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Synthesis and Crystal Structure of $[Cu_4(3\text{-aminopyridine})_8(\mu^3\text{-OH})_4]4BF_4 \bullet 2MeCN$: A Novel Copper(II) Cubane

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A new tetrameric copper species is formed from the reaction of 3-aminopyridine and $[Cu(MeCN)_4]BF_4$. Four molecules per unit cell crystallize in the monoclinic space group $P2_1/c$, having $a = 13.2552(7)$ Å, $b = 17.8202(9)$ Å, $c = 28.527(2)$ Å, $\beta = 91.105(1)$, and a volume of 6737.1 Å [3], giving a calculated density of 1.482 g/mol. 22315 reflections were observed and the structure was refined to a final $R_1 = 0.063$ $[I > 2\sigma(I)]$. The distorted cubic core is composed of four copper(II) cations and four μ^3-OH^- ions. Two pyridine nitrogen atoms from the 3-aminopyridine ligands complete the Jahn-Teller distorted square-pyramidal coordination sphere around each copper. Longer, sixth bonds on two of the copper centers are made to a bridging MeCN. Three of the BF_4^- anions participate in *intra*molecular O–H ⋯ F hydrogen bonding with the bridging hydroxide ions and N–H ⋯ F with the free amino groups, while the remaining (disordered) BF_4 forms *inter*molecular hydrogen bonds between tetramers.

Keywords: Copper(II)compounds, cubanes, Jahn-Teller distortions

INTRODUCTION

The three-dimensional organization of metal ions and their bound and unbound ligands is of extreme import to the proper and efficient functioning of both metalloenzymatic systems [1] and certain industrial catalysts [2]. A common supramolecular structural motif found in the active site of several enzymes is the cubane, where four metal atoms and four μ^3-bridging ligands (*e.g.*, halogen, sulfide, hydroxide) occupy alternating corners of a cube. Probably the most well-known cubanes are the family of Fe—S clusters, now acknowledged as vital to the functioning of nitrogenase [3], and having numerous synthetic analogs [4]. Similarly in copper chemistry, a wide variety of Lewis bases have been used to produce both cuprous [5] and cupric [6] cubanes that have been structurally characterized. A majority of the Cu(I) compounds are bridged with Cl^-, Br^-, or I^-, owing to the affinity of monovalent copper for softer ligands, whereas Cu(II) complexes tend to form with harder, oxygen-donating ligands.

Our initial aim was to create a three-dimensional coordination polymer similar to $[Cu(pyrimidine)_2]^-_\infty$, [7], by using both the

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*Corresponding author.

aromatic nitrogen and the amine nitrogen as σ-donor ligands to two different tetrahedral Cu(I) centers. Using 3-aminopyridine, however, oxidation of the metal to Cu(II) occurs, followed by oligomerization to the tetrameric title compound. The crystal structure we report here constitutes a rare example of a hydroxo-bridged Cu(II) cubane formed from monodentate Lewis bases.

EXPERIMENTAL

Synthesis

All solvents and reagents were used without further purification unless otherwise specified. Single crystals suitable for single-crystal X-ray diffraction (see below) were prepared by solvent vapor diffusion. Specifically, 0.030 g (0.095 mmol) $[Cu(MeCN)_4]BF_4$ [8] was placed in a small vial, and dissolved with 0.5 mL acetonitrile (Fisher) and 2.0 mL nitrobenzene (Aldrich). To this solution was added 0.018 g (0.19 mmol) 3-aminopyridine (3-AP) (Aldrich). The open vial was placed in a larger vial containing 8 mL THF. The solution began to darken almost immediately, and blue crystals formed from the blue-green solution in the inner vial after several days.

Crystal Structure Determination

A transparent-blue, flat, rectangular crystal measuring 0.4 × 0.1 × 0.17 mm that completely extinguished polarized light was mounted on a glass fiber with epoxy. A full hemisphere of data was collected at room temperature using a Siemens SMART system equipped with a CCD area·detector, yielding 22315 reflections, which when integrated left 7012 independent reflections [$R_{int} = 0.048$]. The structure was solved by using direct methods [9] and refined using a full least-squares treatment on F^2 [10]. Disorder of one of the BF_4 anions, B(4), was modeled by assigning six fluorine positions F(13) - F(18), as indicated by difference electron density maps, and then refining on the occupancy of all six fluorine atoms with fixed thermal parameters. The resulting fractional occupancies were adjusted slightly, and fixed to sum to four (0.67, 1.0, 0.67, 1.0, 0.33, 0.33, for F(13) - F(18), respectively), and the thermal parameters were refined. None of the hydroxyl protons, and only three amine protons could be located with confidence from this data set. A complete description of the crystal structure solution, fractional coordinates, complete bond distances and angles, Cu—F and N—F close contact distances, anisotropic thermal parameters, hydrogen positions, as well as structure factor tables, are provided in the supplementary material.

RESULTS AND DISCUSSION

The synthesis of this compoud involves the oxidation of Cu(I) to Cu(II) *via* an unknown mechanism. Our experience with Cu(I) chemistry using related aromatic Lewis bases, suggests that the amine group is the oxidant; acetonitrile/nitrobenzene solutions of Cu(I) with pyrimidine, [7], bipyridine [11], and phenanthroline [12] are oxidatively stable in the presence of air. A partial view of the structure in Figure 1 shows that four metal atoms come together at the four tetrahedral corners of a distorted cube, with the remaining corners occupied by hydroxide ions. The source of the hydroxide ion is unknown, but we assume it comes from residual water present in the solvents [13]. Each copper coordination sphere is completed by two aromatic nitrogen atoms from 3-AP. The result is a Jahn-Teller distorted square-pyramidal coordination, having four short equatorial bonds (two hydroxide and two aminopyridine ligands) and one long axial bond to the third hydroxide. The core can be viewed as two stacked square-planer dimers (solid bonds in Fig. 1) rotated by 90° to connect

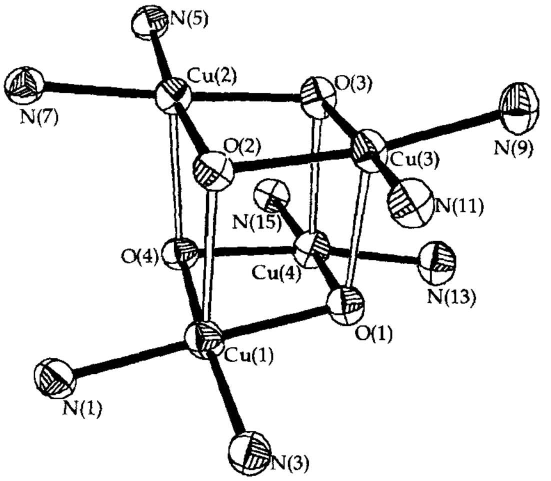

FIGURE 1 Structure of the tetrameric cubane core showing 30% thermal ellipsoids and numbering scheme used in the discussion. All of the shorter equatorial bonds are represented as solid lines, whereas the long, axial bonds are shown as hollow lines.

TABLE I Crystal data and structure refinement parameters

Empirical formula	$Cu_4C_{44}H_{52}N_{18}O_4B_4F_{16}$
Formula weight	
Temperature	293(2) K
Wavelength	0.71070 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 13.2552(7)$ Å $\alpha = 90°$ $b = 17.8202(9)$ Å $\beta = 91.105(1)°$ $c = 28.527(2)$ Å $\gamma = 90°$
Volume	6737.1(6) Å^3
Z	4
Density (calculated)	1.482 g/mol
Absorption coefficient	0.717 mm^{-1}
F(000)	2552
Crystal size	0.4 × 0.1 × 0.17 mm
Theta range for data collection	1.35 to 20.85°
Index ranges	$-13 \leq h \leq 12$, $-17 \leq k \leq 17$, $-28 \leq l \leq 28$
Reflections collected	22315
Independent reflections	7012 [$R_{\text{int}} = 0.0484$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7012/0/913
Goodness-of-fit on F^2	1.056
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.062$, $wR_2 = 0.157$
R indices (all data)	$R_1 = 0.091$, $wR_2 = 0.179$
Largest diff. peak and hole	0.769 and -0.740 e•Å^{-3}

TABLE II Selected bond lengths [Å] for the $Cu_4(OH)_4N_8$ core

	Cu—Cu		
Cu(1) —Cu(4)	2.960(1)	Cu(1) —Cu(2)	3.292(1)
Cu(2) —Cu(3)	2.981(1)	Cu(3) —Cu(4)	3.369 (1)
mean	2.970	*mean*	3.330
	Cu—O		
Cu(1) —O(1)	1.968(5)	Cu(1) —O(2)	2.357(5)
Cu(1) —O(4)	1.974(5)	Cu(2) —O(4)	2.328(5)
Cu(2) —O(2)	1.976(5)	Cu(3) —O(1)	2.372(6)
Cu(2) —O(3)	1.966(5)	Cu(4) —O(3)	2.374(5)
Cu(3) —O(2)	1.971(5)	*mean*	2.358
Cu(3) —O(3)	1.959(5)		
Cu(4) —O(1)	1.967(5)		
Cu(4) —O(4)	1.974(5)		
mean	1.969		
	Cu—N		
Cu(1) —N(1)	1.987(8)		
Cu(3) —N(11)	1.981(7)		
Cu(1) —N(3)	1.989(7)	Cu(3) —N(9)	2.001(8)
Cu(2) —N(7)	2.004(7)	Cu(4) —N(15)	1.994(7)
Cu(2) —N(5)	2.014(7)	Cu(4) —N(13)	1.995(9)
		mean	1.993

via the long fifth bonds (hollow bonds in Fig. 1); according to the classification by Mergehenn and Haase [6b], this constitutes a Class I cubane core. The bond distances and angles relating to the core are collected in Tables II and III, respectively. Although the angles between aminopyridine ligands are almost ideal (ave. 90.4°) notice that the cube is distorted as to cause the expansion of all Cu—O—Cu angles (mean value=97.9°) and a contraction of the interior angles around the copper centers (mean value=80.7°), thereby lowering the symmetry of the faces of the cube from square to rhombic. It is interesting to compare this compound to the structure of the monomeric $[Cu(pyrimidine)_4]^{2+}$ cation synthesized from the same solvent system [14]. In the latter case, all four pyrimidine ligands are bound to the copper center, with BF_4^- anions completing the coordination shells, and no solvate molecules.

The periphery of the cubane core has some unusual characteristics. The complete asymmetric unit contains one $Cu_4(OH)_4$ core, eight monodentate aminopyridine ligands, four tetrafluoroborate anions, and two acetonitriles of solvation. A side-view of the molecule with the anions and solvate molecules removed in Figure 2 shows two important features. Firstly, the orientation of the 3-amino groups *vis-á-vis* the plane of their dimer, is the same for ligands

TABLE III Selected bond angles (degrees) for the $Cu_4(OH)_4N_8$ core

	O —Cu —O		
O(1) —Cu(1) —O(4)	81.4(2)	O(3) —Cu(3) —O(2)	81.1(2)
O(1) —Cu(1) —O(2)	82.2(2)	O(3) —Cu(3) —O(1)	81.0(2)
O(4) —Cu(1) —O(2)	80.4(2)	O(2) —Cu(3) —O(1)	81.8(2)
O(3) —Cu(2) —O(2)	80.8(2)	O(1) —Cu(4) —O(3)	78.6(2)
O(3) —Cu(2) —O(4)	84.2(2)	O(1) —Cu(4) —O(4)	81.5(2)
O(2) —Cu(2) —O(4)	81.1(2)	O(3) —Cu(4) —O(4)	80.5(2)
		mean	80.7
	Cu —O —Cu		
Cu(1) —O(1) —Cu(3)	96.9(2)	Cu(3) —O(3) —Cu(2)	98.8(2)
Cu(4) —O(1) —Cu(1)	97.5(2)	Cu(2) —O(3) —Cu(4)	94.6(2)
Cu(4) —O(1) —Cu(3)	101.5(2)	Cu(3) —O(3) —Cu(4)	98.5(2)
Cu(3) —O(2) —Cu(2)	98.1(1)	Cu(4) —O(4) —Cu(1)	97.1(2)
Cu(3) —O(2) —Cu(1)	97.3(2)	Cu(4) —O(4) —Cu(2)	98.8(2)
Cu(2) —O(2) —Cu(1)	98.4(2)	Cu(1) —O(4) —Cu(2)	99.5(2)
		mean	97.9
	N —Cu —O		
O(4) —Cu(1) —N(1)	93.5(3)	O(2) —Cu(3) —N(11)	92.7(3)
O(1) —Cu(1) —N(3)	92.8(3)	O(3) —Cu(3) —N(9)	95.5(3)
N(1) —Cu(1) —O(2)	102.4(3)	N(11) —Cu(3) —O(1)	102.9(3)
N(3) —Cu(1) —O(2)	106.8(3)	N(9) —Cu(3) —O(1)	105.2(3)
O(2) —Cu(2) —N(7)	92.4(3)	O(4) —Cu(4) —N(15)	93.8(3)
O(3) —Cu(2) —N(5)	93.9(3)	O(1) —Cu(4) —N(13)	94.2(3)
N(7) —Cu(2) —O(4)	101.8(3)	N(13) —Cu(4) —O(3)	98.8(3)
N(5) —Cu(2) —O(4)	101.0(2)	N(15) —Cu(4) —O(3)	104.5(3)
		mean	98.4
O(1) —Cu(1) —N(1)	172.6(3)	O(3) —Cu(3) —N(11)	172.2(3)
O(4) —Cu(1) —N(3)	170.2(3)	O(2) —Cu(3) —N(9)	171.6(3)
O(3) —Cu(2) —N(7)	170.2(3)	O(1) —Cu(4) —N(15)	174.8(3)
O(2) —Cu(2) —N(5)	174.1(3)	O(4) —Cu(4) —N(13)	172.2(3)
		mean	172.7
	N —Cu —N		
N(1) —Cu(1) —N(3)	91.5(3)	N(11) —Cu(3) —N(9)	90.1(3)
N(7) —Cu(2) —N(5)	92.5(3)	N(15) —Cu(4) —N(13)	90.7(3)
		mean	90.4

bound to the same copper. The thermal parameters of every amine-nitrogen atom is significantly larger than the pyridine nitrogen atoms of the same ring, suggesting that there may be slight rotational freedom about the Cu—N bonds. Secondly, the stacking of aminopyridine ligands bound to neighboring copper centers "opens up" the faces of the core for anion and solvent binding as discussed below. A space-filling perspective, Figure 3, looking from the top of Figure 2, shows that both the sixth copper coordination site and the hydroxide ions are relatively accessible.

The symmetry of the cubane core is certainly not retained by the "non-bonded" portions of the structure, as a view of the complete asymmetric unit in Figure 4 attests. Of the three close anions, the shortest Cu—F distance is >2.8 Å

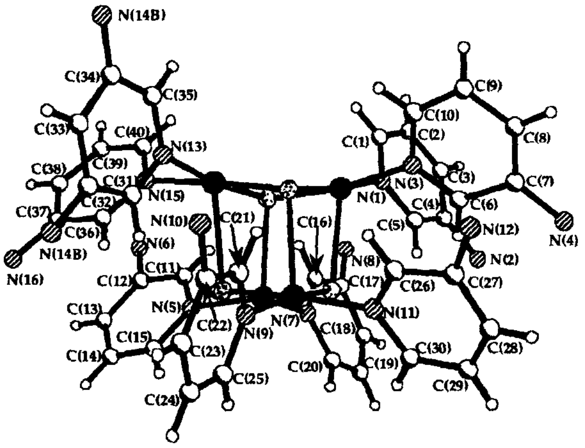

FIGURE 2 A view of the $[Cu_4(OH_4)(3\text{-aminopyridine})_8]^{4+}$ cation indicating the numbering scheme, with the atoms drawn as spheres of arbitrary size. For ease of reference, all pyridine nitrogen atoms have odd-numbered labels, and the amine nitrogen atoms even-numbered labels. The copper (large solid gray spheres) and oxygen (dotted spheres) atom labels are not shown for clarity (see Fig. 1).

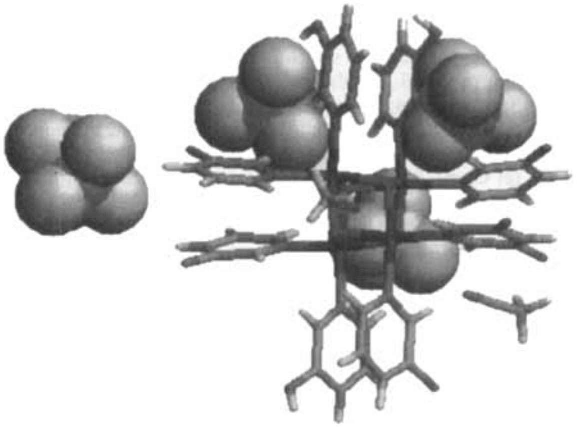

FIGURE 3 Space-filling view of the cation in Figure 2, looking directly onto a Cu_2O_2 rhombic face of the core. The color scheme is as follows: Copper = purple, oxygen = red, nitrogen = blue, carbon = gray, and hydrogen = white.

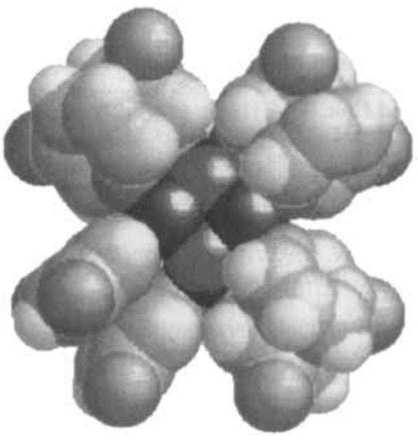

FIGURE 4 The complete asymmetric unit, with all atoms of the cation and the acetonitrile solvent molecules represented as sticks, and the BF_4 anions as their van der Waals spheres. Color scheme is the same as in Figure 3.

(between Cu(2) and F(12)), too long to be considered a true bonding interaction [15]. Instead the BF_4 anions associate with three hydroxide ions to form O–H···F hydrogen bonds at distances ranging from 2.81 Å to 3.03 Å; O(3) has no associated anion. For comparison, the O—H···O distance in ice is 2.76 Å. Additional N—H···F hydrogen bonds, ranging from 2.74–3.29 Å, anchor the anions to the ligands. The two acetonitrile molecules crystallized with this cluster, do not interact with any part of the molecule to any great extent. Figure 4 shows the bridging position of the C—C —N bond of one of these (coming directly out of the plane of the page) across the Cu(1)—O(4)—Cu(4)—O(1) face of the cube, and weakly interacts with these copper atoms: Cu(1) —N = 3.25Å, Cu(4) — N = 2.90Å.

The molecules pack in the solid state with the help of the fourth BF_4 anion that does not participate in intramolecular H-bonding with one cubane, but rather acts as a *inter*molecular H-bonding bridge between two molecules. It is likely that the disorder is caused by the many possible H-bond acceptors accessible to the anions that reside in the open cavities between clusters. Two of the bridging anions are shown in the middle of Figure 5, with the N—H···F interactions denoted with dashed lines.

Other investigators have prepared structurally related $Mn_4(\mu^3\text{-OH})_4$ cubanes and used them as supramolecular synthons for the construction of 3D networks by linking the hydroxide groups cubanes (H-bond donors) with various bifunctional amines (H-bond acceptors) [16]. The

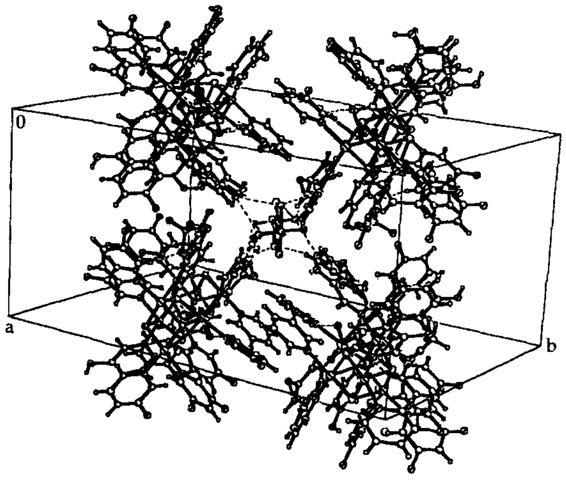

FIGURE 5 Packing view of the unit cell of [Cu_4(3-aminopyridine)$_8$(μ^3-OH)$_4$] 4BF$_4$•2MeCN. The disordered BF_4 anions in the center of the figure act as intermolecular hydrogen bonding-bridges (dashed lines) between neighboring cubanes.

present structure contains additional functionality in the uncoordinated amine nitrogens that are bent away from the Cu—N bond axis. Perhaps if the 3-aminopyridine cubes can be linked *via* their amine groups we will induce a novel three dimensional connectivity. Furthermore, complex Cu—Cu interactions in other Cu_4O_4 cubanes have produced both antiferromagnetic and ferromagnetic exchange interactions, depending on the detailed bond angles and bond distances. Results of these reactivity studies as well as magnetic susceptibility measurements will be presented elsewhere [17].

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