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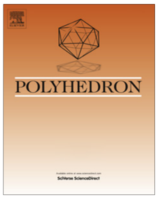

Magnetic properties of five planar defect dicubanes of $[Ln^{III}{}_4(\mu_3\text{-}OH)_2(L)_4(HL)_2]\cdot 2THF$ (Ln = Gd, Tb, Dy, Ho and Er)

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ABSTRACT

A series of five isostructural tetranuclear defect dicubane, or butterfly, topology 4f coordination clusters of formula $[Ln^{III}{}_4(\mu_3\text{-}OH)_2(L)_4(HL)_2]\cdot 2THF$, [$H_2L$ = (E)-2-(2-hydroxy-3-methoxybenzylideneamino)phenol; Ln = Gd(**1**), Tb(**2**), Dy(**3**), Ho(**4**) and Er(**5**)) has been synthesized and characterized. The highly anisotropic Dy_4 and Ho_4 complexes clearly show intramolecular ferromagnetic coupling which arise from dominant intramolecular dipolar–dipolar interactions rather than any significant superexchange effects. Furthermore, the Dy_4 complex shows Single Molecule Magnet (SMM) behavior.

1. Introduction

Coordination chemistry has become an efficient tool for the design and synthesis of new materials ranging from zero dimensional (0D) [1] molecular clusters to multidimensional polymeric networks [2]. Discovering the correct combination of organic ligands and metal ions results in the synthesis of compound which possess various physical properties such as magnetism [1,2], catalysis [3], porosity [4], optical [5], phosphorescence [6].

Initially, the employment of 3d metals ions along with organic ligands represented a successful synthetic strategy for the synthesis of such materials [1]. However, in recent times it has been shown that the incorporation or wholesale use of 4f ions is a useful strategy to target coordination clusters [7] and multidimensional complexes [8] showing unusual and exotic electronic structures. For example, lanthanide compounds can show interesting optical properties [5,6] and are employed as dopants for semiconductors such as GaN to produce light emitting materials operating in the visible region [9]. Moreover, it has been found that some lanthanide compounds absorb UV radiation but emit in the visible region [5,6]. Mixed lanthanide (Gd^{III} and Eu^{III} etc.) compounds have also been developed as materials with high quantum yield phosphorescence [6a]. In addition, trivalent lanthanide ions can provide materials which emit in the Near Infra Red (NIR) region [10].

More recently, it has been recognized that the magnetic properties of the 4f ions present an exciting new area within coordination chemistry [11]. This is largely a result of the very high magnetic anisotropies which certain 4f ions can possess and, in particular, the Ising systems of the Dy^{III}, Tb^{III}, Ho^{III} ions have provided a number unusual molecular-based systems displaying slow relaxation of the magnetization [11]. Thus magnetic clusters comprising 4f ions can display fascinating magnetic properties such as Single Molecule Magnet (SMM) behavior [12]. In addition, an appropriate combination of 4f ions with 3d-paramagnetic metal ions can result in mixed metal 3d–4f compounds showing interesting magnetic properties [11–13].

Because of the intrinsic nature of the 4f electrons, the exchange interactions between Ln^{III} ions in a solely Ln^{III} based cluster are very weak, however they can still have high blocking temperatures and energy barriers as a result of their single ion anisotropies which resist the reversal of magnetization and often show multiple relaxation processes [14].

Part of our current research interest focuses on the study of 4f chemistry from the magnetic [15–17] and synthetic points of view [18]. In the former case, we have synthesized low dimensional compounds consisting of pure Ln coordination clusters and one dimensional (1D) chains showing the magnetically interesting properties of SMM [15] and Single Chain Magnet (SCM) [16] behavior, respectively. In this context we have reported a series of low nuclearity clusters abbreviated as Dy_3 [15a,b], Dy_4 [15c,f,g], Dy_5 [15d], and Dy_6 [15e] showing a variety of SMM properties. In addition, we have developed efficient ways of synthesizing new materials such as SMMs with non-magnetic ground states where SMM behavior arises from excited states as well showing the existence

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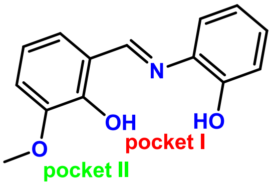

Scheme 1. Structure of ligand ((E)-2-(2-hydroxy-3-methoxybenzylideneamino)phenol, (H_2L) with two types of pocket (I and II).

of spin chirality [15a,17]. From a structural point of view, we have been able to develop a synthetic strategy for the synthesis of multidimensional polymeric compounds using solely monotopic ligands and lanthanides [18].

Building on the combined experience and taking inspiration from our recent work using Schiff base ligands [15a,e] we have been exploring the coordination abilities of the Schiff base H_2L = (E)-2-(2-hydroxy-3-methoxybenzylideneamino)phenol (Scheme 1) ligand which possesses two different pocket sites. The employment of this ligand in 3d/4f chemistry affords tetranuclear compounds with defect dicubane topology formulated as $Ni^{II}_2Ln^{III}_2$ (where Ln is Dy, Tb) [19a] and $Co^{II}_2Ln^{III}_2$ (where Ln is Y, Dy) [19b] and possessing SMM behavior. The next step in our systematic study is to investigate the coordination abilities toward lanthanides. Thus we report herein the synthesis, characterization and magnetic properties of five new clusters with general formula of $[Ln^{III}_4(\mu_3\text{-}OH)_2(L)_4(HL)_2]\cdot 2THF$, (**x**)·2THF where Ln = Gd (**1**), Tb (**2**), Dy (**3**), Ho (**4**) and Er (**5**).

2. Experimental section

2.1. Materials and methodology

All the $LnCl_3\cdot 6H_2O$ salts were prepared by reaction of lanthanide oxide with corresponding acid in hot aqueous solution and crystallized by slow evaporation. The commercially available $CdCl_2\cdot H_2O$, Et_3N, MeOH and THF were used as received without further purification. Fourier Transform IR spectra were measured on a Perkin-Elmer Spectrum One spectrometer with samples prepared as KBr pellets. Powder XRD patterns were recorded at room temperature using a Stoe STADI-P diffractometer with Cu Kα radiation.

2.2. Synthesis of the ligand (E)-2-(2-hydroxy-3-methoxybenzylideneamino)phenol (H_2L)

This ligand was prepared as reported in the literature [20]. An equimolar mixture of *ortho*-vanillin (10 mmol) and 2-aminophenol (10 mmol) was refluxed in MeOH (20 mL) for 30 min. The dark orange-red precipitate obtained was filtered and washed well with cold methanol followed by ether and dried in oven at 60 °C and further purified by recrystallization from hot methanol. Yield is 92%. *Anal.* Calc. for $C_{14}N_1H_{13}O_3$: C, 69.12; H, 5.38; N, 5.76. Found: C, 69.15; H, 5.40; N, 5.70%. IR data (KBr): ν (cm^{-1}): 3150(b), 2991(w), 2902(w), 2817(w), 1644(w), 1627(s), 1616(s), 1541(m), 1509(s), 1461(s), 1361(s), 1333(m), 1305(m), 1278(m), 1245(s), 1166(w), 1104(m), 1064(m), 1032(m), 1970(m), 923(w), 849(w), 738(s), 723(m), 575(w), 431(w).

2.3. Synthesis of the complexes

2.3.1. Synthesis of $[Gd^{III}_4(\mu_3\text{-}OH)_2(L)_4(HL)_2]\cdot 2THF$, (1)·2THF

The same procedure was employed to prepare all complexes and hence only the compound **1** is described here in detail. The mixture of $GdCl_3\cdot 6H_2O$ (0.1 mmol, 38 mg), $CdCl_2\cdot H_2O$ (0.11 mmol, 22 mg) and H_2L (0.2 mmol, 48.6 mg) was stirred in MeOH (20 mL) for 20 min in the presence of Et_3N (0.36 mmol, 36 mg) 20 ml of THF was added to the turbid yellow solution to give a clear orange-red solution. The well-formed rod-shaped orange crystals of **1** were obtained within 3–4 days in 68% yield. *Anal.* Calc. for $C_{92}H_{86}Gd_4N_6O_{22}$: C, 48.96; H, 3.84; N, 3.72. Found: C, 48.86; H, 3.87; N, 3.70%. Selected IR data (KBr): ν (cm^{-1}): 3433(w), 3052(w), 2968(w), 2834(w), 1611(s), 1584(s), 1544(w), 1496(s), 1481(s), 1460(s), 1451(s), 1338(s), 1385(m), 1331(s), 1285(s), 1259(s), 1228(s), 1178(s), 1151(w), 1103(w), 1080(w), 1031(w), 971(w), 911(w), 870(w), 821(w), 735(s), 710(m), 571(w), 498(w), 454(w).

*Compound **2**:* Yield 66%. *Anal.* Calc. for $C_{92}H_{86}Tb_4N_6O_{22}$: C, 48.81; H, 3.84; N, 3.71. Found: C, 48.75; H, 3.86; N, 3.68%. Selected IR data (KBr): ν (cm^{-1}): 3431(w), 3052(w), 2968(w), 2834(w), 1611(s), 1584(s), 1542(w), 1496(s), 1481(s), 1460(s), 1451(s), 1338(s), 1385(m), 1331(s), 1285(s), 1259(s), 1228(s), 1178(s), 1151(w), 1103(w), 1080(w), 1031(w), 971(w), 911(w), 870(w), 821(w), 735(s), 710(m), 571(w), 497(w), 454(w).

*Compound **3**:* Yield 65%. *Anal.* Calc. for $C_{92}H_{86}Dy_4N_6O_{22}$: C, 48.51; H, 3.78; N, 3.65. Found: C, 48.55; H, 3.86; N, 3.68%. Selected IR data (KBr): ν (cm^{-1}): 3431(w), 3052(w), 2968(w), 2834(w), 1611(s), 1584(s), 1542(w), 1496(s), 1481(s), 1460(s), 1451(s), 1338(s), 1385(m), 1331(s), 1285(s), 1259(s), 1228(s), 1178(s), 1151(w), 1103(w), 1080(w), 1031(w), 971(w), 911(w), 870(w), 821(w), 735(s), 710(m), 571(w), 497(w), 454(w).

*Compound **4**:* Yield 65%. *Anal.* Calc. for $C_{92}H_{86}Ho_4N_6O_{22}$: C, 48.30; H, 3.78; N, 3.67. Found: C, 48.35; H, 3.75; N, 3.70%. Selected IR data (KBr, ν/cm^{-1}): 3432(w), 3055(w), 2968(w), 2834(w), 1611(s), 1584(s), 1542(w), 1496(s), 1482(s), 1460(s), 1451(s), 1338(s), 1385(m), 1331(s), 1285(s), 1259(s), 1228(s), 1178(s), 1151(w), 1103(w), 1080(w), 1031(w), 971(w), 911(w), 870(w), 821(w), 735(s), 710(m), 571(w), 497(w), 455(w).

*Compound **5**:* Yield 70%. *Anal.* Calc. for $C_{92}H_{86}Er_4N_6O_{22}$: C, 48.11; H, 3.77; N, 3.66. Found: C, 48.05; H, 3.75; N, 3.62%. Selected IR data (KBr): ν (cm^{-1}): 3432(w), 3054(w), 2969(w), 2834(w), 1611(s), 1585(s), 1542(w), 1496(s), 1482(s), 1460(s), 1452(s), 1338(s), 1385(m), 1331(s), 1285(s), 1259(s), 1228(s), 1178(s), 1151(w), 1103(w), 1080(w), 1031(w), 971(w), 911(w), 870(w), 821(w), 735(s), 710(m), 571(w), 498(w), 453(w).

2.4. Magnetic measurements

Magnetic susceptibility measurements were obtained using a Quantum Design SQUID MPMS-XL susceptometer. This magnetometer works between 1.8 and 300 K for dc applied fields ranging from −7 to +7 T. Measurements for **1**, **2**, **3**, **4** and **5** were performed on 8.8, 9.2, 9.8, 12.4 and 11.4 mg, respectively of polycrystalline powder dispersed in eicosane. The magnetic data were corrected for the sample holder and the diamagnetic contribution. The samples were first checked for the presence of ferromagnetic impurities by measuring the magnetization as a function of the field at 100 K and none were detected.

2.5. X-ray crystallography

Powder XRD patterns (Fig. S1) and the crystal cell parameters (Table 1 and S1) show that compounds **1**–**5** are isostructural. X-ray data for compound **3** (Table 1) and the unit cells of **1**, **2**, **4** and **5** were collected on a Stoe IPDS II area detector diffractometer at 180 K using graphite-monochromated Mo Kα radiation. Semi-empirical absorption corrections were made using *XPREP* in SHELXTL [21]. The structure was solved using direct methods, followed by full-matrix least-squares refinement against F^2 (all data) using SHELXTL [21]. Anisotropic refinement was used for all ordered non-H atoms. Organic H atoms were placed in calculated positions, while coordinates of hydroxo H atoms and amine H atoms were refined with restrained O–H and N–H bond lengths.

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