Electronic Supplementary Information (ESI) for the manuscript:

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

Julia Vallejo, Joan Cano, Isabel Castro,* Miguel Julve, Francesc Lloret, Oscar Fabelo, Laura Cañadillas-Delgado and Emilio Pardo*

Results

Magnetic Properties. The dc magnetic susceptibility data of **2** were analysed through the isotropic spin Hamiltonian for a single dinuclear model by assuming that the two crystallografically independent Gd^{III}_2 units present in the crystal lattice of **2** are magnetically equivalent, $\hat{H} = -J\hat{S}_1 \cdot \hat{S}_2 + g(\hat{S}_1 + \hat{S}_2)\beta H$, where J is the mean intramolecular magnetic coupling parameter and g is the Landé factor of the Gd^{III} ions (with $S_1 = S_2 = S_{Gd} = 7/2$). The least-squares fit of the experimental data through eqn (1) [where N is the Avogadro number, β is the Bohr magneton, k is the Boltzmann constant, and $x = J/kT$]: gave $J = -0.12$ cm^{-1} and $g = 2.00$ with $F = 1.1 \times 10^{-5}$, where F is the agreement factor defined as $F = \sum[(\chi_M T)_{exp} - (\chi_M T)_{calcd}]^2/\sum[(\chi_M T)_{exp}]^2$ (blue solid line in Fig. S3).

$$\chi_M T = (2Ng^2\beta^2/k)\ (A/B) \qquad (S1)$$

$$A = 6e^{x} + 30e^{3x} + 84e^{6x} + 180e^{10x} + 330e^{15x} + 546e^{21x} + 840e^{28x} \qquad (S1.1)$$

$$B = 1 + 3e^{x} + 5e^{3x} + 7e^{6x} + 9e^{10x} + 11e^{15x} + 13e^{21x} + 15e^{28x} \qquad (S1.2)$$

Experimental Section

Preparation of complexes 1–3: A methanolic solution (50 mL) of H_2L (1.54 g, 5 mmol) was treated with a 25% methanolic solution of Me_4NOH (5 mL, 12.5 mmol), and the resulting light yellow solution was stirred at 60 ºC for 30 min in the open air. A methanolic solution (25 mL) of the corresponding hydrated lanthanide chloride salts MCl_3 [M = Pr (**1**), Gd (**2**) and Dy (**3**)] (1.67 mmol) was then added dropwise while the reaction mixture was stirred. The resulting colourless solution was concentrated to a volume of 10 mL in a rotary evaporator, and treated successively with diethyl ether and acetone to give a very hygroscopic product (solid or oil) that was immediately dissolved in acetonitrile (100 mL). KCl (0.37 g, 5 mmol) was added in solid and the resulting suspension was heated for 5 h with vigorous stirring and then filtered to discard residual solid particles. A polycrystalline solid precipitated almost immediately when the solution was allowed to cool to room temperature. It was collected by filtration and air-dried. The presence of coordinated carbonate in complexes **1**–**3** was confirmed by the effervescence observed after addition of concentrated HCl over solid samples of **1**–**3**. Well-shaped, large, hexagonal prisms of **1-3** suitable for X-ray structural analysis were obtained by recrystallization from acetonitrile. Compound **1**: Yield: 2.28 g, 67%; Anal.: calcd for $C_{73}H_{117.75}K_2N_{18}O_{25.875}Pr_2$ (2021.6): C, 43.04; H, 5.91; N, 12.37%. Found: C, 43.12; H, 5.71; N, 12.37%; IR (KBr): $\nu = 1517$ and 1469 cm^{-1} (C=O); Compound **2**: Yield: 2.66 g, 77%; Anal.: calcd for $C_{73}H_{118}K_2N_{18}O_{26}Gd_2$ (2056.5): C, 42.36; H, 5.82; N, 12.18%. Found: C, 42.22; H, 5.71; N, 12.19%; IR (KBr): $\nu = 1521$ and 1467 cm^{-1}

(C=O); Compound **3**: Yield: 2.05 g, 59%; Anal.: calcd for $C_{73}H_{118}K_2N_{18}O_{26}Dy_2$ (2067.0): C, 42.14; H, 5.79; N, 12.12%. Found: C, 42.11; H, 5.90; N, 12.08%; IR (KBr): ν = 1519 and 1471 cm^{-1} (C=O). Electron microscopy analysis (M/K molar ratio): 1.02 [M = Pr (**1**)], 1.01 [M = Gd (**2**)] and 1.03 [M = Dy (**3**)].

Concerning the synthetic method used to isolate complexes **1-3** some points need to be considered:

-The addition of KCl is required to precipitate and crystallise **1-3**. Attempts without K^+ did not allow successful results.

-The reactions under ambient conditions ($T \approx$ 300 K), led to the same complexes **1-3**, but the yields were much poorer. At this respect, the heating of the reaction mixture did not promote CO_2 extraction suggesting a robust character for this family of complexes.

- The syntheses were also carried out under argon atmosphere in order to obtain the lanthanide(III) mononuclear complexes. However, although many experiments were done, we were unable to isolate the targeted species.

Physical Techniques. Elemental analyses (C, H and N) were carried out by the Microanalytical Service of the Universitat de València. IR spectra were recorded on a Perkin-Elmer 882 spectrophotometer as KBr pellets. Variable-temperature direct current (dc) magnetic susceptibility measurements were carried out on powdered samples with a Quantum Design SQUID magnetometer. The alternating current (ac) magnetic susceptibility measurements were carried out on polycrystalline samples with a Quantum Design Physical Property Measurement System (PPMS). The susceptibility data were corrected for the diamagnetism of the constituent atoms and the sample holder.

Crystal Structure Data Collection and Refinement. Single crystals of **1-3** were measured using synchrotron radiation (with λ = 0.73790 Å) at the BM16 Spanish beamline of the ESRF (Grenoble, France) with a CCD detector (ADSCq210rCCD). The data collections consist of phi scans and the oscillation range (Δ φ) used for each image was one degree, in all cases. Fast crystal degradation, in part due to the radiation damage, was observed during the data acquisition, precluding optimal data completeness. All data were collected at 100 K to avoid the fast solvent loss. Nevertheless, the low diffraction power together with the degradation problems preclude a better crystal structure determination. Among the three different measurements, compound **1** present a more realistic model. The data obtained from **2** and **3** are good enough to prove that the three compounds are isomorphous, but the low quality of the data preclude a more accurate discussion based on their crystal structures. The structures were solved by direct methods and subsequent Fourier syntheses using the SHELXS-97 program,[1] and were refined by the full-matrix least-squares technique against F^2 using with the SHELXL-97 program for the first cycles. Due to the high numbers of parameters the SHELXS-97 program was used for the final refinements, programs included in the WINGX software package.[2]

Anisotropic thermal parameters were used to refine all non-H atoms in **1**, while in **2** and **3**, solvent molecules and tetramethylammonium counterions were refined with an isotropic model. The treatment of the hydrogen atoms was calculated geometrically for all compounds. Due to the low data quality, different restrains have been used in **1-3**, involving mainly geometrical description of the tetramethylammonium counterions.

The final geometrical calculations and the graphical manipulations were carried out with PARST95,[3] PLATON[4] and DIAMOND[5] programs. The main crystallographic data and some experimental details are shown in Table S1. Further crystallographic details for compounds **1-3** may be obtained from the Cambridge Crystallographic Data Center [CCDC reference numbers: CCDC-883544 (**1**), CCDC-883545 (**2**) and CCDC-883546 (**3**)].

Table S1. Crystal Data and details of the Structure Determination of **1**-**3**.

Compound	**1**	**2**	**3**
T(K)	100(2)	100(2)	100(2)
Formula	$C_{584}H_{946}Pr_{16}K_{16}N_{144}O_{207}$	$C_{292}H_{485}Gd_{8}K_{8}N_{72}O_{104}$	$C_{292}H_{477}Dy_{8}K_{8}N_{72}O_{104}$
M	16176.70	8239.18	8273.121
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	33.559(7)	33.572(7)	33.506(7)
b, Å	16.070(3)	16.084(3)	16.097(3)
c, Å	36.895(7)	36.841(7)	36.714(7)
β, (º)	92.07(3)	91.62(3)	91.40(3)
V, Å^3	19884(7)	19885(7)	19796(7)
Z	1	2	2
Index ranges	$-42 \leq h \leq 42$ $-20 \leq k \leq 20$ $-47 \leq l \leq 47$	$-35 \leq h \leq 35$ $-17 \leq k \leq 17$ $-39 \leq l \leq 39$	$-42 \leq h \leq 42$ $-20 \leq k \leq 18$ $-45 \leq l \leq 46$
ρ_{calc} (Mg m^{-3})	1.360	1.326	1.326
λ (Mo-K$_\alpha$ Å)	0.73790	0.73790	0.73790
μ (Mo-K$_\alpha$, mm^{-1})	1.233	1.625	1.818
R1, $I > 2\sigma(I)$ (all)	0.1286 (0.1429)	0.1355 (0.1454)	0.1865 (0.2048)
wR2, $I > 2\sigma(I)$ (all)	0.3420 (0.3513)	0.3746 (0.3684)	0.4928 (0.5076)
Measured reflections (Rint)	171243 (0.1211)	97404 (0.0814)	103580 (0.1200)
Independent reflections ($I > 2\sigma(I)$)	43499 (35474)	25216 (21778)	40399 (29714)

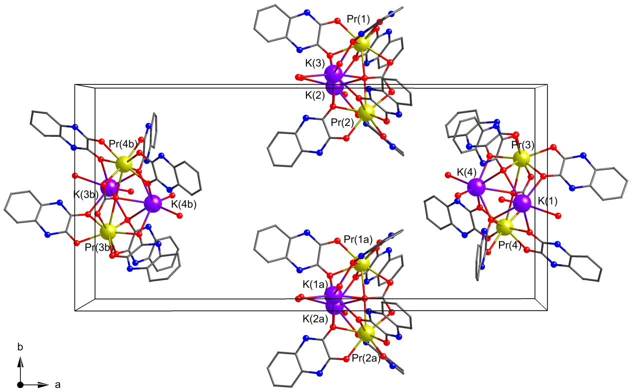

Fig. S1 Perspective view of the unit cell of **1** with the atom-numbering scheme of the metal atoms for the four crystallographically independent $K^{I}_{2}Pr^{III}_{2}$ entities [symmetry code: (a) = *x*, *y* − 1, *z*, (b) = −*x* − 1, −*y* − 1, −*z* – 1]. Praseodymium and potassium atoms are represented by yellow and purple balls, respectively. The hydrogen atoms have been omitted for clarity.

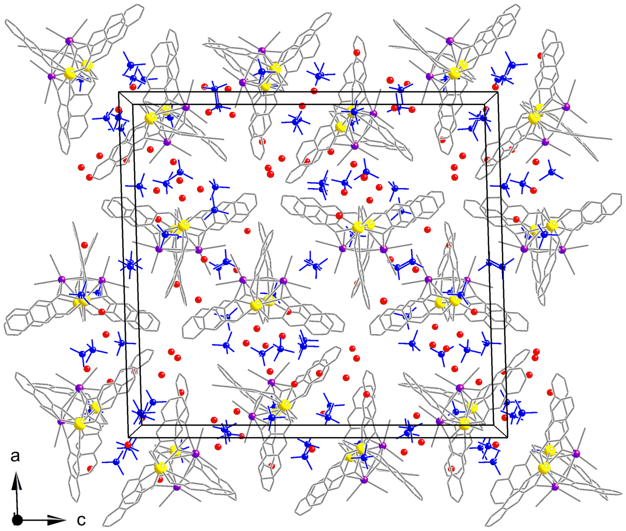

Fig. S2 Projection view of the crystal packing of **1** along the crystallographic *b* axis. Praseodymium and potassium atoms are represented by yellow and purple balls respectively. Tetramethylammonium cations and crystallization water molecules are represented in blue and red, respectively.

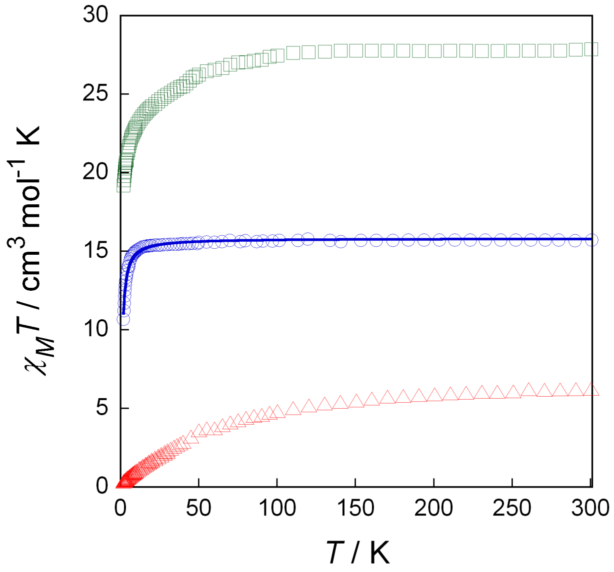

Fig. S3 Temperature dependence of $\chi_M T$ for **1** (Δ), **2** (○) and **3** (□). The solid line for **2** corresponds to the best fit (see text).

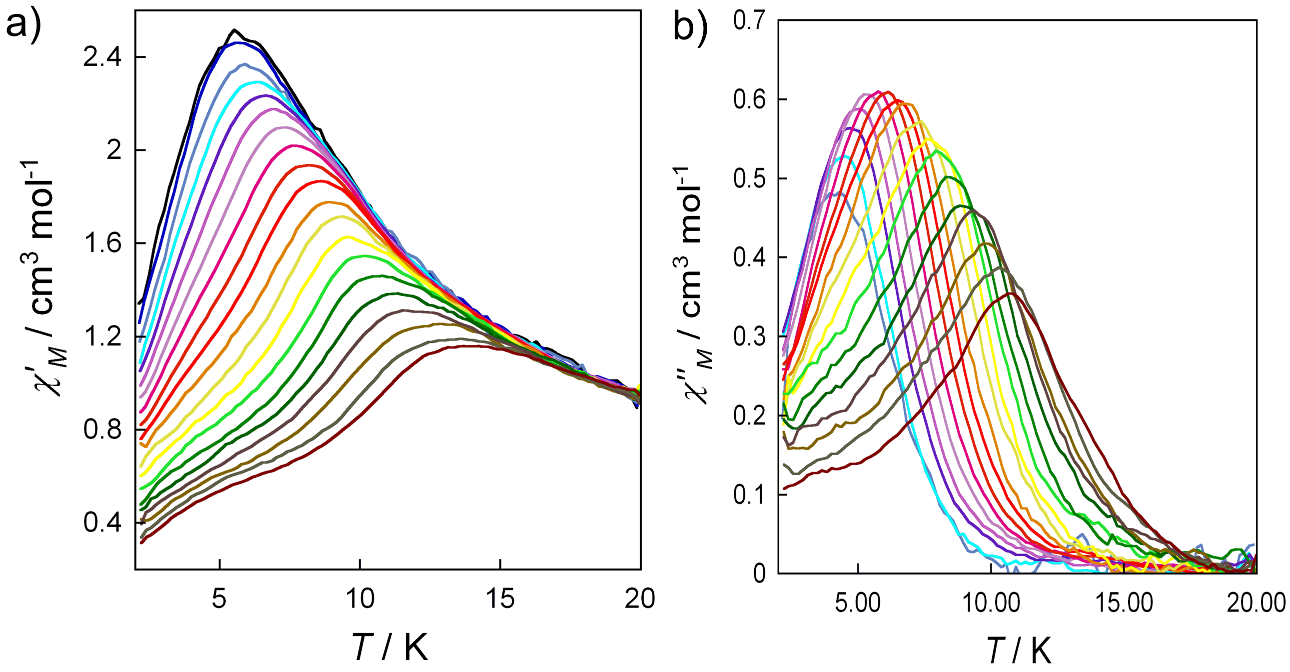

Fig. S4 Temperature dependence of χ_M‘ (a) and χ_M” (b) of **3** under an applied dc field of 5000 G in the frequency range of 14-10000 Hz. The solid lines are only guides for the eye.

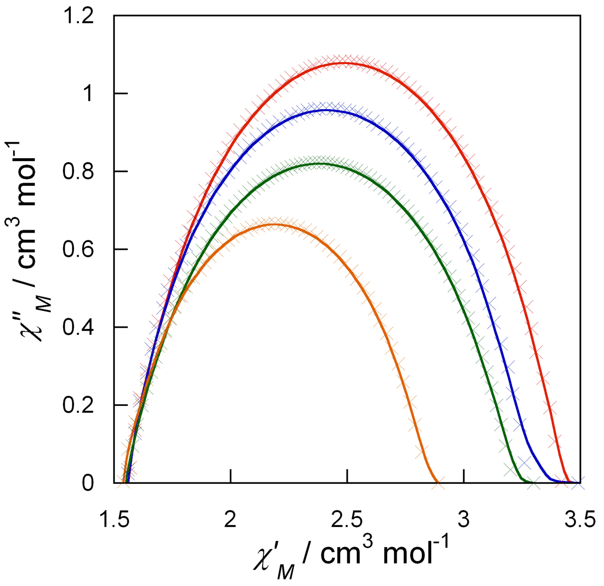

Fig. S5 Cole-Cole plots of **3** at 6 (red), 7 (blue), 8 (green) and 10 (orange) K under a dc applied field of 5000 G.

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