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The Crystal and Molecular Structure of 2,2′,N,N′-bipyridyl Chloro Tricyanoethenolate Copper(0)

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The crystal and molecular structure of 2,2′, N,N′-bipyridyl chloro tricyanoethenolate copper(0) has been determined by three-dimensional X-ray analysis and refined by least-squares methods to conventional residuals of $R = 0.046$ and $R_w = 0.063$. The lattice parameters are a = *9.963(3),* b = *9.922(4),* c = *8.505(3) Å, $\alpha = 101.58(3)$, $\beta = 99.73(3)$, and $\gamma = 67.08(3)°$. The space group is $P\bar{1}$ with two molecules per unit cell. A total of 2222 unique data with $|F_o| \geq 3\sigma_F$ were used in the structure determination. The copper(II) ion is coordinated with two nitrogen atoms from the bipyridyl ligand, a chloride ion and a nitrogen atom from the ethenolate anion in a square planar arrangement. A fifth ligand, a chloride ion from a second molecule, is located above the square plane at a distance of 2.712 Å from the copper atom, while a possible sixth coordinating atom, a nitrogen from a neighbor tricyanoethenolate is located below the square plane at a Cu–N distance of 2.981 Å.*

Introduction

Bipyridyl and bipyridylamine ligands have been used in the synthesis of a variety of five coordinate copper complexes [1–3 and references therein]. Several investigators have discussed the structures of these complexes as 'frozen out' intermediates in the transition between idealized trigonal bipyramidal and square pyramidal structures [1, 3]. We attempted to prepare a complex containing bipyridyl and a decomposition product of tetracyanoethylene (TCNE) hoping to freeze out a formally four coordinate copper(II) complex that would involve charge transfer interaction between TCNE or its decomposition product and a fifth coordination site on the metal atom. The structure discussed in this paper represents a partial success in the effort in that we have succeeded in preparing a four coordinate complex containing the anion $C_5N_3O^-$, a bipyridyl ligand, and relatively weak interactions between the copper(II) ion and a chloride ion and possibly a cyanide nitrogen on adjacent complex molecules. This was accomplished by limiting the complexing abilities of the metal and the ligands by lowering the pH of the solution from which the complex was crystallized.

Experimental

Synthesis

An aqueous solution containing a 1:1:2 mixture of $CuCl_2$, TCNE, and bipyridyl was acidified with a few drops of concentrated HCl. Upon slow evaporation of the solvent dark green crystals of the title compound precipitated. These crystals were used for the X-ray structure determination.

Structure Solution

The crystal chosen for the lattice constant determination and intensity measurements was of irregular shape with approximate dimensions of 0.15 × 0.1 × 0.1 mm. The air stable crystal was mounted on a glass fiber with epoxy glue and placed on a four-circle automated diffractometer previously described [4]. The orientation matrix and lattice constant determination were accomplished by the procedure described earlier [5]. The values for the lattice constants, obtained from the settings of twelve high angle, centered reflections, are $a = 9.963(3)$, $b = 9.922(4)$, $c = 8.505(3)$ Å, $\alpha = 101.58(3)°$, $\beta = 99.73(3)°$, and $\gamma = 67.08(3)°$. Statistical tests indicated the presence of a center of symmetry and the space group was subsequently determined to be $P\bar{1}$. Monochromated molybdenum K_α radiation was used throughout all phases of the data collection process ($\lambda = 0.70954$ Å). Intensity data were collected at ambient temperature to a 2θ maximum of 50°. Of the 3210 data representing a hemisphere of

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the obtainable data, the 2222 reflections that satisfied the condition $|F_o| \geq 3\sigma_F$ were used in the refinement of the structure. Lorentz and polarization effects were corrected for in the data reduction process. The effects of absorption were assumed to be negligible (μ = 16.86 cm^{-1}). The standard deviation of a reflection was computed according to

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

where C_T and C_B represent total and background counts and K_T is a counting time factor.

The copper and chlorine atoms were located from a sharpened Patterson map. The remaining non-hydrogen atoms were located using standard Fourier and least squares techniques. The refinement was then continued using a block diagonal least squares procedure [6]. Anisotropic thermal parameters were used for all the non-hydrogen atoms and the quantity minimized was $\Sigma\omega(||F_o| - |F_c||)^2$. At this stage hydrogen atoms were included for the pyridyl rings from calculated positions assuming 1.03 Å C–H distances and 120° bond angles. The hydrogen atom positions were not refined. Atomic scattering factors for the non-hydrogen atoms were those of Hanson *et al.* [7]. Chlorine and copper scattering factors were modified using real and imaginary terms [8]. The hydrogen atom scattering factor terms were those of Stewart [9]. The final residuals after a full matrix least squares refinement cycle are R = 0.046 and R_w = 0.063. The shift in any parameter after this cycle was less than one standard deviation.

Discussion

The ethenolate ligand was likely formed in solution according to the equation given in reference [10]. An ORTEP [11] view of the molecule is given in Fig. 1. Atom positional parameters for the non-hydrogen atoms are given in Table I. Thermal parameters and hydrogen atom parameters are given in the supplementary material. Bond distances and bond angles are given in Tables II and III.

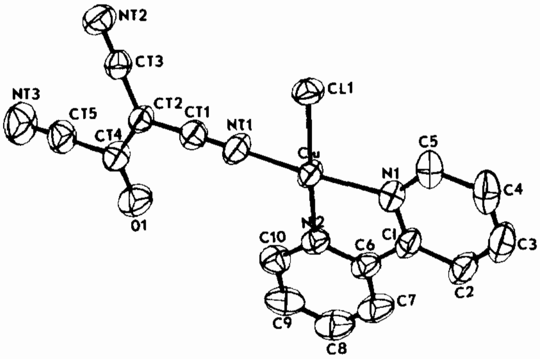

Fig. 1. Computer generated drawing of the title compound using 50% probability ellipsoids.

TABLE I. Positional Parameters for the Non-Hydrogen Atoms (X 10^4).

Atom	x	y	z
Cu	687.8(6)	3448.2(5)	3538.5(6)
Cl1	1228(1)	5517(1)	4190(1)
N1	2344(4)	2244(4)	4961(4)
C1	2398(5)	868(5)	4929(5)
C2	3407(6)	–51(6)	5984(7)
C3	4367(6)	459(8)	7017(7)
C4	4344(5)	1837(7)	7017(6)
C5	3305(5)	2723(6)	5965(6)
C6	1295(5)	451(5)	3760(6)
C7	1237(7)	–945(5)	3457(7)
C8	144(8)	–1192(6)	2370(8)
C9	–881(7)	–57(7)	1620(7)
C10	–778(5)	1316(5)	1968(6)
N2	316(4)	1548(4)	3001(4)
NT3	–5654(6)	6402(6)	–3239(7)
CT5	–4768(6)	5773(6)	–2351(7)
CT2	–2682(5)	5623(5)	–332(5)
O1	–3602(4)	3717(4)	–980(5)
CT3	–2719(5)	6971(5)	–674(5)
CT1	–1606(5)	4921(5)	819(6)
NT2	–2742(5)	8043(5)	–1002(6)
CT4	–3636(5)	4922(5)	–1158(6)
NT1	–734(4)	4321(4)	1764(5)

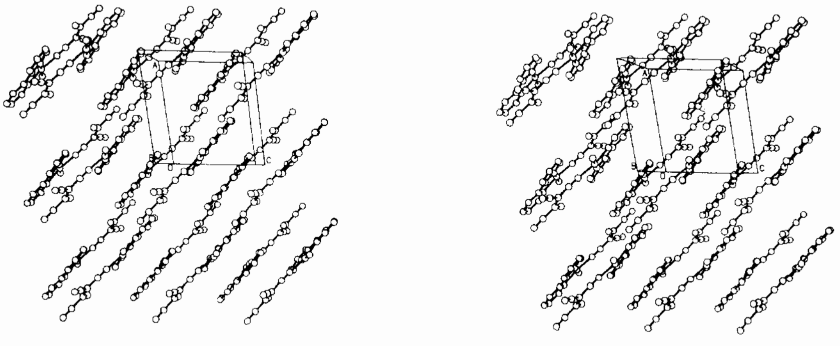

Fig. 2. A stereoscopic view of the unit cell.

TABLE II. Selected Bond Distances.

Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)
Cu	C11	2.261(1)	C7	C8	1.370(9)
Cu	N1	1.996(4)	C8	C9	1.375(9)
Cu	N2	2.010(4)	C9	C10	1.376(8)
Cu	NT1	1.970(5)	N2	C10	1.343(6)
N1	C1	1.340(6)	NT1	CT1	1.144(7)
C1	C2	1.399(7)	CT1	CT2	1.389(6)
C2	C3	1.363(8)	CT2	CT3	1.411(6)
C3	C4	1.36(1)	CT3	NT2	1.143(6)
C4	C5	1.393(7)	CT2	CT4	1.404(6)
C1	C6	1.479(6)	CT4	CT5	1.493(6)
N1	C5	1.337(6)	CT5	NT3	1.128(8)
N2	C6	1.340(6)	CT4	O1	1.223(6)
C6	C7	1.380(6)			

TABLE III. Selected Bond Angles.

Atom 1	Atom 2	Atom 3	Angle°	Atom 1	Atom 2	Atom 3	Angle°
C11	Cu	N1	95.8(1)	C1	N1	C5	119.7(4)
C11	Cu	N2	177.0(1)	N2	C6	C1	114.9(4)
C11	Cu	NT1	89.7(1)	N2	C6	C7	121.2(5)
N1	Cu	N2	81.4(2)	N2	C10	C9	120.9(4)
N1	Cu	NT1	167.8(2)	C6	C7	C8	118.7(5)
N2	Cu	NT1	92.9(2)	C7	C8	C9	120.1(5)
Cu	N1	C1	114.4(3)	C8	C9	C10	118.9(6)
Cu	N1	C5	125.8(3)	CT1	CT2	CT3	118.4(4)
Cu	N2	C6	114.1(3)	NT1	CT1	CT2	178.6(5)
Cu	N2	C10	125.8(3)	NT2	CT3	CT2	177.8(5)
N1	C1	C6	115.0(4)	CT1	CT2	CT4	118.5(4)
N1	C1	C2	120.7(4)	CT3	CT2	CT4	123.0(4)
C1	C2	C3	118.9(5)	CT2	CT4	CT5	114.6(4)
C2	C3	C4	120.4(6)	CT2	CT4	O1	125.9(4)
C3	C4	C5	118.7(5)	O1	CT4	CT5	119.5(4)
C4	C5	N1	121.5(5)	CT4	CT5	NT3	177.9(6)

Carbon–carbon and carbon–nitrogen distances in the bipyridyl rings are normal for copper(II) bipyridyl complexes as is the copper–chlorine distance of 2.261 Å [1–3]. Placement of neighboring molecules are such that the copper complex could be viewed as distorted square prismatic or even distorted octahedral. A chlorine atom in an adjacent molecule is 2.712 Å from the copper atom and essentially along the normal to the basal plane. In addition a terminal nitrogen of an ethenolate group (NT2) is essentially opposite this chlorine and at a distance of 2.981 Å from the copper; the corresponding Cl–Cu–N angle is 173°. Hence, the stacking is such that some intermolecular interaction via the d_{z^2} orbital of the copper may be possible. A packing diagram [12] is shown in Fig. 2. The copper–copper distance 3.512(2) Å would give the crystal a greater than normal metallic character except that the interaction is not continued from the second molecule to a third molecule. Thus, the crystal is expected to exhibit normal electrical conductivity for complexes of transition metals where the molecules are isolated from one another with connections only through van der Waals interactions.

The ethenolate ion is of interest for several reasons. The ethene linkage C2–C4 1.404(6) Å is longer than the range given for C=C distances in the International Tables (1.337(6) Å) [13]. The carbon–oxygen bond distance, 1.223(6) Å, is considerably shorter than the 1.43(1) Å distance expected for a C–O single bond. In fact it is within the range given for C=O double bond systems [13]. One can draw a number of resonance forms for this anion; examination of the distances indicates an important form must be one in which the double bond is between carbon and oxygen and not the normal ethylenic atoms. This is discussed in more detail below. A second feature of this anion is its ability to coordinate to a copper atom through either the oxygen atom or in this structure through one of the nitrogen atoms (NT1). In the compound Cu(bpyamine)$_2$(ethenolate)$_2$ [10], the ethenolate ligands are bonded to the copper atom though the oxygen atom. In this structure the C–O bond distance is 1.260(7) Å, somewhat longer than the C–O distance in the title structure. Evidently the point of attachment of the ligand to a copper atom is not determined by just the inherent basicity of the potential donor atoms in the anion in solution. Also in this structure the double bond resides more between the C–C linkage as evidenced by the relatively shorter 1.372(7) Å distance. To pursue this point further we took the atom coordinates for the ethenolate anion for the Cu–N bonded system and calculated the gross orbital charges using the GAUSSIAN-70 computer program [14] assuming an isolated ligand. The sum of the calculated orbital charges for the 1s, 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals on the carbon, nitrogen and oxygen atoms are given in Table IV. It can be seen from this table that in this geometry the calculated charge on the oxygen atom is about the same as the charges on two of the three nitrogen atoms. Thus in principle it could be expected that the ligand could interact with a metal ion through either one of several nitrogen atoms or through the oxygen atom. The ion would then readjust to form a more stable structure by either shortening or lengthening the C–C and C–O bonds. It is intriguing to speculate whether the ethenolate could be induced to coordinate to two separate metals as a bidentate ligand. The possibility then exists to extend a molecular orbital in two dimensions over perhaps the entire crystal, forming in effect a continuous conduction band.

TABLE IV. Orbital Charge Sums for the Atoms in the Ethenolate Anion.

Atom	Calculated Electronic Charge (Qe)	Qe – Z
NT1	7.318	0.318
NT2	7.312	0.312
NT3	7.250	0.250
O1	8.319	0.319
CT1	5.933	–0.067
CT2	6.180	0.180
CT3	5.944	–0.056
CT4	5.791	–0.209
CT5	5.952	–0.048
		+0.999

The title complex is unusual in that all atoms in the molecule are nearly coplanar. Several least squares planes are given in Table V. The individual pyridyl rings are more or less coplanar. The dihedral angle

TABLE V. Least Squares Planes.

Plane #1

Atoms Cu, N1, N2, C11 & NT1
Equation $0.72951X + 0.03715Y - 0.68296Z + 1.56075 = 0$

Atom	*Distance from plane (Å)*
Cu	–0.084
N1	0.103
N2	–0.068
C11	–0.051
NT1	0.100

Plane #2

Atoms NT1–NT3, CT1–CT5 & O1
Equation $-0.69361X + 0.12526Y + 0.70937Z - 2.04176 = 0$

Atom	*Distance from plane (Å)*
NT1	0.029
NT2	–0.056
NT3	0.054
CT1	0.026
CT2	0.026
CT3	0.002
CT4	–0.016
CT5	0.010
O1	–0.075

Plane #3

Atoms N1, C1–C5
Equation $0.72147X + 0.02237Y - 0.69208Z + 1.53063 = 0$

Atom	*Distance from plane (Å)*
N1	–0.013
C1	0.013
C2	–0.003
C3	–0.007
C4	0.008
C5	0.002

Plane #4

Atoms N2, C6–C10
Equation $0.65711X - 0.12180Y + 0.74389Z - 1.70011 = 0$

Atom	*Distance from plane (Å)*
N2	–0.014
C6	0.007
C7	0.004
C8	–0.008
C9	0.002
C10	0.010

described by the normals to the two least-squares planes of the pyridine rings is 7.42°. The entire molecule is not quite so coplanar, the angle between the least-squares plane of the bipyridyl molecule and the ethenolate molecule being 11.47°. The four atoms making up the coordination sphere in the square planar complex are very nearly coplanar, deviations of these atoms from the least-squares plane are given in Table V.

The rigidity of the molecule was tested as follows using the computer program THMI [15]. Thermal parameters for the individual atoms were calculated from T, L, and S tensors with fixed intramolecular bond distances and angles. The resulting calculated thermal parameters are then compared with the observed values. The goodness of fit of the rigid body approximation can be determined by comparing the sum of the $U_{obs} - U_{calc}$ values with a root mean squares deviation of $U_{observed}$. The values compared are calculated according to the following.

An estimated standard deviation of the weighted ΔU =

$$(\Sigma((\omega(U_{observed} - U_{calculated})^2/(\#\text{ of observations} - \\ - \#\text{ of parameters})\left(\frac{6X\#\text{atoms}}{\Sigma\omega^2}\right)\Bigg)^{1/2}$$

where ω is a weighting factor, and U corresponds to the root mean square value. The results are given in Table VI.

TABLE VI. Rigid Body Motions of the Title Complex.

Rigid Body	Mean σU	Mean ΔU
Bipyridyl Group N1, N2, C1–C10	0.0028	0.0030
Ethenolate Anion O1, NT1–NT3, CT1–CT5	0.0026	0.0046
Entire Molecule	0.0026	0.0049

It can be seen from this table that the rigid body approximation is a good one for the bipyridyl group. The ethenolate anion however does not give as good a fit indicating that it is less rigid in its behavior.

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