Supramolecular “Double-Propeller” Dimers of Hexanuclear Cu\textsuperscript{II}/Ln\textsuperscript{III} Complexes: A \{Cu\textsubscript{3}Dy\textsubscript{3}\} \textsuperscript{2} Single-Molecule Magnet**

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Building molecular organizations with controlled structure is an important point of interest in supramolecular chemistry and materials science.\textsuperscript{[1]} The major force to build a supramolecular architecture is determined by a number of factors: 1) coordination bonding,\textsuperscript{[2]} 2) versatile hydrogen-bonding interactions\textsuperscript{[3]} 3) π–π-stacking interactions,\textsuperscript{[4]} and 4) electrostatic interactions.\textsuperscript{[5]} Hydrogen-bonding and π interactions are frequently employed as driving forces to give well-defined supramolecular architectures.\textsuperscript{[6]} In recent years, a number of metallo-supramolecular structures and their relevant insights into metal-directed self-assembly processes, these polymetallic species can display unique magnetic properties, which result from the assembly of paramagnetic metal ions by bridging ligands.

The design of new materials based on aromatic polycarboxylic acids such as benzene-1,3,5-tricarboxylic acid (trimesic acid) is currently an important research topic for the community of chemists and physicists.\textsuperscript{[9]} We report herein on the molecular structure, the supramolecular association, and unusual magnetic properties of the first examples of three-bladed propellers made with heterometallic compounds (Cu\textsubscript{3}Ln\textsubscript{3}, Ln = Gd, Tb, Dy), which result from the coordination of Cu–Ln entities with trimesic acid.

The reaction of 2-hydroxy-3-(hydroxymethyl)-5-methylbenzaldehyde\textsuperscript{[10]} with propylenediamine (2:1 molar ratio) in methanol, followed by addition of Cu(OAc)\textsubscript{2}2H\textsubscript{2}O, yielded the “compartmental complex ligand” Cu\textsubscript{2}H\textsubscript{2}O (Scheme S1 in the Supporting Information). This complex possesses a flexible O–O\textsubscript{2}, metal binding site (2-phenoxo- and 2-hydroxymethyl oxygen atoms), which could accommodate 4f ions. In addition, the terminal -OH groups can participate in the formation of hydrogen bonds. Dinuclear heterometallic complexes [LCuLn(NO\textsubscript{3})\textsubscript{3}]3.5THF (1) (Ln\textsuperscript{III} = Gd (1a), Tb (1b), Dy (1c)) were synthesized by reaction of Cu\textsubscript{2}H\textsubscript{2}O with Ln(NO\textsubscript{3})\textsubscript{3}6H\textsubscript{2}O in THF. Reaction of these heterobinuclear complexes with trimesic acid in an acetone/THF (1:2 ratio) gave the hexanuclear compounds [(µ\textsubscript{2}-Cu\textsubscript{3}H\textsubscript{2}O)[LCuLn(NO\textsubscript{3})\textsubscript{3}]3]3THF (2) (Ln\textsuperscript{III} = Gd (2a), Tb (2b), Dy (2c)).

The IR spectra of the three compounds 1 were essentially identical, not just in the lower wavenumber “fingerprint” region, but also in the higher wavenumber region corresponding to hydrogen-bonded O–H stretches, indicating that the three compounds are closely isostructural. The same is true of the spectra of the complexes 2 (see the Supporting Information). All the spectra show characteristic vibrations of the coordinated ligand, with the ν\textsubscript{C–N} and ν(C\textsubscript{sp}–O) stretching vibrations observed at 1625–1622 cm\textsuperscript{−1} and 1029–1033 cm\textsuperscript{−1}, respectively. Bands assigned to nitrate ions (for example, in 2c ν\textsubscript{as}(NO\textsubscript{3}) = 1468; ν\textsubscript{s}(NO\textsubscript{3}) = 1298; ν(NO) = 1001 cm\textsuperscript{−1}) are also present. The extent of separation of the two highest frequency bands (170 cm\textsuperscript{−1}) suggested a bidentate chelating mode of coordination for these anions.\textsuperscript{[11]} The supplementary strong bands at 1710 cm\textsuperscript{−1} present in the IR spectra of the hexanuclear compound 2c can be assigned to the ν\textsubscript{as}(COO\textsuperscript{−}) vibration of the trimesate carboxylate groups in a monodentate coordination mode.

The structures of 1b and 2c were determined by single-crystal X-ray diffraction. The structure of 1b consists of LCu\textsubscript{3}Tb\textsuperscript{III} binuclear units (Figure 1 a) in which the metal ions are doubly bridged by the two phenoxy oxygen atoms. Cu1 is located in the inner N\textsubscript{2}O\textsubscript{2} plane of the Schiff base ligand (L\textsuperscript{2}−); these four atoms form a distorted equatorial plane with the apical positions occupied by the oxygen atom of a THF molecule. Cu1–O1A = 2.460(8) Å on one side and the oxygen atom of a nitrate ligand (Cu1–O5 = 2.522(4) Å) on the other side. This nitrate ligand is also chelated to Tb1, so that O5 provides a supplementary π–π Cu–Tb bridge, while the two remaining nitrate anions simply chelate Tb1. The Cu1–Tb1 distance is 3.3216(6) Å and the dihedral angle between the Tb1–O1–O3 and Cu1–O1–O3 planes is 41.62(2)°. The Tb atom in 1b is ten-coordinate, ligated by four oxygen atoms from the ligand, four oxygen atoms from two chelating nitrate anions, and two from the bridging ν\textsubscript{as}(NO\textsubscript{3}) nitrate anion; the Tb1–O bond lengths vary from 2.392(3) to
The two terminal OH groups of each Cu entity form strong hydrogen bonds with the oxygen atoms of two lattice THF molecules (O4···O31 = 2.664(6), O2···O41 = 2.671(6) Å). The structure of complex 2c, which has threefold rotational site symmetry, is shown in Figure 1b,c. Cu1 is five-coordinate and has an approximate square-pyramidal geometry. As for 1b, the N2O2 atom set of the ligand defines the equatorial plane of Cu1, and again an oxygen atom from a nitrate ligand that chelates Dy1 occupies an axial site (Cu1–O5 = 2.501(8) Å). Cu1 and Dy1 are thus linked by two phenoxo bridges (O1 and O3), and O5 also forms a $\eta^2$-$\eta^1$ bridge with a Cu···Dy distance of 3.3035(15) Å.

The DyIII ion is nine-coordinate with a capped square-antiprismatic geometry, and Dy1–O bond lengths range from

Figure 1. a) Molecular structure of complex 1b; b) molecular structure of complex 2c; c) space-filling model of complex 2c (emphasizing the propeller structure); d) dodecanuclear supramolecular assembly of two hexanuclear heterometallic compounds (2c); e) 2c viewed down the crystallographic c axis.
2.320(2) to 2.558(2) Å. The coordination environment comprises four oxygen atoms from the two nitrate ligands, four oxygen atoms from the “compartamental complex ligand” (CuL) and one oxygen atom from the monodentate carboxylate ligand (Dy1–O1I = 2.312(2) Å). This last interaction is reinforced by a strong hydrogen bond from the Schiff base hydroxy oxygen atom O2 to the noncoordinated carboxylate oxygen atom O12. The CuO2Dy core is again not planar, but has a dihedral angle between the CuI–O1I–O3 and Dy1–O1I–O3 planes equal to 45.88(2°). The trimesate ligand thus connects three binuclear [LCu(Dy)(NO3)] units to give a hexanuclear complex, resembling a three-bladed propeller, in which each blade is derived from a CuL moiety. The crystal site symmetry requires that all three blades have the same handedness (either left- (A) or right-handedness (Δ); Figure 1d).

Pairs of hexanuclear compounds [[μ2-C2H3OH][LCu(Dy)(NO3)]]2, related by a crystallographic 3 rotoinversion center, form a supramolecular assembly. The two molecules are linked by six intermolecular hydrogen bonds, each involving the second Schiff base hydroxy group O4 and a noncoordinated carboxylate oxygen atom from the second molecule. In addition, the aromatic rings of the two trimesate ligands are coplanar and their six carbon atoms are perfectly eclipsed, resulting in strong π–π stacking between the rings and separation between their planes of 3.543(4) Å (Figure 1d,e), which strengthens the hexanuclear complex. Similar self-assembly by hydrogen bonds and π–π stacking has been found in a range of organic and coordination compounds,[6] but this compound is the first example involving heterometallic CuLn units.

The magnetic behavior of 1a and 2a is shown in Figure S2 (in the Supporting Information) as a plot of $\chi_M(T)$ against $T$. At 300 K, $\chi_M(T)$ for 1a is equal to 8.27 cm$^3$ mol$^{-1}$ K, which corresponds to the value expected for two uncoupled Cu$^{II}$ and Gd$^{III}$ metal ions (8.25 cm$^3$ mol$^{-1}$ K). Lowering the temperature causes $\chi_M(T)$ to increase to 8.94 cm$^3$ mol$^{-1}$ K at 2 K, confirming the presence of a weak ferromagnetic Cu$^{II}$–Gd$^{II}$ interaction. Compound 2a shows a similar behavior. At 300 K, $\chi_M(T)$ for 2a is 24.92 cm$^3$ mol$^{-1}$ K, increasing slightly to 25.92 cm$^3$ mol$^{-1}$ K at 2 K. As shown previously, 4f/4f magnetic interactions through carboxylate groups are very weak,[22] and the interaction through the trimesate ligand will be even weaker. Quantitative analyses were performed for compounds 1a and 2a on the basis of classical Heisenberg–Dirac–van Vleck (HDVV) formalism derived from the isotropic Hamiltonian $H_{\text{iso}} = -J \mathbf{S}_1 \cdot \mathbf{S}_2 .[19]$ The data were fitted in the simultaneous $\chi_M(T)$ and $\chi_A(T)$ thermal dependences including temperature-independent paramagnetism (TIP), impurity contribution ($\rho$), and intermolecular interaction ($\phi$) according to Equation (1) with $n = 1$ for 1a and $n = 3$ for 2a.

$$\chi = n \frac{4N\beta^4 g_\phi^4 + 7 g_\rho^4 \exp(-4J/kT)}{kT^2} \cdot \frac{9 + 7 \exp(-4J/kT)}{9 + 7 \exp(-4J/kT)} \quad (1)$$

The $g$ values associated with the low lying levels $E(4) = 0$ and $E(3) = 4J$ are $g_a = \gamma(3 g_{\text{Gd}} + g_{\text{Cu}})/8$ and $g_b = (9 g_{\text{Gd}} - g_{\text{Cu}})/8$, respectively.[23] Least-squares fitting of the experimental data with $g_{\text{Gd}}$ fixed at 2.00 led to the following sets of parameters: $g_{\text{Cu}} = 2.16(4)$ and $J = 0.20(4)$ cm$^{-1}$ for 1a, and $g_{\text{Cu}} = 2.13(5)$ and $J = 0.11(4)$ cm$^{-1}$ for 2a; agreement factors of $\chi (\chi_{\text{obsd}} - \chi_{\text{calcld}})^2/\chi (\chi_{\text{obsd}})^2$ are 2.5 x 10$^{-4}$ and 3.5 x 10$^{-4}$, respectively. The experimental magnetization for 1a and 2a at 2.0 K are correctly fitted by Brillouin functions corresponding to coupled Cu$^{II}$ and Gd$^{III}$ ions (see the Supporting Information).

The interpretation of the magnetic data of complexes 1b, 1c, 2b, and 2c is not straightforward since the Tb$^{III}$ and Dy$^{III}$ ions possess first-order angular moments that preclude the use of spin-only Hamiltonians for isotropic exchange. The strong anisotropy of these ions leads to a deviation of the magnetic susceptibility from the Curie law, characterized by a decrease of the $\chi_M(T)$ product at low temperatures and the absence of saturation in the magnetization curves for 1b, 1c, 2b, and 2c (see the Supporting Information). If Cu–Tb or Cu–Dy interactions are active in these compounds, these must coexist alongside the above effect, and the resultant profiles of the $\chi_M(T)$ versus $T$ curves are therefore not necessarily indicative of the sign of the magnetic interaction. Furthermore, we know from the study of the equivalent complexes 1a and 2a that the Cu–Ln interaction is weak. From the experimental results, we can tell that a weak ferromagnetic Cu–Tb interaction is present in 2b. For the other three complexes, 1b, 1c, and 2c, studies to lower temperature would be needed. Because of the weak values of the $J$ parameters, the qualitative method, which consists of replacing the Cu ion by diamagnetic ones and comparing the $\chi_M(T)$ products of the two sets of complexes, is also unlikely to give a reliable answer.[14b]

The ac susceptibility measurements for 2c show frequency-dependent signals, suggesting single molecule magnetic (SMM) behavior. These are rather weak; the $\gamma'/\gamma$ ratios are low, and no maxima could be observed above 1.8 K for the out-of-phase signals. This low intensity is presumably due to population of low-lying excited states, which are a consequence of the weak magnetic interaction.

The magnetizations of single crystals of both 1c [CuDy] and 2c [Cu2Dy], as a function of applied field were studied with a micro-SQUID array in the 0.04–7 K range.[15] For 1c, the measurements at 0.04 K revealed hysteresis loops with a very low coercivity (Figure 2, top). Similar behavior was also found in other series of CuLn (Ln = Dy or Tb) compounds.[16,17] By contrast, measurements on the supramolecularly associated [Cu2Dy]2c, for which the field was applied in the easy plane of the crystal, perpendicular to the threefold axis of the propeller, revealed hysteresis loops with a drastic increase in the coercivity relative to that of 1c. The coercivity is dependent on both temperature and sweep rate (Figure 2, bottom), increasing with both decreasing temperature and increasing field sweep rate, as expected for SMM behavior, and is still large (ca. 0.5 T) above 1 K. The hysteresis loops also present a very large sweep-rate-independent step at zero field, which is due to quantum tunneling of the magnetization through the barrier.

The heterometallic dinuclear units in the case of 1 and 2 involve the same bicompartamental ligand. The coordination geometries about Cu and the lanthanide are similar in both...
cases. In particular, the CuO₂Ln dihedral angles, which determine the Cu-Ln magnetic interaction, are very similar (see the Supporting Information), so we expect very similar intra-{CuLn} behavior in 1c and 2c. Thus, to understand their strikingly different hysteretic behavior, we first note that it cannot be due to supramolecular magnetic interactions only, which are expected to be very weak in 2c (of the order of tens of mK). Therefore, the observed magnetization steps basically originate from intradimer momentum reorientations, whereas the supramolecular interactions between the dimers are mainly responsible for the tunnel window for these transitions. In this respect, the situation is quite different from the case of the [{Mn₄O₃Cl₄(O₂CEt)₃}]²⁻ cluster, for which separation of magnetization steps along the field axis arises as a result of supramolecular magnetic interactions between the two Mn₄ units. The second observation is that in 1c all {CuDy} units (and their anisotropy axes) are parallel to each other, whereas in 2c their magnetic axes form 120° in the ab plane for nearest neighbor ions (our ab initio calculations show that these axes essentially lie in the ab plane). Therefore the observed hysteresis in 2c can be explained as follows: In a (quasi) axial ligand field the ³H₁₅/₂ term of Dy³⁺ ion splits into several well separated Kramers doublets, the ground one having a momentum projection close to J = 15/2. The lowest energy levels of the CuDy dimer arise from the exchange interaction between the S = 1/2 state of the Cu²⁺ ion and the lowest Kramers doublet on the Dy³⁺ site. Since the magnetization curve for 1c shows no activation behavior at low values of field, even at very low temperature (Figure 2), the exchange interaction is most probably of Ising type.

The reversal of magnetic moment on the Dy³⁺ site, which is always directed along the anisotropy axis, can only be induced by the transverse components of the magnetic field, whereas the flipping rate is a very sensitive function of the amplitude of this field. In 1c the applied field probably has a nonnegligible transverse component on the Dy³⁺ ions in all of the CuDy units, which results in an almost completely adiabatic reversal of magnetization through resonance tunneling around the H = 0 point and the lack of hysteresis. However, in 2c the field applied in the ab plane will have different transverse components for the three Dy³⁺ ions in the Cu₃Dy₃ units. It can eventually be oriented in such a way as to become almost parallel to the anisotropy axis of one of the Dy³⁺ ions of the triangle (ions of type a in Figure 3). Then the transverse field on this ion will be small and the adiabatic channel of reversal of magnetization will be practically closed. In contrast, the field on the other two dysprosium sites (b and c in Figure 3) will make an angle of 60° with their anisotropy axes, giving rise to an adiabatic reversal of magnetization at any field sweep rates similar to the behavior of 1c. At large

Figure 2. Single-crystal magnetization (M) versus applied field for complex 1c {CuDy} (top) and 2c {Cu₃Dy₃}²⁻ (bottom) with different field sweep rates at 0.04 K. M is normalized to its saturation value at 1.4 T. For temperature-dependence data, see the Supporting Information.

Figure 3. Evolution of the orientation of magnetic moments on the six dysprosium sites (arrows) of the double-propeller complex {Cu₃Dy₃}²⁻ with the magnetic field applied in the easy plane. Upper and lower dysprosium triangles are shown by solid and dashed lines, respectively.
negative fields, the magnetic moments on the DyIII ions will be oriented as in the upper plot of Figure 3. Increasing the field up to $H > 0$ we cross the tunneling window, where adiabatic flips of magnetic moments on sites b and c occur (middle plot in Figure 3). Since the projection of their magnetic moments on the direction of the field is $\frac{1}{2}$, these flips will reduce the total magnetic moment to a value close to zero. At the same time the quantum tunneling of magnetization will not occur on dysprosium sites of type a, which instead will evolve nonadiabatically into the excited state when the field is swept to the positive region. Later on they will undergo thermal relaxation to the ground Zeeman component. This relaxation is associated with momentum reversal on these dysprosium sites (lowest plot in Figure 3), which will give rise to a second magnetization step at ($H > 0.5$ T in Figure 2), whose position will be dependent on the field sweep rate.

In conclusion, we present herein a supramolecular $[\text{Cu}_3\text{Dy}_3]^2$ compound in which the two hexanuclear complexes are presented in the Supporting Information.

$\text{Experimental Section}$

Experimental details of the synthesis and spectral characterization are presented in the Supporting Information.

Magnetic susceptibility data were collected on powdered samples with a Quantum Design MPMS SQUID magnetometer under a 0.1 T applied magnetic field. All data were corrected for diamagnetism of applied magnetic field. $\chi$ versus $T$ was fitted by using a $\chi(T) = C(1/T)^{\nu}(1 - C_{\chi}/T^{\nu})$ function. The low temperature data were fitted to the Curie-Weiss law, with $\mu_{\text{eff}} = 5.3$ B.M. and $\theta = 55$ K.

X-ray analysis: The X-ray data were collected on Bruker SMART Apex (1b) and Stoe IPDS II (2c) diffractometers using graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). All data were corrected for the Lorentz effect and absorption corrections were applied.

$\text{Supporting Information}$

The Supporting Information contains a more detailed description of the experimental procedures and the data analysis.

Keywords: heterometallic compounds · magnetic properties · single molecule magnets · supramolecular chemistry


