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Heterodinuclear Cu–Tb Single-Molecule Magnet

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A strictly heterodinuclear Cu–Tb complex [LCu(O_2COMe)Tb(thd)$_2$] made with a Schiff base L, thd, and monomethylcarbonate ligands [L^{2-} = *N*,*N*′-2,2-dimethylpropylenedi(3-methoxysalicylideneiminato); thd = tetramethylheptanedionato] behaves like a single-molecule magnet. The monomethylcarbonate ligand, which appears during the reaction pathway, bridges the Cu and Tb ions.

A decade after the discovery of single-molecule-magnet (SMM) behavior in the Mn_{12} cluster,[1,2] the interest directed toward SMMs remains alive. A way to obtain nanometer-scale magnets used diverse types of homopolynuclear transition-metal complexes,[3] while, more recently, heteropolynuclear complexes containing 3d and 4f ions and behaving as SMMs have also been prepared and characterized.[4,5] The nuclearity of these complexes is at least equal to four for the Cu_2Tb_2 complex[4] or greater than four, as in the Dy_6Mn_6 entity.[5] A limiting case could be the chain complex supported by a Cu−Tb skeleton, which despite its high nuclearity, displays single-chain-magnet (SCM) characteristics.[6] Surprisingly, a family of mononuclear complexes (Pc_2Ln with Ln = Tb and Dy and Pc = phthalocyaninato ligand) have been recognized as SMMs.[7] A simple and convenient characterization of the SMM property results from the observation of frequency-dependent out-of-phase signals (χ'') in alternating current (ac) magnetic susceptibility measurements. The diversity of molecules involved in this phenomenon suggests that several mechanisms should be responsible, but in any case, two conditions have to be fulfilled, i.e., high-spin fundamental state and marked anisotropy. In keeping with these considerations, one may wonder whether the low-nuclearity complexes containing perfectly insulated (3d−4f) ion pairs may fill up both conditions. Three complexes involving the same ligand [L^{2-} = *N*,*N*′-2,2-dimethylpropylenedi(3-methoxysalicylideneiminato)] and the Cu−Tb (**1**), Zn−Tb (**2**), and Zn−La (**3**) ion pairs have been prepared,[8] from which two of them have been structurally characterized. These complexes are isostructural and strictly dinuclear, while the magnetic properties lead to the conclusion that **1** is a SMM and **2** a simple paramagnet.

The central parts of the **1** and **3** structures[9] include Cu−Tb or Zn−La pairs (Figures 1 and 2). The 3d−4f ions are triply bridged by two phenoxo oxygen atoms from the L ligand and the oxygen atoms from the bridging monomethylcarbonate anion with a 3d···Ln separation of 3.4598(3) Å for **1** and 3.6174(5) Å for **3**. The 3d ion (Cu or Zn) adopts a square-based 4 + 1 coordination mode; the equatorial N_2O_2 donors are provided by L, while the axial position is occupied by the μ-bridging CO_2 group from the monomethylcarbonate

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(8) $L^1Cu(O_2COMe)Tb(thd)_2$ (**1**) was prepared as follows. A first methanol solution (15 mL) of tetramethylheptanedione (Hthd) (0.55 g, 3 mmol) and LiOH·H_2O (0.13 g, 3 mmol) was stirred at room temperature. A second methanol solution (60 mL) containing LCu·2H_2O (0.47 g, 1 mmol) and $GdCl_3$·6H_2O (0.37 g, 1 mmol) was stirred a few minutes and then poured into the previous one. The resulting solution was stirred at room temperature for 1 h and set aside. Crystals were isolated by filtration 2 days later and air-dried. $L^1Cu(O_2COMe)Tb(thd)_2$ (**1**). Yield: 44%. Elem anal. Calcd for $C_{45}H_{65}CuN_2O_{11}Tb$: C, 52.3; H, 6.3; N, 2.7. Found: C, 52.0; H, 6.1; N, 2.6. The same experimental method yielded **2** and **3** as white microcrystalline powders. $L^1Zn(O_2COMe)Tb(thd)_2$ (**2**). Yield: 0.6 g, 58%. Calcd for $C_{45}H_{65}N_2O_{11}TbZn$: C, 52.3; H, 6.3; N, 2.7. Found: C, 51.9; H, 6.1; N, 2.7. $L^1Zn(O_2COMe)La(thd)_2$ (**3**). Yield: 0.52 g, 50%. Calcd for $C_{45}H_{65}LaN_2O_{11}Zn$: C, 53.4; H, 6.5; N, 2.8. Found: C, 53.0; H, 6.3; N, 2.6.

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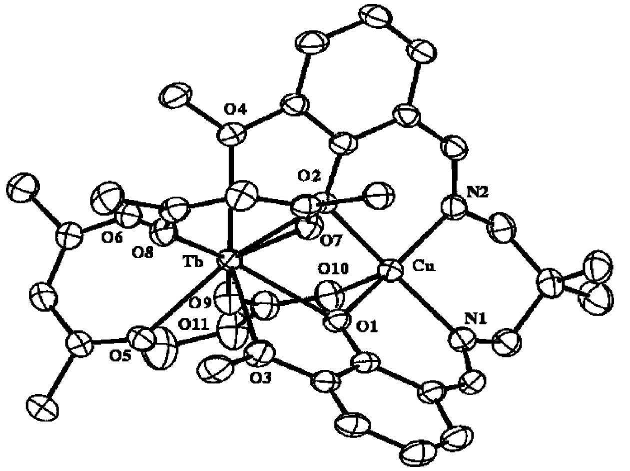

Figure 1. Molecular structure of **1**. H atoms and CH_3 from thd are omitted for clarity.

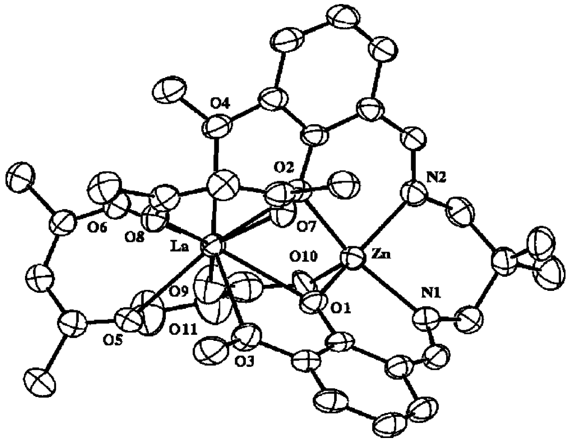

Figure 2. Molecular structure of **3**. H atoms and CH_3 from thd are omitted for clarity.

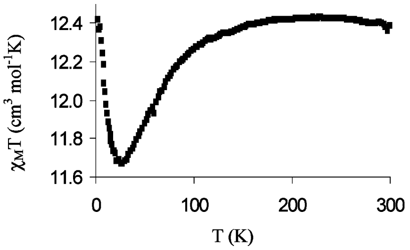

Figure 3. Thermal dependence of $\chi_M T$ for **1**.

anion, with the 3d ion displaced from the mean equatorial N_2O_2 coordination plane by 0.2181(3) Å for **1** and 0.4812(4) Å for **3**, toward the bridging carboxylate function. The Tb or La ion is nine coordinate. In addition to the two phenoxo oxygens, the rare-earth ion completes its environment with two oxygen atoms from the OMe side arms, four oxygens coming from the two bidentate tetramethylheptanedionato units and one oxygen from the bridging carbonate anion. Seven Tb−O bonds vary from 2.321(2) to 2.425(2) Å, while the La−O bonds are larger [2.440(2)−2.541(2) Å], as expected. The two longest Ln−O bonds involve the OMe side arms [2.638(2) and 2.645(2) Å for **1** and 2.684(2) and 2.684(3) Å for **3**). The monomethylcarbonato ion is involved in the rare heterodinuclear bridge (η^1:η^1:μ), with Cu−O and Tb−O bond lengths equal to 2.166(2) and 2.385(2) Å (respectively 2.155(3) and 2.532(3) Å for **3**). The four atoms of the bridging entity, CuO_2Tb and ZnO_2La, lead to a roof-shaped core, with the dihedral angle between the Cu−O1−O2 and Tb−O1−O2 planes being equal to 19.0(2)° [26.7(3)° for **3**]. The separations between metal ions belonging to neighboring molecules are large: the Cu···Cu separation is equal to 6.6583(6) Å, while values of 10.1695(3) and 8.4100(3) Å are respectively observed for Tb···Tb and Cu···Tb. These separations are equal to 6.5996(9), 10.1895(4), and 8.5551(5) Å for **3**. They preclude any significant intermolecular interaction of magnetic nature.

From the synthetic point of view, it is worth noting that the reaction of CO_2 coming from air with methanol yields the monomethylcarbonate ligand acting as a secondary bridging ligand. Such an easy CO_2 uptake was previously observed with monomeric copper(II) and zinc(II) tetraaza-cycloalkane complexes[10] and with the isostructural Cu−Gd complex.[11]

The static magnetic susceptibility χ_M of **1** has been measured in the 2−300 K temperature range in a 0.1-T applied magnetic field. The data obtained for complex **1** are represented in Figure 3. At 300 K, the $\chi_M T$ product is equal to 12.40 cm^3 mol^{-1} K, which is slightly larger than the value (12.22 cm^3 mol^{-1} K) expected for a pair of noninteracting Cu and Tb ions. As the temperature is lowered, $\chi_M T$ keeps a constant value until 150 K, then begins to decrease to 11.67 cm^3 mol^{-1} K at 25 K, and eventually increases to reach a value of 12.42 cm^3 mol^{-1} K at 3 K. The profile of the $\chi_M T$ vs T curve is strongly suggestive of the occurrence of two competitive phenomena. The decrease of $\chi_M T$ on lowering of the temperature in the high-temperature regime is most probably governed by the depopulation of the Tb Stark levels, while the increase of $\chi_M T$ at lower temperatures may be attributed to a ferromagnetic Cu−Tb interaction. It is known that the coupled systems,[12,13] including at least one ion with an orbital momentum, are not amenable to a quantitative analysis.

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(9) Crystal and structure refinement parameters for **1**: $C_{45}H_{65}CuN_2O_{11}Tb$, M = 1032.45, triclinic, space group $P\bar{1}$, a = 13.3990(15) Å, b = 14.7829(17) Å, c = 12.4177(13) Å, α = 95.274(13)°, β = 95.280(13)°, γ = 92.053(14)°, V = 2436.4(5) Å^3, Z = 2, D_c = 1.407 Mg m^{-3}, μ = 1.932 mm^{-1}, T = 293(2) K, F(000) = 1062, R1 = 0.0261 (wR2 = 0.0640) for 8848 unique reflections (R_{int} = 0.0309) with a GOF of 1.080. Complex **3**: $C_{45}H_{65}LaN_2O_{11}Zn$, M = 1014.27, triclinic, space group $P\bar{1}$, a = 13.3566(16) Å, b = 15.1124(18) Å, c = 12.5630(15) Å, α = 95.657(14)°, β = 94.185(15)°, γ = 93.312(14)°, V = 2511.4(5) Å^3, Z = 2, D_c = 1.341 g cm^{-3}, μ = 1.371 mm^{-1}, T = 293(2) K, F(000) = 1048, R1 = 0.0459 (wR2 = 0.0765) for 9110 unique reflections (R_{int} = 0.0393) with a GOF of 1.043. The diffraction intensities were collected with a STOE imaging plate diffractometer system with a graphite monochromator (λ = 0.710 73 Å) using φ oscillation movement mode. The structure was solved by direct methods and refined on F^2 by the SHELXL-97 program. CCDC reference number 262391 for **1** and 262392 for **3**.

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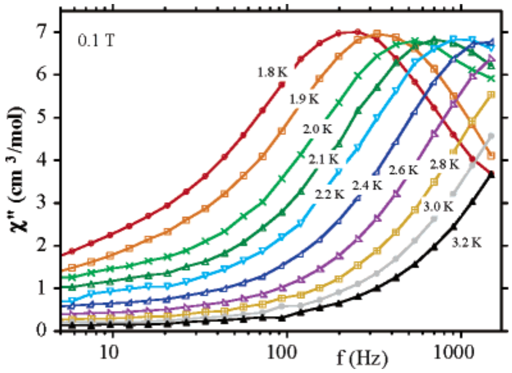

Figure 4. Frequency dependence of the χ'' susceptibility measured at several temperatures for **1**.

More significant are the results of ac field susceptibility measurements. The data are represented in Figure 4, showing the out-of-phase (χ''_M) susceptibilities vs frequency of the ac field (3 Oe) at several temperatures. Note that we applied a static field of 0.1 T in order to avoid tunneling at zero applied field (Figure S1 in the Supporting Information). The profile of these curves is characteristic of a SMM. The maxima of χ''_M were used to determine the relaxation rate τ. An Arrhenius plot of ln(τ) vs 1/T allowed us to determine the effective anisotropy barrier $U_{\mathrm{eff}} = 13.8$ K and the preexponential factor $\tau_0 = 3 \times 10^{-7}$ s (Figure S2 in the Supporting Information). A similar experiment made with the Zn−Tb complex (**2**) confirms the absence of an out-of-phase ac magnetic susceptibility signal, indicating that the SMM behavior cannot be induced by the Tb ion alone.

The SMM behavior of **1** was confirmed by hysteresis loops obtained from magnetization vs dc field scans. These were performed on single crystals using a micro-SQUID apparatus. The applied field was aligned parallel to the easy axis of magnetization of the molecules. Figure 5 presents typical hysteresis loops showing a temperature- and field-sweep-rate-dependent hysteresis (Figure S3 in the Supporting Information). The pronounced step at $H = 0$ is typical for fast resonant tunneling between the spin ground-state doublet. Such a behavior was recently published concerning a Mn$^{\mathrm{III}}$ dinuclear SMM,[14] but the present Cu−Tb complex seems to be the first heterodinuclear SMM. The large separation of the heterodinuclear molecules, as a consequence of the role held by the main and secondary ligands, implies that the observed magnetic behavior is an intramolecular property. The absence of such a behavior in the Zn−Tb complex allows us to confirm that the out-of-phase ac magnetic component observed in the Cu−Tb complex is a property characteristic of the Cu−Tb pair and cannot be attributed to the Tb ion alone. It is clear that this behavior is a consequence of the exchange coupling between the Cu and Tb ions. This observation suggests a way of increasing the SMM quality, i.e., replacement of Cu by a more anisotropic d ion. Work in that direction is in progress. In addition to anisotropy, we know that the occurrence of SMM behavior requires a high-spin ground state. This condition is very often achieved by coupling several ions in a polynuclear species. Interestingly, the present complex **1** shows that a two-ion (3d−4f) system, among which only one has a high spin, is a SMM.

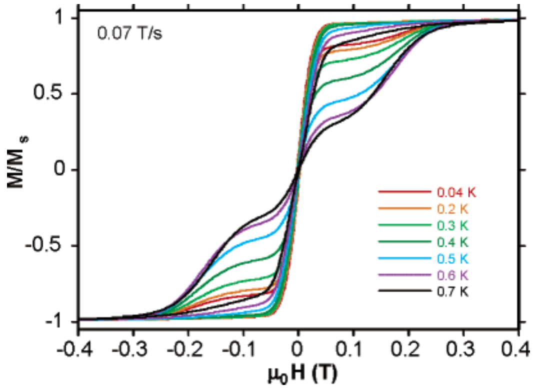

Figure 5. Hysteresis loop measurements of **1** for several temperatures and a field sweep rate of 0.07 T/s. The magnetization is normalized by the saturation value M_s at 1.4 T.

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Supporting Information Available: X-ray crystallographic file in CIF format and figures of the frequency plot of the χ'' susceptibility, Arrhenius plot of the relaxation time (τ) vs 1/T for **1**, and hysteresis loop measurements of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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