The Structure of Chlorobis-(2,2',N,N'-bipyridyl)copper(II)(1,1,2,3,3-pentacyanopropenide)

WILLIAM P. JENSEN

Chemistry Department, South Dakota State University, Brookings, S.D. 57007, U.S.A.

and ROBERT A. JACOBSON*

Ames Laboratory-USDOE and Department of Chemistry, Iowa State University, Ames, Iowa 50011, U.S.A.

The crystal and molecular structure of chlorobis(2,2',N,N'-bipyridyl)copper(II)(1,1,2,3,3-penta-cyanopropenide) was determined by three dimensional X-ray analysis. The lattice parameters are a = 12.278(3), b = 15.769(4), c = 7.331(2) Å, α = 97.73(2), β = 100.01(2), and γ = 106.53(2)°. The space group is P$\bar{1}$. The structure was solved by conventional Patterson and Fourier techniques and refined by full matrix least squares methods to final residuals of R = 0.090 and R_w = 0.102 for a total of 2388 unique data ($F_o \geqslant 3\sigma_F$). The copper atom is five coordinate and the donor atoms are disposed about the copper atom in a distorted trigonal bipyramidal arrangement with the chloride occupying one of the equatorial sites. The pentacyanopropenyl anion is present as a counterion and does not participate in the coordination to the metal atom.

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 solid state species is formed. 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 fomer the stacking environment would be of interest, while in the latter the steric interactions between the bulky ligands would be important.

---

*Author to whom correspondence should be addressed.

Experimental

Synthesis

The compound was prepared by grinding the solid obtained by mixing 1:2 molar amounts of $CuCl_2$ and 2,2'-bipyridyl in water with TCNE using a mortar and pestle. The powdered mixture was allowed to contact a solvent mixture of water and n-hexane. Light green crystals of the title compound precipitated upon slow evaporation of the solvent system. The crystals were used without further treatment. The crystal chosen for the intensity measurements and lattice constant determination was of irregular shape of approximate dimensions 0.2 × 0.2 × 0.2 mm. The air stable crystal was mounted on a glass fiber and oriented on an automated diffractometer. The validity of the indexing procedure was checked using standard techniques [1]. Lattice constants were obtained from twelve accurately centered reflections. Copper radiation was used for the determination (λ = 1.5418 Å). The lattice constants are *a* = 12.278(3), *b* = 15.769(4), *c* = 7.331(2) Å, α = 97.73(2), β = 100.01(2), and γ = 106.53(2)°. Statistical tests indicated a centrosymmetric structure and thus the space group was assumed to be P$\bar{1}$ with two molecules per unit cell. This assumption was verified by the subsequent refinement of the structural parameters. A total of 2388 unique data were taken where $|F_o| \geqslant 3\sigma F_o$. Intensity data were collected at ambient temperature to a 2θ maximum of 50° using the ω scan mode on an automated four-circle diffractometer. Monochromated molybdenum radiation (λ = 0.70954 Å) was used and standard reflections were remeasured every 100 reflections. The crystal exhibited no significant decrease in intensity during the data collection period. The unique data represents a hemisphere of the obtainable data. The data were corrected for Lorentz and polarization

TABLE I. Positional Parameters for the Non-Hydrogen Atoms $\times$ 10^4.

Atom	x	y	z	Atom	x	y	z
Cu	1529(1)[a]	3126(9)	3197(2)	C15	918(10)	4017(8)	6742(16)
Cl	2358(2)	4141(2)	1425(4)	C16	−854(8)	3059(6)	1984(13)
N1	1445(7)	1836(6)	3478(11)	C17	−1926(9)	2921(8)	814(17)
N2	2983(7)	3394(6)	5034(11)	C18	−2132(11)	2504(8)	−1070(16)
C1	2426(9)	1800(7)	4675(14)	C19	−1268(10)	2241(7)	−1719(16)
C2	2524(10)	998(7)	5068(16)	C20	−207(9)	2407(7)	−484(15)
C3	1648(12)	210(8)	4201(18)	CT1	2988(13)	26(11)	156(19)
C4	674(11)	250(7)	2996(17)	NT2	4882(11)	−866(9)	2618(17)
C5	608(10)	1056(7)	2656(15)	CT2	4074(15)	342(12)	1518(21)
C6	3290(9)	2677(7)	5501(13)	CT7	3145(17)	1836(10)	265(23)
C7	4314(9)	2803(8)	6796(15)	NT5	5672(11)	3487(10)	2522(18)
C8	5059(10)	3668(8)	7551(15)	NT3	6752(12)	1728(10)	4155(17)
C9	4734(9)	4397(8)	7099(16)	NT4	2242(16)	1795(10)	−686(23)
C10	3704(9)	4232(7)	5788(15)	CT3	4611(12)	−290(9)	2252(16)
N3	545(7)	3592(5)	4894(11)	NT1	2164(12)	−423(9)	−859(21)
N4	−28(7)	2789(5)	1352(11)	CT5	5840(12)	1447(8)	3262(17)
C11	−544(9)	3519(6)	3977(14)	CT8	5010(14)	2800(11)	1987(20)
C12	−1277(10)	3880(8)	4879(17)	CT6	4242(12)	1936(9)	1393(19)
C13	−856(12)	4341(9)	6744(18)	CT4	4571(16)	1174(11)	1887(22)
C14	226(12)	4393(8)	7671(16)				

[a]In this and succeeding tables numbers in parentheses indicate standard deviations in the least significant figures.

TABLE II. Selected Cation Bond Distances (A).

Cu−Cl	2.277(3)	C5−N1	1.34(1)	C12−C13	1.39(2)
Cu−N1	2.062(9)	C1−C6	1.46(1)	C13−C14	1.36(2)
Cu−N2	1.969(8)	C6−C7	1.38(1)	C14−C15	1.38(2)
Cu−N3	2.118(8)	C7−C8	1.38(2)	C15−N3	1.36(2)
Cu−N4	1.998(8)	C8−C9	1.38(2)	C11−C16	1.47(1)
N1−C1	1.38(1)	C9−C10	1.38(1)	C16−C17	1.38(1)
C1−C2	1.37(1)	C10−N2	1.34(1)	C17−C18	1.39(2)
C2−C3	1.38(2)	N2−C6	1.36(1)	C18−C19	1.38(2)
C3−C4	1.38(2)	N3−C11	1.35(1)	C19−C20	1.38(1)
C4−C5	1.35(2)	C11−C12	1.40(2)	C20−N4	1.35(1)
				N4−C16	1.33(1)

effects but no absorption correction was applied ($\mu = 11.0$ cm^{-1} and transmission factors are estimated to vary by less than 5 percent).

Structure Solution

The copper atom was located from a Patterson map. The positions of the remaining non-hydrogen atoms were determined by electron density and least squares techniques. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were calculated assuming 1.00 Å C−H distances and H−C−C bond angles of 120°. The quantity minimized was $\Sigma\omega(\|F_o|-|F_c\|)^2$ where $\omega = 1/\sigma F_o^2$. Atomic scattering factors used

were those of Hanson *et al.* [2], except for hydrogen where the values of Stewart [3] were used. The copper and chlorine scattering factors were modified by real and imaginary correction terms [4]. The final residual index was R = 0.090 with the corresponding $R_w = 0.102$, where

$$R = \frac{\Sigma(\|F_o|-|F_c\|)}{\Sigma|F_o|}$$

and

$$R_w = \frac{\Sigma\omega(\|F_o|-|F_c\|)}{\Sigma\omega|F_o|}$$

TABLE III. Selected Cation Bond Angles (°).

C1–Cu–N1	138.5(2)	Cu–N3–C11	113.5(5)	C8–C9–C10	118(1)
C1–Cu–N2	93.6(2)	Cu–N3–C15	127.7(7)	C9–C10–N2	122(1)
C1–Cu–N3	114.2(2)	Cu–N4–C16	117.3(6)	C6–N2–C10	119.4(8)
C1–Cu–N4	92.0(2)	Cu–N4–C20	121.8(7)	N3–C11–C16	114.1(8)
N1–Cu–N2	80.3(3)	N1–C1–C6	114.3(9)	N3–C11–C12	121.4(8)
N3–Cu–N4	78.6(3)	N1–C1–C2	121(1)	C11–C12–C13	119(1)
N2–Cu–N3	97.9(3)	C1–C2–C3	119(1)	C12–C13–C14	119(1)
N2–Cu–N4	174.3(3)	C2–C3–C4	119(1)	C13–C14–C15	120(1)
N1–Cu–N4	96.4(3)	C3–C4–C5	120(1)	C11–C16–C17	122.7(9)
N1–Cu–N3	107.3(3)	C4–C5–N1	123(1)	N4–C16–C11	116.0(8)
Cu–N1–C1	113.2(7)	C6–C1–N1	114.3(9)	C16–C17–C18	119(1)
Cu–N1–C5	128.8(7)	C6–C7–C8	120(1)	C17–C18–C19	120(1)
Cu–N2–C6	116.7(7)	C1–C6–C7	124(1)	N4–C20–C19	120.9(9)
Cu–N2–C10	123.7(7)	C7–C8–C9	120(1)		

TABLE IV. Equations of Least Squares Planes.

Plane 1 Fitting N1, N2, C1–C10 (B1PY1)

$-0.63968\,x + 0.09459\,y + 0.76280\,z - 1.36867 = 0$

Atom	Distance (A)	Atom	Distance (A)
N1	−0.023	C5	−0.004
N2	−0.012	C6	−0.065
C1	−0.040	C7	−0.029
C2	+0.012	C8	0.006
C3	0.034	C9	0.070
C4	0.040	C10	0.024

Plane 2 Fitting N3, N4, C11–C20 (B1PY2)

$0.42913\,x + 0.86234\,y - 0.26872\,z - 3.34022 = 0$

Atom	Distance (A)	Atom	Distance (A)
N3	−0.032	C15	−0.016
N4	−0.020	C16	−0.040
C11	−0.038	C17	−0.042
C12	−0.007	C18	−0.002
C13	0.063	C19	−0.041
C14	0.033	C20	0.058

Plane 3 Fitting NT1–NT5, CT1–CT8 (Anion)

$-0.60194\,x + 0.07291\,y + 0.79521\,z + 2.01091 = 0$

Atom	Distance (A)	Atom	Distance (A)
NT1	−0.188	CT3	0.065
NT2	0.039	CT4	0.024
NT3	−0.031	CT5	0.023
NT4	0.123	CT6	0.030
NT5	−0.103	CT7	0.087
CT1	−0.077	CT8	−0.045
CT2	0.052		

Plane 4 Fitting Cu, Cl, N1, N3

$0.66833\,x + 0.03966\,y + 0.74281\,z - 2.66993 = 0$

TABLE IV. *(continued)*

Atom	Distance (A)
Cu	−0.002
Cl	0.001
N1	0.001
N3	0.0005

Results and Discussion

Atom positional parameters for the non-hydrogen atoms are given in Table I. The anisotropic thermal parameters and the positional parameters for the hydrogen atoms are given in the supplementary material. Selected bond distances and angles for the cation are given in Tables II and III. The geometry of the ligands about the copper atom is that of a distorted trigonal bipyramid with the chlorine atom occupying an equatorial position and two nitrogen atoms from different bipyridyl groups occupying the axial positions. This geometrical type rather than the square pyramidal was selected since the bond angles in the equatorial plane sum up to 360.0° and the least squares plane fitting the equatorial atoms (including the copper atom) contains all the atoms within at least 0.002 Å, (Table IV). The axial nitrogen atoms are tipped slightly toward the equatorial atoms N1 and N3 probably due to the rigid nature of the bipyridyl groups. The average N–N distance within a bipyridyl molecule is 2.615(10) Å. The C–N and C–C distances in the cation are normal for this type of ligand. The distortion from planar geometry of the bipyridyl ligands is small as shown in Table IV. The angles between the vectors normal to the least squares planes of N1, C1–C5, and N2, C6–C10,
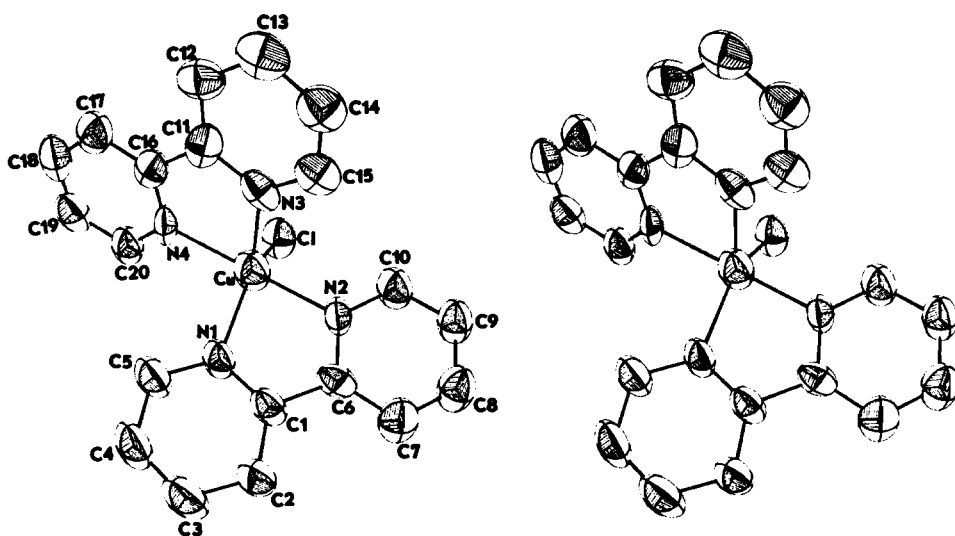
Fig. 1. A stereoscopic view of the chlorobis-(2,2',N,N'-bipyridyl)copper(II) ion showing the non-hydrogen atoms using 50% probability ellipsoids.
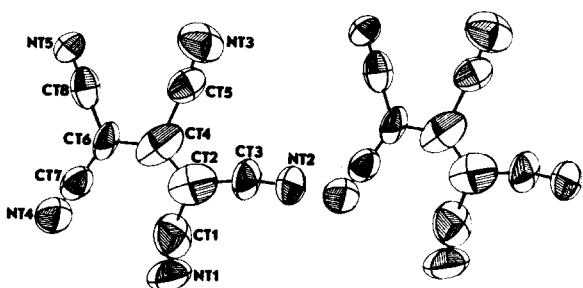

Fig. 2. A stereoscopic view of the 1,1,2,3,3-pentacyano-propenide ion showing the non-hydrogen atoms using 50% probability ellipsoids.
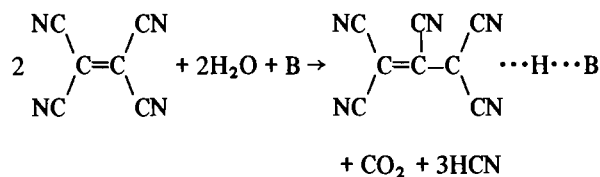
and between the least squares planes of N3, C11—C15 and N4, C16—C20 are zero and three degrees, respectively. The bipyridyl six-membered rings are even closer to being coplanar than in structures such as reference 8 where the tilt angle is given as 7° [8]. An ORTEP [5] drawing of the cation is shown in Fig. 1.

Detailed examination of the angles involving the copper atom however reveals that there are appreciable distortions from trigonal bipyramidal symmetry. Ideally one would expect an approximate two-fold rotation axis containing the copper and chlorine atoms. In fact the complex displays an appreciable deviation from this type of idealized symmetry. The equatorial bond angles N1—Cu—Cl and N3—Cu—Cl are 138.5(2) and 114.2(2)°, respectively. This distortion is observed in similar five-coordinate complexes (reference 10 and references

therein). This type of distortion could be described as an intermediate step in the conversion of a trigonal bipyramid geometry complex moving toward a square pyramidal geometry complex. Indeed a just published paper by Harrison [11] for a similar system treats the distortions observed there in a similar fashion to that which we are proposing [12].

There are no apparent covalent bonding interactions between the cation and the anion. The three closest interactions are between NT1—H5; NT2—H2; and NT4—H20 with distances of 2.31, 2.40, and 2.44 Å, respectively. Other anion—cation distances are greater than 2.70 Å.

The anion, a reaction product of TCNE, is a rather unusual thirteen atom, highly planar group (see Table IV). It is likely formed as a salt in a reaction similar to that reported in reference 9 in which TCNE is allowed to react with water in the presence of a base (B) according to the following:

$$2 \quad \begin{array}{c} NC \\ NC \end{array} C{=}C \begin{array}{c} CN \\ CN \end{array} + 2H_2O + B \rightarrow \begin{array}{c} NC \\ NC \end{array} C{=}C{-}C \begin{array}{c} CN \\ CN \end{array} \cdots H \cdots B$$

$$+ CO_2 + 3HCN$$

In this case the base is probably the hydroxide ion. An ORTEP [5] representation of this group is shown in Fig. 2. Bond distances for this group are given in Table V and bond angles are given in Table VI.

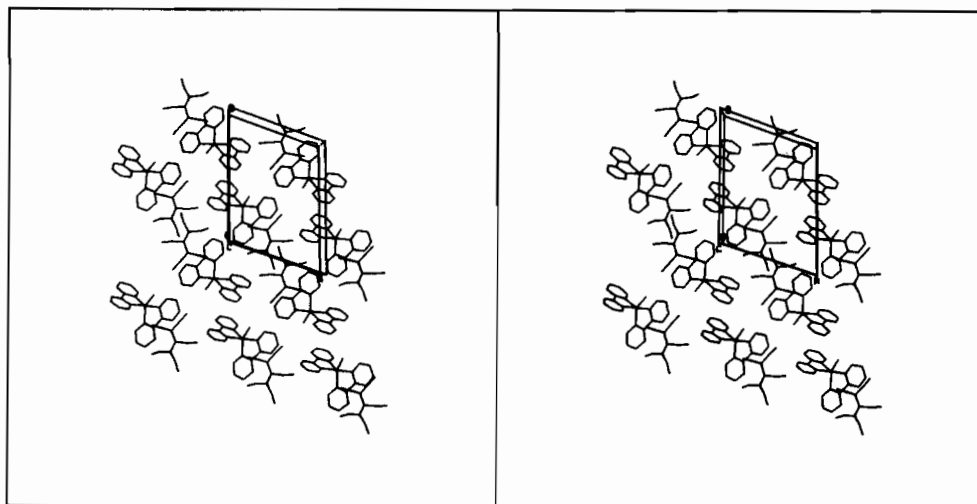It is surprising that this highly nucleophilic group does not coordinate with the copper atom. This

Fig. 3. Stereo view of the unit cell.

TABLE V. Anion Bond Distances (A).

NT1–CT1	1.12(2)	CT5–NT3	1.12(2)
CT1–CT2	1.43(2)	CT4–CT6	1.44(2)
CT2–CT3	1.45(2)	CT6–CT7	1.41(2)
CT3–NT2	1.10(2)	CT7–NT4	1.18(3)
CT2–CT4	1.25(2)	CT6–CT8	1.38(2)
CT4–CT5	1.61(2)	CT8–NT5	1.12(2)

TABLE VI. Selected Anion Bond Angles (°).

NT1–CT1–CT2	163(2)
CT1–CT2–CT3	121(1)
CT2–CT3–NT2	169(1)
CT1–CT2–CT4	116(1)
CT2–CT4–CT5	112(1)
CT4–CT5–NT3	172(1)
CT4–CT6–CT7	122(2)
CT4–CT6–CT8	121(1)
CT6–CT8–NT5	177(2)
CT5–CT4–CT6	114(1)
CT2–CT4–CT6	134(1)
CT7–CT6–CT8	117(1)
CT3–CT2–CT4	123(1)

could be due to the relative inaccessibility of the copper atom, being nearly surrounded by two bipyridyl molecules. The average C–N distances is 1.13 Å, somewhat shorter than the average distance for nitriles given in reference 6. Attempts were made to fit the thermal parameters of the anion atoms to motions of a rigid body [7]. The goodness of fit of the anion atom vibrations to those of a rigid body can be established by comparing the mean weighted ΔU_{ij} ($U_{ijobs} - U_{ijcalc}$ terms) with the mean estimated error in the observed thermal parameters. In this case the model contained librational and translational axes that did not coincide with molecular axes. The mean error in U_{obs} is 0.0086 whereas the weighted mean of ΔU_{ij} is 0.019. The relatively poor agreement indicates a high degree of non-rigid motion of the molecular ion in the crystal. Elimination of the terminal nitrogen atoms from the rigid body model results in an increase of ΔU_{ij} mean to 0.021 again indicating that the entire molecular ion is librating and translating in a highly non-rigid manner. This type of non-rigid thermal activity could account for the somewhat short carbon-nitrogen bond distances observed although with the rather high standard deviations estimated for the anion atom positions, the bond distances are not unreasonable.

The assumption that the anion truly does undergo non-rigid librations and/or translations is supported by the observation that a bipyridyl group of the cation can be fitted, with excellent agreement, to a rigid body model. For the bipyridyl group, N1, N2, C1–C10, the mean error in U_{obs} is 0.0060 and the estimated standard deviation of the weighted ΔU is 0.0044, a fit that is slightly better than what would be expected on the basis of estimated errors. This observation could indicate that the estimated errors in the thermal parameters are on the conservative side. At any rate it does indicate that the bipyridyl group, as expected, behaves as a rigid body in this system.

References

1 R. A. Jacobson, *J. of Appl. Crystallography, 9,* 115 (1976).
2 H. P. Hanson, F. Herman, J. D. Lea and S. Skillman, *Acta Crystallogr., 17,* 1040 (1960).
3 R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys., 42,* 3175 (1965).
4 International Tables for X-Ray Crystallography, Vol. III, p. 215, Table 4-2-4, The Kynoch Press, Birmingham, England (1962).
5 C. K. Johnson, 'ORTEP-II: A Fortran Thermal-Ellipsoid Plot Program for the Crystal Structure Illustrations', U.S. AEC Report ORNL-3794 (Second Revision with Supplemental Instructions), 1971.
6 International Tables for X-Ray Crystallography, Vol. III, p. 276, Tables 4-2-4, The Kynoch Press, Birmingham, England (1962).
7 K. N. Trueblood, Program THMI-2, Department of Chemistry, University of California, Los Angeles, CA. 90024.
8 J. J. Daly, F. Sany, R. P. A. Sanden, H. H. Zeiss, *J. Chem. Soc. Dalton,* 1497 (1973).
9 W. J. Middleton, E. L. Little, D. D. Coffman and V. A. Engelhardt, *J. Am. Chem. Soc., 80,* 2795 (1958).
10 R. A. Jacobson and W. P. Jensen, *Inorg. Chim. Acta, 49,* 199 (1981).
11 W. D. Harrison and B. J. Hathaway, *Acta Cryst., B36,* 1069 (1980).
12 W. P. Jensen and R. A. Jacobson, *Abstracts of the 15th Midwest Regional Meeting,* American Chemical Society, 44, #416 (1979).