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Nitrate-Bridged “Pseudo-Double-Propeller”-Type Lanthanide(III)–Copper(II) Heterometallic Clusters: Syntheses, Structures, and Magnetic Properties

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Supporting Information

ABSTRACT: Two discrete nitrate-bridged novel “pseudo-double-propeller”-shaped hexanuclear Cu/Ln clusters of the formula $[Cu_4Ln_2L_4L'_4(NO_3)_2(OH_2)_2]\cdot 3NO_3\cdot 4H_2O$ [Ln = Dy, Gd; LH = *o*-vanilin; L′H = 2-(hydroxyethyl)-pyridine] were synthesized and characterized. Single-crystal X-ray diffraction studies revealed the trimeric half-propeller-type Cu_2/Ln core connected to other opposite-handed similar trimers by a bridging nitrate ligand. The Dy analogue, $[Cu_4Dy_2L_4L'_4(NO_3)_2(OH_2)_2]\cdot 3NO_3\cdot 4H_2O$, shows frequency-dependent out-of-phase alternating-current magnetic susceptibility, which indicates that this novel discrete $[Cu_4Dy_2]$ heterometallic cluster may exhibit single-molecule-magnet behavior.

Since the discovery of the first single-molecule-magnet (SMM) behavior in the Mn_{12} acetate,[1] compounds exhibiting slow relaxation of magnetization have attracted much attention because of their potential applications in high-density information storage and processing of magnetic information at the molecular level.[2] SMMs are molecular aggregates possessing both high-spin (S) and uniaxial (negative) magnetic anisotropy (D), leading to an anisotropy energy barrier (U) for the reversal of magnetization. To synthesize SMMs, attention was initially focused on polynuclear 3d metal aggregates, especially large manganese complexes.[3] However, recently this research field was redirected more toward mixed 3d–4f clusters as well as 4f-based systems, owing to the significant magnetic anisotropy from the large unquenched orbital angular momentum of 4f metal ions, which increases the D value for the complex, resulting in higher energy barriers. After the observation of slow magnetic relaxation in the case of mononuclear 4f complexes,[4] interest in SMMs based on 4f[5] and 3d–4f ions has grown dramatically.[6] Particularly, SMMs based on lanthanide only with Dy^{III} ions and 3d–4f containing Dy are increasingly reported in the literature.[7] Recently, a number of Ln/Cu-based SMM cluster compounds with different nuclearities have been reported; among them, a “double propeller” hexanuclear Cu/Dy^{III} cluster reported by the Powell group was particularly interesting regarding the design of clusters from dimer to hexamer.[9]

To design such SMMs with varying nuclearities, a rational synthetic approach is necessary. It has been found that *o*-vanillin (HL) and Schiff base ligands based on *o*-vanillin have formed several SMMs because of its favorable binding positions and hard Lewis basic sites to make complexes with hard Lewis acid 4f metal ions.[10] Among them, trinuclear Dy^{III} compounds reported by the Powell group and others showed very interesting magnetic behavior.[11] Furthermore, the SMM based on Cu/Ln using Schiff base ligands derived from *o*-vanillin gave few propeller-type complexes.[12] Moreover, to synthesize clusters based on hard Lewis acid with high hydrooxophilic Ln^{III} and Cu^{II} ions, we have selected pyridine-based ancillary ligands having alkoxide ends, which act as chelating and bridging ligands with hard Lewis base O and N binding sites. Keeping this in mind, we use two different ligands: one with a flexible end, the alkoxide of a 2-(hydroxyethyl)pyridine (L′) and another one with three rigid oxophilic sites, *o*-vanillin (L), to synthesize mixed 3d–4f metal clusters.

Herein, we report the preparation, structural description, and magnetic properties of two hexanuclear Cu_4/Dy_2 and Cu_4/Gd_2 clusters with a “pseudo-double-propeller” architecture using mixed ligands, where the Dy analogue exhibits SMM behavior. After the report of a hexanuclear double-propeller Cu^{II}/Dy^{III} cluster with interesting magnetic behavior, this is the first pseudo-double-propeller structure containing two trimeric mixed Cu_2/Ln metal sites connected directly by a central bridging nitrate ligand. Compounds **1** and **2**, formulated as $[Cu_4Ln_2L_4L'_4(NO_3)_2(OH_2)_2]\cdot 3NO_3\cdot 4H_2O$ [for **1**, Ln = Dy; for **2**, Ln = Gd; L = *o*-vanillin; L′ = 2-(hydroxyethyl)pyridine], were synthesized by a slow evaporation method at room temperature in methanol. Single-crystal X-ray diffraction analysis revealed that both compounds crystallized in monoclinic space group $C2/c$ and contain two Cu and one Ln metal centers and two L and two L′ ligands in their asymmetric unit. Compounds **1** and **2** are isostructural, so we detail here the structure of compound **1** only. Both structures contain Cu_4/Ln_2 hexanuclear units (Figure 1a), in which two trimeric Cu_2/Ln units are connected by three O atoms of the central bridging nitrate, with Ln ions being located at the center

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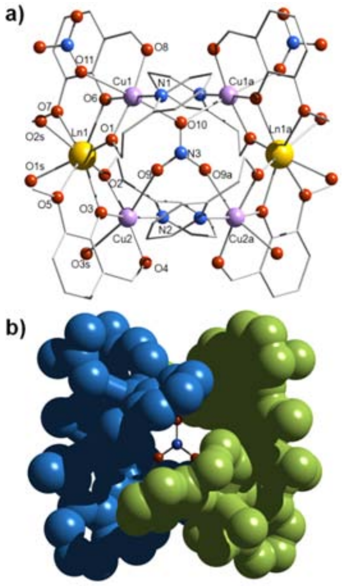

Figure 1. (a) Molecular structures of complexes **1** and **2** (Ln = Dy, Gd). Color code: Dy, yellow; Cu, violet; C, gray; N, blue; O, red. (b) Molecular structure showing the two propellers bridged by a nitrate. H atoms are omitted for clarity.

of the Cu_2/Ln trimeric site. These three metal centers along with an oxo bridge form a “pseudo-double-propeller” arrangement of two opposite-running trimeric units (Cu_2/Ln) interplaned by a central nitrate, which has 2-fold rotational site symmetry, as shown in Figure 1b. The O atoms of the nitrate ligands on the outer side of the molecule occupy the axial positions of Cu1 and Cu1a (Cu1−O11 distance = 2.589 Å) of two opposite trimeric units, and the O atom of a bridging nitrate ligand is coordinated in a μ_2-oxo fashion (Cu1−O10 distance = 2.536 Å) from the center of the molecule. This bridging nitrate ligand is also chelated to Cu2 and Cu2a, so that O9 and O9a provide additional bridges between two sites. The Ln atom is eight-coordinated by four O atoms from two L, two O atoms from two alkoxido O atoms of L′, and two from coordinated water molecules, together making a distorted square-antiprismatic environment around the Ln metal centers. The Dy−O bond lengths vary from 2.247 to 2.680 Å. In addition, there are free water molecules along with the nitrate anions interacting with a cationic complex by making a strong hydrogen bonding with coordinated water molecules of Ln1 and Cu2 and also with a coordinated nitrate of Cu1 (Figure S1 in the SI). Here, Cu1 is six-coordinated and has an octahedral geometry with a N/O-donor atom environment. At the outer equatorial site of Cu1, the phenoxo group of the *o*-vanillin ligand bridges a Ln atom, leading to a Cu1···Dy1 distance of 3.364 Å in **1** and a Cu1···Gd1 distance of 3.385 Å in **2**. Cu1 and Ln1 are thus linked by one phenoxo bridge (O6) and O1 of a μ_2-alkoxido bridge. Cu2 is also six-coordinated except that the water molecule is coordinated from the outer side of the molecule at its axial position, unlike the coordinated nitrate ligand to Cu1.

The two connected trinuclear Cu_2Ln cores give a hexanuclear complex, resembling two opposite-running propellers balanced by a bridging nitrate. Here two blades are derived from the entity CuLL′ with Ln as the center, and this makes a pseudo-double-propeller arrangement lacking two blades of the 4-fold propeller in each side; hence, we called it “pseudo” (Figure 2a−c). These two blades have the same handedness (left- or right-handedness) with respect to two blades of another opposite propeller having opposite handedness (Figure 2d). Henceforth, pairs of cationic trinuclear sites $[Cu_2LnL_2L'_2(NO_3)(OH_2)]$, related by a crystallographic 2-fold axis passing through a central nitrate via N3 and O10, form a stable pseudo-double-propeller supramolecular architecture.

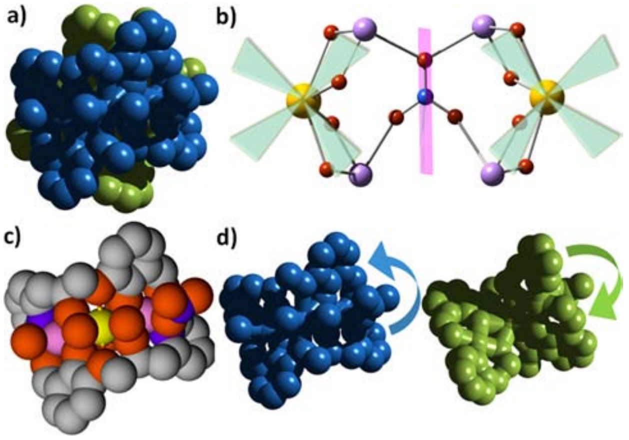

Figure 2. (a) Trimeric Cu_4/Ln_2 core. (b) Double-propeller resemblance of the central core of the molecule. (c) Molecular view showing a single propeller along the *a* axis. (d) Arrangement of opposite-running pseudopropellers.

As for the magnetic properties, it is easier to first examine those of **2** because Gd^{III} does not present first-order spin−orbit coupling. The χT value at room temperature for **2** (18.04 emu·K·mol^{-1}) is slightly higher than the expected value of 17.40 emu·K·mol^{-1} for two Gd^{III} ions ($^8S_{7/2}$; $g = 1.99$) and four Cu^{II} ions ($S = {}^1/_2$; $g = 2.1$);[13] see Figure S5 in the SI. Upon cooling, the χT value increases regularly up to a maximum at around 8 K (23.4 emu·K·mol^{-1}), where it starts to decrease regularly down to 19.7 emu·K·mol^{-1} at 1.8 K. This behavior is characteristic of intramolecular ferromagnetic interactions between the spin carriers. The magnetic coupling via the bridging nitrate group can be considered as negligible. The coupling via the ONO motif of the nitrate group is actually known to be very weak.[14] However, the Cu2−Cu2 coupling occurs via a single O atom of the nitrate group (O10) and could be a priori quite large despite the relatively long Cu−O distance (2.55 Å). Examination of the crystal structure of **2** shows that the coordination sphere of Cu2 is elongated along the O13−O10 axis and, therefore, the magnetic orbital of the Cu2 paramagnetic center ($d_{x^2-y^2}$, considering Cu2−O10 as the *z* axis) has no contribution pointing toward O10. Moreover, the direct overlap between the magnetic orbitals is also negligible because of the large Cu2−O10−Cu2 angle (134°) and the large Cu2−Cu2 distance (4.69 Å). Therefore, Cu2−Cu2 can also be neglected in the first approximation.[15] This is further confirmed by analysis of the magnetic data. The χT versus T curve can actually be fitted in the high-temperature region (above 18 K) considering two noncoupled Cu−Gd−Cu entities, using the following spin Hamiltonian: $\hat{H} = -J\hat{S}_{Gd1}(\hat{S}_{Cu1} + \hat{S}_{Cu2})$.

The fit leads to $J = 4.7$ cm^{-1} and $g = 2.03$, with a very good agreement factor $R = 1.2 \times 10^{-5}$ (Figure S5 in the SI). The subsequent decrease at low field is due to a combination of saturation effects, intermolecular interactions, and antiferromagnetic intramolecular interactions between the two Cu_2/Gd

parts (the zero-field splitting of the ground state is supposed to be quite low, given the very small magnetic anisotropy of the constituting paramagnetic centers). The magnetization versus field curve at 1.8 K also confirms this coupling scheme. Data can be perfectly fitted by a Brillouin function considering two independent entities of spin $^9/_2$ (with $g = 2.05$) corresponding to the ground state resulting from the ferromagnetic alignment of two Cu^{II} and one Gd^{III} cations (Figure S5 in the SI). The alternating-current (ac) susceptibility measurements under a zero direct-current (dc) field show no evidence of a frequency-dependent out-of-phase signal (χ'') down to 1.8 K (Figure S6 in the SI).

For compound **1**, the χT value at room temperature is slightly smaller than the expected one of 29.8 emu·K·mol^{-1} for two Dy^{III} ($S = {}^5/_2$; $L = 5$; $^6H_{15/2}$; $g_J = {}^4/_3$) and four Cu^{II} ($S = {}^1/_2$; $g = 2$) ions.[13] Upon cooling, χT remains almost constant until about 100 K, where it starts to increase to a maximum of 32.9 emu·K·mol^{-1} at 4.9 K (Figure 3a). This behavior indicates the occurrence of intramolecular ferromagnetic interactions between the Dy^{III} and Cu^{II} ions. Below this maximum, the decrease of χT may be due to a combination of intermolecular antiferromagnetic interactions, effects of magnetic anisotropy, and depopulation of excited Stark sublevels.[16]

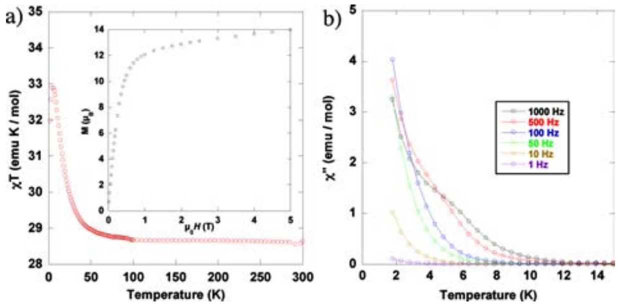

Figure 3. (a) χT versus T plot of compound **1**. Inset: magnetization versus field curve at 1.8 K. (b) Plot of the out-of-phase ac susceptibility (χ'') for compound **1** at different frequencies.

The M versus H curve at low temperature (1.8 K) shows a rapid increase at low fields, with the magnetization being far from reaching saturation at high fields [14 μ_B at 5 T, much lower than the expected value for two Dy^{III} and four Cu^{II} ions (around 22 μ_B)]. This behavior is typical of the effect of anisotropy and crystal-field effects for Dy^{III} ions.[11,16] At 1.8 K, the magnetization does not show hysteresis. Nevertheless, ac susceptibility measurements under zero dc field show a clear uprise of a frequency-dependent out-of-phase signal (χ''), which may indicate SMM behavior (Figure 3b). Yet, this feature should not be taken too rapidly as evidence of SMM behavior; only lower-temperature measurements could precisely determine the exact behavior of the clusters.[17]

In conclusion, we have successfully designed and synthesized mixed-metal 3d−4f Cu/Ln clusters with Dy and Gd using mixed-ligand systems. Rather than using Schiff base ligands, this approach with the use of oxophilic *o*-vanillin and pyridine-based alkoxido ligands made it possible to synthesize novel nitrate-bridged first "pseudo-double-propeller" arrangements of two analogous Cu_4Dy_2 and Cu_4Gd_2 supramolecular magnetic archetypes. Cu_4Dy_2 was found to show frequency-dependent ac susceptibility, which suggests that this compound behaves as a SMM at low temperature.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, synthesis, analysis, magnetic measurements, and X-ray tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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