Copper(II) Complexes of 3,3′-Annelated 2,2′-Bi[1,8]naphthyridine

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Abstract

Four mononuclear Cu(II) complexes prepared from ligands (L) = 2,2′-bi[1,8]naphthyridine as well as its 3,3′-dimethylene-, 3,3′-trimethylene- and 3,3′-tetramethylene-bridged derivatives were studied by ESR spectroscopy and a single crystal X-ray diffraction analysis was carried out on the dimethylene-bridged compound of composition $Cu(L)Cl_2(H_2O)$. Crystals are monoclinic, space group $P2_1/n$, with a = 8.934(3), b = 11.427(4), c = 17.382(5) Å and β = 103.65(3)°; V = 1724.5 Å^3 and D (cal; z = 4) = 1.68 gm cm^{-3}. Final R and R_w factors were 0.0523 and 0.0497, respectively, for 2260 reflections having $I > 3\sigma(I)$. The central Cu(II) ion is five-coordinate as a result of its being bound by the two central nitrogens of the heterocyclic ligand, two chlorides and one water in a distorted trigonal bipyramidal arrangement, the nature of whose distortion is principally due to the small bite (77.1°) of the bidentate ligand. Stereochemical features of similar, five-coordinated trigonal bipyramidal Cu(II) compounds are presented, which combined with our results, reveal that for such d^9 complexes, the more electronegative substituent prefers the axial position of the trigonal bipyramid. Theoretical predictions made elsewhere are compared against the experimental results described above.

Introduction

The 1,8-naphthyridine molecule has received wide attention because of its ability to function as an effective ligand. When acting in a bidentate fashion, it utilizes an exceptionally small 'bite' due to the 1,3-orientation of its two nitrogen atoms. The resulting bis-coordinated metallocycle would therefore involve the formation of a strained four-membered ring. Thus, it has been demonstrated that 1,8-naphthyridine often coordinates in a monodentate fashion [1, 2]. Enwall and Emerson have examined the structure of bis[1,8-naphthyridine] copper(II) chloride and found it to fall into this monodentate category [3]. Fig. 1 illustrates the approximate geometry of this complex about which several important features should be noted. The coordination is close to square planar as shown by the sum of the coordination angles (362°). The complex has *cis* geometry without any intermolecular interactions between the two aromatic rings other than van der Waals contacts. The complex appears favorably disposed toward a covalent bond connecting the 2 and 2′ positions which should not seriously distort the coordination geometry.

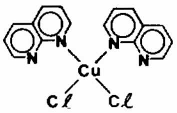
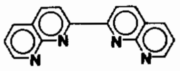


Fig. 1. Approximate geometry of bis[1,8-naphthyridine] copper(II) chloride.

We have been interested in polyaza biaryl type systems in which nitrogens are situated inside a molecular cavity potentially capable of polynuclear metal coordination. These systems would represent extensions of the well-studied 2,2′-bipyridine and 2,2′-biquinoline systems. When more than two nitrogen atoms are present in the coordinating cavity, the possibility exists for different sites of bidentate complexation. This paper will deal with 2,2′-bi[1,8]naphthyridine (**1**) as a multidentate ligand, and reports the first metal complex of this ligand as well as related complexes with its 3,3′-annelated derivatives (**2**–**4**).



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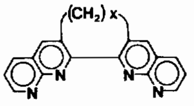
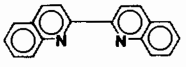


2 x = 2
3 x = 3
4 x = 4



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The ligand 2,2′-biquinoline (**5**) is a well known diaza analog of **1**. It has been shown to form square planar 1:1 complexes with copper(II) chloride [4].

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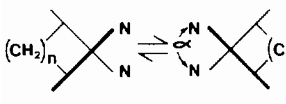
On the other hand, bis-chelated copper(II) complexes of **5** cannot adopt this square planar arrangement and are found instead to be pseudotetrahedral [5]. When **1** or **5** is bridged by two or more methylene units at the 3 and 3′ positions, the lowest energy conformation of the molecule results when the two aromatic rings lie in different planes. The dihedral angle (α) between these planes increases as the 3,3′-bridge becomes longer (Fig. 2). A careful analysis of the 400 MHz NMR spectra of **1–4** revealed that **2** and **3** are inverting (A $\rightleftharpoons$ B) rapidly at room temperature while **4** is conformationally rigid allowing for possible resolution of the conformational enantiomers.

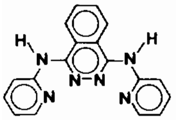


n	α
1	0°
2	20
3	50
4	65

Fig. 2. The angle α between the two ring moieties and the interconversion between the conformational enantiomers.

Rehorek and Thomas have prepared and studied the spectral properties of two complexes of 3,3′-dimethylene derivatives of **5** with copper(II) chloride. Their findings are consistent with distorted tetrahedral structures for these compounds [6].

The systems studied in this paper complement several other tetra-aza ligands (**6–8**) whose copper(II) complexes have been recently investigated [7–9]. In these systems the N_1 and N_2 (or N_3 and N_4) positions bear a 1,4- or 1,5-relationship while N_2 and N_3 bear a 1,2- or 1,3-relationship. These ligands have two 'hinges' while **1–4** and **5** have only one 'hinge'. Not surprisingly, all three ligands **6–8** readily form binuclear copper(II) complexes. We expected that the lower degree of conformational mobility available to our systems would impose constraints which could result in unusual coordination properties.



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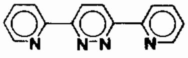

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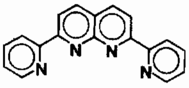

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Experimental

General Procedure for Preparation of Copper Complexes

0.30 mmol of ligand [10] were dissolved in 10 ml of methanol and heated to 50 °C. Ten equivalents (3.0 mmol) of $CuCl_2$ dihydrate in 10 ml of water were added slowly to the hot methanolic solution until a ppt appeared. The solution was cooled and the ppt was collected. Ligand **1** provided a quantitative yield of dark green crystals; ligand **2** provided a 66% yield of light green crystals; ligands **3** and **4** both provided a quantitative yield of black crystals. The complexes were purified by recrystallization from water.

ESR spectra were obtained on a Varian Associates E-4 GHz x-band spectrometer at 77 K on neat powder samples and their traces are shown in Fig. 3. *Anal.* Ligand **1**: $CuCl_2$(**1**) Calcd: C, 48.03 N, 14.01; H, 2.52. Found: C, 48.92; N, 14.27; H, 2.55. Ligand **2**: $CuCl_2(H_2O)$(**2**) Calcd: C, 49.49; N, 12.83; H, 3.23. Found: C, 51.61; N, 13.38; H, 2.87. Ligand **4**: $CuCl_2$(**4**) Calcd: C, 52.89; N, 12.34; H, 3.55. Found: C, 52.77; N, 12.95; H, 3.24.

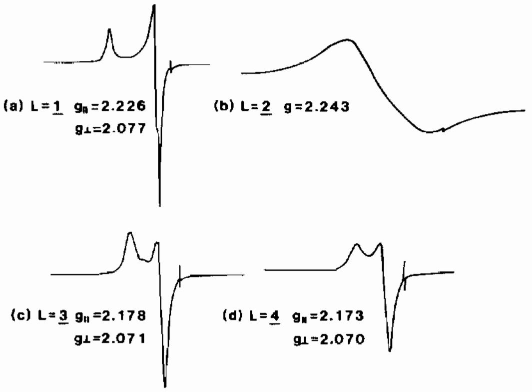


Fig. 3. ESR spectra of the four complexes $Cu(L)Cl_2(H_2O)_x$.

X-Ray Data Collection and Structure Solution and Refinement for Compound II: *$Cu(L)Cl_2(H_2O)$, L = 2*

The crystal used for all X-ray measurements was a small, irregular fragment, having a maximum dimension of *ca.* 0.3 mm. It was highly dichroic, its color varying from dark green to purple. An Enraf-Nonius CAD-4 automated diffractometer was used with Mo-Kα radiation monochromatized by a dense graphite crystal assumed to be ideally imperfect. Final cell constants, as well as other information concerning data collection and refinement are given in Table I. From the systematic absences noted, the space group was shown to be $P2_1/n$. Intensities were measured using the ω–2θ technique, with the scan rate depending on the net count obtained in rapid pre-scans of each reflection. Three standard reflections were monitored every 2 h and they showed no significant variations from the values of the initial measurements. In reducing the data, Lorentz and polarization factors were applied but no absorption correction was made (μ = 15.13 cm^{-1}).

The structure was solved by interpretation of the Patterson map, which gave the coordinates of the Cu atom. The remaining atoms were found in sub-

TABLE I. Summary of Data Collection and Processing Parameters for **II**.

Space group	$P2_1/n$
Cell constants	a = 8.934(3) Å
	b = 11.427(4) Å
	c = 17.382(5) Å
	β = 103.65(3)°
Cell volume	1724.5 $Å^3$
Molecular formula	$CuCl_2ON_4C_{18}H_{14}$
Molecular weight	436.78 g
Density (calc.; z = 4)	1.68 g/cm^3
Radiation	MoKα (λ = 0.71069 Å)
Absorption	15.13 cm^{-1}
Data collection range	$4° \leq 2\theta \leq 55°$
Scan width	$\Delta\theta = (1.00 + 0.35 \tan\theta)°$
Maximum scan time	180s
Scan speed range	0.5 to 4.02 deg/min
Total data collected	4550
Data with $I > 3\sigma(I)$	2260
Total variables	234
$R = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$	0.0523
$R_w = [\Sigma w^2(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w^2\lvert F_o\rvert^2]^{1/2}$	0.0497
Weights	$[\sigma(F_o)]^{-2}$
Goodness of fit	2.66

sequent difference syntheses and refined isotropically. At this stage, it was noted that several residual peaks appeared in the region of the C4–C5 bridge which suggested these two atoms were disordered over their two possible conformations. The two bridge images were allowed to refine with separate occupancy factors while restraining the thermal parameters of the two images to be the same for related atoms. The occupancy factor for the C4–C5 bridge refined to 67%. All hydrogen atoms appeared in difference maps; however, they could not be refined. Consequently, they were placed at idealized positions, except for the hydrogen atoms of the coordinated water which were refined. Upon convergence (shift/e.s.d. ratios less than 0.1, except for the parameters for C5 and C5′ whose ratios were less than 0.4) the values of the crystallographic parameters were those listed in Table II. The atomic scattering factors used were those of Cromer and Mann [11] except for the hydrogen atoms [12]. All calculations were carried out with SHELX-76 [13]. Bond lengths and angles, least-squares planes and torsional angles are presented on Tables III–VI and were calculated from the parameters listed on Table II.

TABLE II. Atomic Coordinates and Thermal Parameters (×1000; Cu × 10 000).

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	0.15371(11)	0.25692(9)	0.34605(6)	320(5)	223(5)	240(5)	22(5)	64(4)	−6(6)
Cl1	0.2058(3)	0.4443(2)	0.3133(1)	61(2)	23(1)	44(1)	−2(1)	21(4)	5(1)
Cl2	0.0114(3)	0.0887(2)	0.3244(1)	34(1)	30(1)	54(2)	−5(1)	7(1)	−12(1)
O	0.2700(7)	0.1968(5)	0.2677(3)	56(4)	36(4)	28(4)	7(3)	13(3)	−7(3)
N1	0.0629(7)	0.3039(5)	0.4365(3)	40(4)	15(4)	19(4)	−1(3)	4(3)	0(3)
N2	0.3426(8)	0.2142(5)	0.4524(4)	45(5)	18(4)	27(4)	−4(3)	4(4)	2(3)
C1	0.1388(9)	0.2790(6)	0.5096(5)	40(5)	15(5)	24(4)	−9(4)	4(4)	−3(3)
C2	0.2992(9)	0.2252(6)	0.5183(5)	35(5)	17(5)	31(5)	−9(4)	5(4)	0(4)
C3	0.3817(11)	0.1905(8)	0.5928(5)	52(7)	38(6)	25(5)	4(5)	−3(5)	−2(4)
C6	0.0868(10)	0.3018(7)	0.5788(5)	53(6)	29(5)	25(5)	−8(4)	11(4)	−4(4)
C7	−0.0545(10)	0.3558(8)	0.5688(5)	50(6)	33(5)	30(5)	−1(5)	18(5)	−6(4)
C8	−0.1393(10)	0.3818(7)	0.4923(5)	40(5)	21(5)	40(6)	−8(4)	17(4)	−5(4)
C9	−0.0829(9)	0.3539(7)	0.4262(5)	37(5)	15(4)	25(5)	−2(4)	12(4)	−2(4)
N10	−0.1593(8)	0.3705(6)	0.3500(4)	34(4)	26(4)	32(4)	8(3)	7(3)	0(3)
C11	−0.2974(10)	0.4170(7)	0.3385(5)	46(6)	27(5)	37(5)	8(4)	9(5)	0(4)
C12	−0.3644(10)	0.4512(8)	0.3990(6)	33(6)	33(5)	54(6)	6(4)	7(5)	1(5)
C13	−0.2910(10)	0.4361(8)	0.4746(6)	41(6)	36(6)	57(7)	0(5)	30(5)	−9(5)
C14	0.5253(11)	0.1478(8)	0.5984(6)	56(7)	37(6)	35(6)	6(5)	−12(5)	6(5)
C15	0.5802(10)	0.1370(7)	0.5307(6)	32(5)	22(5)	45(6)	−2(4)	−3(5)	3(4)
C16	0.4897(9)	0.1691(7)	0.4578(5)	30(5)	14(4)	41(6)	−2(4)	4(4)	3(4)
N17	0.5299(8)	0.1597(6)	0.3884(4)	34(4)	28(4)	44(5)	10(4)	7(4)	10(4)
C18	0.6685(11)	0.1175(8)	0.3895(6)	38(6)	34(6)	70(8)	3(5)	11(6)	12(5)
C19	0.7684(11)	0.0830(8)	0.4598(7)	32(6)	31(6)	89(9)	4(5)	13(6)	7(6)
C20	0.7298(11)	0.0913(8)	0.5316(6)	42(6)	28(5)	71(8)	−1(5)	−2(6)	8(5)
C5	0.1894(21)	0.2810(15)	0.6609(11)	43(5)					
C4	0.2927(17)	0.1809(13)	0.6615(9)	43(4)					
C5′	0.1651(43)	0.2387(30)	0.6560(22)	48(10)					
C4′	0.3514(35)	0.2337(28)	0.6664(17)	49(8)					

(continued overleaf)

TABLE II *(continued)*

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
HA	0.3586	0.1845	0.3090	80					
HB	0.2509	0.1756	0.2377	80					
H7	−0.0967	0.3769	0.6153	80					
H11	−0.3561	0.4301	0.2828	80					
H12	−0.4691	0.4864	0.3857	80					
H13	−0.3390	0.4610	0.5184	80					
H14	0.5908	0.1244	0.6515	80					
H18	0.7023	0.1115	0.3381	80					
H19	0.8707	0.0506	0.4581	80					
H20	0.8024	0.0668	0.5818	80					
H5	0.1175	0.2637	0.7013	80					
H5B	0.2578	0.3573	0.6783	80					
H4	0.3742	0.1801	0.7194	80					
H4B	0.2256	0.1014	0.6555	80					
H5′	0.1405	0.2850	0.7121	80					
H5′B	0.1193	0.1484	0.6635	80					
H4′	0.4092	0.1728	0.7160	80					
H4′B	0.4027	0.3188	0.6825	80					

TABLE III. Intramolecular Bond Distances (Å) for **II**.

Cu–O	2.019(6)	Cu–N1	2.005(7)
Cu–Cl1	2.291(2)	Cu–Cl2	2.287(2)
Cu–N2	2.243(7)	C1–C2	1.535(11)
N1–C1	1.322(9)	N2–C2	1.299(12)
N1–C9	1.396(10)	N2–C16	1.394(11)
C9–C8	1.396(13)	C16–C15	1.383(12)
C8–C7	1.398(11)	C15–C14	1.383(15)
C7–C6	1.379(13)	C14–C3	1.355(14)
C6–C1	1.412(13)	C3–C2	1.388(11)
C9–N10	1.352(10)	C16–N17	1.342(13)
N10–C11	1.314(11)	N17–C19	1.325(12)
C11–C12	1.385(14)	C19–C18	1.390(14)
C12–C13	1.334(13)	C19–C20	1.373(17)
C13–C8	1.456(12)	C15–C20	1.432(13)
C6–C5	1.521(19)	C3–C4	1.588(20)
C6–C5′	1.538(36)	C3–C4′	1.456(34)
C5–C4	1.468(23)	C5′–C4′	1.632(50)
O–HA	0.9(1)	O–HB	0.6(1)
HA•••N17	1.825(6)		
all C(sp3)–H	1.08		
all C(sp2)–H	1.00		

TABLE IV. Intramolecular Bond Angles (°) for **II**.

O–Cu–Cl1	89.0(2)	N1–Cu–Cl1	95.1(2)
O–Cu–Cl2	87.6(2)	N1–Cu–Cl2	92.4(2)
O–Cu–N2	94.3(2)	N1–Cu–N2	77.1(3)
Cl1–Cu–Cl2	151.9(1)	N1–Cu–O	171.2(2)
Cl1–Cu–N2	104.5(2)	Cl2–Cu–N2	103.5(2)
C1–C6–C5	121.5(10)	C2–C3–C4	118.1(9)
C1–C6–C5′	118.9(17)	C2–C3–C4′	123.7(14)
C6–C5–C4	111.6(14)	C3–C4–C5	111.5(12)
C6–C5′–C4′	110.8(27)	C3–C4′–C5′	108.1(21)

TABLE V. Least Squares Planes, out of Plane Distances (Å) and Dihedral Angles for **II**.

1-Plane N2, Cl1, Cl2
$0.728x - 0.347y - 0.591z + 0.485 = 0$
Cu: −0.021(1)   0: 1.990(6)   N1: −1.970(7)

2-Plane N1, N2, O
$0.391x + 0.919y - 0.044z - 2.384 = 0$
Cu: 0.038(1)   Cl1: 2.265(2)   Cl2: −2.175(2)

3-Plane N2, C2, C3, C14, C15, C16
$-0.3637x - 0.9219y - 0.1336z + 3.726 = 0$
Cu: 0.255(1)   C4: 0.36(1)   C4′: −0.39(3)

4-Plane N1, C1, C6, C7, C8, C9
$-0.4293x - 0.9010y - 0.0632z + 3.048 = 0$
Cu: 0.054(1)   C5: −0.10(1)   C5′: 0.45(4)

5-Plane C15, C16, N17, C18, C19, C20
$-0.3634x - 0.9239y - 0.1198z + 3.615 = 0$

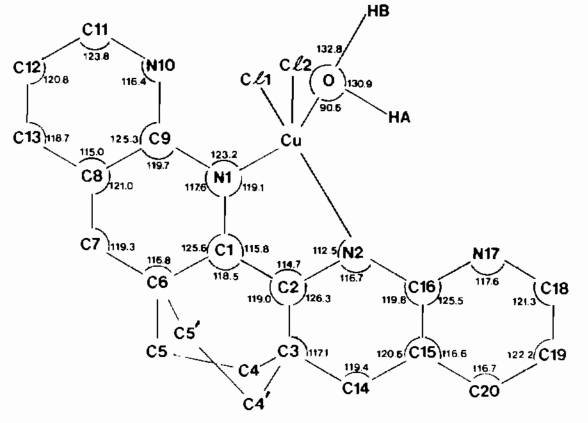
6-Plane C8, C9, N10, C11, C12, C13
$0.3869x - 0.9219y - 0.218z + 2.952 = 0$

Angles between planes

Plane 1	Plane 2	Angle
1	2	90.5°
3	4	5.6°
3	5	0.8°
4	6	3.6°

TABLE VI. Selected Torsion Angles for **II**.

N1–C1–C2–N2	1.95°	C2–C1–C6–C5	3.6°
C3–C2–C1–C6	5.3°	C2–C1–C6–C5′	−19.2°
C1–C2–C3–C4	14.3°	C3–C4–C5–C6	50.6°
C1–C2–C3–C4′	−19.1°	C3–C4′–C5′–C6	−46.6°



II

Results and Description of the Crystal Structure of II

The formulation $Cu(L)Cl_2(H_2O)_x$ can be proposed for the complexes obtained with ligands L = **1**, **2** and **4** on the base of the C, N, H elemental analysis results.

A stereoscopic view of the molecule for compound **II** is shown in Fig. 4. The copper atom lies in a five-coordinate arrangement which has been described [14] as 'triangular bipyramidal' rather than 'trigonal bipyramidal' because of the large Cl–Cu–Cl angle (151.9°) in the equatorial plane. The two chlorines and one nitrogen (N2) of the chelate occupy the equatorial positions, the oxygen of the water and the second chelate nitrogen (N1) the axial positions. The equatorial bond is longer than the axial one by a significant amount (2.24 Å for the equatorial Cu–N bond, 2.00 Å for the axial one). The Cu atom lies only 0.02 Å from the equatorial plane defined by N2, Cl1, and Cl2, and 0.04 Å from the axial plane defined by O, N1, and N2, which is not a large deviation from the ideal geometry. The water molecule forms an intramolecular hydrogen bond with a nitrogen (N17) of the chelate.

The chelate conformation is as follows: each of the naphthyridines retains its planarity but the two are not coplanar. The C4–C5 bridge shows a disorder, being in one position 67% of the time—the one shown in darker outline in Fig. 4, and labelled with unprimed numbers.

ESR Spectra

It is regrettable that, at this juncture, the spectra are useful merely in verifying that these are paramagnetic Cu(II) compounds and that, as solid powders, they give recordable resonance absorptions at reasonable values of g. However, lack of either Cu(II) hyperfine splittings or of N-ligand hyperfine components precludes any attempt to quantify differences in bonding between the metal and the various heterocyclic ligands. In solution, at room temperature, these spectra are broad as a result either of ligand dissociation, ligand torsional motions or both. The outcome is that the spectra thus far recorded in fluid media are no more informative than those shown in Fig. 3. Hopefully, we may be able to remedy this in the future when somewhat sturdier complexes are studied by this method. It is clear, however, from the spectra shown (Fig. 3) that the degree of dipole–dipole interaction and the degree of asymmetry of the ligand field varies widely. For example (a), (c) and (d) show clear differences between axial and equatorial interactions; nearly resolved xx, yy, and zz components in (a), and almost clean separation of the g-tensor components in (c). Finally, either no major differences exist between these tensor components in (b) (complex **II**) or, more likely, there is a large degree of spin–spin interaction between adjacent complexes in the solid. Detailed information on the geometry of complex **II** is given by the X-ray analysis.

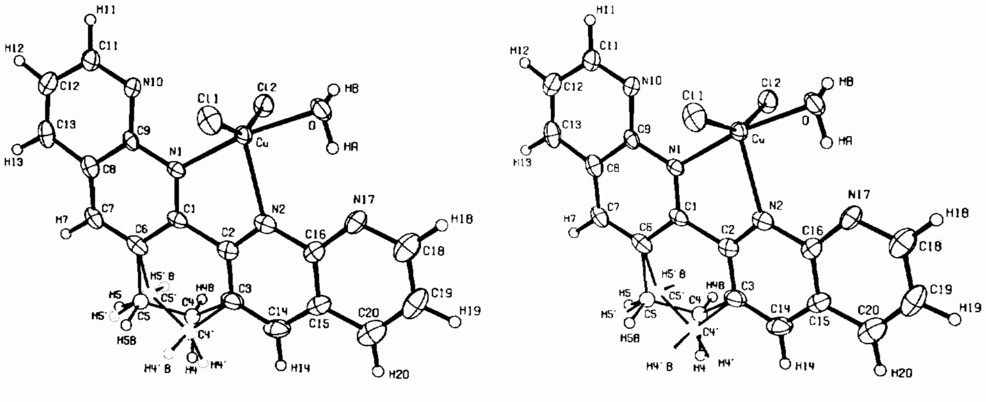


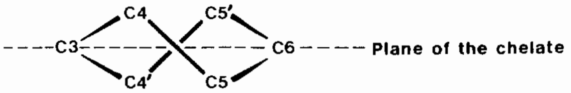
Fig. 4. Stereoscopic view of the molecule of II showing the atom labelling scheme.

Discussion

Stereochemical Features of Compound II *and of Similar Trigonal Bipyramidal Complexes*

The distortion of the complex from the idealized trigonal bipyramidal geometry (the angle N2–Cu–Cl is 104°, instead of 120°) is mainly due to the small bite of the chelate, the N1–Cu–N2 angle being 77.1°. The N1–C1–C2–N2 torsional angle is only 2°, showing that this part of the chelate is forced into planarity by the Cu–N bonds, whereas the free ligand should show a larger torsional angle in order to minimize the repulsion between nitrogen lone pairs [15]. On the other side of the C1–C2 bond, the torsional angle at C6–C1–C2–C3 is 6°, the strain being caused by the two remaining sp^3 hybridized carbons of the ring.

An NMR spectrum [16] of the ligand in solution shows that it exists in two symmetrical conformations exchanging rapidly from one to the other, having a 50–50 population at room temperature.



In the solid state, the two conformations are still symmetrical with respect to the plane defined by the two naphthyridine rings, but the occupancy factors found in the structural study (21 °C) are 67–33%. This change can readily be explained by reference to the packing diagram (Fig. 5) and by calculation of the distances between the hydrogen atoms of the ethylenic (CH_2–CH_2) bridge and atoms of the surrounding molecules which show that there is a short H4'B–Cl distance of 2.65 Å, which is less than the sum of van der Waals' radii (2.9 Å). Furthermore, the anisotropic thermal motion of the chlorine is such that it is capable of an even closer (*ca.* 2.60 Å) approach to the hydrogen. There is no such interaction for the hydrogens of the preferred C4–C5 position, which provides a rationale for the difference in occupancies we observed in the solid.

The only monomeric trigonal bipyramidal Cu(II) complex containing an H_2O ligand, Cu–Cl, and Cu–N bonds reported previously is dichloro–aquo(2,9-dimethyl-1,10-phenanthroline)Cu(II) [14]. It shows the same coordination features at the copper center as does **II** and was reported to have a Cu–O distance of 1.975 Å. If one includes in the tally five complexes related to the two above but having no Cu–Cl bonds, the range of values reported for the Cu–OH_2 bonds is [14, 17–19] 1.975–2.238 Å, which bracket the value of 2.019 Å observed here for **II**. To our knowledge, only 14 structures of monomeric trigonal bipyramidal Cu(II) complexes containing Cu–Cl and Cu–N bonds have been reported in the literature [14, 18–30], with the following ranges for the Cu–Cl and Cu–N bonds:

2.29 [26]–2.41 [27]	Å for the Cu–Cl bonds
1.96 [30]–2.14 [22]	Å for the axial Cu–N bonds
2.00 [27]–2.24 [14]	Å for the equatorial Cu–N bonds.

Cu–N and Cu–Cl bond lengths in **II** fall well within those ranges.

All of the above-cited [14, 17–30] complexes share with **II** the following features:

(1) the axial Cu–N bond is always shorter than the equatorial one,

(2) Cl ligands are always found in equatorial positions.

The first fact has been theoretical justified [31] for a d^9 complex: the d_{z^2} orbital, directed at the axial ligands, contains only one electron; thus, the repulsion between the metal and the axial ligands

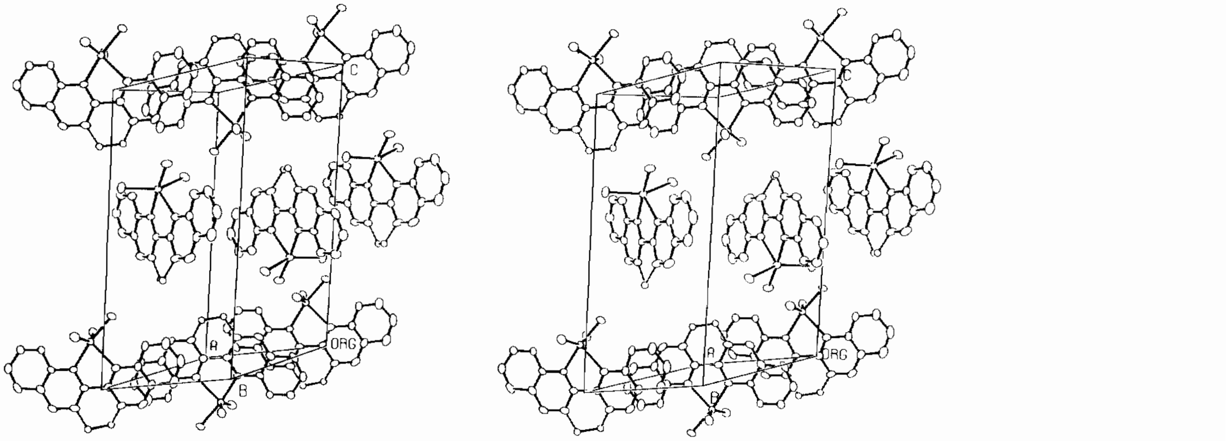


Fig. 5. Stereoscopic view of the molecular packing in the crystal lattice of II, with hydrogens and the disordered bridge omitted for clarity.

is less than for the equatorial ones, in which region the metal orbitals are full. Using extended Hückel calculations, Hoffman and Rossi [32] predicted that, in a d^8 complex, the axial bond would be shorter than the equatorial one, the situation being reversed for a d^{10} complex. Those with a d^9 configuration are at a crossover point and no clear prediction could be made. From experimental evidence, it appears that these Cu complexes are closer to the predictions for the d^8 case.

In the same paper, Hoffman and Rossi [32] studied the preference for axial/equatorial positions as a function of σ- *vs.* π-donor/acceptor properties of the ligands. The σ substituent effects, alone, would favor the more electronegative atoms at equatorial positions in the d^8 case and in axial positions for a d^{10} complex. Using the Mulliken–Jaffe electronegativity tables [33], one obtains the following order of electronegativities:

O(in H_2O) > N(sp^2 hybrid) > Cl

Thus, for a case such as **II** and for dichloroaquo(2,9-dimethyl-1,10-phenanthroline)Cu(II) [14], which are the only two complexes containing H_2O, Cl and N bonds, the more electronegative substituents are located at the axial positions and behave more closely to the predictions for the d^{10} case. The same, by the way, is true of all the complexes previously cited [14, 17–30]. On the other hand, it could be argued that these positional preferences are due only to steric effects, which is indeed the case [26] for $[Cu(bipy)_2Cl]^+$ where the small bite of the bipyridine ligand requires one of the nitrogens to occupy the axial position, so the two bipy ligands allow no choice to the Cl but to occupy an equatorial site. However, this situation does not occur in all other complexes, some of them containing monodentate N ligands [20–22] and, thus, other patterns of coordination are possible. In any case, the argument does not hold for water competing with chloride, thereby voiding all the above arguments. Another electronic effect which must be taken into consideration is the π-donor/acceptor character of the ligands. Here, we have very weak π-acceptor ligands (bipyridine and related systems) and weak π-donors (Cl^- and H_2O); therefore, it is difficult to reach conclusions based on Hoffmann's results [32] as to which is the preferred position, but it seems reasonable to consider the σ-electronic effects to be responsible for the experimentally observed preference. The complexes discussed here belong to a very narrow class of compounds (*i.e.*, monomeric Cu(II) trigonal bipyramidal complexes containing N ligands and terminal Cl) and, consequently, it is desirable to inspect complexes containing other ligands before justified conclusions can be reached. This is particularly true of the suggestion that in the case of d^9 complexes, the most electronegative ligand should occupy the axial site.

In summary, the picture of Hoffmann and Rossi [32], while suitable for the d^8 and d^{10} systems, is, as they recognized, unreliable for d^9 compounds. Systematic experimental evidence is also insufficient in range, at the moment, to permit clear-cut decisions concerning site preferences.

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