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COMMUNICATION

Slow magnetic relaxation in carbonato-bridged dinuclear lanthanide(III) complexes with 2,3-quinoxalinediolate ligands†

Julia Vallejo,^a Joan Cano,^{ab} Isabel Castro,^{*a} Miguel Julve,^a Francesc Lloret,^a Oscar Fabelo,^{cd} Laura Cañadillas-Delgado^{†cd} and Emilio Pardo^{*a}

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The coordination chemistry of the 2,3-quinoxalinediolate ligand with different lanthanide(III) ions in basic media in air affords a new family of carbonato-bridged M_2^{III} compounds ($M = \text{Pr, Gd and Dy}$), the Dy_2^{III} analogue exhibiting slow magnetic relaxation behaviour typical of single-molecule magnets.

Among the different types of molecular magnetic materials¹ that coordination chemistry can offer, discrete polynuclear complexes of highly anisotropic metal ions are of special interest due to the possibility of obtaining the so-called single-molecule magnets (SMMs).¹ These molecules exhibit slow relaxation of the magnetisation below a blocking temperature (T_B) and they have potential applications in high-density magnetic memories, molecular spintronics and quantum computing devices. A SMM requires a ground state with both a high spin (S) and a large negative axial magnetic anisotropy (D), properties that ultimately depend on the nuclearity and topology, but also on the nature of the metal ion and the bridging ligand.² Lanthanide(III) ions are good candidates to obtain SMMs as they have larger spin and single ion anisotropy values than transition metal ions, the best candidates being dysprosium(III), terbium(III) and holmium(III) ions. Hence, a wide variety of lanthanide complexes exhibiting slow relaxation of the magnetisation have been reported in recent years.³

As a part of our first exploratory studies on the coordination chemistry of the tautomeric ligand 1,4-dihydroquinoxaline-2,3-dione (H_2L , Chart 1),⁴ we report herein the synthesis, crystal structure, physical and magnetic properties of a new

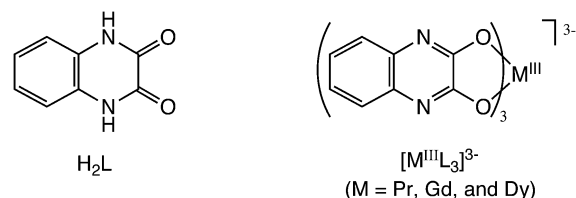


Chart 1

family of dinuclear lanthanide(III) complexes of general formula $(\text{Me}_4\text{N})_6\{\text{K}_2(\text{H}_2\text{O})_4[\text{M}_2^{III}\text{L}_6(\mu\text{-CO}_3)]\} \cdot n\text{H}_2\text{O}$ [$M = \text{Pr}$ (**1**), Gd (**2**) and Dy (**3**)]. Interestingly, complex **3** exhibits slow magnetic relaxation effects typical of SMMs, constituting thus the first example of a 2,3-quinoxalinediolate-based SMM. In this regard, it is worth mentioning the related 2,3-quinoxalinediolate-bridged cobalt(II) chain reported recently by Yang *et al.* that behaves as a single-chain magnet (SCM).^{4e}

Complexes **1–3** were prepared from the reaction of 1,4-dihydroquinoxaline-2,3-dione (H_2L) and the corresponding hydrated lanthanide(III) chloride in basic methanolic solutions in the presence of potassium chloride. The formation of the carbonato-bridged dinuclear complex instead of the expected mononuclear species, $[\text{M}^{III}\text{L}_3]^{3-}$ ($M = \text{Pr, Gd, and Dy}$, Chart 1), would be explained by the well-known CO_2 uptake from the air in basic media.

Complexes **1–3** crystallise in the centrosymmetric $P2_1/c$ space group of the monoclinic system. The crystal structure of **1** as a representative example of this series of isomorphous complexes was solved by single-crystal X-ray diffraction with synchrotron radiation.

The structure of **1** consists of discrete carbonato-bridged dinuclear praseodymium(III) complex anions, $[\text{Pr}_2^{III}\text{L}_6(\mu\text{-CO}_3)]^{8-}$, and coordinated potassium cations, together with tetramethylammonium counteranions and both coordinated and free water molecules (Fig. 1; Fig. S1 and S2, ESI†).

The unit cell of **1** contains two crystallographically independent dinuclear complex anions (Fig. S1, ESI†) that can be described as two propeller-like, tris(chelated) $[\text{Pr}^{III}\text{L}_3]^{3-}$ mononuclear units bridged by a symmetric bis-bidentate CO_3^{2-} ligand (Fig. 1(b) and (c)).⁵ Each of the four crystallographically independent Pr atoms is eight-coordinate. The eight-fold PrO_8 coordination geometry can be described as a bicapped triangular prism with six oxygen atoms from three chelating L^{2-} ligands and two oxygen atoms from the bridging carbonate [$\text{Pr-O} = 2.478(10)\text{--}2.422(11)\text{ \AA}$

^a Departament de Química Inorgànica, Instituto de Ciencia Molecular (ICMOL), Universitat de València, 46980 Paterna, València, Spain. E-mail: Isabel.Castro@uv.es, Emilio.Pardo@uv.es; Fax: +34 3543273; Tel: +34 3544442

^b Fundació General de la Universitat de València (FGUV), Universitat de València, 46980 Paterna, València, Spain

^c Instituto de Ciencia de Materiales de Aragón, CSIC-Universidad de Zaragoza, Zaragoza, 50009, Spain

^d Institut Laue Langevin, Grenoble, 38042, France

† Electronic supplementary information (ESI) available: Preparation and physical characterization data of **1–3**, details of the least-squares fitting of the magnetic data of **2**, additional Fig. S1–S5, crystallographic refinement details for **1–3** (Table S1). CCDC 883544–883546 (**1–3**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc33674j

‡ Present address: Centro Universitario para la Defensa, Academia General Militar, Ctra de Huesca s/n, 50090 Zaragoza, Spain.

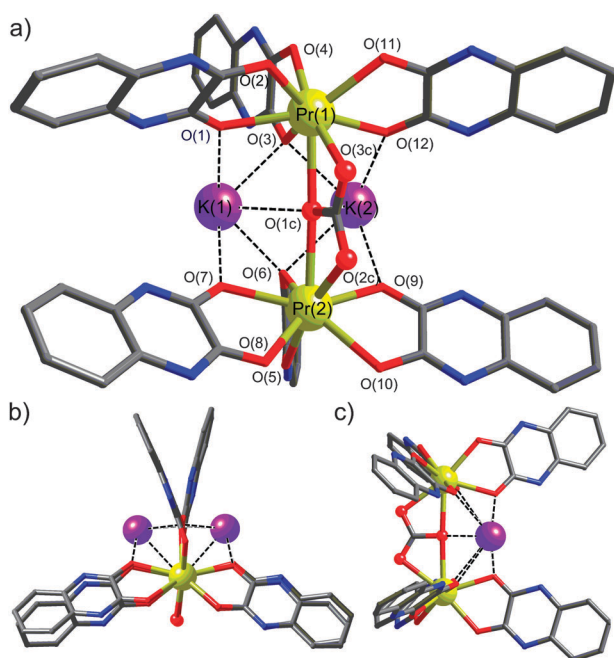


Fig. 1 (a) Perspective view of one of the four crystallographically independent K_2Pr_2 entities of **1** with the atom-numbering scheme of the metal environments (Pr, yellow; K, purple; N, blue; O, red; C, grey). The hydrogen atoms have been omitted for clarity. The dashed lines represent the weak K–O coordinative interactions. (b) Top and (c) side projection views of the anionic K_2Pr_2 unit of **1**. The oxygen atoms from the carbonate group are represented by red spheres. The hydrogen atoms have been omitted for clarity.

and $Pr-OCO_2 = 2.636(9)-2.451(9)$ Å]. Within the dinuclear anion, each $[Pr^{III}L_3]^{3-}$ mononuclear unit is bound to two carbonate-bridged tetra(aqua) potassium(i) units through one of the two quinoxalineolate-oxygen atoms from the three different L^{2-} ligands [$K-O = 2.854(8)-2.716(11)$ Å, $K-Ow = 2.854(11)-2.59(4)$ Å and $K-OCO_2 = 3.010(8)-2.842(8)$ Å]. So, two L^{2-} groups act as bidentate/monodentate ligands towards a Pr and a K atom, respectively, the third one acting as a bidentate/bis-monodentate ligand towards one Pr and two K atoms, respectively (Fig. 1(a)). Hence, the resulting K_2Pr_2 entity has a pseudo two-fold (C_2) symmetry, whereby carbonate acts as both bis-bidentate and bis-monodentate bridges towards the two Pr atoms and the two K atoms, respectively (Fig. 1(a)). The values of the intramolecular Pr–Pr, Pr–K, and K–K distances through the carbonate are in the ranges 5.2666(13)–5.2029(14), 3.967(3)–3.857(4), and 4.019(4)–3.983(5) Å, while the shortest intermolecular Pr–Pr separation is 10.934(2) Å, indicating that the molecules are quite well isolated due to the presence of the tetramethylammonium organic counteranions (Fig. S2, ESI†). These cations are placed between the K_2Pr_2 units along the three crystallographic axes and they are held at the dinuclear anionic complexes only by electrostatic interactions and van der Waals forces ($C-H \cdots N$ distances ranging from 3.69 to 4.42 Å).

The direct current (dc) magnetic properties of **1–3** in the form of the $\chi_M T$ versus T plots (χ_M being the dc molar magnetic susceptibilities per M_2^{III} unit) have been investigated in the temperature range 2.0–300 K (Fig. S3, ESI†). The $\chi_M T$ values of 6.23 (**1**), 15.71 (**2**), and 27.86 $cm^3 mol^{-1} K$ (**3**) at room temperature are very close to those expected for two

non-interacting praseodymium(III) [$\chi_M T = 3.20 cm^3 mol^{-1} K$ with $S = 1$, $L = 5$, 3H_4 , $g = 4/5$ (**1**)], gadolinium(III) [$\chi_M T = 15.76 cm^3 mol^{-1} K$ with $S = 7/2$, $L = 0$, $^8S_{7/2}$, $g = 2$ (**2**)], and dysprosium(III) [$\chi_M T = 28.30 cm^3 mol^{-1} K$ with $S = 5/2$, $L = 5$, $^6H_{15/2}$, $g = 4/3$ (**3**)] ions. The lack of orbital contribution to the magnetic moment of the gadolinium(III) ions makes the magnetic properties of compound **2** the easiest ones to be analysed. Upon cooling, the $\chi_M T$ value for **2** remains constant down to ca. 15 K and then decreases to reach a value of 10.62 $cm^3 mol^{-1} K$ at 2 K. This feature suggests the occurrence of a weak antiferromagnetic interaction between the two gadolinium(III) ions through the CO_3^{2-} bridge. The magnetic properties of **1** and **3** are more complicated because of the intervening first-order angular momentum and crystal field effects of the praseodymium(III) ions and dysprosium(III) ions. Upon cooling, $\chi_M T$ for **1** and **3** decreases gradually and then more rapidly below ca. 50 K to reach values of 0.31 (**1**) and 19.13 $cm^3 mol^{-1} K$ (**3**) at 2.0 K.

Least-squares fitting of the experimental dc magnetic susceptibility data of **2** through eqn (S1) (see ESI†) in the temperature range 2.0–300 K gave $J = -0.12 cm^{-1}$ and $g = 2.00$ (blue solid line in Fig. S3, ESI†), where J is the intramolecular magnetic coupling and g is the Landé factor of the gadolinium(III) ion.

The alternating current (ac) magnetic properties of **3** in the form of the χ'_M and χ''_M versus T plots (χ'_M and χ''_M being the in-phase and out-of-phase ac molar magnetic susceptibilities per Dy_2^{III} unit, respectively) show evidence of slow magnetic relaxation effects which are typical of SMMs (Fig. 2). Thus, both the in-phase (χ'_M) and out-of-phase (χ''_M) components of the ac susceptibility in zero-dc magnetic field show a strong frequency dependence below ca. 16 K, and maxima are observed for χ''_M ranging from 11 ($\nu = 10000$ Hz) to 5.5 K ($\nu = 183$ Hz) (Fig. 2(b)). Moreover, the Cole–Cole plots at different temperatures [the inset of Fig. 2(a)] give almost perfect semicircles which can be fitted by the generalized Debye model.⁶ The calculated values of the α parameter of 0.16, 0.13, 0.20, and 0.14 at 6, 7, 8 and 10 K, respectively, support a single relaxation process discarding thus a spin-glass behaviour ($\alpha = 0$ for a Debye model).⁷ The calculated values of the adiabatic (χ_S) and isothermal (χ_T) susceptibilities are in the ranges of 1.3–2.1 and 3.0–4.9 $cm^3 mol^{-1}$, respectively [solid lines in the inset of Fig. 2(a)].

Interestingly, a fast tunnelling relaxation occurs at zero dc field in **3**, which is marked by the divergence in χ''_M below the blocking temperature (Fig. 2(b)). In fact, this effect almost disappears when a dc field of 5000 G is applied (Fig. S4, ESI†). This behaviour is not rare for lanthanide-based SMMs and it implies that the superparamagnetic blocking is only achieved for high frequencies, because of the fast zero-field quantum tunnelling relaxation.^{3e,f} These quantum tunnelling relaxation effects are likely responsible for the deviations from linearity of the Arrhenius plots in the low temperature region [the inset of Fig. 2(b)]. In the high temperature region, the values of the relaxation time calculated from the maximum of χ''_M at a given frequency ($1/\tau = 2\pi\nu$) follow the Arrhenius law characteristic of a thermally activated mechanism [$\tau = \tau_0 \exp(E_a/k_B T)$] [solid line in the inset of Fig. 2(b)]. The calculated value of the pre-exponential factor for **3** ($\tau_0 = 1.22 \times 10^{-7}$ s) is consistent with those previously reported for other lanthanide-based SMMs, while

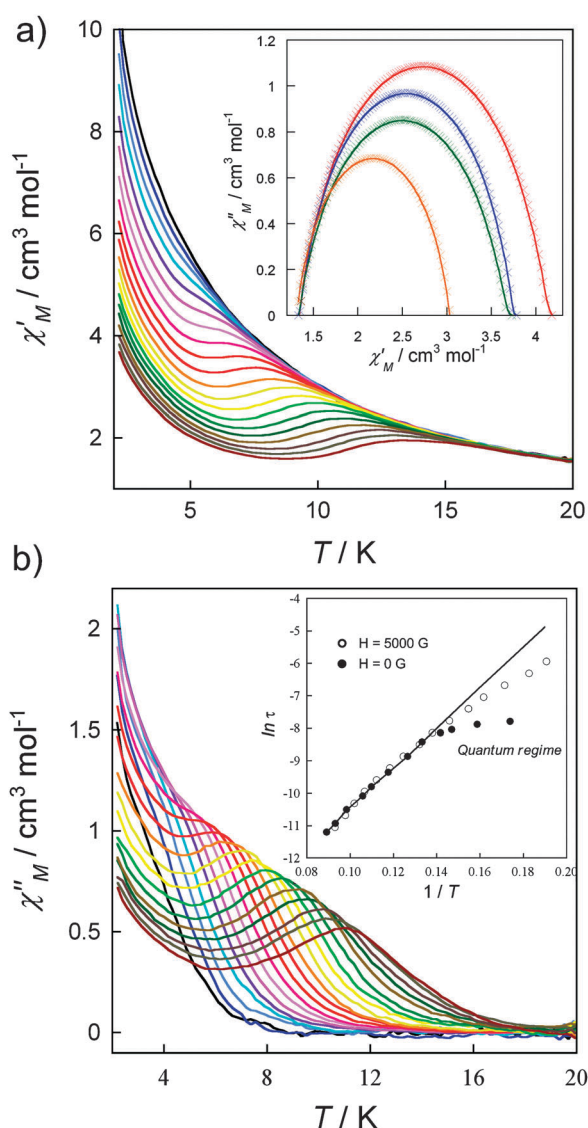


Fig. 2 Temperature dependence of χ'_M (a) and χ''_M (b) of **3** in zero applied static field and under 4 G oscillating field at frequencies in the range of 14–10 000 Hz. The solid lines are only guides for the eye. The insets show the Cole–Cole plots at 6 (red), 7 (blue), 8 (green) and 10 K (orange) (a) and the Arrhenius plots (b) with zero (●) and 5000 G (○) dc magnetic fields. The solid lines are the best-fit curves (see the text).

that of the activation energy ($E_a = 39.1 \text{ cm}^{-1}$) is one of the highest observed for a lanthanide-based SMM.³

In summary, a novel family of carbonato-bridged M_2^{III} compounds ($M = \text{Pr, Gd and Dy}$) has been synthesised using the 2,3-quinoxalinediolate ligand. Although a small but non-negligible intramolecular antiferromagnetic coupling between the gadolinium(III) ions across the carbonate bridge has been found in **2** ($J = -0.12 \text{ cm}^{-1}$), the presence of slow relaxation effects of the Dy_2^{III} derivative strongly suggests the occurrence of an intramolecular ferromagnetic coupling in **3**. This dinuclear dysprosium(III) complex is the first example of quinoxalinediolate-based SMM and exhibits a very large energy barrier. Current efforts are devoted to replace some of the dysprosium(III) ions in **3** by the diamagnetic yttrium(III) ones in order to investigate

the role, if any, of the intramolecular magnetic interactions in the low-temperature magnetic relaxation behaviour. In addition, the synthesis of new examples of quinoxalinediolate-containing dinuclear complexes with other highly anisotropic lanthanide cations such as Tb^{III} and Ho^{III} is also planned in order to get SMMs with even higher values of the blocking temperature.

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