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[*μ*-*N*,*N*,*N*′,*N*′-Tetrakis(2-pyridylmethyl)-1,2-ethanediamine]bis[dichlorocopper(II)]

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Key indicators

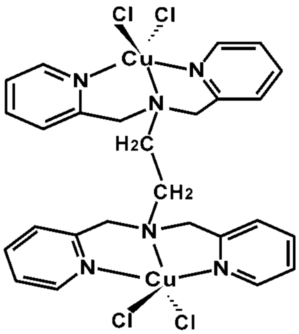
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.009 Å
R factor = 0.057
wR factor = 0.136
Data-to-parameter ratio = 19.3

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

Each Cu^{II} atom in the title complex, [Cu_2Cl_4(tpen)], where tpen is *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-1,2-ethanediamine ($C_{26}H_{28}N_6$), is clearly five-coordinate with approximate square-pyramidal geometry. Four of the coordinating atoms, *viz.* a Cl atom and the three N atoms of a tpen ligand, lie in a distorted square plane around Cu^{II}. The second Cl atom occupies the apical position of the square pyramid. The Cu—Cl distances are 2.262 (1) and 2.478 (1) Å, and the Cu—N distances are 2.006 (4) to 2.089 (4) Å.

Comment

The most interesting aspect in the coordination chemistry of copper(II) is the variety of coordination geometries possible for the central Cu^{II} atom (Anderson *et al.*, 1976). *N*,*N*,*N*′,*N*′-Tetrakis(2-pyridylmethyl)-1,2-ethylenediamine (referred to as tpen) is a ligand. It is expected to form a mononuclear hexadentate octahedral complex. However, because of the steric crowding in mononuclear copper(II) complexes, the formation of dinuclear copper(II) complexes is also possible (Karlin *et al.*, 1992; Mahapatra *et al.*, 1997; Casella *et al.*, 1988; Farrugia *et al.*, 1997). Recently, dinuclear transition-metal complexes containing Cu^{II} with various chelating ligands related to tpen have been reported (Jensen *et al.*, 1997). Furthermore, the high reactivity of the chloro ligand which coordinates to Cu^{II} makes the complexes useful as a starting material for various reactions.



(I)

We report here the crystal structure of the centrosymmetric title complex, (I). In the title complex (Fig. 1), the dinuclear Cu^{II} is contained as a central dimetal unit, which is connected by a tpen bridge and with four coordinated chloro ligands. In the crystal structure, each Cu^{II} is clearly five-coordinate with approximate square-pyramidal geometry. Bond distances and angles are summarized in Table 1. Four of the coordinating atoms, *viz.* one of the Cl atoms (Cl1) and the three N atoms of

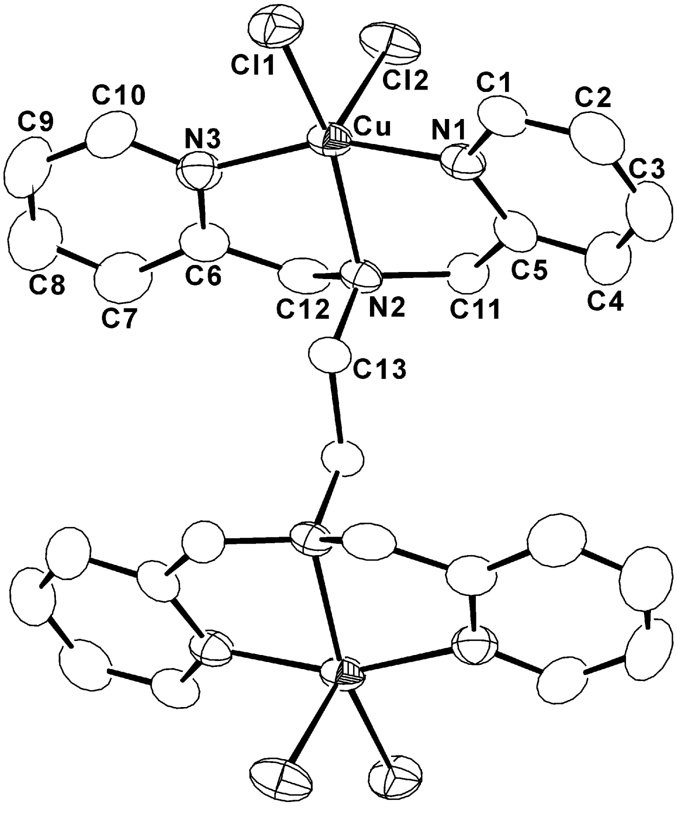


Figure 1
ORTEP-3 (Farrugia, 1997) drawing of (I) with the atom numbering; displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

the tpen ligand, lie at the corners of a distorted square plane around Cu^{II}. The second Cl atom (Cl2) occupies the apical position of the square pyramid. The Cu—Cl bond lengths are not identical and are 2.2618 (14) and 2.4781 (14) Å. The Cu—N bond lengths are 2.006 (4), 2.020 (5) and 2.089 (4) Å. Comparing the Cu—Cl bonds, it is found that the length of the Cu—Cl apical bond is significantly longer than that of the basal one (2.478 Å *versus* 2.262 Å). This axial expansion may be due to the influence of the d^9 electronic configuration on the coordination geometry (Anderson *et al.*, 1976). In addition to interatomic distances, it is noteworthy to mention bond angles. The Cl1—Cu—Cl2 [105.24 (6)°] bond angle is greater than the other bond angles [Cl2—Cu—N1 95.6 (1)°, Cl2—Cu—N2 96.4 (1)° and Cl2—Cu—N3 95.63 (14)°]. This is believed to be a result of repulsion by the lone-pair electrons of Cl1 and Cl2. Two intermolecular C—H···Cl interactions are present in the crystal structure. Also, the Cu···Cu non-bonding distance for (I) is 7.932 (1) Å.

Experimental

A solution of $CuCl_2.5H_2O$ (0.23 g, 1 mmol) in methanol (50 ml) was added to a solution of tpen (0.22 g, 0.5 mmol) in methanol (5 ml). A green precipitate formed immediately after mixing. The mixture containing the precipitate was stirred for 20 min. and then 5 ml of a methanolic solution of sodium acetate (0.1 g, 1.2 mmol) was added. The precipitate dissolved immediately without ligation of acetate. The resulting green solution was stirred for 1 h. After stirring, the green solution was left at room temperature for a few days. A single green crystal suitable for X-ray analysis was then formed. Analysis calculated for the title complex: C 45.03, H 4.07, N 12.12%; found: C 44.85, H 4.13, N, 12.22%.

Crystal data

$[Cu_2Cl_4(C_{26}H_{28}N_6)]$
$M_r = 693.42$
Orthorhombic, *Pbca*
$a = 13.113$ (1) Å
$b = 20.926$ (2) Å
$c = 10.6378$ (8) Å
$V = 2919.1$ (4) Å^3
$Z = 4$
$D_x = 1.589$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 9.6$–10.9°
$\mu = 1.85$ mm^{-1}
$T = 298$ (2) K
Monoclinic, green
0.32 × 0.25 × 0.22 mm

Data collection

Stoe Stadi4 diffractometer
ω–2θ scans
Absorption correction: numerical (Stoe & Cie, 1996)
$T_{min} = 0.665$, $T_{max} = 0.824$
3548 measured reflections
3324 independent reflections
2303 reflections with $I > 2\sigma(I)$

$R_{int} = 0.079$
$\theta_{max} = 27.4°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 26$
$l = 0 \rightarrow 13$
3 standard reflections
frequency: 60 min
intensity decay: 5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.136$
$S = 1.16$
3324 reflections
172 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0328P)^2 + 10.1201P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.79$ e Å^{-3}
$\Delta\rho_{min} = -0.46$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu—N1	2.006 (4)	Cu—Cl1	2.262 (1)
Cu—N3	2.020 (5)	Cu—Cl2	2.478 (1)
Cu—N2	2.089 (4)		
N1—Cu—N3	158.8 (2)	N2—Cu—Cl1	158.4 (1)
N1—Cu—N2	80.7 (2)	N1—Cu—Cl2	95.6 (1)
N3—Cu—N2	80.3 (2)	N3—Cu—Cl2	95.6 (1)
N1—Cu—Cl1	96.8 (1)	N2—Cu—Cl2	96.4 (1)
N3—Cu—Cl1	97.5 (1)	Cl1—Cu—Cl2	105.24 (6)

H atoms were treated as riding atoms using *SHELXL*97 defaults. The measurement of reflections from (459) to (7,12,9) was repeated following some problems during the data collection.

Data collection: *Stadi*4 (Stoe & Cie, 1996); cell refinement: *Stadi*4; data reduction: *X-RED* (Stoe & Cie, 1996); program(s) used to solve structure: *SHELXS*97–2 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97–2 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997).

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