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The binuclear copper(II) complex μ-chloro-μ-methoxy-bis[chloro(di-2-pyridylamine)-copper(II)]

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Key indicators

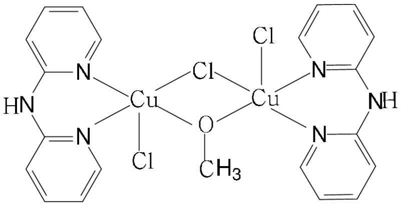
Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.042
wR factor = 0.096
Data-to-parameter ratio = 17.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title binuclear copper(II) complex, $[Cu_2Cl_3(CH_3O)(C_{10}H_9N_3)_2]$, the metal centers adopt distorted trigonal bipyramidal five-coordinate geometry. The molecule possesses a C_2 axis, on which lie the bridging Cl^- anion and the methoxy group. The non-bridging coordinated Cl^- ions participate in N—H···Cl and C—H···Cl inter- and intramolecular hydrogen bonds.

Comment

The ligand di-2-pyridylamine (dpyam) has been used widely to form transition metal complexes. With copper(II) the structures of mononuclear and polynuclear compounds have been reported as well as bridged binuclear species, for example, oxamidate (oa)-bridged $[Cu_2\text{-}(dpyam)_2(oa)(NO_3)_2]$ (Sletten, 1982), dihydroxo-bridged $[Cu_2(dpyam)_2(OH)_2(BF_4)_2]$ and $[Cu(dpyam)_2(OH)_2(H_2O)]Cl_2{\cdot}2H_2O$ (Wu *et al.*, 1992). In recent years, increasing attention has been paid to the dpyam ligand because it has been used as a basic material for the formation of polymeric chain complexes. In the framework of our current work concerning the synthesis and characteristaion of transition metal polynuclear compounds using multidentate N-donor groups as ligands (Shieh *et al.*, 1997; Lai *et al.*, 1999; Peng *et al.*, 2000; Li *et al.*, 2003), copper(II) complexes with the dpyam ligand have been examined.



(I)

As shown in Fig. 1, each Cu^{II} atom in the title compound, (I), is coordinated by two N atoms of one chelating dpyam ligand, two bridging atoms (O1 and Cl1) and a non-bridging Cl atom. Selected geometric parameters are listed in Table 1. The Cu atom has a highly distorted trigonal bipyramidal geometry with a τ value of 0.715 (Addison *et al.*, 1984) (for five-coordinate complexes, $\tau = 0$ for a perfect square pyramid and $\tau = 1$ for a trigonal bipyramid). The bite angle of the dpyam ligand, N1—Cu—N3, of 90.44 (11)° is similar to that observed previously (86–96°; Muñoz, 1993). The individual pyridyl rings are quite planar [maximum deviation 0.0123 (15) Å for atom C2]. However, as in the preceding structure (Muñoz, 1993), the two pyridine rings of the dpyam ligand are inclined to one another by 12.8 (5)°. Atoms Cu, Cl1, Cu1*A* and O1 are coplanar, forming a dihydral angle of 101.4 (14)° with the pyridyl ring involving atom N1. The Cu^{II} atoms, with a

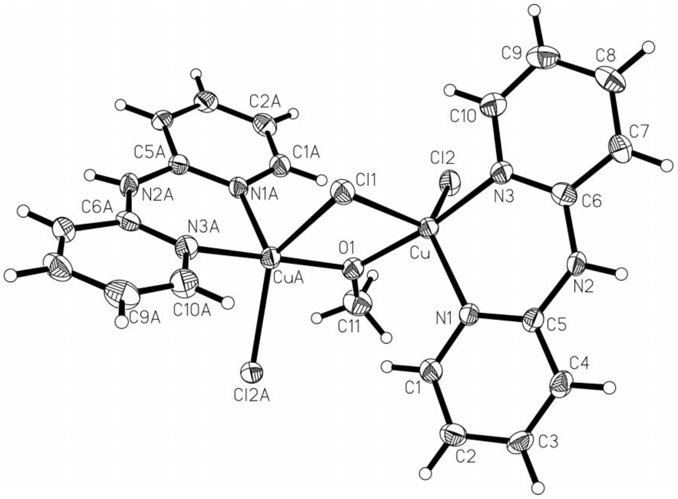


Figure 1
The molecular structure of (I), showing displacement ellipsoids at the 50% probability level and the atom-numbering scheme. The suffix *A* corresponds to symmetry code (i) in Table 1. Only one orientation of the disordered methyl group is shown.

Cu···Cu distance of 3.2615 (5) Å, are linked by a bridging Cl atom and the O-atom of the methoxy group, with angles Cu—Cl1—Cu*A* and Cu—O1—Cu*A* of 82.44 (4) and 116.09 (16)°, respectively. This results in the formation of a discrete neutral binuclear complex which has a C_2 symmetry axis passing through the C—O bond of the methoxy group and bridging Cl1 atom.

This structure is similar to that of the triply bridged μ-Cl-μ-(OMe)$_2$-dicopper(II) complex reported previously (Marsich *et al.*, 1995). It is evident that the bridging effect of the Cl atom is not as strong as that of the methoxy O atom; the bond lengths Cu—O and Cu—Cl are 1.9220 (17) and 2.4748 (10) Å, respectively. The Cu—O bond length is consistent with the sum of the corresponding single bond covalent radii, while the Cu—Cl bond length is significantly longer than the formal single-bond length of 2.27 Å. However, the Cl atoms, both bridging and non-bridging, play an important role in hydrogen bonding. The crystal structure is stabilized by inter- and intramolecular N—H···Cl and C—H···Cl hydrogen bonds, details of which are given in Table 2.

Experimental

Dpyam (0.25 g, 1.46 mmol) and CuCl (0.18 g, 1.8 mmol) were placed in an Erlenmeyer flask, and 25 ml of DMF was added as solvent. The mixture was heated for 10 min at *ca* 393 K, then a solution of potassium *tert*-butoxide (0.164 g, 1.46 mmol) in *n*-butanol (2 ml) was added dropwise. Heating was continued for 30 min, then the mixture was left overnight in air at room temperature. Reoxygenation to a copper(II) species occurred. The solvent was removed using a rotatory evaporator and the residue was washed with hexane. The remaining solid was extracted with methanol and recrystallized from methanol/ether, giving both block-shaped black crystals, of a known linear trinuclear complex (Zeng *et al.*, 2003), and pale-green crystals of the title compound, (I). IR (cm^{-1}): 3453.51 (*m*), 3364.66 (*m*), 1680.4 (*s*), 1626.32 (*s*), 1502.7 (*m*), 1413.85 (*w*), 1205.25 (*s*), 1147.31 (*s*), 849.86 (*m*), 757.14 (*m*), 730.1 (*s*), 513.78 (*m*).

Crystal data

$[Cu_2Cl_3(CH_3O)(C_{10}H_9N_3)_2]$
$M_r = 606.87$
Monoclinic, $C2/c$
$a = 16.9245$ (3) Å
$b = 7.6655$ (2) Å
$c = 19.2417$ (4) Å
$\beta = 112.6724$ (9)°
$V = 2303.41$ (9) Å^3
$Z = 4$
$D_x = 1.750$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9609 reflections
$\theta = 2.3$–27.5°
$\mu = 2.22$ mm^{-1}
$T = 150$ (1) K
Plate, green
0.10 × 0.10 × 0.02 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{min} = 0.836$, $T_{max} = 0.965$
9609 measured reflections
2633 independent reflections
2028 reflections with $I > 2\sigma(I)$
$R_{int} = 0.066$
$\theta_{max} = 27.5°$
$h = -21 \rightarrow 21$
$k = -9 \rightarrow 9$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.096$
$S = 1.05$
2633 reflections
152 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0447P)^2 + 3.9941P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.81$ e Å^{-3}
$\Delta\rho_{min} = -0.54$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu—O1	1.9220 (17)	Cu—Cl2	2.3633 (9)
Cu—N3	1.990 (3)	Cu—Cl1	2.4748 (10)
Cu—N1	2.072 (3)	O1—C11	1.416 (6)
O1—Cu—N3	171.81 (10)	O1—Cu—Cl1	80.73 (8)
O1—Cu—N1	96.00 (8)	N3—Cu—Cl1	92.97 (9)
N3—Cu—N1	90.44 (11)	N1—Cu—Cl1	102.45 (7)
O1—Cu—Cl2	90.44 (6)	Cl2—Cu—Cl1	128.92 (3)
N3—Cu—Cl2	89.47 (8)	Cu^i—Cl1—Cu	82.44 (4)
N1—Cu—Cl2	128.56 (8)	Cu—O1—Cu^i	116.09 (16)

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2*A*···Cl2^{ii}	0.88	2.32	3.188 (3)	170
C1—H1*A*···Cl2^{i}	0.95	2.77	3.684 (4)	162
C3—H3*A*···Cl1^{iii}	0.95	2.83	3.717 (4)	156
C9—H9*A*···Cl2^{iv}	0.95	2.74	3.672 (4)	168
C11—H11*A*···Cl2^{i}	0.98	2.80	3.264 (2)	109
C11—H11*C*···Cl2	0.98	2.68	3.264 (2)	118

Symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $\frac{1}{2} + x, \frac{3}{2} + y, 1 + z$; (iii) $-1 - x, -1 - y, -z$; (iv) $\frac{1}{2} - x, \frac{3}{2} - y, 1 - z$.

H atoms were placed in geometrically idealized positions, with C—H = 0.95–0.98 Å and N—H = 0.88 Å. They were constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$ (CH or NH) and $1.5U_{eq}(C)$ (CH$_3$). The H atoms of the bridging methoxy group are disordered equally over two orientations related by the twofold rotation axis.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL*97

(Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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