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# Synthesis, crystal structure and magnetic properties of $\mu_4$-oxo-centered tetranuclear lanthanide clusters

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**$\mu_4$-Oxo-centered tetranuclear lanthanide (Gd, Tb) clusters with the 1,3-bis(2-hydroxy-3-methoxybenzylamino)propan-2-ol ($H_3L$) ligand have been synthesized and their crystal structure and magnetic properties are presented.**

Over the past few years, many studies have been devoted to polynuclear systems and high-nuclearity clusters of lanthanides, because of their importance in biological and materials chemistry.[1] As a consequence of their unique spectroscopic and electronic properties mainly associated with the $4f^n$ electronic configuration, lanthanide clusters are expected to exhibit interesting magnetic properties[2] and to be an essential component in the preparation of new materials. Several classes of ligands have been utilized for the preparation of polynuclear complexes of lanthanides. These include alkoxides,[3] sulfides,[4] carboxylates[5] and carboranes.[6] In addition, lanthanide clusters assembled with imido[7] and selenido[8] ligands were observed. Recently, we have become interested in the synthesis and the properties of lanthanide complexes containing aminophenol ligands. Two novel neutral $\mu_4$-oxo rhombohedral tetranuclear lanthanide (Gd, Tb) clusters, $[M_4L_2(NO_3)_4(MeOH)_2(\mu_4\text{-}O)]$, (M = Gd, **1** and M = Tb, **2**) were isolated and fully characterized by positive ion FAB-MS, X-ray crystallography and magnetic measurements. The structurally characterized complex consists of a planar $Ln_4O$ core with weak metal–metal bonding interactions, which is very rare, the only known example being $Na_6[\{(C_6H_5SiO_2)_8\}_2Ln_4(\mu_4\text{-}O)]$ (Ln = Gd and Nd).[9] However, in this compound the metal–metal interaction is rather weak and almost negligible. In addition, the nearly planar $Ln_4O$ fragment was shown to be present in the octahedral coordinating core of oxo-hydroxo lanthanide clusters.[10]

The aminophenol ligand 1,3-bis(2-hydroxy-3-methoxybenzylamino)propan-2-ol ($H_3L$) was obtained from $KBH_4$ reduction of the Schiff base derived from the condensation reaction of 1,3-diaminopropan-2-ol and 3 equiv. of *o*-vanillin. The reaction of hydrated lanthanide nitrate (Gd, Tb) with $H_3L$ in a 2 : 1 ratio in methanol afforded complexes **1** and **2** in satisfactory yields. Single crystals of **2** suitable for X-ray analysis were obtained from slow evaporation of the methanol solution at room temperature for a few days.

A perspective drawing of complex **2**, together with some selected bond parameters, is shown in Fig. 1. This analysis revealed that complex **2** consists of a rhombohedral core of four Tb(III) ions bonded to a central $\mu_4$-oxygen atom lying on a crystallographic inversion center. Thus, for reasons of symmetry, the central $Tb_4O$ core is exactly planar. This $Tb_4O$ core is capped by two deprotonated ligands $L^{3-}$ with an $\eta^7$ coordination mode. Each of the two opposite sides are bridged by the two phenolate groups [Tb(1)–Tb(2*), Tb(1*)–Tb(2)] of the deprotonated ligand $L^{3-}$, the alkoxo group of $L^{3-}$ and the hydroxo group [Tb(1)–Tb(2), Tb(1*)–Tb(2*)] of MeOH. Each metal ion is eleven-coordinate with a methoxy group and amino *N*-donor of $L^{3-}$, a bidentate nitrate, two Tb ions and the centered oxo-ligand. The Tb–$\mu_4$-O distances [2.2430(7) and 2.6474(8) Å] are significantly longer than those observed in the trinuclear Tb-carborane cluster $(C_{61}H_{159}B_{24}Li_6O_5Si_{12}Tb_3)\cdot C_6H_6$,[11] [2.170(3)–2.185(3) Å]. This is due to the steric effect of the ligands coordinated to the metal ions. A central planar $Tb_4O$ core is very rare, the

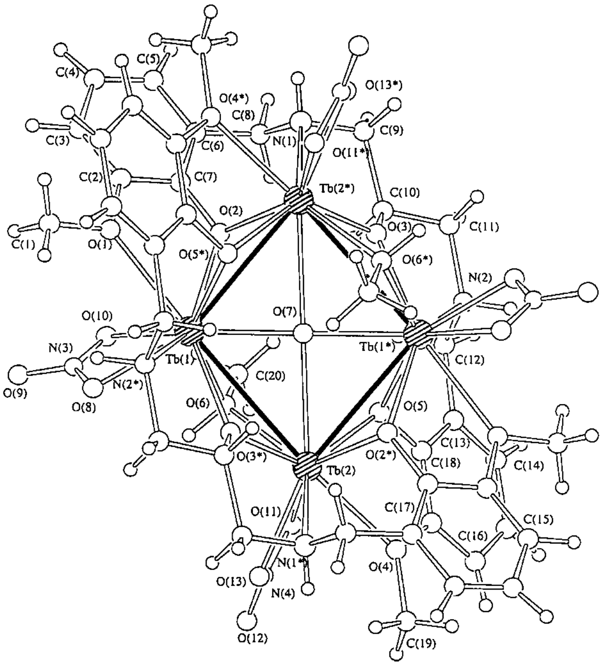

**Fig. 1** Molecular structure of complex **2** with the atomic numbering scheme for non-hydrogen atoms. Selected bond lengths (Å) and angles (°): Tb(1)–Tb(2) 3.548(1), Tb(1)–Tb(2*) 3.389(1), Tb(1)–O(1) 2.61(1), Tb(1)–O(2) 2.50(1), Tb(1)–O(3*) 2.47(1), Tb(1)–O(5*) 2.37(1), Tb(1)–O(6) 2.34(1), Tb(1)–O(7) 2.2430(7), Tb(1)–O(8) 2.19(1), Tb(1)–O(10) 2.85(1), Tb(1)–N(2*) 2.77(1), Tb(2)–O(2*) 2.344(10), Tb(2)–O(3*) 2.084(10), Tb(2)–O(4) 2.444(10), Tb(2)–O(5) 2.288(10), Tb(2)–O(6) 2.59(1), Tb(2)–O(7) 2.6474(8), Tb(2)–O(11) 2.70(1), Tb(2)–O(13) 2.40(1), Tb(2)–N(1*) 2.97(1); Tb(2)–Tb(1)–Tb(2*) 99.46(2), Tb(1)–Tb(2)–Tb(1*) 80.54(2), Tb(1)–O(7)–Tb(2) 92.66(3), Tb(1)–O(7)–Tb(2*) 87.34(3).

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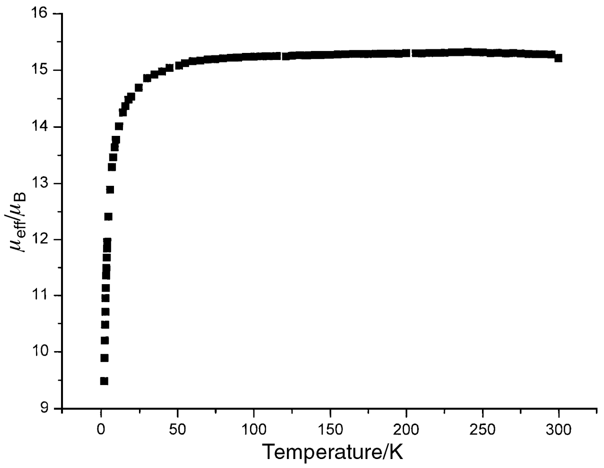

**Fig. 2** Temperature dependence of effective magnetic moment, $\mu_{eff}$, of complex **1** with diamagnetic correction.

geometry around a $\mu_4$-$O^{2-}$ ligand is normally tetrahedral or distorted tetrahedral. This central oxo group bridges the metal ions giving rise to a cluster core, while the hydrophobic groups in the peripheral positions prevent the core from further aggregation. Hence, it functions as an anion template that induces the assembly of the lanthanide ions. The $\mu_4$-oxo ligand is most probably derived from water preserved in the reaction system, as the yield of **1** and **2** decrease dramatically when carefully pre-dried MeOH was used in the synthesis. Karl–Fischer titration indicated that a water content of 0.5% in MeOH is the optimal condition to yield the complexes **1** and **2**.

The magnetic properties of complexes **1** and **2** in the solid state have been investigated at 100 Oe and over the temperature range 2–300 K. The plots of $\chi_M^{-1}$ *vs.* $T$ for **1** and **2** obey the Curie–Weiss law [$\chi = C/(T - \theta)$] with Weiss constants, $\theta$, of $-2.18$ and $-5.22$ K, respectively. For complex **1**, the $\mu_{eff}$ value per molecule is 15.3 $\mu_B$ at room temperature, close to the expected value of 15.9 $\mu_B$ for four free non-interacting $Gd^{3+}$ ions[12] and remains almost constant to *ca.* 50 K, then drops rapidly below 50 K to 9.48 $\mu_B$ at 2 K (Fig. 2). The dramatic decrease in the value of $\mu_{eff}$ at low temperature is mainly attributed to the weak intra-and intermolecular antiferromagnetic coupling between the $Gd^{3+}$ ions,[13] and may also partially arise from the very small splitting of the $^8S_{7/2}$ multiplet at zero field, or additional splitting of the ground state multiplet promoted by a $Gd^{3+}$–$Gd^{3+}$ interaction at low temperature, since the applied field is small (100 Oe). However, for complex **2** there is a continuous decrease in the value of $\mu_{eff}$ as the temperature is lowered from room temperature. The $\mu_{eff}$ value per molecule is 15.0 $\mu_B$ at room temperature, much lower than the expected value of 19.4 $\mu_B$ for four free non-interacting $Tb^{3+}$ ions, indicative of the possible presence of antiferromagnetic coupling between the $Tb^{3+}$ ions. $\mu_{eff}$ decreases abruptly to a value of 11.2 $\mu_B$ at 2 K once below 75 K. This feature is primarily due to the splitting of the ligand field of the $Tb^{3+}$ ion because of strong spin–orbital coupling, and partly contributed to by the possible antiferromagnetic interaction between the $Tb^{3+}$ ions. Further investigations into the magnetic properties of complex **2** are now in progress.

## Experimental

### Syntheses of complexes 1 and 2

1,3-Bis(2-hydroxy-3-methoxybenzylamino)propan-2-ol (0.1 mmol) and $Ln(NO_3)_3 \cdot 5H_2O$ (0.2 mmol) in methanol (10 ml) were stirred at room temperature for 5 days. A white precipitate was collected and washed with methanol (yield: 33%). **1**: mp >350 °C. IR (KBr disc): $\nu$ 3401br, 2942m, 2857m, 1479s, 1383s, 1286m, 1254w, 1048w, 1028w, 937w, 846w cm$^{-1}$. Anal. found: C, 28.4; H, 3.2; N, 6.7%. Calc. for $C_{40}H_{54}N_8O_{25}Gd_4$: C, 28.7; H, 3.3; N, 6.7%. Positive ion FAB MS: *m/z* 1550 (calc. 1550) $[Gd_4L_2(NO_3)_3(\mu_4\text{-}O)]^+$. **2**: mp >350 °C. IR (KBr disc): $\nu$ 3407br, 2944m, 2863m, 1473s, 1383s, 1286m, 1254w, 1049w, 1034w, 935w, 845w cm$^{-1}$. Anal. found: C, 28.4; H, 3.1; N, 6.5%. Calc. for $C_{40}H_{54}N_8O_{25}Tb_4$: C, 28.6; H, 3.2; N, 6.7%. Positive ion FAB MS: *m/z* 1557 (calc. 1557) $[Tb_4L_2(NO_3)_3(\mu_4\text{-}O)]^+$. Colourless single crystals of **2** were obtained *via* slow evaporation of the solvent for a few days.

### Crystallography

Single crystals of **2** suitable for X-ray crystallographic analysis were mounted on a sealed glass capillary using epoxy resin. Diffraction data were collected at ambient temperature on a Bruker AXS Smart CCD diffractometer using graphite-monochromated Mo-K$\alpha$ radiation ($\lambda = 0.71073$) with the $\omega$-scan technique. Crystal data for $C_{40}H_{54}N_8O_{25}Tb_4$, **2**: M = 1682.61, primitive monoclinic, space group $P2_1/a$ (non-standard setting no. 14), $a = 12.9780(8)$, $b = 20.976(1)$, $c = 11.3418(7)$ Å, $\beta = 93.216(1)°$, $U = 3082.6(3)$ Å$^3$, $T = 298$ K, $Z = 2$, $\mu$(Mo-K$\alpha$) = 46.01 cm$^{-1}$, 19046 reflections measured, 7096 unique ($R_{int} = 0.041$), 4869 observed reflections [$I > 1.5\sigma(I)$] were used in all calculations. The structure was solved by direct methods (SIR92)[14] and expanded using Fourier techniques, refined by full-matrix least-squares analysis on $F$ to $R = 0.060$ ($Rw = 0.071$) and a goodness-of-fit of 2.45.

CCDC reference number 156033. See http://www.rsc.org/suppdata/nj/b0/b010193l/ for crystallographic data in CIF or other electronic format.

### Magnetic measurements

Variable temperature magnetization characterizations were performed by using a Quantum Design SQUID magnetometer equipped with a 5 T magnet in the temperature range 2 to 300 K. All data were diamagnetically corrected.

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