X-ray crystal structure of *trans*-dichlorobis(2,4,6-collidine)copper(II)

S. Subramanian and Michael J. Zaworotko^{*,1}

Received July 16, 1993

The X-ray crystal structure of *trans*-dichlorobis(2,4,6-collidine)copper(II) has been determined. Dark blue crystals of the complex crystallize in the monoclinic space group P2₁/c, with cell dimensions a = 7.527(3), b = 14.732(4), c = 7.951(4)Å and $\beta = 92.79(9)^{\circ}$; V = 880.6(6)Å³ and Z = 2. 949 unique reflections with $I_{\text{net}} > 3\sigma(I)$ on refinement afforded values of R = 0.041 and $R_w = 0.048$.

Introduction

Copper(II) complexes exhibit a wide variety of coordination geometries. Whereas five coordinate square pyramidal geometry is predominant in copper(II) complexes, four coordinate copper(II) complexes exhibiting geometries that vary between tetrahedral and square planar geometries have also been encountered. Distorted square planar geometry around copper(II) centers has been claimed where the distinction between a compressed tetrahedron and a distorted octahedron is not sharply distinguishable (Cotton and Wilkinson, 1988). In this regard CuX_4^{2-} anions have been extensively studied (Greenwood and Earnshaw, 1985) and the geometry around Cu in tetrachlorocuprate(II), $CuCl_4^2$, anions has been shown to be very sensitive to the nature of the counterions. $CuCl_4^{2-}$ adapts tetrahedral, square planar or an intermediate geometry depending upon the steric bulkiness of the accompanying cation (Greenwood and Earnshaw, 1985; Cotton and Wilkinson, 1988). Only a few cationic and neutral copper(II) complexes have thus far been structurally characterized that are strictly square planar. This report describes the crystal structure of such a complex, the neutral square planar complex, trans-dichlorobis(2,4,6-collidine)copper(II), trans-(2,4,6-collidine)₂CuCl₂.



Experimental

CuCl was prepared as described elsewhere (Vogel, 1989). All other chemicals were purchased from Aldrich Chemical Co. and used without further purification. The IR spectrum was recorded on a Perkin Elmer 1600 series FTIR instrument.

Synthesis of trans-(2,4,6-collidine)₂CuCl₂

The title complex was prepared by aerial oxidation of CuCl in a solvent mixture of pyridine and collidine. 0.98 g (9.9 mmol) of CuCl was dissolved in 30 ml of pyridine under an atmosphere of nitrogen and 25 ml of 2,4,6-collidine was added. The resulting solution was allowed to stand at room temperature in a partially sealed Erlenmeyer flask allowing for slow diffusion of air. Over a period of seven to ten days dark blue single crystals of *trans*-Cu(2,4,6-collidine)₂Cl₂ were deposited. Yield: 2.10 g (5.6 mmol; 57%). IR (KBr reflectance; cm⁻¹):

¹Department of Chemistry, Saint Mary's University, Halifax, Nova Scotia, Canada B3H 3C3.

2955, 2905(C-H), 1619(C=N), 1569, 1468, 1438, 1413, 1373, 1318, 1238, 1037, 951, 896 and 861.

X-ray crystallography

A single crystal suitable for X-ray diffraction was mounted in a thin-walled glass capillary and three dimensional diffraction data were collected on a Enraf-Nonius CAD-4 diffractometer. Pertinent experimental parameters related to X-ray crystallography are presented in Table 1. The unit cell dimensions were determined using 24 centered reflections in the 2θ range 37-45°. The structure was solved by direct methods using the PC version of the NRCVAX program package (Gabe

 Table 1. Crystallographic data for trans-dichlorobis
 (2,4,6-collidine)copper(II)

Compound	$Cu(2,4,6\text{-collidine})_2Cl_2$		
Colour	dark blue		
Formula wt.	3/6.8		
Crystal system	monoclinic		
Space group	$P2_{i}/c$		
Temp. °C	17		
Cell constants ^a			
a, A	7.527(3)		
b, \dot{A}	14.732(4)		
$c, \mathrm{\AA}$	7.951(4)		
β, °	92.79(9)		
Vol., Å ³	880.6(6)		
F(000)	390		
Ζ	2		
$D_{\rm calc}$ g cm ⁻³	1.42		
$\mu_{\rm calc}' {\rm cm}^{-1}$	14.1		
Scan Type	$\omega/2\theta$		
Radiation	MoK_{α}		
Max. Xtal Dimensions, mm	$0.30 \times 0.30 \times 0.50$		
Scan width	$.80 + .35 \tan \theta$		
Transmission range	.815, .999		
Decay of standards	$\pm 1\%$		
Reflections measured	3287		
2θ range, °	2-45		
Unique reflections	1146		
Reflections observed ^b	949		
Computer programs	NRCVAX		
Structure solution	Direct		
Number of parameters	97		
Weight modifier, k	.00005		
G.O.F.	3.51		
R	0.041		
R_{w}	0.048		
Final diff. map (e/Å ³)	0.39		

^aLeast-squares refinement of $((\sin \theta)/\lambda)^2$ for 25 reflections $\theta > 18^\circ$.

 ${}^{b}I > 3\sigma(I)$. Corrections: Lorentz-polarization and absorption (empirical psi scan).

et al., 1989) implemented on an 80486 based IBM compatible computer. A weighting scheme based upon counting statistics was used. All non-hydrogen atoms were refined anisotropically. The collidine ring hydrogen atoms were fixed in calculated positions (C-H 1.08 Å) and the methyl hydrogen atoms were located via inspection of a difference Fourier map. Hydrogen atoms were assigned isotropic thermal parameters based upon the carbon atoms to which they are bonded and were not refined. Neutral atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The final least square cycle was calculated with 22 atoms and 97 parameters and afforded $R = \Sigma(F_o - F_c)^2/\Sigma F_o = 0.041$ and $R_w = \Sigma[(w(F_o - F_c)^2)/\Sigma(wF_o^2)]^{1/2} = 0.048$.

Results and discussion

As might be expected from it's d⁹ electron configuration, copper(II) complexes tend to adapt five coordinate square pyramidal geometry. However, four coordinate copper(II) centers are also well known in [CuL₄] type complexes, the overall charge varying between +2 and -2 depending upon the nature of L. In most of these cases the copper(II) center is found either in a compressed tetrahedral or a highly distorted octahedral geometry that approaches square planar coordination (Cotton and Wilkinson, 1988; A. F. Wells, 1986). A similar trend is also found in many dimeric complexes containing bidentate (Mitchell et al., 1970) and pyridine N-oxide ligands (Sager et al., 1967). There are several structurally characterized examples of anionic square planar copper(II) complexes. For example, a number of salts containing the $CuCl_4^2$ anion have been characterized and the geometry of $CuCl_4^{2-}$ ion in these salts has been found to vary between tetrahedral (e.g., $((CH_3)_4N)_2[CuCl_4])$ and square planar (e.g., (NH₄)₂[CuCl₄] and (dienH₃)[CuCl₄](Cl)) geometries (Cotton and Wilkinson, 1989; Losee and Hatfield, 1973; Ferguson and Zaslow, 1971). Square planar cationic and neutral copper(II) complexes are, however, less well characterized via X-ray crystallography.

ORTEP (Johnson, 1965) perspective and overhead views of the title complex are presented in Fig. 1. Fractional atomic coordinates and listings of important bond lengths and angles are presented in Tables 2 and 3, respectively. The copper(II) center lies around a crystallographic inversion center and hence half of the ligands, 2,4,6-collidine and chloride, are symmetry generated. The ligands are therefore arranged in a *trans*-geometry.



Fig. 1. (a) Perspective ORTEP view of *trans*-dichlorobis(2,4,6-collidine)copper(II). (b) Overhead view of *trans*-dichlorobis(2,4,6-collidine)copper(II).

The Cl-Cu-N angles are 88.98(12) and 91.02(12)° and the Cl-Cu-Cl and N-Cu-N angles are precisely 180°. These structural parameters, with the crystallographically imposed symmetry, implies a perfect square planar geometry around the copper(II) center. The Cu-Cl and Cu-N distances are 2.2696(23) and 2.003(4)Å, respectively. These distances are comparable to those found in the analogous *trans*-dichlorobis(pyridine)copper(II) complex (Cu-Cl, 2.28 and Cu-N, 2.02 Å) (Dunitz, 1957); however, it should be

 Table 2. Fractional atomic coordinates x, y, z and B_{iso} for transdichlorobis (2,4,6-collidine) copper(II)

-				
	x	у	Z	B_{iso}^{a}
Cu	0	0	0	3.64(4)
Cl	0.14500(19)	0.03854(10)	0.24664(20)	5.19(7)
Ν	-0.1502(5)	0.1115(3)	0.0181(5)	3.35(20)
C1	-0.3039(7)	0.1060(3)	0.0954(7)	3.57(23)
C2	-0.4134(7)	0.1800(4)	0.1103(6)	3.86(24)
C3	-0.3608(7)	0.2647(3)	0.0545(6)	3.99(24)
C4	-0.2006(7)	0.2697(3)	-0.0211(7)	4.0(3)
C5	-0.0959(7)	0.1927(3)	-0.0411(7)	3.78(24)
C6	-0.3486(7)	0.0163(3)	0.1690(8)	4.7(3)
C7	-0.4742(8)	0.3470(4)	0.0784(8)	6.0(3)
C8	0.0750(8)	0.1965(4)	-0.1266(8)	5.4(3)

^aB_{iso} is the mean of the principal axes of the thermal ellipsoid.

Fable 3.	Interatomic bond distances (Å) and angles (°) for trans-
	dichlorobis (2,4,6-collidine) copper(II)

Distances			
Cu-Cl	2.269(2)	C1-C6	1.490(7)
$Cu-Cl^a$	2.269(2)	C2-C3	1.388(8)
Cu-N	2.003(4)	C3-C4	1.375(8)
Cu-N ^a	2.003(4)	C3-C7	1.500(7)
N-C1	1.339(7)	C4-C5	1.395(7)
N-C5	1.355(6)	C5-C8	1.485(8)
C1-C2	1.376(7)		
Angles			
Cl-Cu-Cla	180.0	N-C1-C6	116.8(4)
Cl-Cu-N	88.9(1)	C2-C1-C6	121.4(5)
Cl-Cu-Na	91.0(1)	C1-C2-C3	120.2(5)
Cla-Cu-N	91.0(1)	C2-C3-C4	117.2(4)
Cla-Cu-Na	88.9(1)	C2-C3-C7	120.9(5)
N-Cu-Na	179.9	C4-C3-C7	121.9(5)
Cu-N-C1	119.1(3)	C3-C4-C5	121.2(5)
Cu-N-C5	121.2(3)	N-C5-C4	119.8(5)
C1-N-C5	119.6(4)	N-C5-C8	118.4(4)
N-C1-C2	121.8(4)	C4-C5-C8	121.9(5)

a(-x, -y, -z).

noted that the latter was not a very accurately determined X-ray structure. The aromatic rings are oriented perpendicular to the CuN_2Cl_2 plane, presumably to minimize steric interactions. Such an orientation enhances steric hindrance by the methyl groups along the axial

sites, hence mitigating against axial ligation and distortion towards tetrahedral geometry. Similar observations have been made in cationic pyridine-N-oxide complexes (Lee et al., 1969a and 1969b). However, in the neutral dimeric *trans*-dichlorobis(pyridine-N-oxide) copper(II) complex and in the monomeric trans-dichlorobis(pyridine)copper(II) complexes, the pyridine rings are rotated by only about 70° with respect to the CuN₂Cl₂ plane. In the former case, a significant deviation from square planar geometry is observed and this may account for the observed orientation. However, in the latter case, the geometry around copper(II) center is square planar. Although steric factors are prominent in controlling the orientation of the aromatic rings (pyridine being sterically less demanding than 2,4,6-collidine) π -bonding between the aromatic ring and copper(II) ions has been invoked to explain the earlier observations. In particular, the nature of magnetic interactions between the copper(II) centers has been rationalized on the basis of such π -bonding (Sager et al., 1967).

Most of the cationic square planar copper(II) complexes that have thus far been structurally characterized are those of pyridine-N-oxides with non-coordinating anions (Lee et al., 1969a and 1969b). Similar complexes with coordinating anions form dimeric (Watson, 1969; Sager et al., 1967; Scavnicar and Matkovic, 1969) or monomeric complexes (Sager and Watson, 1969) complexes with distorted square planar or square pyramidal geometry (Sager and Watson, 1969; Sager et al., 1967). A square planar copper(II) cation has also been characterized in tetrakis-(triphenylarsine oxide)copper(II) bis[dichlorocuprate(I)] (Francisco et al., 1981). In the context of neutral complexes, trans-(pyridine)₂CuCl₂ (Dunitz, 1957) and trans-(2,6-Lutidine-Noxide)₂CuCl₂ (Sager and Watson, 1969) represent the only two structures that have been structurally characterized and are monomeric and square planar. In the title complex trans-square planar geometry is enhanced both by electronic and steric factors: the trans disposition of the 2,4,6-collidine and chloride ligands would be expected to enhance π -bonding between the copper(II) ion and the aromatic rings; such an arrangement of ligands is sterically more favorable thereby preventing both axial ligation and distortion from square planar geometry.

Acknowledgment

We gratefully acknowledge financial support from the Natural Sciences and Engineering Council of Canada (operating grant, MJZ) and Saint Mary's University (purchase of the X-ray diffractometer).

References

- Cotton, F. A., and Wilkinson, G. (1988) Advanced Inorganic Chemistry (fifth edition) (Wiley, New York) p. 756.
- Dunitz, J. D. (1957) Acta Cryst. 10, 307.
- Ferguson, G., and Zaslow, B. (1971) Acta Cryst. B27, 849.
- Francisco, R. H. P., De Almeida Santos, R. H., Lechat, J. R., and Massabni, A. C. (1981) Acta Cryst. B37, 232.
- Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L., and White, P. S. (1989) J. Appl. Cryst. 22, 384.
- Greenwood, N. N., and Earnshaw, A. (1985) Chemistry of the elements. (Pergamon Press, Oxford, U.K.) p. 1385.
- International Tables for X-ray Crystallography, Vol. IV. (Kynoch Press, Birmingham, 1974).
- Johnson, C. K. (1976) ORTEP, Report ORNL-3794, revised (Oak Ridge National Laboratory, Oak Ridge, TN).
- Lee, J. D., Brown, D. S., and Melsom, B. G. A. (1969) Acta Cryst. B25, 1378.
- Lee, J. D., Brown, D. S., and Melsom, B. G. A. (1969) Acta Cryst. B25, 1595.
- Losee, D. B., and Hatfield, W. E. (1973) J. Am. Chem. Soc. 95, 8169.
- Mitchell, T. P., Bernard, W. H., and Wasson, J. R. (1970) Acta Cryst. B26, 2096.
- Sager, R. S., and Watson, W. H. (1969) Inorg. Chem. 8, 308.
- Sager, R. S., Williams, R. J., and Watson, W. H. (1967) Inorg. Chem. 6, 951.
- Scavnicar, S., and Matkovic, B. (1969) Acta Cryst. B25, 2046.
- Vogel's textbook of practical organic chemistry (1969) (fifth edition), revised by B. S. Furniss, A. J. Hannaford, P. W. G. Smith, and A. R. Tetchell. (Longman Group U.K. Ltd.), p. 428.
- Watson, W. H. (1969) Inorg. Chem. 8, 1879.
- Wells, A. F. (1986) Structural Inorganic Chemistry (fifth edition) (Clarendon Press, Oxford, U.K.) p. 1122.