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Crystal and Molecular Structure of Bis(1,8-naphthyridine)copper(II) Chloride

BY E. L. ENWALL

Chemistry Department, University of Oklahoma, Norman, OK 73069, *USA*

AND K. EMERSON

Chemistry Department, Montana State University, Bozeman, Montana 59717, *USA*

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Abstract

The structure of $[Cu(C_8H_6N_2)_2]Cl_2, C_{16}H_{12}CuN_4^{2+}.2Cl^-$, has been determined and refined by least squares. The space group is $C2/c$ and the unit-cell parameters are a = 13·786 (1), b = 8·192 (1), c = 16·396 (1) Å, and β = 122·5 (1)°. The number of formula units in the unit cell is four and the density is 1·68 Mg m^{-3}. The structure is composed of isolated molecules, with approximately square-planar coordination about the Cu ion, and with *cis* geometry of the ligands. The 1,8-naphthyridine molecule is monodentate.

The ligand 1,8-naphthyridine (hereafter NN) has attracted wide attention in the last ten years as an example of a strong base ligand with a very small 'bite'. It has been found coordinated in a variety of configurations and the chemistry is complex. In many complexes with first-row transition metals, four NN molecules coordinate bidentately but very unsymmetrically to a central metal ion to give trigonal dodecahedral geometry (Clearfield, Singh & Bernal, 1970; Singh, Clearfield & Bernal, 1971); similar coordination but different geometries have been found for some mercury complexes (Dewan, Kepert & White, 1975; Epstein, Dewan, Kepert & White, 1974). Sacconi and co-workers have reported two complexes in which the NN ligand coordinates in a *syn-syn* bidentate manner to two metal atoms (Gatteschi, Mealli & Sacconi, 1977; Sacconi, Mealli & Gatteschi, 1974), and Dixon and co-workers have described structures in which the NN is primarily coordinated through only one of its two N atoms (Dixon, 1977; Bushnell, Dixon & Khan, 1978). The title compound of this paper is another member of this last class.

Experimental

1,8-Naphthyridine was prepared by the method of Paudler & Kress (1967). Starting materials were practical grade and were used without further purification. The crude product was purified by vacuum sublimation. Bis(1,8-naphthyridine)copper(II) chloride was prepared by mixing solutions of stoichiometric quantities of $CuCl_2$ and NN in water, and allowing excess solvent to evaporate. The product separated as green prismatic crystals on slow evaporation. Analyses: calc. Cu 16·10, C 48·68, H 3·06, Cl 17·96%; found: Cu 15·90, C 48·69, H 2·77, Cl 18·13%.

Crystal data

$C_{16}H_{12}Cl_2CuN_4$, FW 394·74, monoclinic, a = 13·786 (1), b = 8·192 (1), c = 16·396 (1) Å, β = 122·5 (1)°, V = 1561·71 Å^3, Z = 4, $F(000)$ = 796, D_c = 1·68, D_m = 1·68 Mg m^{-3}; λ(Mo $K\alpha$) = 0·7107 Å, μ = 1·73 mm^{-1}.

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Preliminary photographs of the crystals showed a general extinction for $h + k$ odd and a glide extinction on $h0l$ for l odd. These extinctions are consistent with either space group Cc or $C2/c$. These groups are difficult to distinguish between unequivocally, and the centrosymmetric group $C2/c$ was chosen to begin our investigation. If this were not correct, at least one of three things should have indicated a wrong choice: the structure would not refine to a reasonable value of the agreement factor, the final difference map should show unexplained peaks, or some of the temperature factors in the final parameter list should be either very large or very small – or not positive definite. None of these conditions obtains, and their absence indicates the correctness of the space-group assignment.

A prismatic crystal of dimensions 0·84 × 0·63 × 0·37 mm was mounted with the long axis parallel to the goniometer axis. Transmission factors varied from a maximum of 0·53 to a minimum of 0·30, and absorption corrections were made. Intensity measurements were made with Zr-filtered Mo $K\alpha$ radiation on an Enraf–Nonius CAD-4 diffractometer at the University of Oklahoma. Unit-cell parameters were obtained by least-squares refinement of 15 carefully measured θ values. Intensities were collected by the θ–2θ scanning technique and counted with a scintillation counter. 1605 unique reflections were collected within a reciprocal-sphere radius of 0·626. All reflections were included in the final refinement. Less than 4% of the reflections had values less than 3σ, where σ is the e.s.d. of the intensity of a reflection. Three standard reflections were checked at intervals during data collection, and no deterioration of the crystal was observed. The e.s.d.'s for each observation were derived from counting statistics.

The heavy atoms were located from a Patterson synthesis and partially refined; the C and N atoms were then located from a Fourier synthesis using these phases. H atoms were located from a difference Fourier map at a late stage in the refinement. In the final stages of refinement all atoms except the H were refined with anisotropic temperature factors. The function minimized was $\sum w(F_o - F_c)^2$ with $w = 1/\sigma^2$. The weighted agreement factor $r = [\sum w(F_o - F_c)^2/\sum w(F_o)^2]^{1/2}$ was reduced in the final refinement to a value of 0·091; the agreement factor $R = \sum (F_o - F_c)/\sum F_o$ was reduced to a value of 0·074. The standard deviation of an observation of unit weight was 1·0 in the final refinement; in the final difference Fourier map the highest peak was less than 0·1 e Å^{-3}. Final atom parameters are given in Table 1.* Scattering factors for the various atoms were taken from *International Tables for X-ray Crystallography* (1968); corrections for anomalous scattering were included for the Cu and Cl atoms. Computer programs were from the University of Oklahoma crystallographic library, and are all versions of widely used programs. The least-squares program is a version of *ORFLS* (Busing, Martin & Levy, 1962) and the Fourier summation program is a modified version of that originally written by F. R. Ahmed. The absorption corrections were calculated from a version of *TOMPA*, from the library at the University of Washington written by J. R. Stewart.

Results and discussion

In the solid state $Cu(NN)_2Cl_2$ consists of discrete molecules with the configuration shown in Fig. 1; the numbering scheme for the ring atoms is also given. Bond distances and angles are given in Table 2. The distances between Cu and the four principal coordinated atoms are within the normal ranges. The Cu

Table 1. *Final positional parameters* (×10^4) *with e.s.d.'s in parentheses*

	x	y	z
Cu	5000	3162·0 (9)	2500
Cl	4323·0 (8)	1297·0 (13)	3083·3 (7)
N(1)	4763 (3)	4958 (4)	3228 (2)
C(2)	3821 (4)	5754 (5)	2997 (3)
C(3)	3781 (4)	6965 (5)	3587 (4)
C(4)	4767 (4)	7300 (6)	4457 (3)
C(5)	6835 (4)	6645 (6)	5629 (3)
C(6)	7760 (4)	5744 (6)	5808 (3)
C(7)	7631 (4)	4682 (7)	5105 (4)
N(8)	6682 (3)	4426 (4)	4264 (2)
C(9)	5757 (3)	5301 (4)	4091 (3)
C(10)	5775 (3)	6454 (5)	4732 (3)
H(2)	3105 (40)	5438 (54)	2449 (31)
H(3)	3154 (50)	7678 (62)	3453 (40)
H(4)	4773 (47)	8110 (61)	4721 (43)
H(5)	6867 (44)	7347 (62)	6075 (43)
H(6)	8633 (44)	5748 (58)	6527 (36)
H(7)	7991 (37)	4267 (54)	5175 (33)

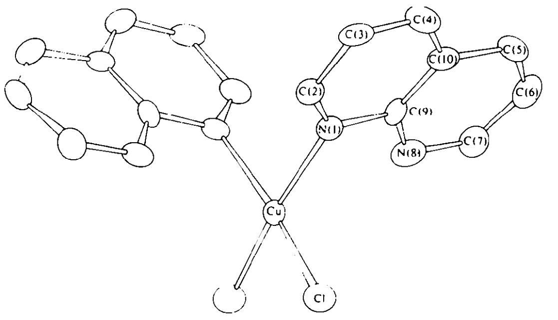

Fig. 1. Perspective view of the molecule of bis(1,8-naphthyridine)-copper(II) chloride.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34628 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected bond distances* (Å) *and angles* (°)

Metal—ligand distances		Metal—ligand angles	
Cu—Cl	2·253 (1)	Cl—Cu—Cl′	94·6 (1)
Cu—N(1)	2·028 (3)	Cl—Cu—N(1)	90·4 (1)
Cu—N(8)	2·764 (3)	N(1)—Cu—N(1′)	87·0 (2)
Ring bond distances		**Ring bond angles**	
C(9)—N(1)	1·369 (5)	C(9)—N(1)—C(2)	118·8 (3)
C(9)—N(8)	1·353 (5)	C(9)—N(8)—C(7)	115·5 (4)
C(2)—N(1)	1·314 (5)	N(1)—C(2)—C(3)	123·3 (4)
C(7)—N(8)	1·310 (6)	N(8)—C(7)—C(6)	126·1 (5)
C(2)—C(3)	1·407 (7)	C(2)—C(3)—C(4)	118·3 (4)
C(7)—C(6)	1·377 (7)	C(7)—C(6)—C(5)	118·5 (4)
C(3)—C(4)	1·369 (7)	C(3)—C(4)—C(10)	119·8 (4)
C(6)—C(5)	1·362 (6)	C(6)—C(5)—C(10)	119·2 (4)
C(4)—C(10)	1·393 (6)	C(4)—C(10)—C(5)	125·0 (4)
C(5)—C(10)	1·419 (6)	N(1)—C(9)—N(8)	114·5 (3)
C(9)—C(10)	1·403 (6)	C(4)—C(10)—C(9)	118·6 (4)
		C(5)—C(10)—C(9)	116·4 (4)
		N(1)—C(9)—C(10)	121·1 (3)
		N(8)—C(9)—C(10)	124·3 (3)

Table 3. *Displacements of atoms from mean planes* (Å)

Mean plane of coordination

Cu	0
N	±0·242 (3)
Cl	±0·202 (2)

Mean plane of 1,8-naphthyridine ring

N(1)	−0·021 (4)	C(6)	−0·029 (5)
C(2)	−0·033 (5)	C(7)	0·007 (6)
C(3)	0·009 (5)	N(8)	0·031 (4)
C(4)	0·028 (5)	C(9)	0·016 (4)
C(5)	−0·022 (5)	C(10)	0·014 (4)

atom lies on a twofold axis which falls in the coordination plane; the coordination is close to square planar as shown by the sum of the coordination angles (362°) and the deviations from the mean plane of the five atoms of 0·24 Å or less. Table 3 gives deviations from the mean planes for the coordination and ring planes, and Table 4 gives equations for these planes. The complex has *cis* geometry, and the units are stacked in columns along the symmetry axis with all units in the same orientation. On the adjacent axes the orientation is reversed. The shortest intermolecular contact between neighboring molecules is 2·87 Å, between a Cl and an adjacent H. All other atom contacts are greater than 3·0 Å. The shortest N—H distance is 3·3 Å between adjacent molecules. There do not appear to be any intermolecular interactions other than van der Waals contacts.

The coordination of NN in this molecule should be described as monodentate. The Cu—N(1)—N(2) angle is 79°; if minimum interaction with the most distant N atom were to occur, one would expect an angle of 90°. The other extreme is to suppose that the N atoms are equally bonded at normal Cu—N distances of about 2·0 Å; this would lead to a value of about 55° for this angle. The N(1)—Cu—N(2) angle is also an indication of the coordination; for the monodentate model the angle should be about 50°, while for the bidentate case with the two N atoms at 2·0 Å from the Cu, it should be about 70°. The calculated angle in this structure is 54°, in agreement with the monodentate model.

Table 4. *Equations of mean planes*

Coordinate system: x parallel to a, y parallel to b, z parallel to c^*.

Equation of coordination plane (calculated from Cu, 2N, 2Cl)

$$0{\cdot}5898x + 0{\cdot}0y + 0{\cdot}8075z = 5{\cdot}5584$$

Equation of 1,8-naphthyridine ring plane (all C and N ring atoms included)

$$0{\cdot}5590x + 0{\cdot}7136y - 0{\cdot}4222z = 3{\cdot}1163$$

These data must be interpreted with caution. The structures cited earlier indicate clearly that NN very seldom coordinates symmetrically. The only cases of symmetrical coordination in the crystal structures which have been evaluated are in dodecahedral structures with four NN molecules, all chelated. In each of these two cases (Singh, Clearfield & Bernal, 1971; Epstein, Dewan, Kepert & White, 1974) one of the four NN molecules is relatively symmetrically bound; the other three are unsymmetrical in varying degrees. In all the other cases studied the coordination of the NN is quite unsymmetric. This compound and the 2,7-dimethyl-1,8-naphthyridine complex (Mealli & Sacconi, 1977) are the only two in which the coordination geometry at the Cu is approximately square planar. There is undoubtedly some interaction between the distant N and the central Cu atoms, but it is not of any steric importance. The complex bis(adenine)copper dibromide, which has been studied by De Meester & Skapski (1973), has been suggested as another example of this case; however, the four nearest ligands to the Cu in that compound are about midway in geometry between square planar and tetrahedral, and the more distant N atoms are not positioned along the tetrad axis.

Clearfield and co-workers have suggested that coordination influences the planarity of the NN ring atoms. In their study of the complex $Fe(NN)_4ClO_4$ (Singh, Clearfield & Bernal, 1971) and of the free ligand (Clearfield, Sims & Singh, 1972) they found the free ligand to be significantly less planar than the coordinated ligands in the complex. Mealli & Sacconi (1977) also found that their substituted NN ring was more nearly planar than that found in the free ligand, but the other workers who have looked at the ring plane have all found deviations from planarity which do not seem to be related to the mode of coordination. Clearfield and co-workers suggested that bidentate coordination of the ring would reduce repulsion between the

N lone pairs and lead to planarity of the ring system. However, all of the other complexes reported since exhibit varying degrees of deviation from planarity and in some cases the deviations are larger than those on the free ligand. No correlation is apparent between mode of coordination and deviation from planarity. The only point of general agreement seems to be that the two ring N atoms always lie on opposite sides of the mean ring plane when there are significant deviations.

The deviations from planarity reported in Table 3 for the title compound are very similar to those reported by Clearfield for the free ligand. The ligand is twisted about its center to put the two N atoms on opposite sides of the mean plane, and also bowed slightly, putting the bridgehead atoms further from the plane than the twist alone would achieve.

The mean plane of the NN ring makes an angle with the coordination plane of 89·3° and the two rings are at an angle of 88·9° with respect to each other. The uncoordinated N(8) atom is on the same side of the coordination plane as the coordination nitrogen, N(1), and is 2·421 Å from the coordination plane. Equations for the two mean planes are given in Table 4.

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