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We report the synthesis, structure and magnetic properties of the first 4d-4f single-molecule magnet. The complex [Ru\textsuperscript{III}\textsubscript{2}Dy\textsuperscript{III}\textsubscript{2}(OMe)\textsubscript{2}(O\textsubscript{2}CPh)\textsubscript{4}(mdea)\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}] displays a butterfly type core, with an anisotropy barrier of 10.7 cm\textsuperscript{-1}. Ab initio and DFT calculations provide insight into the observed magnetic behaviour.

Single-molecule magnets (SMMs) are a class of zero-dimensional compounds with a wide range of properties such as magnetic bistability below a blocking temperature, the ability to exhibit quantum tunnelling of the magnetization (QTM) and quantum coherence.\textsuperscript{1} SMMs have gained great interest due to potential technological applications such as storing and processing digital information,\textsuperscript{2} and as molecular spintronic devices.\textsuperscript{3} Anisotropic 4f ions\textsuperscript{4} have been used to improve upon the properties laid out by the first generation SMMs, which were based on polynuclear 3d complexes, namely the hysteretic blocking temperature properties laid out by the first generation SMMs, which were based on homometallic 4d and 5d compounds, utilizing ions such as Ru\textsuperscript{III}, Mo\textsuperscript{IV}, Mo\textsuperscript{V}, Re\textsuperscript{V}, Os\textsuperscript{IV} and W\textsuperscript{VI}, with a number of these displaying SMM behaviour.\textsuperscript{5} This review notwithstanding, the magnetoo-chemistry of Ln\textsuperscript{III} complexes containing 4d and 5d ions remain little studied, and may be due to the complicated nature of the magnetic anisotropy and the difficulty in modelling the magnetic data. Recent advances in ab initio calculations have proven invaluable in the advancement of our understanding of slow magnetic relaxation in anisotropic 4f coordination compounds.\textsuperscript{6} With this background in mind, we aimed to synthesize new 4d and/or 5d containing clusters with a view to making a theoretical analysis of the magnetic properties and establish some guiding principles and elucidate what factors may allow for the observation of SMM behaviour using 4d or 5d ions. We chose the 4d ion Ru\textsuperscript{III} as starting point for this work. Several 3d-Ru\textsuperscript{III} complexes have recently been isolated,\textsuperscript{7} with a [Mn\textsuperscript{III}Ru\textsuperscript{III}] complex displaying slow relaxation of the magnetization.\textsuperscript{8} Here we incorporate the 4d Ru\textsuperscript{III} ion into a Dy\textsuperscript{III} complex and report the synthesis, structure, magnetic characterization and an ab initio and DFT theoretical analysis of a new Ru\textsuperscript{III} based SMM.

![Molecular structure of I. The H atoms are omitted for clarity. Colour scheme: Ru\textsuperscript{III}, pale green; Dy\textsuperscript{III}, purple; O, red; N, blue; C, light grey. The dashed lines correspond to the main magnetic axes of the Dy\textsuperscript{III} ions and the axes perpendicular to the anisotropy plane of the Ru\textsuperscript{III} ions. The arrows show the orientation of local magnetic moments in the ground exchange doublet state.](image)

The reaction of RuCl\textsubscript{2}-6H\textsubscript{2}O, Dy(NO\textsubscript{3})\textsubscript{3}-6H\textsubscript{2}O, benzoic acid, N-methyl-diethanolamine (mdea\textsubscript{H}\textsubscript{2}) and triethylamine in acetonitrile resulted in a brown solution. Yellow crystals of [Ru\textsuperscript{III}Dy\textsuperscript{III}(OMe)\textsubscript{2}(O\textsubscript{2}CPh)\textsubscript{4}(mdea)\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}] (I) were subsequently
isolated (see ESI for experimental details). Complex 1 (Fig. 1) crystallizes in the monoclinic space group P21/n, with the asymmetric unit containing half the cluster (one RuIII and DyIII ion), which lies upon an inversion centre (see ESI and Table S1 for X-ray details). Overall, 1 is a tetranuclear complex consisting of two RuIII and two DyIII ions, with the metallic core displaying a butterfly type arrangement. The DyIII ions occupy the body (central) sites, with the RuIII ions occupying the outer wing positions. The RuII and DyII ions are bridged via two μ1 methoxide ligands, each coordinating the two DyIII ions to a single RuIII ion. The complex is further stabilized by two [mdea]2- ligands, each of which coordinate via the N-atom to a RuII ion and then bridge via the two μ2-O atoms to a RuII and a DyIII ion. Four benzoate ligands each bridge a RuII to a DyIII ion with the common μ syn-syn bridging mode. The coordination sphere for each DyIII ion is completed by a single chelating nitrate ligand. The RuIII ions are six-coordinate with distorted octahedral geometries, and an average Ru–O3O bond distance of 2.04 Å. The DyIII ions are both eight-coordinate, and display distorted square-antiprismatic geometries, quantified by SHAPE analysis, with a CShM of 1.637. The average Dy-O bond length is 2.36 Å. Selected bond lengths and angles are given in Table S2. Packing diagrams are shown in Fig. S1. Compound 1 is isostructural to {CoIII,DyIII} and {CrIII,DyIII} SMMs.11–12

Direct current (dc) susceptibility measurements on a polycrystalline sample of 1 in the temperature range 2 – 300 K yield the χM/μT (χM = molar magnetic susceptibility) versus T plot (Fig. 2), with a χM/μT value of 29.01 cm³ K mol⁻¹ at 300 K. This is close to the expected value of 29.09 cm³ K mol⁻¹ for an uncoupled [RuII(DyII)₂] moiety. As the temperature is decreased the χM/μT product decreases gradually down to 25 K, below which an upturn is observed. The low temperature behaviour is field dependent, with a further decrease observed under all fields at the lowest temperatures measured due to Zeeman depopulation effects. The high temperature decrease (300 – 25 K) is due to the depopulation of the excited m states of the DyIII ions, while the increase at lower temperatures suggests non-negligible exchange interactions between the RuII and the DyII ions (see ab initio and DFT analysis). The isothermal magnetization (M) measurements (Fig. 2, inset) each display a rapid increase in magnetization below 2 T, before a more gradual linear-like increase, without saturating. This suggests a significant magnetic anisotropy is present. We therefore examined for

M vs H hysteresis, however, no coercivity was observed down to 1.8 K (4 Oe/s) (Fig. S2) using a conventional SQUID magnetometer.

In order to probe for slow magnetic relaxation on a shorter timescale, above 1.8 K, variable temperature and variable frequency alternating current (ac) susceptibility measurements were performed with an oscillating ac field of 3.5 Oe under a zero applied dc field. These measurements revealed frequency and temperature dependence of both

![Fig. 2](image-url)
expect even stronger magnetic exchange,7 and thus the potential for longer relaxation times.13 However the experimental data reveals that the relaxation barrier is much smaller, at 10.7 cm\(^{-1}\), and as a consequence fast(er) relaxation times are observed at the temperatures studied, hence no \( M \) vs \( H \) coercivity was found above 1.8 K. The \( a \) parameters for the \([\text{CrDy}_2]\) analogue are 0.12 and 0.28 at 8.5 and 5.0 K, being larger at 5 K than for \([\text{RuDy}_2]\), the latter showing increases in \( a \) at 1.8 K due to QTM.

To quantify these observations, \textit{ab initio} and DFT calculations were performed using MOLCAS 7.8\(^{11}\) and ORCA 2.9.0\(^{13}\) software, respectively. Details are given in the ESI and Table S3. Fragment CASSCF/SO-RASSI/SINGLE_ANISO\(^{46}\) type calculations have been performed to determine the low-lying energy levels and magnetic properties of individual Dy\(^{III}\) and Ru\(^{III}\) centres. Only one Dy\(^{III}\) and Ru\(^{III}\) centre per complex has been calculated, due to the presence of the inversion centre. Table S4 shows that the ground state for the Ru\(^{III}\) ion is a doublet, which is expected due to the strong crystal field splitting of the 4d orbitals. This is backed up via DFT (BP and B3LYP) methodology, the obtained spectrum of exchange multiplets together with matrix elements of magnetic moments on the corresponding wave functions can be used for the construction of the barrier of reversal of magnetization. On the right side the local magnetic moments shown for one of two components for each exchange doublet state.

The ground KD for the Dy\(^{III}\) sites are highly axial, while the ground KD of Ru\(^{III}\) displays easy anisotropy plane of magnetization, which is much weaker than the anisotropy on the Dy\(^{III}\) sites (Table 1). Consequently, it is the latter which defines the SMM behaviour of the complex.

In order to gain some information about the exchange coupling constants in this system we performed BS-DFT calculations at the B3LYP/SVP level. To estimate the exchange constant for all pairs, we performed calculations on model complexes with the experimental geometries. To examine the exchange between the Ru\(^{III}\) ions we substituted Dy\(^{III}\) ions for Lu\(^{III}\), giving a \([\text{LuIII,RuH}_2]\) complex. To investigate the exchange interaction between the Dy\(^{III}\) ions we substituted Ru\(^{III}\) for V\(^{III}\) and Dy\(^{III}\) for Gd\(^{III}\), giving a \([\text{GdV}_2\text{Y}_{III}]\) complex; the exchange parameters were then rescaled for the spin \( S = 5/2 \) of dysprosium ions compared to the \( S = 7/2 \) of gadolinium. Finally, to examine the Dy\(^{III}\) – Ru\(^{III}\) interactions, we performed calculations on two complexes of the type \([\text{Gd}(I)\text{Lu}(I')\text{Ru}(I)\text{Y}(I')]\) and \([\text{Gd}(I)\text{Lu}(I')\text{Y}(I)\text{Ru}(I')]\), with subsequent rescaling to the spin of Dy\(^{III}\). In all cases we applied Yamaguchi’s formula to estimate the exchange coupling constants.\(^{17}\) The following Hamiltonian was employed to account for exchange interactions, where the interactions with the orbitally degenerate Dy\(^{III}\) ions was accounted for within the Lines model\(^{18}\):

\[
\hat{H}_{\text{exch}} = -J_{Dy-Dy} \hat{S}_D \hat{S}_D' - J_{Dy-Ru} \hat{S}_D \hat{S}_R - 2J_{Ru-Ru} \hat{S}_R \hat{S}_R' - 2J_{Dy-Ru} \hat{S}_D \hat{S}_R' \quad \text{(Eq.1)}
\]

where \( \hat{S} \) are the spin operators of the Dy\(^{III}\) and Ru\(^{III}\) ions, respectively, \( S_{Dy} = 5/2 \), \( S_{Ru} = 1/2 \). The obtained exchange parameters are shown in Table 2.

Magnetic susceptibility data, \( \chi_T(T) \), (Fig. S7) and the \( M(H) \) curves (Fig. S8) were calculated using the DFT determined exchange parameters and including the dipolar interaction. The employed Hamiltonian including exchange and dipolar interactions is of the same form as the one used for description of \([\text{Cr}^{III}\text{Dy}^{III}]\) complex.\(^{12}\) The DFT determined values give a good agreement of the calculated \( \chi_T(T) \) curve with the experimental one, the only fitting parameter being used the intermolecular interaction \( J' \), which is \(-0.021\ cm^{-1}\). The dominant exchange parameters are found between the Dy\(^{III}\) and Ru\(^{III}\) ions and are antiferromagnetic in nature. Due to the strong exchange interaction between Dy\(^{III}\) and Ru\(^{III}\) ions, the local magnetic moments in the ground exchange doublet state of Ru\(^{III}\) centres are aligned along the main anisotropy axes of Dy\(^{III}\) sites (Fig. 1). If we rescale the exchange coupling constants for Dy-Ru pairs (Table 2) to the pseudospin \( 1/2 \) of Dy ions and to the spin \( 3/2 \) of Cr ions from the \([\text{Cr}^{III}\text{Dy}^{III}]\) butterfly complex,\(^{12}\) we obtain the following parameters: \(-5.8\) and \(-6.2\ cm^{-1}\), which are smaller than the same parameters in \([\text{Cr}^{III}\text{Dy}^{III}]\) complex, \(-17\) and \(-20\ cm^{-1}\), respectively. Following a recently proposed methodology, the obtained spectrum of exchange multiplets together with matrix elements of magnetic moments on the corresponding wave functions can be used for the construction of the barrier of reversal of magnetization.\(^{12,19}\)

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**Table 1. Energies of the lowest Kramers doublets (cm\(^{-1}\)) of Dy\(^{III}\) and Ru\(^{III}\) centres and the \( g \) tensor of the ground Kramers doublet.**

<table>
<thead>
<tr>
<th></th>
<th>Dy</th>
<th>Ru</th>
<th>Dy basis1</th>
<th>Dy basis2</th>
<th>Ru basis1</th>
<th>Ru basis2</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3972</td>
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<td>179</td>
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<td>5115</td>
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<td>17874</td>
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<tr>
<td>546</td>
<td>555</td>
<td></td>
<td>18347</td>
<td>18396</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( g_x = 0.0051 )</td>
<td>( g_y = 0.0079 )</td>
<td>( g_x = 2.65 )</td>
<td>( g_y = 2.60 )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( g_x = 0.0057 )</td>
<td>( g_y = 0.0095 )</td>
<td>( g_x = 2.48 )</td>
<td>( g_y = 2.47 )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( g_x = 0.1974 )</td>
<td>( g_y = 0.1976 )</td>
<td>( g_x = 1.54 )</td>
<td>( g_y = 1.58 )</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The ground KD for the Dy\(^{III}\) sites are highly axial, while the ground KD of Ru\(^{III}\) displays easy anisotropy plane of magnetization, which is much weaker than the anisotropy on the Dy\(^{III}\) sites (Table 1). Consequently, it is the latter which defines the SMM behaviour of the complex.

**Table 2. Exchange parameters (cm\(^{-1}\)) between magnetic ions for the \([\text{Ru}^{III}\text{Dy}^{III}]\) complex 1.**

<table>
<thead>
<tr>
<th>Pair</th>
<th>Calculated</th>
<th>Fitted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dy1-Dy1'</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ru1-Ru1'</td>
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<td>-0.4</td>
</tr>
<tr>
<td>Dyl-Ru1</td>
<td>-3.7</td>
<td>-3.7</td>
</tr>
<tr>
<td>Dyl-Ru1'</td>
<td>-3.5</td>
<td>-3.5</td>
</tr>
</tbody>
</table>

Fig. 4. \textit{Ab initio} constructed barrier of relaxation of magnetization. On the right side the local magnetic moments shown for one of two components for each exchange doublet state.
The low-lying exchange spectrum and the position of the magnetization blocking barrier (dotted line) are shown in Fig. 4. The exchange states are placed on the diagram according to their magnetic moments (bold black lines). The horizontal blue arrows show the tunnelling transitions (the energy splitting) within each doublet state, while the non-horizontal arrows show the spin-phonon transition paths. The numbers at the paths are averaged transition moments in μu connecting the corresponding states. Red arrows correspond to the maximal transition probability from a given state, thus outlining the relaxation barrier within the ground exchange doublet. The barrier is of the exchange type, since multiple relaxation paths are involved between several exchange levels (Fig. 4). We would like to stress that the magnetic blocking barrier is constructed without using any fitting parameter other than $\varepsilon J'$ to account for intermolecular interaction. The ab initio built blocking barrier is in excellent agreement (13.9 cm$^{-1}$) with the experimentally determined value (~11 cm$^{-1}$). However, the barrier in I is significantly smaller than in the isostructural $\{\text{Cr}^{II}\text{Dy}^{III}\}$ complex.$^{12}$ This can be explained by two reasons. First, the exchange interaction between the Dy–Ru pairs is weaker than for the Dy–Cr pairs. Since in both complexes the barrier is of the exchange type, it is clear that a weaker exchange interaction would lower the barrier in one of them. Secondly, the spin of I is 3/2, whereas the spin of Ru is 1/2. Therefore, the chromium complex possesses more exchange doublet states and involves, therefore, more levels in the blocking barrier (c.f. the present Fig. 4 and the Fig. 6 in Ref. [12]). A similar situation was observed in a series of $\{\text{Co}^{II}\text{Ln}^{III}\text{Co}^{II}\}$, Ln = Gd, Tb and Dy, where the Gd complex was found to be a much better SMM.$^{19}$ Comparing $\{\text{Cr}^{III}\text{Dy}^{III}\}$ with I shows that the best SMM effect is achieved via an efficient interaction between anisotropic metal ions with a strongly axial ground state and high-spin isotropic metal ions.$^{19}$

In summary, we have synthesised a rare Ru$^{III}$-based polynuclear complex that is the first 4d/4f SMM. Calculations reveal significant Ru–Dy magnetic exchange interactions of ~3.5 and ~3.7 cm$^{-1}$, stronger than usually observed for 4f–4f and the majority of reported 3d–4f complexes.$^{11}$ It is this reason that a thermally activated slow relaxation mechanism is observed in the absence of a static dc field, and stems from an exchange based multilevel mechanism, with only a cross over to a quantum regime observed below 2.5 K (c.f. $\{\text{Co}^{II}\text{Dy}^{III}\}$ complexes, with negligible exchange, where QTM is observed from ~8 K). For I, however, the Ru–Dy pair-wise exchange parameter is smaller than the Cr–Dy pair-wise exchange in an isostructural analogue and this is the major reason for the smaller anisotropy barrier (11 vs 55 cm$^{-1}$). This work highlights that 4d ions can be used to develop new SMMs and will be integral for the targeted synthesis of future heterometallic lanthanide complexes that exhibit strong magnetic exchange and long relaxation times.

Notes and references

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‡ CCDC number 1032631. Electronic Supplementary Information (ESI) available: [experimental details, magnetic data and computational details and information]. See DOI: 10.1039/c000000x/.


