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Supramolecular Templating of the Double-Cubane $[\{Cu_3(Hpz^{tBu})_6(\mu_3\text{-}Cl)(\mu_3\text{-}OH)_3\}_2Cu]Cl_6$ (Hpz^{tBu} = 5-*tert*-Butylpyrazole)**

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While the $[M_4(\mu_3\text{-}X)_4]^{4+}$ (M = transition ion, X = anion or dianion) cubane structure is a common motif in transition metal chemistry and biochemistry, only a few examples of vertex-sharing double-cubane compounds are known.[1–8] We note in particular **1** (bipym = 2,2′-bipyrimidine), which is the only compound with this topology whose magnetochemical properties have been fully elucidated to date.[5] We report here a new example of a heptacopper double-cubane complex, **2**, whose molecular structure and magnetochemistry differ substantially from those of **1**. Moreover, the unusual structure of **2** is supported by a unique pattern of supramolecular cation:anion interactions.

$[\{Cu_3(bipym)_3(OH_2)(\mu_3\text{-}OH)_4\}_2Cu](NO_3)_6$ **1**

$[\{Cu_3(Hpz^{tBu})_6(\mu_3\text{-}Cl)(\mu_3\text{-}OH)_3\}_2Cu]Cl_6$ **2**

Turquoise crystals of $\mathbf{2} \cdot 2\,CH_2Cl_2$ were grown from CH_2Cl_2/pentane mixtures.[9] The asymmetric unit of these crystals contains half a complex molecule with Cu(1) lying on a crystallographic inversion center, forming a $[\{Cu_3(Hpz^{tBu})_6(\mu_3\text{-}Cl)(\mu_3\text{-}OH)_3\}_2Cu]^{6+}$ double-cubane (Figure 1). The shared-vertex Cu(1) is ligated by six OH^- ligands, with an axis of Jahn – Teller elongation along the O(7)-Cu(1)-O(7′) vector. The other Cu ions exhibit tetragonal geometries, with two OH^- and two Hpz^{tBu} ligands in the basal plane and axial contacts to two Cl^- ions. Cu(3) and Cu(4) adopt almost identical geometries, with contacts of 2.7949(5) – 2.9129(6) Å to Cl(62) and one other Cl^- ligand. However, Cu(2) has a shorter distance of 2.5502(5) Å to Cl(62), and a much longer distance of 3.7433(6) Å to Cl(63) (not shown in Figure 1).

In addition to Cl(62) and its symmetry-generated equivalent, there are six Cl^- ions disposed in a ring around the heptacopper core of the molecule (Figure 2). Each of these Cl^- ions accepts three hydrogen bonds, from one OH^- and two Hpz^{tBu} N–H donors. Cl(64) and Cl(65) are in near-

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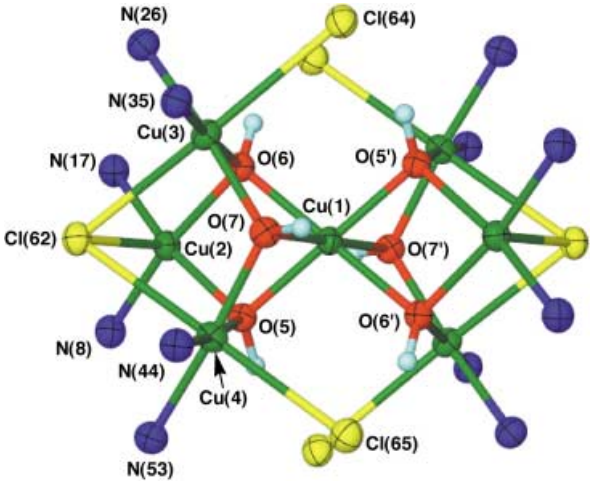


Figure 1. View of the $[\{Cu_3(Hpz^{tBu})_6(\mu_3\text{-}Cl)(\mu_3\text{-}OH)_3\}_2Cu]^{6+}$ core in the crystal structure of $\mathbf{2}\cdot 2CH_2Cl_2$. For clarity, only the coordinated N atoms of the Hpz^{tBu} ligands are shown. Thermal ellipsoids are at the 50% probability level. Color code: Cu: green; O: red; N: blue; Cl: yellow; H: turquoise. Selected bond lengths [Å] and angles [°]: Cu(1)-O(5) 1.9781(13), Cu(1)-O(6) 1.9675(13), Cu(1)-O(7) 2.2957(13), Cu(2)-O(5) 1.9731(14), Cu(2)-O(6) 1.9862(13), Cu(3)-O(6) 1.9940(13), Cu(3)-O(7) 1.9549(14), Cu(4)-O(5) 2.0076(14), Cu(4)-O(7) 1.9493(13); O(5)-Cu(1)-O(6) 81.00(5), O(5)-Cu(1)-O(6′) 99.00(5), O(5)-Cu(1)-O(7) 75.74(5), O(5)-Cu(1)-O(7′) 104.26(5), O(6)-Cu(1)-O(7) 76.06(5), O(6)-Cu(1)-O(7′) 103.94(5), O(5)-Cu(2)-O(6) 80.66(6), O(6)-Cu(3)-O(7) 83.86(6), O(5)-Cu(4)-O(7) 83.51(6), Cu(1)-O(5)-Cu(2) 96.61(6), Cu(1)-O(5)-Cu(4) 102.33(6), Cu(2)-O(5)-Cu(4) 108.97(6), Cu(1)-O(6)-Cu(2) 96.53(6), Cu(1)-O(6)-Cu(3) 101.59(6), Cu(2)-O(6)-Cu(3) 111.11(6), Cu(1)-O(7)-Cu(3) 92.12(5), Cu(1)-O(7)-Cu(4) 93.65(5), Cu(3)-O(7)-Cu(4) 118.55(7). Primed atoms are related to unprimed atoms by the symmetry operation: $1-x, 1-y, 1-z$.

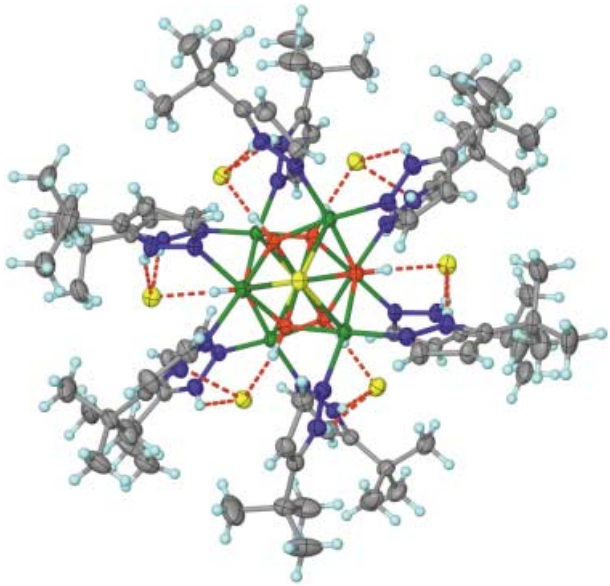


Figure 2. View of the $[\{Cu_3(Hpz^{tBu})_6(\mu_3\text{-}Cl)(\mu_3\text{-}OH)_3\}_2Cu]Cl_6$ molecule in the crystal structure of $\mathbf{2}\cdot 2CH_2Cl_2$, showing the hydrogen-bonding interactions to the Cl^- ions. The view is parallel to the Cl(62)···Cu(1)···Cl(62′) vector in Figure 1. Color code as for Figure 1 with C: gray.

identical environments 2.8–2.9 Å from the closest Cu ion (see above). However Cl(63), which is hydrogen-bonded to the OH^- ligand O(7′) lying on the axis of Jahn–Teller elongation at Cu(1), is displaced from the equivalent site by 0.9 Å away from Cu(2). These hydrogen-bonded Cl^- ions are encapsulated inside the Hpz^{tBu} *tert*-butyl substituents, which enclose the molecule in a hydrophobic sheath.

Magnetic susceptibility data were obtained between 5–330 K from a powder sample of **2**, in an applied field of 2000 G (Figure 3). At 300 K $\chi_M T = 2.4\ cm^3 mol^{-1} K$, which is

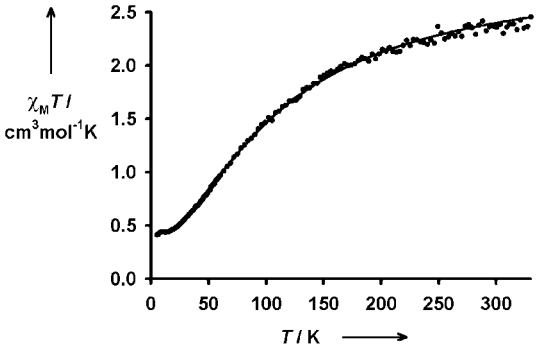
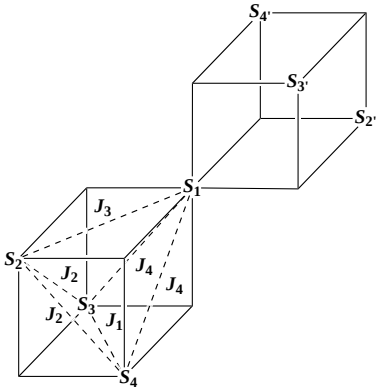


Figure 3. Plot of $\chi_M T$ versus T for a powder sample of **2** (circles), showing the best theoretical fit (line). See text for fitting details.

slightly smaller than the spin-only value expected for seven noninteracting $S = 1/2$ Cu^{II} ions (2.6 $cm^3 mol^{-1} K$).[10] As the temperature is lowered $\chi_M T$ decreases, reaching a plateau of 0.44 $cm^3 mol^{-1} K$ at 15 K which is consistent with a fully populated $S = 1/2$ ground state.[10] These data were interpreted by using the Hamiltonian in Equation (1) (see Scheme 1 for the exchange-coupling scheme adopted).[11]

$$\begin{aligned} H = & -2J_1(S_3S_4 + S_{3'}S_{4'}) - 2J_2(S_2S_3 + S_2S_4 + S_{2'}S_{3'} + S_{2'}S_{4'}) \\ & -2J_3(S_1S_2 + S_1S_{2'}) - 2J_4(S_1S_3 + S_1S_4 + S_1S_{3'} + S_1S_{4'}) \end{aligned} \quad (1)$$



Scheme 1. Exchange-coupling scheme employed to analyze the magnetic data of **2**. Each spin equates to the correspondingly numbered Cu ion in Figure 1 (i.e. $S_1 \equiv$ Cu(1) etc.).

During the analysis it was found that $J_2 \approx J_4$, and that both of these parameters were poorly defined owing to correlation problems. Therefore, these two J values were constrained to be equal for the final fitting, which yielded $g = 2.14$, $J_1 = -72$, $J_3 = -21$ and $J_2 = J_4 = -16\ cm^{-1}$ (Figure 3). The constant J_3 describes superexchange mediated by two OH^- ligands that both lie in the xy magnetic planes of Cu(1) and Cu(2). The observed value for this coupling agrees well with Haase's

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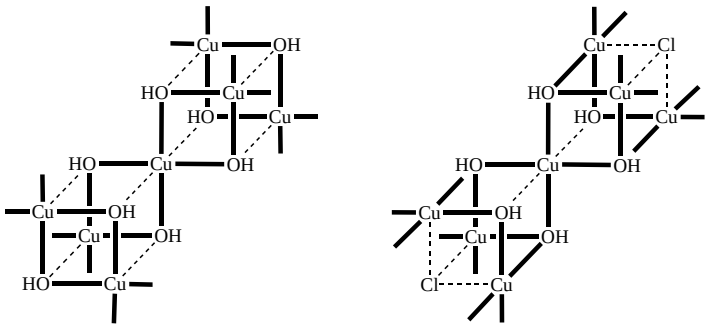
correlation for basal–basal superexchange in $[Cu_4(\mu_3\text{-}OR)_4]^{4+}$ (R = alkyl) cubanes, which predicts $J_3 \approx -30\ cm^{-1}$ for the observed average Cu(1)-O-Cu(2) angle of 96.57(8)°.[12] The other superexchange constants J_1, J_2, and J_4 in **2** are all effectively mediated by $[Cu_2(\mu\text{-}OH)]^{3+}$ bridges, across average Cu-O-Cu angles of 118.55(7)°, 110.04(8)°, and 101.96(8)°, respectively. This is consistent with J_1 being more antiferromagnetic than J_2 or J_4.[12, 13] Since J_1 is the strongest antiferromagnetic coupling in the molecule, this means that Cu(1), Cu(2), and Cu(2′) are spin-frustrated with respect to Cu(3), Cu(4), Cu(3′), and Cu(4′).

While they both have C_s symmetry, the heptacopper cores of **1**[5] and **2** are very different (Scheme 2). Compound **1** can be described structurally and magnetically as a pair of vertex-linked C_2-symmetric $[Cu_4(bipym)_3(\mu_3\text{-}OH)_4]^{4+}$ cubanes. This



1 **2**

Scheme 2. Comparative molecular structures of **1** and **2**, showing the basal (thick lines) and apical (dashed lines) Cu–X (X = O, Cl) bonds.

"dimer of dimers" motif is common in $[Cu_4(\mu_3\text{-}OR)_4]^{4+}$ (R = H, alkyl) cubane compounds.[12, 14] However, the individual $[Cu_4(Hpz^{tBu})_6(\mu_3\text{-}Cl)(\mu_3\text{-}OH)_3]^{4+}$ cubane moieties in **2** are C_s-symmetric, being distorted from C_{3v} symmetry by the Jahn–Teller elongation at Cu(1). This is the first example of this structural type in Cu^{II} chemistry.

There is a small, but growing, number of compounds containing an enclosed guest anion or cation inside a polyoxometalate[15] or polynuclear coordination complex[16] cage. The guest ion in these compounds templates the structure of the surrounding framework, despite interacting with it only through electrostatic and van der Waals interactions. Compound **2** is an inversion of the usual scenario, in that the metal core is encapsulated by a belt of hydrogen-bonded, templating anions. Experiments are in progress to prepare new mono- and bidentate ligands designed as anion receptors, in order to use supramolecular chemistry to prepare other novel metal–oxo or –hydroxo cluster architectures.

Experimental Section

To a mixture of $CuCl_2$ (0.13 g, 1.0 mmol) in MeOH (30 mL) was added a MeOH (20 mL) solution of NaOH (0.040 g, 1.0 mmol) and 3{5}-*tert*-butylpyrazole (0.24 g, 2.0 mmol). The resultant dark green solution was stirred at 293 K for three days, then evaporated to dryness. Extraction of the residue with CH_2Cl_2, and layering of the resultant green solution with pentane, yielded turquoise crystals of **2**. Yield 0.18 g, 54% based on Cu. Elemental analysis calcd (%) for $C_{84}H_{150}Cl_8Cu_7N_{24}O_6$: C 43.47, H 6.51, N 14.49; found: C 43.50, H 6.55, N 14.55.

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