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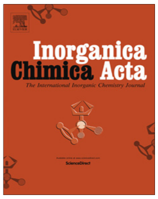

Research paper

Syntheses, structures and magnetic properties of chiral lanthanide tetrahedral clusters supported by symmetrical amidate ligands

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ABSTRACT

Two clusters with formula $[Ln_4(\mu_4\text{-}O)(HL)_3(SCN)_4(H_2O)_2]$ (Ln = Dy (**1**), Er (**2**)) were assembled by the hydrothermal reaction of $Ln(SCN)_3$ hydrate and symmetrical amidate H_3L ligand (2-hydroxy-N-[2-hydroxy-3-[(2-hydroxybenzoyl)amino]propyl]benzamide) in the presence of triethylamine. X-ray crystallographic analysis reveals that **1** and **2** are isostructural and are tetranuclear with a μ_4-O centred Ln_4 tetrahedron core, in which four crystallographically unequivalent lanthanide ions are all seven-coordinated in distorted capped octahedron geometries. Significantly, both clusters show chirality that is induced by coordination of spirally twisted ligands. The magnetic properties of **1** and **2** have been investigated. Both clusters do not exhibit slow magnetic relaxation that may be ascribed to the effect of the symmetry of ligand field on the oblate Dy^{3+} and prolate Er^{3+} ions, as well as the regular tetrahedral core.

1. Introduction

The design and synthesis of polynuclear lanthanides continues to attract attention, due to their aesthetically pleasing structures [1] as well as their potential applications as magnetic [2] and optical materials [3]. Lanthanide compounds, especially of Dy^{3+}, Tb^{3+} and Er^{3+}, are promising candidates for single-molecule magnets (SMMs) [4]. This is because they possess significant inherent magnetic anisotropy arising from the large, unquenched orbital angular momentum [3d,5]. Since the discovery of Dy_3 SMMs with toroidal arrangement of magnetic moments [6], the interest in polymetallic lanthanide SMMs has been developing, and yielded remarkable results including high anisotropy barriers and accessible blocking temperature regime [2c,7]. Dozens of Dy_4 SMMs with different structures, such as linear, planar and polyhedral, have played important roles in such breakthrough [8]. Through analysis of the structural-magnetic relationship of these metallic cores, important features relevant to lanthanide SMMs might be revealed that will provide significant insight for structural assembly and magnetic modulations [9]. In particular, only two Dy_4 tetrahedral SMMs [10], $[Dy_4(\mu_4\text{-}O)(\mu\text{-}OMe)_2(beh)_2(esh)_4]$ (**3**) [10b], $[Dy_4(\mu_4\text{-}O)L_2(C_6H_5COO)_6]$ (**4**) [10a], have been reported to also show coordination-induced chirality. In reality, the isolation of lanthanide compounds incorporating SMMs behavior and chirality represents a challenge. Hence, the studies of structure and magnetic properties of such chiral systems could improve the knowledge of the structure-property relationship.

The common ligands in the reported lanthanide SMMs are mixed N, O-donors with alkoxo, phenoxo and amino groups [7d,11]. Salen-type ligands have been used in the synthesis of lanthanide SMMs [12]. However, C=N double bonds in Salen-type ligand are rigid and limit the diversified coordination. In order to explore the coordination of a flexible ligand, we select a symmetrical amidate ligand, (2-hydroxy-N-[2-hydroxy-3-[(2-hydroxybenzoyl)amino]propyl]benzamide) (H_3L, Scheme 1), to construct lanthanide compounds using the alkoxo, carboxido and phenoxo donors. The ligand has only been used to synthesize transition metal compounds so far [13]. Herein, two lanthanide clusters with molecular formula of $[Ln_4(\mu_4\text{-}O)(HL)_3(SCN)_4(H_2O)_2]$ (Ln = Dy (1), Er (2)) were prepared by using the symmetrical amidate ligand H_3L. X-ray crystallography shows that the isostructural clusters **1** and **2** consist of four lanthanide ions arranged in a tetrahedral geometry around the central μ_4-O atom, which shows chirality that is induced by coordination of spirally twisted ligands. The synthesis, structures, magnetic properties of **1** and **2** were investigated.

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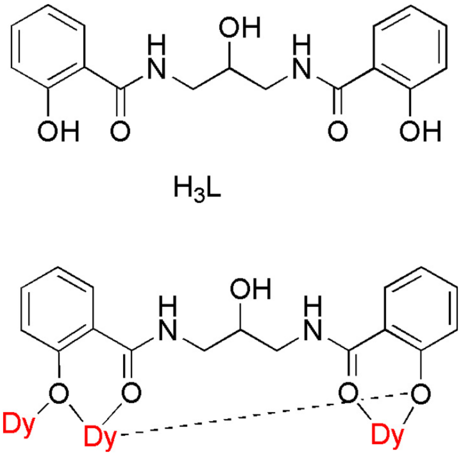

Scheme 1. Ligand H_3L and its coordination formation.

2. Experimental section

2.1. General

All chemicals and solvents used for the syntheses were of A.R. Grade and were used without purification.

Elemental analyses for C, H and N were carried out on a Perkin-Elmer 2400 analyzer. IR spectra (4000–300 cm^{-1}) were measured using KBr pellets by a Fourier transform infrared spectrometer Nicolet 6700. All magnetization data were recorded on a Quantum Design MPMS-XL7 SQUID magnetometer equipped with a 7 T magnet. The variable-temperature magnetization was measured with an external magnetic field of 1000 Oe in the temperature range of 2–300 K. The experimental magnetic susceptibility data are corrected for the diamagnetism estimated from Pascal's tables and sample holder calibration.

2.2. X-ray crystallography

Suitable single crystals were selected for single-crystal X-ray diffraction analysis. Crystallographic data were collected at 293 (2) K on a Bruker Apex II CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods and refined on F^2 with full-matrix least-squares techniques using SHELXS-97 and SHELXL-97 programs [14]. The locations of lanthanide ions were easily determined, and O, N, and C atoms were subsequently determined from the difference Fourier maps. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The H atoms were introduced in calculated positions and refined with a fixed geometry with respect to their carrier atoms. Crystallographic data and refinement details are given in Table S1. CCDC 1497830–1497831 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.3. Synthesis of the clusters

2.3.1. Ligand H_3L was synthesized according to a previously published method [13]

*2.3.1.1. Synthesis of [$Dy_4(\mu_4\text{-}O)(HL)_3(SCN)_4(H_2O)_2$] (**1**).* To a solution of H_3L (0.1 mmol, 33 mg) in a mixed solvent of methanol (3 mL) and acetonitrile (7 mL), triethylamine (0.3 mmol, 300 μL methanol solution of 1 mol L^{-1} triethylamine) and $Dy(SCN)_3\cdot6H_2O$ (0.2 mmol, 88.9 mg) were added. The mixture was stirred at room temperature until it turned to a solution. Then, the solution was transferred to Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 100 °C for two days. After cooling to room temperature, yellow single crystals of cluster **1** were obtained in 50% yield (32 mg, 0.02 mmol) based on the ligand. Elemental analysis (%) calcd for $Dy_4C_{55}H_{52}N_{10}O_{18}S_4$: C, 34.42, H, 2.73, N, 7.30; found C, 34.12, H, 2.60, N, 6.95. IR (KBr, cm^{-1}), shown in Fig. S1: 3355 (br), 2361 (m), 2342 (w), 2076 (vs), 1608 (vs), 1584 (s), 1553 (s), 1474 (m), 1443 (m), 1344 (w), 1299 (m), 1252 (m), 1085 (w), 854 (m), 764 (m).

*2.3.1.2. Synthesis of [$Er_4(\mu_4\text{-}O)(HL)_3(SCN)_4(H_2O)_2$] (**2**).* This cluster was obtained by a similar procedure as described for **1**, substituting $Er(SCN)_3\cdot6H_2O$ for $Dy(SCN)_3\cdot6H_2O$. Yield: 40 mg, 0.02 mmol (61%, based on the ligand). Elemental analysis (%) calcd for $Er_4C_{55}H_{52}N_{10}O_{18}S_4$: C 34.08, H 2.70, N 7.23; found: C 33.83, H 2.58, N 6.91. IR (KBr, cm^{-1}), shown in Fig. S1: 3335 (br), 2961 (s), 2342 (m), 2079 (s), 1607 (s), 1583 (s), 1550 (s), 1473 (w), 1437(w), 1340 (w), 1250 (m), 1150 (w), 1084 (w), 850 (w), 765 (m), 699 (w).

3. Results and discussion

3.1. Crystal structures

The hydrothermal reaction of symmetrical amidate ligand H_3L with $Ln(SCN)_3$ hydrate (Ln = Dy, Er) in a mixed solvent of methanol and acetonitrile in the presence of a base produces tetranuclear clusters **1** and **2**, respectively.

Single-crystal X-ray studies revealed that **1** and **2** were crystallographically isostructural, with the tetranuclear [$Ln_4(\mu_4\text{-}O)(HL)_3(SCN)_4(H_2O)_2$] core, and both crystallizes in the orthorhombic space group *Pna*2_1 with Z = 4. The structure of **1** is described as a representative. As shown in Fig. 1, **1** contains four Dy ions, three ligands HL^{2-}, one $\mu_4\text{-}O^{2-}$, four SCN^-, and two coordinated H_2O. The central $\mu_4\text{-}O^{2-}$ ion bridges four Dy ions to produce a μ_4-O (O1) centred tetrahedral core (Fig. 2a) with Dy–O1 distances of 2.226(11)–2.268(12) Å. All of six edges of the tetrahedron are bridged by singly deprotonated phenol oxygen atoms from HL^{2-} ligands. Within the core, the Dy···Dy distances are in the range 3.5995(14)–3.7140(12) Å, Dy–Dy–Dy angles are 58.32(3)-61.20(2)°. The dihedral angles between the bottom (Dy2, Dy3, Dy4) of the tetrahedral Dy_4 core and the other three sides are

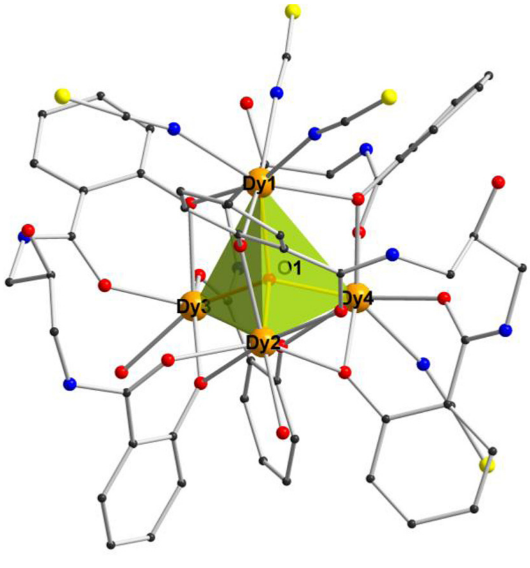

Fig. 1. Structure of **1** with hydrogen atoms omitted for clarity.