Crystal, Molecular, and Electronic Structure of *catena*-μ-oxalato-ammine-copper(II)

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Crystals of formula $Cu(NH_3)(C_2O_4)$, obtained from very dilute ammonia solutions of copper(II) oxalate, are orthorhombic, space-group *Pbca*, with $a = 11{\cdot}19(1)$, $b = 9{\cdot}43(1)$, $c = 8{\cdot}38(1)$ Å, $Z = 8$. The structure was refined by least-squares methods using 587 independent reflections, collected on a diffractometer, to a conventional *R* of 0·050. The structure is polymeric and co-ordination around copper is distorted square bipyramidal, with the ammonia molecule bonding in the more strict co-ordination plane. One oxygen of an oxalate group functions as a bridge between two atoms of copper, and this gives rise to strong antiferromagnetism, the magnetic moment at 302 K being 1·46 and at 94·5 K 0·53 BM. A superexchange mechanism operating through these oxygen atoms is invoked to explain this and a value for *J* of *ca.* -265 cm^{-1} is obtained. E.s.r. spectra of powders confirm this behaviour, and do not show the resonance at 3·1 cm characteristic of binuclear species such as copper(II) acetate. No bands other than those expected for the copper(II) chromophore itself could be found in the reflectance and single-crystal optical spectra. These latter could be interpreted in terms of *ca.* D_{4h} symmetry, and it is found that the $^2A_{1g} \leftarrow {}^2B_{1g}$ transition lies at rather low energy, as expected from the relatively short axial copper(II)–oxygen bond lengths. Solution optical spectra indicate the possible existence of binuclear species.

COPPER(II) oxalate hemihydrate forms many complexes with ammonia, *e.g.* those having five, four, and two molecules[1] of ammonia. The diammines have been shown to exhibit different co-ordination around the copper ion due to differing co-ordination modes of the oxalate ion.[2] The very early literature[3] mentions the existence of the last member of the oxalate series, $Cu(NH_3)(C_2O_4)$, and we have confirmed this. There are few reports on copper(II) complexes containing only one molecule of ammonia, although it is believed that decomposition of $Cu(NH_3)_5Cl_2$ leaves the monoammine complex as a final product.[4] On the basis of spectroscopic results and magnetic moments alone it is difficult to assign a structure to the monoammine oxalate, and the crystal structure has therefore been determined.

EXPERIMENTAL

Freshly prepared copper(II) oxalate hemihydrate (10 g) was added to ammonia solution (75 ml, *d* 0·88) and the blue solution boiled for 15 min, then set aside when the diammine was precipitated. The remaining solution was set aside overnight at 0 °C when pale blue crystals of $Cu(NH_3)_2(C_2O_4),2H_2O$ were obtained. The remaining pale blue-green solution was diluted with water (4 l) and set aside for 1 month. The blue-green crystals finally obtained were washed with ethanol and ether (Found: Cu, 37·5; C, 14·1; NH_3, 10·0. Calc. for $C_2H_3CuNO_4$: Cu, 37·7; C, 14·2; NH_3, 10·2%).

The crystals were flattened prisms, optically biaxial and pleochroic. When observed perpendicular to the flattening, they are light green or blue-green according to whether the electric vector vibrates parallel or perpendicular to the longest edge of the crystals [001]. Crystal

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[1] B. J. Hathaway and A. A. G. Tomlinson, *Co-ordination Chem. Rev.*, 1970, **5**, 1.

[2] H. Langfelderova, J. Garaj, and J. Gazo, *Proc. XIII Internat. Conf. Co-ordination Chem.*, Kraków, Poland, 1970, **11**, 75.

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data were determined from rotation and Weissenberg photographs and refined on a single-crystal automated Siemens diffractometer.

Crystal Data.—$C_2H_3CuNO_4$, $M = 168{\cdot}6$, Orthorhombic, $a = 11{\cdot}19(1)$, $b = 9{\cdot}43(1)$, $c = 8{\cdot}38(1)$ Å, $U = 884$ Å^3, $D_m = 2{\cdot}50$, $Z = 8$, $D_c = 2{\cdot}53$, $F(000) = 664$. Space-group *Pbca*, from systematic absences. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å, $\mu(\text{Cu-}K_\alpha) = 64{\cdot}8$ cm^{-1}.

Intensity data were determined with the same diffractometer by use of Cu-K_α radiation and the ω—2θ scan technique ($2\theta_{\text{max.}} = 140°$). 840 Independent reflections were collected, of which 587 having $I > 2\sigma(I)$ were used in the analysis. After correction for Lorentz and polarisation effects, the structure amplitudes were put on the absolute scale using Wilson's method, which gave a mean isotropic thermal parameter of 3·6 Å^2.

Reflectance spectra were run on a Beckman DK 1A spectrophotometer using magnesium oxide as a standard. Crystal spectra were determined on a Shimadzu MPS 50L microspectrophotometer equipped with a Glan–Thompson prism and external beam balancing.

TABLE 1

Fractional atomic co-ordinates and temperature factors (Å^2) * with estimated standard deviations in parentheses

	x/*a*	*y*/*b*	*z*/*c*	*B* or B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	0·0758(1)	0·2372(1)	0·1236(2)	2·19(4)	1·23(4)	2·14(4)	0·03(4)	−0·07(4)	−0·23(4)
O(1)	−0·0800(5)	0·1454(5)	0·0709(6)	1·40(20)	0·65(17)	1·63(23)	0·33(18)	−0·05(20)	−0·29(16)
O(2)	0·0626(5)	0·3667(5)	−0·1167(7)	3·16(25)	0·68(18)	0·69(22)	0·86(19)	0·40(22)	−0·09(18)
O(3)	0·1458(5)	0·0622(5)	0·0231(6)	1·40(21)	0·72(18)	1·13(24)	−0·01(17)	−0·07(17)	0·07(16)
O(4)	−0·0033(5)	0·4160(5)	0·1892(6)	2·42(23)	0·65(19)	0·62(20)	0·13(17)	0·37(19)	−0·17(17)
N	0·2351(6)	0·3018(7)	0·1994(8)	1·42(28)	1·83(26)	1·11(27)	−0·76(22)	−0·15(24)	0·06(21)
C(1)	−0·0201(7)	0·5151(8)	0·0891(8)	1·66(31)	0·73(25)	0·65(35)	0·01(23)	0·35(25)	−0·26(22)
C(2)	0·0655(6)	−0·0233(7)	−0·0139(9)	1·35(31)	0·97(25)	0·21(28)	0·29(24)	−0·22(24)	0·15(21)
H(1)	0·250(11)	0·225(12)	0·263(14)	1·8(3·0)					
H(2)	0·292(10)	0·300(11)	0·125(14)	1·8(3·2)					
H(3)	0·217(11)	0·388(11)	0·238(15)	1·8(3·2)					

* The anisotropic thermal parameters are in the form: $\exp\left[-0{\cdot}25(h^2B_{11}a^{*2} + \ldots 2klB_{23}b^*c^*)\right]$.

I.r. spectra were determined on a Perkin-Elmer 251 (4000—300 cm^{-1}) and a Hitachi spectrometer (400—60 cm^{-1}), potassium bromide discs were used and there was no evidence of anion exchange.

Magnetic measurements down to liquid nitrogen temperature were performed using a Gouy balance, and were repeated several times. E.s.r. spectra were run on a Varian V 4502 using both polycrystalline samples and single crystals.

RESULTS

Determination of the Structure and Refinement.—The structure was solved by the heavy-atom technique starting from a three-dimensional Patterson calculation, when *R* was 21·4%. Refinement was then carried out with block-diagonal least-squares and unit weights down to *R* 5·3%. After the introduction of the weighting function:[5]

$$w^{-\frac{1}{2}} = [\text{total counts} + (0{\cdot}005 \times \text{intensity})^2]^{\frac{1}{2}}/(Lp\,.\,2\,.\,F_o)$$

R was only reduced to 5·1%. At this point a difference Fourier synthesis showed the positions of the three hydrogen atoms the inclusion of which improved *R* to 5·0%.

Table 1 shows the final atomic co-ordinates and thermal parameters. A Table of observed and calculated structure factors is listed in Supplementary Publication No. SUP 20247 (3 pp., 1 microfiche).* The atomic scattering factors used throughout the calculations were taken from ref. 6 for copper, oxygen, nitrogen, and carbon, and from ref. 7 for hydrogen. Computations were carried out on the CDC 6600 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale (Bologna) using programmes of Immirzi.[8]

Magnetic Properties and Spectra.—The compound is highly antiferromagnetic (Figure 1). The magnetic moment changes regularly from 1·46 at room temperature to 0·53 BM at 94·5 K suggesting there is no gross change in structure in this temperature range. From the broad maximum in the region of 240 K a value for the critical temperature (T_c) of 238 K was obtained. Measurements of the area under the e.s.r. signal confirm this behaviour. The e.s.r. spectrum changed from *g* $2{\cdot}151_2$ at 298 K to *g* $2{\cdot}140_4$ at 98 K (*Q*-band). At *X*-band (room temperature) two *g* values were found, $g_\parallel$ $2{\cdot}315_8$ and $g_\perp$ $2{\cdot}083_4$.

The reflectance spectrum of the compound shows a well defined band at 13·7 kK together with a very broad shoulder at 10·0 kK (Figure 2); no further absorption is observed up to 30 kK. This is considerably different from the spectrum of the preparative solution (the compound appeared to hydrolyse quite readily in water) which has a

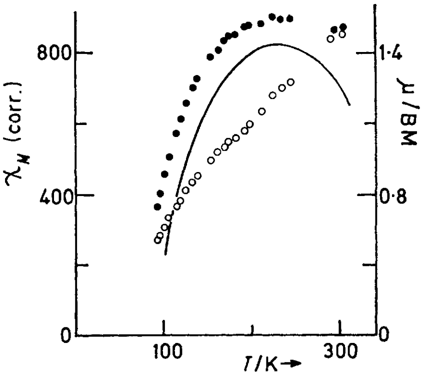

FIGURE 1 Magnetic behaviour with temperature: closed circles, experimental χ_M; open circles, magnetic moment; full line denotes area under e.s.r. curve (arbitrary units)

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. will be supplied as full size copies).

[5] R. C. G. Killean and J. L. Lawrence, *Acta Cryst.*, 1969, **B25**, 1750.

[6] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[7] F. H. Moore, *Acta Cryst.*, 1963, **16**, 1169.

[8] A. Immirzi, *Ricerca Sci.*, 1967, **37**, 743.

single asymmetric band at 15·2 kK with a shoulder at *ca.* 26 kK. Thus the co-ordination changes in solution, and the solution spectrum may be indicative of a solution structure of a dimeric type [copper(II) acetate monohydrate[9] has bands at *ca.* 15 and 27 kK in the optical spectrum]. Gaussian analysis of the reflectance spectrum (performed on a Du Pont 310 curve analyser, and open to the usual criticisms of this kind of resolution) shows three bands are probably present, at 8·5, 11·0, and 14·0 kK. Figure 2 also shows the partial polarised single-crystal spectrum.

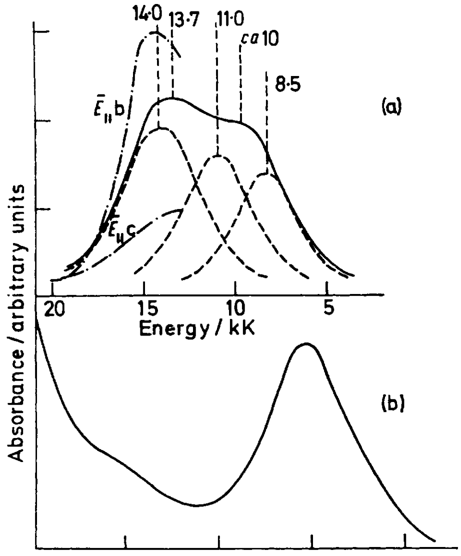


FIGURE 2 (a) Solid-state spectra: full line, reflectance spectrum; dashed line, gaussian analysis of reflectance spectrum; dash dot, partial polarised spectrum. (b) Spectrum of preparative solution

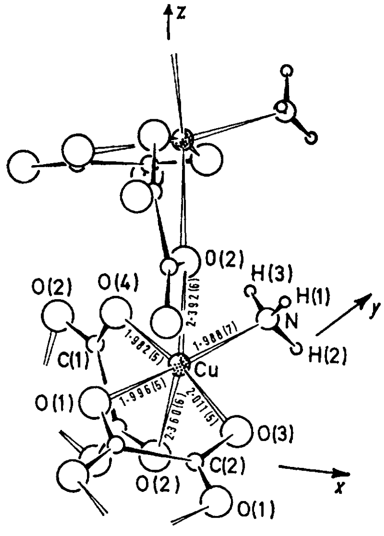
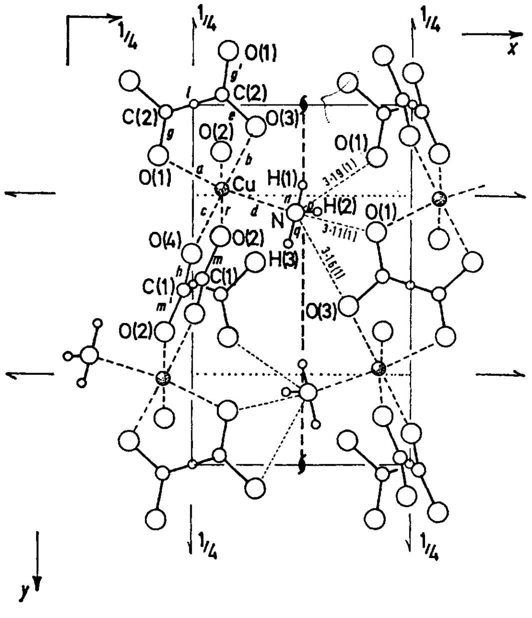


FIGURE 3 Clinographic projection of the structure

DISCUSSION

The structure determination has shown that the compound is not a binuclear polymer, *i.e.* of the copper(II) acetate type, although the strong antiferromagnetism might have suggested this to be the case.

Figures 3 and 4 show two projections of the structure. Co-ordination around the copper is distorted octahedral since it is surrounded by two oxygen atoms, O(1) and O(3), from an oxalate ion, a nitrogen atom from the ammonia molecule and by the oxygen atom, O(4), from an oxalate ion not equivalent to the first one. Co-ordination is not perfectly planar as there are tetrahedral displacements from the mean plane ranging from 0·10—0·16 Å.



Distances (Å)

a	1·996(5)	*h*	1·270(9)
b	2·011(5)	*l*	1·59(2)
c	1·982(5)	*m*	1·234(9)
d	1·988(7)	*n*	0·9(1)
e	1·246(9)	*p*	0·9(1)
f	1·55(2)	*q*	0·9(1)
g	1·257(8)	*r*	2·360(6)

Angles (deg.)

ab	83·8(2)	*ch*	120·6(5)
ac	92·3(2)	*hl*	116·6(6)
bd	92·1(3)	*lm*	116·6(6)
cd	92·9(2)	*hm'*	126·7(7)
cr	76·6(2)	*mr*	109·3(5)
ag	111·6(5)	*np*	105(10)
fg	116·1(6)	*nq*	123(10)
ef	117·5(6)	*pq*	115(10)
eg'	126·5(7)		
be	110·7(5)		

FIGURE 4 Projection of the structure on the (001) plane

Two oxygen atoms, O(2), related to one another by a *c* glide, co-ordinate to the metal ion in *trans*-positions with respect to the co-ordination plane and at a distance longer than the in-plane Cu–O distances. The axial oxygen atoms are in directions tilted with respect to the co-ordination plane: Cu · · · O(2) 78·2° and C · · · O(2^{I}) 87·2° (I denotes atom at x, $\frac{1}{2}-y$, $z+\frac{1}{2}$). The Cu–O distances found in the plane are not significantly

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[9] L. Dubicki and R. L. Martin, *Inorg. Chem.*, 1966, **5**, 2203.

different and agree with those generally found in copper(II) complexes of this type.[10] The two long Cu–O distances are in the lower part of the range of those generally found.

The chelate rings formed by the two oxalate ions are nearly perpendicular to one another, the dihedral angle between them being 94·2°. Both oxalate ions form bridges between adjacent octahedra linking them in layers parallel to (100). A further linkage between adjacent octahedra along (001) is formed by the O(2) atom which is shared by two adjacent copper atoms. These two linkages give rise to a polymeric structure. As observed in other oxalate structures (*e.g.* oxalic acid dihydrate,[11] deuteriated oxalic acid dihydrate,[12] and the double oxalate of yttrium and ammonium [13]) the gravity centres of the oxalate ions are centres of symmetry, so in the asymmetric unit there are two halves of these ions. The C–O distances are not significantly different, the double bond being delocalised in each carboxy-group as normally found in complexes containing ionised carboxy-groups. Both C–C distances are longer than the expected values and the differences are significant; similar differences have been observed.[14]

The ammonia molecule forms NH · · · O contacts joining the layers of the co-ordination polyhedra (Figure 4 and Table 2).

TABLE 2

$N \cdots O(1^{II})$	3·19(1) Å	$N-H(1)-O(1^{II})$	135°
$N \cdots O(1^{III})$	3·11(1)	$N-H(2)-O(1^{III})$	165
$N \cdots O(3^{IV})$	3·16(1)	$N-H(3)-O(3^{IV})$	125

Roman numerals as superscripts denote the following equivalent positions:

II $x + \frac{1}{2}, y, \frac{1}{2} - z$ IV $\frac{1}{2} - x, \frac{1}{2} + y, z$
III $x + \frac{1}{2}, \frac{1}{2} - y, \bar{z}$

Whether or not these contacts indicate the presence of hydrogen bonds is somewhat ambiguous, since they are in the upper part of the range for such NH · · · O hydrogen bonds (2·57—3·28 Å) [15] and also they are bent; one (NH · · · O 3·11 Å) is bifurcated. Consequently, the frequencies of the N–H stretching vibrations do not correlate very well with the curves of ν(NH) against bond distance.[16] However, since bent and bifurcated hydrogen bonds should show high- and low-frequency deviations, respectively, from this curve, it may be concluded that the i.r. spectra indicate only weak hydrogen bonding, in agreement with the crystal structure.

The rest of the i.r. spectrum is complex owing to interactions of skeletal and ligand modes below 900 cm^{-1} (Figure 5), consequently many of the assignments of Table 3 are tentative. ν(M–N) 415 and ν(M–O) (+def.) 455, 462 cm^{-1} seem reasonable,[1,17] but the bands at 265 and 285 cm^{-1} cannot be assigned with certainty, although they are probably δ(O–M–N), δ(O–M–O) modes. ν_{as}(M–O–M) where O–M–O is <180° may rise as high as *ca.* 850 cm^{-1},[18] but the only band which appears assignable to ν_{as}(Cu–O–Cu) is the doublet at 810, 798, which also contains δ(O–C=O).[17] Presumably this lies at lower frequency than other reported ν_{as}(M–O–M) values, because of the long axial Cu–O bonds.

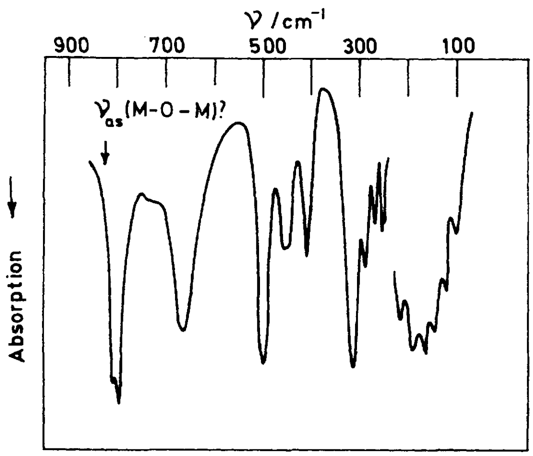

FIGURE 5 I.r. spectrum of $Cu(NH_3)(C_2O_4)$

The reflectance and single-crystal spectra show no bands other than those, between 10 and 14 kK, due to *d–d* transitions of the chromophore (Cu{NO_3 + 2O}).

TABLE 3

I.r. spectrum (cm^{-1})

3360s	ν(N–H)	810s	ν_{as}(Cu–O–Cu)?
3285s		798s	
3200m			
1712sh		663sb	ρ(Cu–NH_3)
1690sh			
ca. 1625sh	ν_{as}(C=O)	508s	δ(O–C=O)
1600s	δ_d(Cu–NH_3)	462	ν(Cu–O) + (def.)
		455	
1365s	ν_s(C–O) + ν(C–O)	414	ν(Cu–N)
1322s	δ_s(Cu–NH_3)	318	π($C_2O_4^{2-}$)
1307s			
1272	ν_s(C–O) + δ(O–C=O)	285sh	δ(O–Cu–N) + δ(O–Cu–O)
1261		265m	
		250m	

216, 193, 167, 145, 124, and 102 cm^{-1} are probably lattice modes; s = strong, sh = shoulder, b = broad, m = medium

This contrasts with the extra absorption at *ca.* 27 kK in dimeric Cu^{II} complexes, said to be characteristic of direct Cu–Cu interaction. It was not found possible to obtain polarised spectra in the 5—12 kK region because of the size of the crystals, so a complete analysis of the Cu^{II} site-symmetry [19] is not possible. However,

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[19] B. J. Hathaway and D. E. Billing, *Co-ordination Chem. Rev.*, 1970, **5**, 143.

the reflectance spectrum shows bands at energies in agreement with those of (Cu$\{O_4 + 2O\}$) systems,[20] which indicates that the spectrum may be treated as that due to an approximate D_{4h} symmetry, in which case a tentative assignment: $^2B_{1g} \rightarrow {}^2A_{1g}$ 8·5, $B_{1g} \rightarrow {}^2B_{2g}$ 11·0, and $B_{1g} \rightarrow {}^2E_g$ 13·7 kK is possible. The polarisation of the highest-energy band confirms that it is the $^2B_{1g} \rightarrow {}^2E_g$ transition. Even if the gaussian analysis is discarded the low energies of the bands indicate that the tetragonal distortion is low, *i.e.* that the axial oxygen atoms significantly influence the *d* orbital energies. Convincing evidence of the importance of the ' axial ' oxygen atoms is obtained from the magnetic susceptibility measurements. Assuming that the structure remains basically the same over the temperature range studied, the antiferromagnetism must be explained by invoking superexchange effects either through the 165·4° bridging oxygen atom or through the oxalate ions, or both. Presumably, the oxygen bridge bonding is predominant in causing superexchange since the carbon atoms of the oxalate group would be expected to ' cushion ' the flow of electron density between Cu^{II} ions. Furthermore, it would be expected that the 94° tilting angle between oxalate groups coordinated to the same metal would be unfavourable for $p_\pi(O)$–$d_{xz,yz}$(Cu) overlap. By use of the approximate equation [21]: $J = 1\cdot6\ kT_c$, a value for J of *ca.* -265 cm^{-1} is obtained (negative since the interaction is antiferromagnetic). This is of the same order as that found both for dimers containing short Cu–Cu distances, such as copper(II) acetate [21] itself, and also of those having longer Cu–Cu distances.[22] The results suggest that a low magnetic susceptibility in the case of copper(II) carboxylate complexes, is not, in itself, indicative of a binuclear structure.

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[1/762 *Received, May* 13*th*, 1971]

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