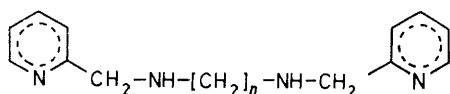


Crystal and Molecular Structure of a Solvate of Chloro-[1,6-bis-(2'-pyridyl)-2,5-diazahexane]copper(II) Chloride

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The structure of the α -form of the title compound has been determined by a three-dimensional *X*-ray structural analysis. Crystals are monoclinic with $a = 9.73(1)$, $b = 13.66(1)$, $c = 14.52(1)$ Å, $\beta = 112.95(5)^\circ$, space group $P2_1/c$, and $Z = 4$. The structure was solved by conventional Patterson and Fourier techniques and refined by block-diagonal least-squares methods to a final R of 0.102, for 1246 independent reflections collected on an automatic diffractometer. The cation is five-co-ordinate with a geometry approximating to a square pyramid. One of the pyridyl nitrogens occupies the axial position with Cu-N 2.21(2) Å. The other bond lengths are normal, although there are distortions of the co-ordination polyhedron resulting from ligand constraints, and some distortions of bond angles in the chelating ligand itself. The chloride anions form hydrogen-bonded 'bridges' between secondary amine nitrogens of screw-related cations. The solvent (water or methanol) is disordered in regions around centres of symmetry; water and/or methanol can be accommodated with small variations of the unit-cell dimensions.

In a recent report¹ of the stereochemistry of some metal compounds of the homologous tetra-amine ligands 1,6-bis-(2'-pyridyl)-2,5-diazahexane (Ia; $n = 2$, abbreviated as bispicen) and 1,7-bis-(2'-pyridyl)-2,6-diazahexane (Ib; $n = 3$, abbreviated as bispictn) we noted that the compound $\text{Cu}(\text{bispicen})\text{Cl}_2 \cdot x\text{H}_2\text{O}$ appeared to be a key one for determining the extent of five-co-ordination in this series of copper(II) compounds.



(I)

a; $n = 2$ b; $n = 3$

In contrast to the compounds $\text{Cu}(\text{bispictn})(\text{NCS})_2$, at least two forms of which now have been shown to be five-co-ordinate,² $\text{Cu}(\text{bispicen})(\text{NCS})_2$ forms an octahedral six-co-ordinate isomer;¹ and, whilst $\text{Cu}(\text{bispicen})\text{Cl}_2$ appeared to contain five-co-ordinate copper(II), we could not eliminate the possibility that it (and perhaps other compounds in the series) might also have a *cis*-octahedral six-co-ordinate structure. Accordingly, and to define more exactly the steric effects of such ligands, we have determined the *X*-ray structure of the chloro-compound.

EXPERIMENTAL

Crystals of the α -form were obtained from methanol¹ usually as blue flattened needles. Zero- and first-level Weissenberg films ($\{0kl\}$ and $\{1kl\}$) generally showed faint signs of a second 'single-crystal' diffraction pattern which increased in intensity with time. The latter presumably corresponds to the β -form which has been characterised by its powder pattern. The crystals were metastable and decayed at a rate that seemed at least partially paralleled by loss of solvent of crystallisation. This decay rate was reduced by coating selected crystals with 'Formvar' dissolved in methylene dichloride.

¹ J. G. Gibson and E. D. McKenzie, *J. Chem. Soc. (A)*, 1971, 1666.

A single crystal of dimensions *ca.* 0.43 × 0.25 × 0.21 mm was used for data collection. Cell constants were determined from precession $\{h0l\}$ and Weissenberg $\{0kl\}$ photographs.

Crystal Data.— $\text{C}_{14}\text{H}_{18}\text{Cl}_2\text{CuN}_4 \cdot x\text{H}_2\text{O}$, $M = 394.8$ ($x = 1$), Monoclinic, $a = 9.73(1)$, $b = 13.66(1)$, $c = 14.52(1)$ Å, $\beta = 112.95(5)^\circ$, $U = 1761.1$ Å³, $D_m = 1.50$ (by flotation), $Z = 4$, $D_c = 1.484$ ($x = 1$), $F(000) = 812$ ($x = 1$). Cu- K_α radiation, $\lambda = 1.5418$ Å; $\mu(\text{Cu-}K_\alpha) = 46.11$ cm⁻¹. Space group $P2_1/c$ (C_{2h}^5 , No. 14) from systematic absences.

Layers $\{0-13kl\}$ were collected on a Philips' 'Pailred' automatic two-circle diffractometer with stationary counter and moving crystal ω -scan technique, by use of silicon-monochromated Cu- K_α radiation. Angular scan-ranges varying from 2.4—3.4° were used, depending on spot-width, with a scan rate of 2.5° min⁻¹. For each reflection, two background counts were accumulated, each over a period of 12 s, with the crystal stationary at each extremity of the scan.

Reflections with intensity $I < 2.5\sigma$ were ignored, as generally were those with background difference $\Delta > 4\sigma$. However, for the $\{1kl\}$ data, where interference from diffraction by the β -form was most acute, such reflections were not omitted, but rechecked later by comparison with Weissenberg films. Three intensities affected by the spurious diffraction were then rejected. The usual Lorentz and polarisation factors were applied, but no allowance was made for absorption or extinction. 1246 Independent reflections were used in the final refinement.

A Patterson synthesis gave the position of the copper atom, and Fourier methods subsequently gave the positions of the non-hydrogen atoms, except those of the solvent molecules. Block-diagonal least-squares refinement reduced R to 0.134, copper and chlorine being assigned anisotropic thermal parameters.

A difference-Fourier synthesis for the region about $(0, \frac{1}{2}, 0)$ showed two diffuse peaks *ca.* 1.3 Å apart and close to the centre of symmetry; these were tentatively assigned as half-population oxygen atoms of disordered water molecules and their positional and isotropic thermal parameters behaved fairly satisfactorily when included in further refinement to R 0.109.

A full difference-Fourier then showed peaks of mean height *ca.* 0.25 eÅ⁻³ in most positions where hydrogen atoms

² N. A. Bailey and E. D. McKenzie, *J.C.S. Dalton*, 1972, 1566; N. A. Bailey, E. D. McKenzie, and J. R. Mullins, *Chem. Comm.*, 1970, 1103.

were to be expected. Accordingly the positions of all hydrogen atoms, except those of the solvent, were calculated. These atoms were included, but not varied, in the final refinement to R 0.102. Atomic scattering factors were taken from ref. 3.

A subsequent preparation of the compound gave a crystal with unit cell: $a = 9.68$, $b = 13.57$, $c = 14.38$ Å, $\beta = 114.1^\circ$, and $U = 1725$ Å³, as measured from precession films (Mo- K_α radiation, $\lambda = 0.71069$ Å). This cell correlates well

TABLE 1

Atomic positions ($\times 10^4$) and calculated hydrogen positions ($\times 10^3$) with isotropic thermal parameters (Å²). Estimated standard deviations are given in parentheses

Atom	x/a	y/b	z/c	B
Cu *	3277(3)	0500(2)	1428(2)	
Cl(1) *	2328(7)	-1062(4)	1252(4)	
Cl(2) *	3654(7)	3670(4)	0942(4)	
N(1)	4227(20)	0549(15)	2934(13)	3.83(6)
N(2)	2813(17)	0713(11)	-0040(11)	2.32(5)
N(3)	4841(19)	1522(13)	1542(13)	3.04(6)
N(4)	1592(21)	1314(14)	1792(14)	3.74(6)
C(1)	1623(24)	0413(18)	-0775(16)	3.56(7)
C(2)	1429(25)	0459(20)	-1782(16)	3.98(7)
C(3)	2655(28)	0926(19)	-1956(19)	4.24(8)
C(4)	3828(29)	1209(20)	-1197(19)	4.79(9)
C(5)	3978(23)	1116(17)	-0205(16)	3.00(7)
C(6)	5236(28)	1424(20)	0664(19)	4.55(9)
C(7)	5990(27)	1454(20)	2544(18)	4.30(8)
C(8)	5258(32)	1310(22)	3263(21)	5.68(10)
C(9)	3069(28)	0480(22)	3350(19)	4.92(9)
C(10)	1892(26)	1214(18)	2801(17)	3.73(8)
C(11)	0978(26)	1708(17)	3171(17)	3.67(8)
C(12)	-0130(28)	2251(19)	2658(18)	4.16(9)
C(13)	-0448(28)	2373(19)	1656(19)	4.35(9)
C(14)	0482(27)	1867(18)	1255(19)	4.11(8)
O(1)	-1460(50)	4610(40)	0280(30)	7.5(2)
O(2)	-0420(40)	4570(30)	-0030(30)	4.3(1)
H(1) †	077	002	-061	5.0
H(2)	037	036	240	5.5
H(3)	257	098	274	6.0
H(4)	474	156	135	6.5
H(6')	567	213	053	6.0
H(6'')	615	090	085	6.0
H(7')	672	084	259	6.0
H(7'')	667	212	274	6.0
H(8')	610	177	404	7.0
H(8'')	464	196	332	7.0
H(9')	255	-023	328	6.5
H(9'')	355	068	414	6.5
H(11)	126	164	400	5.5
H(12)	-082	261	301	5.5
H(13)	-137	285	120	6.0
H(14)	026	195	045	5.5
H(15)[N(1)]	488	-020	318	5.5
H(16)[N(3)]	433	225	150	4.5

* Anisotropic thermal parameters ($\times 10^5$)

Atom	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
Cu	940(5)	271(2)	440(2)	-168(5)	579(6)	-192(8)
Cl(1)	1300(14)	239(4)	524(6)	-36(9)	635(16)	-384(14)
Cl(2)	1459(15)	410(6)	352(6)	74(10)	410(15)	153(16)

The expression for the temperature factor is: $\exp - (h^2b_{11} + k^2b_{22} + l^2b_{33} + hkb_{23} + hlb_{13} + hkb_{12})$.

† Hydrogen on carbon takes the same number as the carbon atom, with pairs on the same carbon distinguished by primes where appropriate. Hydrogen on nitrogen is distinguished by the corresponding nitrogen atom label in brackets.

with the powder pattern obtained from the bulk sample (Co- K_α radiation, $\lambda = 1.7902$ Å). A similar good correla-

* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

tion was observed between the measured cell dimensions from the 'data' crystal and powder photographs of the original bulk sample from which it was selected. Further recrystallisations from different samples of methanol gave powder patterns which showed slight variations in the positions, but not the gross intensities of the lines.

An explanation for these variations in cell dimensions was found by vapour-phase chromatographic analysis of the solvent of crystallisation (including adsorbed and occluded solvent), which established the presence of both water and methanol in the crystals. Those obtained by a simple recrystallisation from reagent-grade methanol (*e.g.*, the 'data' crystal) contained methanol: water *ca.* 1:9; whereas, if the solution was boiled down to half volume to remove water, the amount of methanol in the crystals increased. The batch from which we obtained the crystal giving the second unit-cell dimensions quoted had methanol: water 3:4. Apparently there is a distinct preference for water in the solvent sites in the crystal; but, if it is unavailable, methanol can replace it with a consequent small adjustment in the unit-cell dimensions. Because of uncertainties about the exact methanol: water ratio in the 'data' crystal, and because of the relative paucity of the data collected from such a metastable crystal, we cannot justify any attempt to elaborate, in the least-squares refinement, the model for the disordered solvent.

The final atomic positional and vibrational parameters, with estimated standard deviations, are listed in Table 1. Observed structure amplitudes and calculated structure factors are tabulated in Supplementary Publication No. SUP 20681 (12 pp, 1 microfiche).*

RESULTS AND DISCUSSION

The structural analysis shows the presence in the crystals of five-co-ordinate $[\text{Cu}(\text{bispicen})\text{Cl}]^+$ cations and chloride anions, together with disordered solvent of

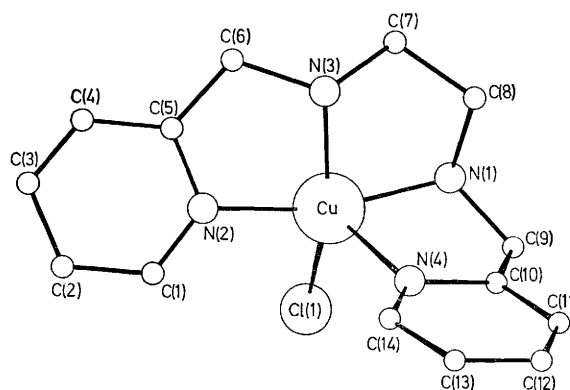


FIGURE 1 The structure of the molecular cation and the atomic labelling

crystallisation around the centres of symmetry at $(0, \frac{1}{2}, 0)$ and $(0, 0, \frac{1}{2})$. The molecular geometry of the cation is shown in Figure 1, together with the atom labelling scheme; details of the various bond lengths and angles are given in Table 2. There are no contacts between the molecular cations shorter than the

* 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, 202.

generally accepted sums of the van der Waal's radii. Relevant equations of least-squares planes and interplanar angles are listed in Table 3.

TABLE 2

Interatomic distances and angles with estimated standard deviations in parentheses

(a) The co-ordination sphere of the metal			
(i) Bond lengths (Å)			
Cu-Cl	2.298(6)	Cu-N(3)	2.02(2)
Cu-N(1)	2.01(2)	Cu-N(4)	2.21(2)
Cu-N(2)	2.02(2)		
(ii) Bond angles (°)			
Cl(1)-Cu-N(1)	95.1(6)	N(1)-Cu-N(3)	85.3(8)
Cl(1)-Cu-N(2)	95.8(5)	N(1)-Cu-N(4)	79.8(7)
Cl(1)-Cu-N(3)	155.0(6)	N(2)-Cu-N(3)	80.7(7)
Cl(1)-Cu-N(4)	101.0(6)	N(2)-Cu-N(4)	107.4(7)
N(1)-Cu-N(2)	165.4(7)	N(3)-Cu-N(4)	103.7(7)
(b) The bispicen ligand			
(i) Bond lengths (Å)			
N(2)-C(1)	1.30(3)	C(8)-N(1)	1.49(4)
C(1)-C(2)	1.41(3)	N(1)-C(9)	1.47(3)
C(2)-C(3)	1.41(4)	C(9)-C(10)	1.50(3)
C(3)-C(4)	1.30(4)	C(10)-N(4)	1.38(3)
C(4)-C(5)	1.39(4)	C(10)-C(11)	1.38(4)
C(5)-N(2)	1.36(3)	C(11)-C(12)	1.28(4)
C(5)-C(6)	1.44(4)	C(12)-C(13)	1.37(4)
C(6)-N(3)	1.47(3)	C(13)-C(14)	1.43(4)
N(3)-C(7)	1.45(3)	C(14)-N(4)	1.30(3)
C(7)-C(8)	1.49(4)		
(ii) Bond angles (°)			
Cu-N(1)-C(8)	107.1(16)	N(2)-C(5)-C(6)	116(2)
Cu-N(1)-C(9)	110.1(16)	C(4)-C(5)-C(6)	126(2)
Cu-N(2)-C(1)	125.7(15)	C(5)-C(6)-N(3)	111(2)
Cu-N(2)-C(5)	112.7(14)	C(6)-N(3)-C(7)	120(2)
Cu-N(3)-C(6)	108.0(15)	N(3)-C(7)-C(8)	109(2)
Cu-N(3)-C(7)	107.4(15)	C(7)-C(8)-N(1)	109(2)
Cu-N(4)-C(10)	109.5(15)	C(8)-N(1)-C(9)	112(2)
Cu-N(4)-C(14)	132.0(17)	N(1)-C(9)-C(10)	110(2)
N(2)-C(1)-C(2)	122(2)	C(9)-C(10)-C(11)	127(2)
C(1)-C(2)-C(3)	117(2)	N(4)-C(10)-C(9)	116(2)
C(2)-C(3)-C(4)	119(3)	N(4)-C(10)-C(11)	118(2)
C(3)-C(4)-C(5)	124(3)	C(10)-C(11)-C(12)	125(2)
C(4)-C(5)-N(2)	117(2)	C(11)-C(12)-C(13)	118(3)
C(1)-N(2)-C(5)	121(2)	C(12)-C(13)-C(14)	117(2)
		C(13)-C(14)-N(4)	123(2)
		C(10)-N(4)-C(14)	118(2)
(c) The hydrogen-bonded chain. Primed atoms are at $1-x, \frac{1}{2}+y, \frac{1}{2}-z$			
(i) Interatomic distances (Å)			
N(3) ... Cl(2)	3.15(2)	Cl(2) ... H(16)	2.11
Cl(2) ... N(1')	3.20(2)	Cl(2) ... H(15')	2.15
(ii) Interatomic angles (°)			
N(3) ... Cl(2) ... N(1')	118.4(5)		
H(16) ... Cl(2) ... H(15')	113		
N(3) ... H(16) ... Cl(2)	157		
Cl(2) ... H(15') ... N(1')	165		

The Copper(II) Co-ordination Polyhedron.—The copper(II) cation has a distorted (or intermediate)⁴ five-coordinate geometry, but it more closely approaches the square pyramidal extreme and will be described in these terms.

The 'basal plane' of the square pyramid contains three nitrogen atoms [N(1)—(3)] and the chloride Cl(1). Because of the different ligands in this 'basal plane', definition of a least-squares plane for the atoms is in-

appropriate; but the angles N(1)-Cu-N(2) 165.4(7) and N(3)-Cu-Cl(1) 155.0(6)° are close to those expected for a square pyramid with the metal out of the basal plane in the normal manner. The bond lengths are normal covalent ones Cu-N 2.01(2), 2.02(2), and 2.02(2) Å, and

TABLE 3

Equations to the least-squares planes given in the form $lX + mY + nZ = d$ (where X , Y , and Z are coordinates in Å referred to the axes a , b , and c^*). The deviations of the various atoms from these planes are given in square brackets

	l	m	n	d
Plane (1):				
Cl(1), N(3), N(4)	-0.1146	0.1812	-0.9768	-2.0759
[Cu 0.062]				
Plane (2):				
Cl(1), N(3), N(4), Cu	-0.1183	0.1828	-0.9760	-2.0654
[Cl(1) -0.017, N(3) -0.020, N(4) -0.008, Cu 0.045]				
Plane (3):				
Cl(1), N(1), N(2)	-0.9044	0.4255	-0.0331	-2.0787
[Cu 0.155, N(3) -0.0574]				
Plane (4):				
Cl(1), N(1), N(2), Cu	-0.9111	0.4106	-0.0349	-2.0620
[Cl(1) -0.009, N(1) -0.050, N(2) -0.050, Cu 0.108]				
Plane (5):				
Cu, N(1), N(3)	0.6937	-0.7189	-0.0443	1.0749
[C(7) 0.390, C(8) -0.288]				
Plane (6):				
N(2), C(1)—(5)	-0.4124	0.9103	-0.0358	-0.2546
[C(1) -0.026, C(2) 0.034, C(3) -0.022, C(4) 0.001, C(5) 0.009, C(6) 0.049, N(2) 0.005, N(3) 0.492, Cu -0.174]				
Plane (7):				
N(4), C(10)—(14)	-0.5771	-0.7909	-0.2036	-2.2188
[C(9) 0.161, C(10) -0.002, C(11) -0.002, C(12) 0.005, C(13) -0.003, C(14) -0.001, N(1) -0.490, N(4) 0.003, Cu -0.083]				
Plane (8):				
N(1)—(3)	-0.7205	0.6934	0.0045	-1.3128
[Cu 0.081, Cl(1) -0.806]				
Plane (9):				
N(1), N(2), N(4)	0.4505	0.8857	0.1120	2.0987
[Cu -0.209]				
Plane (10):				
N(2), N(3), C(5), C(6)	-0.3429	0.9040	-0.2552	-0.0043
[N(2) -0.048, N(3) 0.043, C(5) 0.086, C(6) -0.080, Cu -0.682]				
Plane (11):				
N(4), C(9), C(10), Cu	0.5745	0.7706	0.2761	0.0424
[N(1) 0.575, N(4) -0.048, C(9) -0.032, C(10) 0.059, Cu 0.021]				
Angles between planes (°)				
(1)-(3)	77.7	(8)-(9)	73.1	
(1)-(8)	78.2	(6)-(7)	118.3	
(1)-(9)	90.0	(6)-(10)	13.2	
(3)-(9)	92.0	(7)-(11)	175.7	

Cu-Cl(1) 2.298(6) Å. The fourth nitrogen is 2.21(2) Å from the copper and essentially at the axial site of the square pyramid. There are no other close contacts to the copper.

⁴ E. L. Muettterties and R. A. Schunn, *Quart. Rev.*, 1966, 245.

Most of the angular distortions of the co-ordination polyhedron are directly attributable to ligand steric constraints. Such distortions include: (a) the chelate ring angles of $85.8(9)^\circ$ for the ethylenediamine ring, and $80.7(7)$ and $79.9(7)^\circ$ for the terminal picolylamine rings; (b) N(4) is constrained away from the ideal axial site by *ca.* $14(1)^\circ$ approximately in the plane defined by N(1), N(2), N(4), and Cu; and (c) the angles Cu-N(2) \cdots C(3) and Cu-N(4) \cdots C(12) are, respectively, $9(1)$ and $12(1)$ from the ideal 180° .

Although elongations of the axial bonds in square pyramidal copper(II) compounds are firmly documented,

$2.148(17)$ Å. [To assist comparison, we have labelled the atoms in our present structure by the same system⁷ used for (II). N(3) is not strictly comparable, being an azomethine nitrogen in (II).] Thus, there is a similar distinction between 'axial' and 'basal' bond lengths in both structures, although it is not as great in (II).

Furthermore, both molecules have the same overall configuration of the tetra-amine. This is imposed by steric constraints in (II), but not in the present bispicen compound, which (as noted later) would be less strained in the more symmetrical configuration¹ (equivalent to the configuration in a *cis- α* -octahedral species). Thus

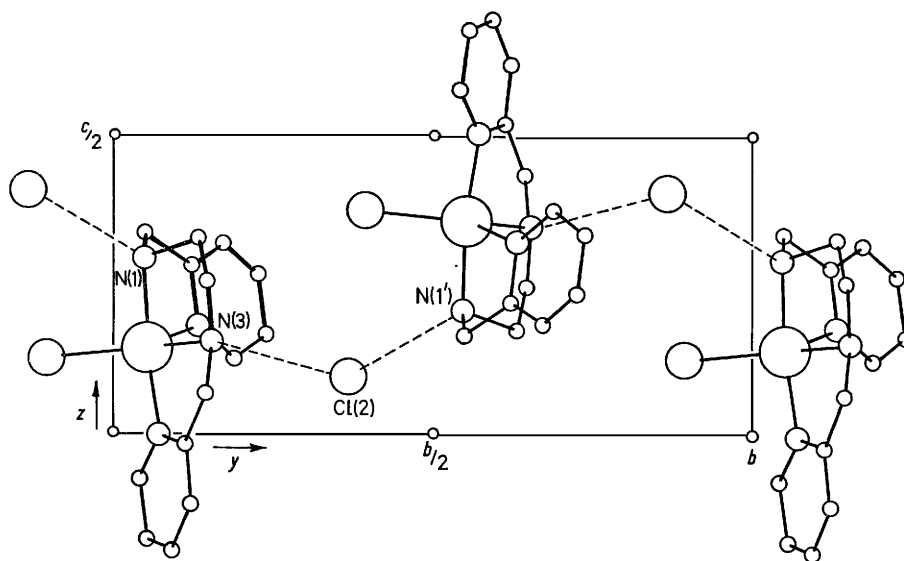
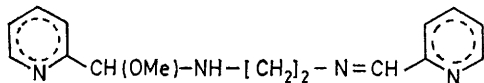


FIGURE 2 The arrangement of the atoms in half the unit cell viewed along the *a* axis. Disordered solvent molecules are omitted. N(1') is at $1-x, \frac{1}{2}+y, \frac{1}{2}-z$

there are few previous examples^{5,6} of such an elongation of a Cu-N distance in a five-co-ordinate species. There is, however, one recent example⁷ which is particularly pertinent here. It is the 'alcohol-addition' compound⁸ [Cu(bpe,MeOH)Br]ClO₄ [(II), where bpe,MeOH is the ligand (III)]. Here the X-ray structural analysis⁷



(III)

showed a co-ordination polyhedron which is very similar indeed to the present one, although both cations are in very different crystalline environments (*cf.* Figure 2 with the corresponding Figure in ref. 7).

The comparable bonds are of similar length in both structures. For the alcohol-addition compound (II), N(1) and N(2) are respectively $2.053(15)$ and $2.034(15)$ Å from the copper, whereas the axial Cu-N(4) bond is

the observed geometry appears to be, at least partially, a result of a stereochemical preference of the metal.

The quite minor variations of structure which are observed between the two cations are easily rationalised as resulting from the different geometries of the portions of the quadridentate ligands which make up the N₃ unit in the basal plane of the square pyramid {*viz.* NH·CH₂·CH₂·NH·CH₂·py vs. NH·CH₂·CH₂·N·CH·py}.

The Amine Ligand.—The ethylenediamine chelate ring has a *gauche* configuration, with C(7) and C(8) lying, respectively, 0.39 and 0.29 Å above and below the Cu, N(1), N(3) plane. The asymmetry arises from the configuration of the total tetra-amine, which is equivalent to that in a *cis- β* -octahedral species.¹ The strain involved for the ligand in this configuration is shown by: (a) the large angle C(6)-N(3)-C(7) of $120(2)^\circ$ [*cf.* C(8)-N(1)-C(9) $112(2)^\circ$, which is much closer to the expected tetrahedral angle]; and (b) the copper atom is significantly less co-planar with the pyridyl group in the basal

⁵ H. S. Preston and C. H. L. Kennard, *J. Chem. Soc. (A)*, 1969, 2955.

⁶ D. L. Cullen and E. C. Lingafelter, *Inorg. Chem.*, 1970, **9**, 1865.

⁷ B. F. Hoskins and F. D. Whillans, *J. Chem. Soc. (A)*, 1970, 123.

⁸ C. M. Harris and E. D. McKenzie, *Nature*, 1962, **196**, 424; *J. Chem. Soc. (A)*, 1969, 746; M. Cressy, E. D. McKenzie, and S. Yates, *ibid.*, 1971, 2677.

plane of the 'square pyramidal' polyhedron than it is with the other pyridyl (Table 3).

Such strain would be significantly relieved in an alternative configuration of the tetra-amine, *i.e.* one in which the terminal picolyl groups are both axial substituents of the nitrogens of the *gauche* ethylenediamine. This is equivalent to the configuration at a *cis- α* -octahedral species.¹

significance of O(1) and O(2) is ambiguous. Figure 3(a) shows the geometry of the centres of electron density determined in the region of the disordered solvent molecules. The contacts involving O(1) and O(2), and their symmetry-related neighbours are either too short or too long for normally acceptable hydrogen-bonded distances. However, our interpretation is that the peaks represent a composite model of the electron density at

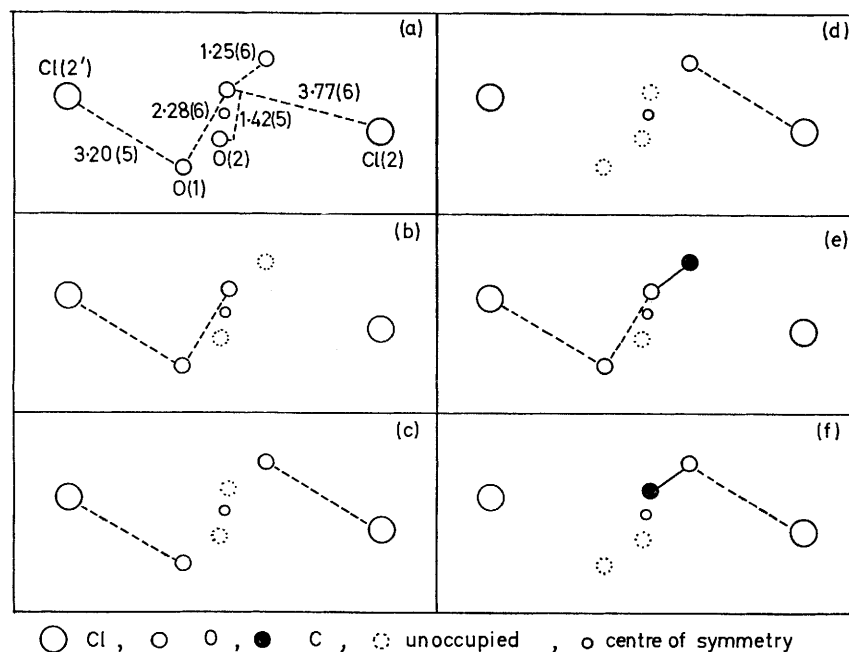


FIGURE 3 (a) The observed centres of electron density corresponding to solvent molecules (water or MeOH). The possible modes of occupancy of these sites are: (b), (c), and (d), by water alone, (e) by both water and methanol, and (f) by methanol alone

Both pyridyl residues are closely planar (Table 3).

The Hydrogen-bonded Network and Solvent.—Figure 2 illustrates the formation of the infinite hydrogen-bonded chains in which the chloride ions form 'bridges' between atoms N(3) and N(1') of neighbouring cations related by the screw axis. The $N \cdots Cl$ contacts are, respectively, 3.15(2) and 3.20(2) Å; the $N-H \cdots Cl$ angles are within the range expected for hydrogen-bonding,⁹ and the calculated $H \cdots Cl \cdots H$ angle of 113° is close to tetrahedral.

Interpretation of the situation in the disordered solvent region is rather speculative, since the physical

⁹ M. Iwata, K. Nakatsu, and Y. Saito, *Acta Cryst.*, 1969, **B25**, 2562; B. L. Holian and R. E. Marsh, *ibid.*, 1970, **B26**, 1049.

these sites; possible modes of solvent occupancy which may be contributing to the observed electron density are given in Figure 3(b)–(f). In view of the observed variation in cell dimensions with solvent composition, it is not difficult for such different individual arrangements of the solvent molecules to satisfy both electron-density and symmetry requirements.

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