

The Crystal and Molecular Structure of Bis(O-tricyanoethyleneoate)-bis(2,2',N,N'-bispyridylamine)copper(II)

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The crystal and molecular structure of bis(O-tricyanoethyleneoate)bis(2,2',N,N'-bispyridylamine)copper(II), (triclinic, $P\bar{1}$, $a = 10.075(2)$, $b = 10.911(2)$, $c = 7.841(2)$ Å, $\alpha = 107.98(2)$, $\beta = 104.78(2)$, $\gamma = 108.40(2)^\circ$, $V = 716.19$ Å³, $Z = 1$, MoK_α radiation), has been determined by three dimensional x-ray analysis. The structure was solved by conventional Patterson and Fourier techniques, and refined by a full matrix least-squares procedure to a final conventional residual index, $R = (\sum \|F_o| - |F_c||) / \sum |F_o|$, of 7.2% for 1984 unique observed reflections ($F_o > 3\sigma F_o$). The copper atom is hexacoordinate ($\sim D_{4h}$ symmetry) with the four equatorial sites occupied by pyridyl nitrogens, and the two axial positions each occupied by an oxygen atom of a tricyanoethylene moiety. The molecule itself has a center of inversion.

Introduction

We have recently embarked on a program of preparation and structural study of products obtained from reaction mixtures containing tetracyanoethylene (TCNE) and a variety of organometallic complexes. In general one of two possibilities might be realized when a mixed state species is obtained. Either the two moieties would be found to be only weakly interacting, or TCNE, or one of its derivatives, could coordinate to the metal. In the former case the stacking environment would be of interest, while in the latter the steric interactions between the bulky ligands would be important.

Moreover, extensive structural studies of complexes containing the bispyridylamine ligand have been carried out in this laboratory. In particular, the structure of bispyridylamine itself was reported by Johnson and Jacobson in 1973 [1], and two

copper complexes with that ligand were also reported [2, 3] as was a related bispyridylmethyl compound [4].

Combining these two areas of interest, this paper reports the results of reacting tricyanoethyleneol with the square planar copper complex bispyridylamine-copper(II) dichloride.

Experimental

Crystal Data

The title compound was prepared by mixing stoichiometric amounts of copper(II) bispyridylamine dichloride in aqueous solution with tetracyanoethylene (TCNE) in butyl alcohol solution, and allowing this mixture to go to dryness at room temperature. Well-formed golden brown single crystals were thus formed as a major reaction product and used without further purification. A crystal of approximate dimensions 0.2 × 0.2 × 0.2 mm was mounted on a glass fiber using Duco cement, and preliminary oscillation photographs indicated that the compound crystallizes in the triclinic system. A Howells, Phillips, and Rogers test [5] did not unambiguously resolve the question of the presence or absence of a crystallographic center of symmetry, but subsequent structure refinement showed that such a center does exist, thus fixing the space group as $P\bar{1}$. Final unit cell parameters, obtained from a least-squares fit of $\pm 2\theta$ values ($2\theta > 25^\circ$) for twenty-eight independent reflections (MoK_α radiation, $\lambda = 0.70954$ Å) at 27° yielded $a = 10.075(2)$, $b = 10.911(2)$, $c = 7.841(2)$ Å, $\alpha = 107.98(2)$, $\beta = 104.78(2)$, $\gamma = 108.40(2)^\circ$, $V = 716.19$ Å³, $D_{calc} = 1.489$ g cm⁻³.

Collection and Reduction of X-Ray Intensity Data

Data were collected at room temperature using a technique and apparatus described by Rohrbaugh and Jacobson [6]. Within a 2θ sphere of 50° ($\sin\theta/\lambda = 0.596$ Å⁻¹) all data in the hkl , $hk\bar{l}$, $h\bar{k}l$, and $h\bar{k}\bar{l}$ octants were measured. As a general check on crystal and electronic stability, the intensities of six standards were remeasured periodically (after every 75

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TABLE 1a. Final Positional^a Parameters.

Atom	x	y	z	Atom	x	y	z
Cu	5000	5000	5000	N(2)	2672(8)	-718(7)	-1665(11)
N(A)	6623(6) ^b	3064(5)	3890(8)	N(3)	730(7)	3894(7)	1037(10)
N(PA)	5578(5)	3753(5)	6190(7)	C(1)	1447(7)	989(6)	-946(9)
C(PA1)	6160(6)	2898(6)	5360(9)	C(2)	2237(7)	2337(7)	535(10)
C(PA2)	6371(7)	1878(7)	5979(11)	C(3)	-107(8)	515(7)	-2166(11)
C(PA3)	6009(8)	1765(8)	7492(12)	C(4)	2150(7)	57(7)	-1339(10)
C(PA4)	5466(8)	2695(8)	8438(11)	C(5)	1361(7)	3199(7)	781(10)
C(PA5)	5277(7)	3660(7)	7746(9)	H(A)	691(9)	242(8)	330(12)
N(PB)	6911(5)	5395(5)	4534(7)	H(PA2)	688(9)	123(8)	533(12)
C(PB1)	7310(6)	4352(6)	3825(9)	H(PA3)	622(8)	177(8)	819(12)
C(PB2)	8421(7)	4518(7)	3027(10)	H(PA4)	525(9)	275(9)	941(13)
C(PB3)	9212(7)	5827(8)	3130(10)	H(PA5)	481(9)	435(8)	838(12)
C(PB4)	8934(7)	6974(7)	4079(10)	H(PB2)	857(9)	367(8)	235(12)
C(PB5)	7772(7)	6718(6)	4721(9)	H(PB3)	1003(9)	600(8)	252(11)
O	3606(5)	2910(5)	1700(7)	H(PB4)	946(9)	795(8)	423(12)
N(1)	-1333(7)	126(6)	-3175(11)	H(PB5)	744(9)	741(8)	533(12)

^aThe positional parameters are presented in fractional coordinates ($\times 10^4$ for the non-hydrogen atoms, $\times 10^3$ for the hydrogen atoms). ^bIn this and succeeding tables, estimated standard deviations are given in parentheses for the least significant figures.

TABLE 1b. Thermal Parameters.^{a,b}

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	109(2)	83(1)	233(3)	59(1)	97(2)	66(2)
N(A)	122(8)	86(6)	247(15)	64(6)	97(9)	65(8)
N(PA)	103(7)	82(6)	204(13)	39(5)	74(8)	59(7)
C(PA1)	97(8)	78(7)	202(15)	35(6)	63(9)	48(9)
C(PA2)	139(10)	104(8)	277(20)	64(8)	76(12)	87(11)
C(PA3)	160(11)	118(9)	293(22)	60(8)	58(13)	105(12)
C(PA4)	138(10)	143(10)	211(18)	50(8)	76(11)	98(12)
C(PA5)	122(9)	117(9)	185(16)	43(7)	61(10)	61(10)
N(PB)	110(7)	71(5)	172(12)	45(5)	75(8)	42(7)
C(PB1)	98(8)	100(7)	170(14)	49(6)	64(9)	54(9)
C(PB2)	112(9)	122(9)	217(17)	64(7)	91(10)	69(10)
C(PB3)	121(9)	164(11)	240(18)	78(8)	108(11)	117(12)
C(PB4)	124(9)	124(9)	255(19)	49(8)	106(11)	98(11)
C(PB5)	122(9)	95(8)	207(16)	40(7)	85(10)	62(9)
O	113(6)	120(6)	248(12)	51(5)	51(7)	16(7)
N(1)	147(10)	116(8)	457(24)	48(8)	30(13)	84(12)
N(2)	235(12)	141(9)	394(22)	124(9)	123(13)	72(12)
N(3)	190(10)	174(10)	342(20)	124(9)	122(12)	90(12)
C(1)	117(9)	91(7)	208(16)	53(7)	62(10)	56(9)
C(2)	124(10)	121(9)	200(16)	64(7)	88(11)	57(10)
C(3)	138(11)	84(8)	283(20)	45(8)	70(12)	60(10)
C(4)	145(10)	98(8)	233(18)	59(8)	74(11)	54(10)
C(5)	129(10)	108(8)	224(17)	62(8)	68(11)	44(10)

^aThe β_{ij} are defined by: $T = \exp\{-h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}\}$. Isotropic temperature factors of 4.0 \AA^2 were assumed for all hydrogen atoms. ^bNumbers shown are $\times 10^4$.

reflections) during the data collection period of 56.8 hours for the 3317 reflections. No significant decrease in intensity was detected during the data collection period for these standards, and therefore no correction was made for crystal decomposition.

The intensity data were corrected for Lorentz and polarization effects, but as the crystal was small and the linear absorption coefficient was low ($\mu = 5.70 \text{ cm}^{-1}$), no absorption correction was made. The estimated error in each intensity was calculated by

$$\sigma_I^2 = C_T + K_I C_B + (0.03 C_T)^2 + (0.03 C_B)^2$$

where C_T , K_I and C_B are the total count, counting time factor, and background count, respectively, and the factor 0.03 represents an estimate of non-statistical errors. The estimated deviations in the structure factors were calculated by the finite difference method [7]. Of the 3317 reflections measured, 2378 were considered observed ($>3\sigma_{F_o}$), and of these 1984 were unique, and thus used in subsequent calculations.

Solution and Refinement of Structure

The position of the copper atom was fixed by symmetry arguments to be at a center of symmetry. (The position $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) was chosen for convenience.) The remaining non-hydrogen atoms were found by successive structure factor [8] and electron density map calculations [9]. The positional and anisotropic thermal parameters of all non-hydrogen atoms were refined, via minimization of the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma_F^2$, resulting in a conventional residual index $R = \sum \|F_o| - |F_c|\| / \sum |F_o| = 8.3\%$. The hydrogen positions in the bispyridylamine group were then calculated, and also allowed to refine, although the isotropic thermal parameters for the hydrogen atoms were fixed at 4.0 \AA^2 . A final R factor of 7.2% resulted. No appreciable secondary extinction effect was noted. The scattering factors for the non-hydrogen atoms were those of Hanson *et al.* [10], modified for the real and imaginary parts of anomalous dispersion [11]. For hydrogen, the scattering factors of Stewart *et al.* were used [12].

The final positional parameters are listed in Table I; the anisotropic temperature factors are listed in the supplementary material. Bond lengths and bond angles are listed in Tables II and III, respectively, with a tabulation of least squares planes information being given in Table IV. A list of the observed and calculated structure factors may be obtained from the authors.

Description and Discussion

Although the two starting compounds in this study were TCNE and the square planar copper complex bispyridylaminecopper(II) dichloride, solution of the crystal structure showed that the TCNE had undergone a reaction, losing one CN group which was replaced by a hydroxyl. This reaction took place via a Michael addition as

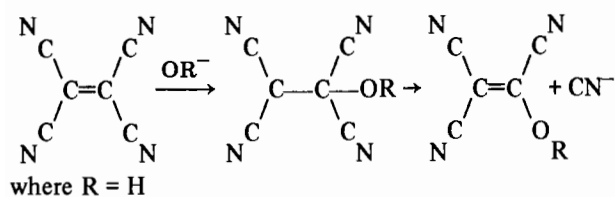


TABLE IIa. Selected Intramolecular Interatomic Distances (Å).

Cu–N(PA)	2.016(6)	O–C(2)	1.260(7)
Cu–N(PB)	1.989(6)	C(1)–C(2)	1.372(7)
Cu–O	2.520(4)	C(1)–C(3)	1.433(9)
N(PA)–C(PA1)	1.342(9)	C(1)–C(4)	1.414(11)
C(PA1)–C(PA2)	1.396(12)	C(2)–C(5)	1.483(12)
C(PA2)–C(PA3)	1.356(14)	N(1)–C(3)	1.138(10)
C(PA3)–C(PA4)	1.404(13)	N(2)–C(4)	1.128(12)
C(PA4)–C(PA5)	1.365(13)	N(3)–C(5)	1.138(12)
C(PA5)–N(PA)	1.356(10)	N(A)–H(A)	0.88(10)
N(PB)–C(PB1)	1.334(9)	C(PA2)–H(PA2)	1.08(10)
C(PB1)–C(PB2)	1.406(10)	C(PA3)–H(PA3)	1.00(11)
C(PB2)–C(PB3)	1.364(11)	C(PA4)–H(PA4)	0.84(11)
C(PB3)–C(PB4)	1.396(12)	C(PA5)–H(PA5)	1.07(10)
C(PB4)–C(PB5)	1.373(11)	C(PB2)–H(PB2)	1.00(9)
C(PB5)–N(PB)	1.367(18)	C(PB3)–H(PB3)	1.05(10)
N(A)–C(PA1)	1.388(10)	C(PB4)–H(PB4)	0.98(9)
N(A)–C(PB1)	1.379(9)	C(PB5)–H(PB5)	0.96(10)

TABLE IIb. Selected Intermolecular Interatomic Distances (Å).

N(2)–H(A) ^{1 a}	2.14(9)
N(1)–H(PB5) ¹	2.55(8)
N(3)–H(PB2) ¹	2.61(10)
N(3)–H(PB3) ¹	2.64(9)
N(1)–H(PA2) ¹	2.69(10)
C(3)–H(PB4) ²	2.71(10)
O–H(PA4) ¹	2.74(11)
N(3)–H(PB3) ²	2.75(9)
N(1)–H(PB4) ²	2.83(10)
N(2)–H(PB2) ²	2.87(9)
N(2)–H(PA3) ²	2.93(10)
N(2)–H(PA2) ²	2.93(10)

^aExplanation of symmetry operations: ¹Position related to (x, y, z) by unit cell translations. ²Position related to (–x, –y, –z) by unit cell translations.

Two of these enol compounds subsequently lose one hydrogen each and react with the copper complex, which itself loses both Cl^- ions, thus producing the title compound.

As noted above, the complex possesses inversion symmetry and is thus a *trans* complex. As can be seen in Tables IIa and III, interatomic distances and angles in this compound are in keeping with those found in similar molecules. In particular, it might be noted that the copper–(pyridyl ring) nitrogen distances (2.016(6) and 1.989(6) Å) are comparable to similar distances found in other copper bispyridylamine compounds (1.94–2.09 Å) [2, 3]; likewise the copper–oxygen distances of 2.520(4) Å is quite similar to the distance of 2.46 Å given as typical for axial oxygens in D_{4h} compounds [13].

TABLE III. Selected Bond Angles (Degrees).

N(1)–C(3)–C(1)	178.3(11)	C(PB2)–C(PB3)–C(PB4)	119.3(8)
N(2)–C(4)–C(1)	178.0(8)	C(PB3)–C(PB4)–C(PB5)	118.6(7)
N(3)–C(5)–C(2)	177.4(6)	C(PB4)–C(PB5)–N(PB)	122.7(7)
C(3)–C(1)–C(2)	120.0(7)	N(A)–C(PA1)–N(PA)	119.3(7)
C(4)–C(1)–C(2)	121.2(6)	N(A)–C(PB1)–N(PB)	119.1(6)
C(5)–C(2)–C(1)	115.5(6)	N(A)–C(PA1)–C(PA2)	118.6(7)
C(3)–C(1)–C(4)	118.7(5)	N(A)–C(PB1)–C(PB2)	118.5(6)
C(5)–C(2)–O	117.2(5)	C(PA1)–N(A)–C(PB1)	125.1(5)
C(1)–C(2)–O	127.3(8)	C(PA1)–C(PA2)–H(PA2)	121(6)
O–Cu–N(PA)	90.26(17)	C(PA3)–C(PA2)–H(PA2)	120(6)
O–Cu–N(PB)	89.30(16)	C(PA2)–C(PA3)–H(PA3)	127(6)
N(PA)–Cu–N(PB)	86.28(23)	C(PA4)–C(PA3)–H(PA3)	112(6)
Cu–N(PA)–C(PA1)	120.6(5)	C(PA3)–C(PA4)–H(PA4)	128(7)
Cu–N(PB)–C(PB1)	121.3(4)	C(PA5)–C(PA4)–H(PA4)	114(7)
Cu–N(PA)–C(PA5)	121.3(5)	C(PA4)–C(PA5)–H(PA5)	120(6)
Cu–N(PB)–C(PB5)	120.9(5)	N(PA)–C(PA5)–H(PA5)	116(6)
Cu–O–C(2)	130.8(5)	C(PB1)–C(PB2)–H(PB2)	119(5)
C(PA1)–N(PA)–C(PA5)	117.8(6)	C(PB3)–C(PB2)–H(PB2)	122(5)
C(PB1)–N(PB)–C(PB5)	117.4(6)	C(PB2)–C(PB3)–H(PB3)	122(5)
N(PA)–C(PA1)–C(PA2)	122.0(7)	C(PB4)–C(PB3)–H(PB3)	119(5)
C(PA1)–C(PA2)–C(PA3)	119.2(8)	C(PB3)–C(PB4)–H(PB4)	124(6)
C(PA2)–C(PA3)–C(PA4)	119.6(9)	C(PB5)–C(PB4)–H(PB4)	117(6)
C(PA3)–C(PA4)–C(PA5)	118.1(8)	C(PB4)–C(PB5)–H(PB5)	126(5)
C(PA4)–C(PA5)–N(PA)	123.2(7)	N(PB)–C(PB5)–H(PB5)	111(5)
N(PB)–C(PB1)–C(PB2)	122.4(6)	C(PA1)–N(A)–H(A)	116(7)
C(PB1)–C(PB2)–C(PB3)	118.8(7)	C(PB1)–N(A)–H(A)	112(6)

TABLE IVa. Equations of Least Squares Planes.^{a,b}

<i>Plane A.</i>		<i>Plane B.</i>	
Fitting O, N(1), N(2), N(3), C(1), C(2), C(3), C(4), C(5)		Fitting Cu, N(PA), N(PB)	
0.38108X + 0.68934Y – 0.61610Z = 1.82530		0.01964X + 0.44587Y + 0.89487Z = 4.70888	
Atom	Distance	Atom	Distance
O	0.0279	Cu	0.0000
N(1)	0.0249	N(PA)	0.0000
N(2)	–0.0171	N(PB)	0.0000
N(3)	–0.0242		
C(1)	–0.0116	NA	–1.3666
C(2)	0.0091		
C(3)	–0.0046		
C(4)	–0.0015		
C(5)	–0.0026		
Cu	–0.5976		
<i>Plane C.</i>		<i>Plane D.</i>	
Fitting N(PA), C(PA1), C(PA2), C(PA3), C(PA4), C(PA5)		Fitting N(PB), C(PB1), C(PB2), C(PB3), C(PB4), C(PB5)	
0.63947X + 0.44538Y + 0.62665Z = 5.50474		0.41809X – 0.17520Y + 0.89206Z = 3.86811	
Atom	Distance	Atom	Distance
N(PA)	–0.0216	N(PB)	–0.0438
C(PA1)	0.0153	C(PB1)	0.0459
C(PA2)	0.0035	C(PB2)	–0.0061
C(PA3)	–0.0155	C(PB3)	–0.0335

(continued on facing page)

TABLE IVa. (continued)

Atom	Distance	Atom	Distance
C(PA4)	0.0089	C(PB4)	0.0348
C(PA5)	0.0094	C(PB5)	0.0026
Cu	-0.2830	Cu	-0.4496
N(A)	0.1195	N(A)	0.2082
H(PA2)	0.0712	H(PB2)	-0.0653
H(PA3)	0.0897	H(PB3)	-0.1013
H(PA4)	0.0375	H(PB4)	0.0301
H(PA5)	-0.0257	H(PB5)	-0.0004

^aPlanes are defined as $c_1X + c_2Y + c_3Z = d$, where X, Y, and Z are cartesian coordinates which are related to the triclinic cell coordinates (x, y, z) by the transformations:

$$X = xa \sin \gamma + zc(\cos \beta - \cos \alpha \cos \gamma) / \sin \gamma$$

$$Y = xa \cos \gamma + yb + zc \cos \alpha$$

$$Z = zc(1.0 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma)^{1/2} / \sin \gamma$$

TABLE IVb. Inter-plane Angles (°).

Plane	Plane	Angle
A	B	76.32
B	C	39.47
B	D	43.11
C	D	41.41

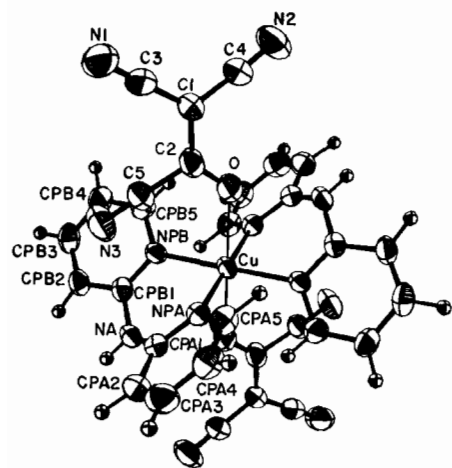


Fig. 1. Computer generated view of the title compound. 50% probability ellipsoids are shown with isotropic temperature factors of 1.0 Å² used for the hydrogen atoms for reasons of clarity.

The immediate environment about the copper atom has approximate D_{4h} symmetry although the bispyridylamine group's bite of 86.28° is slightly smaller than 90° due to steric reasons. Indeed, similar steric reasons account for a puckering of the bispyridylamine group of 41.41° (*cf.* Table IVb), an

effect that can be seen in Fig. 1 [14]. As noted by Johnson and Jacobson [3], the bispyridylamine ligand is more flexible than the bispyridyl ligand, allowing it to assume a great variety of geometric and bonding configurations. For example, in the copper complexes $CuL_2(ClO_4)_2$ [2] and $(CuL_2I)_2 \cdot I(ClO_4)$ [3], (L = bispyridylamine), the interplanar angles between the pyridyl groups are 9.6°, and 33 and 37° (for two groups), respectively; in the palladium complex (PdL_2) reported by Freeman and Snow the interplanar angle is 38.2° [15], in the related nickel complex $NiL'Br_2$, (L' = dimethyl-di-(2-pyridylmethylamine)) [4], reported by Rodgers and Jacobson, the group is tridentate and planar, and the pyridyl nitrogens are axially bound to a trigonal bipyramidal nickel. The small value of 9.6° for $CuL_2(ClO_4)_2$ is consistent with the fact that the N–Cu–N angle has opened from 90° to 95.6° with the copper atom having more tetrahedral than square planar environment, while the angles of 30° or more pertain to the complexes having approximate square planar metal atom geometries.

The angle Cu–O–C2 is 130.8(5)°, indicating considerable sp^2 character for the oxygen. This is in keeping with the extensive π character of the tricyanoethylene molecule. One might also expect a certain amount of $d-\pi$ bonding between the copper and oxygen atoms. However, the torsional angle C(2)–O–Cu–N(PB) is 28.18°, rather than the 0° angle to be expected. Such a twist might still be indicative of appreciable $d-\pi$ bonding if considerable steric or hydrogen bonding effects are operative. Table IIb lists all such intermolecular interatomic distances less than 3.00 Å, and Fig. 2, in which all atoms within 8.0 Å of the copper atom are shown, shows the packing of the crystalline structure. Neither Table IIb nor Figure 2 make very convincing arguments in favor of hydrogen bonding sufficient to force a $d-\pi$ bond to twist by almost 30°.

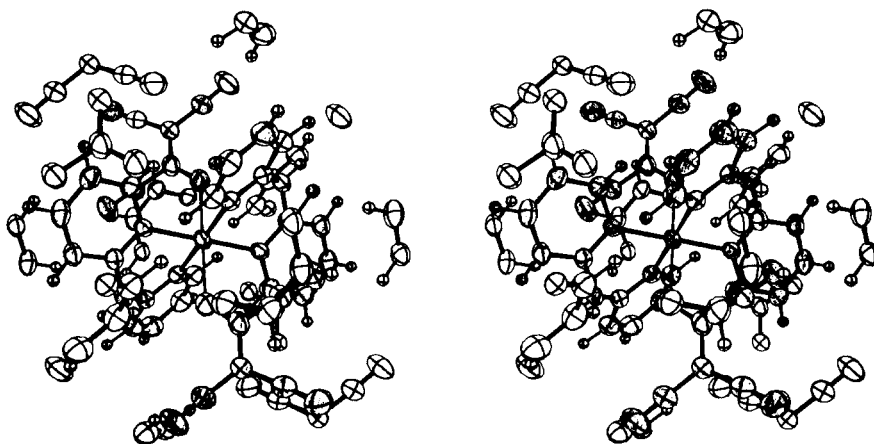


Fig. 2. ORTEP picture in which all atoms within 8.0 Å of the copper atom are shown.

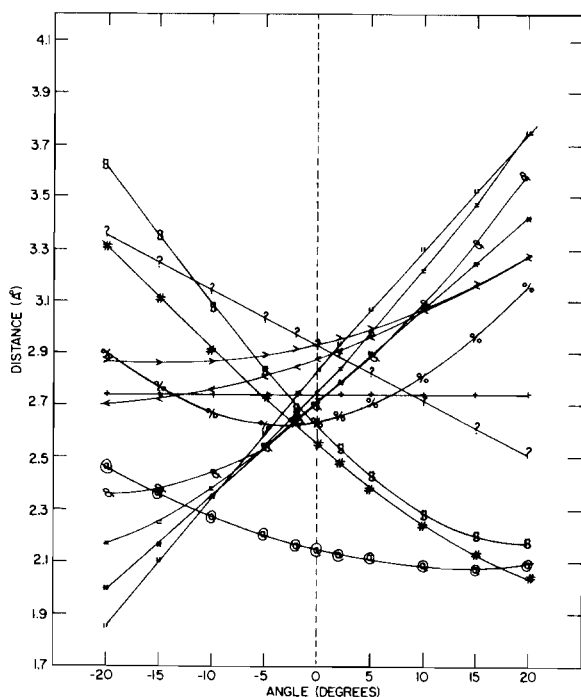


Fig. 3. Plot of selected intermolecular interatomic distances as a function of the departure of the torsional angle C(2)-O-Cu-N(PB) from the observed value of 28.18°. Legend: @ N(2)-H(A)²; # N(1)-H(PB5)¹; \$ N(3)-H(PB2)¹; % N(3)-H(PB3)¹; & N(1)-H(PA2)¹; * C(3)-H(PB4)²; + O-H(PA4)¹; = N(3)-H(PB3)²; " N(1)-H(PB4)²; < N(2)-H(PB2)²; > N(2)-H(PA3)²; ? N(2)-H(PA2)². Explanation of symmetry operations are given in Table IIb.

In Fig. 3, the interatomic distances from the ethylene moiety atoms to atoms in bispyridylamine moieties adjacent to this group are shown as a function of the departure of the torsional angle about the

Cu-O bond from the measured value of 28.18°. To make this illustration, the ethylene moiety was rotated about an axis defined by the Cu-O bond, and the interatomic distances were followed for those dozen intermolecular atomic pairs separated by less than 3.0 Å in the actual crystalline structure. It might be noted at the outset that although this illustration shows calculated values over a range of $\pm 20^\circ$, in fact it is unlikely that a rotation of anything like 20° could occur without gross changes occurring in the overall crystalline structure. Indeed, in the case of a simpler molecule reported by Bernstein and Hagler, rotations of greater than 7.5° seem impossible without changing the crystalline structure [16].

Examination of this figure shows that rotation from the observed case in either direction decreases some distances representative of repulsive interactions while of course increasing other distances. Thus the observed geometry appears reasonable since increasing the torsional angle would rapidly decrease two distances N(1)-H(PB5)¹ and N(3)-H(PB2)²; decreasing the torsional angle would rapidly decrease four others (N(1)-H(PA2)¹, N(3)-H(PB3)², C(3)-H(PB4)², and N(1)-H(PB4)²). The actual torsional angle of 28.18° can be seen as one which avoids the van der Waals crowding which would otherwise occur with other rotations. It should be noted that the only intermolecular interatomic distance less than 3.0 Å that should properly be called a 'hydrogen bond' (N(2)-H(A)²), is relatively insensitive to the torsional angle. One must therefore conclude that the Cu-O bond is largely, σ in character.

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