The Crystal Structure of the Bis(2,7-dimethyl-1,8-naphthyridine)dichlorocopper(II) Complex with the *trans* Configuration

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The crystal structure of the bis(2,7-dimethyl-1,8-naphthyridine)dichlorocopper(II) complex, $C_{20}H_{20}N_4CuCl_2$, has been determined by X-ray diffraction. Crystal data are: $a = 10\cdot515$ (2), $b = 11\cdot095$ (3), $c = 8\cdot677$ (2) Å, $\beta = 102\cdot00$ (4)°, $Z = 2$; monoclinic, space group $P2_1/n$; $D_c = 1\cdot51$ g cm^{-3}. The final R is $0\cdot047$. The geometry of the complex is *trans*-square planar with two Cl atoms and two N atoms from two different monodentate ligand molecules coordinated to the Cu. The Cu–Cl bond distance is $2\cdot279$ (3) Å and the Cu–N distance to the bonded N atom is $1\cdot982$ (9) Å. The steric interference of the methyl groups favours the *trans*-square-planar configuration.

Introduction

The potentially bidentate ligand 1,8-naphthyridine (NN) can function under different circumstances either as a monodentate or a bidentate molecule. At least one example of each binding mode is known. The binucleating capacity of NN was first ascertained in this laboratory in the complex [Ni$_2$(NN)$_4$Br$_2$]B(C$_6$H$_5$)$_4$ (Sacconi, Mealli & Gatteschi, 1974) whose formation is attained through a reduction of bivalent Ni to the unusual formal oxidation number $+1\cdot5$. NN behaves as a monodentate ligand in the monomeric complex Cu(NN)$_2$Cl$_2$, with *cis*-square-planar configuration (Enwall & Emerson, 1968; and private communication). Recently we decided to extend our investigation of the ligating power of NN and its 4-methyl (MeNN) and 2,7-dimethyl (Me$_2$NN) derivatives to Cu salts. We have now obtained two novel compounds of formulae Cu$_2$(MeNN)$_2$Cl$_3$ and Cu(Me$_2$NN)$_2$Cl$_2$ respectively. A report on the features of the former compound which confirms the binucleating capacity of naphthyridines and the connexion between this binding mode and the unusual mixed-valence states of the coordinated metals will be published elsewhere (Sacconi, Mealli & Gatteschi, 1976). Here we wish to report the crystallographic details of the latter compound.

Experimental

To a hot solution (60 °C) of 1 mmol of CuCl$_2$.2H$_2$O in 15 ml of ethanol, a solution containing 2 mmol of Me$_2$NN in 15 ml of the same solvent was added. Green-brown crystals were obtained on cooling the reaction mixture, and these were recrystallized from DMF. The precipitate was filtered, washed with ethanol and petroleum spirit and dried in vacuum at 60°C. The purity of the product obtained was confirmed by elemental analysis.

Crystal data

$C_{20}H_{20}N_4CuCl_2$, F.W. 767·26; monoclinic, $P2_1/n$; $a = 10\cdot515$ (2), $b = 11\cdot095$ (3), $c = 8\cdot677$ (2) Å, $\beta = 102\cdot00$ (4)°, $V = 990\cdot17$ (6) Å^3, $Z = 2$; $F(000) = 768$, $D_c = 1\cdot51$, $D_m = 1\cdot52$ g cm^{-3}; λ(Mo $K\alpha$) = $0\cdot7093$ Å, $\mu = 13\cdot9$ cm^{-1}.

A prismatic crystal, having a volume of $0\cdot33 \times 10^{-2}$ mm^3, was chosen for the determination of the lattice constants and space group and was used throughout data collection. All measurements were made with Mo $K\alpha$ radiation, monochromatized with a flat graphite crystal, on a PW 1100 Philips automated diffractometer. The lattice constants were obtained by least-squares refinement of 18 reflexions automatically found and centred by the machine. The crystal chosen had faces of the forms {10$\bar{1}$} and {110}, with distances between parallel faces of the same form of $0\cdot24$ and $0\cdot11$ mm respectively. The θ–2θ scan technique was employed with a scan range of $0\cdot7°$ in θ (corrected for dispersion) at a scan rate of $0\cdot05°$ s^{-1}. The background measurement time at each side of the scan was determined as (scan time)/2. 1072 unique reflexions were measured up to $\theta = 20°$, 601 of which were considered observed, having intensities greater than three times their estimated standard deviations; these were calculated as previously described (Mealli, Midollini & Sacconi, 1975) with a value of $0\cdot03$ for the instability factor. The usual corrections were carried out, including one for absorption. The transmission factors, calculated by the program *AGNOST* written by David Cahen, varied between $0\cdot86$ and $0\cdot97$.

The structure was solved by direct methods with *MULTAN*. All the unique atoms in the asymmetric unit

(the Cu atoms are in special positions $0,0,\frac{1}{2}$ and $\frac{1}{2},\frac{1}{2},0$) could be localized in the initial E map, except for two atoms in the Me_2NN molecule. These were introduced at calculated positions with the program *BMFIT* (Nyburg, 1974) which fits a molecule in a given cell to a fragment of a comparable molecule in the cell of the latter. In the present case we used one refined NN molecule from our previous structural determination (Sacconi, Mealli & Gatteschi, 1974). Subsequent least-squares refinement, with the observed reflexions only, proceeded smoothly. The function minimized was $\Sigma\, w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$; intermediate discrepancy values were $R = 0\cdot105$ and $R_w = 0\cdot107$ with a fully isotropic model $\{R = \Sigma\, ||F_o| - |F_c||/\Sigma F_o$ and $R_w = [\Sigma\, w(|F_o| - |F_c|)^2/\Sigma\, wF_o^2]^{1/2}\}$. The use of a fully anisotropic model lowered R to $0\cdot059$ and R_w to $0\cdot062$. After introduction of H atoms at calculated positions (in particular the positions of the H atoms belonging to the methyl groups were derived with a least-squares procedure which fitted a partially observed model from a ΔF map to an ideal methyl model) and including the effects of anomalous dispersion in the calculation of F_c's, the final R values were $r = 0\cdot047$ and $R_w = 0\cdot049$. Atomic parameters are listed in Table 1.* The reported standard deviations of the atomic

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32192 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

parameters, and particularly those relative to the thermal parameters, appear somewhat higher than usual; this is probably a result of the limited number of reflexions used throughout the refinement. Scattering factors and computer programs are those mentioned elsewhere (Mealli, Midollini & Sacconi, 1975).

Results and discussion

The structure of $Cu(Me_2NN)_2Cl_2$ consists of discrete molecules with the configuration shown in Fig. 1, where the labelling scheme and the main bond distances and angles about the Cu atom are also reported. Fig. 2 summarizes bond distances and angles within the ligand. A packing diagram for the whole complex is shown in Fig. 3. The Cu atom lies on a centre of inversion and is coordinated by two *trans* Cl atoms and two *trans* N atoms of two different Me_2NN molecules; this results in an exactly planar arrangement. The coordination is almost square planar as the angles Cl—Cu—N deviate from 90° by not more than four times their estimated standard deviations. This coordination is not uncommon in Cu^{II} complexes, but frequently the approach of one or two extra donors along the fourfold axis is observed. In the present compound this role can possibly be played by the N(2) atoms of the Me_2NN molecules, which are $2\cdot801$ Å from the Cu and give Cl—Cu—N(2) and N(1)—Cu—N(2) angles of $92\cdot9$ and $53\cdot7°$ respectively; at this distance, mainly imposed by the rigidity

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Table 1. *The final atomic parameters* ($\times 10^4$)

(a) Non-hydrogen atoms. Standard deviations are in parentheses. The anisotropic temperature factor is
$$\exp\,[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)].$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	5000	5000	10000	515 (13)	381 (11)	465 (13)	−5 (11)	110 (10)	−30 (12)
Cl	7027 (3)	4566 (2)	9606 (3)	545 (21)	569 (19)	529 (23)	34 (14)	147 (18)	−10 (15)
N(1)	4230 (8)	4710 (9)	7744 (11)	606 (65)	400 (65)	520 (71)	−40 (49)	43 (52)	−134 (65)
N(2)	4552 (8)	6734 (10)	7593 (11)	470 (64)	544 (67)	533 (78)	25 (54)	127 (56)	−6 (71)
C(1)	3831 (11)	3651 (11)	7148 (16)	459 (82)	593 (96)	445 (105)	14 (65)	151 (76)	−67 (85)
C(2)	3221 (11)	3561 (10)	5529 (18)	538 (89)	551 (83)	591 (111)	7 (65)	32 (82)	−75 (84)
C(3)	3100 (11)	4532 (12)	4564 (13)	606 (89)	687 (91)	307 (80)	15 (72)	8 (66)	−48 (81)
C(4)	3531 (10)	5656 (11)	5204 (15)	419 (81)	502 (90)	362 (99)	−10 (61)	12 (75)	−85 (83)
C(5)	3469 (11)	6745 (13)	4357 (15)	615 (90)	661 (93)	625 (99)	198 (75)	191 (79)	139 (75)
C(6)	3918 (12)	7779 (11)	5124 (20)	713 (91)	563 (96)	644 (113)	50 (71)	131 (85)	251 (87)
C(7)	4445 (11)	7745 (11)	6714 (19)	463 (83)	470 (99)	762 (107)	81 (62)	142 (80)	134 (88)
C(8)	4089 (10)	5709 (11)	6808 (16)	331 (72)	430 (87)	485 (101)	6 (62)	50 (69)	−40 (84)
C(9)	4049 (11)	2564 (10)	8171 (14)	794 (95)	587 (79)	502 (88)	−74 (68)	273 (75)	81 (73)
C(10)	4917 (12)	8879 (10)	7589 (16)	811 (94)	586 (84)	991 (93)	−118 (70)	123 (91)	−38 (81)

(b) Hydrogen atoms. Positional parameters used in the last cycle of least-squares refinement. The isotropic temperature factors used are 10% higher than the corresponding isotropic values of the C atoms to which the H atoms are attached.

	x	y	z		x	y	z
H(1)—C(2)	2879	2771	5112	H(2)—C(9)	3423	1929	7810
H(1)—C(3)	2708	4437	3430	H(3)—C(9)	4901	2216	8234
H(1)—C(5)	3074	6738	3219	H(1)—C(10)	4996	8805	8734
H(1)—C(6)	3861	8540	4550	H(2)—C(10)	5786	9113	7460
H(1)—C(9)	3978	2750	9243	H(3)—C(10)	4362	9562	7270

of the ligand, a certain amount of Cu—N interaction can be thought to be operative. In fact, in the compound tetrakis(1,8-naphthyridine)iron(II) perchlorate (Singh, Clearfield & Bernal, 1971), the Fe atom has been considered octacoordinated in spite of four rather
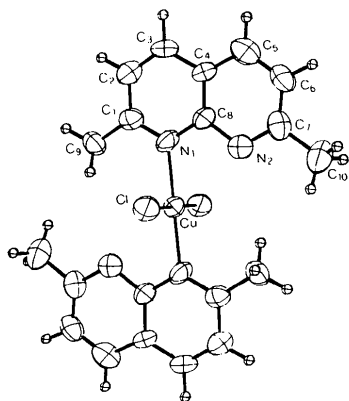

Fig. 1. *ORTEP* drawing of the molecule scaled to include 50% probability. Independent bond distances and bond angles about the Cu atom are: Cu—N(1) 1·982 (9), Cu—Cl 2·279 (3) Å, Cl—Cu—N(1) 91·2 (3)°.
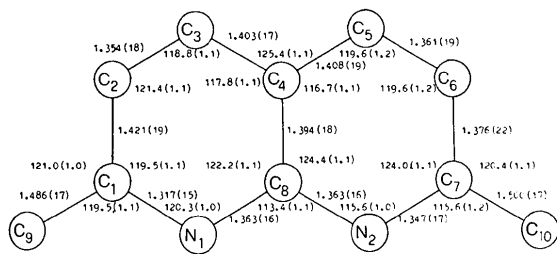
long Fe—N distances, one of which is 2·756 (11) Å. Also, in the compound hydridotris(3,5-dimethyl-1-pyrazolyl)boratocopper(I) (Mealli, Arcus, Wilkinson, Marks & Ibers, 1976) a residual Cu—N bridge bonding seems to take place at a distance of 2·777 (4) Å.

The Cu—Cl [2·279 (3)] and Cu—N [1·982 (9) Å] bond distances within the planar array are normal. The Cu—N distances in the square-planar complexes with *cis* configuration Cu(1,8-naphthyridine)$_2$Cl$_2$ (Enwall & Emerson, 1968; and private communication) and [Cu(adenine)$_2$Br$_2$]$^{2+}$ (De Meester & Skapski, 1973) (both ligand molecules contain the non-linear triatomic group N—C—N functioning as a monodentate) are somewhat longer [2·032 (2) and 2·013 (5) Å respectively]. In these compounds the halide atoms may be responsible for a *trans* effect, lessening the strength of the Cu—N interaction.

The formation of a *trans* isomer in the present case, in contrast to the *cis* configuration of the two previous compounds, can be rationalized in terms of the intramolecular steric hindrance exerted by the two methyl groups in positions 2 and 7. A least-squares fitting of the Me$_2$NN molecule to the NN molecule as oriented within the *cis* isomer results in unreasonably short con-

Fig. 2. Summary of bond distances (Å) and angles (°) in the Me$_2$NN molecule.

Table 2. *Displacements* (Å) *of the* 2,7-*dimethyl*-1,8-*naphthyridine atoms from the mean plane*

N(1)	0·009	C(3)	0·001	C(7)	—0·008
N(2)	—0·007	C(4)	—0·003	C(8)	—0·005
C(1)	0·018	C(5)	0·015	C(9)*	0·095
C(2)	—0·022	C(6)	0·003	C(10)*	—0·053

* Atoms not included in the calculation.
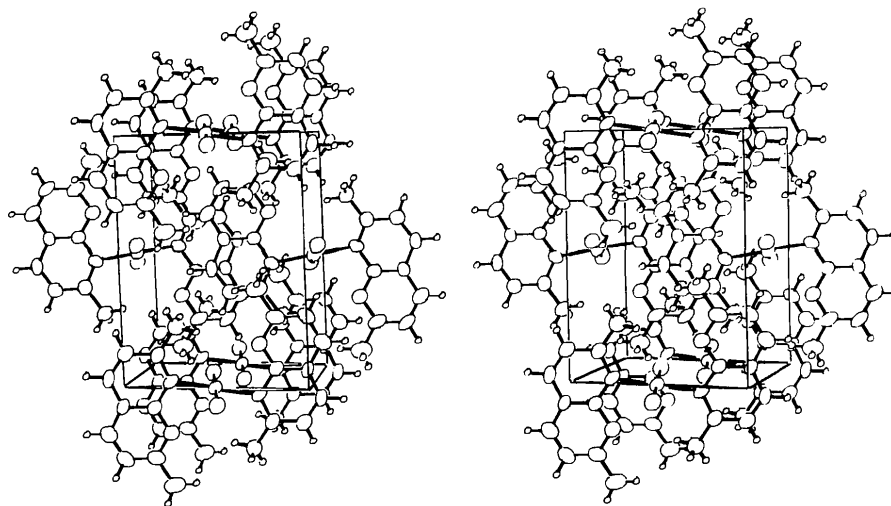

Fig. 3. View of the whole cell in Cu(Me$_2$NN)$_2$Cl$_2$ showing the packing in the crystal.

tact distances involving the C atoms of the methyl groups.

In Table 2 the displacements of the ligand atoms from the least-squares plane calculated considering only the aromatic part of the molecule are reported. Here the system approaches planarity to a degree (highest displacement 0·022 Å) which was only found in the naphthyridine molecules of the octacoordinated complex $[Fe(NN)_4](ClO_4)_2$ (Singh, Clearfield & Bernal, 1971); in all the other 1,8-naphthyridine complexes whose structures have been reported, and even in the free molecule (Clearfield, Sims & Singh, 1972), the displacements are very much higher. Finally it is worth noting that the plane containing the ligand molecule is almost orthogonal to the coordination plane defined by the Cu, Cl and N atoms, the dihedral angle being 87·4°.

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Electron-Density Distributions in Crystals of γ-Fe₂SiO₄ and γ-Co₂SiO₄

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Electron-density distributions in crystals of γ-Fe₂SiO₄ and γ-Co₂SiO₄ have been experimentally determined from single-crystal X-ray diffraction data. Evidence for trigonally deformed distributions of 3d electrons around the transition-metal atoms in the compounds was observed on the final difference Fourier maps. The residual electron-density distribution for γ-Fe₂SiO₄ is significantly different from that for γ-Ni₂SiO₄, in conformity with the difference in the number of 3d electrons. The difference Fourier map of γ-Co₂SiO₄ has an intermediate feature between those of γ-Ni₂SiO₄ and γ-Fe₂SiO₄. Residual electron densities were also observed on the Si—O bonds.

Introduction

Evidence for the aspherical distribution of 3d electrons around the transition-metal atoms in crystals of $[Co(NH_3)_6][Co(CN)_6]$ (Iwata & Saito, 1973) and γ-Ni₂SiO₄ (Marumo, Isobe, Saito, Yagi & Akimoto, 1974) has been obtained by single-crystal X-ray diffraction. The transition-metal atoms are octahedrally coordinated. The two independent Co^{III} atoms in the former crystal are in the low-spin state, and the six 3d electrons occupy the t_{2g} orbitals in the ground state. The distribution of the 3d electrons in the t_{2g} or-

bitals has maxima on the eight threefold rotation axes of the coordination octahedron. Residual densities indicating such an aspherical distribution were clearly observed on the difference Fourier maps of $[Co(NH_3)_6]$-$[Co(CN)_6]$. In the case of γ-NiSiO₄, the Ni^{2+} cation has eight 3d electrons, six of which are in the t_{2g} orbitals, and two in the e_g orbitals in the ground state. Since the sum of the electron-density distributions of three 3d electrons in the t_{2g} and two in the e_g orbitals should be approximately spherical, the electron-density distribution around the Ni^{2+} cation is expected to show an asphericity similar to those observed in $[Co(NH_3)_6]$-