Metallacyclophanes

Rational Design of an Enneanuclear Copper(II) Complex with a Metallacyclophane Core[**]

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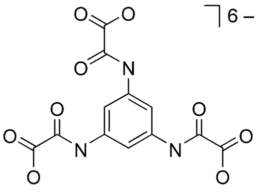
Design of complex molecular architectures starting from constituent subunits is a central theme in inorganic chemistry.[1] Among such species, those containing magnetic ions are of particular interest because their magnetic properties directly stem from the geometrical arrangement of the constituent subunits.[2] The main challenge in this field is the synthesis of single-molecule magnets whose ground states have high spin and considerable negative axial anisotropy.[3] Pathways to such complex molecular entities are based on two orthogonal synthetic schemes: self-assembly methods[4] and step-by-step strategies.[5] In the former, the nature of the final products cannot be determined a priori. In contrast, the latter provide an efficient means to control both nuclearity and dimensionality of the polymetallic edifice.

Following a step-by-step approach, we prepared the new ligand *N,N′,N″*-1,3,5-benzenetris(oxamate) (**1**). Being incapable of hexadentate ligation to a single metal center, this ligand rather self-assembles with $\mathrm{Cu^{II}}$ ions in a 2/3 ligand/metal ratio to give the trinuclear complex $\mathrm{Na_6[Cu^{II}_3(\mathbf{1})_2]\cdot 11.5\,H_2O}$ ($\mathrm{Na_6\text{-}\mathbf{2}\cdot 11.5\,H_2O}$). In the $[\mathrm{Cu^{II}_3(\mathbf{1})_2}]^{6-}$ core **2**, each ligand adopts a tris(N,O-bidentate) coordination mode (vide infra). Thus, the three bis(oxamate)copper(II) spin-bearing residues are bridged by two 1,3,5-benzenetriyl moieties, which have already proved to be efficient ferromagnetic spin-coupling units in π-conjugated organic polyradicals[6] and metal complexes.[7–10] Additionally, **2** is a potential hexakis-bidentate ligand that can coordinate six other metal ions through its external oxygen atoms. Using this "complex-as-ligand strategy" with ancillary ligands on the additional metal ions to avoid polymerization, we obtained the novel homometallic enneanuclear complex $[\{\mathrm{Cu^{II}_3(\mathbf{1})_2}\}\{\mathrm{Cu^{II}(pmdien)}\}_6]\mathrm{(ClO_4)_6\cdot 12\,H_2O}$ ($\mathbf{3}\text{-}\mathrm{(ClO_4)_6\cdot 12\,H_2O}$; pmdien = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine).



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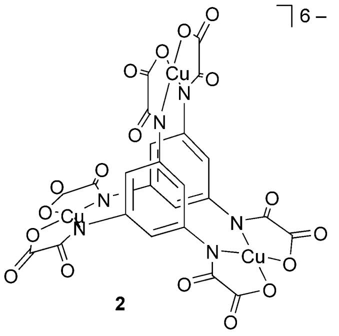

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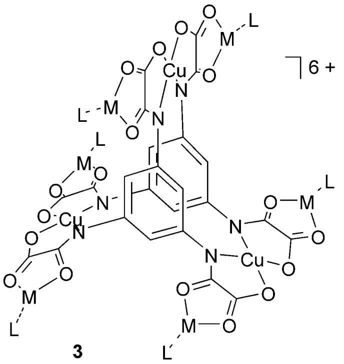

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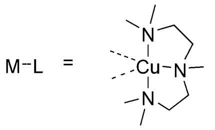

Single-crystal X-ray characterization of **3** revealed the desired structure. The unit cell ($R\bar{3}$ space group) contains two types of hexacationic enneacopper molecules, one of which is disordered, as well as perchlorate ions and water molecules. The well-ordered enneanuclear molecules exhibit the anticipated pattern of six external $[\mathrm{Cu(pmdien)}]^{2+}$ subunits ligated to a central $[\mathrm{Cu_3(\mathbf{1})_2}]^{6-}$ unit (Figure 1). To the best of our knowledge, **3** is the second crystallographically characterized example of a 1,3,5-metallacyclophane.[11]

The central $\mathrm{Cu^{II}}$ ions have an elongated square-pyramidal (Cu2 and Cu4) or elongated octahedral (Cu5) geometry with distant axial ligands. These environments can be approximated as square-planar, created by one oxamate moiety of each ligand (maximum deviation from average $\mathrm{N_2O_2}$ plane: 0.148 Å). The $[\mathrm{Cu_3(\mathbf{1})_2}]^{6-}$ core is twisted to accomodate a noneclipsed disposition of the aromatic rings, with a distance of 3.237 Å between their average planes. In comparison to the binuclear 1,3-metallacyclophane analogue of **2**, [Cu$_2$-*m*],[10] coordination of the third Cu atom brings the aromatic rings closer, enhances electronic repulsions, and results in greater overall twisting of the molecule: the C-C-N-Cu torsion angles are farther from 90° in **3** (65.0–79.6°, av 73.8°) than in [Cu$_2$-*m*] (73.4–89.3°, av 78.9°). In the peripheral $[\mathrm{Cu(pmdien)}]^{2+}$ subunit, the $\mathrm{Cu^{II}}$ ions are five-coordinate, close to square-pyramidal with τ values[12] ranging from 0.27 to 0.39, and with one Cu–O bond longer than the other (2.20 versus 1.97 Å on average).

The magnetic properties of **2** and **3** are depicted in Figure 2. Complex **2** exhibits ferromagnetic coupling between the three $\mathrm{Cu^{II}}$ ions: $\chi_M T$ continuously increases with decreasing temperature. A good fit to the experimental data was obtained with $g = 2.07$, $J = +11.6\ \mathrm{cm^{-1}}$ and a Weiss constant $\theta = +0.41$ K (see Experimental Section). Despite the large separation between the $\mathrm{Cu^{II}}$ ions of about 6.9 Å, a strong ferromagnetic coupling J is present, as in [Cu$_2$-*m*]

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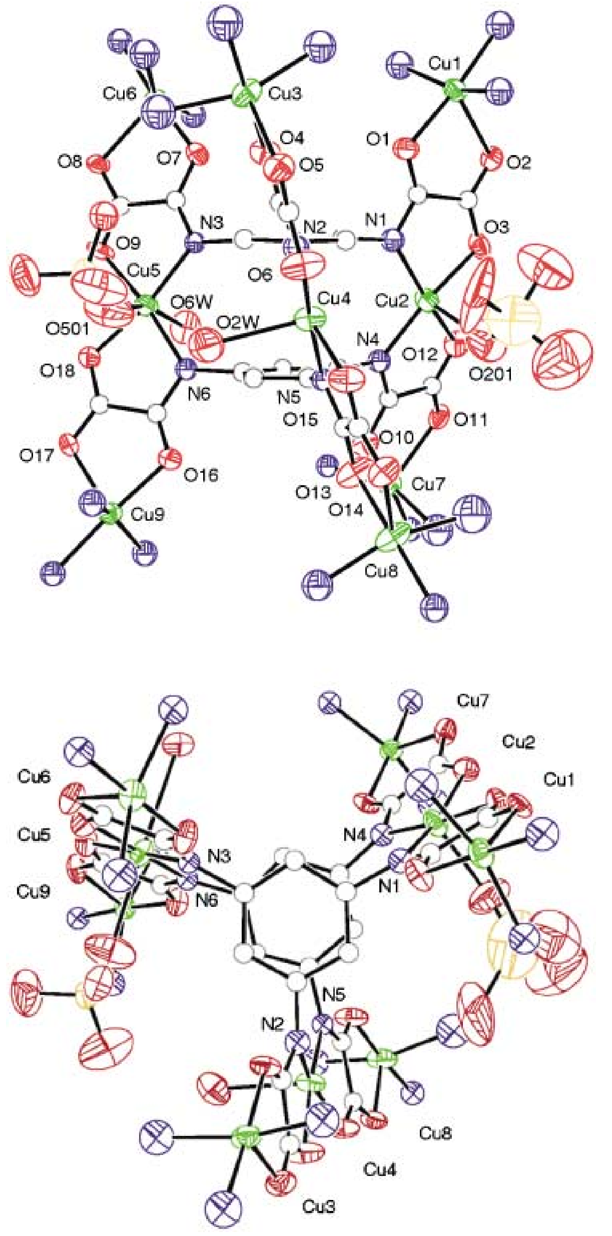

Figure 1. Side and top views of the well-ordered enneacopper unit **3**. Selected interatomic distances [Å] and angles [°]: Cu2-Cu4 6.899(7), Cu2-Cu5(7) 7.051, Cu4-Cu5(7) 6.836, Cu2-N1 1.980(6), Cu2-N4 1.957(6), Cu2-O201 2.417(7), Cu4-N2 1.961(5), Cu4-N5 1.980(5), Cu4-O2W 2.424(8), Cu5-N3 1.998(6), Cu5-N6 1.950(5), Cu5-O501 2.468(7), Cu5-O6W 2.835(8); N1-Cu2-N4 104.9(3), N2-Cu4-N5 105.1(2), N3-Cu5-N6 105.7(2).

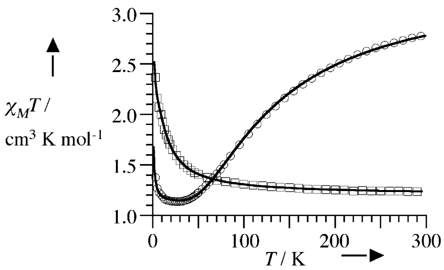

Figure 2. Magnetic behavior of **2** (squares) and **3** (circles); the solid lines are the calculated curves.

(+16.8 cm^{-1}),[10] due to spin-polarization effects through the aromatic *meta* linkage.[13] Aside from the organoiron complex reported by Lapinte et al.,[8] the couplings in **2** and [Cu$_2$-*m*] are larger than in other metal complexes.[9,14] This is due to the particular geometry of **2** in which the copper basal planes are nearly perpendicular to the benzene rings, which leads to a strong interaction between the Cu $d_{x^2-y^2}$ orbitals through the π system of the benzene rings.[10]

When the sample is cooled, $\chi_M T$ for **3** first decreases, then reaches a plateau between 20–30 K with a value of 1.17 cm^3 K mol^{-1} corresponding to three uncoupled 1/2 spins, and then increases below 20 K to reach 1.44 cm^3 K mol^{-1} at 2 K. This reproduces the expected behavior of **3**: antiferromagnetically coupled (J_{AF}) oxamato-bridged trinuclear Cu^{II} subunits, and, in the low-temperature region, ferromagnetic coupling (J_F) between the $S = 1/2$ ground states of the trinuclear subunits through the central [Cu$_3$(**1**)$_2$]$^{6-}$ core. A good fit of the experimental data was obtained with $J_{AF} = -106$ cm^{-1}, $J_F = +7.8$ cm^{-1}, and $g = 2.03$. The value of J_{AF} is in good agreement with that found for oxamate-bridged tricopper(II) complexes with pmdien as terminal ligand.[15,16] The magnitude of J_F was confirmed by the fit of the magnetization versus field at 2 K, which gave $J_F = +8.4$ cm^{-1}.[17] The smaller value of J_F in **3** (+7.8 cm^{-1}) compared to **2** (+11.6 cm^{-1}) and [Cu$_2$-*m*] (+16.8 cm^{-1}) likely originates from less efficient overlap between the aforementioned orbitals as a consequence of the greater helical twist in **3**.

In conclusion, ligand **1** allows the assembly of three Cu^{II} ions in a *meta* arrangement around bridging aromatic rings to give complex **2**. Being hexakis-bidentate, **2** is an efficient building block for larger assemblies with advantageous chelation of the peripheral metal ions, as observed in **3**. Through its rational construction, the enneanuclear complex **3** may be described as a first-generation metallodendrimer based on **2**. Importantly for magnetic assemblies, the ferromagnetic coupling by a spin-polarization mechanism in **2** is also operative in **3**. To extend these promising results, we aim at using this new class of ligands for the synthesis of 1) enneanuclear heterometallic complexes as potential single-molecule magnets, and 2) extended networks for molecule-based magnets.

Experimental Section

1,3,5-Triaminobenzene: A mixture of 3,5-dinitroaniline (1.46 g, 8.0 mmol) and 10% Pd/C (150 mg) in methanol (150 mL) was stirred overnight under hydrogen (40 bar). The suspension was filtered over Celite under inert atmosphere and washed with degassed methanol until the filtrate was colorless. Evaporation of the solvent gave 1,3,5-triaminobenzene as a light brown oil in quantitative yield. ^{1}H NMR (250 MHz, degassed [D$_6$]DMSO): $\delta = 4.34$ (br s, 6H; NH$_2$), 5.12 ppm (s, 3H; aromatic H).

1: The ligand was isolated as its triethyl ester. Under inert atmosphere, a solution of 1,3,5-triaminobenzene (972 mg, 7.9 mmol) in DMF (50 mL) was added to ethyloxalyl chloride (5.5 mL, 49 mmol). After the mixture had been stirred for 5 min, diisopropylethylamine (8.5 mL, 49 mmol) was added, and the solution was stirred at about 90 °C for 2 h, after which it was handled in air. After evaporation of the solvent, water (200 mL) was added to the resulting oil, to yield a white solid, which was collected by filtration, washed with water to neutrality of the filtrate, and dried under vacuum (2.7 g, 80% yield). Elemental analysis (%) calcd for $C_{18}H_{21}N_3O_9$ (423): C 51.06, H 5.00, N 9.95; found: C 49.66, H 4.91, N 9.91; ^{1}H NMR ([D$_6$]DMSO): $\delta = 1.30$ (t, 9H; 3 CH_3), 4.29 (q, 6H; 3 CH_2O), 7.91 (s, 3H; aromatic H), 10.91 ppm (s, 3H; 3 NH); IR (KBr): $\tilde{\nu} = 3277$ (NH), 1739, 1695 cm^{-1} (C=O).

2: The trinuclear Cu^{II} complex was obtained by reaction of the proligand of **1** (2 equiv) with $Cu^{II}(NO_3)_2$ (3 equiv) in basic aqueous medium (6 equiv of NaOH), and isolated as its sodium salt (95%).[18] Elemental analysis (%) calcd for $C_{24}H_6Cu_3N_6Na_6O_{18}(H_2O)_{11.5}$ (1202): C 23.98, H 2.43, N 6.99; found: C 23.94, H 2.42, N 6.99; IR (KBr): $\tilde{\nu} = 1654$, 1598 cm^{-1} (C=O).

3: Caution: Perchlorate-containing salts are potentially explosive and should be handled in very small quantities. The enneacopper(II) complex **3** was synthesized in a manner similar to that described in the literature,[16] with the appropriate 6:1 ratio of [Cu(pmdien)]$(ClO_4)_2$ and **2** in water. After addition, the mixture was stirred for 10 min, then the precipitate was collected by filtration, washed with water and methanol, and dried under vacuum (75%). Crystallization of **3** as green rods occurred over a few days on slow evaporation of a saturated aqueous solution. Elemental analysis (%) calcd for $C_{78}H_{144}Cl_6Cu_9N_{24}O_{42}(H_2O)_{12}$ (3091): C 30.31, H 5.48, N 10.88, Cl 6.88, Cu 18.50; found: C 29.72, H 5.27, N 10.76, Cl 7.15, Cu 17.36; IR (KBr): $\tilde{\nu} = 1607$ br (C=O), 1088–1145 cm^{-1} (ClO).

Crystal data for **3**: $C_{91}H_{196}Cl_7Cu_{10.5}N_{28}O_{67}$, $M_r = 3270.08$, trigonal, space group $R\bar{3}$, $a = b = 65.137(9)$ Å, $c = 18.861(4)$ Å, $V = 69303(20)$ Å^3, $T = 123(2)$ K, $Z = 18$, $\rho_{calcd} = 1.410$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 1.616$ mm^{-1}. Data were corrected for Lorentzian and polarization effects and absorption. 23008 unique reflections, of which 9362 with $I > 2\sigma(I)$ were taken as as observed. The structure was solved by direct methods using SHELXS97 and refined by using the full-matrix least-squares method on F^2 using SHELXL97. The hydrogen atoms were neither found nor calculated. Refinement of 1296 variables with anisotropic thermal parameters gave $R = 0.1290$, $R_w = 0.3311$, and $S = 1.065$. CCDC-208622 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

The moderate quality of the resolution likely arises from disorders. Two perchlorate ions (Cl3, Cl4) are disordered, as is a molecule of complex **3** (Cu10, Cu11, C88, C89, N28, O19, O21) lying on the $\bar{3}$ axis and disordered on two positions with occupancy factors of 0.5. The latter appear as dodecanuclear entities by superposition of the two enantiomers of a $[Cu_3[\mathbf{1}]_2[Cu(pmdien)]_6]^{6+}$ complex. Even though a rigorous metrical analysis is precluded by the disorder, all Cu environments are very similar to those in well-ordered molecules.

Magnetic measurements were carried on a SQUID magnetometer on powdered samples in the range 2–300 K. The susceptibility curves were fitted with an analytical law with the $-J$ convention for **2**,[19] and by full Hamiltonian diagnalization for **3** with the Hamiltonian $\mathcal{H} = -J_F(S_2S_4 + S_2S_5 + S_4S_5) - J_{AF}(S_2S_1 + S_2S_7 + S_4S_3 + S_4S_8 + S_5S_6 + S_5S_9) + g\beta(S_1 + S_2 + S_3 + S_4 + S_5 + S_6 + S_7 + S_8 + S_9)\mathrm{B}$.

For **2**, at the lowest temperature attainable, $\chi_M T$ is 2.5 cm^3 K mol^{-1}, a value higher than expected for the $S = 3/2$ ground state. This is due to weak intermolecular ferromagnetic interactions, which were taken into account by a Weiss constant θ.[19]

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[17] The magnetization of **3** at low temperature can also be fitted in terms of an effective interaction between the doublet ground states of the trinuclear subunits. The best fit is obtained with a J_{eff} value of $+0.9$ cm^{-1}, which corresponds to a J_F value of $+8.4$ cm^{-1} ($J_F = 9J_{eff}$).

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