Magnetic Properties of Heterometallic Ruthenium-based Clusters

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This thesis describes the synthesis of ruthenium based molecular clusters and their characterisation. Chapter 2 introduces the concept that the very large zero-field splitting \(D = 2.9 \text{ cm}^{-1}\) in the \(S = 5/2\) ground state of \([\text{Ru}_2\text{Mn}(\mu_3\text{-O})(\text{BuCO}_2)_6(\text{py})_3]\) can be modelled by antisymmetric exchange effects. This is supported by measurement of the single ion \(D\) values from the Fe\(_2\)Mn analogue. The same model is applied to the Ru\(_2\)Ni analogue to describe the zero-field splitting in the \(S = 1\) ground state, \((D_{GS} = +8.0 \text{ cm}^{-1} \text{ from } D_{\text{Ni}} = -4.0 \text{ cm}^{-1})\) in Chapter 3.

Chapters 3 and 4 give the full characterisation of each of the two families, \([\text{M}^{\text{III}}_2\text{M}^{\text{II}}(\mu_3\text{-O})(\text{BuCO}_2)_6(\text{py})_3]\) (\(\text{M}^{\text{III}} = \text{Ru or Fe, } \text{M}^{\text{II}} = \text{Mn, Co, Ni or Zn}\)), through IR, electronic absorption and NMR spectroscopy and are structurally characterised by X-ray diffraction. The total spin ground states and zero-field splitting of those ground states have been ascertained by SQUID magnetometry and EPR spectroscopy. Due to the redox activity of the Ru\(_2\)M complexes chemical oxidations led to the isolation of \([\text{Ru}^{\text{III}}_2\text{Co}^{\text{III}}\text{O}(\text{BuCO}_2)_6(\text{py})_3]^+\) (5) and \([\text{Ru}^{\text{III}}\text{Ru}^{\text{IV}}\text{Ni}^{\text{II}}\text{O}(\text{BuCO}_2)_6(\text{py})_3]^+\) (6); the locus of their oxidation was determined with the aid of X-ray absorption spectroscopy (XAS).

Chapter 5 shows that due to the ease of the substitution of the terminal ligand in Ru\(_2\)M they can be linked to other molecular clusters with N-donor ligands, in this case \([\text{Cr}_7\text{NiF}_8(\text{BuCO}_2)_{15}(\text{O}_2\text{CC}_5\text{H}_4\text{N})][\text{NH}_2\text{Pr}_2]\) in order to synthesise \([\text{Ru}_2\text{NiO}(\text{BuCO}_2)_6(\text{py})_3(\text{Cr}_7\text{NiF}_8(\text{BuCO}_2)_{15}(\text{O}_2\text{CC}_5\text{H}_4\text{N}))_2][\text{NH}_2\text{Pr}_2]\). In situ oxidation experiments have also been carried out to assess the switchability of the redox active linker.

Chapter 6 demonstrates a new structural archetype for tetranuclear ruthenium mixed-metal complexes, with the formula, \([\text{Ru}_2\text{M}_2(\mu_3\text{-OH})_2(\text{BuCO}_2)_7(\text{py})_4]\), where M is either Co (1) or Ni (2). SQUID magnetometry and EPR spectroscopy have determined the spin ground states as, \(S_{\text{eff}} = 1/2\) in 1 and \(S = 3/2\) in 2. The magnetic anisotropy in 2 has been determined as \(+2.02 \text{ cm}^{-1}\) for the \(S = 3/2\) ground state.
Declaration

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## List of Abbreviations

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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>Acac</td>
<td>Acetylacetone</td>
</tr>
<tr>
<td>ASE</td>
<td>Antisymmetric Exchange</td>
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<tr>
<td>Bta</td>
<td>Benzotriazole</td>
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<tr>
<td>CIF</td>
<td>Crystal Information File</td>
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<td>Cp</td>
<td>Cyclopentadiene</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic volammetry</td>
</tr>
<tr>
<td>EPR</td>
<td>Electron Paramagnetic Resonance</td>
</tr>
<tr>
<td>ESI-MS</td>
<td>Electrospray Ionisation Mass Spectrometry</td>
</tr>
<tr>
<td>Et</td>
<td>Ethyl</td>
</tr>
<tr>
<td>Et&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>Diethyl ether</td>
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<td>EtOH</td>
<td>Ethanol</td>
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<tr>
<td>Et-sao</td>
<td>2-hydroxyphenylpropanone oxime</td>
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<tr>
<td>Him</td>
<td>Imidazole</td>
</tr>
<tr>
<td>H&lt;sub&gt;3&lt;/sub&gt;L</td>
<td>2, 6 – bis(hydroxyl-methyl)-4-methylphenol</td>
</tr>
<tr>
<td>H&lt;sub&gt;3&lt;/sub&gt;thme</td>
<td>1,1,1-tris(hyroxymethyl)ethane</td>
</tr>
<tr>
<td>H&lt;sub&gt;3&lt;/sub&gt;tmp</td>
<td>1,1,1-tris(hydroxymethyl)propane</td>
</tr>
<tr>
<td>INS</td>
<td>Inelastic neutron scattering</td>
</tr>
<tr>
<td>IR</td>
<td>Infra-red</td>
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<td>JT</td>
<td>Jahn-Teller</td>
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<td>Methyl</td>
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<td>Acetonitrile</td>
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<tr>
<td>MeOH</td>
<td>Methanol</td>
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<tr>
<td>MMCT</td>
<td>Metal-to-metal charge transfer</td>
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<tr>
<td>n-Bu</td>
<td>n-butyl</td>
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<tr>
<td>Nitph</td>
<td>2-phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl-3-N-oxide</td>
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<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
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<tr>
<td>Abbreviation</td>
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<tr>
<td>19Pr</td>
<td>n-propyl</td>
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<td>pdmH</td>
<td>Pyridine-2, 6-dimethanol</td>
</tr>
<tr>
<td>Ph</td>
<td>Phenyl</td>
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<td>Phenazine</td>
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<tr>
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<td>Pyrazine</td>
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<td>SOC</td>
<td>Spin-Orbit Coupling</td>
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<td>SMM</td>
<td>Single Molecule Magnet</td>
</tr>
<tr>
<td>SQUID</td>
<td>Super-Conducting Quantum Interference Device</td>
</tr>
<tr>
<td>1Bu</td>
<td>Tert-butyl</td>
</tr>
<tr>
<td>TIP</td>
<td>Temperature Independent Paramagnetism</td>
</tr>
<tr>
<td>tpaMes</td>
<td>Tris-mesityltris(pyrrolylmethyl)amine</td>
</tr>
<tr>
<td>XAS</td>
<td>X-ray Absorption Spectroscopy</td>
</tr>
<tr>
<td>UV-Vis-NIR</td>
<td>Ultra-violet visible near-infra-red</td>
</tr>
<tr>
<td>ZFS</td>
<td>Zero-Field Splitting</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
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<td>-------------</td>
</tr>
<tr>
<td>A</td>
<td>Hyperfine interaction</td>
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<td>B</td>
<td>Magnetic field</td>
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<td>c</td>
<td>Zero-field splitting coefficient</td>
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<tr>
<td>d</td>
<td>Antisymmetric exchange vector</td>
</tr>
<tr>
<td>D</td>
<td>Axial zero-field splitting parameter or anisotropic exchange constant</td>
</tr>
<tr>
<td>E</td>
<td>Rhombic zero-field splitting parameter</td>
</tr>
<tr>
<td>E</td>
<td>Potential or energy</td>
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<tr>
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<td>g-value</td>
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<td>G</td>
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<td>Current</td>
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<tr>
<td>I</td>
<td>Nuclear spin</td>
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<td>J</td>
<td>Isotropic exchange constant or total angular momentum</td>
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<td>L</td>
<td>Orbital angular momentum</td>
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<td>M</td>
<td>Molar magnetisation</td>
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<td>Avogadro’s number</td>
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<td>Residual factor</td>
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<td>Total spin</td>
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<tr>
<td>T</td>
<td>Tesla or Temperature</td>
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<tr>
<td>U</td>
<td>Energy barrier to slow relaxation</td>
</tr>
<tr>
<td>wR₂</td>
<td>weighted residual factor</td>
</tr>
<tr>
<td>z</td>
<td>Charge</td>
</tr>
<tr>
<td>β</td>
<td>Electronic Bohr magneton</td>
</tr>
<tr>
<td>δ</td>
<td>Chemical shift</td>
</tr>
<tr>
<td>ΔE</td>
<td>Energy barrier or peak-to-peak separation</td>
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ε  Extinction coefficient
κ  Orbital reduction factor
λ  Wavelength
σ  Orbital reduction parameter
µ_B  Bohr magneton
χ_M  Molar magnetic susceptibility
Chapter One - Introduction

1.1 Rationale for submitting the thesis in an alternative format

The author of this thesis has been fortunate in being able to publish some of her results in a high impact peer review journal. Timely publication of results is critical in this field for several reasons; firstly the work is highly interdisciplinary and collaborative, with chemists and physicists around the world working in tandem, and so up-date research in the public domain is highly important. Secondly, the requirement for specialised instruments by accessing expensive and specialised national resources (e.g. Diamond Light Source), which require evidence of high level publications. Therefore it has been preferable to publish research during the course of the author’s PhD, with one paper published in a high impact journal and further research contained in this thesis prepared as manuscripts ready for publication. These cover all aspects of the author’s work throughout her PhD and so it has been deemed acceptable to submit the thesis in this format.

1.2 Organisation of thesis

Chapter one provides an introduction to the thesis, reviews the work within this field up to the present time and outlines the aims of the project. Chapter two contains a peer-reviewed publication. Chapters three to six consist of manuscripts ready for publication which are representative of the research undertaken by the author. Chapter seven provides the conclusion to the research as a whole carried out for this thesis and suggests further work.
1.3 Contributing authors

Paper 1, entitled “Large Zero-Field Splitting of the Ground Spin State Arising from Antisymmetric Exchange Effects in Heterometallic Triangles” is a communication written by the thesis author. Synthesis was performed by the author and Grigore Timco. X-ray crystallography was performed by the thesis author. Magnetic measurements and fits were performed by the author. EPR data and simulations were performed by the author, Stephen Sproules and Eric McInnes. High-Field EPR spectra were collected in collaboration with Anne-Laure Barra. Matrix calculations were carried out by Nicholas Chilton and Eric McInnes.

Manuscript 1, entitled “Ground State Description of Heterometallic Clusters [Ru₂MO(²BuCO₂)₆(py)₃]²⁻ (M = Mn, Co, Ni, Zn; py = pyridine; z = 1, 0)” is a full paper written by the thesis author. Synthesis, X-ray crystallography, cyclic voltammetry and electronic spectroscopy were performed by the thesis author. Magnetic measurements and data fits were performed by the thesis author. EPR data and simulations were performed by the thesis author and Stephen Sproules. High-Field EPR spectra were collected in collaboration with Anne-Laure Barra. X-ray absorption spectroscopy was carried out by Kyle Lancaster.

Manuscript 2, entitled “Characterisation of Heterometallic Clusters [Fe₂M(μ₃-O)(²BuCO₂)₆(py)₃] (M = Mn, Co, Ni; py = pyridine) using Multi-frequency EPR spectroscopy” is a full paper written by the author. Synthesis was performed by the author and Grigore Timco. X-ray crystallography, cyclic voltammetry and magnetic measurements and fits were performed by the thesis author. EPR data and simulations were performed by the thesis author and Stephen Sproules. High-Field EPR spectra were collected in collaboration with Anne-Laure Barra.
Manuscript 3, entitled “The Electrochemical Behaviour of a Switchable Ru$_2$Ni Linker between Two Cr$_7$Ni Rings Examined using Cyclic Voltammetry, EPR and UV-vis-NIR Spectroscopy”, is a communication written by the thesis author. Synthesis, cyclic voltammetry and magnetic measurements and fits were performed by the thesis author. X-ray crystallography was carried out by George Whitehead. EPR data and simulations were performed by the thesis author and Stephen Sproules. High-Field EPR spectra were collected in collaboration with Anne-Laure Barra.

Manuscript 4, entitled “Synthesis, Structure and Characterisation of Two New Ruthenium Mixed-Metal Butterfly Type Complexes, [Ru$_2$M$_2$(μ$_3$-OH)$_2$(BuCO$_2$)$_7$(py)$_4$] (M = Co (1), Ni (2) and py = pyridine)” is a full paper written by the author. Synthesis, electronic spectroscopy, cyclic voltammetry and magnetic measurements and fits were performed by the thesis author. X-ray crystallography was carried out primarily by the thesis author with contributions from Iñigo Vitorica-Yrezabal. EPR data and simulations were performed by the thesis author and Stephen Sproules. High-Field EPR spectra were collected in collaboration with Anne-Laure Barra.
1.4 Single molecule magnets: An introduction

Single molecule magnets, or SMMs, are characterised by their ability to be magnetised by an applied magnetic field and then retain this magnetisation for a significant amount of time below a certain temperature (known as the blocking temperature) upon removal of the magnetic field. This slow relaxation of magnetisation is the property that has led to these molecules being considered for high density information storage.

The behaviour of SMMs is directly related to $D$ and $E$, which are the anisotropic zero-field splitting parameters of the system. $D$ is the axial zero-field splitting parameter and $E$ is the rhombic term, illustrated by the Hamiltonian below in Eq. 1.

$$\hat{H} = D\hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2)$$  \hspace{1cm} (1)

In order for a molecule to be an SMM, $D$ is crucial and must be negative. This makes the $M_s = \pm S$ states lowest in energy, and therefore allows exclusive population of these levels. This is often described pictographically by a double well of the $\pm M_s$ states, (Figure 1), which depicts the energy barrier to spin reversal (further illustrated in Figure 2) that is responsible for the slow relaxation of magnetisation.
Figure 1. Diagram showing the double well description of SMMs. Left: $-D$ splits the $\pm M_s$ levels (the lowest energy $\pm M_s$ levels are equally populated at zero-field). Centre: The largest value $-M_s$ level is most stabilised in applied field and is exclusively populated. Right: Upon removal of the field the $\pm M_s$ states return to degeneracy and $\pm M_s$ states with the largest magnitude are equally populated by a series of steps over the barrier.

At zero field the $M_s = -S$ and $M_s = +S$ form degenerate pairs and are equally populated. However once a field is applied, the $M_s = -S$ level becomes lower in energy. Upon removal of the magnetic field, the system returns to thermal equilibrium through a series of steps over the barrier to spin reversal; therefore, the larger the barrier, the longer the relaxation times. The size of the energy barrier ($U_{\text{eff}}$) can be determined from the ground state spin, $S_T$, and the zero-field splitting of the ground state, $D$, (Eq. 2).

$$U = |D|S^2 \quad (2)$$
1.4.1 Single molecule magnets: A brief history

Mn$_{12}$

The first and most famous SMM is Mn$_{12}$, [Mn$^{\text{III}}_{8}$Mn$^{\text{IV}}_{4}$O$_{12}$(O$_2$CMe)$_{16}$(H$_2$O)$_4$] (Figure 3), which was synthesised in 1993.$^{1,2}$ Mn$_{12}$ has an $S = 10$ ground state, resulting from the antiferromagnetic coupling of the eight Mn(III) ions with the four Mn(IV) ions, with a zero-field splitting of $D = -0.46$ cm$^{-1}$. This zero-field splitting results from the Jahn-Teller (JT) distorted Mn(III) ions. The JT axes of the individual ions align in a near parallel orientation such that the single ion anisotropies can combine to give the molecule’s overall anisotropy.

Figure 2. Illustration of the energy barrier to spin reversal and therefore slow relaxation to magnetisation for an $S = 10$ ground state.
Figure 3. Molecular structure of Mn$_{12}$. Key: Mn, purple; O, red; C, black (H atoms omitted for clarity).

Experimental evidence has shown that the $S = 10$ zero-field splitting of $D = -0.46$ cm$^{-1}$ results in an energy barrier $U_{\text{eff}} = 46$ cm$^{-1}$. Mn$_{12}$ also shows magnetic hysteresis at low temperature, below approximately 4 K (Figure 4). Therefore, much of the research to date has concentrated on increasing this energy barrier in order to create SMMs that could be used in data storage.

Figure 4. Hysteresis loops for Mn$_{12}$ in a 0-2 T magnetic field for 2.2 K (●) and 2.8 K (○). Taken directly from reference 3.
1.4.2 A Route to Better SMMs: Increasing \( S \)

One widespread idea to increase the energy barrier to slow relaxation and to create better SMMs was to maximise the total spin of the molecule, and this has been extensively studied using high nuclearity Mn(III) clusters.\(^4\)–\(^8\) Mn(III) clusters are ideal candidates for SMMs, due to their large ground state spins and large anisotropies which are induced by their Jahn-Teller distorted ions. This approach has led to some success although the largest \( U_{\text{eff}} \) value has only increased by about sixty percent from Mn\(_{12}\). However, it has resulted in the synthesis of many interesting and aesthetically pleasing high-nuclearity clusters. The largest SMM to be synthesised is the Mn\(_{84}\) torus-wheel, [Mn\(^{\text{III}}\)\(_{84}\)O\(_{72}\)(O\(_2\)CMe)\(_{78}\)(OMe)\(_{24}\)(MeOH)\(_{12}\)(H\(_2\)O)\(_{42}\)(OH)\(_6\)]\(\cdot\)xH\(_2\)O\(-y\)CHCl\(_3\), shown in Figure 5.\(^4\)

![Figure 5](image)

**Figure 5.** [Mn\(^{\text{III}}\)\(_{84}\)O\(_{72}\)(O\(_2\)CMe)\(_{78}\)(OMe)\(_{24}\)(MeOH)\(_{12}\)(H\(_2\)O)\(_{42}\)(OH)\(_6\)]\(\cdot\)xH\(_2\)O\(-y\)CHCl\(_3\), torus-wheel. Key: Mn\(^{\text{III}}\), purple; O, red; C, black, (H atoms or solvent molecules omitted for clarity).\(^4\)

This complex was obtained using Mn\(_{12}\) as a starting material in a reaction with \((\text{NBu}_4)\text{(MnO}_4\)) in methanol and acetic acid. Sadly, due to the dominant antiferromagnetic exchange interactions between the Mn(III) ions, the ground state of Mn\(_{84}\) is only \( S = 6 \), resulting in a \( U_{\text{eff}} \) of 12.6 cm\(^{-1}\) and hysteresis below 1.5 K, thus Mn\(_{84}\) performs less well as
an SMM than Mn_{12}. This example therefore illustrates the difficulty in controlling the interaction between metal ions within clusters. Other very high nuclearity clusters have also been synthesised in the quest for enhanced SMMs, e.g. [Mn_{30}O_{24}(OH)_{8}(tBuCH_{2}CO_{2})_{32}(H_{2}O)_{2}(MeNO_{2})_{4}], which is isolated from the recrystallisation of [Mn_{12}O_{12}(BuCH_{2}CO_{2})_{16}(H_{2}O)_{4}] in CH_{2}Cl_{2} and MeNO_{2}. Mn_{30} consists of one Mn(IV) ion, twenty-six Mn(III) ions and three Mn(II) ions but it was also found to have a low ground state spin of $S = 5$ with a total anisotropy of $D = -0.51$ cm$^{-1}$. This gave a $U_{\text{eff}}$ of 10.5 cm$^{-1}$, therefore again it is a worse performing SMM than Mn_{12}.

![Molecular structure of [Mn_{25}O_{18}(OH)_{2}(N)_{3}(pdm)_{6}(pdmH)_{6}]Cl_{2}](image)

**Figure 6.** Molecular structure of [Mn_{25}O_{18}(OH)_{2}(N)_{3}(pdm)_{6}(pdmH)_{6}]Cl_{2}, (H atoms and solvent molecules omitted for clarity). Key: Mn, purple; O, red; N, blue; C, black.

Another example is Mn_{25}, [Mn_{25}O_{18}(OH)_{2}(N)_{3}(pdm)_{6}(pdmH)_{6}]Cl_{2}, (pdmH = pyridine-2, 6-dimethanol) (Figure 6). Mn_{25} consists of six Mn(II) ions, eighteen Mn(III) ions and one Mn(IV) ion. It was found to have one of the largest ground state spins known at $S = \frac{51}{2} \pm 1$ but with a very small zero-field splitting of $D = -0.022$ cm$^{-1}$, giving rise to an energy barrier of $U_{\text{eff}} = 8.3$ cm$^{-1}$. The extremely large ground state spin of Mn_{25} is in fact not the largest observed; that title goes to a Mn_{19} complex, [Mn^{III}_{12}Mn^{II}_{7}(\mu_{4}-O)_{8}(\mu_{3}-
N\textsubscript{3})\textsubscript{8}(HL)\textsubscript{12}(MeCN)\textsubscript{6}]\textsubscript{2} \cdot 10\text{MeOH} \cdot \text{MeCN} \quad (\text{H}_{3}\text{L} = 2, 6 – \text{bis(hydroxyl-methyl)-4-methylphenol}) \quad (\text{Figure 7}), \quad \text{which due to dominant ferromagnetic interactions has a ground state spin of a staggering} \quad S = \frac{83}{2}. \quad \text{Unfortunately, Mn}_{19} \quad \text{performs very poorly as an SMM due to its minute zero-field splitting} \quad (U_{\text{eff}} = 4.1 \text{ cm}^{-1}).

\textbf{Figure 7.} \quad \text{The vertex-sharing supertetrahedron} \quad [\text{Mn}^{\text{III}}\text{III}_{12}\text{Mn}^{\text{II}}\text{II}_{7}\text{O}_{8}(\text{N}_{3})_{8}(\text{HL})_{12}(\text{MeCN})_{6}]\text{Cl}_{2} \cdot 10\text{MeOH} \cdot \text{MeCN. Key: Mn, purple; O, red; C, grey; N, blue; (H atoms and solvent molecules are omitted for clarity)}.^5

This research demonstrates that the alignment of the individual ion anisotropies is important, because if they cancel out then the molecule’s anisotropy will be small or zero, resulting in poor SMMs. Since this is due to the geometry of the complex it is almost impossible to control. However in spite of this, some improvements on Mn\textsubscript{12} have been made with 3d metal ions; a hexametallic manganese complex, Mn\textsubscript{6}, [Mn\textsuperscript{III}_{6}O\textsubscript{2}(Et-sao)\textsubscript{6}(O\textsubscript{2}CPh(Me))\textsubscript{2}(EtOH)\textsubscript{4}], (Et-saoH\textsubscript{2} = 2-hydroxyphenylpropanone oxime) (\text{Figure 8}), was found to have a ground state spin of $S = 12$ with a total anisotropy of $D = -0.43 \text{ cm}^{-1}$, thus enhancing the energy barrier to magnetic reversal to $U_{\text{eff}} = 60.5 \text{ cm}^{-1}$, which is approximately 10 cm$^{-1}$ larger than Mn\textsubscript{12}.\textsuperscript{10}
Figure 8. Molecular structure of the hexametallic manganese complex, $[\text{Mn}^{\text{III}}_6\text{O}_2(\text{Et-sao})_6(\text{O}_2\text{CPh}\text{Me})_2\text{(EtOH)}_4]$, (H atoms and solvent molecules omitted for clarity).\(^{10}\) Key: Mn\(^{\text{III}}\), purple; O, red; N, blue; C, black.

Synthesising high nuclearity complexes with large ground state spins may not be the best approach to creating new SMMs with larger energy barriers, so the next section will discuss the importance of the zero-field splitting.

1.4.3 Single molecule magnets: The importance of $D$

In Mn\(_{12}\), the ground state zero-field splitting is equal to $D = -0.46$ cm\(^{-1}\) (discussed above), and a similar value is obtained for Mn\(_6\), $D = -0.43$ cm\(^{-1}\). These values are an order of magnitude smaller than mononuclear axially elongated Mn(III) complexes, which have typical zero-field splittings of $D = -4.5$ cm\(^{-1}\) (e.g. [Mn(acac)]\(_3\), $D = -4.52$ cm\(^{-1}\)).\(^{11}\) This decrease in total anisotropy is due to the projection of the local anisotropies onto the total spin ground state. Therefore, perhaps efforts to increase the zero-field splitting should be the main focus in the search for SMMs with increased energy barriers. This has been
supported by Neese et al. who concluded that $D$ is in fact inversely proportional to $S^2$, Eq. 3.

\[ D \propto -1/S^2 \quad (3) \]

A suggestion which has been supported by theoretical calculations and modelling is that the zero-field splitting of metal ions can be increased by adopting coordination environments and electronic configurations which promote orbital near-degeneracies that are able to maximise spin-orbit coupling (SOC). An example of this is given by high-spin $d^6$ systems in a flat-based trigonal pyramidal geometry, which results in the orbital configuration shown below in Figure 9. In this arrangement two sets of degenerate orbital are observed with $xz$ and $yz$ being the lowest, $xy$ and $x^2-y^2$ the middle and $z^2$ the highest in energy.

Figure 9. Trigonal pyramidal high-spin Fe(II) complex, $K[(tpaMes)Fe]$ (tpaMes = tris-mesityltrim(5-methyl)pyrrolidinyl)amine) and the corresponding idealised $d$-orbital configuration. Key: Fe, orange; O, red; N, blue; C, black; (H atoms omitted for clarity).

The magnetic susceptibility data for the high-spin Fe(II) compound $K[(tpaMes)Fe]$, (Figure 9) were fitted with a zero-field splitting of $D = -39.6 \text{ cm}^{-1}$. Therefore, theoretically this large anisotropy could lead to a spin reversal barrier of $U_{eff} = 158 \text{ cm}^{-1}$.
which is significantly larger than all the polynuclear 3d SMMs known to date. Unfortunately, the experimental data gave a much lower value ($U_{\text{eff}} = 42 \text{ cm}^{-1}$). This lower than predicted value is due to quantum tunnelling through the energy barrier which becomes allowed due to transverse anisotropy, $E$, that arises from a slight distortion from three-fold symmetry at the Fe(II) centre. A small $E$ value ($E = 0.4 \text{ cm}^{-1}$) must be included to gain an accurate fit of the susceptibility data discussed above.

Another way to promote SOC and thus increase the zero-field splitting within a complex could be to use metal ions that already possess large SOC, i.e. the heavier metals (4d and 5d), as SOC increases on descending the periodic table. Comparing the free-ion SOC coefficients of ruthenium and iron, there is a large increase from iron to ruthenium ($\xi_{\text{Ru}} = 1180 \text{ cm}^{-1}$ and $\xi_{\text{Fe}} = 460 \text{ cm}^{-1}$). Extremely large zero-field splittings are common in ruthenium tetracarboxylate complexes, for example $[\text{Ru}_2(\text{RCO}_2)_4(L)_2]^{0/+}$ (RCO$_2$ = carboxylate, L = solvent or bridging ligand), which can exhibit zero-field splittings up to $D = \sim 300 \text{ cm}^{-1}$ in its $S = 1$ ground state.

1.5 Larger $D$: Ruthenium dimers

Such tetracarboxylate dimers, often referred to as lantern or paddle wheel complexes, are known for a variety of metals (Cr, Mo, W, Tc, Re, Ru, Os, Co, Rh, Ir, Ni and Cu). Ruthenium is one of the newest, and potentially the most interesting, members of this family of complexes.$^{16}$ Ruthenium tetracarboxylate dimers were first synthesised in 1966, by Stephenson and Wilkinson, as the mixed-valent chloride bridged chain complexes, $[\text{Ru}_2(\text{RCO}_2)_4\text{Cl}]^{0/+}$ (R = Me, Et or $^8\text{Pr}$), from the reaction of RuCl$_3$.xH$_2$O with the appropriate carboxylic acid and anhydride under reflux.$^{17}$ Ruthenium tetracarboxylate complexes can be found as either discrete molecules, $[\text{Ru}_2(\text{RCO}_2)_4\text{L}_2]^{0/+}$ or as linear or bent chains, $[\text{Ru}_2(\text{RCO}_2)_4\text{X}]^{0/+}$ (X = bridging ligand) (Figure 10).
Ruthenium tetracarboxylate complexes are of particular interest due to their magnetic properties, as the mixed valent Ru$_2$(II,III) complexes have three unpaired electrons ($S = \frac{3}{2}$ ground state) with the odd electron delocalised between the two metals, *i.e.* Ru$_2$(II$^{1/2}$/II$^{1/2}$).

The three unpaired electrons result from the near degeneracy of the $\pi^*$ and $\delta^*$ molecular orbitals that make up the metal-metal bond. It has been postulated by Norman and co-workers that the electronic configuration of the $S = \frac{3}{2}$ ground state is; $\sigma^2\pi^2\delta^2\pi^*^2\delta^{*1}$ (Scheme 1a).\textsuperscript{18} The $\delta^*<\pi^*$ configuration would be favoured if the bonding was entirely metallic in nature. However, this is not the case as the $\delta^*$ orbital interacts significantly with the low lying carboxylate orbitals.\textsuperscript{19}

**Figure 10.** Molecular structure of tetracarboxylate complex, [Ru$_2$(tBuCO$_2$)$_4$(H$_2$O)$_2$]$^+$.\textsuperscript{16}

Key: Ru, violet; O, red; C, black; (H atoms and counter ion omitted for clarity).
Scheme 1. (a) left; molecular orbital scheme for \([\text{Ru}_2(\text{RCO}_2)_4]^+\), (b) right; the more favoured molecular orbital scheme for \([\text{Ru}_2(\text{RCO}_2)_4]\).

These complexes also exist in the usually air-sensitive homovalent form \([\text{Ru}_2(\text{II},\text{II})]\) with two unpaired electrons in the \(\pi^*\) and \(\delta^*\) manifold to give an \(S = 1\) ground state, \((\sigma^2\pi^2\delta^2\pi^*\delta^*\pi^*\delta^*\delta^*\pi^*\delta^*\delta^*)\), (Scheme 1b).\(^19\) The configuration \((\pi^*)^2(\delta^*)^2\) has been favoured more recently over \((\pi^*)^3(\delta^*)^1\), as DFT calculations yielded a \((\pi^*)^2(\delta^*)^2\) ground state with the \((\pi^*)^3(\delta^*)^1\) triplet lying slightly higher in energy \((0.012 \text{ au})\).\(^19\) Both the hetero and homovalent forms are characterised by very large zero-field splitting, at \(D = \sim +70 \text{ cm}^{-1}\) and \(\sim +250 \text{ cm}^{-1}\) respectively.\(^16\) These huge values are due to the complexes containing 4d metals and with closely spaced electronic states. A lot of research has been conducted into the interdimer communication in these linked chains, towards molecular wires. Early variable temperature magnetic susceptibility studies on the mixed valent bent chain complex \([\text{Ru}_2(\text{PrCO}_2)_4\text{Cl}]\_\infty\) found that the data were best modelled as isolated dimeric units with \(D = +77 \text{ cm}^{-1}\) according to the Hamiltonian below in Eq. 4.\(^20\)

\[
\hat{H} = \beta(gS)H + D \left[\hat{S}_z^2 - \left(\frac{1}{3}\right)S(S+1)\right] + E(\hat{S}_x^2 - \hat{S}_y^2) \tag{4}
\]

Attempts to fit the data with an exchange between the dimer units, resulted in a poorer fit. It may seem surprising that no communication was observed but when considering the bent
arrangement of the polymeric chain, the lack of an interaction becomes apparent. The X-ray structure shows the Ru-X-Ru angle is 125°, and therefore the overlap between the magnetic orbitals between adjacent clusters will be poor. It was thought that the interdimer interaction would be optimised in a linear arrangement. Attempts to obtain linearity started with the use of linear bidentate ligands such as pyrazine. One investigation conducted by Cukiernik et al. found that in polymeric \([\text{Ru}_2(\text{MeCO}_2)_4(pz)]_n(\text{BPh}_4)_n\) there was an antiferromagnetic exchange interaction between the Ru\(_2\) dimeric units, but the interaction was very small at \(J = \sim -2.0\) cm\(^{-1}\). Similar \(J\)-values were also observed for the homovalent derivative \([\text{Ru}_2(\text{CF}_3\text{CO}_2)_4(\text{phz})]_\infty\) (\text{phz} = phenanzine) \((J = -3.0\) cm\(^{-1}\)).\(^{21,22}\) Changing from a diamagnetic to a radical linker, such as nitph (2-phenyl-4,4,5,5-tetramethyl-4,5-dinydro-1\(H\)-imidazol-1-oxyl-3-N-oxide) in \([\text{Ru}_2(\text{BuCO}_2)_4(\text{nitph})]_n(\text{BPh}_4)_n\) was thought to increase the interaction between the dimeric units.\(^{23}\) However, this zig-zag structure only shows a strong antiferromagnetic interaction between the Ru\(_2\) dimer and the radical linker \((J = -100\) cm\(^{-1}\)).

1.6 Carboxylate chemistry: Ruthenium oxo-centered carboxylate triangles

1.6.1 An introduction to oxo-centered carboxylate triangles

The most common type of trinuclear carboxylate clusters are those known as oxo-centered carboxylate triangles, often referred to as basic metal carboxylates.\(^{24,25}\) These compounds were first synthesised in the 19\textsuperscript{th} century but the correct structure was not realised until 1928, when Welo postulated the triangular structure on the basis of the magnetic data.\(^{26,27}\) This was further supported in 1960 by Orgel, who successfully modelled the triangular unit with a central oxide ion and X-ray diffraction studies later confirmed the proposed structure.\(^{28,29}\) Trinmetallic oxo-centered carboxylate clusters have the general formula \([\text{M}_3(\mu_3-O)(\text{RCO}_2)_6(\text{L})_3]^{0/+}\) (\(\text{L} = \text{solvent, CO or N-heterocycles}\)), and are common
throughout the d-block, with examples in 3d, 4d and 5d.\textsuperscript{24,25,31,32} The versatile chemistry of these clusters has led to the synthesis of homo and heterovalent homometallic complexes as well as homo and heterovalent heterometallic clusters with a variety of carboxylate bridges and terminal ligands. The heterometallic clusters extend across the periodic table with mixed-metal complexes containing different 3d metals, 3d-s/p block metals, 3d-4d, 4d-4d and 4d-5d combinations.\textsuperscript{25,30,32-38} A schematic representation of an oxo-centered carboxylate ruthenium triangle is shown in Figure 11.

\textbf{Figure 11.} Schematic representation of an oxo-centered trinuclear ruthenium carboxylate cluster, \textit{(R = carboxylate ligands and L = solvent or N-heterocyclic ligands)}.\textsuperscript{24}

The triangular arrangement of the metal ions is reinforced by a central $\mu_3$-oxide ion, which lies flat in the plane of the molecule, and six bridging carboxylates, which are canted $\sim60^\circ$ above and below the metal core. The coordination sphere of each metal ion is completed by a terminal solvent or $N$-donor ligand.\textsuperscript{25,24} However, with the molybdenum and tungsten analogues there are two central $\mu_3$-oxide ions above and below the triangular plane.\textsuperscript{30,31}
1.6.2 Properties:

Isotropic exchange interactions, $J$

The magnetic properties of many of the oxo-centered carboxylate triangles known to date are well understood and dominated by strong antiferromagnetic exchange interactions between the three metal ions.\textsuperscript{25,27,39,40} Initial attempts to fit the magnetic data of the iron and chromium analogues used a single isotropic exchange parameter, $J$, assuming threefold symmetry, according to Eq. 5, where the symbols have their usual meanings, and $S_i$ is the spin of the individual metal ion.\textsuperscript{25}

$$\hat{H} = -2J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_2 \cdot \hat{S}_3 + \hat{S}_3 \cdot \hat{S}_1)$$ \hspace{1cm} (5)

However, a much better description is usually that the metal ion triangles are significantly distorted and are best described as isosceles, and therefore the Hamiltonian is transformed in the equation shown below, with two different $J$ parameters (Eq. 6).

$$\hat{H} = -2J_{12}(\hat{S}_1 \cdot \hat{S}_2) - 2J_{12-3}(\hat{S}_1 \cdot \hat{S}_3 + \hat{S}_2 \cdot \hat{S}_3)$$ \hspace{1cm} (6)

The isosceles model is also required to fit data from inelastic neutron scattering (INS) and Mössbauer studies, which could not be fitted with an equilateral triangle model.\textsuperscript{41,42} For example, a best fit for the magnetic data of iron acetate, [Fe\textsuperscript{III}_3(\text{μ}_3-O)(\text{MeCO}_2)_6(\text{H}_2\text{O})_3]Cl, yielded $J_{12} = -38.2$ cm\textsuperscript{-1} and $J_{12-3} = -28.9$ cm\textsuperscript{-1}.\textsuperscript{43}

1.6.3 Antisymmetric and anisotropic exchange interactions and spin frustration

The basic description of exchange coupled triangular complexes is given by the exchange interactions in the isotropic Hamiltonians shown above in Eqs. 5 and 6. However, this scheme is unable to explain the observed experimental data (EPR, optical and Mössbauer spectra) collected on some trinuclear clusters.\textsuperscript{44,45} We take Cu\textsuperscript{II}_3 as the simplest example. A
Cu$^{II}_3$ triangle has an $S = \frac{3}{2}$ and two $S = \frac{1}{2}$ states as a result of the exchange coupling. They can be easily justified by explaining the interactions of each of the metal ions, as each Cu(II) ion can interact with its neighbouring spins; i.e. two $S = \frac{1}{2}$ Cu(II) centres can interact to give either an $S = 1$ or $S = 0$ unit which can then interact with the remaining Cu(II) $S = \frac{1}{2}$ ion to give an $S_T = \frac{3}{2}$ and $S_T = \frac{1}{2}$ and another $S_T = \frac{1}{2}$ respectively. In the isotropic coupling scheme the two $S_T = \frac{1}{2}$ states are accidentally degenerate and are the ground state (Figure 12); this degeneracy is known as spin frustration. One definition of the term ‘frustration’ defines a system that cannot effectively cancel its pair-wise interactions. Although the interactions are antiferromagnetic, each configuration shown in Figure 13 results in a pair of spins that align parallel to each other.

**Figure 12.** Energy diagram of three antiferromagnetically coupled Cu(II) trimetallic complexes, adapted from reference 45. The experimental data on such competing spin configurations often leads to the requirement of higher-order exchange terms being included in the exchange Hamiltonian (Eq. 6). Antisymmetric and anisotropic exchange effects have been suggested as the two largest non-Heisenberg contributions, which are first and second-order in spin-orbit coupling effects respectively. Simplifying the example to an interaction between two
centres, the exchange Hamiltonian can then be rewritten as Eq. 7, where $D$ is the anisotropic exchange tensor and $\vec{g}$ is the antisymmetric exchange vector.

\[ \vec{H}_{12} = -2J \hat{S}_1 \cdot \hat{S}_2 + \hat{S}_1 \cdot \hat{D} \cdot \hat{S}_2 + \vec{g}(\hat{S}_1 \times \hat{S}_2) \] (7)

Figure 13. Illustration of the competing spin configurations of the spin frustrated ground state $^2E$ in a Cu$^{II}_3$ triangle complex, adapted from reference 45.

Anisotropic and antisymmetric exchange effects give rise to off-diagonal elements of the exchange matrix and become important when strong SOC effects are present. These effects arise from superexchange between the ground state on one metal with the excited state of another, whereas isotropic exchange ($J$) is between the metal ion ground states.46-48
1.6.4 The chemistry of ruthenium oxo-centered carboxylate triangles

The basic synthetic procedure for these complexes has been described by Spencer and Wilkinson (Scheme 2) and involves refluxing ethanol solutions containing RuCl$_3$.xH$_2$O, the appropriate carboxylic acid and sodium carboxylate.  

![Scheme 2. Synthesis of [Ru$_3$(μ$_3$-O)(RCO$_2$)$_6$(S)$_3$]$^+$ (RCO$_2$ = carboxylate and S = solvent), taken from reference 24.](image)

The reaction mechanism for the synthesis of these compounds has not been investigated but it has been proposed that the reaction proceeds via a dinuclear complex, [Ru$_2$O(RCO$_2$)$_2$], as an intermediate species, which would explain the formation of Ru$_2$M and not RuM$_2$ when synthesising mixed-metal derivatives.$^{50,51}$

The triangular structure of [Ru$_3$(μ$_3$-O)(RCO$_2$)$_6$(S)$_3$]$^+$ gives rise to interesting chemical properties, because of the close proximity of the metal ions. This results in strong electronic and magnetic interactions, allowing the stabilisation of a series of successive oxidation states, characterised by electrochemistry, in which four or five reversible redox waves are observed corresponding to:

Ru$_3^{IV,IV,III}$O/Ru$_3^{IV,III,III}$O/Ru$_3^{III,III,III}$O/Ru$_3^{III,II,II}$O/Ru$_3^{III,II,II}$O/Ru$_3^{II,II,II}$O. The separation between each wave is ~1 V, thus showing extensive electronic delocalisation within the molecule (Figure 14).

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Figure 14. Cyclic voltammograms of the [Ru$_3$O(MeCO$_2$)$_6$(pz)$_3$] cluster (3 mM) obtained at several scan speeds, in acetonitrile ([NEt$_4$ClO$_4$] 0.1 M), in the 2.0 to −2.0 V range taken directly from reference 24.$^{24,52}$

Ruthenium oxo-centered carboxylate triangles can be used as starting materials for larger clusters. There has been extensive research into linking oxo-centered ruthenium triangles with bridging ligands, such as pyrazine or 4,4'-bipyridine exploiting the lability of the terminal solvent ligands.$^{24}$ The replacement of one of these terminal ligands with a bridging ligand results in ligand bridged dimers (Figure 15).
Further substitution and rational design leads to polymeric structures, for example using [Ru₃O(MeCO₂)₆(CO)(MeOH)]₂ with pyrazine in MeOH, a cyclic hexamer is produced [Ru₃O(MeCO₂)₆(CO)(pz)]₆ (Figure 16).²⁴

The interaction between the Ru₃O units is reflected in their electrochemistry, which is dependent upon both the nature of the bridging ligand and the electron density of the Ru₃O
unit. This interaction is particularly strong with the pyrazine bridged units, due to favourable overlap between the Ru$_3$O cluster d-orbitals and the ligand $\pi^*$ orbitals. The electronic coupling was found to increase on reduction of the complex and electronic spectroscopic studies on a mixed pyrazine bridged cluster, [Ru$_3$O$^{\text{III,II,II}-\text{pz}}$Ru$_3$O$^{\text{III,II,II}}$], supported its classification as a delocalised class III system, according to the Robin-Day classification of mixed valence charge transfer complexes.

The ease of substitution of the terminal solvent ligands on Ru$_3$O clusters is clearly illustrated in the synthesis of the complexes discussed above. However, the kinetics of ruthenium and therefore the rate of substitution at the terminal site is much slower than other d-block metals. The rate of substitution of pyridine ligands on ruthenium in [Ru$_2$M$_3$-O)(MeCO$_2$)$_6$(py)$_3$] (10$^{-4}$ s$^{-1}$), where M = Zn or Mg, were compared to the rates in [Ru$_3$($\mu_3$-O)(MeCO$_2$)$_6$(py)$_3$]$^+$ (2.4x10$^{-7}$ s$^{-1}$) and it was revealed that Zn and Mg ions in the former showed an induced labilization effect on the Ru(III) ions, as the rate of substitution increased 500 fold. Hence, the enhanced reactivity of the mixed-metal ruthenium complexes over the homometallic ruthenium triangles, may provide a facile route for synthesising larger ruthenium based clusters from smaller preformed clusters.

### 1.6.5 Mixed-metal ruthenium oxo-centered triangles

The 4d-3d mixed-metal clusters [Ru$_2$M$_3$-O)(RCO$_2$)$_6$(L)$_3$] (M = Mn, Co, Ni, Zn, Mg; L = H$_2$O, py), briefly discussed in the previous section, can be made through a simple synthetic procedure similar to the homometallic ruthenium triangles. Much of the literature on this family of compounds suggests that the magnetic properties are that of the divalent metal. This is explained by the much stronger interaction of the two ruthenium ions than with the 3d metal ion. The two ruthenium ions are so very strongly
antiferromagnetically coupled that they are effectively diamagnetic \((S = 0)\), so the magnetic data appears close to that of the isolated divalent metal ion (Figure 17).  

![Graph showing magnetic moment vs. temperature](image)

**Figure 17.** Effective magnetic moment of mixed-metal ruthenium acetate trinuclear clusters \([\text{Ru}_2M(\mu_3-O)(\text{MeCO}_2)_6(\text{py})_3]\), \((M = \text{Mn} = \bullet, \text{Co} = \bigtriangleup, \text{Ni} = \square, \text{Zn} = \bigcirc\) and \(\text{Mg} = \Delta\)) figure taken directly from reference 32.

The strong interaction between the ruthenium ions and the interaction of the ruthenium ions with a heterometal has not been fully described in the literature and is worth investigating, as most reports ascribed different properties to be due to either the \(\text{Ru}_2\) unit (electronic and redox) or the heterometal (magnetic) rather than the cluster as a whole, so further study is clearly required to discover how the metals interact with each other in the cluster.

The properties intrinsic to ruthenium and ruthenium-based complexes; *i.e.* the large spin-orbit coupling of ruthenium, the extensive electronic delocalisation (reversible redox chemistry of \(\text{Ru}_3\text{O}\)) and large zero-field splitting of \([\text{Ru}_2(\text{RCO}_2)_4\text{L}]^{0+}\), may be able to be exploited in the quest for new magnetic materials, *e.g.* SMMs and switchable molecular devices.
1.7 References


1.8 Aims

The majority of the research into single molecule magnets (SMMs) has involved 3d metals or 3d/4f complexes, with recent work more focused on the lanthanide ions. However, little research has involved the use of 4d metals for the same purpose. Therefore the aim of my project was to extend this chemistry to 4d metals, with the anticipation of understanding the electronic and magnetic properties of these complexes, leading to their use as tool for increasing anisotropy of magnetic clusters and as starting materials in the synthesis of larger assemblies or as a linker between other metallic clusters.

The main focus of my project was to use ruthenium as a tool for increasing the anisotropy in molecular magnets, by initially synthesising small heterometallic ruthenium clusters, \([\text{Ru}_2\text{MO'(BuCO}_2\text{)}_6\text{(py)}_3]\) (M = Mn, Co, Ni and Zn, py = pyridine) and fully characterising them and then comparing them to their 3d metal counter parts, \([\text{Fe}_2\text{MO'(BuCO}_2\text{)}_6\text{(py)}_3]\).

The next step was then to use the smaller trinuclear units as starting materials in larger assemblies or as linkers between molecular clusters, due to the extensive redox chemistry of ruthenium compounds and the ease of substitution of their terminal ligands, thus allowing us to study the interaction between the individual components within the linked system.
Chapter Two – Paper 1

“Large Zero-Field Splittings of the Ground Spin State Arising from Antisymmetric Exchange Effects in Heterometallic Triangles”

... of the electronic exchange interaction (also known as Dzyaloshinski-Moriya exchange) is often overlooked in modeling the magnetic data of molecular species, but in the Communication by E. J. L. McInnes and co-workers on page 5310 ff., it is shown to be responsible for the large magnetic anisotropy in the $S = 5/2$ ground state of a trimetallic complex. The illustration plays on the concept of “antisymmetry” and triangles with an Escher triangle.
Large Zero-Field Splittings of the Ground Spin State Arising from Antisymmetric Exchange Effects in Heterometallic Triangles**

Samantha A. Magee, Stephen Sproules, Anne-Laure Barra, Grigore A. Timco, Nicholas F. Chilton, David Collison, Richard E. P. Winpenny, and Eric J. L. McInnes*

Abstract: \[\text{[Ru}_2\text{Mn(O)(O}_2\text{CtBu)}_6\text{(py)}_3\text{]}\] has an \(S = \frac{1}{2}\) ground state with a very large zero-field splitting (ZFS) of \(D = 2.9 \text{ cm}^{-1}\), as characterized by EPR spectroscopy at 4–330 GHz. This is far too large to be due to the MnII ion (\(D < 0.2 \text{ cm}^{-1}\)), as shown from the \([\text{Fe}_2\text{Mn}]\) analogue, but can be modeled by antisymmetric exchange effects.

The magnetic anisotropy in transition-ion clusters is of fundamental importance in areas such as molecular magnetism, for example giving rise to memory effects\(^{[3]}\) through to the characterization of metalloenzyme active sites\(^{[2]}\). When the ground state can be described by a total electron spin \(S > \frac{1}{2}\), arising from dominant isotropic exchange, the magnetic anisotropy tends to be dominated by the zero-field splitting (ZFS) of the \((2S + 1)\)-fold multiplet. This is generally assumed to be dominated by the projection of the local ZFSs of the metal ions\(^{[5]}\) when the local spins are \(s = \frac{1}{2}\) (and have no ZFS) or when they are intrinsically isotropic, such as the \(\text{S Mn}^2+\) ion, it is well understood that anisotropic components of the exchange are the main contributions to the ZFS. In contrast, the general significance of the antisymmetric component of the exchange interaction on \(S > \frac{1}{2}\) states is not so clear: here we introduce an example where it provides the source of very large ZFS effects.

Antisymmetric exchange (ASE; also known as Dzyaloshinski–Moriya exchange) is the origin of spin canting (weak ferromagnetism) in extended lattices. In terms of molecular systems, ASE was first observed and discussed in trigonal clusters of half-integer spins\(^{[4]}\). This is because they provide the simplest discrete systems in which spin frustration can be studied\(^{[6]}\). Since antiferromagnetic coupling in an equilateral triangle leads to two degenerate \(S = \frac{1}{2}\) lowest energy states (\(\text{E}^\text{term}\) state). ASE provides a mechanism for breaking the \(\text{E}^\text{term}\) degeneracy and these effects can be quantified by EPR spectroscopy as they are manifested as unusual g-values\(^{[3, 4]}\).

The unusual EPR signatures of some trimetallic Cu\(^{[7]}\) and FeS\(^{[8]}\) enzymes can be explained by these effects. ASE effects on \(S > \frac{1}{2}\) states are much less studied, although it has been proposed as a mechanism for otherwise-forbidden magnetization quantum tunneling steps in Mn\(_{12}\) and other single molecule magnets\(^{[9]}\) and also for the origin of high-order ZFS effects\(^{[10]}\).

Belinsky\(^{[11]}\) and Tsukerblat et al.\(^{[12]}\) have calculated the effects of the ASE on the maximum \(S = \frac{1}{2}\) state (as ground or excited state) in Cu\(^{2+}\) and V\(^{4+}\) triangles. They showed that components of the ASE within the M\(_3\) triangle could break the degeneracy, that is, introduce a ZFS. However, in-plane components are symmetry forbidden when the M\(_3\) triangle lies on a mirror plane\(^{[5]}\). They further showed that symmetry-allowed components normal to the triangle do not split the quartet unless there is a large isosceles distortion. Here we show that this can explain the huge ZFSs in the \(S > \frac{1}{2}\) ground state of the heterometallic triangle \([\text{Ru}_2\text{Mn(O)}-(t\text{BuCO}_2)_6\text{(py)}_3\text{]}\) which we have characterized by multifrequency EPR spectroscopy from 4 to 330 GHz.

\([\text{Ru}_2\text{Mn}]\) and its \([\text{Fe}_2\text{Mn}]\) analogue both crystallize in the \(P_2_1\) space group with one molecule per asymmetric unit (ESI): the Mn site is not crystallographically resolved. They have the classic structure of basic metal carboxylate triangles\(^{[13]}\), with bridging pivalate and terminal pyridine groups (Figure 1). The acetate analogues of these complexes have been reported\(^{[14, 15]}\) and we find similar magnetic susceptibility (\(\chi\)) behavior. \([\text{Ru}_2\text{Mn}]\) has \(\chi T = 4.42 \text{ cm}^2\text{Kmol}^{-1}\) (Figure 2), the

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Figure 1. Molecular structure of \([\text{Ru}_2\text{Mn}]\).\(^{[26]}\) Scheme: \(\text{Ru/Mn}\) (large spheres), O (gray), N (white), C (black). H omitted for clarity. Average M–M and M–O distances: 3.36(4) and 1.94(4) Å in \([\text{Ru}_2\text{Mn}]\) and 3.32(4) and 1.91(5) Å in \([\text{Fe}_2\text{Mn}]\), respectively.
value expected for an isolated $S = \frac{1}{2}$ state, hence the magnetic properties appear at first sight to be those of the isolated Mn$^{III}$ ion. Using the isotropic Hamiltonian $H_{\text{iso}}$ [Eq. (1)]:

$$H_{\text{iso}} = \sum_i g_i \beta \mathbf{H} - 2J_i \left( \mathbf{s}_i \cdot \mathbf{s}_j \right) - D \left( \mathbf{s}_i \cdot \mathbf{S} \right)$$  \hspace{1cm} (1)$$

where $s_i = s_j = \frac{1}{2}$ (Ru$^{III}$, low-spin d$^4$) and $s_i = \frac{3}{2}$ (Mn$^{II}$, high-spin d$^5$), this corresponds to the $|0,0\rangle$ ground state ($|S,0\rangle$). A simple Kambé treatment gives this ground state for $J_{\text{ru}}/J_{\text{mn}} > 3.5$, with the first excited state ($|1,3/2\rangle$) at a relative energy of $7J_{\text{ru}} - 2J_{\text{mn}}$. Test calculations show that $|J_{\text{mn}}|$ must be greater than ca. 10$^{10}$ cm$^{-1}$ and that $J_{\text{ru}}/J_{\text{mn}}$ must be greater than ca. 10 for there to be no evidence of excited-state population in $\chi(T)$ at high temperature. Large $|J_{\text{rs}}|$ values are justified by the large radial extent of the 4d wavefunctions, and indeed direct overlap as opposed to super-exchange is possible. Couplings of this magnitude have been observed in homometallic Ru$^{III}$ cages.$^{[19]}$

Fitting the low-temperature drop in $\chi(T)$, and magnetization ($M$) data (Figure 2), for an isolated $S = \frac{1}{2}$ with $H_{\text{ZFS}}$ [Eq. (2)], gives the axial ZFS parameter $|D| = 3.0$ cm$^{-1}$ ($E = 0$, with fixed $g = 1.98$).$^{[20]}

$$H_{\text{ZFS}} = g_i \beta \mathbf{H} + D \left( S_i \cdot \frac{S(S + 1)}{3} \right) + E \left( S_i^z \right)$$  \hspace{1cm} (2)$$

This is much larger than estimated previously for the acetate analogue by low-frequency EPR spectroscopy.$^{[21]}$ Therefore, we have measured the value of $D$ directly by high-frequency EPR spectroscopy.$^{[21]}$ Spectra at low frequencies are those of an axial effective spin $\frac{1}{2}$ with $g_{\text{eff}} \approx 6$ and $R_{\text{ZFS}} \approx 2$, consistent with a ground-state $M = \pm \frac{1}{2}$ Kramers doublet, with resolved $^{55}$Mn hyperfine for frozen solution samples (Figure 3a and see Figure S1 in the Supporting Information). Spectra recorded at 220 and 330 GHz (Figure 3) unambiguously define the $S = \frac{1}{2}$ multiplet, and simulation$^{[22]}$ with $H_{\text{ZFS}}$ gives $D = +2.9$ cm$^{-1}$ ($E = 0$) with $g = 1.98$ (see Figure S2 in the Supporting Information).

In this simple model the ZFS of the $|0,0\rangle$ state should correspond to that of the isolated Mn$^{III}$ site. However, this is absurd: the largest values reported for six-coordinate Mn$^{III}$ ions with ON donor sets are $|D| < 0.2$ cm$^{-1}$. To test the model we have prepared and studied the equivalent 3d complex [Fe$_2$Mn] in which the Mn$^{III}$ ion has the same coordination environment. Fitting $\chi(T)$ for [Fe$_2$Mn] to $H_{\text{iso}}$ with $s_i = s_j = \frac{1}{2}$ gives $J_i = -63.5$ and $J_j = -21.9$ cm$^{-1}$ with $g = 2.0$ (Figure 2), similar to its acetate analogue.$^{[23]}$ This gives the $|1,3/2\rangle$ ground state, as confirmed by low-temperature magnetization and EPR measurements. Modeling the latter with $H_{\text{ZFS}}$ for $S = \frac{3}{2}$ gives $D = +0.25$, $|E| = 0.04$ cm$^{-1}$ (fixed $g = 2.0$; Figures 2 and 4). While the $|1,3/2\rangle$ ZFS has contributions from all three metal ions, assuming it arises entirely from Mn$^{III}$ (an over-estimation) gives $D_{\text{iso}} = +0.13$ cm$^{-1}$. This is in the range known for ON-donor six-coordinate Mn$^{III},$[20] but negligible compared to the ground-state ZFS of [Ru$_2$Mn]. Hence [Ru$_2$Mn] has a contribution of about 3 cm$^{-1}$ to its ZFS from another source.

Given the predictions for AE effects in the high-spin state of $x = \frac{1}{2}$ triangle$^{[11]}$ we have investigated this model by the Hamiltonian $H_{\text{iso}} + H_{\text{ext}}$, where $\mathbf{d}$ are the ASE vectors,$^{[20]}$ and $H_{\text{ext}}$ is defined in Equation (3).

$$H_{\text{ext}} = d_i \left( \mathbf{s}_i \times \mathbf{S} \right) + d_i \left( \mathbf{s}_i \times \mathbf{S} \right)$$  \hspace{1cm} (3)$$

If we neglect the torsion angles of the terminal pyridine ligands, then [Ru$_2$Mn] is an isoceles triangle with $C_3$ symmetry. We define the normal to the trimetallic plane as the $z$ axis to maintain consistency with the literature reports.
A system that is isosceles not only in terms of the strength of the identity of the spins themselves.

\[ J_{1} \]

In this case, all three metal–metal vectors lie on a mirror plane and the only non-zero components of \( \mathbf{d} \) are \( d_{z} \). Such components do not lead to ZFS in the high-spin states of equilateral triangles.\(^{[10,11]} \) In our case we have a system that is isosceles not only in terms of the strength of the \( J \) coupling (often seen in homometallic triangles), but in the identity of the spins themselves.

Hamiltonian \( H_{\text{iso}} \) gives the 24 \( \times \) 24 energy matrix comprising the ground \( |1/2,2\rangle \) (with eigenvalue \( +3J/2 \)) and excited \( |1,3/2 \) \((-J/2+7J/2), |1,5/2 \) \((-J/2+2J/2), and \( |1,7/2 \) \((-J/2−5J/2)\) states. Applying \( H_{\text{iso}} \) with only \( d_{z} \neq 0 \), as a perturbation to this coupled basis gives the non-zero matrix elements (labeling states as \( |S_{i},M_i\rangle \)):

\[
\begin{align*}
\{1, \frac{7}{2}, \frac{5}{2}\} \ R_{\text{Antiferro}} \{0, \frac{5}{2}, \frac{5}{2}\} &= -i \left( \frac{d_{z}^{2} - 5d_{z}^{2}}{\sqrt{14}} \right) \\
\{1, \frac{5}{2}, \frac{3}{2}\} \ R_{\text{Antiferro}} \{0, \frac{3}{2}, \frac{3}{2}\} &= \pm i \left( \frac{d_{z}^{2} + 2d_{z}^{2}}{\sqrt{7}} \right) \\
\{1, \frac{3}{2}, \frac{1}{2}\} \ R_{\text{Antiferro}} \{0, \frac{1}{2}, \frac{1}{2}\} &= -i \left( 10 \frac{d_{z}^{2} - 5d_{z}^{2}}{2\sqrt{21}} \right) \\
\{1, \frac{5}{2}, \frac{7}{2}\} \ R_{\text{Antiferro}} \{0, \frac{7}{2}, \frac{7}{2}\} &= \pm 3i \left( \frac{d_{z}^{2} + 2d_{z}^{2}}{\sqrt{35}} \right) \\
\{1, \frac{3}{2}, \frac{5}{2}\} \ R_{\text{Antiferro}} \{0, \frac{5}{2}, \frac{5}{2}\} &= \left( \frac{d_{z}^{2} + 7d_{z}^{2}}{\sqrt{15}} \right) \\
\{1, \frac{1}{2}, \frac{3}{2}\} \ R_{\text{Antiferro}} \{0, \frac{3}{2}, \frac{3}{2}\} &= -i \left( \frac{d_{z}^{2} - 5d_{z}^{2}}{\sqrt{7}} \right) \\
\{1, \frac{3}{2}, \frac{7}{2}\} \ R_{\text{Antiferro}} \{0, \frac{7}{2}, \frac{7}{2}\} &= \pm 7i \left( \frac{d_{z}^{2} + 2d_{z}^{2}}{\sqrt{35}} \right) \\
\{1, \frac{1}{2}, \frac{5}{2}\} \ R_{\text{Antiferro}} \{0, \frac{5}{2}, \frac{5}{2}\} &= \left( \frac{d_{z}^{2} + 7d_{z}^{2}}{\sqrt{15}} \right) \\
\{1, \frac{1}{2}, \frac{3}{2}\} \ R_{\text{Antiferro}} \{0, \frac{3}{2}, \frac{3}{2}\} &= -i \left( \frac{d_{z}^{2} - 5d_{z}^{2}}{\sqrt{7}} \right) \\
\{1, \frac{1}{2}, \frac{1}{2}\} \ R_{\text{Antiferro}} \{0, \frac{1}{2}, \frac{1}{2}\} &= \left( \frac{d_{z}^{2} + 7d_{z}^{2}}{\sqrt{15}} \right) \\
\{1, \frac{3}{2}, \frac{1}{2}\} \ R_{\text{Antiferro}} \{0, \frac{1}{2}, \frac{1}{2}\} &= -i \left( \frac{d_{z}^{2} - 5d_{z}^{2}}{\sqrt{7}} \right)
\end{align*}
\]

There are no first-order corrections to the eigenvalues, but each ground-state \( M \) component mixes with all excited states with \( \Delta M = 0 \). The three Kramers doublets are separated and, to second order, the \( |M = \frac{1}{2}, \frac{1}{2}\rangle \) gap is half the \( |\frac{1}{2}, \frac{1}{2}\rangle \) gap. This is the form of an isolated \( S = \frac{1}{2} \) state under Hamiltonian \( (2) \), with separations of \( 2D \) and \( 4D \), respectively. To second order, \( D \) is then given by Equation (4),

\[
D = \frac{-(2d_{z}J_{1} + d_{z}J_{2})^{2}}{(2J_{1} - H_{I}(2J_{1} + 2J_{2}))}
\]

where the denominator is the product of the gaps to the three excited states.

Excellent simulations of the EPR spectra (Figure 3 and see Figure S3 in the Supporting Information), including variable-temperature and hyperfine effects, are obtained by full diagonalization of \( H_{\text{iso}} + H_{\text{antiferro}} \) (with \( g_{\text{Mn}} = 1.98 \) and \( g_{\text{Ru}} = 2.0 \); the simulations are insensitive to the latter), and fits to the low-temperature \( \chi(T) \) and \( M(H) \) are indistinguishable from those in Figure 2. For these calculations we have taken \( J_{1} = -1000 \text{ cm}^{-1} \) with \( J_{2}/J_{1} = 10 \) (see above). Clearly, more than one set of \( d_{z}/d_{z} \) components can generate a given \( D \) value. If we take \( d_{z} = 0 \), then we find \( d_{z} = 66 \text{ cm}^{-1} \) (Figure 3; calculations are insensitive to the sign of \( d_{z} \)).

much larger values of \( d_{z} \) are required to generate equivalent \( D \) values [see Eq. (4)]. Adjustment of \( J_{1} \) and \( J_{2} \), will give different \( d_{z} \) values, but the conclusion does not change: very large ZFS effects (several cm\(^{-1}\)) have been introduced to the \( S = \frac{1}{2} \) ground state by ASE effects in second-order. (There are also higher-order contributions: the calculated \( |M = \frac{1}{2}, 0\rangle \) \( \frac{1}{2} \) gap is not exactly double the \( \frac{1}{2} \) to \( \frac{1}{2} \) gap from those in Figure 2. For these calculations we have taken \( J_{1} = -1000 \text{ cm}^{-1} \) with \( J_{2}/J_{1} = 10 \) (see above). Clearly, more than one set of \( d_{z}/d_{z} \) components can generate a given \( D \) value.)

The ASE parameters we have found here are entirely reasonable: \( d_{z} \) values of greater than \( 100 \text{ cm}^{-1} \) have been found for antiferromagnetically coupled \( \text{Cu}^{II} \) triangles.\(^{[10,11]} \) It has been argued that the latter are due to the favorable alignment of ground- and excited-state \( d \) orbitals,\(^{[10,11]} \) because ASE arises from exchange between the electronic ground state of one ion and the excited state of another through spin-orbit coupling (SOC). In \( \text{Ru}^{II} \text{Mn} \), the ASE will be favored both by the large SOC of \( \text{Ru}^{III} \), and the strong exchange interactions arising from the large radial extent of the 4d orbitals. The perturbative expressions above show that this can also be viewed as mixing of the ground-state \( \text{Mn}^{II} \) functions (\( S_{z} = 0 \)) with the “ferromagnetic” excited state (\( S_{z} = 1 \)) of the \( \text{Ru}^{II} \) unit. This is equivalent to an alternative description of the electronic structure proposed for some oxo-bridged \( \text{Ru}^{III} \) oligomers, where direct exchange between the 4d functions results in delocalized singlet and “low lying” (in electronic spectroscopy terms) triplet states.\(^{[12,24]} \)

In summary, we have shown the ASE interaction can lead to very large spin ground-state ZFSs in polymetallic complexes, even through a second-order perturbation on the isotropic exchange. The model reproduces spectroscopic observations across two orders of magnitude in field/frequency regime of EPR spectroscopy. The results show that these effects cannot be ignored, particularly when 2nd and 3rd

\[ J_{1} \]

Figure 4. EPR spectra of polycrystalline \( \text{Fe}^{II}\text{Mn} \) measured at 10 K and a) 8.76 and b) 13.97 GHz (8 K), with simulations (red) based on Hamiltonian \( H_{\text{iso}} \), with the parameters in the text. Gaussian linewidth is 300 G.
row metal ions are involved, as is becoming popular as a route to introduce magnetic anisotropy into molecular magnets. Furthermore, it is possible that ASE is much more widespread than generally imagined in coupled systems, and assigned to anisotropic exchange or local ZFS effects; for example, a ground state \( D = 0.25 \text{ cm}^{-1} \) for \( \text{Fe}_{3} \text{Mn} \) can equally well be derived from \( d_{z}^{2} = 0.67 \text{ cm}^{-1} \), similar to values observed in \( \text{Fe}_{3} \) triangles.\(^{[9,25]} \) This is important because different anisotropy terms in the spin Hamiltonian result in different mixing derived from exchange coupling · zero-field splitting. **Electron Spin Resonance (ESR)** · exchange coupling · zero-field splitting. **Keywords:**

antisymmetric exchange · electronic structure · EPR spectroscopy · exchange coupling · zero-field splitting

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[26] CCDC 926362 and 926363 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
Supporting Information
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69451 Weinheim, Germany

Large Zero-Field Splitting of the Ground Spin State Arising from Antisymmetric Exchange Effects in Heterometallic Triangles**

Samantha A. Magee, Stephen Sproules, Anne-Laure Barra, Grigore A. Timco, Nicholas F. Chilton, David Collison, Richard E. P. Winpenny, and Eric J. L. McInnes*

anie_201400655_sm_miscellaneous_information.pdf
Supplementary Information

Synthesis. Solvents and reagents were from commercial sources and used without further purification, with the exception of manganese pivalate which was made by literature methods.\[1\]

{Ru₂Mn}: Pivalic acid (22.1 g, 219 mmol) and RuCl₃·xH₂O (0.15 g, 0.57 mmol) in 4:1 EtOH/H₂O (25 mL) were heated at 70 °C for 10 min. After cooling, manganese pivalate (0.52 g, 2.01 mmol) was added with stirring. After standing overnight, the purple solution was filtered, the solvent removed under vacuum, and the resultant oil filtered to remove excess manganese pivalate. The filtrate was diluted with MeCN (10 mL) and excess pivalic acid removed by successive cooling (-40 °C) and filtration. The solvent was removed, the residue stirred in distilled water (200 mL) for 30 min then filtered to give a dark purple solid which was washed with 4:1 H₂O/MeCN (3 x 10 mL) and air dried (0.1 g). The solid was dissolved in MeCN (30 mL) and pyridine (10 mL), stirred overnight and filtered. The solvent was removed and the purple residue recrystallised from a minimum amount of pyridine (25 mg, 26%). Microanalysis: (C₄₅H₆₉MnN₃O₁₃Ru₂) calcd: C, 48.38; H, 6.23; N, 3.76; Mn, 4.92%. Found: C, 48.38; H, 6.32; N, 3.79; Mn 4.47%. IR (KBr): 1405, 1369, 1356 sh cm⁻¹. ESI-MS +ve (m/z): 1018 [M – (C₅H₉O₂)]⁺. ¹H NMR (CDCl₃): δ 2.04 s (36H, CH₃), δ 3.13 s (18H, CH₃) ppm.

{Fe₂Mn}: Pivalic acid (50.0 g, 490 mmol) and Fe(NO₃)₃·9H₂O (10.0 g, 24.8 mmol) were heated for 4 h with stirring at 160 °C, in a 2-neck round-bottom flask with condenser, to remove NO₂. Manganese acetate (3.00 g, 12.2 mmol) was added under N₂, and acetic acid removed by addition of toluene (2 x 100 mL) and distillation of the azeotrope. After cooling to room temperature, MeCN (50 mL) was added and the solution stirred for 15 min. The solid was filtered off and washed with MeCN (3 x 15 mL). The solid was dissolved in CH₂Cl₂ (0.2 g in 20 mL) and excess pyridine (200 mg) with stirring for 20 min. After removing the solvent under vacuum, the residue was recrystallised from diethyl ether/MeCN to give large brown crystals of {Fe₂Mn} (0.102 g, 53%). Microanalysis: (C₄₅H₆₀Fe₂MnN₃O₁₃) calcd: C, 52.64; H, 6.77; N, 4.09; Fe, 10.88; Mn, 5.35%. Found: C, 52.60; H, 6.89; N, 4.14; Fe, 10.76; Mn, 5.20%. IR (KBr): 1408, 1371, 1357 sh cm⁻¹. ESI-MS +ve (m/z): 846 [M – (C₅H₁₀O₂) – (C₅H₅N)]⁺. ¹H NMR (CDCl₃): δ 3.09 s (18H, CH₃), δ 3.13 s (18H, CH₃) ppm.
**X-ray crystallography.** X-ray diffraction data were collected on an OXFORD Diffraction XCaliber2 CCD diffractometer using Mo Kα radiation. The structures were solved with SHELXS, and SHELXL was used for the refinement.[2] Crystallographic information files were produced using OLEX2.[3]

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Physical measurements. Magnetic measurements were performed in the temperature range 1.8 – 300 K using a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T magnet. Corrections for diamagnetism were made using Pascal’s constants and magnetic data were corrected for diamagnetic contributions from the sample holder. Fits were performed using the program PHI.\(^4\) S-, X-, Q- and W-band EPR spectra were measured on Bruker instrumentation at the EPSRC National UK EPR Facility and Service at The University of Manchester. High-frequency, high-field EPR spectra were recorded at the LNCMI-CNRS at Grenoble on a home-built spectrometer.\(^5\) Simulations and data analysis were performed using software written by Weihe,\(^6\) Piligkos\(^7\) and some test calculations performed with Stoll’s EasySpin.\(^8\)

Fig. S1 Multi-frequency EPR spectra of \( \{\text{Ru}_2\text{Mn}\} \) at 10 K recorded in \( \text{CH}_2\text{Cl}_2/\text{toluene} \) solution at S-(3.874 GHz), X- (9.388 GHz) and Q-band (33.95 GHz), and as a polycrystalline solid at W-band (93.99 GHz).
Fig. S2 331.2 GHz EPR spectrum (black) of polycrystalline \{\text{Ru}_2\text{Mn}\} at 10 K, with simulation (red) according to Hamiltonian $\mathcal{H}_{\text{DFS}}$ (2) with $S = 5/2$, $g_{\text{iso}} = 1.98$ and $D = +2.9$ cm$^{-1}$, $E = 0$ and a Gaussian linewidth of 1500 G with 5% $D$-strain.
Fig. S3 Variable temperature 331.2 GHz EPR spectra (black) of polycrystalline \{Ru$_2$Mn\} at (top to bottom) 5, 10 and 15 K. Simulations (red) with Hamiltonian $H_{iso} + H_{anti}$ and the parameters in the main text (Gaussian linewidth of 1500 G with 5% strain in $d^2$).
Fig. S4 Variable temperature 331.2 GHz EPR spectra of polycrystalline $\{\text{Fe}_2\text{Mn}\}$. 
Chapter Three – Manuscript 1

“Ground State Description of Heterometallic Clusters

$[\text{Ru}_2\text{MO}^{1+}(\text{BuCO}_2)_6(\text{py})_3]^\pm$ (M = Mn, Co, Ni, Zn; py = pyridine; $z = 1+,$ 0)”

S. A. Magee, A.-L. Barra, K. M. Lancaster, S. Sproules, E. J. L. McInnes
Ground State Description of Heterometallic Clusters

\[ \text{[Ru}_2\text{MO}^{(t\text{BuCO}_2)_6(\text{py})_3]}^z \ (M = \text{Mn, Co, Ni, Zn}; \ \text{py} = \text{pyridine}; \ z = 1+, 0) \]

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Abstract. A family of mixed metal, oxo-centered clusters of the general formula [Ru\textsuperscript{III}\textsubscript{2}M\textsuperscript{II}O(tBuCO\textsubscript{2})\textsubscript{6}(py\textsubscript{3})] (M = Co (2), Ni (3), Zn (4)) have been synthesized and characterized by IR, electronic absorption and NMR spectroscopy. The manganese homologue (1) has been reported previously (Magee, S. A., et al. Angew. Chem. Int. Ed. 2014, 53, 5310 – 5313). The molecular structures have been determined by X-ray crystallography. The total spin ground state has been ascertained by SQUID magnetometry and EPR spectroscopy as $S = \frac{5}{2}$ in 1, $S_{\text{eff}} = \frac{1}{2}$ in 2, $S = 1$ in 3, and $S = 0$ in 4. A large magnetic anisotropy at $D = +8.1 \text{ cm}^{-1}$ was determined for 3 by high frequency/high field EPR measurements. Cyclic voltammetry measurements revealed two one-electron oxidation processes; the first defined as fully reversible giving access to the monocationic clusters. The oxidation is defined as confined to the divalent metal in the case of 2, and localized on the [Ru\textsubscript{2}] fragment in 3 and 4. This led to the isolation of [Ru\textsuperscript{III}\textsubscript{2}Co\textsuperscript{III}O(tBuCO\textsubscript{2})\textsubscript{6}(py\textsubscript{3})]\textsuperscript{+} (5) and [Ru\textsuperscript{III}Ru\textsuperscript{IV}\textsuperscript{II}O(tBuCO\textsubscript{2})\textsubscript{6}(py\textsubscript{3})]\textsuperscript{+} (6); their electronic structure confirmed by X-ray crystallography, magnetometry, and EPR and X-ray absorption spectroscopy (XAS).
Introduction

Oxo-centered, carboxylate-bridged triangular clusters are ubiquitous in coordination chemistry and are most numerous for first-row transition metal ions. They possess a distinctive $\text{M}_3\text{O}$ planar structure with the metal ions positioned at the corners of an equilateral triangle. Examples with heavier metals are less common; the first containing three Ru(III) was originally mis-assigned by Mond as a binuclear species. The correct composition and connectivity was provided by Spencer and Wilkinson by analogy to first-row counterparts with tervalent Cr, Mn, and Fe which at that time had been crystallographically characterized.

![Figure 1](image)

**Figure 1.** Depiction of the molecular structure of $[\text{Ru}^{\text{III}}_2\text{M}^{\text{II}}\text{O}^\text{BuCO}_2\text{(py)}_3]$ (1). Mn turquoise, Ru violet, O red, N blue, C black. Hydrogen atoms have been omitted for clarity.

Interest in these polynuclear complexes has ranged from models for biological centres, to electron transfer, metal mixed-valency, ligand exchange reactions and analysis of intermetallic interactions and magnetic properties. Sasaki, Ito and co-workers pioneered the preparation of mixed-metal triangular clusters with 3d and 4d metal ions. Their progress produced the acetate linked entities $[\text{Ru}^{\text{III}}_2\text{M}^{\text{II}}]$ ($\text{M} = \text{Mg, Mn, Co, Ni}$,
Zn)$^{19,20}$ and [Ru$^{III}_2$M$^{III}$]$^+$ (M = Cr, Fe, Rh).$^{20-22}$ The invariance of the structural dimensions across this type of cluster enabled comparison with mixed-metal homologues of the first-row. It was shown the spin ground state is that of the heterometal brought about by very strong anti-ferromagnetic coupling between the Ru(III) ions,$^{20,22-24}$ which is in stark contrast to the relatively weak anti-ferromagnetic interaction between 3d metals.$^{25}$ However, the impact of the ruthenium ions on the electronic properties of the 3d ion has only recently been uncovered. We communicated the preparation and structural characterization of a [Ru$^{III}_2$Mn$^{II}$] oxo-centered cluster with bulkier pivalate ligands (Figure 1).$^{26}$ Magnetic and high-frequency/field EPR spectroscopic examination of the $S = \frac{5}{2}$ ground state revealed a very large magnetic anisotropy of $D = 3.0$ cm$^{-1}$, far too large to be due to the Mn(II) ion. We were able to explain the origin of this large magnetic anisotropy in terms of antisymmetric exchange interactions (ASE), i.e. exchange interactions between the electronic ground state of one ion and an excited state of another via spin-orbit coupling (SOC).$^{26}$ It is favoured here due to the large SOC constant of Ru(III) and the strong exchange interaction due to the large radial extent of the 4d orbitals. Herein, we extend the series of trigonal mixed-metal pivalate clusters, [Ru$^{III}_2$M$^{II}$O($t$BuCO$_2$)$_6$(py)$_3$] to include the divalent metal ions Co (2), Ni (3), and Zn (4). Each has been structurally characterized and their ground state electronic structure examined by magnetometry and multifrequency EPR measurements. Electrochemical studies reveal these charge-neutral species can be reversibly one-electron oxidized, and the molecular structures of monocationic clusters of Co (5) and Ni (6) are reported. The locus of this redox event is revealed by magnetometry, EPR and X-ray absorption spectroscopy (XAS). In our pursuit of new molecular devices, the unique redox and magnetic properties of these clusters make them attractive components to include in more elaborate molecular constructs.$^{11,27}$
Experimental Section

Syntheses

All solvents and reagents were purchased from commercial sources and used without further purification. Cobalt and nickel pivalate, \([\text{M}_2(\text{H}_2\text{O})_4(\text{tBuCO}_2)_4(\text{BuCO}_2\text{H})_4]\), were synthesized according to literature procedures.\(^{28}\) Zinc pivalate was prepared by an adaption of the synthesis of manganese pivalate, using zinc acetate as a starting material.\(^{29}\)

\([\text{Ru}_2\text{MO}(\text{tBuCO})_6(\text{py})_3]\), \(\text{M} = \text{Co} \ (2), \ \text{Ni} \ (3), \ \text{Zn} \ (4)\). A mixture of RuCl\(_3\) (0.15 g; 0.57 mmol) and pivalic acid (22.1 g; 219 mmol) in 4:1 EtOH/H\(_2\)O (25 mL) was heated for 10 min at 70 °C. After cooling to room temperature, \([\text{M}_2(\text{H}_2\text{O})_4(\text{tBuCO}_2)_4(\text{BuCO}_2\text{H})_4]\) (\(\text{M} = \text{Co or Ni}\)) (0.95 g; 2.01 mmol) or \([\text{Zn}(\text{tBuCO})_2]_o\) (0.54 g; 2.01 mmol) was added, and the reaction mixture stirred until all had dissolved and the colour changed from red to purple. The solution was left to stand overnight and then filtered. The solvent was removed by rotary evaporation and the resultant oil was filtered to remove excess metal pivalate, treated with MeCN (10 mL) then placed in the freezer (−40 °C) overnight. Repeated freeze-filter cycles ensured the removal of excess pivalic acid. The solvent was then stripped under vacuum before distilled water (200 mL) was added to the purple residue, and stirred for 30 min. The solution was filtered to yield a dark purple solid, which was washed with 4:1 H\(_2\)O/MeCN (3 × 10 mL) and dried in air. The desired complex was obtained by dissolving 100 mg of the purple solid in MeCN (30 mL) and pyridine (10 mL), then stirring the solution overnight and filtering. The solvent was removed by rotary evaporation and the purple residue recrystallized from a minimum amount of pyridine.

2: Yield = 0.06 g, 19%. Anal. Calcd for C\(_{45}\)H\(_{69}\)O\(_{13}\)N\(_3\)CoRu\(_2\): C, 48.21; H, 6.20; N, 3.75; Co, 5.26. Found: C, 48.69; H, 6.34; N, 3.72; Co, 5.11 %. IR: \(\nu_{as}(\text{OCO})\) 1620, 1601 cm\(^{-1}\).
ESI-MS: \textit{m/z} 1066 [M–py+Na]^+. \textsuperscript{1}H NMR (CDCl\textsubscript{3}): \(\delta\) -6.73 (18H, s, \((CH_3)_3\)), 16.77 (36H, s, \((CH_3)_3\)), 9.30 (4H, m, Ru-py), 7.95 (4H, m, Ru-py), 7.52 (2H, m, Ru-py) ppm.

3: Yield = 0.06 g, 19%. Anal. Calcd. for C\textsubscript{45}H\textsubscript{69}O\textsubscript{13}N\textsubscript{3}NiRu\textsubscript{2}: C, 48.22; H, 6.20; N, 3.75; Ni, 5.24. Found: C, 48.39; H, 6.27; N, 3.76; Ni, 4.95 %.

ESI-MS: \textit{m/z} 1038 [M–py+H]^+. \textsuperscript{1}H NMR (CDCl\textsubscript{3}): \(\delta\) 0.67 (18H, s, \((CH_3)_3\)), 4.16 (36H, s, \((CH_3)_3\)) ppm.

4: Yield = 0.04 g, 13%. Anal. Calcd for C\textsubscript{45}H\textsubscript{69}O\textsubscript{13}N\textsubscript{3}ZnRu\textsubscript{2}: C, 47.93; H, 6.17; N, 3.73; Zn, 5.80. Found: C, 48.18; H, 6.07; N, 3.73; Zn, 5.24 %.

ESI-MS: \textit{m/z} 979 [M–(C\textsubscript{5}H\textsubscript{9}O\textsubscript{2})–py+(CH\textsubscript{3}OH)]^+. \textsuperscript{1}H NMR (CDCl\textsubscript{3}): \(\delta\) 0.56 (18H, s, \((CH_3)_3\)), 0.92 (36H, s, \((CH_3)_3\)) ppm.

Significantly higher yields of 2 and 3 were obtained by carboxylate substitution of the acetate analogues. Purple [Ru\textsubscript{2}MO(MeCO\textsubscript{2})\textsubscript{6}(H\textsubscript{2}O)\textsubscript{3}] (M = Co, Ni; 0.15 g; 0.22 mmol)\textsuperscript{20,28} dissolved in toluene (30 mL) was refluxed with pivalic acid (0.40 g; 3.88 mmol) for 3 h. The solvent was then removed by distillation and fresh toluene was added. The process was repeated thrice. Pivalic acid (0.40 g; 3.88 mmol) was added on the final addition of solvent, and the distillation process repeated twice. The resultant purple residue was dissolved in CH\textsubscript{2}Cl\textsubscript{2} (20 mL), treated with pyridine (0.07 g; 0.88 mmol) and stirred for 30 min. The solvent was removed under vacuum and the solid recrystallized from Et\textsubscript{2}O/MeCN. Yield = 0.20 g, 82% (2); 0.22 g, 89% (3).

[Ru\textsubscript{2}MO\textsuperscript{tBuCO\textsubscript{2}}\textsubscript{6}(py)\textsubscript{3}](PF\textsubscript{6}), M = Co (5), Ni (6). Under an N\textsubscript{2} atmosphere, a dark purple solution of 2 or 3 (100 mg; 0.09 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (20 mL) was combined with [FeCp\textsubscript{2}](PF\textsubscript{6}) (0.03 g; 0.08 mmol) and stirred for 30 min. The deep purple solution was left to stand for 10 min before being filtered. Hexane (20 mL) was added, the solution concentrated to a third of the volume and placed in the freezer (-40 °C) to crystallize.
5: Yield = 0.06 g, 56%. Anal. Calcd for C_{45}H_{69}O_{13}N_{3}F_{6}PCoRu_2: C, 42.69; H, 5.49; N, 3.32; P, 2.45; Co, 4.69. Found: C, 42.40; H, 5.38; N, 3.19; P, 2.28; Co, 4.02 %. IR: ν_{as}(OCO) 1555 br cm\(^{-1}\). ESI-MS: m/z 1043 [M–py]\(^+\). \(^1\)H NMR (CDCl\(_3\)): δ -0.61 (18H, s, (CH\(_3\)_3), 3.89 (36H, s, (CH\(_3\)_3) 6.54 (4H, m, Ru-py), 7.62 (4H, m, Ru-py), 9.60 (2H, m, Ru-py) ppm.

6: Yield = 0.07 g, 64%. C\(_{45}\)H\(_{69}\)O\(_{13}\)N\(_3\)F\(_6\)PNiRu\(_2\): C, 42.68; H, 5.50; N, 3.32; P, 2.45; Ni, 4.64. Found: C, 42.31; H, 5.46; N, 3.16; P, 2.46; Ni, 4.26 %. IR: ν_{as}(OCO) 1604 br cm\(^{-1}\). ESI-MS: m/z 1041 [M–py]\(^+\). \(^1\)H NMR (CDCl\(_3\)): δ 1.50 (18H, s, (CH\(_3\)_3), 1.69 (36H, s, (CH\(_3\)_3), 5.46 (4H, m, Ru-py), 9.41 (4H, m, Ru-py), 10.73 (2H, m, Ru-py) ppm.

**X-ray crystallographic data collection and refinement of the structures.** Single crystals of 2 were mounted in the nitrogen cold stream of an Oxford Supernova diffractometer, using micro-focus Mo-K\(\alpha\) radiation (\(\lambda = 0.71073 \text{ Å}\)). Single crystals of 3 and 4 were mounted in the nitrogen cold stream of an Oxford Diffraction XCalibur 2 diffractometer. Graphite monochromated Mo-K\(\alpha\) radiation (\(\lambda = 0.71073 \text{ Å}\)) was used throughout. Crystals of 5 and 6 were measured at 100 K on beamline I19 at the Diamond Light Source. The structures were solved by direct methods and refined by full-matrix least-squares method with anisotropic thermal parameters for all atoms using SHELXS, and SHELXL was used for the refinement.\(^{30}\) CIF files were generated using Olex2.\(^{31}\)
<table>
<thead>
<tr>
<th>Table 1. Crystallographic Data</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
</tr>
<tr>
<td>C₄₅H₆₀N₃O₁₃CoRu₂</td>
</tr>
<tr>
<td>Fw</td>
</tr>
<tr>
<td>crystal system</td>
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<tr>
<td>space group</td>
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<tr>
<td>a, Å</td>
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<tr>
<td>b, Å</td>
</tr>
<tr>
<td>c, Å</td>
</tr>
<tr>
<td>α, °</td>
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<tr>
<td>β, °</td>
</tr>
<tr>
<td>γ, °</td>
</tr>
<tr>
<td>V, Å³</td>
</tr>
<tr>
<td>T, K</td>
</tr>
<tr>
<td>Z</td>
</tr>
<tr>
<td>ρ calcld, g cm⁻³</td>
</tr>
<tr>
<td>λ, Å/μ, mm⁻¹</td>
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<tr>
<td>refl. collected / 2θ max</td>
</tr>
<tr>
<td>unique refl. / I &gt; 2σ(I)</td>
</tr>
<tr>
<td>no. of param. / restr.</td>
</tr>
<tr>
<td>R₁ a / goodness of fit b</td>
</tr>
<tr>
<td>wR₂ c / (I &gt; 2σ(I))</td>
</tr>
<tr>
<td>residual density, e Å⁻³</td>
</tr>
</tbody>
</table>

a) Observation criterion: I > 2σ(I). R₁ = Σ||F₀| - |Fₑ||Σ|F₀|; b) GoF = [Σ[w(F₀² - Fₑ²)]²]/(n-p); c) wR₂ = [Σ[w(F₀² - Fₑ²)²]/Σ[w(F₀²)]]¹/² where w = 1/σ²(F₀)² + (aP)² + bP, P = (F₀²+2Fₑ²)/3
Physical Measurements: Electronic absorption spectra were recorded using a Perkin-Elmer Lambda 1050 spectrophotometer (300 – 2800 nm). Infrared data were collected using a ThermoScientific iD5 ATR, Nicolet iS5 spectrometer. $^1$H NMR spectra of the complexes in CDCl$_3$ solutions were recorded using a Bruker 400 FT NMR spectrometer. Chemical shifts are referenced to internal CHCl$_3$ ($\delta = 7.26$ ppm). Cyclic voltammograms were measured using an Autolab potentiostat AUT71194. Redox potentials are referenced to the internal ferrocenium/ferrocene (Fc$^{+/0}$) couple. Multifrequency EPR spectra were recorded at the EPSRC National UK EPR Facility and Service at The University of Manchester. High frequency/field EPR measurements were carried out at LNCMI Grenoble on a custom built instrument.$^{32}$ Spectral simulations were performed using Bruker’s Xsophe software package$^{33}$ or Easyspin.$^{34}$ Magnetic data were recorded using a SQUID magnetometer (Quantum Design MPMS-XL) over a temperature range 2 – 300 K with applied magnetic fields up to 7 T. Corrections for diamagnetism were made using Pascal’s constants and magnetic data were corrected for diamagnetic contributions from the sample holder. Fits were performed using the program PHI.$^{35}$ XAS data were measured at the Stanford Synchrotron Radiation Lightsource (SSRL) under ring conditions of 3.0 GeV and 300 mA. Data were measured on beamline 7-3 as previously described.$^{36}$ ESI-MS and elemental analyses were carried out by the University’s mass spectrometry and microanalytical services.

Results and Discussion

Synthesis and Characterization

The synthesis of this series of mixed-metal triangles begins with the formation of [Ru$_2$O($^t$BuCO$_2$)$_2$]$^{2+}$ as the precursor to trinuclear mixed-metal clusters.$^{15,20,37}$ This is followed by addition of a pivalate complex of the divalent metal; [M$_2$(H$_2$O)($^t$BuCO$_2$)$_4$($^t$BuCO$_2$H)$_4$] for M = Co or Ni,$^{28}$ and [M($^t$BuCO$_2$)$_2$]$_c$ for M = Mn or
The development of a purple reaction mixture signals the formation of the trinuclear cluster. After purification to remove unreacted metal pivalates and excess pivalic acid, the purple solid collected by vacuum filtration has water molecules filling the terminal sites, \([\text{Ru}_2\text{M}O(\text{BuCO}_2)_6(\text{H}_2\text{O})_3]\). These are exchanged by stirring in an acetonitrile/pyridine solvent mixture which ultimately gives the neutral clusters \([\text{Ru}_2\text{M}O(\text{BuCO}_2)_6(\text{py})_3]\) (\(\text{M} = \text{Mn} (1), \text{Co} (2), \text{Ni} (3), \text{Zn} (4)\)) in low yields (13-19%). The alternative preparation of 2 and 3 follows carboxylate substitution of the known acetate derivates\(^{20}\) by refluxing in excess pivalic acid. The final step of exchanging terminal water for pyridine gave both complexes in higher yields (~80-90%). The chemical oxidation of 2 and 3 is readily achieved from the reaction with 1 equiv. of \([\text{FeCp}_2](\text{PF}_6)\) under an inert atmosphere, affording the complex salts 5 and 6, respectively, in ca. 60% yield.

The compound formulation was confirmed by microanalysis and mass spectrometry, and all IR spectra exhibited the signature antisymmetric vibration of the pivalate bridge.\(^{38}\) The presence of the divalent metal introduces two-fold symmetry into the cluster, which is evidenced by the 2:1 ratio of proton resonances for the bridging pivalate ligands in \(^1\text{H}\) NMR spectra. Each compound exhibits this pattern though there is considerable variation in their appearance and position by virtue of the paramagnetism in some of these complexes. For 2, 5 and 6, the three proton environments for the pyridine ligands coordinated to the Ru(III) ions can be identified based on their relative intensity. The corresponding proton resonances for the pyridine bound to the heterometal were not readily defined for any of the complexes. This is surprising in the case of 5 as it is isoelectronic to \([\text{Ru}_2\text{Rh}O(\text{MeCO}_2)_6(\text{py})_3]^+\) which gave a very sharp spectral profile.\(^{21}\)

The deep purple hue of each complex is due to two intense absorption peaks in the visible region of the electronic spectrum (Figure S1). These peaks fall into the narrow ranges of 543 – 566 and 351 – 382 nm, respectively (Table 2). The lower energy feature is assigned as an excitation between states composed of combinations of Ru dπ and O pπ orbitals of the Ru-O-Ru unit,\(^{10,13,21}\) and bear a striking resemblance to diruthenium complexes with
the same ligands. There is a slight shift in the peak position with variation in the divalent metal but each possesses a weak intensity shoulder on the low-energy side.

**Figure 2.** Top: Overlay of the electronic spectra of 5 (bold line) and 2 (dashed line). Bottom: Overlay of the electronic spectra of 6 (bold line) and 3 (dashed line). Spectra were recorded in CH₂Cl₂ solutions at ambient temperature.

In the case of the oxidized species, 5 and 6, a modest blue shift is observed for these two principal transitions together with a noticeable increase in their intensity (Figure 2). This effect was previously noted for the acetate homologues of 2 and 5. Dong *et al.* described that upon oxidation of the neutral cluster, [Ru₂CoO(MeCO₂)₆(py)₃] to [Ru₂CoO(MeCO₂)₆(py)₃]⁺ an obvious blue shift from 570 nm to 551 nm was observed and the same is true here for 5 and 6. For the first time, a weak band in the near-IR (NIR) region is seen for the oxidized clusters, which is not present in their precursors (Figure 2, inset). At this stage, the transition cannot be unambiguously assigned but may correspond to an intracluster metal-to-metal charge transfer (MMCT) mediated by the central oxo ligand. The intensity would be proportional to the occupancy and energetic matching of 3d and 4d orbitals of appropriate symmetry that are stabilized when the cluster is oxidized. Although there is no precedence for similar low energy bands for complexes with oxide
and carboxylate bridges, a low-energy band (~1190 nm) of equivalent intensity ($\epsilon \sim 400$ M$^{-1}$ cm$^{-1}$) was recently described as an intervalence charge transfer transition in Class III mixed-valent Ru$^{III}$-O-Ru$^{IV}$ complexes. The similarity of both spectra suggest that this process is the same in each case and is related to a mixed valence Ru$_2^{III/IV}$ unit, which corroborates with the entire analyses of 6 (spectroscopic, electrochemical and magnetic experiments) but conflicts with the conclusions drawn from the other characterisation methods on 5 discussed later (spectroscopic and magnetic measurements).

### Table 2. Electronic Spectral Data

<table>
<thead>
<tr>
<th>complex</th>
<th>$\lambda_{\text{max}}$, nm ($\epsilon$, $10^4$ M$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>653 (sh, 0.38), 543 (0.64), 351 (1.51), 244 (3.42)</td>
</tr>
<tr>
<td>2</td>
<td>645 (sh, 0.22), 566 (0.62), 382 (1.19), 246 (2.46)</td>
</tr>
<tr>
<td>3</td>
<td>669 (sh, 0.13), 561 (0.78), 382 (1.37), 248(2.57)</td>
</tr>
<tr>
<td>4</td>
<td>636 (sh, 0.16), 544 (0.59), 369 (1.28), 245 (2.51)</td>
</tr>
<tr>
<td>5</td>
<td>1678 (0.02), 543 (1.42), 490 (sh, 0.82), 329 (1.69), 294 (2.45), 239 (5.59)</td>
</tr>
<tr>
<td>6</td>
<td>1720 (0.04), 739 (0.19), 586 (sh, 0.49) 529 (0.73), 358 (0.85), 295 (1.55), 259 (2.65)</td>
</tr>
</tbody>
</table>

**Crystal structures.** The molecular structures of charge-neutral 2 – 4 and complex salts 5 and 6 were determined by X-ray crystallography. Selected bond lengths and angles are presented in Table 3. The crystal structure of 1 has been reported previously (Figure 1).²⁶

**Figure 3.** Depiction of the asymmetric unit and molecular structure in crystals of 2 – 4. Ru violet, Co/Ni/Zn green, O red, N blue, C black. Hydrogen atoms have been omitted for clarity.
Structural determination of compounds 2 – 4 were carried out using X-ray crystallography at either 100 or 150 K. All crystallized in the monoclinic space group $P2_1/n$. Two molecules can be found in the asymmetric unit, with one molecule orthogonal to the other (Figure 3). It was not possible to identify to position of the divalent metal as the metal ions are statistically disordered over the three sites, a common outcome in mixed-metal and mixed-valent trimetallic clusters.\(^1\) The metals ions sit at the vertices of an isosceles triangle with a mean separation of 3.3306(4) Å in 2, 3.3116(4) Å in 3 and 3.3344(5) Å in 4. The acetate variants of 2 and 3 have the same dimensions though solved in trigonal space group $R32$.\(^20\) The central oxide lies flat within the $M_3$ plane. The average $M$–$O_{\text{oxo}}$ distance progressively shortens with increasing nuclear charge across the series 1 – 3. The six bridging pivalates lie above and below the molecule, canted ~60° to the $[M_3O]$ plane. The pyridine ligands reside in two different orientations. One pyridine ligand lies flat with the triangular plane of the complex, whereas the other two pyridine molecules rest perpendicular to this plane. The average $N$–$M$–$O_{\text{oxo}}$ bond angles are; 178.5(1)°, 178.6(1)° and 178.2(2)° for 2, 3 and 4, respectively. This average bond angle is slightly smaller in 1 at 176.5(2)°. The only distortion from idealized octahedral geometry is seen in the displacement of the metal ions by ~0.14 Å out of the $O_4$ equatorial plane in 1 – 4. These metrics are comparable to a wide range of structurally characterized $\mu_3$-oxo trinuclear carboxylate complexes.\(^1\)
Table 3. Selected Average Bond Distances (Å) and Angles (deg) for 1 – 6

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>M···M</td>
<td>3.3587(7)</td>
<td>3.3306(4)</td>
<td>3.3116(4)</td>
<td>3.3344(5)</td>
<td>3.284(2)</td>
<td>3.3046(7)</td>
</tr>
<tr>
<td>M–O(_{\text{oxo}})</td>
<td>1.939(3)</td>
<td>1.923(2)</td>
<td>1.912(2)</td>
<td>1.925(3)</td>
<td>1.896(11)</td>
<td>1.909(3)</td>
</tr>
<tr>
<td>M–N</td>
<td>2.188(5)</td>
<td>2.147(3)</td>
<td>2.120(3)</td>
<td>2.137(3)</td>
<td>2.073(15)</td>
<td>2.108(4)</td>
</tr>
<tr>
<td>M–O(_{\text{oxo}})–M</td>
<td>120.0(2)</td>
<td>120.0(1)</td>
<td>120.0(1)</td>
<td>120.3(1)</td>
<td>120.0(6)</td>
<td>120.0(2)</td>
</tr>
<tr>
<td>N–M–O(_{\text{oxo}})</td>
<td>176.5(2)</td>
<td>178.5(1)</td>
<td>178.6(1)</td>
<td>178.2(2)</td>
<td>177.7(5)</td>
<td>176.8(2)</td>
</tr>
</tbody>
</table>

\(^a\) Data taken from ref 26.

Both 5 and 6 crystallize in the triclinic space group \(P\bar{1}\) with one monocationic trimetallic cluster, hexafluorophosphate counterion, and a solvent molecule per asymmetric unit. The monocation of 6 has identical dimensions to the parent compound 3 (within experimental error; Table 3). On the other hand, the average M–O\(_{\text{oxo}}\) distance in 5 is ~0.03 Å shorter than in 2, as are the average M–N and equatorial M–O bonds. This indicates oxidation of the high-spin Co(II) ion producing a low-spin Co(III), as supported by the diamagnetic ground state measured by magnetometry. The same distortion from idealized octahedral geometry is observed with the metal ions displaced by ~0.14 and ~0.13 Å out of the O\(_4\) equatorial plane in 5 and 6, respectively. In contrast to the neutral species, two pyridine units are parallel to the trigonal plane (Figure 4).

Figure 4. Structure of the monocation in crystals of 5 and 6. Ru violet, Co/Ni green, O red, N blue, C black. Hydrogen atoms have been omitted for clarity.
**Electrochemistry.** The cyclic voltammograms (CV) of complexes 1 – 4 were recorded in CH$_2$Cl$_2$ solution containing 0.1 M [N($n$-Bu)$_4$]PF$_6$ as supporting electrolyte using a glassy carbon working electrode at ambient temperature (Figure 5). The reduction potentials listed in Table 4 are referenced to the ferrocenium/ferrocene (Fc$^+$/Fc) couple.

**Table 4. Redox Potentials (V) of Complexes 1 – 4 Versus Fe$^+$/Fc**

<table>
<thead>
<tr>
<th></th>
<th>$E^{1/2}_1$</th>
<th>$E^{1/2}_2$</th>
<th>$E^3_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>+0.88</td>
<td>-0.47</td>
<td>-1.94</td>
</tr>
<tr>
<td>2</td>
<td>+0.79</td>
<td>-0.32</td>
<td>-1.89</td>
</tr>
<tr>
<td>3</td>
<td>+1.18</td>
<td>-0.24</td>
<td>-1.74</td>
</tr>
<tr>
<td>4</td>
<td>+1.04</td>
<td>-0.22</td>
<td>-1.74</td>
</tr>
</tbody>
</table>

$^a$ 2+/1+ couple, $^b$ 1+/0 couple, $^c$ 0/1– couple.

Each voltammogram exhibits three features, two one-electron oxidations and a single one-electron reduction. Only the first oxidation is judged fully reversible, the second is quasi-reversible in 1 – 3 and irreversible in 4. The acetate homologues$^{20,42}$ also displayed three redox processes at more positive potential commensurate with the smaller $pK_a$ value for the free carboxylic acid: 4.76 for acetic acid, and 5.01 for pivalic acid.$^{45}$ Each process was described as reversible, and the consistent energy gap between successive events led the authors to define these as localized within the [Ru$_2$] portion of the molecule, *i.e.* the first oxidation as $[\text{Ru}^{III}_2\text{M}^{II}]^0 \rightarrow [\text{Ru}^{III}\text{Ru}^{IV}\text{M}^{II}]^+$. There is a positive shift of the potential of the first oxidation as the series is traversed 1 – 4. The one-electron oxidation of 4 affords a mixed-valent $[\text{Ru}^{III}\text{Ru}^{IV}\text{Zn}^{II}]$ moiety, and likewise for 3 based on the similarity in potential. Compound 2 is more easily oxidized, and considering the noticeable structural changes in 5, its aforementioned diamagnetic ground state and Co K-edge measurements (vide infra), we can assign the product as $[\text{Ru}^{III}_2\text{Co}^{III}]^+$. Oxidation of 1 is the most facile, however
initial attempts failed to generate the monocation of 1. Further efforts should be undertaken in order to ascertain whether it is $[\text{Ru}^{\text{III}}_2\text{Mn}^{\text{III}}]^+$ that is produced.

![Cyclic voltammograms](image)

**Figure 5.** Cyclic voltammograms of 1 – 4 recorded in CH$_2$Cl$_2$ solutions containing 0.1 M [N(n-Bu)$_4$](PF$_6$) at room temperature with a scan rate of 200 mV s$^{-1}$. Potentials are referenced versus the Fc$^{+/0}$ couple.

**X-ray absorption spectroscopy.** The locus of one-electron oxidation of compounds 2 and 3 has been probed by X-ray absorption spectroscopy (XAS). Co and Ni K-edge data were recorded on dilute samples of 2 and 5, and 3 and 6, respectively, and the spectra are compared in Figure 6. The edge region occurs because of the 1s $\rightarrow$ 4p + continuum transition, and relative shifts of the edge position reflect changes in the effective nuclear charge for a given element. The qualitative interpretation is a 1 eV increase corresponds to
an increase of the oxidation state by one unit.\textsuperscript{36,46} In 5, the rising-edge shifts up by 1.6 eV relative to 2, indicating an increase in the oxidation state of cobalt. The loss in edge intensity in 5 is consistent with other Co(III) complexes.\textsuperscript{47} In contrast, the Ni K-edge spectra for 3 and 6 are superimposable, with only a minute shift to higher energy for the monocationic species provided by the additional charge. Clearly, the oxidation of 3 is centered at the [Ru\textsubscript{2}] unit, as supported by magnetometry and EPR spectroscopy (vide infra).

**Figure 6.** Overlay of the normalized (a) Co K-edge spectra of 2 (blue) and 5 (cyan), and (b) Ni K-edge spectra at 10 K of 3 (red) and 6 (pink).

**Magnetism.** Temperature-dependent (2 – 300 K) magnetic susceptibility measurements of solid samples of 1 – 3 and 6 are presented in Figure 7. The room temperature $\chi_M T$ values of 4.42 cm$^3$ K mol$^{-1}$ for 1 and 1.22 cm$^3$ K mol$^{-1}$ for 3 equate to the spin-only values for $S = \frac{5}{2}$ and $S = 1$ respectively, and are temperature independent to about 20 K. Therefore, the exchange coupling between the Ru(III) ions is very strongly antiferromagnetic and greatly exceeds the interaction between each Ru(III) and the divalent metal ion. Some Ru(III) dinuclear complexes with both oxide and carboxylate bridging ligands are strongly antiferromagnetically coupled and diamagnetic at room temperature.\textsuperscript{40}
Figure 7. Overlay of the temperature dependence of the magnetic susceptibility of 1 (△), 2 (◇), 3 (○), and 6 (□). The red line represents a best fit to the data.

The magnetic susceptibility data for 1 and 3 can be fit using the spin-Hamiltonian described in Eq. 1, where the isolated spin ground state is that of the divalent metal ion \( S = \frac{5}{2} \) (1) and \( S = 1 \) (3)) given the strong antiferromagnetic coupling between the two Ru(III) \( S = \frac{1}{2} \) centers. This gave the following values; \( g = 1.962 \) and \( |D| = 3.0 \text{ cm}^{-1} \) (and \( E = 0 \)) for the Mn(II) ion in 1 and \( g = 2.174 \) and \( |D| = 8.1 \text{ cm}^{-1} \) (and \( E = 0 \)) for the Ni(II) ion in 3. The downturn in the magnetic moment is hence due to zero-field splitting (parameterized by \( D \) and \( E \)).

\[
\hat{H}_{GS} = g_{GS}\beta\hat{S}\hat{H} + D_{GS}\left(\hat{S}_x^2 - \frac{\hat{S}(\hat{S}+1)}{3}\right) + E_{GS}(\hat{S}_x^2 - \hat{S}_y^2) \tag{1}
\]

Simulations of the field dependency of the magnetization collected at 2 and 4 K were achieved for 1 and 3 with the same parameters (Figure S2).\textsuperscript{26} These spin-Hamiltonian parameters have been corroborated by high-frequency/field EPR measurements.

For 1 this large \( D \) value is unfeasible for an isotropic octahedral Mn(II) ion and is best modelled through antisymmetric exchange interactions (ASE).\textsuperscript{26} In a previous communication this interaction was modelled using the Hamiltonian in Eq. 2:
\[ H = -2J_1(\hat{S}_{Ru1} \cdot \hat{S}_{Ru2}) - 2J_2(\hat{S}_{Ru1} \cdot \hat{S}_{Mn} + \hat{S}_{Ru2} \cdot \hat{S}_{Mn}) + \mathbf{d}_1 \cdot [\hat{S}_{Ru1} \times \hat{S}_{Ru2}] + \mathbf{d}_2 \cdot [\hat{S}_{Ru1} \times \hat{S}_{Mn} + \hat{S}_{Mn} \times \hat{S}_{Ru2}] \]  \hspace{1cm} (2)

\( \mathbf{d}_1 \) and \( \mathbf{d}_2 \) are the ASE vectors.\(^{48} \) Good fits of the magnetic data can be obtained using the following values: \( J_1 = -1000 \text{ cm}^{-1} \), \( J_2 = -100 \text{ cm}^{-1} \), \( s_{Ru1} = s_{Ru2} = \frac{1}{2} \) and \( s_{Mn} = \frac{5}{2} \) and if \( \mathbf{d}_1 \cdot \mathbf{z} = 0 \) then \( \mathbf{d}_2 \cdot \mathbf{z} = 66 \text{ cm}^{-1}.^{26} \) The same treatment can be applied to \( 3 \) and values of a similar magnitude are obtained. The ground state of \( 3 \) is described as \( |0, 1> \) (|\( S_{Ru-Ru}, S_T > \)), and the magnetic data can be modelled using Eq. 3 with the values: \( J_1 = -1000 \text{ cm}^{-1} \), \( J_2 = -100 \text{ cm}^{-1} \), \( s_{Ru1} = s_{Ru2} = \frac{1}{2} \) and \( s_{Ni} = 1 \) and if \( \mathbf{d}_1 \cdot \mathbf{z} = 0 \) then \( \mathbf{d}_2 \cdot \mathbf{z} = 138.4 \text{ cm}^{-1} \) with \( D_{Ni} = -4.0 \text{ cm}^{-1} \) from EPR simulations of \([\text{Fe}_2\text{Ni}(\mu_3-\text{O})(\text{tBuCO}_2)\text{py}]_6(\text{py})_3\), \( \text{Fe}_2\text{Ni} \) (Chapter 4). The same approximations and limitations on these values apply as for \( 1 \).

\[ \tilde{H} = -2J_1(\hat{S}_{Ru1} \cdot \hat{S}_{Ru2}) - 2J_2(\hat{S}_{Ru1} \cdot \hat{S}_{Ni} + \hat{S}_{Ru2} \cdot \hat{S}_{Ni}) + \mathbf{d}_1 \cdot [\hat{S}_{Ru1} \times \hat{S}_{Ru2}] + \mathbf{d}_2 \cdot [\hat{S}_{Ru1} \times \hat{S}_{Ni} + \hat{S}_{Ni} \times \hat{S}_{Ru2}] + D_{Ni}[\hat{S}_{Ni}^2 \cdot \frac{\hat{S}_{Ni}(\hat{S}_{Ni}+1)}{3}] \]  \hspace{1cm} (3)

The magnetic susceptibility plot for \( 2 \) is typical of an octahedral, high-spin Co(II) center. Its profile is identical to that measured for the acetate derivative.\(^{20,42} \) The unquenched orbital angular momentum elevates the room temperature \( \chi_M T \) value to 3.11 cm\(^3\) K mol\(^{-1}\), well above the spin-only value for a spin-quartet. The first-order orbital angular momentum of the \( ^4T_{1g} \) ground state in octahedral Co(II) is coupled to the electron spin (\( S = \frac{3}{2} \)) by spin orbit coupling (SOC), therefore \( S \) and \( L \) are no longer good quantum numbers, so we must consider \( J \), the total angular momentum. The fit in Figure 7 was achieved via the Hamiltonian in Eq. 4 with \( g = 2.155 \), an orbital reduction parameter (\( \sigma \)) of -0.9, and a spin-orbit coupling constant (\( \lambda \)) of -171.5 cm\(^{-1}\). The orbital reduction parameter \( \sigma = A \kappa \), where \( A = \frac{3}{2} \) and \( \kappa \) is the usual orbital reduction factor (\( 0 \leq \kappa \leq 1 \)), and can therefore take the values -1.5-0. The A parameter acts to simplify the calculation by creating a fictitious \( L \)
=1 due to the T-P isomorphism, where the factor \((-^3/2)\) defines the conversion of the matrix of the angular momentum operator \(\hat{l}\) within the \(^4T_1\) \((^4T)\) state to the matrix of \(\hat{l}\) in the atomic p-basis.

\[
\hat{H} = \beta (\sigma \hat{L}_\text{Co} + g \hat{S}_\text{Co}) H + \lambda (\sigma \hat{L}_\text{Co} \cdot \hat{S}_\text{Co})
\]

(4)

\[
\phi(J, m_J) = \sum_{\text{ml}} C_{\text{1}}^{m_J} \frac{m_J}{2} \frac{m_J}{2} |l = 1, m_l, s = \frac{3}{2}, m_s\rangle
\]

(5)

\[
\phi \left( \frac{1}{2}, \pm \frac{1}{2} \right) = \left( \frac{1}{\sqrt{6}} \right) |1, \mp 1, \frac{3}{2}, \pm \frac{1}{2} \rangle - \left( \frac{1}{\sqrt{3}} \right) |1, 0, \frac{3}{2}, \mp \frac{1}{2} \rangle + \left( \frac{1}{\sqrt{2}} \right) |1, \pm 1, \frac{3}{2}, \mp \frac{3}{2} \rangle
\]

(6)

Eq. 4 gives a \(J = 1/2\) ground state, and can be explained by normal octahedral Co(II) behaviour made of components \(|m_l, m_s\rangle\) for \(|J = 1/2, m_J = \pm 1/2\rangle\) given by Clebsch-Gordon in Eq. 6, due to the antiferromagnetically coupling of the two Ru(III) ions to give \(S = 0\).\(^{49}\)

The Clebsch-Gordon coefficients can be calculated using Eq. 5.

Compound 4 is diamagnetic but shows residual paramagnetism from the sizeable TIP contribution from ruthenium (Figure S3).\(^{18,23,24}\) Compound 5 was also found to be diamagnetic (\(S = 0\)) over the entire temperature range. Its Ni counterpart, 6, has a \(\chi_M T\) value of 0.45 cm\(^3\) K mol\(^{-1}\) at 2 K which corresponds to the spin-only value for an \(S = 1/2\) with a \(g\)-value ~2.2. This spin ground state is generated by antiferromagnetic coupling of the unpaired electron on the \([\text{Ru}_2]^{7+}\) unit with the Ni(II) \(S = 1\) ion. Thermal population of the excited state (\(S = 3/2\)) is responsible for the steady increase in the magnetic moment reaching a maximum of 1.27 cm\(^3\) K mol\(^{-1}\) at room temperature. This excludes the formation of Ni(III) upon oxidation of this cluster. The data were fitted for \(g = 2.18\) and an exchange coupling constant of \(J = -145\) cm\(^{-1}\) for the antiferromagnetic interaction between the Ni(II) \(S = 1\) ion and the \([\text{Ru}_2]^{7+} S = 1/2\) center (Eq. 7).

\[
\hat{H} = -2J_{\text{Ru2-Ni}} (S_{\text{Ru2}} \cdot S_{\text{Ni}}) + g \beta (S_{\text{Ru2}} + S_{\text{Ni}}) H
\]

(7)
Figure 8. EPR spectra of 2 recorded in CH$_2$Cl$_2$/toluene solution at X-band (9.3869 GHz) and Q-band (34.033 GHz) at 10 K. Experimental data are shown in black and simulations as the red trace.

**EPR Spectroscopy.** Frozen solution EPR spectra of 2 at X- and Q-band at 10 K are typical of high-spin Co(II) centers with unquenched orbital angular momentum (Figure 8). These spectra were simulated as an effective $S = \frac{1}{2}$ giving rhombic $g = (5.61, 4.05, 2.77)$; the acetate derivative displayed similar parameters. The average $g$-value of 4.14 is comparable to the calculated value of 4.19 for the $J = \frac{1}{2}$ ground state in the fitting of the magnetic data. Coupling of the electron spin to the $I = \frac{7}{2}$ nuclear spin of $^{59}$Co (100% natural abundance) is evident on $g_1$ and $g_2$ at X-band. Simulation of this spectrum gave $A = (180, 138, 20) \times 10^{-4}$ cm$^{-1}$. At W-band frequency (94 GHz), the spectrum exhibit additional lines centered at $g_1$ and $g_3$ (Figure S4), which is even more apparent at 331.2 GHz, which suggests two similar but distinct paramagnetic species. The spectra were simulated using two sets of $g$-values with equal weighting: $g_A = (6.377, 4.247, 2.888)$ and $g_B = (5.354, 4.247, 2.640)$. The propensity and ease with which terminal solvent molecules exchange has been well documented, and one way to rationalize these overlapping signals may arise from the loss of one or more pyridine ligands by adventitious water during the sample preparation (grinding to a fine powder for high frequency
measurements). The introduction of water would weaken the ligand field and hence change the g-values. Due to the loss of these additional lines in the CH$_2$Cl$_2$/toluene frozen solution spectra (Figure 8 and S5), this hypothesis may be dismissed as these are non coordinating solvents, and therefore the same spectra should be observed. However, the spectrum is simplified, therefore the solid state spectra are more likely to be the result of more than one crystallographically distinct molecule and the effect is averaged upon dissolution of the complex. This is supported by the X-ray data, as the asymmetric units of compounds 2-4 (Figure 3) contain two crystallographically distinct molecules, with small variations in bond distances and angles between molecules (Table S1).

**Figure 9.** Crystal packing of 1 within the unit cell along axes a (left), b (centre) and c (right). Hydrogen atoms omitted for clarity.
Figure 10. Crystal packing of 2-4 within the unit cell along axes a (top left), b (top right) and c (bottom). Hydrogen atoms omitted for clarity.

This argument is further reinforced by the crystal packing diagrams of 1-4 along each of the unit cell axes, $a$, $b$ and $c$ are shown in Figures 9 and 10. The crystal packing of 1 (Figure 9) is much simpler than in 2-4 and the solid state EPR can be simulated using one set of parameters. The same is true for the iron derivatives in Chapter 4, ([Fe$_2$M($\mu_3$-$O$)(BuCO$_2$)$_6$(py)$_3$], where M = Mn and Co), in which these compounds show the same crystal packing and the EPR can be simulated using one set of parameters. In 2 and 3, due to the arrangement of the molecules in the solid state, the disorder of the divalent metal within the triangular core and crystallographically distinct molecules within the asymmetric units, EPR simulations require more than one set of parameters to obtain good
fitting of the data. Similar reasoning could also explain the multiple lines observed in the EPR spectrum of Fe₂Ni, as this again crystallizes differently in the hexagonal space group, \( P6_122 \).

![EPR spectrum](image)

**Figure 11.** EPR spectrum of polycrystalline 3 recorded at 331.2 GHz and 5 K. Experimental data is shown in black and simulation in red.

An EPR spectrum of 3 is unobtainable on standard laboratory spectrometers due to the large zero-field interaction. This is in stark contrast to the experimental X-band spectrum reported for a polycrystalline sample of the acetate analogue.\(^{24}\) we surmise this spectrum arises from either a mononuclear Ru(III) impurity or trace amounts of trinuclear \([\text{Ru}_3\text{O}]^+\), based on the reported \( g \)-values.\(^{18}\) The large splitting of the \( m_s \) levels of the spin-triplet is only bridged using 331.2 GHz radiation, and this spectrum is shown in Figure 11. Again, the multiple lines appearing at a resonant field position of 2500 mT arise from small variations in the individual molecules within the asymmetric units of the crystalline material, as discussed above. The crystallographic disorder of the divalent metal should also be remembered here as it is statistically disordered over the 3 sites. This, in turn may give rise to further disturbances of the anisotropy within the molecule, which nickel and cobalt ions appear to be particularly sensitive to. This spectrum has been simulated for \( g = \)
2.20 and three sets of zero-field splitting parameters: $D_A = +8.10 \text{ cm}^{-1}$ and $E_A = 2.20 \text{ cm}^{-1}$; $D_B = +8.10 \text{ cm}^{-1}$ and $E_B = 1.27 \text{ cm}^{-1}$; $D_C = +7.67 \text{ cm}^{-1}$ and $E_C = 0.3 \text{ cm}^{-1}$, using the spin-Hamiltonian presented in Eq. 1. The spectral intensity was mapped by weighting the subspectra in a ratio of 1:2.8:1.1 (Figure S6). These values for $g$ and $D$ (note this is only a 5 % spread in $D$) agree with the magnetic susceptibility data (vide supra).

EPR studies of Fe$_2$Ni (Chapter 4) give $D_{Ni} = 4.0 \text{ cm}^{-1}$, hence the large $D = -8.0 \text{ cm}^{-1}$ for 3 has another large contribution and can be explained by the ASE model given for complex 1.\textsuperscript{26} The EPR spectrum of 3 can be simulated with the ASE parameters discussed above, using Eq. 3, again with a range of $D$ values and similar weighting as above of each individual spectrum. The spectrum in Figure 12, has been simulated for $g_{Ni} = 2.20$ and $g_{Ru} = 2.00$ with the $J$ and $d_i^z$ values discussed in the previous section, again with a range of zero-field splitting values, taking the zero-field splitting of the Ni$^{II}$ ion of $D_{Ni} = -4.0 \text{ cm}^{-1}$ in Fe$_2$Ni (Chapter 4), as a starting point: $D_1 = -2.7 \text{ cm}^{-1}$; $D_2 = -3.5 \text{ cm}^{-1}$ and $D_3 = -4.25 \text{ cm}^{-1}$.

The spectral intensity was mapped by weighting the subspectra in a ratio of 1.4:2.2:1 (Figure S7).

![Figure 12](image-url)

**Figure 12.** EPR spectrum of polycrystalline 3 recorded at 331.2 GHz and 5 K. Experimental data is shown in black and simulation in red.

Chemical oxidation of 3 produces a monocationic cluster with a spin-doublet ground state. The frozen solution spectrum recorded at X-band is axial with $g_{\perp} > g_{||}$; the perpendicular $g$
components are resolved at Q-band (Figure 13). Simulation of the experimental data at these two frequencies gave $g = (2.338, 2.306, 2.035)$. This $S = \frac{1}{2}$ ground state arises from antiferromagnetic exchange between the Ru$_2$ ($S = \frac{1}{2}$) unit and the Ni(II) ion ($S = 1$), theory states that the $g$-value of this ground state arises from Eq 8.

$$g_{GS} = \frac{4g_{Ni} - g_{Ru2}}{3}$$  \hspace{1cm} (8)

Therefore, if we take the $g$-value of the Ru$_2$ moiety as $g = (2.414, 1.758, 1.381)$, obtained from the EPR simulation of the chemical oxidation of 4, and $g_{Ni} = 2.17$ (from fitting the magnetic data) then Eq. 8 yields the following values, $g_{Ru2Ni^+} = (2.433, 2.307, 2.089)$, which fit well with the values used in the simulations of 6.

![EPR spectra of 6 recorded in a CH$_2$Cl$_2$/toluene frozen glass at X-band (9.7313 GHz) and Q-band (34.104 GHz) at 30 K. Experimental data are shown in black and simulations as the dashed trace.](image)

**Figure 13.** EPR spectra of 6 recorded in a CH$_2$Cl$_2$/toluene frozen glass at X-band (9.7313 GHz) and Q-band (34.104 GHz) at 30 K. Experimental data are shown in black and simulations as the dashed trace.

The EPR spectrum of 6 is neatly contrasted by the in situ oxidation of 4, where the large $g$-anisotropy is consistent with an unpaired spin on the diruthenium moiety (Figure 14). Furthermore, the monocationic cluster gave a fluid solution spectrum (Figure S8). Simulation was achieved for $g = (2.414, 1.758, 1.381)$, which are similar to mixed-valent diruthenium(III,IV) complexes of the formula [Ru$_2$O(RCO$_2$)L$_6$]$^{3+}$ ($R = \text{Me, C}_8\text{H}_{17}p$-OMe, $\text{C}_8\text{H}_{17}p$-OMe, ...).
C$_6$H$_4$-p-Me; L = imidazole) reported by Chakravarty and co-workers.\textsuperscript{41} It is worthwhile mentioning that 4 gave no EPR signal contrary to the spectrum recorded by Kobayashi \textit{et al.}\textsuperscript{23} on a polycrystalline sample of the acetate analogue which conceivably stems from a Ru(III) impurity.

![EPR spectrum image]

**Figure 14.** X-band (9.436 GHz) EPR spectrum of in situ oxidation 4 in CH$_2$Cl$_2$/toluene solution at 30 K. Experimental data is shown in black and simulation as the red trace.

**Conclusions**

It has been shown that although the ground state for a series of neutral triangular clusters of the formula [Ru\textsuperscript{III}$_2$M\textsuperscript{II}O(C$_5$H$_9$O$_2$)$_6$(py)$_3$] (M = Mn, Co, Ni, Zn) can be described as derived exclusively from the spin state of the divalent metal, the explanation of the large magnetic anisotropies in 1 and 3 comes from ASE.\textsuperscript{26} This explanation gives a good description of the electronic interactions within each complex as ASE will be favoured by both the large SOC constant of Ru(III) and the larger radial extent of the 4d orbital. The unquenched orbital angular momentum of the octahedral Co(II) ion in 2 sees this centre best described as a $J = \frac{1}{2}$ ground state.

Comparing these complexes against their iron counter parts also gave a better understanding of their electronic ground states, (Chapter 4).
These pivalate-bridged mixed metal clusters are more easily oxidized than their acetate congeners. For 2, this redox event appears to be localized to the heterometal, when considering the low temperature data (EPR, X-ray crystallography, magnetic measurements and XAS) forming a \([\text{Ru}^\text{III}_2\text{M}^\text{III}]^+\) species. However, the similarity of the room temperature electronic spectra and cyclic voltammograms counter this argument and further investigation is required. This discrepancy may be an effect of temperature, \textit{i.e.} the charge is localised on the cobalt ion at low temperature. Therefore variable temperature XAS and UV-vis-NIR spectroscopy may provide the answer. In contrast, one electron is clearly removed from the diruthenium(III) component of the cluster in 3 and 4, the 3d orbitals are more stabilized as the series is traversed. The doublet spin ground state in 6 is generated by a relatively weak antiferromagnetic coupling between the Ni(II) \(S = 1\) ion and the mixed-valent \([\text{Ru}_2]^{7+}\) \(S = \frac{1}{2}\) center. This interaction may give rise to the low energy MMCT band seen in the electronic spectrum. With the electronic structure clearly defined, we can begin to integrate these units into larger assemblies.

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**Supporting Information Available.** Electronic spectra for 1 − 4; field dependent magnetization curves for 3; magnetic susceptibility data for 4; high frequency EPR spectra for 2; EPR simulation composition of 3; EPR spectrum of in situ oxidized 4. This material is available free of charge via the internet at http://pubs.acs.org.
References


23. Kobayashi, H.; Uryû, N.; Miyamoto, R.; Ohba, Y.; Iwaizumi, M.; Sasaki, Y.; Ohto,


   Trans.* **1985**, 2509.


27. (a) Affronte, M.; Casson, I.; Evangelisti, M.; Candini, A.; Carretta, S.; Muryn, C. A.;
   Muryn, C. A.; McInnes, E. J. L.; Ghirri, A.; Candini, A.; Santini, P.; Amoretti, G.;


Supporting Information

Ground State Description of Heterometallic Clusters

\[ \text{[Ru}_2\text{MO}^{(t)}\text{BuCO}_2\text{]}_6\text{(py)}_3^\text{z} \] (M = Mn, Co, Ni, Zn; py = pyridine; \( z = 1+, 0 \))

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Figure S1. Overlay of the electronic absorption spectra for 1 – 4 recorded in CH$_2$Cl$_2$ solutions at ambient temperature.

Figure S2. $M = f(H/T)$ plots at $T = 2$ and 4 K for compound 3. Experimental data shown as symbols and best fits represented by the red lines.
Figure S3. Temperature-dependence of the magnetic susceptibility of 4. The data are fit exclusively with TIP ($1603 \times 10^{-6}$ cm$^3$ K mol$^{-1}$) depicted by the red trace.

Figure S4. High-frequency/field EPR spectra of polycrystalline samples of 2 recorded at 94.2 GHz (10 K) and 331.2 GHz (5 K). Experimental data is shown in black and simulation in red.
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<th>3</th>
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**Table S1.** Selected bond distances (Å) and angles (deg) for each molecule in the asymmetric unit of 2 and 3.
Figure S5. Q-band (33.902 GHz) EPR spectrum of polycrystalline sample of 2 at 10 K. Experimental data is shown in black and simulation as the red trace.
Figure S6. Illustration of the three subspectra required to reproduce the simulation of the 331.2 GHz experimental spectrum of 3 measured at 5 K.
Figure S7. Illustration of the three subspectra required to reproduce the simulation of the 331.2 GHz experimental spectrum of 3 using ASE measured at 5 K.
Figure S8. X-band (9.407 GHz) EPR spectrum of in situ oxidation 4 in CH₂Cl₂/toluene solution at 293 K. Experimental data is shown in black and simulation in red.

CCDC numbers: (2) 986162, (3) 986163, (4) 986164, (5) 986165, (6) 986166.
“Characterisation of Heterometallic Clusters \([\text{Fe}_2\text{M}(\mu_3-\text{O})(\text{tBuCO}_2)_6(\text{py})_3]\) (\text{M} = \text{Mn, Co, Ni}; \text{py} = \text{pyridine}) using Multi-frequency EPR Spectroscopy”

S. A. Magee, A.-L. Barra, G. A. Timco, S. Sproules, D. Collison and E. J. L. McInnes
Characterisation of Heterometallic Clusters $[\text{Fe}_2\text{M}(\mu_3\text{-O})(^t\text{BuCO}_2)_6(\text{py})_3]$ (M = Mn, Co, Ni; py = pyridine) using Multi-frequency EPR Spectroscopy

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Abstract. A family of mixed metal, oxo-centered clusters with the general formula $[\text{Fe}^{\text{III}}\text{M}^{\text{II}}(\mu_3-\text{O})(\text{BuCO}_2)_6(\text{py})_3]$ (M = Mn (1), Co (2), Ni (3) and py = pyridine) have been synthesised and characterised by elemental analysis, cyclic voltammetry, IR and electronic absorption spectroscopy. The molecular structures have been determined by X-ray crystallography. The total spin ground states of 1-3 have been determined from SQUID magnetometry and for the first time by EPR spectroscopy as, $S = \frac{3}{2}$ in 1, $S_{\text{eff}} = \frac{1}{2}$ in 2 and $S = 1$ in 3. The manganese derivative (1) has been reported previously (S. A. Magee, et al. *Angew. Chem. Int. Ed.* 2014, 53, 5310-5313). High frequency/high field EPR measurements enabled us to determine a negative magnetic anisotropy of $D_{\text{Ni}} = -4.0 \text{ cm}^{-1}$ for the Ni$^{\text{II}}$ ion in 3.

Introduction

Oxo-centered iron carboxylate triangles can be synthesised from a variety of carboxylic acids and with a large number of different terminal ligands. These labile terminal ligands can be substituted with ease and therefore permit these triangles to be used as useful linkers to larger assemblies. Originally, the only well known example of this rational approach to covalently linked clusters was with the use of triruthenium basic carboxylates, linked by bridging ligands such as 4,4′-bipyridine and pyrazine. Oxo-centered iron carboxylate triangles were among the first polynuclear clusters to be studied magnetically, and have since been studied extensively. These clusters are characterised by a strong antiferromagnetic exchange interaction between the three metal ions, to give an $S = \frac{1}{2}$ ground state resulting from the interaction of three high spin, $s = \frac{5}{2}$ Fe$^{\text{III}}$ ions. The interaction is best illustrated using the spin Hamiltonian in Eq. 1, which describes an isosceles triangle.

$$\hat{H} = -2J_{\text{Fe1-Fe2}}(\hat{S}_{\text{Fe1}} \cdot \hat{S}_{\text{Fe2}}) - 2J_{\text{Fe1,2-Fe3}}(\hat{S}_{\text{Fe1}} \cdot \hat{S}_{\text{Fe3}} + \hat{S}_{\text{Fe2}} \cdot \hat{S}_{\text{Fe3}})$$ (1)
$J_{\text{Fe1-Fe2}}$ and $J_{\text{Fe1,2-Fe3}}$ are the isotropic exchange constants between the three metal ions and $S_{\text{Fe1}}$, $S_{\text{Fe2}}$ and $S_{\text{Fe3}}$ are the individual spins of each metal ion. The isosceles model is also required to fit the data from INS and Mössbauer studies, which could not be fitted with an equilateral triangle model. A best fit for the acetate complex, [Fe$_3$(μ$_3$-O)(MeCO$_2$)$_6$(H$_2$O)$_3$]Cl, was achieved using $J$ values of $J_{\text{Fe1-Fe2}} = -38.2$ cm$^{-1}$ and $J_{\text{Fe1,2-Fe3}} = -28.9$ cm$^{-1}$. A poorer fit can be obtained with a single $J$ of $J_{\text{Fe}} = -29.0$ cm$^{-1}$ assuming an equilateral triangle, thus showing the requirement for an isosceles model even with magnetically equivalent ions. Oxo-centered iron carboxylate triangles also exist as heterometallic complexes, where one iron ion is replaced with another 3d or s-block metal. The introduction of a heterometal in the +2 oxidation state, dramatically alters the exchange interaction between the three metals. The Hamiltonian shown in Eq. 1, is still relevant here, however there is a two-fold increase in the Fe1-Fe2 interaction compared to the Fe$_2$O analogue, which is approximately independent of the M$^{\text{II}}$ ion present. This phenomenon is well known in terms of fitting the magnetic data of [Fe$^\text{III}$]$_2$M$^{\text{II}}$(μ$_3$-O)(RCO$_2$)$_6$(L)$_3$] (M = Mn, Co, Ni, RCO$_2^-$ = carboxylate and L = H$_2$O, pyridine) complexes. In this work we show a multi-frequency EPR investigation of a family of mixed metal iron pivalate complexes, [Fe$^\text{III}$]$_2$M$^{\text{II}}$(μ$_3$-O)(tBuCO$_2$)$_6$(py)$_3$] (M = Mn, Co, Ni), providing the first EPR investigation of the low-lying electronic state of this family. This provides further insight into the magnetic properties of the divalent metal in each complex and aids our understanding of the electronic and magnetic properties of the Ru$_2$M family, [Ru$^\text{III}$]$_2$M$^{\text{II}}$(μ$_3$-O)(tBuCO$_2$)$_6$(py)$_3$] (M = Mn, Co, Ni) in Chapter 3.
Experimental Section

Synthesis

All solvents and reagents were purchased from commercial sources and used without further purification unless otherwise stated. Nickel pivalate, \([\text{Ni}_2(\mu-\text{OH}_2)(\text{BuCo}_2)_4(\text{BuCO}_2\text{H})_4]\), was synthesised according to literature procedures.\(^{40}\)

\[\text{Fe}_2\text{M}(\mu_3-\text{O})(\text{BuCO}_2)_6(\text{py})_3], \text{M} = \text{Mn} \ (1), \text{Co} \ (2):\] Pivalic acid (50.0 g, 490 mmol) and \(\text{Fe(NO}_3)_3.9\text{H}_2\text{O} \ (10.0 \ g, \ 24.8 \ \text{mmol})\), were heated at 160°C with stirring in a 2 neck round bottom flask (250 mL) for 4 hours to remove all \text{NO}_2 gas. Then \(\text{M(MeCO}_2)_2.4\text{H}_2\text{O} \ (\text{M} = \text{Mn, Co}) \ (3.00 \ \text{g}, \ 12.2 \ \text{mmol})\) was added to the flask under \text{N}_2 along with toluene (100 mL), which was removed by distillation to ensure the removal of acetic acid. The reaction was then left overnight and fresh toluene (100 mL) was added and the process repeated. The reaction was kept at 160°C under \text{N}_2, some of the excess pivalic acid evaporated and the product began to crystallise. The reaction was then cooled slowly to room temperature, with stirring. MeCN (50 mL) was added and the solution was stirred for approximately 15 minutes before being filtered and washed with MeCN (3 x 15 mL). Yields of \([\text{Fe}_2\text{M}(\mu_3-\text{O})(\text{BuCO}_2)_6(\text{BuCO}_2\text{H})_3] : 12.0 \ \text{g} \ (88.3\%) \ \text{and} \ 12.5 \ \text{g} \ (91.7\%) \ \text{for} \ 1 \ \text{and} \ 2 \ \text{respectively were achieved}.\]

Single crystals of \([\text{Fe}_2\text{M}(\mu_3-\text{O})(\text{BuCO}_2)_6(\text{py})_3]\) were obtained by dissolving 200 mg of \([\text{Fe}_2\text{M}(\mu_3-\text{O})(\text{BuCO}_2)_6(\text{BuCO}_2\text{H})_3]\) in \text{CH}_2\text{Cl}_2 (20 mL) and excess pyridine (200 mg) with stirring for approximately 30 minutes. The solvent was removed on the rotary evaporator and the brown residue was redissolved in a minimum amount of diethyl ether, and an equivalent amount of MeCN was added. The solution was left to slowly evaporate to give large brown crystals.

1: Yield 100 mg (53.3%). Anal. Calcd for \(\text{Fe}_2\text{Mn}_1\text{C}_{46}\text{H}_{69}\text{O}_{13}\text{N}_3: \text{C}, \ 52.64; \ \text{H}, \ 6.77; \ \text{N}, \ 4.09; \ \text{Fe}, \ 10.88; \ \text{Mn}, \ 5.35\%. \ \text{Found: C, 52.60; H, 6.89; N, 4.14; Fe, 10.76; Mn, 5.20\%}. \ \text{IR:}
νas(OCO) 1612, 1597 cm⁻¹. ESI-MS: m/z (%) 846 (20) [M-(piv)-(py)]⁺. ¹H NMR (CDCl₃): δ 4.33 (36H, s, (CH₃)₃–Fe-Mn pivalates), δ 3.09 (18H, s, (CH₃)₃–Fe-Fe pivalates).

2: Yield 100 mg (53.3%). Anal. Calcd for Fe₂Co₁C₄₅H₆₉O₁₃N₃: C, 52.44; H, 6.75; N, 4.08; Fe, 10.84; Co, 5.72%. Found: C, 52.55; H, 6.66; N, 4.03; Fe, 10.45; Co, 5.53%. IR: νas(OCO) 1620, 1598 cm⁻¹. ESI-MS: m/z (%) 1078 (60) [M-(py)+(THF)]+MeOH+Na⁺.

[Fe₂Ni(μ₃-O)(⁵BuCO₂)₆(py)₃] (3): Pivalic acid (50.0 g, 490 mmol) and Fe(NO₃)₃·9H₂O (10.0 g, 24.8 mmol), were heated at 160°C with stirring for 5 hours to remove all NO₂ gas. The flask was then cooled to 100°C and [Ni₂(μ-OH)(⁵BuCO₂)₄(⁵BuCO₂H)₄], (5.83 g, 12.4 mmol) was added along with toluene (25 mL), and heating was continued for 1 hour. After 1 hour the temperature was increased to 165°C and the reaction continued overnight. The reaction was then cooled to 65°C with stirring and MeCN (50 mL) was added in small portions. After 1 hour the solution was cooled to room temperature, filtered and washed with MeCN (3 × 25 mL) and dried in air. Yield of [Fe₂Ni(μ₃-O)(⁵BuCO₂)₆(⁵BuCO₂H)₃]: 13.0 g (95.2%). Single crystals of [Fe₂Ni(μ₃-O)(⁵BuCO₂)₆(py)₃] were obtained by dissolving 200 mg of [Fe₂Ni(μ₃-O)(⁵BuCO₂)₆(⁵BuCO₂H)₃] in CH₂Cl₂ (20 mL) and excess pyridine (200 mg) with stirring for approximately 30 minutes. The solvent was removed on the rotary evaporator and the brown residue was redissolved in a minimum amount of diethyl ether, and an equivalent amount of MeCN was added. The solution was left to slow evaporate to give large brown crystals. Yield 150 mg (80.2%).

Anal. Calcd for Fe₂Ni₁C₄₅H₆₉O₁₃N₃: C, 52.45; H, 6.75; N, 4.08; Fe, 10.84; Ni, 5.70%. Found: C, 51.39; H, 6.77; N, 3.96; Fe, 10.33; Ni, 5.40%. IR: νas(OCO) 1624, 1600 cm⁻¹. ESI-MS: m/z (%) 857 (70) [M-(py)₃+(MeOH)₂]+H⁺.
X-ray crystallographic data collection and refinement of the structures. Single crystals of 1-3 were mounted in the nitrogen cold stream of an Oxford Diffraction XCalibur 2 diffractometer. Graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) was used throughout. The structures were solved by direct methods and refined by full-matrix least-squares method with anisotropic thermal parameters for all atoms using SHELXS, and SHELXL was used for the refinement. The three metal ions are crystallographically equivalent in 1 and 2 and so were statistically disordered over the three sites using the SUMP command. In 3 two metals are observed in the asymmetric unit and the third is generated by symmetry from metal 2. The divalent metal is disordered accordingly. The occupancy factors and thermal and positional parameters for the metal sites were fixed according to the disorder model used. The split atoms model was used to account for the disorder in some of the (CH₃)₃CCO₂ groups. CIF files were generated using Olex2. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the CCDC, (986172 (2) and 986173 (3))
Table 1. Crystallographic Data

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<td>P6₁22</td>
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<td>b, Å</td>
<td>19.7175(8)</td>
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<td>c, Å</td>
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<td>wR2 (I &gt;2σ(I))</td>
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<td>0.1750</td>
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<td>residual density, e Å⁻³</td>
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<td>1.20 / -0.94</td>
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a) Observation criterion: I > 2σ(I), R₁ = Σ|Fₒ|−|Fc|/Σ|Fₒ|; b) GoF = [Σ[w(Fₒ²−Fᶜ²)]²/(n−p)]⁻¹/²; c) wR² = [Σ[w(Fₒ²−Fᶜ²)²]/Σ[w(Fₒ²)]²]⁻¹/² where w = 1/σ²(Fₒ²)⁺+(aP)²+bP, P = (Fₒ²+2Fᶜ²)/3

Physical Measurements. Electronic absorption spectra were recorded using an Agilent 8453 spectrometer (190-1100 nm). Infrared data were collected using a ThermoScientific iD5 ATR, Nicolet iS5 spectrometer. ¹H NMR spectrum of 1 in CDCl₃ solutions was recorded using a Bruker 400 FT NMR spectrometer. Chemical shifts are referenced to internal CHCl₃ (δ = 7.26 ppm). Cyclic voltammograms were measured using an Autolab potentiostat AUT71194. Redox potentials are referenced to the internal ferrocenium/ferrocene (Fc⁺/0) couple. Multifrequency EPR spectra were recorded at the EPSRC National UK EPR Facility and Service at The University of Manchester. High frequency/high-field EPR measurements were carried out at LNCMI Grenoble on a custom built instrument. Multifrequency EPR spectra were performed using Easyspin. Magnetic data

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were recorded using a SQUID magnetometer (Quantum Design MPMS-XL) over a
temperature range 2 – 300 K with applied magnetic fields to 7 T. Corrections for
diamagnetism were made using Pascal’s constants and magnetic data were corrected for
diamagnetic contributions from the sample holder. Fits were performed using the program
PHI.\textsuperscript{45} ESI-MS and microanalyses were carried out by Manchester School of Chemistry,
Mass spectrometry service and micro analytical laboratory.

**Results and Discussion**

**Synthesis and Characterisation**

The pivalate compounds 1-3 were synthesised by direct synthesis, using a procedure based
on the synthesis of the acetate derivatives, [Fe\textsubscript{2}M(μ\textsubscript{3}-O)(MeCO\textsubscript{2})\textsubscript{6}(py)\textsubscript{3}].\textsuperscript{29} Single crystals
can then be isolated through pyridine substitution of terminal pivalic acid ligands on
[Fe\textsubscript{2}M(μ\textsubscript{3}-O)(t\textsubscript{BuCO}\textsubscript{2})\textsubscript{6}(t\textsubscript{BuCO\textsubscript{2}H})\textsubscript{3}] \textsubscript{2} and then slow evaporation of a 1:1 Et\textsubscript{2}O:MeCN
solution.

1-3 were characterised by elemental analysis, ESI-MS, IR, UV-Vis, EPR spectroscopy,
SQUID magnetommetry, cyclic voltammetry and X-ray crystallography. The pale brown
colour of these solutions results in very weak absorption bands in the visible region of the
spectrum (350-800 nm) (Figure 1). However, the transitions that are observed are typical
of the metals present in these compounds.\textsuperscript{46}
Figure 1. UV-Vis spectra of 1-3 in CH₂Cl₂. Red = 1, blue = 2, Green = 3 (5x10⁻⁴ M).

Table 2. UV-Vis absorption spectral data for compounds 1-3 in CH₂Cl₂

<table>
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<tr>
<th>Complex</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt;, nm (ε, 10&lt;sup&gt;4&lt;/sup&gt;M⁻¹cm⁻¹)</th>
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</thead>
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<tr>
<td>1</td>
<td>583 (0.05), 485 (0.08), 428 (0.12), 348 (0.39)</td>
</tr>
<tr>
<td>2</td>
<td>572 (0.03), 464 (0.09), 325 (0.45)</td>
</tr>
<tr>
<td>3</td>
<td>558 (0.02), 457 (0.08), 359 (0.34)</td>
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</table>

Crystal structures. The molecular structures of 1-3 were determined by X-ray crystallography, selected bond lengths and angles are shown in Table 3. It was not possible to identify the divalent metal site, as the metal ions are statistically disordered over the three sites.

Complexes 1 and 2 crystallise in the monoclinic space group P2₁, with one molecule in the asymmetric unit. Complex 3 crystallises in the hexagonal space group P6<sub>1</sub>22, with half of a molecule in the asymmetric unit. The triangular shape of the molecule is held together by a central μ₃-oxide, which lies flat within the M₃ plane. The triangular structure is further reinforced by the bridging carboxylate ligands (Figures 2 and 3), lying above and below the plane. In complex 3 the pyridine ligands lie perpendicular to the Fe₂M plane in contrast to 1 and 2 where they lie flat in the plane. This change in orientation of the terminal
ligands is most likely due to crystal packing effects. The average N-M-O\textsubscript{oxo} bond angle increases across the series with 175.96(14)$^\circ$, 176.46(13)$^\circ$ and 176.93(13)$^\circ$ for 1, 2 and 3 respectively. The average intermetal separation is comparable to similar oxo-centered trinuclear carboxylate clusters in the literature, at 3.316(11) Å in 1, and slightly shorter in 2 and 3 at 3.288(8) Å and 3.277(13) Å respectively.\cite{29-39} The M-O distances are 1.914(3) Å in 1, and slightly shorter in 2 and 3 at 1.898(3) Å and 1.892(4) Å respectively.\cite{37}

\begin{figure}[h]
\centering
\includegraphics[width=0.7\textwidth]{molecular_structure.png}
\caption{Depiction of the molecular structure of 1 and 2. Fe Orange, Mn or Co Turquoise, O red, N lilac, C black.}
\end{figure}
Figure 3. Depiction of the molecular structure of 3. Fe Orange, Ni light green, O red, N lilac, C black.
Table 3. Selected bond distances [Å] and angles [°] for 1, 2 and 3

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<tr>
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<th>1 \textsuperscript{a}</th>
<th>2</th>
<th>3 \textsuperscript{b}</th>
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<td>M···M</td>
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<td>M2-O1</td>
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\textsuperscript{a}Data taken from ref 37. \textsuperscript{b}Metal 3 generated by symmetry from Metal 2.

**Electrochemistry.** The cyclic voltammograms (CVs) of complexes 1-3 were recorded in a CH\textsubscript{2}Cl\textsubscript{2} solution containing 0.1 M [N\textsubscript{n-Bu\textsubscript{4}}](PF\textsubscript{6}), as supporting electrolyte, using a glassy carbon working electrode and a scan rate of 200 mV s\textsuperscript{-1} at ambient temperature. The redox processes listed in Table 4 are referenced versus the ferrocenium/ferrocene (Fc\textsuperscript{+}/Fc\textsuperscript{0}) couple. Cyclic voltammetry of 3 (Figure 4) revealed that the complex undergoes one quasi-reversible one-electron oxidation process and two irreversible reductions. Complexes 1 and 2 undergo one irreversible one-electron oxidation process and one irreversible reduction, shown in Figure 4, and labelled I and II respectively. The daughter products to each irreversible process occur at \textasciitilde-0.5 V (close to process IV) and only occur when the
potential is swept past that of the parent process, *i.e.* +0.29 and +0.72 V for process I in 1 and 2 respectively and -1.71 and -1.87 V for process II in 1 and 2 respectively. Both process I and II are classed as irreversible due to the large peak to peak separation ($\Delta E_p$), which is -0.82 and -1.30 V for oxidative process in 1 and 2 respectively and -1.37 and -1.46 V for reductive process in 1 and 2 respectively. These are similar to the acetate homologues.\(^{46-52}\)

**Figure 4.** Cyclic voltammograms of 1-3 recorded in CH\(_2\)Cl\(_2\) solutions containing 0.1 M [N\((n\text{-Bu})_3\)](PF\(_6\)) at room temperature with a scan rate of 200 mV s\(^{-1}\). Potentials are referenced versus the Fc\(^{+\/0}\). Red = 1, Blue = 2, Green = 3, Black = [Fe\(^{\text{III}}\)\(_2\)Fe\(^{\text{II}}\)(μ\(_3\)-O)(\(^{1}\)BuCO\(_2\))\(_6\)(py)\(_3\)]\(^{\text{53}}\).

**Table 4.** Electrochemical data of 1-3 and [Fe\(^{\text{III}}\)\(_2\)Fe\(^{\text{II}}\)(μ\(_3\)-O)(\(^{1}\)BuCO\(_2\))\(_6\)(py)\(_3\)] Versus Fe\(^{+\/0}\).

<table>
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<tr>
<th></th>
<th>$E_{1/2,i}$ I</th>
<th>$E_{1/2,i}$ II</th>
<th>$E_p$ III</th>
<th>$E_{1/2}$ IV</th>
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<tr>
<td>1</td>
<td>+0.29</td>
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<td>2</td>
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<tr>
<td>3</td>
<td>+0.76</td>
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<tr>
<td>[Fe(^{\text{III}})(_2)Fe(^{\text{II}})(μ(_3)-O)((^{1})BuCO(_2))(_6)(py)(_3)]</td>
<td></td>
<td></td>
<td>-0.79</td>
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The case of 3 differs somewhat, as the oxidative process is now quasi-reversible, with the peak-peak separation significantly reduced. A second reduction wave is also observed at a more negative potential. Process IV which is present only in 1 and 2, was found to be an impurity, as the intensity of this reduction potential is not of a comparable size to the other waves in the voltammogram, so does not originate from the major species. The feature was characterised as an Fe$^\text{III}$/Fe$^\text{II}$ reduction resulting from an iron triangle impurity by recording the electrochemical behaviour of [Fe$^\text{III}$$_2$Fe$^\text{II}$(μ$_3$-O)(BuCO$_2$)$_6$(py)$_3$] for comparison, shown in Figure 4.

![Figure 5](image-url)  

**Figure 5.** Plots of $\chi_M T$ vs T for compounds 1-3 at H = 0.5 T. Experimental data shown as symbols and fits shown as red line (○ = 1, △ = 2, □ = 3).

**Magnetism.** The magnetic susceptibilities of 1, 2 and 3 are strongly temperature dependent. The observed profiles shown in Figure 5, are similar to analogous acetate triangles in the literature.$^{26,31,32}$ In each case competing antiferromagnetic exchange interactions between the three metal ions gives rise to a room temperature $\chi_M T$ value which is far removed from that calculated for fully uncoupled systems. The room temperature $\chi_M T$ values are 4.02, 3.64 and 2.17 cm$^3$ K mol$^{-1}$ for 1, 2 and 3 respectively. The $\chi_M T$ values decrease with decreasing temperature in 1 and 2, resulting in a $\chi_M T$ value of 1.66 and 1.62 cm$^3$ K mol$^{-1}$ at 2 K for 1 and 2, respectively. The non-zero values are consistent with
paramagnetic ground states.\textsuperscript{19,26,31,32} The low temperature value of 1 corresponds to an \( S = \frac{3}{2} \) state born out of antiferromagnetic coupling of the \( S_{\text{Mn}} = \frac{5}{2} \) ion with the triplet state of the Fe pair, as discussed in a previous communication (see below).\textsuperscript{37} Whereas in 2, the low temperature value corresponds to a \( J \) (total angular momentum) = \( \frac{1}{2} \) state, with contributions from both \( S \) and \( L \) (orbital angular momentum) of high spin octahedral \( \text{Co}^{II} \).\textsuperscript{32,36} The susceptibility profile of 3 is unlike 1 and 2, although it does decrease with decreasing temperature, there is a slight increase from 40 K before the value begins to decrease again at 8 K. Compound 3 also shows a paramagnetic ground state with a \( \chi_M T \) value of 0.95 cm\(^3\) K mol\(^{-1}\) at 2 K, corresponding to an \( S = 1 \) state due to the antiferromagnetic coupling of the \( S_{\text{Ni}} = 1 \) ion with the singlet state of the Fe pair (see below).\textsuperscript{19,26,32}

The exchange coupling pattern of \( J_{\text{Fe-Fe}} > J_{\text{Fe-M}} \) previously described for these triangles is utilised here, and the data were fit according to the Heisenberg spin Hamiltonian given in Eq. 2 where the symbols have their usual meanings, and the coupling pathways are presented in Scheme 1.

\[
\hat{H} = (g_{\text{Fe1}} + g_{\text{Fe2}} + g_M)\beta (\hat{S}_{\text{Fe1}} + \hat{S}_{\text{Fe2}} + \hat{S}_M)H - 2J_{\text{Fe-Fe}}(\hat{S}_{\text{Fe1}} \cdot \hat{S}_{\text{Fe2}}) - 2J_{\text{Fe-M}}(\hat{S}_{\text{Fe1}} \cdot \hat{S}_M)
\]  \hspace{1cm} (2)
Scheme 1. Magnetic exchange pathways in the trinuclear core.

The Hamiltonian in Eq. 2 can be solved by Kambe’s notation and the energy level diagrams for 1 and 3 can be plotted using Eq. 3, where $S_{Fe} = \frac{5}{2}$; $S_{M}$ is the spin of the $M^{ll}$ ($S_{M} = \frac{5}{2}$ for Mn$^{ll}$ and $S_{M} = 1$ for Ni$^{ll}$); $S^{+} = S_{Fe1} + S_{Fe2}$ and $S_{T} = S^{+} + S_{M}$.\(^{54}\)

\[
E(S_{T}, S^{+}) = -J_{Fe-M}[S_{T}(S_{T} + 1) - S^{+}(S^{+} + 1) - S_{M}(S_{M} + 1)] - J_{Fe-M}[S^{+}(S^{+} + 1) - S_{Fe1}(S_{Fe1} + 1) - S_{Fe2}(S_{Fe2} + 1)]
\]

(3)

Using this approach $S^{+}$ can take the value $|S_{Fe1} + S_{Fe2}|$ to $|S_{Fe1} - S_{Fe2}|$, i.e. $S^{+}$ ranges from 0 to 5 in integral values. $S_{T}$ can take values from $|S^{+} + S_{M}|$ to $|S^{+} - S_{M}|$, the differing possibilities are given in Tables S1 and S2.

Excellent fits for both temperature-dependant magnetic susceptibility (Figure 5) and field dependant magnetisation (Figure S1) were obtained for each of the three complexes. The best fit parameters for 1 were: $J_{Fe-Fe} = -63.5$ cm$^{-1}$ and $J_{Fe-Mn} = -21.9$ cm$^{-1}$ with $g$ fixed at 2.0 according to Eq. 2. This combination of $J$ values are similar to the acetate analogue and give rise to a $|\frac{5}{2}, 1\rangle$ ground state.\(^{37}\)
Figure 6. Energy diagram for low lying spin levels of 1.

The energy diagram of the spin states of 1 revealed a quartet ground state, \(|S, S^\uparrow\rangle = |3/2, 1\rangle\) with a sextet excited state \(|5/2, 0\rangle \ 26.3 \text{ cm}^{-1}\) above it. Therefore, the 2 K \(\chi_MT\) value of 1.66 cm\(^3\) K mol\(^{-1}\) arises solely from the \(|3/2, 1\rangle\) ground state.

These parameters lead to a well separated ground state and therefore the field dependant magnetisation data can also be fit as an \(S = 3/2\) ground state with a small zero-field splitting, giving \(D = +0.25 \text{ cm}^{-1}\) and \(E = 0.04 \text{ cm}^{-1}\), using the giant spin approximation (Eq. 4).

\[
\vec{H}_{GS} = g_{GS} \beta \vec{S} \vec{H} + D_{GS} \left( \frac{S_x^2}{2} - \frac{S(S+1)}{3} \right) + E_{GS} (\vec{S}_x^2 - \vec{S}_y^2) \tag{4}
\]

However, due to the nature of the \(|3/2, 1\rangle\) ground state, the zero-field splitting of the total spin ground state, as determined by EPR (discussed later), arises from a contribution from each of the metal ions. Assuming it arises solely due to Mn\(^{II}\), then a single ion \(D\) value, \(D_{Mn}\), is calculated as 0.13 cm\(^{-1}\). Using the equations shown below (Eq.5-7), the total zero-field splitting in Eq. 4 can be projected back to the Mn\(^{II}\) ion using Bencini and Gatteschi’s method (Eq. 7). The symbols have their usual meanings: \(c_{Mn}\) is the zero field splitting coefficient for \(D_{Mn}\) of the Mn\(^{II}\) ion and \(D_{GS}\) is the zero field splitting of the total spin ground state. \(S_i\) is the spin of the individual ions, \(S\) is the total spin of the system, and \(S^\prime = \)}
2S+1. The last term in Eq. 7 is known as a six J symbol. This is discussed in a previous communication.\(^3\)

\[\hat{H} = -2J_{\text{Fe-Fe}} (\hat{S}_{\text{Fe1}} \cdot \hat{S}_{\text{Fe2}}) - 2J_{\text{Fe-Mn}} (\hat{S}_{\text{Fe1}} \cdot \hat{S}_{\text{Mn}} + \hat{S}_{\text{Fe2}} \cdot \hat{S}_{\text{Mn}}) + g\beta (\hat{S}_{\text{Fe1}} + \hat{S}_{\text{Fe2}} + \hat{S}_{\text{Mn}})H + D_{\text{Mn}} (\hat{S}_{\text{Mn}}^2 - \frac{S_{\text{Mn}}(S_{\text{Mn}}+1)}{3}) \]  

\[D_{\text{Mn}} = \frac{D_{\text{GS}}}{c_{\text{Mn}}} \]  

\[c_{\text{Mn}} = (-1)^{2S_{\text{Fe1}} + 2S_{\text{Fe2}} + 2S_{\text{Mn}} + 3S_{\text{Fe1Fe2}}} S \left\{ \left[ (2S_{\text{Mn}} + 1)S_{\text{Mn}}^2 (2S_{\text{Mn}} - 1)S_{\text{Mn}} (S_{\text{Mn}} + 1) \right]^{\frac{1}{2}} \left[ ((2S + 3)S^2 (2S - 1)S (S + 1))^{\frac{1}{2}} \right] \right\} \]

The magnetic susceptibility fitting for 3 was achieved using the following values; \(J_{\text{Fe-Fe}} = -69.6\ \text{cm}^{-1}\) and \(J_{\text{Fe-Ni}} = -31.0\ \text{cm}^{-1}\) with \(g_{\text{Fe}}\) fixed at 2.0 and \(g_{\text{Ni}}\) set at 2.21 according to Eq. 2. The inclusion of zero-field parameters were also required to obtain a good fit of the field dependant magnetisation data, \(D_{\text{Ni}} = -4.0\ \text{cm}^{-1}\) and \(E_{\text{Ni}} = 0.40\ \text{cm}^{-1}\) (Eq. 8). The values of \(J\) and \(D\) are similar in magnitude to couplings in related triangles.\(^{17,19}\) This exchange coupling scheme reveals a triplet ground state \(|1,0\rangle\), with an \(S = 0\) first excited state \(|0,1\rangle\), which resides 15.2 cm\(^{-1}\) above it. The second excited state, \(S = 1\) \(|1,1\rangle\) is 62.0 cm\(^{-1}\) above the first excited state. This is apparent from the shape of the \(\chi_M T\) vs. \(T\) plot (Figure 5). When the temperature is decreased the diamagnetic singlet state is populated, resulting in the decrease in \(\chi_M T\), then as the temperature is decreased further the population of the \(S = 1\) \(|1,0\rangle\) ground state increases resulting in a low \(T\) peak. The ordering of the spin states is observed in the energy diagram of 3 shown below (Figure 7).

\[\hat{H} = (g_{\text{Fe1}} + g_{\text{Fe2}} + g_{\text{Ni}})\beta (\hat{S}_{\text{Fe1}} + \hat{S}_{\text{Fe2}} + \hat{S}_{\text{Ni}})H + D_{\text{Ni}} \left[ \hat{S}_{\text{Ni}}^2 - \frac{S_{\text{Ni}}(S_{\text{Ni}}+1)}{3} \right] + E_{\text{Ni}} (\hat{S}_{\text{Ni}}^2 - \hat{S}_{\text{Ni}}) - 2J_{\text{Fe-Fe}} (\hat{S}_{\text{Fe1}} \cdot \hat{S}_{\text{Fe2}}) - 2J_{\text{Fe-Ni}} (\hat{S}_{\text{Fe1}} \cdot \hat{S}_{\text{Ni}} + \hat{S}_{\text{Fe2}} \cdot \hat{S}_{\text{Ni}}) \]  

(8)
Due to the $|1, 0>$ nature of the ground state of $3$ the zero-field splitting is a result of the Ni$^{II}$ ion with no contributions from the two Fe ions, which mutually cancel to give the $S^+ = 0$ state.

The magnetic behaviour of $2$ is more complicated, as the orbital angular momentum, $L$, must also be considered, due to the orbital triplet ground state of the high spin octahedral Co$^{II}$ ion. The first-order orbital angular momentum of the $^4T_{1g}$ ground state in octahedral Co$^{II}$ is coupled to the total electron spin ($S = 3/2$) by spin-orbit coupling (SOC), therefore $S$ and $L$ are no longer good quantum numbers, so we must consider $J$, the total angular momentum. Therefore, SOC must also be taken into account when fitting the data. The best fit for $2$ was obtained using Eq. 9, according to the Lines coupling model with the following values; $J_{Fe-Fe} = -68.8 \text{ cm}^{-1}$ and $J_{Fe-Co} = -15.8 \text{ cm}^{-1}$ with $g$ fixed at $2.0$ and the inclusion of an orbital reduction parameter ($\sigma$) of $-1.35$, along with a spin-orbit coupling parameter ($\lambda$) of $-168 \text{ cm}^{-1}$ $^{19,32,36}$ The orbital reduction parameter $\sigma = A\kappa$, where $A = -3/2$ and $\kappa$ is the usual orbital reduction factor ($0 \leq \kappa \leq 1$), and can therefore take the values $-1.5 - 0$.

Using the T-P isomorphism the $^4T_1 (^4T)$ state can be viewed as a fictitious $L = 1$: the factor $A (-3/2)$ defines the conversion of the matrix of the angular momentum operator $\hat{L}$ within the $^4T_1 (^4T)$ state to the matrix of $\hat{l}$ in the atomic p-basis. These exchange couplings reveal a
$J = \frac{1}{2}$ ground state. The ground state of 2 can be explained by normal octahedral Co$^{II}$ behaviour made of components $|m_l, m_s>$ for $|J = \frac{1}{2}, m_J = \pm \frac{1}{2}>$ given by Clebsch-Gordon in Eq. 11, due to the antiferromagnetically coupling of the two Fe$^{III}$ ions to give $S = 0.57$.

The Clebsch-Gordon coefficients can be calculated using Eq. 10.

$$\hat{H} = \beta \left( \sigma \hat{L}_{Co} + g \left( \hat{S}_{Fe1} + \hat{S}_{Fe2} + \hat{S}_{Co} \right) \right) H - 2J_{Fe-Fe} \left( \hat{S}_{Fe1} \cdot \hat{S}_{Fe2} \right) - 2J_{Fe-Co} \left( \hat{S}_{Fe1} \cdot \hat{S}_{Co} + \hat{S}_{Fe2} \cdot \hat{S}_{Co} \right) + \lambda (\sigma \hat{L}_{Co} \cdot \hat{S}_{Co})$$

(9)

**Figure 8.** Energy diagram for low lying spin levels of 2.

$$\phi(J, m_J) = \sum_{m_l, m_s} C^{J m_l}_{m_J m_s} |l = 1, m_l, s = \frac{3}{2}, m_s>$$

(10)

$$\phi \left( \frac{1}{2}, \pm \frac{1}{2} \right) = \left( \frac{1}{\sqrt{6}} \right) |1, \pm 1, \frac{3}{2}, \pm \frac{1}{2}> - \left( \frac{1}{\sqrt{3}} \right) |1, 0, \frac{3}{2}, \pm \frac{1}{2}> + \left( \frac{1}{\sqrt{2}} \right) |1, \mp 1, \frac{3}{2}, \pm \frac{3}{2}>$$

(11)

From the parameters discussed above for 2 an energy level diagram can be plotted (Figure 8) showing a well isolated $J = \frac{1}{2}$, ground state with the next excited state ($J = \frac{1}{2}$) ~83 cm\textsuperscript{-1} above it.
**EPR Spectroscopy.** The X- and Q-band EPR experimental data and simulations for 1 are reported elsewhere. 37 High frequency/high field EPR spectra of 1 could be simulated using the same parameters (with Eq. 4), with an $S = \frac{3}{2}$ ground state spin with zero-field splitting parameters, $D = +0.25 \text{ cm}^{-1}$ and $E = 0.04 \text{ cm}^{-1}$, yielded from Q-band simulations, (Figures S2 and S3).

![EPR Spectroscopy Image](image)

**Figure 9.** Multi-frequency powder EPR spectra of 2 recorded at X- (9.777 GHz) at 10 K and Q- band (33.99 GHz) at 10 K. Experimental data is shown in black and simulations in red.

Due to the well isolated $J = \frac{1}{2}$ ground state of 2, only this Kramer’s doublet is observed in the low temperature EPR experiments. The spectra shown in Figures 9 and 10 are consistent with a large $g$-anisotropy, and were simulated using effective $g$-values, $g_{\text{eff}} = 6.10, 3.55, 2.81$. A hyperfine interaction of $A = 185, 100, 33 \times 10^{-4} \text{ cm}^{-1}$, was included in the simulation as there is identifiable coupling of the $I = \frac{7}{2}$ nuclear spin of $^{59}\text{Co}$ nucleus (100% natural abundance) to the total orbital angular momentum $J = \frac{1}{2}$, on $g_1$ at X-band (Eq. 12).

$$\hat{H} = g\beta \hat{S} \hat{H} + \hat{S} \hat{A} \hat{I} \quad \text{(12)}$$
The average effective $g$-value of 2 extracted from EPR is 4.15, which is comparable to the effective $g$-value of 4.23 obtained by fitting the magnetic data.

Due to the large zero-field splitting observed in 3, this compound is EPR silent at conventional frequencies. However, a signal can be obtained at 331.2 GHz (Figure 11). The multiple lines observed in the spectrum relate to a range of $D$ values, due to slight differences in individual molecules within the crystalline material, as discussed previously in Chapter 3. There is no evidence of this phenomenon in the EPR spectra of 1 and 2, which both crystallise with one molecule in the asymmetric unit, in the monoclinic space group $P2_1$. The simulation for the $S=1$ ground state yielded $g = 2.21$, $D = -4.0$ cm$^{-1}$ and $E = 0.4$ cm$^{-1}$ ($E/D = 0.10$), using the spin Hamiltonian shown in Eq. 4. These parameters gave a simulation with the main features at the correct field positions with accurate separations between them. However, the experiment is not fully defined with a single set of zero-field splitting parameters, as discussed in Chapter 3 for Ru$_2$Ni, the multiple lines are due to a range of $D$ values. The parameters used here are very similar to those obtained from the magnetic data. Unlike 1, 3 possesses a negative zero-field splitting parameter, which is comparable to similar compounds in the literature.$^{19}$

**Figure 10.** Polycrystalline powder spectrum (331.2 GHz) of 2 at 5 K. Experimental data is shown in black and simulations in red.
Figure 11. Polycrystalline powder spectrum (331.2 GHz) of 3 at 5 K. Experimental data is shown in black and simulations in red.

Conclusions

It has been shown previously that antiferromagnetic exchange interactions dominate between the three metal ions within oxo-centered carboxylate triangles.21-26,31,32 Here, for the first time, we have been able to determine the ground states and associated magnetic anisotropies by EPR spectroscopy for 1 – 3. As previously reported, the $S = \frac{3}{2}$ ground state of 1 possesses a magnetic anisotropy of $D = +0.25$ cm$^{-1}$.37 The $D$ value of -4.0 cm$^{-1}$ for 3, arising solely from the Ni(II) ion, has been obtained through the use of high frequency/high field EPR spectroscopy. Interestingly, in the two cases the signs are different; the negative zero-field splitting in 3 is comparable and within the range of similar compounds in the literature.17,19 The ground state spin of 2 is that of an $J = \frac{1}{2}$, with very anisotropic $g$-values, which fits well with the magnetic data and the model discussed by Tsukerblat et al. on a similar acetate compound, [Fe$_2$Co(MeCO$_2$)$_6$(3-Cl-py)$_3$] (3-Cl-py = 3-chloro-pyridine).32
Acknowledgments

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References


Supporting Information For

“Characterisation of Heterometallic Clusters \([\text{Fe}_2\text{M}(\mu_3-\text{O})(\text{tBuCO}_2)_6(\text{py})_3]\) (M = Mn, Co, Ni; py = pyridine) using Multi-frequency EPR Spectroscopy”

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Figure S1. $M = f(H/T)$ plots at $T = 2$ and 4 K for compounds 1-3. Experimental data shown as symbols and best fits represented by the red lines, ($\bigcirc = 1$, $\triangle = 2$, $\square = 3$).

Figure S2. Polycrystalline powder spectrum (331.2 GHz) of 1 at 5 K. Experimental data is shown in black and simulation in red.
**Figure S3.** Polycrystalline powder spectra (331.2 GHz) of 1 at 5, 10, 15 and 20 K. Experimental data is shown in black and simulations in red.
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Table S1. Calculated energies for the spin states of 1 using Kambe’s notation. The ground state of 1 is highlighted in red.
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**Table S2.** Calculated energies for the spin states of 3 using Kambe’s notation. The ground state of 3 is highlighted in red.
### Table S3

Percentage composition of the ground state in 2 from mixing of the $m_s$ states and the $M_l$ states of the one Co$^{II}$ ion and the $m_s$ states of the two Fe$^{III}$ ions.

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Chapter Five – Manuscript 3

“The Electrochemical Behaviour of a Switchable Ru$_2$Ni Linker between Two Cr$_7$Ni Rings Examined using Cyclic Voltammetry, EPR and UV-vis-NIR Spectroscopy”

S. A. Magee, S. Sproules, A.-L. Barra, G. F. S Whitehead, D. Collison, R. E P. Winpenny and E. J. L. McInnes
The Electrochemical Behaviour of a Switchable Ru\textsubscript{2}Ni Linker between Two Cr\textsubscript{7}Ni Rings Examined using Cyclic Voltammetry, EPR and UV-vis-NIR Spectroscopy

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Abstract. A linked heterometallic chromium ring system has been synthesised, \([\text{Ru}_2\text{NiO}^{(\text{BuCO}_2)_6}(\text{py})(\text{Cr}_7\text{NiF}_8(\text{BuCO}_2)_{15}(\text{O}_2\text{CC}_3\text{H}_4\text{N}))_{22}\text{][NH}_2\text{Pr}_2]_2\), \(1\), \((\text{py} = \text{pyridine}, \text{pr} = \text{n-propyl and HO}_2\text{CC}_3\text{H}_4\text{N} = \text{isonicotinic acid})\) using well established carboxylate chemistry. The molecular structure has been determined by X-ray crystallography. Electronic properties of \(1\) have been determined by cyclic voltammetry, EPR and UV-Vis-NIR spectroscopy. In situ oxidation experiments have also been carried out to assess the switchability of the redox active linker.

Introduction

Recent literature has discussed the idea that polymetallic clusters may be used as components within molecular devices.\(^1\)-\(^7\) This requires linking together polymetallic components that interact weakly with each other.\(^2\) These polymetallic clusters have magnetic, redox and spectroscopic properties, which we can exploit to control the communication between them. One family of clusters that have attracted a lot of interest for this purpose are antiferromagnetically coupled octametallic \(\text{Cr}_7\text{Ni}\) rings, where each ring possesses an \(S = \frac{1}{2}\) ground state.\(^2\) These \(\text{Cr}_7\text{Ni}\) rings can be linked together by first functionalising the ring with a carboxylic acid that also contains a nitrogen-donor group (\(e.g.\) pyridyl) that can then bind to other metal centres with labile terminal ligands. Thus, once linked coupling is introduced between the molecular components.\(^1\)-\(^4\) In this communication we discuss the use of a redox active mixed-metal ruthenium pivalate triangle, \([\text{Ru}_2\text{NiO}^{(\text{BuCO}_2)_6}(\text{py})_3]\), as a linker between two octametallic rings, \([\text{Cr}_7\text{NiF}_8(\text{BuCO}_2)_{15}(\text{O}_2\text{CC}_3\text{H}_4\text{N})][\text{NH}_2\text{Pr}_2]\). Cyclic voltammetry reveals that the ruthenium-nickel triangle has a reversible oxidative process that is easily accessible with \([\text{FeCp}_2](\text{PF}_6)\), (see Chapter 3). This reversible oxidation is retained in \(1\), allowing us to obtain the oxidised product, \([1](\text{PF}_6)\), which can be studied by EPR spectroscopy.
Experimental Section

Synthesis

All solvents and reagents were purchased from commercial sources and used without further purification unless otherwise stated. [Ru₂NiO(tpy)₃] and [Cr₇NiF₈(tpc)(O₂CC₅H₄N)][NH₂Pr₂] have been synthesised according to Chapter 3 and a literature procedure respectively.

\[
\text{[Ru₂NiO(tpc)(Cr₇NiF₈(tpc)(O₂CC₅H₄N))][NH₂Pr₂]₂ (1)}
\]

[Cr₇NiF₈(tpc)(O₂CC₅H₄N)][NH₂Pr₂]² (0.500 g, 0.216 mmol), was dissolved in hot acetone (15 mL), and [Ru₂NiO(tpc)(py)₃] (0.119 g, 0.106 mmol) was added. The resultant purple solution was stirred with heating for 3 hours. The solution was then allowed to cool, before being sealed and left to stand. After 1 week red/purple crystals were obtained from the reaction solution. Yield 0.243 g, 40.9%. Anal. Calcd for C₂₀₉H₃₅₉O₇₇N₅F₁₆Cr₁₄Ni₃Ru₂: C, 44.87; H, 6.65; N, 1.25; Cr, 13.01; Ni, 3.15. Found: C, 44.69; H, 6.66; N, 1.24; Cr, 13.53; Ni, 3.25 %.

X-ray crystallographic data collection and refinement of the structures. Single crystals of 1 were measured at 150 K on beamline I19 at the Diamond Light Source. The structure was solved by direct methods and refined by full-matrix least-squares method with anisotropic thermal parameters for all atoms using SHELXS, and SHELXL was used for the refinement. The three metal ions of the Ru₂Ni triangle are crystallographically equivalent, so were statistically disordered over the three sites using the SUMP command. The occupancy factors and thermal and positional parameters for the metal sites were fixed according to this disorder model. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the CCDC (1004944).
Physical Measurements: Electronic absorption spectra were recorded using a Perkin-Elmer Lambda 1050 spectrophotometer (300 – 2800 nm). Cyclic voltammograms were measured using an Autolab potentiostat AUT71194. Redox potentials are referenced to the internal ferrocenium/ferrocene (Fc⁺/0) couple. Multifrequency EPR spectra were recorded at the EPSRC National UK EPR Facility and Service at The University of Manchester. High frequency/field EPR measurements were carried out at LNCMI Grenoble on a custom built instrument. Spectral simulations were performed software written by Weihe and Piligkos with some test calculations performed using EasySpin. Magnetic data were recorded using a SQUID magnetometer (Quantum Design MPMS-XL) over a temperature range 2 – 300 K with applied magnetic fields to 7 T. Corrections for diamagnetism were made using Pascal’s constants and magnetic data were corrected for diamagnetic contributions from the sample holder. Microanalysis was carried out by Manchester School of Chemistry micro analytical laboratory.

Results and Discussion

Synthesis and Characterisation

Compound 1 was synthesised in a reaction between [Ru₂NiO(BuCO₂)₆(py)₃] and [Cr₇NiF₈(BuCO₂)₁₅(O₂CC₅H₄N)][NH₂Pr₂]. Two of the terminal pyridine ligands on [Ru₂NiO(BuCO₂)₆(py)] were replaced with two [Cr₇NiF₈(BuCO₂)₁₅(O₂CC₅H₄N)][NH₂Pr₂] to give 1 (Reaction 1). [Cr₇NiF₈(BuCO₂)₁₅(O₂CC₅H₄N)][NH₂Pr₂] binds to the ruthenium-nickel triangle through the py-N atom of the isonicotinate group, thus behaving as a very large substituted pyridine ligand.

\[
[Ru₂NiO(BuCO₂)₆(py)] + 2 [Cr₇NiF₈(BuCO₂)₁₅(O₂CC₅H₄N)][NH₂Pr₂] \rightarrow \\
[Ru₂NiO(BuCO₂)₆(py)(Cr₇NiF₈(BuCO₂)₁₅(O₂CC₅H₄N))₂][NH₂Pr₂]₂ + 2 (py) \quad (1)
\]
The in situ oxidation of 1 can be achieved from the reaction with 1 equiv. of [FeCp$_2$](PF$_6$) under an inert atmosphere, affording the monocation [1](PF$_6$).

**Figure 1.** Depiction of the asymmetric unit and molecular structure of 1. Hydrogen atoms omitted for clarity.

**Crystal structure.** Structural determination of 1 was carried out using X-ray crystallography at 150 K. The compound crystallises in the hexagonal space group $P6_1$, with one molecule in the asymmetric unit (Figure 1). It was not possible to identify the position of Ni$^{II}$ ion within the triangular unit, as the metal ions are statistically disordered over the three sites. The same is true within the heterometallic ring units, as the Ni$^{II}$ ion can be in one of two sites, *i.e.* on either site bound to the isonicotinate group, due to the faster reaction kinetics of Ni$^{II}$ compared with Cr$^{III}$.$^{13}$ Selected bond distances and angles are shown in Table 1. The metrics of the triangular linker show some variation when compared to the isolated unit, [Ru$_2^{III}$NiO($^t$BuCO$_2$)$_6$(py)$_3$] (Chapter 3). In 1 the average intermetal distance within the triangle unit is 3.3177(9) Å compared to 3.3116(4) Å in [Ru$_2^{III}$NiO($^t$BuCO$_2$)$_6$(py)$_3$], showing an increase in the average separation. However, there is little difference in the average M-O$_{oxo}$ distance which remains pretty much constant from 1.912(2) Å in the isolated triangle to 1.915(4) Å in 1.
Table 1. Selected average bond distances [Å] and angles [°] for 1

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**Magnetism.** Temperature-dependent (2 – 300 K) magnetic susceptibility measurements on a solid sample of 1 is presented in Figure 2, along with the magnetic susceptibility of [Ru$_2$NiO(′BuCO$_2$)$_6$(py)$_3$], taken from Chapter 3 and the sum of the $\chi_M T$ values of two [Cr$_7$NiF$_8$(′BuCO$_2$)$_{15}$(O$_2$CC$_5$H$_4$N)][NH$_2$Pr$_2$]. Subtracting the $\chi_M T$ values of two [Cr$_7$NiF$_8$(′BuCO$_2$)$_{15}$(O$_2$CC$_5$H$_4$N)][NH$_2$Pr$_2$] from 1 gives the red line, shown in Figure 2, which gives the observed $\chi_M T$ value for [Ru$_2$NiO(′BuCO$_2$)$_6$(py)$_3$].
Figure 2. Temperature dependence of magnetic susceptibility ($\chi_M T$) of 1 (circles) and [Ru$_2$NiO($^t$BuCO$_2$)$_6$(py)$_3$] (triangles) (Chapter 3), with the calculated plot of the sum of the $\chi_M T$ values of two [Cr$_7$Ni$_8$(BuCO$_2$)$_{15}$(O$_2$CC$_5$H$_4$N)]$_2$[NH$_2$Pr$_2$] (squares) and their subtraction from 1 (red line).

Field dependant magnetisation studies were also carried out and the same analysis was applied to this data, resulting in the red line shown below in Figure 3, which again corresponds to the values of the Ru$_2$Ni triangle linker. These results show that: (i) the exchange couplings within the Cr$_7$Ni and Ru$_2$Ni components are unchanged from the parent clusters, and (ii) the couplings between the cluster components are very small.
Figure 3. Plot of magnetisation (M) against field (H) of 1 (circles) and [Ru$_2$NiO( BuCO$_2$)$_6$(py)$_3$] (triangles) (Chapter 3), with the calculated plot of the sum of the M values of two [Cr$_7$NiF$_8$(BuCO$_2$)$_{15}$(O$_2$CC$_3$H$_4$N)] [NH$_2$Pr$_2$] (squares) and their subtraction from 1 (red line).

**Electrochemistry.** The cyclic voltammograms (CVs) of complex 1 were recorded in a CH$_2$Cl$_2$ solution containing 0.1 M [N($n$-Bu)$_4$](PF$_6$), as supporting electrolyte, at a glassy carbon working electrode and a scan rate of 200 mV s$^{-1}$ at ambient temperature. The redox processes listed in Table 2 are referenced versus the ferrocenium/ferrocene (Fc$^{+}$/0) couple.

Figure 4 displays the CVs of 1 and [Ru$_2$NiO( BuCO$_2$)$_6$(py)$_3$] (Chapter 3) as a reference. Cyclic voltammetry of 1 revealed that the complex undergoes one reversible one-electron oxidation and one quasi-reversible one-electron reduction process. The observed voltammogram show processes similar to the isolated triangle, [Ru$_2$NiO( BuCO$_2$)$_6$(py)$_3$], which exhibits three features, two one-electron oxidations and a single one-electron reduction. Only the first oxidation is judged fully reversible, the second is quasi-reversible. The reversibility of the first oxidation is retained in 1, labelled in Figure 4 as process I, and is chemically accessible with the use of the ferrocenium ion ([FeCp$_2$](PF$_6$)), as a oxidising agent to attain the one electron oxidation product of 1, [1](PF$_6$). Due to the similarity of the CVs shown in Figure 4, the origin of process I is assigned as the Ru$_2^{III/III}$ to Ru$_2^{III/IV}$
oxidation. This is also supported by the observation of the transition in the near-IR region in the absorption spectra (Figure 6). Interestingly, the second oxidation process, III, is lost completely in 1.

![Cyclic voltammogram](image)

**Figure 4.** Cyclic voltammogram of 1 (black line) and [Ru₂NiO(tBuCO₂)₆(py)₃] (red line) in CH₂Cl₂ solution (0.1 M [N(n-Bu)₄](PF₆) supporting electrolyte) at room temperature with a scan rate of 200 mV s⁻¹ (glassy carbon working electrode). Potentials are referenced versus the ferrocenium/ferrocene (Fc⁺/Fc) couple.

The reversibility of process I can be tested using variable scan speeds, shown in Figure 5. The E₁/₂ and peak to peak ratio (ΔE), remain constant at different scan speeds allowing it to be classed as a fully reversible process.
**Figure 5.** Cyclic voltammograms of process I in 1 in CH₂Cl₂ solution (0.1 M [N(n-Bu)₄](PF₆) supporting electrolyte) at room temperature at various scan rates, (black – 50 mV s⁻¹, red – 100 mV s⁻¹, green – 200 mV s⁻¹, blue – 400 mV s⁻¹, light blue – 800 mV s⁻¹) (glassy carbon working electrode). Potentials are referenced versus the ferrocenium/ferroene (Fc⁺/Fc) couple.

**Table 2.** Redox Potentials (V) of Complexes 1 and [Ru₂NiO(BuCO₂)₆(py)₃] Versus Fc⁺/Fc.

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ᵃ 1+/0 couple. ᵇ 0/1– couple. ᶜ 2+/1+ couple. ᵈ Data taken from Chapter 3.
Figure 6. Near-IR region of UV-Vis-NIR spectra of 1 (red line), [1](PF₆) (blue line) and [Ru₂^{III,IV}NiO(tBuCO₂)₆(py)₃] (black line) in CH₂Cl₂ solutions at ambient temperature.

The UV-Vis-NIR spectrum of [Ru₂^{III,IV}NiO(tBuCO₂)₆(py)₃], was discussed in Chapter 3. The weak band in the near-IR (NIR) region for [Ru₂^{III,IV}NiO(tBuCO₂)₆(py)₃] (Figure 6) is also observed in [1](PF₆) but is not present in 1, as with the neutral species, [Ru₂^{III}NiO(tBuCO₂)₆(py)₃], (Chapter 3). Therefore, it is believed that this transition at 1716 nm and 1720 nm in 1 and [Ru₂^{III,IV}NiO(tBuCO₂)₆(py)₃](PF₆), respectively results from the oxidation of the Ru₂^{III} centres to Ru₂^{III,IV} within the triangle linker. The transition in [Ru₂^{III,IV}NiO(tBuCO₂)₆(py)₃] may correspond to an intracluster metal-to-metal charge transfer (MMCT) but cannot be clearly assigned, as discussed previously (Chapter 3).

EPR Spectroscopy. The weak exchange couplings, J, between the cluster components in 1 and [1](PF₆) can be determined by EPR spectroscopy. EPR spectra obtained for 1 show two distinct features at X- and Q-band and one broad asymmetric signal at S-band (Figure 7). The observed signals are not a result of the sum of the individual components as found with fitting the magnetic data but are due weak exchange interactions between each of the cluster units. If the EPR spectra were a result of the individual components then very different EPR spectra would be observed, as [Ru₂^{III}NiO(tBuCO₂)₆(py)₃] is EPR silent under
these conditions due to the very large zero-field splitting of its $S = 1$ ground state and the EPR spectrum of $[\text{Cr}_7\text{NiF}_8(\text{BuCO}_2)_{15}(\text{O}_2\text{CC}_3\text{H}_4\text{N})][\text{NH}_2\text{Pr}_2]$ corresponds to an $S = \frac{1}{2}$ signal at $g = 1.8$. Simulations of I at S-, X- and Q-band were achieved according to the Hamiltonian in Eq. 1, using the ground state spin of each individual component of the complex, ($S = \frac{1}{2}$ for each of the Cr$\text{Ni}$ rings and $S = 1$ for the Ru$\text{Ni}$ triangle), (Figure 7).

$$
\mathcal{H} = (g_{\text{Cr}_7\text{Ni}} + g_{\text{Ru}_2\text{Ni}} + g_{\text{Cr}_7\text{N}i_2})\beta(\hat{S}_{\text{Cr}_7\text{Ni}} + \hat{S}_{\text{Ru}_2\text{Ni}} + \hat{S}_{\text{Cr}_7\text{N}i_2})H \\
+ \frac{D_{\text{Ru}_2\text{Ni}}}{3} \left[ \hat{S}_{\text{Cr}_7\text{Ni}}^2 - \frac{S_{\text{Ru}_2\text{Ni}}(S_{\text{Ru}_2\text{Ni}} + 1)}{3} \right] + E_{\text{Ru}_2\text{Ni}}(\hat{S}_{\text{Cr}_7\text{Ni}}^2 - \hat{S}_{\text{Ru}_2\text{Ni}}^2) \\
- 2J_{\text{Ru}_2\text{Ni}-\text{Cr}_7\text{Ni}}(\hat{S}_{\text{Ru}_2\text{Ni}} \cdot \hat{S}_{\text{Cr}_7\text{Ni}}) - 2J_{\text{Ru}_2\text{Ni}-\text{Cr}_7\text{N}i_2}(\hat{S}_{\text{Ru}_2\text{Ni}} \cdot \hat{S}_{\text{Cr}_7\text{N}i_2})
$$

(1)

According to the model in Eq. 1 two different exchange couplings, $J$, are required in order to obtain good simulations at each frequency. Attempts to use one exchange interaction, $J$, between the three sites failed to accurately simulate the positions and intensities of the peaks in the spectrum for each frequency (S-, X- and Q-band) with one set of parameters. Simulations yielded the following values; $g_{\text{Cr}_7\text{Ni}} = (1.78, 1.78, 1.74)$, $(g$-values are taken from previous simulations on Cr$\text{Ni}$ rings), $g_{\text{Ru}_2\text{Ni}} = 2.20$, $D_{\text{Ru}_2\text{Ni}} = +8.00 \text{ cm}^{-1}$, $E_{\text{Ru}_2\text{Ni}} = 1.30 \text{ cm}^{-1}$ (see Chapter 3), $J_{\text{Ru}_2\text{Ni}-\text{Cr}_7\text{Ni}} = 0.10 \text{ cm}^{-1}$ and $J_{\text{Ru}_2\text{Ni}-\text{Cr}_7\text{N}i_2} = 0.00 \text{ cm}^{-1}$. This leads to the interpretation that the Cr$\text{Ni}$ rings are coordinated to the Ni site and one of the Ru ions of the triangular unit. This explanation is highly plausible due to the faster kinetics of the Ni$^{\text{II}}$ ion compared to the Ru$^{\text{III}}$ ion. Therefore, similar to the Cr$\text{Ni}$ wheels, the Ni site is substituted first.$^{13}$ Chapter 3 showed the two Ru$^{\text{III}}$ ions antiferromagnetically couple to give an $S = 0$ unit, therefore it is reasonable to assume that an interaction will only be observed with the Ni$^{\text{II}}$ ion ($S = 1$), and the EPR data can be simulated with only one exchange interaction, with no interaction to wheel bound to the Ru$^{\text{III}}$ ion, illustrated in Scheme 1.
Scheme 1. Magnetic exchange pathways and ground spin states in 1.

Figure 7. Polycrystalline EPR spectra of 1 at S- (3.8750 GHz), X- (9.6100 GHz) and Q-band (33.9232 GHz) at 5 K. Experimental data shown in black and simulations shown in red.

The coupling scheme for 1 gives rise to a total of twelve states with one state being doubly degenerate. These twelve states arise from the different orientations of the spin of each component in the system when coupled with each other, resulting in three quartets which arise due to the zero-field splitting of the system. The lowest energy states result from coupling the $S = \frac{1}{2}$ Cr$_7$Ni rings to the $M_S = 0$ component of the $S = 1$ state of the Ru$_2$Ni unit (where the exchange is much weaker than the ZFS of the $S = 1$ state), where as the two higher energy quartet states result from the coupling of the $S = \frac{1}{2}$ Cr$_7$Ni rings with the $M_S$
= ±1 states of the $S = 1$ of Ru$_2$Ni. The levels within each quartet state are degenerate at zero-field and once a field is applied this degeneracy is lifted. The three quartet states are separated by the positive zero-field splitting of the system, $D$, splits the $M_S = 0$ and $|M_S| = 1$ with the former lower in energy. The states that arise from the $|M_S| = 1$ component are then split further by $E$. This is illustrated in Figure 8 for the Z direction, which is defined by the principal axis of the zero-field splitting tensor of the Ru$_2$Ni (X and Y orientations are shown in Figure S3).

Figure 8. Zeeman splitting diagram of 1 in the Z direction.

High-frequency/high-field EPR measurements were conducted on 1, (Figure S2), but due to the population of low lying excited states at higher fields, the experiment cannot be simulated using this simple model.

Chemical oxidation of 1 gave the monocationic product [1](PF$_6$). The locus of this oxidation remains as the Ru$_2$ unit ($S = 0$ to $S = \frac{1}{2}$), evident from the cyclic voltammetry and UV-Vis-NIR data, discussed previously. Each of the three components of the cluster now possess an $S = \frac{1}{2}$ ground state, ($S = \frac{1}{2}$ for each of the Cr$_7$Ni rings and the Ru$_2$Ni triangle). The $S = \frac{1}{2}$ ground state of the Ru$_2$Ni triangle results from antiferromagnetic exchange within the triangular core between the $S = \frac{1}{2}$ Ru$_2$ unit and the $S = 1$ Ni$^{II}$, this is discussed in more detail elsewhere (Chapter 3).
\[ \hat{H} = (g_{Cr7Ni} + g_{Ru2Ni+} + g_{Cr7Ni2}) \beta (\hat{s}_{Cr7Ni} + \hat{s}_{Ru2Ni} + \hat{s}_{Cr7Ni2}) H - 2J_{Ru2Ni+ - Cr7Ni} (\hat{s}_{Ru2Ni} \cdot \hat{s}_{Cr7Ni1}) - 2J_{Ru2Ni+ - Cr7Ni2} (\hat{s}_{Ru2Ni} \cdot \hat{s}_{Cr7Ni2}) \]

(2)

The frozen solution spectra at X- and Q-band (Figure 9) of [1](PF₆) appear more complicated than its neutral counterpart, 1 and the sum of the individual components. The use of one exchange interaction, \(J\), again failed to simulate features in the spectra at the correct field positions and with accurate intensities. It was also considered that the oxidation reaction may not have gone to completion resulting in the observed spectra being due to a mixture of the oxidised and reduced components (1 and [1](PF₆)). However inclusion of both species did not significantly improve the simulation. A best fit was achieved for both frequencies (X- and Q-band) according to the Hamiltonian in Eq. 2, using the same \(g_{Cr7Ni}\) values as above and the \(g_{Ru2Ni+}\) values obtained in Chapter 3, from simulations of \([Ru_2^{III/IV}NiO('BuCO_2)['_3(py)_3]^+\) \((g = 2.338, 2.306, 2.035)\). The change in the electronic structure of the triangle unit creates a feasible exchange pathway between the \(Ru_2^{III/IV}\) unit and the \(Cr7Ni\) bound to one of the Ru ions as well as the \(Ni^{II}\) ion, illustrated in Scheme 2. The simulation yielded \(J_{Ru2Ni+ - Cr7Ni1} = 0.068 \text{ cm}^{-1}\) and \(J_{Ru2Ni+ - Cr7Ni2} = 0.020 \text{ cm}^{-1}\) to give reasonable fittings for both X- and Q-band using this simple model.

[Scheme 2. Magnetic exchange pathways and ground spin states in [1](PF₆).]
Figure 9. EPR spectra of in situ oxidation of 1 with 1 Eq. [FeCp₂](PF₆) in a CH₂Cl₂/toluene solution at X- (9.3792 GHz) and Q-band (33.9826 GHz) at 5 K. Experimental data shown in black and simulations shown in red.

The coupling scheme above for three $S = \frac{1}{2}$ components in [1](PF₆) gives rise to a total of eight states, a quartet and two doublets. This is illustrated by the Zeeman splitting diagrams shown in Figures 10 and S4 (the direction is defined by the $g$-values of the system). At zero-field the quartet state is lowest in energy and each of the levels within that state are degenerate, however once a field is applied these levels diverge. This results in the lowest energy state arising from each of the three electrons in the spin down orientation ($|\downarrow\downarrow\downarrow>$) and the highest energy state is due to the opposite configuration ($|\uparrow\uparrow\uparrow>$). The remaining states are a result of a mixture of the spin up and spin down configurations (i.e. $|\uparrow\downarrow\downarrow>$, $|\uparrow\uparrow\downarrow>$, $|\uparrow\uparrow\uparrow>$).
Conclusion

In summary, we have shown that a linked system with a redox active linker can be synthesised in a simple manner, with the preservation of an easily accessible redox process. This allows us to probe and study its electronic structure in both a reduced and oxidised state, and therefore aiding our understanding in the development of switchable molecular devices. However, due to the choice of linker, \([\text{Ru}_2\text{NiO(}^\text{tBu}CO_2)_6\text{(py)}_3]\), which has an \(S = 1\) state in the reduced form and an \(S = 1/2\) state in the oxidised form, the interaction is constantly ‘on’, \(i.e.\) there is always communication. A system using a redox active linker which is diamagnetic in its reduced state and possesses an \(S = 1/2\) ground state once oxidised, would be better as an ‘off/on’ switch for communication. Therefore, the next step in this research may be to develop linked systems using with this aim in mind.

Acknowledgments

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References


Supporting Information For

“The Electrochemical Behaviour of a Switchable Ru₂Ni Linker between Two Cr₇Ni Rings Examined using Cyclic Voltammetry, EPR and UV-vis-NIR spectroscopy”

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**Figure S1.** Polycrystalline EPR spectra of 1 at S-band (3.8750 GHz) at variable temperatures.

**Figure S2.** Polycrystalline EPR spectrum of 1 (331.2 GHz) at 5 K.
Table S1. Crystallographic Data

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\(^a\) Observation criterion: \(I \geq 2σ(I)\). \(R1 = \frac{Σ||F_o|| - |F_c||}{Σ|F_o|}\); \(^b\) GoF = \(\frac{[Σ[w(F_o^2-F_c^2)^2]/(n-p)]^{1/2}}{[Σ[w(F_o^2)^2]/Σw(F_o^2)]^{1/2}}\); \(^c\) wR2 = \(\frac{[Σ[w(F_o^2-F_c^2)^2]/Σw(F_o^2)^2]}{[Σw(F_o^2)]^{1/2}}\) where \(w = \frac{1}{σ^2(F_o^2)+(aP)^2+bP}\), \(P = (F_o^2+2F_c^2)/3\)
Figure S3. Zeeman splitting diagrams of 1 in X (top), Y (bottom) orientations.
Figure S4. Zeeman splitting diagrams of [1](PF₆) in X (top), Y (bottom) orientations.
Chapter Six – Manuscript 4

“Synthesis, Structure and Characterisation of Two New Ruthenium Mixed-Metal Butterfly Type Complexes, [Ru₂M₂(µ₃-OH)₂(C₅H₄CO₂)₇(py)₄] (M = Co (1), Ni (2) and py = pyridine)”

S. A. Magee, I. Vitorica-Yrezabal, A.-L. Barra, S. Sproules, D. Collison and E. J. L. McInnes
Synthesis, Structure and Characterisation of Two New Ruthenium Mixed-Metal Butterfly Type Complexes, 

$$[\text{Ru}_2\text{M}_2(\mu_3-\text{OH})_2(\text{iBuCO}_2)_7(\text{py})_4] (\text{M} = \text{Co (1), Ni (2)})$$

and py = pyridine)

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Abstract. A new structural archetype has been synthesised for tetranuclear ruthenium mixed-metal complexes, with the formula [Ru₂M₂(μ₃-OH)₂(4-BuCO₂)₇(py)₄], where M is either Co (1) or Ni (2). It is the first time this ‘butterfly’ arrangement has been reported with ruthenium. These complexes have been characterised by elemental analysis, electronic spectroscopy and cyclic voltammetry. Molecular structures of 1 and 2 and their precursor compounds have been determined by X-ray crystallography. SQUID magnetometry and EPR spectroscopy have determined the spin ground states as $S_{\text{eff}} = \frac{1}{2}$ in 1 and $S = \frac{3}{2}$ in 2. The zero-field splitting in 2 has been determined as $+2.02$ cm$^{-1}$ for the $S = \frac{3}{2}$ ground state and $-/+4.65$ cm$^{-1}$ for the Ni$^{II}$ ions using isotropic $J$ coupling scheme.

Introduction

Over the years there has been a great deal of interest into the synthesis of larger assemblies of ruthenium carboxylate complexes due to their extensive redox chemistry, interesting magnetic properties and versatile substitution chemistry. Until recently the main focus of this chemistry was the linkage of oxo-centered ruthenium carboxylate triangles, [Ru₃O(RCO₂)₆(L)₃]$^+$ (R = carboxylate and L = terminal or bridging ligand), with 4,4’-bipyridine and pyrazine or creating single chain magnets from bridging diruthenium tetracarboxylate complexes, [Ru₂(RCO₂)₄L₂]$^{0+\text{-}1\text{-}4}$ However, in a recent publication by Upadhyay et al. a homometallic hexameric ruthenium cluster was synthesised, [Ru₆(μ₃-O)₂(μ-OH)₂(4-BuCO₂)₁₂(py)₂]$_{5}$. This is one of the largest carboxylate-based ruthenium clusters characterised by X-ray diffraction and the first structure of two Ru₃O units linked by OH$^{-}$ bridges. Variable-temperature magnetic susceptibility measurements reveal a significantly lower room temperature $\chi_M T$ value (0.96 cm$^3$ K mol$^{-1}$) than expected for six uncoupled Ru$^{III}$ ions (2.25 cm$^3$ K mol$^{-1}$) and a singlet ground state at low temperature, indicating a dominant antiferromagnetic exchange interaction between the metal ions. Fitting the magnetic data yielded rather large isotropic exchange parameters, $J$, ranging
from +63.4 to -800.6 cm\(^{-1}\). These values are some of the largest reported for polynuclear transition-metal complexes.\(^6,7\)

Our efforts into the synthesis of larger ruthenium based clusters focused on mixed-metal complexes using 3d metal ions. Until now the only discrete molecules of ruthenium-3d mixed-metal carboxylate complexes are the oxo-centered heterometallic ruthenium carboxylate triangles.\(^7-17\) Here we concentrate on the synthesis of tetranuclear mixed-metal ruthenium ‘butterfly’ complexes, \([\text{Ru}_2\text{M}_2(\mu_3{-}\text{OH})_2(\text{BuCO}_2)_7(\text{py})_4] (M = \text{Co} (1) \text{ or Ni} (2), \text{ py} = \text{pyridine})\). This structural motif is relatively common among 3d metals and 3d/4f clusters but little has been reported with 4d metal ions.\(^{18-29}\) One example of a ‘butterfly’ complex containing a 4d metal which has a similar structural motif as our complexes above is \([\text{Mo}_4(\mu_3{-}\text{O})_2\text{O}_4(\text{MeCO}_2)_8\text{Cl}_2]\), which has a room temperature magnetic moment of 2.25 B.M. This value is lower than expected for four uncoupled Mo\(^V\) ions, this is again due to dominant antiferromagnetic exchange interactions between the four metal centres.\(^30\)

**Experimental**

**Synthesis**

All solvents and reagents were purchased from commercial sources and used without further purification unless otherwise stated. \([\text{M}_2(\text{H}_2\text{O})_2(\text{BuCO}_2)_4(\text{BuCO}_2\text{H})_4] (\text{M} = \text{Co or Ni})\), were synthesised according to the literature procedures.\(^{18,31}\)

\([\text{Na}(\text{BuCO}_2)]\): NaOH (5.00 g, 0.13 mmol) and pivalic acid (20.70 g, 0.20 mmol) were stirred at 100°C, until most of the NaOH had dissolved and a thin film started to form on the surface. EtOH (60 mL) was added and a condenser was fitted. The reaction was continued for 1 hour before cooling to room temperature. The solvent was removed using a rotary evaporator and hexane (160 mL) was added to the flask and the solution was stirred
for a further 20 minutes to give a white precipitate, which was filtered and washed with hexane. Yield 12.03 g (77.6 %).

\[ \text{[Ru}_2\text{M}_2(\mu_3-\text{OH})_2(\text{BuCO}_2)_7(\text{py})_4] \quad (\text{M} = \text{Co (1), Ni (2))} \]

was dissolved in a mixture of EtOH (20 mL), H_2O (5 mL) and pivalic acid (4.43 g, 43.70 mmol). The solution was heated at 70°C for approximately 10 minutes until the solution had changed from brown to red. After the solution was allowed to cool to room temperature, [M_2(H_2O)(BuCO_2)_4(BuCO_2H)_4] (M = Ni or Co) (0.95 g, 2.01 mmol) and [Na(BuCO_2)] (0.25 g, 1.72 mmol) were added to the solution and stirred until dissolved, upon which the colour changed from red to purple. The solution was left overnight and then filtered. The solvent was removed on the rotary evaporator, after which the colour changed from purple to reddish brown. To this, MeCN (10 mL) was added to give a brown precipitate and the solution was stirred for 3 hours and then placed in the fridge overnight. The brown solid was collected by filtration and washed with a small amount of cold MeCN, then dried in air. Single crystals can be obtained by dissolving 0.10 g of the brown solid in hexane and filtering to remove a white solid (<0.01 g). The hexane was then removed on rotary evaporator and the solid residue was dissolved in Et_2O (1 mL) and pivalic acid (0.01 g). An equivalent amount of MeCN was layered on top and the solution was left to slowly evaporate to give orange crystals of [Ru_2Co_2(\mu_3-O)(\mu_3-OH)(BuCO_2)_6(BuCO_2H)_4(MeCN)(H_2O)] \text{ (1a)} \] and \text{ [Ru}_2\text{Ni}_2(\mu_3-OH)_2(BuCO_2)_7(BuCO_2H)_4] \text{ (2a): yield 0.39 g (46.3%). Single crystals of [Ru}_2\text{Co}_2(\mu_3-OH)_2(BuCO_2)_7(BuCO_2H)_4] \text{ (1b) and additional crystals of 2a can be obtained directly from the reaction solution after 1 week, yield 0.15 g (17.8%). Then 0.10 g of the crystalline material of 1a or 1b and 2a was dissolved in CH_2Cl_2 (10 mL) and excess pyridine was added (approximately 0.10 g). The solution was stirred for at least 1 hour and the solvent removed. The yellow/brown residue was then redissolved in the minimum volume of Et_2O. An equivalent amount of MeCN was added and the solution was left to evaporate slowly.}
Orange/brown crystals form after 2 weeks, 0.08 g (82.8%). 1 can also be synthesized from crystallisation of the crude material of 1a by slow evaporation of a pyridine solution. Anal. Calcd for C$_{55}$H$_{85}$N$_4$O$_{16}$Ru$_2$M$_2$ (M= Co (1), Ni (2)): (1) - C = 47.93, H=6.22, N= 4.06, Co = 8.55%. Found: C= 47.77, H=6.25, N=4.17, Co = 8.49%. (2) - C = 47.94, H=6.22, N= 4.07, Ni = 8.52%. Found: C= 47.81, H=6.08, N=3.86, Ni = 8.07%.

ESI-MS: m/z (%) 1104 (100) [M-(py)$_3$+(MeOH)$_2$]$^+$ (1) and 1103 (100) [M-(py)$_3$+(MeOH)$_2$]$^+$ (2).

**X-ray crystallographic data collection and refinement of the structures.** Single crystals of 1 and 2 were measured at 100 K on beamline I19 at the Diamond Light Source and on a Bruker Prospector 3-circle diffractometer with an APEX II detector respectively. The structures were solved by direct methods and refined by full-matrix least-squares method with anisotropic thermal parameters for all atoms using SHELXS, and SHELXL was used for the refinement. CIF files were generated using Olex2. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the CCDC (1004949 (1) and 1004952 (2)).
Table 1. Crystallographic Data

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<td>refl. collected / $2\Theta_{\text{max}}$</td>
<td>38176 / 49.09</td>
<td>145475 / 117.86</td>
</tr>
<tr>
<td>unique refl. / $I &gt; 2\sigma(I)$</td>
<td>38176 / 19162</td>
<td>37515 / 28884</td>
</tr>
<tr>
<td>no. of param. / restr.</td>
<td>1310 / 84</td>
<td>3020 / 12</td>
</tr>
<tr>
<td>R1$^a$ / goodness of fit$^b$</td>
<td>0.0825 / 0.917</td>
<td>0.0893 / 1.112</td>
</tr>
<tr>
<td>wR2$^c$ (I &gt; 2\sigma(I))</td>
<td>0.2254</td>
<td>0.2056</td>
</tr>
<tr>
<td>residual density, e Å$^{-3}$</td>
<td>2.64 / -2.25</td>
<td>3.03 / -1.14</td>
</tr>
</tbody>
</table>

a) Observation criterion: $I > 2\sigma(I)$. R1 = $\Sigma||F_o||-|F_c||/\Sigma|F_o|$; b) GoF = $[\Sigma[w(F_o^2-F_c^2)^2]/(n-p)]^{1/2}$; c) wR2 = $[\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$ where $w = 1/\sigma^2(F_o^2)+(aP)^2+bP$, $P = (F_o^2+2F_c^2)/3$
Physical measurements: Electronic absorption spectra were recorded using a Perkin-Elmer Lambda 1050 spectrophotometer (300 – 2800 nm). Cyclic voltammograms were measured using an Autolab potentiostat AUT71194. Redox potentials are referenced to the internal ferrocenium/ferrocene (Fc⁺/Fc⁻) couple. Multifrequency EPR spectra were recorded at the EPSRC National UK EPR Facility and Service at The University of Manchester. High frequency/field EPR measurements were carried out at LNCMI Grenoble on a custom built instrument. Spectral simulations were performed using Easyspin. Magnetic data were recorded using a SQUID magnetometer (Quantum Design MPMS-XL) over a temperature range 2 – 300 K with applied magnetic fields up to 7 T. Corrections for diamagnetism were made using Pascal’s constants and magnetic data were corrected for diamagnetic contributions from the sample holder. Fits were performed using the program PHI. ESI-MS and elemental analyses were carried out by the University’s mass spectrometry and microanalytical services.

Results and Discussion

Synthesis and Characterisation

Compounds 1 and 2 were synthesised using a similar procedure to the mixed-metal ruthenium pivalate triangles in Chapter 3, but with a different ratio of pivalic acid and the addition of sodium pivalate into the reaction mixture. Single crystals suitable for X-ray diffraction can be obtained through pyridine substitution of the terminal pivalic acid ligands of the precursor molecule, [Ru₂M₂(μ₃-OH)₂(BuCO₂)₂(BuCO₂H)₄], and then slow evaporation of a 1:1 Et₂O:MeCN solution.

The deep orange colour of both complexes provides weak absorptions in the visible range (350-800 nm) of the electronic spectrum (Figure 1) with slight shifts in the peak positions depending on the divalent metal. A very broad transition is observed in the near-IR range.
at 1356 and 1334 nm for 1 and 2 respectively. This low energy band has been assigned to a metal-metal charge transfer (MMCT) between the two ruthenium ions mediated through the two $\mu_3$-OH bridges suggesting the Ru$_2$ core is mixed valence Ru$_{\text{II}/\text{III}}$, which is required for charge balance (see below). A similar NIR band is observed in the mixed-valent complexes [Ru$_2$MO($^{t}$BuCO$_2$)$_6$(py)$_3$]$^+$ (M = Co, Ni) (Chapter 3) and [Ru$_2$NiO($^{t}$BuCO$_2$)$_6$(py)(Cr$_7$NiF$_8$(O$_2$CC$_5$H$_4$N)(NH$_2$Pr$_2$)$_2$)$_2$]$^+$ (NH$_2$Pr$_2$ = isopropylamine) (Chapter 5) although at a lower energy (~1700 nm).

**Figure 1.** Electronic spectra of 1 (red) and 2 (green) in CH$_2$Cl$_2$ solutions at ambient temperature.

**Table 2.** Electronic Spectral Data for 1 and 2.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\lambda_{\text{max}}$, nm ($\varepsilon$, 10$^4$ M$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>448 (0.14), 559 (0.06), 703 (0.03), 1356 (0.05)</td>
</tr>
<tr>
<td>2</td>
<td>404 (0.22), 640 (0.02), 751 (0.02), 1334 (0.07)</td>
</tr>
</tbody>
</table>

**Crystal structures.** The molecular structures of 1 and 2 were determined by X-ray crystallography (Figure 2). Selected bond lengths and angles are displayed in Table 3. Bond lengths and angles for each molecule in the asymmetric unit are shown in Tables S2 and S3.
Structural determination of both compounds was carried out at 100 K. Complex 1 crystallises in the triclinic space group $P\overline{1}$, with two molecules in the asymmetric unit and a solvated pyridine (Figure S3). 2 crystallises in the monoclinic space group $P2_1/n$, with four molecules in the asymmetric unit and six acetonitrile solvent molecules (Figure S4).

Each metal site is localised, with the two ruthenium ions at the centre and the 3d metals at the periphery, in a bent arrangement of the metal core. The metal core is made up of a Ru$_2$-(μ$_3$-OH)$_2$-M$_2$ unit (M = Co or Ni), where the ruthenium ions and the two bridging hydroxides sit in one plane and the 3d metal ions lie ~22° out of this Ru$_2$-(μ$_3$-OH)$_2$ plane. The 4d/3d metal core is held together by two μ$_3$-OH and six bridging pivalates between the ruthenium ions to the 3d metals. A seventh bridging pivate connects the two ruthenium ions and the coordination spheres of the 3d ions are completed by two terminal pyridine ligands. The compound is charge neutral as no counter ion is found, so due to charge balance the two ruthenium ions must be mixed-valent and in the Ru$^{II/III}$ oxidation states, which is supported by the MMCT band in the NIR region of the electronic spectra. The arrangement of the metal centres may be described as two edge sharing hydroxo-centred triangles. However, they are far from equilateral as the Ru···Ru distances of 2.4740(14) and 2.4623(12) Å for 1 and 2, respectively, is much shorter than the mean Ru···M distances of 3.4543(2) and 3.4418(2) Å for 1 and 2, respectively. The Ru···Ru distance is almost 1 Å shorter than the Ru···M distance. However this short distance is expected due to the two μ$_3$-OH bridges resulting in an edge-sharing biocahedral arrangement.$^{37-39}$
Figure 2. Depiction of the molecular structure of 1 and 2. Ru violet, Co/Ni turquoise, O red, N blue, C black. Hydrogen atoms have been omitted for clarity.

The bent structure of the Ru$_2$-(µ$_3$-OH)$_2$-M$_2$ unit adds further support to the central bridging ligand being OH$^-$ rather than O$^{2-}$, it is common in the literature that O$^{2-}$ lies flat to the plane of the molecule (Chapters 2-6) and the OH$^-$ is offset from the molecular plane.$^{18-29}$ The average Ru-µ$_3$-OH and M-µ$_3$-OH distance shortens from 1 to 2 from 1.938(9) and 1.965(9) Å, respectively, for 1 and from 1.926(7) and 1.949(8) Å for 2.
Table 3. Selected Bond Distances (Å) and Angles (deg) for 1 and 2.

<table>
<thead>
<tr>
<th></th>
<th>1&lt;sup&gt;a&lt;/sup&gt;</th>
<th>2&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru1···Ru2</td>
<td>2.4740(14)</td>
<td>2.4623(12)</td>
</tr>
<tr>
<td>Ru1···M1</td>
<td>3.475(2)</td>
<td>3.494(2)</td>
</tr>
<tr>
<td>Ru1···M2</td>
<td>3.440(2)</td>
<td>3.407(2)</td>
</tr>
<tr>
<td>Ru2···M1</td>
<td>3.429(2)</td>
<td>3.413(2)</td>
</tr>
<tr>
<td>Ru2···M2</td>
<td>3.473(2)</td>
<td>3.453(2)</td>
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<tr>
<td>Ru1—O1&lt;sub&gt;Hydroxo&lt;/sub&gt;</td>
<td>1.939(8)</td>
<td>1.929(7)</td>
</tr>
<tr>
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<td>1.938(9)</td>
<td>1.917(7)</td>
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<tr>
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<td>1.979(9)</td>
<td>1.948(7)</td>
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<tr>
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<td>1.922(8)</td>
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<td>1.934(7)</td>
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<td>1.950(8)</td>
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<td>M1—N1</td>
<td>2.201(11)</td>
<td>2.123(9)</td>
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<td>M1—N2</td>
<td>2.158(10)</td>
<td>2.083(9)</td>
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<td>M2—N3</td>
<td>2.218(11)</td>
<td>2.152(11)</td>
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<td>2.147(11)</td>
<td>2.090(11)</td>
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<td>Ru1—O1&lt;sub&gt;Hydroxo&lt;/sub&gt;—Ru2</td>
<td>79.3(4)</td>
<td>79.6(3)</td>
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<tr>
<td>Ru1—O1&lt;sub&gt;Hydroxo&lt;/sub&gt;—M1</td>
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<td>128.6(4)</td>
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<td>Ru2—O1&lt;sub&gt;Hydroxo&lt;/sub&gt;—M1</td>
<td>122.2(4)</td>
<td>124.0(4)</td>
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<td>79.3(3)</td>
<td>79.4(3)</td>
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<tr>
<td>Ru2—O2&lt;sub&gt;Hydroxo&lt;/sub&gt;—M2</td>
<td>126.0(4)</td>
<td>125.5(4)</td>
</tr>
<tr>
<td>Ru1—O2&lt;sub&gt;Hydroxo&lt;/sub&gt;—M2</td>
<td>124.8(4)</td>
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<tr>
<td>O1&lt;sub&gt;Hydroxo&lt;/sub&gt;—M1—N1</td>
<td>89.2(3)</td>
<td>86.9(3)</td>
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<td>176.9(4)</td>
<td>176.5(3)</td>
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<td>O2&lt;sub&gt;Hydroxo&lt;/sub&gt;—M2—N3</td>
<td>90.3(4)</td>
<td>88.3(4)</td>
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<td>O2&lt;sub&gt;Hydroxo&lt;/sub&gt;—M2—N4</td>
<td>177.0(4)</td>
<td>179.8(5)</td>
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</tbody>
</table>

<sup>a</sup> Values taken from molecule 1 in the asymmetric unit, full set of bond distances (Å) and angles (°) are shown in supporting information, Tables S3 and S4.
**Electrochemistry.** The cyclic voltammograms (CVs) of complexes 1 and 2 were recorded in CH$_2$Cl$_2$ solution containing 0.1 M [N(n-Bu)$_4$](PF$_6$) as supporting electrolyte using a glassy carbon working electrode at ambient temperature (Figure 3). The reduction potentials listed in Table 4 are referenced to the ferrocenium/ferrocene (Fc$^{+/0}$) couple.

**Figure 3.** Cyclic voltammograms of 1 and 2 recorded in CH$_2$Cl$_2$ solutions containing 0.1 M [N(n-Bu)$_4$](PF$_6$) at room temperature with a scan rate of 200 mV s$^{-1}$. Potentials are referenced versus the Fc$^{+/0}$ couple.

The CVs of both compounds show three features, two one-electron oxidations and a single one-electron reduction (Figure 3). In both cases the reductive process is irreversible. The two oxidative processes in 1 are described as quasi-reversible, whereas in 2 the two processes are only separated by $\sim$0.08 V making it very difficult to accurately determine the reversibility of these processes (Figures S5 and S6). It is likely that only one of these processes belongs to 2, where as the other is due to an impurity, which is a result of unsuccessful terminal ligand substitution on the 3d metal, thus leading to very similar but chemically different molecules. This theory is supported by the low frequency EPR data discussed later, as it cannot be effectively simulated with one set of parameters. The first oxidation process in both complexes is chemically accessible with the ferrocenium ion but
attempts to chemically isolate the oxidised products failed, possibly due to the processes being quasi-reversible and unstable under those conditions.

Table 4. Redox Potentials (V) of Complexes 1 and 2 Versus Fe$^+/\text{Fc}$

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E^{1/2}$</th>
<th>$E^{2/2}$</th>
<th>$E^{3/2}$</th>
<th>$E^{4p}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.19</td>
<td>–</td>
<td>0.39</td>
<td>-1.33</td>
</tr>
<tr>
<td>2</td>
<td>-0.14</td>
<td>0.06</td>
<td>–</td>
<td>-1.48</td>
</tr>
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</table>

Magnetism. Temperature-dependent (2 – 300 K) magnetic susceptibility measurements of solid samples of 1 and 2 are presented in Figure 4. The room temperature $\chi_M T$ values are 5.81 and 1.98 cm$^3$ K mol$^{-1}$ for 1 and 2 respectively. The $\chi_M T$ values for 1 decrease as the temperature decreases resulting in a low temperature $\chi_M T$ value (2 K) of 2.88 cm$^3$ K mol$^{-1}$. In 2 the $\chi_M T$ value is increases slightly as temperature decreases until ~15 K where it decreases to 1.76 cm$^3$ K mol$^{-1}$. The non-zero values are consistent with paramagnetic ground states.

Figure 4. Plots of $\chi_M T$ vs T for compounds 1 and 2 at H = 0.5 T. Experimental data shown as symbols and fits shown as red line (○ = 1, □ = 2).
The low temperature $\chi_M T$ value of 1 corresponds to a $J = \frac{1}{2}$ ground state, with contributions from both $S$ and $L$ due to the nature of high spin octahedral Co$^{II}$. The $\chi_M T$ value at 2 K in 2 is due to an $S = \frac{3}{2}$ ground state that results from antiferromagnetic exchange interaction between the central Ru$_2$ unit ($S = \frac{1}{2}$) with both the $S = 1$ Ni ions. The Ru$_2^{III/II}$ unit (low spin $d^5, d^6$) has a single unpaired electron and hence is $S = \frac{1}{2}$.

\[ M_1^J \text{(Ru)} \cdot M_2 \]

\[ \text{Scheme 1. Exchange coupling scheme between the Ru$_2$ central unit and the two 3d metal ions.} \]

The magnetic data for 2 can be fit with the exchange coupling scheme shown above (Scheme 1) using the Heisenberg spin Hamiltonian given in Eq. 1 where the symbols have their usual meanings.

\[ H = (g_{Ni1} + g_{(Ru)2} + g_{Ni2})\beta (\hat{S}_{Ni1} + \hat{S}_{(Ru)2} + \hat{S}_{Ni2}) \hat{H} - 2J_{(Ru)2-Ni1,2}(\hat{S}_{(Ru)2} \cdot \hat{S}_{Ni1} + \hat{S}_{(Ru)2} \cdot \hat{S}_{Ni2}) \]

\[ (1) \]

The Hamiltonian in Eq. 1 can be solved by Kambe’s notation and the energy level diagrams for 2 can be plotted using Eq. 2, where $S_{Ni} = 1$; $S_{(Ru)2} = \frac{1}{2}$; $S^+ = S_{Ni1} + S_{Ni2}$ and $S_T = S^+ + S_{(Ru)2}$.\(^{40}\)

\[ E(S_T, S^+) = -J_{(Ru)2-Ni1,2}[S_T(S_T + 1) - S^+(S^+ + 1) - S_{(Ru)2}(S_{(Ru)2} + 1)] \]

\[ (2) \]

Using this approach $S^+$ can take the value $|S_{Ni1} + S_{Ni2}|$ to $|S_{Ni1} - S_{Ni2}|$, i.e. $S^+$ ranges from 2 to 0 in integral values. $S_T$ can take values from $|S^+ + S_{(Ru)2}|$ to $|S^+ - S_{(Ru)2}|$, the differing possibilities are given in Tables S1.
Figure 5. Energy level diagram for the possible spin states of 2.

An excellent fit for temperature-dependant magnetic susceptibility (Figure 4) was obtained for 2. The best fit parameters were: $J_{(Ru)2-Ni1,2} = -240.0 \text{ cm}^{-1}$ with $g_{Ru2} = 2.01$, $g_{Ni1,2} = 2.12$ according to Eq. 1. This $J$ value gives rise to a $|3/2\rangle, 2\rangle$ ground state, which is observed in energy diagram of spin states (Figure 5).

The inclusion of a zero-field splitting parameter for the nickel ions in 2, $D_{Ni1,2} = -/+/4.65 \text{ cm}^{-1}$, resulted in a better fit for the low temperature magnetisation data (Figure 6) according to Eq. 3. Unfortunately, using this set of parameters the sign of $D_{Ni}$ cannot be determined, but with the assistance of high field/high frequency EPR the correct sign was resolved (discussed later). The exchange coupling scheme revealed a well isolated $S = \frac{3}{2}$ ground state, with the first excited state $S = \frac{1}{2}, (|1/2, 1\rangle), 240.0 \text{ cm}^{-1}$ above it.

$$\hat{H} =$$

$$\left( g_{Ni1} + g_{(Ru)2} + g_{Ni2} \right) \beta \left( \hat{S}_{Ni1} + \hat{S}_{(Ru)2} + \hat{S}_{Ni2} \right) H + D_{Ni1,2} \left[ \hat{S}_{Ni1,2}^2 - \frac{S_{Ni1,2}(S_{Ni1,2}+1)}{3} \right] -$$

$$2J_{(Ru)2-Ni1,2} \left( \hat{S}_{(Ru)2} \cdot \hat{S}_{Ni1} + \hat{S}_{(Ru)2} \cdot \hat{S}_{Ni2} \right)$$

(3)
Due to the well separated ground state the field dependent magnetisation of 2 can also be fit using Hamiltonian in Eq. 4 for an $S = \frac{3}{2}$ ground state with a total anisotropy for the ground state of 2.00 cm$^{-1}$ and $g = 2.12$, using the giant spin approximation (Figure S7).

$$\hat{H}_{GS} = g_{GS} \beta \hat{S} \beta H + D_{GS} \left( \hat{S}_{z}^{2} - \frac{S(S+1)}{3} \right) \quad (4)$$

**Figure 6.** $M = f(H/T)$ plots at $T = 2$ and 4 K for compounds 1 (left) and 2 (right). Experimental data shown as symbols and best fits (according to Eq.5 and Eq.3 for 1 and 2 respectively) represented by the red lines.

Excellent fits for both temperature dependent magnetic susceptibility (Figure 4) and field dependent magnetisation (Figure 6) were also attained for 1. The first-order orbital angular momentum of the $^{4}T_{1g}$ ground state in octahedral Co$^{II}$ is coupled to the electron spin ($S = \frac{3}{2}$) through spin orbit coupling (SOC), therefore the total angular momentum $J$, must now be considered as $S$ and $L$ are no longer good quantum numbers. The fitting for 1 was achieved according to the Lines model$^{41}$ using the Hamiltonian in Eq. 5, with the following values: $J_{(Ru)2-Co1,2} = -108.2$ cm$^{-1}$ with $g$ fixed at 2.0, an orbital reduction parameter ($\sigma$) of -1.17 and a spin orbit coupling constant ($\lambda$) of -170.0 cm$^{-1}$. The orbital reduction parameter $\sigma = A \kappa$, where $A = -\frac{3}{2}$ and $\kappa$ is the usual orbital reduction factor ($0 \leq \kappa \leq 1$), and can therefore take the values -1.5-0. The A parameter takes advantage of T-P isomorphism,
where the factor \((-3/2)\) defines the conversion of the matrix of the angular momentum operator \(\hat{l}\) within the \(^4T_1\) \((^4T)\) state to the matrix of \(\hat{l}\) in the atomic p-basis, creating a fictitious \(L = 1\). This set of parameters gives rise to a well isolated \(J = 1/2\) ground state, with the first excited state, \(J = 3/2, \sim217.0\) cm\(^{-1}\) above it.

\[
\hat{H} = \beta \left( \sigma \hat{L}_{Co1,2} + g (\hat{S}_{Co1} + \hat{S}_{(Ru)2} + \hat{S}_{Co2}) \right) H \\
- 2J_{(Ru)2-Co1,2} (\hat{S}_{(Ru)2} \cdot \hat{S}_{Co1} + \hat{S}_{(Ru)2} \cdot \hat{S}_{Co2}) + \lambda (\sigma \hat{L}_{Co1,2} \cdot \hat{S}_{Co1,2})
\]

(5)

**EPR Spectroscopy.** Frozen solution EPR spectra of 1 at X- and Q-band at 10 K are typical of high spin Co\(^{II}\) ions with unquenched orbital angular momentum (Figure 7). The spectra are simulated as an effective \(S = 1/2\) due to the well isolated doublet ground state with very anisotropic \(g\)-values, \(g_{eff} = 8.22, 4.15, 3.35\) (Eq. 6). The average \(g\)-value from EPR is 5.24, which is comparable to the calculated \(g\)-value of 5.57 of the \(J = 1/2\) ground state in the fitting of the magnetic data.

![EPR spectra](image)

**Figure 7.** EPR spectra of 1 recorded in a CH\(_2\)Cl\(_2\)/toluene frozen glass at X-band (9.3867 GHz) and Q-band (33.935 GHZ) at 10 K. Experimental data shown in black and simulations shown in red.

\[
\hat{H} = g\beta \hat{S} H
\]

(6)
The EPR spectra of 2 at very low temperature are consistent with an appreciable rhombic zero-field splitting on an $S = \frac{3}{2}$ ground state spin (Figures 8 and 9). In order, to obtain an accurate value of the size and sign of the zero-field splitting parameters in 2 a multi-frequency EPR investigation was conducted. Simulations of the high-field/high frequency EPR spectra (331.2 GHz) yielded the following values for $S = \frac{3}{2}$ ground state: $g = 2.21, 2.20, 2.18, D = +2.02$ and $E = 0.44$ cm$^{-1}$, according to Eq. 7. $D$-strain is required to gain accurate simulations at a range of temperatures from 5 - 20 K (25 %) (Figure S8). However, it should be noted that the simulations were very sensitive to changes in $g_x$, $g_y$ and $E$, giving a variety of parameters which could provide an adequate simulation of the major features in the spectrum. Therefore further experiments are required to provide a definite value of the zero-field splitting parameters in this compound and single crystal EPR measurements may provide the answer.

\[ \hat{H}_{GS} = g_{GS} \beta \hat{S}H + D_{GS} \left( \hat{S}_z^2 - \frac{S(S+1)}{3} \right) + E_{GS} (\hat{S}_x^2 - \hat{S}_y^2) \]  
\[ (7) \]

Unfortunately, one set of parameters cannot be used to simulate the spectra observed at lower frequencies, (X- and Q-band) but the major features of the spectra are observed using the parameters discussed above (Figures S9 and S10). This is believed to be due co-
crystallisation of slightly different molecules, *i.e.* the pyridine substitution of the terminal ligands on $\text{M}^{\text{II}}$ has not gone to completion (see CV data). This then leads to slight differences in the observed $D$ values going from an N-donor to an O-donor ligand. However, respectable simulations can be achieved at X- and Q-band at 5 K using two sets of parameters, which approximately average to those yielded from the high field/high frequency simulations. The following values were used to simulate the $S = \frac{3}{2}$ ground state: $g_1 = 2.20$, $D_1 = +2.00$ and $E_1 = 0.20 \text{ cm}^{-1}$ and $g_2 = 2.20$, $D_2 = +2.00$ and $E_2 = 0.60 \text{ cm}^{-1}$ in a 10:1 weighting ratio, with $D$-strain required in each case (10 and 28 \% for parameter set 1 and 2 respectively) (Figure 9).

**Figure 9.** EPR spectra of 2 recorded in a CH$_2$Cl$_2$/toluene frozen glass at X-band (9.3878 GHz) and Q-band (33.904 GHZ) at 5 K. Experimental data shown in black and simulations shown in red.

**Conclusion**

Here we present the first examples of mixed-metal ruthenium pivalate ‘butterfly’ complexes, $[\text{Ru}_2\text{M}_2(\mu_3\text{-OH})_2(\text{tBuCO}_2)_7\text{(py)}_4]$ (M = Co, Ni). Unfortunately, attempts to synthesise Mn and Zn derivatives failed but other metals would be worth investigating. Fitting the magnetic data ($\chi_M T \text{ vs. } T$ and $M \text{ vs. } H$) gave a well-isolated $J = \frac{1}{2}$ ground state
for 1 and an $S = 3/2$ ground state for 2, thus showing a dominant antiferromagnetic exchange interaction between the metal ions. EPR spectra of 1 were simulated as an effective $S = 1/2$ and high field/high frequency EPR allowed us to determine the sign and size of the anisotropy of the $S = 3/2$ ground state in 2 as $D = +2.02\ \text{cm}^{-1}$ and $E = 0.44\ \text{cm}^{-1}$.

**Acknowledgements**

This work is supported by the EPSRC (UK), The National EPR Research Facility and Service and The University of Manchester.

**References**


Supporting information

Synthesis, Structure and Characterisation of Two New Ruthenium Mixed-Metal Butterfly Type Complexes, 

\[ \text{[Ru}_2\text{M}_2(\mu_3-\text{OH})_2(\text{tBuCO}_2)_7(\text{py})_4] (M = \text{Co (1), Ni (2)}) \]

and py = pyridine)

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X-ray crystallographic data collection and refinement of the structures. Single crystals of **1a**, **1b** and **2a** were measured at 100 K on beamline I19 at the Diamond Light Source, Oxford Diffraction XCalibur 2 diffractometer and Enraf-Nonius X-ray diffractometer (Graphite monochromated Mo-Kα radiation (\(\lambda = 0.71073 \text{ Å}\)) respectively. The structures were solved by direct methods and refined by full-matrix least-squares method with anisotropic thermal parameters for all atoms using SHELX, and SHELXL was used for the refinement.\(^1\) The disorder modelled in **2a** was done using WinGX.\(^2\) CIF files were generated using Olex2.\(^3\) Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the CCDC (1004950, 1004951, 1004953) for **1a**, **1b** and **2a** respectively.

**Figure S1.** Depiction of the molecular structure of **1b** and **2a**. Ru violet, Co/Ni turquoise, O red, N blue, C black. Hydrogen atoms have been omitted for clarity.
Figure S2. Depiction of the molecular structure of 1a. Ru violet, Co turquoise, O red, N blue, C black. Hydrogen atoms have been omitted for clarity.

Table S1. Crystallographic data of 1a, 1b and 2a.

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<th>1a</th>
<th>1b</th>
<th>2a</th>
</tr>
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<tbody>
<tr>
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<td>Ru$_2$Co$<em>2$C$<em>5$H$</em>{101}$O$</em>{24}$</td>
<td>Ru$_2$Ni$<em>2$C$<em>5$H$</em>{101}$O$</em>{24}$</td>
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<td>Triclinic</td>
</tr>
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<td>space group</td>
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<td>P $\overline{1}$</td>
<td>P $\overline{1}$</td>
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<td>Z</td>
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<td>2</td>
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<td>0.71073 / 0.94</td>
<td>0.71073 / 1.01</td>
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<td>24342 / 52.8</td>
<td>16854 / 56.0</td>
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<tr>
<td>unique refl. / $I &gt; 2\sigma(I)$</td>
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<td>14521 / 8940</td>
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<td>753 / 0</td>
<td>798 / 0</td>
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<td>0.104 / 1.07</td>
<td>0.059 / 1.09</td>
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<td>0.292</td>
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<td>2.78 / -2.62</td>
<td>1.75 / -1.75</td>
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a) Observation criterion: $I > 2\sigma(I)$. R1 = Σ||$F_o$|−|$F_c$||/Σ$|F_o$|; b) GoF = [Σ[w($F_o^2$−$F_c^2$)²]/(n−p)]$^{1/2}$; c) wR2 = [Σ[w($F_o^2$−$F_c^2$)²]/Σ[w($F_o^2$)²]]$^{1/2}$ where $w = 1/σ^2(F_o^2)+(aP)^2+bP$, $P = (F_o^2+2F_c^2)/3$
**Figure S3.** Depiction of the asymmetric unit of 1. Ru violet, Co turquoise, O red, N blue, C black. Hydrogen atoms have been omitted for clarity.

**Figure S4.** Depiction of the asymmetric unit of 2. Ru violet, Ni turquoise, O red, N blue, C black. Hydrogen atoms have been omitted for clarity.

**Elemental analyses**

**1b, 2a:** $C_{55}H_{105}M_2O_{24}Ru_2$ (M = Co (1b), Ni (2a)): Anal. Calcd. – 1b; C = 44.93, H = 7.20, N = 0.00, Co = 8.02 %. Found – C = 44.96, H = 7.36, N = 0.00, Co = 7.72 %. 2a; C = 44.94, H = 7.20, N = 0.00, Ni = 7.99 %. Found – C = 44.99, H = 7.22, N = 0.00, Ni = 7.76%.

**1a:** $C_{52}H_{100}Co_2NO_{23}Ru_2$: Anal. Calcd. – C = 43.76, H = 7.06, N = 0.98, Co = 8.26%. Found – C = 42.98, H = 7.21, N = 0.92, Co = 8.56%.
Figure S5. Cyclic voltammograms of 1 recorded in CH₂Cl₂ solutions containing 0.1 M [N(n-Bu)₄](PF₆) at room temperature with variable scan rates. Potentials are referenced versus the Fc⁺/₀ couple.

Figure S6. Cyclic voltammograms of 2 recorded in CH₂Cl₂ solutions containing 0.1 M [N(n-Bu)₄](PF₆) at room temperature with variable scan rates. Potentials are referenced versus the Fc⁺/₀ couple.
Table S2. Calculated energies for the spin states of 2 using Kambe’s notation. The ground state of 2 is highlighted in red.

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<tr>
<th>$S^+$</th>
<th>$S_T$</th>
<th>$S_{(Ru})$</th>
<th>E (cm$^{-1}$)</th>
<th>Energy level</th>
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<td>2</td>
<td>2.5</td>
<td>0.5</td>
<td>480</td>
<td>5</td>
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<td>2</td>
<td>1.5</td>
<td>0.5</td>
<td>-720</td>
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</tr>
<tr>
<td>1</td>
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<td>0.5</td>
<td>240</td>
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<td>0.5</td>
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Figure S7. $M = f(H/T)$ plots at $T = 2$ and 4 K for compound 2. Experimental data shown as symbols and best fits represented by the red lines. Fitting the data using the $S = \frac{3}{2}$ ground state spin and the total zero-field splitting, $D = +2.02$ cm$^{-1}$ of the ground state.
Table S3. Bond Distances (Å) and Angles (deg) for 1.

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Table S4. Bond Distances (Å) and Angles (deg) for 2.

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**Figure S8.** Polycrystalline powder spectra (331.2 GHz) of 2 at 5, 10, 15 and 20 K. Experimental data is shown in black and simulations in red.

**Figure S9.** EPR spectrum of 2 recorded in a CH\(_2\)Cl\(_2\)/toluene frozen glass at X-band (9.3878 GHz) at 5 K. Simulated with the same parameters used for the 331.2 GHz data. Experimental data shown in black and simulations shown in red.
Figure S10. EPR spectrum of 2 recorded in a CH$_2$Cl$_2$/toluene frozen glass at Q-band (33.904 GHz) at 5 K. Simulated with the same parameters used for the 331.2 GHz data. Experimental data shown in black and simulations shown in red.

References


Chapter Seven - Conclusions and further work

A large proportion of recent publications in the field of polynuclear transition metal complexes have been in the pursuit of new SMMs or materials for quantum information processing. The main focus of this thesis was to increase the anisotropy in molecular magnets using the 4d metal ruthenium. Although the ruthenium compounds discussed in this thesis proved not to show any SMM phenomena, they did however amplify the magnetic anisotropies of the 3d metal ions within the clusters.

This effect described in Chapters 2 and 3 was found to be due to ASE interactions, which resulted in very large ground spin state ZFS. Ru$_2$Mn has a ZFS of +2.9 cm$^{-1}$ in its $S = 5/2$ ground state. Previously, the $S = 5/2$ ground state had been assigned solely to the Mn$^{II}$ ion due to the strongly antiferromagnetically coupled Ru$^{III}$ ions ($S = 0$). However, this ZFS value is absurdly large and is an order of magnitude larger than any value in the literature for six-coordinate Mn$^{II}$. Using Fe$_2$Mn (Chapters 2 and 4) as a comparison the single ion anisotropies can be calculated and the effect from the Mn$^{II}$ ion is negligible in comparison to the ZFS in ground state of Ru$_2$Mn. This model accurately reproduced the magnetic and EPR data for this compound as well as that obtained for Ru$_2$Ni. This shows that these effects cannot be ignored for heavy metals and are important because different anisotropy terms in the spin Hamiltonian result in different mixings between ground and excited states: ASE interactions have previously been discussed as a possible origin of quantum tunnelling in molecular magnets. In Ru$_2$M ASE is favoured due to the large SOC in Ru$^{III}$ and the large radial extent of the 4d orbitals, therefore a greater effect is likely to be seen with Os$^{III}$, due to its even larger SOC and the greater extent of its 5d orbitals. Hence, the next step in this research would be to synthesise the osmium analogues to test this effect.

The chemical oxidation of Ru$_2$Co and Ru$_2$Ni in Chapter 3 allowed us to determine the locus of this redox process, which is on the heterometal in the former (Co$^{II} \rightarrow$ Co$^{III}$) and at
the Ru$_2$ unit in the latter (Ru$_2^{III/III}$ $\rightarrow$ Ru$_2^{III/IV}$). The oxidised products were isolated in each case and structurally characterised by X-ray diffraction, to give the first X-ray structure of oxidised mixed-metal ruthenium carboxylate triangles. However, due to conflicting evidence from the UV-vis-NIR data, in which both complexes show the same near-IR band, further experiments are required, e.g. variable temperature UV-vis-NIR and X-ray absorption spectroscopy. Therefore, in order to fully understand the electronic structures of this family of compounds attempts to isolate the oxidised products of the Mn and Zn derivatives should be continued.

The ground state and exchange interactions of heterometallic iron triangles have been well understood since the 1980s. In this thesis the EPR spectra of a family of mixed-metal iron pivalate complexes [Fe$_2$MO(tBuCO$_2$)$_6$(py)$_3$] (M = Mn, Co and Ni) were reported and accurately simulated (Chapters 2 and 4). This gave further support to assigning the ground spin of these complexes as well as determining the size and sign ZFS in each case. Understanding the electronic structure of these heterometallic iron carboxylate compounds led to the conclusions drawn in Chapters 2 and 3, thus aiding our understanding of electronic structure of the Ru$_2$M family and their ZFS origins in the ASE interactions.

The lability of the terminal ligands on ruthenium oxo-centered triangles has led to countless examples of rationally linked trimetallic clusters. In chapter 5 we exploited this ability in Ru$_2$Ni in our efforts to synthesis switchable linked heterometallic chromium carboxylate rings for quantum information processing. This proved successful through the substitution of two of the terminal pyridine ligands on [Ru$_2$NiO(tBuCO$_2$)$_6$(py)$_3$] for two bulkier pyridine ligands [Cr$_7$NiF$_8$(tBuCO$_2$)$_{15}$(O$_2$CC$_5$H$_4$N)$_5$], creating a switchable link between two Cr$_7$Ni rings. Due to the redox activity of Ru$_2$Ni it can be oxidised to an $S = \frac{1}{2}$ from an $S = 1$ ground state, thus altering the communication between each of the building block units. Unfortunately, due to the nature of this linker in either the oxidised or reduced form there is always some communication between the individual components of the
cluster, *i.e.* the switch is always ‘on’ to some extent. Therefore, the next step in this research would be to develop a linker that could genuinely switch between ‘off’ and ‘on’, allowing communication in the ‘on’ state and preventing communication in its ‘off’ state. Perhaps, if it were possible to selectively substitute the pyridine ligands on the two Ru\textsuperscript{III} ions for two [Cr\textsubscript{7}NiF\textsubscript{8}(\textit{t}BuCO\textsubscript{2})\textsubscript{15}(O\textsubscript{2}CC\textsubscript{5}H\textsubscript{4}N)] in [Ru\textsubscript{2}ZnO(\textit{t}BuCO\textsubscript{2})\textsubscript{6}(py)\textsubscript{3}], which is diamagnetic ($S = 0$), then upon oxidation of the Ru\textsubscript{2} unit to an $S = \frac{1}{2}$ the interaction would be switched ‘on’ between the two rings.

Chapter 6 gave us the first examples of mixed-metal ruthenium pivalate ‘butterfly’ complexes, [Ru\textsubscript{2}M\textsubscript{2}(\textit{μ}-OH)\textsubscript{2}(\textit{t}BuCO\textsubscript{2})\textsubscript{7}(py)\textsubscript{4}] ($M = \text{Co, Ni}$), although this is a common structural motif for 3d and lanthanide ions there are few examples of this type of complex with 4d metals. One example is a homometallic molybdenum carboxylate cluster, [Mo\textsubscript{4}(\textit{μ}-O)\textsubscript{2}O\textsubscript{4}(MeCO\textsubscript{2})\textsubscript{6}Cl\textsubscript{2}] which has the same structural arrangement as our compounds. Unfortunately, attempts to synthesise Mn and Zn derivatives failed but other metals would be worth investigating. The molybdenum example above shows there may be further scope to expand this synthetic strategy to other heavy metals.

This research has shown that there is potential in the use of heavier d-block metals as a tool for increasing the magnetic anisotropy in molecular magnets and further research should be conducted to expand our understanding in this area.