

# Dalton Transactions

An international journal of inorganic chemistry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: M. Murrie, E. Lowe, H. Hourston, T. Sharma, S. K. Dugmore, C. Wilson and G. Rajaraman, *Dalton Trans.*, 2025, DOI: 10.1039/D5DT01565K.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

## ARTICLE

## Leveraging anion selection to modulate crystallographic symmetry in Yb(III) single-molecule magnets

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Ethan Lowe,<sup>a</sup> Hamish Hourston,<sup>a</sup> Tanu Sharma,<sup>b</sup> Sarah K. Dugmore,<sup>a</sup> Claire Wilson,<sup>a</sup> Gopalan Rajaraman<sup>\*b</sup> and Mark Murrie<sup>\*a</sup>

Distortions in the local symmetry around Ln(III) ions in SMMs significantly impacts slow magnetic relaxation by introducing transverse crystal field parameters that enhance quantum tunnelling of the magnetisation (QTM). Minimising these distortions, often using macrocyclic or sterically hindered ligands, or by tuning intermolecular interactions, is essential for suppressing QTM. A less-explored strategy involves aligning the molecular symmetry elements within the crystal lattice to generate a high-symmetry crystal lattice with symmetry enforced bond angles and lengths. Here, we demonstrate that aligning the  $S_4$  axes of  $[\text{YbCl}_2(\text{Ph}_3\text{AsO})_4]^+$  and  $[\text{BPh}_4]^-$  in  $[\text{YbCl}_2(\text{Ph}_3\text{AsO})_4]\text{BPh}_4$  (**1**) enforces tetragonal symmetry and a strict  $180^\circ$  Cl–Yb–Cl angle. In contrast,  $[\text{YbCl}_2(\text{Ph}_3\text{AsO})_4]\text{PF}_6$  (**2**) does not possess aligned molecular rotational axes and therefore lacks the crystallographically enforced symmetry leading to a smaller Cl–Yb–Cl angle. While both compounds exhibit similar slow relaxation of the magnetisation, due to efficient Raman relaxation processes, **2** shows a significant decrease in the *ab initio* calculated collinearity of the anisotropy axes of the excited Kramers doublets, alongside a change in the ground  $m_J = \pm 7/2$  state composition, with an increased admixture of the  $m_J = \pm 1/2$  states. These findings highlight the potential of crystallographically enforced symmetry in designing high-performance Yb(III)-based SMMs.

## Introduction

Lanthanide ions have come to dominate the field of single-molecule magnets (SMMs) producing large magnetisation reversal ( $U_{\text{eff}}$ ) barriers, extremely slow magnetic relaxation times and large coercive fields.<sup>1–3</sup> However, within the large family of Ln(III) metal ions, the field is saturated with Dy(III),<sup>4,5,6</sup> Tb(III)<sup>7,8</sup> and Er(III)<sup>9,10</sup> SMMs,<sup>11</sup> accompanied by a small number of complexes containing other Ln(III) ions.<sup>12,13</sup> Tuning the ligand field of these other Ln(III) ions, to enhance slow magnetic relaxation, has become a key area of interest for obtaining new multifunctional SMMs.<sup>14,15,16</sup>

The time reversal symmetry imposed in Kramers ions results in the generation of a bistable ground state, irrespective of the ligand field.<sup>17</sup> As such, this property gives rise to a much greater number of SMMs based on Kramers ions, due to the flexibility of available ligand fields and geometries.<sup>11</sup> However, the Kramers ion Yb(III) presents an interesting case. Despite its

Kramers nature there is only one known example of a Yb(III) SMM displaying slow magnetic relaxation without the presence of an applied dc field.<sup>18</sup> Furthermore, this example was only achieved through isotopic enrichment using  $^{174}\text{Yb(III)}$ , which possesses a nuclear spin  $I = 0$ . This suggests that Yb(III) is an unusual case among Ln(III) ions and may be highly susceptible to efficient relaxation of its magnetisation through hyperfine, dipolar or other mechanisms.<sup>18b</sup>

The startling absence of other 'zero-field' Yb(III) SMMs, may also be related to the design of Yb(III) SMMs based on ligand field environments and geometries which complement other 'prolate ions' such as Er(III).<sup>19,20</sup> Whilst both Yb(III) and Er(III) are both described as prolate, the 4f charge density approximations of the larger  $m_J$  states clearly possess different profiles.<sup>21</sup> This may begin to explain why many Yb(III) complexes based on either Er(III) SMMs or geometries that favour strictly prolate ions, produce only modest  $U_{\text{eff}}$  barriers and regularly require an applied dc field to observe slow magnetic relaxation.<sup>22–26</sup>

The 4f charge density approximation of the Yb(III)  $m_J$  states may also suggest a third possible reason for the efficient magnetic relaxation in Yb(III) SMMs.<sup>21</sup> Small changes in the local symmetry of Ln(III) ions are known to rapidly introduce transverse crystal field parameters (CFPs).<sup>27,28</sup> These transverse CFPs result in a mixing of  $m_J$  states and the introduction of rapid magnetic relaxation through mechanisms such as quantum tunnelling of the magnetisation (QTM).<sup>29,30,31</sup>

<sup>a</sup> School of Chemistry, University of Glasgow, University Avenue, Glasgow G12 8QQ, UK. E-mail: mark.murrie@glasgow.ac.uk

<sup>b</sup> Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai, Maharashtra 400076, India. E-mail: rajaraman@chem.iitb.ac.in

† Electronic supplementary information (ESI) available: Experimental section, crystallographic details, magnetic and computational studies. CCDC 2469525–2469526. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/x0xx00000x>.



One powerful way to control the local symmetry and distortions around a Ln(III) ion is to modify the second coordination sphere.<sup>32,33</sup> Second coordination sphere modifications have been shown to significantly change the magnetic properties of many SMMs through a variety of interactions.<sup>34,35</sup>

In this work we propose to utilise the inherent point group symmetry of two different anions; the octahedral ( $O_h$ )  $PF_6^-$  anion and the tetrahedral ( $T_d$ )  $[BPh_4]^-$  anion. By replacing the  $[BPh_4]^-$  anion with the  $PF_6^-$  anion we break the tetragonal crystallographic symmetry of the compound, generating distortions within the primary coordination sphere. As such we investigate the structural and magnetic properties of  $[YbCl_2(Ph_3AsO)_4]BPh_4$  (**1**) and  $[YbCl_2(Ph_3AsO)_4]PF_6$  (**2**) and employ computational studies to probe ground state composition, crystal field splitting and possible relaxation mechanisms.

## Experimental

**$[YbCl_2(Ph_3AsO)_4]BPh_4$  (**1**)** To a colourless solution of triphenylarsine oxide (0.4 mmol, 128.9 mg) and sodium tetraphenylborate (0.1 mmol, 34.2 mg) in ethanol (5 mL), warmed to 70 °C, was added ytterbium(III) chloride hexahydrate (0.1 mmol, 38.7 mg). The mixture was stirred for 1 h at 70 °C, quickly forming a white precipitate. While still warm, the solution was filtered through filter paper and the white solid was collected and dried. Once dry, the solid was dissolved in dichloromethane (5 mL), filtered through cotton wool, and the filtrate was used for layer and vapour diffusions with diethyl ether. Colourless block-like crystals suitable for single-crystal X-ray diffraction were obtained from vapour diffusion and confirmed to be  $[YbCl_2(Ph_3AsO)_4]BPh_4$ . The crystals were isolated and washed with  $Et_2O$  and dried, yielding 96.1 mg (52 % yield) of the product. Elemental analysis calculated % for  $[YbCl_2(Ph_3AsO)_4]BPh_4$  C:62.3 %, H:4.4 %, N:0 %, found: C:62.1 %, H:4.4 %, N:0 %. IR:  $\bar{\nu}$  ( $cm^{-1}$ ): 681, 732, 901, 962, 1086, 1437, 1479, 1580, 1977, 2019, 2161, 3050.

**$[YbCl_2(Ph_3AsO)_4]PF_6$  (**2**)** To a solution of triphenylarsine oxide (0.4 mmol, 128.9 mg) and sodium hexafluorophosphate (0.1 mmol, 16.8 mg) in ethanol (5 mL), warmed to 70 °C, was added ytterbium(III) chloride hexahydrate (0.1 mmol, 38.7 mg). The mixture was stirred for 1 h at 70 °C, quickly forming a white precipitate. While still warm, the solution was filtered through filter paper and the solid was collected and dried. Once dry, the solid was dissolved in dichloromethane (5 mL), filtered through cotton wool, and the filtrate was used for layer and vapour diffusions with diethyl ether. Colourless block-like crystals suitable for single-crystal X-ray diffraction were obtained from vapour diffusion and confirmed to be  $[YbCl_2(Ph_3AsO)_4]PF_6$ . The crystals were isolated and washed with  $Et_2O$  and dried, yielding 114.1 mg (68 % yield) of the product. Elemental analysis calculated % for  $[YbCl_2(Ph_3AsO)_4]PF_6$  C:51.5 %, H:3.6 %, N:0 %, found: C:51.4 %, H:3.6 %, N:0 %. IR:  $\bar{\nu}$  ( $cm^{-1}$ ): 684, 738, 835, 897, 996, 1087, 1186, 1320, 1439, 1480, 1580, 2328, 2369, 3058.

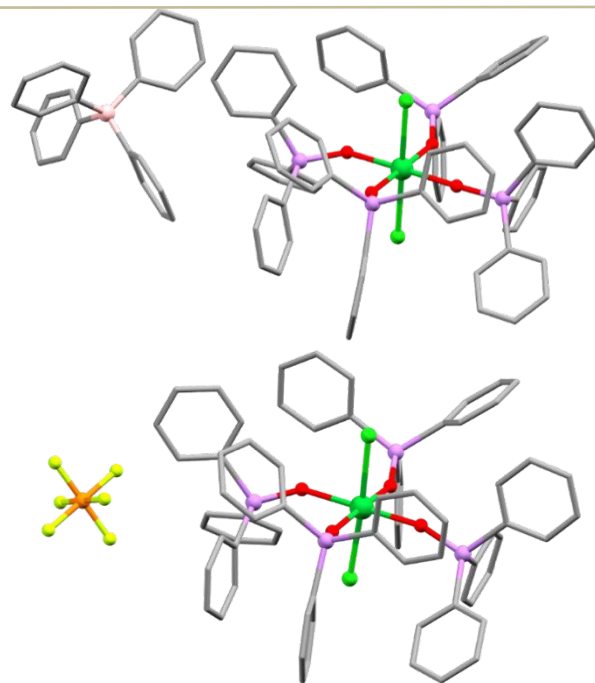
## Results and Discussion

### Crystal structures

$[YbCl_2(Ph_3AsO)_4]BPh_4$  (**1**) crystallises in the tetragonal space group  $I4_1/a$  and  $[YbCl_2(Ph_3AsO)_4]PF_6$  (**2**) crystallises in the lower symmetry triclinic space group  $P\bar{1}$  (Fig. 1. One quarter of the  $[Yb(Ph_3AsO)_4Cl_2]^+$  cation and one quarter of the  $[BPh_4]^-$  anion are found within the asymmetric unit of **1**, whilst one full  $[Yb(Ph_3AsO)_4Cl_2]^+$  cation and one  $PF_6^-$  anion are located in the asymmetric unit of **2**. The increase in the asymmetric unit in **2** is attributed to the introduction of the  $PF_6^-$  anion, which is found in an octahedral environment, and the misalignment of the primary rotational axes of the  $[Yb(Ph_3AsO)_4Cl_2]^+$  and  $PF_6^-$  ions. This results in a breaking of tetragonal symmetry within the crystal lattice of **2** (*vide infra*).

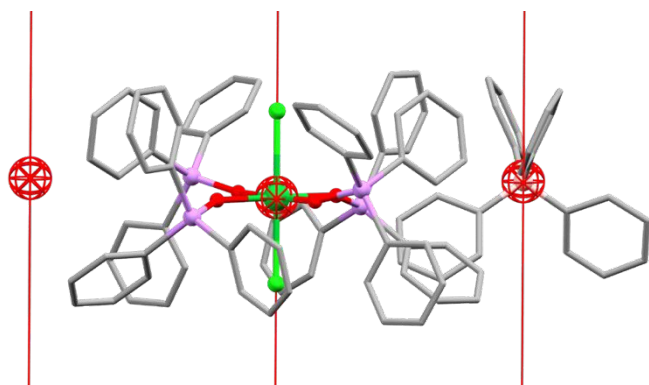
Similar average axial Yb-Cl bond lengths of 2.641 Å and 2.633(1) Å are observed for **1** and **2**, respectively. However, **2** possesses two differing Yb-Cl bond lengths (2.626(1) Å and 2.640(1) Å), already indicating an increased distortion in **2**. Axial Cl- $\bar{Y}b$ -Cl angles of 180° in **1** and 176.24(4)° in **2** further highlights the increased distortion in **2**. The perfectly linear 180° Cl- $\bar{Y}b$ -Cl angle in **1** is enforced by the four-fold rotoinversion axis that lies along the Cl- $\bar{Y}b$ -Cl bond (Fig. 2. Equatorial Yb-O bond lengths observed in **1** (2.163 Å) and **2** (2.190(3), 2.174(3), 2.166(3) and 2.168(3) Å again highlight the increased distortion of the  $\{YbO_4Cl_2\}$  unit present in **2**.

Both Yb(III) centres are determined to have distorted octahedral geometry ( $O_h$ ) by continuous shape measures analysis (CSHMs) (0.942 for **1** and 0.898 for **2**).<sup>36</sup> It should be noted that CSHMs does not produce a score for a  $D_{4h}$  geometry and the elongation of the axial Yb-Cl bonds means that a better description for the structure of the Yb(III) centres in **1** and **2** is *pseudo- $D_{4h}$* . This also explains the unusual reduction in the  $O_h$

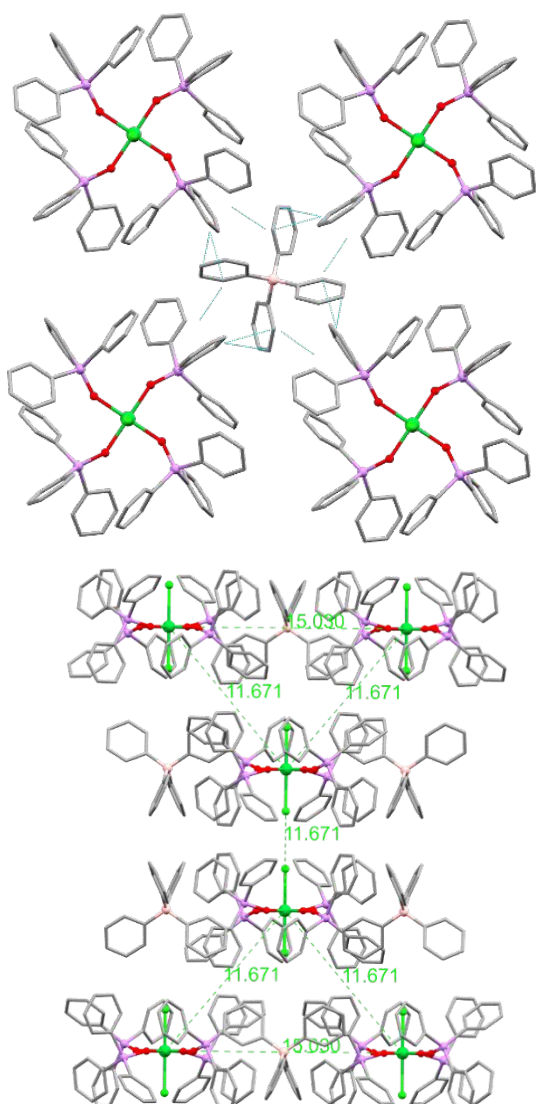


**Fig. 1** The structure of compounds **1** (top) and **2** (bottom). As, purple; B, pink; C, grey; Cl, light green; F, yellow; O, red; P, orange; Yb, green; with H atoms omitted for clarity.





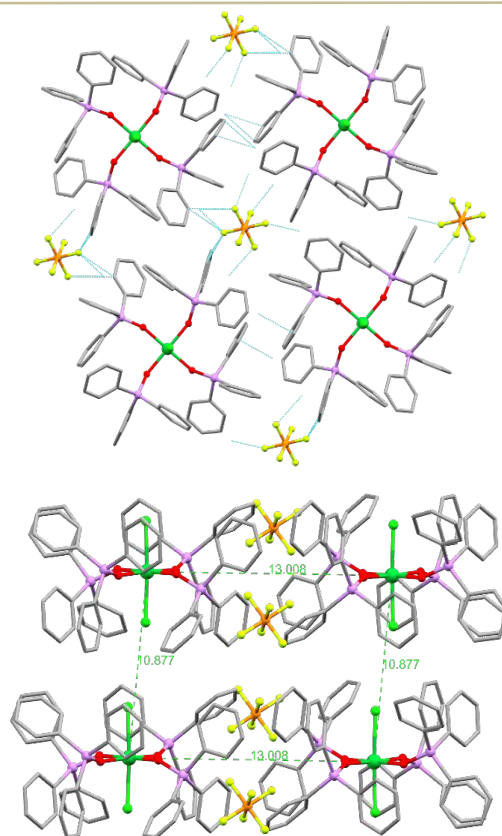
**Fig. 2** The structure of **1** highlighting the  $S_4$  rotoinversion axes (red lines). As, purple; B, pink; C, grey; Cl, light green; O, red; Yb, green; with H atoms omitted for clarity.



**Fig. 3** The crystal packing of **1** looking along the crystallographic  $c$ -axis, highlighting the intermolecular interactions between complexes in the same layer (top). The crystal packing between layers in **1** looking down the crystallographic  $b$ -axis, where the Yb(III)...Yb(III) distances are in green (bottom). As, purple; B, pink; C, grey; Cl, light green; O, red; Yb, green; with H atoms omitted for clarity.

CSHMs value for **2**, which displays the more distorted structure. A slight elongation of the axial bonds in **1** likely results in the larger  $O_h$  CSHMs score. To give a better representation of the equatorial distortion in **2** caused by the loss of tetragonal symmetry, we investigated the  $D_{4h}$  CSHMs score for the square planar fragment  $\{YbO_4\}$  (Fig. S1). Compound **1**  $\{YbO_4\}$  gives a  $D_{4h}$  CSHMs value of 0.004 whilst **2**  $\{YbO_4\}$  gives a  $D_{4h}$  CSHMs value 0.019. This is equivalent to a roughly five-fold increase in equatorial distortion in compound **2**.

Furthermore, investigation of the  $S_4$  symmetry operation using continuous symmetry measures reveals a deviation away from perfect  $S_4$  symmetry in the  $\{YbO_4Cl_2\}$  unit of compound **2**.<sup>36b</sup> This is characterised by the increased continuous symmetry measure (CSM) for the  $S_4$  symmetry operation of 0.0310 for **2** vs. 0 for compound **1**, which possesses an ideal  $S_4$  axis. In the crystal packing of compound **1**, *pseudo*-2D layers arise from intermolecular edge-to-face interactions between phenyl rings of the  $OAsPh_3$  ligand and the  $[BPh_4]^-$  anion ( $C_{centroid} \cdots C$ , 3.58 and 3.86 Å) (Fig. 3). The shortest intermolecular Yb(III)...Yb(III) distances of 11.67 Å occur between both staggered and head-to-tail complexes which crystallise along the crystallographic  $c$ -axis (Fig. 3). Intermolecular  $\pi$ - $\pi$  interactions between phenyl ( $OAsPh_3$ ) rings of neighbouring complexes ( $C \cdots C$ , 3.43 – 3.62 Å) alongside interactions between the phenyl rings of  $OAsPh_3$  and the  $PF_6^-$  anion ( $C \cdots F$ , 3.04 – 3.51 Å) also afford complex **2** a



**Fig. 4** The crystal packing of **2** highlighting the intermolecular interactions between complexes and  $PF_6^-$  anions in the same layer (top). The crystal packing between layers in **2** showing the closest intra-layer and inter-layer intermolecular Yb(III)...Yb(III) distances in Å (bottom). As, purple; C, grey; Cl, light green; F, fluorescent yellow; O, red; P, orange; Yb, green; with H atoms omitted for clarity.



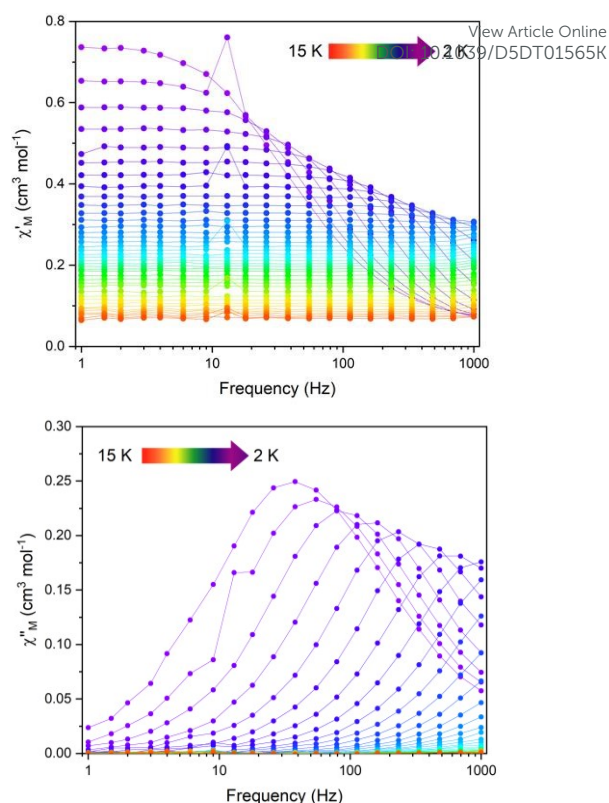


similar *pseudo*-2D layer structure and packing as observed in **1** (Fig. 4). The nearest intermolecular Yb(III)⋯Yb(III) distance of 10.88 Å occurs between staggered molecules within different layers along the crystallographic *a*-axis (Fig. 3). The phase purity of compounds **1** and **2** was confirmed by powder X-ray diffraction (Fig. S2).

The significant difference in space group between **1** (*I*4<sub>1</sub>/*a*) and **2** (*P*1̄) can be rationalised by considering not only the structure of the anions, but also their orientation and intermolecular interactions with the [Yb(Ph<sub>3</sub>AsO)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup> cations. Incorporation of a large [BPh<sub>4</sub>]<sup>−</sup> anion in **1** results in highly directional edge-to-face interactions with only the equatorial component of the SIM unit. As such, the [BPh<sub>4</sub>]<sup>−</sup> anion is locked into a pre-determined orientation. This reduced rotational degree of freedom results in an alignment of the *S*<sub>4</sub> axes (Fig. 2) and the perpetuation of tetragonal symmetry throughout the crystal lattice. Conversely, the smaller size, higher symmetry and weak intermolecular interactions of the PF<sub>6</sub><sup>−</sup> anion result in a much greater rotational degree of freedom in **2**. The PF<sub>6</sub><sup>−</sup> anion acts as an effective spherical charge with only a limited directional dependence. As such, both molecules are orientated where their ~C<sub>2</sub> Cl–Yb–Cl axes are mis-aligned, resulting in the absence of a C<sub>2</sub> crystallographic axis in the crystal structure of **2**. Whilst controlling crystal packing is not trivial, a sound understanding of the geometry, symmetry and potential interactions between molecules can allow for a rational design of crystal structures with both high and low symmetry.

### Magnetic characterisation

The magnetic properties of polycrystalline samples of **1** and **2**, suspended in eicosane, were measured in an applied dc field of 1000 Oe from 280 – 2 K (Fig. S3). The χ<sub>M</sub>T values at 280 K for complexes **1** and **2**, of 2.33 and 2.45 cm<sup>3</sup> mol<sup>−1</sup> K, respectively are slightly lower than the theoretical value (2.57 cm<sup>3</sup> mol<sup>−1</sup> K). This slight decrease is attributed to ligand field effects<sup>37,38</sup> and the values are in excellent agreement with those observed in other Yb(III) SMMs.<sup>39,40,41</sup> Upon cooling, χ<sub>M</sub>T decreases steadily for both compounds until reaching 1.57 and 1.68 cm<sup>3</sup> mol<sup>−1</sup> K for **1** and **2**, respectively. This decrease is attributed to the depopulation of excited Stark states, where the uneven separation of the excited states explains the non-linear decrease across the temperature range.<sup>42,43</sup> Magnetisation vs. field measurements were conducted on **1** and **2** at 2, 4 and 6 K from 0 – 7 T (Fig. S4). At 2 K under an applied dc field of 7 T experimental magnetisation values (M<sub>exp</sub>) of 1.82 and 1.94 Nβ are observed for **1** and **2**, respectively. These values are in good agreement with the expected M<sub>sat</sub> value (≈ 2 Nβ) for a highly anisotropic *m*<sub>J</sub> = ±7/2 ground state (1/4 *g*<sub>zz</sub>).<sup>27</sup> Variable temperature ac susceptibility measurements were conducted on **1** and **2** to probe for the presence of slow magnetic relaxation. Neither complex displayed any out-of-phase (χ'') magnetic susceptibility peaks under zero applied field, likely a result of efficient QTM. To probe for field-induced slow magnetic relaxation, variable-field χ' and χ'' vs. frequency measurements were conducted from 0 – 4000 Oe, across a 1 – 941 Hz frequency range at 3 and 2 K for **1** and **2**, respectively



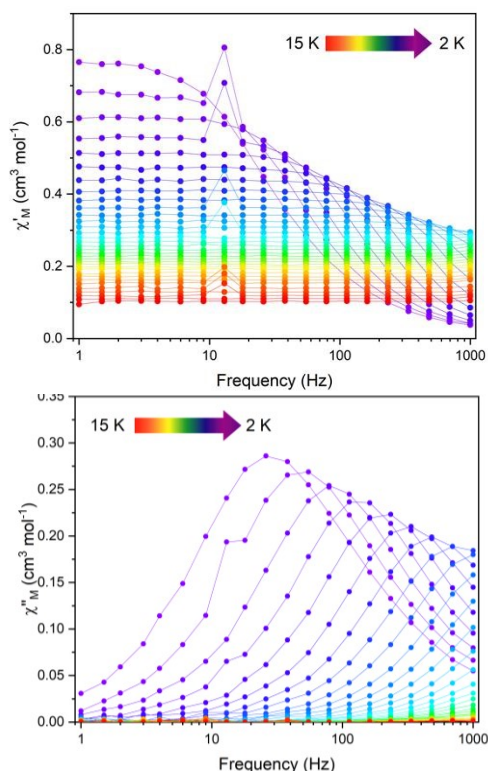
**Fig. 5** The frequency dependence of the in-phase (top) and out-of-phase (bottom) ac susceptibility signals in the temperature range 2 – 15 K under an applied field of 600 Oe for **1**.

(Fig. S5 and S6). Cole-Cole plots were then constructed from the χ' vs. χ'' data and fitted across a 200 – 4000 Oe range to a generalised Debye equation using CCFIT2 to obtain tau values.<sup>44,45</sup> The tau values were then plotted vs. applied dc field to obtain the optimum applied field for the suppression of QTM (Fig. S7). Both compounds display a similar field dependence of their tau values, characteristic of a suppression of QTM under small magnetic fields and the onset of direct relaxation at large fields. Optimum applied dc fields of 600 Oe and 1000 Oe were then selected to conduct variable-temperature ac susceptibility measurements for **1** and **2**, respectively.

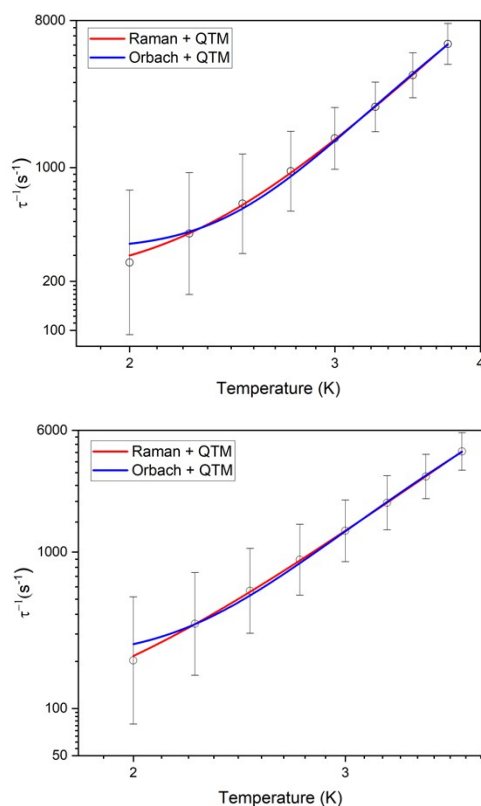
Variable-temperature ac susceptibility measurements conducted from 2 – 15 K and 1 – 941 Hz under an applied field of 600 and 1000 Oe for compounds **1** and **2**, respectively, are shown in Fig. 5 and Fig. 6. Spikes in the data around 10.65 Hz are artefacts. Frequency dependant peaks in the χ'' data are present up to 3.75 K for both compounds, with a clear frequency dependence of χ' below 4 K. Cole-Cole plots were then constructed from the χ' and χ'' data and variable-temperature tau values were extracted by fitting the 2 – 3.75 K temperature range to a generalized Debye law using CCFIT2 (Fig. S8).<sup>44,45</sup> Plotting of the relaxation rate (τ<sup>−1</sup>) vs. temperature (Fig. 7) allows for the relaxation rate to be modelled and the extraction of the relaxation parameters using either Orbach and QTM or Raman and QTM relaxation mechanisms, using equations 1 and 2:

$$\tau^{-1} = \tau_{QTM}^{-1} + CT^n \quad (1); \quad \tau^{-1} = \tau_{QTM}^{-1} + \tau_0^{-1} \exp\left(-\frac{U_{eff}}{T}\right) \quad (2)$$





**Fig. 6** The frequency dependence of the in-phase (top) and out-of-phase (bottom) ac susceptibility signals in the temperature range 2 – 15 K under an applied field of 1000 Oe for **2**.



**Fig. 7** The relaxation rates for **1** (top) and **2** (bottom) from 2 – 3.75 K where the red and blue lines represent the best fit to Raman + QTM or Orbach + QTM relaxation mechanisms, respectively (top). Black vertical bars are estimated standard deviations in the relaxation times derived from Debye fits according to ref 44.

The parameters  $\tau_{QTM}^{-1} = 196(9) \text{ s}^{-1}$ ,  $C = 1.0(1) \text{ K}^{-n} \text{ s}^{-1}$  and  $n = 6.52(8)$  were obtained from fitting the tau values of **1** across a 2 – 3.75 K range using equation 1. For **2**, the parameters  $\tau_{QTM}^{-1} = 71(11) \text{ s}^{-1}$ ,  $C = 3.5(2) \text{ K}^{-n} \text{ s}^{-1}$  and  $n = 5.40(4)$  were obtained using equation 1. Attempts to model the relaxation rate using a Direct process resulted in a poor quality of fit and unreasonable parameters. A decrease in  $\tau_{QTM}^{-1}$  is observed in compound **2**, which is surprising due to its more distorted structure and shorter intermolecular Yb(III)···Yb(III) distances. However, the use of a larger applied dc magnetic field in the ac measurements is consistent with a decrease in  $\tau_{QTM}^{-1}$  for **2**. Furthermore, a significant change in Raman relaxation is observed, as might be expected for a change in intermolecular packing and the introduction of an anion that possesses different Raman active vibrational modes.<sup>46,47,48</sup>

Alternatively, compounds **1** and **2** can be fitted using Orbach and QTM relaxation mechanisms and equation 2. This fit produces a noticeably poorer fit at low temperatures (Fig. 7). However, at higher temperatures the Orbach mechanism provides an accurate fit to the tau values. The parameters obtained from the alternative fit for compounds **1** and **2** are  $\tau_{QTM}^{-1} = 316(41) \text{ s}^{-1}$ ,  $U_{\text{eff}} = 23.2(8) \text{ K}$  and  $\tau_0 = 3.8(8) \times 10^{-7} \text{ s}$  and  $\tau_{QTM}^{-1} = 213(32) \text{ s}^{-1}$ ,  $U_{\text{eff}} = 19.4(6) \text{ K}$ , and  $\tau_0 = 1.4(2) \times 10^{-6} \text{ s}$ , respectively. A summary of all extracted parameters can be found in Table 1.

A small increase in  $U_{\text{eff}}$  observed in **1** could be attributed to an increased crystal field splitting resulting from the tetragonal symmetry imposed by the  $[\text{BPh}_4]^-$  anion. However, from the magnetic data alone it is impossible to discern whether Raman or Orbach relaxation are observed in compounds **1** and **2**. However, as Orbach relaxation is only permitted to proceed through a ‘real state’, *ab initio* calculations were conducted to determine the crystal field splitting of the Kramers doublets and probe for the presence of a real Kramers doublet around 20 K.

### Theoretical studies

The *ab initio* calculations for estimating the spin Hamiltonian parameters have been performed using the MOLCAS programme package.<sup>49</sup> SINGLE\_ANISO<sup>50</sup> calculations were carried out to determine the  $g$ -tensors of the low-lying eight Kramers Doublets (KDs). The  $U_{\text{cal}}$  values,  $g$  factor anisotropy, crystal field parameters and the direction of  $g_{zz}$  of the ground KD were extracted. The energy distribution of the  $m_J$  states, composition of the  $m_J$  states,  $g$  tensors and angle of the excited state  $g_{zz}$  tensors with respect to the ground  $g_{zz}$  tensor of **1** and **2** are shown in Table 2.

**Table 1** A comparison of the QTM, Raman and Orbach parameters extracted from the different fits of the relaxation rates for compounds **1** and **2**.

	Raman + QTM			Orbach + QTM		
	C ( $\text{K}^{-n} \text{ s}^{-1}$ )	n	$\tau_{QTM}^{-1}$ ( $\text{s}^{-1}$ )	$U_{\text{eff}}$ (K)	$\tau_0 \times 10^{-7}$ (s)	$\tau_{QTM}^{-1}$ ( $\text{s}^{-1}$ )
<b>1</b>	1.0(1)	6.52(8)	196(9)	23.2(8)	3.8(8)	316(41)
<b>2</b>	3.5(2)	5.40(4)	71(11)	19.4(6)	14(2)	213(32)



**Table 2** The energy distribution and composition of the states,  $g$  tensors and angle of the excited state  $g_{zz}$  tensors with respect to the ground  $g_{zz}$  tensor of compounds **1** and **2**. DOI: 10.1039/D5DT01565K

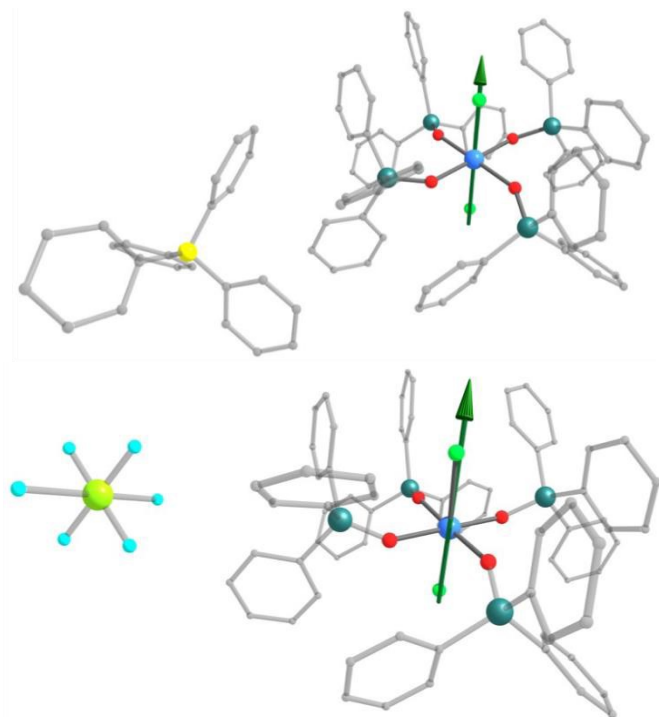
Compound 1						
Multiplet	Energy (cm <sup>-1</sup> )	Composition	$g_{xx}$	$g_{yy}$	$g_{zz}$	Angle with the ground state
1	0.0	0.94   $\pm 7/2$ > + 0.06   $\pm 5/2$ >	0.165	0.343	7.455	-
2	429.0	0.63   $\pm 5/2$ > + 0.37   $\pm 3/2$ >	3.994	3.607	2.315	0.01
3	600.2	0.06   $\pm 7/2$ > + 0.93   $\pm 1/2$ >	4.566	4.045	0.657	0.1
4	698.9	0.37   $\pm 5/2$ > + 0.63   $\pm 3/2$ >	3.970	3.645	0.085	0.1
Compound 2						
Multiplet	Energy (cm <sup>-1</sup> )	Composition	$g_{xx}$	$g_{yy}$	$g_{zz}$	Angle with the ground state
1	0.0	0.91   $\pm 7/2$ > + 0.05   $\pm 1/2$ >	0.121	0.335	7.500	-
2	430.8	0.62   $\pm 5/2$ > + 0.36   $\pm 3/2$ >	3.951	3.664	2.298	6.7
3	578.8	0.92   $\pm 1/2$ >	5.092	3.527	0.662	2.4
4	679.1	0.36   $\pm 5/2$ > + 0.62   $\pm 3/2$ >	4.600	3.054	0.042	4.2

The four Kramers doublets in the  $^2F_{7/2}$  ground state of **1** span 699 cm<sup>-1</sup>. The ground state comprises relatively pure  $m_J = \pm 7/2$  states with a small contribution from the  $m_J = \pm 5/2$  states (Table 2). The ground Kramers doublet also possesses only small transverse  $g$  tensor components ( $g_{xx} = 0.165$ ,  $g_{yy} = 0.343$ ) with  $g_{zz} = 7.455$ , which generates a large axial magnetic anisotropy.

Whilst the excited KDs (2–4) possess highly admixed states and significant transverse anisotropy, the  $g_{zz}$  angles remain highly collinear with the ground state. This is attributed to the high degree of axial symmetry within **1** (*vide supra*).

The four Kramers doublets in the  $^2F_{7/2}$  ground state of **2** span 679 cm<sup>-1</sup>, similar to the splitting in **1**. A small decrease in the purity of the ground state is observed (94 %  $\pm 7/2$  in **1** and 91%  $\pm 7/2$  in **2**), with an increased contribution from the more oblate  $m_J = \pm 1/2$  states. This can be rationalised by the increased distortion in **2** which generate larger calculated transverse crystal field parameters (see Table S5) resulting in an increased admixture of  $m_J$  states. The ground Kramers doublet possesses a large magnetic anisotropy with  $g_{zz} = 7.500$  and small transverse  $g_{xx} = 0.121$  and  $g_{yy} = 0.335$  terms, similar to **1**. Most notable is the decrease in collinearity of the excited KD  $g_{zz}$  tensors with the ground state  $g_{zz}$  tensor, compared to **1**. This indicates that the breaking of tetragonal symmetry in **2** generates a significant loss of axuality in the excited states, which has been attributed to faster relaxation of the magnetisation in a number of SMMs. As such, symmetry enforcing of perfect L-Yb-L bond angles is an important route to generate SMMs that display strong axuality throughout the excited Kramers doublets.

The  $g_{zz}$  anisotropy axis is aligned along the Cl-Yb-Cl (180°) axis coincident with the  $S_4$  rotoinversion axis in **1**, whereas in **2** the  $g_{zz}$  anisotropy axis deviates from the Cl-Yb-Cl (~176°) axis (Fig. 8). In **1** and **2** the first excited Kramers doublets at 429 and 431 cm<sup>-1</sup> are an admixture of the  $\pm 5/2$  and  $\pm 3/2$   $m_J$  states and possesses a significant transverse contribution ( $g_{xx} = 3.994$ ,  $g_{yy} = 3.607$  for **1** and  $g_{xx} = 3.951$ ,  $g_{yy} = 3.664$  for **2**). Despite the collinear anisotropy axis of the first excited Kramers doublet in **1**, the large transverse anisotropy indicates that relaxation of the magnetisation cannot proceed through an energy barrier larger than the splitting between the ground and first excited



**Fig. 8** The calculated anisotropy axis (dark green arrow) of the ground state Kramers doublet of **1** (top) and **2** (bottom), where As, green-blue; B, yellow; C, grey; Cl, light green; F, cyan; O, red; P, lime; Yb, blue; with H atoms omitted





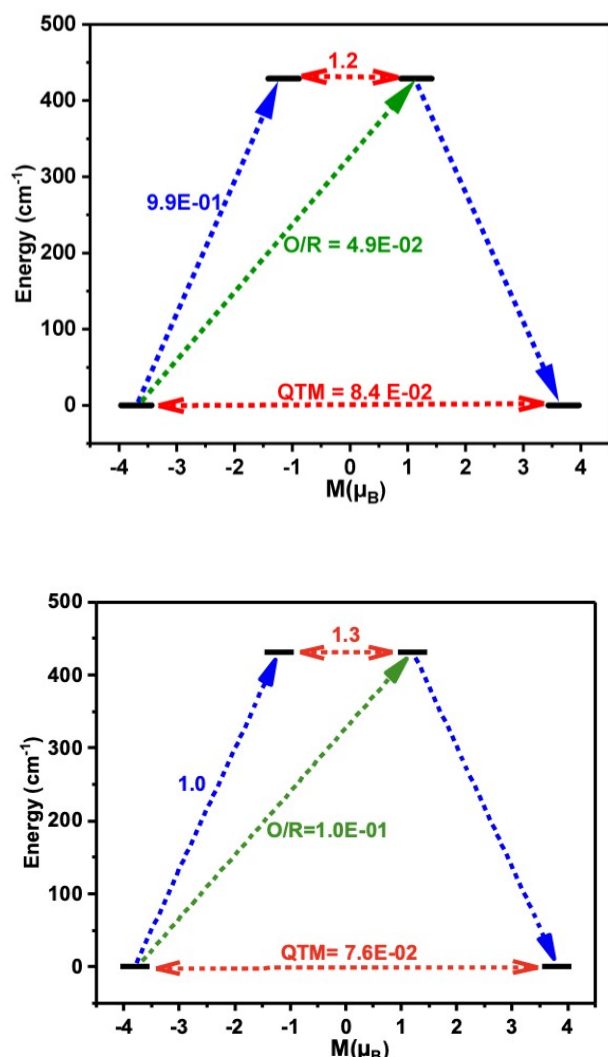


Fig. 9 *Ab-initio* calculated relaxation dynamics and energy splitting between the ground and first excited Kramers doublets for **1** (top) and **2** (bottom). The arrows show the connected energy states and the accompanying number represents the transverse matrix element for the transition magnetic moments. Where QTM = red, Orbach/Raman = Green, Orbach = blue.

Kramers doublet. This gives rise to a large  $U_{\text{cal}}$  value of  $429 \text{ cm}^{-1}$  (Fig. 9). Compound **2** also displays significant transverse anisotropy and a decrease in collinearity in the first excited Kramers doublet, with a similar  $U_{\text{cal}}$  value of  $431 \text{ cm}^{-1}$ .

In both compounds, relaxation of the magnetisation is predicted to proceed through the first excited Kramers doublet (Fig. 9). However, this does not correlate well with the absence of signal in the out-of-phase magnetic susceptibility under no external applied field. This indicates that other factors contribute towards a fast relaxation of the magnetic moment in **1** and **2**. Under an applied magnetic field, the extracted  $U_{\text{eff}}$  barriers of  $23.2(8)$  and  $19.4(6)$  K for **1** and **2**, respectively are far too small compared to the calculated splitting of the Kramers doublets and  $U_{\text{cal}}$ . It should be noted that the crystal field states for Yb(III) are generally overestimated in the computational methodology employed, as seen in other Yb(III) complexes,<sup>23</sup> and that there is significant transverse anisotropy that will

reduce the calculated barrier height due to QTM. Nevertheless, the absence of a real  $m_J$  state around 20 K indicates that Raman relaxation is likely the dominant mechanism controlling magnetic relaxation in **1** and **2**. This is consistent with the use of Raman and QTM to fit the dynamic magnetic data in **1** and **2** and suggests that these Yb(III) complexes display highly efficient Raman relaxation.

## Conclusions

We have demonstrated that by judicious choice of anion, it is possible to generate high symmetry Yb(III) SMMs. The alignment of the molecular  $S_4$  axes of both  $[\text{Yb}(\text{Ph}_3\text{AsO})_4\text{Cl}_2]^+$  and  $[\text{BPh}_4]^-$  molecules generates a tetragonal crystal lattice and enforces a perfectly linear Cl-Yb-Cl bond angle within the SMM unit of **1**, aligning the anisotropy axis of the first excited Kramers doublet in particular. Whilst the breaking of tetragonal symmetry in compound **2** does not lead to drastic changes in the observed slow magnetic relaxation, a significant decrease in the *ab initio* calculated collinearity of the anisotropy axes of the excited Kramers doublets is observed, alongside a change in the ground  $m_J = \pm 7/2$  state composition with a small admixture of the  $m_J = \pm 1/2$  states.

Even with the  $180^\circ$  Cl-Yb-Cl angle and very small distortion of the equatorial ligand field in **1**, the calculated relaxation barrier ( $U_{\text{cal}} \sim 430 \text{ cm}^{-1}$ ) is not observed. We suggest that this is due to a highly efficient Raman relaxation, that occurs in compounds **1** and **2**. Many Yb(III) complexes display a similar relaxation profile to **1** and **2**, hinting that Yb(III) ions may be highly susceptible to Raman relaxation or, as proposed by other groups, other efficient relaxation mechanisms. This may indicate that a suitable ligand field has not been found to complement the unusual electron density distribution of the  $m_J = +7/2$  state. The identification and suppression of this relaxation mechanism now proves the next major hurdle to overcome in the search for high-performance Yb(III) SMMs. Nonetheless, we propose that symmetry enforcing of perfect L-Ln-L bond angles, through careful anion selection, may prove a powerful strategy for obtaining future high-performance Yb(III) SMMs.

## Author contributions

EL and HH carried out the synthesis, sample characterisation, magnetic measurements and data analysis, advised by MM. EL and SD carried out the crystallographic measurements and data analysis, advised by CW. Calculations were carried out by TS, advised by GR. MM and EL devised and supervised the project. The manuscript was written by EL and MM with input from all authors.

## Conflicts of interest

There are no conflicts to declare.

## Data availability





Crystallographic data for **1** and **2** have been deposited under CCDC 2469525-2469526 and can be obtained from <https://www.ccdc.cam.ac.uk/structures/>.

## Acknowledgements

MM thanks EPSRC UK (EP/T517896/1) for funding. GR thanks DST/SERB (SB/SJF/2019-20/12; CRG/2022/001697) for funding. For the purpose of open access, the authors have applied a Creative Commons Attribution (CC BY) licence to any Author Accepted Manuscript version arising from this submission.

## References

- C. A. P. Goodwin, F. Ortu, D. Reta, N. F. Chilton and D. P. Mills, *Nature*, 2017, **548**, 439–442.
- F.-S. Guo, B. M. Day, Y.-C. Chen, M.-L. Tong, A. Mansikkamäki and R. A. Layfield, *Science*, 2017, **362**, 1400–1403.
- W. Xu, Q. Luo, Z. Li, Y. Zhai and Y. Zheng, *Adv. Sci.*, 2024, **11**, 2308548.
- J. Liu, Y.-C. Chen, J.-L. Liu, V. Vieru, L. Ungur, J.-H. Jia, L. F. Chibotaru, Y. Lan, W. Wernsdorfer, S. Gao, X.-M. Chen and M.-L. Tong, *J. Am. Chem. Soc.*, 2016, **138**, 5441–5450.
- Y. Ding, T. Han, Y. Zhai, D. Reta, N. F. Chilton, R. E. P. Winpenny and Y. Zheng, *Chem. Eur. J.*, 2020, **26**, 5893–5902.
- A. B. Canaj, S. Dey, C. Wilson, O. Céspedes, G. Rajaraman and M. Murrie, *Chem. Commun.*, 2020, **56**, 12037–12040.
- N. Ishikawa, M. Sugita, T. Ishikawa, S.-y. Koshihara and Y. Kaizu, *J. Am. Chem. Soc.*, 2003, **125**, 8694–8695.
- Y. Chen, F. Ma, X. Chen, B. Dong, K. Wang, S. Jiang, C. Wang, X. Chen, D. Qi, H. Sun, B. Wang, S. Gao and J. Jiang, *Inorg. Chem.*, 2017, **56**, 13889–13896.
- M. G. Bernbeck, A. P. Orlova, J. D. Hilgar, M. Gembicky, M. Ozerov and J. D. Rinehart, *J. Am. Chem. Soc.*, 2024, **146**, 7243–7256.
- A. P. Orlova, M. S. Varley, M. G. Bernbeck, K. M. Kirkpatrick, P. C. Bunting, M. Gembicky and J. D. Rinehart, *J. Am. Chem. Soc.*, 2023, **145**, 22265–22275.
- Y. Duan, L. E. Rosaleny, J. T. Coutinho, S. Giménez-Santamarina, A. Scheie, J. J. Baldoví, S. Cardona-Serra and A. Gaita-Ariño, *Nat. Commun.*, 2022, **13**, 7626.
- H. Kwon, K. R. McClain, J. G. C. Kragoskow, J. K. Staab, M. Ozerov, K. R. Meihaus, B. G. Harvey, E. S. Choi, N. F. Chilton and J. R. Long, *J. Am. Chem. Soc.*, 2024, **146**, 18714–18721.
- S. K. Gupta, T. Rajeshkumar, G. Rajaraman and R. Murugavel, *Chem. Commun.*, 2016, **52**, 7168–7171.
- J. Chen, T.-D. Zhou and W. Sun, *Dalton Trans.*, 2023, **52**, 4643–4657.
- Y. Liu, B.-H. Lyu, S.-N. Du, G.-Z. Huang, Z.-Y. Ruan, S.-G. Wu, J.-L. Liu and M.-L. Tong, *Dalton Trans.*, 2021, **50**, 6778–6783.
- R. Marin, G. Brunet and M. Murugesu, *Angew. Chem. Int. Ed.*, 2021, **60**, 1728–1746.
- M. J. Klein, *Am. J. Phys.*, 1952, **20**, 65–71.
- J. Flores Gonzalez, H. Douib, B. Le Guennic, F. Pointillart and O. Cador, *Inorg. Chem.*, 2021, **60**, 540–544; K. S. Pedersen, J. Dreiser, H. Weihe, R. Sibille, H. V. Johannesen, M. A. Sørensen, B. E. Nielsen, M. Sigrist, H. Mutka, S. Rols, J. Bendix and S. Piligkos, *Inorg. Chem.*, 2015, **54**, 7600–7606.
- G. K. Gransbury, H. M. Nicholas, S. R. Murphy, J. Emerson-King, M. Vonci, C. A. P. Goodwin, R. E. P. Winpenny, N. F. Chilton, M. J. Giansiracusa and D. P. Mills, *Inorg. Chem.*, 2024, **63**, 22422–22434.
- K. R. Meihaus and J. R. Long, *J. Am. Chem. Soc.*, 2013, **135**, 17952–17957; P. Zhang, L. Zhang, C. Wang, S.-Y. Lin and J. Tang, *J. Am. Chem. Soc.*, 2014, **136**, 4484–4487.
- J. D. Rinehart and J. R. Long, *Chem. Sci.*, 2011, **2**, 2078–2085.
- J. Wang, J. J. Zakrzewski, M. Heczko, M. Zychowicz, K. Nakagawa, K. Nakabayashi, B. Sieklucka, S. Chorazy and S.-i. Ohkoshi, *J. Am. Chem. Soc.*, 2020, **142**, 3970–3979.
- A. Borah, S. Dey, S. K. Gupta, M. G. Walawalkar, G. Rajaraman and R. Murugavel, *Chem. Commun.*, 2020, **56**, 11879–11882.
- K. Soussi, J. Jung, F. Pointillart, B. Le Guennic, B. Lefevre, S. Golhen, O. Cador, Y. Guyot, O. Maury and L. Ouahab, *Inorg. Chem. Front.*, 2015, **2**, 1105–1117.
- S. P. Petrosyants, K. A. Babeshkin, A. V. Gavrikov, A. B. Ilyukhin, E. V. Belova and N. N. Efimov, *Dalton Trans.*, 2019, **48**, 12644–12655.
- P.-H. Lin, W.-B. Sun, Y.-M. Tian, P.-F. Yan, L. Ungur, L. F. Chibotaru and M. Murugesu, *Dalton Trans.*, 2012, **41**, 12349.
- J.-L. Liu, Y.-C. Chen and M.-L. Tong, *Chem. Soc. Rev.*, 2018, **47**, 2431–2453.
- D. N. Woodruff, R. E. P. Winpenny and R. A. Layfield, *Chem. Rev.*, 2013, **113**, 5110–5148.
- A. B. Canaj, S. Dey, E. R. Martí, C. Wilson, G. Rajaraman and M. Murrie, *Angew. Chem. Int. Ed.*, 2019, **58**, 14146–14151.
- S. Liu, Y. Gil, C. Zhao, J. Wu, Z. Zhu, X.-L. Li, D. Aravena and J. Tang, *Inorg. Chem. Front.*, 2022, **9**, 4982–4989.
- P. K. Sahu, A. Mondal and S. Konar, *Chem. Eur. J.*, 2023, **29**, e202203664.
- E. Lowe, C. Wilson, A. B. Canaj and M. Murrie, *Dalton Trans.*, 2025, **54**, 477–481; A. B. Canaj, M. K. Singh, C. Wilson, G. Rajaraman and M. Murrie, *Chem. Commun.*, 2018, **54**, 8273–8276.
- R. Herchel, P. Zoufalý and I. Nemec, *RSC Adv.*, 2019, **9**, 569–575.
- S. S. Leiszner, M. Perfetti, E. Damgaard-Møller, Y.-S. Chen and B. B. Iversen, *Dalton Trans.*, 2024, **53**, 19246–19255.
- Y. Gil, L. Llanos, P. Cancino, P. Fuentealba, A. Vega, E. Spodine and D. Aravena, *J. Phys. Chem. C*, 2020, **124**, 5308–5320.
- M. Pinsky, D. Avnir, *Inorg. Chem.*, 1998, **37**, 5575–5582; G. Alon and I. Tuvi-Arad, *J. Math. Chem.*, 2018, **56**, 193–212.
- O. A. Blackburn, R. M. Edkins, S. Faulkner, A. M. Kenwright, D. Parker, N. J. Rogers and S. Shuvaev, *Dalton Trans.*, 2016, **45**, 6782–6800.
- D. Parker, E. A. Suturina, I. Kuprov and N. F. Chilton, *Acc. Chem. Res.*, 2020, **53**, 1520–1534.
- S. Chorazy, M. Rams, J. Wang, B. Sieklucka and S.-i. Ohkoshi, *Dalton Trans.*, 2017, **46**, 13668–13672.
- A. V. Gavrikov, A. Ilyukhin, I. V. Taydakov, M. T. Metlin, N. Datskevitch, M. E. Buzoverov, K. A. Babeshkin and N. N. Efimov, *Dalt. Trans.*, 2023, **52**, 17911–17927.
- X. Yi, K. Bernot, V. Le Corre, G. Calvez, F. Pointillart, O. Cador, B. Le Guennic, J. Jung, O. Maury, V. Placide, Y. Guyot, T. Roisnel, C. Daiguebonne and O. Guillou, *Chem. Eur. J.*, 2014, **20**, 1569–1576.
- D. Gatteschi and C. Benelli, *Introduction to Molecular Magnetism: From Transition Metals to Lanthanides*, Wiley-VCH, 2015.
- M. L. Kahn, C. Mathonière and O. Kahn, *Inorg. Chem.*, 1999, **38**, 3692–3697.
- D. Reta and N. F. Chilton, *Phys. Chem. Chem. Phys.*, 2019, **21**, 23567–23575.
- W. J. A. Blackmore, G. K. Gransbury, P. Evans, J. G. C. Kragoskow, D. P. Mills and N. F. Chilton, *Phys. Chem. Chem. Phys.*, 2023, **25**, 16735–16744.
- G. Handzik, M. Magott, M. Arczyński, A. M. Sheveleva, F. Tuna, S. Baran and D. Pinkowicz, *Dalton Trans.*, 2020, **49**, 11942–11949.
- W. Huang, R. A. Wheeler and R. Frech, *Spectrochim. Acta A*, 1994, **50**, 985–996.



## Journal Name

## ARTICLE

- 48 X. Xuan, J. Wang and H. Wang, *Electrochim. Acta*, 2005, **50**, 4196–4201.
- 49 G. Karlström, R. Lindh, P.-Å. Malmqvist, B. O. Roos, U. Ryde, V. Veryazov, P.-O. Widmark, M. Cossi, B. Schimmelpfennig, P. Neogady and L. Seijo, *Comput. Mater. Sci.*, 2003, **28**, 222–239.
- 50 L. F. Chibotaru and L. Ungur, *J. Chem. Phys.*, 2012, **137**, 064112.

View Article Online  
DOI: 10.1039/D5DT01565K



View Article Online  
DOI: 10.1039/D5DT01565K

## Data availability

Crystallographic data for **1** and **2** have been deposited under CCDC 2469525-2469526 and can be obtained from <https://www.ccdc.cam.ac.uk/structures/>.

