

Bis(2,2-bipyridine-*N,N'*)tetra- μ -chloro-tetracopper(I)

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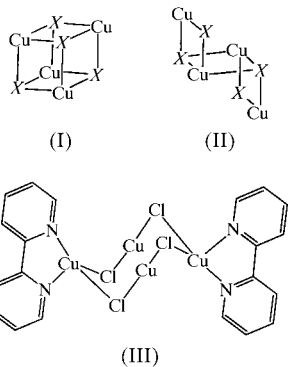
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A novel centrosymmetric chair-like dimer, bis(2,2'-bipyridine)- $1\kappa^2N,N';3\kappa^2N,N'$ -tetra- μ -chloro-1:2 κ^2Cl ;2:3 κ^2Cl ;3:4 κ^2Cl ;1:4 κ^2Cl -tetracopper(I), $[Cu_4Cl_4(C_{10}H_8N_2)_2]$, has been solvothermally synthesized and structurally characterized. The complex self-assembles into a three-dimensional network *via* C—H \cdots Cl hydrogen bonds, π - π stacking and weak Cu \cdots Cl electrostatic interactions.

Comment

Lewis-base adducts of copper(I) halides yield a large number of structural types resulting from the oligomerization of $Cu^I X$ (X = halide; Caulton *et al.*, 1990). A frequently observed tetranuclear structure is that of a cube, (I), in which four vertices are occupied by copper(I) ions and the other four by halides. By suitably unfolding the cube, its structure may be topologically transformed into a step configuration, (II), in which ten edges are defined by ten Cu— X bonds (Hu *et al.*, 1995; Churchill & Rotella, 1974). By separating the opposite



faces of the cube or severing the step, independent dimeric species are also possible (Healy *et al.*, 1983). A crown-like Cu_4I_4 framework supported by the S atoms of an $M(mnt)$ moiety (M = Pd, Pt; mnt is 1,2-dicyano-1,2-ethylenedithiolate) has recently been reported by Sugimoto *et al.* (1999).

In this report, we describe the solvothermal synthesis and X-ray crystal structure of a novel tetranuclear copper complex $[Cu_4Cl_4(bipy)_2]$ (bipy is 2,2'-bipyridine), (III), containing a chair-like Cu_4Cl_4 framework. Interestingly, the tetramers are connected through C—H \cdots Cl hydrogen bonds, π - π stacking and weak Cu \cdots Cl interactions, giving rise to a three-dimensional network.

Secondary bonding interactions have been the focus of increased interest for several years. The classical hydrogen bond is a well known structural phenomenon; the non-classical C—H \cdots O/N/Cl hydrogen bonds, at first a controversial postulate, are now accepted as an important factor in determining the nature and stability of solid-state structures. Numerous experiments have been performed and several reviews have documented C—H \cdots O and C—H \cdots N interactions (Steiner, 1997; Steiner & Desiraju, 1998; Davies *et al.*, 1996). By comparison, C—H \cdots Cl interactions have been less extensively studied (Freytag & Jones, 2000). Recently, Aakeroy *et al.* (1999) have demonstrated the existence and universality of C—H \cdots Cl hydrogen bonds by a statistical analysis of data extracted from the Cambridge Structural Database (Allen & Kennard, 1993). Complex (III) offers a unique case of a three-dimensional structure constructed through this type of non-conventional hydrogen bond and is an excellent model for investigation of the effects of C—H \cdots Cl hydrogen bonds on crystal packing and molecular recognition.

The title complex, (III), consists of a discrete $[Cu_4Cl_4(bipy)_2]$ molecule lying across a crystallographic inversion centre as shown in Fig. 1. The eight-membered Cu_4Cl_4 ring forms a distorted chair, with the dihedral angle between the strictly planar systems $Cl1/Cu2/Cl2/Cu1^i/Cl2^i$ and $Cl1/Cu1/Cl2^i$ being 108.4° [symmetry code: (i) $1-x, 1-y, 1-z$]. The copper(I) ions within the molecule are in two different coordination environments; Cu1 is coordinated by a chelating bipy and two Cl atoms forming a distorted tetrahedron, with the most distorted angle $N1-Cu1-N2$ being $81.2(2)^\circ$, while Cu2 is linearly coordinated by two chlorides with a $Cl1-Cu2-Cl2$ angle of $175.93(8)^\circ$. The copper environments in (III) are significantly different from those in the cubane and step structures, where both centres adopt a tetrahedral geometry or have both triangular and tetrahedral geometries. The Cu1—Cl bond lengths of 2.3184 (17) and 2.4556 (18) Å clearly lie within the bond-distance range expected for related Cu_4Cl_4 complexes (Hu *et al.*, 1995; Churchill & Rotella, 1974), are obviously longer than the Cu2—Cl bond lengths of 2.1176 (18) and 2.1196 (18) Å, typical for linear copper(I) chlorides (Siemeling *et al.*, 1997), and are a consequence of the higher coordination number of the Cu1 atom. The Cu1 \cdots Cu2 and Cu1 \cdots Cu2ⁱ distances within the chair are 2.8327 (12) and 2.8008 (12) Å, respectively, falling into the range of metal-metal distances found in other Cu_4X_4 complexes (Hu *et al.*, 1995; Churchill & Rotella, 1974; Healy *et al.*, 1983). The present Cu_4Cl_4 core is thus very different from the cubane and the step-type structures so far observed in isolated tetranuclear copper(I) halides. In fact, the transformation from the step structure (II) to the chair structure (III) requires only a

net breaking of two Cu—X bonds. Therefore, the present case is unique among Cu₄X₄ systems and constitutes a new structural variant in metal-halide chemistry.

The extended structure of (III) involves three distinct kinds of secondary interactions: C—H···Cl hydrogen bonds, π – π stacking and weak Cu···Cl interactions. The H atoms of the bipy rings have been activated by electron donation from the bipy to the copper(I) ions upon coordination. Some of these are then suitably disposed to yield weak hydrogen bonds with neighbouring Cl atoms. In this case, two H atoms of each coordinated bipy ligand are involved in hydrogen-bonding interactions with Cl1 atoms of adjacent Cu₄Cl₄ molecules, giving a two-dimensional layer structure. The C2—H2A···Cl1ⁱⁱ and C4—H4A···Cl1ⁱⁱⁱ distances [symmetry codes: (ii) $-x, -y, 2 - z$; (iii) $-x, 1 - y, 2 - z$] are 2.93 and 2.99 Å, respectively, within the range 2.7–3.0 Å of reported C—H···Cl hydrogen-bond lengths (Aakeroy *et al.*, 1999). The corresponding angles are 148 and 158°, respectively, further supporting the existence of hydrogen bonds. A more detailed inspection shows that adjacent layers are further linked *via* π – π stacking interactions and Cu···Cl electrostatic interactions, leading to a three-dimensional network structure, as shown in Fig. 2. The interplanar distances between adjacent bipy planes of 3.46 and 3.53 Å indicate significant π – π interactions. The geometry of the bipy ligand is unexceptional and similar to that in bipy groups involved in π – π interactions (Ye *et al.*, 1998). The Cu2···Cl1^{iv} distance [symmetry code: (iv) $-x, 1 - y, 1 - z$] is 3.43 Å, slightly less than the sum of the corresponding van der Waals radii (3.51 Å), and therefore indicative of a weak interaction.

In conclusion, we have characterized a novel chair-like tetranuclear copper(I) chloride, which is self-assembled into a stable three-dimensional network *via* three different kinds of secondary interactions. The structure described here indicates that the combination of metal chlorides (hydrogen-bond acceptors) with heterocyclic bases such as 2,2-bipy, 1,10-phenanthroline and pyridine (hydrogen-bond donors) has enormous potential for generating secondary interactions such as C—H···Cl hydrogen bonds and π – π stacking, and for assembling multicomponent systems in which the subunits are

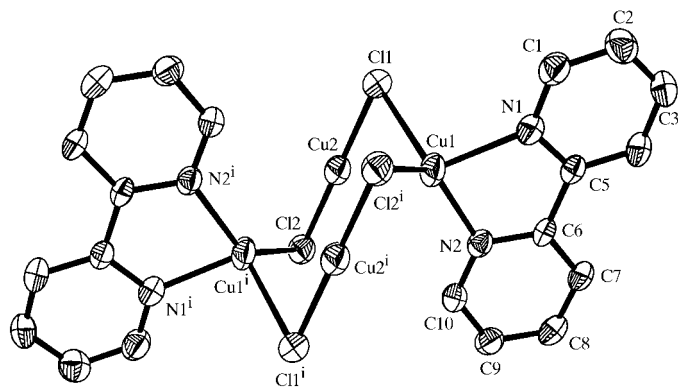


Figure 1
A view of the molecular structure of [Cu₄Cl₄(bipy)₂] showing 40% probability displacement ellipsoids. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

mono- or polynuclear complexes. Polymers of this type are interesting and important for their potential as useful conductive, porous and magnetic materials (Subramanian *et al.*, 1994).

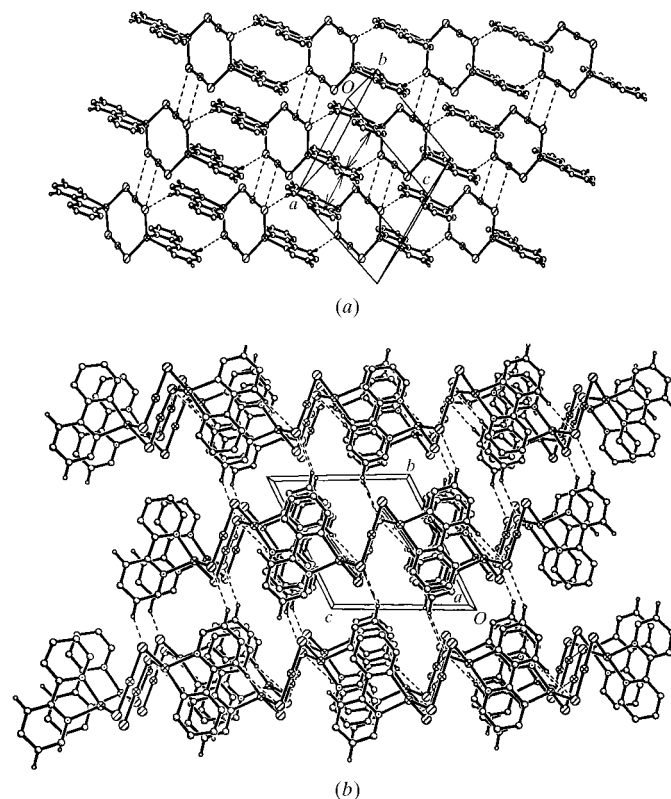


Figure 2
(a) A view of the π – π stacking and Cu···Cl interactions in (III) and (b) a view of the three-dimensional network structure in (III). With the exception of H2 and H4, H atoms have been omitted for clarity.

Experimental

A mixture of CuCl₂·2H₂O (1 mmol), bipy (1 mmol) and H₃BO₃ (1.5 mmol) was suspended in water (10 ml) and EtOH (3 ml) and transferred to a stainless steel bomb, which was sealed, heated at 443 K for 3 d, and then slowly cooled to room temperature to give purple crystals of the title complex in 30% yield. The product is air stable and insoluble in common organic solvents, such as benzene, EtOH, MeCN, DMF, DMSO and THF. H₃BO₃ played an important role in growing crystals of (I) and may function as a mineral agent (Sheldrick & Wachhold, 1997). No crystals were obtained when the above reaction was performed in the absence of this agent.

Crystal data

[Cu₄Cl₄(C₁₀H₈N₂)₂]
M_r = 708.33
 Triclinic, *P*1
a = 7.4252 (8) Å
b = 9.4231 (7) Å
c = 9.4957 (9) Å
 α = 64.253 (2)°
 β = 74.117 (2)°
 γ = 88.504 (2)°
V = 572.28 (9) Å³

Z = 1
D_x = 2.055 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 1649 reflections
 θ = 2.41–25.03°
 μ = 4.150 mm⁻¹
T = 293 (2) K
 Plate, purple
 0.15 × 0.15 × 0.10 mm

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.526$, $T_{\max} = 0.661$
 2994 measured reflections

2006 independent reflections
 1596 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$
 $\theta_{\max} = 25.03^\circ$
 $h = -8 \rightarrow 8$
 $k = -11 \rightarrow 8$
 $l = -11 \rightarrow 9$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.055$
 $wR(F^2) = 0.162$
 $S = 1.053$
 2006 reflections
 146 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.104P)^2 + 0.663P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.90 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.84 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cu1—N1	2.085 (5)	Cu2—Cl1	2.1176 (18)
Cu1—N2	2.032 (5)	Cu2—Cl2	2.1196 (18)
Cu1—Cl1	2.4556 (18)	Cu1—Cu2	2.8327 (12)
Cu1—Cl2 ⁱ	2.3184 (17)	Cu1—Cu2 ⁱ	2.8008 (12)
N1—Cu1—N2	81.2 (2)	Cl2 ⁱ —Cu1—Cl1	103.44 (6)
N2—Cu1—Cl2 ⁱ	129.91 (14)	Cl1—Cu2—Cl2	175.93 (8)
N1—Cu1—Cl2 ⁱ	112.52 (14)	Cu2—Cl1—Cu1	76.15 (6)
N2—Cu1—Cl1	121.91 (14)	Cu2—Cl2—Cu1 ⁱ	78.12 (6)
N1—Cu1—Cl1	100.12 (15)		

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

H atoms were placed geometrically at a distance of 0.93 \AA from their carrier C atoms and were refined riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1994); data reduction: SAINT and SHELXTL (Siemens, 1994); program(s) used to solve structure: SHELXTL; program(s)

used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1430). Services for accessing these data are described at the back of the journal.

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