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COMMUNICATION

Slow magnetic relaxation in a \{\text{Co}^{II}\text{Co}^{III} \}_{2}\ complex containing a high magnetic anisotropy trigonal bipyramidal \text{Co}^{II} centre

Alexandra Collet,\textsuperscript{a} Gavin A. Craig,\textsuperscript{b} María José Heras Ojea,\textsuperscript{a} Lakshmi Bhaskaran,\textsuperscript{b} Claire Wilson,\textsuperscript{a} Stephen Hill\textsuperscript{b} and Mark Murrie*\textsuperscript{a}

We report a trinuclear mixed-valence \{\text{Co}^{II}\text{Co}^{III}) \}_{3}\ complex, where the \text{Co}^{0} centre adopts a trigonal bipyramidal geometry, leading to a large easy-plane magnetic anisotropy and field-induced slow magnetic relaxation with a Raman-like relaxation process.

Single-Molecule Magnets (SMMs) show promise in a number of technological applications such as molecular spintronics,\textsuperscript{1} high-density information storage,\textsuperscript{2} and qubits for quantum computation.\textsuperscript{3} When the magnetic properties arise from a single paramagnetic ion in an appropriate ligand field, these molecules are often referred to as Single-Ion Magnets (SIMs). The origin of SMM and SIM behaviour is the presence of an energy barrier \(\Delta E/k_B\) that prevents the reorientation of the magnetisation between the \(M_z = \pm S\) components of the ground state \(S\). The magnetic anisotropy, which depends on the spin-orbit contribution,\textsuperscript{4} is difficult to control in polymeric systems, and hence recent research has focused on mononuclear systems. Mononuclear \text{Co}^{II} complexes have been found to exhibit both large negative (easy-axis) and large positive (easy-plane) magnetic anisotropy when found in tetracoordinate, pentacoordinate and hexacoordinate geometries.\textsuperscript{5} More specifically, \text{Co}^{II} ions with ideal trigonal bipyramidal geometry are expected to exhibit high easy-plane anisotropy.\textsuperscript{6}

We are working towards the synthesis of coordination complexes containing at least one high magnetic anisotropy centre, such as trigonal bipyramidal (TBP) \text{Co}^{II}, in order to boost the barrier \(\Delta E/k_B\). Herein, we report the complex \(\text{[Co}^{II}\text{Co}^{III}_{2}(\mu_2-\text{OH})(\mu-\text{pz})_3\text{DBM}]_2\cdot2\text{MeCN} (1\cdot2\text{MeCN})\) (Fig. 1), which is a new solvate of a previously reported \text{Co}$_{3}$ complex, obtained by a different synthetic procedure.\textsuperscript{7}

Figure 1. The molecular structure of 1. Colour code: \text{Co}^{II}: dark pink (the dark pink polyhedron represents the TBP geometry), \text{Co}^{III}: light pink (the light pink polyhedra represent the octahedral geometry), O: red, N: blue, C: grey. Hydrogen atoms are omitted for clarity.

Complex 1 is a mixed-valence isosceles triangle of \text{Co}^{II}/\text{Co}^{III} ions synthesised from the reaction of \text{CoCl}_2\cdot6\text{H}_2\text{O} with \text{Hpz} (pyrazole) and \text{HDBM} (dibenzoylemethane) in MeOH/MeCN in the presence of \text{NET}_3 (see ESI\textsuperscript{‡}). The crystallographic data can be found in Table S1 (see ESI\textsuperscript{‡}). The \text{Co}^{II} centre (Co1) is five-coordinate adopting a slightly distorted TBP geometry, while the two diamagnetic \text{Co}^{III} ions (Co2 and Co3) adopt an octahedral geometry. The oxidation states of \text{Co}^{II} and \text{Co}^{III} were confirmed using Bond Valence Sum (BVS) analysis.\textsuperscript{8} Continuous shape measures (CShMs),\textsuperscript{9} which provide an estimate of the distortion from the ideal TBP geometry for Co1, give a value of 0.33 (where 0 corresponds to the ideal polyhedron), confirming a small distortion (Table S2, Fig. S3 ESI\textsuperscript{‡}). The crystal packing is shown in Figure S4. Intermolecular interactions are present through hydrogen-\(\pi\) and \(\pi-\pi\) interactions between the phenyl and pyrazolate rings of neighbouring molecules, while the shortest intermolecular Co1--Co1' distance is \(\sim9.3\ \text{Å} \).

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\textsuperscript{a} WestCHEM, School of Chemistry, University of Glasgow, University Avenue, Glasgow, G12 8QQ, UK. E-mail: mark.murrie@glasgow.ac.uk

\textsuperscript{b} Department of Physics and NHMFL, Florida State University, Tallahassee, USA

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\textsuperscript{‡} Current address: Institute for Integrated Cell-Material Science (WPI-iCeMS), Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan.

\textsuperscript{§} Current address: Department of Physics and NHMFL, Florida State University, Tallahassee, USA

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Direct current (dc) magnetic susceptibility measurements were performed on a polycrystalline sample of 1 restrained in eicosane in the 290 - 2 K temperature range in an applied magnetic field of 1000 Oe (Fig. 2). The $\chi_M^T$ value at room temperature (2.45 cm$^{-1}$ mol$^{-1}$K) corresponds to a high-spin Co$^{II}$ and indicates a spin-orbit coupling contribution (the Co$^{III}$ ions are diamagnetic so for $g = 2$, $S = \frac{3}{2}$, $\chi_M^T = 1.88$ cm$^{-1}$ mol$^{-1}$ K). Upon cooling, $\chi_M^T$ decreases slowly until ~50 K to reach 2.16 cm$^{-3}$ mol$^{-1}$K and then decreases rapidly below ~50 K to reach 1.40 cm$^{-3}$ mol$^{-1}$ K at 2 K, indicating zero-field splitting of the ground state. Additionally, magnetisation versus field plots at 2, 4 and 6 K did not saturate at the highest available field of 5 T, a further indication of the presence of magnetic anisotropy (Fig. 2 inset).

Microanalysis and powder X-ray diffraction carried out on ground and non-ground samples (Fig. S1, S2) show that the lattice solvent is easily lost. Such desolvation could cause changes in the crystal packing, resulting in small changes of the local cobalt environment and hence small changes to the Co$^{II}$ $g$ values and zero-field splitting (ZFS) parameters. High frequency EPR studies on a polycrystalline sample of 1 in a field of 1000 Oe (Fig. 2 inset). Magnetisation versus field plot at temperatures 2, 4 and 6 K for 1. The red solid lines represent the fit (see text for details).

The relatively high value of the transverse anisotropy indicates significant mixing of the $M_5 = \pm \frac{1}{2}$ and $\pm \frac{5}{2}$ levels, and can be attributed to the small deviation from the ideal TBP geometry and/or the different nature of the ligands in the equatorial positions. Only a few examples of Co$^{II}$ in TBP geometry with easy-plane anisotropy have been found to show slow relaxation of magnetisation. Therefore, we performed alternating current (ac) magnetic susceptibility measurements. In zero applied dc field 1 does not display any out-of-phase ac signals, due to efficient zero-field quantum tunnelling. However, by using an applied ac field to suppress tunnelling, compound 1 does display slow magnetic relaxation at low temperature. Variable dc fields (500 – 5000 Oe) were applied to 1 at 2 K in order to obtain the optimum dc field, at which the characteristic relaxation time of the magnetisation ($\tau$) possesses the largest value (Fig. S7, ESI†). The characteristic relaxation times for each field were calculated using CC-FIT, and the $\tau_{\text{max}}$ value was obtained at 1000 Oe. The frequency dependence of the in-phase and out-of-phase magnetic susceptibility was measured under the optimum dc field, for the range of temperatures 1.8 – 8 K (Fig. 3).

$$\mathbf{H} = D S_\perp^2 + E (S_x^2 - S_z^2) + \mu_B g \mathbf{B} \mathbf{S} \quad (1)$$

The first and second terms represent the axial and rhombic ZFS terms, parameterised by $D$ and $E$, respectively, $\mathbf{S}$ is the spin operator with components $S_i (i = x, y, z)$, and the final term denotes the Zeeman interaction with the local magnetic field, $\mathbf{B}$, parameterised through the Landé $g$ tensor. Fixing the values of $g_x = g_y = 2.025$ and $g_z = 2.075$, and $\chi_{\text{IP}} = 0.0009$ cm$^{-1}$ mol$^{-1}$, where $\chi_{\text{IP}}$ stands for the contribution of temperature-independent paramagnetism arising from two Co$^{II}$ and one TBP Co$^{II}$, we were able to extract the ZFS parameters $D = +23.85 (\pm 0.17)$ cm$^{-1}$ and $E = + 4.04 (\pm 0.09)$ cm$^{-1}$. The $E/D$ ratio extracted from the fitting of the magnetic data is ~0.17, consistent with the EPR studies. The magnitude of $D$ is also consistent with previously reported Co$^{II}$ centres in TBP geometry with easy-plane anisotropy.

![Figure 2](image1.png)

**Figure 2.** Variable temperature dc susceptibility data for 1 in a field of 1000 Oe from 290 – 2 K. Inset: Magnetisation versus Field plot at temperatures 2, 4 and 6 K for 1. The red solid lines represent the fit (see text for details).

![Figure 3](image2.png)

**Figure 3.** Frequency dependent in-phase (top) and out-of-phase (bottom) susceptibility signals for complex 1 in a 1000 Oe dc applied magnetic field, in the temperature range 1.8 – 8 K. The solid lines correspond to the fit (CC-FIT).
The fitting of the Cole–Cole plot (out-of-phase versus in-phase signals) for 1 was performed using CC-FIT\textsuperscript{14} (Fig. 4), resulting in small values of the Cole–Cole parameter $\alpha$ (0.08 – 0.02) indicative of a relatively narrow distribution of relaxation times. The $\tau$ values were used to construct an Arrhenius plot for the temperatures 1.8 – 5 K, from which the relaxation parameters of $\Delta E/k_B$ (energy barrier) and $\tau_0$ (pre-exponential factor) at higher temperatures were extracted for 1 (Fig. S8, ES\textsuperscript{I}I). Fitting within the linear region (Orbach relaxation mechanism) the values $\Delta E/k_B = 23.18$ (± 2.2) K and $\tau_0 = 1.14 \times 10^{-5}$ s were extracted. However, the value of $\Delta E/k_B$ is smaller than the calculated energy difference between the ground and first exited state of $\sim 50$ cm$^{-1}$ ($\Delta E_{\text{shear}} = 2\sqrt{D^2 + 3E^2}$), a clear indication that other relaxation processes need to be considered. Using Equation 2, we attempted to fit the $\tau$ versus $T$ data but we were not able to extract reasonable values. The terms are the direct, tunnelling, Raman and Orbach contributions, in that order.\textsuperscript{15}

$$\tau^{-1} = A H^m T + \frac{B_1}{1+B_2 H^m} + CT^n + \tau_0^{-1}\exp\left(\frac{\Delta E}{k_B T}\right)$$ (2)

$$\tau^{-1} = B + CT^n$$ (3)

In order to avoid over-parameterisation we attempted to fit the $\tau$ versus Field ($H$) plot using only the terms for direct and tunnelling processes (which are dependent on field) to extract the parameters $A$, $B_1$, and $B_2$. However, all efforts were unsuccessful, an indication that there is a more complicated dependence of $\tau$ with the field. Therefore, using only the tunnelling (expressed as the parameter $B$) and Raman contributions (see Equation 3) we were able to fit the $\tau^{-1}$ versus $T$ plot (Fig. 4) affording the values $B = 926$ s$^{-1}$, $C = 2.3$ K$^{-n}$ s$^{-1}$ and $n = 6.6$.

**Figure 4.** Cole–Cole plot of the ac magnetic susceptibility of 1 at 1000 Oe (top). The solid lines correspond to the fit (CC-FIT). Plot of $\tau$ versus $T$ for 1 in the temperature range 1.8 – 5 K (bottom). The red solid line corresponds to the fit using Equation 3 (see text for details).

The exponent factor $n$ in the Raman process should be equal to 9 for Kramer's ions, or 5 in the presence of low-lying states. However, lower values for $n$ have been reported in cases where acoustic and optical phonons are involved.\textsuperscript{15,16} In conclusion, [Co$^\text{III}$Co$^\text{II}$]$_2$(µ$_2$-OH)(µ$_2$-pz)(DBM)$_2$\textsuperscript{+} is the only reported example of mixed-valence Co$^\text{III}$/Co$^\text{II}$ polynuclear complex containing a single trigonal bipyramidal Co$^\text{III}$ centre that gives rise to slow magnetic relaxation.\textsuperscript{17} In the case of 1, this arises from a large easy-plane magnetic anisotropy. To obtain the zero-field splitting parameters, we used high frequency EPR measurements to extract the $g$ factors. These were then fixed in the simultaneous fitting of the dc magnetic susceptibility data and the magnetisation data to give the parameters $D = + 23.85$ (± 0.17) cm$^{-1}$ and $E = + 4.04$ (± 0.09) cm$^{-1}$. Furthermore, it has been demonstrated recently how the magnetic anisotropy of octahedral Co$^\text{II}$ is transferred to the overall magnetic anisotropy of a polymeric [Cr$_2$Co$_4$] system. This is of interest for quantum information processing, especially in relation to molecules with a large spin ground state that is characterised by a large easy-plane anisotropy.\textsuperscript{18} Hence, the next step is to develop a route to incorporate high magnetic anisotropy trigonal bipyramidal Co$^\text{II}$ centres into exchange-coupled polymeric systems that contain multiple paramagnetic centres.

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**Notes and references**

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