Inorg. Chem. **2004**, *43*, 4540–4542

Inorganic Chemistry

Communication

Self-Assembly of High-Nuclearity Metal Clusters: Programmed Expansion of a Metallasiloxane Cage to an Octacopper(II) Cluster

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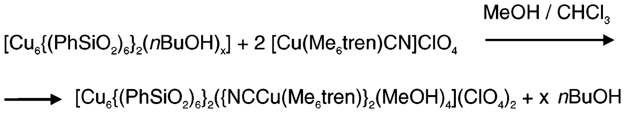
Received January 26, 2004

The novel octanuclear copper(II) cluster $[Cu_6\{(PhSiO_2)_6\}_2\{NCCu(Me_6tren)\}_2(MeOH)_4]^{2+}$ (**1**) has been isolated as a perchlorate salt by reacting the hexacopper(II) metallasiloxane cage $[Cu_6\{(PhSiO_2)_6\}_2(n\mathrm{BuOH})_x]$ (x = 4, 6) with $[Cu(Me_6tren)CN]ClO_4$ in a methanol/chloroform mixture (Me_6tren = tris(2-(dimethylamino)-ethyl) amine). Crystal data for $\mathbf{1}(ClO_4)_2{\cdot}MeOH$: monoclinic, space group $P2_1/n$ (no. 14), $a = 16.8490(3)$ Å, $b = 22.2966(4)$ Å, $c = 17.2508(3)$ Å, $\beta = 94.7658(5)°$, $V = 6458.3(2)$ Å^3, $Z = 2$. The structure comprises a highly distorted hexagonal Cu_6 array linked to two $[Cu(Me_6tren)]$ units via cyanide bridges. Magnetic measurements reveal that the addition of the copper cyanide complexes dramatically affects the magnetism of the Cu_6 unit, whose ground spin state changes from $S = 3$ to $S = 0$.

The rational design of high-nuclearity magnetic clusters represents a major goal of current research in the field of magnetic molecular materials. Compounds of this class, in particular those exhibiting a high-spin ground-state, are of fundamental interest in nanomagnetism[1a] and molecular electronics,[1b] and suitable synthetic techniques need to be developed for constructing and controlling their architectures. Possible strategies include site-specific ligand replacement[2] on preformed clusters and supramolecular self-assembly of highly informed magnetic components.[3] Following the latter approach, we have recently used high-spin metallasiloxanes as templates for the controlled organization of specifically functionalized magnetic units. The metallasiloxane cage $[Cu_6\{(PhSiO_2)_6\}_2(n\mathrm{BuOH})_x]$ (**2**, x = 4, 6),[4a] for instance, reacts smoothly with the copper(II) cyanide complex $[Cu(tmpa)CN]^+$ to afford a decanuclear cluster, $[Cu_6\{(PhSiO_2)_6\}_2\{NCCu(tmpa)\}_4]^{4+}$ (**3**),[4,5] bearing four cyano-bridged [Cu(tmpa)] units.

Scheme 1



$$[Cu_6\{(PhSiO_2)_6\}_2(n\mathrm{BuOH})_x] + 2\,[Cu(Me_6tren)CN]ClO_4 \xrightarrow{MeOH\,/\,CHCl_3} [Cu_6\{(PhSiO_2)_6\}_2(\{NCCu(Me_6tren)\}_2(MeOH)_4](ClO_4)_2 + x\ n\mathrm{BuOH}$$

Herein we report the synthesis, structure, and magnetic properties of an octacopper(II) cluster, $[Cu_6\{(PhSiO_2)_6\}_2\{NCCu(Me_6tren)\}_2(MeOH)_4]^{2+}$ (**1**)[5] obtained by a similar strategy. The compound $\mathbf{1}(ClO_4)_2{\cdot}MeOH$ was synthesized as outlined in Scheme 1.[6] $[Cu(Me_6tren)CN]ClO_4$ (**4**)[5−7] (0.122 mmol) was dissolved in methanol (10.0 mL) with heating and mixed with a solution of **2** (0.019 mmol) in anhydrous chloroform (10.0 mL). Heating to reflux (5 h) followed by cooling and layering of diethyl ether afforded large, air-unstable light-blue prisms of $\mathbf{1}(ClO_4)_2{\cdot}MeOH$ in about 1 week with low yield.[6,8] The crystalline material was suitable for X-ray diffraction analysis[9] and bulk magnetic

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(5) tmpa = tris(2-pyridylmethyl)amine, Me_6tren = tris(2-(dimethylamino)-ethyl)amine.

(6) **Warning!** Appropriate care should be taken in the use of perchlorate salts. The described compounds have not displayed any explosive tendencies, but caution is advised.

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(8) Anal. Calcd. for $\mathbf{1}(ClO_4)_2$: N, 4.89; C, 41.06, H, 4.22. Found (vacuum-dried sample, 0.1−0.2 mmHg, 75 min): N, 4.80; C, 40.86; H, 4.29. IR (KBr pellets): $\nu = 2167$ cm^{-1} (w, CN$^-$).

(9) Crystal data for $\mathbf{1}(ClO_4)_2{\cdot}MeOH$: $Cu_8C_{103}H_{140}Cl_2N_{10}O_{37}Si_{12}$, fw = 3026.56, space group $P2_1/n$ (no. 14), $a = 16.8490(3)$ Å, $b = 22.2966(4)$ Å, $c = 17.2508(3)$ Å, $\beta = 94.7658(5)°$, $V = 6458.3(2)$ Å^3, $Z = 2$, $T = -45(2)$°C, $\lambda = 0.71073$ Å, $D_{calcd} = 1.554$ g cm^{-3}, μ(Mo Kα)= 1.523 mm^{-1}. R1[F_o^2, $I > 2\sigma(I)$] = 0.0322, wR2 (F_o^2, all data) = 0.0926. The oxygen atom O13 and the phenyl groups C7−C12 and C13−C18 were found to be disordered over two positions and refined with half-occupancy. The perchlorate anions and the MeOH molecules are disordered in general positions.

10.1021/ic049898+ CCC: $27.50

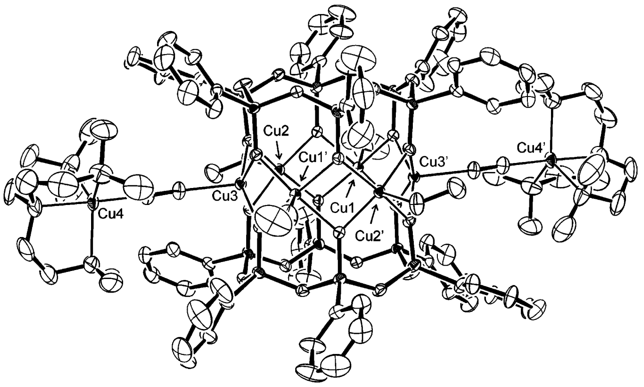

Figure 1. ORTEP[13] drawing showing the molecular structure of the cation **1** with 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

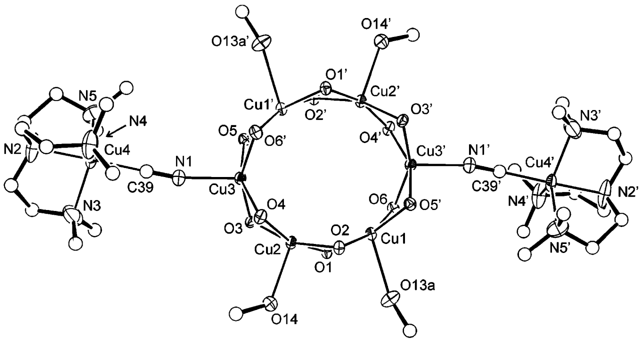

Figure 2. ORTEP[13] plot of **1** viewed perpendicular to the Cu_6 plane, with the atom labeling scheme and 50% probability thermal ellipsoids for Cu, O, and N atoms. C atoms are represented as spheres with arbitrary radius. The Si−O−Si skeleton and the phenyl rings of the cyclohexasiloxanolate ligand, as well as hydrogen atoms, have been omitted. Selected interatomic distances (Å) and angles (deg): Cu⋯Cu1′ 5.4275(5), Cu2⋯Cu2′ 5.6334(5), Cu3⋯Cu3′ 6.1150(5), Cu1⋯Cu2 2.8688(3), Cu1⋯Cu3′ 2.8640(3), Cu2⋯Cu3 2.8732(3), Cu1−O1 1.9660(13), Cu1−O2 1.9575(13), Cu1−O5′ 1.9618(13), Cu1−O6 1.9371(13), Cu1−O13a 2.421(5), Cu1−O13b 2.462(5), Cu2−O1 1.9725(13), Cu2−O2 1.9610(13), Cu2−O3 1.9454(13), Cu2−O4 1.9582(13), Cu2−O14 2.270(2), Cu3−O3 1.9708(13), Cu3−O4 1.9765(13), Cu3−O5 1.9932(13), Cu3−O6′ 1.9844(13), Cu3−N1 2.1822(18), Cu4−C39 1.954(2), Cu4−N2 2.030(2), Cu4−N3 2.161(3), Cu4−N4 2.136(2), Cu4−N5 2.156(2), N1−C39 1.146(3), Cu3′⋯Cu1⋯Cu2 126.946(10), Cu1⋯Cu2⋯Cu3 122.011(10), Cu2⋯Cu3⋯Cu1′ 111.042(10), Cu1−O1−Cu2 93.50(6), Cu1−O2−Cu2 94.13(6), Cu2−O3−Cu3 94.39(6), Cu2−O4−Cu3 93.81(6), Cu1′−O5−Cu3 92.79(5), Cu1−O6−Cu3′ 93.82(6), C39−N1−Cu3 169.28(19), N1−C39−Cu4 176.9(2).

measurements.[10] The structure of **1** (Figures 1 and 2) features an inner, nearly planar hexagonal array of six square-pyramidal (SP) copper(II) ions [maximum deviation from mean plane = ±0.0029(1) Å] linked through cyanide bridges to two trigonal-bipyramidal (TB) [Cu(Me_6tren)] units. Four methanol molecules complete the external coordination environment of the [$Cu_6\{(PhSiO_2)_6\}_2$] cage. Close inspection of the structure shows that the linked [Cu(Me_6tren)] units induce large distortions in the [$Cu_6\{(PhSiO_2)_6\}_2$] moiety. The range spanned by the distances between opposite copper(II) ions [5.4275(5)−6.1150(5) Å] is considerably wider than that observed in Cu_6 cages surrounded by six equivalent ligands, such as [$Cu_6\{(PhSiO_2)_6\}_2(n\text{BuOH})_6$] [5.625(4)−5.801(4) Å].[4a] The structure is markedly elongated along the line joining Cu3 and Cu3′, which exhibit more pronounced shifts from their oxygen basal planes than the remaining ions [0.4395(7) vs 0.2407(7)−0.3065(7) Å]. The cluster features a nonlinear Cu−C−N−Cu bridge in a *cisoid* conformation with N−C−Cu(TB) and Cu(SP)-N−C angles of 176.9(2)° and 169.28(19)°, respectively. Noticeably, the linkage isomer Cu(TB)−N−C−Cu(SP) leads to a less satisfactory structure refinement, showing that the binding mode of the cyanide group in **4** is fully retained. The coordination environment of Cu4 is also quite similar to that observed in the cyanide complex **4**, with only slight deviations from trigonal symmetry [$\tau = 0.956(3)$].[7,11]

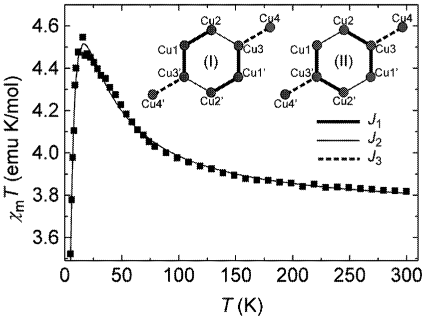

Figure 3. Experimental $\chi_m T$ vs T data for **1**$(ClO_4)_2$ with the exchange-coupling schemes I and II discussed in the text. The best-fit calculated curves for (a) $g = 2.224$, $J_1 = J_2 = -19.7$ cm^{-1}, $J_3 = 15.2$ cm^{-1} and (b) $g = 2.225$, $J_1 = -24.4$ cm^{-1}, $J_2 = 5.9$ cm^{-1}, $J_3 = -1.2$ cm^{-1} are also shown as overlapping solid lines.

The molar magnetic susceptibility χ_m of **1**$(ClO_4)_2$ was measured in the range 5.0−300.0 K.[10] The $\chi_m T$ product at 300 K (3.82 emu·K/mol) is higher than expected for eight uncoupled $S_i = {}^1/_2$ spins (3.00 emu·K/mol with $g = 2.00$) and slowly increases upon cooling, reaching a maximum of 4.56 emu·K/mol at ca. 16 K and then rapidly decreasing to 3.52 emu·K/mol at 5.0 K (see Figure 3). In a first attempt to explain the observed behavior, an isotropic spin Hamiltonian was used assuming identical exchange coupling constants in the Cu_6 ring, as suggested by the narrow range of Cu−O−Cu angles [92.79(5)−94.13(6)°]. This simple model gives very good agreement with experimental data using $g = 2.224(3)$, $J_1 = J_2 = -19.7(6)$ cm^{-1}, and $J_3 = 15.2(3)$ cm^{-1} [set (a) in Figure 3]. However, it does not account for the observed field dependence of the molar magnetization (M_m) at low temperature (Figure 4). In fact, the best-fit J values result in a well-isolated $S = 2$ ground spin state for the cluster and the M_m vs H/T curves at low temperature are expected to saturate at about 2.5 emu·T/mol (dashed curves). By contrast, the experimental molar magnetization at 2 K and 6 T exceeds 4 emu·T/mol, pointing to the presence of low-lying spin states with $S > 2$. The model was then refined by assuming the presence of two different coupling constants in the Cu_6 ring. Because of the centrosymmetric structure of the cluster, two alternative exchange coupling patterns can be envisaged, corresponding

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[10] Crystalline samples of **1**$(ClO_4)_2$·MeOH were dried under vacuum (0.1−0.2 mmHg, 75 min) before experiments. A magnetic field of 1.0 T was used in magnetic susceptibility vs T runs, and magnetization experiments were performed at 2.0 and 4.6 K in the field range 0−6.0 T on a Teflon-restrained sample.

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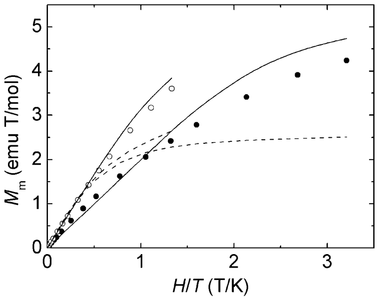

Figure 4. Experimental M_m vs H/T data for **1**$(ClO_4)_2$ at 2.0 (●) and 4.6 K (○), and data calculated with the parameter sets a (dashed lines) and b (solid lines).

to Heisenberg Hamiltonians 1 and 2 (schemes I and II, respectively, in Figure 3).

$$\mathbf{H} = J_1[\mathbf{S}_1\cdot(\mathbf{S}_2 + \mathbf{S}_{3'}) + \mathbf{S}_{1'}\cdot(\mathbf{S}_{2'} + \mathbf{S}_3)] + J_2(\mathbf{S}_2\cdot\mathbf{S}_3 + \mathbf{S}_{2'}\cdot\mathbf{S}_{3'}) + J_3(\mathbf{S}_3\cdot\mathbf{S}_4 + \mathbf{S}_{3'}\cdot\mathbf{S}_{4'}) \quad (1)$$

$$\mathbf{H} = J_1[\mathbf{S}_3\cdot(\mathbf{S}_{1'}+\mathbf{S}_2) + \mathbf{S}_{3'}\cdot(\mathbf{S}_1 + \mathbf{S}_{2'})] + J_2(\mathbf{S}_1\cdot\mathbf{S}_2 + \mathbf{S}_{1'}\cdot\mathbf{S}_{2'}) + J_3(\mathbf{S}_3\cdot\mathbf{S}_4 + \mathbf{S}_{3'}\cdot\mathbf{S}_{4'}) \quad (2)$$

Both schemes give excellent agreement with experimental $\chi_m T$ vs T data using the set of parameters $g = 2.225(2)$, $J_1 = -24.4(10)$ cm^{-1}, $J_2 = 5.9(4)$ cm^{-1}, and $J_3 = -1.2(12)$ cm^{-1} [set (b) in Figure 3]. Notice that the two Hamiltonians are physically indistinguishable for $J_3 \approx 0$, so that the real pattern of magnetic interactions in the Cu_6 core cannot be uniquely determined. A vanishingly small value of J_3 is reasonable, considering the symmetry and relative orientation of magnetic orbitals on Cu(SP) and Cu(TB), and is consistent with previous results.[4,12] Because of the presence of both ferro- and antiferromagnetic exchange interactions, the Cu_6 core has an $S = 0$ ground spin state as compared with $S = 3$ in **2**.[4a] Because of the vanishingly small coupling to the peripheral $S_i = {}^1/_2$ units, the ground manifold of the cluster comprises quasidegenerate $S = 0$ and $S = 1$ states. The state with maximum spin multiplicity ($S = 4$), however, lies only ca. 8 cm^{-1} above the ground manifold, and the predicted field dependence of the magnetization (Figure 4, solid curves) is now in reasonable agreement with the observed data.

In conclusion, a novel octanuclear copper(II) cluster has been synthesized by linking two copper cyanide complexes to a central metallasiloxane cage with $S = 3$. The addition dramatically influences the magnetism of the inner Cu_6 core, whose ground spin state changes to $S = 0$. Nevertheless, this result generalizes the value of metallasiloxane cages as building blocks for the synthesis of high-nuclearity clusters and provides a simple way to design and isolate specifically functionalized compounds. Further experiments aimed at exploring the controlled arrangement of radicals and spin-crossover units around $[M_6\{(PhSiO_2)_6\}_2]$ templates are currently under way.

Acknowledgment. Thanks are expressed to Prof. Vincenzo Albano and Prof. Magda Monari (Department of Chemistry "G. Ciamician", University of Bologna) for help in X-ray experiments and preliminary data treatment and to Dr. Yulia A. Pozdniakova (A. N. Nesmeyanov Institute, Moscow) for helpful discussions. This work was financially supported by EU networks MOLNANOMAG HPRN-CT-1999-00012 and QUEMOLNA MRTN-CT-2003-504880, Italian CNR (Agenzia2000-CNRG002EF2), and MIUR.

Supporting Information Available: Listings of molar magnetic susceptibility vs temperature and molar magnetization vs field data. X-ray crystallographic file for **1**$(ClO_4)_2\cdot$MeOH in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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