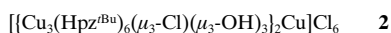
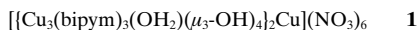


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Supramolecular Templating of the Double-Cubane $[\{\text{Cu}_3(\text{Hpz}^{\text{tBu}})_6(\mu_3\text{-Cl})(\mu_3\text{-OH})_3\}_2\text{Cu}]\text{Cl}_6$ ($\text{Hpz}^{\text{tBu}} = 5\text{-tert-Butylpyrazole}$)**

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While the $[\text{M}_4(\mu_3\text{-X})_4]^{4+}$ ($\text{M} = \text{transition ion}$, $\text{X} = \text{anion or dianion}$) 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.



Turquoise crystals of $\mathbf{2} \cdot 2\text{CH}_2\text{Cl}_2$ 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 $[\{\text{Cu}_3(\text{Hpz}^{\text{tBu}})_6(\mu_3\text{-Cl})(\mu_3\text{-OH})_3\}_2\text{Cu}]^{6+}$ double-cubane (Figure 1). The shared-vertex Cu(1) is ligated by six OH^- ligands, with an axis of Jahn–Teller elongation along the $\text{O}(7)\text{-Cu}(1)\text{-O}(7')$ 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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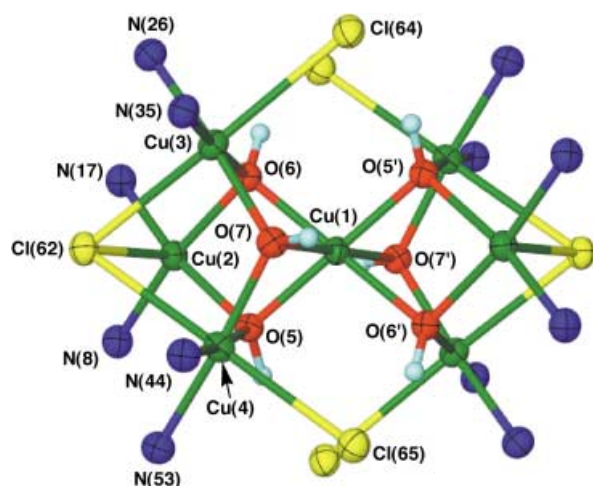


Figure 1. View of the $[\text{Cu}_3(\text{Hpz}^{\text{tBu}})_6(\mu_3\text{-Cl})(\mu_3\text{-OH})_3]_2\text{Cu}^{6+}$ core in the crystal structure of $2 \cdot 2 \text{CH}_2\text{Cl}_2$. For clarity, only the coordinated N atoms of the Hpz^{tBu} ligands are shown. Thermal ellipsoids are at the 50% probability 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(7) 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: $1-x, 1-y, 1-z$.

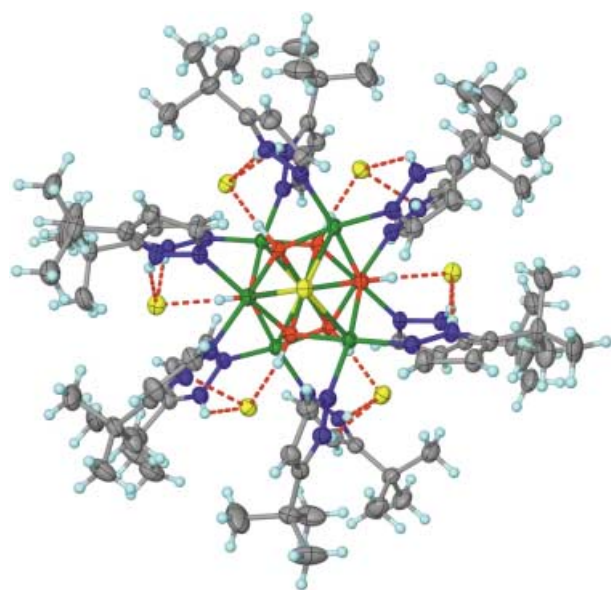


Figure 2. View of the $[\text{Cu}_3(\text{Hpz}^{\text{tBu}})_6(\mu_3\text{-Cl})(\mu_3\text{-OH})_3]_2\text{Cu}\text{Cl}_6$ molecule in the crystal structure of $2 \cdot 2 \text{CH}_2\text{Cl}_2$, showing the hydrogen-bonding interactions to the Cl^- ions. The view is parallel to the $\text{Cl}(62) \cdots \text{Cu}(1) \cdots \text{Cl}(62')$ 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 encapsu-

lated 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 $\chi_{\text{M}}T = 2.4 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, which is

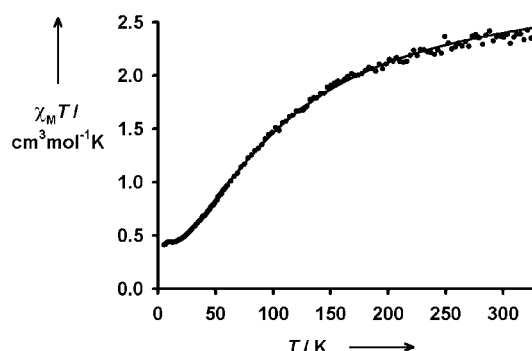
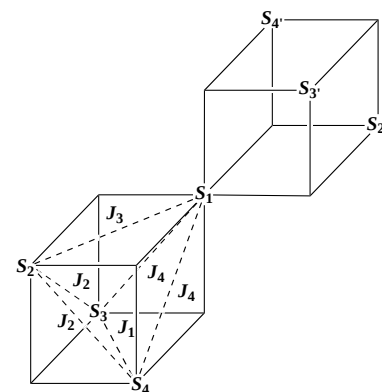


Figure 3. Plot of $\chi_{\text{M}}T$ versus T for a powder sample of **2** (circles), showing the best theoretical fit (line). See text for fitting details.

slightly smaller than the spin-only value expected for seven noninteracting $S = 1/2$ Cu^{II} ions ($2.6 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$).^[10] As the temperature is lowered $\chi_{\text{M}}T$ decreases, reaching a plateau of $0.44 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ 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]

$$H = -2J_1(S_3S_4 + S_3S_4) - 2J_2(S_2S_3 + S_2S_4 + S_2S_3 + S_2S_4) - 2J_3(S_1S_2 + S_1S_2) - 2J_4(S_1S_3 + S_1S_4 + S_1S_3 + S_1S_4) \quad (1)$$

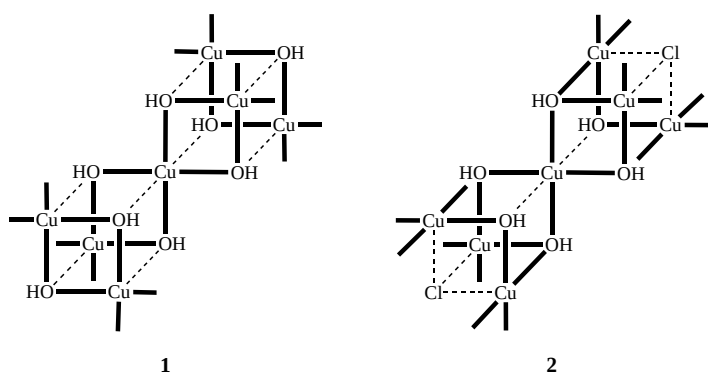


Scheme 1. Exchange-coupling scheme employed to analyze the magnetic data of **2**. Each spin equates to the correspondingly numbered Cu ion in Figure 1 (i.e. $S_1 \equiv \text{Cu}(1)$ etc.).

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 $J_2 = J_4 = -16 \text{ cm}^{-1}$ (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

correlation for basal–basal superexchange in $[\text{Cu}_4(\mu_3\text{-OR})_4]^{4+}$ (R = alkyl) cubanes, which predicts $J_3 \approx -30 \text{ cm}^{-1}$ for the observed average Cu(1)–O–Cu(2) angle of $96.57(8)^\circ$.^[12] The other superexchange constants J_1 , J_2 , and J_4 in **2** are all effectively mediated by $[\text{Cu}_2(\mu\text{-OH})]^{3+}$ bridges, across average Cu–O–Cu angles of $118.55(7)^\circ$, $110.04(8)^\circ$, and $101.96(8)^\circ$, 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 $[\text{Cu}_4(\text{bipym})_3(\mu_3\text{-OH})_4]^{4+}$ cubanes. This



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 $[\text{Cu}_4(\mu_3\text{-OR})_4]^{4+}$ (R = H, alkyl) cubane compounds.^[12, 14] However, the individual $[\text{Cu}_4(\text{Hpz}^{\text{Bu}})_6(\mu_3\text{-Cl})(\mu_3\text{-OH})_3]^{4+}$ 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 $\text{C}_{84}\text{H}_{150}\text{Cl}_8\text{Cu}_7\text{N}_{24}\text{O}_6$: C 43.47, H 6.51, N 14.49; found: C 43.50, H 6.55, N 14.55.

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