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The Crystal Structure of the Mixed Valence Copper Cyanide Ethylenediamine Complex: Aquobis(en)copper(II) Di-[catena-di-μ-cyanocuprate(I)], $Cu_3(en)_2(CN)_4.H_2O$*

By R. J. Williams,† Allen C. Larson and Don T. Cromer

University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87544, *U.S.A.*

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The crystal structure of the mixed valence copper cyanide ethylenediamine complex: aquobis(en)copper(II) di-[catena-di-μ-cyanocuprate(I)], $Cu_3(en)_2(CN)_4.H_2O$, has been solved from three-dimensional X-ray counter data and refined by least-squares methods, with anisotropic thermal parameters, to a conventional R index of 3·75%. The crystals are monoclinic, space group Cc, with $a=14{\cdot}774(10)$, $b=7{\cdot}749(4)$, $c=14{\cdot}272(9)$ Å, and $\beta=112°39(3)'$. There are four formula units per unit cell. The structure consists of discrete aquobis(ethylenediamine)copper(II) cations and a polymeric $[Cu_2(CN)_4^{-2}]_x$ anion. The coordination about the Cu(II) atom of the cation is square-pyramidal with two bidentate ethylenediamine molecules occupying basal positions and with a water molecule at the apex. The anion is a pseudocentrosymmetric three-dimensional cage-like network of Cu(I) ions tetrahedrally linked together by cyanide ions. The cations fit into holes in this network. Refinement included all hydrogen atoms in positions constrained to give reasonable geometry. Two of the four cyanide ions are probably ordered, but the other two may be disordered. The ethylenediamine groups have large thermal motion. Large corrections were made to the C–C bond lengths on the assumption that the groups are either dynamically flipping or statically disordered.

Introduction

Recently Cooper & Plane (1966) reported the preparation and partial characterization of some mixed valence copper cyanide complexes containing ammonia and ethylenediamine. These compounds were shown to contain copper(I) and copper(II) in a ratio of 2:1. It was postulated from spectral data that the complexes contained the ions $Cu(NH_3)_4^{2+}$ and $Cu(en)_2^{2+}$ and that it was possible that bridging could occur with the anion, thought to be $Cu(CN)_2^-$. We recently determined the structure of the ammonia complex, $Cu_3(NH_3)_3(CN)_4$ (Williams, Cromer & Larson, 1971), and found it to have an unusual neutral polymeric structure containing Cu(II)–CN–Cu(I) bridges. As a continuation of our studies of complex copper cyanides (see *e.g.*, Roof, Larson & Cromer, 1968, and references contained therein), we have now determined the structure of one of the two mixed valence ethylenediamine copper cyanide complexes which we have prepared. The compound reported here crystallizes as pale purple monoclinic crystals. The second compound, perhaps an anhydrous modification, crystallizes as blue triclinic crystals. These triclinic crystals decompose in a few days and only the unit cell has been determined, which is $a=20{\cdot}80$, $b=8{\cdot}67$, $c=7{\cdot}79$ Å, $\alpha=64{\cdot}9$, $\beta=87{\cdot}0$, and $\gamma=88{\cdot}5°$.

Experimental

Pale purple crystals of $Cu_3(en)_2(CN)_4.H_2O$ were prepared by method (a) of Cooper & Plane (1966). A few of the blue triclinic crystals were intermixed. Preliminary precession photographs showed the crystals to be monoclinic. Systematic absences are hkl if $h+k\neq 2n$ and $h0l$ if $l\neq 2n$; these absences are consistent with space groups Cc or $C2/c$, and subsequent analysis showed that the former is correct. Lattice constants were obtained from a least-squares analysis of 12 reflections measured with Mo $K\alpha_1$ radiation ($\lambda=0{\cdot}70926$ Å) on an automated Picker diffractometer (Busing & Levy, 1967). Crystallographic data are given in Table 1.

Table 1. *Crystallographic data for* $Cu_3(en)_2(CN)_4.H_2O$

Space group Cc
$a=14{\cdot}774$ (10) Å
$b=\ 7{\cdot}749$ (4)
$c=14{\cdot}272$ (9)
$\beta=112°39$ (3)′
$Z=4$
Formula: $Cu_3C_8N_8OH_{18}$
$F(000)=868$ (without $\Delta f'$)
$d_{calc}=1{\cdot}907$ g.cm^{-3}
$d_{obs}\ =1{\cdot}889$ g.cm^{-3}
(by flotation in bromoform and 1,1,2-trichlorethane)

A second, simpler method of preparation is to dissolve CuCN in a solution of about 50% ethylenediamine in water and let it stand at room temperature. Oxidation of the copper by air takes place and well-shaped crystals soon grow. Bubbling oxygen through the solution will speed the process. Only the purple form was observed in this preparation. The crystals are usually rhombohedral in shape and show the forms {110} and {001}.

A crystal obtained from the second method of preparation was used for the intensity measurements. In-

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† Present address: Chemistry Department, Midwestern University, Wichita Falls, Texas 76308, U.S.A.

tensities were measured by means of an automated Picker diffractometer using the programs of Busing, Ellison, Levy, King & Roseberry (1968). Intensities were obtained from θ–2θ scans with steps of 0·05° in 2θ over a 2θ range of 2°, plus the α_1–α_2 dispersion and a 2-sec count at each step. Background was measured for 20 sec at each end of the scan range and assumed to vary linearly over the range. Reflections were measured for the quadrant with $h, k \geq 0$ and all values of l to a maximum 2θ of 70° with graphite monochromated Mo $K\alpha$ radiation. A total of 3456 reflections was measured. The crystal used was approximately rhombohedral in shape with a volume of $6{\cdot}2 \times 10^{-3}$mm^3. Absorption corrections ($\mu = 44$ cm^{-1}) were applied by the method of Busing & Levy (1957) through use of a modified version of Burnham's (1962) program. Maximum and minimum transmission factors calculated were 0·567 and 0·482. A total of 2689 reflections was observed greater than zero according to the criterion:

$$(I-B) \geq 2\sigma(I) = 2[I+B+(0{\cdot}02\ I)^2]^{1/2}, \qquad (1)$$

where I is the integrated peak intensity, B is the normalized background intensity, and $\sigma(I)$ is the estimated standard deviation of I.

Structure determination

A three-dimensional Patterson function was calculated and could be interpreted only as having arisen from copper atoms in three general positions of space group Cc. These copper atoms were given isotropic temperature factors and submitted to three cycles of full-matrix least-squares refinement. This led to values of $R = 0{\cdot}23$ and $R_w = 0{\cdot}27$, where $R = \sum|\Delta F|/\sum|F_o|$ and $R_w = [\sum w(\Delta F)^2/\sum wF_o]^{1/2}$ (Hamilton, 1964), with observed reflections omitted. An electron density map phased by the heavy atoms was calculated, and all atoms, except the four carbon atoms in the ethylenediamine groups and the hydrogen atoms, were located. The remaining carbon atoms were located, with some difficulty, from subsequent electron density maps phased by the more complete partial model. The electron density at these carbon atom positions ranged from 4·0 to 5·0 e.Å^{-3} as compared with values of 6·5 to 9·0 e.Å^{-3} for the cyanide groups and the nitrogen atoms in the ethylenediamine groups. These low-peak electron densities suggest a high degree of thermal motion or positional disorder, or both, associated with the carbon atoms in the ethylenediamine groups.

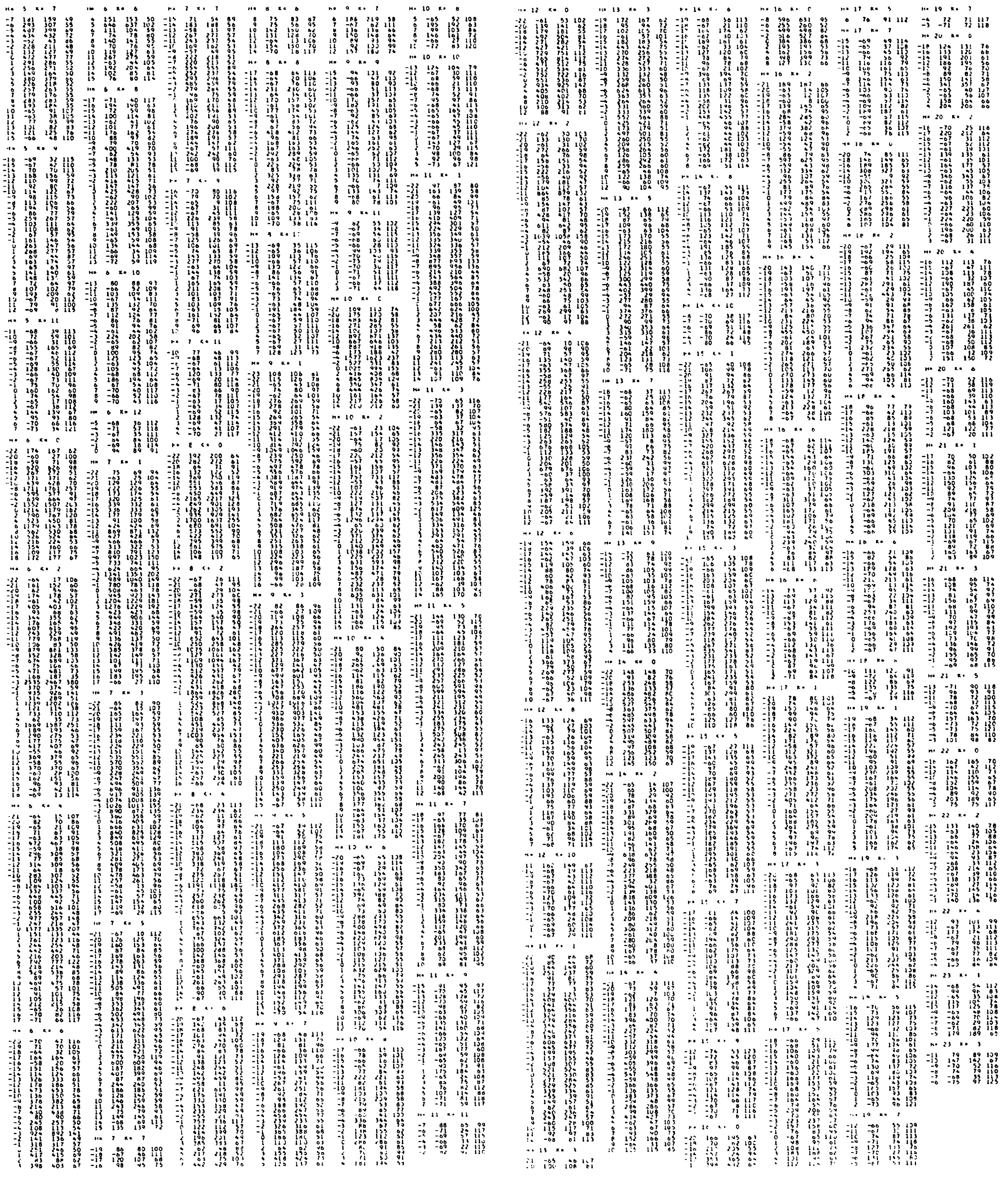
The orientations of the four independent cyanide groups were difficult to assign. From our previous work we have found that Cu–N distances are about 0·1 Å longer than Cu–C distances and on this criterion, at this stage of the structure determination, CN(1) and CN(4) seemed to be correctly oriented and probably ordered (see Table 2). The orientations of CN(2) and CN(3) could not be definitely established on the basis of bond lengths or thermal parameters. Instead, we used Stewart's (1969, 1970) generalized scattering fac-

Table 2. *Observed and calculated structure factors for* $Cu_3(en)_2(CN)_4.H_2O$

Column headings are l, 10 F_o/K, 10 F_c and 100 σ (F_o/K). A minus sign preceding F_o means 'less than', and the value given is that derived from $2\sigma(I)$.

[illegible]

Table 2 (*cont.*)



tors and *L*-shell projection method. Details of the application of generalized scattering factors to the identification of carbon and nitrogen in the present compound and in other CuCN complexes will be published at a later time (Larson & Cromer, 1972). Briefly, the scattering factors used for these atoms were composed of an average of the carbon and nitrogen core scattering factors and an average of the carbon and nitrogen valence scattering factors. A population parameter was applied to the valence scattering factors. The member of each pair that had the larger electron population parameter was then presumed to be nitrogen. The results were consistent with the orientations already selected for CN(1) and CN(4), and they provided a rationale for the orientations for CN(2) and CN(3) given in this paper. It will later be shown that CN(1) and CN(2) are probably ordered but, because of pseudosymmetry, CN(3) and CN(4) may be disordered.

This model without hydrogen atoms, when refined with anisotropic thermal parameters, yielded $R=0{\cdot}0401$ and $R_w=0{\cdot}0487$. A difference Fourier map at this time gave some indication of hydrogen atoms. Hydrogen atoms were then included in constrained positions (Waser, 1963; Rollett, 1970), with $\text{C–H}\simeq 1{\cdot}0$, $\text{N–H}\simeq 0{\cdot}95$, $\text{O–H}\simeq 0{\cdot}90$ Å (with standard deviations of 0·05 Å) and near-neighbor distances such that approximately tetrahedral geometry was insured. For the water molecule, only O–H and H–H distances were constrained so the orientation of the molecule was free to vary. Isotropic hydrogen thermal parameters were held constant at 10·0 Å^2. This model gave $R=0{\cdot}0374$ and $R_w=0{\cdot}0435$.

To determine whether the correct absolute configuration has been chosen, the signs of all $\Delta f''$ were reversed and the least-squares calculation was repeated. This calculation gave $R=0{\cdot}0374$ and $R_w=0{\cdot}0434$, and the ratio of R_w for the two refinements is 1·002. With about 2400 degrees of freedom and one parameter (the sign of $\Delta f''$), the difference between the two cases is significant at the 99·5% confidence level if the ratio exceeds 1·0017 (Hamilton, 1965).

The initial absolute configuration that had been selected was therefore probably wrong, and the signs of all coordinates were thus changed. The final refinement was made with fixed isotropic hydrogen thermal parameters of 1·0 Å^2, plus the anisotropic parameters of the atom to which the hydrogen atoms were bonded, and gave $R=0{\cdot}0375$ and $R_w=0{\cdot}0434$.

The final parameters are given in Table 3, and the observed and calculated structure factors are listed in Table 2. The quantity minimized in the least-squares calculations is $\sum w(F_o-KF_c)^2$, where $w=1/\sigma^2(F_o)$ is the weight derived from equation (1) (Stout & Jensen, 1968), K is a scale factor, and F_c is the ordinary calculated structure factor. Extinction was small and was ignored. For unobserved reflections $w=0$. Anisotropic thermal parameters were in the form:

$$\exp\left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})\right].$$

Scattering factors for copper and nitrogen were from Doyle & Turner (1968), for hydrogen from Stewart, Davidson & Simpson (1965), and a Hartree–Fock valence state scattering factor was used for carbon (Cromer, 1968). Both $\Delta f'$ and $\Delta f''$ were used for all atoms (Cromer & Liberman, 1970).

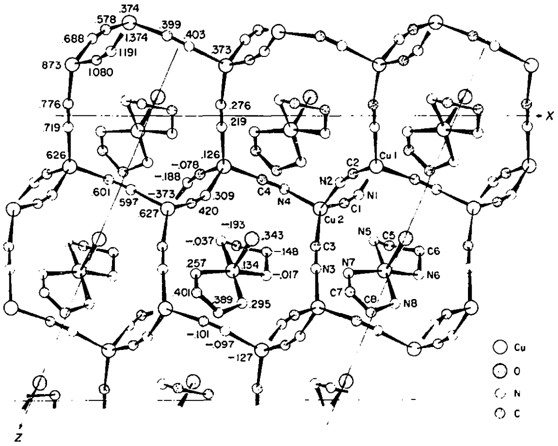


Fig. 1. View of the structure of $Cu_3(en)_2(CN)_4.H_2O$ down the b axis. Numbers beside some atoms are the y coordinates.

Table 3. *Positional and thermal parameters* $\times 10^4$ *with standard deviations for* $Cu_3(en)_2(CN)_4.H_2O$

The x and z for Cu(1) were arbitrarily chosen to fix the origin.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	3127	1263 (1)	1783	39 (1)	156 (1)	43 (1)	15 (1)	30 (1)	38 (1)
Cu(2)	1873 (1)	6265 (1)	3217 (1)	42 (1)	150 (1)	42 (1)	−16 (1)	31 (1)	−32 (1)
Cu(3)	4818 (1)	1335 (1)	5512 (1)	25 (1)	127 (1)	33 (1)	−2 (1)	16 (1)	8 (1)
C(1)	2580 (3)	4199 (6)	3061 (3)	31 (2)	114 (6)	37 (2)	−1 (6)	15 (3)	1 (6)
C(2)	2480 (3)	−0784 (6)	2041 (3)	38 (2)	101 (6)	40 (2)	−25 (6)	21 (4)	4 (6)
C(3)	2237 (3)	2759 (6)	−0409 (3)	36 (2)	140 (7)	32 (2)	33 (6)	29 (3)	28 (6)
C(4)	−0435 (3)	6009 (5)	2244 (3)	31 (2)	114 (7)	34 (2)	9 (5)	26 (3)	5 (5)
N(1)	2927 (3)	3092 (6)	2775 (4)	43 (2)	144 (7)	51 (2)	18 (9)	35 (4)	−6 (7)
N(2)	2174 (4)	−1883 (6)	2369 (3)	45 (2)	168 (8)	46 (2)	−6 (7)	35 (4)	−3 (7)
N(3)	2520 (3)	2194 (6)	5400 (3)	40 (2)	159 (7)	42 (2)	17 (6)	33 (3)	26 (6)
N(4)	0409 (3)	5973 (5)	2577 (3)	36 (2)	148 (7)	37 (2)	−0 (6)	29 (3)	−17 (6)
C(5)	4641 (5)	−1933 (8)	4585 (5)	70 (4)	171 (10)	67 (4)	−75 (11)	59 (6)	−68 (10)
C(6)	5685 (5)	−1483 (8)	4822 (4)	66 (4)	171 (10)	44 (3)	36 (9)	42 (5)	−16 (8)
C(7)	3967 (7)	4012 (11)	6242 (9)	68 (5)	256 (17)	145 (9)	74 (15)	92 (11)	−91 (20)
C(8)	4930 (8)	3892 (12)	6974 (8)	88 (6)	322 (22)	114 (8)	68 (18)	50 (11)	−219 (21)
N(5)	4057 (3)	−0373 (6)	4445 (3)	40 (2)	161 (8)	47 (2)	−58 (7)	9 (4)	−8 (7)
N(6)	5985 (3)	−0168 (5)	5624 (3)	35 (2)	119 (6)	36 (2)	15 (5)	26 (3)	20 (5)
N(7)	3652 (3)	2575 (7)	5572 (4)	35 (2)	214 (9)	59 (3)	52 (7)	41 (4)	64 (8)
N(8)	5599 (3)	2955 (6)	6639 (4)	40 (2)	122 (7)	59 (3)	12 (6)	14 (4)	−21 (6)
O	5046 (3)	3430 (5)	4343 (3)	43 (2)	198 (7)	51 (7)	34 (6)	42 (4)	34 (6)

Table 3 (*cont.*)

Hydrogen atom positions × 10^3
$B=1·0$ Å^2 + anisotropic parameters of bonded atom.

	x	y	z	Bonded atom
H(1)	469	−240	522	C(5)
H(2)	442	−258	401	C(5)
H(3)	611	−242	512	C(6)
H(4)	571	−089	424	C(6)
H(5)	355	444	643	C(7)
H(6)	429	467	580	C(7)
H(7)	480	287	741	C(8)
H(8)	514	481	734	C(8)
H(9)	394	003	378	N(5)
H(10)	347	−071	449	N(5)
H(11)	646	050	556	N(6)
H(12)	615	−074	625	N(6)
H(13)	331	180	586	N(7)
H(14)	324	292	494	N(7)
H(15)	611	252	718	N(8)
H(16)	584	382	630	N(8)
H(17)	551	349	410	O
H(18)	448	380	387	O

Table 4. *Bond distances and angles in* $Cu_3(en)_2(CN)_4.H_2O$, *uncorrected for thermal motion*

Cu(1)-C(2)	1·959 (4) Å	C(2)—Cu(1)-C(4)	113·4 (2)°
-C(4)	1·977 (4)	C(2)—Cu(1)-N(1)	102·4 (2)
-N(1)	2·103 (5)	C(2)—Cu(1)-N(3)	114·8 (2)
-N(3)	1·964 (4)	C(4)—Cu(1)-N(1)	104·8 (2)
Cu(2)-C(1)	1·971 (5)	C(4)—Cu(1)-N(3)	112·8 (2)
-C(3)	1·973 (4)	N(1)—Cu(1)-N(3)	107·5 (2)
-N(2)	2·033 (5)	C(1)—Cu(2)-C(3)	118·0 (2)
-N(4)	2·012 (4)	C(1)—Cu(2)-N(2)	105·1 (2)
Cu(3)-N(5)	2·004 (4)	C(1)—Cu(2)-N(4)	112·5 (2)
-N(6)	2·034 (4)	C(3)—Cu(2)-N(2)	106·4 (2)
-N(7)	2·004 (4)	C(3)—Cu(2)-N(4)	109·2 (2)
-N(8)	2·017 (4)	N(2)—Cu(2)-N(4)	104·7 (2)
-O	2·441 (4)	N(5)--Cu(3)-N(6)	83·9 (2)
N(5)—C(5)	1·454 (9)	N(5)--Cu(3)-N(7)	96·2 (2)
N(6)—C(6)	1·469 (7)	N(6)--Cu(3)-N(8)	94·9 (2)
N(7)—C(7)	1·424 (11)	N(7)—Cu(3)-N(8)	84·5 (2)
N(8)—C(8)	1·448 (10)	N(5)—Cu(3)-O	96·5 (2)
C(5)—C(6)	1·488 (10)	N(6)—Cu(3)-O	97·2 (2)
C(7)—C(8)	1·408 (14)	N(7)—Cu(3)-O	92·8 (2)
C(1)—N(1)	1·152 (7)	N(8)—Cu(3)-O	87·4 (2)
C(2)—N(2)	1·145 (7)	N(1)--C(1)—Cu(2)	166·6 (4)
C(3)—N(3)	1·153 (5)	N(2)--C(2)--Cu(1)	167·6 (4)
C(4)—N(4)	1·152 (5)	N(3)--C(3)—Cu(2)	175·1 (4)
C(5)—H(1)	0·96	N(4)--C(4)—Cu(1)	173·8 (4)
C(5)—H(2)	0·91	C(1)—N(1)—Cu(1)	159·7 (4)
C(6)—H(3)	0·95	C(2)—N(2)—Cu(2)	168·3 (4)
C(6)—H(4)	0·96	C(3)—N(3)—Cu(1)	174·6 (4)
C(7)—H(5)	0·83	C(4)—N(4)—Cu(2)	171·8 (4)
C(7)—H(6)	1·05	Cu(3)-N(5)—C(5)	108·4 (3)
C(8)—H(7)	1·07	Cu(3)-N(6)—C(6)	110·1 (3)
C(8)—H(8)	0·87	Cu(3)-N(7)—C(7)	109·9 (4)
N(5)—H(9)	0·94	Cu(3)-N(8)—C(8)	108·8 (5)
N(5)—H(10)	0·92	N(5)--C(5)—C(6)	110·2 (5)
N(6)—H(11)	0·91	N(6)--C(6)—C(5)	108·3 (5)
N(6)—H(12)	0·94	N(7)--C(7)—C(8)	114·9 (6)
N(7)—H(13)	0·97	N(8)--C(8)—C(7)	114·4 (7)
N(7)—H(14)	0·92		
N(8)—H(15)	0·91		
N(8)—H(16)	0·96		
O——H(17)	0·88		
O——H(18)	0·90		

Discussion

A list of interatomic distances and angles is given in Table 4. A view of the structure along the *b* axis is shown in Fig. 1. The structure consists of a polymeric $[Cu_2(CN)_4^{2-}]_\infty$ anion composed of a three-dimensional array of copper(I) ions linked tetrahedrally by cyanide ions to form a cage-like array. The holes in this array are occupied by discrete aquobis(en)copper(II) cations, as shown best in Fig. 2 which is a stereo view of the structure along the *b* axis. For clarity, only one cation is shown in Fig. 2.

In the cation, the coordination about the copper(II) is square pyramidal with two ethylenediamine molecules occupying basal positions and with the water molecule at the apex. A stereo view of the cation is shown in Fig. 3. The four nitrogen atoms in the basal plane are somewhat puckered and lie alternately 0·055 Å above and below their least-squares plane. The copper atom is 0·105 Å from the plane and the oxygen atom is 2·442 Å from the copper atom and on the same side of the plane as the copper atom. The Cu(II)–N bonds, which average 2·014 Å (before corrections), are within the normal range (Brown, Lee & Melsom, 1968; Brown & Lingafelter, 1964; Morosin, 1969).

C(5) is 0·44 Å and C(6) is 0·17 Å from the Cu(3), N(5), N(6) plane. C(7) is 0·17 Å and C(8) is 0·21 Å from the Cu(3), N(7), N(8) plane. Most of the apparent bond lengths in the ethylenediamine groups are short, particularly the C(7)–C(8) bond, and deserve comment. All of the carbon atoms have large motions normal to the plane of the nitrogen atoms. These motions suggest that the ethylenediamine groups are disordered or that there is a dynamic flipping of the carbon atoms across the appropriate Cu–N–N plane. These two possibilities cannot be distinguished in the diffraction data, but in either case the effect on the apparent bond length is the same and corresponds closely to the upper limit model of two atoms having displacement components perpendicular to the bond and 180° out of phase (Johnson, 1970). Before applying these corrections, it is appropriate to subtract the motion of the copper atom from the other atoms. The corrected interatomic distances in the cation and the basis for the correction are given in Table 5. For atoms bonded directly to the copper atom, corrections based on either a riding model or a rigid-body model are intuitively satisfactory and lead to essentially the same small corrections. The upper limit model for the C–C bond corrections has produced a reasonable result for the C(5)–C(6) bond but has somewhat overcorrected the C(7)–C(8) bond. It is difficult to choose a correction model for the C–N distances. If the dynamic or static flipping of the group is correct, the C–N bond is in a sense rotating about an axis through the nitrogen atom. The actual C–N bond lengths probably lie somewhere between the lower limit and the riding model.

The anion network alone has a pseudocenter of symmetry and the origin has been chosen to emphasize

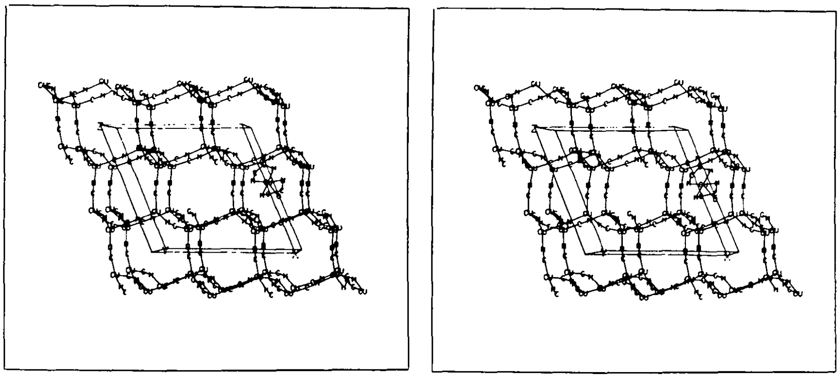


Fig. 2. Stereo view of the structure of $Cu_3(en)_2(CN)_4.H_2O$ looking approximately along the *b* axis. Only one cation is shown.

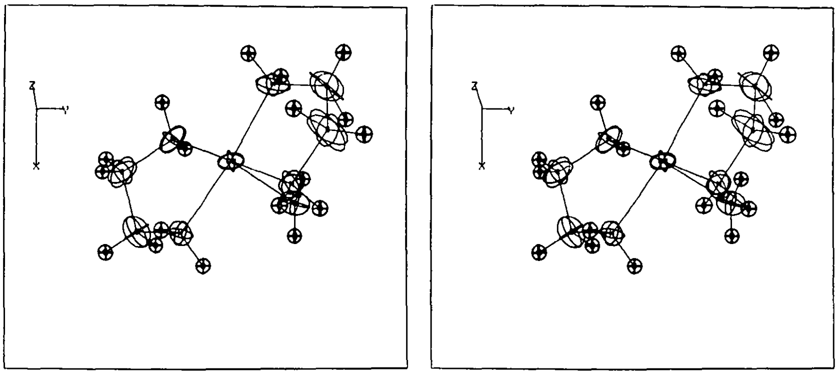


Fig. 3. Stereo view with thermal ellipsoids, of the $Cu(en)_2.H_2O^{2+}$ cation.

this fact. This pseudocentric structure probably accounts for the small difference in R_w, when the absolute configuration was changed. The atoms C(1) and C(2) are closely related by the pseudocenter, as are the atoms N(1) and N(2), and C(3) and N(3). Also, the two Cu(I) ions and the atoms C(4) and N(4) are related by a pseudo twofold axis at $x\simeq 0$ and $z\simeq\frac{1}{4}$. There is a pseudo 2_1 screw axis at $x\simeq\frac{1}{4}$ and $z\simeq\frac{1}{4}$. If the anion network were by itself and in space group $C2/c$, cyanide groups 3 and 4 would have to be disordered. The difference between the Cu–C and Cu–N distances for groups 3 and 4 is markedly less than for the other two cyanide groups, and Cu(2)–C(3) is even slightly greater than Cu(1)–N(3). Because of the pseudosymmetry, cyanide groups 3 and 4 might well be randomly ordered. The bond lengths tend to support the concept of disorder, although the electron counts, as mentioned earlier, support the ordered structure. Quite apart from the pseudosymmetry of the anion, it should also be noted that N(5) and N(6) in one of the ethylenediamine groups are closely related by the pseudo twofold axis.

It is rather surprising to find the polar cation filling the holes in the anion network in an ordered manner. Within experimental error, the anion network is centrosymmetric provided that CN(3) and CN(4) are disordered. There are two orientations of the cation, related by a center of symmetry, which lead to the same packing. However, there is no evidence in the Patterson map suggesting that the copper atom of the cation is in a half-filled site in the centric space group $C2/c$. The indirect argument might then be made that because the polar cation is ordered, the anion must also be ordered and is therefore not centrosymmetric.

The water molecule is quite isolated. The only suggestion of a hydrogen bond is O–H(18)–N(1) for which the O–N(1) distance is 3·09 Å, the H(18)–N(1) distance is 2·34 Å, and the angle is 141°.

Calculations were performed on CDC-6600 and 7600 computers using programs developed at this laboratory, except for the rigid-body program for which we are indebted to K. N. Trueblood.

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Table 5. *Bond distances in the* Cu(II)(en)$_2$.H$_2$O *cation, corrected for thermal motion*

For C–C bonds the motion of the copper atom has been subtracted from the carbon atoms.

Bond	Uncorrected	Lower limit	Riding	Rigid body	Upper limit
Cu(3)–N(5)	2·004 Å	2·005 Å	2·015 Å	2·014 Å	
Cu(3)–N(6)	2·034	2·034	2·036	2·042	
Cu(3)–N(7)	2·004	2·006	2·017	2·012	
Cu(3)–N(8)	2·017	2·018	2·026	2·027	
Cu(3)–O	2·441	2·442	2·449	2·450	
C(5)—N(5)	1·454	1·456	1·463	1·458	
C(6)—N(6)	1·469	1·478	1·486	1·475	
C(7)—N(7)	1·424	1·445	1·465	1·429	
C(8)—N(8)	1·448	1·469	1·499	1·452	
C(5)—C(6)	1·488	1·491		1·492	1·528 Å
C(7)—C(8)	1·408	1·408		1·411	1·586

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The Crystal Structure of Tin(II) Sulphate

By J. D. Donaldson and D. C. Puxley

Department of Chemistry, Chelsea College of Science and Technology, Manresa Road, London, S.W.3., *England*

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Tin(II) sulphate, $SnSO_4$, crystallizes in the orthorhombic system, space group *Pnma*, with four formula units in a cell with $a=8·799$, $b=5·319$, $c=7·115$ Å. The intensities of 418 independent reflexions were obtained by counter methods and the structure refined by least-squares methods to a conventional *R* value of 4·4%. The structure consists of a framework of sulphate groups linked by O–Sn–O bridges. The tin(II) atoms have typical pyramidal three coordination with Sn–O bond distances of 2·27, 2·27 and 2·25 Å and O–Sn–O angles of 79·0, 77·1 and 77·1°.

Introduction

Rentzeperis (1962) described a crystal-structure determination of $SnSO_4$ on the basis of measurement of the intensities of 58 powder reflexions. This structure was based on the assumption that $SnSO_4$ had the barite structure (James & Wood, 1925) although it had previously been suggested by Donaldson & Moser (1960) that this was unlikely in view of the large difference in the ionic radii of Ba^{2+} and Sn^{2+}. This $SnSO_4$ structure, along with the other known tin(II) structures (Donaldson, 1967), has been used in the interpretation of ^{119}Sn Mössbauer data. (Donaldson & Senior, 1969) It is however important to have a more accurate knowledge of the details of the environment of the tin atoms in $SnSO_4$ and for this reason we have carried out a full single-crystal three-dimensional structure analysis on the material.

Experimental

The crystals of $SnSO_4$ which were prepared by Donaldson & Moser's (1960) method are not hygroscopic as previously reported.