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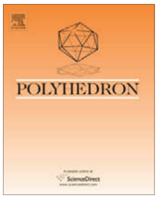

Coordination enhancement of single-molecule magnet behavior of Tb(III)–Cu(II) dinuclear systems

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ABSTRACT

Tb(III)–Cu(II) based single-molecule magnets (SMMs) were synthesized to investigate the relationship between magnetic anisotropy and the symmetry of the ligand field, by the reaction of [TbCu(*o*-vanilate)$_2$(NO$_3$)$_3$] with 2,2-dimethyl-1,3-propanediamine (**3**), followed by the reaction of one another equivalent of *o*-vaniline (**4**). Both complexes behave as SMM in the temperature range of 2.8–4.0 K (**3**) and 2.8–5.2 K (**4**), showing semi-circle shapes of Cole–Cole plots with α parameters in the ranges of 0.27–0.41 and 0.11–0.32. The energy barriers Δ/k_B for the spin flippings were estimated from the Arrhenius plots to be 29(2) K for **3** and 32.2(6) K for **4**, respectively.

Single-molecule magnets (SMMs) [1–3], which show magnetic properties not observed previously, are chemically and physically fascinating compounds. The origin of the SMM behavior is the easy-axis magnetic anisotropy ($D < 0$), which causes the formation of an energy barrier that prevents reversal of the molecular magnetization and causes a slow relaxation of the magnetization at low temperature. SMMs form due to a combination of a large spin multiplicity of the ground state and an easy-axis (or Ising type) magnetic anisotropy of the entire molecule. Utilization of heavy lanthanide ions [4–6], such as terbium(III) and dysprosium(III), has been one of the most elegant ways to design SMMs [4,5], because they have large angular momenta ($J = 6$ with $g_J = 3/2$ is known for Tb^{III}) in the ground multiplet state, which is derived from the strong spin-orbit coupling. Moreover, these metal ions are assumed to have a large Ising-type magnetic anisotropy [4e,4h,7]. In the previous paper, we have reported the structures and magnetic properties of two Tb–Cu dinuclear complexes, [TbCu(**L1**)$_2$(NO$_3$)$_3$] (**1**) and [TbCu(**L2**)$_2$(NO$_3$)$_3$] (**2**) (structures of Schiff base ligands H**L1** and H**L2** are given in Scheme 1), and we have discussed the relationship between the symmetry of the ligand field and the magnetic anisotropy [8], on the bases of the special matching between electronic distributions of the Stalk sub-levels of Tb(III) ion and the shape of crystal field formed by donating oxygen atoms. The Tb(III) ion with an f^8 configuration takes the ^{7}F$_6$ ground state of $|J, J_z\rangle = |6, J_z\rangle$ ($J_z = \pm6, \pm5, \ldots, 0$). In this configuration, two sub-levels corresponding to the $J_z = \pm6$ states and the $J_z = 0$ state have different special distributions; the former has an oblate spheroidal profile, whereas the later has a prolate spheroidal profile. When the donor ligand are surrounding in a symmetrical and an equatorial manner, which was found in **2**, the prolate shaped $J_z = 0$ state can be stabilized, and as a result, an easy-plane magnetic anisotropy could be observed. In **1**, the less symmetrical coordination partially disrupted such an equatorial crystal field, and this led to an easy-axis anisotropy of Tb(III) which is commonly observed for Tb(III) ion. This easy-axis anisotropy would be enhanced when the crystal field is more unsymmetrical, or two large negative charges are located in a uni-axial manner, since in these conditions the oblate shaped $J_z = \pm6$ states can be more stabilized. Along this line, we investigated the relationship between the morphology of crystal field and SMM features of two new complexes, [TbCu(**L3**)(NO$_3$)$_3$(H$_2$O)] (**3**) and [TbCu(**L3**)(*o*-vanilate)(NO$_3$)(MeOH)]NO$_3$ (**4**), which are formed with the hexa-dentate Schiff base ligand **L3**$^{2-}$ [9] shown in Scheme 1. Syntheses, structures, and SMM behaviors of **3** and **4** will be discussed in this communication.

Complex **3**[1] was synthesized according to the Gd(III)–Cu(II) analog complex reported by Costes et al. [9], using methanol as a solvent except for acetone. A reaction of **3** with one equivalent of *o*-vaniline and one equivalent of tetrabutylammonium hydroxide in methanol afforded a formation of green crystals of complex **4**.[2]

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[1] *Crystallographic data for* **3**: Green prism, triclinic, space group $P\bar{1}$, $a = 9.3293(15)$ Å, $b = 10.5346(17)$ Å, $c = 14.683(2)$ Å, $\alpha = 73.608(3)^\circ$, $\beta = 84.113(3)^\circ$, $\gamma = 89.636(3)^\circ$, $V = 1376.7(4)$ Å^3, $T = 153$ K, $Z = 2$, 13556 reflections were observed, of which 6296 were independent, $R_1 = 0.0358$ ($I > 2\sigma(I)$) and $wR_2 = 0.0768$ (all data) for 391 parameters, goodness-of-fit = 0.944.

[2] *Crystallographic data for* **4**: Green prism, triclinic, space group $P\bar{1}$, $a = 9.244(4)$ Å, $b = 12.126(5)$ Å, $c = 16.322(6)$ Å, $\alpha = 92.351(7)^\circ$, $\beta = 97.361(7)^\circ$, $\gamma = 103.226(7)^\circ$, $V = 1761.7(12)$ Å^3, $T = 100$ K, $Z = 2$, 12190 reflections were observed, of which 5072 were independent, $R_1 = 0.0496$ ($I > 2\sigma(I)$) and $wR_2 = 0.1120$ (all data) for 477 parameters, goodness-of-fit = 1.175.

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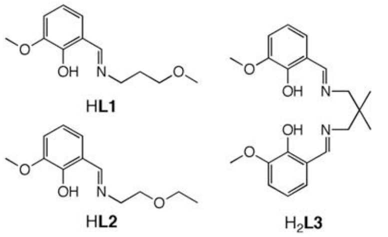

Scheme 1. Structures of Schiff base ligands described in the main text.

Figs. 1 and 2 show crystal structures of two complexes. Both complexes crystallized in triclinic crystal system with space group $P\bar{1}$, and each unit cell involves two molecules related by the inversion center. In each complex, the Schiff base ligand $\mathbf{L3}^{2-}$ behaves as tetradentate O_2N_2 ligand for Cu(II) ion and tetradentate O_4 ligand for Tb(III) ion, and Tb and Cu are doubly bridged by two phenoxo oxygens (O2 and O4). O_2N_2 donor atoms are almost coplanar (maximum deviations from ideal planes are 0.0030(19) and 0.104(3) Å, respectively), and each Cu atom is located on the plane with deviations of 0.1385(19) and 0.103(3) Å, respectively. Coordination distances are in a range of 1.957(3)–1.989(4) Å for **3** and 1.954(4)–1.975(6) Å for **4**, and each apical position of the Cu atom is occupied by water oxygen atom (O14) or nitrate oxygen atom (O12) with the distances of 2.299(4) and 2.405(5) Å, respectively. Both Cu atoms in **3** and **4** are in an axially elongated pyramidal coordination, and the magnetic orbital ($d_{x^2-y^2}$) of Cu(II) ion with d^9 electronic configuration is located on the equatorial plane directing toward four donating atoms. The Schiff-base ligands are slightly bending from the O_2N_2 plane, with the dihedral angles of two phenyl rings being 21.5(2)° and 43.1(3)°. In the O_4 site of the ligand, four donor atoms are also arranged in a quite flat manner (maximum deviations from the ideal planes are 0.009(2) Å (**3**) and 0.065(3) Å (**4**)), and the Tb(III) are located 0.711(3) Å (**3**) and 0.6262(19) Å (**4**) above the planes, with the bonding distances ranging in 2.331(3)–2.495(3) Å for **3** and 2.333(4)–2.589(5) Å for **4**, respectively. The bridging angles of Tb–O–Cu were found to be 107.48(13)° and 108.35(13)° for **3** and 106.94(19)° and 107.06(19)° for **4**, and as a result, the core structures of $\{\mathrm{TbCu}(\mathbf{L3})\}^{3+}$ moieties are quite similar in both complexes. Tb in **3** were further coordinated by three nitrate anions in a bidentate manner to complete the deca-coordination. The coordination modes are unsymmetrical among three nitrate anions; one is parallel to the Tb–Cu axis whereas two are skew to the axis. Consequently, the coordination geometry of Tb(III) ion can be assumed as a square-antiprism capped by two methoxo oxygen atoms (O1 and O3) with quite large distortion, which would be advantageous to realize an SMM character. In **4**, the nona-coordination of Tb(III) ion was completed by three additional ligands, a nitrate anion (O5 and O6) and an *o*-vanilate anion (O9 and O10) both in a chelating fashion, and a methanol molecule (O11) in a monodentate fashion. The phenoxo oxygen of the *o*-vanilate anion (O9) is collinear with Tb(III) and Cu(II) ions, and located on the opposite side of the two phenoxo oxygens of $\mathbf{L3}^{2-}$. As was described in the previous paper, the negative charge distribution of phenoxo oxygen atom is larger than other oxygen donors such as oxygen atom(s) in a nitrate anion, a methoxo group, and also a methanol molecule. Consequently, the axial positions of Tb(III) is occupied with more negative phenoxo oxygen atoms (O2, O4, and O9) and the equatorial positions were occupied by less negative oxygen donors (O1, O3, O5, O6, O10, and O11). The uni-axial crystal filed found in **4** might be advantageous for the enhancement of the easy-axial magnetic anisotropy of Tb(III) ion.

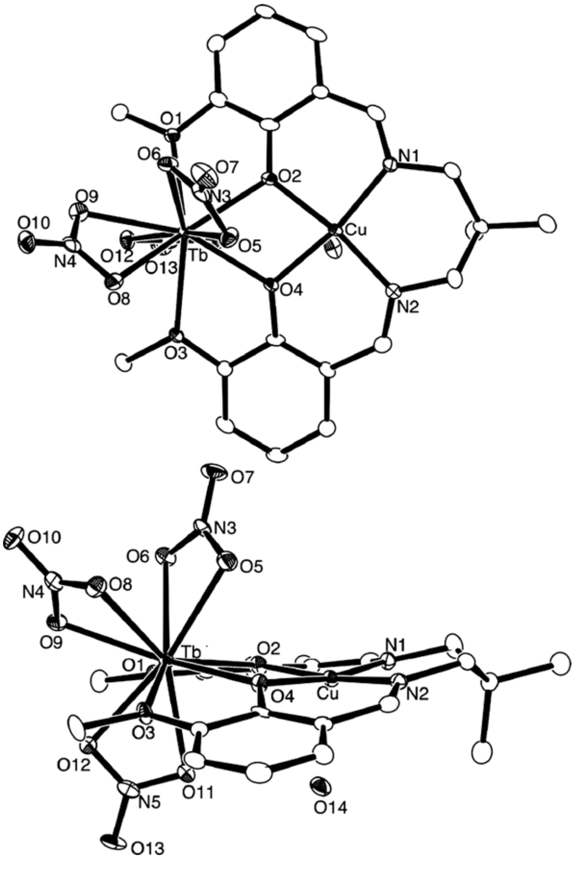

Fig. 1. Top view (upper) and side view (bottom) of ORTEP drawings of the complex **3** at 50% probability. Hydrogen atoms are omitted.

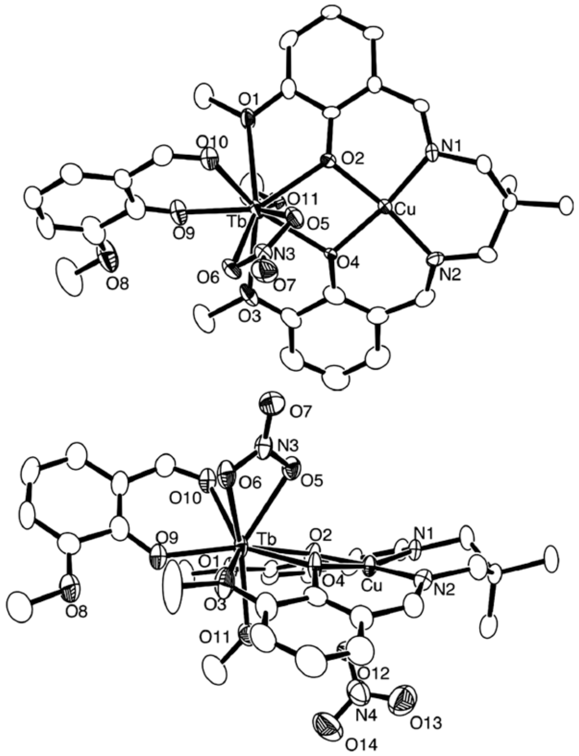

Fig. 2. Top view (upper) and side view (bottom) of ORTEP drawings of the complex **4** at 50% probability. Hydrogen atoms are omitted.