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A step further in the comprehension of the magnetic coupling in gadolinium(III)-based carboxylate complexes

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ABSTRACT

Three new gadolinium(III) complexes of formula $[Gd_4(bta)_3(H_2O)_{16}]_n \cdot 12nH_2O$ (**1**), $[Gd_4(bta)_3(H_2O)_{12}]_n \cdot 18nH_2O$ (**2**) and $[Gd_2(H_2bta)(bta)(H_2O)_2]_n \cdot 4nH_2O$ (**3**) (H_4bta = 1,2,4,5-benzenetetracarboxylic acid) have been synthesized and their structures determined by X-ray diffraction. **1** and **3** are three-dimensional compounds whereas **2** exhibits a two-dimensional structure. The ability of the bta^{4-} to adopt different coordination modes accounts for these high dimensionalities although it precludes a rational structural design. The structures of **1**–**3** have in common the double oxo-carboxylate bridge between gadolinium(III) ions (μ-*O*:κ^2*O*,*O*′) either as a discrete units (**1** and **2**) or as a chain (**3**) and one (**3**) or two (**2**) *syn*–*syn* carboxylate bridges that reinforce this bridging pathway in **2** and **3**. The values of the gadolinium-gadolinium separation through the double μ-*O*:κ^2*O*,*O*′ skeleton are 4.1801(4) (**1**), 3.9345(7) (**2**) and 3.93279(13) Å (**3**) and those of the angle at the oxo-carboxylate bridge (θ) are 113.29(10) (**1**), 106.65 (**2**) and 104.42(6) and 108.22(6)° (**3**). The magnetic properties of **1** and **3** have been investigated in the temperature range 1.9–300 K and they show the occurrence of very weak ferro- (**1**) and weak antiferromagnetic (**3**) interactions [$J = +0.00120(4)$ (**1**) and $-0.0149(1)\ cm^{-1}$ (**3**), the Hamiltonians being defined as $\boldsymbol{H} = -J\boldsymbol{S}_1 . \boldsymbol{S}_2$ and $\boldsymbol{H} = -J\Sigma_{i=1} \boldsymbol{S}_i . \boldsymbol{S}_{i+1}$, respectively]. The magneto–structural data of **1** and **3** show that the nature of the magnetic coupling between two gadolinium(III) ions is governed by the geometrical parameters at the μ-O:κ^2*O*,*O*′ digadolinium(III) core. Although a quantitative magneto–structural correlation for this family cannot be established because the small number of reported examples nowadays, the present data do not follow the semi-empirical law proposed by Baggio et al. [1].

1. Introduction

In the last years, the design and synthesis of gadolinium based metal–organic frameworks have attracted increasing attention due to their potential applications in catalysis [2], magnetism [3], molecular adsorption [4], magneto–caloric effect [5] and particularly in magnetic resonance imaging contrast agents [6]. Dealing with the field of molecule-based magnets, lanthanide ions have been used as sources of large and anisotropic magnetic moments in the search of high coercivity. Nevertheless the internal character of their 4*f* unpaired electrons, produce weak magnetic interactions between the spin carriers. Between the different rare-earth catons, Gd(III) has an $^8S_{7/2}$ ground state without first-order orbital momentum. This feature makes it the best candidate among the lanthanides for the exploration of magneto–structural correlations as illustrated by the theoretical and experimental studies on gadolinium-based complexes that have been reported by different research groups [1–7].

Previous works on metal–organic frameworks (MOFs) based on the 1,2,4,5-benzenetetracarboxylic acid (H_4bta, commonly known as pyromellitic acid) in combination with homometallic and heterometallic nodes have shown that H_4bta is a good choice for the construction of MOFs owing to the versatility as ligands of their deprotonated forms, although the variety of coordination modes precludes a rational design of the final products [8].

Herein, in the context of our systematic studies on carboxylate-containing lanthanide complexes and aiming at checking the ability of rare-earth ions to afford high-dimensional materials, we present three novel pyromellitate-containing gadolinium(III)

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complexes of formula $[Gd_4(bta)_3(H_2O)_{16}]_n{\cdot}12nH_2O$ (**1**), $[Gd_4(bta)_3(H_2O)_{12}]_n{\cdot}18nH_2O$ (**2**) and $[Gd_2(H_2bta)(bta)(H_2O)_2]_n{\cdot}4nH_2O$ (**3**) that were obtained by three different synthetic routes. The magnetic properties of **1** and **3** have been investigated and discussed in the light of previous magneto–structural studies.

2. Experimental

2.1. Material and methods

Gadolinium(III) nitrate hexahydrate, tetramethoxysilane, sodium hydroxide, sodium carbonate and 1,2,4,5-benzenetetracarboxylic acid were purchased from commercial sources and used as received. X-ray quality crystals of **1** were grown by the silica gel technique described by Henisch [9]. Compound **2**, was obtained through the slow evaporation technique at room temperature and single crystals of **3** have been grown through the hydrothermal techniques described by Byrappa and Yoshimura [10].

Elemental analyses (C, H) were performed on an EA 1108 CHNS-O microanalytical instrument.

2.2. Preparation of the complexes

2.2.1. Synthesis of $[Gd_4(bta)_3(H_2O)_{16}]_n{\cdot}12nH_2O$ (1)

An aqueous solution (9.5 mL) of 1,2,4,5-benzenetetracarboxylic acid (0.2 M), and whose pH was adjusted to 4.5 with sodium hydroxide (0.2 M), was added to a 0.9 ml of tetramethoxysilane. The resulting mixture was introduced into a test tube, covered with parafilm, and stored for one day at room temperature to allow the gel formation. Finally, an aqueous solution (5 mL) of gadolinium(III) nitrate hexahydrate (0.2 M) was carefully layered on the gel in order to prevent any damage of its surface, and the test tubes were stored at 30 °C. X-ray quality colourless prisms of **1** appeared after two days. Yield: 60%. *Anal.* Calc. for $C_{15}H_{31}Gd_2O_{26}$ (**1**): C, 19.12; H, 3.32%. Found: C, 19.23; H, 3.28%.

2.2.2. Synthesis of $[Gd_4(bta)_3(H2O)_{12}]_n{\cdot}15nH_2O$ (2)

An aqueous solution of 1,2,4,5-benzenetetracarboxylic acid 0.2 M (15 mL) was allowed to react with solid sodium carbonate (2 mmol, 212 mg). To the resulting clear mixture a water solution (16 mL) of gadolinium(III) nitrate hexahydrate (0.02 M) was added. The mixture was stored at room temperature, and colourless prisms suitable for X-ray analysis were obtained after a few days. Yield: 23%. *Anal.* Calc. for $C_{30}H_{60}Gd_4O_{51}$ (**2**): C, 19.30; H, 3.24%. Found: C, 19.38; H, 3.19%.

2.2.3. Synthesis of $[Gd_2(H_2bta)(bta)(H_2O)_2]_n{\cdot}4nH_2O$ (3)

An aqueous solution (10 mL) of 1,2,4,5-benzenetetracarboxylic acid (1.5 M) was poured into an aqueous solution (20 mL) of gadolinium(III) nitrate hexahydrate (1 M). The resulting mixture was sealed in a 45 mL stainless-steel reactor with a teflon liner, and heated at 150 °C for 48 hours. After cooling, colourless prismatic crystals were collected from the teflon-liner and air dried. This crystalline material was suitable for X-ray analyses and therefore it was used in all the measurements. Yield: 77%. *Anal.* Calc. for $C_{10}H_9GdO_{11}$ (**3**): C, 25.96; H, 1.96%. Found: C, 25.91; H, 2.01%.

2.3. Physical techniques

Magnetic susceptibility measurements on polycrystalline samples of **1** and **3** were performed in the temperature range of 2–300 K with a Quantum Design SQUID magnetometer under an applied magnetic field of 0.5 T ($T > 20$ K) and 100 G ($T < 20$ K). Diamagnetic corrections of the constituent atoms were estimated from Pascaĺs constants [11] to be -142.13×10^{-6} (**1**) and -110.11×10^{-6} $cm^3\ mol^{-1}$ (**3**) (per gadolinium atom). Experimental susceptibilities were also corrected for the temperature independent paramagnetism and the magnetization of the sample holder.

Table 1
Crystal data and details of structure determination of compounds **1-3**.

Compound	1	2	3
T (K)	293(2)	293(2)	293(2)
Formula	$C_{15}H_{31}Gd_2O_{26}$	$C_{30}H_{60}Gd_4O_{51}$	$C_{10}H_9GdO_{11}$
M	941.90	1865.78	462.42
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	10.0662(6)	9.0486(7)	10.7329(5)
b (Å)	11.4492(6)	11.5197(7)	7.1849(2)
c (Å)	12.7746(7)	14.3603(9)	17.1753(8)
α (°)	108.730(4)	87.389(6)	90
β (°)	96.948(5)	80.262(7)	97.160(4)
γ (°)	96.802(5)	85.699(7)	90
V (Å^3)	1364.56(13)	1470.33(17)	1314.14(9)
Z	2	1	4
Index ranges	$-13 \le h \le 13$ $-14 \le k \le 14$ $-16 \le l \le 16$	$-10 \le h \le 11$ $-14 \le k \le 14$ $-18 \le l \le 18$	$-13 \le h \le 13$ $-9 \le k \le 6$ $-22 \le l \le 22$
ρ_{calc} (Mg m^{-3})	2.292	2.107	2.337
λ (Mo Kα) (Å)	0.71073	0.71073	0.71073
μ (Mo Kα) (mm^{-1})	4.930	4.573	5.107
R_1, $I > 2\sigma(I)$ (all)	0.0288 (0.0476)	0.0399 (0.0632)	0.0167 (0.0204)
wR_2, $I > 2\sigma(I)$ (all)	0.0437 (0.0472)	0.0849 (0.0929)	0.0382 (0.0398)
Measured reflections (R_{int})	27644 (0.0421)	14646 (0.0365)	13724 (0.0219)
Independent reflections ($I > 2\sigma(I)$)	6174 (4932)	6629 (5135)	2972 (2747)
Crystal size (mm)	0.18 × 0.16 × 0.08	0.2 × 0.2 × 0.16	0.14 × 0.1 × 0.04

Table 2
Selected bond lengths and angles of compound **1**.

Gd(1)–O	Distance (Å)	Gd(2)–O	Distance (Å)
Gd(1)–O(1)	2.433(3)	Gd(2)–O(4d^1)	2.452(3)
Gd(1)–O(1b^1)	2.570(3)	Gd(2)–O(7)	2.583(3)
Gd(1)–O(2b^1)	2.458(3)	Gd(2)–O(8)	2.452(3)
Gd(1)–O(3)	2.397(3)	Gd(2)–O(9)	2.369(3)
Gd(1)–O(5c^1)	2.469(3)	Gd(2)–O(4w)	2.391(3)
Gd(1)–O(6c^1)	2.468(3)	Gd(2)–O(5w)	2.519(3)
Gd(1)–O(1w)	2.450(3)	Gd(2)–O(6w)	2.444(3)
Gd(1)–O(2w)	2.402(3)	Gd(2)–O(7w)	2.376(3)
Gd(1)–O(3w)	2.337(3)	Gd(2)–O(8w)	2.413(3)
Gd···Gd	Distance (Å)	Gd–O–Gd	Angle (°)
Gd(1)···Gd(1b^1)	4.1801(4)	Gd(1)–O(1)–Gd(1b^1)	113.29(10)

Symmetry code: $b^1 = -x, -y, -z + 1$; $c^1 = -x, -y + 1, -z + 1$; $d^1 = x - 1, y, z$.

2.4. X-ray crystallography data collection and refinement

Single crystals of **1**–**3** were mounted on a Nonius Kappa CCD diffractometer. Data were collected at 293(2) K using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), and they were indexed, integrated and scaled using the EVALCCD program [12]. The data were corrected for absorption through sphere numerical methods. The structures were solved by direct methods and refined with full-matrix least-squares technique on F^2 using the Shelxs-97 and Shelxl-97 programs [13] included in the WINGX software package [14]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the 1,2,4,5-benzenetetracarboxylate ligand (**1**–**3**) were located from difference maps and refined with a riding