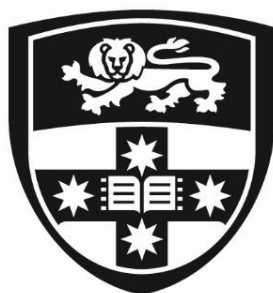


Investigations of Ruthenium Charge-Transfer Complexes and Extended Materials

A thesis submitted in fulfilment of requirements for the
degree of Doctor of Philosophy

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Statement of Student Contribution

I declare that all the work presented in this thesis is my own except where otherwise stated. The work presented in this thesis has not been submitted in any other form for another diploma or dissertation at any other institution. The work derived from the published or unpublished work of others has been acknowledged in the text and a list of references is provided.

Harrison Samuel Moore

January 2024

Abstract

The Creutz-Taube ion, synthesised in 1969 by Carol Creutz and Henry Taube, initiated decades of research into intramolecular electron transfer between dinuclear metal centres. In particular, significant efforts have been devoted to ruthenium and osmium dinuclear complexes with pyridyl and polypyridyl bridges. Such systems are significant by virtue of their easily accessible redox couples and high electron densities, resulting in pronounced charge transfer behaviour. The electronic properties of such complexes are not straightforward, owing to competing effects from π -donor and π -acceptor ligands. While these systems have been used to develop 1D polymers, 2D and 3D materials are relatively unexplored.

A family of coordination complexes *trans*-[Ru(acac)₂(X)₂] (X = N-donor ligands) have been developed. These complexes have been used to produce coordination polymers with closely related behaviours. This work aims to elucidate electronic trends and relationships within this family of ruthenium complexes and coordination polymers by leveraging several analytical techniques, including electrochemistry, spectroscopy, crystallography, and density functional theory. By applying these analytical techniques to discrete, polymer and host-guest systems that incorporate similar Ru motifs, we can describe the competing effects inherent to these systems, demonstrate their similarities and differences, and identify trends that could lead to functionalised systems in the future.

This thesis is divided into three primary works. Chapter 3 describes the synthesis and characterisation of the *trans*-[Ru(acac)₂(X)₂] family of discrete complexes, and discusses their spectroscopic, electrochemical and crystallographic trends.

Chapter 4 discusses the synthesis and characterisation of coordination polymers with *trans*-[Ru(acac)₂(X)₂] metalloligands, including a 3D diamondoid coordination polymer with Robin-Day Class I mixed-valency. The various properties of the coordination polymers are contrasted with their discrete counterparts.

Chapter 5 presents the synthesis of a host-guest material with charge-transfer behaviour. A ruthenium-pyrazine complex was incorporated into the pores of a metal-organic framework, in order to investigate the mechanics of charge-transfer within a controlled, solid-state outer-sphere environment.

List of Publications

Chapter 1 of this thesis is based in part on the following publications:

I **7.11 – Molecular Electron Transfer**

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Comprehensive Coordination Chemistry III, **2021**, 376-392

II **Mixed Valency in Extended Materials**

Moore, H. S.[†]; Kearns, E. R.[†]; van Koeeverden, M. P.[†]; D'Alessandro, D. M.*.

Mixed-Valence Systems, **2023**, 393-429

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Author Attribution Statement

I This thesis contains material published in I, which is present in Sections 1.2.1 and 1.2.2. This component was adapted from Section 2 of Publication I, titled ‘Fundamental Aspects of Mixed Valency’. I contributed the writing and figures.

II This thesis contains material published in II, which is present in Section 1.5. This component was adapted in part from Section 2 of Publication II, titled ‘Electron Transfer in Extended Mixed-Valence Materials’. I contributed the writing.

Harrison Samuel Moore

June 2023

Deanna D’Alessandro

June 2023

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Abbreviations and Symbols

CV	Cyclic Voltammetry
SWV	Square Wave Voltammetry
SEC	Spectroelectrochemistry
FTIR	Fourier-Transform Infrared
TGA	Thermogravimetric Analysis
w	Weak Signal Intensity
m	Medium Signal Intensity
s	Strong Signal Intensity
sh	Shoulder Signal
br	Broad Signal
$E_{1/2}$	Half-Wave Potential
E_p	Peak-To-Peak Separation
$i_{p,c}$	Cathodic Peak Current
$i_{p,a}$	Anodic Peak Current
ν	Vibrational Peak Maxima
λ	Electronic Peak Maxima
1D	One-Dimensional
2D	Two-Dimensional
3D	Three-Dimensional

CIF	Crystallographic Information File
MOF	Metal-Organic Framework
CP	Coordination Polymer
MeCN	Acetonitrile
DMF	<i>N,N</i> -Dimethyl Formamide
pyz	pyrazine
bpy	4,4'-bipyridine
BPE	1,2-bis(4-pyridyl)ethylene
Py	Pyridine

Chapter 1

Introduction

1.1. Ruthenium

Ruthenium is a second-row transition metal belonging to group 8 of the periodic table. It is a significant metal in the history of transition metal chemistry, particularly in regards to the development of early charge-transfer materials, such as the Creutz Taube ion, as well as Marcus-Hush theory.¹⁻⁴ The coordination chemistry of ruthenium is diverse, with 11 documented oxidation states.⁵ The chemistry of ruthenium is similar to that of iron and osmium, with lability and orbital diffusion properties intermediate of its group 8 neighbours. Ruthenium has been extensively investigated for its photochemistry, particularly in the tris(2,2'-bipyridine)ruthenium motif and its derivatives.⁶⁻⁸ Ruthenium has also attracted significant attention in the field of catalysis, as a metal,⁹ in perovskites,¹⁰ nanoparticles,¹¹ and metal complexes.¹²

1.2. Charge-transfer

1.2.1. General Principles

Charge-transfer studies have been conducted with a variety of materials, including discrete coordination complexes,¹³ supramolecular assemblies,¹⁴ and solid-state materials.¹⁵ Typically, the term refers to the excitation of an electron from one component of a material to another. This can include transfer between metals and ligands in metal complexes, between the donor and acceptor of a charge-transfer complex, or between different nodes or linkers of a coordination polymer (CP). Of particular interest to this work are charge-transfer behaviours associated with transition metal *d* orbitals.¹⁶ These include metal-to-ligand charge-transfer (MLCT), ligand-to-metal charge-transfer (LMCT) and intervalence charge-transfer (IVCT). Such processes are typically mediated by π -backbonding (Figure 1.1); a two-fold interaction that involves charge donation from the ligand to the metal *via* a σ -bond, and charge donation

from the metal to the ligand *via* a π -bond.¹⁷⁻¹⁸ Crucially, the π -bond involves the valence d orbitals, which can donate or accept excited electrons under different conditions.

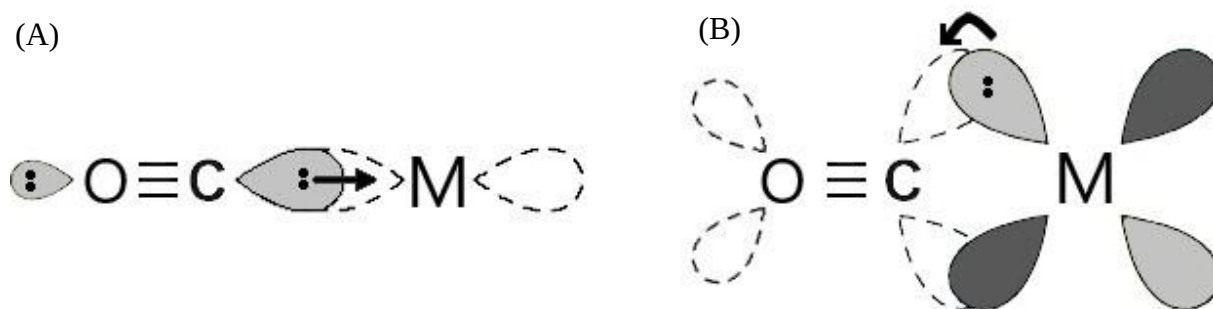


Figure 1.1. π -backbonding in a generic metal CO complex; (A) σ -bond; (B) π -bond. Figure reprinted and altered with permission from Atlanta Publishing House LLC.¹⁹

Mixed-valence systems have been prominent in molecular electron transfer research in the field of coordination chemistry for over five decades, as exemplified by historically important pigments, such as Prussian Blue, $\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3$, which has been known since the late 18th century. The innate mixed-valence nature of the iron centres in Prussian Blue (i.e., present in both their Fe(II) and Fe(III) oxidation states) gives rise to IVCT upon absorption of light in the visible region of the electromagnetic spectrum, which results in its distinctive blue colour. More generally, the IVCT phenomenon in mixed-valence systems involves electron transfer between two redox-active sites that are present in different formal redox states.³⁻⁴ The IVCT phenomenon was first described in reference to the Creutz-Taube ion, a dinuclear ruthenium complex (Figure 1.2).

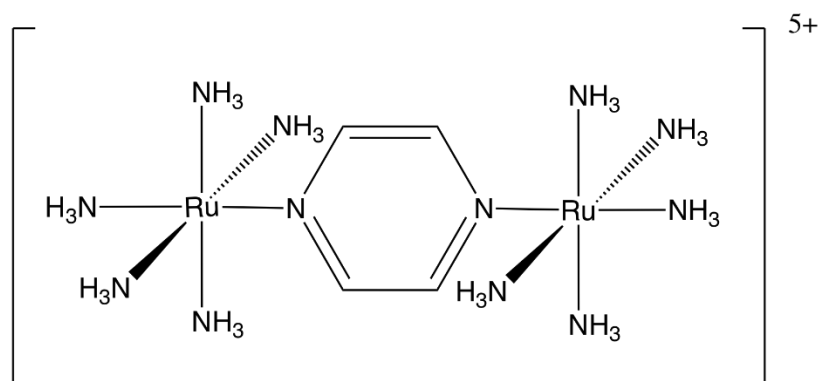


Figure 1.2. The Creutz-Taube Ion¹

1.2.2. Robin Day Classifications

The degree of charge localisation across a mixed-valence system is determined by multiple factors. Robin and Day developed a classification system for mixed-valence systems by considering the wavefunctions of two distinct atoms with different oxidation states, from which they produced a method to determine the class of delocalisation between the two charge centres.²⁰ The Robin-Day classification scheme is primarily concerned with changes in charge delocalisation due to differences in ions, relative ligand field strength and ligand field symmetry. The scheme does not consider the nature of the bridging ligand, which has a significant impact on the degree of delocalisation.²¹

Robin and Day described three distinct classes of mixed-valence systems. The Robin-Day Classification Scheme has been more quantitatively defined with Marcus-Hush theory - Hush specifically introducing several equations used in the current definition of the Robin-Day classes.²⁻⁴ Marcus described electron transfer with the use of potential energy surfaces, which are commonly used to elucidate the optical and thermal reaction pathways of mixed-valence systems.^{4,22}

Class I systems exhibit complete or near-complete localisation. Neither mixing between potential energy surfaces, nor electronic coupling is observed (Figure 1.3). IVCT is not present, as the two ions have little to no electronic interaction. The potential energy surfaces in these systems are all adiabatic, meaning they are consistent with the Born-Oppenheimer approximation.²³⁻²⁴ Class I systems typically exist when there are substantial differences in ligand field symmetry between ions, or because of the absence of a bridging ligand, which can help mediate charge-transfer. Examples include oxides of Cr(III) and Cr(IV), and GaCl₂.^{20,25}

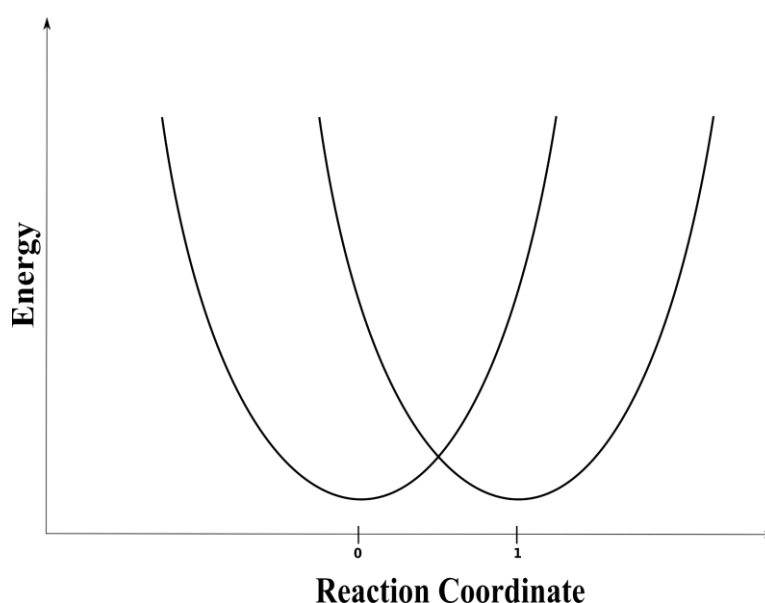


Figure 1.3. Class I mixed-valence potential energy surfaces for a symmetric system.

Mathematically, Class II and III are defined by a comparison of H_{ab} , the electronic coupling parameter, and λ , the reorganisation energy, also known as the optical transition energy. H_{ab} is a measurement of how strongly coupled the two metal centres are., given by the following equation:²⁻³

$$H_{ab} = \frac{|\mu_{12}|}{er_{ab}} v_{max} \quad (1.1)$$

where e is electron charge, and r_{ab} is the distance between the adiabatic potential energy curves.

$|\mu_{12}|$ is the dipole moment associated with the transition between potential energy curves.

From Marcus-Hush theory, λ is notably given by the following equation:

$$\lambda = \lambda_i + \lambda_o \quad (1.2)$$

where λ_i is the inner-sphere reorganisation energy. This term is associated with changes in bond lengths and angles. λ_o is the outer-sphere reorganisation energy, which is associated with changes in solvent polarisability,²⁶ solvent order, and intermolecular interactions such as hydrogen bonding and π -stacking.²⁷ λ_i can also be influenced by interactions with solvent, which result in changes in bond length and ligand conformations.²⁷ As a result, λ can vary substantially for solvents of differing polarity for some molecules. The energy absorbed in the optical transition process is given as $E_{op} = h\nu$, where ν is the frequency of the light absorbed by the species, and h is Planck's constant. The relationship between λ and E_{op} can be simplified as $E_{op} = \lambda$ for symmetrical systems, where ions have identical ionisation potentials and electronic configurations.³ This means the reorganisation energy is typically measurable directly from the electronic absorption spectrum of the molecule.

Class II mixed-valence systems exhibit partial delocalisation of the metal valence electrons. Due to orbital overlap and similar ligand field symmetry, the potential energy surfaces mix, and IVCT occurs. The metal ions have distinguishable oxidation states. This means that charge transitions, vibrational modes and bond distances unique to both oxidation states are observable.²⁰ In these systems, H_{ab} is given as the separation between the upper and lower adiabatic surfaces. The system is weakly coupled, and mathematically defined where $2H_{ab} \ll \lambda$.

Class II mixed-valence systems typically exist where ions have nearly identical ligand field symmetries, and valence electron molecular orbitals can partially overlap.²⁰ Class II systems

typically have a bridging ligand capable of mediating charge-transfer, such as π -backbonding ligands that bridge transition metals.¹³ Examples of Class II systems include Prussian Blue, and crocidolite ($\text{Na}_2(\text{Fe}^{\text{II}}_3\text{Fe}^{\text{III}}_2)\text{Si}_8\text{O}_{22}(\text{OH})_2$).²⁰

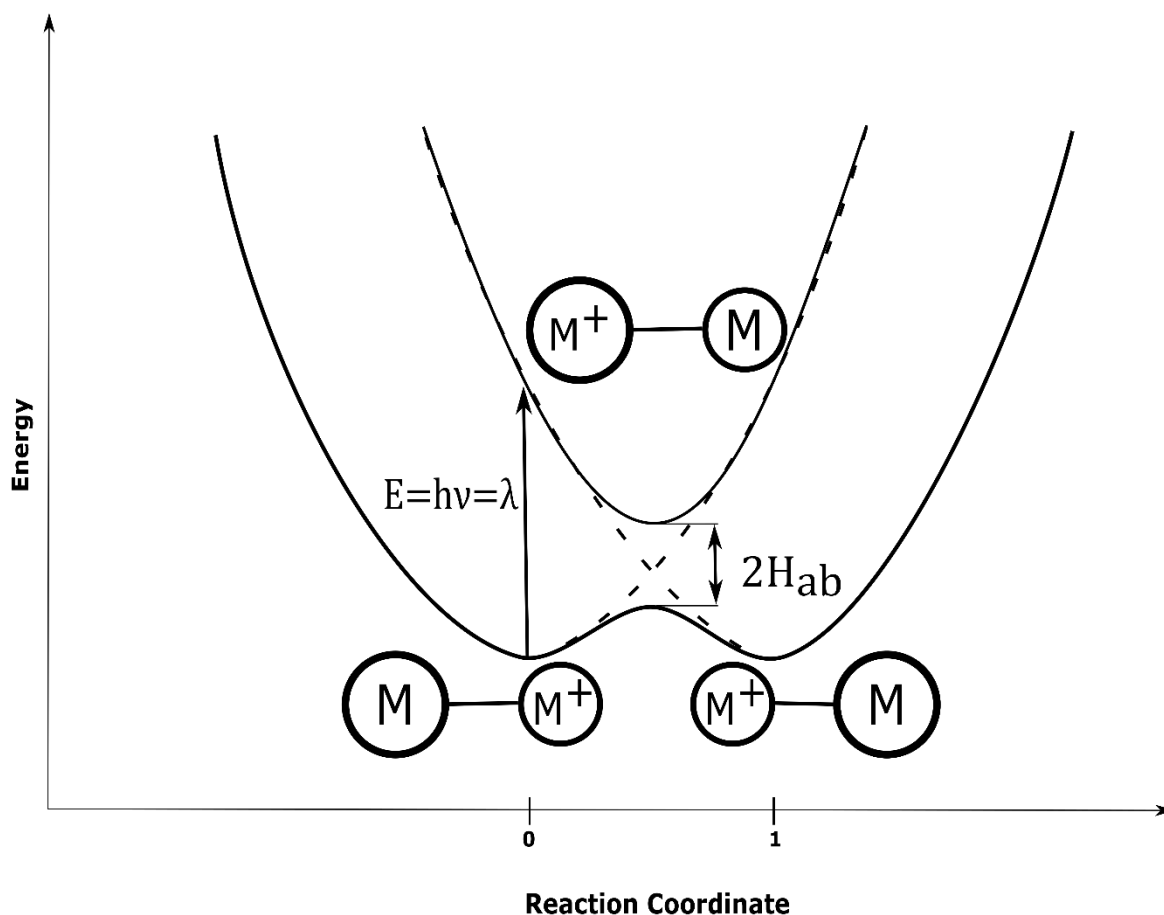


Figure 1.4. Class II mixed-valence potential energy curves for a symmetric system. Solid lines are adiabatic potential energy surfaces, and dotted lines are diabatic potential energy surfaces.²⁸ Figure adapted with permission from John Wiley & Sons, Inc.¹³

Class III mixed-valence systems exhibit complete delocalisation of the metal valence electrons. Mixing between potential energy surfaces occurs to such an extent that the thermal electron transfer barrier disappears, and the system exists in a state of equilibrium where excess charge is shared between the two metal ions. Therefore, both atoms have averaged oxidation states (which can be non-integers) and are thus indistinguishable. Class III systems often exhibit fully conducting behaviour because of delocalised charge. Class III systems exist when

there is complete overlap between orbitals, and ligand field symmetry is identical between ions. These systems employ bridging ligands that are capable of mediating charge-transfer, and short enough to facilitate complete orbital overlap.²⁹⁻³⁰ Examples of Class III systems include ruthenium red ($[(\text{NH}_3)_5\text{RuORu}(\text{NH}_3)_4\text{ORu}(\text{NH}_3)_5]^{6+}$) and the oxidised form of tetrathiafulvalene (TTF^+).^{20,31}

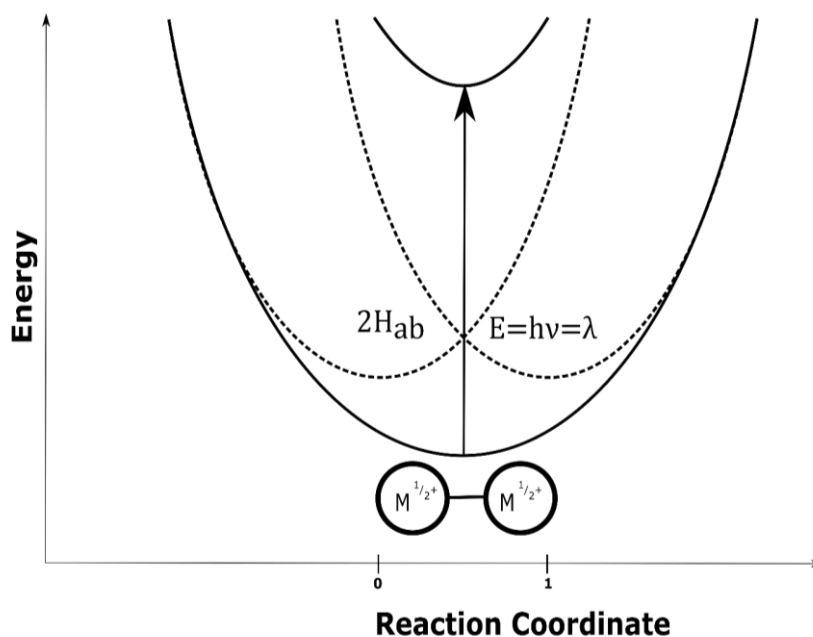


Figure 1.5. Class III mixed-valence potential energy curves for a symmetrical system. Solid lines are adiabatic potential energy surfaces, and dotted lines are diabatic potential energy surfaces. Figure adapted with permission from John Wiley & Sons, Inc.¹³

1.2.3. MLCT and LMCT

The number of fundamental studies on IVCT and mixed-valency, as opposed to MLCT and LMCT, are in part a product of the relative simplicity of the IVCT mechanism. IVCT can be categorised as resulting from simple mixing of similar atomic (molecular in the case of organic IVCT) orbitals with comparable symmetries. MLCT and LMCT mechanisms, by comparison, cannot easily be reduced to transitions between separate orbital structures, but instead must be

considered in the context of the entire molecular orbital (MO) structure of a coordination complex.³²⁻³⁴ This can make predicting and identifying MLCT and LMCT transitions difficult if the electronic structure of a complex is not well understood.

1.3. The d^5 - d^6 Boundary

The oxidation state of a group 8 metal (of which ruthenium is a member) within a coordination complex can have dramatic effects on the electronic and magnetic properties of the material. Due to the importance of the π -backbonding interaction, synthetic properties such as coordination number, geometry, and affinity for certain ligands can all be affected by the oxidation state of the central metal. The most pronounced one-electron transition in the group 8 metals is arguably that from low-spin d^5 (III) to low-spin d^6 (II). Magnetically, low-spin d^5 is paramagnetic, while low-spin d^6 is diamagnetic. In octahedral materials with the point group O_h , low-spin d^5 metal centres have incomplete t_{2g} orbitals, typically resulting in π -accepting behaviour, while the full t_{2g} orbitals of low-spin d^6 complexes results in π -donating behaviour.

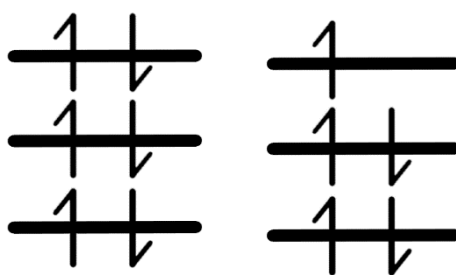


Figure 1.6. Low-energy d orbitals, occupancy for Ru(II) and Ru(III) respectively.

The oxidation states of ruthenium relevant to this work are primarily Ru(II) and Ru(III), with d orbital configurations of low-spin d^6 and d^5 respectively. For ruthenium complexes within the O_h point group, Ru t_{2g} orbitals are largely non-degenerate due to crystal field distortions and spin-orbit coupling.³⁵⁻³⁹ This results in three energetically distinct Kramer's doublets (Figure 1.6). The materials discussed in this work largely fall into lower symmetry point groups

than O_h ; however, the above relationship can exist in such point groups. For example in D_{2h} , the non-degenerate B_{1g} , B_{2g} and B_{3g} orbitals can all lie below the A_g orbitals, producing the same d^5 and d^6 electron configuration shown in Figure 1.6. In π -backbonded systems the orbitals in question are molecular but conform to the same description.

1.4. Acetylacetonone Complexes

Pentane-2,4-dione, or acetylacetonone ($H(acac)$), is a diketone commonly used in the preparation of metal acetylacetonates ($acac^-$), where the compound acts as a negatively charged bidentate ligand.⁴⁰ The acetylacetonate ligand has a delocalised π -structure, that interacts electronically with coordinated transition metals through π -bonding.⁴¹ Unlike most pyridyl ligands, acetylacetonone is a π -donating ligand.⁴² and will also donate charge through σ bonds.

Ruthenium acetylacetonate complexes have appeared sporadically throughout the literature. The most simple combination of acetylacetonone and Ru are the two enantiomers of tris(acetylacetonato)ruthenium(III) (Figure 1.7A).⁴³ This complex prompted several spectroscopic studies, in which there remain some unidentified transitions.⁴⁴⁻⁴⁵ Synthetic work on ruthenium acetylacetonates led to the discovery of the system *trans*-bis(acetylacetonato)dipyrazineruthenium(II) by Hasegawa, *et al.* (Figure 1.7B),⁴⁵ as well as a one-dimensional coordination polymer $[Ru(acac)_2(pyz)]_n$.⁴⁵ The foundation of much of the current work and application of the *trans*- $[Ru(acac)_2(X)_2]$ motif as a linear metalloligand for reticular and polymer synthesis stems from this work.

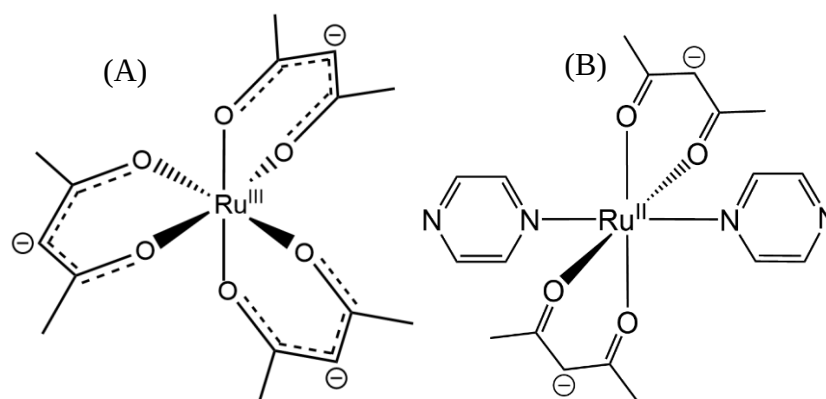


Figure 1.7. (A) Δ -[Ru^{III}(acac)₃]; (B) *trans*-[Ru^{II}(acac)₂(py)₂]

A recent contribution by Vinum, *et al.* to the literature on acetylacetonate complexes provided compelling evidence for the existence of the acac^{2-} oxidation state,⁴⁶ which was previously believed inaccessible. The researchers employed the motif *trans*-[Cr(acac)₂(X)₂] (X = pyridine, 4-(trifluoromethyl)pyridine), or 4-(dimethylamino)pyridine)), and discovered the complexes were Robin-Day Class III mixed-valence, where acac^- and acac^{2-} ligands were present simultaneously, observationally producing two valence-averaged $\text{acac}^{-1.5}$ ligands.

Acetylacetonate derivatives have also been employed for polymer synthesis. Domasevitch and coworkers prepared coordination polymers from discrete four-coordinate beryllium complexes.⁴⁷⁻⁴⁹ While these materials are well studied in the solution phase, their behaviour when immobilised is less explored. This avenue holds exciting possibilities for future synthetic and spectroscopic research.

1.5. Extended Materials

1.5.1. Coordination Polymers and Metal-Organic Frameworks

The term coordination polymer (CP) refers to a broad range of organometallic extended materials that exist as periodic structures in one-, two- or three-dimensions (Figure 1.8).⁵⁰⁻⁵¹ CPs can incorporate the already variable behaviour of coordination complexes into new and potentially synergistic arrangements, a capacity demonstrated by most metal-organic frameworks (MOFs). MOFs are a subset of coordination polymers that consist of metal-containing nodes connected by organic linkers⁵²⁻⁵³. The architecture of CPs is possible thanks to rigid and highly variable coordination bonds, which also contribute to the charge-transfer and conductive properties of such materials through the prevalent π -backbonding phenomenon. The coordination geometry of the nodes within CPs varies across the periodic table, which results in unique and potentially targetable architectures.⁵⁴⁻⁵⁵

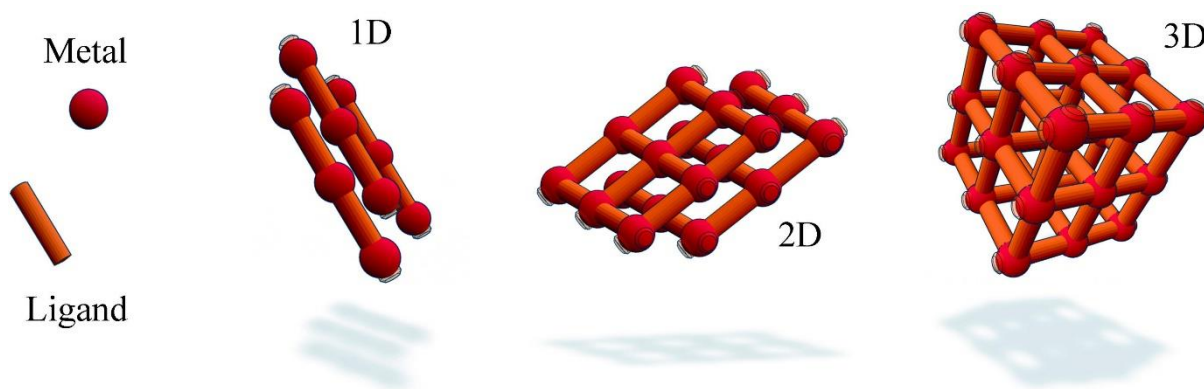


Figure 1.8. Simple schematic of 1D, 2D and 3D CPs. Figure reprinted with permission from Elsevier.⁵⁶ MOFs are strictly two- or three-dimensional nanoporous materials, with a large percentage of the framework volume consisting of pores or channels.⁵³ MOFs are highly designable materials, and can incorporate a range of behaviors specific to their component groups, including conductivity,⁵⁷⁻⁶⁰ charge-transfer,⁶¹ luminescence,⁶²⁻⁶⁴ ferromagnetism,⁶⁵⁻⁶⁷

redox activity,⁶⁸ spin crossover,⁶⁹ host-guest chemistry.⁷⁰ MOFs are often synthesised under mild conditions relative to conditions used for other inorganic solids, such as zeolites.⁵⁰ MOFs are insoluble in most solvents and can be modified post-synthetically. Consequently, MOFs have been developed and investigated at length for their synergistic properties, particularly in combination with their high surface areas.⁷¹ Some applications include nanowires,⁷² catalysis,⁷⁰ porous sensors,⁷³ kinetic separation,⁷⁴ gas capture and storage.⁷⁵ Post synthetic modification (PSM) of MOFs is an increasingly relevant technique employed by MOF chemists to further tune the properties of frameworks.⁷⁶ There are four main categories of PSM, broadly defined by the component of the framework to be added, substituted or removed. These include the metal-based, ligand-based, metal and ligand-based, and guest-based PSM methods.

MOFs have been long investigated for reaction-targeting capabilities, specifically as templates for reactions involving guest molecules.⁷⁰ The highly variable geometry, size, dimensionality, and functionality of pore spaces within MOFs can restrict and orient guest molecules with respect to the pore apertures of the framework.⁷⁰ Templatation of reactions can improve yields,⁷⁷⁻⁷⁸ reaction times,⁷⁹ or change the selectivity of reactions.⁸⁰ The degree of control over reactions afforded by MOFs has led to the templated synthesis of polymers and oligomers.⁸¹⁻⁸⁴ Monomers are first impregnated into the framework pores, upon which they are polymerised or oligomerised through a variety of methods. This process can result in individual polymer or oligomer units isolated within the structure of a MOF, which can permit fine control over the functionality of a polymer system. From the perspective of this work, isolating a charge-transfer oligomer through the process above will produce a unique outer-sphere environment, thereby altering the mechanisms of charge-transfer. This sensitivity of the pores to the environment can also result in highly versatile sensors that can change in colour, vibrational spectroscopy, and electrochemical properties such as the preferred redox state, dependent on the outer-sphere effects with pore content. The framework chosen for these investigations was

$\text{Zr}_6\text{O}_4(\text{OH})_4 \cdot (\text{C}_8\text{H}_6(\text{SO}_3\text{H})_6) \cdot (\text{DMF})_{0.7} \cdot (\text{H}_2\text{O})_{47}$ (**UiO-66-(HSO₃)₂**), which reportedly has an average pore width of 0.524 nm and volume of 0.196 cm³/g.⁸⁵ This material was chosen for its pore size and stability under low pH environments.

1.5.2. Charge-Transfer and Mixed-Valency within Coordination Polymers

There exists a complex relationship between the design of a framework and its function. The chosen topology, clusters, linkers and their spatial and orbital relationships can all contribute to charge transfer and various emergent properties within the framework. Mixed-valence MOFs frequently exhibit emergent properties either because of, or for reasons relating to mixed-valency. The best example of this relationship is the prevalence of conductive and semiconductive extended systems exhibiting mixed-valency.¹⁵ For example, a family of mixed-valence iron-based triazolate frameworks $[\text{Fe}(\text{tri})_2](\text{BF}_4)_x$ (Htri = 1,2,3-triazole; $x = 0.09, 0.22$, and 0.33) were produced by Park *et al.* via chemical oxidation of the valence-pure Fe(II) framework $[\text{Fe}(\text{tri})_2]$.⁸⁶ All three MV frameworks exhibited an IVCT band; however, the full band shapes were not observed due to the low wavelengths of the IVCT transitions.⁵⁷ ⁵⁷Fe Mössbauer spectroscopy at 290 K indicated all three frameworks contained valence averaged Fe(III)/Fe(II), a strong indication of class III Robin–Day mixed valency.²⁵ All three frameworks were electrically conductive; however, $[\text{Fe}(\text{tri})_2](\text{BF}_4)_{0.33}$ exhibited an unusually high electronic conductivity value due to charge delocalisation in the MV system.

As CT interactions are entirely dependent on orbital interactions, CT can occur through one of two avenues; through-bond and through-space.⁸⁷ Ligand design and framework structure are, therefore, extremely important factors to consider when attempting to produce a charge-transfer framework, as the spatial relationship between mixed-valence functional groups is integral to the mechanism and extent of coupling.⁶⁰ Engineering through-bond CT in extended materials is readily achieved by the judicious selection of metals and ligands, to ensure close matching in energy levels and efficient orbital overlap.⁸⁸ In contrast, through-space CT in

supramolecular systems is an uncommon phenomenon, which has appeared in only a handful of examples.⁸⁹⁻⁹¹ The requirements for through-space CT to occur are restrictive to the extent that the structure of a material must be carefully considered and designed to produce the desired supramolecular orbital overlaps between the MV moieties. In particular, the crystal packing arrangements of metals and ligands in MOFs can sometimes be difficult to control, especially as a consequence of pore space, precluding the supramolecular interactions required for through-space CT to be predictably engineered.

1.5.3. Functionalised Frameworks and Metalloligands

The most simple approach to CP design is to employ functionalised ligands as a basis for functionalisation of a framework.⁹² For example, the organic motif phenalenyl is an aromatic system with a stabilised, delocalised radical.⁹³ The phenalenyl core can easily be incorporated into larger organic molecules that include ligands for framework synthesis. Koo, *et al.* synthesised a new molecule, 2,5,8-tri(4-pyridyl)-1,3-diazaphenalene,⁹⁴ which upon deprotonation and one-electron oxidation, produced a neutral radical species. This radical underwent reversible oxidation and reduction, and was used to produce cadmium-based frameworks, which preserved the radical behaviour of the phenalenyl core.⁹⁵

So-called ‘metalloligands’ are coordination complexes that can behave both as nodes and building units in polymeric systems.⁹⁶⁻⁹⁷ Metalloligands offer several advantages over organic ligands. Firstly, metalloligands can be used to finely control the structure of coordination polymers, through the coordination geometry of the metalloligand, and selective functionalisation organic components.⁹⁶ A wide range of coordination geometries are possible when considering these two factors, including 2-,⁴⁷ 3-,⁴⁸ 4-,⁹⁸ and 6- coordinate geometries of various angles.⁹⁹ The rigidity of metal coordination geometries is also advantageous for MOFs, where permanent porosity is more easily achieved than with flexible organic ligands.

Furthermore, properties unique or more readily accessible to coordination complexes may be preserved through polymerisation, to produce emergent properties. Producing CPs *via* metalloligands with spin-crossover,¹⁰⁰ charge-transfer,¹⁰¹⁻¹⁰² and mixed-valency can result in guest-dependent interactions unique to this class of material. Catalysis, a common target for MOF materials, can be achieved *via* metalloligands employing chiral stereocentres,¹⁰³ or redox-activity.¹⁰⁴

Depending on the design of the coordination polymer, some of these properties are more readily accessible than others. For example, retaining the conductivity of a metalloligand upon polymerisation requires careful consideration of coordination polymer geometry and orbital interactions.⁸⁸ Reversibility of redox reactions requires the other components of the polymer to be inert or at least have reversible behaviors under the same conditions as the metalloligand.¹⁰⁵

1.5.4. Ruthenium Coordination Polymers

Ruthenium is a second-row transition metal in the platinum group and is relatively inert when compared to traditional metals used in CPs and MOF synthesis, such as iron, cobalt, copper, zinc and zirconium. Inert metals participate poorly in the self-assembly process and as a result are generally unsuited as nodes in CPs. The small number of CPs incorporating ruthenium in the literature approach this issue through pre-synthesised metalloligands and electropolymerisation. A popular motif is $[\text{Ru}(\text{2,2'-'bpy})_3]^{n+}$ and its derivatives,¹⁰⁶⁻¹⁰⁷ although other motifs have been explored.¹⁰⁸⁻¹¹¹ However, Liu, *et al.* were able to incorporate ruthenium directly into a cage SBU using traditional reticular synthesis.¹¹²

The properties of the above polymers are varied, but largely rely on the pre-existing behaviour of the metalloligands. For example, polymers employing the $[\text{Ru}(\text{2,2'-'bpy})_3]^{n+}$ or similar motifs tend to exhibit luminescent behaviour, and have been employed as functional thin films.¹⁰⁶⁻¹⁰⁷ Redox-activity of ruthenium metalloligands has facilitated production of flip-flop memory

devices,¹⁰⁹ electrosensors, and the elucidation of unique electron-transport behaviour.^{112,110-111} Alternatively, side chain polymerisation of the ruthenium complex $[\text{Ru}(2,2'\text{-bpy})(2,2'\text{-bpyCH}_2\text{O})]^+$ resulted in emergent long-range charge transport between mixed-metal sites.¹⁰⁸

Characterisation Techniques

1.6. Cyclic Voltammetry

Cyclic Voltammetry (CV) is the most widely employed analytical electrochemical technique. By applying a constantly ramping potential to a sample and measuring the current response, an electrochemical profile for an analyte can be obtained. CV employs a three-electrode setup, with a working, counter and reference electrode.¹¹³⁻¹¹⁴ Typically the working electrode is a cylinder of graphite, gold or platinum, which is encased in an inert material with the bottom face exposed. This face is smooth and has a known surface area. For diffusion-controlled processes, this configuration produces the duck-shape hysteresis commonly associated with the technique (Figure 1.9), due to consistent diffusion of ions into the bulk solution.

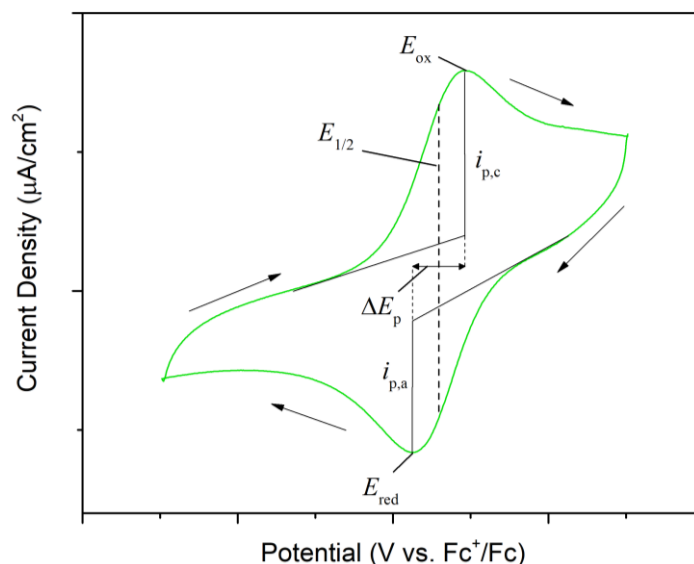


Figure 1.9. A typical cyclic voltammogram of a reversible or *quasi*-reversible analyte in the solution state. E_{ox} and E_{red} are the oxidative and reductive peak potentials, respectively. $E_{1/2}$ is the half-wave potential, the halfway point between E_{ox} and E_{red} . ΔE_p is the peak separation, measured as the difference between E_{ox} and E_{red} .

The reference electrode is used to accurately determine the potential across the working and counter electrodes. For aqueous experiments there are several viable reference electrode systems, including Ag/AgCl, saturated calomel electrode (SCE) and the reversible hydrogen electrode (RHE), which all have stable redox couples. Non-aqueous measurements are more difficult, as the only options for reference electrodes with stable redox couples are liquid junctions, which can contribute to voltage loss across the cell. Instead, electrochemists typically employ a *quasi*-reference electrode such as Ag^+/Ag , which has a redox couple of variable potential within a set range. An internal standard, such as ferrocene, with a stable redox couple is then introduced to the electrochemical cell and the data calibrated with respect to the internal standard.

Perhaps the most significant conclusion that can be drawn from cyclic voltammograms is the electrochemical reversibility of an analyte. A redox reaction is reversible if mass transport of ions is thermodynamically unhindered in both the oxidation and reduction steps of the reaction,

and electron transfer is much faster than mass transport.¹¹³ There are several quantitative markers for reversibility in freely diffusing analytes:

1. The peak separation ΔE_p should be approximately 59 mV at 25°C for an electrochemically reversible process.¹¹⁴
2. The relationship between scan rate ν and peak current i can be described for a reversible redox reaction by the Randles-Sevcik equation:

$$i = 0.446nFAC^0 \left(\frac{nF\nu D_o}{RT} \right)^{\frac{1}{2}} \quad (1.3)$$

Where i is peak current in amperes, n is the electron count of the redox process, F is Faraday's constant, A is electrode surface area in cm^2 , C_0 is analyte concentration in mol/mL , ν is scan rate in mV/s , D_o is the diffusion coefficient of the oxidised sample in cm^2/s , R is the universal gas constant and T is temperature in Kelvin.¹¹³ Given an ideal experiment, all variables are constant except i and ν , which gives the following relationship for freely diffusing reversible analytes:

$$i \propto \sqrt{\nu} \quad (1.4)$$

3. The ratio of cathodic peak current to anodic peak current, $|i_{p,c}/i_{p,a}|$, should be approximately 1
4. E_{ox} , E_{red} and the half-wave potential, $E_{1/2}$, should all be scan-rate independent.

The term *quasi-reversible* applies where the heterogenous electron transfer is comparable or slower than mass transport and/or a fast coupled chemical process occurs during electron transfer. As a result, *quasi-reversible* voltammograms have a peak separation ΔE_p larger than 59 mV at 25 °C.¹¹⁵

The majority of solution-state measurements involve generating freely diffusing redox species, i.e. diffusion of the generated species (a volume of analyte called the diffusion layer) occurs restricted only by the intramolecular forces present between solvated molecules, ions and solvent.¹¹⁶ However, if an analyte is in the solid-state, transport of charge rarely occurs *via* free diffusion. Instead, for a process occurring at the surface of an electrode, the following equation is used in place of Equation 1.3:¹¹³

$$i = \frac{n^2 F^2}{4RT} v A \Gamma \quad (1.5)$$

Where Γ is surface coverage in mol/cm². Again, considering an ideal measurement, the following relationship is obtained:

$$i \propto v \quad (1.6)$$

Additionally, for an electrochemically reversible surface process, $\Delta E_p = 0$ and $|i_{p,c}/i_{p,a}| \sim 1$. Diffusion of charge in a solid-state experiment becomes more complex when considering measurements on crystalline materials, such as CPs or MOFs. Such materials may have rigid internal structures, nanoporosity, ionic, neutral and/or bulky guests. Additionally, many polymeric materials are measured as bulk powders or microcrystals, without a homogenous orientation. All of these factors can contribute to a far more complex picture of charge diffusion than in the simple free diffusion model.¹¹⁷ Such diffusion can be assessed practically for MOF samples. Considering the diffusion of counterions contrary to that of electrons through a framework, the problem can be approached by producing a diffusion coefficient dependent on that of the counterions.¹¹⁸

1.7. UV-Vis-NIR Spectroscopy

There are a variety of techniques and instruments employed throughout this work that rely on the absorption of light in the ultraviolet (UV), visible (Vis) and near-infrared (NIR) regions by an analyte. Known as UV-Vis-NIR spectroscopy or electronic absorption spectroscopy, this technique is primarily used to observe transitions from electronic ground states to excited states upon absorption of photons.¹¹⁹⁻¹²⁰ Electronic transitions are typically described in terms of the atomic orbitals (AOs) or molecular orbitals (MOs) from which electrons are excited or to which they transfer. Transitions commonly observed in aromatic systems typically involve bonding, non-bonding and antibonding orbitals such as σ , σ^* , π , π^* and n . Transition metal complexes often exhibit transitions to or from atomic d orbitals. Transitions such as MLCT ($d \rightarrow \pi^*$), LMCT ($\pi^* \rightarrow d$), IVCT, and $d \rightarrow d$, in addition to higher energy $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$ transitions, can often dominate absorption spectra.¹²¹ Metal complexes with π -backbonding behaviour are of particular interest because of the above transitions.

Transitions between molecular orbitals can be described with respect to the point group character table for a molecule.¹²⁰ Such definitions can be useful when considering the electronic symmetry of molecules in the ground and excited states, which will differ with orbitals and their electronic occupation, and are important factors in transition probabilities.

Thus, electronic absorption spectroscopy gives enormous insight into the electronic structure, electronic occupation, and symmetry of a system. There are many variations of the technique and the type of measurement. These include spectroelectrochemistry (SEC), polarised and circularly polarised measurements, magnetic circular dichroism (MCD), measurements on single crystals, bulk powders, or solutions.

1.8. Microcrystal UV-Vis Spectroscopy

Single-crystal polarised UV-Vis-NIR spectroscopy is a specialised technique well-suited to the analysis of materials that only exist in the solid-state. This technique is distinct from traditional electronic absorption spectroscopy in that it measures a single orientation of a chromophore in a crystal structure, as opposed to the average of all possible orientations, such as in solution-state or solid-state diffuse reflectance measurements. Anisotropy of the electronic transitions arising from chromophores within a material can be observed directly with this technique, which can also result in better resolved spectra than diffuse reflectance spectroscopy due to reduced inhomogeneous broadening.¹²² In recent years, this technique has been employed for valuable analysis of solid-state materials, including quantification of solid-state IVCT,¹²³ and analysis of solid-state charge-transfer behaviour.¹²⁴ This technique has also been used to investigate the CT behaviour of $[\text{Ru}(\text{bpy})_3]^{2+}$ in the solid-state. Krausz and Ferguson noted the improved resolution of the technique compared to solution-state, and were able to identify the symmetries of several transitions *via* the polarised absorption component of the technique.¹²⁵

1.9. Vibrational Spectroscopy

The term ‘vibrational spectroscopy’ usually refers to two complementary techniques - infrared and Raman spectroscopies. Both techniques involve the excitation of vibrational or rotational states that result from corresponding vibrational modes of atoms within molecules. Thus, vibrational spectroscopy is used to identify bonds or molecules, differentiate between isomers, and gain insight into the symmetry of crystalline materials.¹²⁶ Each technique provides a complimentary set of vibrational bands corresponding to modes - infrared spectroscopy is only sensitive to modes corresponding to a change in dipole moment, while Raman spectroscopy can only be used to observe modes corresponding to a change in polarisability.¹²⁷

1.9.1. Infrared Spectroscopy

Fourier transform infrared (FTIR) spectroscopy is a relatively simple photon absorption technique, which operates on a similar principle to electronic absorption spectroscopy. FTIR spectroscopy, however, is particularly limited in terms of available wavelengths. Low energy IR signals, in the ‘far-infrared’ region, are typically much lower in intensity than those in the mid-IR or NIR. As a result, specialised instruments are usually required for measurements in this region, in which most metal-ligand modes occur. Raman spectroscopy does not exhibit this limitation and is well suited for observing bands due to low-energy vibrational modes.

1.9.2. Raman and Resonance Raman Spectroscopy

Normal Raman spectroscopy relies on an inelastic interaction of light with electrons, called Raman scattering. A Raman spectroscopy measurement involves excitation by a monochromatic light source, which is then frequency shifted on scattering from a Raman-active vibrational mode.¹²⁸ Raman scattering involves the excitation of a vibrational ground state to a series of superimposed eigenstates, known as a virtual state, with no defined eigenstate of its own.¹²⁹

Resonance Raman spectroscopy is an extension of normal Raman spectroscopy, which takes advantage of the chromophore-specific scattering involved in the process.^{128,130} The incident laser wavelength is chosen to correspond with the wavelength of an absorbance band of a chromophore. This process enhances the intensity of bands associated with vibrational modes of a specific chromophore up to 10^6 -fold.

Electronic transitions typically involve orbitals of differing symmetries. Therefore, resonance Raman enhancement is associated with the symmetry of the electronic excited state corresponding to the excitation wavelength. Resonance Raman spectroscopy can provide information about the symmetry of a molecule and its electronic orbitals.

There are four categories of resonance Raman enhancement, which are dependent on the symmetry of the Raman modes present in the spectrum.¹³¹ *A-term* enhancement occurs with fundamental modes that are totally symmetric. This phenomenon is described by Franck-Condon scattering, which involves interactions between vibrational wavefunctions during electronic transitions.¹³² *A-term* scattering is the most commonly observed enhancement phenomena in resonance Raman spectroscopy. *B-term* enhancement only occurs with fundamental modes with symmetry corresponding to the direct product of the electronic orbital irreducible representations. *B-term* scattering is typically observed for non-totally symmetric Raman modes. This phenomenon is described by Herzberg-Teller vibronic coupling, where a vibrational excitation couples two excited states. *C-term* enhancement occurs when the excitation wavelength coincides with a sideband produced by vibronic coupling with the 0-0 transition. *D-term* scattering occurs when the excitation wavelength is on-resonance with a 0-1 transition.¹³³⁻¹³⁴ Both phenomena result in enhancement of overtones or a combination tone of two fundamental modes.

This technique is valuable for charge-transfer materials, which typically have strong absorbance features in the NIR, Vis and UV regions. Ideally, using on-resonance laser wavelengths would vastly improve the visibility of these small vibrational modes. A variety of excitation wavelengths were used throughout the present investigation to study the resonance enhancement of the Raman vibrational modes.

1.9.3. A Note on ‘Deuteration’:

Syntheses of certain metalloligands were repeated with deuterated ligands (e.g. pyrazine-*d*₄). This was done in order to more easily identify vibrational modes in the infrared and Raman spectra of metalloligands used throughout this work. From the harmonic oscillator model of molecular vibration, the mass term μ was expressed as the following:¹³⁵

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad (1.7)$$

where m_1 and m_2 are the constituent masses involved in the vibration. The frequency of the vibration ν is inversely proportional to the square root of μ , as shown in the following expression:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (1.8)$$

Thus, employing a deuterated ligand in synthesis will result in an observable and quantifiable difference in the wavelength of vibrational modes associated with the deuterium atoms compared to the sample synthesised without a deuterated ligand. This allows precise identification of the modes in question.

1.10. Spectroelectrochemistry:

1.10.1. General Principles:

SEC is a valuable technique for analysis of redox-active materials, where *in situ* electrochemical oxidation and reduction of an analyte can be used in conjunction with a variety of spectroscopic techniques, including ultraviolet, visible, near-infrared, infrared, Raman, X-ray absorption (XAS) and electron paramagnetic resonance (EPR) spectroscopies.

In situ generation of the oxidised or reduced forms of an analyte has distinct advantages over other approaches. Air sensitivity is a common phenomenon in reduced metal complexes and radical compounds,¹³⁶ and photosensitivity is commonly observed in XAS SEC.¹³⁷ Both issues can be addressed by *in situ* techniques. Additionally, *in situ* measurements allow for the analysis of the transition of an analyte from one oxidation state to another. For example, in UV-Vis-NIR spectroscopy, the presence of an isosbestic point (Figure 1.10), i.e. a wavelength where the absorbance is unchanged over the course of the transition, indicates the stoichiometry of the transition is stable and that undesired compounds are not being produced.¹³⁸

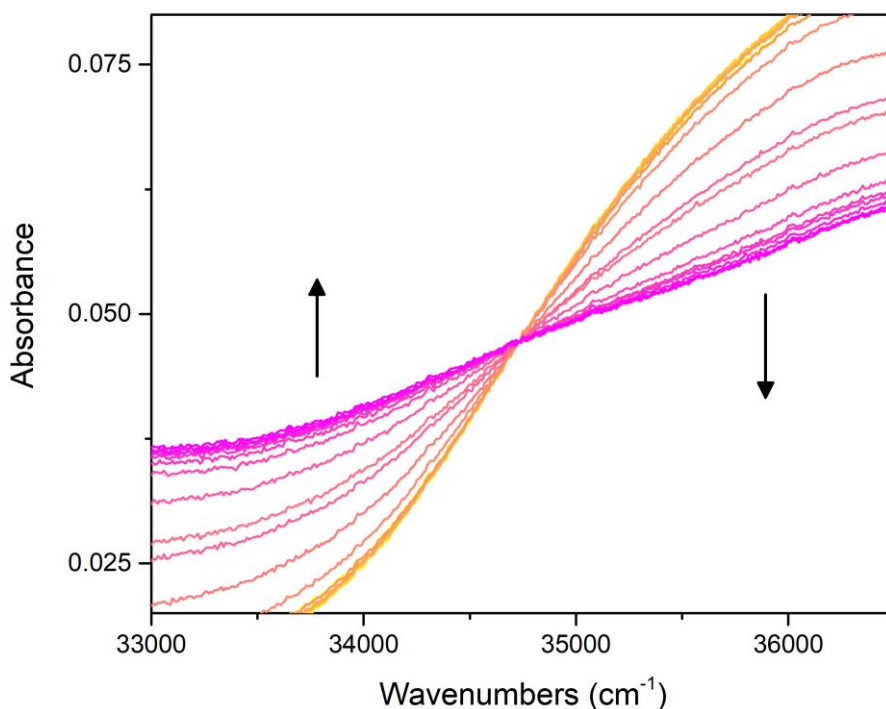


Figure 1.10. Isosbestic point in the solution-state SEC of *trans*-[Ru(acac)₂(pyz)₂], in TBAPF₆ (0.1 M) in MeCN. Arrows indicate spectral progression.

Similar to other analytical electrochemical techniques, SEC setups require the standard three electrode system of working, counter and reference electrodes. For solution-state measurements, the working electrode typically has a large surface area to facilitate bulk

electrolysis. The reference electrode will differ based on the electrolyte medium, but is typically an Ag/Ag⁺ pseudo-reference electrode. As a result, SEC results are rarely quantitative with respect to the applied potential on the system, and rely on supplemental measurements such as CV and SWV.

1.10.2. UV-Vis-NIR SEC

UV-Vis-NIR SEC is one of the primary techniques for analysis of electrochromic materials. For metal complexes and some coordination polymers the technique can be used to observe different charge-transfer interactions, many of which alternate or are only present in a single oxidation state. The d^5 - d^6 boundary (Section 1.3) is an underlying cause of the above behavior in group 8 transition metals, and under the right conditions can result in MLCT, LMCT and IVCT. The non-degeneracy of low-spin ruthenium d orbitals described in Section 1.3 results in multiple transitions to excited state orbitals, consequently, spectra of these complexes are often convoluted with many overlapping absorption features.

UV-Vis-NIR SEC can be used to observe transitions within organic materials, ligands, and CPs. Transitions within, or between, organic species can result from radical formation, or more exotic behaviours like through-space charge-transfer in solid-state materials.

The technique has also been used for decades for *in situ* analysis of mixed-valence materials, in order to observe IVCT bands between ions.¹³⁹

1.10.3. Infrared SEC

IR SEC is a technique primarily used to observe structural changes in materials upon reduction or oxidation.¹⁴⁰ Changes in bond lengths, at metal clusters,¹⁴¹ and ligand structure are all observable with this technique.¹⁴² Chemical reactions involving reduced or oxidised analytes are also easily observed by the breaking and formation of bonds.¹⁴³⁻¹⁴⁵ A recent application of IR SEC to charge-transfer materials was performed by Safari, who extensively investigated the

correlation between CO stretching bands and electron transfer rates within bimetallic mixed-valence ruthenium complexes.¹⁴⁶ To our knowledge, this technique has not been applied to ruthenium CPs.

1.11. X-Ray Diffraction

X-ray diffraction (XRD) in this work refers to two techniques, performed on powders (PXRD) and single crystals (SCXRD). Both techniques are powerful methods of analysing crystalline materials. XRD operates on the diffraction of photons by the lattice planes of crystal structures. Constructive interference of photons will occur when the space between two lattice planes d is related to the angle of incidence θ according to Bragg's law:¹⁴⁷

$$n\lambda = 2d \sin \theta \quad (1.9)$$

where n is an integer and λ is the wavelength of light.

In an ideal PXRD measurement, the analyte is composed of crystals in every possible orientation relative to the incident photons. As a result, the incident angle θ can be varied according to the needs of the experiment. This produces a two-dimensional diffraction pattern. PXRD patterns of sufficient quality and phase purity can be indexed and the space group identified.¹⁴⁸ As PXRD is a bulk measurement, it can be used to detect different phases and the presence of amorphous materials, which is not possible in SCXRD.

SCXRD is a substantially more complex technique. In an ideal SCXRD experiment, the analyte is a single crystal, which has only one single orientation relative to the incident photon.¹⁴⁹ The orientation of the crystal as well as θ is altered over the course of the experiment in order to produce multiple two-dimensional diffraction patterns (called 'frames') that are collated into a three-dimensional diffraction pattern. SCXRD is an extremely useful technique for analysis of solid-state materials as it facilitates the production of three-dimensional models of materials

via crystallography, which can provide high-resolution data on bond distances and angles, as well as information about connectivity, ions, ligand orientation and solvent presence. For polymeric structures, SCXRD can give information about crystal habits, pore spaces and guests.¹⁵⁰

1.12. Thesis Outline

Our aims are to elucidate electronic trends and relationships within a family of related ruthenium systems by leveraging several analytic techniques, including electrochemistry, spectroscopy, crystallography and density functional theory. By applying these analytical techniques to discrete, polymer and host-guest systems that incorporate similar Ru motifs, we hope to demonstrate similarities and differences between these systems, as well as trends that could lead to functionalised materials in the future.

Chapter 2 details the experimental details of syntheses and characterisations performed throughout this thesis.

Chapter 3 presents a detailed investigation of several discrete complex metalloligands belonging to the *trans*-[Ru(acac)₂X₂] family. This analysis provides extensive detail on the charge-transfer and redox-active behaviour of these complexes, as well as trends observed across the entire family. Several trends across the family are related due to the interplay between the d^5 - d^6 boundary, electronic contributions from ligands and strong π -backbonding behaviour.

Chapter 4 discusses coordination polymers constructed from metalloligands in Chapter 3. A comparison of their properties and the role of competing interactions within the metalloligands is provided.

Chapter 5 presents an analysis of an incorporated charge-transfer material, in order to investigate the mechanics of charge-transfer within a controlled, solid-state outer sphere environment. Comparisons between this new material and behaviour observed in discrete material are provided.

The reader will note the extensive nature of Chapter 3 compared to 4 and 5. This was required to properly identify trends fundamental to the discrete family, and provide context for later research.

Chapter 2

Experimental Procedures and Sample Preparation

2.1. Notes on Safety

Many of the techniques and materials detailed below are hazardous and require special training or equipment to safely handle. All hazardous materials were handled with appropriate PPE, including safety glasses, lab coat and nitrile/latex gloves. Open-source and Class 4 lasers were operated with laser safety glasses appropriate to the wavelength used. Volatile chemicals were handled within a fume cupboard, and were only removed from sealed containers. The reader should take particular note of the following hazardous chemicals:

Chloroform is a Category 2 suspected carcinogen, and a Category 2 suspected reproductive toxin.

Dichloromethane is a Category 2 suspected carcinogen.

N,N-Dimethyl formamide is a Category 1B presumed reproductive toxin.

Methanol is highly toxic to the central nervous system and retina, and potentially fatal if ingested.

2.2. Synthetic Procedures

2.2.1. Synthesis of tetraphenylphosphonium *trans*-bis(acetylacetonato)dichloridoruthenium(III), $\text{Ph}_4\text{P}\{\textit{trans}\text{-}[\text{Ru}(\text{acac})_2\text{Cl}_2]\}$:

A method by Hasegawa, *et al.* was adapted for the synthesis of this compound.⁴⁵ Acetylacetone (100 mL, 0.98 mol) was shaken with a small volume of aqueous NaOH (0.92 g, 0.04 mol, 20 mL), and then washed with water, until the washings were slightly basic. After acetylacetone (10 mL) was collected, the liquid was dried over activated 4 Å molecular sieves for 72 hr. The solvent was then distilled through a Vigreux Column into a sealed flask to produce a clear, colourless liquid.¹⁵¹

Ruthenium(III) trichloride hydrate (~ 2 g, ~ 10 mmol) was added to a flask containing aqueous KCl (0.75 g, 0.01 mol, 10 mL) and purified acetylacetone (10 mL, 0.098 mol). The mixture was refluxed for 30 min to give a dark red-purple mixture. The mixture was then carefully evaporated to dryness to remove any remaining acetylacetone. Water (50 mL) was then added to the solid and the flask was sonicated to ensure dissolution. The mixture was then filtered to remove any remaining solid.

Aqueous Ph₄PCl (1.79 g, 4.8 mmol, 10 mL) was prepared, and 1 mL was added to the mixture with stirring. A purple solid immediately precipitated, which was then filtered off and discarded. The remaining Ph₄PCl solution (9 mL) was then added to the mixture with stirring. The resulting orange precipitate was collected *via* filtration and washed with deionised water (~30 ml). A mixture of chloroform/acetonitrile (50 mL, 50% v/v) was added to the solid with stirring. The mixture was then filtered to remove a small mass of insoluble orange solid. The solution was then evaporated to dryness and dried overnight under vacuum.

The solid was then dissolved in a minimum volume of chloroform:acetonitrile (50% v/v), and run through a silica column (15 cm x 6 cm), with chloroform:acetonitrile (50% v/v) as the eluent. The first two fractions (light pink and purple) were discarded, and the third fraction (deep red) was collected. The third fraction was evaporated to dryness and the solid was recrystallised in methanol:acetone (50% v/v) to give large, deep red crystals. Many of these crystals were appropriate for single-crystal X-ray diffraction. Yield: 1.619 g, ~ 23%.

IR (neat, cm⁻¹): ν 1519 (m), 1434 (w), 1381 (m), 1265 (w), 1162 (m), 1106 (m), 722 (s), 693 (s), 659 (m), 525 (s), 455 (s). **UV-vis (cm⁻¹, M⁻¹cm⁻¹):** Exp (MeOH): λ_{max} (ϵ), 19,200 (1480) , 27,900 (6300), 36,200 (16,000). Lit (MeOH, Ph₄As{*trans*-[Ru(acac)₂Cl₂]}): λ_{max} (ϵ), 19,190 (1500), 26,600 (5300), 27,900 (5800), 36,000 (11,300), 36,800 (12,100), 37,700 (9800).⁴⁵

Elemental: Theoretical %: C: 57.55, H: 4.83, Experimental %: C: 57.58, H: 4.83.

2.2.2. Synthesis of *trans*-bis(acetylacetonato)dipyrazineruthenium(II), *trans*-[Ru(acac)₂(pyz)₂], (RuML1)

A method by Hasegawa, *et al.* was adapted for the synthesis of this compound.⁴⁵ Ph₄P{*trans*-[Ru(acac)₂Cl₂]} (132.9 mg, 0.19 mmol) and pyrazine (305 mg, 3.7 mmol) were dissolved in methanol (10 mL), and the solution was sparged with Ar for 30 min. At the same time, three small pieces of Zn amalgam were activated in dilute HCl (0.1 M), 50 mL for 20 min. The amalgam was washed with distilled water and methanol, then added to the mixture, which rapidly darkened. The reaction was sealed and refluxed under an N₂ or Ar atmosphere for 1 hr. The resulting solution was left to cool and the amalgam was collected *via* vacuum filtration, washed with DCM until all soluble material was removed from the filter. The filtrate was then evaporated to dryness, then thoroughly washed with water (200 mL) and diethyl ether (100 mL) to remove residual pyrazine, polar Ru salts and Ph₄P⁺ salts. The remaining dark purple solid was then dissolved in a minimum volume of chloroform and loaded onto an alumina column (Brockmann Grade I neutral, 9 cm x 6 cm). The first fraction (purple) was obtained with chloroform as the eluent. Other fractions were discarded. The product was evaporated to dryness and dried under vacuum overnight to give a deep purple crystalline solid in quantitative yield (91 mg).

The sample was crystallised by vapour diffusion. The sample was dissolved in chloroform in a small vial (2 mL), which was placed inside a larger vial (25 mL). The larger vial was then carefully filled up until just below the lip of the smaller vial with diethyl ether. The larger vial was then sealed and left overnight. The sample crystallised as thin purple needles.

IR (neat, cm⁻¹): ν 1570 (m), 1539 (w-m), 1512 (s), 1403 (m), 1005 (m), 823 (m), 617 (s). **UV-vis (cm⁻¹, M⁻¹cm⁻¹):** Exp (MeCN): λ_{max} (ϵ), 17,500 (14,800), 24,800 (8500), 36,500 (17,700), 38,600 (21,300). Lit (MeOH): λ_{max} (ϵ), 17,600 (14,000), 24,900 (9300), 36,800 (20,000),

38,800 (22,000). **MS** (ESI, MeCN): m/z calculated for $C_{18}H_{22}N_4O_4Ru$ $[M+H]^+$: 461.08, found: 460.05. **^1H NMR** (300 MHz, $CDCl_3$, ppm): δ 8.51 (s, 4H), 8.27 (d, 8.27, 8.28, 4H), 5.12 (s, 2H), 1.90 (s, 12H). **Elemental**: Theoretical %: N: 12.19, C: 47.05, H: 4.83, Experimental %: N: 12.11, C: 47.25, H: 4.59.

The above method was repeated on a smaller scale for the synthesis of *trans*-bis(acetylacetonate)di(pyrazine- d_4)ruthenium(II), employing pyrazine- d_4 (150 mg, 1.78 mmol). The only deviations between this compound and RuML1 are in vibrational spectroscopy and mass spectrometry. Yield: 35.4 mg, 81.4 %

IR (neat, cm^{-1}): ν 1535 (w-m), 1523 (m), 1512 (s), 1402 (m), 1332 (w), 1283 (m), 980 (s), 781 (m), 648 (m), 599 (s), 474 (s). **MS** (ESI, MeOH): m/z calculated for $C_{18}H_{14}D_8N_4O_4Ru$ $[M+H]^+$: 468.12, found: 468.06.

2.2.3. Synthesis of *trans*-bis(acetylacetonato)dipyrazineruthenium(III) Iodide, *trans*-[Ru(acac) $_2$ (pyz) $_2$]I, ([RuML1]I)

trans-[Ru(acac) $_2$ (pyz) $_2$] (2 mg, 4.4 mmol) was dissolved in DCM (5 mL) in a glass vial (25 mL). A small piece of I_2 (~ 1 mg, 7.9 mmol) was added to the vial. The mixture was then sonicated for 5 min, after which the dark purple solution had turned to a lighter orange. The vial was then opened and evaporated to dryness overnight to remove excess I_2 , and then dried under vacuum for 24 hr. The product was obtained as a deep orange solid in quantitative yield (2.6 mg).

IR (neat, cm^{-1}): ν 1590 (w), 1518 (s, br), 1420 (m), 1277 (s), 1062 (m), 937 (m), 810 (m), 691 (m), 501 (s). **Elemental**: Theoretical %: N: 9.56, C: 36.87, H: 3.78, Experimental %: N: 8.73, C: 36.99, H: 3.407. **MS** (ESI, MeOH): m/z calculated for $C_{18}H_{22}N_4O_4Ru$ $[M+H]^+$: 460.07, found: 460.03.

2.2.4. Synthesis of *trans*-bis(acetylacetonato)di(4,4'-bipyridine)ruthenium(II), *trans*-[Ru(acac)₂(bpy)₂], RuML2 and *trans*-bis(acetylacetonato)(4,4'-bipyridine)ruthenium(III) chloride, *trans*-[Ru(acac)₂(bpy)₂]Cl, ([RuML2]Cl)

Ph₄P{*trans*-[Ru(acac)₂Cl₂]} (132 mg, 0.19 mmol) and 4,4'-bipyridine (585 mg, 3.7 mmol) were dissolved in methanol (10 mL), and the solution sparged with Ar for 30 min. At the same time, three small pieces of zinc amalgam were activated in dilute hydrochloric acid (0.1 M, 50 mL) for 20 min. The amalgam was washed with distilled water and methanol, then added to the mixture, which rapidly darkened. The reaction was sealed and refluxed under an inert atmosphere for 1 hr. The resulting solution was left to cool, and the mixture filtered and washed from any zinc amalgam pieces with DCM.

Similar to RuML1, the crude product contained numerous impurities, including 4,4'-bipyridine, Ph₄P{*trans*-[Ru(acac)₂Cl₂]}, Ph₄P⁺ salts and the salt, [RuML2]Cl. This mixture was dried, washed with water and diethyl ether. The mixture was then dissolved in a minimum volume of chloroform and run through an alumina column (Brockmann Grade I neutral, 15 cm x 4 cm) with chloroform as the initial eluent. The first fraction (dark blue) was obtained by eluting the column with chloroform, and the second fraction (pink) was obtained by eluting the column with ethanol. Both fractions were evaporated to dryness and dried under vacuum for 24 hr. The dark blue fraction was RuML2 and the pink fraction was [RuML2]Cl. Further purification of [RuML2]Cl was performed by washing the solid with diethyl ether (50 mL). However, not all impurities could be removed.

The sample was crystallised by vapour diffusion, using the same method as RuML1. The sample crystallised as small blue-violet needles.

A further polymorph of the material was crystallised *via* vial-in-vial liquid diffusion of a chloroform solution of RuML2 into acetonitrile, after which RuML2 was obtained as large, brown, prismatic crystals.

[RuML2]Cl was crystallised by vapour diffusion. The sample was dissolved in ethanol in a small vial (2 mL), which was placed inside a larger vial (25 mL). The larger vial was then carefully filled up until just below the lip of the smaller vial with diethyl ether. The larger vial was then sealed and left overnight. The sample crystallised as deep red rods.

Yield: RuML2: 16.4 mg, 14.3 % RuML2Cl: 103.2 mg, 84.9 %

RuML2:

IR (neat, cm⁻¹): 2921 (m), 2851 (m), 1616 (w), 1592 (s), 1520 (m), br, 1505 (s), 1479 (s), 1399 (s), 1362 (m), 1231 (m), 1217 (w), 1008 (s), 991 (w), sh, 955 (w), 932 (m), 864 (w), 852 (w), 810 (s), 782 (m), 763 (m), 728 (m), 693 (w), 668 (w), 656 (w), 641 (m), 490 (m). **UV-vis** (cm⁻¹, M⁻¹cm⁻¹): Exp (DMF): λ_{max} (ϵ) 16,200 (14,000), 23,200 (9300), 38,000 (22,000). **MS** (ESI, MeCN): m/z calculated for C₃₀H₃₀N₄O₄Ru₁ [M+H]⁺: 613.14, found: 612.19. **Elemental:** Theoretical %: N: 9.16, C: 58.91, H% 4.94, Experimental %: N: 9.32, C: 58.85, H: 4.5.

RuML2Cl:

IR (neat, cm⁻¹): 1616 m, 1594 m, sh, 1585 m, 1521 (s br), 1483 m, 1438 s, 1403 m, 1362 m, br, 1278 m, 1106 vs, 1066 m, 1024 m, 986 m, 984 w, 936 m, 807 m, 770 m, 763 m, 757 m, sh, 750 m, 737 w, 722 s, 689 s, 629 m, 617 w, 608 m, 524 s, 466 m, 434 m. **UV-vis** (cm⁻¹, M⁻¹cm⁻¹): Exp (DMF): λ_{max} (ϵ), 18,300 (5400), 30,200 (11,600), 39,200 (24,700). **MS** (ESI, MeCN): m/z calculated for C₃₀H₃₀N₄O₄Ru₁ [M+H]⁺: 613.14, found: 612.16. **Elemental:** Theoretical %: N: 8.66, C: 55.68, H% 4.67, Experimental %: N: 8.16, C: 55.67, H: 5.223.

2.2.5. Synthesis of *trans*-bis(acetylacetonate)di(methyl-isonicotinate)ruthenium(II), *trans*-[Ru(acac)₂(Py(4-COOMe))₂], (RuML2.5)

Ph₄P{*trans*-[Ru(acac)₂Cl₂]} (132 mg, 0.19 mmol) and methylisonicotinate (0.4 mL, 3.4 mmol) were dissolved in methanol (10 mL), and the solution was sparged with Ar for 30 min. At the same time, three small pieces of zinc amalgam were activated in dilute hydrochloric acid (0.1 M, 50 mL) for 20 min. The amalgam was washed with distilled water and methanol, then added to the mixture, which rapidly darkened. The reaction was sealed and refluxed under an inert atmosphere for 1 hr. The resulting solution was left to cool, and the dark brown crystalline solid was collected *via* vacuum filtration and washed with methanol and acetone. The sample was purified using the same method as RuML1. Yield: 107 mg yield: 98 %

The sample was crystallised using the same method as RuML1.

IR (neat, cm⁻¹): 2953 (w), 1720 (s), 1587 (m), 1542 (m), 1508 (vs), 1423 (m), 1401 (s), 1314 (w), 1275 (vs), 1259 (vs), 1190 (s), ~1100 (multiple peaks) (m), 1045 (vw), 1020 (vw), 1002 (vs), 959 (w), 936 (w), 858 (m), 828 (w), 801 (vw), 785 (s), 771 (vs), 699 (s), 691 (s), 648 (s), 507 (w), 480 (m). **MS** (ESI, MeCN): *m/z* calculated for C₂₄H₂₈N₂O₈Ru [M+H]⁺: 575.10, found: 574.13 **Elemental:** Theoretical %: N: 4.88, C: 50.26, H% 4.92, Experimental %: N: 4.96, C: 50.28, H: 4.895.

2.2.6. Synthesis of *trans*-bis(acetylacetonate)bis(1,2-bis(4-pyridyl)ethylene)ruthenium(II), *trans*-[Ru(acac)₂(BPE)₂], (RuML4)

Ph₄P{*trans*-[Ru(acac)₂Cl₂]} (131.5 mg, 0.19 mmol) and 1,2-bis(4-pyridyl)ethylene (BPE) (683 mg, 3.75 mmol) were dissolved in methanol (10 mL), and the solution was sparged with Ar for 30 min. At the same time, three small pieces of zinc amalgam were activated in dilute hydrochloric acid (0.1 M, 50 mL) for 20 min. The amalgam was washed with distilled water and methanol, then added to the mixture, which rapidly darkened. The reaction was sealed and

refluxed under an inert atmosphere for 1 hr. The resulting solution was left to cool, and the dark green-purple solid was collected *via* vacuum filtration and washed through the filter paper with chloroform or DCM to remove any small pieces of zinc amalgam. The solution was evaporated to dryness and dried under vacuum for 24 hr.

As with RuML1 and RuML2, the crude product was a mixture of di(4,4'-ethylene)pyridyl, RuML4, [RuML4]Cl, RuMLPRE, Ph₄PCl and unidentified Ru oxides and hydrates. di(4,4'-ethylene)pyridyl proved very difficult to separate from [RuML4]Cl effectively, which affected yields and purity. The filtrate was evaporated to dryness, then washed with H₂O (50 mL). The mixture was immersed in diethyl ether (25 mL) and placed in an ultrasonic bath for 5 min to maximise dissolution of BPE. The mixture was then filtered, and the filtrate was dry-loaded onto an alumina column (Brockmann Grade I neutral, 6 cm x 15 cm) with chloroform as the eluent. The first fraction (dark green-blue) was obtained with chloroform as the eluent. The second fraction (light blue) was obtained with ethanol as the eluent. The first band contained RuML4 and some BPE, and the second band contained [RuML4]Cl and small quantities of BPE. Crystallography suggested that [RuML4]Cl contained chloroform molecules.

Both fractions were evaporated to dryness and dried under vacuum to give a dark blue-green powder of [Ru(acac)₂(BPE)₂]. RuML4 Yield: 11.1 mg, 9.0 % [RuML4]Cl Yield: 78.1 mg, 60.4 %

[RuML4]Cl was crystallised *via* vapour diffusion of hexane into a saturated chloroform solution of crude RuML4. The sample crystallised as small, dark violet needles.

RuML4:

IR (neat, cm⁻¹): 2990 (m), 2972 (m), 2901 (m), 1632 (w), 1612 (w), 1590 (s br), 1533 (m), 1509 (s), 1405 (s br), 1394 (s), 1259 (m), 1249 (m), 1241 (m), 1075 (m), 1067 (s), 1058 (s), 1053 (m), 1028 (m), 1010 (s), 998 (m), 989 (m), 971 (m), 965 (m), 935 (m), 892 (m), 879 (m),

827 (s), 668 (m), 650 (m), 641 (m), 552 v(s), 431 w. **UV-vis** (cm^{-1} , $\text{M}^{-1}\text{cm}^{-1}$): Exp (MeCN): λ_{max} (ϵ), 15,200 (9100), 23,100 (6900), 34,900 (26,000) (b). **MS** (ESI, MeOH): m/z calculated for $\text{C}_{34}\text{H}_{34}\text{N}_4\text{O}_4\text{Ru}$ $[\text{M}+\text{H}]^+$: 664.16, found: 664.27. **Elemental**: Theoretical %: N: 8.44, C: 61.53, H: 5.16, Experimental %: N:8.55, C: 61.56, H: 5.4.

[RuML4]Cl:

IR (neat, cm^{-1}): 2990 m, 2972 m, 2901 m, 1612 m, 1596 m, 1518 s, br, 1411 m, 1394 w, 1373 m, 1362 m, 1347 m, 1342 m, 1278 m, 1241 m, 1209 m, 1109 m, 1074 m, 1066 s, 1058 s, 1053 m, 1028 m, 991 m, 979 s, 937 m, 831 vs, 797 s, 781 m, 725 m, 721 m, 696 m, 668 m, 652 m, 554 vs, 527 s, 470 s, 461 m, 429 m. **UV-vis** (cm^{-1} , $\text{M}^{-1}\text{cm}^{-1}$): Exp (MeCN): λ_{max} (ϵ), 19,300 (3100), ~27,000 (br) (11,000), 33,600 (27,000). **MS** (ESI, MeOH): m/z calculated for $\text{C}_{34}\text{H}_{34}\text{N}_4\text{O}_4\text{RuCl}$ $[\text{M}+\text{H}]^+$: 664.16, found: 664.19. **Elemental**: Theoretical % calculated for $\text{C}_{34}\text{H}_{34}\text{N}_4\text{O}_4\text{RuCl} \cdot 2.16(\text{CHCl}_3) \cdot 1.78(\text{EtOH})$: N: 5.39, C: 45.91, H: 4.54, Experimental %: N: 5.02, C: 46.26, H: 4.172.

2.2.7. Synthesis of *trans*-bis(acetylacetonato)dipyridineruthenium(III) chloride, *trans*-[Ru(acac)₂(py)₂]Cl, (RuML0)

$\text{Ph}_4\text{P}\{\text{trans}[\text{Ru}(\text{acac})_2\text{Cl}_2]\}$ (132 mg, 0.19 mmol) and pyridine (300 mg, 3.7 mmol) were dissolved in methanol (10 mL), and the solution was sparged with Ar for 30 min. At the same time, three small pieces of zinc amalgam were activated in dilute hydrochloric acid (0.1 M, 50 mL) for 20 min. The amalgam was washed with distilled water and methanol, then added to the mixture, which rapidly darkened. The reaction was sealed and refluxed under an inert atmosphere for 1 hr. The resulting solution was left to cool, and the dark brown solid was collected *via* vacuum filtration, washed with methanol (15 mL) and diethyl ether (15 mL), and the filtrate was retained. The solid was then washed from the filter paper with chloroform or DCM (20 mL) to remove any small pieces of zinc amalgam. Yield: 36.0 mg, 42.3 %.

The sample was crystallised into several polymorphs.

Crystals of RuML0 and [RuML0]Cl were both obtained by slow evaporation of an acetonitrile solution. RuML0 crystallised as dark red needles, while [RuML0]Cl crystallised as dark red plates.

[RuML0]Cl·2MeOH was crystallised *via* slow vapour diffusion of diethyl ether into a methanol solution of crude RuML0. The sample crystallised as deep red plates.

IR (neat, cm⁻¹): 1591 (m), 1560 (m), 1534 (m), 1511 (s), 1470 (m), 1445 (w), 1404 (s), 1344 (m), 1279 (w), 1260 (m), 1243 (w), (sh), 1203 (m), 1146 (m), 1062 (m), 1041 (w), 1015 (m), 997 (s), 930 (s), 864 (w), 779 (s), 766 (s), 689 (s), 660 (w), 640 (s), 629 (s), 489 (m), 437 (m). **UV-vis** (cm⁻¹, M⁻¹cm⁻¹): Exp (MeCN): λ_{max} (ϵ), 20,000 (19,000), 22,400 (22,000), 36,200 (25,000), 40,100 (17,000). **MS** (ESI, MeCN): *m/z* calculated for C₂₀H₂₄N₂O₄Ru [M+H]⁺: 458.08, found: 458.05. **Elemental:** Theoretical %: N: 5.68, C: 48.73, H: 4.91, Experimental %: N: 5.67, C: 48.43, H: 4.98.

2.2.8. Synthesis of [Ag(RuML2)₂](SbF₆)_n

[Ru(acac)₂(bpy)₂]Cl (12.2 mg, 0.02 mmol) was measured into a small vial (2 mL). Silver hexafluoroantimonate (6.8 mg, 0.03 mmol) was measured into a large vial (25 mL). A vial-in-vial liquid diffusion was set up, with chloroform in the small vial, and ethanol in the large vial. The reaction was left undisturbed for at least two weeks, after which [Ag(RuML2)₂](SbF₆)_n was obtained as small red plates. The crystals were separated by hand, as oxide powder was also present in the reaction vessel. Single crystals were obtained from the reaction vessel for diffraction experiments. The yield was not calculated due to the difficulty in isolating the crystals from the powder.

IR (neat, cm⁻¹): 1605 (w), 1518 (m), 1488 (w), 1429 (w), 1413 (w), 1413 (w), 1355 (m), 1338 (w), 1278 (w), 1219 (w), 1095 (w), 1068 (w), 1046 (m), 1028 (m), 1005 (w), 940 (w), 819 (m),

730 (w) 690 (w), 668 (w), 657 (w), 637 (m), 487 (w), 470 (m), 435 (w) **UV-vis** (cm^{-1}): Exp (Solid-state): λ_{max} , 18,000, ~29,900 (br).

2.2.9. Synthesis of $[\text{Ag}_n(\text{RuML2})_n](\text{PF}_6)_n$

The above reaction was repeated with silver hexafluorophosphate (5 mg, 0.02 mmol). The product was obtained as small red crystals. The crystals were removed by hand, as oxide powder was also present in the reaction vessel. The yield was not calculated due to the difficulty in isolating the crystals from the powder.

2.2.10. Synthesis of $[\text{ZnCl}_2(\text{RuML4})]$

trans- $[\text{Ru}(\text{acac})_2(\text{BPE})_2]\text{Cl}$ (13 mg, 0.02 mmol) was measured into a small vial (2 mL). Zinc chloride (1.5 mg, 0.01 mmol) was measured into a large vial (25 mL). A vial-in-vial liquid diffusion was set up, with chloroform in the small vial, and ethanol in the large vial. The reaction was left undisturbed for two weeks, after which $[\text{ZnCl}_2(\text{RuML4})]$ was obtained as small red-purple crystals. The crystals were removed by hand, as oxide powder and other solid impurities were also present in the reaction vessel. Single crystals were obtained from the reaction vessel for diffraction experiments. The yield was not calculated due to the difficulty in isolating the crystals from impurities.

IR (neat, cm^{-1}): 2966 (m), 1615 (s), 1594 (m), 1532 (m), 1511 (s), 1404 (m), 1367 (w), 1336 (m), 1279 (w), 1263 (m), 1219 (m), 1198 (m), 1065 (m), 1045 (m), 1030 (s), 1007 (s), 973 (m), 933 (m), 882 (s), 832 (s), 774 (m), 661 (m), 644 (s), 569 (m), 551 (s), 437 (m). **UV-vis** (cm^{-1}): Exp (Solid-state): λ_{max} : ~18,000, ~25,000 (br).

2.2.11. Synthesis of $[\text{ZnBr}_2\text{RuML4}]$

trans- $[\text{Ru}(\text{acac})_2(\text{BPE})_2]\text{Cl}$ (13 mg, 0.02 mmol) was measured into a small vial (2 mL). Zinc bromide (2.5 mg, 0.01 mmol) was measured into a large vial (25 mL). A vial-in-vial liquid diffusion was set up, with chloroform in the small vial, and ethanol in the large vial. The

reaction was left undisturbed for at least 2 weeks, after which $[\text{ZnCl}_2\text{RuML}_4]$ was obtained as small red-purple crystals. The crystals were removed by hand, as oxide powder and other solid impurities were also present in the reaction vessel. Single crystals were obtained from the reaction vessel for diffraction experiments. The yield was not calculated due to the difficulty in isolating the crystals from impurities.

IR (neat, cm^{-1}): 1612 (w), 1591 (w), 1519 (m), 1432 (w), 1411 (w), 1360 (m), 1347 (w), 1276 (m), 1230 (w), 1204 (m), 1025 (m), 975 (m), 937 (w), 838 (m), 829 (m), 751 (m), 689 (m).

UV-vis (cm^{-1}): Exp (Solid-state): λ_{max} : $\sim 18,000$, $\sim 25,000$ (br).

2.2.12. Synthesis of pentaammine(chlorido)ruthenium(III) chloride, $[\text{RuCl}(\text{NH}_3)_5]\text{Cl}_2$

The synthetic procedure of this material was adapted from that of Allen *et al.*¹⁵² $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (2 g, ~ 10 mmol) was dissolved in water (10 mL) in a sealed reaction vessel with an outlet tube. Hydrazine hydrate (80 %, 20 mL, 0.5 mol) was carefully added dropwise over 1 hr with stirring. Vigorous effervescence and an exothermic reaction were observed. The reaction was left to stir overnight.

The mixture was then filtered, and the filtrate was retained. The pH of the mixture was then adjusted carefully with hydrochloric acid (0.1 M), until the pH value was measured at 2. The mixture was then boiled with stirring, which precipitated a yellow solid. The solution was boiled until no more precipitation was observed. The solid was extracted *via* vacuum filtration and washed with aqueous hydrochloric acid (0.1 M, 5 mL) and diethyl ether (25 mL).

The product was purified *via* recrystallisation in hydrochloric acid. First the crude $[\text{RuCl}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (3 g) was added to water (10 mL), which was then heated to 60 °C with stirring. Concentrated ammonia solution was then added dropwise until the complex dissolved

to give a wine-red solution. The solution was filtered hot, and the filtrate was cooled in an ice bath. Concentrated hydrochloric acid was added to precipitate the product.

IR (neat, cm^{-1}): 3150 (m,b), 1603 (m), 1300 (s), 800 (m). **Elemental:** Theoretical %: N: 23.94, C: 0.00, H: 5.17, Experimental %: N: 24.48, C: 0.0, H: 5.12.

2.2.13. Synthesis of pentaammine(dinitrogen)ruthenium(II) chloride, $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]\text{Cl}_2$

The synthetic procedure of this material was adapted from that of Allen *et al.*¹⁵² A slurry of $[\text{RuCl}(\text{NH}_3)_5]\text{Cl}_2$ (1 g, 3.5 mmol) in water (25 mL) was heated to 60 °C with stirring. Concentrated ammonia solution (~ 1 mL) was added dropwise until the solid dissolved to give a wine-red solution.

The solution was then cooled on an ice bath. Methane sulfonic acid (~ 5 mL) was carefully added dropwise with stirring until the solution was at pH 2. The solution became a light red colour as the solution became more acidic.

Sodium azide (5 g, 77 mmol) was added to the mixture with slow stirring. The colour of the solution immediately changed to a red-orange (note: this colour is due to the presence of $[\text{Ru}(\text{N}_3)(\text{NH}_3)_5]^{2+}$ ions,¹⁵² which is explosive out of solution. Under no circumstances should solid be precipitated at this point, and the precipitation step should not be performed until the solution is no longer red, or has been left in acidic conditions for at least 10 hr.). Methane sulfonic acid was carefully added dropwise to the solution, to maintain the pH value at 2-3. At pH 3, the solution began to effervesce gently. The reaction was monitored for several hours and then left until the colour changed to yellow.

The solution was placed in an ice bath, and sodium chloride (4.5 g, 0.077 mol) was added to precipitate the product as a light orange-yellow powder over 1 hr. The product was then collected *via* vacuum filtration and washed with ethanol and acetone.

Yield: 0.808 g, 81.2 %.

IR (neat, cm^{-1}): 3150 (m, b), 2070 (m), 1603 (m), 1300 (s), 800 (m). **Elemental:** Theoretical %: N: 34.39, C: 0.00, H: 5.30, Experimental %: N: 25.57, C: 0.36, H: 5.19.

2.2.14. Synthesis of pentaammine(trifluoromethanesulfonato)ruthenium(III) trifluoromethanesulfonate, $[\text{Ru}(\text{OSO}_2\text{CF}_3)(\text{NH}_3)_5](\text{CF}_3\text{SO}_3)_2$

This synthetic procedure was adapted from the literature.¹⁵³ $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]\text{Cl}_2$ (0.72 g, 2.5 mmol) was dissolved in trifluoromethanesulfonic acid (10 mL, 0.11 mol). The solution was sparged with Ar in a sealed round bottom flask. Bromine (0.5 mL, 10 mmol) was injected into the mixture, and the vessel was heated to 55 °C. After 15 min, the reaction was then heated to 110 °C and left for at least 15 min, and only cooled when bromine gas was not visible in the vessel. The solution was then cooled in an ice bath, and diethyl ether (30 mL) was carefully added dropwise with stirring. A light yellow or grey precipitate formed immediately, and the vessel was kept in a fridge overnight. The product was collected by vacuum filtration and washed with diethyl ether (50 mL). The product cannot be purified further, as dissolution of the complex causes substitution of the triflate ligand. The pure product is a light grey colour, yellow colouring is due to the presence of $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$.

Yield: 1.37 g, ~ 86 %.

IR (neat, cm^{-1}): 3300 (m, b), 1634 (w-m), 1230 (s), 1175 (s), 1024 (s), 1007(s), 814 (m), 625 (s) **Elemental:** Theoretical %: N: 11.06, C: 5.69, H: 2.39, S: 15.18, Experimental %: N: 10.27, C: 5.39, H: 2.83, S: 13.41.

2.2.15. Synthesis of decaammine- μ -(pyrazine)diruthenium(II) chloride, $[(\text{NH}_3)_5\text{Ru}(\mu\text{-pyz})\text{Ru}(\text{NH}_3)_5]\text{Cl}_4\cdot\text{H}_2\text{O}$

Pyrazine (4 mg, 0.05 mmol) was dissolved in dry acetone (1 mL) in a micro-test tube. The solution was sparged with Ar and $[\text{Ru}(\text{OSO}_2\text{CF}_3)(\text{NH}_3)_5](\text{CF}_3\text{SO}_3)_2$ (45.5 mg, 0.07 mmol) was added and the reaction sealed. The mixture was stirred overnight, with a colour change from light yellow to cloudy red was observed. The test tube was opened and aqueous HCl (0.2 M) was added. The crude product contained the dimer $[(\text{NH}_3)_5\text{Ru}(\mu\text{-pyz})\text{Ru}(\text{NH}_3)_5]\text{Cl}_4\cdot\text{H}_2\text{O}$ and the monomer $[(\text{NH}_3)_5(\text{pyz})\text{Ru}]\text{Cl}_2\cdot\text{H}_2\text{O}$. The mixture was purified by cation exchange chromatography, with dilute hydrochloric acid (0.0001 M) as the eluent.

Yield: $[(\text{NH}_3)_5\text{Ru}(\mu\text{-pyz})\text{Ru}(\text{NH}_3)_5]\text{Cl}_4\cdot\text{H}_2\text{O}$: 21.1 mg, 43.0 %; $[(\text{NH}_3)_5(\text{pyz})\text{Ru}]\text{Cl}_2\cdot\text{H}_2\text{O}$:

$[(\text{NH}_3)_5\text{Ru}(\mu\text{-pyz})\text{Ru}(\text{NH}_3)_5]\text{Cl}_4\cdot\text{H}_2\text{O}$:

IR (neat, cm^{-1}): 1586 (m, br), 1435 (w), 1418 (w), 1370 (w), 1329 (s), 1310 (s), 1150 (m), 840 (s), 774 (s), 549 (w), 506 (w), 463 (w) **UV-vis (cm^{-1}):** Exp (H_2O): λ_{max} : 17,800, 38,900.

2.2.16. Synthesis of pentaamine(pyrazine)ruthenium(II) triflate, $[(\text{NH}_3)_5\text{Ru}(\text{pyz})](\text{CF}_3\text{SO}_3)_2$

This reaction was adapted from the literature.¹⁵³ Pyrazine (10 g, 0.12 mol) was heated to 70 °C under N_2 with stirring. $[\text{Ru}(\text{OSO}_2\text{CF}_3)(\text{NH}_3)_5](\text{CF}_3\text{SO}_3)_2$ (0.29 g, 0.45 mmol) was added and the mixture was stirred for 2 hr. The reaction was allowed to cool, then washed with diethyl ether (50 mL) to obtain a purple solid.

Yield: 140 mg, 56 %

IR (neat, cm^{-1}): 1625 (m, br), 1350 (m), 1242 (s), 1226 (s), 1170 (m), 1026 (s), 811 (m), 629 (s), 577 (w), 518 (m), 485 (w) **UV-vis (cm^{-1}):** Exp (H_2O): λ_{max} : 21,200, 33,400, 38,400.

2.2.17. Synthesis of Ru(pyz)@UiO-66-(HSO₃)₂

Pyrazine (8 mg, 0.1 mmol) and UiO-66-(HSO₃)₂ (50 mg) were added to diethyl ether (2 mL) and stirred in a sealed container for 30 min. The mixture was then dried under vacuum overnight. [Ru(OSO₂CF₃)(NH₃)₅](CF₃SO₃)₂ (90 mg, 0.14 mmol) was dissolved in dry acetone (1 mL) and the activated pyz@UiO-66-(HSO₃)₂ was added. The mixture was sparged with Ar, sealed and stirred overnight. The product was then filtered and washed with acetone and dried under vacuum overnight. Ru(pyz)@UiO-66-(HSO₃)₂ was obtained as a light pink powder.

Yield: 23.0 mg

IR (neat, cm⁻¹): 1658 (m), 1581 (s), 1487 (w), 1417 (s), 1331 (w), 1233 (m), 1174 (s), 1120 (s), 1020 (s), 780 (w), 654 (s), 481 (s) **UV-vis (cm⁻¹):** Exp (Solid-state): 18,800, ~ 35,000 (sh), 41,300.

2.3. Experimental Methods

2.3.1. Electrochemistry

Cyclic voltammetry (CV) was performed using a BASi Epsilon potentiostat, employing *iR* compensation. The degree of compensation varied between experiments due to inconsistencies in electrode position and small differences in electrolyte concentration (Appendix A). The electrode configuration differed depending on the experiment. Before measurements were performed, the electrolyte solutions were sparged with Ar for approximately 30 min. The solutions remained under Ar for the duration of the experiment. Background measurements were taken that corresponded to the scan ranges and rates used for the analyte. This was performed for two reasons; to determine that the electrochemical cell, electrodes and electrolyte contained no contaminants or faults, and to provide an electrochemical profile of the electrolyte

that could later be subtracted from that of the sample for accurate determination of the peak current i . This value was one factor required to identify the reversibility of a redox reaction.

Spectroelectrochemical (SEC) measurements were performed using an eDAQ e-corder 410 potentiostat. For solution-state UV-vis-NIR SEC, the working electrode was platinum gauze, the counter electrode was platinum wire and the reference electrode was silver wire immersed in the electrolyte solution to form an Ag^+/Ag *quasi*-reference electrode, or an Ag/AgCl electrode in KCl (0.1 M) for aqueous measurements. SEC measurements involving single-process, reversible oxidations were performed in atmospheric conditions. This was done due to the proclivity of the electrolyte to evaporate over the several hours required for a full measurement, thereby increasing the concentration of the analyte and preventing accurate data collection. For all other experiments, sample solutions were sparged with Ar for approximately 30 min beforehand. The samples remained under Ar for the duration of the experiment.

For IR SEC, the working electrode was a IRUBIS Universal basic single reflection ATR crystal wafer coated with a thin layer (~ 20 nm) of indium tin oxide (ITO), deposited *via* radio frequency sputter deposition. The layer was annealed at 300 °C for 1 hr to decrease resistance and to provide a conductive layer on the top face of the crystal.¹⁵⁴ The exposed face of the working electrode was a flat circle with a 6 mm diameter. The counter electrode was coiled Pt wire. For aqueous measurements, the reference electrode was an Ag/AgCl wire immersed in a saturated KCl solution in a glass casing with a CoralPor[®] tip. For non-aqueous measurements, the reference electrode was an Ag^+/Ag wire.

Solution-state bulk electrolysis was performed in a standard single vial electrochemical cell, with stirring. The working electrode was carbon sponge, the counter electrode was coiled Pt wire and the reference electrode was an Ag^+/Ag wire. The electrolyte was KCl (0.1 M) in H_2O , pH = ~ 5 . To generate the oxidised complexes $[(\text{NH}_3)_5\text{Ru}^{\text{III}}(\text{pyz})]^{3+}$ and $[(\text{NH}_3)_5\text{Ru}^{\text{III}}(\mu-$

pyz)Ru^{III}(NH₃)₅]⁶⁺, the samples were stirred as the potentiostat was set to 1 V vs. Ag⁺/Ag for approximately 30 min. After the redox process was fully complete (based on colour change), a small volume of the solution was extracted with a syringe, and placed in a quartz cuvette with path length 1 cm. The spectrum of the solution was then recorded with a Cary5000 spectrometer.

An Ag/AgCl reference electrode was prepared according to the method detailed by Rootare and Powers.¹⁵⁵ A silver wire was cleaned with 70% nitric acid, sanded with P1200 sandpaper and washed with water. The wire was then connected to a potentiostat as the working electrode and another cleaned silver wire as the counter electrode. The wires were immersed in HCl (1.0 M) and a potential of 120 mV was applied to the system for 5 min. A dark purple layer quickly formed on the wire, which was then washed with deionised water and placed within a Vycor-capped electrode house, filled with KCl (0.1 M) solution. The electrode was stored long term in a KCl (0.1 M) solution.

2.3.1.1. Sample Preparation: Cyclic Voltammetry

For the CVs of Ph₄P{*trans*-[Ru(acac)₂Cl₂]}, RuML1, RuML2, RuML4, RuML0 and [ZnX₂RuML4] (X = Cl, Br), the electrolyte was tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) (0.1 M) dissolved in HPLC grade acetonitrile. TBAPF₆ electrolytes were prepared from TBAPF₆, recrystallised three times from ethanol. Ferrocene was purified by sublimation.¹⁵⁶ The working electrode was a glassy carbon cylinder with a diameter of 1 mm. Before analysing a new sample, the electrode was thoroughly polished on a Buehler Microcloth polishing pad with alumina slurry, then washed with water and methanol. For solid-state experiments, the crystalline solid was mixed into a slurry on a glass slide and then ground onto the surface of the electrode, after which the solvent was allowed to dry. The counter electrode was coiled Pt wire. Before analysing a new sample, the wire was dipped in nitric acid (70%), washed with water and acetone and then placed in a blowtorch flame until red hot. The

reference electrode was a silver wire, used *in situ* as an Ag^+/Ag *quasi* reference electrode. Before analysing a new sample, the wire was sanded until shiny with P1200 grade sandpaper, then washed with deionised water and acetone.

The majority of solution-state experiments in this work involved samples that were insoluble in aqueous media, with redox processes close to or overlapping the ferrocene redox couple at 0.56 V vs. Normal Hydrogen Electrode (NHE). As a result, electrochemical measurements were performed twice, once in the presence of ferrocene, and once without. Figures relating to these measurements did not include the ferrocene redox process for the sake of clarity but were adjusted to the standard V vs. Fc^+/Fc reference used for non-aqueous electrochemistry.

Due to the limited solubility of RuML1, 2 and 4 in acetonitrile, the signals observed in CV experiments were generally in the μA range. Consequently, electromagnetic noise believed to originate from mains power in the laboratory produced a sinusoidal pattern in many CV experiments, particularly in scans recorded between 400 and 800 mV/s. To mitigate the effect this interference, a Faraday cage was employed for all experiments described in Chapters 3 and 4. Unfortunately, the cage was not able to eliminate all the interference, and these patterns are still observable in much of the electrochemical data within this work. This resulted in a small source of uncertainty in electrochemical data.

RuML1, RuML2 and RuML4:

The electrolyte was TBAPF_6 (0.1 M) in HPLC grade acetonitrile (~ 10 mL). Due to the poor solubility of RuML1, RuML2 and RuML4 in acetonitrile, the solutions were brought to their saturation points (1-5 mg of all samples) *via* ultrasonication. Measurements involving ferrocene were performed with an approximately equimolar quantity of ferrocene (~ 1 mg) to maintain the sensitivity of the instrument.

$\text{Ph}_4\text{P}\{\text{trans}[\text{Ru}(\text{acac})_2\text{Cl}_2]\}$ and RuML0:

The electrolyte was TBAPF₆ (0.1 M) in HPLC grade acetonitrile (~ 10 mL). The sample (~15 mg) was dissolved in the electrolyte *via* swirling. Measurements involving ferrocene were performed with an approximately equimolar quantity of ferrocene (~ 3 mg).

[Ag(RuML2)₂](SbF₆)₃·*n*EtOH, [ZnX₂(RuML4)]·*n*EtOH (X = Cl, Br):

The electrolyte was TBAPF₆ (0.1 M) in HPLC grade acetonitrile (~ 10 mL). The samples were pipetted as a suspension onto a glass slide. Before the solvent evaporated fully, the sample was ground onto the working electrode, ensuring the glassy carbon was sufficiently covered. The working electrode was quickly immersed in the electrolyte to prevent degradation of the sample. Measurements involving ferrocene were performed with a small mass of ferrocene (~1 mg).

UiO-66-(HSO₃)₂ and CTI@UiO-66-(HSO₃)₂:

For the electrochemical analysis of UiO-66-(HSO₃)₂ and CTI@UiO-66-(HSO₃)₂, a glassy carbon electrode with diameter 1 mm was employed, upon which the sample was drop cast and pressed onto the electrode. Electrolytes were TBAPF₆ (0.1 M) in MeCN (~ 10 mL), LiCl (0.1 M) in MeCN (~ 10 mL), LiBF₄ (0.1 M) in DMF (~ 10 mL), KCl (0.1 M) in D₂O (~ 10 mL), pH = ~ 5. The counter electrode was a coiled Pt wire, and the reference electrode was Ag⁺/Ag. Cleaning procedures for the counter and reference electrodes were identical to those detailed above.

2.3.2. X-Ray Diffraction

2.3.2.1. Single-Crystal X-Ray Diffraction

Three different instruments were used for single-crystal X-ray diffraction (SCXRD) experiments. Instruments were chosen based on crystal size and quality, as well as instrument availability. An Agilent Technologies SuperNova Dual Source diffractometer with an Atlas

CCD detector was used with mirror-monochromated Cu-K α ($\lambda = 1.54178 \text{ \AA}$) and Mo-K α ($\lambda = 0.71073 \text{ \AA}$) X-rays from a SuperNova microfocus source. A Bruker APEX2 FR591 diffractometer with a Bruker APEX-II CCD detector was used with mirror-monochromated Mo-K α ($\lambda = 0.71073 \text{ \AA}$) X-rays from an Incoatec I μ S 2.5 source. Both diffractometers were equipped with an Oxford Cryosystems Cryostream 700. Diffraction experiments were performed at 100 K and room temperature (Appendix B).

Weakly diffracting samples were measured at the macromolecular crystallography (MX2) beamline at the Australian Synchrotron. The instrument was equipped with an EIGER X 16M pixel detector, and X-rays were delivered by an in-vacuum undulator source from the 3 GeV synchrotron storage ring.¹⁵⁷

Single crystals were placed on glass slides as dry crystals or suspensions in the mother liquor. Crystals were immobilised with Paratone-N oil, and then loaded onto loops for analysis.

Reflection intensities were integrated from a sphere of data recorded in 1° increments about ω rotation. Unit cell determination, data integration, frame scaling, and absorption corrections were performed in CrysAlisPro or APEX2.¹⁵⁸⁻¹⁵⁹ Structure solutions were obtained by dual-space iterative methods from SHELXT and were refined by a full-matrix least-squares on all unique F² values using SHELXL within OLEX2 v1.3.¹⁶⁰⁻¹⁶² Non-hydrogen atoms were refined with anisotropic thermal parameters, except where otherwise stated, with hydrogen atoms being added geometrically and refined using riding thermal parameters. The full details used in each structure refinement model can be found in the respective crystallographic information file (CIF). PLATON SQUEEZE was used to account for disordered solvent molecules that could not be sensibly modelled.¹⁶³ Molecular graphics were generated from CrystalMaker® v10.7.3.¹⁶⁴

2.3.2.2. Powder X-Ray Diffraction

Powder X-ray diffraction (PXRD) was performed on a PANalytical X'Pert Powder diffractometer for flatplate measurements, with a Cu-K α ($\lambda = 1.54178 \text{ \AA}$) X-ray source. Flatplate measurements were loaded as dry, crystalline powders onto zero diffraction silicon plates.

Measurements covered a 2θ range of 4-50°, with a data interval of 0.0263°, and step time of 1.67 s.

2.3.3. X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Fisher K-Alpha⁺ instrument. Samples were dried under vacuum overnight before loading onto adhesive squares on the XPS sample plate. Samples were analysed with general surveys as well as for specific elements, including Ru, Cl, N, C and O. Each scan contained 30 accumulations. Two points were analysed per sample to ensure homogeneity.

2.3.4. Elemental Microanalysis

Samples were sent to the Elemental Microanalysis Service in the Department of Molecular Sciences at Macquarie University. Samples were run on Vario MICRO cube elemental analysers using an electronic micro balance, and analysed for C, N and H by technical staff.

2.3.5. Ultraviolet-Visible-Near-Infrared Spectroscopy

Solution-state and solid-state diffuse reflectance spectroscopy in the ultraviolet, visible and near-infrared regions was performed with an Agilent Cary 5000 Spectrophotometer, except where stated otherwise.

Solution-state spectroscopy was performed in a 1 cm quartz cuvette, with the instrument in single-beam mode. Scans were taken between 5000 and 55000 cm^{-1} , with a bandwidth of 2 nm. Spectral resolution varied between experiments (Appendix A).

Solid-state diffuse reflectance spectroscopy was performed using a Harrick UV-Vis-NIR Praying Mantis diffuse reflectance accessory. Baseline measurements were performed using BaSO_4 , and the solid sample was diluted in BaSO_4 before loading in the sample compartment. Scans were taken between 5000 and 50000 cm^{-1} with a spectral resolution of 11 cm^{-1} .

Solution-state SEC was performed using the Optically Transparent Thin Layer Electrochemical (OTTLE) cell (Figure 2.1).¹⁶⁵⁻¹⁶⁶ The OTTLE cell was constructed of quartz and includes a thin cuvette with path length 0.5 mm, attached to a tubular body used to house the working and reference electrodes. Thin platinum gauze was placed within the cuvette (in the beam path) and a platinum wire was run from the gauze to the top of the cell to form the working electrode. An Ag^+/Ag reference electrode and a coiled Pt counter electrode were placed in separate sintered glass frits filled with the electrolyte solution, which were then placed within the tube section of the OTTLE cell. The cell was fitted with a Teflon lid with holes for the three electrodes and one for a sparging needle to prevent oxygen from entering the solution. The cell was then mounted within a custom Teflon block, used to immobilise the cell and support the structure. Measurements were taken in dual beam mode, and a piece of Pt gauze was placed in the second beampath to ensure consistent results.

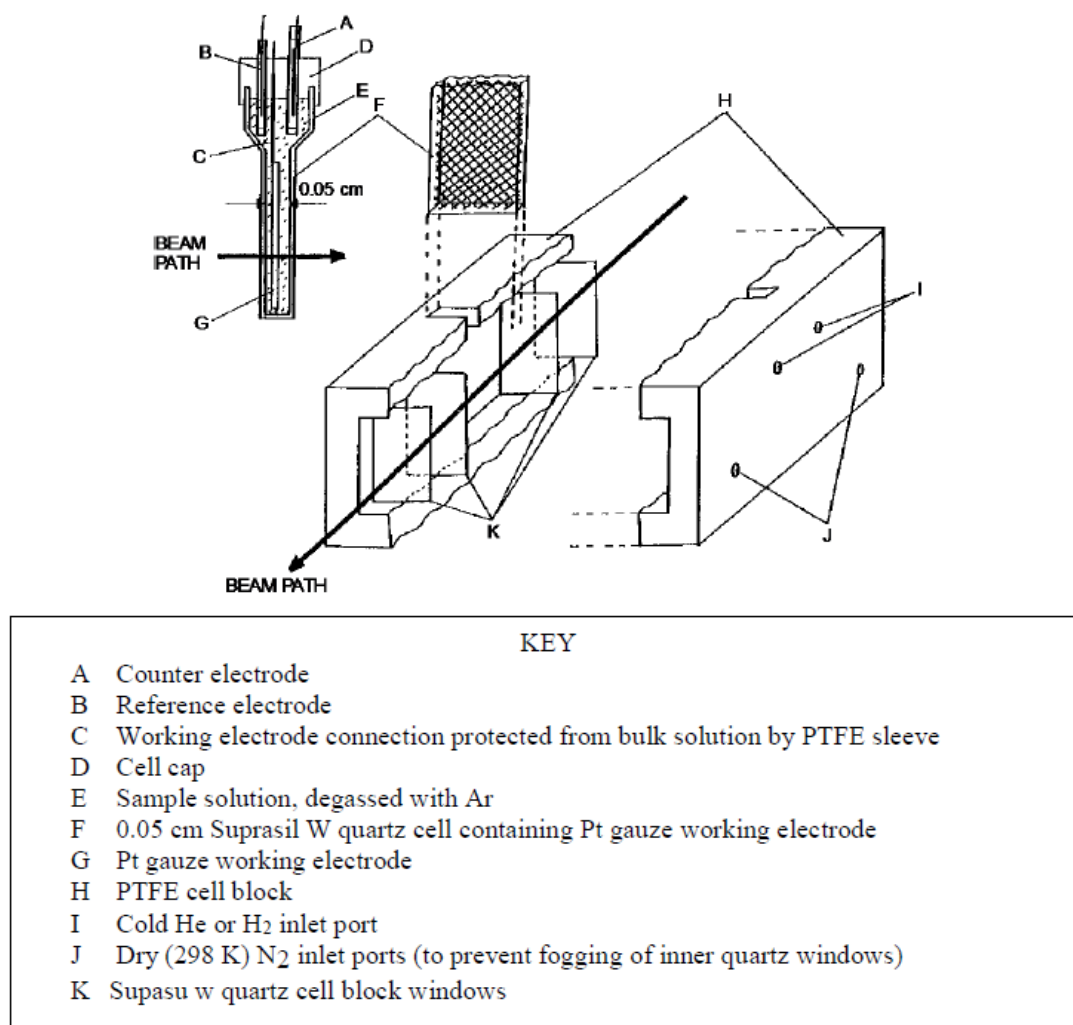


Figure 2.1. Schematic of the OTTLE cell, used for UV-vis-NIR spectroelectrochemistry.¹⁶⁵⁻¹⁶⁶

2.3.5.1. Sample Preparation

$\text{Ph}_4\text{P}\{\text{trans-}[\text{Ru}(\text{acac})_2\text{Cl}_2]\}$:

For solution-state spectroscopy the solvent was HPLC grade methanol (10 mL). The sample (5.3 mg, 0.0075 mmol) was dissolved in the solvent to give a solution of concentration 0.75 mM.

RuML1 :

For solution-state spectroscopy the solvent was HPLC grade chloroform (10 mL). The sample (1.3 mg, 0.0028 mmol) was dissolved in the solvent, giving a solution of concentration 0.028

mM. An additional stock solution was made using HPLC grade acetonitrile (25 mL). The sample (0.9 mg, 0.0020 mmol) was dissolved, giving a concentration of 78 μ M.

For solution-state SEC the electrolyte was TBAPF₆ (0.1 M) dissolved in HPLC grade acetonitrile (25 mL). RuML1 (0.9 mg) was dissolved in the electrolyte to give a solution of concentration 78 μ M.

RuML2:

For solution-state spectroscopy the solvent was PureSolv DMF (100 mL). The sample (1.4 mg, 0.0023 mmol) was dissolved in the solvent, giving a solution of concentration 0.024 mM.

For solution-state SEC the electrolyte was TBAPF₆ (0.1 M) dissolved in PureSolv DMF (25 mL). RuML2 (1.3 mg) was dissolved in the electrolyte to give a solution of concentration 85 μ M.

RuML4:

For solution-state spectroscopy the solvent was HPLC grade acetonitrile (100 mL). The sample (0.5 mg, 0.75 μ mol) was dissolved in the solvent, giving a solution of concentration 7.5 μ M.

For solution-state SEC the electrolyte was TBAPF₆ (0.1 M) dissolved in HPLC grade acetonitrile (25 mL). RuML4 (1.4 mg) was dissolved in the electrolyte to give a solution of concentration 84 μ M.

RuML0:

For solution-state SEC the electrolyte was TBAPF₆ (0.1 M) dissolved in HPLC grade acetonitrile (10 mL). RuML0Cl (1.9 mg, 3.8 mmol) was dissolved in the electrolyte to give a solution of concentration 0.38 mM.

[Ag(RuML2)₂](SbF₆)₃·*n*EtOH, [ZnX₂(RuML4)]·*n*EtOH (X = Cl, Br):

For solid-state diffuse reflectance spectroscopy, the sample was washed *via* centrifuge with ethanol (100 mL). The sample was pipetted into a small mortar and the solvent allowed to dry. The sample was then mixed with BaSO₄ powder.

Single-crystal polarised spectroscopy in the near-infrared, visible and ultraviolet regions were performed with a custom spectrophotometer designed by Krausz.¹²² The instrument is composed of optics obtained from a CARY14 spectrophotometer equipped with a 24 V/150 W quartz halogen lamp and a Spec 1704, 1 (m), high-resolution Czerny-Turner monochromator and a high-speed stepper motor. Single crystals were mounted over a 1 mm aperture and data were collected in both horizontal and vertical polarisation modes. For visible spectra, a grating blazed at 500 nm was used in conjunction with an EMI 9659QB Photomultiplier Tube. Spectra were then collected over the range 350 to 750 nm (13330-28570 cm⁻¹) in 1 nm increments. For NIR spectra, a grating blazed at 1000 nm was used in conjunction with an OSRAM BXP-65 Silicon PIN Photodiode. Spectra were collected in the range 700 to 1100 nm (9090-14290 cm⁻¹) in 1 nm increments. A baseline correction was applied to the data by measuring the absorbance spectrum of the empty aperture, which was then manually subtracted from the absorption spectrum of the crystal. All spectra were collected using two orthogonal polarisations. These have been labelled as 0° and 90° and do not reflect the absolute orientations of the crystals.

2.3.6. Mass Spectrometry

Electrospray ionisation (ESI) and direct probe atmospheric pressure chemical ionisation (APCI) measurements were performed on a Bruker AmaZon SL ion trap mass spectrometer. This technique was used for low resolution spectroscopy.

Inductively coupled plasma mass spectrometry (ICPMS) was performed on a PerkinElmer Nexion 300X inductively coupled plasma mass spectrometer. Samples were run with 1 second dwell time per element and all elements were measured in kinetic energy discrimination mode using helium as the collision gas (4 L/min). Rh and Ir were used as internal standards.

For ESI MS, samples of approximately 1 mg were dissolved in spectroscopic grade methanol or acetonitrile (depending on the solubility of the analyte) and the solution diluted by a factor of 10^{3-4} .

For APCI MS, samples were analysed as solid powders or crystals.

For ICPMS, the sample was dissolved in the minimum amount of nitric acid (70%), and diluted by a factor of 100.

2.3.7. Raman Spectroscopy

Two instruments were used for Raman spectroscopy. A Renishaw inVia Qontor confocal Raman microscope was used for laser lines 288 nm, 355 nm, 532 nm, 785 nm. A Renishaw inVia confocal Raman microscope was used for laser lines 488 nm, 514 nm, 633 nm and 830 nm.

Wavelengths were chosen to coincide with different features of the absorbance spectra of the samples.¹⁶⁷

All samples were solid powder or crystals, with the exception of $[\text{Ag}(\text{RuML}_2)_2](\text{SbF}_6)_3 \cdot n\text{EtOH}$ and $[\text{ZnX}_2(\text{RuML}_4)] \cdot n\text{EtOH}$ ($\text{X} = \text{Cl}, \text{Br}$), which were analysed as solid crystallites dispersed in a mixture of ethanol and chloroform. The solvent was observed to evaporate over the course of the measurements.

2.3.8. Infrared Spectroscopy

Attenuated total reflectance infrared spectroscopy (ATR-IR) was performed on a PerkinElmer UATR Two FTIR spectrometer. Samples were collected at a spectral resolution of 2 cm^{-1} with 32 accumulations.

Infrared SEC was performed on a Bruker Vertex 80v, using a Pike Technologies JackFish 2 surface enhanced infrared absorption spectroscopy (SEIRAS) SEC cell,¹⁶⁸ mounted on a Pike Technologies VeeMAX III variable angle specular reflection angular accessory. The JackFish features a specialised design for attenuated total reflectance (ATR) spectroscopy, employing an IRUBIS silicon wafer as both the ATR crystal and working electrode.

All FTIR samples were solid powder or crystals, with the exception of $[\text{Ag}(\text{RuML}2)_2](\text{SbF}_6)_n \cdot 8\text{EtOH}$ and $[\text{ZnX}_2(\text{RuML}4)] \cdot n\text{EtOH}$ ($\text{X} = \text{Cl}, \text{Br}$), which were analysed as solid crystallites dispersed in a mixture of ethanol and chloroform.

For JackFish measurements, due to the large volume of the cell, limited amount of analyte available and poor solubility in common solvents, solution-state measurements in the JackFish cell were deemed unsuitable due to low signal. Instead, the analyte was deposited onto the working electrode surface by evaporating a concentrated solution of the analyte in DCM, and an electrolyte system was chosen within which the analyte was insoluble or sparingly soluble. For all measurements the electrolyte was KCl (0.1 M) in H_2O .

2.3.9. Nuclear Magnetic Resonance Spectroscopy

^1H Nuclear Magnetic Resonance (NMR) spectra were collected on a Bruker NEO 300 MHz NMR spectrometer. Analysis was performed in Topspin ver. 4.1.0.

2.3.10. Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) measurements were collected on a Discovery TGA analyser. Air was used, with a flow rate of 10 mL/min. The samples were taken to 700 °C at a ramp rate of 3 °C/min.

2.3.11. Density Functional Theory

In order to properly describe the electronic and vibrational spectroscopies within this work, three complexes in two oxidation states were modelled with DFT, in Gaussian 16.¹⁶⁹ Electronic excitation spectra were calculated with the CAM-B3LYP¹⁷⁰/def2-SVP¹⁷¹ method. The long-range corrected¹⁷² CAM-B3LYP method was employed to ensure the proper description of any prospective charge-transfer excitations. The choice of the def2-SVP basis set is based on previous studies,¹⁷³⁻¹⁷⁴ which show that it provides an efficient and adequate means to account for the relative absorption energies. The Tamm-Dancoff approximation¹⁷⁵ was applied to further accelerate the computation of the electronic excited states with minimal loss of accuracy. Molecular orbitals used in the discussion correspond to the CAM-B3LYP/def2-SVP level.¹⁶⁹ Geometries were optimised with the B3LYP¹⁷⁶/def2-SVP¹⁷¹ method. Vibrational frequency computations were carried out at the same level for the calculation of infrared and Raman spectra, as well as to confirm the nature of the optimized geometries as equilibrium structures. This protocol, or similar ones, is widely used for these tasks. Its accuracy has been validated, for example, by Chan *et al.*¹⁷⁷⁻¹⁷⁸

Chapter 3

Coordination Complexes



Project Goals

The research within this Chapter draws inspiration from the Creutz-Taube complex and the decades of inorganic chemistry that followed in its wake. Dinuclear complexes of several second- and third-row metals bridged by pyridyl ligands have produced charge-delocalisation.¹³ These metals include complexes of ruthenium, rhodium, rhenium, osmium and iridium. The simple geometries of these coordination complexes and the existing pathway for charge transfer made the motif an enticing pathway towards conductive and redox-active polymer materials. Early targets in this project were the complexes *trans*-[Ru^{III}(pyz)₂(NH₃)₄]³⁺ and *trans*-[Os^{III}(pyz)₂(NH₃)₄]³⁺ (Figure 3.1). However, it soon became clear that the synthetic pathways for these complexes involved hazardous starting materials or the synthetic pathways were low-yielding.¹⁷⁹⁻¹⁸³

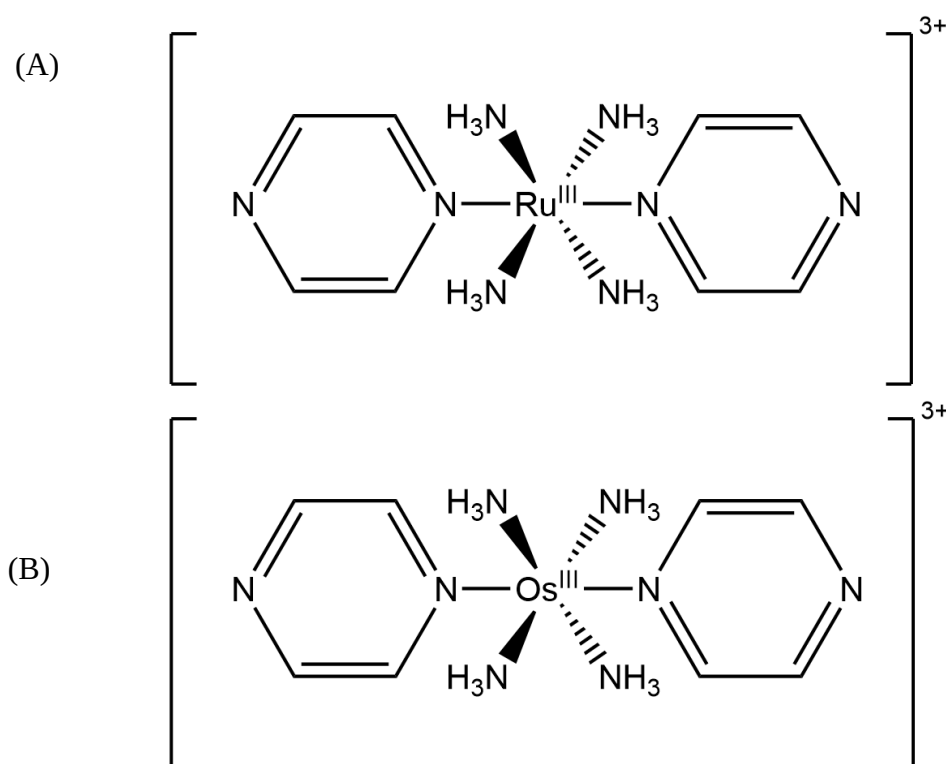


Figure 3.1. The complexes (A) *trans*-[Ru^{III}(pyz)₂(NH₃)₄]³⁺; and (B) *trans*-[Os^{III}(pyz)₂(NH₃)₄]³⁺

A viable alternative motif was reported by Hasegawa *et al.*,⁴⁵ that involved a two-step synthesis of the complex $trans\text{-}[\text{Ru}^{\text{II}}(\text{acac})_2(\text{pyz})_2]$ from ruthenium trichloride. The intermediate material, $\text{Ph}_4\text{As}\{trans\text{-}[\text{Ru}^{\text{III}}(\text{acac})_2\text{Cl}_2]\}$ or $\text{Ph}_4\text{P}\{trans\text{-}[\text{Ru}^{\text{III}}(\text{acac})_2\text{Cl}_2]\}$,¹⁸⁴ also provides an interesting subject of analysis. The synthetic pathway primarily results in the *trans*- isomer, and can be adapted to incorporate a variety of N-donor ligands. Applicability of the motif to reticular or polymer synthesis is discussed in Chapter 4.

In this chapter, various members of the family $trans\text{-}[\text{Ru}(\text{acac})_2(\text{pyz})_2]$, are reported in terms of their crystallographic, spectroscopic and electrochemical properties. The π -backbonding and π -bonding mechanisms dominate trends among members of this family.

3.2. Identification of Ruthenium Oxidation State

The reduction potentials of $trans\text{-}[\text{Ru}(\text{acac})_2(\text{X})_2]$ species, where X is a π -acid tend to lie at negative potentials vs SHE, and thus oxidation of the Ru centre occurred in the presence of weak oxidants. As a result, both the Ru(II) and Ru(III) oxidation states are readily synthesised (Chapter 2), with the exception of $trans\text{-}[\text{Ru}(\text{acac})_2(\text{pyz})_2]$, which is only present as Ru(II) in the reaction product. Identification of the relative composition of Ru(II) and Ru(III) in synthetic workups was determined by X-ray Photoelectron Spectroscopy (XPS), from their slightly different Ru 3d 5/2 emission energies.¹⁸⁵ Calibrating the energies of these spectra is difficult, because Ru produces 3d 3/2 emissions that overlap with carbon XPS emissions.¹⁸⁵ Instead of using the calibrated eV of the Ru 3d 5/2 emissions, the difference between the 3d 3/2 and 3d 5/2 emissions was used to provide a more reliable measure of the oxidation state of the materials (Table 3.1). The difference is clear between the two oxidation states, with Ru(II) complexes producing a $\Delta 3d$ of 4.3-4.8 eV, and Ru(III) producing a $\Delta 3d$ of ~ 2.7 eV.

Table 3.1. Comparison of Ru 3d 3/2 and Ru 3d 5/2 XPS signals across the *trans*-[Ru(acac)₂(X)₂] family

Compound/Spot no.	Ru 3d 3/2 and Cs peak	Ru 3d 5/2 peak	Difference
RuML4	285.2115	280.442	-4.7695
[RuML4]Cl	285.3615	282.641	-2.7205
RuML2	285.2765	280.5795	-4.697
[RuML2]Cl	285.328	282.6045	-2.7235
RuML1	284.8105	280.4405	-4.37
RuML0	285.823	281.158	-4.669

Also apparent is the identity of the counterion in the Ru(III) complexes, which was determined by comparison of the Cl 2p energies in *trans*-[Ru(acac)₂(X)₂] materials and their oxidised counterparts. Chloride ions are most likely sourced from displaced Cl ligands upon reduction of *trans*-Ph₄P[Ru(acac)₂Cl₂]. The oxidation of the *trans*-[Ru(acac)₂(X)₂] motif during the synthetic step exists in equilibrium with the formation of the salt Ph₄PCl, the balance of which is dependent on the redox potential of the Ru system. For example, the synthesis of *trans*-[Ru(acac)₂(pyz)₂] produces a negligible quantity of the chloride in the product, while the synthesis of *trans*-[Ru(acac)₂(BPE)₂] produces the chloride as the major product, due to the significantly lower barrier to oxidation. As a result, the synthesis in Chapter 2 cannot be straightforwardly altered to avoid production of chloride salts.

Isolation of the Ru(II) component can generally be achieved by column chromatography through an alumina stationary phase and a sufficiently non-polar eluent such as chloroform. The Ru(III) component can sometimes be isolated *via* a more polar eluent such as ethanol, but may have a very similar R_f to the precursor ion *trans*-[Ru(acac)₂Cl₂]⁻, and the ligand X.

Colour changes between Ru(II) and Ru(III) oxidation states in the *trans*-[Ru(acac)₂(X)₂] motif are surprisingly variable, largely due to the substantial variation in π -acceptor behaviour exhibited by the ligand. For example, *trans*-[Ru(acac)₂(BPE)₂] changes from a dark green Ru(II) solution to a light orange Ru(III) solution, but *trans*-[Ru(acac)₂(Py)₂] changes from an

orange Ru(II) solution to a deep red Ru(III) solution. The visual appearance of any *trans*-[Ru(acac)₂(X)₂] complex, therefore, is not sufficient to determine oxidation state.

3.3. Crystallography

3.3.1. Ph₄P{*trans*-[Ru^{III}(acac)₂Cl₂]}

The complex Ph₄P{*trans*-[Ru^{III}(acac)₂Cl₂] } crystallised in the triclinic space group $P\bar{1}$, with one molecule of each ion in the asymmetric unit, and two molecules of each ion in the unit cell (Figure 3.2).

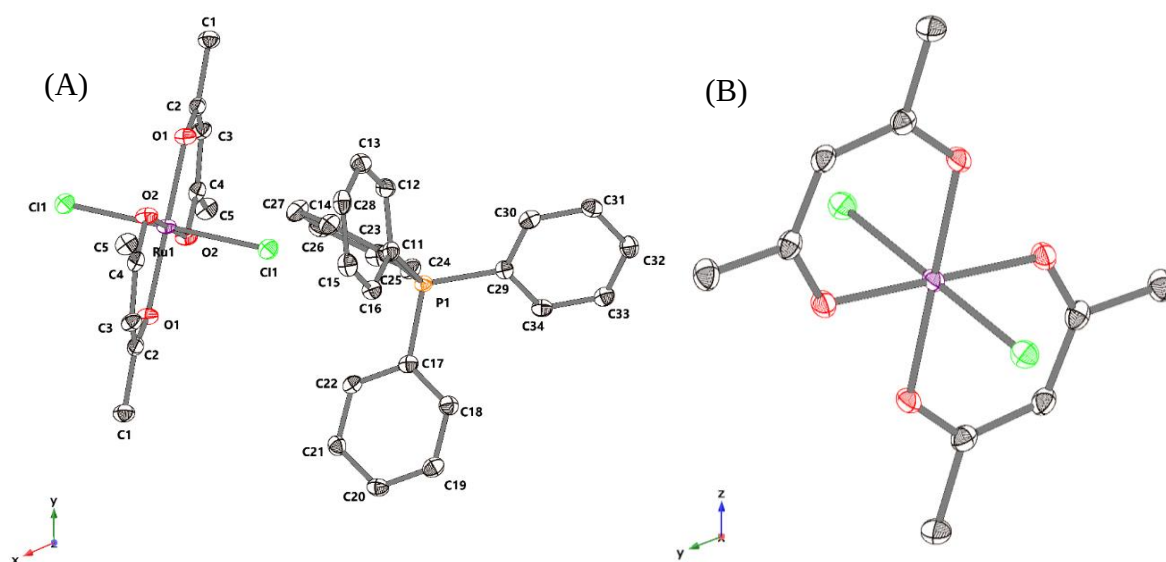


Figure 3.2. (A) Ph₄P{*trans*-[Ru^{III}(acac)₂Cl₂] } molecular unit, viewed down the *c* axis; (B) *trans*-[Ru(acac)₂Cl₂]⁺ ion, viewed down the *a* axis. Both structures in $P\bar{1}$. Hydrogens omitted for clarity. Colour scheme: C, black; O, blue; Ru, purple; Cl, green; P, orange. Figures were produced using CrystalMaker X.

3.3.2. RuML1, *trans*-[Ru^{II}(acac)₂(pyz)₂]

The coordination complex *trans*-[Ru^{II}(acac)₂(pyz)₂] crystallised in the monoclinic space group $P2_1/n$, with two neutral complexes in the unit cell (Figure 3.3). Unsurprisingly, the crystal structure of this material indicates substantial bond and angular distortion around the ruthenium coordination sphere. Tetragonal distortion is observable in the axial positions, where two *trans* ligands are more strongly bonded to the metal centre and thus produce a contraction of the axial bond lengths.¹⁸⁶

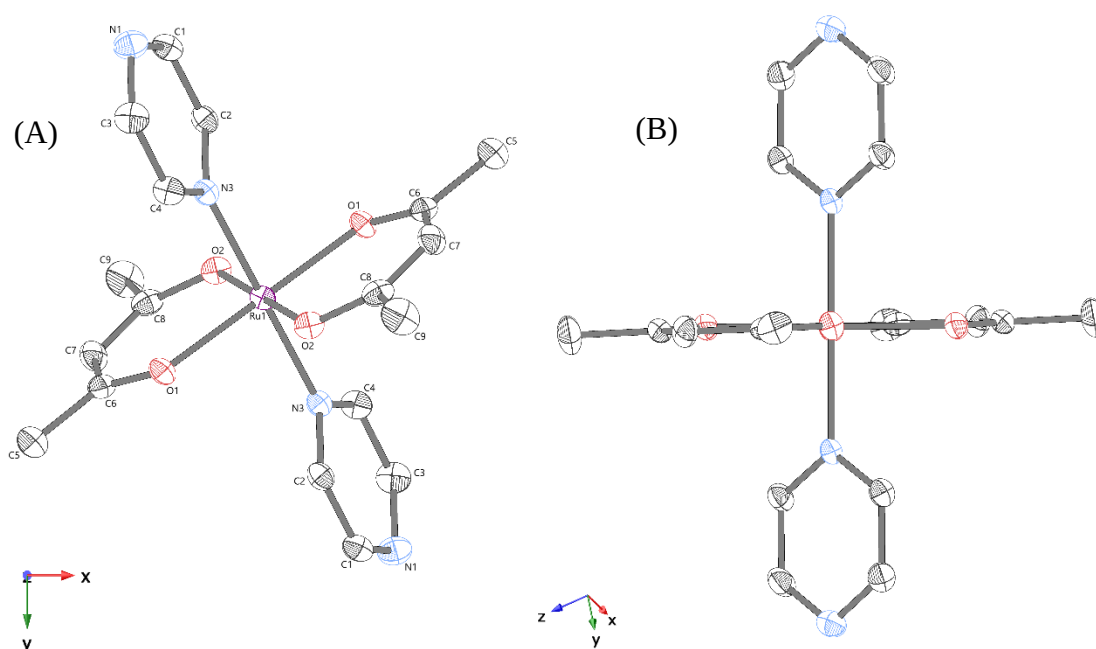


Figure 3.3. *trans*-[Ru(acac)₂(pyz)₂] molecular unit in $P2_1/n$. (A) viewed down the c axis; (B) viewed along the equatorial plane. Hydrogens omitted for clarity. Colour scheme: N, blue; C, black; O, red; Ru, purple. Figures were produced using CrystalMaker X.

Similar values for Ru-N and Ru-O bond distances were observed. (Table 3.2).

Table 3.2. Coordination bond lengths in *trans*-[Ru(acac)₂(pyz)₂]

Ru-N _{pyz} Bond Length (Å)	Ru-O _{acac} Bond Length (Å)
2.038 (3)	2.041 (2), 2.046 (2)

The pyrazine ligands are not perfectly orthogonal to the acetylacetonate ligands, due either to crystal packing, or distortion of the coordination sphere. The plane made from atoms C3, C3a, C1 and C1a and the plane with atoms O1, O1a, O2 and O2a are at an angle of $88.00 \pm 0.15^\circ$, calculated with Olex2 (Figure 3.4).¹⁶²

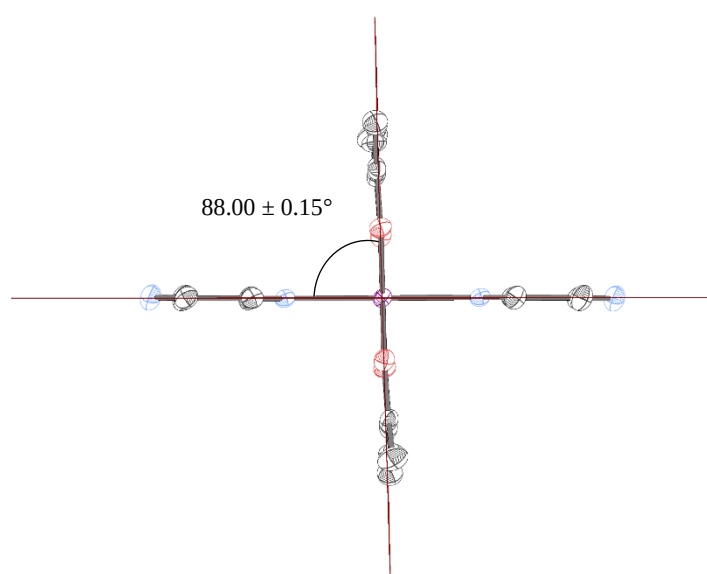


Figure 3.4. Comparison of ligand planes in *P*₂₁/*n* structure of *trans*-[Ru(acac)₂(pyz)₂]. Molecule oriented for clarity. Hydrogens omitted for clarity. Colour scheme: N, blue; C, black; O, blue; Ru, purple. Figure was produced using CrystalMaker X.

3.3.3. RuML2, *trans*-[Ru^{II}(acac)₂(bpy)₂]

The coordination complex *trans*-[Ru^{II}(acac)₂(bpy)₂] crystallised in the unusual orthorhombic space group *Fdd*2. This space group is non-centrosymmetric, and the asymmetric unit contains one entire molecule (Figure 3.5). There are sixteen neutral molecules per unit cell. The crystal structure of *trans*-[Ru^{II}(acac)₂(bpy)₂] exhibits strong static disorder at both the acetylacetonate

and 4,4'-bipyridine ligands. The disordered parts had an occupancy determined by a free variable, refined to a value of 0.53348. This resulted in a major part with occupancy of approx. 53.3% and minor part with occupancy of approx. 46.7%. The disorder at the acetylacetonate groups represented a 'wagging' motion of the two coordinating O atoms relative to the Ru centre. On the other hand, the disorder at the 4,4'-bipyridine groups represented a rotational freedom of the pyridine rings on the axis of the C14, C15; C19, C20; C24, C25; C29, C30 atom pairs.

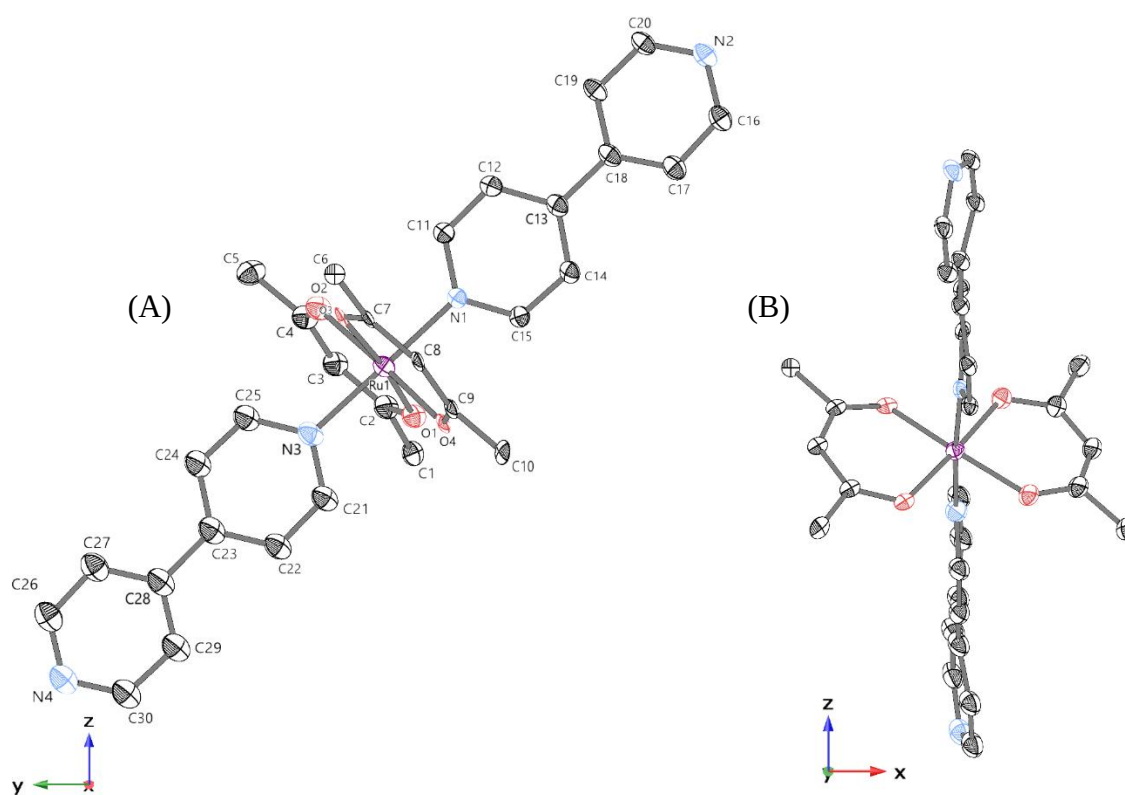


Figure 3.5. Molecular and asymmetric unit of *trans*-[Ru(acac)₂(bpy)₂] in *Fdd2*. Disorder omitted for clarity. (A) viewed down the *a* axis; (B) viewed down the *b* axis. Hydrogens omitted for clarity. Colour scheme: N, blue; C, black; O, red; Ru, purple. Figures were produced using CrystalMaker X.

A polymorph of *trans*-[Ru^{II}(acac)₂(bpy)₂] was obtained *via* slow liquid-liquid diffusion of a chloroform solution of *trans*-[Ru^{II}(acac)₂(bpy)₂] into acetonitrile. The complex crystallised into the monoclinic space group *C2/c*. The asymmetric unit contained one molecule, and there were

eight molecules per unit cell. The monoclinic polymorph of *trans*-[Ru^{II}(acac)₂(bpy)₂] exhibited virtually no disorder in contrast to the *Fdd2* crystal structure, possibly due to π -stacking between pyridyl rings along the *b* axis (Figure 3.6). π -stacking occurs as a non-covalent attractive interaction between aromatic π -systems.¹⁸⁷⁻¹⁹² The cofacial or ‘sandwich’ π -stacking configuration was observed between the inner pyridyl rings of the complex. In the *C2/c* structure of *trans*-[Ru^{II}(acac)₂(bpy)₂], the rings in question were within 5 Å, offset by approx. 1.1 Å. The angle between the planes of the pyridyl rings is 4.8° and the electron-withdrawing nitrogens are offset by approx. 90°. These conditions are in good agreement with the qualitative rules for face-to-face π -stacking interactions in heteroaromatic systems.¹⁸⁷

The only indication of disorder is the presence of electron density close to the outer pyridyl rings, similar to the disorder observed in the same position in the *Fdd2* structure. This electron density is too small to effectively model any disordered fragment.

The angle between the pyridyl rings in 4,4'-bipyridine determined the degree of overlap between the two ring π orbital systems. The angle had a direct impact on the degree of charge delocalisation in ruthenium bipyridine systems.¹⁹³ The complex *trans*-[Ru^{II}(acac)₂(bpy)₂] displayed a low degree of charge delocalisation, with very little apparent overlap between π orbitals of the respective bpy rings in both the *Fdd2* and *C2/c* structures of *trans*-[Ru^{II}(acac)₂(bpy)₂] (Table 3.3).

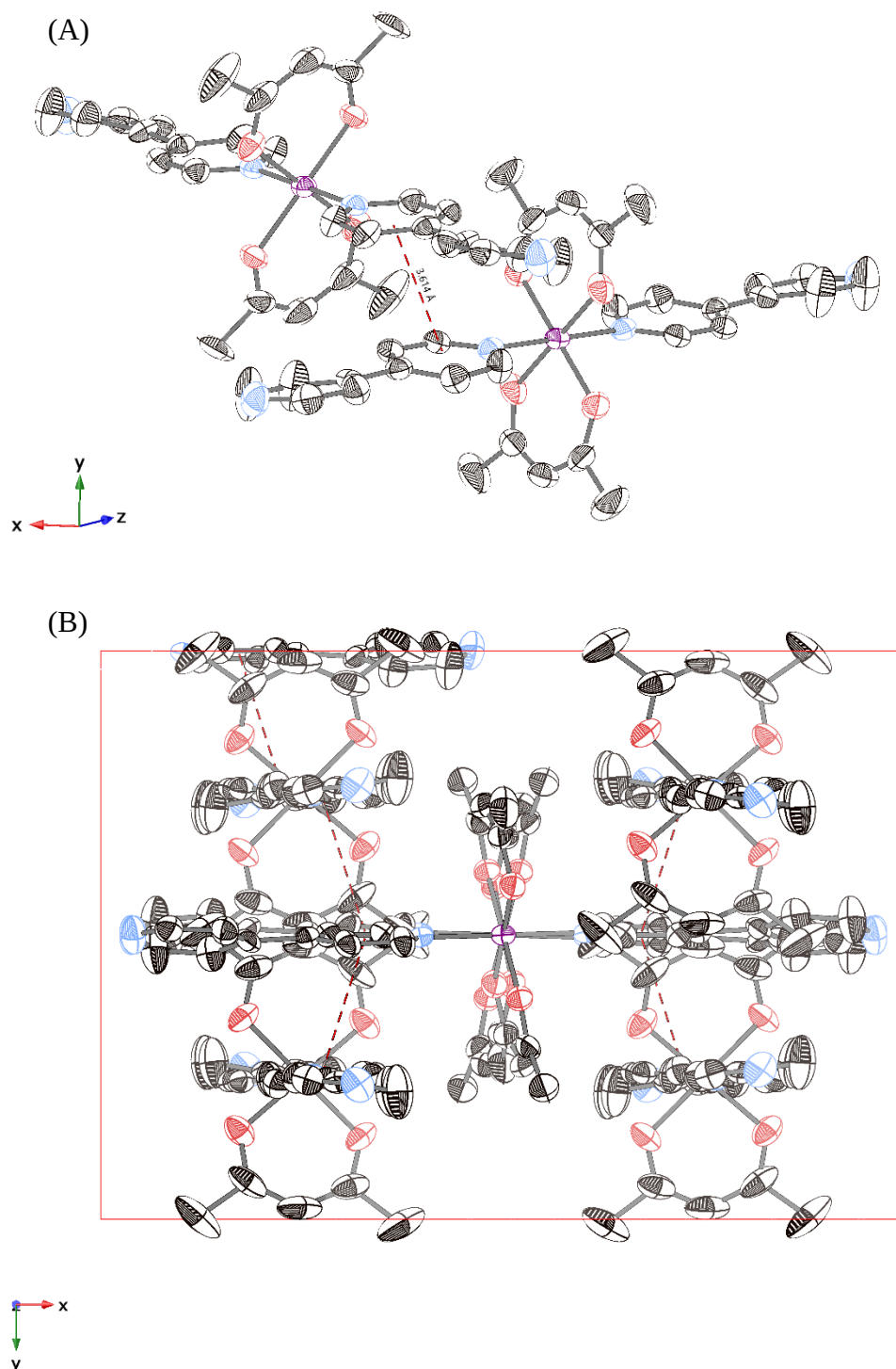


Figure 3.6. $trans\text{-}[\text{Ru}^{\text{II}}(\text{acac})_2(\text{bpy})_2]$ crystal structure in $C2/c$. (A) Two molecules, oriented for clarity. (B) Unit cell, viewed down the c axis. π -stacking indicated by dotted line between ring centroids. Hydrogens omitted for clarity. Colour scheme: N, blue; C, black; O, blue; Ru, purple. Figures were produced using CrystalMaker X.

The Ru-N bond distances were also comparable between the two polymorphs. The range of bond distances with respect to uncertainty were between 2.021 and 2.058 Å in the *Fdd2* structure, while the *C2/c* structure had bond distances between 2.036 and 2.057 Å with respect to uncertainty. These distances were in relatively good agreement with each other, and were consistent with Ru(II). On average the Ru-N bond distances in both *trans*-[Ru(acac)₂(bpy)₂] polymorphs were longer than those observed in *trans*-[Ru^{II}(acac)₂(pyz)₂], which resulted from weaker π -backbonding between Ru-bpy compared to Ru-pyz.

The angular distortion was notably lower in the *C2/c* polymorph than the *Fdd2* structure. The difference was attributed to more favourable packing and intermolecular interactions in the *C2/c* polymorph compared with the *Fdd2* structure. Notably, the *cis* O-Ru-O angle between the ‘arms’ of the coordinating acetylacetonate groups was within 1° for both *trans*-[Ru^{II}(acac)₂(bpy)₂] polymorphs, as well as *trans*-[Ru^{II}(acac)₂(pyz)₂]. The bulk of the angular distortion in both *Fdd2* and *C2/c* polymorphs of *trans*-[Ru^{II}(acac)₂(bpy)₂] was, therefore, attributable to the ‘bowed out’ acetylacetonate coordinating groups.

The complex, *trans*-[Ru^{III}(acac)₂(bpy)₂]⁺, crystallised in the monoclinic space group *P2₁/c* with solvents of crystallization as the salt *trans*-[Ru^{III}(acac)₂(bpy)₂]Cl·EtOH·H₂O. The asymmetric unit contained a RuML₂⁺ molecule, one ethanol molecule, one water molecule and one chloride ion. The unit cell contained four molecules of RuML₂⁺, ethanol, water, and four chloride ions.

Curiously, the angle between the pyridyl rings was notably smaller than in either of the Ru(II) structures (Table 3.3). The origin of this is unclear- clearly the smaller angle is not as a result of electronic interactions between the metal centre and the bpy π^* system, as such an interaction would be far more favourable in the Ru(II) system. The smaller angle may therefore be explained by crystal packing, especially considering the much larger angle between the other pyridyl rings in the Ru(III) structure.

Table 3.3. Angle between pyridyl rings of 4,4'-bipyridine in the *trans*-[Ru(acac)₂(bpy)₂] crystal structures.

Crystallographic Fragment	Ru Oxidation State	Space Group	Angle between bpy rings (degrees)	Average angle between pyridyl rings (Degrees)
Major fragment (53%)	II	<i>Fdd2</i>	19.44, 10.77	15.11
Minor disordered fragment (47%)	II	<i>Fdd2</i>	21.17, 19.27	20.22
Major fragment (~100%)	II	<i>C2/c</i>	12.99, 18.79	15.89
Major fragment (~100%)	III	<i>P2₁/c</i>	6.54, 18.76	12.65
Average				17.66

3.3.4. RuML4, *trans*-[Ru^{III}(acac)₂(BPE)₂]

The complex, *trans*-[Ru^{III}(acac)₂(BPE)₂]⁺ (RuML4⁺), crystallised in the triclinic space group $P\bar{1}$ containing CHCl₃ as the solvent of crystallization as the salt *trans*-[Ru(acac)₂(BPE)₂]Cl·3CHCl₃. The asymmetric unit contained one entire molecule of RuML4⁺, three chloroform molecules and a chloride ion (Figure 3.7). The unit cell contained two molecules of RuML4⁺, six chloroform molecules and two chloride ions. The staggering of the BPE ligands occurs in the same direction. The crystal structure was solved and refined from a twinned dataset, which may have contributed to the thermal ellipsoids appearing slightly larger than other crystal structures presented in this Chapter.

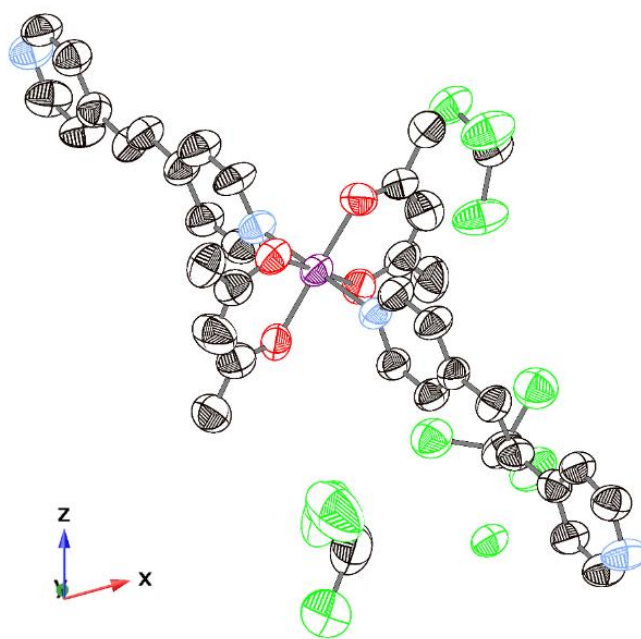


Figure 3.7. The asymmetric unit of *trans*-[Ru^{III}(acac)₂(BPE)₂]Cl·3CHCl₃ in $P\bar{1}$, viewed down the *b*-axis. Hydrogens omitted for clarity. Colour scheme: N, blue; C, black; O, blue; Cl, green; Ru, purple. Figure was produced using CrystalMaker X.

3.3.5. RuML2.5, *trans*-[Ru^{II}(acac)₂(PyCOOMe)₂]

The coordination complex, *trans*-[Ru^{II}(acac)₂(PyCOOMe)₂], crystallised in the triclinic space group $P\bar{1}$, with a half molecule in the asymmetric unit and a full molecule in the unit cell (Figure 3.8).

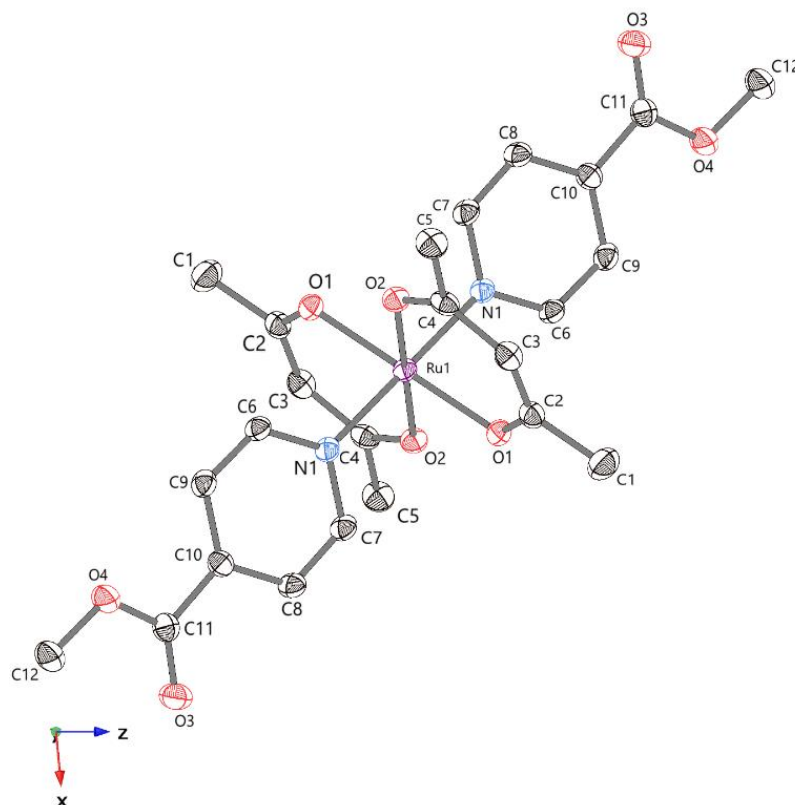


Figure 3.8. *trans*-[Ru^{II}(acac)₂(PyCOOMe)₂] molecular unit in $P\bar{1}$, viewed down the b-axis. Hydrogens omitted for clarity. Colour scheme: N, blue; C, black; O, blue; Ru, purple. Figure was produced using CrystalMaker X.

3.3.6. RuML0, *trans*-[Ru^{II}(acac)₂(Py)₂]

The coordination complex, *trans*-[Ru^{II}(acac)₂(Py)₂], crystallised in the monoclinic space group $P2_1/n$, with half a molecule in the asymmetric unit and two molecules in the unit cell (Figure 3.9).

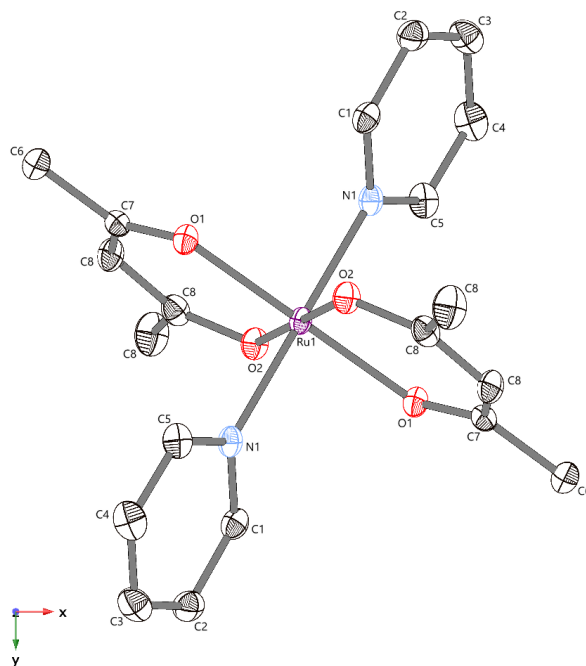


Figure 3.9. *trans*-[Ru^{II}(acac)₂(Py)₂] molecular unit in *P*2₁/*n*, viewed down the *c* axis. Hydrogens omitted for clarity. Colour scheme: N, blue; C, black; O, blue; Ru, purple. Figure was produced using CrystalMaker X.

The complex, *trans*-[Ru^{III}(acac)₂(Py)₂]⁺, crystallised as a chloride salt in the monoclinic space group *C*2/*m* (Figure 3.10). The crystal structure featured significant static disorder that resulted from the central Ru atom lying on an inversion centre, bisected by a mirror plane and two-fold rotation axis (Figure 3.10B). Consequently, the crystal structure features two crystallographically identical molecules of *trans*-[Ru(acac)₂(Py)₂] lying on the ruthenium atom, offset by 35–50°. These complexes were formally treated as having a crystallographic occupancy of 0.5 each, meaning two overlapping molecules form one complete molecule. A half-occupied chloride ion was modelled in the asymmetric unit. The asymmetric unit contained a Ru of 0.25 occupancy and an acetylacetonate and pyridine of 0.5 occupancy. Thus, the asymmetric unit contains a quarter molecule. The unit cell contains two complete molecules of *trans*-[Ru^{III}(acac)₂(Py)₂]⁺ and one chloride ion.

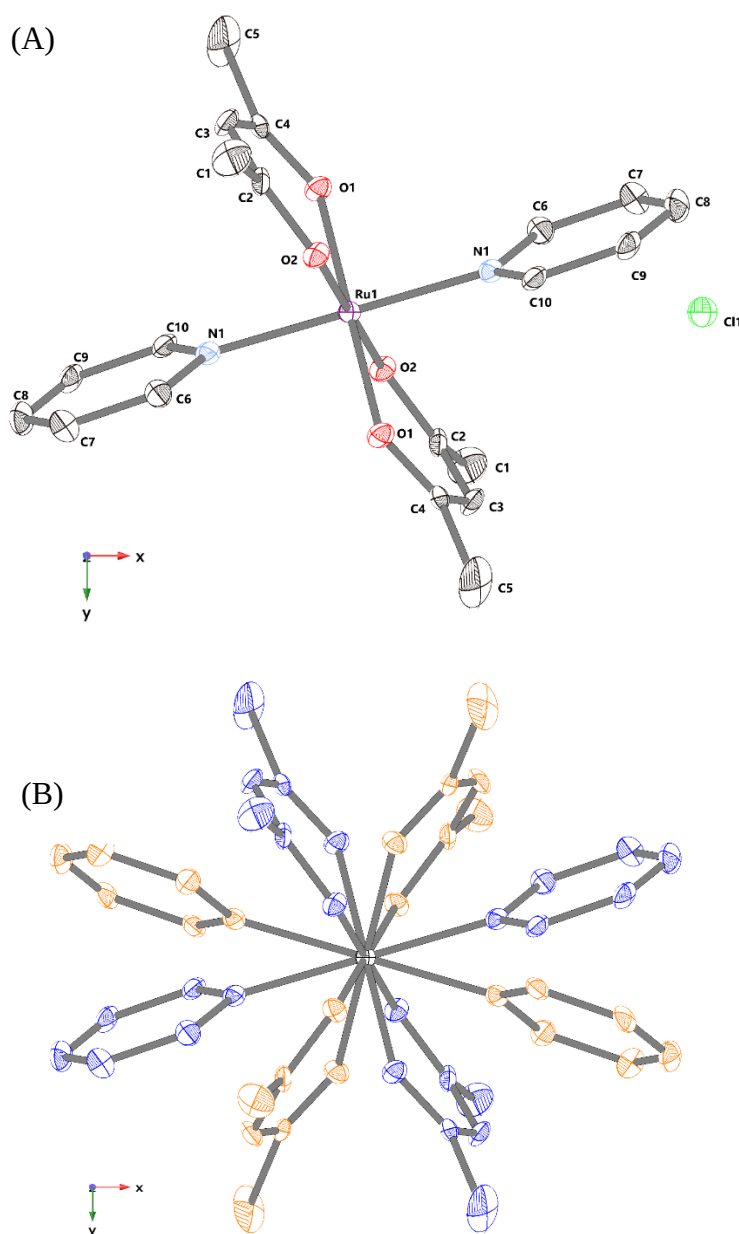


Figure 3.10. *trans*-[Ru^{III}(acac)₂(Py)₂]Cl in *C2/m*. (A) Molecular unit viewed down the *c* axis, disorder excluded. Colour scheme: N, blue; C, black; O, blue; Ru, purple; (B) Disordered molecular unit viewed down the *c* axis, Cl⁻ excluded. Hydrogens omitted for clarity. Figure was produced using CrystalMaker X.

A polymorph of this complex was crystallised by slow vapour diffusion of diethyl ether into a methanol solution of [Ru^{III}(acac)₂(Py)₂]Cl. The complex with methanols of crystallization, *trans*-[Ru^{III}(acac)₂(Py)₂]Cl·2MeOH crystallised in the monoclinic space group *P2₁/n*, and was solved from a twinned dataset. The asymmetric unit contained one full molecule of *trans*-

$[\text{Ru}^{\text{III}}(\text{acac})_2(\text{Py})_2]^+$, two disordered methanol molecules and one chloride molecule. The unit cell contained four molecules of *trans*- $[\text{Ru}^{\text{III}}(\text{acac})_2(\text{Py})_2]^+$, eight methanol molecules and four chloride molecules.

The angular distortion parameter in *trans*- $[\text{Ru}^{\text{III}}(\text{acac})_2(\text{pyridine})_2]$ was the lowest observed in this family of complexes. As noted earlier, the largest contribution to the angular distortion in these complexes was the *cis* O-Ru-O angles between the arms of the coordinating acetylacetonate groups. This angle was much lower in *trans*- $[\text{Ru}^{\text{III}}(\text{acac})_2(\text{pyridine})_2]$ than any of those observed in the other discrete ruthenium complexes. Both of the above factors are consistent with a Ru(III) centre.

3.3.7. General Trends

There are a number of crystallographic trends observable across the family of *trans*- $[\text{Ru}^{\text{III/II}}(\text{acac})_2(\text{X})_2]^{n+}$ complexes. The dominant factors are of course the oxidation state of the ruthenium ion and the relative π -acceptor behaviour of the ligand X. We will consider coordination bond lengths, distortion of the octahedral field,³⁹ and distortion of the acetylacetonate ligands.

3.3.7.1. C-O bond lengths

An interesting point of comparison lies with the chromium analogue of RuML0 *trans*- $[\text{Cr}(\text{acac})_2(\text{Py})_2]$.⁴⁶ A Robin-Day Class III mixed-valence $(\text{acac})_2^{\cdot 3-}$ pair was observed in this chromium complex which was in part determined crystallographically by comparison of the C-O bond distances.⁴⁶ Vinum *et al.* analysed approximately 3000 crystal structures that included coordinated acetylacetonate, and a Gaussian fit with central tendency of 1.2731 Å and standard deviation of 0.0180 Å was applied.⁴⁶ The coordination complexes exhibiting the mixed-valence $(\text{acac})_2^{\cdot 3-}$ radical pair exhibited statistically larger C-O bond lengths, between ~1 standard deviations in *trans*- $[\text{Cr}(\text{acac})_2(\text{CF}_3\text{Py})_2]$ (CF_3Py = 4-(trifluoromethyl)pyridine) and ~2

standard deviations in *trans*-[Cr(acac)₂(Me₂NPpy)₂] (Me₂NPpy = 4-(dimethylamino)pyridine) larger than the central tendency. The elongation of the C-O bonds is due to a population of the π^* antibonding orbital of the acetylacetonate ligands.¹⁹⁴

A charge delocalised relationship like that observed in *trans*-[Cr(acac)₂(Py)₂] would be unexpected in the Ru analogues. While Cr(III) and Ru(III) (d^3 and d^5 respectively) are both stabilised by crystal field splitting energy (CFSE), Cr(II) (d^4) is much more poorly stabilised by CFSE than Ru(II) (d^6). Ru(II) is also less reducing than Cr(II). Crystallographic evidence also appears to point away from the presence of the (acac)₂³⁻ pair in the ruthenium analogues (Table 3.4). The average C-O bond lengths in the *P2₁/n* structure of *trans*-[Ru^{II}(acac)₂(Py)₂] and the *P2₁/n* structure of *trans*-[Ru^{III}(acac)₂(Py)₂]Cl·2MeOH both lie firmly within one standard deviation of the central tendency, as do the average C-O bond lengths of *trans*-[Ru^{II}(acac)₂(pyz)₂], the *Fdd2* structure of *trans*-[Ru^{II}(acac)₂(bpy)₂], Ph₄P{*trans*-[Ru^{III}(acac)₂Cl₂]} and *trans*-[Ru^{II}(acac)₂(PyCOOMe)₂]. The outliers include the *C2/c* structure of *trans*-[Ru^{II}(acac)₂(bpy)₂] and the *C2/m* structure of *trans*-[Ru^{III}(acac)₂(Py)₂]Cl, where the high uncertainties of the C-O bond lengths give values that lie above and below the first standard deviation line. We can conclude that the *trans*-[Ru(acac)₂(X)₂] family of metal complexes do not meet this condition for the presence of the (acac)₂³⁻ pair.

Table 3.4. Comparison of C-O bond lengths in the *trans*-[Ru(acac)₂(X)₂] family

Formula	Space Group	Ru Oxidation State	Acac C-O Bond Lengths (Å)	Average C-O Bond Lengths (Å)
<i>trans</i> -[Ru(acac) ₂ (pyz) ₂] (RuML1)	<i>P2₁/n</i>	II	1.271 (4), 1.276 (4)	1.274 (5)
<i>trans</i> -[Ru(acac) ₂ (bpy) ₂] (RuML2)	<i>Fdd2</i>	II	1.270 (17), 1.270 (17), 1.285 (16), 1.274 (17), 1.274 (16), 1.278 (17), 1.278 (16), 1.273 (17)	1.275 (8)
<i>trans</i> -[Ru(acac) ₂ (bpy) ₂]	<i>C2/c</i>	II	1.282 (13), 1.258 (11), 1.278 (12), 1.268 (11)	1.272 (12)
<i>trans</i> -[Ru(acac) ₂ (Py) ₂] (RuML0)	<i>P2₁/n</i>	II	1.2715 (19), 1.273 (2)	1.2723 (19)
<i>trans</i> -[Ru(acac) ₂ (Py) ₂]Cl	<i>C2/m</i>	III	1.290 (12), 1.282 (12)	1.286 (11)
<i>trans</i> -[Ru(acac) ₂ (Py) ₂]Cl·2MeOH	<i>P2₁/n</i>	III	1.281 (4), 1.275 (5), 1.283 (5), 1.280 (4)	1.280 (5)
<i>trans</i> -[Ru(acac) ₂ (PyCOOMe) ₂]	<i>P1̄</i>	II	1.264 (3), 1.268 (3)	1.266 (4)
<i>trans</i> -[Ru ^{III} (acac) ₂ (bpy) ₂]Cl·EtOH·H ₂ O	<i>P2₁/n</i>	III	1.295 (4), 1.295 (4), 1.290 (5), 1.282 (5)	1.291 (6)
<i>trans</i> -Ph ₄ P[Ru(acac) ₂ Cl ₂] (RuMLPRE)	<i>P1̄</i>	III	1.282 (3), 1.274 (3)	1.278 (5)

3.3.7.2. Angular Distortion

The angular distortion parameter Σ is a measure of the deviation from ideal octahedral geometry and is given as:¹⁹⁵

$$\Sigma = \sum_{i=1}^{12} |90 - \phi_i| \quad (3.1)$$

Where ϕ_i is a *cis* angle in the octahedral coordination sphere.

Table 3.5 displays a clear correlation between oxidation state and angular distortion. The Ru(II) complexes all had substantially higher Σ values ($\Sigma > 20$) than their Ru(III) analogues, with the exception of $\text{Ph}_4\text{P}\{\text{trans}[\text{Ru}^{\text{III}}(\text{acac})_2\text{Cl}_2]\}$. All reported crystal structures display some form of distortion between coordinating groups due to steric interactions, most notable in the heavily distorted *Fdd2* structure of *trans*- $[\text{Ru}^{\text{II}}(\text{acac})_2(\text{bpy})_2]$.

The primary contribution to this distortion was the bite angle α (Figure 3.11) of the acetylacetonate groups. This bite angle was uncommonly large for transition metal acetylacetonate complexes,¹⁹⁶ and is especially pronounced for the Ru(II) d^6 complexes (Figure 3.12). The size of α changed dramatically between the low-spin d^5 and d^6 configurations of the *trans*- $[\text{Ru}(\text{acac})_2(\text{X})_2]^{\text{n}+}$ motif (Figure 3.12, Table 3.5). Interestingly, the distance between the donor atoms d is observed to differ by nearly 0.15 Å between Ru(II) and Ru(III) complexes, in contrast to the traditional treatment of the ‘rigid’ bite distance d .¹⁹⁷⁻¹⁹⁹ However, it has been noted that the distance d varied across transition metal complexes with the same ligand.^{196,200-201}

Table 3.5. Angular distortion parameters Σ for *trans*-[Ru(acac)₂(X)₂] crystal structures

Complex/Coordination Polymer	Space Group	Ru Oxidation State	Σ at Ru coordination sphere
<i>trans</i> -[Ru(acac) ₂ (pyz) ₂]	<i>P2₁/n</i>	II	25.96
<i>trans</i> -[Ru(acac) ₂ (bpy) ₂]	<i>Fdd2</i>	II	45.68
<i>trans</i> -[Ru(acac) ₂ (bpy) ₂] disordered acac	<i>Fdd2</i>	II	41.67
<i>trans</i> -[Ru(acac) ₂ (bpy) ₂] 1 st metal centre	<i>C2/c</i>	II	36.33
<i>trans</i> -[Ru(acac) ₂ (PyCOOMe) ₂]	<i>P$\bar{1}$</i>	II	29.6
<i>trans</i> -[Ru(acac) ₂ (Py) ₂]	<i>P2₁/n</i>	II	20.28
<i>trans</i> -[Ru(acac) ₂ (Py) ₂]Cl·2MeOH	<i>P2₁/n</i>	III	10.8
<i>trans</i> -[Ru(acac) ₂ (Py) ₂]Cl	<i>C2/m</i>	III	9.98
<i>trans</i> -[Ru ^{III} (acac) ₂ (bpy) ₂]Cl·EtOH·H ₂ O 1 st	<i>P2₁/c</i>	III	9.61
<i>trans</i> -[Ru ^{III} (acac) ₂ (bpy) ₂]Cl·EtOH·H ₂ O 2 nd	<i>P2₁/c</i>	III	14.72
<i>trans</i> -[Ru(acac) ₂ (BPE) ₂]Cl·3CHCl ₃	<i>P$\bar{1}$</i>	III	15.31
Ph ₄ P{ <i>trans</i> - [Ru(acac) ₂ Cl ₂]} 1 st	<i>P$\bar{1}$</i>	III	24.28
Ph ₄ P{ <i>trans</i> -[Ru(acac) ₂ Cl ₂]} 2 nd	<i>P$\bar{1}$</i>	III	35.56

Bite is typically quantified with a normalised bite parameter b , which can be described in reference to d , r (the M-donor bond length) and α (Equations 3.2, 3.3).

$$b = \frac{d}{r} \quad (3.2)$$

$$b = 2\sin\left(\frac{\alpha}{2}\right) \quad (3.3)$$

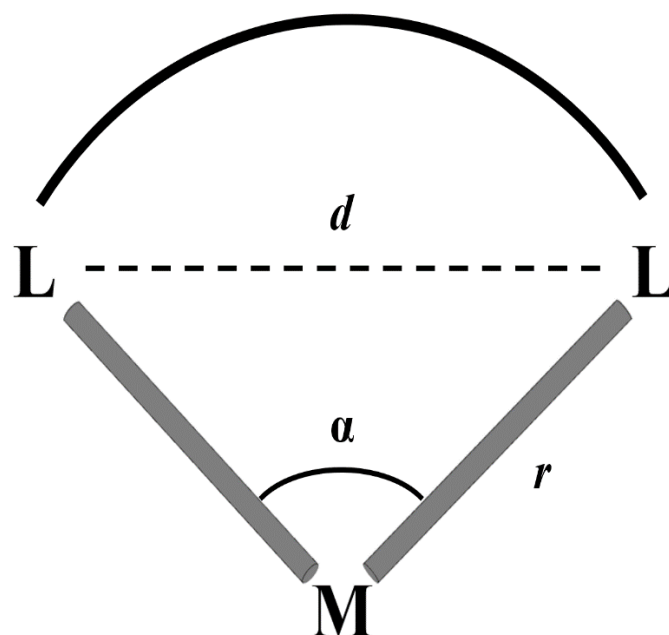


Figure 3.11. Schematic representation of the bidentate bite

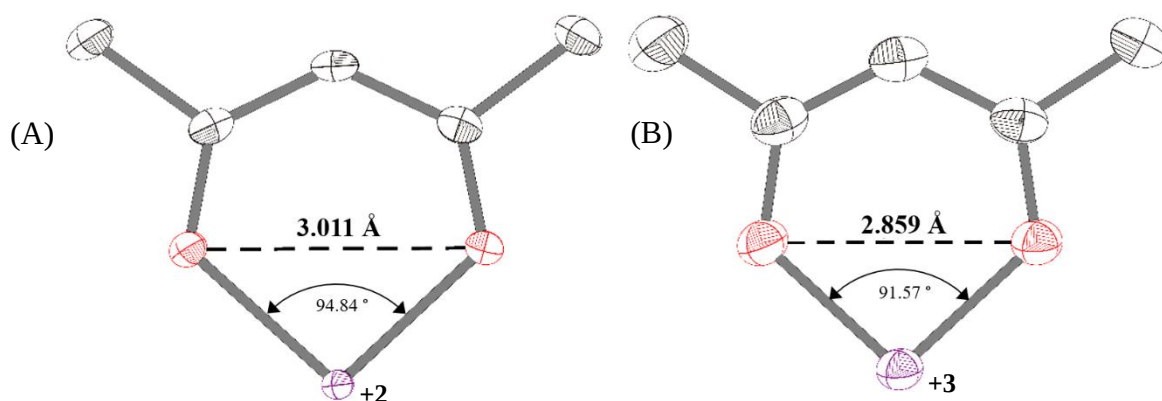


Figure 3.12. Ru acetylacetonate coordination in (A) *trans*-[Ru^{II}(acac)₂(Py)₂] (B) *trans*-[Ru^{III}(acac)₂(Py)₂]Cl·2MeOH. Figures were produced using CrystalMaker X.

The unusual variability in d , α and b between d^5 and d^6 complexes in the *trans*-[Ru(acac)₂(X)₂]^{*n*+} may be a result of two factors (Table 3.6, Table 3.7). A minor contribution may be the change in atomic radius between Ru(II) and Ru(III), due to van der Waals forces, which resulted in a larger van der Waals radius for Ru(II) compared with Ru(III).²⁰²⁻²⁰³ However, the primary cause of this interaction was likely to be electronic interactions between

the metal centre and acetylacetonate ligands. As has been established spectroscopically (Section 3.5), electronic transitions are observed between the π -donating acetylacetonate ligands and the Ru metal centres, including the π -donating Ru(II) and π -accepting Ru(III) configurations. Optimisation of metal-ligand orbital overlap interactions was postulated to influence the normalised bite,^{196,199,201} and outcompete steric interactions within the acetylacetonate ligands to a larger degree than previously observed.

The bite angle of the acetylacetonate ligand in both enantiomers of the coordination complex $[\text{Ru}^{\text{III}}(\text{acac})_3]$ has been discussed several times in the literature.²⁰⁴⁻²⁰⁶ The enantiomers are approximately equivalent in terms of α ; $\sim 93^\circ$, and d ; 2.91 Å. These values lie between the observed values of α and d for the Ru(II) and Ru(III) species of the *trans*- $[\text{Ru}(\text{acac})_2(\text{X})_2]$ family.

Another question is the precursor complex $\text{Ph}_4\text{P}\{\text{trans}-[\text{Ru}^{\text{III}}(\text{acac})_2\text{Cl}_2]\}$, which had a large Σ value, a *cis* O-Ru-O angle and O-O distance comparable to *trans*- $[\text{Ru}^{\text{II}}(\text{acac})_2(\text{X})_2]$ crystal structures. Similar to $[\text{Ru}^{\text{III}}(\text{acac})_3]$, $\text{Ph}_4\text{P}\{\text{trans}-[\text{Ru}^{\text{III}}(\text{acac})_2\text{Cl}_2]\}$ had only π -donating ligands. Symmetry considerations aside, we can infer a relationship between α , d , b and the relative π -backbonding present in the $[\text{Ru}(\text{acac})_2(\text{X})_n]$ system. Systems with only π -donating ligands (such as acac^- and Cl^-) exhibited increased distortion in the Ru(III) oxidation state, where π -bonding interactions are stronger. On the other hand, systems with π -accepting ligands (such as pyz, bpy, BPE, etc.) produced more distorted acac^- ligands in the Ru(II) oxidation state, where π -backbonding interactions are strongest.

To understand the above trend, we first considered the factors at play. The first is the bite angle of the acetylacetonate ligands, which produce the strongest π -bonding interaction when the bite angle is 90° . The second factor is the considerable steric strain on the acetylacetonate ligand itself, which favours larger values of α and d , particularly given the short Ru-O bond distances

observed in these complexes. Competition between these two factors produced the bite angle distortions and was largely altered by the extent of π -bonding between the metal centre and the ligand. The lower σ - and π -acceptor ability of Ru(II) produces substantially distorted bite angles as the acetylacetonate ligands relax to lower steric strain. The higher distortion exhibited by $[\text{Ru}^{\text{III}}(\text{acac})_3]$ and $\text{Ph}_4\text{P}\{\text{trans}-[\text{Ru}^{\text{III}}(\text{acac})_2\text{Cl}_2]\}$ compared with other Ru(III) complexes such as $\text{trans}-[\text{Ru}(\text{acac})_2(\text{Py})_2]\text{Cl}$ resulted from the additional π -donor ligands present in the former complexes, which reduced the overall σ - and π -acceptor capacities of the Ru(III) metal centre.

Table 3.6. *cis* angles and O-O distances across acetylacetonate O-Ru-O coordination

	Space Group	Ru Oxidation State	Individual α (degrees)	Average α (degrees)	O-O distance d (Å)
$\text{trans}-[\text{Ru}(\text{acac})_2(\text{pyz})_2]$	$P2_1/n$	II	94.77 (9)	94.77 (9)	3.008 (3)
$\text{trans}-[\text{Ru}(\text{acac})_2(\text{bpy})_2]$	$Fdd2$	II	95.9 (10), 93.6 (7)	94.8 (14)	3.00 (2) , 3.04 (3)
$\text{trans}-[\text{Ru}(\text{acac})_2(\text{bpy})_2]$ disordered acac	$Fdd2$	II	93.3 (11), 94.3 (8)	93.8 (10)	2.98 (3), 3.02 (3)
$\text{trans}-[\text{Ru}(\text{acac})_2(\text{bpy})_2]$	$C2/c$	II	94.4 (3), 94.4 (3)	94.4 (2)	2.975 (8), 2.981 (9)
$\text{trans}-[\text{Ru}(\text{acac})_2(\text{PyCOOMe})_2]$	$P\bar{1}$	II	94.65 (6)	94.65 (6)	3.003 (2)
$\text{trans}-[\text{Ru}(\text{acac})_2(\text{Py})_2]$	$P2_1/n$	II	94.84 (4)	94.84 (4)	3.0110 (14)
$\text{trans}-[\text{Ru}(\text{acac})_2(\text{Py})_2]\text{Cl}\cdot 2\text{MeOH}$	$P2_1/n$	III	91.09 (1) 91.56 (1)	91.33 (24)	2.853 (4), 2.859 (3)
$\text{trans}-[\text{Ru}(\text{acac})_2(\text{Py})_2]\text{Cl}$	$C2/m$	III	91.4 (3)	91.4 (3)	2.85 (1)
$\text{trans}-[\text{Ru}(\text{acac})_2(\text{BPE})_2]\text{Cl}\cdot 3\text{CHCl}_3$	$P\bar{1}$	III	92.3 (4) 92.9 (4)	92.6 (5)	2.895 (13), 2.909 (14)
$\text{trans}-[\text{Ru}^{\text{III}}(\text{acac})_2(\text{bpy})_2]\text{Cl}\cdot \text{EtOH}\cdot \text{H}_2\text{O}$	$P2_1/c$	III	90.8 (1) 90.8 (1)	90.8 (1)	2.844 (4), 2.848 (4)
$\text{trans}-\text{Ph}_4\text{P}[\text{Ru}(\text{acac})_2\text{Cl}_2]$	$P\bar{1}$	III	94.11 (6), 93.44 (6)	93.78 (28)	2.936 (2), 2.950 (2)

Table 3.7. Normalised bite values, taken with average *d* and *r* values.

	Space Group	Ru Oxidation State	Normalised Bite <i>b</i>
<i>trans</i> -[Ru(acac) ₂ (pyz) ₂]	<i>P2₁/n</i>	II	1.472 (2)
<i>trans</i> -[Ru(acac) ₂ (bpy) ₂]	<i>Fdd2</i>	II	1.471 (11)
<i>trans</i> -[Ru(acac) ₂ (bpy) ₂] disordered acac	<i>Fdd2</i>	II	1.460 (11)
<i>trans</i> -[Ru(acac) ₂ (bpy) ₂]	<i>C2/c</i>	II	1.468 (4)
<i>trans</i> -[Ru(acac) ₂ (PyCOOMe) ₂]	<i>P1̄</i>	II	1.470 (1)
<i>trans</i> -[Ru(acac) ₂ (Py) ₂]	<i>P2₁/n</i>	II	1.473 (1)
<i>trans</i> -[Ru(acac) ₂ (Py) ₂] <i>Cl</i> ·2MeOH	<i>P2₁/n</i>	III	1.430 (2)
<i>trans</i> -[Ru(acac) ₂ (Py) ₂] <i>Cl</i>	<i>C2/m</i>	III	1.430 (6)
<i>trans</i> -[Ru(acac) ₂ (BPE) ₂] <i>Cl</i> ·3CHCl ₃	<i>P1̄</i>	III	1.445 (5)
<i>trans</i> -[Ru ^{III} (acac) ₂ (bpy) ₂] <i>Cl</i> ·EtOH·H ₂ O	<i>P2₁/c</i>	III	1.424 (2)
<i>trans</i> -Ph ₄ P[Ru(acac) ₂ Cl ₂]	<i>P1̄</i>	III	1.460 (1)

3.3.7.3. Coordination Bond Lengths

The lengths of coordination bonds have long been understood to correlate to bond valence.²⁰⁷⁻

²⁰⁸ In the *trans*-[Ru(acac)₂(X)₂] family of complexes, Ru-N and Ru-O bond distances demonstrably change with oxidation state (Table 3.8, 3.9). The Ru(II) complexes are associated with shorter Ru-N bond lengths (< 2.06 Å) and slightly longer Ru-O bond lengths, corresponding to the weaker π -backbonding behaviour of acac-Ru vs pyridyl-Ru coordination. In the Ru(III) oxidation state, the inverse behavior is observed- the Ru-N bond lengths are longer (>2.075 Å) and Ru-O bonds much shorter (~2.0 Å). The Ru-N bonds lengthen because of a loss of π -backbonding on transition from d^6 to d^5 , and the Ru-O bonds shorten because the π -accepting Ru(III) forms a stronger π -backbonding relationship with the π -donating acetylacetonate ligands than Ru(II).

The Ru-N bonds also differ depending on the relative π -acceptor behaviour of the pyridyl ligand. *trans*-[Ru(acac)₂(pyz)₂] produces a much shorter Ru-N bond length than *trans*-[Ru(acac)₂(Py)₂] as pyrazine is a substantially stronger π -acid than pyridine.

Table 3.8. Ru-N bond lengths

Formula	Space Group	Ru Oxidation State	Ru-N Bond Lengths (Å)	Average Ru-N Bond length (Å)
<i>trans</i> -[Ru(acac) ₂ (pyz) ₂]	<i>P2₁/n</i>	II	2.038 (3)	2.038 (3)
<i>trans</i> -[Ru(acac) ₂ (bpy) ₂]	<i>Fdd2</i>	II	2.033 (12) 2.047 (11)	2.040 (8)
<i>trans</i> -[Ru(acac) ₂ (bpy) ₂]	<i>C2/c</i>	II	2.051 (6) 2.041 (5)	2.046 (4)
<i>trans</i> -[Ru(acac) ₂ (PyCOOMe) ₂]	<i>P1</i> [−]	II	2.0425 (17)	2.0425 (17)
<i>trans</i> -[Ru(acac) ₂ (Py) ₂]	<i>P2₁/n</i>	II	2.0501 (12)	2.0501 (12)
<i>trans</i> -[Ru(acac) ₂ (Py) ₂]Cl·2MeOH	<i>P2₁/n</i>	III	2.079 (3) 2.073 (3)	2.076 (2)
<i>trans</i> -[Ru(acac) ₂ (Py) ₂]Cl	<i>C2/m</i>	III	2.077 (8)	2.077 (8)
<i>trans</i> -[Ru(acac) ₂ (BPE) ₂]Cl·3CHCl ₃	<i>P1</i> [−]	III	2.07 (1) 2.09 (1)	2.08 (1)
<i>trans</i> -[Ru ^{III} (acac) ₂ (bpy) ₂]Cl·EtOH·H ₂ O	<i>P2₁/c</i>	III	2.074 (3) 2.071 (3)	2.073 (2)
decaammine- μ -(pyrazine)diruthenium(III,III) hexachloride	<i>P2₁/n</i>	III	2.111 (2)	2.111 (2)

Table 3.9. Ru-O bond lengths for acetylacetonate coordination

Formula	Space Group	Ru Oxidation State	Ru-O Bond Lengths (Å)	Average Ru-O Bond length (Å)
<i>trans</i> -[Ru(acac) ₂ (pyz) ₂]	<i>P2₁/n</i>	II	2.041 (2), 2.046 (2)	2.044 (1)
<i>trans</i> -[Ru(acac) ₂ (bpy) ₂]	<i>Fdd2</i>	II	2.039 (14), 2.041 (14), 2.055 (14), 2.075 (14)	2.053 (7)
<i>trans</i> -[Ru(acac) ₂ (bpy) ₂] disordered acac	<i>Fdd2</i>	II	2.064 (15), 2.051 (15), 2.049 (15), 2.048 (15)	2.053 (8)
<i>trans</i> -[Ru(acac) ₂ (bpy) ₂]	<i>C2/c</i>	II	2.045 (5), 2.009 (6), 2.028 (6), 2.035 (5)	2.029 (3)
<i>Trans</i> -[Ru(acac) ₂ (PyCOOMe) ₂]	<i>P1̄</i>	II	2.0442 (14), 2.0402 (13)	2.0422 (10)
<i>Trans</i> -[Ru(acac) ₂ (Py) ₂]	<i>P2₁/n</i>	II	2.0419 (1), 2.0474 (1)	2.04470 (7)
<i>Trans</i> - [Ru(acac) ₂ (Py) ₂]Cl·2MeOH	<i>P2₁/n</i>	III	1.999 (3), 1.998 (2), 1.995 (2), 1.994 (2)	1.997 (1)
<i>Trans</i> -[Ru(acac) ₂ (Py) ₂]Cl	<i>C2/m</i>	III	1.991 (7), 1.995 (7)	1.993 (5)
<i>Trans</i> - [Ru(acac) ₂ (BPE) ₂]Cl·3CHCl ₃	<i>P1̄</i>	III	2.013 (9), 2.000 (1), 2.007 (9), 2.006 (1)	2.007 (3)
<i>Trans</i> - [Ru ^{III} (acac) ₂ (bpy) ₂]Cl·EtOH·H ₂ O	<i>P2₁/c</i>	III	1.999 (2), 1.995 (3), 2.001 (3), 1.998 (3)	1.998 (1)
<i>Trans</i> -Ph ₄ P[Ru(acac) ₂ Cl ₂]	<i>P1̄</i>	III	2.011 (2), 2.012 (2), 2.017 (1), 2.022 (2)	2.0155 (9)

A crystallographic effect not discussed in this work is the influence of π -backbonding on the shape of pyridyl rings. In theory, stronger π -backbonding should cause rings to constrict, giving smaller aromatic C-C and C-N bond lengths in stronger π -backbonded ligands.²⁰⁹ This analysis

was attempted between Ru(II) and Ru(III) structures of RuML2, but experimental error on these bond lengths was too large to determine any difference.

3.4. Electrochemistry

3.4.1. $\text{Ph}_4\text{P}\{\text{trans}[\text{Ru}(\text{acac})_2\text{Cl}_2]\}$

$\text{Ph}_4\text{P}\{\text{trans}[\text{Ru}(\text{acac})_2\text{Cl}_2]\}$ exhibits complex electrochemistry, largely owing to its labile ligands. At least five electrochemical processes can be observed in the full voltammogram (Figure 3.13), including two irreversible reductions at $E_{\text{red}} = -1.52$ V vs Fc^+/Fc and $E_{\text{red}} = -2.27$ V vs Fc^+/Fc , a *quasi*-reversible process at $E_{1/2} = 0.322$ V vs Fc^+/Fc and $\Delta E_p = 60$ mV, and a *quasi*-reversible oxidation at $E_{1/2} = 0.842$ V vs Fc^+/Fc $\Delta E_p = 69$ mV.

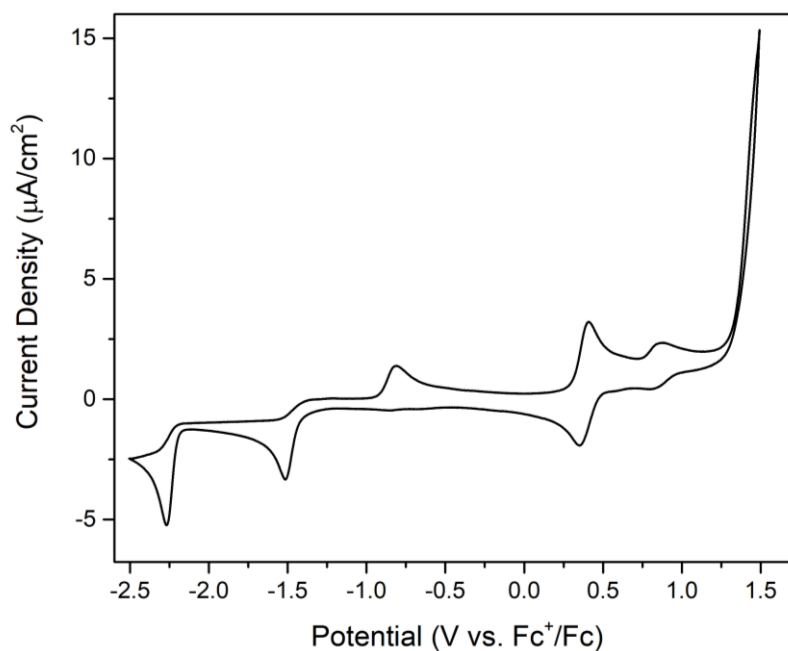


Figure 3.13. Cyclic voltammogram of $\text{Ph}_4\text{P}\{\text{trans}[\text{Ru}(\text{acac})_2\text{Cl}_2]\}$, starting at -0.54 and taken from to -2.5 to 1.5 V vs Fc^+/Fc at 100 mV/s. W.E.: Glassy carbon

The most negative irreversible reduction at $E_{\text{red}} = -2.27$ V vs Fc^+/Fc is most likely associated with the Ph_4P^+ cation, which has been observed at approx. -2.2 V vs Fc^+/Fc in the literature.²¹⁰

The process at $E_{1/2} = 0.322$ V vs Fc^+/Fc , $\Delta E_p = 60$ mV and $|i_{p,c}/i_{p,a}| = 1.08$ at 100 mV/s is a chemically reversible oxidation (Figure 3.14). This process is associated with the Ru(IV/III) couple. The ruthenium(IV) oxidation state is stabilised by the σ - and π -donor Cl^- and acac^- ligands.²¹¹⁻²¹²

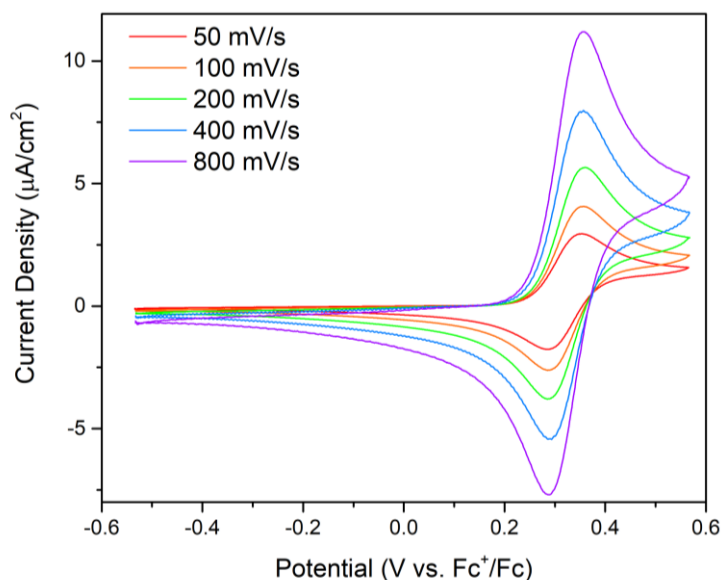


Figure 3.14. Cyclic voltammogram of $\text{Ph}_4\text{P}\{\text{trans}[\text{Ru}(\text{acac})_2\text{Cl}_2]\}$, taken from -0.53 to 0.57 V vs Fc^+/Fc at various scan rates. W.E.: Glassy carbon

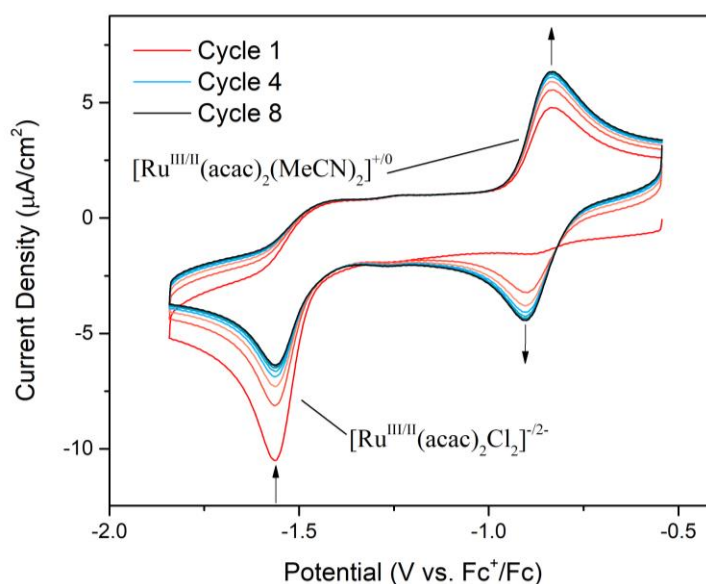
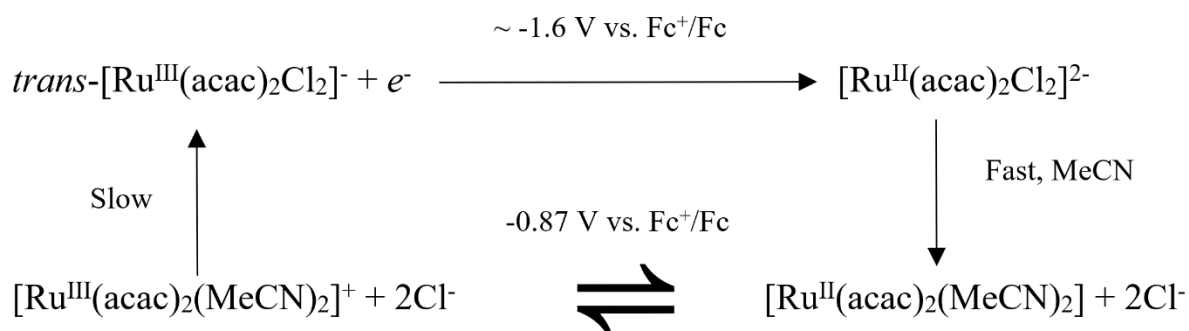


Figure 3.15. Cyclic voltammogram of $\text{Ph}_4\text{P}\{\text{trans}[\text{Ru}(\text{acac})_2\text{Cl}_2]\}$, taken from -0.54 to -1.84 V vs Fc^+/Fc at 800 mV/s. Sample was cycled 8 times without pause. W.E.: Glassy carbon

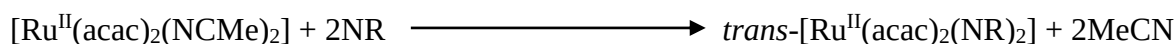
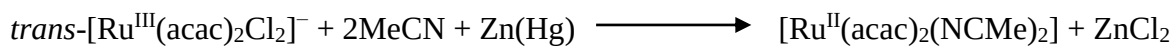
The irreversible reduction process at $E_{\text{red}} = -1.52$ V vs Fc^+/Fc is the most unique feature in the electrochemical profile of $\text{Ph}_4\text{P}\{\text{trans}[\text{Ru}(\text{acac})_2\text{Cl}_2]\}$ (Figure 3.15). Unlike other Ru(II/III) couples discussed in this chapter, the process is an irreversible reduction, which showed that a fast chemical reaction occurs after reduction to Ru(II). This is consistent with the following reaction scheme (Scheme 3.1), whereby the π base chloride ligands are substituted with the π -base MeCN ligands in the Ru(II) oxidation state. This is also relevant to the intermediates present in the substitution reactions of $\text{Ph}_4\text{P}\{\text{trans}[\text{Ru}^{\text{III}}(\text{acac})_2\text{Cl}_2]\}$ when chemically reduced in the presence of other π acids.



Scheme 3.1. Proposed reaction pathway of $\text{trans}[\text{Ru}^{\text{III}}(\text{acac})_2\text{Cl}_2]^-$ in a reducing environment

The above assignment of the irreversible process at $E_{\text{red}} = -1.52$ V vs Fc^+/Fc also directly affects the current density of the process at $E_{1/2} = -0.87$ V vs Fc^+/Fc , $\Delta E_p = 69$ mV and $|i_{p,c}/i_{p,a}| = 1.22$ (Figure 3.15). As the sample is repeatedly cycled past -1.52 V vs Fc^+/Fc , the current density of the $[\text{Ru}^{\text{III/II}}(\text{acac})_2\text{Cl}_2]^{-/2-}$ process reduces. Simultaneously the process at $E_{1/2} = -0.87$ V vs Fc^+/Fc appears *after* the irreversible process occurs and increases in current density with repeated cycles. Both phenomena together support the proposed reaction scheme 3.1, with the new process at $E_{1/2} = -0.87$ V vs Fc^+/Fc corresponding with the *quasi*-reversible Ru(III/II) redox couple of $[\text{Ru}^{\text{III/II}}(\text{acac})_2(\text{MeCN})_2]^{+/0}$. Both phenomena are diffusion controlled.

The *in situ* production of $[\text{Ru}^{\text{II}}(\text{acac})_2(\text{MeCN})_2]$ as an intermediate $\text{trans}-[\text{Ru}^{\text{III}}(\text{acac})_2\text{Cl}_2]$ offers a simple synthetic pathway for the synthesis of $\text{trans}-[\text{Ru}(\text{acac})_2(\text{X})_2]$ complexes:



Scheme 3.2. Proposed reaction pathway for synthesis of $[\text{Ru}(\text{acac})_2(\text{NR})_2]$ in MeCN, where NR is any π -acid with a nitrogen Lewis base e.g., pyrazine, bipyridine, BPE.

$\text{Ph}_4\text{P}\{\text{trans}-[\text{Ru}^{\text{III}}(\text{acac})_2\text{Cl}_2]\}$ can thus be used to produce a variety of symmetrical coordination complexes. However, as noted in Section 3.2., a mixture of Ru(II) and Ru(III) products are observed in the syntheses of RuML2 and RuML4, despite the Zn(Hg) reducing agent. Given the mechanism above, we must conclude that the product $\text{trans}-[\text{Ru}^{\text{II}}(\text{acac})_2(\text{NR})_2]$ may undergo a further reaction to produce the ion $\text{trans}-[\text{Ru}^{\text{III}}(\text{acac})_2(\text{NR})_2]^+$, although the exact mechanism is unclear.

3.4.2. RuML1

The coordination complex $\text{trans}-[\text{Ru}^{\text{II}}(\text{acac})_2(\text{pyz})_2]$ displays simple electrochemical behaviour, reflecting the relatively inert ligands acetylacetonate and pyrazine. A one-electron *quasi-reversible* Ru(III/II) couple was observed at $E_{1/2} = -0.342$ V vs Fc^+/Fc , $E_p = 72$ mV and $|i_{p,c}/i_{p,a}| = 1.30$ at 100 mV/s (Figure 3.16).

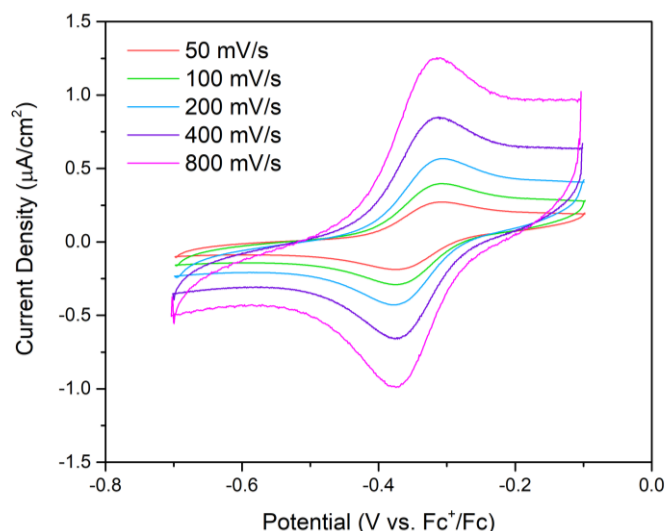


Figure 3.16. Cyclic voltammogram of the *quasi*-reversible process observed in RuML1, taken from -0.7 to -0.1 V vs Fc^+/Fc . W.E.: Glassy carbon

Additionally, other redox processes were observed at high positive and negative potentials in the measurement window (Figure 3.17). A *quasi*-reversible couple was observed at $E_{1/2} =$ approx. -2.2 V vs Fc^+/Fc . This process may be due to the Ru(II/I) couple, which is observed in at a similar potential in Ru pyridyl complexes in the literature.²¹³ The large positive spike in current towards 1.5 V vs Fc^+/Fc is likely the oxidation of TBAPF₆.¹¹³

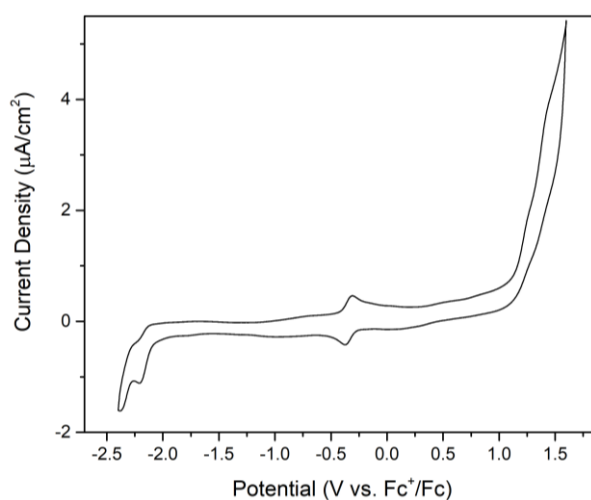


Figure 3.17. Cyclic voltammogram of RuML1, taken from -2.5 to 1.5 V vs Fc^+/Fc at 100 mV/s. W.E.: Glassy carbon.

3.4.3. RuML2

Similar redox processes are observed for RuML2 to those of RuML1. A reversible, single electron redox process occurs at -0.517 V vs Fc^+/Fc , $\Delta E_p = 71.8$ mV and $|i_{p,c}/i_{p,a}| = 0.90$, corresponding with the Ru(III/II) couple (Figure 3.18).

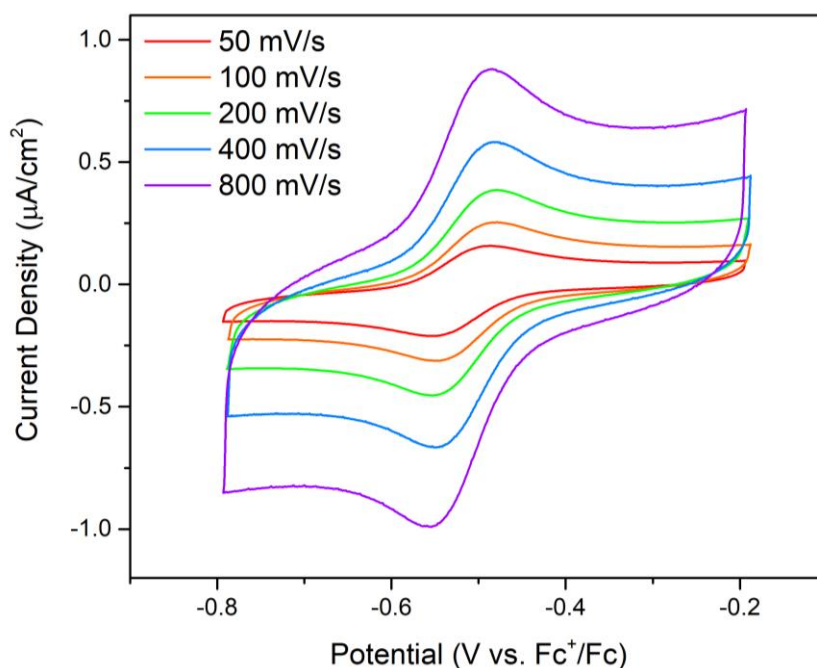


Figure 3.18. Cyclic voltammogram of RuML2, taken from -0.79 to -0.19 V vs Fc^+/Fc . W.E.: Glassy carbon

Additionally, several processes are observable at the highly positive and negative potentials in the window (Figure 3.19). The origin of these processes is similar to RuML1. The *quasi*-reversible process at approx. -2.3 V vs Fc^+/Fc is likely due to the Ru(II/I) couple, the *quasi*-reversible process at approx. 1.1 V vs Fc^+/Fc and the sharp oxidation at the most positive end of the potential window are attributable to the TBAPF_6 electrolyte.

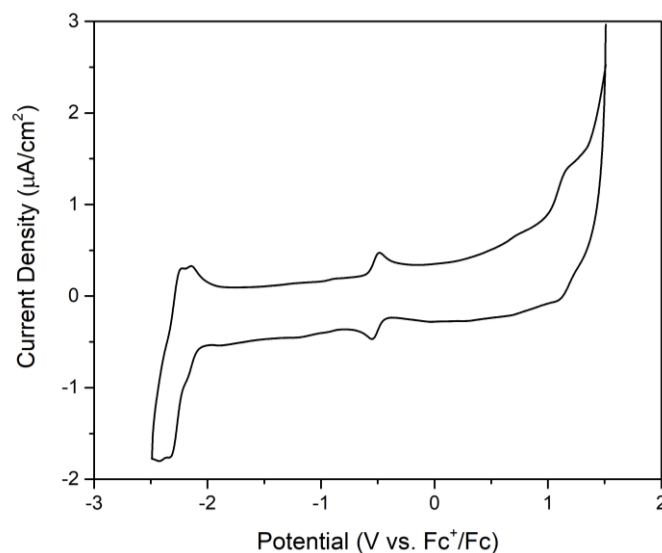


Figure 3.19. Cyclic voltammogram of RuML2, taken from -2.49 to 1.51 V vs Fc^+/Fc at 100 mV/s. W.E.: Glassy carbon

3.4.4. RuML4

Similar redox processes are observed for RuML4 to RuML1. A *quasi*-reversible one-electron Ru(III/II) couple occurs at $E_{1/2} = -0.550$ V vs Fc^+/Fc , $E_p = 72.3$ mV and $|i_{p,c}/i_{p,a}| = 1.10$ at 100 mV/s (Figure 3.20).

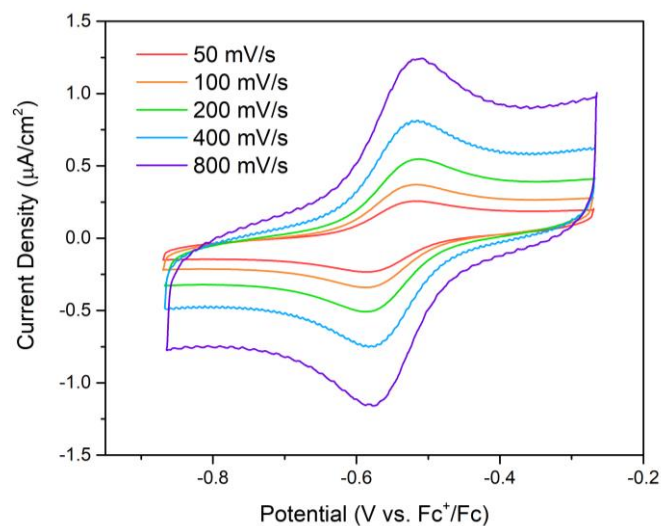


Figure 3.20. Cyclic voltammogram of the reversible process observed in RuML4, taken from -0.87 to -0.27 V vs Fc^+/Fc . W.E.: Glassy carbon

The full voltammogram of RuML4 reveals a multitude of processes (Figure 3.21). The weak processes at $E_{1/2} = \sim -0.96$ V vs Fc^+/Fc and $E_{\text{ox}} = 0.72$ V vs Fc^+/Fc are most likely associated with small impurities, present due to the difficulty in separating RuML4 from its precursors and synthetic side products. The large process at $E_{1/2} = -2.033$ V vs Fc^+/Fc is may be due to a reduction of the BPE ligand, and the process at $E_{1/2} = \sim -2.3$ V vs Fc^+/Fc is likely the Ru(II/I) couple.

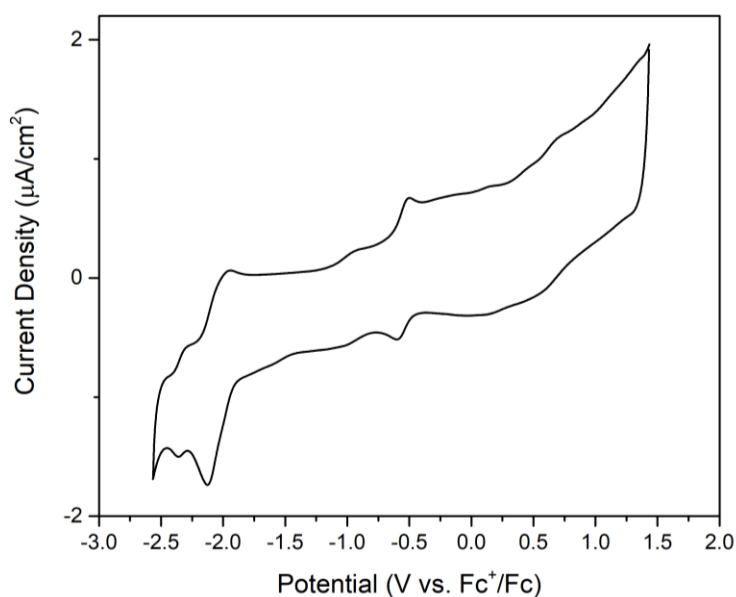


Figure 3.21. Cyclic voltammogram of RuML4, taken from -2.5 to 1.5 V vs Fc^+/Fc at 100 mV/s. W.E.: Glassy carbon

3.4.5. RuML0

Similar redox processes are observed for RuML0 to those of RuML1. Two *quasi-reversible* redox processes are observable at -0.596 and 1.083 V vs Fc^+/Fc .

The *quasi-reversible* one-electron process at -0.596 V vs Fc^+/Fc , $E_p = 62.8$ mV and $|i_{p,c}/i_{p,a}| = 1.04$ at 100 mV/s is the Ru(III/II) couple (Figure 3.22). The more negative potential of this couple compared to the other metalloligands in this chapter is as a result of the poor π -acceptor behaviour of pyridine, resulting in a less stabilised Ru(II) oxidation state than in RuML1. The

material is very easily reduced however, forming $trans\text{-}[\text{Ru}^{\text{II}}(\text{acac})_2(\text{Py})_2]^+$ salts readily in solution.

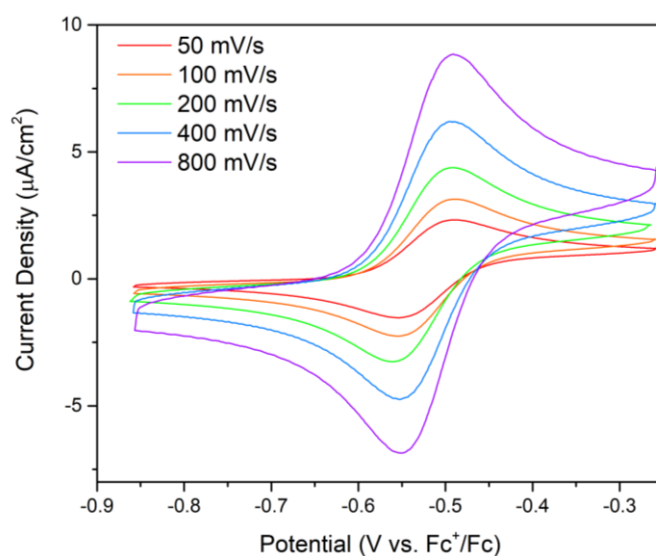


Figure 3.22. Cyclic voltammogram of RuML0, taken from -0.85 to -0.25 V vs Fc^+/Fc . W.E.: Glassy carbon. The origins of the *quasi*-reversible process at 1.083 V vs Fc^+/Fc , $E_p = 72.2$ mV and $|i_{p,c}/i_{p,a}| = 1.37$ at 100 mV/s are unknown (Figure 3.23).

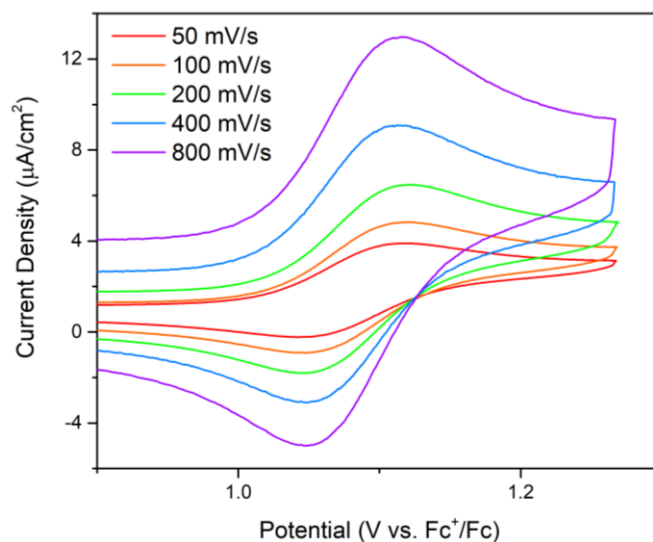


Figure 3.23. Cyclic voltammogram of RuML0, taken from -0.73 to 1.27 V vs Fc^+/Fc . W.E.: Glassy carbon

3.4.6. Trends and General Discussion

A trend in the redox potentials of the Ru(III/II) couples in the above metal complexes can be observed (Table 3.10). This trend is attributable to the relative strength of the π -acid ligands coordinated to the metal centres. The fully occupied low-energy orbitals of Ru(II) are much stronger π -bases than the partially filled Ru(III) low spin orbitals, and hence, π -backbonding is much stronger in Ru(II). This results in much more positive Ru(III/II) potentials with the stronger π ligands. In order from strong to weak π -backbonding: pyrazine, 4,4'-bipyridine, 1,2-bis(4-pyridyl)ethylene, pyridine and acetonitrile.

As observed in Section 3.2., the synthesis of *trans*-[Ru(acac)₂(X)₂] tends to produce both Ru(II) and Ru(III) products, with the exception of RuML1. This phenomenon could be related to the reduction potential of the complex, where low oxidation potentials result in Ru(III) products. RuML4 and RuML0 in particular appear to produce the Ru(III) complex as a major product due to their relatively low oxidation potentials. Oxidation processes tend to be fast for Ru(II), hence traces of oxygen in a reaction will produce a mixture of Ru(II) and Ru(III).

Table 3.10. Variation of half wave potentials of Ru(III/II) couple in the *trans*-[Ru(acac)₂(X)₂] family of complexes, averaged across scan rates 50, 100, 200, 400 and 800 mV/s

Complex Formula	$E_{1/2}$ of Ru(III/II) Couple (V vs Fc ⁺ /Fc)
[Ru(acac) ₂ (pyz) ₂] ⁺⁰	−0.342
[Ru(acac) ₂ (bpy) ₂] ⁺⁰	−0.517
[Ru(acac) ₂ (BPE) ₂] ⁺⁰	−0.550
[Ru(acac) ₂ (Py) ₂] ⁺⁰	−0.596
[Ru(acac) ₂ (MeCN) ₂] ⁺⁰	−0.867

3.5. UV-vis Spectroscopy

This Section discusses the optical and ultra-violet electronic transitions observed in the family of *trans*-[Ru(acac)₂(X)₂] complexes described above. In order to effectively probe the d^5 - d^6 boundary, SEC measurements were performed to obtain the electronic transition profiles of the Ru(III/II) couples.

Given the deep colours of the metal complexes, and the well-established electronic behaviour of ruthenium pyridyl complexes,¹³ we anticipated several charge transfer bands between metals and ligands, as well as intra-ligand transitions in the UV region. The inclusion of both pyridyl and acetylacetonate ligands resulted in complex and highly convoluted spectra with identifiable similarities between different members of the family.

In order to properly identify and deconvolute the transitions three complexes in two oxidation states were modelled with DFT, in Gaussian 16.¹⁶⁹

3.5.1. Ph₄P{*trans*-[Ru(acac)₂Cl₂]}

The electronic absorption spectrum of Ph₄P{*trans*-[Ru(acac)₂Cl₂] } contains numerous convoluted absorption features (Figure 3.24). As the metal centre is Ru(III), LMCT occurs to the π -accepting metal from the π -donor acac⁻ and Cl⁻ ligands. These transitions are present in the visible region of the spectrum. Deconvolution was achieved by comparison with Ru(III) spectra of *trans*-[Ru(acac)₂(X)₂] complexes.

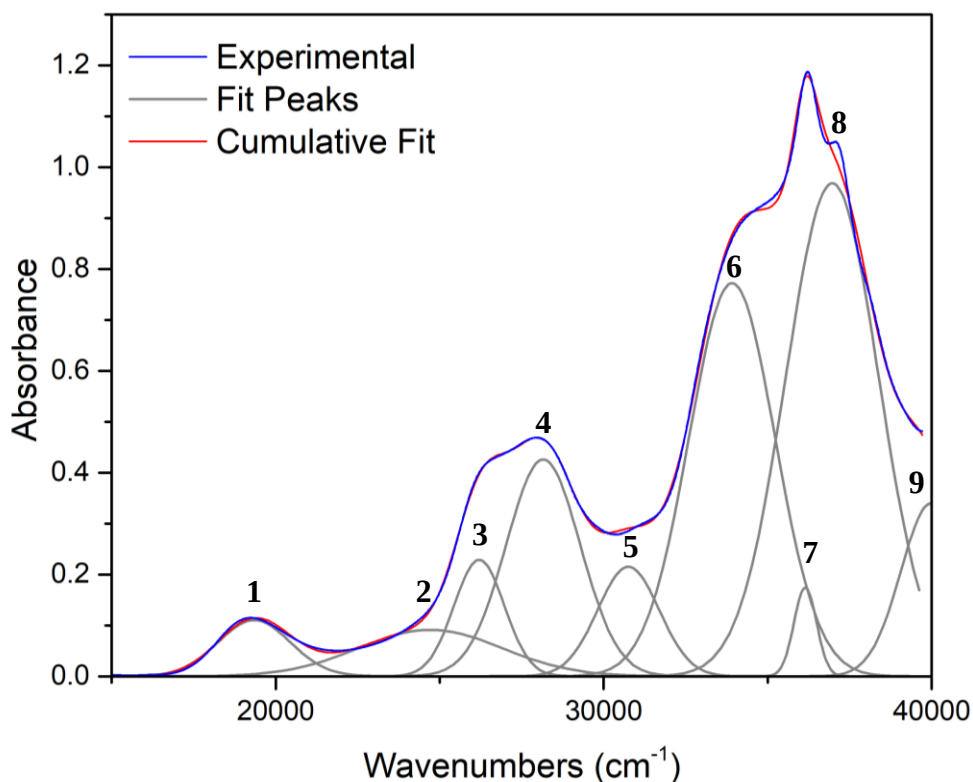


Figure 3.24. Deconvoluted spectrum of $\text{Ph}_4\text{P}\{\text{trans}[\text{Ru}(\text{acac})_2\text{Cl}_2]\}$ in chloroform. Deconvolution was performed with Peak Analyser in Origin 2016, using Gaussian functions.

Table 3.11. Deconvoluted electronic band assignments for $\text{Ph}_4\text{P}\{\text{trans}[\text{Ru}(\text{acac})_2\text{Cl}_2]\}$

Transition Number	Experimental λ ($\times 10^3 \text{ cm}^{-1}$)	Molar Absorption Coefficient ($\times 10^3 \text{ M}^{-1}\text{cm}^{-1}$)
1	19.3	1.5
2	24.7	1.2
3	26.2	3.1
4	28.2	5.7
5	30.8	2.9
6	33.9	10
7	36.2	2.3
8	37.0	13
9	40.0	4.6

3.5.2. RuML1

UV-vis SEC of RuML1 presents a motif that is preserved in observations of analogous materials (Figure 3.25). In the Ru(II) oxidation state, three convoluted bands are observed in the visible region, with multiple overlapping transitions between 30,000 and 45,000 cm^{-1} , and extremely intense transitions above 45,000 cm^{-1} . When oxidised to Ru(III), many features in the visible region disappear, leaving a weakly absorbing band under 20,000 cm^{-1} . Multiple overlapping bands appear around 30,000 cm^{-1} . The near-UV transitions change shape, becoming more broad and increasing in energy slightly. The remaining UV transitions also increase significantly in intensity. The SEC yields reversible spectroscopic changes.

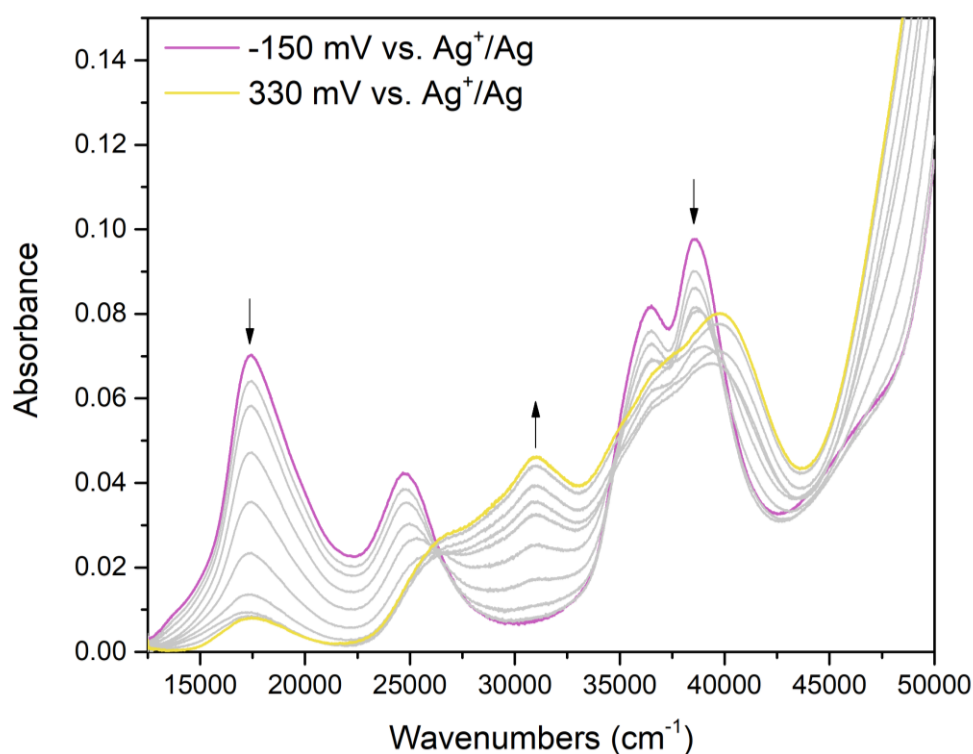


Figure 3.25. UV-vis SEC of *trans*-[Ru(acac)₂(pyz)₂] in 0.1 M TBAPF₆ in MeCN. Concentration 78 μM .

While RuML1 presents typical behaviour of the *trans*-[Ru^{III/II}(acac)₂(X)₂]⁺⁰, the spectroelectrochemistry itself is not quantitative. At some intermediate step during the

oxidation of the complex, the concentration of the sample notably starts to increase. This results in drifting isosbestic points at 26,400, 34,700 and 39,900 cm^{-1} . Isosbestic points may drift under some conditions- namely if there is a change in concentration, if more than two species are involved in the reaction, or if the molar absorptivity of the precursor is altered.²¹⁴⁻²¹⁵

Normalisation of the spectrum was achieved by applying a factor to all cycles to equate the absorbance at the 34,700 cm^{-1} isosbestic point (Figure 3.26). The other isosbestic points are in good agreement after this process, meaning the drifting isosbestic points are due to a change in concentration and not some other source.

The change in concentration over the course of the experiment occurs in both MeCN and DMF, and is likely due to the changing surface properties of the Pt working electrode. RuML1 has a very low solubility in acetonitrile, and saturated solutions were used for UV-vis SEC. Small changes in surface properties could conceivably cause precipitation of the sample. Another possibility is that microscopic particles of RuML1 remain undissolved in the Ru(II) spectrum, and oxidation of the system causes solvation of these particles, thereby increasing the concentration.

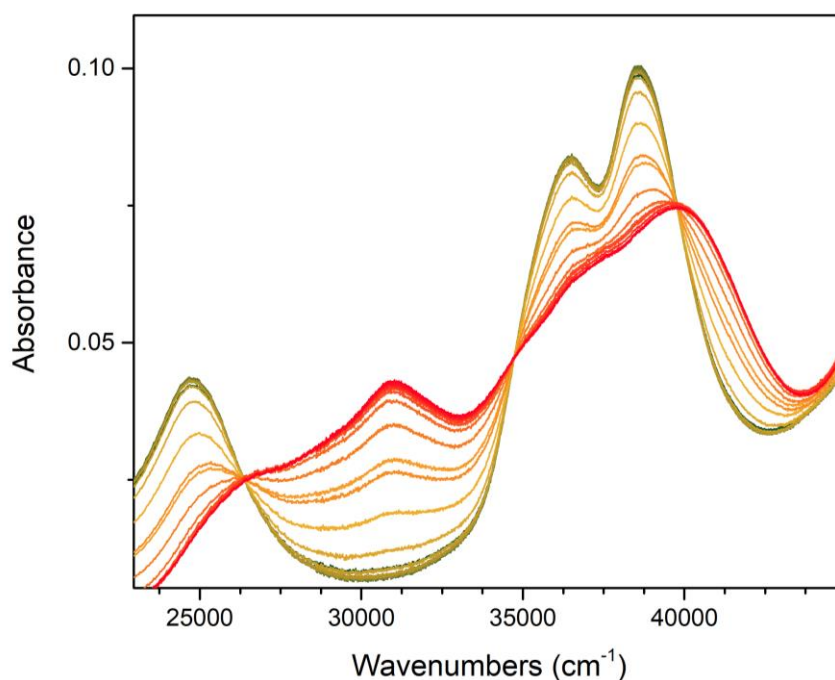


Figure 3.26. Isosbestic points of RuML1 SEC after normalisation at $34,700\text{ cm}^{-1}$, in 0.1 M TBAPF_6 in MeCN

The spectrum of RuML1 was deconvoluted with reference to the simulated spectrum (Figure 3.27A). The simulated spectrum generally gave estimates for band maxima $\sim 7000\text{--}10,000\text{ cm}^{-1}$ higher than experimental observations. This combined with highly convoluted UV bands, resulted in substantial difficulty in assigning the high energy region of the spectrum. Particularly, it is difficult to determine if transition **10** occurs after the trough at $42,600\text{ cm}^{-1}$ in the experimental spectrum, and thus it was excluded from the deconvolution. Due to its minimal impact on the spectrum, transition **5** was also excluded. Even with these concessions the deconvolution is far from perfect and should only be considered accurate below $30,000\text{ cm}^{-1}$. Primarily, the simulated spectrum was used to predict the order and relative area of each Gaussian function during deconvolution. Comparisons of simulated and experimental band maxima are found in Table 3.12.

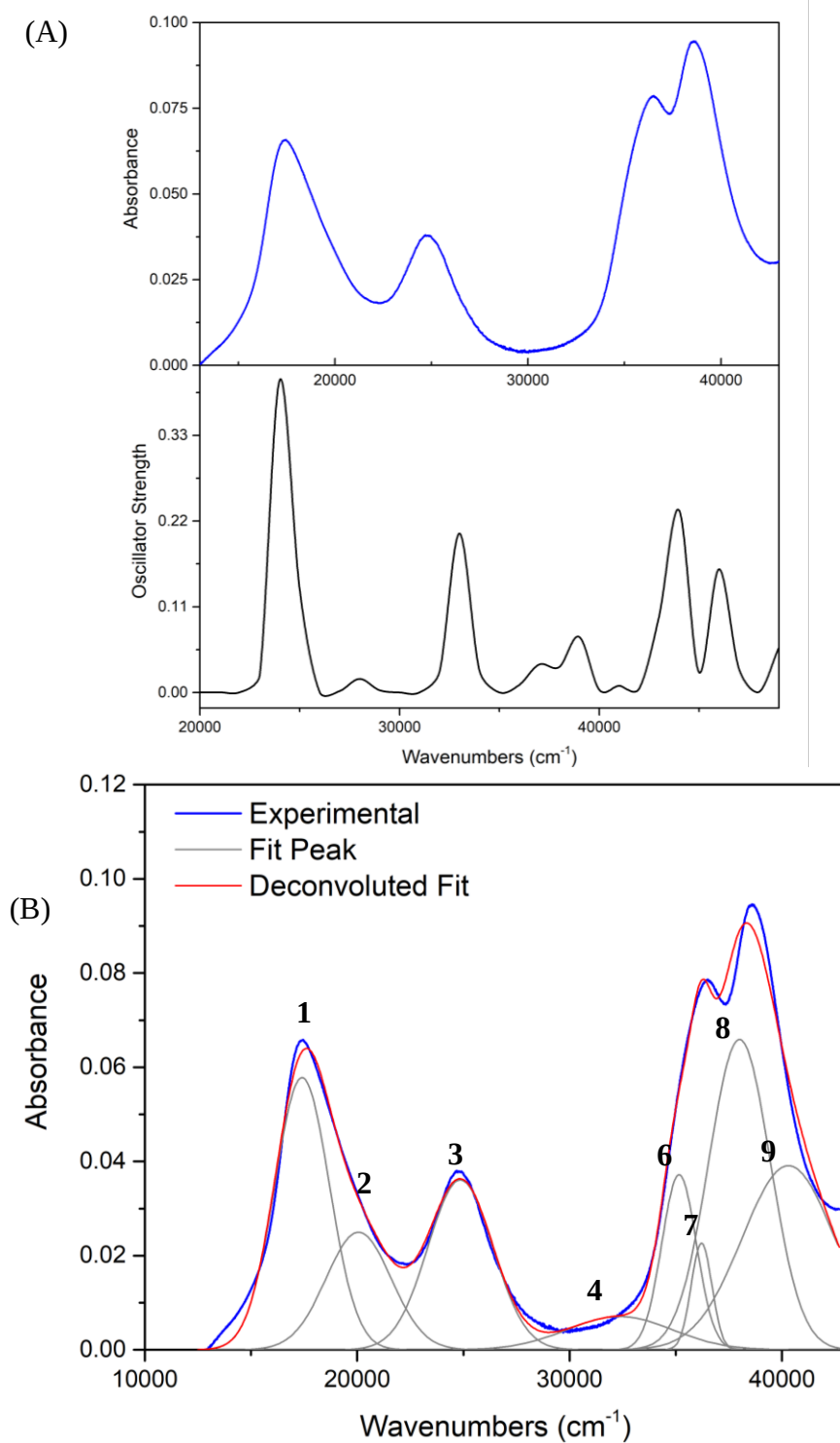


Figure 3.27. (A) Comparison of the experimental and simulated electronic spectrum of RuML1. Top: RuML1 in 0.1 M TBAPF₆ in MeCN. Bottom: Simulated Spectrum, calculated with Gaussian 16. X-axis has been adjusted to account for blueshift and to improve clarity. (B) Deconvoluted spectrum of RuML1 in 0.1 M TBAPF₆ in MeCN. Deconvolution was performed with Peak Analyser in Origin 2016, using Gaussian functions.

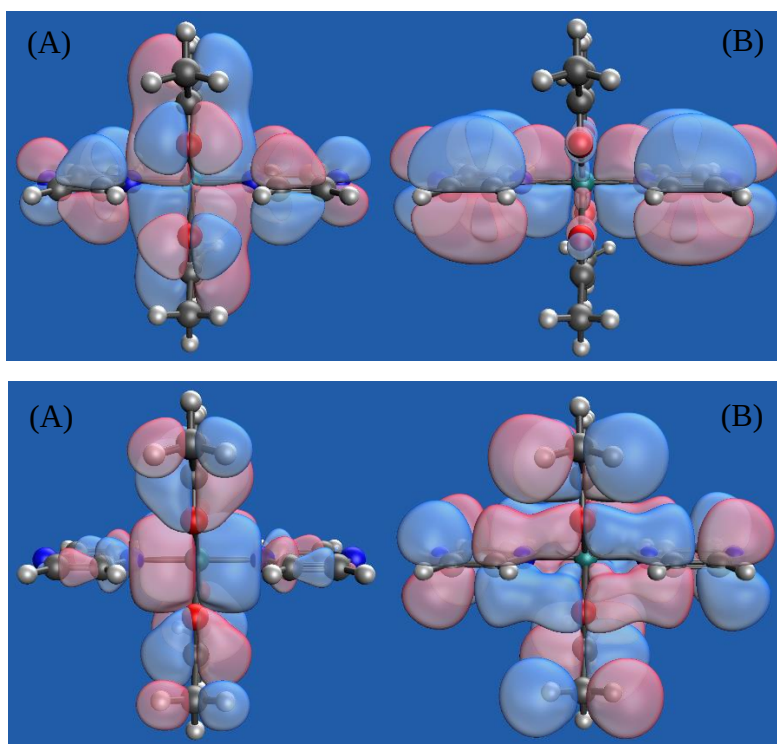


Figure 3.28. Selected simulated molecular orbitals for electronic transitions in *trans*-[Ru^{II}(acac)₂(pyz)₂], calculated with the CAM-B3LYP/def2-SVP method.¹⁷⁰ (A) Transition 1; (B) Transition 3. See Appendix C for excluded figures.

Table 3.12. Modelling of the UV-vis spectrum of RuML1:

Transition Number	RuML1 experimental deconvoluted λ ($\times 10^3 \text{ cm}^{-1}$)	RuML1 simulated λ ($\times 10^3 \text{ cm}^{-1}$)	Molar Absorption Coefficient ($\times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$)	Symmetry	Character
1	17.4	24.2	13	$B_{1g} \rightarrow B_{2u}$	MLCT
2	20.1	28.1	5.7	$B_{1g} \rightarrow A_u$	MLCT
3	24.9	33.0	8.3	$B_{2g} \rightarrow A_u$	MLCT
4	32.4	36.8	5.2	$B_{2g} \rightarrow A_u$	MLCT
5	-	37.2	15	$A_g \rightarrow B_{2u}$	Pyz internal
6	35.2	38.7	8.6	$B_{1g} \rightarrow B_{2u}$	MLCT
7	36.2	41.3	1.6	$B_{3u} \rightarrow B_{1g}$	
8	38.0	43.7	9.0	$B_{1g} \rightarrow A_u$	
9	40.3	46.1	15	$B_{3g} \rightarrow B_{2u}$	Pyz internal
10	-	49.7	13	$B_{3u} \rightarrow B_{2g}$	Acac internal

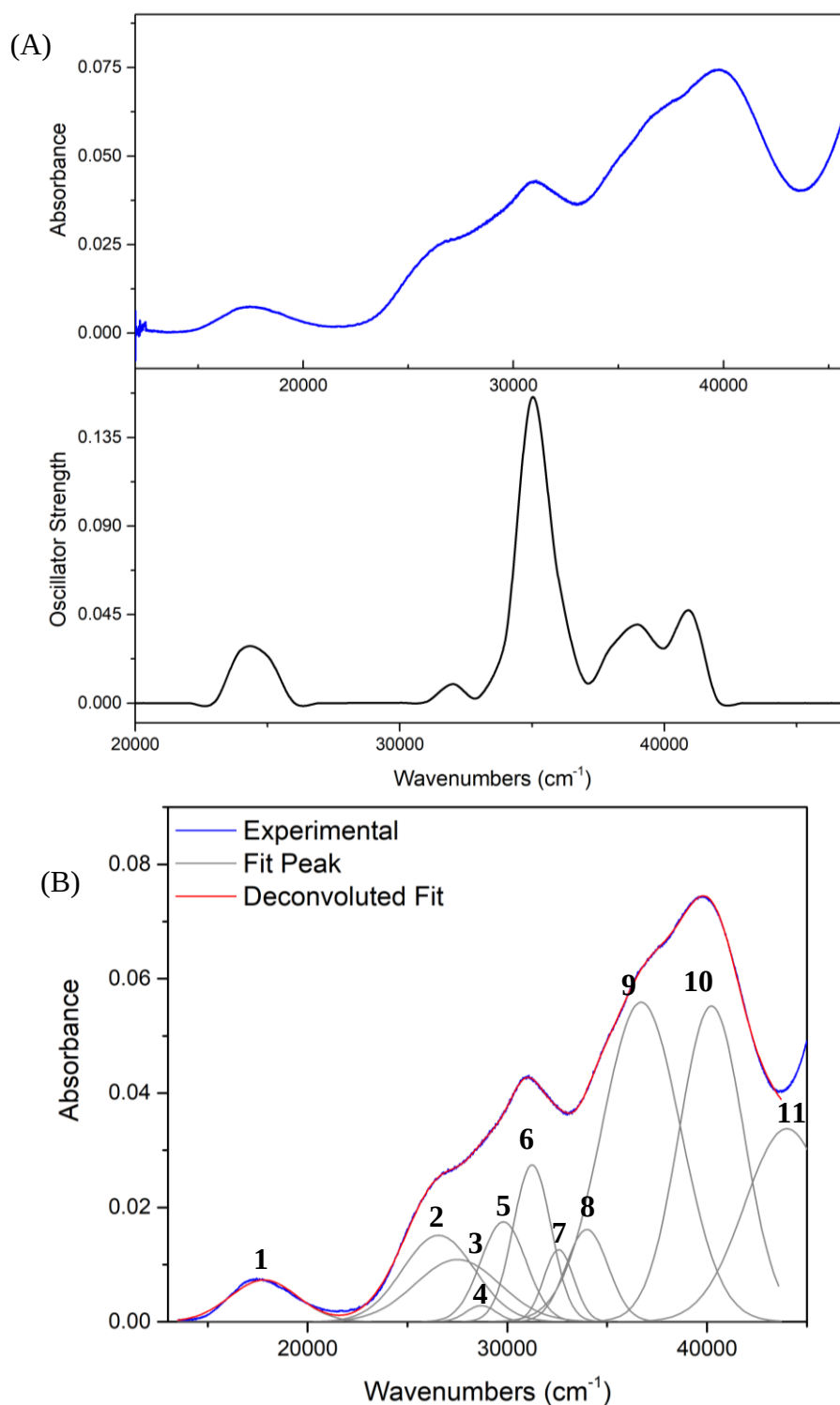
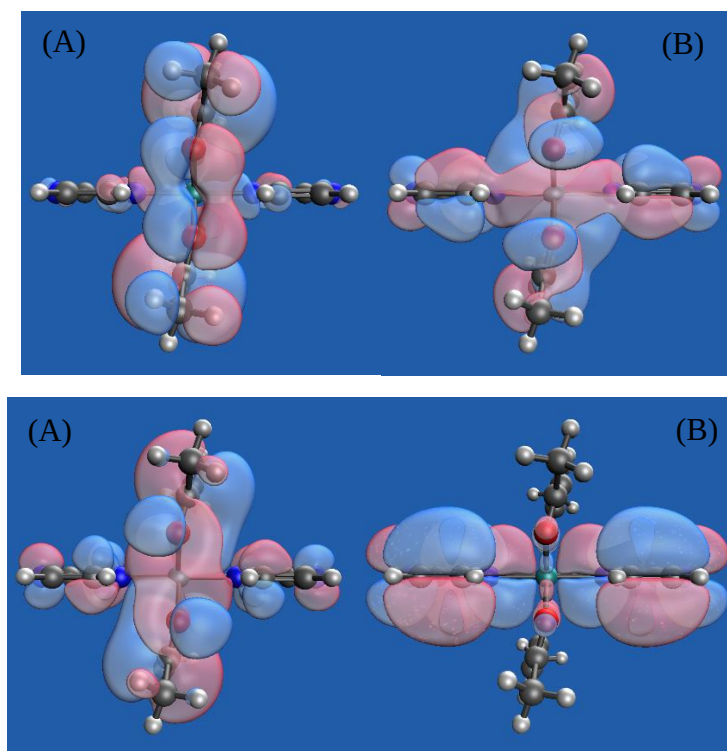


Figure 3.29. (A) Comparison of the experimental and simulated electronic spectrum of RuML1⁺. Top: RuML1⁺ in 0.1 M TBAPF₆ in MeCN. Bottom: Simulated Spectrum, calculated with Gaussian 16. X-axis has been adjusted to account for blueshift and to improve clarity. (B) Deconvoluted spectrum of RuML1⁺ in 0.1 M TBAPF₆ in MeCN. Deconvolution was performed with Peak Analyser in Origin 2016, using Gaussian functions.

Table 3.13. Modelling of the UV-vis spectrum of RuML1⁺:

Transition Number	RuML1 experimental deconvoluted λ ($\times 10^3$ cm ⁻¹)	RuML1 simulated λ ($\times 10^3$ cm ⁻¹)	Molar Absorption Coefficient ($\times 10^3$ M ⁻¹ cm ⁻¹)	Symmetry	Character
1	17.8	24.5	1.7	$B_{3u} \rightarrow B_{1g}$	LMCT
2	26.6	32.2	3.5	$B_{1g} \rightarrow B_{2u}$	MLCT
3	28.7	34.3	4.0	$A_g \rightarrow B_{2u}$	Pyz internal
4	29.8	34.9	0.65	$B_{1g} \rightarrow B_{2u}$	MLCT
5	31.2	35.5	6.3	$B_{1g} \rightarrow A_u$	Acac internal
6	32.6	36.2	2.9	$B_{2u} \rightarrow B_{1g}$	LMCT
7	27.5	36.5	2.5	$B_{2u} \rightarrow B_{1g}$	LMCT
8	34.0	38.4	3.7	$B_{2g} \rightarrow A_u$	Acac internal
9	36.7	38.8	13	$B_{1g} \rightarrow A_u$	Acac internal
10	40.2	40.6	13	$B_{1g} \rightarrow A_u$	Acac internal
11	44.0	40.8	7.8	$B_{1g} \rightarrow B_{2u}$	MLCT

**Figure 3.30.** Selected simulated molecular orbitals for electronic transitions in *trans*-[Ru^{III}(acac)₂(pyz)₂]⁺, calculated with the CAM-B3LYP/def2-SVP method.¹⁷⁰ (A) Transition 1; (B) Transition 2. See Appendix C for excluded figures.

3.5.3. RuML2

RuML2 differs from other members of the *trans*-[Ru(acac)₂(X)₂] family in that it is too insoluble in acetonitrile to produce a sufficiently intense absorption spectrum within the OTTLE cell. As a result, the measurements were performed in DMF. While the features of the Ru(II) and Ru(III) spectra are similar to RuML1, there were no consistent isosbestic points on redox cycling (Figure 3.31). The most visible example of this is the shifting wavelengths of the crossover around 24,800 cm⁻¹, but more examples were observed at 34,400 cm⁻¹ and between 17,000 and 22,000 cm⁻¹.

Unlike RuML1, the drifting isosbestic points do not appear to be related directly to concentration since normalisation at a single isosbestic point does not produce clean isosbestic points at other wavelengths. While changing surface properties at the working electrode may partially explain the unusual transition from the Ru(II) to Ru(III) species, it is not a complete explanation. One possibility is that DMF is substituting 4,4'-bipyridine as the sample is oxidised; however, this runs contrary to the established behaviour of the *trans*-[Ru(acac)₂(X)₂], which is more reactive in the Ru(II) oxidation state, and would likely favour 4,4'-bipyridine over DMF due to stronger π -backbonding interactions. Additionally, the SEC yields reversible spectroscopic changes, which seems to preclude any substitution reactions.

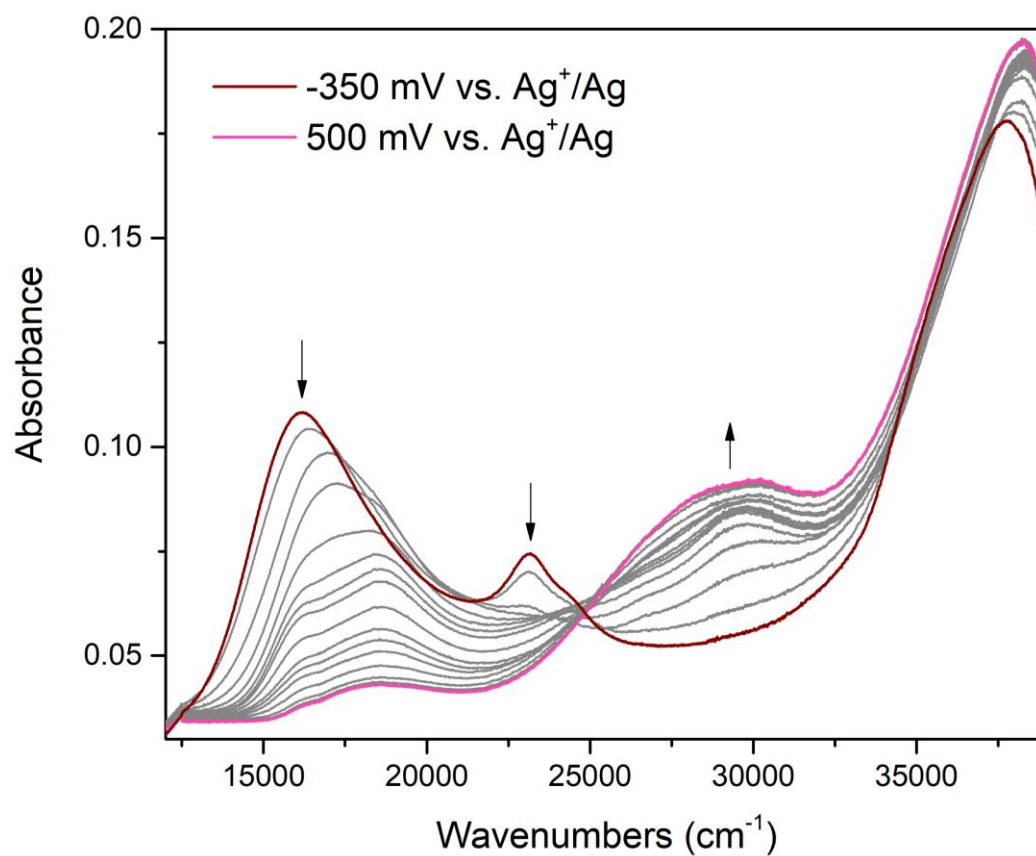


Figure 3.31. UV-vis SEC of *trans*-[Ru(acac)₂(bpy)₂] in 0.1 TBAPF₆ in DMF. Concentration 85 μ M.

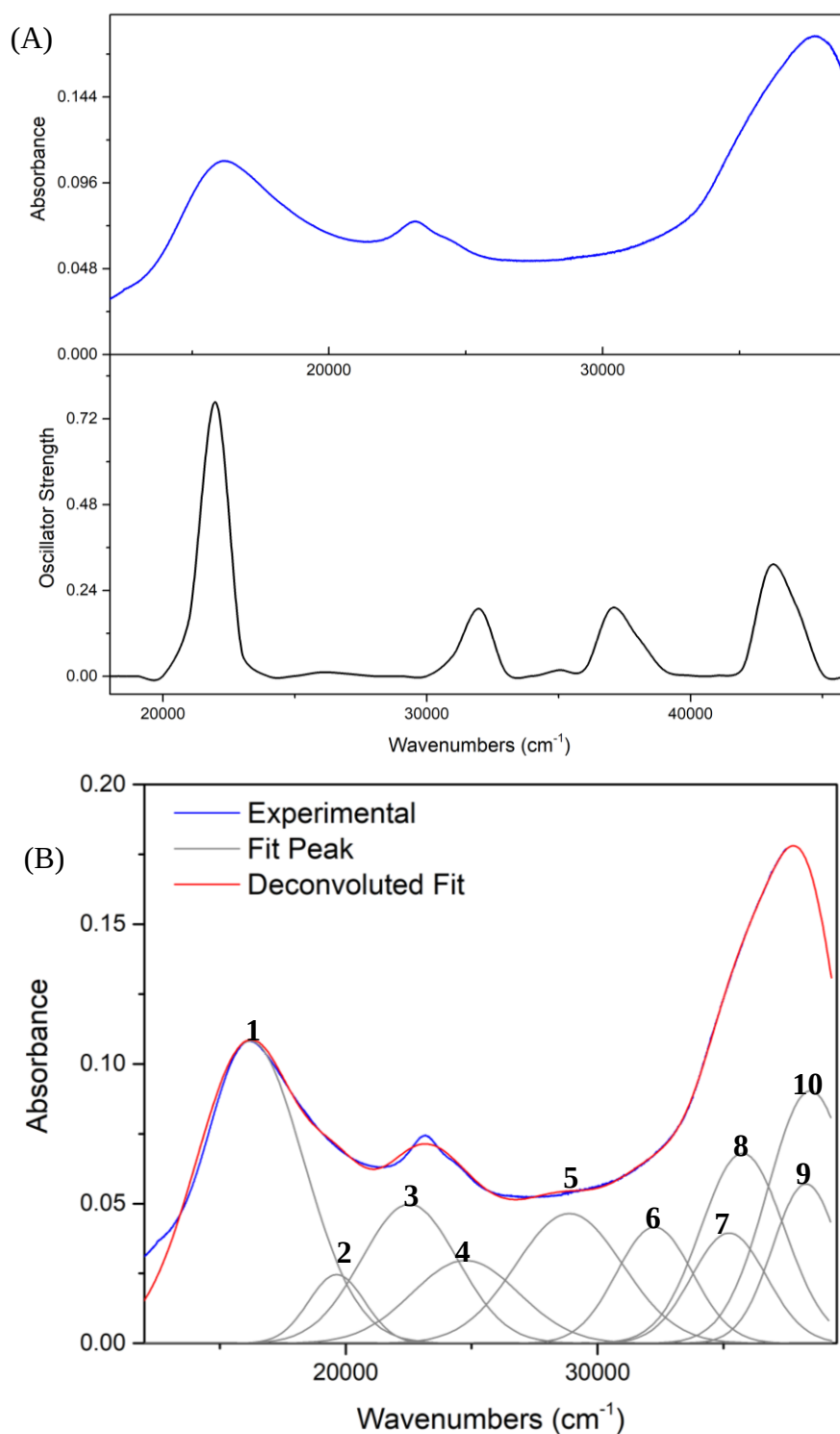


Figure 3.32. (A) Comparison of the experimental and simulated electronic spectrum of RuML2. Top: RuML2 in 0.1 M TBAPF₆ in DMF. Bottom: Simulated Spectrum, calculated with Gaussian 16. X-axis has been adjusted to account for blueshift and to improve clarity. (B) Deconvoluted spectrum of RuML2 in 0.1 M TBAPF₆ in DMF. Deconvolution was performed with Peak Analyser in Origin 2016, using Gaussian functions.

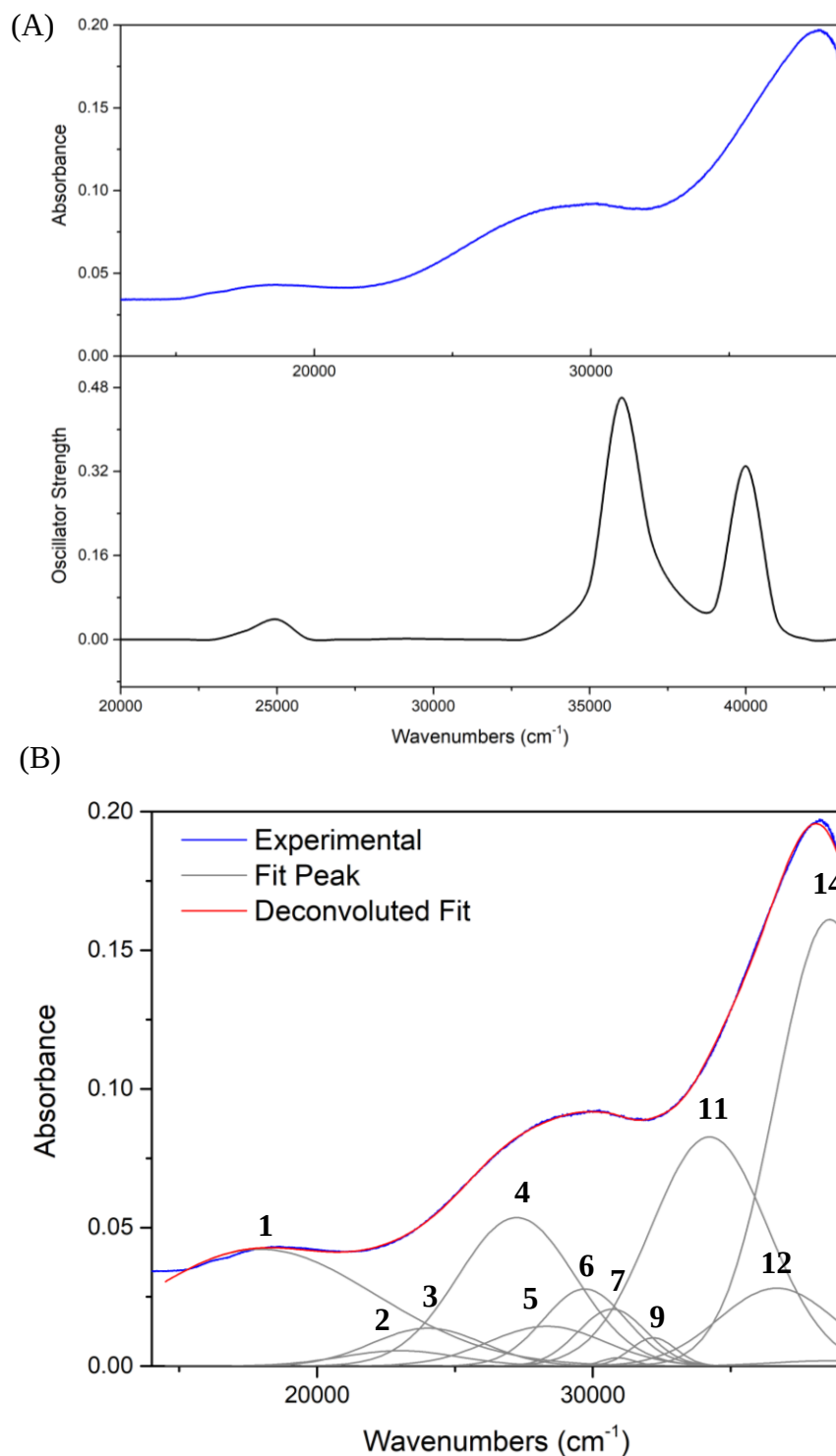


Figure 3.33. (A) Comparison of the experimental and simulated electronic spectrum of RuML2⁺. Top: RuML2⁺ in 0.1 M TBAPF₆ in DMF. Bottom: Simulated Spectrum, calculated with Gaussian 16. X-axis has been adjusted to account for blueshift and to improve clarity. (B) Deconvoluted spectrum of RuML2⁺ in 0.1 M TBAPF₆ in DMF. Deconvolution was performed with Peak Analyser in Origin 2016, using Gaussian functions.

The question of symmetry is more complex in RuML2 than RuML1.²¹⁶⁻²¹⁸ There are multiple configurations of the outer 4,4'-bipyridine rings with respect to each other, which could lead to several possible point group descriptions of the molecule. As observed in Section 3.3 as well as literature examples,¹⁹³ the rings of 4,4'-bipyridine are rarely planar with respect to each other and will twist depending on electronic and steric factors. Highly delocalised systems such as the Class III mixed-valence complex $[(\text{NH}_3)_5\text{Os}^{\text{II}}(4,4'\text{-bpy})\text{Os}^{\text{III}}(\text{NH}_3)_5]^{5+}$ favour a flat bpy bridge because π -orbital overlap is maximised when the rings are planar to each other. Therefore, when considering symmetry in RuML2, we can disregard the outer rings in order to approximate the point group of the molecule. Another factor that may impact the symmetry of the molecule is distortion of the pyridyl rings due to π -backbonding. This was not observed in crystallographic measurements.

Crystallographic data in Section 3.3. shows that the asymmetric unit of RuML2 in the solid state contains both bpy ligands, which suggests that the lowest symmetry C_1 point group is the most accurate description. However, solid state measurements are rarely reflective of the precise geometry of a material in the solution state, due to crystal packing considerations. In fact, the crystal structure of one polymorph of RuML2 contains strong evidence for π -stacking interactions, which do not occur in the solution state. Therefore, we can approximate the symmetry of RuML2 as D_{2h} , the same as RuML1 (Table 3.14, Table 3.15).

Table 3.14. Modelling of the UV-vis spectrum of RuML2:

Transition number	Experimental λ ($\times 10^3 \text{ cm}^{-1}$)	Simulated λ ($\times 10^3 \text{ cm}^{-1}$)	Molar Absorption Coefficient ($\times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$)	Symmetry	Character
1	16.2	21.9	14	$B_{1g} \rightarrow B_{2u}$	MLCT
2	19.6	26.4	3.1	$B_{1g} \rightarrow A_u$	MLCT
3	22.5	31.8	6.2	$B_{2g} \rightarrow A_u$	MLCT
4	24.8	35.5	3.7	$B_{2g} \rightarrow A_u$	MLCT
5	28.9	37.4	5.8	$A_g \rightarrow B_{2u}$	MLCT
6	-	39.0	5.2	$B_{1g} \rightarrow B_{2u}$	Acac internal
7	32.3	42.8	8.5	$B_{3u} \rightarrow B_{1g}$	
8	35.8	43.0	4.9	$B_{1g} \rightarrow A_u$	Bpy internal
9	35.2	43.1	7.1	$B_{3g} \rightarrow B_{2u}$	
10	38.3	43.1	11	$B_{3u} \rightarrow B_{2g}$	
11	38.5	43.7	14	$B_{3g} \rightarrow B_{2u}$	

Table 3.15. Modelling of the UV-vis spectrum of RuML2⁺:

Transition number	Experimental λ ($\times 10^3 \text{ cm}^{-1}$)	Simulated λ ($\times 10^3 \text{ cm}^{-1}$)	Molar Absorption Coefficient ($\times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$)	Symmetry	Character
1	17.9	24.7	5.3	$B_{3u} \rightarrow B_{1g}$	LMCT
2	23.0	34.1	0.70	$B_{1g} \rightarrow B_{2u}$	MLCT
3	24.0	34.6	1.7	$B_{1g} \rightarrow A_u$	
4	27.2	35.9	6.7	$B_{1g} \rightarrow B_{2u}$	MLCT
5	28.3	36.1	1.8	$B_{2u} \rightarrow B_{1g}$	LMCT
6	29.7	37.1	3.5	$B_{1g} \rightarrow B_{2u}$	MLCT
7	30.7	37.5	2.6	$B_{2g} \rightarrow A_u$	Acac internal
8	-	37.5	-	$B_{1g} \rightarrow A_u$	Acac internal
9	32.2	37.6	1.3	$B_{2g} \rightarrow A_u$	Acac internal
10	30.9	39.7	0.38	$B_{3g} \rightarrow B_{1g}$	LMCT
11	34.2	39.7	10	$A_u \rightarrow B_{1g}$	LMCT
12	36.7	39.9	3.5	$B_{1g} \rightarrow A_u$	
13	38.6	40.0	0.24	$B_{2u} \rightarrow B_{1g}$	
14	38.6	40.2	20	$A_u \rightarrow B_{1g}$	

3.5.4. RuML4

The solution-state UV-vis SEC of RuML4 contains the same features as RuML1, 2 and 0 (Figure 3.34). The spectrum features two identifiable isosbestic points at $24,200\text{ cm}^{-1}$ and $35,000\text{ cm}^{-1}$. The SEC yields reversible spectroscopic changes.

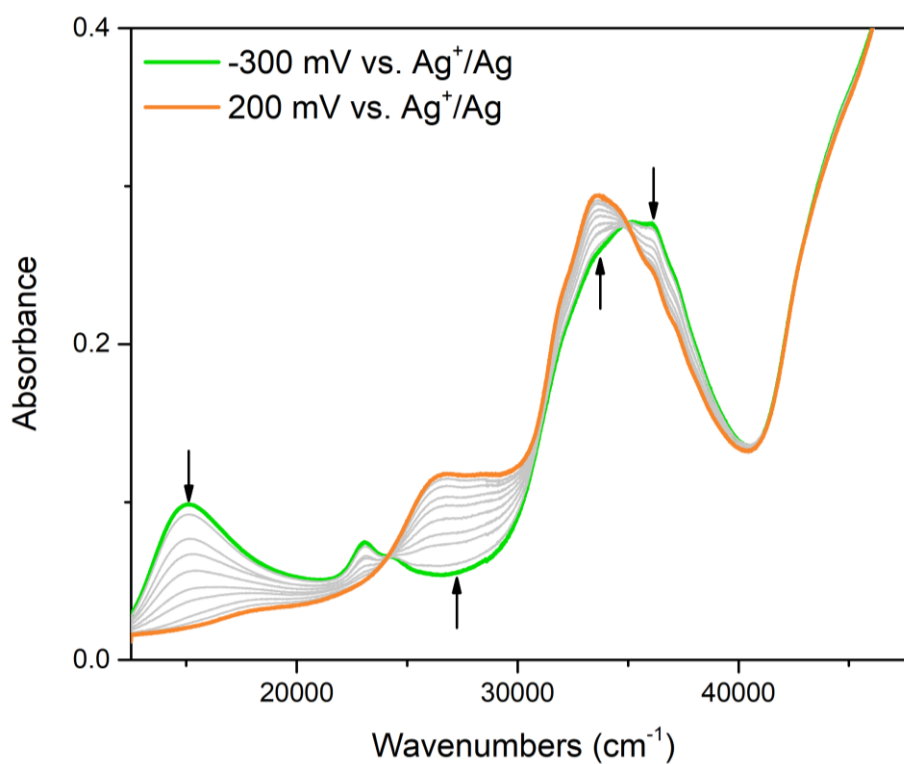


Figure 3.34. UV-vis SEC of *trans*-[Ru(acac)₂(BPE)₂] in 0.1 M TBAPF₆ in MeCN. Concentration 84 μM .

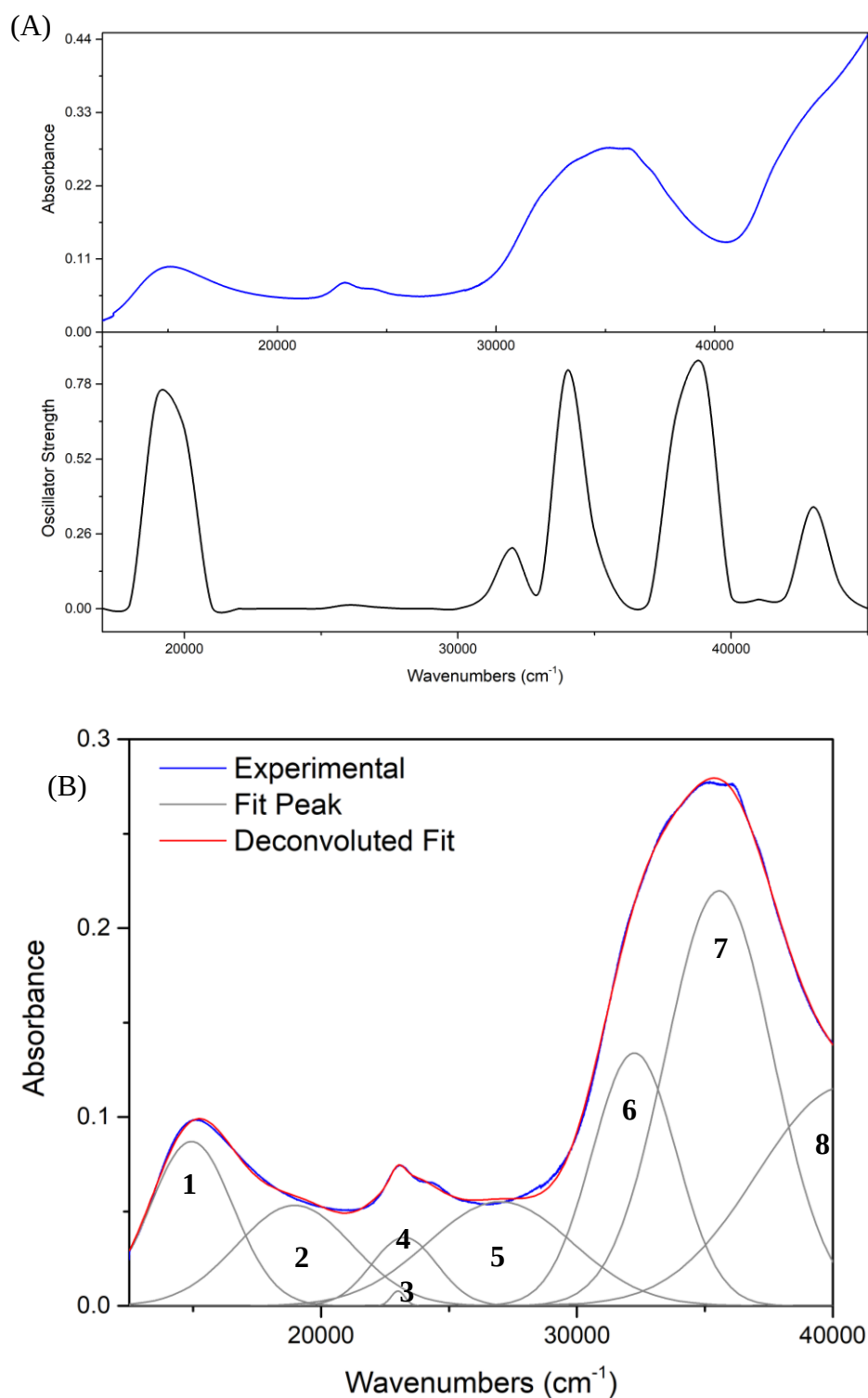


Figure 3.35. (A) Comparison of the simulated and experimental electronic spectrum of RuML4 in 0.1 M TBAPF₆ in MeCN. (B) Deconvoluted spectrum of RuML4 in 0.1 M TBAPF₆ in MeCN. Deconvolution was performed with Peak Analyser in Origin 2016, using Gaussian functions.

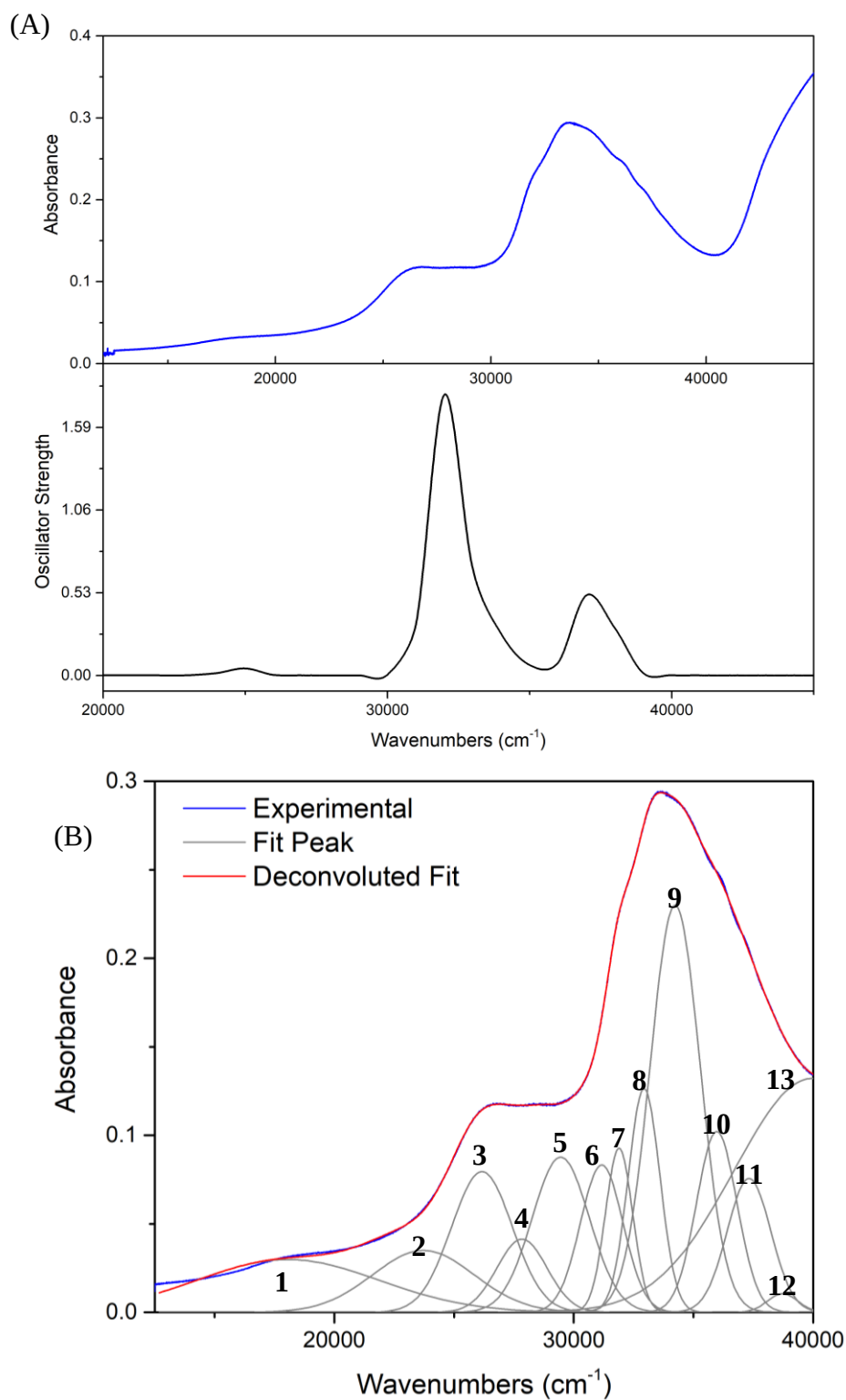


Figure 3.36. (A) Comparison of the simulated and experimental electronic spectrum of RuML4⁺ in 0.1 M TBAPF₆ in MeCN. (B) Deconvoluted spectrum of RuML4⁺ in 0.1 M TBAPF₆ in MeCN. Deconvolution was performed with Peak Analyser in Origin 2016, using Gaussian functions.

The symmetry of RuML4 is similarly difficult to determine as RuML2. There are two possible configurations of the molecule, both of which are observed crystallographically (Figure 3.37). A similar approximation to that made for RuML2, where the ethylene group and outer rings of the BPE ligand can be disregarded because of poor coupling with the metal centre. This produces an approximation of D_{2h} . However, unlike RuML2, there is evidence in the resonance Raman spectroscopy that the ethylene group of RuML4 is participating in electronic coupling with the metal centre (Section 3.6.2.). The ethylene groups break the D_{2h} symmetry of the molecule, which can be described as C_{2v} or C_{2h} . The symmetries of both point groups have been included below (Table 3.16, Table 3.17).

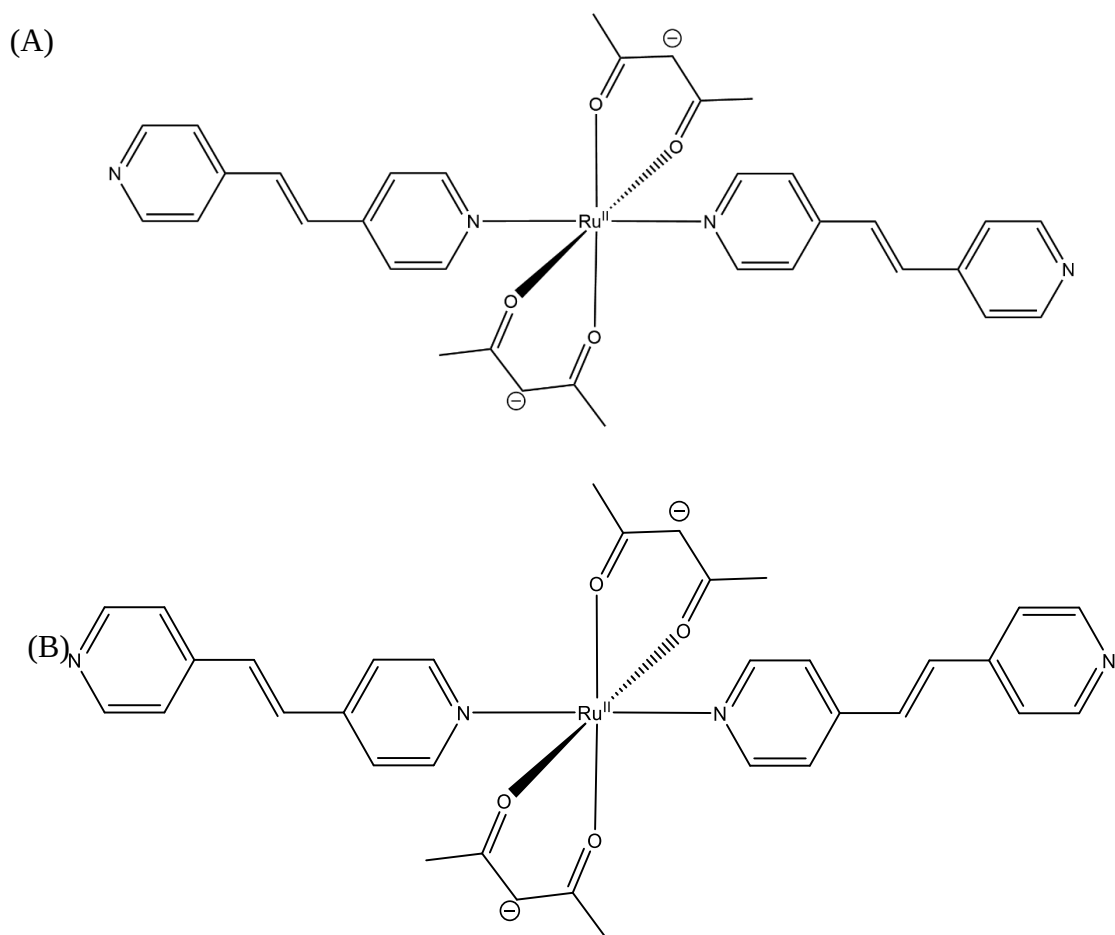


Figure 3.37. Configurations of RuML4. (A) α -RuML4 (B) β -RuML4

Table 3.16. Modelling of the UV-vis spectrum of RuML4:

Transition number	Experimental λ ($\times 10^3 \text{ cm}^{-1}$)	Simulated λ ($\times 10^3 \text{ cm}^{-1}$)	Molar Absorption Coefficient ($\times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$)	Symmetry C_{2v}	Symmetry C_{2h}	Character
1	14.9	19.5	21	$A_2 \rightarrow B_2$	$B_g \rightarrow A_u$	MLCT
2	19.0	26.3	13	$A_2 \rightarrow A_2$	$B_g \rightarrow A_u$	
3	23.0	31.9	1.9	$B_1 \rightarrow A_2$	$A_g \rightarrow A_u$	
4	23.3	34.2	8.6	$A_2 \rightarrow B_2$	$A_g \rightarrow A_u$	MLCT
5	27.0	36.2	13	$B_1 \rightarrow A_2$	$A_g \rightarrow A_u$	MLCT
6	32.2	38.6	32	$A_2 \rightarrow B_2$	$B_g \rightarrow A_u$	BPE internal
7	35.6	40.2	52	$B_2 \rightarrow B_2$	$B_g \rightarrow A_u$	BPE internal
8	40.5	41.4	27	$B_2 \rightarrow B_2$	$B_g \rightarrow A_u$	BPE internal
9	-	43.1		$A_2 \rightarrow A_2$	$A_g \rightarrow A_u$	Acac internal
10	-	43.3		$A_2 \rightarrow B_2$	$B_g \rightarrow A_u$	MLCT

Table 3.17. Modelling of the UV-vis spectrum of RuML4⁺:

Transition number	Experimental λ ($\times 10^3 \text{ cm}^{-1}$)	Simulated λ ($\times 10^3 \text{ cm}^{-1}$)	Molar Absorption Coefficient ($\times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$)	Symmetry C_{2v}	Symmetry C_{2h}	Character
1	18.1	24.8	7.1	$B_1 \rightarrow A_2$	$B_u \rightarrow B_g$	LMCT
2	23.7	31.8	8.3	$A_2 \rightarrow B_2$	$B_g \rightarrow A_u$	MLCT
3	26.2	32.4	19	$A_2 \rightarrow B_2$	$B_g \rightarrow A_u$	
4	27.8	33.8	9.8	$A_2 \rightarrow B_2$	$B_g \rightarrow A_u$	
5	29.5	34.2	21	$A_2 \rightarrow A_2$	$B_g \rightarrow A_u$	LMCT
6	31.2	35.4	20	$A_2 \rightarrow B_2$	$B_g \rightarrow A_u$	
7	31.9	36.7	22	$B_2 \rightarrow A_2$	$A_u \rightarrow B_g$	Acac internal
8	32.9	36.8	30	$A_2 \rightarrow B_2$	$A_u \rightarrow B_g$	BPE internal
9	34.2	37.1	55	$A_2 \rightarrow A_2$	$B_g \rightarrow A_u$	Acac internal
10	36.0	37.3	24	$A_2 \rightarrow B_2$	$B_g \rightarrow A_u$	
11	37.3	37.4	18	$B_1 \rightarrow A_2$	$A_g \rightarrow A_u$	Acac internal
12	38.7	37.5	2.5	$B_2 \rightarrow B_2$	$B_g \rightarrow A_u$	BPE internal
13	40.0	38.4	31	$A_2 \rightarrow B_2$	$B_g \rightarrow A_u$	

3.5.5. RuML0

The solution-state UV-vis SEC of RuML0 produced results consistent with the *trans*-[Ru(acac)₂(X)₂] family. The other distinctive features are present in the UV region, with two bands at 36,100 and 40,000 cm⁻¹ in Ru(II) that drop substantially in intensity upon oxidation to Ru(III). This is in contrast to the comparable intensity of the $n \rightarrow \pi^*$ transitions between Ru(II) and Ru(III) spectra in other members of the *trans*-[Ru(acac)₂(X)₂] family.

The transition from Ru(II) to Ru(III) is remarkably clean over the course of the measurement, with stable isosbestic points at 27,200 cm⁻¹, 34,700 cm⁻¹ and 41,200 cm⁻¹ (Figure 3.38). However, the isosbestic point at 17,600 cm⁻¹ was lost at around -70 mV vs Ag⁺/Ag and higher potentials (Figure 3.39). The SEC yields reversible spectroscopic changes.

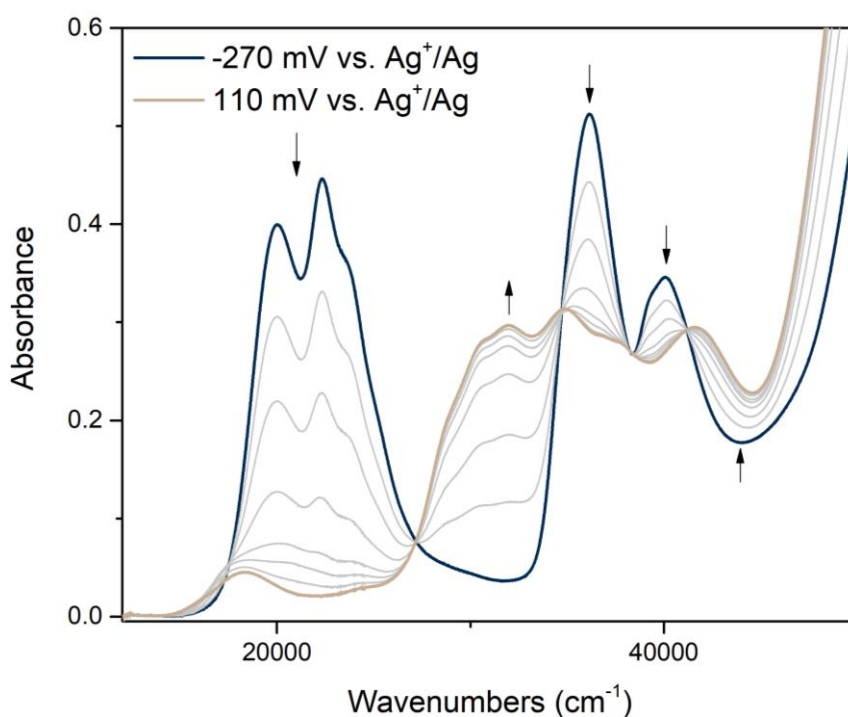


Figure 3.38. UV-vis SEC of *trans*-[Ru(acac)₂(Py)₂] in 0.1 M TBAPF₆ in MeCN. Concentration was 0.38 mM.

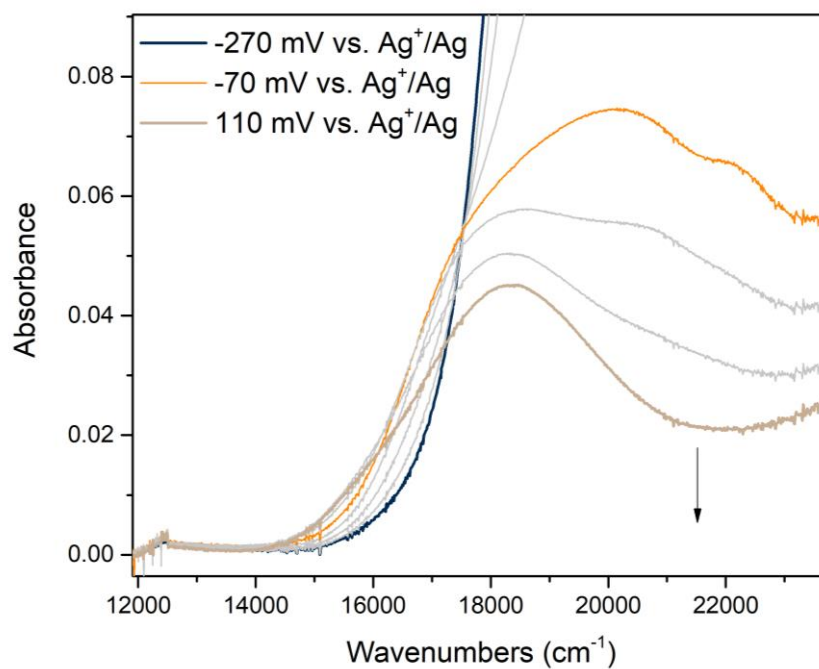


Figure 3.39. Low energy visible SEC of *trans*-[Ru(acac)₂(Py)₂] in 0.1 M TBAPF₆ in MeCN.

The deconvolution of RuML0 and RuML0⁺ was achieved by replicating the order of transitions observed in RuML1 (Figure 3.40). The symmetry of the molecule is D_{2h} , and the symmetries of the orbitals involved in the transitions is expected to follow the description of RuML1 (Table 3.18, Table 3.19).

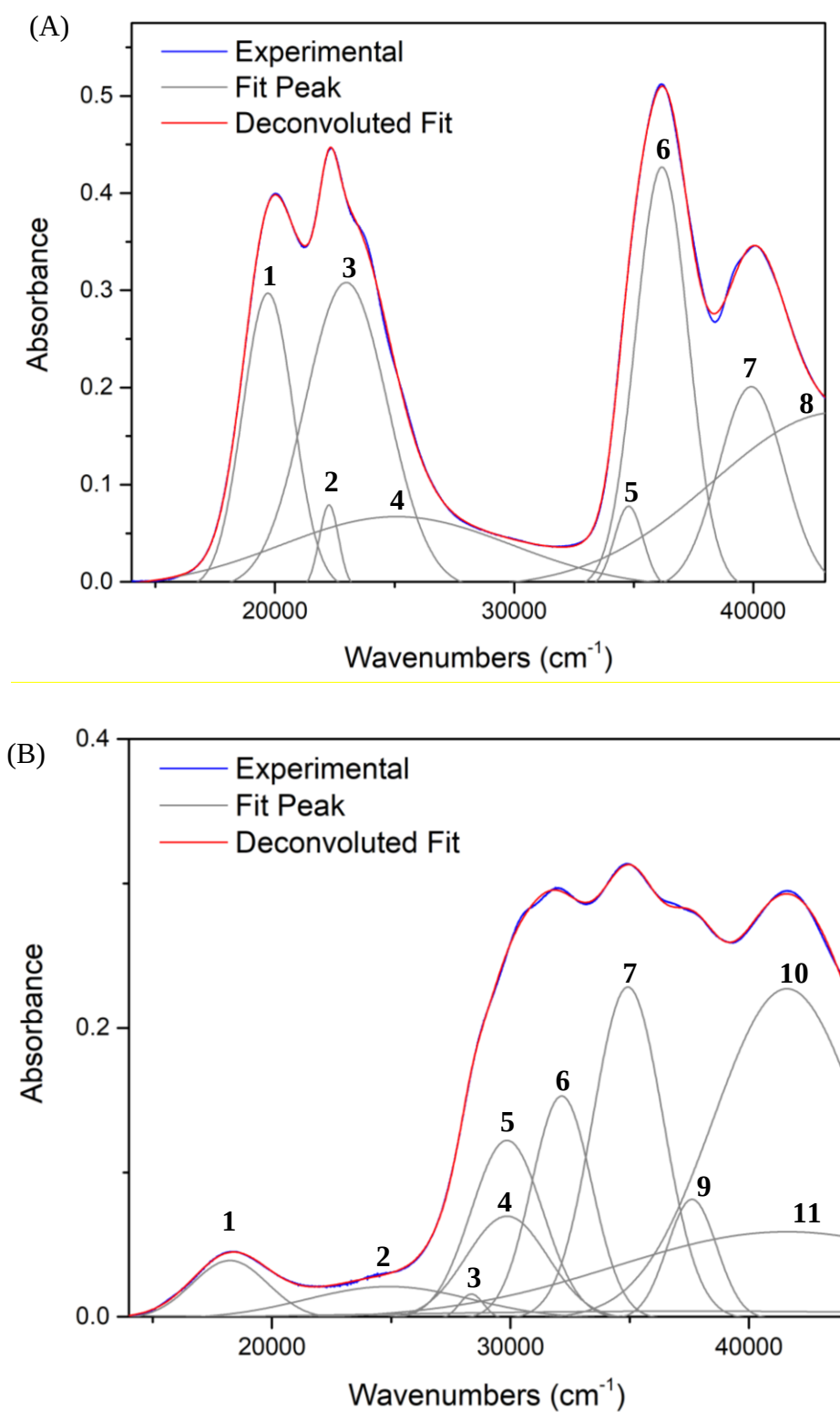


Figure 3.40. (A) Deconvoluted spectrum of RuML0 in 0.1 TBAPF₆ in MeCN. (B) Deconvoluted spectrum of RuML0⁺ in 0.1 M TBAPF₆ in MeCN. Deconvolution was performed with Peak Analyser in Origin 2016, using Gaussian functions.

Table 3.18. Modelling of the UV-vis spectrum of RuML0:

Transition number	Experimental λ ($\times 10^3 \text{ cm}^{-1}$)	Molar Absorption Coefficient ($\times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$)	Symmetry
1	19.7	16	$B_{1g} \rightarrow B_{2u}$
2	22.3	4.2	$B_{1g} \rightarrow A_u$
3	23.0	16	$B_{2g} \rightarrow A_u$
4	25.1	3.6	$B_{2g} \rightarrow A_u$
5	34.8	4.1	$A_g \rightarrow B_{2u}$
6	36.2	23	$B_{1g} \rightarrow B_{2u}$
7	39.9	11	$B_{3u} \rightarrow B_{1g}$
8	43.5	9.3	$B_{1g} \rightarrow A_u$

Table 3.19. Modelling of the UV-vis spectrum of RuML0⁺:

Transition number	Experimental λ ($\times 10^3 \text{ cm}^{-1}$)	Molar Absorption Coefficient ($\times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$)	Symmetry
1	18.2	2.1	$B_{3u} \rightarrow B_{1g}$
2	24.9	1.1	$B_{1g} \rightarrow B_{2u}$
3	28.4	0.83	$A_g \rightarrow B_{2u}$
4	29.9	3.7	$B_{1g} \rightarrow B_{2u}$
5	29.9	6.5	$B_{1g} \rightarrow A_u$
6	32.2	8.1	$B_{2u} \rightarrow B_{1g}$
7	34.9	12	$B_{2u} \rightarrow B_{1g}$
8	37.6	0.21	$B_{2g} \rightarrow A_u$
9	37.6	4.3	$B_{1g} \rightarrow A_u$
10	41.6	3.1	$B_{1g} \rightarrow A_u$
11	41.6	12	$B_{1g} \rightarrow B_{2u}$

3.5.6. Trends and General Discussion

The character of transitions were assessed from the primary orbitals of each transition in the simulated model. The character of some transitions were ambiguous, as some simulated orbitals were present at the metal and both ligands. Many CT transitions were identified through this technique. Additionally, it was clear from the simulations that the Ru(acac)₂ motif was delocalised in both Ru(II) and Ru(III) oxidation states. As a result, MLCT and LMCT transitions in the *trans*-[Ru(acac)₂(X)₂] family always involve the Ru(acac)₂ motif.

A clear relationship is present between the various species presented in this Section. The most apparent similarities are between complexes with the same Ru oxidation state.

The electronic profiles of the Ru(III) complexes Ph₄P{*trans*-[Ru^{III}(acac)₂Cl₂]}, RuML1⁺, RuML2⁺, RuML4⁺ and RuML0⁺ match the general behaviour observed for transition metal acetylacetonate complexes, including [Ru(acac)₃].^{44,219} One question that remains unresolved to our knowledge is the identity of an absorption band at 19,600 cm⁻¹ in the spectrum of [Ru(acac)₃],⁴⁴ which is identified as a *d* → *d* transition by Grobelny *et al.*⁴⁴ This assignment is disputed by Hasegawa *et al.*,⁴⁵ but no alternative assignment was proposed. This transition is present in all of the Ru(III) complexes in this work, at similar wavenumbers (Table 3.20). According to orbital simulations (Figure 3.30), this transition can be described in two ways; an internal transfer within the delocalised Ru(acac)₂ motif, or LMCT from the acac ligands to the metal centre. This also explains the relatively stable position of the transition, as the X ligands (from *trans*-[(Ru(acac)₂(X)₂]) contribute very little to the excited state orbital.

Table 3.20. Comparison of transition **1** energies in Ru(III) acac complexes

Metal Complex	Deconvoluted Experimental λ , Transition 1 ($\times 10^3 \text{ cm}^{-1}$)
[Ru(acac) ₃] (<i>a</i>)	19.6
Ph ₄ As{ <i>trans</i> -[Ru ^{III} (acac) ₂ Cl ₂]} (<i>b</i>)	19.2
Ph ₄ P{ <i>trans</i> -[Ru ^{III} (acac) ₂ Cl ₂]}	19.3
<i>trans</i> -[Ru ^{III} (acac) ₂ (pyz) ₂] ⁺	17.8
<i>trans</i> -[Ru ^{III} (acac) ₂ (bpy) ₂] ⁺	17.9
<i>trans</i> -[Ru ^{III} (acac) ₂ (BPE) ₂] ⁺	18.1
<i>trans</i> -[Ru ^{III} (acac) ₂ (py) ₂] ⁺	18.2

Note: *a*: ref ⁴⁴ *b*: ref ⁴⁵

The remainder of the transitions in the Ru(III) spectra are heavily convoluted, and do not conform closely to the intensities suggested by simulations. According to these simulations, the most intense feature of the blue-UV region is primarily a HOMO-LUMO MLCT transition from the metal centre to the X ligands, in the case of RuML1⁺ and RuML4⁺ (Table 3.21). These orbitals make up a fraction of the equivalent transition in the RuML2⁺ spectrum. This is clearly not the case for Ph₄P{*trans*-[Ru(acac)₂Cl₂]}, where the primary feature below 30,000 cm⁻¹ is most likely LMCT from the Cl⁻ ligands to the metal centre. Similar convoluted features have been observed in Os(III) pyridyl complexes.^{216-218,220}

The trend of the experimental data does not agree with the simulations of these transitions. There are a range of spectroscopic techniques that could assist with a more accurate deconvolution of these spectra, including MCD, single-crystal polarised spectroscopy and resonance Raman. These techniques are discussed in Chapter 6.

Table 3.21. Comparison of HOMO-LUMO transition energies in *trans*-[Ru^{III}(acac)₂(X)₂]⁺ complexes

Metal Complex	Deconvoluted Experimental Band Maxima, HOMO-LUMO transition ($\times 10^3 \text{ cm}^{-1}$)	Simulated Band Maxima, HOMO-LUMO transition ($\times 10^3 \text{ cm}^{-1}$)
RuML4 ⁺	26.2	32.4
RuML2 ⁺	27.2	35.9
RuML0 ⁺	28.4	-
RuML1 ⁺	29.8	34.9

The remaining transitions in RuML1⁺, RuML2⁺, RuML4⁺ and RuML0⁺ are a mixture of LMCT, MLCT and internal X ligand and acac⁻ excitations. Although it is not possible to accurately deconvolute this region, simulations suggest very similar transitions are occurring across all four spectra. Ph₄P{*trans*-[Ru^{III}(acac)₂Cl₂]} by contrast would not exhibit any MLCT or internal X ligand excitations. Instead, The structure between 30,000 and 40,000 cm⁻¹ is characteristic of $\pi \rightarrow \pi^*$ transitions within the phenyl groups of the tetraphenyl phosphonium ion,²²¹ as well as internal acac⁻ transitions.

The spectra of the Ru(II) complexes RuML1, RuML2, RuML4 and RuML0 are consistent with other Ru-pyridyl systems.¹³ The visible region of these spectra is dominated by three or four MLCT bands, typically resulting in two distinct peaks in the convoluted spectra. The UV region contains a mixture of MLCT, internal X ligand and acac⁻ excitations. The UV region is too difficult to accurately model; however, the features of the visible region are much easier to deconvolute. Unsurprisingly, the visible MLCT transitions vary substantially with ligand X. The most intense feature of these spectra is also the lowest energy, primarily composed of the HOMO $\rightarrow$ LUMO transition from the Ru^{II}(acac)₂ motif to the ligands X. Deconvolution of this transition is straightforward and the order of simulated band maxima agrees with the experimental data. A similar transition occurs in the Ru(III) complexes, but at a much higher

energy than in the Ru(II) complexes, because the Ru(III) ground state MO involves a Ru *d* orbital of lower energy.

The trend in band maxima is due to competing effects in both the HOMO and LUMO orbital energies across the family (Table 3.22). The HOMO orbitals vary due to the π -backbonding interaction, which lowers the energy of the Ru *d* orbitals. The LUMO orbitals vary in energy due to MO differences between different ligands X. These competing effects result in a trend that does not reflect either effect in isolation. For example, changes in the LUMO energy of RuML1-4 are outcompeted by the π -backbonding effect, resulting in a lower energy HOMO for RuML1 than RuML2 or RuML4. On the other hand, the π -backbonding interaction in RuML0 is very weak, but the LUMO lies at a much higher energy than that in pyz, bpy or BPE, resulting in a much higher energy transition.

Table 3.22. Comparison of transition **1** MLCT energies in Ru(II) acac complexes

Metal Complex	Deconvoluted Experimental Band Maxima, Transition 1 ($\times 10^3 \text{ cm}^{-1}$) ⁻¹
RuML4	14.9
RuML2	16.2
RuML1	17.4
RuML0	19.7
<i>trans</i> -[Ru(NH ₃) ₄ (pyz)] ²⁺ 222	20.6
<i>trans</i> -[Ru(NH ₃) ₄ (py)] ²⁺ 182	23.6

Comparison with the ammine analogues of RuML1 and RuML0 agrees with a trend noted by Hasegawa.^{45,182,222} One acac⁻ ligand is more electron donating than two ammine ones, resulting in a higher HOMO energy and smaller energy of transition **1**.

This MLCT is largely responsible for the colour of the Ru(II) metal complexes, with RuML4, RuML2, RuML1, RuML0 appearing green-blue, blue, purple and red, respectively.

Another prominent feature in the visible region is primarily composed of the HOMO(-2) $\rightarrow$ LUMO (+2) transition (Table 3.23). Surprisingly, this transition does not exhibit the same

ligand dependency as transition **1**. This is due to the less predictable nature of the HOMO(−2) and LUMO(+2) orbital energies, which do not vary according to a clear trend.

Table 3.23. Comparison of transition **3** energies in *trans*-[Ru^{II}(acac)₂(X)₂] complexes

Metal Complex	Deconvoluted Experimental Band Maxima, Transition 3 ($\times 10^3 \text{ cm}^{-1}$)	Simulated Band Maxima, Transition 3 ($\times 10^3 \text{ cm}^{-1}$)
RuML4	23.3	31.9
RuML2	22.5	31.8
RuML1	24.9	33.0
RuML0	23.0	N/A

Ultimately, the highly convoluted nature of spectra discussed in this Section reflects the complex nature of molecular orbitals in π -backbonded systems. Without simulations, predicting and identifying MLCT and LMCT transitions is far more difficult than IVCT. The traditional model of transitions to and from metal *d* orbitals breaks down completely when considering π -backbonded complexes. Fortunately, given the scope of this project, several trends can be identified within this family of ruthenium acetylacetonate complexes, involving π -backbonding and ligand MOs.

3.6. Vibrational spectroscopy

This Section discusses the infrared and Raman spectroscopies observed for the family of *trans*-[Ru(acac)₂(X)₂] complexes. ATR SEC was performed on several complexes in order to probe the d^5 - d^6 boundary, but only produced meaningful data for one complex. Instead, the chemically oxidised metal complexes were analysed with IR spectroscopy in order to compare the vibrational transitions. Raman and resonance Raman spectroscopy were used to analyse several Ru(II) complexes, in order to gain insight into the electronic behaviour and symmetry of the molecules.

In order to properly describe the vibrational profiles and symmetries of these complexes, three complexes in two oxidation states were modelled with DFT, in Gaussian 16.¹⁶⁹ Characterisation of infrared and Raman spectra was achieved in part by reference to these models. The modelled spectra matched observations closely at lower energies but tended towards higher energy estimations towards the mid and near-infrared regions.

3.6.1. RuML1

The infrared spectrum of RuML1 involves two vibrationally distinct ligands, thus the spectrum has multiple bands that are often convoluted. As a result, band identification was performed by comparing the spectrum of [Ru^{II}(acac)₂(pyz)₂] to that of [Ru^{II}(acac)₂(*d*₄-pyz)₂], to literature sources,²²³⁻²²⁶ and a simulated model (full characterisation can be found in Appendix C). Bands that redshifted between the deuterated and undeuterated complexes were associated with pyrazine. For example, the pyz ring bend at 1570 cm⁻¹ in the non-deuterated ligand was observed at 1523 cm⁻¹ in the spectrum of the deuterated complex. Thus, this band was associated with pyrazine.

As RuML1 was incompatible with IR SEC instrumentation, the neutral complex was oxidised with I₂ to produce the complex *trans*-[Ru^{III}(acac)₂(pyz)₂]I. The FTIR spectra of these materials (Table 3.24, Figure 3.41) show several distinct changes. Many of the same infrared vibrational modes were exhibited by each oxidation state, with varying increases and decreases in energy. Vibrational modes associated with the acetylacetonate ligands exhibit only very slight changes between oxidation states. These changes are discussed further in Section 3.6.6.

Table 3.24. Comparison of acac vibrational modes in the infrared spectrum of RuML1 and [RuML1]I

$\nu_{\max}$ and intensity, acac modes, <i>trans</i> -[Ru ^{II} (acac) ₂ (pyz) ₂]	$\nu_{\max}$ and intensity, acac modes, <i>trans</i> -[Ru ^{III} (acac) ₂ (pyz) ₂]I	Band Assignments
1560 m, sh	1518 s, br	Acac $\nu(\text{C}=\text{O})_{\text{asym}}$, $\delta(\text{C}-\text{HC}=\text{C})$, $\rho(\text{CH}_3)$
1539 w,		Acac $\nu(\text{C}=\text{C})_{\text{asym}}$
1512 s		$\nu(\text{Acac})_{\text{asym}}$
	1420 m	Acac $\delta(\text{CH}_3)$
1404 s	1412 w, sh	Acac $\delta(\text{CH}_3)$
	1355 m	Acac $\delta(\text{CH}_3)$
1340 w	1336 m	Acac $\delta(\text{CH}_3)$
1260 w	1277 s	Acac $\delta(\text{C}-\text{CH}_3)$
1205 w	1194 w	Acac $\rho(\text{CH})$
934 m	937 m	Acac $\nu(\text{C}-\text{CH}_3)$
781 m	810 m	Acac $\pi(\text{CH})$
	691 m	Acac $\pi(\text{C}-\text{C}-\text{O})$, $\rho(\text{CH}_3)$,
649 m	644 m	Acac $\nu(\text{O}-\text{Ru}-\text{O})_{\text{sym}}$, $\rho(\text{CH}_3)$
450 w	466 m	Acac $\nu(\text{O}-\text{Ru}-\text{O})_{\text{sym}}$ $\nu(\text{CH}_3)$
440 w	428 w	Acac $\rho(\text{acac})$

vw = very weak, *w* = weak, *m* = medium, *s* = strong, *vs* = very strong, *sh* = shoulder, ν = stretching mode, δ = bending mode, π = wagging mode, ρ = rocking mode

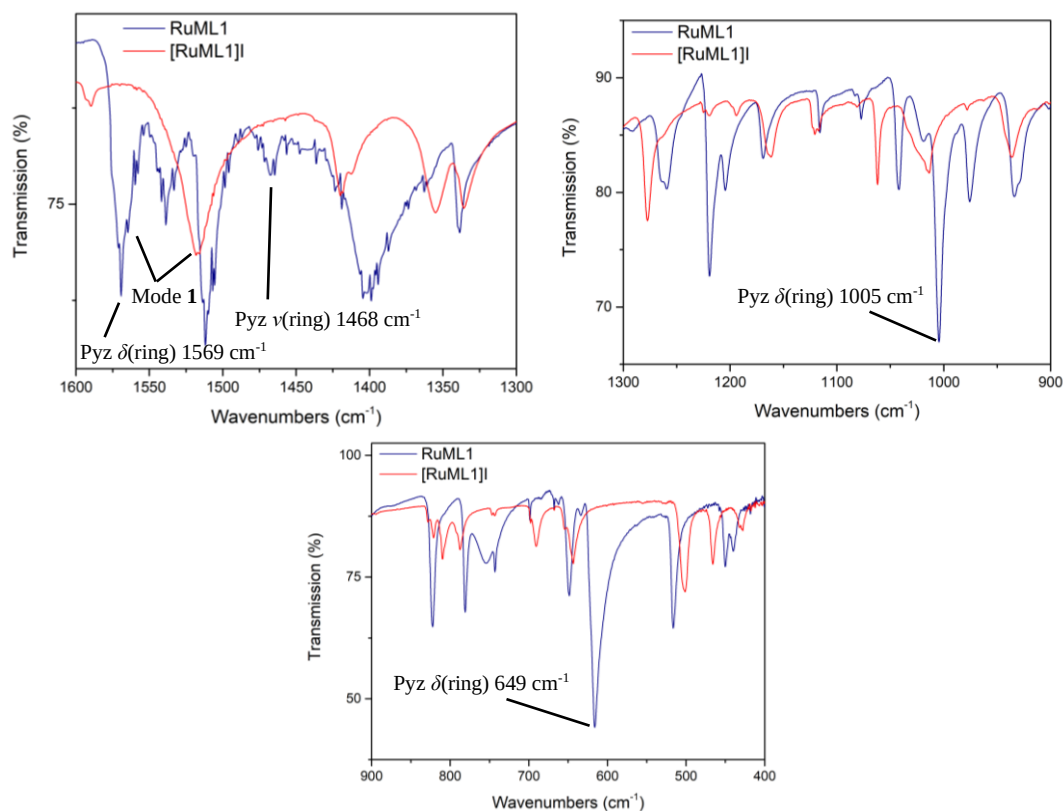


Figure 3.41. FTIR spectra of RuML1 and [RuML1]I

The Raman and resonance Raman spectra of RuML1 were highly populated, due to the pyz and acac ligands (Table 3.25). Bands were assigned with reference to simulated modes and literature values.²²⁷⁻²²⁸ The symmetries of several fundamental modes in D_{2h} were determined by reference to the simulated model.

Table 3.25. Experimental Raman spectra of $[\text{Ru}^{\text{II}}(\text{acac})_2(\text{pyz})_2]$ and $[\text{Ru}^{\text{II}}(\text{acac})_2(d_4\text{-pyz})_2]$, excitation wavelengths: 785, 532, 514 and 488 nm, and simulated Raman spectrum of $[\text{Ru}^{\text{II}}(\text{acac})_2(\text{pyz})_2]$. Because the relative intensity of each band varied between spectra due to enhancement effects, the experimental intensity of each band could not be compared to the simulated intensity.

ν_{max} and Intensity, $[\text{Ru}^{\text{II}}(\text{acac})_2(\text{pyz})_2]$ (cm^{-1})	ν_{max} and Intensity, $[\text{Ru}^{\text{II}}(\text{acac})_2(d_4\text{-pyz})_2]$ (cm^{-1})	Simulated ν_{max} and Intensity, $[\text{Ru}^{\text{II}}(\text{acac})_2(\text{pyz})_2]$ (cm^{-1})	Band Assignment ^{227- 228}	Symmetry
	1708			
1656			Combination	
1596	1542	1687 s	Pyz $\nu(\text{Ring})$, $\delta(\text{CH})$ Acac $\nu(\text{CO})$	A_g
1586	1542	1678 s	Pyz $\nu(\text{Ring})$, $\delta(\text{CH})$ Acac $\nu(\text{CO})$	A_g
1568				
1547				
1485	1480	1547, 1529 w	Acac $\nu(\text{OC-}$ $\text{C=CO})_{\text{asym}}$, $\delta(\text{CH})_3$ Pyz $\rho(\text{CH})$	B_{3g}, A_g
		1463 w		
1359		1397 w	Acac $\pi(\text{CH}_3)$	
	1331			
1259	1260	1311 w	Acac $\nu(\text{CCH}_3)$	A_g
1222		1259 w, 1248 m	Pyz $\nu(\text{Ring})$, $\delta(\text{CH})$	A_g
1167	1168	1239 vw	Acac $\delta(\text{CH})$	A_g
1116		1165 m	Pyz $\rho(\text{CH})$	A_g
1075, 1063	1055	1098 s	Pyz $\delta(\text{Ring})$	A_g
1033				
1013	987	1059 w	Pyz $\delta(\text{Ring})$	
1006		1053 w	Acac $\delta(\text{CH})$, $\delta(\text{CH}_3)$	A_g
933		960 w	Acac $\delta(\text{CH})$, $\delta(\text{CH}_3)$	A_g
	908			
	865			
817				
720	720	726 vw	Pyz $\delta(\text{Ring})$	
686	685	697 w	Acac $\nu(\text{Ring})$	A_g
	663			
650	631	662 m	Pyz $\delta(\text{Ring})$	A_g

454	454	458 vw	Acac $\nu(\text{Ring})_{\text{sym}}$	A_g
317	319			
278				
262	259	271 vw	$\delta(\text{acac-Ru-acac})$	B_{3g}
207	207	211 vw	$\delta(\text{pyz-Ru-acac})$	B_{1g}, A_g

Vw = very weak, w = weak, m = medium, s = strong, vs = very strong, b = broad, v = stretching mode, δ = bending mode, π = wagging mode, ρ = rocking mode, Oop. = out of plane mode.

The Raman spectroscopy of RuML1 was analysed with seven laser lines of differing wavelength. Comparison of the electronic spectra with these laser lines produced five broad categories according to the hypothetical model of transition symmetry assigned to each orbital in D_{2h} (Figure 3.42).

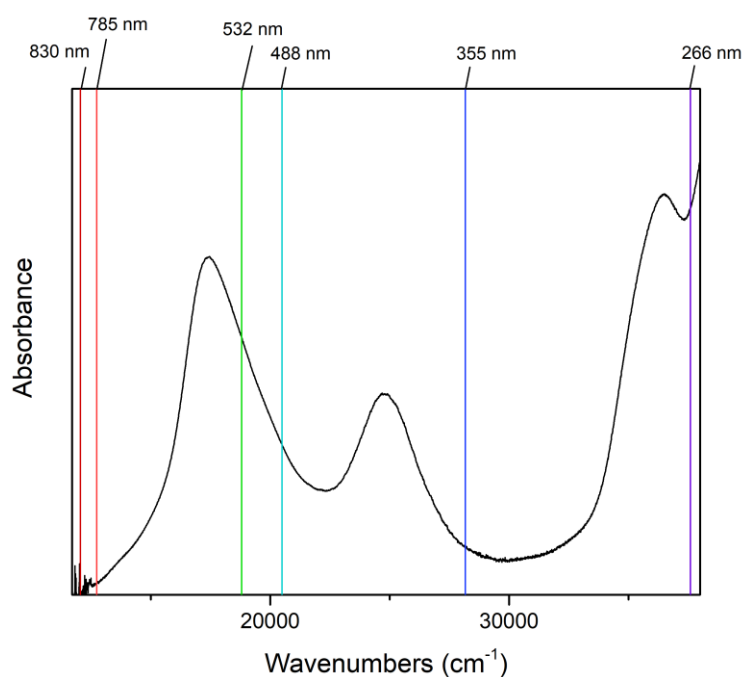


Figure 3.42. Raman excitation wavelengths compared with the UV-vis spectrum of RuML1

1. 830 nm was off-resonance
2. 785 nm was slightly on-resonance with transition **1**
3. 532, 488 nm were on-resonance with transitions **1** and **2**
4. 355 nm was on-resonance with transitions **3** and **4**
5. 266 nm was on-resonance with several transitions, most likely **8** and **9** but possibly including **4-7**.

The distinction between all categories is clearly visible in the relative integrated peak intensity of each band (Figure 3.43). 830 nm clearly exhibited little or no resonance enhancement, and we can comfortably categorise this as a normal Raman spectrum. 785 nm exhibited slightly higher resonance enhancement, consistent with the categorisation of slightly on-resonance. 532 and 488 nm exhibited the highest degree of resonance enhancement for many of the more intense bands, including 1596 cm^{-1} , 1583 cm^{-1} , 1220 cm^{-1} , 687 cm^{-1} and 212 cm^{-1} .

There was little information to be gleaned from the 355 nm spectrum- the main features visible were A-terms between $1500\text{--}1600\text{ cm}^{-1}$, which general exhibit lower resonance enhancement than other excitation wavelengths. 288 nm produced an entirely different resonance pattern, and produced the highest enhancement for several intense modes, including 651 cm^{-1} , 932 cm^{-1} , 1007 cm^{-1} and 1258 cm^{-1} .

Most resonance enhanced bands were A-terms, being totally symmetric fundamental modes. However, there were several features that did not correspond to fundamental modes that experienced enhancement. A broad feature at $\sim 300\text{ cm}^{-1}$ was visible all on-resonance spectra except 355 nm. This may be due to a combination of FIR modes. Bands at $\sim 1660\text{ cm}^{-1}$ and $\sim 1675\text{ cm}^{-1}$ were visible in several spectra but were most pronounced for the higher energy excitation wavelengths. 1660 cm^{-1} was likely a combination mode of 1007 cm^{-1} and 683 cm^{-1} ; 1675 cm^{-1} , only visible in the 514 nm spectrum, was possibly a combination of 1259 cm^{-1} and 454 cm^{-1} . Other unidentified modes occur at 817, 1034, 1548 and 1568 cm^{-1} .

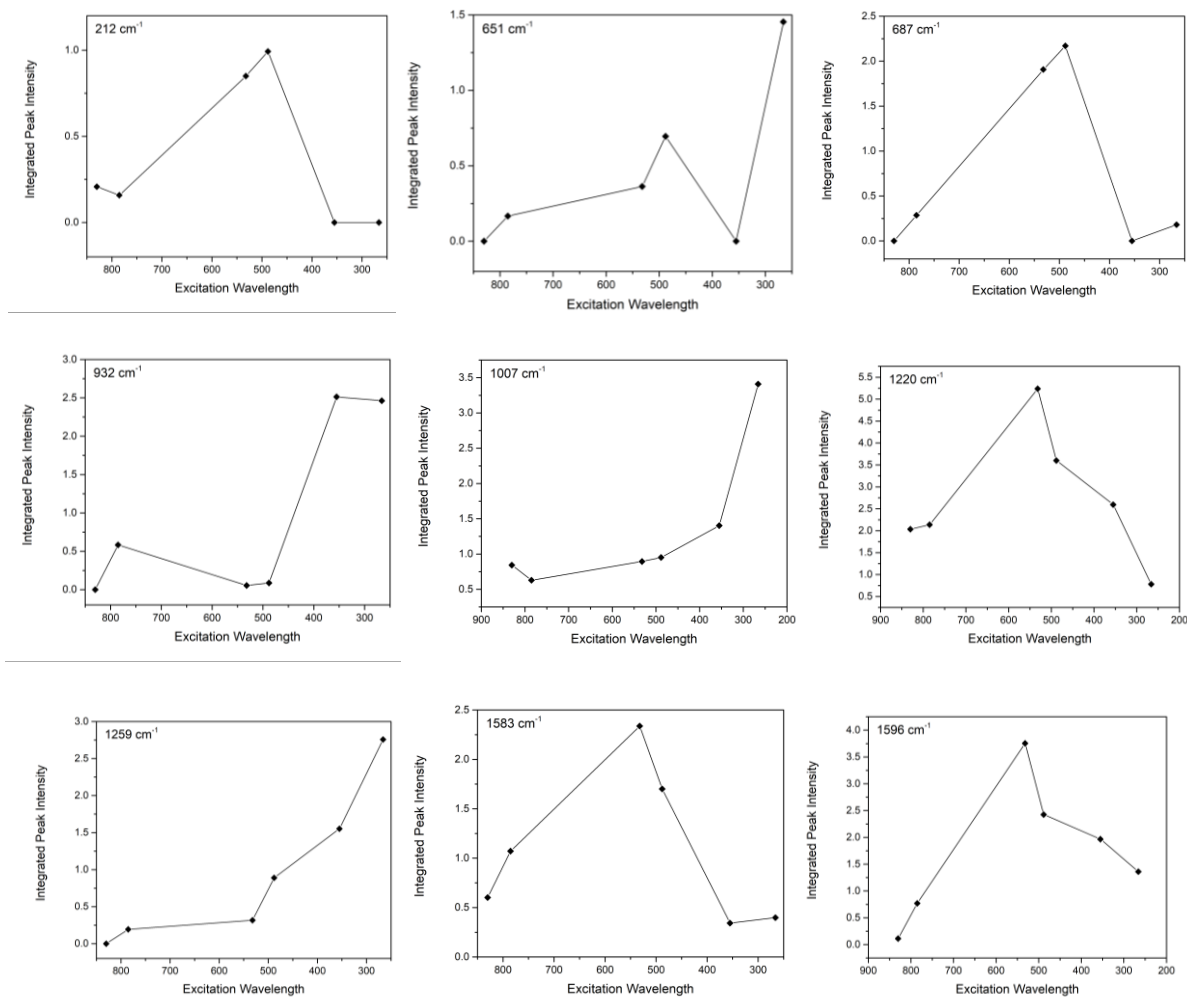


Figure 3.43. Raman excitation profiles for 212, 651, 687, 932, 1007, 1220, 1259, 1583 and 1596 cm^{-1} bands of RuML1 at excitation wavelengths 830, 785, 532, 488, 355 and 266 nm. All bands were integrated and divided by the integral of a reference peak at 446 cm^{-1} .

3.6.2. RuML2

The FTIR spectrum of RuML2 is similarly complex to RuML1. Vibrational modes were assigned by comparison of the spectra of RuML2 to RuML1, [RuML2]Cl to [RuML1]I, as well as a simulated model (Appendix C, Figure 3.44). The difference in ligand resulted in significant differences between the spectra, although the acac vibrational modes were largely unaffected. Oxidation of RuML2 also produced several small changes throughout the spectrum. These comparisons are discussed further in Section 3.6.6.

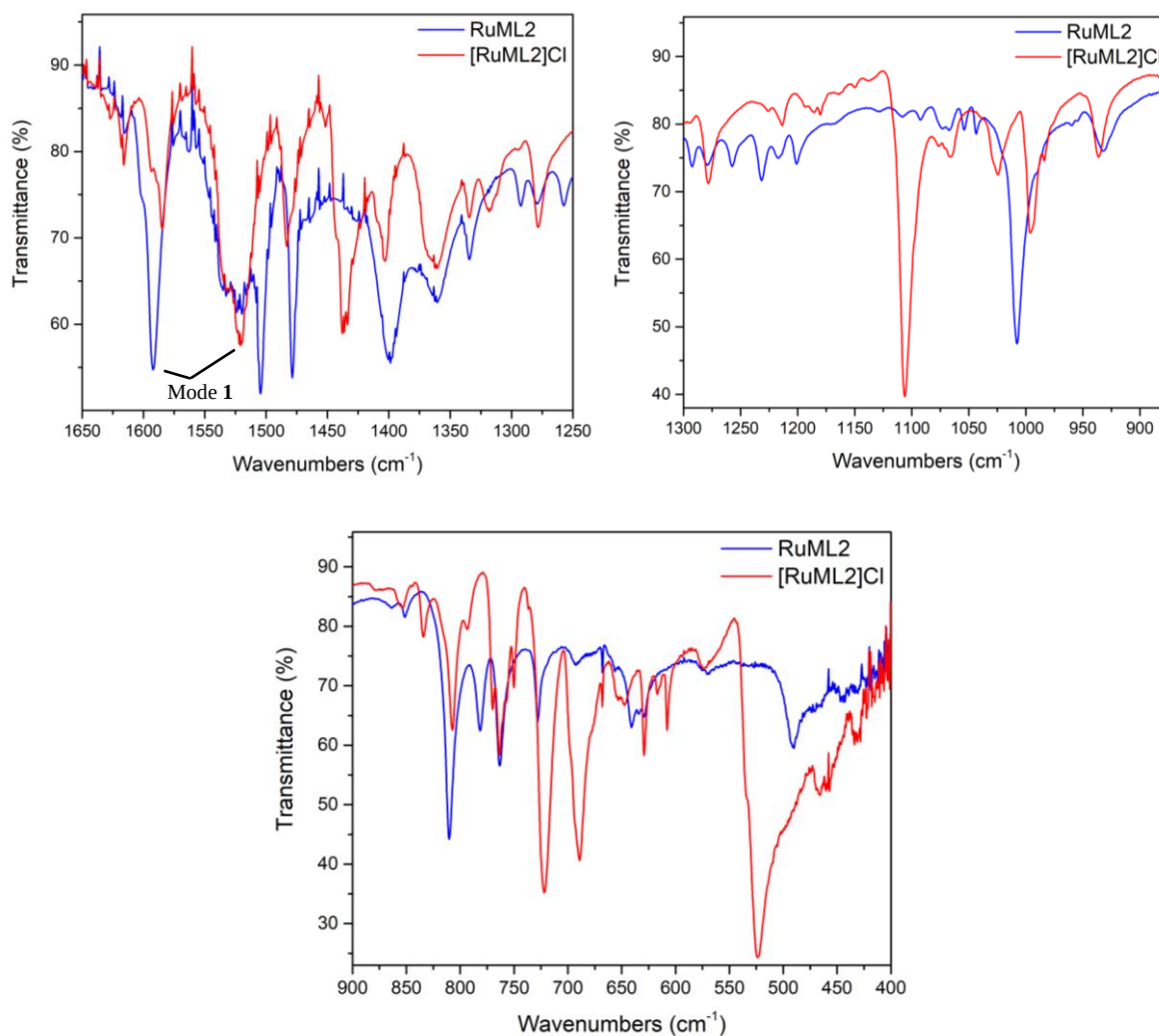


Figure 3.44. FTIR spectra of RuML2 and [RuML2]Cl

The Raman and resonance Raman spectra of RuML2 were characterised with reference to a simulated model and literature values (Table 3.26).²²⁹ The symmetries of several fundamental modes in D_{2h} were assessed by reference to the simulated model.

Table 3.26. Raman spectrum of $[\text{Ru}^{\text{II}}(\text{acac})_2(\text{bpy})_2]$, excitation wavelength: 532 nm.

ν_{max} and Intensity, $[\text{Ru}^{\text{II}}(\text{acac})_2(\text{bpy})_2]$ (cm^{-1})	Simulated ν_{max} and Intensity, $[\text{Ru}^{\text{II}}(\text{acac})_2(\text{bpy})_2]$ (cm^{-1})	Band Assignment ²²⁹	Symmetry
1605 s	1662 s	Bpy $\delta(\text{ring})$	A_g
1593 m, sh	1648 s	Bpy $\delta(\text{Ring})$	A_g
1560 w	1623 s	Acac $\nu(\text{CO})$, $\delta(\text{CH}_3)$	A_g
1511 w	1541 s	Bpy $\rho(\text{CH})$	A_g
1291 s	1318 s	Bpy $\rho(\text{CH})$, $\nu(\text{CC})$	A_g
1254 w, sh	1289 m	Acac $\nu(\text{OCC})_{\text{sym}}$, $\pi(\text{CH}_3)$	A_g
1234 m	1241 s	Bpy $\rho(\text{CH})$	A_g
1212 m	1226 s	Bpy $\rho(\text{CH})$	A_g
1163 w			
1061 w	1085 s	Bpy $\rho(\text{CH})$	A_g
1043 w	1057 w	Bpy $\delta(\text{Ring})$	A_g
1027 m	1046 s	Bpy $\delta(\text{Ring})$	A_g
1016 m	1012 m, 1015 w	Bpy Oop. $\delta(\text{CH})$, $\delta(\text{Ring})$	A_u
887 w	891 w	Bpy Oop $\pi(\text{CH})$	A_u
854 w	865 w	Bpy Oop $\pi(\text{CH})$	A_u
768 m	779 w	Bpy. $\delta(\text{Ring})$	A_g
682 w	684 w	Acac $\pi(\text{CH}_3)$	A_g
645 m	674 w	Bpy $\delta(\text{ring})$	B_{2g}
625 m	639 w	Bpy $\delta(\text{ring})$	A_g
447 m	448 m	$\nu(\text{O-Ru-O})_{\text{sym}}$ Acac $\delta(\text{acac})$	A_g
394 w	413 w	Bpy Oop. $\delta(\text{ring})$	A_u
255 w	257 w	Acac $\pi(\text{CH}_3)$	A_g
176 w	173 w	$\nu(\text{acac-Ru-acac})$	A_g

vw = very weak, *w* = weak, *m* = medium, *s* = strong, *vs* = very strong, *sh* = shoulder, *b* = broad, ν = stretching mode, δ = bending mode, π = wagging mode, ρ = rocking mode, Oop. = out of plane mode.

The Raman spectroscopy of RuML2 was analysed with seven lasers of differing wavelength (Figure 3.45).

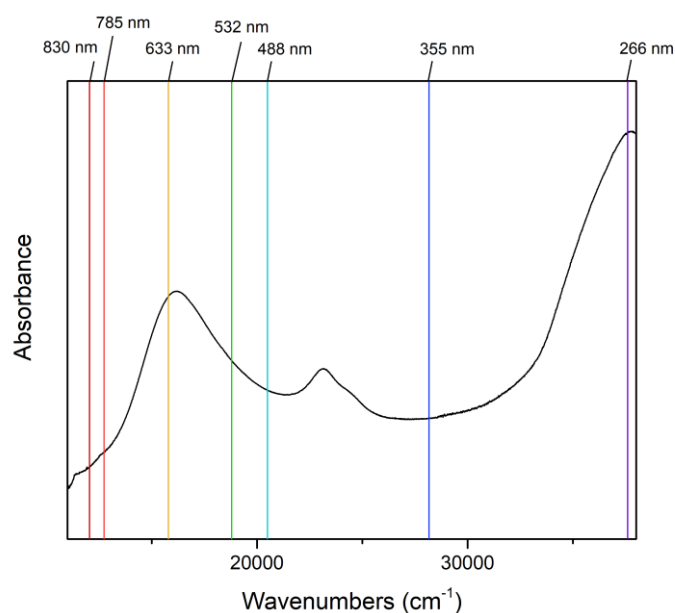


Figure 3.45. Raman excitation wavelengths compared with the UV-vis spectrum of RuML2

Unlike RuML1, all the excitation wavelengths in the D_{2h} approximation of RuML2 excited different transitions with different symmetries. This was reflected in the excitation profiles, which were substantially more varied than those of RuML1. Additionally, the longer wavelength 830 and 785 nm spectra produced fluorescence from the sample, which masked many of the weaker fundamental modes. It was difficult to pick a reference peak to produce excitation profiles for this complex, as most, if not all bands exhibited some form of resonance enhancement or quenching. The totally symmetric ring stretch at 1291 cm^{-1} was eventually chosen as it appeared to change the least between spectra.

The majority of fundamental Raman modes observed in the spectra were totally symmetric; however, the simulation of RuML2 indicates several bands have A_u symmetry, which is Raman forbidden. This was a product of approximating RuML2 as D_{2h} . All but one of these A_u modes occurs on the outer rings of the bpy ligands, which were disregarded in approximating RuML2 as D_{2h} . Most of these modes had very weak Raman intensity, and none exhibited resonance enhancement, although the regions in question were highly populated by other modes. This

suggests that the excited state of the transitions above do not significantly impact the outer rings of the bpy ligands, which supports the point group approximation.

830 and 785 nm produced very similar excitation profiles, and generally exhibited the lowest integrated peak intensity. However, the most apparent outlier was the symmetric stretch and bend of the acetylacetone ligands at 451 cm^{-1} . This mode was totally symmetric and had the highest integrated Raman intensity in the 830 nm spectrum. This may indicate resonance enhancement by the 830 nm laser line or quenching by the smaller wavelength lines. It could also indicate that the 1291 cm^{-1} reference peak was resonance enhanced more than the 451 cm^{-1} mode in subsequent spectra.

The 633 nm profile exhibited moderate resonance enhancement and produced the largest resonance enhancement for the totally symmetric 1546 cm^{-1} acac stretching and bending mode. 532 nm produced weak-to-moderate resonance enhancement. Excitation at 488 nm exhibited the strongest resonance enhancement in this complex, with the A_g bpy CH bend at 992 cm^{-1} , A_g ring bend at 1595 cm^{-1} and A_g ring bend at 1605 cm^{-1} greatly enhanced. Excitation at 355 nm produced moderate enhancement, giving the largest integrated Raman intensity for the A_g bpy CH bend at 1511 cm^{-1} . 266 nm exhibited poor to no resonance enhancement, with a very low intensity.

All identified resonance enhancement was A-term in nature. Additionally, no combination modes or overtones were identified in the resonance enhanced spectra.

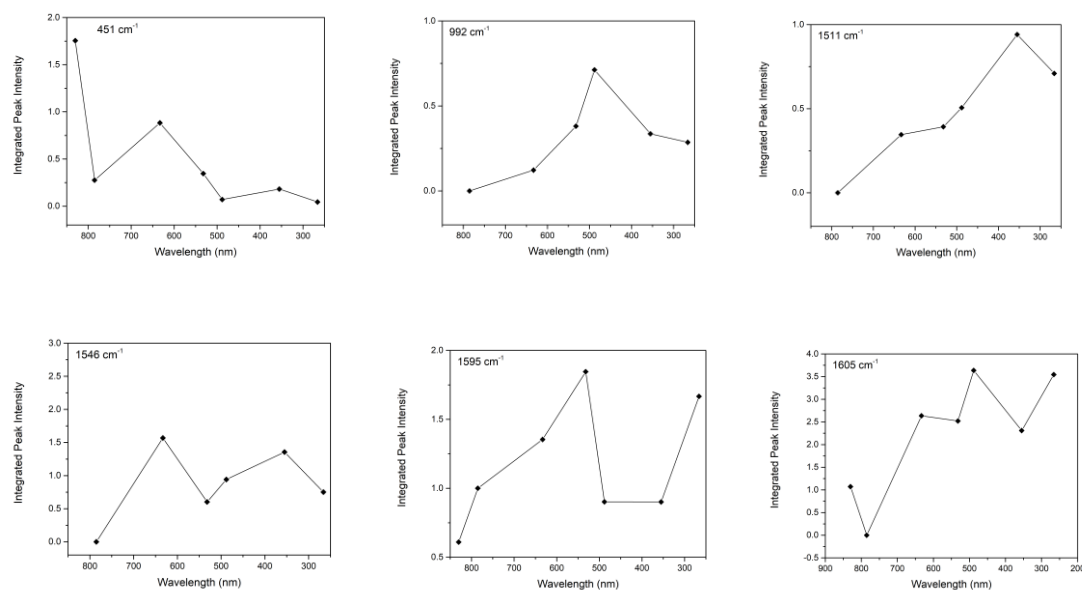


Figure 3.46. Raman excitation profiles for 451, 992, 1511, 1546, 1595, and 1605 cm⁻¹ bands of RuML2 at excitation wavelengths 830, 785, 633, 532, 355 and 266 nm. All bands were integrated and divided by the integral of a reference peak at 1291 cm⁻¹.

3.6.3. RuML4

The FTIR spectrum of RuML4 is similarly complex to RuML1 and RuML2. Vibrational modes were assigned by comparison to other metalloligands, literature values,²³⁰ as well as a simulated model (Appendix C). Comparisons between complexes and oxidation states are discussed further in Section 3.6.6.

ATR SEC of RuML4 was consistent with the FTIR spectra of RuML4 and RuML4Cl on major absorptions (Figure 3.47, Table 3.27). The transition from Ru(II) to Ru(III) is characterised by several clean isosbestic points, and the reversibility of the SEC showed that the complexes were substitutionally stable over the minutes to hours timescale.

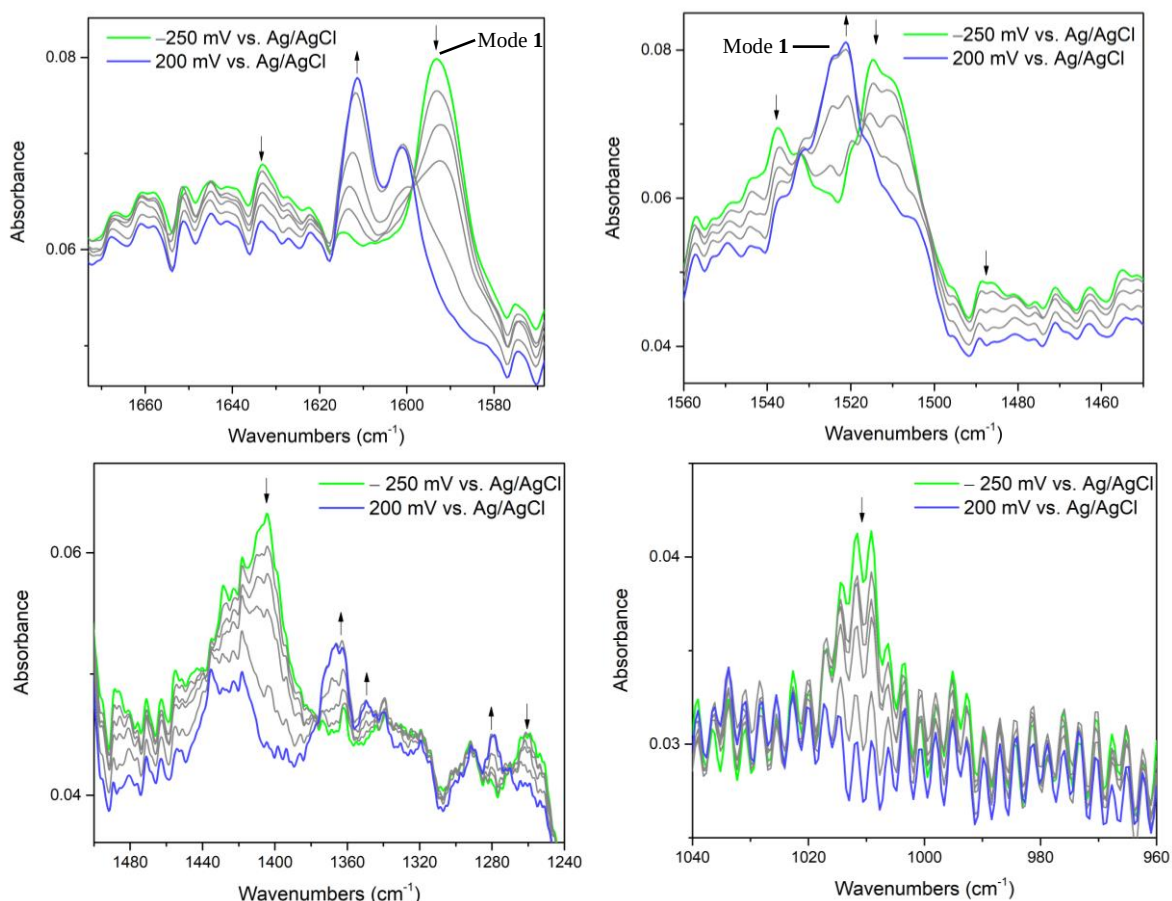


Figure 3.47. Solid-state FTIR SEC of RuML4. Electrolyte was 0.1 M KCl in H₂O. W.E.: ITO layer on silicon crystal.

Table 3.27. FTIR SEC of RuML4

$\nu_{\max}$ RuML4 (cm ⁻¹)	$\nu_{\max}$ RuML4 ⁺ (cm ⁻¹)	Assignment
1633		$\delta(\text{C}_2\text{H}_2)$
	1611	BPE $\delta(\text{inner ring})$
1593	1601, 1521	BPE $\nu(\text{outer ring})_{\text{asym}}$, $\nu(\text{inner ring})_{\text{asym}}$ Acac $\nu(\text{C=O})_{\text{sym}}$, $\delta(\text{C-HC=C})$, $\rho(\text{CH}_3)$
1538		Acac $\delta(\text{CCHC})$
1515		BPE $\rho(\text{CH})$
1404		Acac $\rho(\text{CH}_3)$, BPE $\delta(\text{CH})$
	1363	Acac $\delta(\text{CH}_3)$
	1350	BPE $\rho(\text{CH})$
	1280	BPE $\rho(\text{CH})$, $\delta(\text{ring})$, Acac $\nu(\text{C-CH}_3)$
1261		BPE $\rho(\text{CH})$, $\nu(\text{CC})$
~1010		Acac $\rho(\text{CH}_3)$, BPE $\delta(\text{inner ring})$

ν = stretching mode, δ = bending mode, π = wagging mode, ρ = rocking mode, Oop.= out of plane mode.

The Raman and resonance Raman spectra of RuML4 were characterised with reference to RuML1, RuML2, and a simulated model (Table 3.28). The symmetries of several fundamental modes in C_{2v} and C_{2h} were assessed by reference to the simulated model.

Table 3.28. Experimental and simulated Raman spectrum of RuML4. Excitation wavelength: 532 nm.

$\nu_{\max}$ and Intensity [Ru(acac) ₂ (BPE) ₂] (cm ⁻¹)	Simulated $\nu_{\max}$ and Intensity [Ru(acac) ₂ (BPE) ₂] (cm ⁻¹)	Band Assignment	C_{2v} Symmetry	C_{2h} Symmetry
2801 m, br	3150 m	BPE outer ring $\nu(\text{CH})$	A_1	A_g
1630 s	1695 s	$\delta(\text{C}_2\text{H}_2)$	A_1	A_g
1602 s	1623 s, 1642 s, 1658 s	Acac $\nu(\text{CO})$, $\delta(\text{CH}_3)$ BPE $\delta(\text{CH})$, $\delta(\text{outer ring})$, $\delta(\text{inner ring})$	A_1	A_g
1531 m	1577 m	Acac $\nu(\text{ring})_{\text{asym}}$	B_1	A_g
1492 w	1519 m	BPE $\rho(\text{CH})$	A_1	A_g
1426 w	1450 w	BPE outer ring $\delta(\text{CH})$	A_1	A_g
1339 m	1349 m	BPE $\delta(\text{CH})$	B_1	A_g
1311 w, br	1333 m	C_2H_2 $\delta(\text{ring-CH})$	A_1	A_g
~1215 m, sh	1225 m	BPE $\delta(\text{CH})$	A_1	A_g
1198 s	1215 vs	BPE inner ring $\delta(\text{CH})$	A_1	A_g
1060 w	1078 w	BPE inner ring $\delta(\text{CNC})$, $\rho(\text{CH})$	A_1	A_g
~1029, m				
1017 m	1047 m	BPE $\delta(\text{inner ring})$	A_1	A_g
969 w	1012 w	BPE $\delta(\text{outer ring})$	A_1	A_g
887 w	894 w	BPE $\rho(\text{CH})$, C_2H_2 $\delta(\text{ring-CH})$, $\delta(\text{ring-C=C})$	A_1	A_g
839 w				
809 w				
742 w				
723 w				
683 w				
665 m	685 w	Acac $\pi(\text{CH}_3)$, $\delta(\text{OCC})$	A_1	A_g
591	607 w	Acac $\nu(\text{O-Ru-O})_{\text{asym}}$	B_2	B_g

576 w				
553 w	566 w	BPE inner ring $\rho(\text{CH})$	A_2	B_g
449 w	448 w	$\nu(\text{O-Ru-O})_{\text{sym}}$ Acac $\delta(\text{acac})$	A_1	A_g
404 w				
~ 337 m, b				
266 m	257 w	Acac $\pi(\text{CH}_3)$	A_1	A_g
188 w, br				

vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder, b = broad, ν = stretching mode, δ = bending mode, π = wagging mode, ρ = rocking mode, Oop. = out of plane mode.

The Raman spectroscopy of RuML4 was analysed with six laser lines of differing wavelength (Figure 3.48). 785 nm produced a spectrum with very poor Raman signal, due to laser-induced fluorescence.

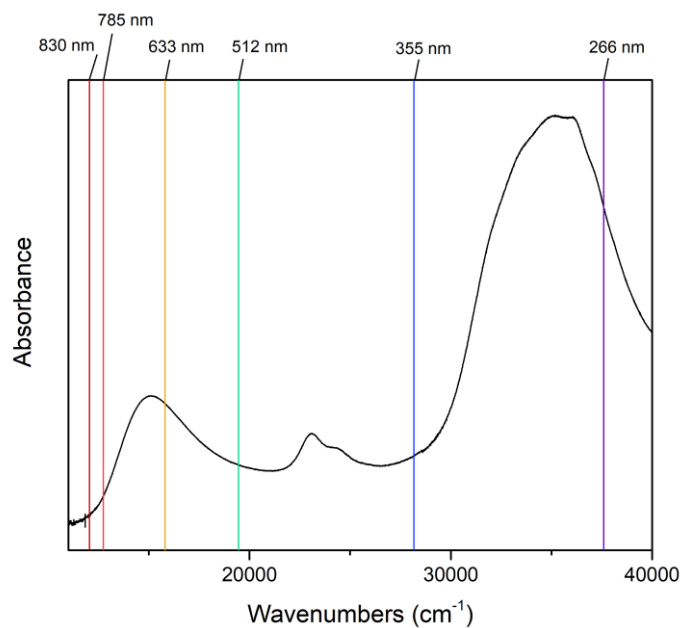


Figure 3.48. Raman excitation wavelengths compared with the UV-vis spectrum of RuML4

The resonance Raman profiles of RuML4 were less distinct from each other than RuML1 or RuML2 (Figure 3.49), which conforms to the lower symmetry descriptions of the molecule as C_{2v} or C_{2h} .

None of the laser lines employed were off-resonance, due to the relatively low energy HOMO→LUMO transition **1**. This made selecting a reference peak difficult, as resonance effects were unclear across the excitation profiles. We settled on the totally symmetric BPE CH bending mode at 1196 cm^{-1} .

There were only small differences between the excitation profiles of 830, 633 and 512 nm, which suggests the excited state symmetries produced by these excitation wavelengths were all the same. This is consistent with the C_{2h} point group.

355 and 266 nm by comparison produced very weak Raman spectra, possibly due to quenching. Most of the modes in the longer wavelength spectra were not visible in the 355 and 266 nm spectra. A band at 591 cm^{-1} was only visible in the 266 nm spectrum. The fundamental mode in this region was B_2 in C_{2v} and B_g in C_{2h} , but neither of these bands could be enhanced by A- or B-term mechanisms by 266 nm. Thus the band may be a combination mode.

One of the most variable bands across the excitation profiles was the totally symmetric C_2H_2 stretch at 1630 cm^{-1} . This band was one of the few visible in the smaller wavelength profiles, and increased in relative integrated intensity across 830, 633 and 512 nm excitation profiles. This indicates the ethylene group was subject to resonance effects, which means ethylene contributed to the π^* MO of the BPE group, and electronically interacted with the Ru centre. This further indicates that the lower symmetry C_{2v} or C_{2h} descriptions are more appropriate than approximating the molecule as D_{2h} by excluding the ethylene group and outer rings.

Again, most vibrational modes were totally symmetric in both C_{2v} and C_{2h} . All resonance enhancement was A-term in nature. There were few modes that represented the correct

symmetry for B-term enhancement in C_{2v} , including those with B_1 symmetry at 1531 and 1339 cm^{-1} , but neither band exhibited any notable enhancement.

Unfortunately, there was little insight offered by the resonance Raman profiles of RuML4, other than an indication that the molecule conforms to a low symmetry description.

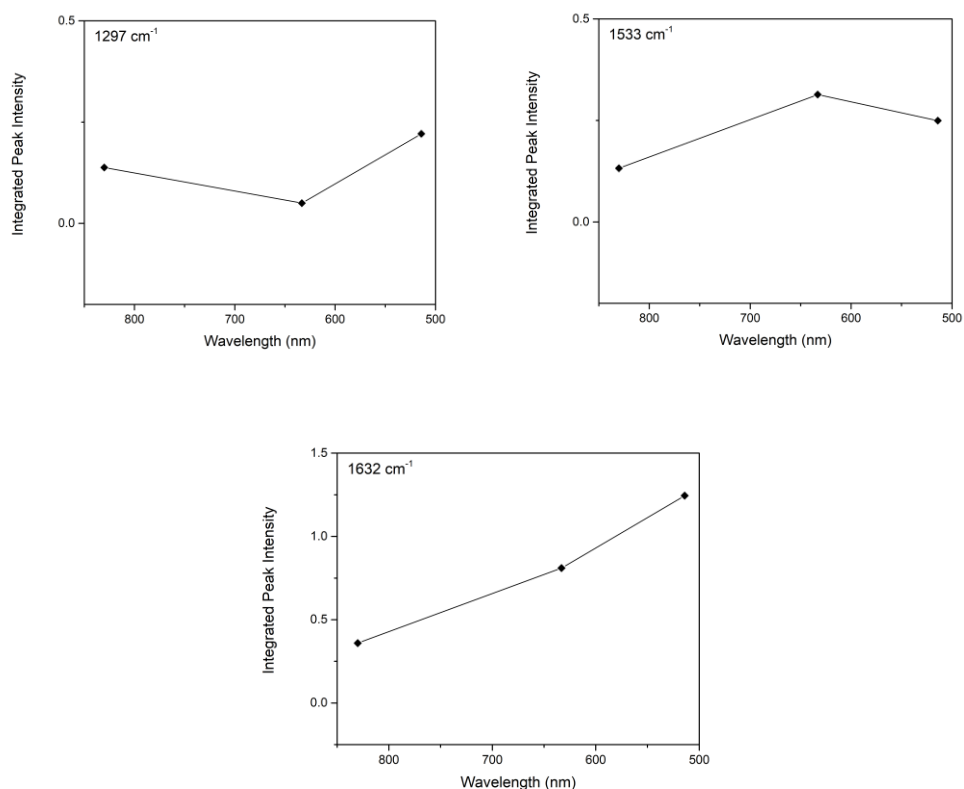


Figure 3.49. Raman excitation profiles for 1297, 1533 and 1632 cm^{-1} bands of RuML4 at excitation wavelengths 830, 785 and 512 nm. All bands were integrated and divided by the integral of a reference peak at 1196 cm^{-1} .

3.6.4. RuML0

The FTIR and Raman spectra of RuML0 most closely resemble RuML1. IR and Raman vibrational modes were characterised by comparison with other metalloligands, and literature values (Table 3.29, Table 3.30).²³¹⁻²³³ Comparisons between complexes and oxidation states are discussed further in Section 3.6.6.

Table 3.29. FTIR spectrum of RuML0

ν_{max} and Intensity [Ru ^{II} (acac) ₂ (Py) ₂] (cm ⁻¹)	Band Assignment ²³¹
1591 m	Py
1560 m	Acac $\nu(\text{C}=\text{O})_{\text{sym}}$, $\delta(\text{C}-\text{HC}=\text{C})$, $\rho(\text{CH}_3)$
1534 m	Acac $\nu(\text{C}=\text{C})_{\text{asym}}$
1511 s	$\nu(\text{Acac})_{\text{asym}}$
1470 m	Py
1445 w	Py
1404 s	Acac $\delta(\text{CH}_3)$
1344 m	Acac $\delta(\text{CH}_3)$
1279 w	Py
1260 m	Acac $\delta(\text{C}-\text{CH}_3)$
1243 w, sh	
1203 m	Acac $\rho(\text{CH})$
1146 m	Py
1062 m	Py
1041 w	Py
1015 m	
997 s	Py
930 s	Acac $\nu(\text{C}-\text{CH}_3)$
864 w	Py
779 s	Acac $\pi(\text{CH})$
766 s	Py
689 s	Py
660 w	
640 s	Acac $\nu(\text{O}-\text{Ru}-\text{O})_{\text{sym}}$, $\rho(\text{CH}_3)$
629 s	
489 m	
437 m	Acac $\rho(\text{acac})$

vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder, b = broad, ν = stretching mode, δ = bending mode, π = wagging mode, ρ = rocking mode, Oop. = out of plane mode.

Table 3.30. Raman spectrum of RuML0. Excitation wavelength 833 nm.

$\nu_{\max}$ and Intensity [Ru(acac) ₂ (Py) ₂] (cm ⁻¹)	Band Assignment
1595 s	Py
1569 m	Py
1543 m	
1473 w	Acac $\nu(\text{OC-C=CO})_{\text{asym}}$
1257 m	Acac $\nu(\text{CCH}_3)$
1207 s	Py
1148 w	Acac $\delta(\text{CH})$
1068 m	Py
1048 m	Py $\nu(\text{ring})$
1013 vs	Acac $\delta(\text{CH})$, $\delta(\text{CH}_3)$, Py $\nu(\text{ring})$
997 m	Py $\nu(\text{ring})$
924 w	Acac $\delta(\text{CH})$, $\delta(\text{CH}_3)$
900 m	
686 m	Acac $\nu(\text{Ring})$
648 s	Py
452 s	Acac $\nu(\text{Ring})_{\text{sym}}$
317 w	
261 m	$\delta(\text{acac-Ru-acac})$
204 m	$\delta(\text{pyz-Ru-acac})$
177 w	

vw = very weak, *w* = weak, *m* = medium, *s* = strong, *vs* = very strong, *sh* = shoulder, *b* = broad, ν = stretching mode, δ = bending mode, π = wagging mode, ρ = rocking mode, *Oop.* = out of plane mode.

3.6.5. Ph₄P{*trans*-[Ru(acac)₂Cl₂]}

The infrared and Raman spectroscopies of Ph₄P{*trans*-[Ru(acac)₂Cl₂] } differ substantially from other members of the *trans*-[Ru(acac)₂(X)₂] family. IR modes were assigned by comparison with [RuML1]I (Table 3.31). Notably, the acac modes of Ph₄P{*trans*-[Ru(acac)₂Cl₂] } differ substantially in energy to those observed in [RuML1]I. This is likely due to the presence of electron donating Cl⁻ ligands, which demonstrably change the geometry of the complex, as shown in Section 3.3. Raman modes were assigned by comparison with literature values (Table 3.32).²²⁸

Table 3.31. FTIR spectrum of $\text{Ph}_4\text{P}\{\text{trans-}[\text{Ru}(\text{acac})_2\text{Cl}_2]\}$

ν_{max} and Intensity [$\text{Ru}(\text{acac})_2\text{Cl}_2$] (cm^{-1})	$\text{Ph}_4\text{P}\{\text{trans-}$	Band Assignment
1586 vw		
1543 sh		Acac $\rho(\text{CH})$, $\nu(\text{C}=\text{C}-\text{C})$, Acac $\nu(\text{C}=\text{O})_{\text{asym}}$
1519 s		
1483 vw		
1434 w		Acac $\delta(\text{CH}_3)$
1381 m		Acac $\delta(\text{CH}_3)$
1265 w		Acac $\nu(\text{C}-\text{CH}_3)_{\text{sym}}$
1199 vw		Acac $\rho(\text{CH})$
1162 vw		
1106 m		
1019 w		
998 w		Acac $\nu(\text{C}-\text{CH}_3)$
932 w		
809 w		
787 w		
767 w		
755 w		
751 w		
722 s		
693 s		
659 m		Acac $\nu(\text{O}-\text{Ru}-\text{O})_{\text{sym}}$, $\rho(\text{CH}_3)$
525 vs		
455 s		Acac $\nu(\text{O}-\text{Ru}-\text{O})_{\text{sym}}$ $\nu(\text{CH}_3)$
415 sh		Acac $\rho(\text{acac})$

vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder, b = broad, ν = stretching mode, δ = bending mode, π = wagging mode, ρ = rocking mode, Oop. = out of plane mode.

Table 3.32. Raman spectrum of $\text{Ph}_4\text{P}\{\text{trans}[\text{Ru}(\text{acac})_2\text{Cl}_2]\}$

ν_{max} and Intensity [$\text{Ru}^{\text{III}}(\text{acac})_2\text{Cl}_2$] (cm^{-1})	Ph ₄ P{ <i>trans</i> - [$\text{Ru}^{\text{III}}(\text{acac})_2\text{Cl}_2$]} Band Assignment ²²⁸
1585 m	Acac $\nu(\text{C-O})$
1364 w	
1322 w	
1269 m	
1199 w	
1164 w	
1110 w	
1095 m	
1026 m	
1001 s	
933 m	
726 w	
691 m	
615 m	
554 w	
460 s	$\nu(\text{Ru-O})$
327 sh	
284 s	
256 s	
187 sh	

vw = very weak, *w* = weak, *m* = medium, *s* = strong, *vs* = very strong, *sh* = shoulder, *b* = broad, ν = stretching mode.

3.6.6. General Discussion

The vibrational spectroscopy of the *trans*-[Ru(acac)₂(X)₂] family was very complex, owing to both acetylacetonate and pyridyl vibrational profiles. While there were shared features between complexes of differing ligand X, the distinct contributions of the pyridyl ligands produced mostly distinct, convoluted spectra. The shared features were modes belonging to the acetylacetonate ligands, which were relatively similar between spectra. Comparison of metal complexes and their oxidised salts revealed very similar vibrational profiles. Most vibrational modes are present in both spectra, with only a small number observable in only one.

Given the highly complex nature of the spectra in this Section, it would be impossible to effectively characterise the spectra of the *trans*-[Ru(acac)₂(X)₂] family without simulations.

There were very few notable trends between the IR spectra of corresponding Ru(II) and Ru(III) metal complexes. Comparison of equivalent vibrational modes revealed mostly small shifts ($\sim 10\text{ cm}^{-1}$) in absorption energy between oxidation states. This result was consistent with the characterisation of bands in the relevant region, which included ring modes, acetylacetonate vibrations and many methyl, aromatic and acetylacetonate CH modes. We anticipated that the largest changes would occur at Ru-N and Ru-O vibrations, which occurred at lower energies than permitted by instrumentation. One of the most prominent vibrational modes notably redshifted upon oxidation of the metal. This mode was characterised by a direct oscillation of the C=O bonds as well as a bending vibration of the acetylacetonate bite (Figure 3.50). The same vibrational mode is observed in both RuML1, 2, 4 and 0, and consistently redshifts upon oxidation of the metal complex (Table 3.33). The relative intensity of this mode did not change upon oxidation, as seen in the SEC of RuML4 (Figure 3.47).

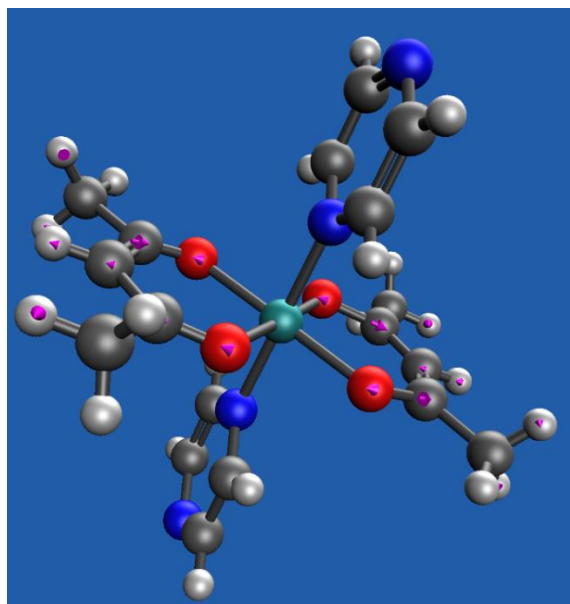


Figure 3.50. Mode 1 in RuML1, as simulated in Gaussian 16.¹⁶⁹

Additionally, Table 3.33 demonstrates a trend between different members of the RuML family. As opposed to the majority of acac vibrational modes, mode **1** increased in energy from RuML1 to RuML2 and RuML4.

The above results appears to suggest a physical change in the acetylacetonate bite upon oxidation of the metal complex. Given the trend across the family, changes in the band are likely related to electronic effects such as π -backbonding. The change in energy of this band is almost certainly related to the distortion of the acac^- ligand observed in Ru(II) crystal structures within this family of complexes. The energy of ν_{max} appears to be correlated to magnitude of distortion at the acac^- ligand.

Table 3.33. Comparison of mode **1** energies across the *trans*-[Ru(acac)₂(X)₂] family

	ν_{max} , Ru(II) (cm ⁻¹)	ν_{max} , Ru(III) (cm ⁻¹)
RuML1	1560	1518
RuML0	1560	-
RuML2	1592	1533
Ph ₄ P{ <i>trans</i> -[Ru ^{III} (acac) ₂ Cl ₂]}	-	1543
RuML4	1590	1518

3.7. Analytical Trends and Summary

The Ru(III/II) redox couple of the *trans*-[Ru(acac)₂X₂] complexes directly reflects the changing degree of π -backbonding occurring across the family. Comparison of the $E_{1/2}$ of this couple with the energy of CT transitions gives insight into the orbitals of the Ru(II) and Ru(III) complexes (Figure 3.51). As discussed in Section 3.5, the energy of the lowest energy transition (**1**) in the Ru(II) complexes (MLCT, HOMO $\rightarrow$ LUMO) do not directly reflect the changing π -backbonding throughout the family. π -backbonding primarily lowers the HOMO energy. The LUMO is also subject to change across the family, due to changing π^* MOs within the ligands themselves (Figure 3.51A). However, the energy of the lowest energy transition (**1**) in the Ru(III) complexes (LMCT) *do* reflect this trend (Figure 3.51B). The LUMO of this orbital (primarily the Ru *d* orbitals) is subject to the same stabilisation due to π -backbonding. However, the HOMO orbital does not appreciably change in energy across the family, as the ligand stays the same; therefore, we see a correlation between negative magnitude of the $E_{1/2}$ potential and the magnitude of transition **1**.

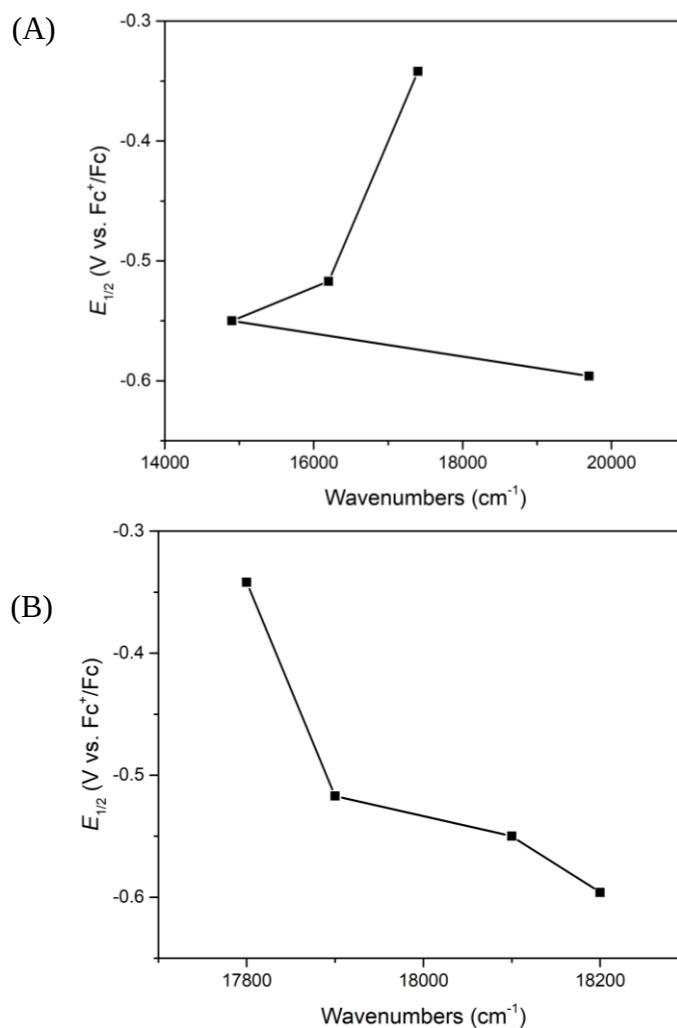


Figure 3.51. Comparison of RuML0, RuML1, RuML2 and RuML4 Ru(III/II) $E_{1/2}$ potentials with maxima energy of transition **1** in (A) Ru(II) (B) Ru(III)

Comparison of the half-wave potential of the Ru(III/II) couples with crystallographic values do not reveal clear trends between different members of the family. This is largely attributable to experimental error, but the specific packing conditions of crystal structures can produce substantial differences in these parameters between polymorphs of the same complex, as shown in Section 3.3. Additionally, the lack of SCXRD data of *trans*-[Ru(III)(acac)₂(pyz)₂]⁺ and *trans*-[Ru^{II}(acac)₂(BPE)₂] in the present work represent potential targets for future work. However, the distinction between both bond lengths and the normalised bite of the acac ligand

across the d^5 - d^6 boundary is very apparent when plotted against the half-wave potential (Figure 3.52).

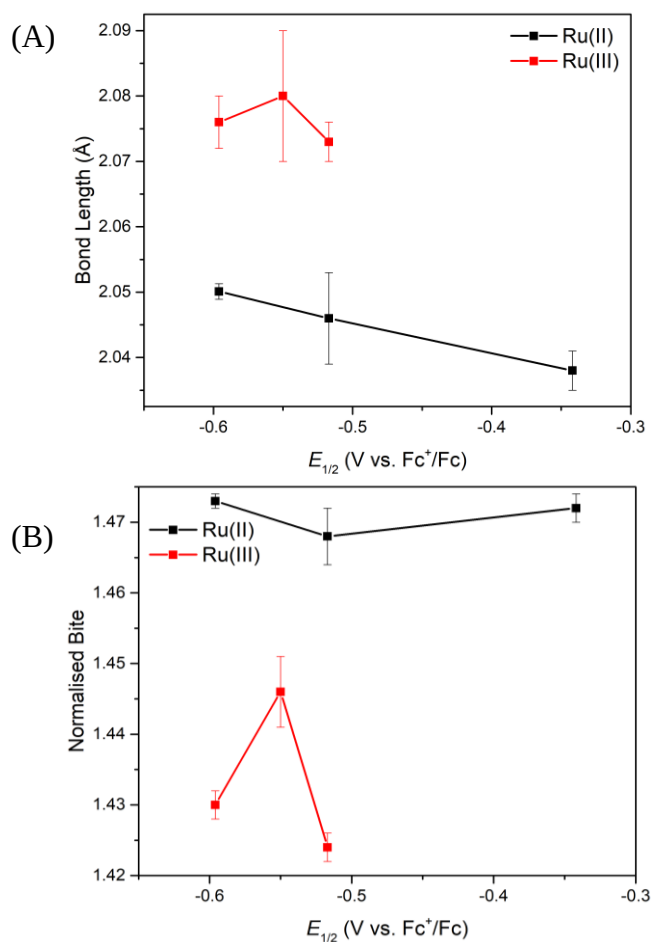


Figure 3.52. Comparison of RuML0, RuML1, RuML2, RuML4 Ru(III/II) $E_{1/2}$ potentials with (A) Average Ru-N bond lengths (B) Normalised bite values

Throughout this Chapter we have presented an extensive investigation of the crystallographic, electrochemical and spectroscopic properties of the discrete *trans*-[Ru(acac)₂(X)₂] family. This foundational work is the basis for further analysis of closely related CPs found in Chapter 4.

Chapter 4

Coordination Polymers with the Moiety $[Ru(acac)_2(X)_2]$

Reticular Synthesis with *trans*-[Ru(acac)₂(X)₂]

Metalloligands

The metalloligands discussed in Chapter 3 display a number of potentially valuable properties, including chemically reversible Ru(III/II) couples at readily accessible reduction potentials, electrochromism and charge transfer. The complexes are also uncharged in the Ru(II) oxidation state and have a +1 charge in the Ru(III) oxidation state, which is ideal for reactions with metal salts. These metalloligands were initially considered as ligand candidates for CPs with long-range charge transfer; however, the metalloligand motif proved challenging in the synthesis of extended materials, for several reasons. The greatest barrier was the geometry of the metalloligands - the acac⁻ ligands were sufficiently bulky and interfered with the self-assembly process. This was especially pronounced with octahedrally coordinating nodes, which have yet to produce identifiable crystalline materials with any *trans*-[Ru(acac)₂(X)₂] metalloligand in the system studied. This was an impediment in producing certain classes of coordination polymers that would exhibit long-range charge transfer, which would require nodes of comparable ligand-field symmetry to the Ru metal.²⁹⁻³⁰ Another barrier was the sensitivity of the metalloligands to high temperatures. At high temperatures the ligand X may exchange with solvents such as MeCN and DMF, which may outcompete self-assembly reactions in solvothermals.

In this Chapter, we report analytical investigations of three coordination polymers employing the *trans*-[Ru(acac)₂(X)₂] motif, including a three-dimensional diamondoid CP with Robin-Day Class I mixed-valency. The crystallographic, electrochemical, and spectroscopic properties of these materials are contrasted with their metalloligands in order to gain a better perspective on the transition from discrete complex to extended material.

4.2. Silver-Bridged Polymers of RuML2

A range of polymer syntheses were investigated with the RuML2 metalloligand. Of these, only two systems produced crystalline materials, and only one has been definitively identified structurally. These materials were synthesised by the reaction of *trans*-[Ru^{III}(acac)₂(bpy)₂]⁺ with bulky silver salts AgPF₆ and AgSbF₆. It is unclear why the Ru(III) complex reacts more favourably with Ag(I) than the Ru(II) complex. One possibility is that Ag(I) is reduced to Ag(0) by the Ru(II) complex, which would prevent formation of a CP. However, as discussed later, Ru(II) is present as a minor component of the CP, possibly as a result of reduction by Ag(I). Reactions that failed to produce crystals involve silver halides and nitrates. Considering the salts that did not produce crystals, and the larger, more strongly diffracting crystals produced by the antimony salt compared with the phosphate salt, we suggest that the crystal systems may help to template cations with more bulky ligands during the self-assembly process. The crystal system identified in this section appears to support these claims.

4.2.1. Crystallography

The coordination polymer [Ag[Ru(acac)₂(bpy)₂]₂](SbF₆)_n·(C₂H₅OH)₈ crystallised in the monoclinic space group *P*2₁/*c*, with a full [Ag[Ru(acac)₂(bpy)₂]₂](SbF₆)₃ monomer in the asymmetric unit and four monomers in the unit cell (Figure 4.1). Additionally, a solvent mask was calculated and 811 electrons were found in a volume of 2382 Å³ in four voids per unit cell. This was consistent with eight ethanol molecules per asymmetric unit, which accounted for 832 electrons per unit cell. The polymer was modelled with three fully-occupied SbF₆[−] counterions per [Ag[Ru(acac)₂(bpy)₂]₂] monomer.

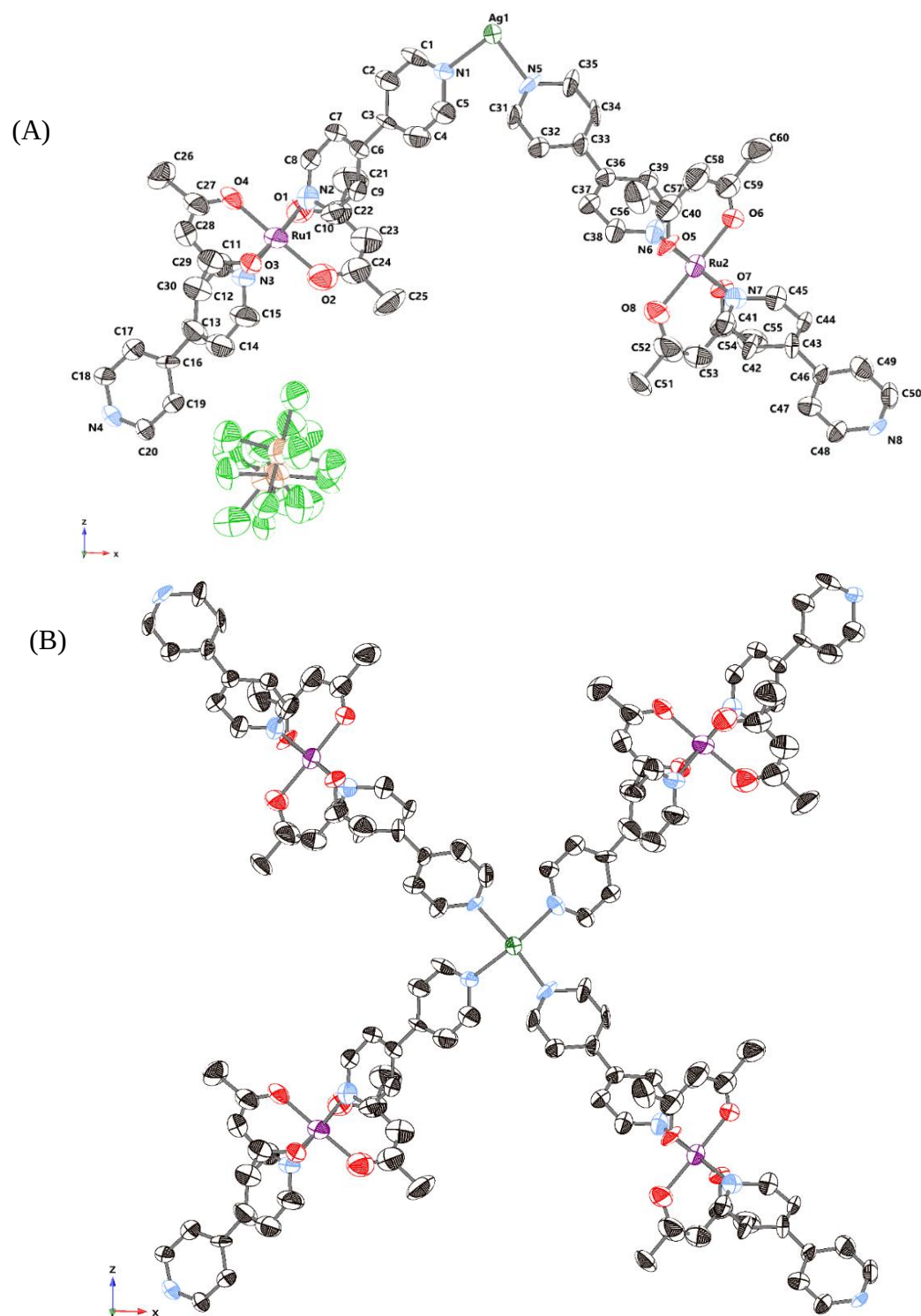
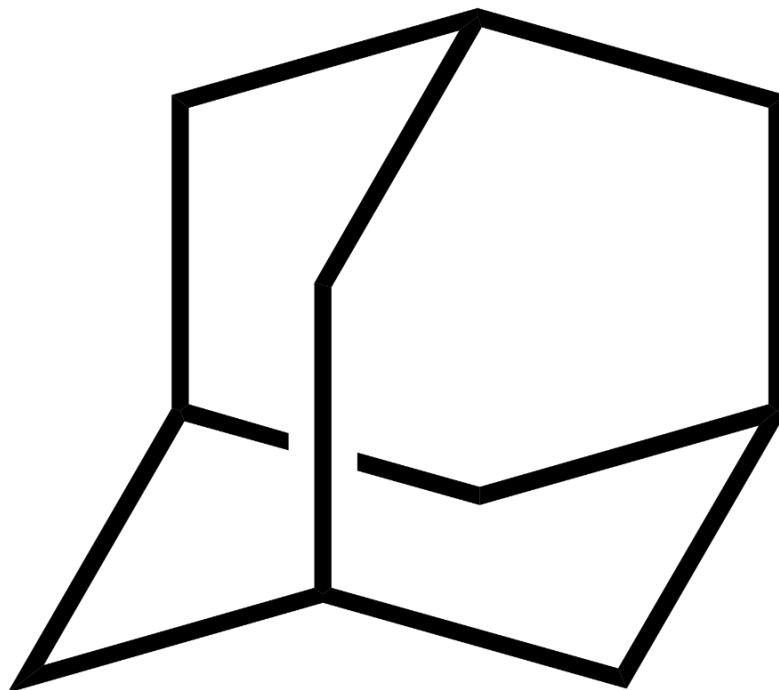


Figure 4.1. $[\text{Ag}(\text{RuML}_2)_2](\text{SbF}_6)_3$ monomer units in $P2_1/c$. (A) Asymmetric unit viewed down the b -axis; (B) Ag tetragonal node viewed down the b -axis, SbF_6 ions omitted. Colour scheme: N, blue; C, black; O, red; Ru, purple; Ag, dark green; F, green; Sb, light brown. Hydrogens atoms were omitted for clarity. Plotted in CrystalMaker X Ver. 10.8.1.

Although spectroscopic data indicated the presence of Ru(II), crystallographic data quality was too low to identify a precise stoichiometry of cation to anion, and the solution with the lowest R value had three fully-occupied SbF_6^- anions and monovalent Ru(III) metalloligands. This indicated a high ratio of Ru(III) to Ru(II) metalloligands within the CP.

Ag(I) ions coordinated tetragonally to the *trans*-[Ru(acac)₂(bpy)₂]⁺ moieties (Figure 4.1B), to form a diamondoid network with pseudo-adamantane units that have a vertex to vertex distance of approximately 40 Å (Figure 4.2). The polymer was eight-fold interpenetrated (Figure 4.3A), owing to the extremely large cavities of the isolated network. One-dimensional channels were observed down the *b*-axis (Figure 4.3B), that were largely occupied by bulky SbF_6^- counterions. These channels were approx. 5 Å in diameter and had the potential to host different ions than SbF_6^- *via* ion exchange. Although the RuML2 metalloligand in theory provided more rigidity to the framework than a traditional organic ligand, the stability of the framework without the large counterions is uncertain. We concluded that the self-assembly process was optimised with a larger counterion.

(A)



(B)

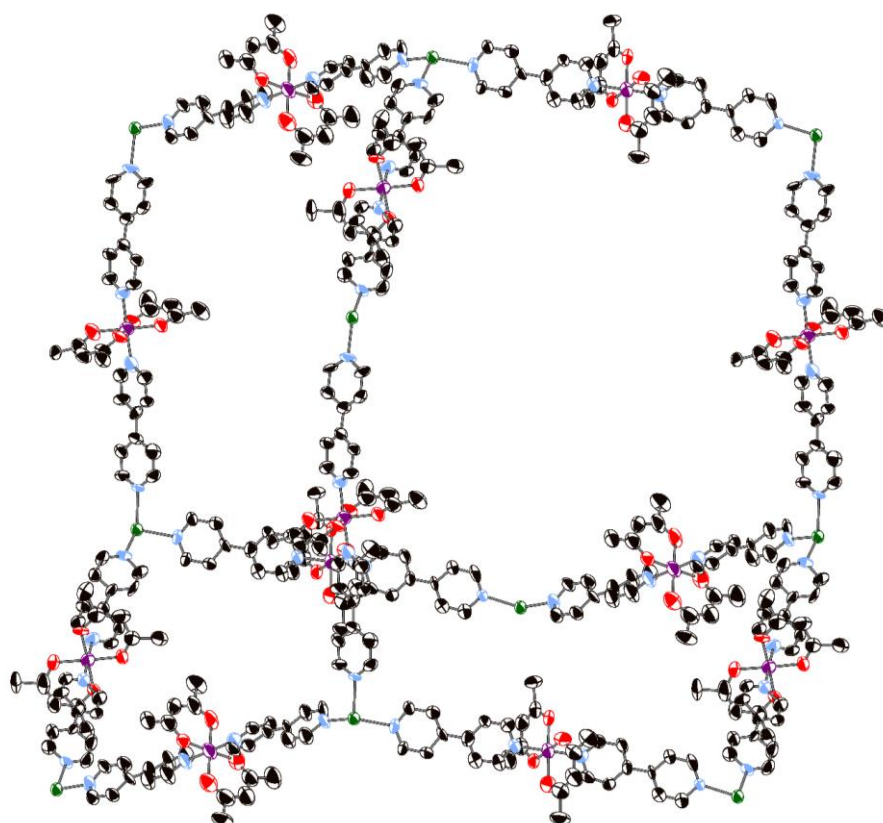


Figure 4.2. (A) Adamantane unit; (B) $[\text{Ag}(\text{RuML}_2)_2](\text{SbF}_6)_3$ cage in $P2_1/c$. SbF_6^- ions omitted for clarity. Colour scheme: N, blue; C, black; O, red; Ru, purple; Ag, dark green; F, green; Sb, light brown. Hydrogens atoms were omitted for clarity. Plotted in CrystalMaker X Ver. 10.8.1.

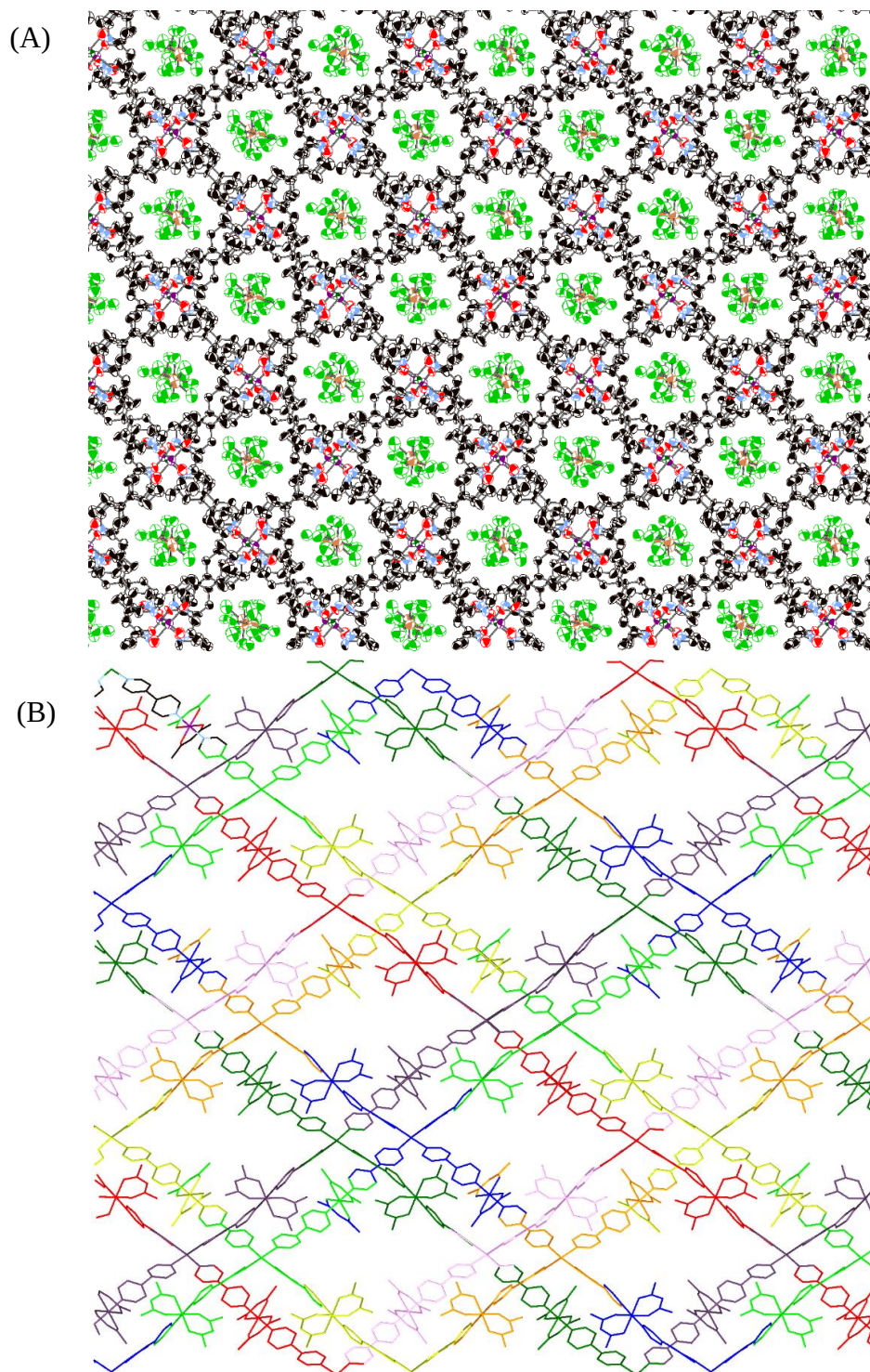


Figure 4.3. $[\text{Ag}(\text{RuML}_2)_2](\text{SbF}_6)_3$ polymer in $P2_1/c$. (A) 1D channels occupied by SbF_6^- counterions, viewed down the b -axis. Colour scheme: N, blue; C, black; O, red; Ru, purple; Ag, dark green; F, green; Sb, light brown; (B) network viewed down the c -axis. Colours represent distinct networks. Hydrogens atoms were omitted for clarity. Plotted in CrystalMaker X Ver. 10.8.1.

Identification of approximately eight unordered ethanol molecules per unit cell suggests the material possesses a degree of porosity. A different counterion or solvent system may permit ordering of additional guests.

The significant sigma distortion parameters of $[\text{Ag}[\text{Ru}(\text{acac})_2(\text{bpy})_2]_2](\text{SbF}_6)_3 \cdot (\text{C}_2\text{H}_5\text{OH})_8$ were large enough to warrant attention (Table 4.1). Unlike the discrete *trans*- $[\text{Ru}(\text{acac})_2(\text{X})_2]^n+$ complexes, the angular distortion within this material was less localised to one ligand. Distortion occurred for steric reasons rather than electronic ones, with the metalloligand distorting to accommodate the structure of the polymer.

Table 4.1. Crystallographic values for $[\text{Ag}[\text{Ru}(\text{acac})_2(\text{bpy})_2]_2](\text{SbF}_6)_n \cdot 8\text{EtOH}$

Parameter	Individual Values	Average Value
Σ Angular Distortion ($^\circ$)	20.03, 14.80	17.42
Acetylacetonate Bite Angles α ($^\circ$)	90.1 (7), 91.4 (8), 92.5 (9), 91.2 (8)	91.3 (1)
O-O distance d ($\text{\AA}$)	2.85 (2), 2.82 (2), 2.83 (2), 2.86 (2)	2.84 (1)
Ru-O Donor Bond Length r ($\text{\AA}$)	1.97 (2), 1.96 (2), 2.01 (2), 1.99 (2), 1.98 (2), 1.98 (2), 1.98 (2), 2.03 (2)	1.99 (2)
Normalised Bite b		1.43 (2)
Ru-N Donor Bond Length N-Ru ($\text{\AA}$)	2.05 (2), 2.08 (2), 2.05 (2), 2.03 (2)	2.05 (2)
Acetylacetonate C-O Bond Lengths ($\text{\AA}$)	1.26 (2), 1.34 (3), 1.26 (2), 1.27 (2), 1.30 (3), 1.27 (2), 1.25 (3), 1.34 (2)	1.29 (3)
Pyridyl Ring Angles ($^\circ$)	15.57, 14.64, 10.06, 22.50	15.69

Based on the analysis performed in Chapter 3, there was a clear relationship between the oxidation state of the Ru metal centre and crystallographic features of *trans*- $[\text{Ru}(\text{acac})_2(\text{X})_2]^n+$ complexes. These features included the Ru-O and Ru-N donor bond lengths, as well as the bite angle, α , the acac O-O distance, d , and the normalised bite value, b . Compared to the *Fdd2* crystal structure of *trans*- $[\text{Ru}^{\text{II}}(\text{acac})_2(\text{bpy})_2]$, the polymer had smaller Ru-O bond lengths, acac bite angles, O-O distances and normalised bite, significant with regards to the crystallographic

uncertainty. Due to the data quality, the length of the Ru-N bonds (2.03-2.07 Å) is too uncertain to make a valid comparison. Coupled with the proposed charge balance of the crystal structure, the ruthenium centres exhibit the features of Ru(III). The parameters in Table 4.1. are largely consistent with those of $[\text{Ru}^{\text{III}}(\text{acac})_2(\text{bpy})_2]\text{Cl}\cdot\text{EtOH}\cdot\text{H}_2\text{O}$. The values of the Ru-O bond lengths, bite angles, O-O distances and normalised bite are marginally larger in the polymeric system (within 1%), suggesting a minimal impact on the π -backbonding relationship exhibited in the metalloligand. There is very little evidence of Ru(II) ligands present within the framework, which suggests the ratio of Ru(III) to Ru(II) is high.

Bond-valence analysis was performed on the two Ru centres in the crystal structure, using literature bond valence parameters for $\text{Ru}^{\text{III}}\text{-N}$ and $\text{Ru}^{\text{III}}\text{-O}$.²³⁴ The calculated values of V were 3.25 ± 0.07 and 3.28 ± 0.07 , which agrees with the analysis performed above.

The angle between the pyridyl rings of 4,4'-bipyridine was similar to those observed in the three discrete crystal structures of the RuML2 metalloligand. The rings would be flat to maximise long range charge transfer, which was precluded by the tetragonal Ag nodes.

4.2.2. Electrochemistry

The CV scans for $[\text{Ag}(\text{RuML2})_2](\text{SbF}_6)_n\cdot 8\text{EtOH}$ were substantially different to those of RuML2. The most prominent features are a *quasi-reversible* processes at -0.533 and two irreversible processes at -0.076 V and 0.043 V vs. Fc^+/Fc (Figure 4.4). The process at -0.533 V vs. Fc^+/Fc , $E_p = 96$ mV, $|i_{p,c}/i_{p,a}| = \sim 0.4$ corresponded to the Ru(III/II) couple observed in RuML2 (Figure 4.5); however, very little oxidative response was observed. This process may coincide with a reduction of Ag(I) to Ag(0), which would immediately cause degradation of the framework. Literature values for the standard reduction potential of Ag(I/0) couples are highly variable, but primarily lie between -1 to 0.1 V vs. Fc^+/Fc .²³⁵⁻²³⁶ This value was reported as 0.077 V vs. Fc^+/Fc for the Ag(I/0) couple of AgNO_3 in MeCN,²³⁶ and would lie at a lower

potential due to the electron-donating bpy ligands. Another possible contribution to this feature and the high $|i_{p,c}/i_{p,a}|$ value was rate-limited counterion release and incorporation into the CP structure, although this does not account for the observed depolymerisation.

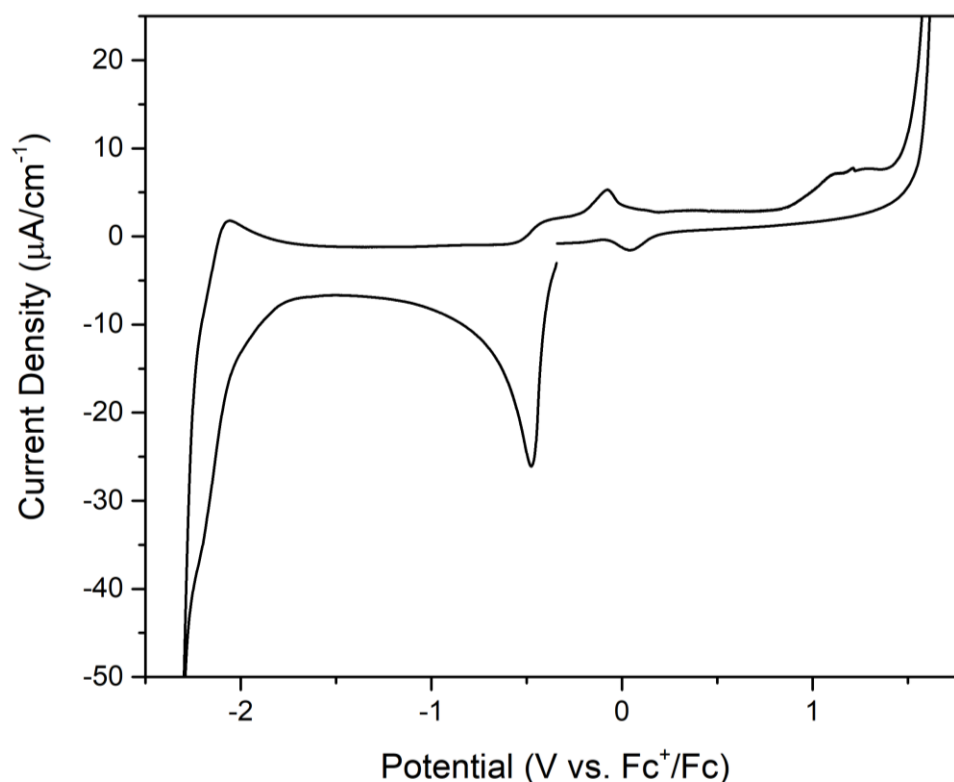


Figure 4.4. Cyclic voltammogram of $[\text{Ag}(\text{RuML}2)_2](\text{SbF}_6)_n \cdot 8\text{EtOH}$, starting at -0.343 V vs. Fc^+/Fc and between -2.35 to 1.35 V vs. Fc^+/Fc at 100 mV/s. Electrolyte: 0.1 M TBAPF_6 in MeCN. Working electrode: 1 mm glassy carbon.

Reduction of the framework at this potential coincided with solvation of the material. Consequently, this process is not chemically reversible. A *quasi*-reversible couple was observed at $E_{1/2} = -0.562$ V vs. Fc^+/Fc , $E_p = 102$ mV after repeated cycles of the solvated material, which corresponded to the $\text{Ru}(\text{III}/\text{II})$ couple of the uncoordinated metalloligand.

This overlap of irreversible Ag electrochemistry with that of the Ru centre unfortunately precluded studies of long-distance electron-transfer in the polymers. As the reduction potential

of the Ru(III) centres in the polymer is within 10 mV of that in the metalloligand, this analysis showed only a small impact on the π -backbonding interaction within the polymerised RuML2.

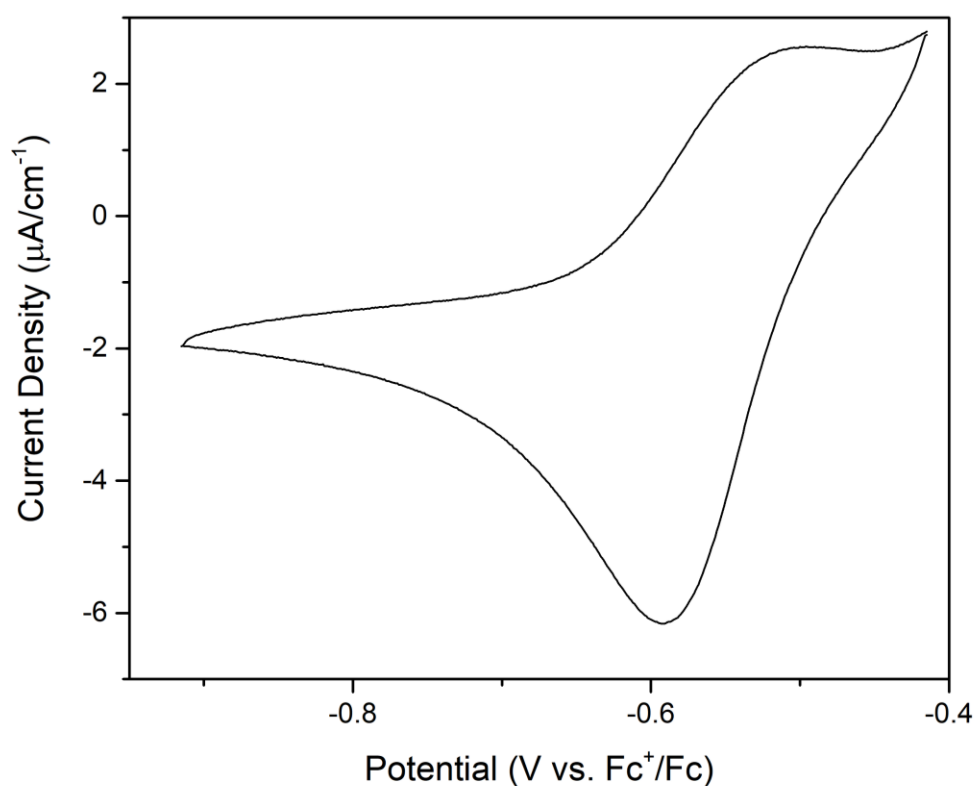


Figure 4.5. Cyclic voltammogram of the *quasi*-reversible process observed in [Ag(RuML2)₂](SbF₆)_n·8EtOH, taken from -0.4 to -0.9 V vs. Fc⁺/Fc at 100 mV/s. Electrolyte: 0.1 M TBAPF₆ in MeCN. Working electrode: 1 mm glassy carbon.

The two irreversible processes at -0.076 V vs. Fc⁺/Fc, $i_{p,c} = 5.7 \mu\text{A}/\text{cm}^2$ and 0.043 V vs. Fc⁺/Fc, $i_{p,a} = -4.8 \mu\text{A}/\text{cm}^2$ were unusual features of the voltammogram. The oxidation may correspond to the Ag(II/I) couple, which has been observed at similar potentials in other Ag (I) complexes.²³⁵ The nature of the reduction is unclear, and both features are candidates for future work.

4.2.3. UV-vis Spectroscopy

The electronic absorption spectroscopy of $[\text{Ag}(\text{RuML2})_2](\text{SbF}_6)_n \cdot 8\text{EtOH}$ over the UV-vis region differed from both the Ru(II) and Ru(III) oxidation states of RuML2. The spectrum contained features of both Ru(II) and Ru(III) oxidation states. The pronounced feature at $17,900\text{ cm}^{-1}$ resembled transitions **1** and **2** from the spectrum of RuML2 and transition **1** from the spectrum of RuML2^+ , and lay between these two bands. The shoulder from $23,000$ to $26,000\text{ cm}^{-1}$ may be due to superimposition of the RuML2 and RuML2^+ spectra in the same region. Single-crystal polarised UV spectra of the CP revealed some small anisotropy, but little-to-no change in the absorption wavelength of the band at $17,900\text{ cm}^{-1}$ (Figure 4.6B).

Evidence against this description came from the SEC of RuML2, where spectra of intermediate potentials representing a mixture of RuML2 and RuML2^+ did not adequately resemble the features of the spectrum of $[\text{Ag}(\text{RuML2})_2](\text{SbF}_6)_n \cdot 8\text{EtOH}$ in Figure 4.6.

As discussed in Section 4.2.2., reduction of the Ru centres coincided with reduction of Ag(I) nodes to Ag(0), which resulted in framework degradation. No loss of crystallinity or colour change was observed over the course of the experiment, suggesting that Ru(II) is not present as a result of reaction with the environment. If the above description is correct, $[\text{Ag}(\text{RuML2})_2](\text{SbF}_6)_n \cdot 8\text{EtOH}$ is not monovalent as modelled crystallographically, and is in fact a mixed-valent system.

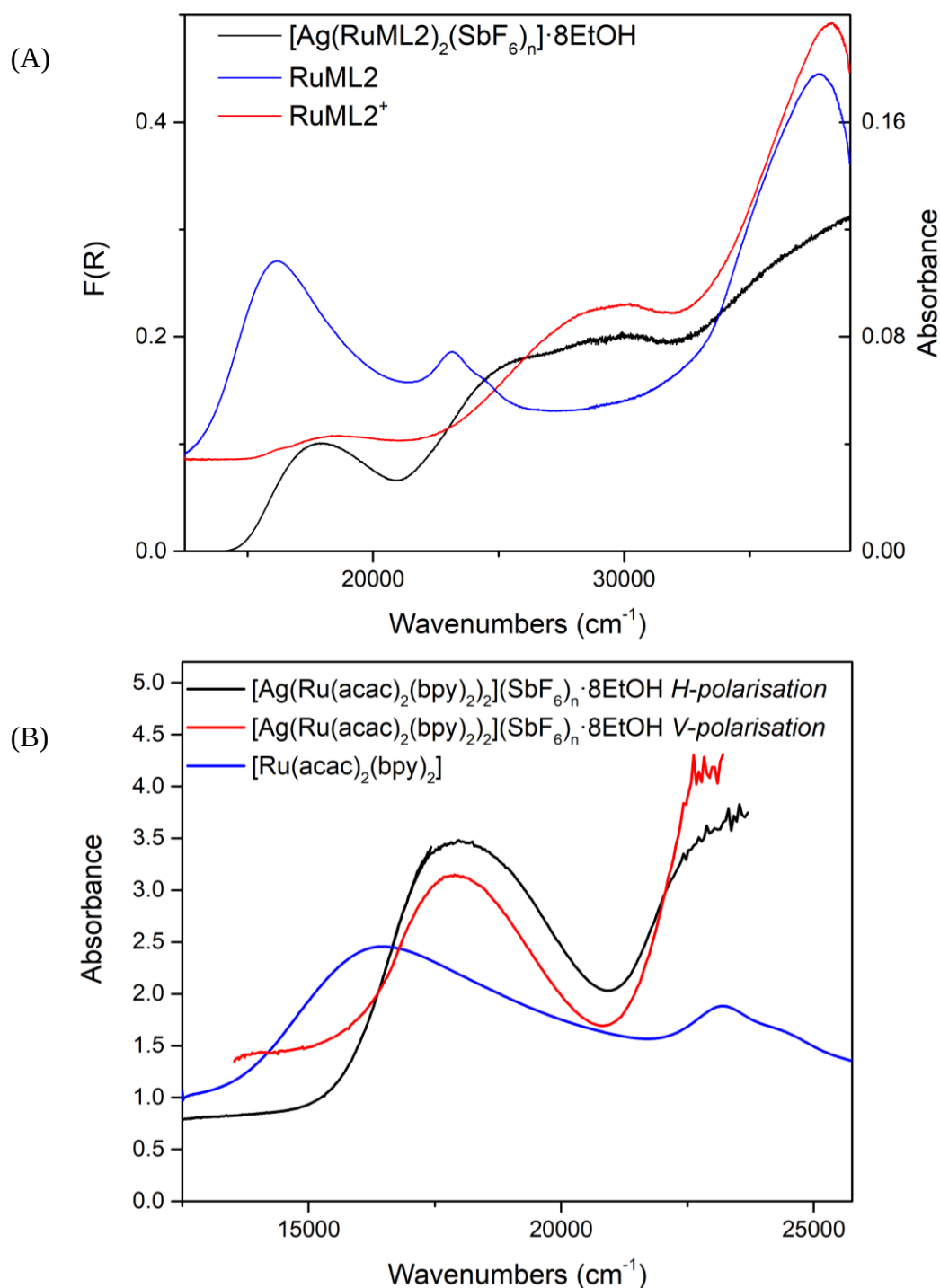


Figure 4.6. UV-vis spectra of $[\text{Ag}(\text{RuML2})_2](\text{SbF}_6)_n \cdot 8\text{EtOH}$ polymer and RuML2 monomers. (A) Solid-state diffuse reflectance spectrum of $[\text{Ag}(\text{RuML2})_2](\text{SbF}_6)_n \cdot 8\text{EtOH}$ compared to solution-state spectra of RuML2 and RuML2⁺ in 0.1 M TBAPF₆ in DMF. (B) Solid-state polarised single crystal transmission spectrum of $[\text{Ag}(\text{RuML2})_2](\text{SbF}_6)_n \cdot 8\text{EtOH}$ compared to solution-state spectrum of RuML2. Polarised spectra are of the same crystal, at orthogonal polarisations on the flat plate face of the crystal.

The blueshift in the lowest energy maxima of $[\text{Ru}^{\text{II}}(\text{acac})_2(\text{bpy})_2]$ to $[\text{Ag}(\text{RuML}2)_2](\text{SbF}_6)_n \cdot 8\text{EtOH}$ of 1500 cm^{-1} suggests that the ratio of Ru(III) to Ru(II) is large within the CP. This is consistent with the crystallography, which indicated Ru(III) was present. Given the differing symmetries of the Ru and Ag coordination spheres, and crystallographic evidence of bpy ring twisting, we can characterise this CP as a Robin-Day Class I material, with no charge transfer between Ru metal centres.²⁵

4.2.4. Vibrational Spectroscopy

4.2.4.1. FTIR Spectroscopy

The FTIR spectrum of $[\text{Ag}(\text{RuML}2)_2](\text{SbF}_6)_n \cdot 8\text{EtOH}$ exhibited features of both RuML2 and $[\text{RuML}2]\text{Cl}$ (Figure 4.7, Table 4.2). The spectra were largely similar between 900 and 1650 cm^{-1} , with some notable wavenumber shifts at 1604 , 1488 , 1413 , 1338 , 1095 , 1068 and 939 cm^{-1} . Many of these are fundamental modes associated with CH groups on bpy or CH_3 groups on acac⁻. Some of these changes may be due to intermolecular interactions between the framework and guest ethanol molecules. Other changes are largely attributable to distortion of the metalloligand within the polymer structure (as noted in Section 4.2.1.). Indeed, the most pronounced difference in this region was the wavenumber change in the bpy ring stretches at 1616 and 1585 cm^{-1} to form one band at 1604 cm^{-1} , which reflected the distortion of the 4,4'-bipyridine units within the polymer. The 400 to 900 cm^{-1} region contained fewer similarities between spectra. This may be due to impurities or chemical differences between analytes – the spectrum of the CP may have contained a small quantity of Ag oxide, which was difficult to isolate from the CP crystals. Unfortunately, observation of the Ag-N modes was not possible with the instrumentation used, as these tend to lie between 270 - 280 cm^{-1} .²³⁷ Similar to the UV-vis spectroscopy of this material, the FTIR spectrum appeared to contain a mixture of Ru(II) and Ru(III) oxidation states, supporting the characterisation of the polymer as mixed-valent.

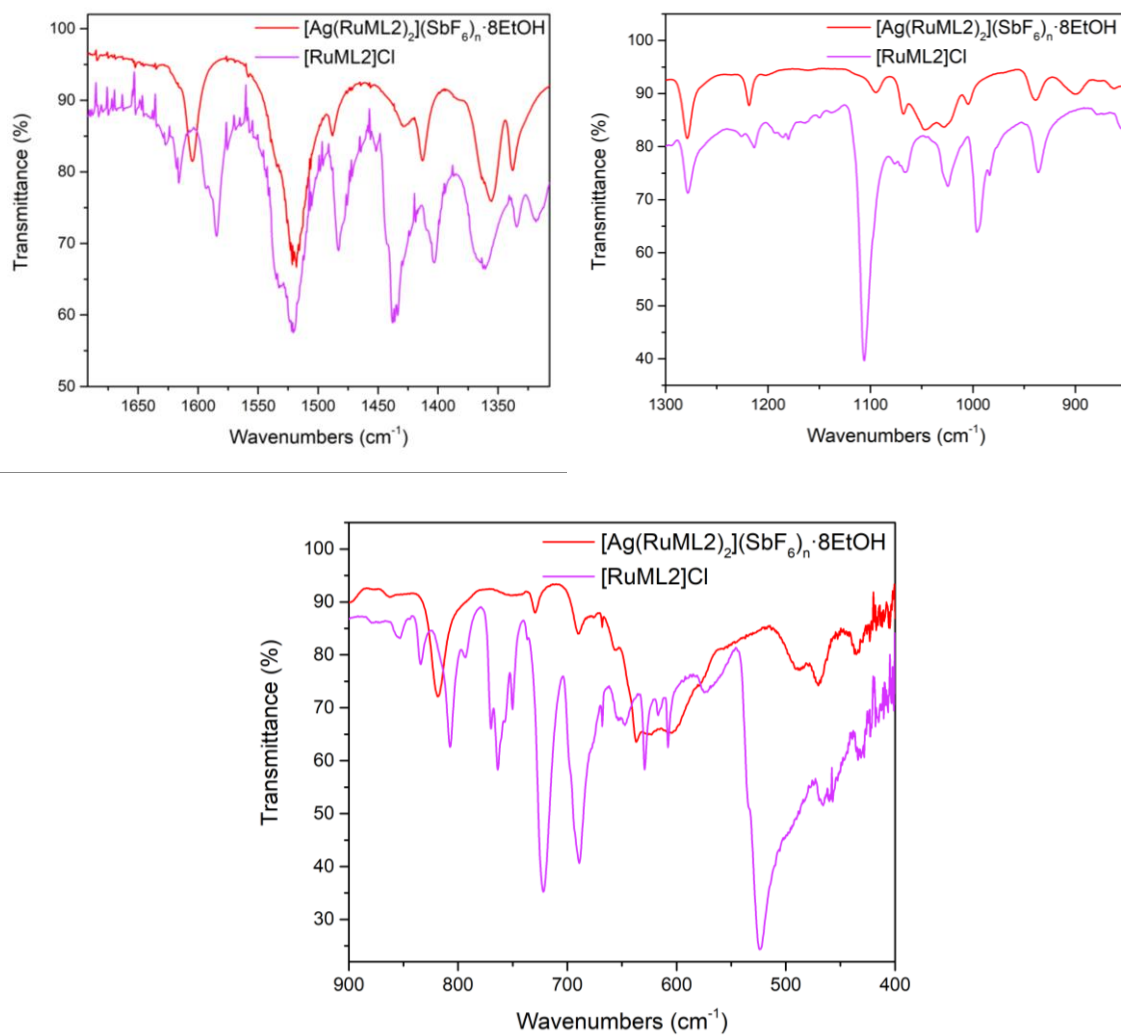


Figure 4.7. FTIR spectra of the Ru(III) salt $[\text{RuML}_2]\text{Cl}$ and polymer $[\text{Ag}(\text{RuML}_2)_2](\text{SbF}_6)_n \cdot 8\text{EtOH}$

Table 4.2. Comparison of the FTIR spectra of $[\text{Ag}(\text{RuML}_2)_2](\text{SbF}_6)_n \cdot 8\text{EtOH}$, $[\text{Ru}^{\text{II}}(\text{acac})_2(\text{bpy})_2]$ and $[\text{Ru}^{\text{III}}(\text{acac})_2(\text{bpy})_2]\text{Cl}$

ν_{max} and Intensity, $[\text{Ag}(\text{RuML}_2)_2](\text{SbF}_6)_n \cdot 8\text{EtOH}$ (cm^{-1})	ν_{max} and Intensity, RuML_2 (cm^{-1})	ν_{max} and Intensity, $[\text{RuML}_2]\text{Cl}$ (cm^{-1})	Band Assignment
	2921 m		Bpy $\nu(\text{CH})$, $\nu(\text{CH}_3)$
	1616 w	1616 w	Bpy $\delta(\text{ring})$
1605 w	1592 s	1533 m, sh, 1585 m	Acac $\nu(\text{C}=\text{O})_{\text{sym}}$, $\delta(\text{C}-\text{HC}=\text{C})$, $\rho(\text{CH}_3)$ Bpy $\delta(\text{ring})$
1518 m	1520 m, br 1505 s	1533 m, sh 1521 s, br	Bpy inner ring $\nu(\text{ring})_{\text{asym}}$ $\rho(\text{CH})$ Acac $\nu(\text{C}=\text{O})_{\text{sym}}$, $\delta(\text{C}-\text{HC}=\text{C})$, $\rho(\text{CH}_3)$ Bpy $\rho(\text{CH})$ Acac $\delta(\text{CCHC})$
1488 w	1479 s	1483 m	Bpy $\delta(\text{CH})$, Acac $\nu(\text{CCHC})_{\text{asym}}$, $\rho(\text{CH}_3)$
		1443 m, sh	Bpy inner ring $\delta(\text{CH})$ Acac $\delta(\text{CH}_3)$
		1438 s	Acac $\delta(\text{CH}_3)$
1429 w		1410 w, sh	Acac $\delta(\text{CH}_3)$
1413 w		1403 m	Acac $\delta(\text{C}-\text{CH}_3)$
1413 w	1399 s		Acac $\rho(\text{CH}_3)$, $\delta(\text{CH}_3)$, Bpy $\delta(\text{CH})$,
1355 m	1362 m	1362 m, br	Acac $\delta(\text{CH}_3)$
1338 w	1335 w	1334 w	Bpy $\rho(\text{CH})$
1278 w	1279 w	1278 m	Acac $\delta(\text{C}-\text{CH}_3)$ Bpy $\rho(\text{CH})$, $\nu(\text{C}-\text{C})$
1219 w	1217 w		Bpy $\delta(\text{CH})$
	1201 w		Acac $\pi(\text{CH})$ Bpy $\delta(\text{CH})$
	1092 w	1185 w	Bpy inner ring $\delta(\text{CH})$
1095 w		1106 vs	
1068 w	1054 w	1066 m	Bpy inner ring $\delta(\text{CH})$
1046 m			
1028 m	1043 w	1024 m	Bpy $\rho(\text{CH})$
1005 w	1008 s		Acac $\rho(\text{CH}_3)$ Bpy $\delta(\text{ring})$
	991 w, sh		Bpy $\delta(\text{ring})$
		986 m	Acac $\rho(\text{CH})$
		984 w	Acac $\rho(\text{CH}_3)$, $\rho(\text{CH})$
	955 w		Bpy $\rho(\text{CH})$
940 w	932 m	936 m	Acac $\nu(\text{C}-\text{CH}_3)$
	864 w	834 w	Bpy $\pi(\text{CH})$
819 m	852 w, 810 s	807 m	Bpy $\rho(\text{CH})$
	782 m	793 w	Acac $\pi(\text{CH})$

	763 m	770 m	Bpy Oop. ρ (ring)
730 w	728 m	763 m	Bpy Oop. ρ (ring)
690 w		689 s	Acac π (C-CH-C), ρ (CH ₃)
668 w	668 w	668 w	Acac δ (CCH), π (CH)
657 w	668 w 656 w	629 m	Bpy δ (ring) Acac ν (O-Ru-O) _{asym} , ρ (CH ₃)
637 m	641 m		Acac ν (O-Ru-O) _{sym} , ρ (CH ₃)
		574 w, br	Acac ρ (C-CH ₃)
	570 vw	524 s	Bpy Oop. ρ (ring)
487 w	490 m	~490 m, sh	Bpy Oop. ρ (ring)
470 m		466 m	Acac δ (acac), ν (O-Ru-O) _{sym} , ν (CH ₃)
435 w	445 w	433	δ (acac)

w= weak, m= medium, s= strong, sh= shoulder, b= broad, ν = stretching mode, δ = bending mode, Oop.= out of plane mode.

The spectrum was characterised by comparison with RuML2.

4.2.4.2. Raman Spectroscopy

There were no meaningful deviations from RuML2 in the Raman spectrum of the CPs (Table 4.3). However, there was evidence of a Ag-N stretching mode around 200 cm⁻¹ in both CP spectra.²³⁸

Table 4.3. Raman spectrum of [Ag(RuML2)₂](SbF₆)_n·8EtOH, [Ag(RuML2)₂](PF₆)₃·xEtOH and [Ru^{II}(acac)₂(bpy)₂]. Excitation wavelength: 532 nm.

$\nu_{\max}$ and Intensity, [Ag(RuML2) ₂](SbF ₆) _n ·8EtOH (cm ⁻¹)	$\nu_{\max}$ and Intensity, [Ag(RuML2) ₂](PF ₆) _n ·xEtOH (cm ⁻¹)	$\nu_{\max}$ and Intensity, [Ru ^{II} (acac) ₂ (bpy) ₂] (cm ⁻¹)	Band Assignment
1622 s	1620 s		
1604 s	1609 s	1600 s	Bpy δ (ring)
1547 w	1553 w	1548 w	Acac ν (CO), δ (CH ₃)
1511 w	1519 w	1510 w	Bpy ρ (CH)
~1483 w		1476 w	
1292 s	1299 s	1291 s	Bpy ρ (CH), ν (CC)
		1254 w, sh	Acac ν (OCC) _{sym} , π (CH ₃)
1235 m	1236 m	1234 m	Bpy ρ (CH)
1223 m	~1220 m	1212 m	Bpy ρ (CH)
1080 m	1081 m		

~1066 w, sh	~1066 w, sh	1062 w	Bpy $\rho(\text{CH})$
1049 w	1047 w	1043 w	Bpy $\delta(\text{Ring})$
1027 s	1033 s	1027 m	Bpy $\delta(\text{Ring})$
~1014 w, sh	~1021 w, sh	1017 m	Bpy Oop. $\delta(\text{CH})$, $\delta(\text{Ring})$
940 w	940 w		
~865 w, b	864 w	887 w	Bpy Oop $\pi(\text{CH})$
774 w	773 m	768 m	Bpy. $\delta(\text{Ring})$
696 w	689 m	683 w	Acac $\pi(\text{CH}_3)$
657 w			$\nu(\text{SbF}_4)$
642 w	641 m	~644 m	Bpy $\delta(\text{ring})$
	~625 w, sh	626 m	Bpy $\delta(\text{ring})$
~ 570 w	574 w	566 w	
468 m	470 m	447 m	$\nu(\text{O-Ru-O})_{\text{sym}}$ Acac $\delta(\text{acac})$
	454 m		
396 w	384 m, b	394 w	Bpy Oop. $\delta(\text{ring})$
379 m, b	~380 m, b		
290 w			
~ 260 w	263 w, sh	256 w	Acac $\pi(\text{CH}_3)$
246 m	236 s, br		
202 w	~206 w, sh		$\nu(\text{Ag-N})$

w= weak, m= medium, s= strong, sh= shoulder, b= broad, ν = stretching mode, δ = bending mode, Oop.= out of plane mode.

The spectrum was characterised with reference to literature and simulations of RuML2.²³⁸⁻²³⁹

4.2.5. Comparison with Metalloligand

The CP $[\text{Ag}(\text{RuML2})_2](\text{SbF}_6)_n \cdot 8\text{EtOH}$ differed substantially from the metalloligand RuML2. Electrochemically, the Ru(III/II) couple was not reversible, likely due to the presence of Ag(I) nodes within the framework. The CP also appeared to contain both Ru(II) and Ru(III), with features of both oxidation states of the complex in the electronic and vibrational spectroscopy. It is difficult to estimate the ratio of Ru(II) to Ru(III) in the polymer, given the relatively low quality of the crystallographic data, and the highly complex electronic absorption spectroscopy of the material. Ultimately, the CP diverges substantially from the discrete complex, but the RuML2 ligand exhibited very little changes upon polymerisation. Differences between the two are largely structural in nature.

4.3. Zinc Halide Polymers of RuML4

A different approach was required to crystallise a polymer incorporating RuML4 in comparison with RuML2. The distinction arises from the geometry of the BPE ligand, which can produce one of two configurations of RuML4 (Figure 4.8). The α configuration (observed in the polymers discussed in this chapter) of the metalloligand produces two coordinate bonds, separated by at least 2 Å from the axis of the bond. The β configuration (observed in the complex *trans*-[Ru(acac)₂(BPE)₂]Cl·3CHCl₃) produces two coordinate environments roughly in line, but the bulk of the ligand lies out of the plane of coordination. This is in comparison to RuML2, which is mostly linear. The BPE ligands are also twisted, which results in different coordination angles at either end of the metalloligand.

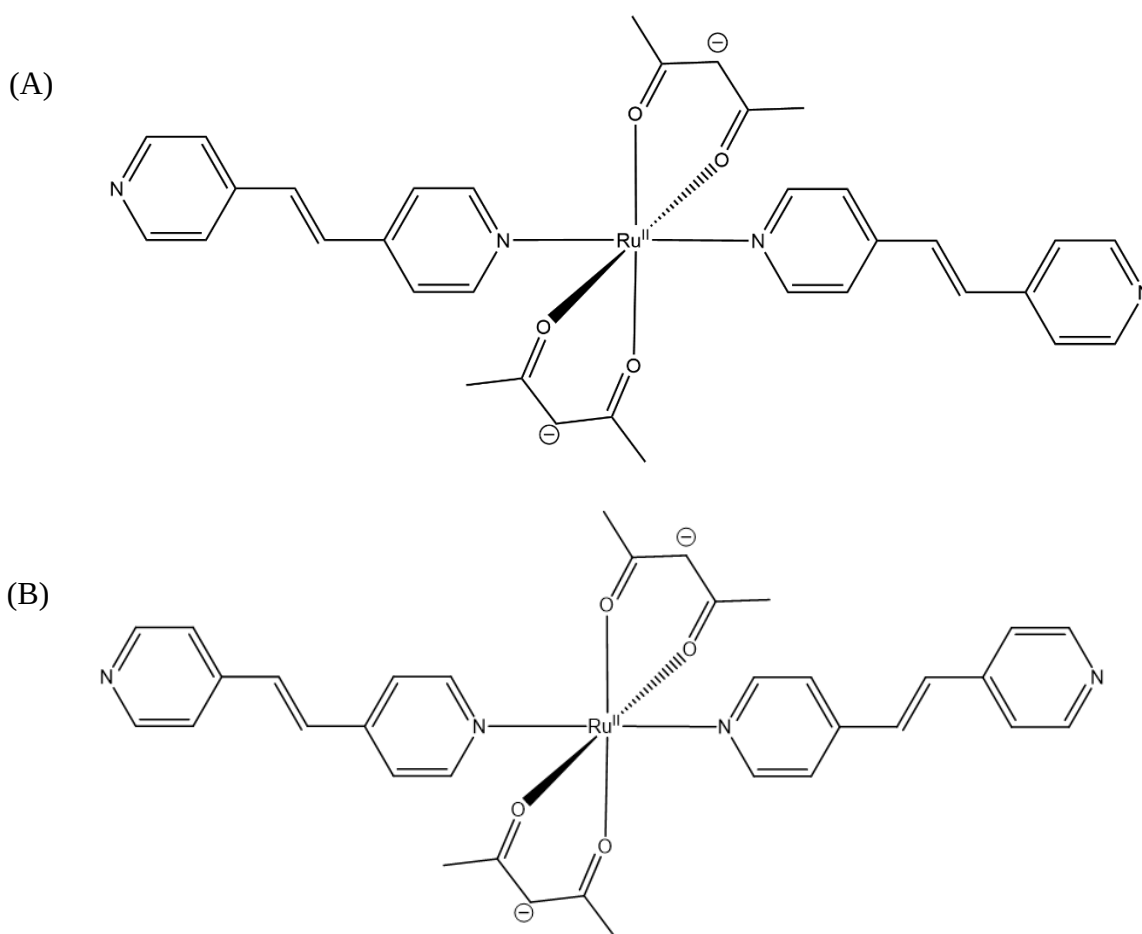


Figure 4.8. Configurations of RuML4. (A) α -RuML4 (B) β -RuML4

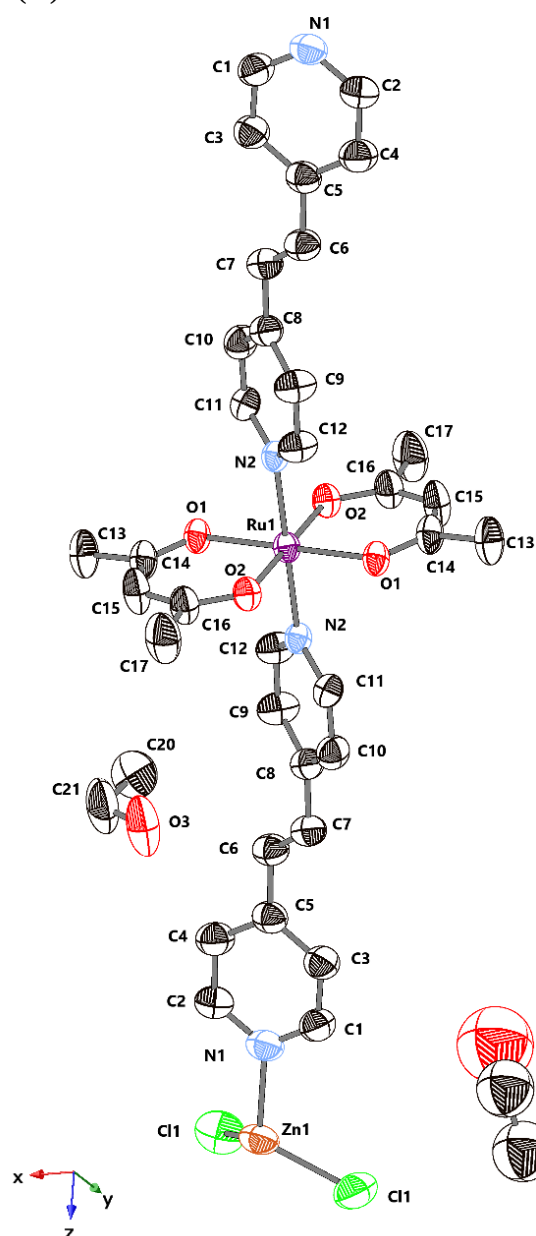
Given these factors, and the electronic differences between the metalloligands discussed in Chapter 3, we can see that RuML2 and RuML4 are not analogous ligands, and will not produce isorecticular CPs. Reactions of RuML4 with silver salts under various conditions have yet to produce crystals, while reactions of RuML2 with zinc halides produced amorphous solids that did not diffract. The latter result is interesting because it suggests that the staggered position and angular misalignment of the coordination sites inherent to the α configuration of RuML4 are crucial to crystallisation of a material.

4.3.1. Crystallography

The coordination polymer $[\text{ZnCl}_2(\text{Ru}(\text{acac})_2(\text{BPE})_2)] \cdot 1.5(\text{EtOH})$ crystallised in the monoclinic space group $C2/c$. The asymmetric unit contained half a $[\text{ZnCl}_2(\text{Ru}(\text{acac})_2(\text{BPE})_2)]$ monomer, one half-occupied and one quarter-occupied ethanol molecule. The unit cell contained four $[\text{ZnCl}_2(\text{Ru}(\text{acac})_2(\text{BPE})_2)]$ monomers, eight half-occupied and eight quarter-occupied ethanol molecules, giving an equivalent of six ethanol molecules per unit cell (Figure 4.9A). The coordination polymer $[\text{ZnBr}_2(\text{Ru}(\text{acac})_2(\text{BPE})_2)] \cdot (\text{EtOH})$ similarly crystallised in the monoclinic space group $C2/c$. The asymmetric unit contained half of a $[\text{ZnBr}_2(\text{Ru}(\text{acac})_2(\text{BPE})_2)]$ monomer, and one half-occupied ethanol molecule. The unit cell contained four $[\text{ZnBr}_2(\text{Ru}(\text{acac})_2(\text{BPE})_2)]$ monomers and eight half-occupied ethanol molecules, giving an equivalent of four ethanol molecules per unit cell (Figure 4.9B).

In both CPs, zinc nodes coordinated to two RuML4 linkers and two halide ligands each, which resulted in a 1D polymer chain in a zig-zag pattern (Figure 4.10). While the Zn nodes were aligned along all three unit cell axes, when viewed along the Zn-N bonds, the staggering effect of the RuML4 metalloligand was observed, with ~ 1.1 and $1.7 \text{ \AA}$ displacement between each node in $[\text{ZnCl}_2(\text{Ru}(\text{acac})_2(\text{BPE})_2)] \cdot 1.5(\text{EtOH})$ and $[\text{ZnBr}_2(\text{Ru}(\text{acac})_2(\text{BPE})_2)] \cdot (\text{EtOH})$ respectively.

(A)



(B)

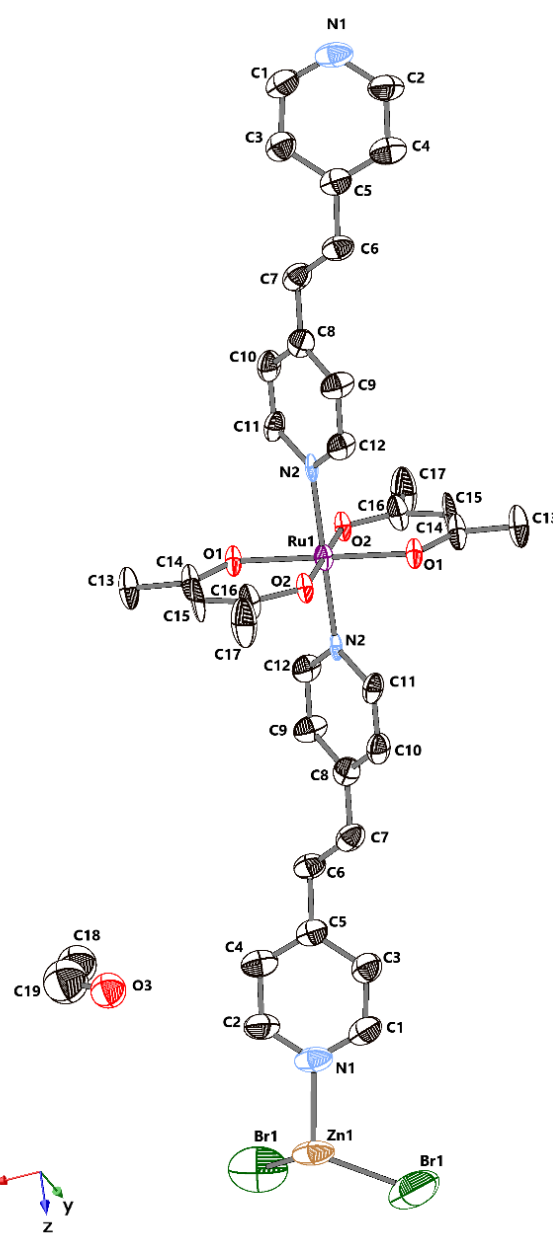


Figure 4.9. (A) $[\text{ZnCl}_2(\text{RuML4})]$ monomer in $C2/c$, including one half-occupied and one quarter-occupied ethanol molecule. (B) $[\text{ZnBr}_2(\text{RuML4})]$ monomer in $C2/c$, including one half-occupied ethanol molecule. Orientated for clarity. Hydrogens were omitted for clarity. Colour scheme: N, blue; C, black; O, red; Ru, purple; Zn, brown; Cl, green; Br, dark green. Plotted in CrystalMaker X Ver. 10.8.1.

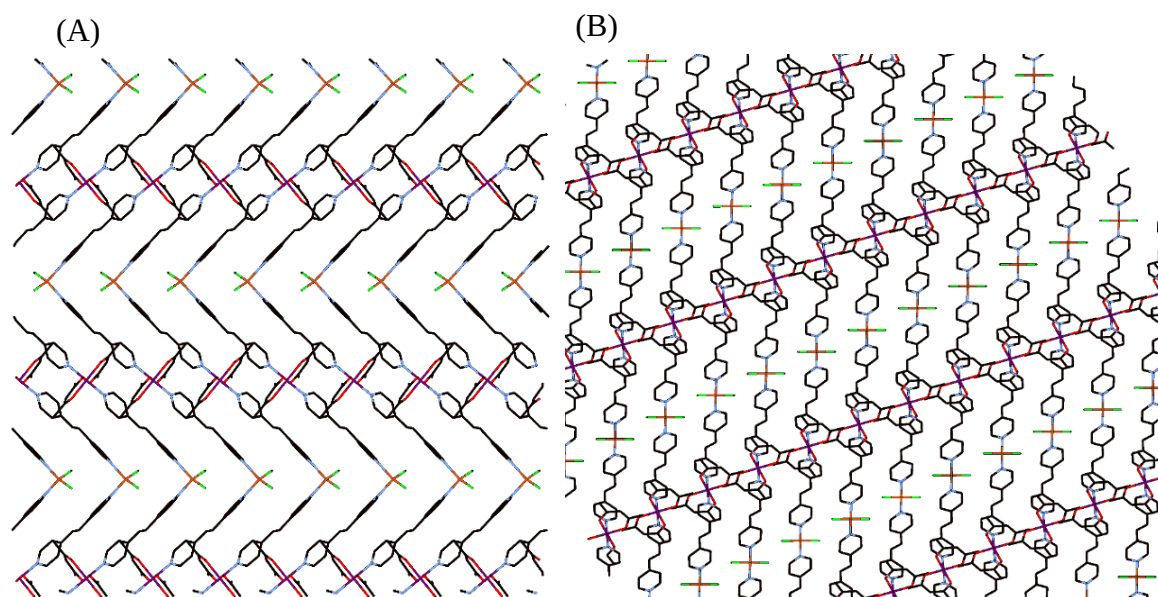


Figure 4.10. Crystal structure of [ZnCl₂(RuML₄)], (A) along the *a*-axis. (B) along the *b*-axis. Hydrogens and solvent molecules omitted for clarity. Colour scheme: N, blue; C, black; O, red; Ru, purple; Zn, brown; Cl, green. Plotted in CrystalMaker X Ver. 10.8.1.

The polymers discussed in this section bear a number of crystallographic differences to the crystal structure of *trans*-[Ru^{III}(acac)₂(BPE)₂]Cl·3CHCl₃; both polymers had larger Σ values, acac bite angles, O-O distances, normalised bite values, Ru-O bond lengths, and shorter Ru-N bonds than the discrete complex, all significant with regards to crystallographic error (Table 4.4). These results were consistent with a Ru(II) oxidation state within the polymers, which agreed with the charge balancing of the crystal structures. As no crystallographic data could be obtained for the Ru(II) discrete complex, direct comparisons were not possible, and the impact of polymerisation on the material could not be assessed crystallographically.

Bond-valence parameters for Ru^{II}-N and Ru^{II}-O could not be located in the literature. As a result, parameters were estimated from the Ru(II) complexes in Chapter 3. Approximating *b* as 0.37,²⁴⁰⁻²⁴¹ *R*₀ was estimated as 1.6365 ± 0.002 for Ru^{II}-N and 1.6375 ± 0.002 for Ru^{II}-O. Bond valences for both CPs using these parameters were very close to 2 (Table 4.4), with small uncertainties.

Table 4.4. Crystallographic values for $[\text{ZnCl}_2(\text{RuML4})] \cdot 1.5(\text{EtOH})$ and $[\text{ZnBr}_2(\text{RuML4})] \cdot (\text{EtOH})$

Parameter	Individual Values [$\text{ZnCl}_2(\text{RuML4})$] · 1.5(EtOH)	Average Value [$\text{ZnCl}_2(\text{RuML4})$] · 1.5(EtOH)	Individual Values [$\text{ZnBr}_2(\text{RuML4})$] · (EtOH)	Average Value [$\text{ZnBr}_2(\text{RuML4})$] · (EtOH)
Σ Angular Distortion	24.24		23.58	
Acetylacetonate Bite Angles α (degrees)	94.96 (14)		95.1 (2)	
O-O distance d (Å)	3.014 (5)		3.021 (8)	
O-Ru Donor Bond Length r (Å)	2.041 (3), 2.048 (3)	2.045 (2)	2.051 (5), 2.044 (5)	2.048 (4)
Normalised Bite b		1.474 (3)		1.475 (5)
N-Ru Donor Bond Length N-Ru (Å)	2.055 (4)		2.042 (7)	
Acetylacetonate C-O Bond Lengths (Å)	1.277 (7), 1.272 (7)	1.275 (7)	1.272 (11), 1.268 (11)	1.270 (9)
Bond Valence V	1.978 (8)		1.99 (1)	

4.3.2. Electrochemistry

The solid-state cyclic voltammetry of $[\text{ZnCl}_2(\text{RuML4})]$ was performed in 0.1 M TBAPF₆ in MeCN, at scan rates from 50 to 800 mV/s. The CV displayed many of the features of RuML4. Unsurprisingly, the Ru(III/II) couple occurred at a similar potential, with $E_{1/2} = -0.533$ V vs. Fc⁺/Fc, $E_p = 97.5$ mV, $|i_{p,c}/i_{p,a}| = 1.2$ at 100 mV/s in the polymer (Figure 4.11A), compared to $E_{1/2} = -0.550$ vs. Fc⁺/Fc, $E_p = 72.3$ mV and $|i_{p,c}/i_{p,a}| = 1.05$ at 100 mV/s in the metalloligand. The slight shift to a more positive potential may indicate a slight stabilisation of the Ru(II) oxidation state due to coordination with zinc chloride linkers. However, outer-sphere contributions to the thermodynamics of electron transfer were also very different between measurements of the solution-state metalloligand and solid-state polymers. E_p increased with

scan rate in the polymer from 90.5 mV at 50 mV/s to 108 mV at 800 mV/s. $|i_{p,c}/i_{p,a}|$ also increased with scan rate in the polymer from 1.2 at 50 mV/s to 1.4 at 800 mV/s. Both of these trends, as well as the increased E_p and $|i_{p,c}/i_{p,a}|$ in the polymer compared to the discrete complex, were due to rate-limited counterion diffusion and/or structural rearrangement within the framework.

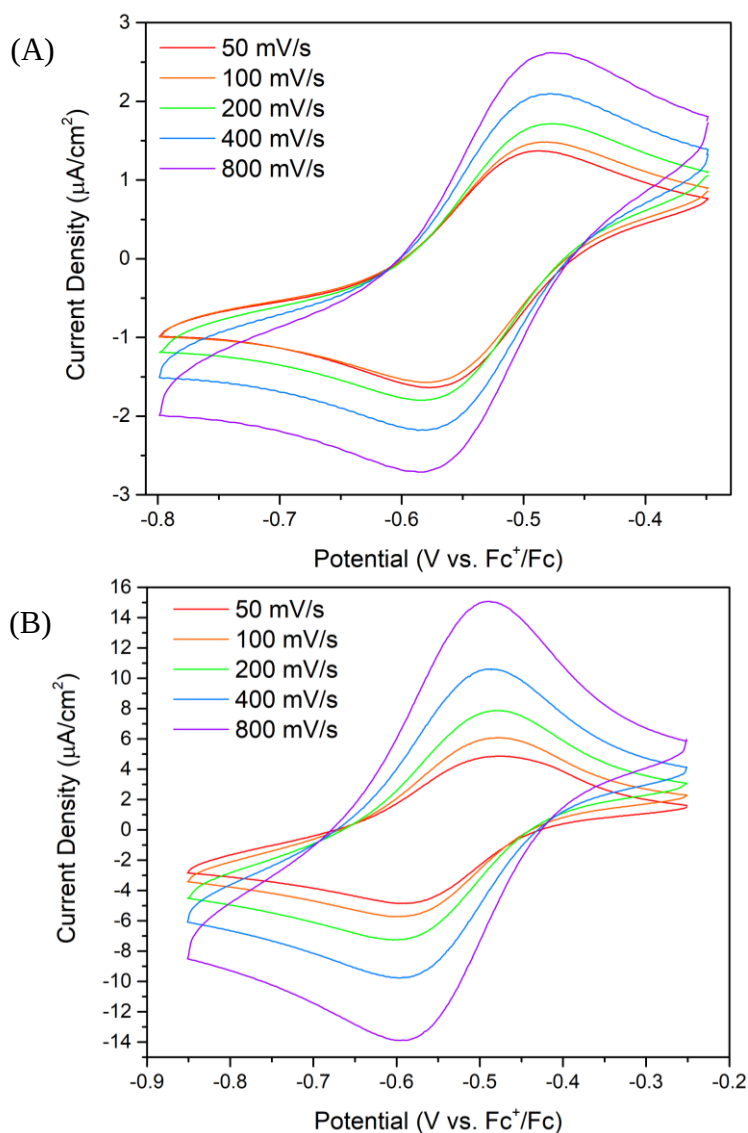


Figure 4.11. Cyclic voltammogram of the *quasi*-reversible processes observed in (A) [ZnCl₂(RuML₄)] starting at -0.48 V vs. Fc⁺/Fc and between -0.8 and 0.45 V vs. Fc⁺/Fc, and (B) [ZnBr₂(RuML₄)] starting at -0.55 mV vs. Fc⁺/Fc and between -0.85 and -0.25 mV vs. Fc⁺/Fc. Electrolyte: 0.1 M TBAPF₆ in MeCN. Working Electrode: 1 mm glassy carbon.

The polymer was observed to degrade with repeat cycles of this redox process. A linear relationship between scan rate and peak current was observed between 50-800 mV/s, giving an R^2 value of 0.9841 for the oxidation and 0.9832 for the reduction current peaks (Appendix D). This result is consistent with behaviour expected for a surface process, where charge diffusion occurs through the solid-state material, rather than a freely-diffusing species.

This large peak-to-peak separation showed the rate of electron transfer was controlled by slow counterion diffusion and/or structural rearrangement of the polymer. When recording the voltammogram for the process at $E_{1/2} = -0.434$ V vs. Ag/AgCl, the sample was left on the working electrode for multiple cycles at different scan rates. Degradation of the sample was observed inconsistently, where changes in the peak potential stopped increasing with increasing scan rate after one or more cycles. This may be due to the *quasi*-reversible nature of the process, or structural changes caused by adjacent, irreversible processes.

The solid-state CV of [ZnBr₂(RuML4)] was also performed in 0.1 M TBAPF₆ in MeCN, at scan rates from 50 to 800 mV/s. The CV was comparable with that of [ZnCl₂(RuML4)] and RuML4, with some small differences. The Ru(III/II) redox couple was present at $E_{1/2} = -0.540$ V vs. Fc⁺/Fc, $E_p = 124$ mV, $|i_{p,c}/i_{p,a}| = 0.87$ at 100 mV/s (Figure 4.11B). This couple was more stable on cycling than in the zinc bromide polymer, and was cycled several times before degradation was observed. E_p did not vary according to a clear trend in the polymer. The peak separation increased from 115 mV at 50 mV/s to 127 mV at 200 mV/s, but then decreased to 106 mV at 800 mV/s. $|i_{p,c}/i_{p,a}|$ increased with scan rate, from 0.83 at 50 mV/s to 0.92 at 800 mV/s. The increased E_p , and $|i_{p,c}/i_{p,a}|$ scan-rate dependence compared to [ZnCl₂(RuML4)], RuML4, indicated counterion diffusion was rate-limited and more inhibited in [ZnBr₂(RuML4)]. However, this was made unclear by the lack of consistent E_p scan-rate dependence and low $|i_{p,c}/i_{p,a}|$ values. The latter was likely due to the restricted potential window in the experiment.

This process displayed similar *quasi-reversible* behaviour to the equivalent process in $[\text{ZnCl}_2(\text{RuML}4)]$. The peak current was plotted vs. the scan rate between 50-800 mV/s to determine the nature of diffusion within the process. The oxidation gave an R^2 of 0.9775 and the reduction an R^2 of 0.9425 (Appendix D). Plotting the peak currents vs. the square root of the scan rate gives a very similar result, with an R^2 of 0.9957 and 0.8535 for the oxidation and reduction respectively.

The polymer $[\text{ZnCl}_2(\text{RuML}4)]$ exhibited a series of multi-electron irreversible reductions at -1.62 V vs. Fc^+/Fc , $i_{p,a} = -46.2 \mu\text{A}/\text{cm}^2$; -1.89 V vs. Fc^+/Fc , $i_{p,a} = -113 \mu\text{A}/\text{cm}^2$, and -2.22 V vs. Fc^+/Fc , $i_{p,a} = 96.3 \mu\text{A}/\text{cm}^2$ (Figure 4.12). Many of these processes were attributable to the reduction of the BPE ligand; however, the additional features observed at -1.62 V vs. Fc^+/Fc and -1.89 V vs. Fc^+/Fc were unique to this polymer, suggesting the reduction of the ZnCl_2 nodes was occurring in this region. The reduction of Zn(II) has been observed at similar potentials,²³⁵ and above -1.32 V vs. Fc/Fc^+ in MeCN.²⁴²⁻²⁴³ Coordination with electron-donating BPE ligands lowers the reduction potential of this couple. The irreversibility of the processes observed at lower potentials in $[\text{ZnCl}_2(\text{RuML}4)]$ may be a result of depolymerisation at zinc sites as Zn(0) is formed. It may also be an indication of rate-limited charge transport within the polymer. The current response of the polymer dramatically reduced after a single cycle, indicating a large structural change was occurring.

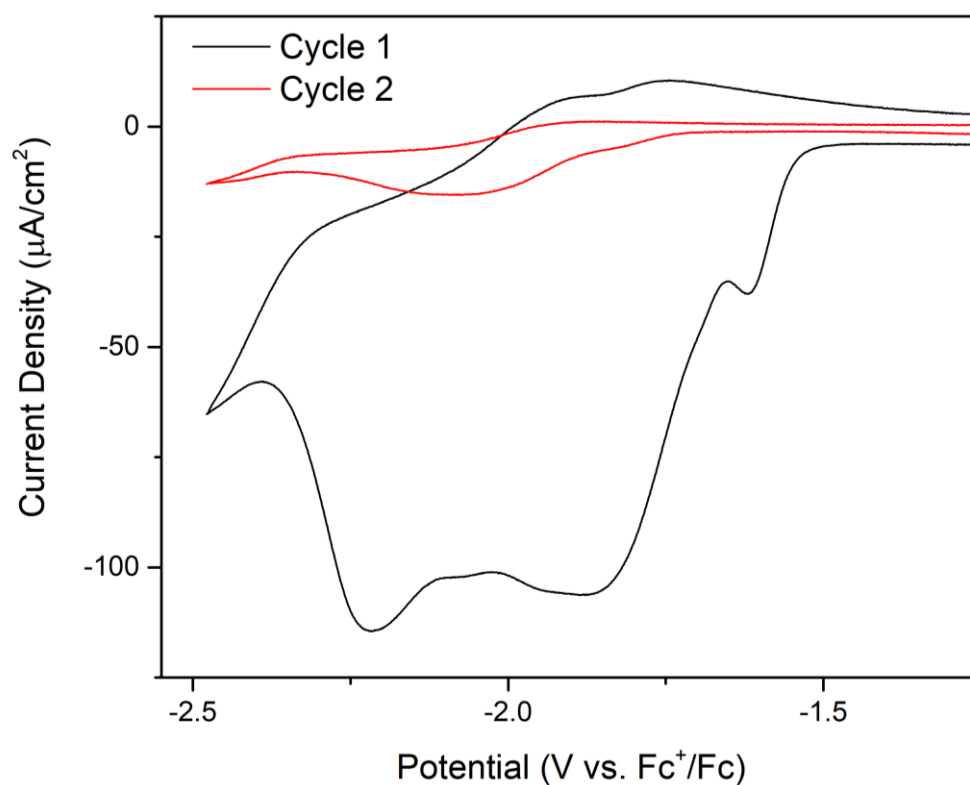


Figure 4.12. Cyclic voltammogram of the processes at high negative potentials in $[\text{ZnCl}_2(\text{RuML4})]$, from -0.478 to -2.5 V vs. Fc^+/Fc , at 100 mV/s. Electrolyte: 0.1 M TBAPF_6 in MeCN. Working Electrode: 1 mm glassy carbon.

4.3.3. UV-vis Spectroscopy

The electronic absorption spectroscopy of $[\text{ZnCl}_2(\text{RuML4})]$ and $[\text{ZnBr}_2(\text{RuML4})]$ differed significantly from that of RuML4. While the crystallography of the polymers strongly suggested that the Ru metalloligands were Ru(II), the crystals themselves were deep red in colour (Figure 4.13), in contrast to the dark green colour of the complex *trans*- $[\text{Ru}^{\text{II}}(\text{acac})_2(\text{BPE})_2]$.

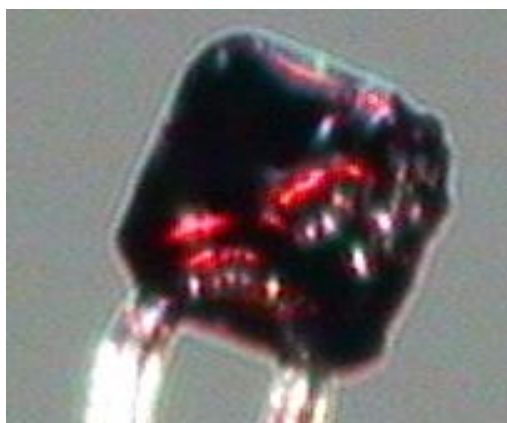


Figure 4.13. Single crystal of $[\text{ZnCl}_2(\text{RuML4})]$

Electronic absorption spectroscopy revealed that the change in colour was due to blueshifting of the MLCT band energies in the visible region, by $\sim 3000 \text{ cm}^{-1}$ (Figure 4.14). These changes in absorption energy were a result of polymerisation of the RuML4 metalloligand. There are two possible contributions to these blueshifts. Firstly, the presence of ordered ethanol molecules within the crystal structures of both CPs may have introduced a significant outer-sphere reorganisation contribution to the charge-transfer mechanism, increasing the energy of the transition. Further, intermolecular interactions between polymer chains may have altered the energies of the LUMO orbitals in these MLCT transitions. One possibility was a π -stacking interaction between acac^- ligands and the inner ring of BPE ligands on different polymer chains (Figure 4.15). These groups were on the boundary for attractive interactions between orthogonal π -systems in both polymers, with a distance of approximately $4.5 \text{ \AA}$ and an offset of approximately $2 \text{ \AA}$.¹⁸⁷ Such a π -stacking relationship may increase the energy of the BPE LUMO and thereby blueshift transitions into the ligand.

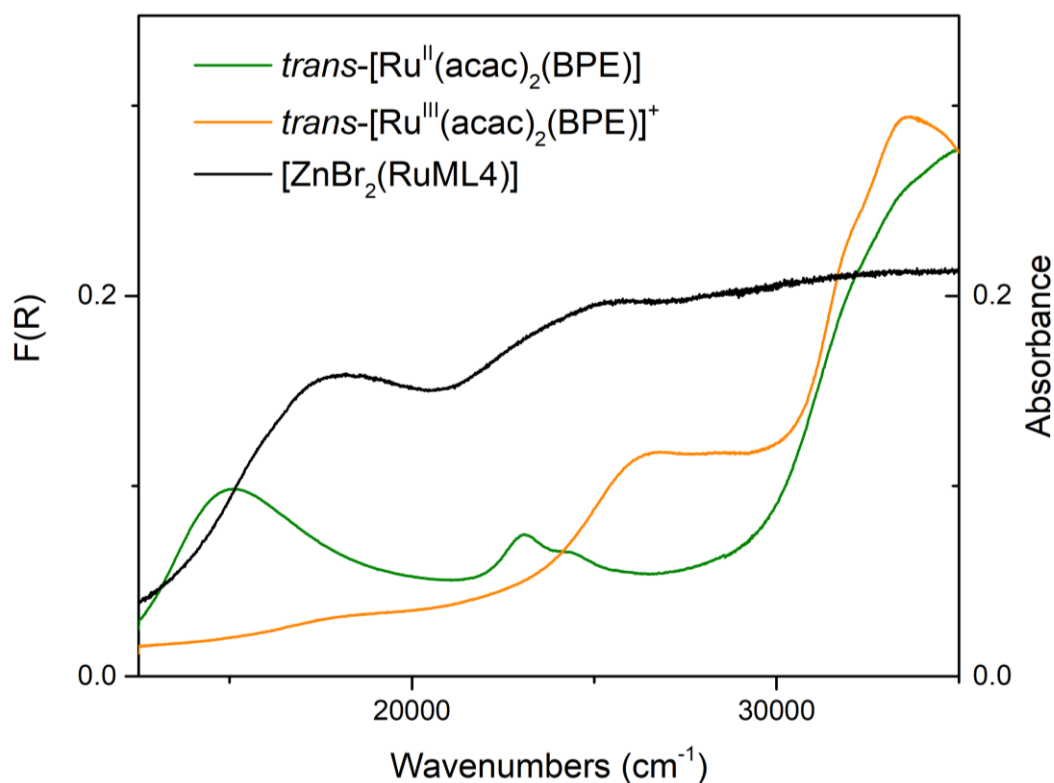


Figure 4.14. Comparison of the electronic absorption spectra of [ZnBr₂(RuML4)], RuML4, and [RuML4]⁺. Spectrum of [ZnBr₂(RuML4)] was a solid-state diffuse reflectance measurement. The spectra of RuML4 and RuML4⁺ were solution-state transmission measurements. Solvent: 0.1 M TBAPF₆ in MeCN.

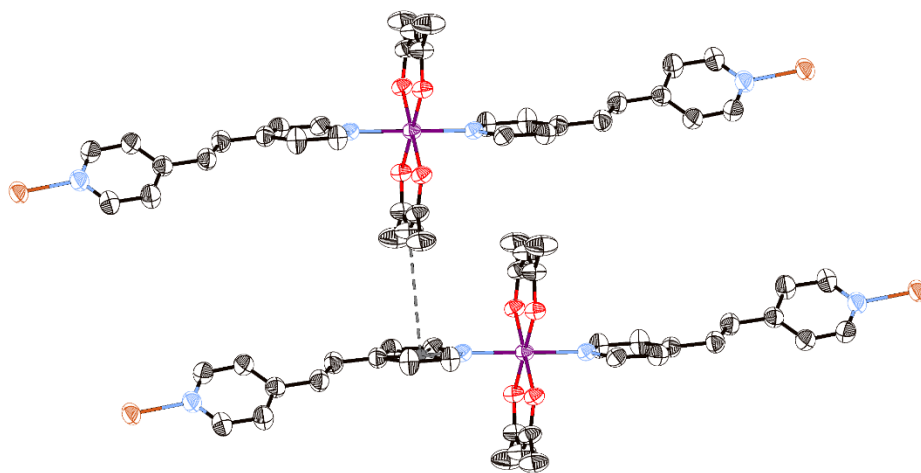


Figure 4.15. Possible π -stacking interaction between acac⁻ and BPE ligands of adjacent chains of [ZnCl₂(RuML4)]. Hydrogens were omitted for clarity. Colour scheme: N, blue; C, black; O, red; Ru, purple; Zn, brown; Cl, green; Centroid, dark grey. Plotted in CrystalMaker X Ver. 10.8.1.

The near-UV region also featured stronger absorbance, resembling the Ru(III) spectrum of the metalloligand. This may be due to partial oxidation of the polymer on exposure to air.

The single-crystal absorption spectroscopy of $[\text{ZnCl}_2(\text{RuML4})]$ revealed substantial anisotropy within the CP (Appendix D). Low data quality was attributed to crystal quality and the highly absorbing nature of the crystals, which permitted only a small analysis window. There was also evidence that the crystal partially oxidised upon exposure to air over the course of several hours, resulting in more weakly absorbing MLCT features below $20,000\text{ cm}^{-1}$.

Due to poor charge penetration and/or insufficient contact with the working electrode, we were unable to perform an electronic absorption SEC measurement on either polymer.

4.3.4. Vibrational Spectroscopy

4.3.4.1. Infrared spectroscopy

FTIR spectra of $[\text{Zn}(\text{RuML4})\text{Cl}_2]$ and $[\text{Zn}(\text{RuML4})\text{Br}_2]$ were obtained on crystals suspended in ethanol. The CP spectra were very similar to that of RuML4 (Table 4.5). Although many of the fundamental frequencies associated with ZnCl_2 and ZnBr_2 were out of range of the instrumentation employed for this experiment,²⁴⁴ at least one vibrational mode associated with ZnCl_2 was present in the $[\text{Zn}(\text{RuML4})\text{Cl}_2]$ spectrum, at 1615 cm^{-1} .²⁴⁵ Other differences between spectra were attributed to lower IR absorbance by both polymers, particularly $[\text{Zn}(\text{RuML4})\text{Br}_2]$. This made it impossible to resolve several low absorbance bands visible in the spectrum of RuML4.

Table 4.5. Comparison of the infrared spectra of [ZnCl₂(RuML4)], [ZnBr₂(RuML4)], and [Ru^{II}(acac)₂(BPE)₂]

$\nu_{\max}$ and Intensity, ZnCl ₂ polymer (cm ⁻¹)	$\nu_{\max}$ and Intensity, ZnBr ₂ polymer (cm ⁻¹)	$\nu_{\max}$ and Intensity RuML4 (cm ⁻¹)	Band Assignment
2966 m		2972 m	Acac ν (CH)
2915 w			
2873 w		2901 m	Acac ν (CH ₃)
1630 w		1632 w	δ (C ₂ H ₂)
1615 s	1612 w	1612 w	BPE δ (ring)
1615 s			ZnCl ₂
1594 m	1591 w	1590 s, br	BPE ν (outer ring) _{asym} , Acac ν (C=O) _{sym} , δ (C-HC=C), ρ (CH ₃)
1553 w			
1532 m		1533 m	Acac δ (CCHC)
1511 s	1519 m	1509 s	BPE ρ (CH)
		1496 w	BPE ρ (CH)
1488 w		1485 w	Acac ν (CCHC) _{asym} , ρ (CH ₃), ρ (CH)
		1450 w	
~1428 m, br	1432 w	1423 m, sh	BPE δ (inner ring)
1404 m	1411 w	1405 s, br	Acac ρ (CH ₃), BPE δ (CH)
		1394 s	Acac δ (CH ₃)
1367 w	1360 m		
	1347 w	1340 w	BPE ν (ring) _{sym}
1336 m		1336 w	Acac δ (CH ₃)
		1295 w	BPE ρ (CH)
1279 w	1276 m	1277 w	BPE ν (ring) _{asym} , C ₂ H ₂ δ (ring-CH), δ (ring-C=C)
1263 m		1259 m	BPE ρ (CH), ν (CC)
		1249 m	Acac ν (C-CH ₃)
		1241 m	
	1230 w	1231 w	
1219 m	1220 vw	1221 w	BPE δ (CH)
1202 m, sh	1204 m	1204 w	BPE inner ring, C ₂ H ₂ δ (CH)
1198 m		1197 w	Acac ρ (CH)
1106 w	1107 w	1100 w, sh	BPE inner ring δ (CH)
~1086 m, sh		1090 w, sh	BPE outer ring δ (CH)
	1070 w	1075 m	
1065 m		1067 s	
	1061 w	1058 s	BPE inner ring δ (CNC), ρ (CH)
		1053 m	
1045 m	1049 w	1038 w	
1030 s	1025 m	1028 m	
1007 s		1010 s	Acac ρ (CH ₃) BPE δ (inner ring)
		998 m	BPE δ (outer ring)

		989 m	BPE outer ring Oop. $\delta(\text{CH})$, C_2H_2 $\pi(\text{CH})$
973 m	975 m	971 m	
		965 m	
952 w	967 vw	953 w	
933 m	937 w	935 m	Acac $\nu(\text{C-CH}_3)$
~890 w, sh		892 m	
		883 w	
882 s	~882 w, br	879 m	BPE $\rho(\text{CH})$, C_2H_2 $\delta(\text{ring-CH})$, $\delta(\text{ring-C=C})$
832 s	838 m	~835 m, sh	
	829 m	827 s	BPE $\pi(\text{CH})$
811 w		812 w	
		805 w	
	797 w	797 w	BPE $\pi(\text{CH})$
774 m		782 w	Acac $\pi(\text{CH})$
		764 w	
744 w	751 m	742 w	
		726 w	
722 w	~722 w, br	721 w	
690 w	689 m	693 w	
	668 w	668 m	BPE $\delta(\text{inner ring})$
661 m	657 w	650 m	BPE $\delta(\text{ring})$, $\delta(\text{C}_2\text{H}_2)$
644 s	646 m	641 m	Acac $\nu(\text{O-Ru-O})_{\text{asym}}$, $\rho(\text{CH}_3)$
569 m	571 m		
551 s	553 s	552 vs	BPE Oop. $\rho(\text{ring})$
489 w	489 w	492 w	
		483 w	
470 w	469 m	470 w	BPE inner ring $\rho(\text{CH})$, C_2H_2 $\delta(\text{ring-CH})$, $\delta(\text{ring-C=C})$
448 m			
437 m	435 m		
430 w, sh	428 w	431 w	Acac $\delta(\text{acac})$, $\pi(\text{CH}_3)$

w= weak, m= medium, s= strong, sh= shoulder, b= broad, ν = stretching mode, δ = bending mode, Oop.= out of plane mode. ZnCl_2 polymer was $[\text{Zn}(\text{Ru}(\text{acac})_2(\text{BPE})_2)\text{Cl}_2]$, ZnBr_2 polymer was $[\text{Zn}(\text{Ru}(\text{acac})_2(\text{BPE})_2)\text{Br}_2]$.

The spectra were characterised by comparison with RuML4 and literature values.²⁴⁵

4.3.4.2. FTIR SEC

The FTIR SEC spectrum of $[\text{Zn}(\text{Ru}(\text{acac})_2(\text{BPE})_2)\text{Cl}_2]$ featured very small changes in absorption over the course of the experiment. There were two possible explanations for this observation. Firstly, the depth of electrochemical charge penetration into the solid-state sample on the electrode surface may have been too small to observe a general change in the spectrum of $[\text{Zn}(\text{Ru}(\text{acac})_2(\text{BPE})_2)\text{Cl}_2]$. Alternatively, electrical contact between the sample and the

working electrode may have been inconsistent, leading to only partial oxidation of the sample in range of the evanescent wave. The cause could be distinguished by the uniformity of colour change across the sample; however, the design of the Jackfish ATR SEC cell prevented this observation. To compensate for this, the spectrum at the starting potential (i.e. the Ru(II) material) was treated as a background and subtracted from that at the final potential (Figure 4.16). These changes were subtle, given the low intensity of the spectra. It was estimated only 25% of the material in range of the evanescent wave underwent a redox reaction. Due to noise below 1200 cm^{-1} , data in this region was disregarded entirely. Despite this, several key changes were present between initial and final potentials (Table 4.6). Many of these changes correspond with those observed in the FTIR SEC of RuML4.

Table 4.6. Comparison of bands gained with bands lost in differential SEC spectrum of $[\text{ZnCl}_2(\text{RuML}_4)]$. Bands gained and lost represent changes upon oxidation.

ν_{max} Band Gained (cm^{-1})	ν_{max} Band Lost (cm^{-1})	Assignment
	1653	$\delta(\text{C}_2\text{H}_2)$
1612		BPE $\delta(\text{inner ring})$
	1595	BPE $\nu(\text{outer ring})_{\text{asym}}$, Acac $\nu(\text{C=O})_{\text{sym}}$, $\delta(\text{C-HC=C})$, $\rho(\text{CH}_3)$
1559		
	1540	Acac $\delta(\text{CCHC})$
1522		Acac $\nu(\text{C=O})_{\text{sym}}$, $\delta(\text{C-HC=C})$, $\rho(\text{CH}_3)$
	1514	BPE $\rho(\text{CH})$
	1489	
1473		BPE inner ring $\delta(\text{CH})$
1436		Acac $\delta(\text{CH}_3)$
	1403	Acac $\rho(\text{CH}_3)$, BPE $\delta(\text{CH})$
1375		Acac $\delta(\text{CH}_3)$
1280		BPE $\rho(\text{CH})$, $\delta(\text{ring})$ Acac $\nu(\text{C-CH}_3)$
	1264	BPE $\rho(\text{CH})$, $\nu(\text{CC})$
	1226	BPE $\delta(\text{CH})$
1206		BPE $\delta(\text{CH})$

w= weak, m= medium, s= strong, sh= shoulder, b= broad, ν = stretching mode, δ = bending mode, Oop.= out of plane mode.

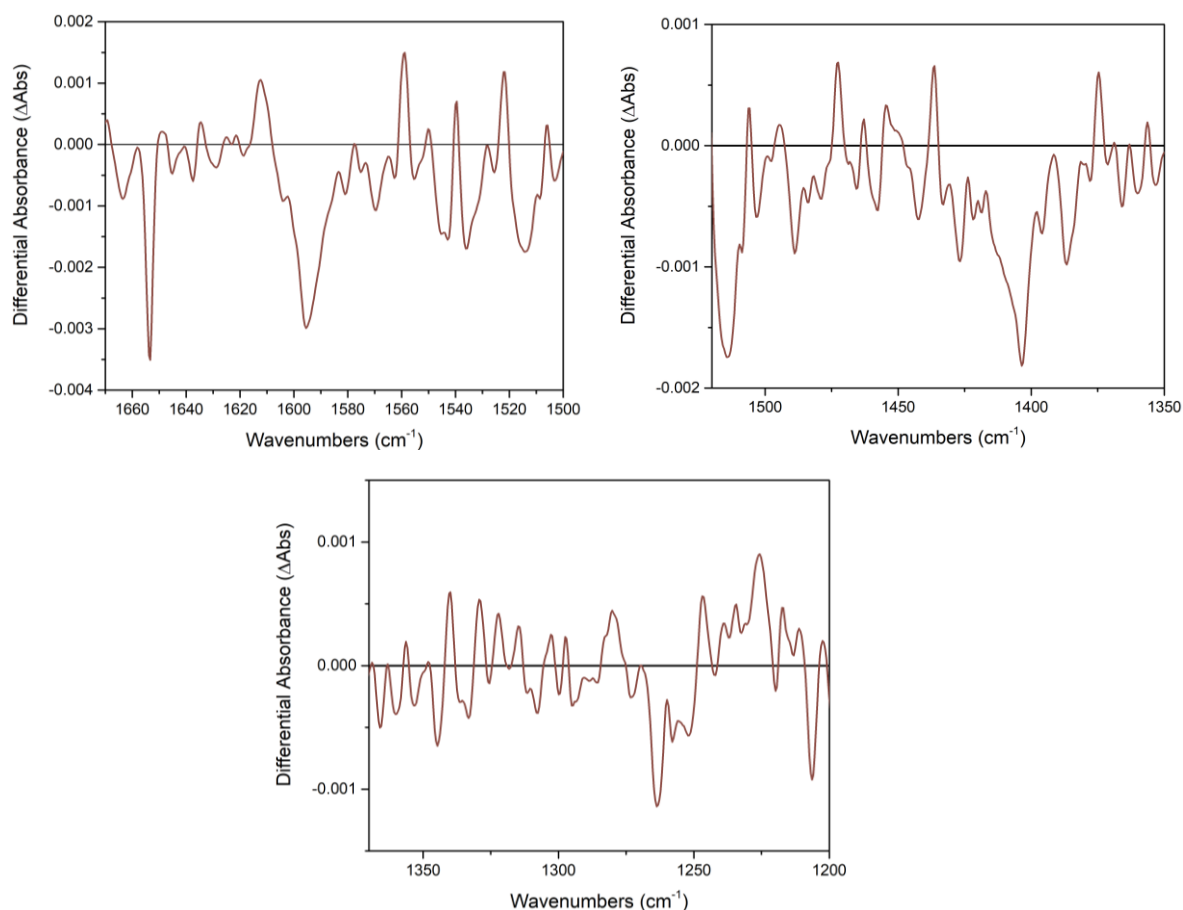


Figure 4.16. Differential ATR IR SEC spectra of $[\text{ZnCl}_2(\text{RuML4})]$, which was performed with crystals dropcast onto the electrode surface. Electrolyte: 0.1 M TBAPF₆ in MeCN. Working electrode: ITO coated silicon wafer (20 nm). Spectrum at initial potential (-0.35 V vs. Ag^+/Ag) was subtracted from spectrum at final potential (0.2 V vs. Ag^+/Ag).

4.3.4.3. Raman spectroscopy

The Raman spectra of the RuML4 CPs are very similar (Table 4.7). One notable change is the blueshift of the symmetric stretch of acac with the Ru metal centre in the CPs. This change is small, but may reflect a change in the bonds between the discrete complex and the extended material. The Zn-N stretch in the CPs is convoluted with a CH_3 wag in the acac^- ligands.

Table 4.7. Comparison of Raman spectra of [ZnCl₂(RuML4)], [ZnBr₂(RuML4)] and [Ru^{II}(acac)₂(BPE)₂]. Excitation wavelength: 532 nm.

$\nu_{\max}$ and Intensity ZnCl ₂ Polymer (cm ⁻¹)	$\nu_{\max}$ and Intensity ZnBr ₂ Polymer (cm ⁻¹)	$\nu_{\max}$ and Intensity RuML4 (cm ⁻¹)	Band Assignment ²⁴⁶
	2978 w	2972 m	Acac ν (CH)
	2931 m	2901 m	Acac ν (CH ₃)
	2877 w		
2802 w	2806 w	2801 br	BPE outer ring ν (CH)
	2627 w		
	2221 w		
2007 w	2005 w		
1631 m	1636 s	1632	δ (C ₂ H ₂)
1605 s	1605 s	1602	Acac ν (CO), δ (CH ₃) BPE δ (CH), δ (outer ring), δ (inner ring)
1542 m	1549 m	1531 m	Acac ν (ring) _{asym}
1490 w	1490 w	1492 w	BPE ρ (CH)
1429 w	1428 w	1426 w	BPE outer ring δ (CH)
1339 w	1340 m	1339 m	BPE δ (CH)
	1311 w	1311 w, br	C ₂ H ₂ δ (ring-CH)
1275 w	1271 w		
~1215 m, sh	1216 m, sh	~1215 m, sh	BPE δ (CH)
1200 s	1201 s	1198 s	BPE inner ring δ (CH)
1063 w	1059 w	1060 w	BPE inner ring δ (CNC), ρ (CH)
1029 m	1027 m	~1029, m	
~1021 m	1018 m	1017 m	BPE δ (inner ring)
969 w	976 w	969 w	BPE δ (outer ring)
	958 w		
888 w	885 w	887 w	BPE ρ (CH), C ₂ H ₂ δ (ring-CH), δ (ring-C=C)
802 w	805 w	809 w	
744 w	744 w	742 w	
721 w		723 w	
693 w	688 w	683 w	
676 w			
665 w	665 w	665 m	
574 w	574 w	576 w	
	554 w	553 w	BPE inner ring ρ (CH)
461 m	462 m	449 w	ν (O-Ru-O) _{sym} Acac δ (acac)
401 w	405 w	404 w	
~337 w, br	~346 w, br	~337 m, b	
~279 w, br	283 w, br		ν (Zn-N)
~279 w, br	283 w, br	266 m	Acac π (CH ₃)
189 w, br	190 w, br	188 w, br	

w= weak, *m*= medium, *s*= strong, *sh*= shoulder, *b*= broad, *v*= stretching mode, *δ*= bending mode, *Oop.*= out of plane mode.

The spectra were characterised by comparison to RuML4 and literature.²⁴⁶

Resonance Raman experiments were performed on both CPs; however, due to the blueshift observed in MLCT transitions in the spectra of the CPs, many of the excitation wavelengths coincided only with transition **1** of the RuML4 metalloligand (Figure 4.17). As a result, there are no notable distinctions between the excitation profiles of the metalloligand and polymers. For example, the $\nu(\text{C}_2\text{H}_2)$ stretch increased in integrated intensity with decreasing wavelength, similar to the metalloligand (Figure 4.18). Although we anticipated that the CPs may more clearly conform to the C_{2v} point group description than the metalloligand, different excitation wavelengths would be required to verify this.

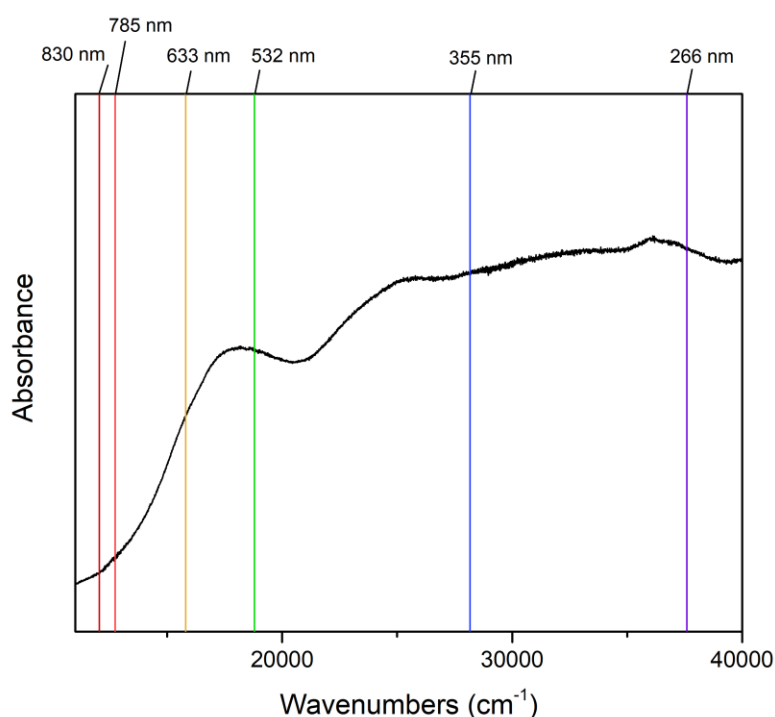


Figure 4.17. Raman excitation wavelengths compared with the UV-vis spectrum of $[\text{ZnBr}_2(\text{RuML4})]$

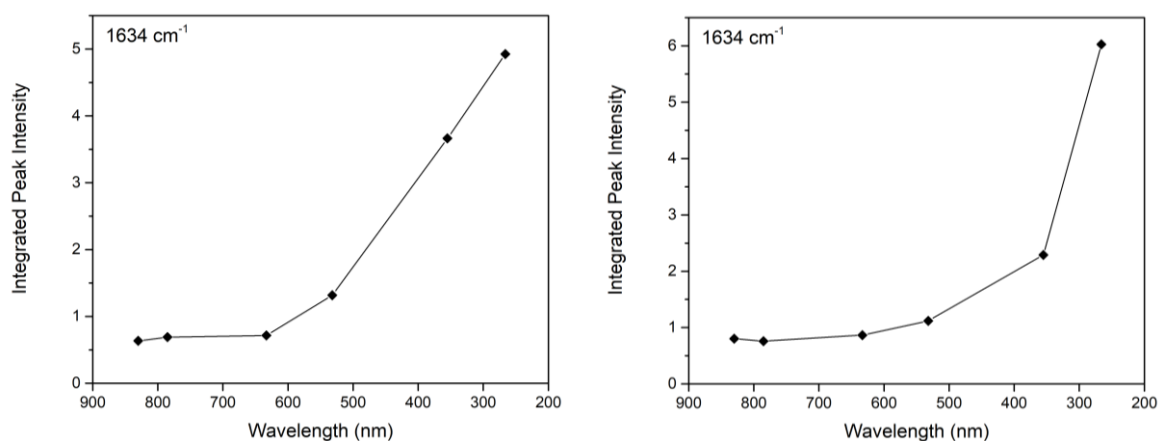


Figure 4.18. Raman excitation profiles for 1633 cm^{-1} bands of $[\text{ZnCl}_2(\text{RuML}_4)]$ and $[\text{ZnBr}_2(\text{RuML}_4)]$ at excitation wavelengths 830, 785, 633, 532, 355 and 266 nm.

4.3.5. Comparison with Metalloligand

Although the spectroscopic behaviour, electrochemistry and crystallography of $[\text{ZnCl}_2(\text{RuML}_4)]$ and $[\text{ZnBr}_2(\text{RuML}_4)]$ is very similar, comparison of the CPs $[\text{ZnCl}_2(\text{RuML}_4)]$ and $[\text{ZnBr}_2(\text{RuML}_4)]$ with the discrete metalloligand RuML4 reveal substantial changes in electronic absorption. They feature very small changes to the vibrational spectroscopy and electrochemistry of the RuML4 motif. The Ru(III/II) couple is *quasi*-reversible and occurs at a comparable potential. The vibrational spectroscopy only shows small differences. The vibrational mode at $\sim 1590 \text{ cm}^{-1}$ in the infrared spectrum that is correlated to the bite angle of the acac^- ligands does not deviate noticeably between metalloligands and CP. Evidently, there is very little difference in the π -backbonding behaviour and electronic structure of the RuML4 metalloligand within the CPs, which suggests differences in electronic absorption are primarily due to outer-sphere reorganisational effects.

4.4. Summary

Throughout this Chapter, we have presented the synthesis of several CPs which employ the *trans*-[Ru(acac)₂(X)₂] motif. We have demonstrated that the spectroscopic and crystallographic behaviours of the metalloligands are subject to the structural influence of polymerisation, resulting in contributions to outer-sphere reorganisation energies and the configuration of the RuML4 metalloligand. Although the electrochemical properties of the *trans*-[Ru(acac)₂(X)₂] motifs themselves do not significantly change upon polymerisation, the accessibility of different oxidation states of the Ru centres may be absent due to the presence of other electroactive species within frameworks, or due to inhibition of charge transport by CP structures.

We hope that the work presented in this Chapter will lead to further investigations into this class of material.

Chapter 5

Guest Chemistry of a Ruthenium Pyrazine Complex

5.1. Project goals

The Creutz-Taube Ion (CTI) sits among the most famous examples of mixed-valency and IVCT in the literature. Early models of charge transfer were demonstrated with the Creutz-Taube Ion because the IVCT mechanism occurs between ruthenium centres of comparable ligand-field energies and orbital symmetries.^{1,25} As a result, IVCT in the CTI can be classically represented by an electronic transition between the metal *d* orbitals of ruthenium, as opposed to the substantially more complex MO theory model required to describe MLCT or LMCT. Therefore, CTI is an excellent candidate for investigations into the effect of host-guest interactions on charge transfer. The initial goal of this project was to identify the impact of such interactions within the modified MOF $\text{Zr}_6\text{O}_4(\text{OH})_4 \cdot (\text{C}_8\text{H}_6(\text{SO}_3\text{H})_2)_6 \cdot (\text{DMF})_{0.7} \cdot (\text{H}_2\text{O})_{47}$ (**UiO-66-(HSO₃)₂**),⁸⁵ which has a calculated BET surface area of 285.05 m²/g. The pore aperture of **UiO-66-(HSO₃)₂** was large enough to allow infiltration of a $[\text{Ru}^{\text{III}}(\text{NH}_3)_5(\text{CH}_3)_2\text{CO}]^{3+}$ monomer.

In this Chapter, we discuss the impregnation of pyrazine and guest oligomerisation of a ruthenium hexaammine monomer within the pores of the framework **UiO-66-(HSO₃)₂**.⁸⁵ We compare the charge transfer and spectroscopic behaviour of this new material to those of the free CTI and its monomer.

5.2. Host-Guest Design

The synthesis of the complex, $[(\text{NH}_3)_5\text{Ru}(\text{pyz})\text{Ru}(\text{NH}_3)_5]^{n+}$, within the pores of **UiO-66-(HSO₃)₂** was attempted by first impregnating the framework with the pyrazine bridging ligand. Immobilisation of pyrazine guaranteed that any subsequent coordination of Ru and pyz would occur either within the pores or on the surface of the MOF particles. The pyrazine impregnated material (pyz@UiO-66-(HSO₃)₂) was then reacted with the Ru monomer $[\text{Ru}^{\text{III}}(\text{NH}_3)_5(\text{OSO}_2\text{CF}_3)](\text{CF}_3\text{SO}_3)_2$ in acetone. The triflate ligand is highly labile on Ru(III) and readily exchanged with solvent molecules to give the complex $[\text{Ru}^{\text{III}}(\text{NH}_3)_5((\text{CH}_3)_2\text{CO})]^{3+}$.²⁴⁷ $[\text{Ru}^{\text{III}}(\text{NH}_3)_5((\text{CH}_3)_2\text{CO})]^{3+}$ could then substitute pyrazine directly or *via* Ru(II), due to base-catalysed disproportionation of Ru(III) to Ru(II) and Ru(IV) in the presence of the weak base, pyrazine, which was present in solution and incorporated into the framework.²⁴⁸⁻²⁵⁰ Thus, as the complex infiltrated the pores of pyz@UiO-66-(HSO₃)₂, the acetone ligands exchanged for the pyz ligands, and produced either the monomer $[\text{Ru}(\text{NH}_3)_5(\text{pyz})]^{n+}$ or the dimer $[(\text{NH}_3)_5\text{Ru}^{\text{II}}(\mu\text{-pyz})\text{Ru}^{\text{II}}(\text{NH}_3)_5]^{n+}$. The product was pink in colour and exhibited no sign of solvatochromism or leeching in a range of organic solvents, including acidic water and D₂O. This suggests that a coordination complex was successfully immobilised within or on the framework. Digestion of Ru(pyz)@UiO-66-(HSO₃)₂ in nitric acid (70%) followed by ICPMS revealed a Ru concentration of 0.43%. Attempts to identify the guest are detailed throughout this Chapter.

5.3. Electrochemistry

Attempts to electrochemically oxidise the Ru centres within Ru(pyz)@UiO-66-(HSO₃)₂ were unsuccessful when using TBAPF₆ as an electrolyte. This was likely due to poor charge penetration or diffusion of counterions through the **UiO-66-(HSO₃)₂** framework. Several

alternate electrolytes were employed, including 0.1 M KCl in D₂O at pH 5, 0.1 M LiBF₄ in MeCN, and 0.1 M LiCl in DMF. The Li electrolytes produced strong and irreversible signals at 0.118 and 1.08 V vs. Ag⁺/Ag which were not observed in the equivalent measurement for the MOF (Figure 5.1). These processes were not present in subsequent cycles.

The oxidation at 0.118 V vs. Ag⁺/Ag, $i_{p,c} = 103 \mu\text{A}/\text{cm}^2$ at 100 mV/s was a Ru(III/II) couple which occurs at a similar potential as that described in the literature.²⁵¹ This couple was not investigated further in the current work due to time restraints, and is a candidate for future work. The second process at 1.08 V vs. Ag⁺/Ag, $i_{p,c} = 429 \mu\text{A}/\text{cm}^2$ may have involved the second Ru(III/II) couple, i.e. [(NH₃)₅Ru(pyz)Ru(NH₃)₅]^{5/6+}, but also contained a more intense yet unidentified oxidation process. It was unclear why the electrochemical processes observed in Ru(pyz)@UiO-66-(HSO₃)₂ were irreversible. However, the capacitance of **UiO-66-(HSO₃)₂** demonstrably reduces after one cycle, similar to the host-guest system. Thus, the irreversibility may be due to the framework rather than a host-guest interaction. There was no evidence that the Ru complex leached into solution after cycling.

The oxidation process observed in the cyclic voltammograms of the host-guest system was not replicated in bulk electrolysis experiments, and thus we were unable to perform NIR SEC experiments on Ru(pyz)@UiO-66-(HSO₃)₂.

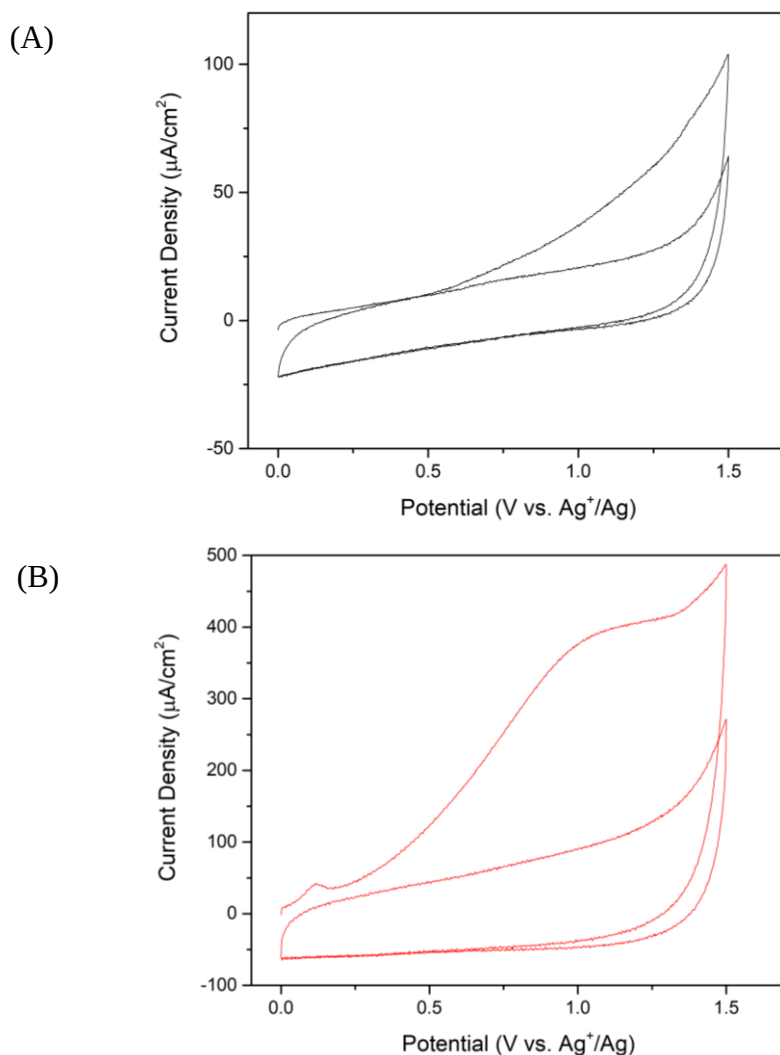


Figure 5.1. Cyclic voltammograms of (A) **UiO-66-(HSO₃)₂**, (B) **Ru(pyz)@UiO-66-(HSO₃)₂** in 0.1 M LiBF₄ in MeCN, collected between 0 and 1.5 V vs. Ag⁺/Ag at 100 mV/s. Working electrode: 1 mm glassy carbon.

5.4. Powder X-Ray Diffraction

PXRD was employed to characterise the MOF and the two guests (Figure 5.2). Both host-guest materials had a lower crystallinity than the MOF, while Ru(pyz)@UiO-66-(HSO₃)₂ produced lower intensity and broader peaks. This was a product of a higher degree of mosaicity in Ru(pyz)@UiO-66-(HSO₃)₂, meaning a higher average degree of misalignment between adjacent microcrystalline domains.²⁵² This could also represent partial filling of internal

structures, as a result of very large unit cells or a lack of regular unit cells due to distortions around incorporated complexes. It could also be a result of inhomogeneous incorporation of the guest into the framework.

Indexation and Le Bail refinement of the three powder patterns revealed each structure adopted the non-centrosymmetric cubic space group $F23$, with small variations in the unit cell parameters and volumes (Table 5.1). $\text{Ru}(\text{pyz})@\text{UiO}-66-(\text{HSO}_3)_2$ had smaller unit cell parameters than **UiO-66-(HSO₃)₂** and $\text{pyz}@\text{UiO}-66-(\text{HSO}_3)_2$, with an a value 0.01-0.03 Å smaller and a volume 16-38 Å³ smaller than the MOF. While both changes were less than 1%, they indicated that a contraction of the unit cell occurred due to guest incorporation. This was most likely due to intermolecular interactions occurring between the host and guest, which were stronger for the $\text{Ru}(\text{pyz})$ guest due to the presence of hydrogen bonding of the ammine ligands. Such an interaction is expected to contribute to the outer-sphere reorganisation energy during charge-transfer.²⁷

Ultimately, the PXRD patterns indicate small crystallographic differences between the MOF and guest incorporated $\text{Ru}(\text{pyz})@\text{UiO}-66-(\text{HSO}_3)_2$, consistent with the presence of $[\text{Ru}^{\text{II}}(\text{NH}_3)_5(\text{pyz})]^{2+}$ or $[(\text{NH}_3)_5\text{Ru}^{\text{II}}(\mu\text{-pyz})\text{Ru}^{\text{II}}(\text{NH}_3)_5]^{4+}$.

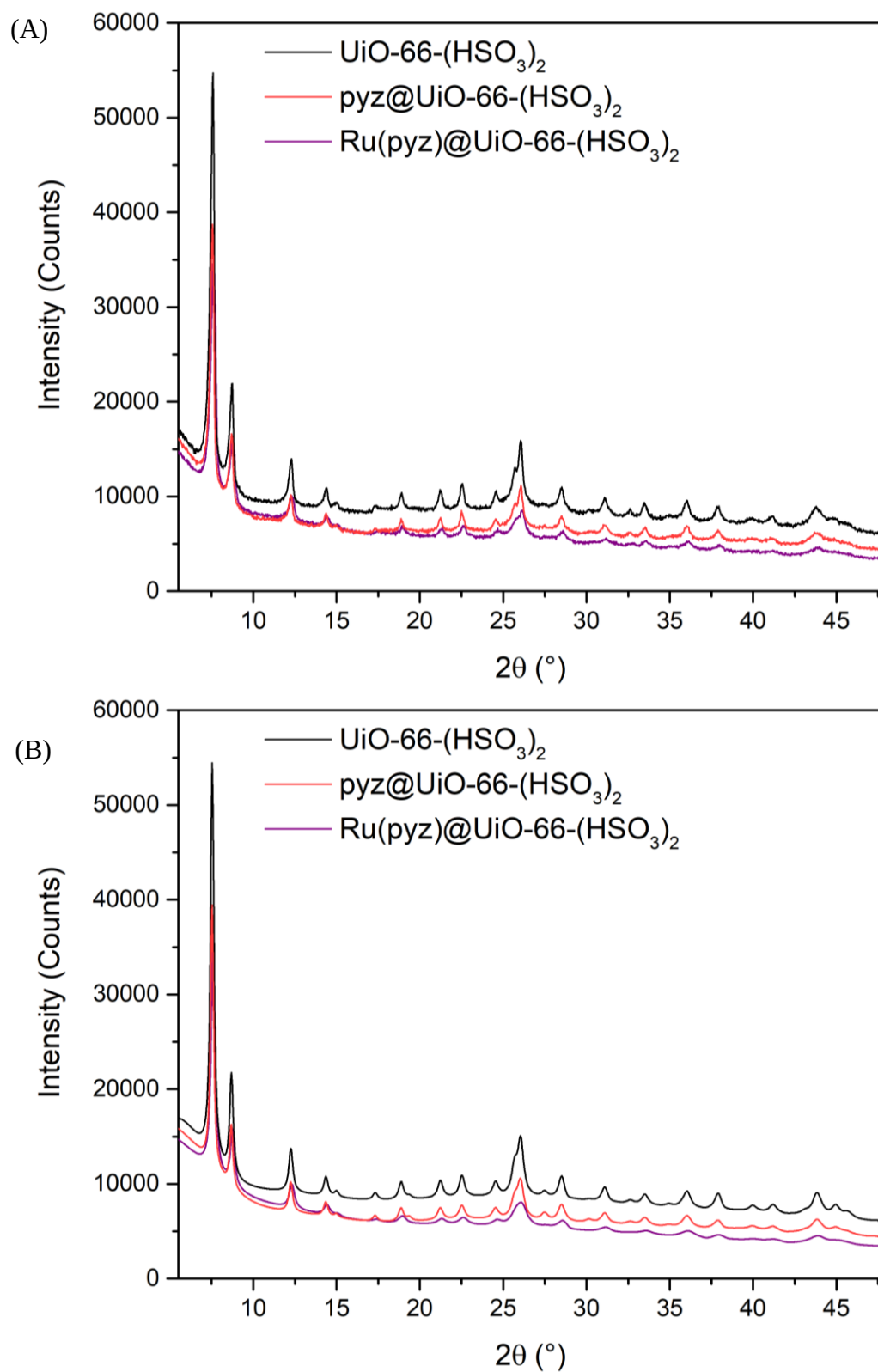


Figure 5.2. PXRD patterns of the host and host-guest materials. (A) Experimental; (B) calculated in *F23* using GSAS-II Ver. 5585.

Table 5.1. Unit cell parameters of UiO-66-(HSO₃)₂, pyz@UiO-66-(HSO₃)₂, and Ru(pyz)@UiO-66-(HSO₃)₂ as refined in *F*23 using GSAS-II Ver. 5585.

Material	<i>a</i> (Å)	<i>V</i> (Å ³)	<i>wR</i>
UiO-66-(HSO ₃) ₂	20.598 (3)	8740 (4)	3.377
pyz@UiO-66-(HSO ₃) ₂	20.606 (6)	8750 (7)	3.119
Ru(pyz)@UiO-66-(HSO ₃) ₂	20.577 (6)	8713 (7)	3.308

5.5. UV-Vis Spectroscopy

The colour of pyz@UiO-66-(HSO₃)₂ changed from white-light yellow to light pink upon reaction with [Ru(NH₃)₅(OSO₂CF₃)](SO₃CF₃)₂. Comparison of the optical spectroscopies of Ru(pyz)@UiO-66-(HSO₃)₂ and **UiO-66-(HSO₃)₂** revealed a new absorption band in Ru(pyz)@UiO-66-(HSO₃)₂ at 18,800 cm⁻¹, as well as a broad shoulder between 22,000 and 30,500 cm⁻¹ (Figure 5.3). These features were responsible for the colour change of the material. Subtraction of the host-guest spectrum by the MOF spectrum revealed several new strongly-absorbing features in the UV region. These new features represented MLCT between Ru and pyz, as well as internal $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions characteristic of pyrazine. These features were indicative of bonding between the *d*⁶ [Ru^{II}(NH₃)₅] monomer and pyrazine ligands within the pores of the MOF.

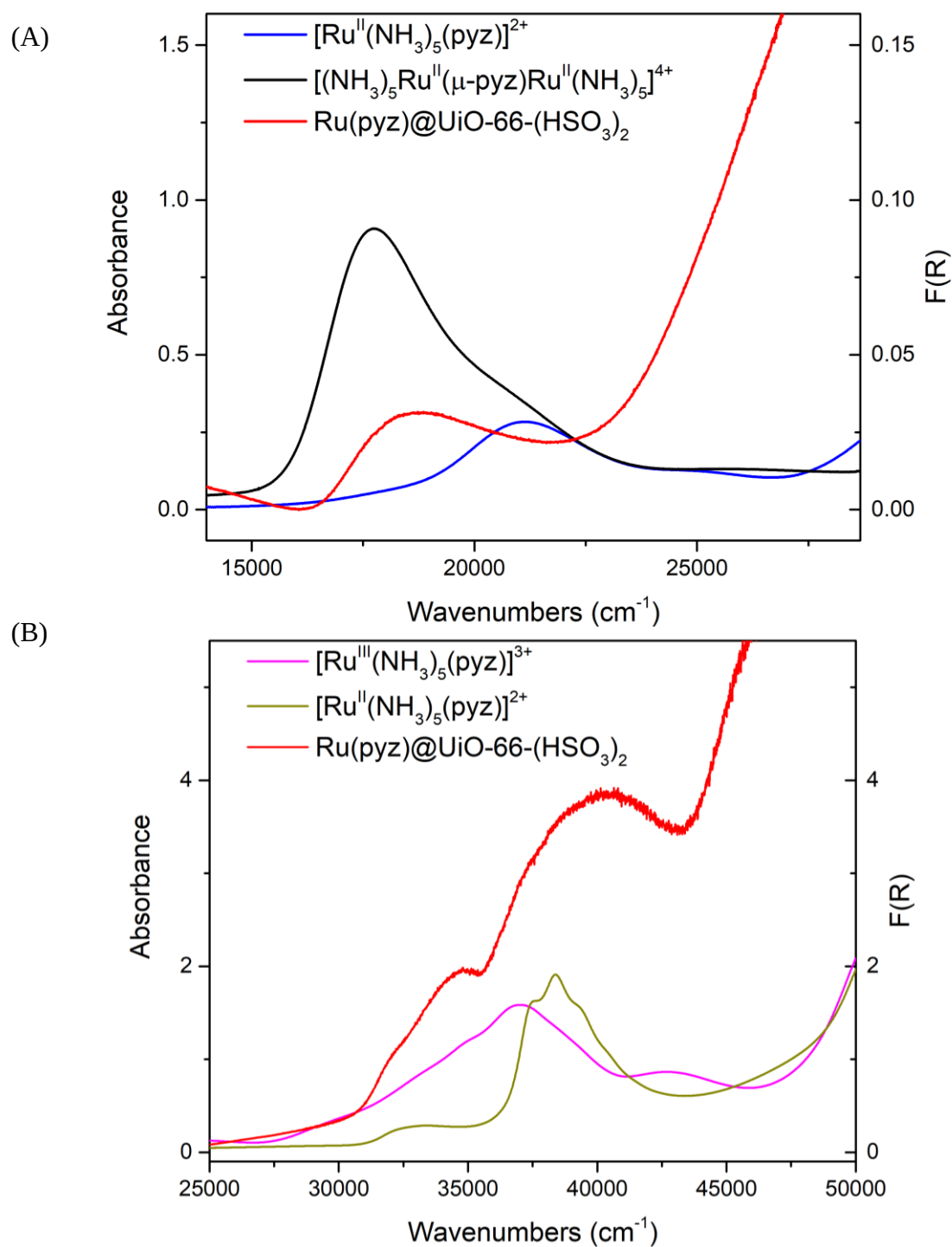


Figure 5.3. Comparison of UV-vis transition spectra of Ru(pyz), [(NH₃)₅Ru(μ-pyz)Ru(NH₃)₅]ⁿ⁺, and [(NH₃)₅Ru(pyz)]ⁿ⁺. (A) Vis region; (B) UV region. Spectrum of ‘Ru(pyz)’ was obtained by subtracting the diffuse reflectance spectrum of UiO-66-(HSO₃)₂ from that of Ru(pyz)@UiO-66-(HSO₃)₂. The spectra of [(NH₃)₅Ru(μ-pyz)Ru(NH₃)₅] and [(NH₃)₅Ru(pyz)] were solution state transmission measurements. Solvent: 0.1 M KCl in H₂O, pH = 5.

Comparison between the spectra of the monomer and dimer complex revealed spectral similarities with the Ru(II) complexes, $[(\text{NH}_3)_5\text{Ru}^{\text{II}}(\mu\text{-pyz})\text{Ru}^{\text{II}}(\text{NH}_3)_5]^{4+}$ and $[(\text{NH}_3)_5\text{Ru}^{\text{II}}(\text{pyz})]^{2+}$, with the MLCT band of $\text{Ru}(\text{pyz})@\text{UiO-66-(HSO}_3)_2$, which lay in between that of the monomer and dimer complex (Figure 5.3A). This may suggest a mixture of monomer and dimer are present within the host-guest material. However, given the undetermined contribution to the transition energy by outer-sphere reorganisation within the host-guest system due to both dielectric continuum and specific effects such as hydrogen bonding,²⁷ we cannot make any confident conclusion.

The UV region resembled both Ru(II) and Ru(III) monomer and dimer, which contain several convoluted bands. However, it most strongly resembled the $[(\text{NH}_3)_5\text{Ru}^{\text{II}}(\text{pyz})]^{2+}$ monomer which was blueshifted by $\sim 2000\text{ cm}^{-1}$ (Figure 5.3B). The ratio of absorbance in the visible region compared with the UV region suggests that uncoordinated pyrazine is present within the pores of $\text{Ru}(\text{pyz})@\text{UiO-66-(HSO}_3)_2$.

Similar features have been observed in the UV-vis regions of several Ru(II) pyridyl complexes,¹³ and the coordination complex $[(\text{NH}_3)_5\text{Os}^{\text{II}}(\mu\text{-bpy})\text{Os}^{\text{II}}(\text{NH}_3)_5]\text{Cl}_6$.²¹⁶⁻²¹⁸

5.6. Vibrational Spectroscopy

Due to the low concentration of guest relative to host in $\text{Ru}(\text{pyz})@\text{UiO-66-(HSO}_3)_2$, vibrational spectroscopy was performed with the expectation that only subtle differences would manifest between the host and host-guest materials. While this expectation was met, FTIR, Raman and resonance Raman spectroscopy were successfully employed in identifying characteristic features of the guest molecules.

Infrared spectra of the new material, the intermediate, and the MOF were very similar (Figure 5.4). The only significantly intense band unique to $\text{Ru}(\text{pyz})@\text{UiO-66-(HSO}_3)_2$ occurred at

1658 cm^{-1} , which did not correspond to the infrared spectrum of $[(\text{NH}_3)_5\text{Ru}(\mu\text{-pyz})\text{Ru}(\text{NH}_3)_5]$. However, the second derivative of both host-guest spectra revealed several subtle details (Appendix E). In $\text{pyz}@ \text{UiO-66-(HSO}_3)_2$, several bands associated with pyrazine were observed, at 1151, 1072, 1036, 804 and 787 cm^{-1} .²²⁵ In $\text{Ru}(\text{pyz})@ \text{UiO-66-(HSO}_3)_2$, bands at ~ 1145 and 805 cm^{-1} corresponded to pyrazine. Weak features at 1633, 1582 and 740 cm^{-1} were associated with ammine ligands in the ruthenium monomer and dimer.²⁵³ Features at 1435 and 1083 cm^{-1} were associated with coordinated pyrazine in $[(\text{NH}_3)_5\text{Ru}(\mu\text{-pyz})\text{Ru}(\text{NH}_3)_5]^{n+}$.²⁵⁴

Both host-guest systems had a lower baseline absorbance with a corresponding reduction of approximately 25%. Differences between the three materials may have arisen from particulate size and surface properties.

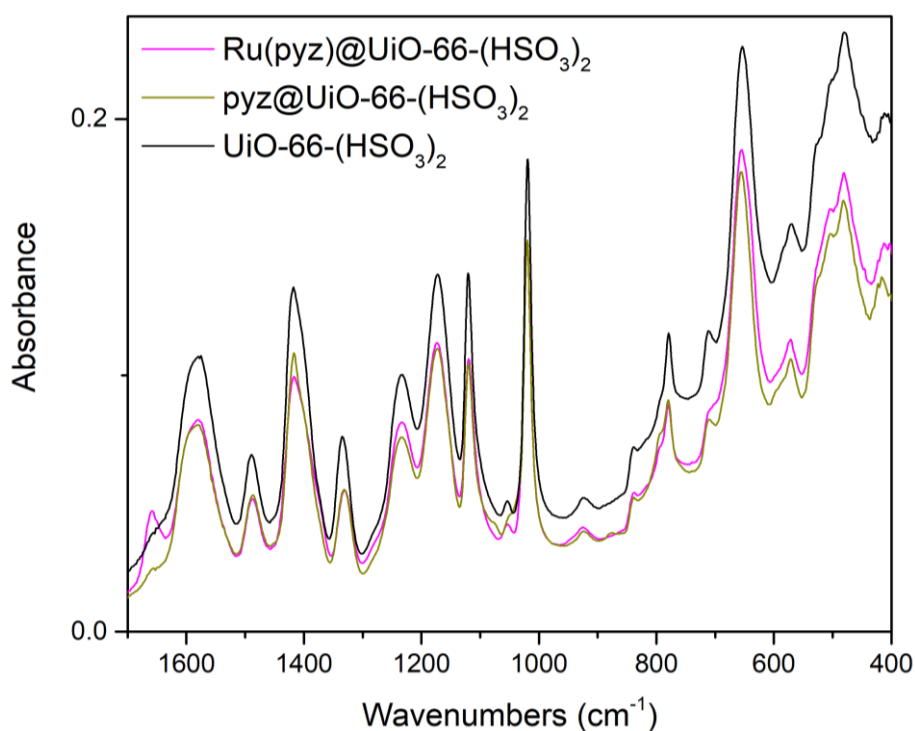


Figure 5.4. FTIR spectra of $\text{UiO-66-(HSO}_3)_2$, $\text{pyz}@ \text{UiO-66-(HSO}_3)_2$, and $\text{Ru}(\text{pyz})@ \text{UiO-66-(HSO}_3)_2$.

Resonance Raman spectroscopy of **UiO-66-(HSO₃)₂** and host-guest materials employing the framework were hindered by laser-induced fluorescence and resonance Raman excitation of the MOF (Figure 5.5). Fluorescence was observed at all excitation wavelengths, but was most prevalent at 633 and 355 nm, with which no Raman spectra were observed. When a Raman signal was observed, differences between the MOF and host-guest materials were minimal. For example, at 255 nm, no difference was observed between any of the analytes, due to resonance enhancement of the MOF.

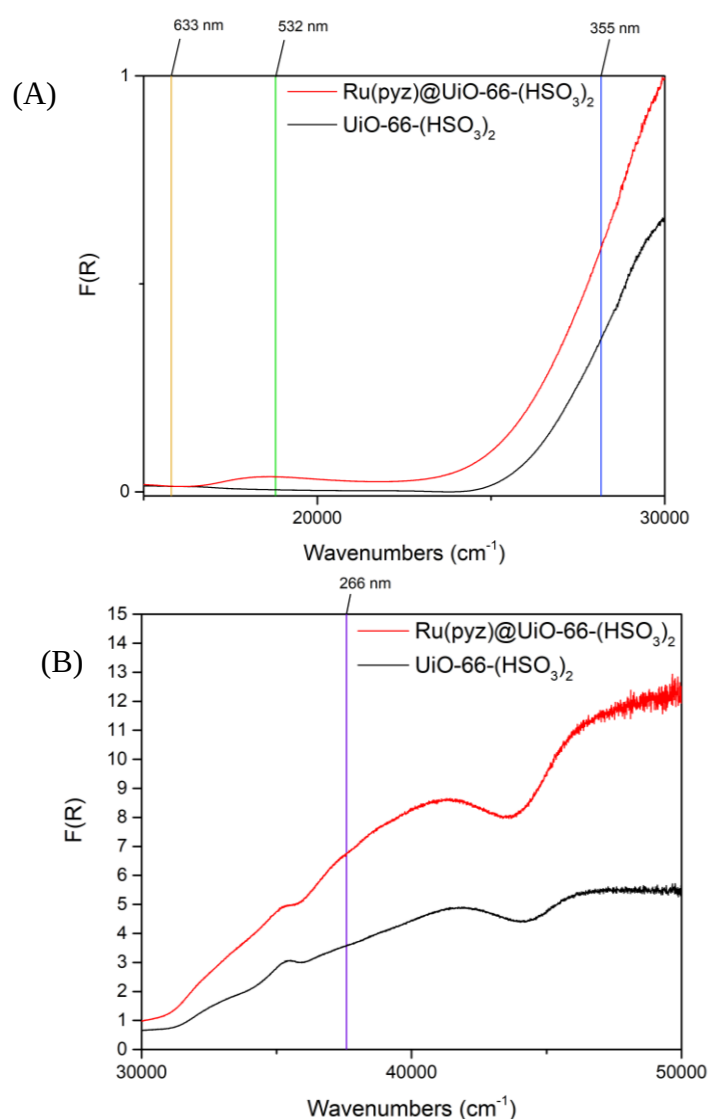


Figure 5.5. Raman excitation wavelengths compared with the UV-vis spectra of **UiO-66-(HSO₃)₂** and **Ru(pyz)@UiO-66-(HSO₃)₂**. (A) Vis region; (B) UV region.

At 833 nm excitation wavelength, small variations were observed between **UiO-66-(HSO₃)₂** and Ru(pyz)@UiO-66-(HSO₃)₂ (Figure 5.6). Comparison of the second derivative spectra revealed the positions of several small features in the host-guest system (Appendix E). Features at 1226, 1090 and 681 cm⁻¹ were indicative of the [(NH₃)₅Ru^{II}(μ-pyz)Ru^{II}(NH₃)₅]⁴⁺ dimer.²⁵⁵ Features at 1226, 1090, 1017 and 681 cm⁻¹ corresponded to the [(NH₃)₅Ru^{II}(pyz)]²⁺ monomer.²⁵⁶ However, the feature at 1017 cm⁻¹ may also correspond to uncoordinated pyrazine, in addition to scattering at 596 cm⁻¹.²⁵⁷

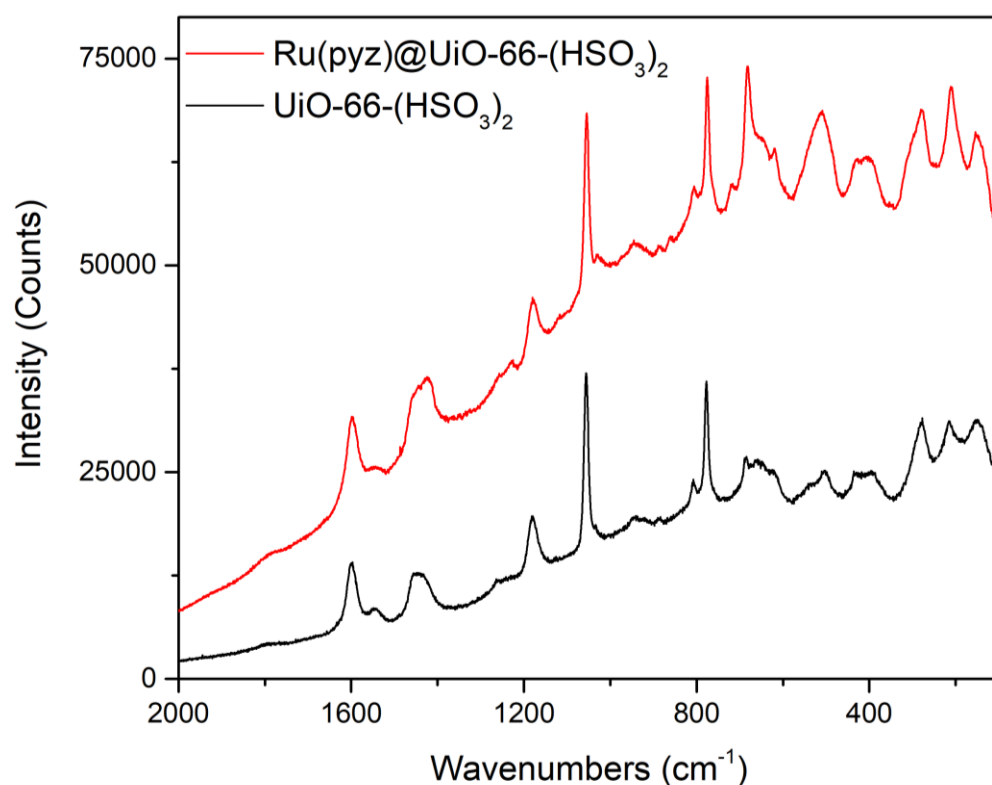


Figure 5.6. Raman spectra of **UiO-66-(HSO₃)₂** and Ru(pyz)@UiO-66-(HSO₃)₂ collected with an excitation wavelength of 830 nm.

Although 532 nm excitation produced significant laser-induced fluorescence, unique features were observed in the spectrum of Ru(pyz)@UiO-66-(HSO₃)₂ (Appendix E). Laser excitation at 532 nm was directly on resonance with the MLCT band at 18,800 cm⁻¹, enhancing bands

unobserved at 830 nm enhancement. This was consistent with resonance Raman measurements of the free dimer and monomer.²⁵⁵⁻²⁵⁶ These features included a broad feature at $\sim 311\text{ cm}^{-1}$ and a sharp peak at 663 cm^{-1} , corresponding to the Ru-N stretch and coordinated pyz ring bend respectively, in both $[(\text{NH}_3)_5\text{Ru}^{\text{II}}(\mu\text{-pyz})\text{Ru}^{\text{II}}(\text{NH}_3)_5]^{4+}$ and $[(\text{NH}_3)_5\text{Ru}^{\text{II}}(\text{pyz})]^{2+}$ complexes.²⁵⁵⁻²⁵⁶

5.7. General Comments

Our attempts to identify the nature of coordination bonding within the host-guest system $\text{Ru}(\text{pyz})@\text{UiO-66-(HSO}_3)_2$ were partially successful. The reduction in unit cell volume and crystallinity of the host-guest system indicate polar guests were present within the framework, likely in low concentration and variable orientations. This is consistent with the presence of ammine ligands, which experience substantial hydrogen bonding interactions with polar solvents, counterions and negatively charged regions of the framework. Additionally, the visible profile of the material is consistent with the presence of MLCT transitions characteristic of coordination between pyrazine and Ru(II), and vibrational spectroscopy revealed several modes consistent with $[(\text{NH}_3)_5\text{Ru}^{\text{II}}(\text{pyz})]^{2+}$ and $[(\text{NH}_3)_5\text{Ru}^{\text{II}}(\mu\text{-pyz})\text{Ru}^{\text{II}}(\text{NH}_3)_5]^{4+}$, as well as resonance Raman enhancement characteristic of the Ru(II) complexes. Thus, we can conclude with reasonable certainty that the motif, $[(\text{NH}_3)_5\text{Ru}^{\text{II}}(\text{pyz})]^{n+}$, is present in the material, as one or both of $[(\text{NH}_3)_5\text{Ru}^{\text{II}}(\text{pyz})]^{2+}$ and $[(\text{NH}_3)_5\text{Ru}^{\text{II}}(\mu\text{-pyz})\text{Ru}^{\text{II}}(\text{NH}_3)_5]^{4+/5+}$. Additionally, UV-vis and Raman spectra revealed a degree of uncoordinated pyrazine still present within the pores of $\text{Ru}(\text{pyz})@\text{UiO-66-(HSO}_3)_2$, which suggests that $[\text{Ru}^{\text{III}}(\text{NH}_3)_5((\text{CH}_3)_2\text{CO})]^{3+}$ had limited access to the pores of **UiO-66-(HSO₃)₂** or coordination sites of incorporated pyrazine.

As we were unable to oxidise the Ru centres in SEC experiments, it was not possible as yet to prove if the dimer was present. Without further investigation of host-guest interactions between **UiO-66-(HSO₃)₂** and pyrazine, we can only speculate on which complex would be

synthetically preferred. For example, if the pyrazine guests are oriented and positioned consistently by the shape or nature of available supramolecular interactions of the framework pores, then it is possible that the monomer or dimer complex may be preferred. However, given that there are no significant differences between the PXRD patterns of **UiO-66-(HSO₃)₂** and **pyz@UiO-66-(HSO₃)₂**, it appears unlikely that pyrazine molecules are oriented consistently within the pores, and instead are oriented randomly or variably according to pore shape and supramolecular interactions. In this case, formation of both monomer and dimer is possible depending on the orientation of the pyrazine ligand within the pores.

Additionally, depending on the orientation of incorporated pyrazine, dimer or monomer formation may occur at pore apertures, impeding further penetration of $[\text{Ru}(\text{NH})_3((\text{CH}_3)_2\text{CO})]^{3+}$ into the pores and thus limiting the concentration of incorporated Ru. Formation of the monomer may also impede formation of the dimer by a similar interaction.

Further, if the orientation of pyrazine and Ru complexes is variable within the pores of the framework, then any outer-sphere reorganisation effects in electron transfer will be averaged over all such molecules observed in the material.

Host-guest interactions are likely to occur in the form of hydrogen bonds. The pores of **UiO-66-(HSO₃)₂** feature protruding HSO₃ groups (Figure 5.7) which likely form hydrogen bonds with the ammine hydrogens. The charged complex may also replace protons in the HSO₃ groups, resulting in hydrogen bonds between complex and SO₃⁻ groups. Given that each pore of **UiO-66-(HSO₃)₂** has six of these polar HSO₃ groups sitting on or within the pore, hydrogen bonding will not necessarily favour one orientation of the guest molecule, which is consistent with observations.

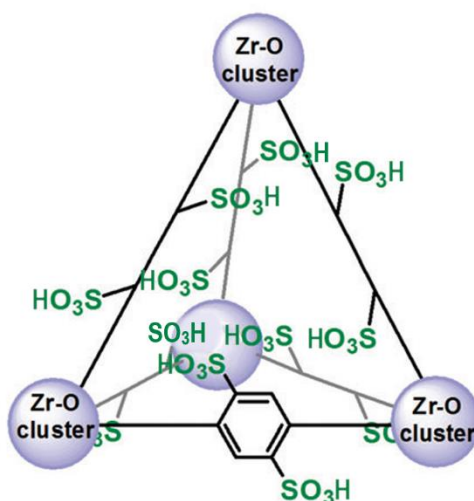


Figure 5.7. Schematic of the pore environment of UiO-66-(HSO₃)₂. Figure reproduced and edited with permission from the Royal Society of Chemistry.⁸⁵

Another consequence of the electrochemical inaccessibility of the Ru centres within Ru(pyz)@UiO-66-(HSO₃)₂ is that the mixed-valence [(NH₃)₅Ru^{II}(μ-pyz)Ru^{III}(NH₃)₅]⁵⁺ ion, and consequently the IVCT transitions, could not be produced within the host-guest system.

We have thus concluded that **UiO-66-(HSO₃)₂** is unsuited to preserving the electrochemical properties of [(NH₃)₅Ru^{II}(pyz)]²⁺ and [(NH₃)₅Ru^{II}(μ-pyz)Ru^{III}(NH₃)₅]⁵⁺, and does not appear to selectively template the formation of either the monomer or dimer molecules. Outer-sphere interactions are expected to play a role in the absorption energy of CT transitions within the host-guest material, but these could not be quantified.

Chapter 6

Epilogue and Future Work

6.1. Epilogue

In this work several trends and relationships are described amongst related Ru pyridyl complexes, as discrete, polymer and host-guest systems. Chapter 3 highlighted spectroscopic and electrochemical trends within the *trans*-[Ru(acac)₂(X)₂] family, and the underlying and competing factors that lead to these trends. In Chapter 4 novel CPs employing *trans*-[Ru(acac)₂(X)₂] complexes as metalloligands is described and contrasted with the behaviours of these extended materials to their discrete counterparts. In Chapter 5 a new host-guest material was described, which employed a Ru pyridyl motif. The impact of the host upon the spectroscopic and electrochemical behaviour of the guest was then described, and contrasted to those of the discrete complex. There are numerous iterations and future research that could be performed with these materials. Several of these are discussed in the following sections.

6.2. Future Work- Synthesis

6.2.1. Metalloligands

Given the comprehensive description of trends within the *trans*-[Ru(acac)₂(X)₂] family in the current work, future synthetic work in this area should be aimed at extended materials. One approach is the functionalisation of metalloligands with different coordinating groups. Preliminary studies in the current work were aimed towards the coordination complex, *trans*-bis(acetylacetonato)di(*iso*-nicotinatic acid)ruthenium(II) (Figure 6.1), with an intention to produce redox-active frameworks with paddlewheel topologies.²⁵⁸⁻²⁶¹

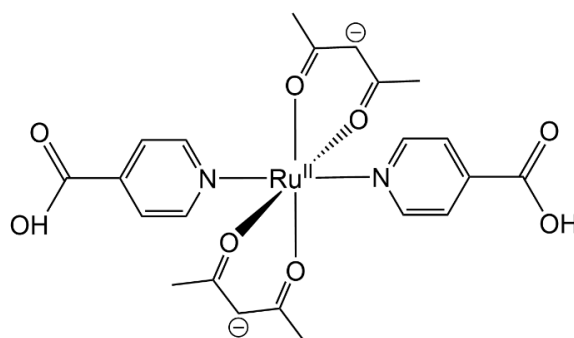


Figure 6.1. *trans*-bis(acetylacetonato)di(*iso*-nicotinic acid)ruthenium(II)

Another route of functionalisation or modification not yet discussed is *via* the bidentate acetylacetonato ligands. Functionalisation of this motif could be achieved by employing the diketone dimer 1,1,2,2-tetraacetylane (TAE), which would radically alter the coordination environment and geometry of the metalloligand. For example, the coordination complex *trans*-bis(1,1,2,2-tetraacetylane)di(4,4'-bipyridine)ruthenium(II) ($[\text{Ru}^{\text{II}}(\text{TAE})_2(\text{bpy})_2]^{2+}$) (Figure 6.2) could be employed as a four-coordinate metalloligand with a unique coordination geometry. Given the reactivity of RuCl_3 with acetylacetone, more exotic materials are conceivable, such as a functionalised 1D polymer $[\text{trans-Ru}(\text{TAE})\text{Cl}_2]_n$. TAE has previously been employed in the synthesis of 1- and 2D CPs with Cu.²⁶²⁻²⁶⁴

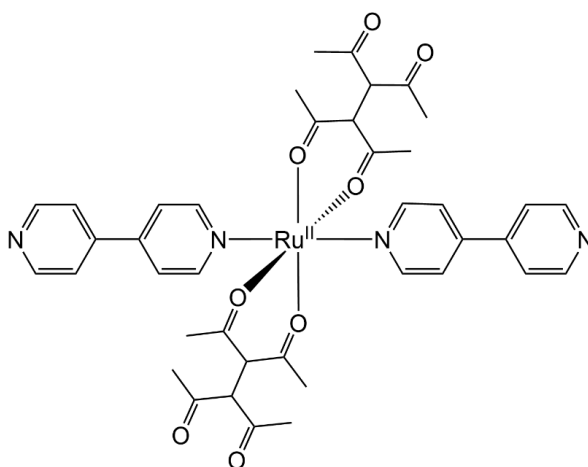


Figure 6.2. *trans*-bis(1,1,2,2-tetraacetylane)di(4,4'-bipyridine)ruthenium(II)

The *trans*-[Ru(acac)₂(X)₂] family may also be a viable candidate for combination with other ruthenium synthons. One highly versatile complex is [Ru^{II}(DMSO)₄Cl₂],²⁶⁵⁻²⁶⁶ which in both *cis*- and *trans*- isomers has been used to produce numerous coordination complexes, including [Ru(py)₄Cl₂],²⁶⁵ which indicates that four-coordinate metalloligands, such as [Ru^{II}(4,4'-bpy)₄Cl₂] should be viable (Figure 6.3A). Furthermore, employing *trans*-[Ru(acac)₂(X)₂] metalloligands as the substituting ligand could lead to exotic metalloligands, such as the pentamer *trans*-[Ru^{II}(*trans*-Ru^{II}(acac)₂(bpy)₂)₄Cl₂] (Figure 6.3B). Such a material would have unique redox chemistry and spectroscopic qualities.

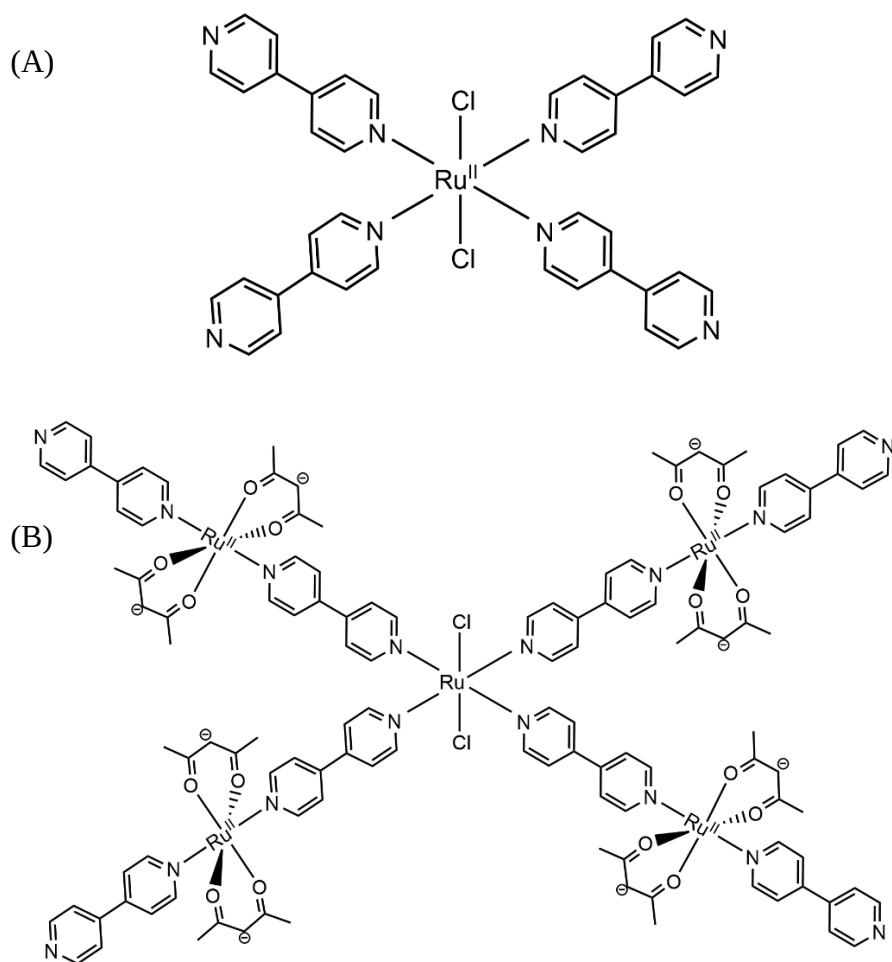


Figure 6.3. Possible metalloligands employing the *trans*-tetrakis-[Ru(X)₄Cl₂] motif. (A) *trans*-[Ru^{II}(4,4'-bpy)₄Cl₂] (B) *trans*-[Ru^{II}(*trans*-Ru^{II}(acac)₂(bpy)₂)₄Cl₂]

The current work has shown the variable nature of electronic-adjacent properties depending on the ligand X in the *trans*-[Ru(acac)₂(X)₂] family. However, geometric trends such as ligand flexibility were not explored in depth and pose interesting possibilities for future framework design. For example, attempts to synthesise RuML2 analogues of the 1D zinc polymers [ZnX₂RuML₄]_n (X = Cl, Br) resulted in an amorphous solid product. This result indicated that the coordination geometry of RuML₄ facilitated true crystallisation of the framework. The geometric flexibility of BPE permits several distinct coordination angles for the RuML₄ metalloligand, which marks it as unique among the materials discussed in this work. Applying the RuML₄ metalloligand, and related, similarly flexible systems such as *trans*-[Ru(acac)₂(1,2-bis(4-pyridyl)ethane)₂] and *trans*-[Ru(acac)₂(4,4'-trimethylenedipyridine)₂] (Figure 6.4) could lead to solid-state materials that are highly flexible and thereby capable of many phase-transitions and tuneable porosity.

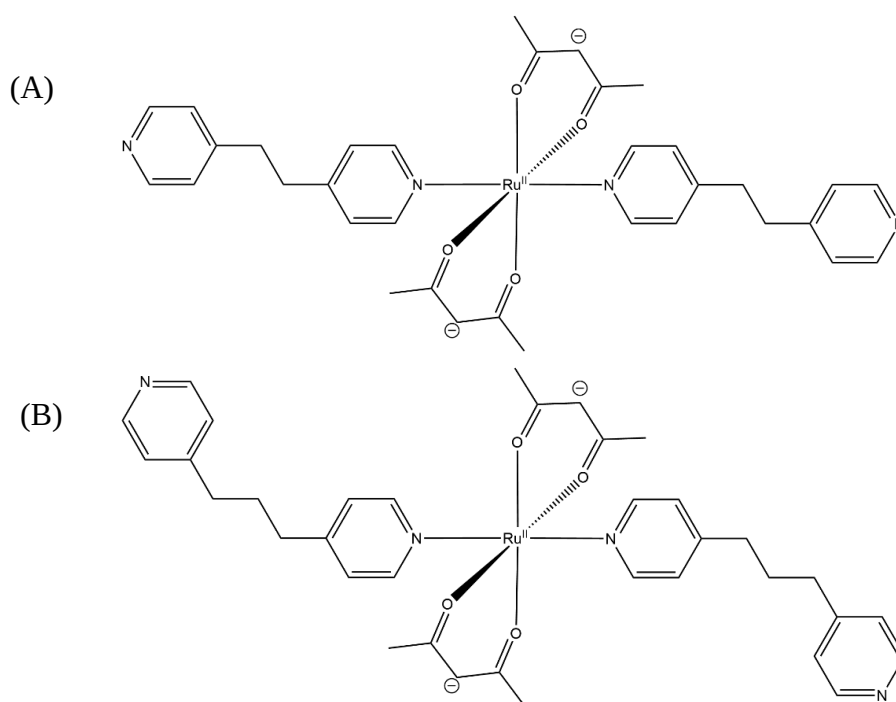


Figure 6.4. Potential *trans*-[Ru(acac)₂(X)₂] metalloligands with flexible pyridyl ligands (A) *trans*-[Ru^{II}(acac)₂(1,2-bis(4-pyridyl)ethane)₂] (B) *trans*-[Ru^{II}(acac)₂(4,4'-trimethylenedipyridine)₂]

6.2.2. Polymers

An initial target of this work that has not yet been achieved was the production of long-range charge transport *via* π -backbonded bridges. A major hurdle for this goal was the difficulty in producing polymers with the same symmetry as the metalloligand metals. The polymers described in Chapter 4 have tetrahedral nodes. Attempts to use octahedral nodes, such as Fe(II) and Fe(III) were unsuccessful, either due to steric restrictions or reagent inertness. However, some promising targets exist for the *trans*-[Ru(acac)₂(X)₂] family. Porphyrin paddlewheel frameworks (PPFs) are a uniquely variable family of MOFs.²⁶⁷⁻²⁷¹ Choi, *et al.* demonstrated that this family of frameworks have topologies dependent on the coordination environment of chelated metals within the porphyrin ligand,²⁶⁸ which was used to produce a linear chain of [Co(4,4'-bpy)] with the octahedral porphyrin CoTCCP (TCCP = tetrakis(4-carboxyphenyl)porphine) (Figure 6.5). With this topology in mind, we can envision an extended material with a similar linear chain employing a *trans*-[Ru(acac)₂X₂] metalloligand. Octahedral metallocorroles would have to be chosen to facilitate long-range charge transport, such as iron,²⁷²⁻²⁷⁵ and ruthenium.^{270,276-277}

Ligand-exchange reactions with acetylacetonato ligands are well-documented in the literature.²⁷⁸⁻²⁷⁹ Post-synthetic modification of a metallopolymer *via* ligand exchange of acetylacetonato ligands was first achieved by Dobrzynski, who exchanged acac ligands for ϵ -caprolactone on a Zr node.²⁸⁰ Similar ligand exchange mechanisms may be possible for the polymers discussed in Chapter 4. For example, exchange of acac for 2,4-diketones with functionalised 1-, 5-, or 3- positions in the 3D CP [Ag(RuML₂)₂](SbF₆)₃ may lead to entirely different framework topologies, pore sizes and shapes.

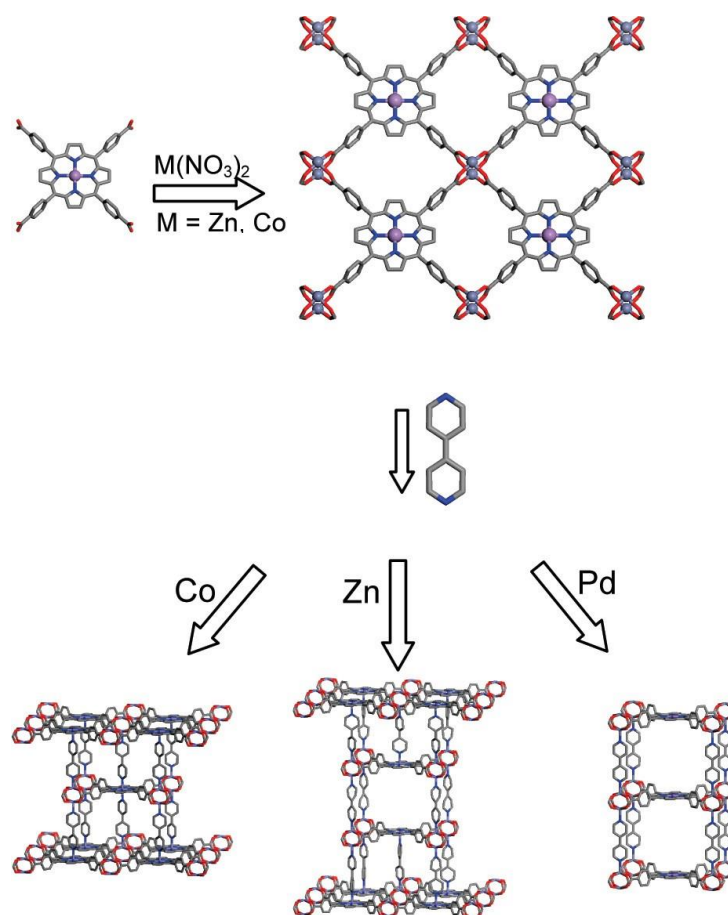


Figure 6.5. Schematic representation of the differing topologies produced by altering the metal coordinated by TCCP in PPF syntheses. Figure reprinted with permission from ACS.²⁶⁸

6.3. Future Work- Spectroscopy

6.3.1. Pressure-Dependent Studies

The range of flexibility and coordination angle of the RuML4 metalloligand provides an interesting avenue of investigation to derived polymer materials. Pressure-dependent Raman spectroscopy (PDRS) and pressure-dependent single-crystal X-ray diffraction (PDSCXRD) are achieved by applying pressure in a diamond anvil cell (DAC). These techniques could be used to investigate the crystallinity, phase and bond environment of RuML4 polymers under high pressures. As discussed in Section 6.2.1, there is potential in the *trans*-[Ru(acac)₂(X)₂] family

for an enormous range of flexibility of ligand, and thus future polymer materials. Investigation of these materials with high-pressure spectroscopy and XRD may lead to new polymer topologies, phases and porosity.

6.3.2. Magnetic Circular Dichroism

Circular dichroism (CD) is a spectroscopic technique that measures the difference between absorbance of left circularly polarised (LCP) and right circularly polarised (RCP) light. Without a magnetic field, this technique is only applicable to chiral materials, which interact with LCP and RCP differently.²⁸¹ Magnetic circular dichroism (MCD) is a more widely applicable technique, capable of producing a signal with non-chiral materials. MCD involves the application of a magnetic field in the same direction as the propagation of light.¹⁸⁶ The introduction of a magnetic field to a CD measurement influences the differential absorption of light. The magnetic field in an MCD experiment interacts with the electronic orbitals of a material *via* the Zeeman effect, in which the degeneracy of orbitals is broken by an applied magnetic field.

Low-temperature MCD measurements can provide substantial information about the ground state of a material. This includes identifying molecular G-values, zero-field splitting, and band polarisations.²⁸² This has led to the identification of transitions and their polarisations in numerous Group 8 charge-transfer complexes.^{125,220,283-286}

6.3.3. Depolarisation Ratios for Raman Spectroscopy

In Chapter 3 and 4, we presented several resonance Raman studies of related metal complexes. In most cases, this provided information about the symmetry of the molecule and the excited state orbitals of the many transitions in these complexes. In these analyses, we characterised Raman modes and their symmetry by reference to DFT models of the molecules. However,

this system was far from perfect, as Raman modes in the simulated spectra typically occurred at higher energies than was observed experimentally.

The depolarisation ratio of a Raman mode is used to establish its symmetry experimentally.^{131,287-288} This can be achieved by linearly polarising the outgoing Raman signal of a measurement before it reaches the detector. By polarising the signal perpendicular and parallel to the polarisation of the initial excitation, the depolarisation ratio (ρ) is obtained by dividing the signal of the perpendicular polarised spectrum by the parallel polarised spectrum.

Smaller values of ρ result from higher symmetry vibrational modes.^{167,289} Therefore, we would expect most Raman modes described in Chapters 3 and 4 to have depolarisation ratios close to 0. However, the technique may reveal mischaracterisations, as well as formerly forbidden modes present in the Raman spectra *via* vibronic coupling. Thus, the technique would allow a more complete picture of the resonance Raman spectroscopy presented in Chapters 3 and 4.

6.3.4. Basicity Calculations

Protonation of pyridyl complexes can provide insight into the competing electronic interactions within a molecule. Hasegawa *et al.* reported the pK_a of *trans*-[Ru(acac)₂(pyz)₂] and *trans*-[Ru(acac)₂(pyz)(pyzH)]⁺, showing the substantial contribution of acac⁻ ligands to the basicity of the pyz ligands in this complex.²⁹⁰ Similar investigations with other members of the *trans*-[Ru(acac)₂(X)₂] family were planned, but ultimately not performed due to time constraints. One significant obstacle to these measurements was the insolubility of *trans*-[Ru^{II}(acac)₂(X)₂] in H₂O. Hasegawa, *et al.* employed a mixture of H₂O and MeOH as the solvent in their measurements, which introduces error into the pK_a measurement, as the activity of H₂O:MeOH in the protonation equilibria is significantly different to H₂O. However, the solubility of RuML2 and RuML4 in MeOH is negligible, which would prevent a proper comparison of the basicity of each complex. One approach to this problem would be to use the Ru(III) complexes,

which dissolve in more polar media. However, as demonstrated throughout Chapter 3, the electronic delocalisation of electron density over the pyridyl ligands in the Ru(II) and Ru(III) complexes are vastly different, and would likely produce very different results.

6.4. Future Work- Chapter 5

There are several routes of investigation open to the work presented in Chapter 5. Further electrochemical measurements would likely enable more precise description of the host material/s within Ru(pyz)@UiO-66-(HSO₃)₂ as the dimer [(NH₃)₅Ru^{II}(μ-pyz)Ru^{II}(NH₃)₅]⁴⁺ or the monomer [(NH₃)₅Ru^{II}(pyz)]²⁺. Additionally, further bulk electrolysis and SEC experiments may permit observation of the IVCT transition present in the [(NH₃)₅Ru^{III}(μ-pyz)Ru^{II}(NH₃)₅]⁵⁺ dimer.

EPR spectroscopy would detect the presence of Ru(III) or a mixed-valence dimer, although spectroscopic data presented in Chapter 5 are already indicative of Ru(II).

6.5. Conclusion

The future of charge-transfer materials remains an exciting field of study, particularly with regards to ruthenium. Throughout this work we have demonstrated that many of the more desirable attributes of ruthenium complexes, including charge-transfer, stable electrochemistry and electrochromism are within reach for ruthenium extended materials. This work has also elucidated trends unique to the *trans*-[Ru(acac)₂(X)₂] family of complexes, due to competing interactions between ligands. We believe that this family of complexes, and ruthenium pyridyl complexes in general are exciting targets for future investigations into extended materials.

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Appendix A

Supplementary Information

Table A.1. List of iR compensation values for CV measurements in Chapters 3, 4, 5.

Sample	Target Couple	Scan Rate (mV/s)	iR Compensation (Ω)
RuMLPRE	Ru(III/II)	800	239
	Ru(IV/III)	50	297
		100	297
		200	297
		400	297
		800	297
RuML1	Ru(III/II)	50	458
		100	456
		200	446
		400	453
		800	512
RuML2	Ru(III/II)	50	463
		100	463
		200	463
		400	463
		800	463
RuML4	Ru(III/II)	50	488
		100	463
		200	439
		400	439
		800	463

RuML0	Ru(III/II)	50	597
		100	595
		200	595
		400	592
		800	592
[Ag(RuML2) ₂](SbF ₆) ₃ · <i>n</i> EtOH	Ru(III/II)	100	403
[ZnCl ₂ (RuML4)]	Ru(III/II)	50	514
		100	499
		200	246
		400	263
		800	289
[ZnBr ₂ (RuML4)]	Ru(III/II)	50	511
		100	511
		200	511
		400	490
		800	484
UiO-66-(HSO ₃) ₂	N/A	100	465
Ru(pyz)@UiO-66-(HSO ₃) ₂	Ru(III/II)	100	465

Table A.2. List of spectral resolution parameters for UV-vis measurements in Chapters 3, 4, 5.

Sample	Experiment	UV-vis Data Interval (cm ⁻¹)	UV-vis Scan Rate (cm ⁻¹ 1/min)	NIR Data Interval (cm ⁻¹)	NIR Scan Rate (cm ⁻¹ 1/min)
RuML0	Solution- state SEC	10	6000	-	-
RuML4	Solution- state SEC	10	9090.9	2.75	5000
RuML1	Solution- state SEC	10	6000	-	-
RuML2	Solution- state SEC	10	6000	-	-
RuMLPRE	Solution- state	10	9090.9	2.0	3636.4
UiO-66-(HSO ₃) ₂	Diffuse reflectance	10	6000	11.08	8000
Ru(pyz)@UiO-66-(HSO ₃) ₂	Diffuse reflectance	10	6000	11.08	8000
[Ag(RuML2) ₂](SbF ₆) ₃ ·nEtOH	Diffuse reflectance	10	6000	-	-
[(NH ₃) ₅ Ru ^{II} (pyz)] ³⁺	Solution- state	10	6000	-	-

$[(\text{NH}_3)_5\text{Ru}^{\text{III}}(\text{pyz})]^{2-}$	Solution-state	10	6000	-	-
$[(\text{NH}_3)_5\text{Ru}^{\text{II}}(\mu\text{-pyz})\text{Ru}^{\text{II}}(\text{NH}_3)_5]^{6-}$	Solution-state	10	6000	-	-
$[(\text{NH}_3)_5\text{Ru}^{\text{III}}(\mu\text{-pyz})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{4-}$	Solution-state	10	6000	-	-

Appendix B

Crystallographic Data Tables

Table B.1. Crystallographic data for RuMLPre

Chemical Formula	C ₂₄ H ₂₀ P · C ₁₀ H ₁₄ O ₄ Cl ₂ Ru
<i>M_r</i>	709.58
Temperature/K	100(2)
Crystal System	Triclinic
Space Group	<i>P</i> $\bar{1}$
<i>a</i> /Å	9.8414(4)
<i>b</i> /Å	13.3460(5)
<i>c</i> /Å	14.1566(5)
α /°	103.325(3)
β /°	106.915(3)
γ /°	107.891(3)
<i>V</i> /Å ³	1585.00(11)
<i>Z</i> (<i>Z'</i>)	2(1)
Radiation Type	CuK α
ρ_{calc} /gcm ⁻³	1.491
μ /mm ⁻¹	6.329
<i>F</i> (000)	730
Crystal Size/mm ³	0.27 x 0.159 x 0.051
2 θ range for data collection/°	3.485 to 72.456
<i>T_{min}</i> , <i>T_{max}</i>	0.456, 1.000
Reflections Collected	6106
<i>R_{int}</i>	0.0289
<i>R_{sigma}</i>	0.0391
<i>R</i> ₁ [<i>I</i> ≥ 2σ(<i>I</i>), all data] ^[a]	0.0280, 0.0318
<i>wR</i> ₂ [<i>I</i> ≥ 2σ(<i>I</i>), all data] ^[b]	0.0703, 0.0733
Data/restraints/parameters	6106/0/386
GoF	1.026
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ / e Å ⁻³	0.676, -0.733

^[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^[b] $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$.

Table B.2. Crystallographic data for RuML1

Chemical Formula	C ₁₈ H ₂₂ N ₄ O ₄ Ru
M_r	459.46
Temperature/K	100(2)
Crystal System	Monoclinic
Space Group	$P2(1)/n$
$a/\text{\AA}$	8.0342(4)
$b/\text{\AA}$	9.1936(5)
$c/\text{\AA}$	12.9978(5)
$\alpha/^\circ$	90
$\beta/^\circ$	93.522(4)
$\gamma/^\circ$	90
$V/\text{\AA}^3$	958.25(8)
$Z(Z')$	2(0.5)
Radiation Type	CuK α
$\rho_{\text{calc}}/\text{gcm}^{-3}$	1.592
μ/mm^{-1}	6.896
$F(000)$	468
Crystal Size/ mm^3	0.009 x 0.013 x 0.231
2θ range for data collection/ $^\circ$	5.899 to 72.482
$T_{\text{min}}, T_{\text{max}}$	0.560, 1
Reflections Collected	1846
R_{int}	0.0287
R_{sigma}	0.0415
$R_1 [I \geq 2\sigma(I), \text{all data}]^{[a]}$	0.0285, 0.0390
$wR_2 [I \geq 2\sigma(I), \text{all data}]^{[b]}$	0.0653, 0.0697
Data/restraints/parameters	1846/0/126
GoF	1.038
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}} / \text{e \AA}^{-3}$	0.473, -0.447

$$^{[a]} R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|. \quad ^{[b]} wR_2 = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}.$$

Table B.3. Crystallographic data for RuML2 in *Fdd2*

Chemical formula	C ₃₀ H ₃₀ N ₄ O ₄ Ru
M_r	611.65
Temperature/K	100.01(10)
Crystal system	orthorhombic
Space group	<i>Fdd2</i>
$a/\text{\AA}$	13.7968(5)
$b/\text{\AA}$	33.4689(14)
$c/\text{\AA}$	24.0029(9)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
$V/\text{\AA}^3$	11083.6(7)
$Z(Z')$	16(1)
$\rho_{\text{calc}}/\text{gcm}^{-3}$	1.466
μ/mm^{-1}	4.926
$F(000)$	5024.0
Crystal size/ mm^3	0.097 x 0.020 x 0.014
Radiation Type	CuK α
2Θ range for data collection/ $^\circ$	7.85 to 144.116
Reflections collected	7837
$T_{\min}, T_{\max}$	0.783, 0.981
R_{int}	0.0344
R_{sigma}	0.0501
$R_1 [I \geq 2\sigma(I), \text{all data}]^{[a]}$	0.0597, 0.0733
$wR_2 [I \geq 2\sigma(I), \text{all data}]^{[b]}$	0.1405, 0.1467
Data/restraints/parameters	4112/2015/605
GoF	1.306
$\Delta\rho_{\max}, \Delta\rho_{\min} / \text{e \AA}^{-3}$	0.537, -0.685
Flack parameter	0.51(2)

^[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. ^[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$.

Table B.4. Crystallographic data for RuML2 in $C2/c$

Chemical formula	$C_{30}H_{30}N_4O_4Ru$
M_r	611.65
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$C2/c$
$a/\text{\AA}$	23.975(5)
$b/\text{\AA}$	13.787(3)
$c/\text{\AA}$	20.549(4)
$\alpha/^\circ$	90
$\beta/^\circ$	125.42(3)
$\gamma/^\circ$	90
$V/\text{\AA}^3$	5535(3)
$Z(Z')$	8(1)
$\rho_{\text{calc}}/\text{gcm}^{-3}$	1.468
μ/mm^{-1}	0.609
$F(000)$	2512.0
Crystal size/ mm^3	0.05, 0.05, 0.1
Radiation Type	$\text{MoK}\alpha$
2Θ range for data collection/ $^\circ$	3.62 to 57.42
Reflections collected	24581
$T_{\min}, T_{\max}$	0.4201, 0.7464
R_{int}	0.1114
R_{sigma}	0.0881
$R_1 [I \geq 2\sigma(I), \text{all data}]^{[a]}$	0.1074, 0.1180
$wR_2 [I \geq 2\sigma(I), \text{all data}]^{[b]}$	0.2669, 0.2736
Data/restraints/parameters	7116/0/359
GoF	1.049
$\Delta\rho_{\max}, \Delta\rho_{\min} / \text{e \AA}^{-3}$	3.269, -1.565

$$^{[a]} R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^{[b]} wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$$

Table B.5. Crystallographic data for RuML2Cl · EtOH · H₂O in *P*2₁/*c*

Chemical formula	C ₃₀ H ₃₀ ClN ₄ O ₄ Ru · C ₂ H ₆ O · H ₂ O
<i>M</i> _r	711.18
Temperature/K	100.15
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	20.0291(11)
<i>b</i> /Å	9.1148(2)
<i>c</i> /Å	20.2899(10)
<i>α</i> /°	90
<i>β</i> /°	119.390(7)
<i>γ</i> /°	90
<i>V</i> /Å ³	3227.4(3)
<i>Z</i> (<i>Z'</i>)	4(1)
<i>ρ</i> _{calc} /gcm ⁻³	1.464
<i>μ</i> /mm ⁻¹	0.618
<i>F</i> (000)	1468.0
Crystal size/mm ³	0.059 x 0.103 x 0.331
Radiation Type	MoK _α
2 Θ range for data collection/°	4.016 to 54.968
Reflections collected	40938
<i>T</i> _{min} , <i>T</i> _{max}	0.528, 1
<i>R</i> _{int}	0.0724
<i>R</i> _{sigma}	0.0675
Data/restraints/parameters	7320/0/409
<i>R</i> ₁ [<i>I</i> ≥ 2σ(<i>I</i>), all data] ^[a]	0.0495, 0.0998
<i>wR</i> ₂ [<i>I</i> ≥ 2σ(<i>I</i>), all data] ^[b]	0.1003, 0.1178
GoF	1.041
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ / e Å ⁻³	0.985, -0.887

^[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. ^[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$.

Table B.6. Crystallographic data for RuML4Cl · (CHCl₃)₃ in $P\bar{1}$

Empirical formula	C ₃₄ H ₃₄ ClN ₄ O ₄ Ru · (CHCl ₃) ₃
M_r	2108.50
Temperature/K	100.15
Crystal system	triclinic
Space group	$P\bar{1}$
$a/\text{\AA}$	12.2256(5)
$b/\text{\AA}$	13.0790(5)
$c/\text{\AA}$	16.5973(5)
$\alpha/^\circ$	80.131(3)
$\beta/^\circ$	75.002(3)
$\gamma/^\circ$	89.599(3)
$V/\text{\AA}^3$	2523.60(17)
$Z(Z')$	1(0.5)
$\rho_{\text{calc}}/\text{gcm}^{-3}$	1.391
μ/mm^{-1}	7.700
$F(000)$	1066.0
Crystal size/ mm^3	0.022 x 0.208 x 0.250
Radiation Type	CuK α
2Θ range for data collection/ $^\circ$	5.6 to 146.112
Reflections collected	47195
$T_{\min}, T_{\max}$	0.528, 1
R_{int}	0.2112
R_{sigma}	0.0991
Data/restraints/parameters	9356/0/509
$R_1 [I \geq 2\sigma(I), \text{all data}]^{[a]}$	0.0951, 0.1257
$wR_2 [I \geq 2\sigma(I), \text{all data}]^{[b]}$	0.2627, 0.2952
GoF	1.082
$\Delta\rho_{\max}, \Delta\rho_{\min} / \text{e \AA}^{-3}$	2.011, -1.1

^[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. ^[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$.

Table B.7. Crystallographic data for RuML2.5 in $P\bar{1}$

Empirical formula	C ₂₄ H ₂₈ N ₂ O ₈ Ru
M_r	573.55
Temperature/K	293(2)
Crystal system	triclinic
Space group	$P\bar{1}$
$a/\text{\AA}$	7.1786(3)
$b/\text{\AA}$	8.0523(3)
$c/\text{\AA}$	11.0484(5)
$\alpha/^\circ$	78.204(4)
$\beta/^\circ$	83.585(3)
$\gamma/^\circ$	84.695(3)
$V/\text{\AA}^3$	619.65(5)
$Z(Z')$	1(0.5)
$\rho_{\text{calc}}/\text{gcm}^{-3}$	1.537
μ/mm^{-1}	5.560
$F(000)$	294.0
Crystal size/ mm^3	0.153, 0.063, 0.028
Radiation Type	CuK α
2Θ range for data collection/ $^\circ$	8.212 to 144.636
Reflections collected	5693
$T_{\min}, T_{\max}$	0.580, 0.946
R_{int}	0.0234
R_{sigma}	0.0272
Data/restraints/parameters	2399/0/163
$R_1 [I \geq 2\sigma(I), \text{all data}]^{[a]}$	0.0229, 0.0231
$wR_2 [I \geq 2\sigma(I), \text{all data}]^{[b]}$	0.0565, 0.0563
GoF	1.035
$\Delta\rho_{\max}, \Delta\rho_{\min} / \text{e \AA}^{-3}$	0.460, -0.646

^[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table B.8. Crystallographic data for RuML0 in $P2_1/n$

Empirical formula	$C_{20}H_{24}N_2O_4Ru$
M_r	457.48
Temperature/K	100.15
Crystal system	monoclinic
Space group	$P2_1/n$
$a/\text{\AA}$	8.13840(10)
$b/\text{\AA}$	9.40190(10)
$c/\text{\AA}$	13.12800(10)
$\alpha/^\circ$	90
$\beta/^\circ$	96.5170(10)
$\gamma/^\circ$	90
$V/\text{\AA}^3$	998.017(18)
$Z(Z')$	2(0.5)
$\rho_{\text{calc}}/\text{gcm}^{-3}$	1.522
μ/mm^{-1}	6.588
$F(000)$	468.0
Crystal size/ mm^3	$0.35 \times 0.04 \times 0.03$
Radiation Type	$\text{CuK}\alpha$
2Θ range for data collection/ $^\circ$	11.602 to 144.788
Reflections collected	19454
$T_{\min}, T_{\max}$	0.206, 0.827
R_{int}	0.0241
R_{sigma}	0.0115
Data/restraints/parameters	1958/0/126
$R_1 [I \geq 2\sigma(I), \text{all data}]^{[a]}$	0.0162, 0.0181
$wR_2 [I \geq 2\sigma(I), \text{all data}]^{[b]}$	0.0406, 0.0416
GoF	1.099
$\Delta\rho_{\max}, \Delta\rho_{\min} / e \text{\AA}^{-3}$	0.051

$$^{[a]} R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|. \quad ^{[b]} wR_2 = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}.$$

Table B.9. Crystallographic data for RuML0Cl in *C2/m*

Empirical formula	C ₂₀ H ₂₄ ClN ₂ O ₄ Ru
<i>M_r</i>	492.93
Temperature/K	100.0
Crystal system	monoclinic
Space group	<i>C2/m</i>
<i>a</i> /Å	19.5427(11)
<i>b</i> /Å	7.5070(4)
<i>c</i> /Å	8.3835(4)
α /°	90
β /°	96.537(2)
γ /°	90
<i>V</i> /Å ³	1221.92(11)
<i>Z</i> (<i>Z'</i>)	2(0.25)
$\rho_{\text{calc}}/\text{gcm}^{-3}$	1.340
μ/mm^{-1}	0.775
<i>F</i> (000)	502.0
Crystal size/mm ³	0.3 x 0.3 x 0.05
Radiation Type	MoK α
2 Θ range for data collection/°	4.196 to 63.122
Reflections collected	19594
<i>T_{min}</i> , <i>T_{max}</i>	0.624, 1
<i>R_{int}</i>	0.0529
<i>R_{sigma}</i>	0.0264
Data/restraints/parameters	2189/0/130
<i>R</i> ₁ [<i>I</i> ≥ 2σ(<i>I</i>), all data] ^[a]	0.0932, 0.0935
<i>wR</i> ₂ [<i>I</i> ≥ 2σ(<i>I</i>), all data] ^[b]	0.2625, 0.2629
GoF	1.191
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ / e Å ⁻³	8.868, -1.117

$$^{[a]}R_1 = \sum||F_o| - |F_c|| / \sum|F_o|. \quad ^{[b]}wR_2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}.$$

Table B.10. Crystallographic data for RuML0Cl · (CH₄O)₂ in *P*2₁/*n*

Formula	C ₂₀ H ₂₄ ClN ₂ O ₄ Ru · (CH ₄ O) ₂
<i>M</i> _r	550.02
Temperature/K	100.15
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	7.93990(10)
<i>b</i> /Å	17.5151(3)
<i>c</i> /Å	17.8330(2)
<i>α</i> /°	90
<i>β</i> /°	93.1450(10)
<i>γ</i> /°	90
<i>V</i> /Å ³	2476.27(6)
<i>Z</i> (<i>Z'</i>)	4(1)
<i>ρ</i> _{calc} /gcm ⁻³	1.475
<i>μ</i> /mm ⁻¹	6.395
<i>F</i> (000)	1132.0
Crystal size/mm ³	0.333, 0.258, 0.055
Radiation Type	CuK _α
2 Θ range for data collection/°	7.08 to 144.846
Reflections collected	9696
<i>T</i> _{min} , <i>T</i> _{max}	0.345, 1
<i>R</i> _{int}	0.1086
<i>R</i> _{sigma}	0.0035
Data/restraints/parameters	9696/30/321
<i>R</i> ₁ [<i>I</i> ≥ 2σ(<i>I</i>), all data] ^[a]	0.0629, 0.0644
<i>wR</i> ₂ [<i>I</i> ≥ 2σ(<i>I</i>), all data] ^[b]	0.1929, 0.1951
GoF	1.095
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ / e Å ⁻³	1.718, -1.216

^[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. ^[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$.

Table B.11. Crystallographic data for $[\text{Ag}(\text{RuML}2)_2](\text{SbF}_6)_3 \cdot (\text{C}_2\text{H}_6\text{O})_8$ in $P2_1/c$

Formula	$[\text{AgC}_{76}\text{F}_{18}\text{H}_{108}\text{N}_8\text{O}_{16}\text{Ru}_2\text{Sb}_3]_n$
M_r	2406.998
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
$a/\text{\AA}$	14.0097(9)
$b/\text{\AA}$	22.183(4)
$c/\text{\AA}$	28.444(2)
$\alpha/^\circ$	90
$\beta/^\circ$	90.867(7)
$\gamma/^\circ$	90
$V/\text{\AA}^3$	8838.8(18)
$Z(Z')$	4(1)
$\rho_{\text{calc}}/\text{gcm}^{-3}$	1.809
μ/mm^{-1}	12.529
$F(000)$	4813.7
Crystal size/ mm^3	0.078 x 0.065 x 0.018
Radiation Type	CuK_α
2Θ range for data collection/ $^\circ$	7.38 to 147.2
Reflections collected	37797
$T_{\min}, T_{\max}$	0.604, 0.897
R_{int}	0.2451
R_{sigma}	0.3438
Data/restraints/parameters	17077/988/909
$R_1 [I \geq 2\sigma(I), \text{all data}]^{[a]}$	0.1349, 0.3267
$wR_2 [I \geq 2\sigma(I), \text{all data}]^{[b]}$	0.3269, 0.5086
GoF	0.930
$\Delta\rho_{\max}, \Delta\rho_{\min} / \text{e \AA}^{-3}$	2.364, -1.623

^[a] $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. ^[b] $wR_2 = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}$.

Table B.12. Crystallographic data for [RuML4ZnCl₂] · (C₂H₆O)_{1.5} in C2/c

Empirical formula	[C ₃₄ H ₃₄ Cl ₂ N ₄ O ₄ RuZn · (C ₂ H ₆ O) _{1.5}] _n
<i>M_r</i>	884.61
Temperature/K	293(2)
Crystal system	monoclinic
Space group	C2/c
<i>a</i> /Å	11.2877(2)
<i>b</i> /Å	11.59170(10)
<i>c</i> /Å	34.5763(4)
<i>α</i> /°	90
<i>β</i> /°	96.779(2)
<i>γ</i> /°	90
<i>V</i> /Å ³	4492.46(10)
<i>Z</i> (<i>Z'</i>)	4(0.5)
<i>ρ</i> _{calc} /gcm ⁻³	1.308
<i>μ</i> /mm ⁻¹	4.825
<i>F</i> (000)	1814.0
Crystal size/mm ³	0.073 x 0.194 x 0.206
Radiation Type	CuK _α
<i>T</i> _{min} , <i>T</i> _{max}	0.48207, 1
2Θ range for data collection/°	10.306 to 148.204
Reflections collected	83776
<i>R</i> _{int}	0.0557
<i>R</i> _{sigma}	0.0168
Data/restraints/parameters	4430/3/255
<i>R</i> ₁ [<i>I</i> ≥ 2σ(<i>I</i>), all data] ^[a]	0.0641, 0.0677
<i>wR</i> ₂ [<i>I</i> ≥ 2σ(<i>I</i>), all data] ^[b]	0.1886, 0.1934
GoF	1.183
Δ <i>ρ</i> _{max} , Δ <i>ρ</i> _{min} / e Å ⁻³	1.936, -0.816

$$^{[a]}R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| \quad ^{[b]}wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$$

Table B.13. Crystallographic data for [RuML4ZnBr₂] · (C₂H₆O) in C2/c

Empirical formula	[(C ₃₄ H ₃₄ Br ₂ N ₄ O ₄ RuZn) · (C ₂ H ₆ O)] _n
<i>M_r</i>	934.98
Temperature/K	293(2)
Crystal system	monoclinic
Space group	C2/c
<i>a</i> /Å	11.2977(3)
<i>b</i> /Å	11.5836(3)
<i>c</i> /Å	34.9293(8)
<i>α</i> /°	90
<i>β</i> /°	97.740(3)
<i>γ</i> /°	90
<i>V</i> /Å ³	4529.5(2)
<i>Z</i> (<i>Z'</i>)	4(0.5)
<i>ρ</i> _{calc} /gcm ⁻³	1.371
<i>μ</i> /mm ⁻¹	5.728
<i>F</i> (000)	1872.0
Crystal size/mm ³	0.005 x 0.132 x 0.206
Radiation Type	CuK _α
2 Θ range for data collection/°	10.224 to 144.748
Reflections collected	19363
<i>T</i> _{min} , <i>T</i> _{max}	0.46445, 1
<i>R</i> _{int}	0.1422
<i>R</i> _{sigma}	0.0793
Data/restraints/parameters	4415/24/226
<i>R</i> ₁ [<i>I</i> ≥ 2σ(<i>I</i>), all data] ^[a]	0.1141, 0.1212
<i>wR</i> ₂ [<i>I</i> ≥ 2σ(<i>I</i>), all data] ^[b]	0.2996, 0.3037
GoF	1.122
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ / e Å ⁻³	3.461, -2.143

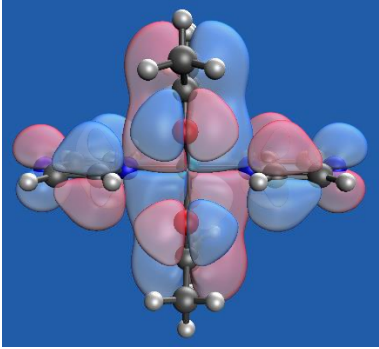
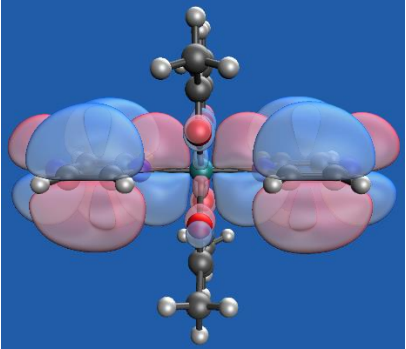
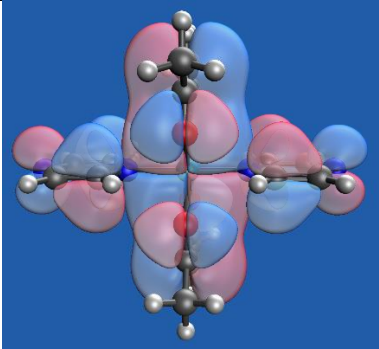
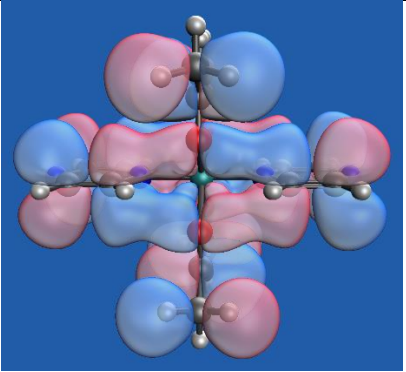
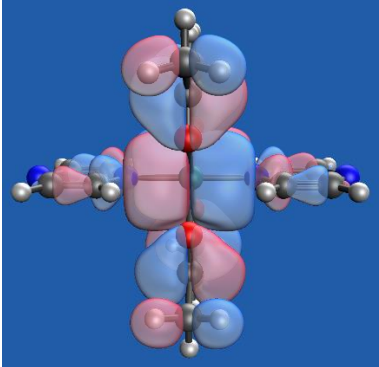
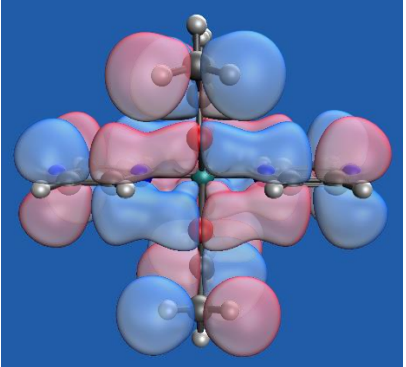
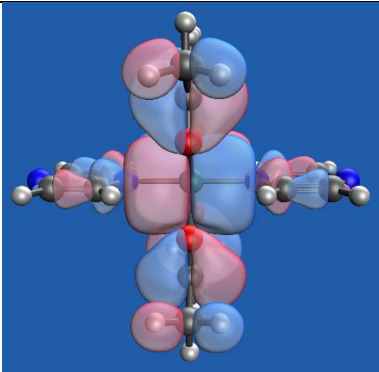
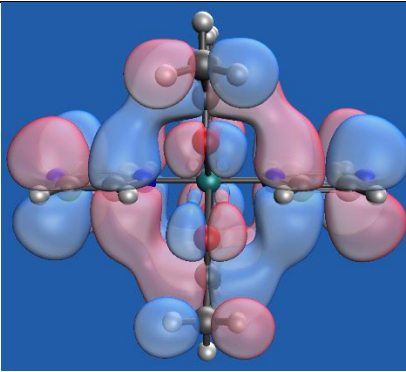
^[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. ^[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$.

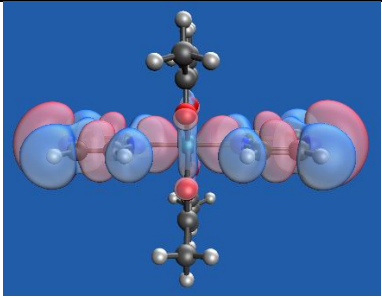
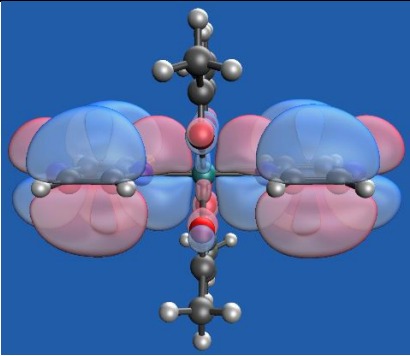
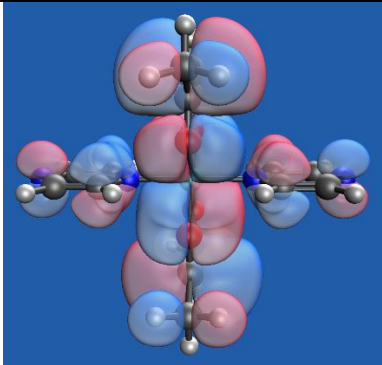
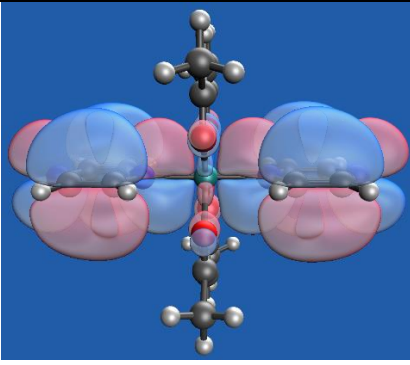
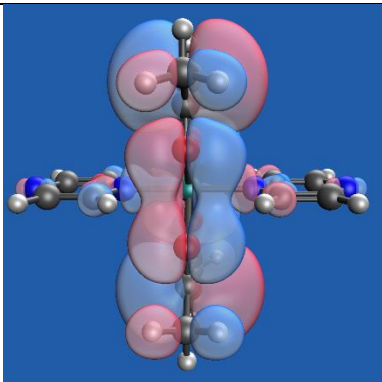
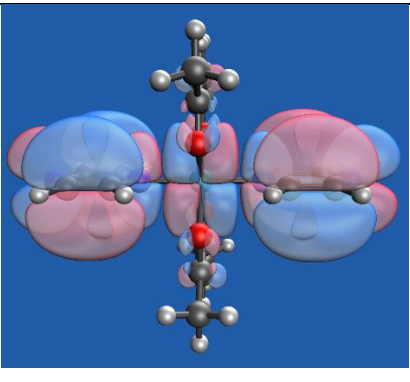
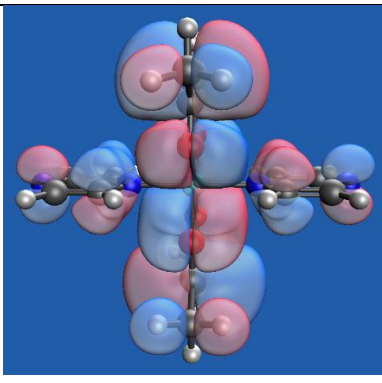
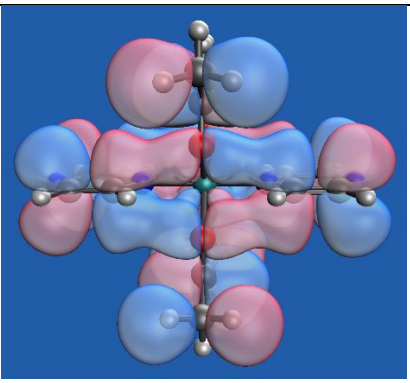
Appendix C

Supplementary Information,

Chapter 3

Table C.1. Simulated molecular orbitals for electronic transitions in *trans*-[Ru^{II}(acac)₂(pyz)₂], calculated with the CAM-B3LYP/def2-SVP method.¹⁷⁰

Transition Number	Orbital From	Orbital To
1		
2		
3		
4		

5		
6		
7		
8		

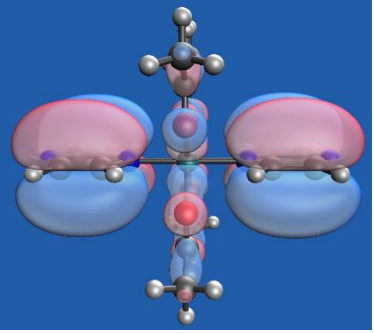
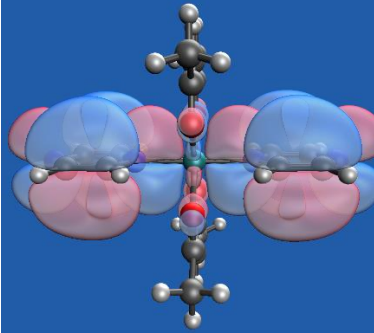
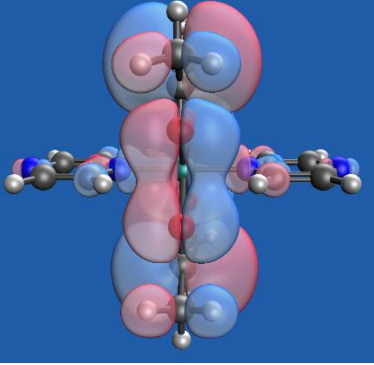
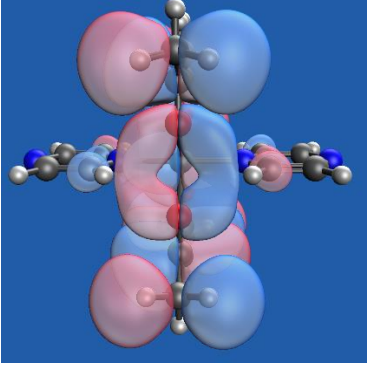
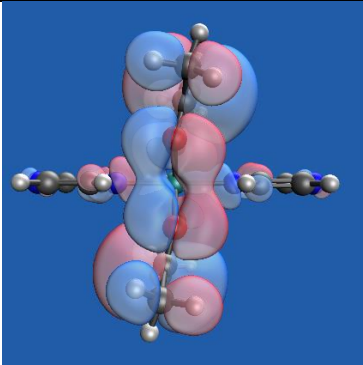
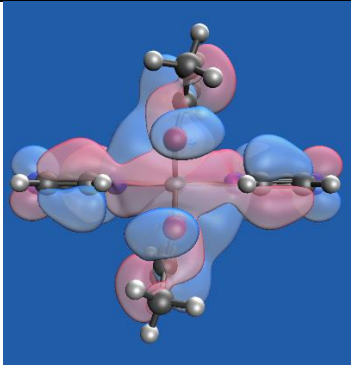
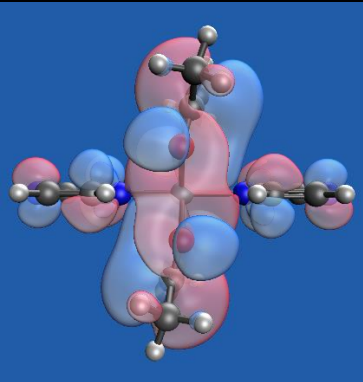
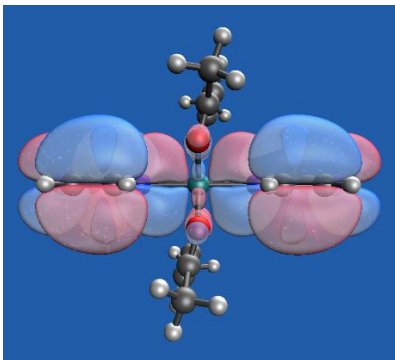
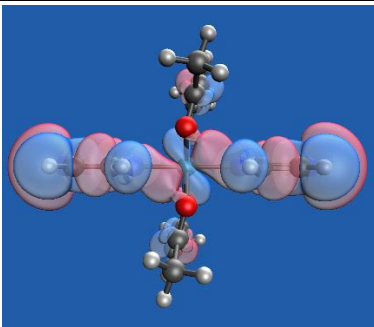
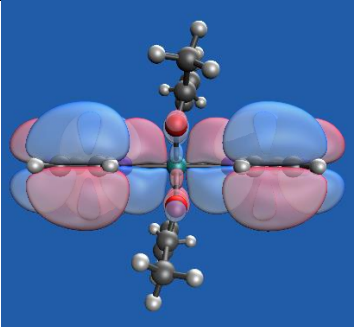
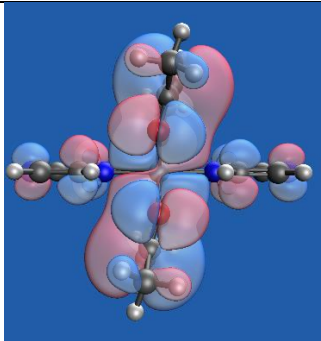
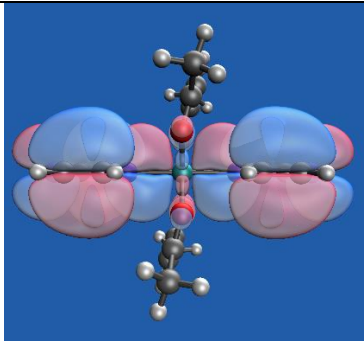
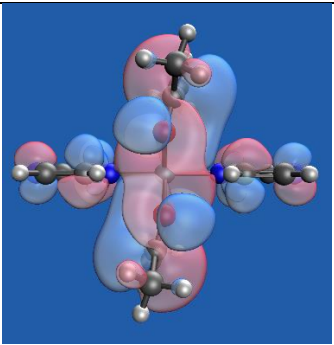
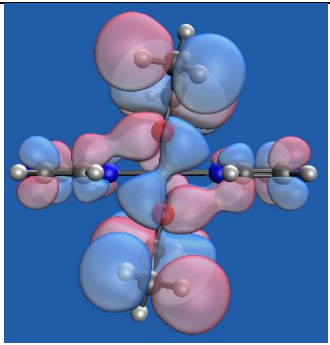
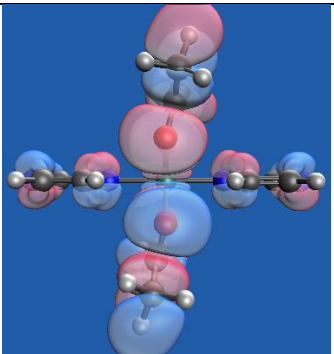
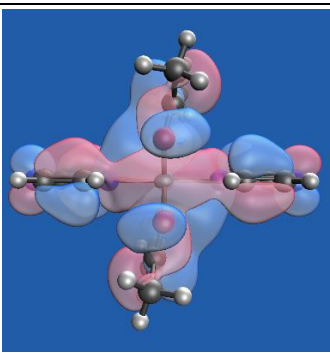
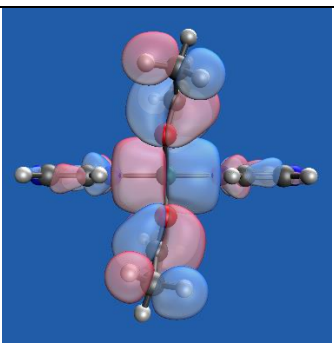
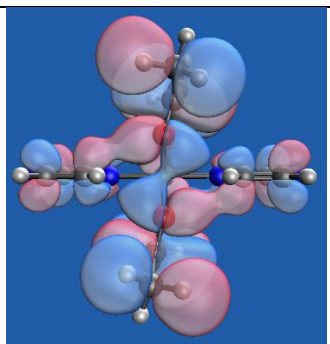
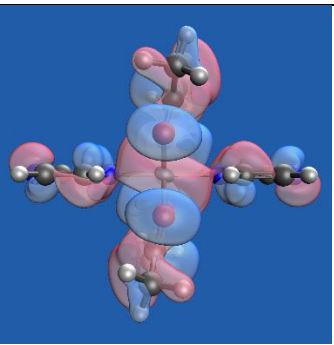
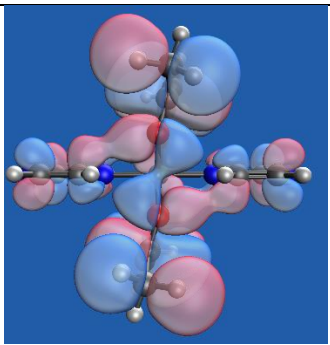
9		
10		

Table C.2. Simulated molecular orbitals for electronic transitions in *trans*-[Ru^{III}(acac)₂(pyz)₂]⁺, calculated with the CAM-B3LYP/def2-SVP method.

Transition Number	Orbital From	Orbital To
1		
2		
3		
4		

5		
6, 7		
8		
9, 10		

11

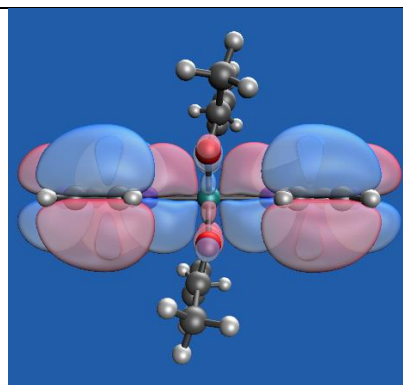
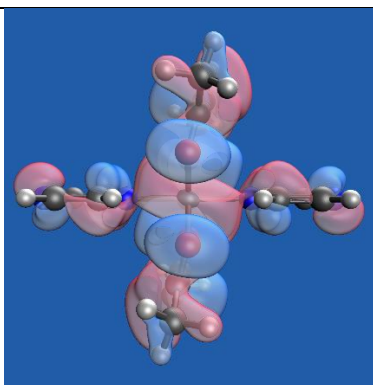
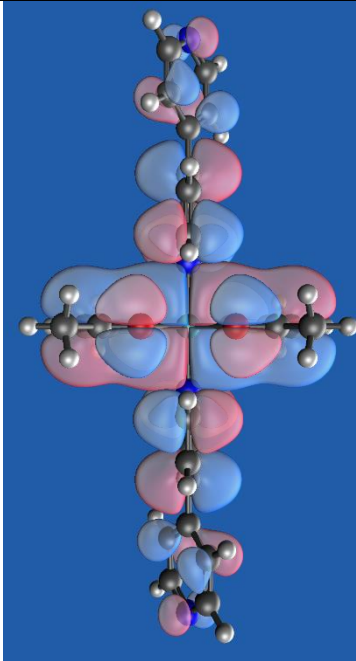
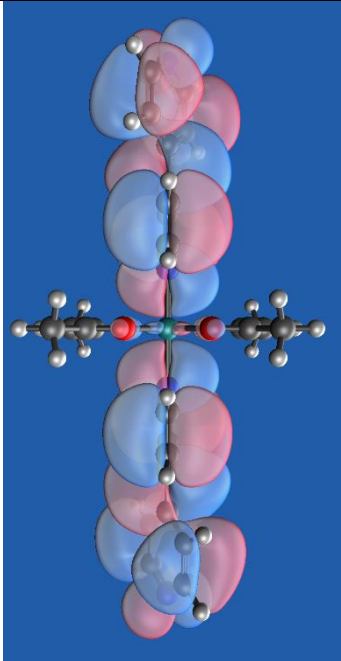
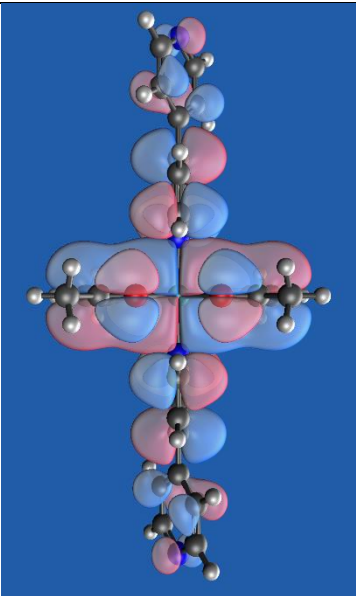
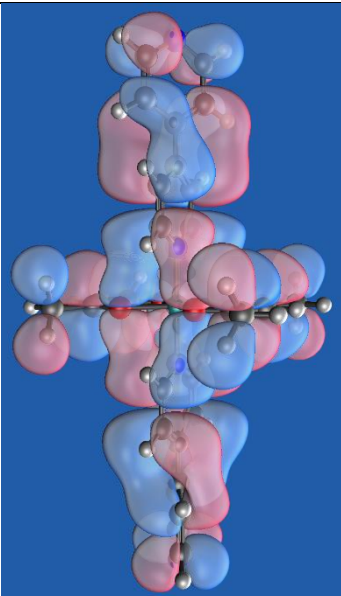
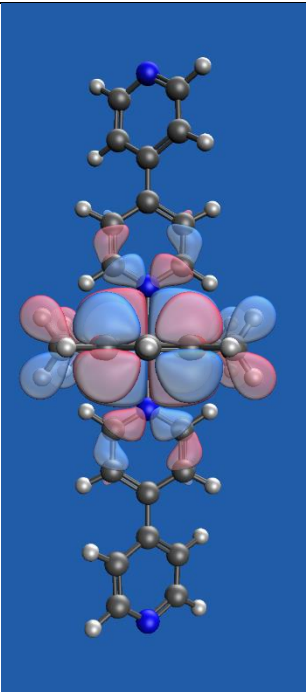
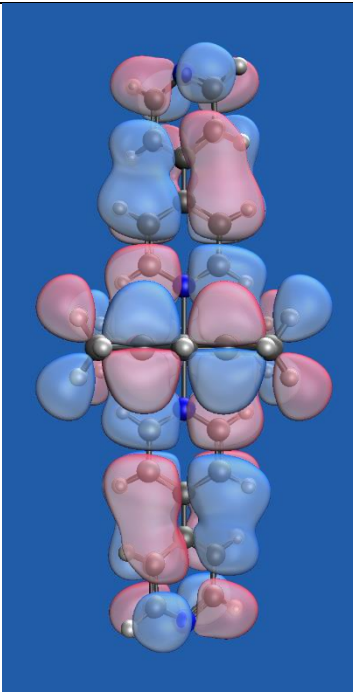
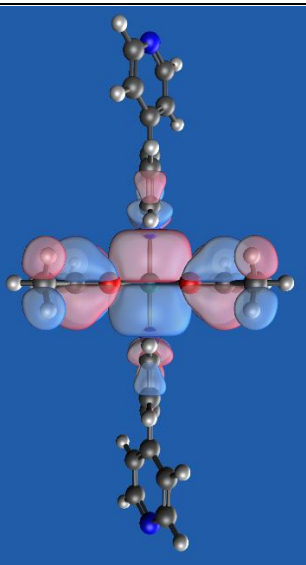
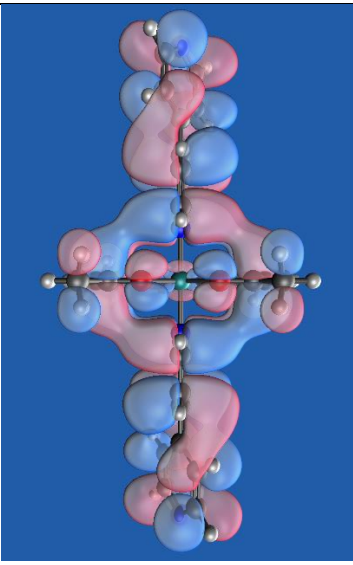
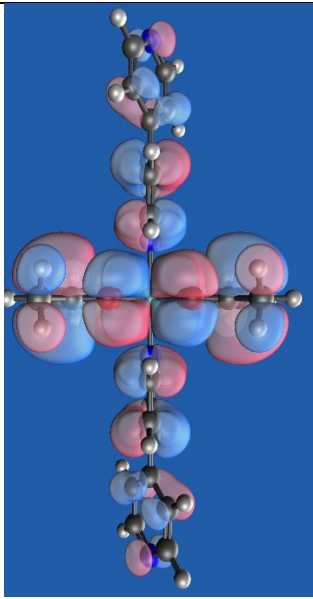
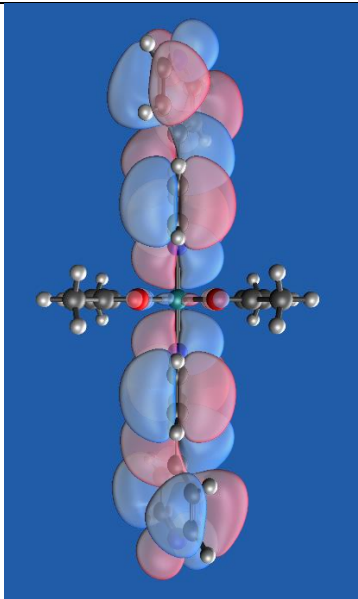
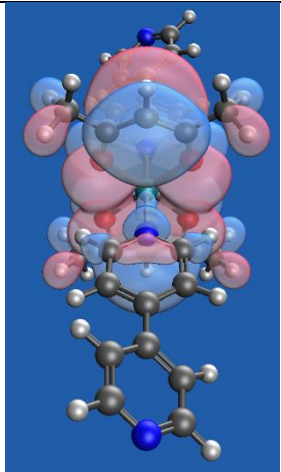
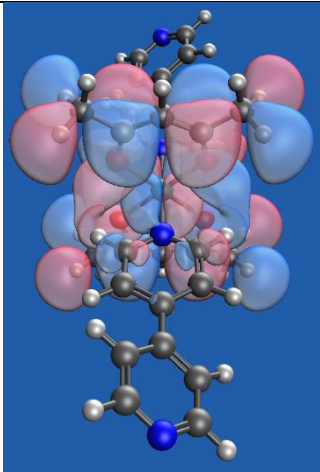
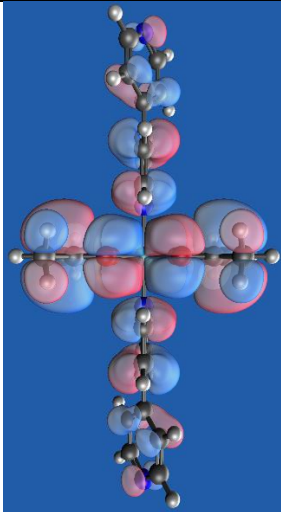
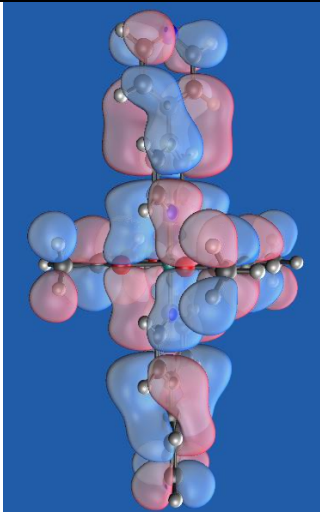


Table C.3. Simulated molecular orbitals for electronic transitions in *trans*-[Ru^{II}(acac)₂(bpy)₂], calculated with the CAM-B3LYP/def2-SVP method.

Transition Number	Orbital From	Orbital To
1		
2		

3		
4		

5		
6		
7		

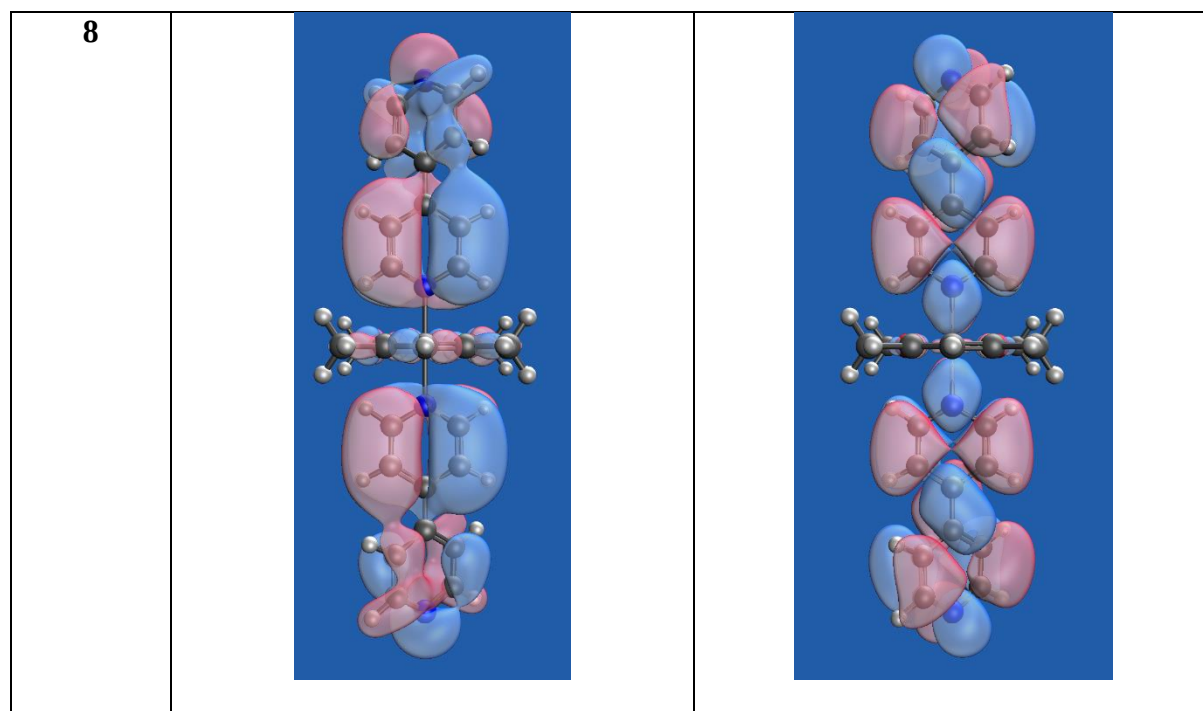
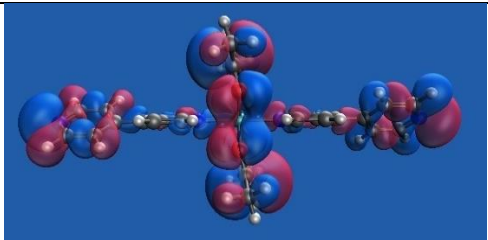
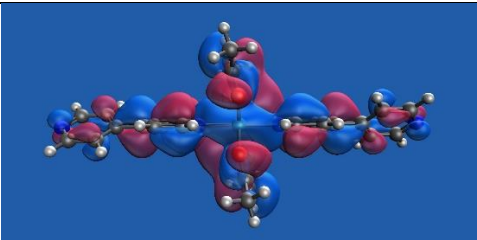
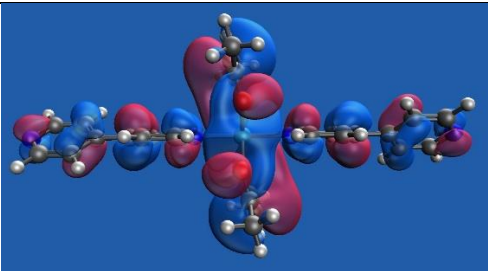
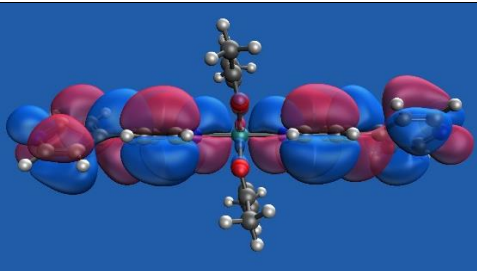
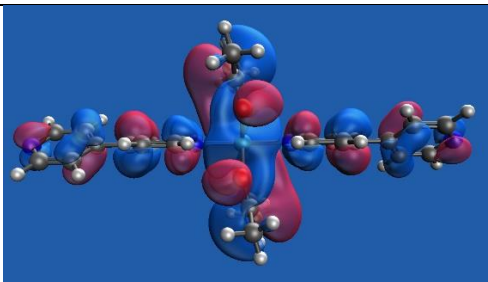
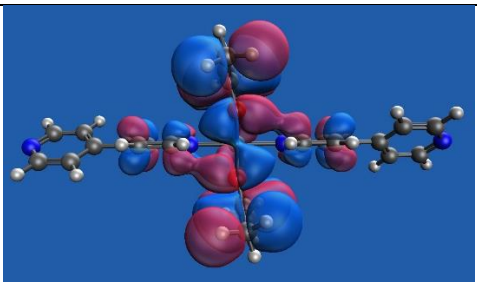
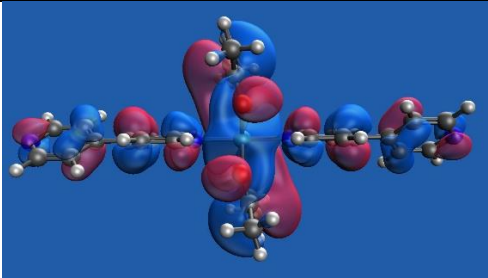
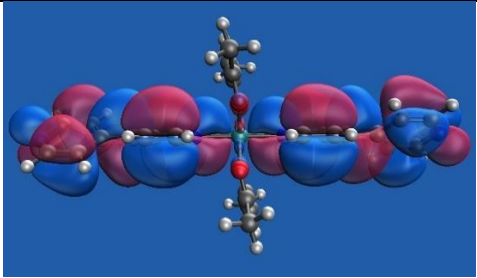
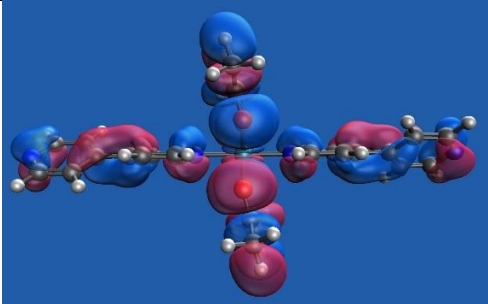
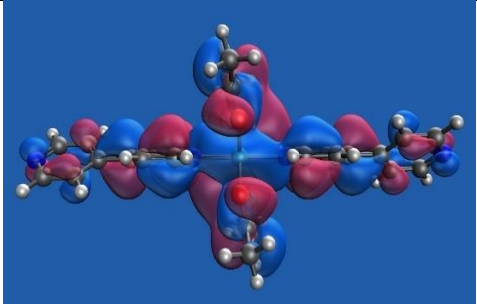
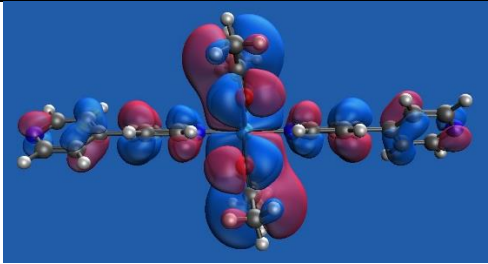
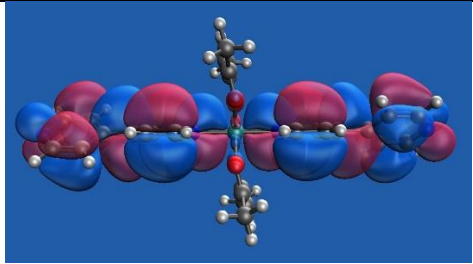
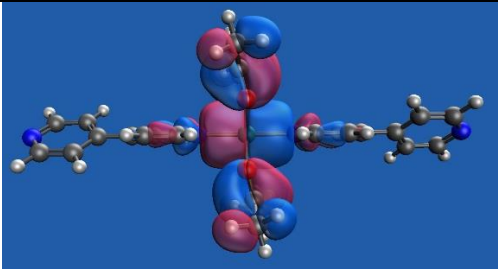
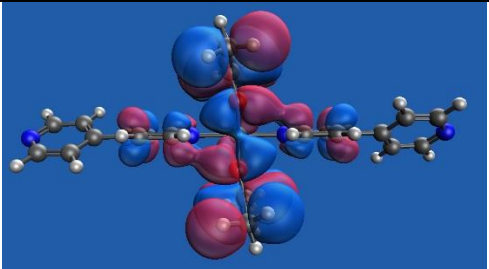
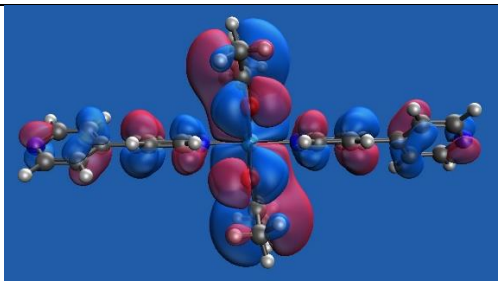
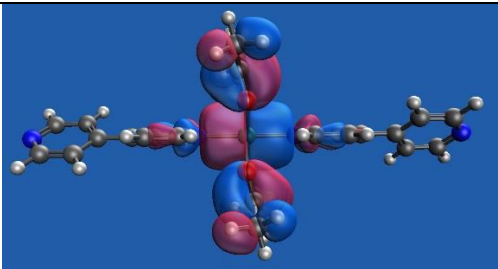
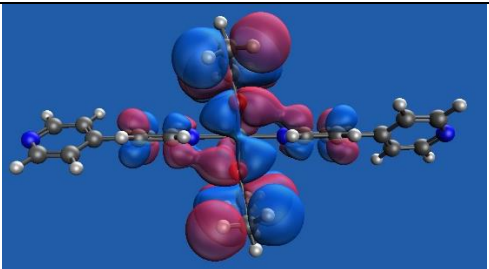
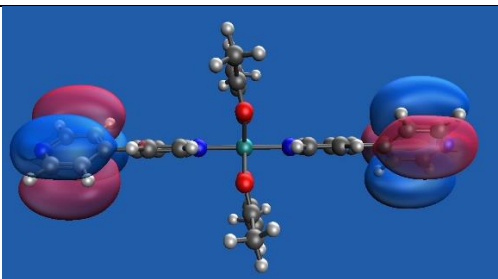
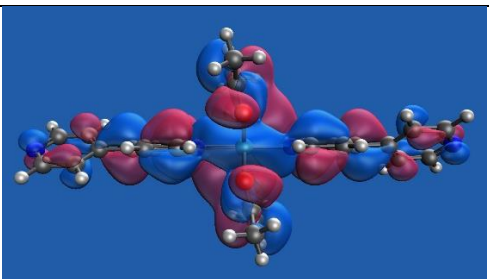
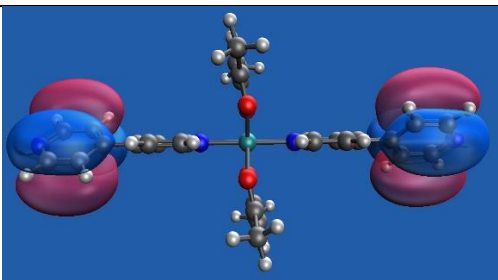
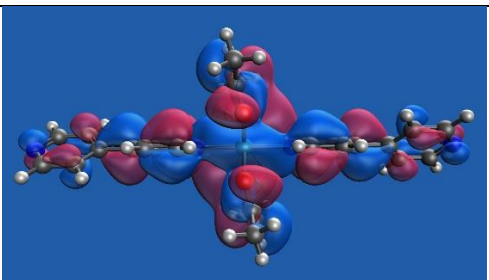


Table C.4. Simulated molecular orbitals for electronic transitions in *trans*-[Ru^{III}(acac)₂(bpy)₂]⁺, calculated with the CAM-B3LYP/def2-SVP method.

Transition Number	Orbital From	Orbital To
1		
2		
3		
4		
5		

6		
7		
8		
9		
10		
11		

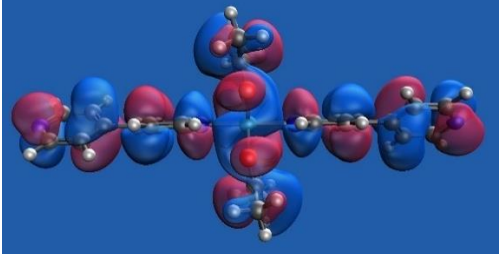
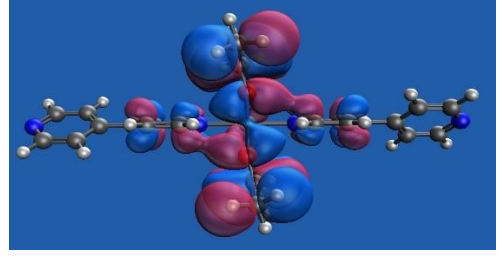
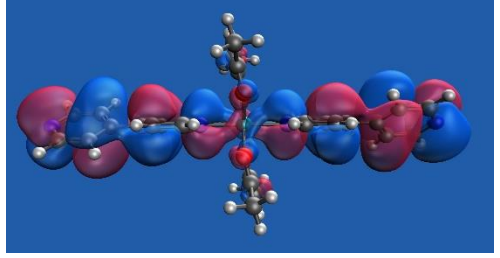
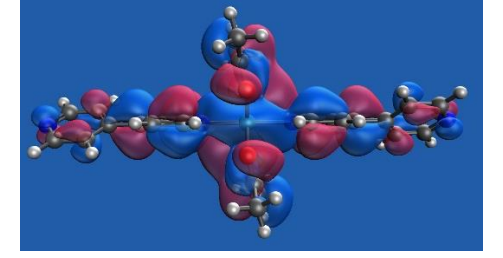
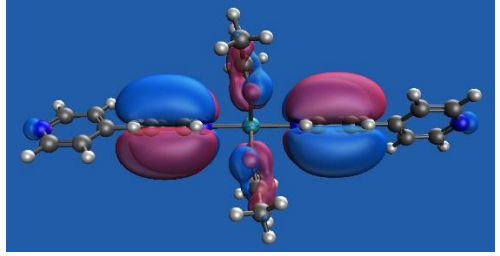
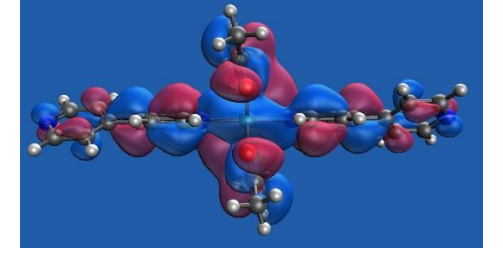
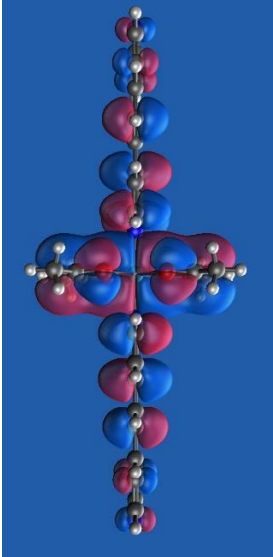
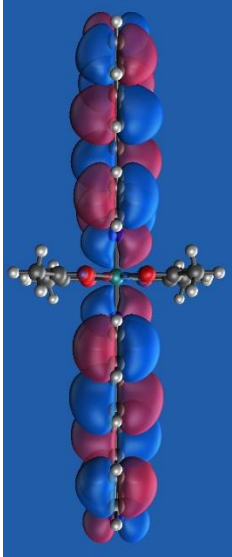
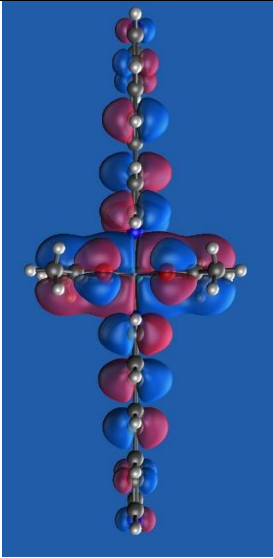
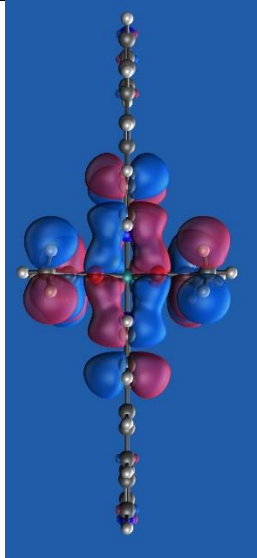
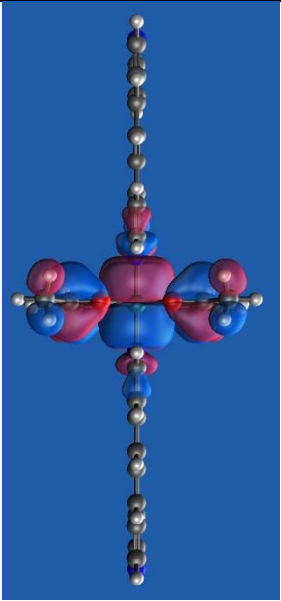
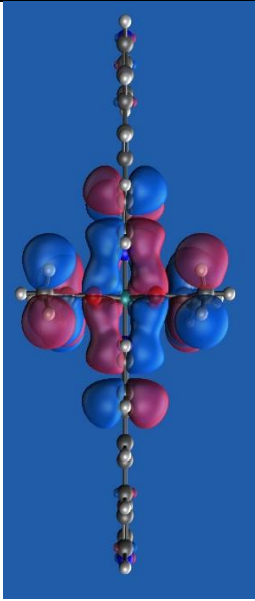
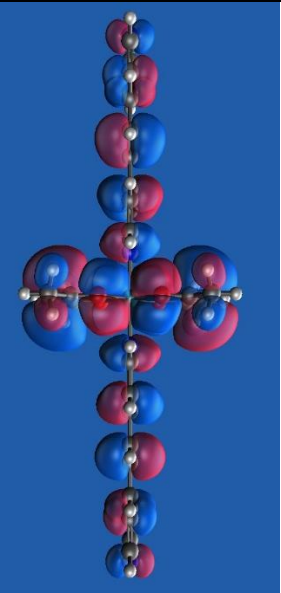
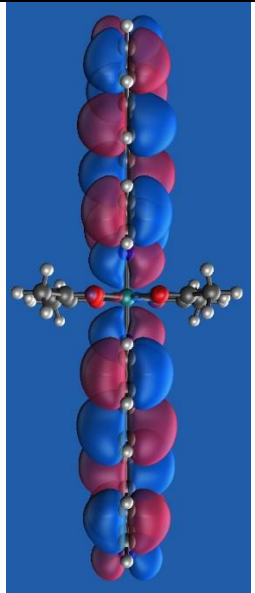
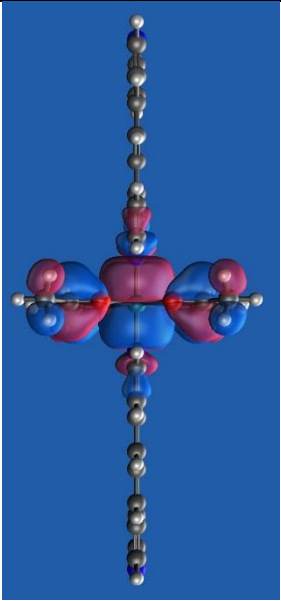
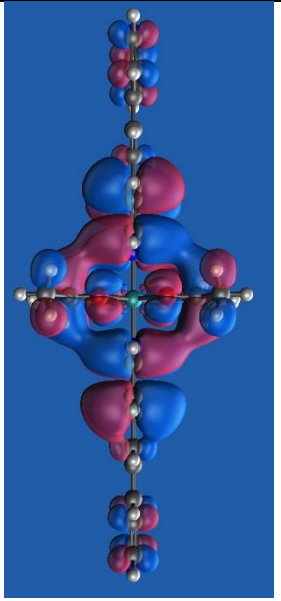
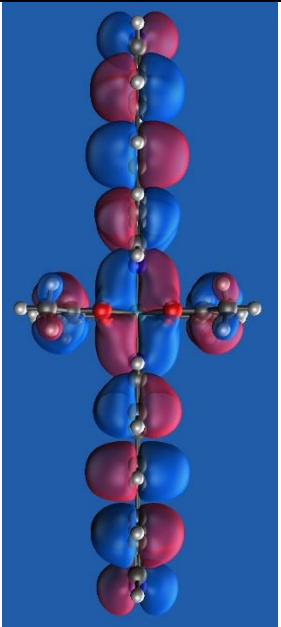
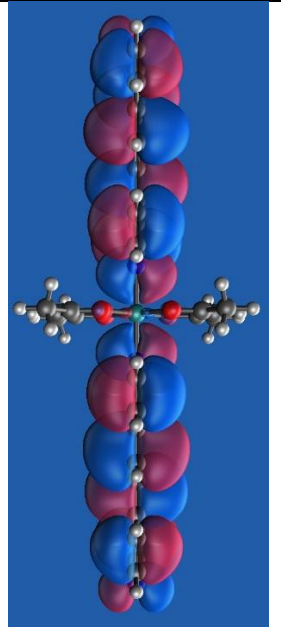
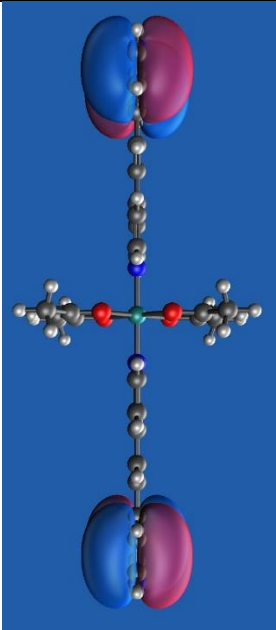
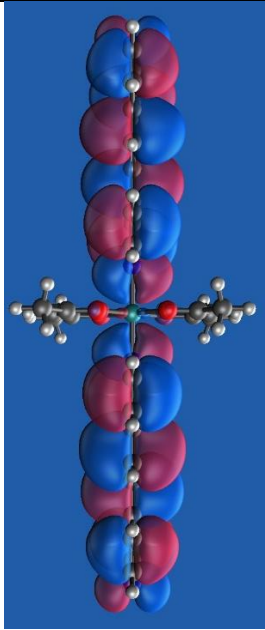
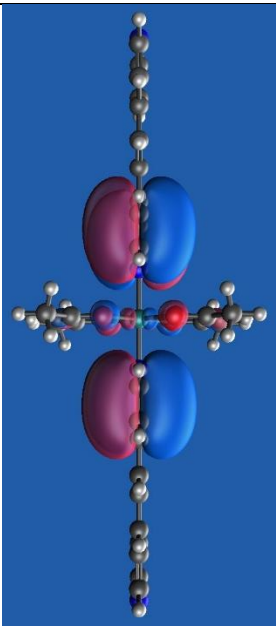
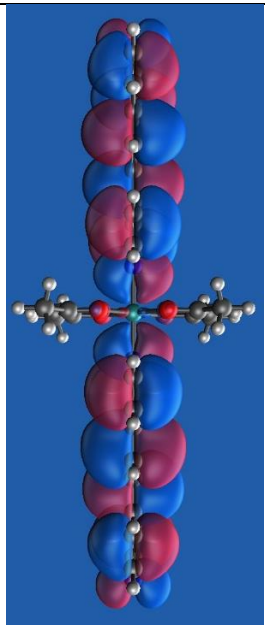
12		
13		
14		

Table C.5. Simulated molecular orbitals for electronic transitions in *trans*-[Ru^{II}(acac)₂(BPE)₂], calculated with the CAM-B3LYP/def2-SVP method.

Transition Number	Orbital From	Orbital To
1		
2		

3	 Molecular orbital visualization for molecule 3, left view. The molecule is oriented vertically. The central part shows a cross-like arrangement of blue and red lobes, indicating a high-symmetry orbital. The vertical axis is decorated with a series of small, alternating blue and red spheres.	 Molecular orbital visualization for molecule 3, right view. The molecule is oriented vertically. The central part shows a cross-like arrangement of blue and red lobes, indicating a high-symmetry orbital. The vertical axis is decorated with a series of small, alternating blue and red spheres.
4	 Molecular orbital visualization for molecule 4, left view. The molecule is oriented vertically. The central part shows a cross-like arrangement of blue and red lobes, indicating a high-symmetry orbital. The vertical axis is decorated with a series of small, alternating blue and red spheres.	 Molecular orbital visualization for molecule 4, right view. The molecule is oriented vertically. The central part shows a cross-like arrangement of blue and red lobes, indicating a high-symmetry orbital. The vertical axis is decorated with a series of small, alternating blue and red spheres.

5	 Molecular orbital visualization for state 5, left view. The molecule is oriented vertically. The central region shows a complex arrangement of blue and red lobes, indicating a high-order orbital. The lobes are symmetric about the vertical axis.	 Molecular orbital visualization for state 5, right view. The molecule is oriented vertically. The central region shows a complex arrangement of blue and red lobes, indicating a high-order orbital. The lobes are symmetric about the vertical axis.
6	 Molecular orbital visualization for state 6, left view. The molecule is oriented vertically. The central region shows a complex arrangement of blue and red lobes, indicating a high-order orbital. The lobes are symmetric about the vertical axis.	 Molecular orbital visualization for state 6, right view. The molecule is oriented vertically. The central region shows a complex arrangement of blue and red lobes, indicating a high-order orbital. The lobes are symmetric about the vertical axis.

7	 A side-view visualization of a molecular orbital for state 7. The molecule is oriented vertically. The central part of the molecule features a cross-like structure with red and grey spheres. Above and below this center are two large, vertically elongated lobes, each split into a blue half and a red half. The entire structure is set against a solid blue background.	 An end-view visualization of a molecular orbital for state 7. The molecule is oriented vertically. The central part of the molecule features a cross-like structure with red and grey spheres. Above and below this center are two large, vertically elongated lobes, each split into a blue half and a red half. The entire structure is set against a solid blue background.
8	 A side-view visualization of a molecular orbital for state 8. The molecule is oriented vertically. The central part of the molecule features a cross-like structure with red and grey spheres. Above and below this center are two large, vertically elongated lobes, each split into a blue half and a red half. The entire structure is set against a solid blue background.	 An end-view visualization of a molecular orbital for state 8. The molecule is oriented vertically. The central part of the molecule features a cross-like structure with red and grey spheres. Above and below this center are two large, vertically elongated lobes, each split into a blue half and a red half. The entire structure is set against a solid blue background.

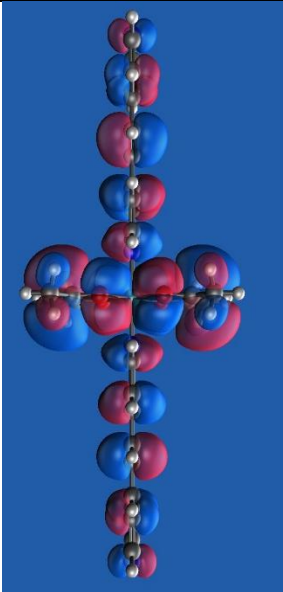
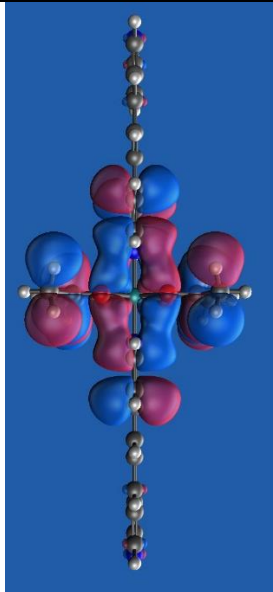
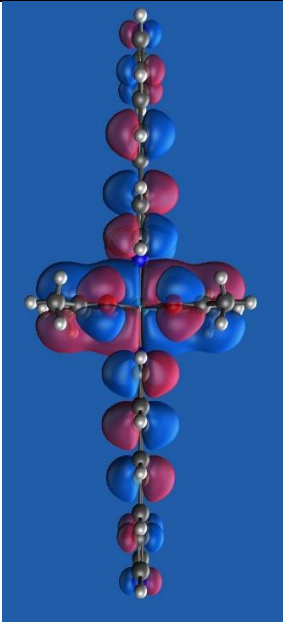
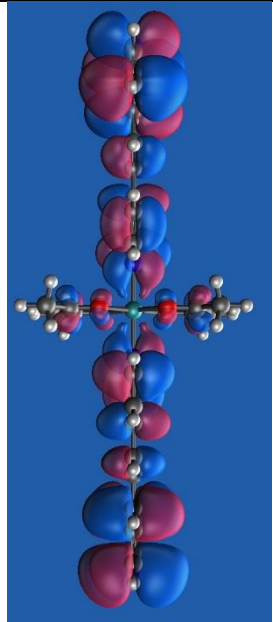
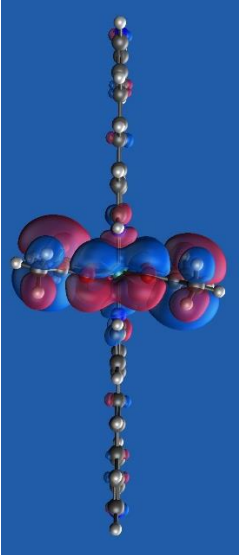
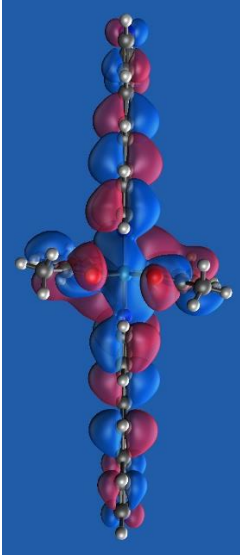
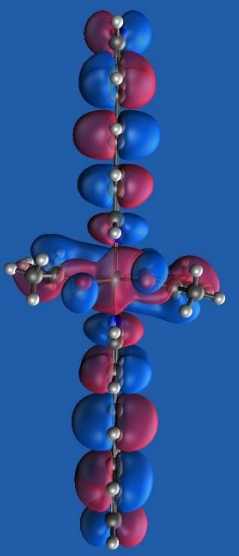
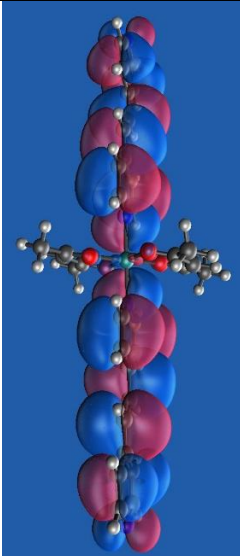
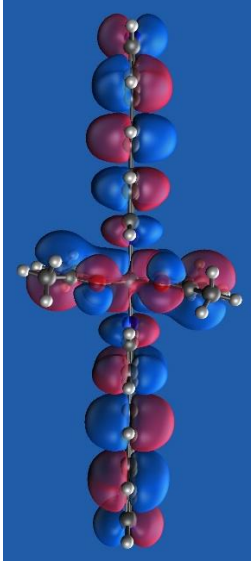
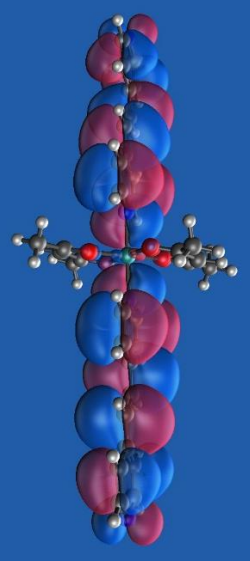
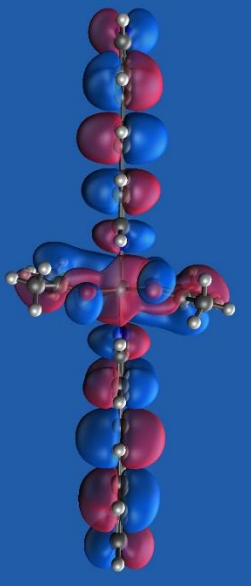
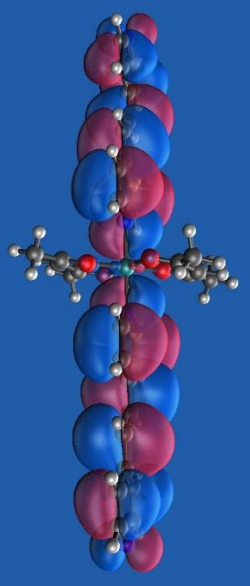
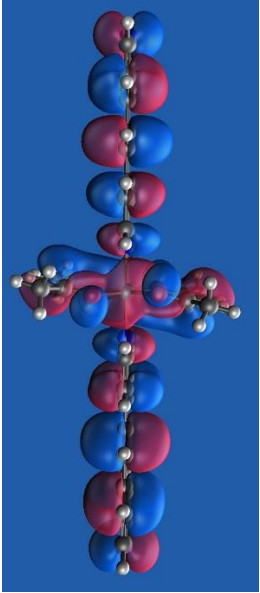
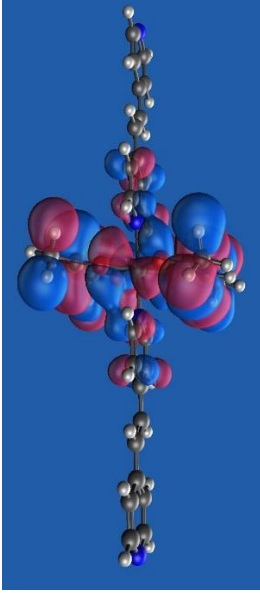
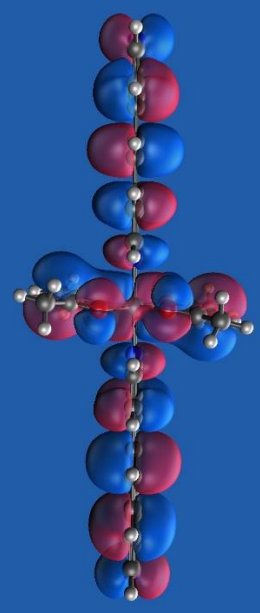
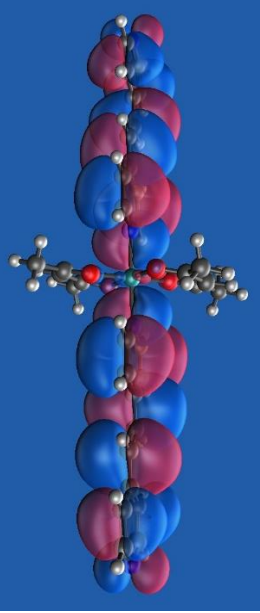
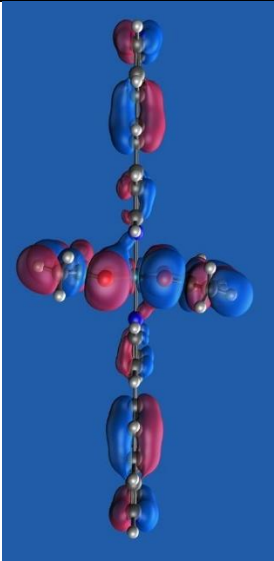
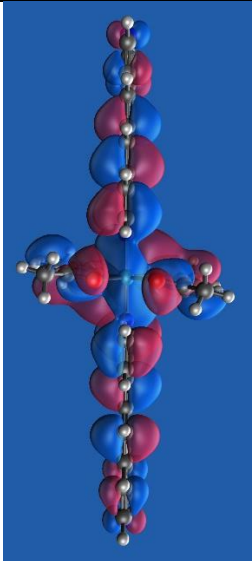
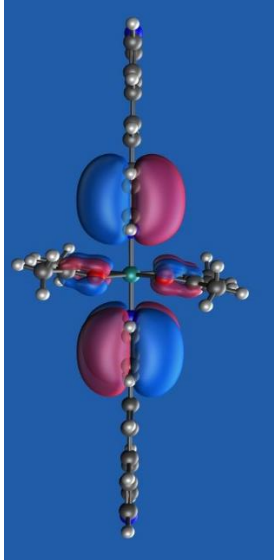
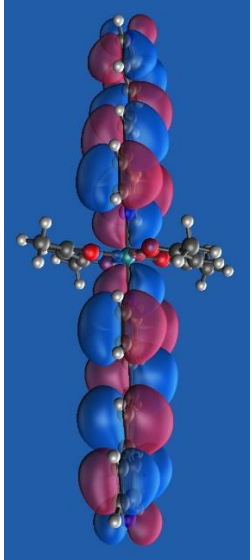
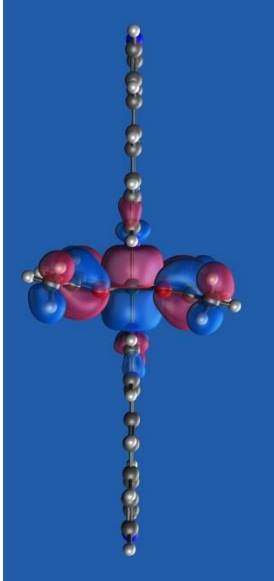
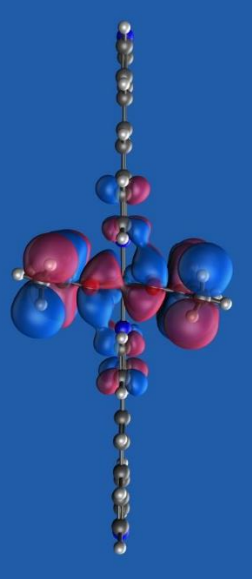
9	 Molecular orbital visualization for state 9, left view. The molecule is oriented vertically. The orbital is primarily localized along the vertical axis, with a central region of high electron density (red and blue lobes) and smaller lobes extending upwards and downwards. The background is blue.	 Molecular orbital visualization for state 9, right view. The molecule is oriented vertically. The orbital is primarily localized along the vertical axis, with a central region of high electron density (red and blue lobes) and smaller lobes extending upwards and downwards. The background is blue.
10	 Molecular orbital visualization for state 10, left view. The molecule is oriented vertically. The orbital is primarily localized along the vertical axis, with a central region of high electron density (red and blue lobes) and smaller lobes extending upwards and downwards. The background is blue.	 Molecular orbital visualization for state 10, right view. The molecule is oriented vertically. The orbital is primarily localized along the vertical axis, with a central region of high electron density (red and blue lobes) and smaller lobes extending upwards and downwards. The background is blue.

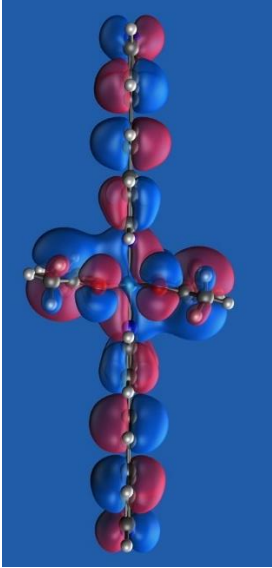
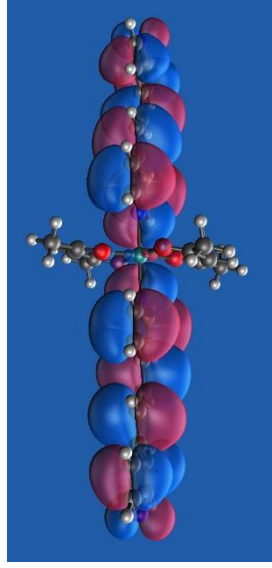
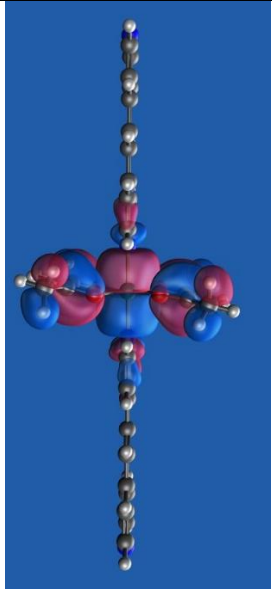
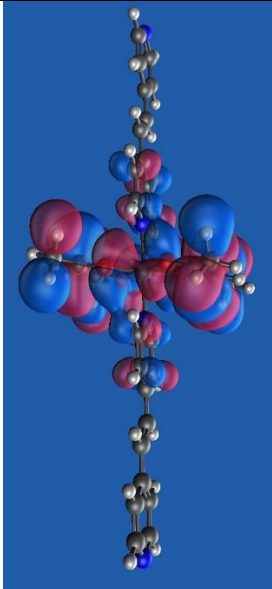
Table C.6. Simulated molecular orbitals for electronic transitions in *trans*-[Ru^{III}(acac)₂(BPE)₂]⁺, calculated with the CAM-B3LYP/def2-SVP method.

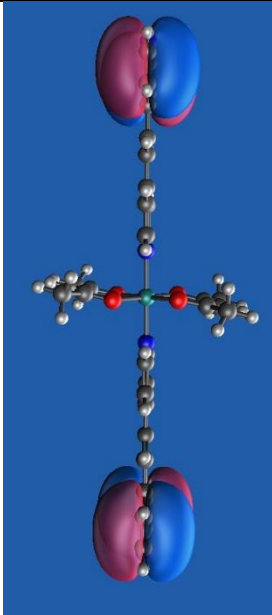
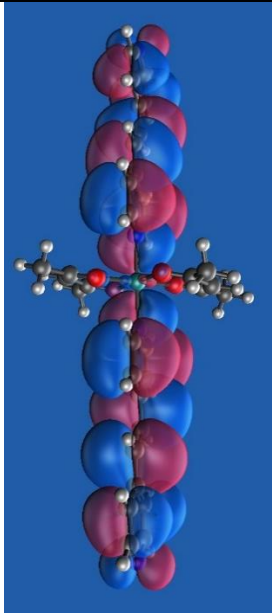
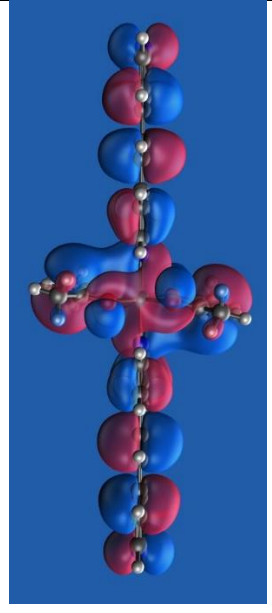
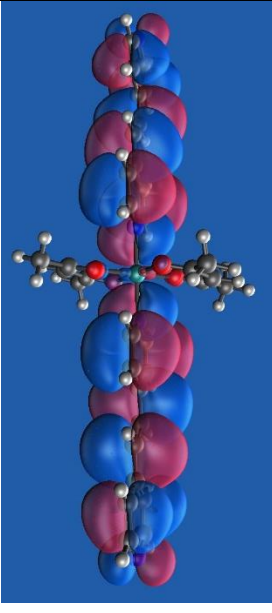
Transition Number	Orbital From	Orbital To
1		
2		

3	 Molecular orbital visualization for molecule 3, left view. The molecule is oriented vertically, showing a central cross-like structure. The visualization displays blue and red lobes representing the positive and negative phases of the molecular orbital, with a central core of atoms.	 Molecular orbital visualization for molecule 3, right view. The molecule is oriented vertically, showing a central cross-like structure. The visualization displays blue and red lobes representing the positive and negative phases of the molecular orbital, with a central core of atoms.
4	 Molecular orbital visualization for molecule 4, left view. The molecule is oriented vertically, showing a central cross-like structure. The visualization displays blue and red lobes representing the positive and negative phases of the molecular orbital, with a central core of atoms.	 Molecular orbital visualization for molecule 4, right view. The molecule is oriented vertically, showing a central cross-like structure. The visualization displays blue and red lobes representing the positive and negative phases of the molecular orbital, with a central core of atoms.

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7	 Molecular orbital visualization for entry 7, left view. The molecule is oriented vertically, showing a central chain of atoms with large blue and red lobes representing the orbital density. The lobes are arranged in a cross-like pattern around the central axis.	 Molecular orbital visualization for entry 7, right view. The molecule is oriented vertically, showing a central chain of atoms with large blue and red lobes representing the orbital density. The lobes are arranged in a cross-like pattern around the central axis.
8	 Molecular orbital visualization for entry 8, left view. The molecule is oriented vertically, showing a central chain of atoms with large blue and red lobes representing the orbital density. The lobes are arranged in a cross-like pattern around the central axis.	 Molecular orbital visualization for entry 8, right view. The molecule is oriented vertically, showing a central chain of atoms with large blue and red lobes representing the orbital density. The lobes are arranged in a cross-like pattern around the central axis.
9	 Molecular orbital visualization for entry 9, left view. The molecule is oriented vertically, showing a central chain of atoms with large blue and red lobes representing the orbital density. The lobes are arranged in a cross-like pattern around the central axis.	 Molecular orbital visualization for entry 9, right view. The molecule is oriented vertically, showing a central chain of atoms with large blue and red lobes representing the orbital density. The lobes are arranged in a cross-like pattern around the central axis.

10	 Molecular orbital visualization for state 10, left view. The molecule is oriented vertically. The central region shows a complex arrangement of blue and red lobes, indicating a high-order molecular orbital. The lobes are symmetric about the vertical axis.	 Molecular orbital visualization for state 10, right view. The molecule is oriented vertically. The central region shows a complex arrangement of blue and red lobes, indicating a high-order molecular orbital. The lobes are symmetric about the vertical axis.
11	 Molecular orbital visualization for state 11, left view. The molecule is oriented vertically. The central region shows a complex arrangement of blue and red lobes, indicating a high-order molecular orbital. The lobes are symmetric about the vertical axis.	 Molecular orbital visualization for state 11, right view. The molecule is oriented vertically. The central region shows a complex arrangement of blue and red lobes, indicating a high-order molecular orbital. The lobes are symmetric about the vertical axis.

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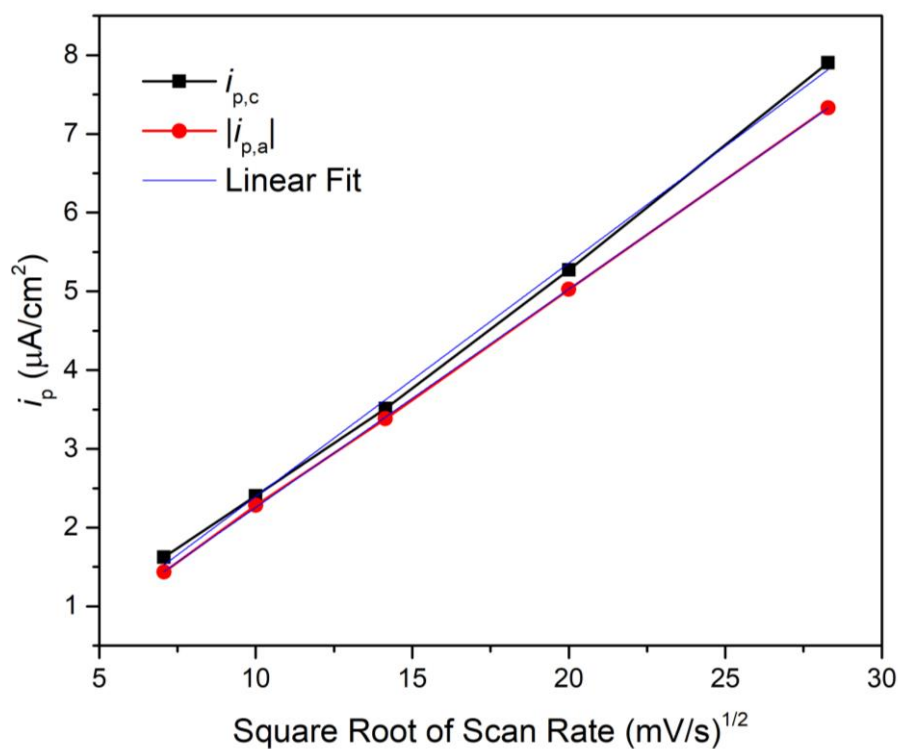


Figure C.1. i_p values for the *quasi*-reversible process observed in $\text{Ph}_4\text{P}\{\text{trans}[\text{Ru}(\text{acac})_2\text{Cl}_2]\}$ vs square root of scan rate. Linear regression goodness-of-fit values (R^2): $i_{p,c}$ 0.9992, $i_{p,a}$ 0.9996.

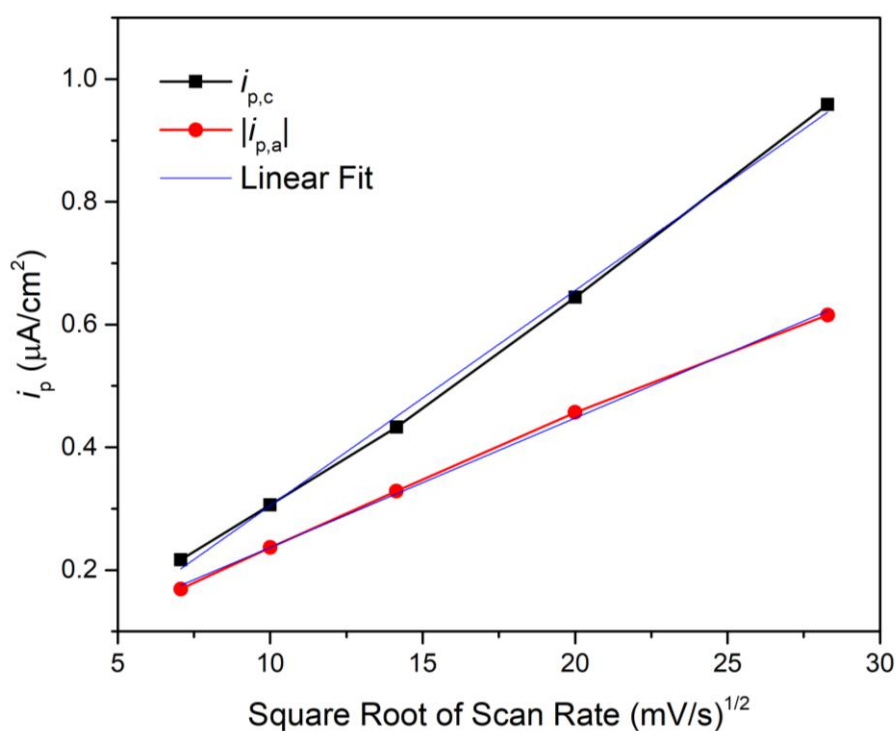


Figure C.2. i_p values for the *quasi*-reversible process observed in RuML1 vs square root of scan rate. Linear regression goodness-of-fit values (R^2): $i_{p,c}$ 0.9970, $i_{p,a}$ 0.9981.

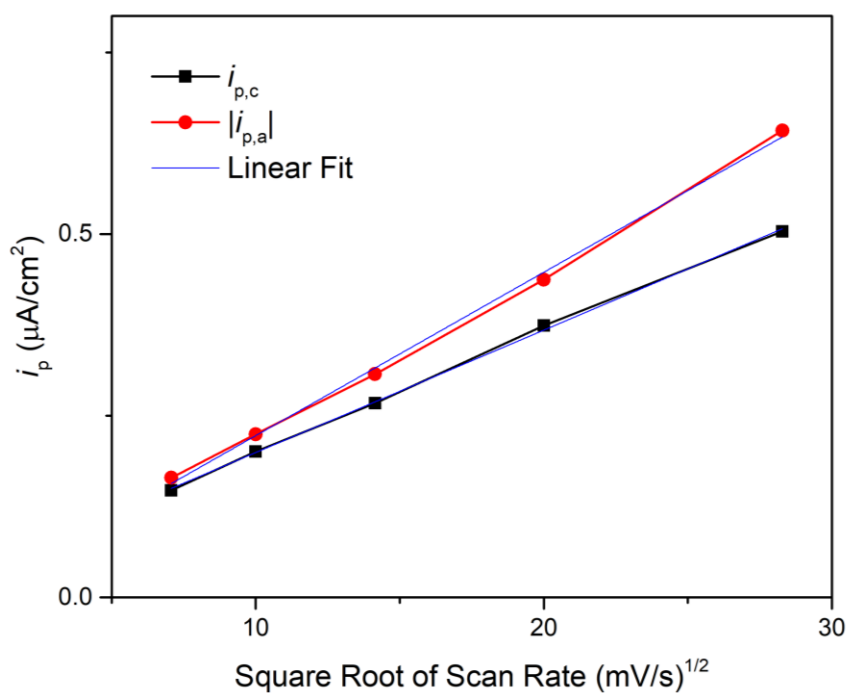


Figure C.3. i_p values for the *quasi*-reversible process observed in RuML2 vs square root of scan rate. Linear regression goodness-of-fit values (R^2): $i_{p,c}$ 0.9989, $i_{p,a}$ 0.9971.

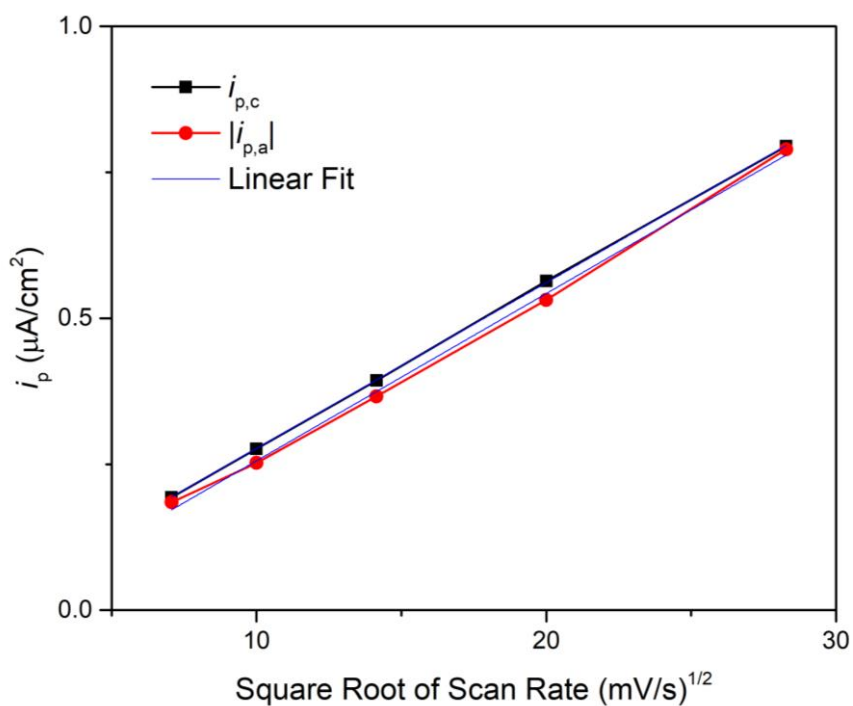


Figure C.4. i_p values for the *quasi*-reversible process observed in RuML4 vs square root of scan rate. Linear regression goodness-of-fit values (R^2): $i_{p,c}$ 0.9999, $i_{p,a}$ 0.9974.

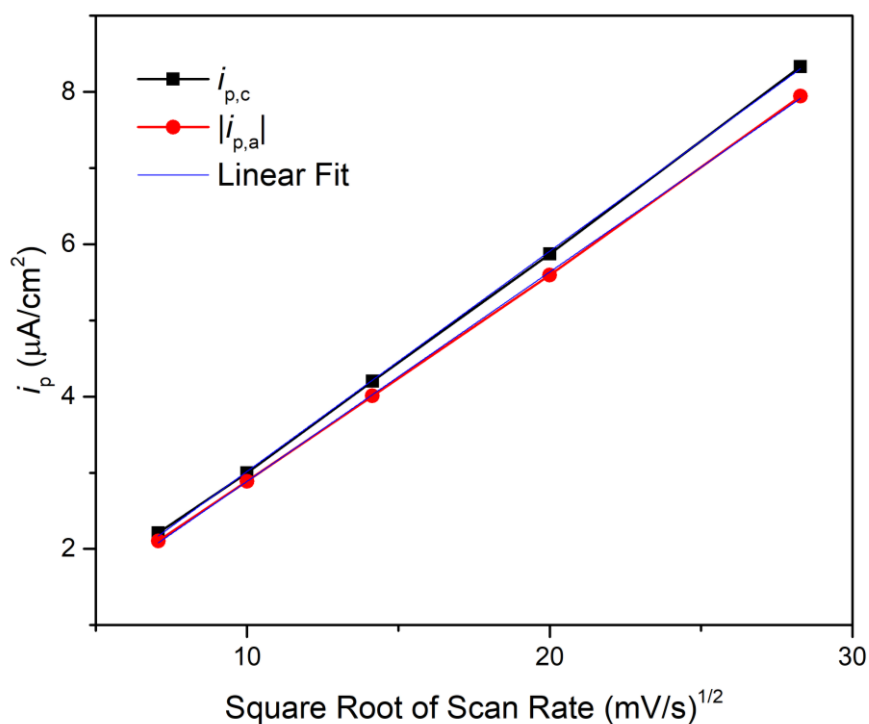


Figure C.5. i_p values for the *quasi*-reversible process observed in RuML0 at -0.596 V vs Fc^+/Fc , vs square root of scan rate. Linear regression goodness-of-fit values (R^2): $i_{p,c}$ 0.9998, $i_{p,a}$ 0.9998.

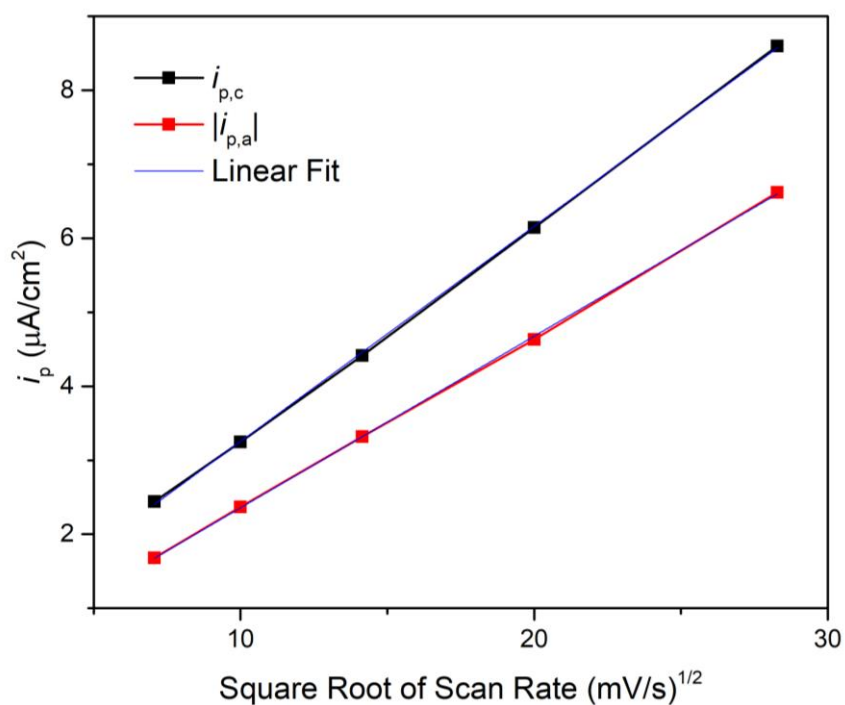


Figure C.6. i_p values for the *quasi*-reversible process observed in RuML0 at 1.083 V vs Fc^+/Fc , vs square root of scan rate. Linear regression goodness-of-fit values (R^2): $i_{p,c}$ 0.9998, $i_{p,a}$ 0.9998.

Table C.7. Experimental IR spectra of $[\text{Ru}^{\text{II}}(\text{acac})_2(\text{pyz})_2]$, $[\text{Ru}^{\text{II}}(\text{acac})_2(\text{d}_4\text{-pyz})_2]$ and simulated spectrum of $[\text{Ru}^{\text{II}}(\text{acac})_2(\text{pyz})_2]$.

ν_{max} and Intensity, [$\text{Ru}^{\text{II}}(\text{acac})_2(\text{pyz})_2$] (cm^{-1})	ν_{max} and Intensity, [$\text{Ru}^{\text{II}}(\text{acac})_2(\text{d}_4\text{-pyz})_2$] (cm^{-1})	Simulated ν_{max} and Intensity, [$\text{Ru}^{\text{II}}(\text{acac})_2(\text{pyz})_2$] (cm^{-1})	Band Assignments
		3194 vw	Pyz $\nu(\text{CH})_{\text{sym}}$, $\nu(\text{CH})_{\text{asym}}$
1569 m	1523 m	1677 s	Pyz $\delta(\text{ring})$
1560 m, sh	1561 w	1670 vs	Acac $\nu(\text{C}=\text{O})_{\text{asym}}$, $\delta(\text{C}-\text{HC}=\text{C})$, $\rho(\text{CH}_3)$
1570 m	1523 m		
1539 w	1532 w	1588 vs	Acac $\nu(\text{C}=\text{C})_{\text{asym}}$
1512 s	1512 s	1539 vs	$\nu(\text{Acac})_{\text{asym}}$
1468 w	1436 w	1526 w	Pyz $\nu(\text{ring})_{\text{asym}}$
1404 s	1402 s	1449 m	Acac $\delta(\text{CH}_3)$
1340 w	1331 w	1387 w	Acac $\delta(\text{CH}_3)$
	1283		
1260 w	1262 w	1310	Acac $\nu(\text{C}-\text{CH}_3)_{\text{sym}}$
1220 m		1248 w	Pyz $\nu(\text{CH})_{\text{sym}}$
1205 w	1205 w	1239 m	Acac $\rho(\text{CH})$
1169 w			
1116 w			
1077 w			
1042 m		1078 w	Pyz $\delta(\text{ring})$, $\nu(\text{CH})_{\text{asym}}$
1019 w			

1005 s	979	1058	Pyz $\delta(\text{ring})$, $\nu(\text{NC})_{\text{asym}}$
976 m			
934 m	935 w	979 w	Acac $\nu(\text{C-CH}_3)$
930 sh			
823 m		848 m	Pyz $\pi(\text{CH})$
781 m	781 m	805 w	Acac $\pi(\text{CH})$
743 vw	738 vw	779 vw	Pyz $\delta(\text{ring})$
699 w			
649 m	648 m	653 m	Acac $\nu(\text{O-Ru-O})_{\text{sym}}$, $\rho(\text{CH}_3)$
617 s	599 s	637 s	Pyz $\delta(\text{ring})$
516	474		Pyz $\pi(\text{ring})$
450 w	446 w	453 w	Acac $\nu(\text{O-Ru-O})_{\text{sym}}$ $\nu(\text{CH}_3)$
440 w		447 w	Acac $\rho(\text{acac})$

vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder, ν = stretching mode, δ = bending mode, π = wagging mode, ρ = rocking mode

Table C.8. Experimental IR spectrum of [RuML1]I and simulated spectrum of RuML1⁺.

ν_{max} and Intensity, [Ru ^{III} (acac) ₂ (pyz) ₂]I (cm ⁻¹)	ν_{max} and Intensity, [Ru ^{III} (acac) ₂ (pyz) ₂] ⁺ (cm ⁻¹)	Band Assignment ²²³⁻²²⁶
1590 w	1689 w	Pyz δ (ring)
1518 s, br	1601 s, 1642 s	Acac ρ (CH), ν (C=C-C), ν (C=O) _{asym}
1420 m	1465 s, 1474 s, 1482 m	Acac δ (CH ₃), ρ (CH) Pyz δ (CH)
1412 w, sh	1450 s	Acac δ (CH ₃)
1355 m	1430 s	Acac δ (CH ₃)
1336 m	1390 s	Acac δ (CH ₃)
1277 s	1331 s	Acac δ (C-CH ₃)
1225 w		
1219 w	1260 w	Pyz ν (ring) _{asym}
1194 w	1234 w	Acac ρ (CH)
1162 m		
1121 w	1169 m	Pyz δ (CH)
1081 vw	1122 vw	Pyz δ (CH)
1062 m	1095 m	Pyz δ (ring)
1014 m, br	1049 m, 1060 s	Acac ρ (CH ₃), ρ (CH)
978 vw	1039 vw	Acac ρ (CH ₃), ρ (CH)
937 m	986 m	Acac ν (C-CH ₃)
821 w	844 m	Pyz π (CH)
810 m	833 m	Acac π (CH)
788 w		

744 vw	783 w	Pyz $\pi(\text{C-N-C})$, $\pi(\text{CH})$
698 w, sh	703 m	Acac $\pi(\text{acac})$
691 m	691 m	Acac $\pi(\text{C-C-O})$, $\rho(\text{CH}_3)$,
654 w, sh	656 vw	Pyz $\delta(\text{ring})$
644 m	649 m	Acac $\nu(\text{O-Ru-O})_{\text{sym}}$, $\rho(\text{CH}_3)$
501 s	529 s	Pyz Oop $\delta(\text{ring})$
466 m	477 w	Acac $\nu(\text{O-Ru-O})_{\text{sym}}$ $\nu(\text{CH}_3)$
428 w	444 w	Acac $\rho(\text{acac})$

vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder, ν = stretching mode, δ = bending mode, π = wagging mode, ρ = rocking mode

Table C.9. Experimental and simulated infrared spectrum of *trans*-[Ru^{II}(acac)₂(bpy)₂].

ν_{max} and Intensity, [Ru ^{II} (acac) ₂ (bpy) ₂] (cm ⁻¹)	Simulated ν_{max} and Intensity, [Ru ^{II} (acac) ₂ (bpy) ₂] (cm ⁻¹)	Band Assignment
2957 w, sh	3200 m	Acac $\nu(\text{CH})$
2921 m	3151 s, 3148 m, 3147 m,	Bpy $\nu(\text{CH})$, $\nu(\text{CH}_3)$
2851 m	3036 m	Acac $\nu(\text{CH}_3)$
1616 w	1659 m	Bpy $\delta(\text{ring})$
1592 s	1614 s, 1645 s	Acac $\nu(\text{C=O})_{\text{sym}}$, $\delta(\text{C-HC=C})$, $\rho(\text{CH}_3)$ Bpy $\delta(\text{ring})$
1520 m, br	1578 s	Bpy $\nu(\text{ring})$
1505 s	1556 s	Acac $\delta(\text{CCHC})$
1479 s	1508 s, 1510 s	Bpy $\delta(\text{CH})$, Acac $\nu(\text{CCHC})_{\text{asym}}$, $\rho(\text{CH}_3)$
1399 s	1440 s, 1443 w, 1446 m, 1451 s	Acac $\rho(\text{CH}_3)$, $\delta(\text{CH}_3)$, Bpy $\delta(\text{CH})$,
1362 m	1376 m	Acac $\delta(\text{CH}_3)$
1335 w	1343 w	Bpy $\delta(\text{CH})$
1292 w		
1279 w	1318 m	Bpy $\delta(\text{ring})$
1257 w	1289 s	Acac $\nu(\text{C-CH}_3)$
1231 m		
1217 w	1241 w	Bpy $\delta(\text{CH})$
1201 w	1224 m, 1226 m,	Acac $\pi(\text{CH})$ Bpy $\delta(\text{CH})$

1128 w		
1108 w		
1092 w	1128 w	Bpy $\delta(\text{CH})$
1073 w		
1067 w		
1054 w	1094 w	Bpy $\delta(\text{CH})$
1043 w	1077 w	Bpy $\delta(\text{CH})$
1008 s	1028 s, 1034 s	Acac $\rho(\text{CH}_3)$ Bpy $\delta(\text{ring})$
991 w, sh	1012 w	Bpy $\delta(\text{ring})$
955 w	995 w	Bpy $\rho(\text{CH})$
932 m	958 w	Acac $\nu(\text{C-CH}_3)$
864 w	877 w	Bpy $\pi(\text{CH})$
852 w	866 w	Bpy $\rho(\text{CH})$
810 s	835 s	Bpy $\pi(\text{CH})$
782 m	799 w	Acac $\pi(\text{CH})$
763 m	773 s	Bpy $\delta(\text{ring})$
728 m	755 w	Bpy Oop $\delta(\text{ring})$
693 w		
668 w	690 vw	Bpy $\delta(\text{ring})$
656 w	679 w	Acac $\nu(\text{O-Ru-O})_{\text{sym}}, \pi(\text{CH}_3)$
641 m	641 m	Acac $\nu(\text{O-Ru-O})_{\text{sym}}, \rho(\text{CH}_3)$
634 w		
629 w		

570 vw	583 w	Bpy Oop δ (ring)
490 m	523 m	Bpy Oop δ (ring)
445 w	445 w	δ (acac)

vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder, b = broad, v = stretching mode, δ = bending mode, π = wagging mode, ρ = rocking mode, Oop. = out of plane mode.

Table C.10. Experimental infrared spectrum of *trans*-[Ru^{III}(acac)₂(bpy)₂]Cl and simulated infrared spectrum of *trans*-[Ru^{III}(acac)₂(bpy)₂]⁺.

ν_{max} and Intensity, [Ru ^{III} (acac) ₂ (bpy) ₂]Cl (cm ⁻¹)	Simulated ν_{max} and Intensity, [Ru ^{III} (acac) ₂ (bpy) ₂]Cl (cm ⁻¹)	Band Assignment
1616 m	1672 s	Bpy δ (inner ring)
1594 m, sh		
1585 m	1645 m	Bpy outer ring $\nu(\text{ring})_{\text{asym}}$ δ (CH)
1533 m, sh	1590 m, 1595 s	Bpy inner ring $\nu(\text{ring})_{\text{asym}}$ ρ (CH) Acac $\nu(\text{C=O})_{\text{sym}}$, $\delta(\text{C-HC=C})$, $\rho(\text{CH}_3)$
1521 s, br	1544 m, 1570 s,	Bpy ρ (CH) Acac $\delta(\text{CCHC})$
1483 m	1514 m	Bpy ρ (CH)
1443 m, sh	1466 m	Bpy inner ring δ (CH) Acac $\delta(\text{CH}_3)$
1438 s	1452 s	Acac $\delta(\text{CH}_3)$
1410 w, sh	1442 m, 1443 m	Acac $\delta(\text{CH}_3)$
1403 m	1418 s	Acac $\delta(\text{C-CH}_3)$
1362 m, br	1380 s	Acac $\delta(\text{CH}_3)$
1334 w	1350 w	Bpy ρ (CH)
1318 w		
1294 vw		
1278 m	1308 s, 1317 m	Acac $\delta(\text{C-CH}_3)$ Bpy ρ (CH), $\nu(\text{C-C})$

1227 vw		
1214 w		
1193 w		
1185 w	1233 m	Bpy inner ring $\delta(\text{CH})$
1180 w	1220 w	Acac $\rho(\text{CH})$
1163 w		
1149 w		
1138 w		
1106 vs		
1077 w		
1071 w		
1066 m	1134 w	Bpy inner ring $\delta(\text{CH})$
1024 m	1089 m	Bpy $\rho(\text{CH})$
986 m	1045 m	Acac $\rho(\text{CH})$
984 w	1036 m	Acac $\rho(\text{CH}_3)$, $\rho(\text{CH})$
936 m	967 w	Acac $\nu(\text{C-CH}_3)$
853 w		
834 w	883 w	Bpy $\pi(\text{CH})$
807 m	831 w, 832 s	Bpy $\pi(\text{CH})$
793 w	823 w	Acac $\pi(\text{CH})$
770 m	774 w	Bpy Oop. $\rho(\text{ring})$
763 m	757 w	Bpy Oop. $\rho(\text{ring})$
757 m, sh		
750 m		

737 w		
722 s		
689 s	692 w	Acac $\pi(\text{C-CH-C})$, $\rho(\text{CH}_3)$
668 w	678 m	Acac $\delta(\text{CCH})$, $\pi(\text{CH})$
656 w		
647 w		
629 m	635 s, 639 m	Bpy $\delta(\text{ring})$ Acac $\nu(\text{O-Ru-O})_{\text{asym}}$, $\rho(\text{CH}_3)$
617 w		
608 m		
574 w, br	569 w	Acac $\rho(\text{C-CH}_3)$
533 m, sh		
524 s	522 m	Bpy Oop. $\rho(\text{ring})$
~490 m, sh	517 w	Bpy Oop. $\rho(\text{ring})$
466 m	466 m	Acac $\delta(\text{acac})$, $\nu(\text{O-Ru-O})_{\text{sym}}$, $\nu(\text{CH}_3)$
434 m	440 w	Acac $\rho(\text{acac})$, $\pi(\text{CH}_3)$

vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder, b = broad, ν = stretching mode, δ = bending mode, π = wagging mode, ρ = rocking mode, Oop. = out of plane mode.

Table C.11. Experimental and simulated infrared spectrum of RuML4.

$\nu_{\max}$ and Intensity [Ru(II)(acac) ₂ (BPE) ₂] (cm ⁻¹)	Simulated $\nu_{\max}$ and Intensity [Ru(II)(acac) ₂ (BPE) ₂] (cm ⁻¹)	Band Assignment ²³⁰
2990 m	3150 s	BPE $\nu(\text{CH})$
2972 m	3108 s	Acac $\nu(\text{CH})$
2901 m	3036 m	Acac $\nu(\text{CH}_3)$
1632 w	1694 m	$\delta(\text{C}_2\text{H}_2)$
1612 w	1638 s	BPE $\delta(\text{ring})$
1590 s, br	1607 m, 1614 s	BPE $\nu(\text{outer ring})_{\text{asym}}$, Acac $\nu(\text{C=O})_{\text{sym}}$, $\delta(\text{C-HC=C})$, $\rho(\text{CH}_3)$
	1581 s	BPE $\nu(\text{inner ring})_{\text{asym}}$
1533 m	1556 s	Acac $\delta(\text{CCHC})$
1509 s	1530 s	BPE $\rho(\text{CH})$
1496 w	1517 m	BPE $\rho(\text{CH})$
1485 w	1509 s	Acac $\nu(\text{CCHC})_{\text{asym}}$, $\rho(\text{CH}_3)$, $\rho(\text{CH})$
1450 w		
1423 m, sh	1467 m	BPE $\delta(\text{inner ring})$
1405 s, br	1446 m, 1450 m, 1451 s	Acac $\rho(\text{CH}_3)$, BPE $\delta(\text{CH})$
1394 s	1440 s	Acac $\delta(\text{CH}_3)$
1340 w		BPE $\nu(\text{ring})_{\text{sym}}$

1338 w		
1336 w	1376 m	Acac $\delta(\text{CH}_3)$
1295 w	1348 m	BPE $\rho(\text{CH})$
1277 w	1319 w	BPE $\nu(\text{ring})_{\text{asym}}$, C_2H_2 $\delta(\text{ring-CH})$, $\delta(\text{ring-C=C})$
1259 m	1302 m	BPE $\rho(\text{CH})$, $\nu(\text{CC})$
1249 m	1290 m	Acac $\nu(\text{C-CH}_3)$
1241 m		
1231 w		
1221 w	1247 w	BPE $\delta(\text{CH})$
1204 w, br	1215 s, 1224 m	BPE inner ring, C_2H_2 $\delta(\text{CH})$ Acac $\rho(\text{CH})$
1100 w, sh	1126 w	BPE inner ring $\delta(\text{CH})$
1090 w, sh	1113 w	BPE outer ring $\delta(\text{CH})$
1075 m		
1067 s		
1058 s	1070 m	BPE inner ring $\delta(\text{CNC})$, $\rho(\text{CH})$
1053 m		
1038 w		
1028 m		
1010 s	1029 s, 1035 s	Acac $\rho(\text{CH}_3)$ BPE $\delta(\text{inner ring})$
998 m	1012 m	BPE $\delta(\text{outer ring})$

989 m	1009 m	BPE outer ring Oop. $\delta(\text{CH})$, C_2H_2 $\pi(\text{CH})$
971 m		
965 m		
953 w		
935 m	959 m	Acac $\nu(\text{C-CH}_3)$
892 m		
883 w		
879 m	893 m	BPE $\rho(\text{CH})$, C_2H_2 $\delta(\text{ring-CH})$, $\delta(\text{ring-C=C})$
827 s	854 m, 860 w	BPE $\pi(\text{CH})$
812 w		
805 w		
797 w	826 w	BPE $\pi(\text{CH})$
782 w	799 m	Acac $\pi(\text{CH})$
764 w		
742 w		
726 w		
721 w		
693 w		
668 m	680 w	BPE $\delta(\text{inner ring})$
650 m	660 s	BPE $\delta(\text{ring})$, $\delta(\text{C}_2\text{H}_2)$
641 m	642 m	Acac $\nu(\text{O-Ru-O})_{\text{asym}}$, $\rho(\text{CH}_3)$
552 vs	572 m	BPE Oop. $\rho(\text{ring})$

492 w		
483 w		
470 w	480 w	BPE inner ring $\rho(\text{CH})$, C_2H_2 $\delta(\text{ring-CH})$, $\delta(\text{ring-C=C})$
431 w	444 w	Acac $\delta(\text{acac})$, $\pi(\text{CH}_3)$

vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder, b = broad, ν = stretching mode, δ = bending mode, π = wagging mode, ρ = rocking mode, Oop. = out of plane mode.

Table C.12. Experimental infrared spectrum of [RuML4]Cl and simulated infrared spectrum of RuML4⁺.

$\nu_{\max}$ and Intensity [Ru(II)(acac) ₂ (BPE) ₂]Cl (cm ⁻¹)	Simulated $\nu_{\max}$ and Intensity [Ru(II)(acac) ₂ (BPE) ₂]Cl (cm ⁻¹)	Band Assignment
2990 m	3173 m	C ₂ H ₂ ν (CH)
2972 m	3161 m	BPE ν (CH)
2901 m	3118 w	Acac ν (CH ₃)
	1698 m	δ (C ₂ H ₂)
1612 m	1665 s	BPE δ (inner ring)
1596 m	1643 w	BPE δ (outer ring)
1532 m, sh	1612 s	BPE ν (outer ring) _{asym}
1518 s, br	1570 s, 1591 m, 1596 s	Acac δ (CCHC), ν (C=O) _{sym} , δ (C- HC=C), ρ (CH ₃) BPE ν (inner ring) _{asym}
1501 w	1522 w, 1534 m	BPE ρ (CH)
1435 w	1469 m, 1474 w	Acac δ (CH ₃), ρ (CH) BPE inner ring δ (CH)
1418 w, sh	1450 m, 1452 s	BPE outer ring δ (CH) Acac δ (CH ₃)
1411 m	1443 m	Acac δ (CH ₃)
1394 w	1419 s	Acac ρ (CCH ₃)

1373 m		
1362 m	1380 m	Acac $\delta(\text{CH}_3)$
1347 m	1351 m	BPE $\rho(\text{CH})$
1342 m		
1340 w		
1338 w		
1336 w		
1298 w		
1278 m	1303 w, 1307 s	BPE $\rho(\text{CH})$, $\delta(\text{ring})$ Acac $\nu(\text{C-CH}_3)$
1249 vw		
1241 m		
1221 w	1250 m	BPE $\delta(\text{CH})$
1209 m	1220 s	BPE $\delta(\text{CH})$
1109 m	1133 w	BPE inner ring $\delta(\text{CH})$
1090 w, sh		
1074 m	1090 w	BPE outer ring $\rho(\text{CH})$
1066 s	1084 m	BPE inner ring $\delta(\text{CNC})$, $\rho(\text{CH})$
1058 s		
1053 m		
1034 w	1045 m	Acac $\rho(\text{CH}_3)$ BPE $\delta(\text{inner ring})$
1028 m	1036 m	Acac $\rho(\text{CH}_3)$, $\pi(\text{CH})$

991 m	1017 w	BPE outer ring, C ₂ H ₂ Oop. ρ (CH)
979 s	1014 m	BPE outer ring, C ₂ H ₂ Oop. ρ (CH)
963 w	990 w	BPE Oop. ρ (CH)
937 m	966 m	Acac ν (C-CH ₃)
892 w	935 w	BPE inner ring π (CH), π (C ₂ H ₂)
883 w		
879 w		
868 w		
841 w, sh	870 w	BPE π (CH)
831 vs	856 m, 857 m	BPE π (CH), C ₂ H ₂ δ (ring-CH), δ (ring- C=C)
806 w		
797 s	822 w	Acac π (CH)
781 m		
766 w		
761 w		
756 w		
725 m		
721 m		

696 m		
668 m	692 w	Acac $\rho(\text{C-CH}_3)$
652 m	678 m	Acac $\delta(\text{CCH}), \pi(\text{CH})$
584 w, br	641 m	Acac $\nu(\text{O-Ru-O})_{\text{asym}},$ $\rho(\text{CH}_3)$
554 vs	575 m	BPE Oop. $\rho(\text{ring})$
527 s	561 s	BPE $\delta(\text{ring}), \delta(\text{ring-}$ $\text{C}_2\text{H}_2\text{-ring})$
509 w		
470 s	480 w	BPE $\rho(\text{CH}), \text{C}_2\text{H}_2$ $\delta(\text{ring-CH}), \delta(\text{ring-}$ $\text{C=C})$
461 m	465 m	Acac $\delta(\text{acac}), \nu(\text{O-Ru-}$ $\text{O})_{\text{sym}},$
429 m	441 w	Acac $\rho(\text{acac}), \pi(\text{CH}_3)$

vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder, b = broad, ν = stretching mode, δ = bending mode, π = wagging mode, ρ = rocking mode, Oop. = out of plane mode.

Table C.12. Experimental and simulated Raman spectrum of RuML4. Excitation wavelength: 532 nm.

$\nu_{\max}$ and intensity, acac modes, <i>trans</i> -[Ru ^{II} (acac) ₂ (pyz) ₂]	$\nu_{\max}$ and intensity, acac modes, <i>trans</i> -[Ru ^{III} (acac) ₂ (pyz) ₂] I	Band Assignments
1560 m, sh	1518 s, br	Acac $\nu(\text{C}=\text{O})_{\text{asym}}$, $\delta(\text{C}-\text{HC}=\text{C})$, $\rho(\text{CH}_3)$
1539 w,		Acac $\nu(\text{C}=\text{C})_{\text{asym}}$
1512 s		$\nu(\text{Acac})_{\text{asym}}$
	1420 m	Acac $\delta(\text{CH}_3)$
1404 s	1412 w, sh	Acac $\delta(\text{CH}_3)$
	1355 m	Acac $\delta(\text{CH}_3)$
1340 w	1336 m	Acac $\delta(\text{CH}_3)$
1260 w	1277 s	Acac $\delta(\text{C}-\text{CH}_3)$
1205 w	1194 w	Acac $\rho(\text{CH})$
934 m	937 m	Acac $\nu(\text{C}-\text{CH}_3)$
781 m	810 m	Acac $\pi(\text{CH})$
	691 m	Acac $\pi(\text{C}-\text{C}-\text{O})$, $\rho(\text{CH}_3)$,
649 m	644 m	Acac $\nu(\text{O}-\text{Ru}-\text{O})_{\text{sym}}$, $\rho(\text{CH}_3)$
450 w	466 m	Acac $\nu(\text{O}-\text{Ru}-\text{O})_{\text{sym}}$ $\nu(\text{CH}_3)$
440 w	428 w	Acac $\rho(\text{acac})$

vw = very weak, *w* = weak, *m* = medium, *s* = strong, *vs* = very strong, *sh* = shoulder, ν = stretching mode, δ = bending mode, π = wagging mode, ρ = rocking mode

Appendix D

Supplementary Information,

Chapter 4

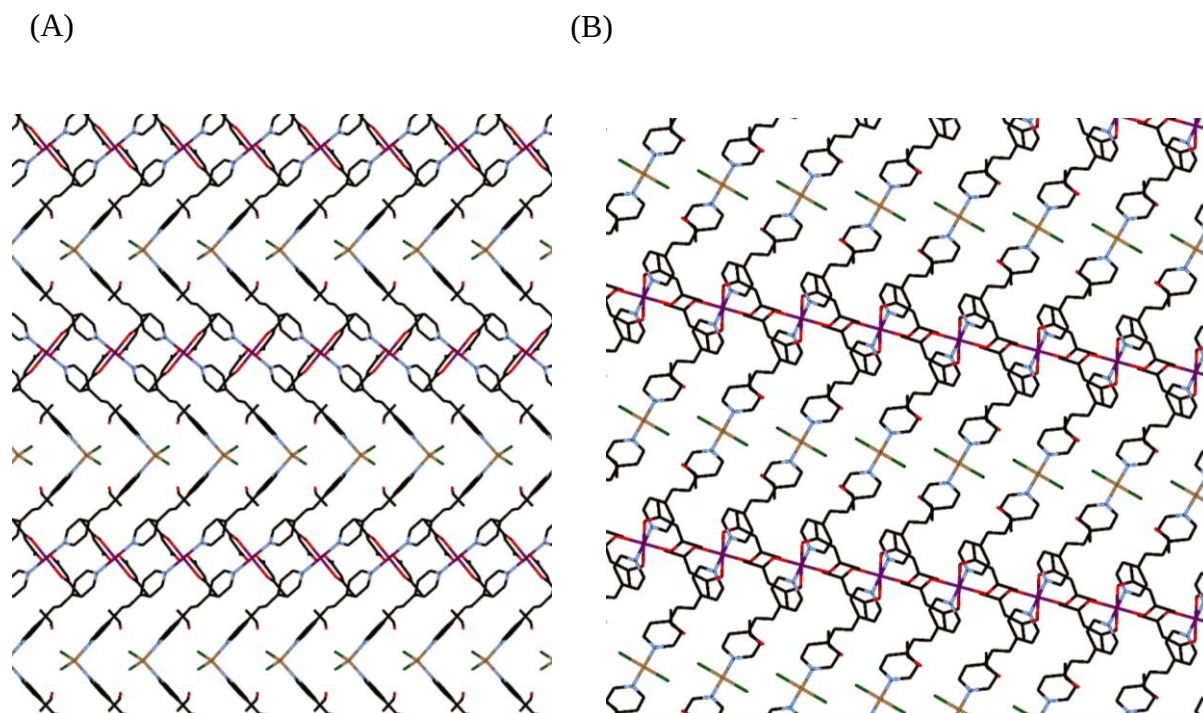


Figure D.1. Crystal structure of [ZnBr₂(RuML₄)], (A) along the *a*-axis. (B) along the *b*-axis. Hydrogens and solvent molecules omitted for clarity. Colour scheme: N, blue; C, black; O, red; Ru, purple; Zn, brown; Br, brown. Plotted in CrystalMaker X Ver. 10.8.1.

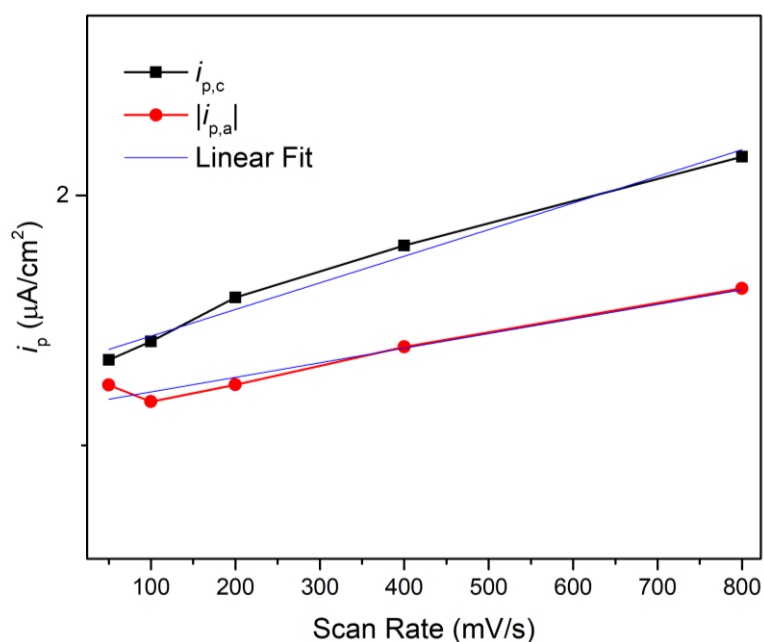


Figure D.2. i_p values for the *quasi*-reversible process observed in [ZnCl₂(RuML₄)] vs scan rate. Linear regression goodness-of-fit values (R^2): $i_{p,c}$ 0.9775, $i_{p,a}$ 0.9425.

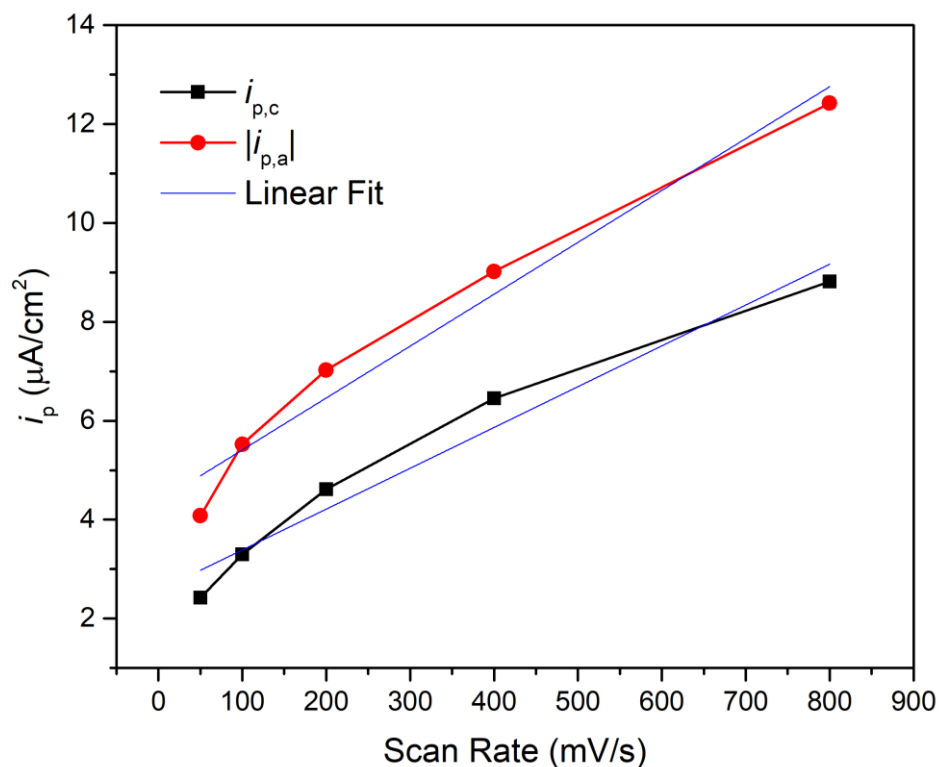


Figure D.3. i_p values for the *quasi*-reversible process observed in $[\text{ZnCl}_2(\text{RuML4})]$ vs scan rate. Linear regression goodness-of-fit values (R^2): $i_{p,c}$ 0.9519, $i_{p,a}$ 0.9587.

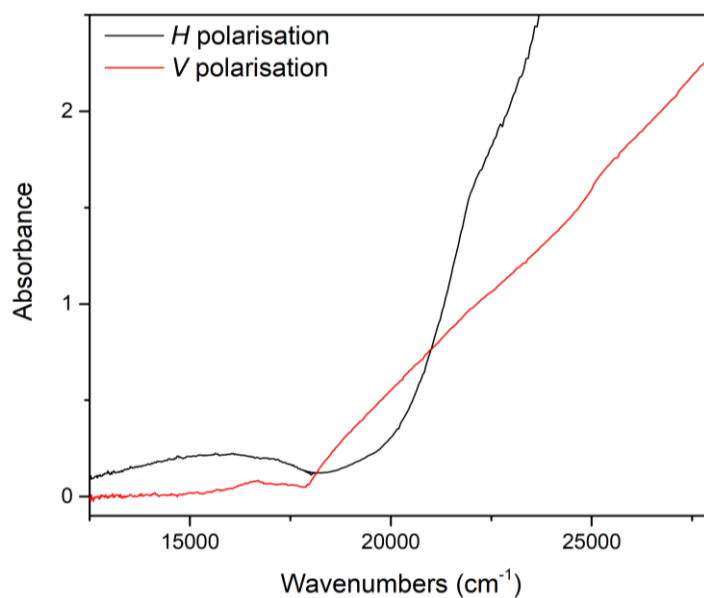


Figure D.4. Single crystal polarised Visible spectrum of $[\text{ZnCl}_2(\text{RuML4})]$. Polarised spectra are of the same face of the crystal, at orthogonal polarisations.

Appendix E

Supplementary Information,

Chapter 5

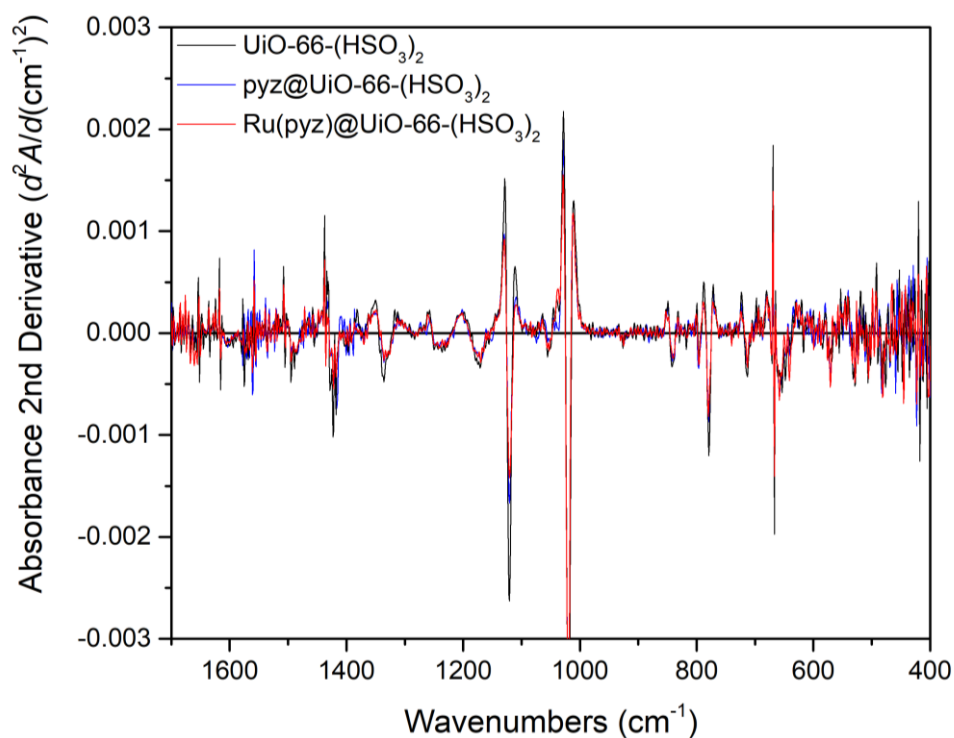


Figure E.1. Second derivative FTIR spectra of MOF and host-guest materials

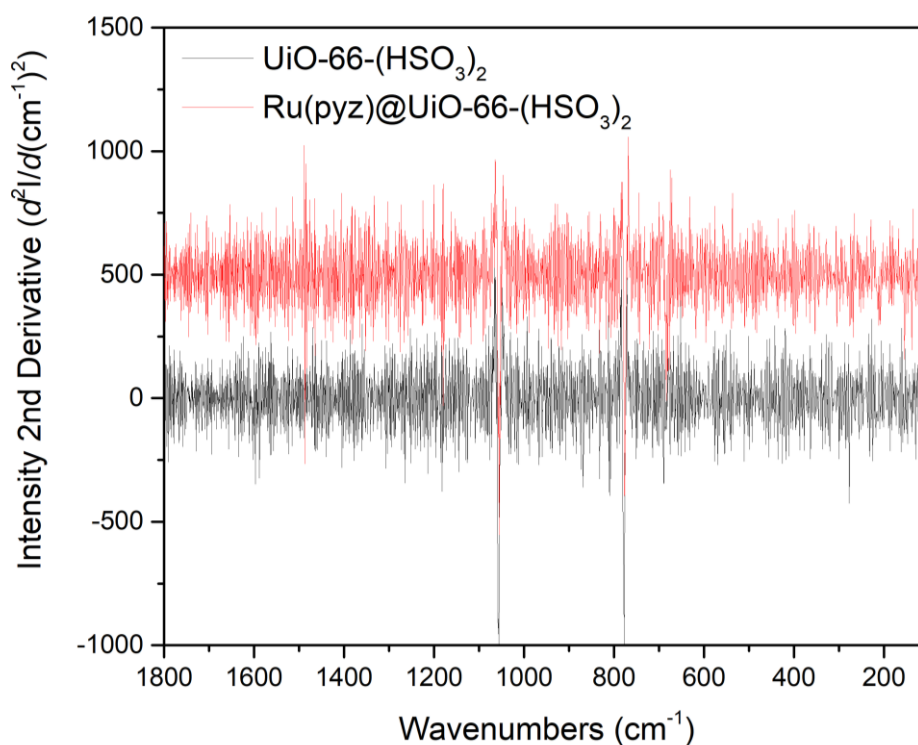


Figure E.2. Second derivative Raman spectra of **UiO-66-(HSO₃)₂** and Ru(pyz)@ UiO-66-(HSO₃)₂. Excitation wavelength: 830 nm. Y axis of 'Ru(pyz)@ UiO-66-(HSO₃)₂' was offset by +500 for clarity.

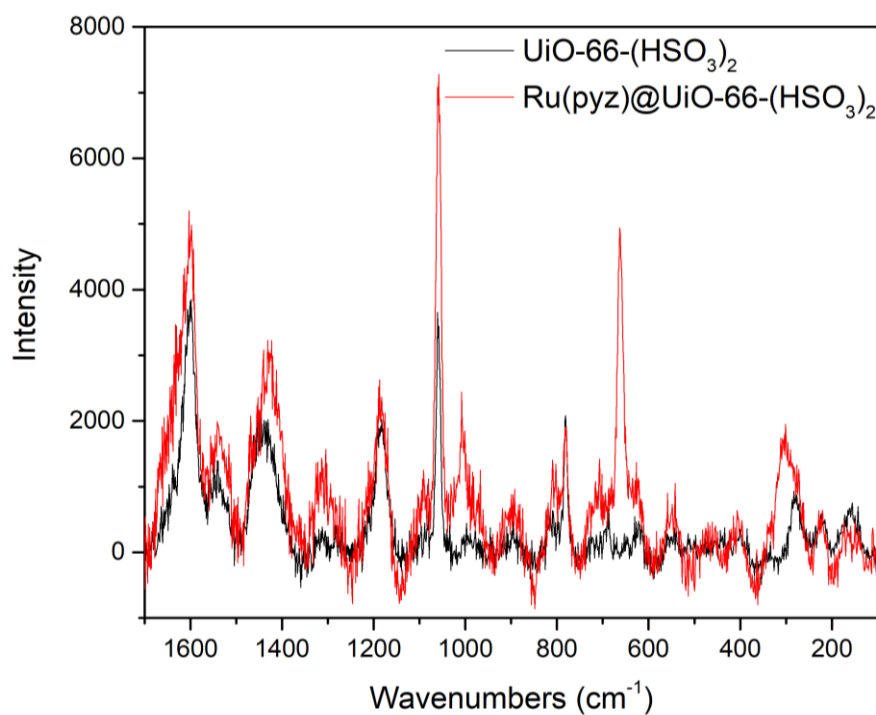


Figure E.3. Raman spectra of $\text{UiO-66-(HSO}_3)_2$ and $\text{Ru(pyz)@UiO-66-(HSO}_3)_2$. Excitation wavelength: 532 nm. Background subtractions were performed with WiRE 5.2.

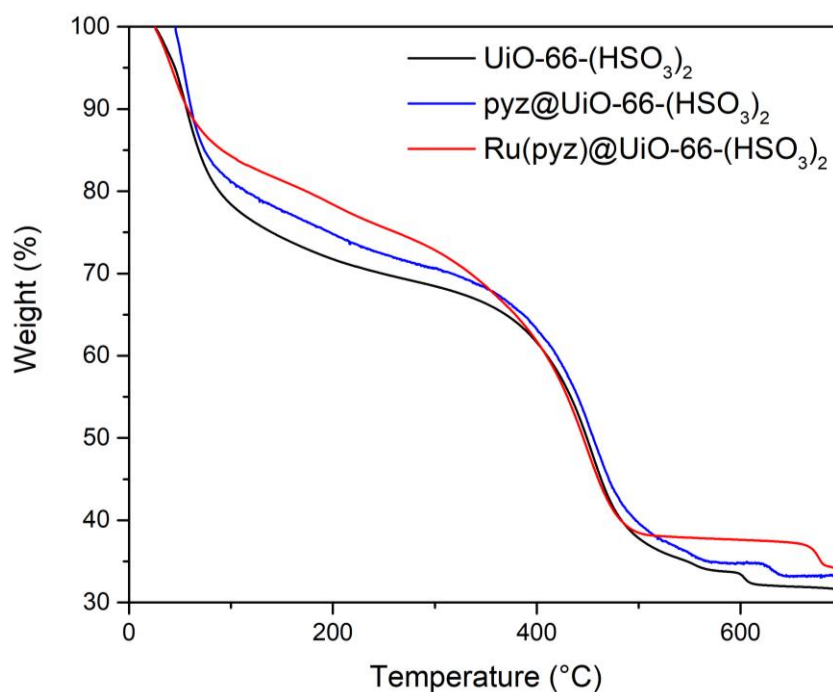


Figure E.4. TGA of $\text{UiO-66-(HSO}_3)_2$, $\text{pyz@UiO-66-(HSO}_3)_2$ and $\text{Ru(pyz)@UiO-66-(HSO}_3)_2$ in air.

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