
Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1066). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 1877–1879

Di-μ-chloro-bis{chloro[2-(*N*-propylaminomethyl)pyridine-*N*,*N'*]copper(II)}

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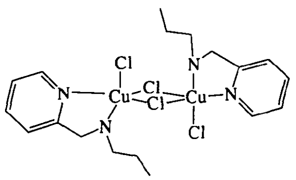
(*Received 6 November 1995; accepted 8 March 1996*)

Abstract

The structure of the title compound, $[Cu_2Cl_2(C_9H_{14}N_2)_2(\mu\text{-}Cl)_2]$, has been determined. The geometry about the Cu atom is square pyramidal. The complex exists as a dimer about an inversion centre with the Cu atoms linked by two asymmetric chlorine bridges. The dimeric structure of this complex differs from the polymeric dihalo-bridged chain of CuLX_2 complexes, where L is 2-(aminomethyl)pyridine.

Comment

The *cis*-diaquo complexes of copper(II) generated in aqueous solution from the corresponding dichloro complexes have been studied (Morrow & Trogler, 1988; Chin, Jubian & Mrejan, 1990; Wahnon, Hynes & Chin, 1994) for their potential as functional enzyme models of phosphodiesterases and peptidases. We have prepared $[Cu_2Cl_2(C_9H_{14}N_2)_2(\mu\text{-}Cl)_2]$, (I), as part of our interest in the reactivity and structure of such complexes.



(I)

The title complex exists as a dimer which is well separated from the other dimers in the cell. The dimer exists about an inversion centre. The bridging Cu_2Cl_2 unit is planar with a Cu$\cdots$Cu' distance of 3.4137 (13) Å. The chlorine bridges are unsymmetrical, with a Cu—Cl(1) distance of 2.2705 (14) Å and a Cu—Cl(1') distance of 2.8336 (16) Å. The geometry about the Cu atom is distorted square pyramidal, with atoms N(1), N(2), Cl(1) and Cl(2) defining the basal plane, and Cl(1') located in the apical position.

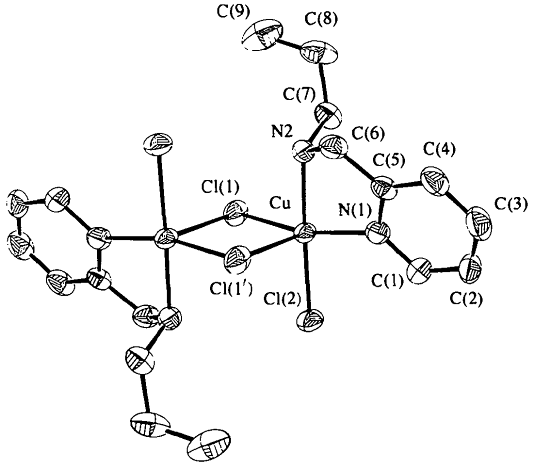


Fig. 1. *ORTEP*II plot (Johnson, 1976) of the title complex showing the atom-numbering scheme. Ellipsoids are shown at the 50% probability level.

The geometry about the Cu atom and the structural characteristics of (I) are similar to other CuLX_2 complexes, where L is a bidentate diammine ligand such as *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (Estes,

Estes, Hatfield & Hodgson, 1975) or *N*,*N*-dimethylethylenediamine (Phelps, Goodman & Hodgson, 1976). In all three complexes, the Cu—N and short Cu—Cl bonds are comparable. Interestingly, the reported structures of di-μ-bromobis{bromo[2-(aminomethyl)-pyridine]copper(II)} (Helis, Goodman, Wilson, Morgan & Hodgson, 1977) and di-μ-chloro-bis{chloro[2-(aminomethyl)pyridine]copper(II)} (O'Connor & Edouk, 1985) show that these compounds exist as polymeric dihalo-bridged chains in which one bridging halide ligand serves to propagate the chain. This is in contrast to (I) which is a discrete dimeric structure. The ligand in our complex differs only by an additional *N*-propyl group. The Cu—N and short Cu—Cl distances are comparable to those in di-μ-chloro-bis{chloro[2-(aminomethyl)pyridine]copper(II)}. The long Cu—Cl distance [2.8336 (16) Å] in (I), however, is shorter than that in the polymeric structure of di-μ-chloro-bis[chloro(2-aminomethylpyridine)copper(II)] [3.206 (1) Å].

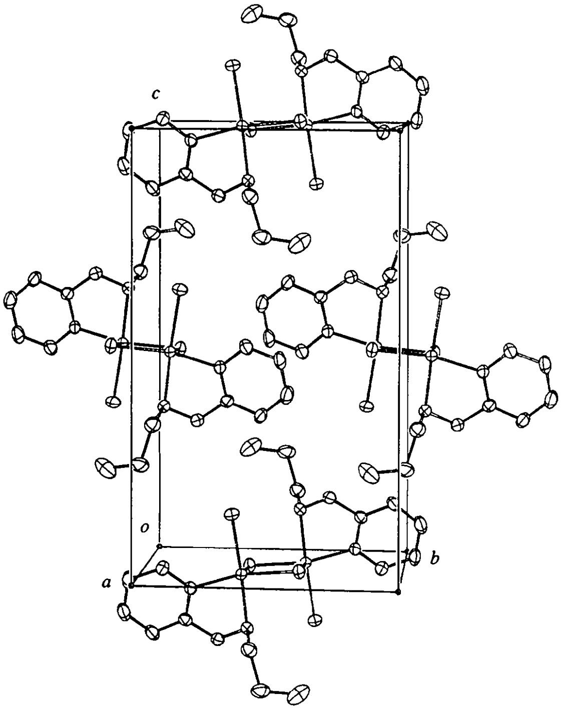


Fig. 2. Packing diagram (*ORTEPII*; Johnson, 1976) with ellipsoids drawn at the 30% probability level.

Experimental

2-(*N*-Propylaminomethyl)pyridine was prepared from the reductive amination of 2-pyridinecarboxaldehyde and propylamine (Borch, Berstein & Durst, 1971). The title complex was obtained by combining one equivalent of 2-(*N*-propylaminomethyl)pyridine and one equivalent of $CuCl_2.2H_2O$ in methanol. Slow recrystallization of the compound from methanol resulted in crystals suitable for analysis.

Crystal data

[$Cu_2Cl_4(C_9H_{14}N_2)_2$]
$M_r = 569.35$
Monoclinic
$P2_1/c$
$a = 7.0801\ (19)$ Å
$b = 10.0072\ (13)$ Å
$c = 16.4820\ (21)$ Å
$\beta = 90.298\ (18)^\circ$
$V = 1167.8\ (4)$ Å^3
$Z = 2$
$D_x = 1.619$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 17.5–20.0^\circ$
$\mu = 2.30$ mm^{-1}
$T = 293$ K
Block
0.33 × 0.25 × 0.20 mm
Blue

Data collection

Rigaku AFC-6 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (Gabe, Le Page, Charland, Lee & White, 1989)
$T_{\min} = 0.5952$, $T_{\max} = 0.6339$
1920 measured reflections
1484 independent reflections

1178 observed reflections [$I_{\rm net} > 2.5\sigma(I_{\rm net})$]
$R_{\rm int} = 0.012$
$\theta_{\max} = 22.43^\circ$
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 17$
3 standard reflections monitored every 150 reflections intensity decay: 0.3%

Refinement

Refinement on F
$R = 0.032$
$wR = 0.031$
$S = 1.55$
1178 reflections
127 parameters
H atom parameters not refined
$w = 1/[\sigma^2(F) + 0.00005F^2]$

$(\Delta/\sigma)_{\max} = 0.011$
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cu	0.31859 (9)	0.61232 (6)	0.99881 (3)	0.0322 (4)
Cl(1)	0.28263 (19)	0.38789 (12)	0.98572 (7)	0.0415 (8)
Cl(2)	0.32591 (19)	0.65004 (13)	0.86373 (7)	0.0438 (8)
N(1)	0.2981 (6)	0.8056 (4)	1.0308 (2)	0.036 (2)
N(2)	0.3129 (5)	0.5892 (4)	1.1210 (2)	0.034 (2)
C(1)	0.2495 (7)	0.9094 (5)	0.9822 (3)	0.043 (3)
C(2)	0.2486 (8)	1.0394 (5)	1.0102 (3)	0.047 (3)
C(3)	0.2983 (8)	1.0633 (5)	1.0898 (4)	0.055 (4)
C(4)	0.3464 (8)	0.9587 (5)	1.1403 (3)	0.047 (3)
C(5)	0.3444 (7)	0.8300 (5)	1.1085 (3)	0.034 (3)
C(6)	0.4019 (7)	0.7097 (5)	1.1569 (3)	0.040 (3)
C(7)	0.1159 (7)	0.5665 (5)	1.1496 (3)	0.045 (3)
C(8)	0.1030 (9)	0.5212 (6)	1.2390 (3)	0.060 (4)
C(9)	0.1661 (10)	0.3824 (7)	1.2528 (4)	0.081 (5)

Table 2. *Selected geometric parameters (Å, °)*

Cu···Cu$^{\rm i}$	3.4137 (13)	Cu—Cl(2)	2.2591 (13)
Cu—Cl(1)	2.2705 (14)	Cu—N(1)	2.010 (4)
Cu—Cl(1$^{\rm i}$)	2.8336 (16)	Cu—N(2)	2.028 (4)

N(1)—C(1)	1.355 (6)	C(3)—C(4)	1.379 (8)
N(1)—C(5)	1.343 (6)	C(4)—C(5)	1.391 (7)
N(2)—C(6)	1.481 (6)	C(5)—C(6)	1.499 (7)
N(2)—C(7)	1.492 (6)	C(7)—C(8)	1.546 (7)
C(1)—C(2)	1.381 (7)	C(8)—C(9)	1.477 (9)
C(2)—C(3)	1.376 (9)		
Cl(1)—Cu—Cl(1^{i})	96.83 (5)	Cl(2)—Cu—N(1)	95.70 (12)
Cl(1)—Cu—Cl(2)	94.29 (5)	Cl(2)—Cu—N(2)	176.91 (11)
Cl(1)—Cu—N(1)	165.60 (11)	N(1)—Cu—N(2)	81.24 (15)
Cl(1)—Cu—N(2)	88.80 (11)	Cu—Cl(1)—Cu^{i}	83.17 (4)
Cl(1^{i})—Cu—Cl(2)	93.49 (5)	Cu—N(1)—C(1)	127.0 (3)
Cl(1^{i})—Cu—N(1)	92.89 (12)	Cu—N(1)—C(5)	114.0 (3)
Cl(1^{i})—Cu—N(2)	86.29 (12)		

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

The structure was solved by direct methods and refined by full-matrix least-squares methods, with all non-H atoms anisotropic. H atoms were included in calculated positions. All computing was performed using the *NRCVAX* system (Gabe *et al.*, 1989).

Data collection: *TEXSAN* (Molecular Structure Corporation, 1992). Cell refinement: *TEXSAN*.

The authors wish to thank the Natural Sciences and Engineering Council of Canada and the US Army Research Office for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: BK1213). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 1879–1881

Bis[di(2-aminoethyl)amine-*N*,*N*′,*N*″]-nickel(II) Chloride Monohydrate, a Redetermination

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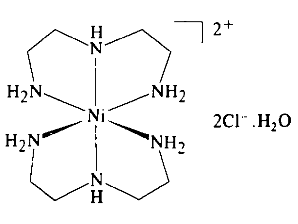
(*Received 1 March 1996; accepted 7 May 1996*)

Abstract

A redetermination of the structure of the title compound, $[Ni(C_4H_{13}N_3)_2]Cl_2.H_2O$, from diffractometer data leads to considerably more accurate geometric parameters than those obtained in a previous determination using film data. The coordination geometry around the Ni^{II} atom in the $[Ni(C_4H_{13}N_3)_2]^{2+}$ cation is a distorted octahedron, with the Ni—N distances in the range 2.083 (4)–2.166 (4) Å and the *trans*-N—Ni—N angles in the range 161.9 (2)–177.5 (2)°.

Comment

We have been interested in the coordination chemistry of transition metal complexes with alkoxy ligands (Bradford, Hynes, Payne, & Willis, 1990; Hynes, Willis & Payne, 1990, 1992; Willis, 1988). In the course of our investigation on the coordination chemistry of the $HOC(CF_3)_2OH$ ligand, $[Ni(dien)_2][HOC(CF_3)_2O]_2$ [dien is di(2-aminoethyl)amine] was prepared (Hynes, 1989). On recrystallization from a mixture of CH_2Cl_2 and CH_3OH, purple hexagonal plates of $[Ni(dien)_2]Cl_2.H_2O$, (I), were obtained as the main product. The structure of this compound is reported here.



(I)

The structure of (I) was previously determined from multiple-layer Weissenberg photographs; the intensity data were measured photometrically and refined to $R_{obs} = 0.092$ (Paoletti, Biagini & Cannas, 1969; Biagini & Cannas, 1970); no absorption correction was applied. This redetermination, using modern diffraction appara-

Acta Crystallographica Section C
ISSN 0108-2701 © 1996