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Heterometallic tetranuclear 3d–4f complexes: Syntheses, structures and magnetic properties

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ABSTRACT

Four novel heterometallic tetranuclear 3d–4f complexes $M_2Dy_2L_{10}(phen)_2$ (M = Co (**1**), Ni (**2**), Cu (**3**) and Zn (**4**); HL = 4-trifluoromethylbenzoic acid, phen = phenanthroline) have been synthesized hydrothermally and characterized by single crystal X-ray diffraction study, IR, elemental analysis and thermal gravimetric analyses. The structures of **1** and **4** are isostructural and the completely deprotonated L ligands adopt μ_2: η^1, η^1 coordination mode to bridge adjacent metal ions which further connect into 1D chains by hydrogen bonds. The tetranuclears in complex **2** were linked by L ligands with μ_2: η^1, η^2 and μ_2: η^1, η^1 coordinated patterns and spread into 2D layers through hydrogen bonds. In complex **3** L ligands possess the same coordinated styles with **2** and a 3D supramolecular network was fabricated via hydrogen-bonding interactions. Dynamic magnetic susceptibility studies reveal slow magnetic relaxation processes for **1** and **3**, suggesting SMM type behavior for these compounds.

Researches on polynuclear metal complexes have received much attention in view of their wide range of potential applications in many fields, including physics, chemistry, biology, nanotechnology and materials science [1–5]. Polynuclear metal complexes as good candidates to construct molecular magnets have also attracted great interest in magnetochemistry for their diverse and interesting magnetic properties [6]. Nowadays, many efforts have been devoted to the rational design and synthesis of 3d–4f heterometallic polynuclear complexes because they have been proved to be promising materials for potential applications as luminescence, catalysis and magnetic materials [7–9].

In recent years, single-molecule magnets (SMMs) have attracted considerable attention owing to their potential applications in magnetic storage and molecular spintronics associated with the magnetic bistability [10]. In recent years, synthesis of SMMs containing lanthanide ions, such as dysprosium, has led to a rapid increase in the field of molecule-based magnetic materials because of the large inherent anisotropy of most lanthanide ions [11]. One major concern of coordination chemistry is currently the synthesis and investigation of 3d–4f polynuclear coordination compounds possessing slow relaxation of the magnetization. However, only a few 3d–4f polynuclear complexes have been shown to display SMM behavior [12]. Thus, the ligand is of paramount signification for constructing 3d–4f polynuclear complexes with this property.

Carboxylate ligands are widely employed in the synthesis of 3d–4f complexes, owing to the ligand system which is prone to coordinate to both transition and lanthanide metal ions acting as chelating and/or bridging agent. Our group was dedicated to the construction of coordination complexes from various carboxylate ligands with interesting topologies and magnetic properties. In consideration of all the above, we have chosen 4-trifluoromethylbenzoic acid (HL) as the main ligand to synthesize new 3d–4f complexes in the presence of auxiliary coligands [13]. A variety of homometallic complexes have been successfully prepared because of the diversity of coordination modes of HL, while no article concerning heterometallic complexes of HL with both transition and lanthanide metal ions has been documented [14].

Fortunately, we successfully prepared four novel 3d–4f complexes $M_2Dy_2L_{10}(phen)_2$ (M = Co (**1**), Ni (**2**), Cu (**3**), Zn (**4**)) based on HL in the presence of auxiliary N-donor co-ligand 1,10-phenanthroline (phen). They exhibit tetranuclear structure character, while adopt distinct coordination modes and various supramolecular frameworks. To the best of our knowledge, complexes **1**–**4** are first series of 3d–4f heterometallic complexes for HL. The magnetic behaviors of the compounds were investigated. Complexes **1** and **3** exhibit slow magnetic relaxation processes, suggesting SMM type behavior for these compounds.

Single-crystal X-ray diffraction measurements reveal that complexes **1**, **2** and **4** crystallize in the triclinic space group *P*-1, and complex **3** crystallizes in the monoclinic space group *C*2/*c*. The asymmetric units of complexes **1**–**4** contain one crystallographically unique Dy(III) center, one crystallographically independent M(II) center (hereafter referred to as M = Co (**1**), Ni (**2**), Cu (**3**), Zn (**4**)), five deprotonated L^- ligands and one phen (Figs. 1a, 2a, 3a). Complexes **1**–**4** are tetranuclears bridged by L^- ligands.

The structures of **1** and **4** are isostructural, thus only the structure of **1** as a representative is described here in detail. In complex **1**, the Dy1 site is coordinated by seven oxygen atoms from seven distinct L ligands

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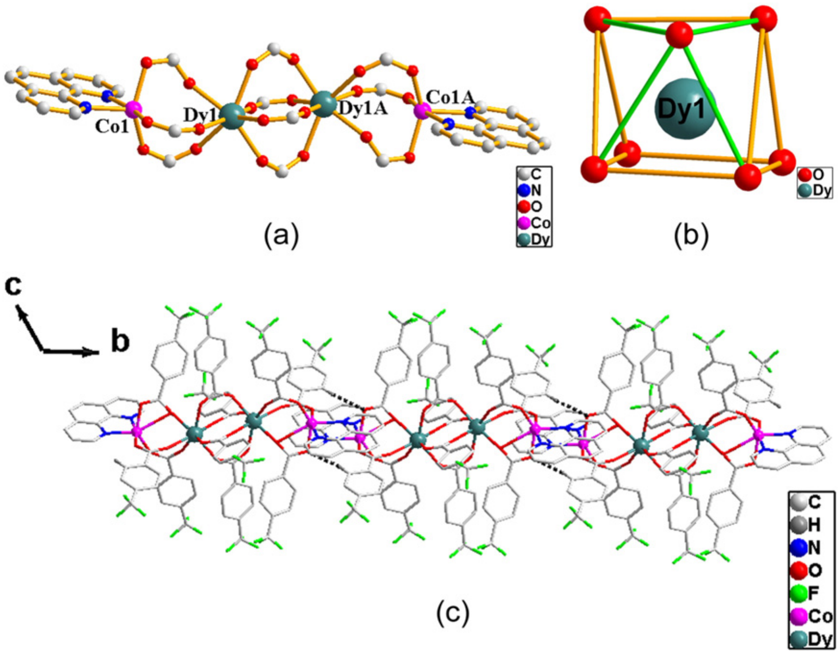

Fig. 1. (a) Coordinated environments of the metal centers in **1**. (b) Coordination polyhedron of Dy(III) ion in complex **1**. (c) The supramolecular framework of **1** (some hydrogen, carbon and fluorine atoms omitted for clarity).

to create a distorted monocapped trigonal prism coordination environment (Fig. 1b). The Co1 site is bonded with three oxygen atoms and two nitrogen atoms from three L^{-} ligands and one phen ligand, which exhibits a slightly twisted trigonal bipyramid geometry. The Dy–O and Co–O/N bond lengths are in the normal range [15]. In **1**, the completely deprotonated L ligands adopt μ_2: η^1, η^1 coordination mode (Scheme 1 I). The intramolecular metal-to-metal distance is 4.1664(17) Å for Co1···Dy1, 4.1223(14) Å for Dy1···Dy1A. The discrete molecules can aggregate into 1D chain via hydrogen bonds between L ligands (C(19)–H(19)···O(6) 3.204(11) Å, 139°) along *b* axis (Fig. 1c).

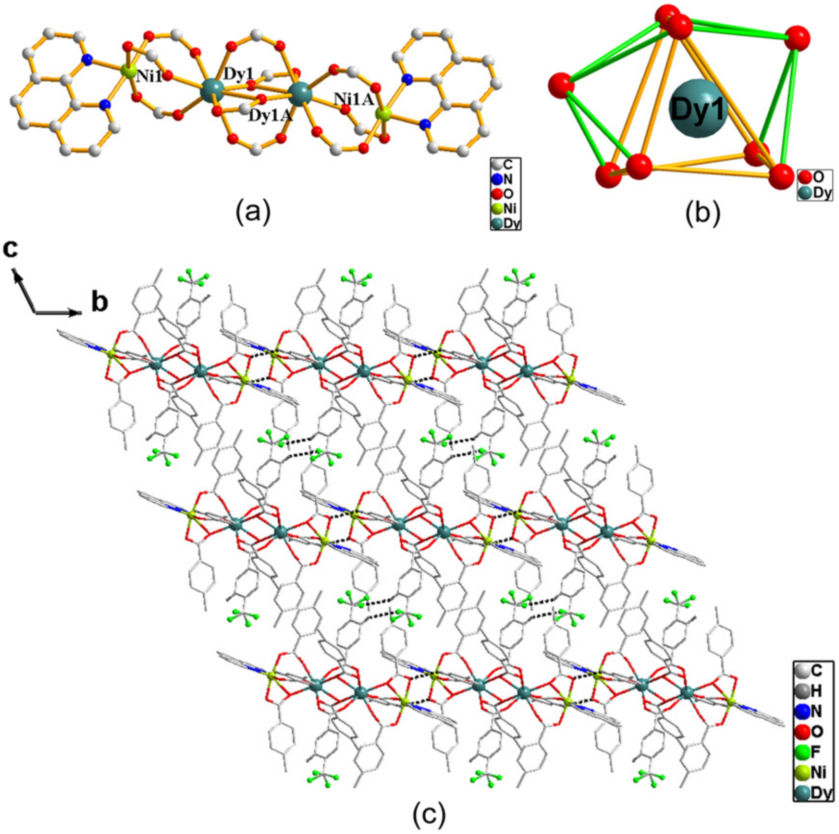

Fig. 2. (a) Coordinated environments of the metal centers in **2**. (b) Coordination polyhedron of Dy(III) ion in complex **2**. (c) The supramolecular framework of **2** (some hydrogen, carbon and fluorine atoms omitted for clarity).