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Slow magnetic relaxations in azide or formate bridged chains based on dicubane-like 3d-4f clusters

Man-Xiu Nie, Qi-Long Wu, Jiong-Peng Zhao*, Su-Hua Gao**, Fu-Chen Liu***

School of Chemistry and Chemical Engineering, TKL of Organic Solar Cells and Photochemical Conversion, Tianjin University of Technology, Tianjin, 300384, PR China

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ABSTRACT

Dicubane-like 3d-4f subunits are linked by azide or formate giving a series of 1D chains. The linkers of azide or formate have little influence on the structure of the M_2Ln_2 subunits. Magnetic study indicated that ferromagnetic interactions exist in the chains of those complexes. At low temperature all the involved cobalt complexes exhibit slow magnetic relaxation.

1. Introduction

Single-chain magnets (SCMs) are one-dimensional (1D) magnetic chains exhibiting slow magnetic relaxation, which have potential applications as ultimate memory or quantum spintronic devices [1]. SCMs require uniaxial type magnetic anisotropy, large ratio of the intrachain and interchain magnetic interactions [2]. The first SCM was reported by Gatteschi et al. [3], presented an attractive alternate to discrete molecular clusters SMMs (single molecule magnets) [4]. After that, different synthetic strategies were developed in constructing such magnetic chains. There are three structure types of SCMs: (i) magnetic chains assembled by metal ions and bridge ligands directly [5], (ii) 2D and 3D networks based on ferro- or ferrimagnetic Ising chains with long interchains bridge ligands [6], (iii) connecting magnetic cluster into 1D chains through bridging ligands, which conducting magnetic interactions effectively [7].

The discrete magnetic cluster, even SMMs with high magnetic anisotropy and diversity structure are desired candidate for extending 1D magnetic systems (type iii) [8]. The ligand 2-Hydroxymethylpyridine (Hhmp) with bridge and chelate coordinated modes is a good choice in assembling cluster structures [9]. In this work, we report five 1D magnetic chains based dicubane-like 3d-4f clusters constructed by hmp ligands, high magnetic anisotropic ions Dy^{III}/Tb^{III} and Co^{II}/Ni^{II} ions. The clusters are linked by double azide/formate bridges [10,11] in forming the final 1D chains. Magnetic studies indicate the ferromagnetic interactions between the ions in those complexes. Obvious slow magnetic relaxation is detected in the Co^{II}–Dy^{III} complexes despite formate or azide bridges between the clusters.

2. Materials and methods

2.1. Experimental section

The solvothermal reaction of Hhmp with sodium azide/formate, Cobalt(II) acetate tetrahydrate/Nickel acetate tetrahydrate and $Dy(NO_3)_3 \cdot 6H_2O$/$Tb(NO_3)_3 \cdot 6H_2O$ in MeOH give brownish red/green crystals of those complexes $[CoDy(hmp)_3(NO_3)(N_3)]_n$ (**1**), $[CoDy(hmp)_3(NO_3)(HCO_2)]_n$ (**2**), $[CoTb(hmp)_3(NO_3)(N_3)]_n$ (**3**), $[CoTb(hmp)_3(NO_3)(HCO_2)]_n$ (**4**) and $[NiDy(hmp)_3(NO_3)(N_3)]_n$ (**5**).

Preparation of **1**: **1** was synthesized by solvothermal reaction.

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* Corresponding author.
** Corresponding author.
*** Corresponding author.
E-mail addresses: horryzhao@yahoo.com, zhaojp@tjut.edu.cn (J.-P. Zhao), gaosuhua@tjut.edu.cn (S.-H. Gao), fuchenliutj@yahoo.com (F.-C. Liu).

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1.5 mmol Cobalt(II) acetate tetrahydrate, 0.75 mmol $Dy(NO_3)_3 \cdot 6H_2O$, 1 mmol HL, 2 mmol NaN_3 and 10 mL of methanol were added into a Teflon lined stainless steel autoclave. The autoclave was sealed and heated at 140 °C for two days. The solution cooled down to room temperature after 18 h and brownish red crystals were collected in ca 25% yield. Element analysis (%): Calcd. for $C_{18}H_{18}CoDyN_7O_6$(649.82): C 33.27, H 2.79, N 15.09; found: C 33.40, H 3.20, N 14.73.

Preparation of **2**: **2** was synthesized with similar protocol of **1** by replacing NaN_3 with $NaHCO_2$. Element analysis (%): Calcd. for $C_{19}H_{17}CoDyN_4O_8$ (652.81): C 34.96, H 2.94, N 8.58; found: C 35.23, H 3.21, N 9.67.

Preparation of **3**: **3** was synthesized with similar protocol of **1** by replacing $Dy(NO_3)_3 \cdot 6H_2O$ with $Tb(NO_3)_3 \cdot 6H_2O$. Element analysis (%): Calcd. for $C_{18}H_{18}CoTbN_7O_6$ (646.24): C 33.45, H 2.81, N 15.17; found: C 33.75, H 3.22, N 14.96.

Preparation of **4**: **4** was synthesized with similar protocol of **1** by replacing NaN_3 with $NaHCO_2$. Element analysis (%): Calcd. for $C_{19}H_{19}CoTbN_4O_8$ (649.23): C 35.15, H 2.95, N 8.63; found: C 33.35, H 3.13, N 8.94.

Preparation of **5**: **5** was synthesized with similar protocol of **1** by replacing Cobalt(II) acetate tetrahydrate with Nickel acetate tetrahydrate. Element analysis (%): Calcd. for $C_{18}H_{18}NiDyN_7O_6$ (649.60): C 33.28, H 2.79, N 15.09; found: C 33.50, H 3.13, N 15.41.

2.1.1. X-ray crystallography

The single-crystal X-ray diffraction datas of **1**–**5** were collected on a Rigaku SCX-mini diffractometer at 293(2) K. The program *CrystalClear* [12] was used for the integration of the diffraction profiles. The structure was solved by direct method using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL (semi-empirical absorption corrections were applied by using the SADABS program) [13]. The non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2. All hydrogen atoms of were generated theoretically at the specific atoms and refined isotropically with fixed thermal factors. Detailed crystallographic data are summarized in Tables S1 and S2.

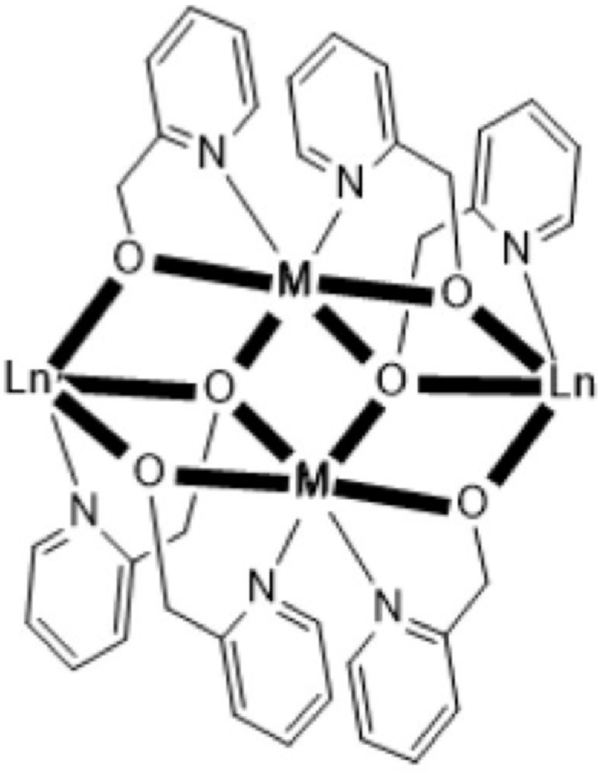
2.1.2. Magnetic measurements

The magnetic measurements were performed by an MPMS XL-5 SQUID magnetometer with monoclinic of **1**–**5**. Measurements can be performed down to 0.5 K. Diamagnetic corrections were estimated by using Pascal constants and background corrections by experimental measurement on sample holders.

3. Results

The phase purity are confirmed by XRPD (Fig. S1, ESI†). Single-crystal X-ray diffraction (Table S1, ESI†) of those complexes indicates that they crystallize in the space *C2/c* group and have 1D chains structure. In the crystallographic asymmetric unit of **1**, there are one Co^{II} ions, one Dy^{III} ions, one azide anions, one nitrate anions and three hmp anions. The Co1 is coordinated by four hmp ligands in a compressed octahedral geometry with equatorial position taking by N1, N2A, O3, O3A and axial position with O1, O2A (Table S3, ESI†). The coordination sphere around the Dy^{III} ions are formed by three nitrogen atoms from two azide ions and one hmp ligand and five oxygen atoms from the bridging hydroxymethyl group of three hmp and two oxygen atoms of the chelating nitrate anions. The eight-coordinate Dy^{III} ions are characterized by a distorted square-antiprismatic environment, in which the atoms O1, N6B, N3, O3 lie approximately on one face, and the atoms O2, N4, O4, O6 on the other face. The selected bond lengths and angles are given in Tables S3–S7. Three hmp ligands taking two types of coordination modes by chelating and bridging ways, in which one of the hmp contained N1 and N2 chelates to the Co^{II} ion and bridges to Dy^{III} ions using the oxygen and nitrate atoms, while the other two hmp ligands chelate to one Dy^{III} ions and bridge two Co^{II} ions. A dicubane-like 3d-4f cluster contained two Co^{II} and two Dy^{III} ions are formed by six hmp ligands (Scheme 1 and Fig. 1). The Dy^{III} ions in the adjacent cluster are linked by double EE azide anions giving 1D chain (Fig. 2). The complexes **3** and **5** have the same structure with **1** but with different metal ions. The formate bridged complexes **2**, **4** have the similar chain with **1** but the dicubane-like 3d-4f clusters are linked by double *syn,syn* formate anions. There are solvent accessible voids about 224–239 Å^3 in the complexes with azide as bridges between the dicubane clusters. Thus, using azide or formate as bridges is valid in directing the arrangement of the polynuclear building blocks. The structure of **1**–**5** is quite different with 1D chain with hmp ligand bridged $Mn^{III}{}_2Mn^{II}{}_2$ dicubane cluster as subunit, in which the double azide bridges the clusters through the Mn^{II} ions in forming the 1D chain and the Mn^{III} ions locate in the center of the dicubane [14]. The dicubane unit in 1–5 is also different with $Gd^{III}{}_4M^{II}{}_8$ complex in which the hmp ligands and metal ions Gd^{III} and M^{II} form a cubane subunit [15].

The magnetic susceptibility data collected on crystalline samples of those complexes in the 2–300 K temperature range are shown in Fig. 3, in which the date of **1**, **2** and **4** are under 1 kOe while **3** and **5** are under 2 kOe. The values of χmT at 300 K are 17.47, 17.07, 14.00 and 14.36 cm^3 Kmol^{-1} for **1** to **4** respectively, which are in reasonably good agreement with the expected values for one Ln^{III} ions (Dy^{III}: $^6H_{15/2}$, S = 5/2, L = 5, g = 4/3, 14.17 cm^{3}Kmol^{-1}; Tb^{III}: $^7F_6$, S = 3, L = 3, g = 3/2, 11.82 cm^{3}Kmol^{-1}) and one Co^{II} ($^4T_{1g}$, S = 3/2, g = 2.0) with unquenched orbital monument (2.8–3.4 cm^{3}Kmol^{-1}) [16]. In the Ni^{II} involved complex **5** the room temperature of values of $\chi_m T$ is 16.36 cm^{3}Kmol^{-1} which is higher than that of uncoupled Dy^{III} and Ni^{II} ions. That indicates strong ferromagnetic coupling



Scheme 1. The dicubane-like 3d-4f subunits constructed by Ln (Dy/Tb), M (Co/Ni) and hmp ligands.