An Investigation of the Interaction Between Copper(II) Ion, Oxalyldihydrazide, and Molecular Oxygen: Crystal and Molecular Structures of Products resulting from the Addition of an Excess of Acetaldehyde

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The end products of the reaction between copper(II) ion, an oxalyldihydrazide, ammonia, and excess of acetaldehyde, in air, have been isolated for oxalyldihydrazide itself and *N*-phenyloxalyldihydrazide. The two products are purple (I) and green (II) respectively and show very high absorption (ε 20 000—30 000 $dm^3\ mol^{-1}\ cm^{-1}$) in the visible region of the spectrum. *X*-Ray analysis reveals that (I) crystallises in the monoclinic system [a = 9.373(2), b = 14.34(2), c = 26.129(4) Å, β = 102.25(1)° with space group $P2_1/c$] whereas the latter is orthorhombic [a = 16.331(2), b = 15.319(2), c = 15.336(4) Å with space group $Cmc2_1$]. Both crystal structures contain anionic complex ions which have cage-like structures resulting from ring-closing reactions with acetaldehyde. The structures were solved from diffractometer data by the heavy-atom-method and refined by least-squares techniques to R 0.088 (1 836 reflections) and 0.077 (1 184 reflections).

DURING a study of the reactions of oxalyldihydrazide Nilsson[1,2] observed that a number of its condensation products with aldehydes and ketones reacted with copper salts to give a very intense blue colour. The reaction did not occur with aromatic carbonyls but was so striking with aliphatic members as to lead to the use of cyclonexanone–oxalyldihydrazide as an analytical reagent for trace amounts of copper. Apart from its sensitivity an advantage lay in the specificity of the reagent. Later it was realised that in the presence of excess of aldehyde, but not ketone, the blue colour became an even more intense purple with an unusually high molar absorption coefficient, reported[3] as ε 29 500 $dm^3\ mol^{-1}\ cm^{-1}$ at 515 nm. Subsequently there have been a number of studies of this system aimed at identifying species and the conditions necessary for their formation. Various structures have been suggested for the coloured products involving the tautomeric state of the carbonyl[4] and imine functions,[1] the choice of donor atoms[5] and geometrical isomerism.[6] Frieden[7] reported that molecular oxygen was also involved in the reaction since the intense colours only appeared in its presence. The reaction with dioxygen was said to be reversible. This work was further in disagreement with some earlier reports in claiming that the number of acetaldehyde residues needed in the formation of the blue species was four rather than two. The structure suggested by Frieden for this compound is of interest in that it includes a dioxygen ligand as part of a bis-co-ordinate copper(II) complex. More recently the purple complex formed by the addition of excess acetaldehyde has been formulated as also containing molecular oxygen.[3]

Interest in the role of metal ions in biological processes and the inference that the oxalyldihydrazide complexes are not only oxygen carriers but also show intense electronic absorption in the visible region reminiscent of 'blue' cuproproteins[8] has led us to a further investigation of this system. We report here the results of *X*-ray structural examinations of a purple complex (I) prepared from oxalyldihydrazide and acetaldehyde and of a green complex (II) prepared from *N*-phenyloxalyldihydrazide.

EXPERIMENTAL

Both compounds were prepared in a similar manner by mixing a hot aqueous solution of oxalyldihydrazide (or the *N*-phenyl derivative) with an ammoniacal solution of copper(II) perchlorate followed, after cooling, by the addition of excess of acetaldehyde. In the presence of air the reactions led to a purple (or green) product. Crystals of the purple compound (I) suitable for *X*-ray work were difficult to obtain but some resulted from a vapour diffusion process by use of propan-2-ol and dichloromethane. The green product (II) crystallised more readily by slow evaporation of an ammoniacal solution.

A number of subsidiary experiments were undertaken during the course of the *X*-ray analysis for reasons which will become obvious and these established that both compounds contained ammonium ions (i.r. bands at 1 400 and 3 175 cm^{-1} and liberation of ammonia by alkali), that both complex species were anionic (electrophoresis), and that the purple complex (I) also contained perchlorate ions (i.r. bands at 630 and 1 100 cm^{-1}). Compound (I) gave no chemical tests for a secondary amine (nitrous acid, Hinsberg reagents) nor did it reveal a ν(NH) band in the i.r. after the ammonium ions were exchanged for sodium. A large band at 3 400 cm^{-1} remained however; this was undoubtedly due to the presence of water in the crystal. Elemental analysis, after mild drying, was consistent with $[NH_4]_2[CuC_{16}H_{24}N_8O_6\cdot H_2O]\cdot\frac{3}{4}NH_4ClO_4$ a formulation which only became clear from the *X*-ray analysis (Found: C, 31.05; H, 5.65; N, 22.7%. $C_{16}H_{34}CuN_{10}O_7\cdot\frac{3}{4}NH_4ClO_4$ requires C, 29.80; H, 5.62; N, 23.33%). Elemental analysis of the green product was consistent with the formulation $[NH_4]_2[CuC_{24}H_{26}N_8O_5\cdot H_2O]\cdot 4H_2O$ (Found: C, 41.15; H, 6.2; N, 19.4%. $C_{24}H_{44}CuN_{10}O_{10}$ requires C, 41.41; H, 6.37; N, 20.12%).

Crystal Data.—Purple Complex, (I). $C_{16}H_{34}CuN_{10}O_7\cdot$

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[1] G. Nilsson, *Acta Chem. Scand.*, 1950, **4**, 205.

[2] G. Nilsson, *Z. analyt. Chem.*, 1956, **153**, 161.

[3] J. F. Boas, J. R. Pilbrow, C. J. Troup, C. Moore, and T. D. Smith, *J. Chem. Soc.* (*A*), 1969, 965.

[4] E. Jacobsen, F. J. Langmhyr, and A. R. Selmer-Olsen, *Analyt. Chim. Acta*, 1961, **24**, 579.

[5] A. Comte, J. Podu, A. Boucherle, and A. Badinand, *Bull. Trav. Soc. pharm. Lyon*, 1961, **4**, 1021.

[6] A. Badinand and J. J. Vallon, *Chim. analyt.*, 1966, **48**, pp. 313, 396.

[7] E. Frieden, in 'Oxidases and Related Redox Systems,' eds. T. E. King, H. S. Mason, and M. Morrison, vol. 1, 1965, Wiley, New York.

[8] R. J. P. Williams, in 'The Biochemistry of Copper,' eds. J. Peisach, P. Aisen, and W. E. Blumberg, Academic Press, London, 1966.

$5H_2O\cdot\frac{3}{4}NH_4ClO_4$ (from subsequent *X*-ray analysis), M = 720.3, Monoclinic, a = 9.373(2), b = 14.34(2), c = 26.129(4) Å, β = 105.25(1)° (from least-squares fit to the diffractometer co-ordinates of 12 reflections in θ range of 24—35°), U = 3 388 Å^3, D_m = 1.45 (by flotation), Z = 4, D_c = 1.43. Cu-K_α radiation, λ = 1.5418 Å; μ(Cu-K_α) = 22.7 cm^{-1}. Space group $P2_1/c$.

Data were collected to θ 50° on a plate-like crystal bounded by the (100), ($\bar{1}$00); (010); (0$\bar{3}$2); (001), and (00$\bar{1}$) faces which had dimensions of 0.06 × (0.23—0.31) × 0.023 mm in the *a*, *b*, and *c* directions. A Hilger-Watts four-circle computer-controlled diffractometer was used in the 2θ—ω step-scan mode covering 90 increments of 0.01° (*i.e.* 1.80° in 2θ) at 1 s intervals. Backgrounds were counted for 15 s on either side of the sweep. The primary beam collimator was 0.5 mm in diameter and the diffracted beam aperture 3.5 mm. The intensities of standard reflections 2,2,2, $\bar{3}$,1,7, and 3,1,5 monitored periodically, remained within 3% of their respective initial values. Of 3 684 independent reflections examined, 1 836 having intensity $\geqslant 2.5\sigma(F^2)$ were subsequently employed in structure solution. The standard deviation, σ, is related to the total counts, I, the background counts, B_1 and B_2, and the counting times t, t_1, and t_2, by the relation $\sigma(F^2) = \{I + (t/(t_1 + t_2))^2(B_1 + B_2) + (pI)^2\}^{\frac{1}{2}}$. The parameter,[9] p, was set at 0.05. After adjustment for Lorentz and polarisation effects data were finally corrected for absorption by the analytical method of Busing and Levy [10] after the composition of the material had become clear from initial structure solution with uncorrected amplitudes.

Crystal Data.—Green complex, (II). $C_{24}H_{36}CuN_{10}O_6\cdot H_2O$, M = 804.3, Orthorhombic, a = 16.331(2), b = 15.319(2), c = 15.336(4) Å (from least-squares fit to diffractometer co-ordinates of 12 reflections in θ range 11—17°), U = 3 837 Å^3, D_m = 1.43 (by flotation), Z = 4, D_c = 1.40. Mo-K_α radiation, λ = 0.710 7 Å; μ(Mo-K_α) = 6.9 cm^{-1}. Space group *Cmcm*, *Cmc*2$_1$, or *C*2*cm* (non-standard *Ama*2).

Data were collected from a crystal bounded by (110), ($\bar{1}\bar{1}$0); ($\bar{1}$10), (1$\bar{1}$0); (001), (00$\bar{1}$) which had dimensions 0.10 × 0.12 × 0.52 mm between pairs of faces. The 2θ—ω step scan was again used, this time over 70 increments of 0.1° at 1 s intervals. Backgrounds were counted for 15 s. The collimator sizes were as before, and the intensities of three standard reflections, 3,5,4, $\bar{7}$,7,1, and 6,6,0 monitored periodically as before, did not vary by >3%. All reflections *hkl* and $\bar{h}$*kl* were collected to a Bragg angle of 27° and then a weighted average obtained for 2 225 independent intensities, 1 184 being then $>2.5\sigma(F^2)$. The normal corrections were applied but later, when the composition of the crystal had become clear, data were also corrected for absorption effects.[10]

Structure Solutions.—(*a*) *Purple complex*, (I). The phase problem was solved by the conventional heavy-atom approach but the position of the copper atom at x = 0.065, y = 0.25, z = 0.146 nevertheless introduced interpretative problems because of the non-space-group symmetry in the initial electron-density map. The presence of the water molecules added to the confusion but after a number of trials a satisfactory atomic arrangement emerged. Block-diagonal least-squares refinement was then undertaken with a weighting scheme in the form $w = 4F^2/\sigma^2(F^2)$. Scattering factors were taken from ref. 11 for oxygen, nitrogen, carbon, and hydrogen and from ref. 12 for copper and chlorine, the values for the two last-named being corrected for the real part of the anomalous dispersion effect. As refinement progressed hydrogen atoms were added to the model of the complex anion at calculated positions after initial location on electron-density difference syntheses. They were assigned a common isotropic temperature factor of 5.0 Å^2 but anisotropic thermal parameters were assumed for the remaining atoms of the complex except for the oxygen of the co-ordinated water molecule. During the course of the refinement it became clear that the perchlorate ion did not have an occupancy factor of unity and it was assumed to have a weight of 0.75. Other discrete peaks, nine in number, were assigned as water molecules for refinement purposes, two of them, O(19) and O(20), having occupancy factors of 0.5. Three of them must, of course, be ammonium ions, one with an occupancy factor of 0.75, but it was not possible to make the distinction on crystallographic grounds. More pressing was the need to decide if the atoms of the complex ion labelled O(5) and O(6) were really oxygens. As will be seen from Figure 1 the heterocyclic structures formed in the reaction are unexpected and it is not immediately obvious what the atoms are likely to be. The crystallographic evidence is equivocal in that although O(5) and O(6) best fit an oxygen scattering curve, and do not have accompanying hydrogen peaks on a difference map, their distances from neighbouring carbons [1.49(2), 1.51(2) and 1.5((2), 1.54(2) Å] are much more indicative of carbon–nitrogen rather than carbon–oxygen bonds. The lack of chemical evidence for the presence of a secondary amine led us to conclude, however, that the atoms are indeed oxygens.

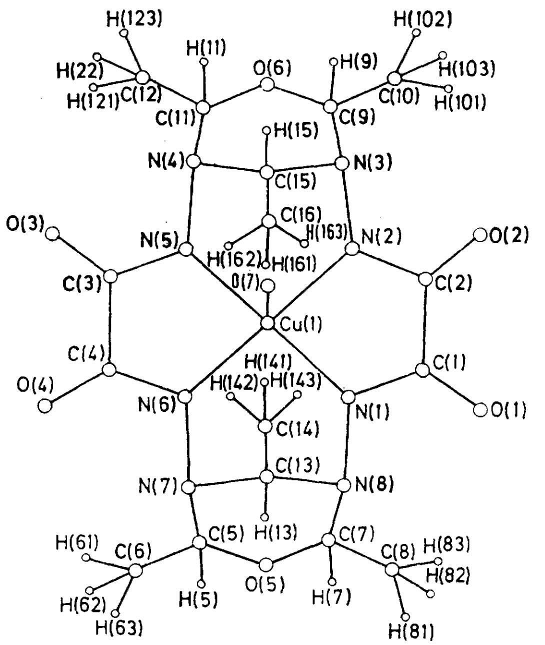

FIGURE 1 The numbering scheme for the cation of the purple complex, (I). Perchlorate oxygen atoms are numbered O(8)—(11), solvent oxygen atoms O(12)—(20)

The final *R* factor was 0.088. Atom co-ordinates are

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[9] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 197.

[10] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.

[11] 'International Tables for *X*-Ray Crystallography,' vol. III. 1962, Kynoch Press, Birmingham.

[12] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

listed in Table 1, calculated bond lengths and angles in Tables 2 and 3. The numbering scheme is shown in Figure 1. Structure-factor data and thermal parameters, together with those for the green complex, are listed in Supplementary Publication No. SUP 21690 (35 pp., 1 microfiche).*

TABLE 1

Positional parameters, with standard deviations in parentheses, for (I)

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Cu(1)	0.062 5(2)	0.239 07(14)	0.146 82(8)
C(1)	0.028 0(16)	0.368 9(11)	0.217 6(6)
C(2)	−0.075 3(17)	0.397 7(12)	0.164 8(6)
C(3)	0.174 9(18)	0.166 9(11)	0.071 2(6)
C(4)	0.280 6(17)	0.140 5(11)	0.123 2(6)
C(5)	0.272 5(17)	0.067 8(12)	0.240 2(6)
C(6)	0.250 6(21)	−0.019 6(14)	0.206 1(8)
C(7)	0.140 8(17)	0.177 8(11)	0.287 0(6)
C(8)	−0.003 4(20)	0.196 4(12)	0.297 8(7)
C(9)	−0.308 3(19)	0.294 9(12)	0.065 1(6)
C(10)	−0.394 0(20)	0.307 3(15)	0.105 5(7)
C(11)	−0.189 3(17)	0.178 0(12)	0.020 0(7)
C(12)	−0.153 4(20)	0.076 5(12)	0.015 8(7)
C(13)	0.334 8(16)	0.229 4(11)	0.250 5(6)
C(14)	0.403 2(20)	0.310 0(13)	0.228 3(7)
C(15)	−0.091 0(18)	0.336 2(12)	0.037 1(6)
C(16)	0.043 7(23)	0.396 5(14)	0.044 0(8)
N(1)	0.091 3(14)	0.285 2(9)	0.215 2(5)
N(2)	−0.081 9(13)	0.332 4(9)	0.127 9(4)
N(3)	−0.172 8(14)	0.349 0(9)	0.076 1(5)
N(4)	−0.053 6(14)	0.235 2(9)	0.031 7(5)
N(5)	0.051 6(13)	0.204 7(8)	0.077 7(4)
N(6)	0.231 6(13)	0.163 4(9)	0.163 9(5)
N(7)	0.321 0(14)	0.147 2(9)	0.214 9(5)
N(8)	0.195 5(13)	0.253 7(9)	0.261 0(4)
O(1)	0.043 2(12)	0.419 4(7)	0.257 4(4)
O(2)	−0.144 7(13)	0.470 3(8)	0.161 6(4)
O(3)	0.204 0(12)	0.147 7(9)	0.028 0(4)
O(4)	0.400 5(12)	0.103 8(8)	0.124 0(4)
O(5)	0.127 0(13)	0.088 7(9)	0.253 2(5)
O(6)	−0.275 8(13)	0.192 5(9)	0.059 7(5)
O(7)	−0.125 1(12)	0.101 9(8)	0.163 0(4)
Cl(1)	0.690 1(7)	0.055 7(5)	0.354 5(3)
O(8)	0.589(2)	0.002 9(21)	0.361 8(11)
O(9)	0.788(2)	0.009 4(16)	0.337 0(9)
O(10)	0.764(3)	0.095 8(19)	0.400 1(10)
Cl(11)	0.635(2)	0.127 9(16)	0.320 6(9)
O(12)	−0.345 0(17)	0.119 4(11)	0.208 8(6)
O(13)	0.187 7(14)	0.414 5(9)	0.361 3(5)
O(14)	0.039 6(25)	0.313 7(17)	0.423 9(9)
O(15)	0.496 6(20)	0.425 4(13)	0.403 4(7)
O(16)	0.201(3)	0.112 1(20)	0.425(11)
O(17)	0.470 2(17)	0.103 9(12)	0.009 5(6)
O(18)	−0.275 1(19)	0.310 2(13)	0.383 1(7)
O(19)	0.385(5)	0.465(4)	0.003 6(19)
O(20)	0.437(4)	0.187(3)	0.426 5(16)

(*b*) *Green complex*, (II). The three-dimensional Patterson map showed clearly that *Cmc*2_1 was the correct space group and on this assumption the co-ordinates of the copper atom were obtained as $x = 0$, $y = 0.354$, $z = 0$. Again, therefore, extra symmetry was injected into the initial heavy-atom electron-density map: in this instance in addition to the mirror plane already imposed on the molecule by the space group. Fortunately, a phenyl group was unambiguously identified and proved a helpful starting point for the correct allocation of atom positions. When the structure of the complex ion had been established, block-diagonal least-squares refinement was begun, with scattering curves and weighting scheme as described previously for (I). Electron-density maps were computed at appropriate stages and allowed the placing of six full-weighted and two half-weighted solvent molecules in the asymmetric unit. With R 0.116 a difference map allowed identification of the hydrogen atoms of the complex and these were then included in the model at calculated positions with an isotropic temperature factor of 5.0 Å^2. Refinement continued with anisotropic thermal parameters for the non-hydrogen atoms of the complex. The heterocyclic ring atom, O(3) of Figure 2, was found to be oxygen after application of the crystallographic

TABLE 2

Bond lengths (Å), with standard deviations in parentheses, for (I)

Cu(1)–N(1)	1.86(1)	C(9)–C(10)	1.50(2)
Cu(1)–N(2)	1.87(1)	C(9)–N(3)	1.45(2)
Cu(1)–N(5)	1.85(1)	C(9)–O(6)	1.51(2)
Cu(1)–N(6)	1.88(1)	C(11)–C(12)	1.50(2)
Cu(1)–O(7)	2.74(1)	C(11)–N(4)	1.48(2)
C(1)–C(2)	1.52(2)	C(11)–O(6)	1.49(2)
C(1)–N(1)	1.35(2)	C(13)–C(14)	1.51(2)
C(1)–O(1)	1.24(2)	C(13)–N(7)	1.49(2)
C(2)–N(2)	1.34(2)	C(13)–N(8)	1.45(2)
C(2)–O(2)	1.22(2)	C(15)–C(16)	1.50(2)
C(3)–C(4)	1.50(2)	C(15)–N(3)	1.44(2)
C(3)–N(5)	1.33(2)	C(15)–N(4)	1.51(2)
C(3)–O(3)	1.26(2)	N(1)–N(8)	1.41(2)
C(4)–N(6)	1.31(2)	N(2)–N(3)	1.42(2)
C(4)–O(4)	1.24(2)	N(4)–N(5)	1.41(2)
C(5)–C(6)	1.52(2)	N(6)–N(7)	1.40(2)
C(5)–N(7)	1.45(2)	Cl(1)–O(8)	1.26(3)
C(5)–O(5)	1.52(2)	Cl(1)–O(9)	1.31(2)
C(7)–C(8)	1.48(2)	Cl(1)–O(10)	1.34(3)
C(7)–N(8)	1.45(2)	Cl(1)–O(11)	1.37(2)
C(7)–O(5)	1.54(2)		

TABLE 3

Bond angles (°), with standard deviations in parentheses, for (I)

N(1)–Cu(1)–N(2)	85.0(8)	N(7)–C(13)–N(8)	112.1(12)
N(1)–Cu(1)–N(5)	172.5(11)	C(16)–C(15)–N(3)	115.4(13)
N(1)–Cu(1)–N(6)	94.4(9)	C(16)–C(15)–N(4)	110.9(13)
N(1)–Cu(1)–O(7)	92.6(8)	N(3)–C(15)–N(4)	111.7(11)
N(2)–Cu(1)–N(5)	94.7(9)	Cu(1)–N(1)–N(8)	126.8(5)
N(2)–Cu(1)–N(6)	169.1(11)	Cu(1)–N(1)–C(1)	114.1(6)
N(2)–Cu(1)–O(7)	96.0(7)	N(8)–N(1)–C(1)	117.4(12)
N(5)–Cu(1)–N(6)	84.5(8)	Cu(1)–N(2)–N(3)	125.7(5)
N(5)–Cu(1)–O(7)	94.9(8)	Cu(1)–N(2)–C(2)	114.6(7)
N(6)–Cu(1)–O(7)	94.9(6)	N(3)–N(2)–C(2)	118.3(13)
N(1)–C(1)–O(1)	127.1(14)	N(2)–N(3)–C(15)	110.8(12)
N(1)–C(1)–C(2)	112.4(12)	N(2)–N(3)–C(9)	112.0(12)
C(2)–C(1)–O(1)	120.4(12)	C(9)–N(3)–C(15)	113.2(13)
C(1)–C(2)–O(2)	119.7(13)	C(11)–N(4)–C(15)	110.2(12)
N(2)–C(2)–O(2)	128.9(16)	C(11)–N(4)–N(5)	112.0(12)
C(1)–C(2)–N(2)	111.3(12)	N(5)–N(4)–C(15)	110.2(12)
N(5)–C(3)–O(3)	127.3(16)	Cu(1)–N(5)–N(4)	126.7(5)
N(5)–C(3)–C(4)	112.0(12)	Cu(1)–N(5)–C(3)	114.1(7)
C(4)–C(3)–O(3)	120.6(13)	N(4)–N(5)–C(3)	117.0(13)
C(3)–C(4)–O(4)	120.2(13)	Cu(1)–N(6)–N(7)	125.6(5)
C(3)–C(4)–N(6)	112.5(12)	Cu(1)–N(6)–C(4)	114.0(7)
N(6)–C(14)–O(4)	127.2(16)	C(4)–N(6)–N(7)	119.0(13)
C(6)–C(5)–N(7)	113.1(12)	N(6)–N(7)–C(13)	113.4(12)
C(6)–C(5)–O(5)	107.6(12)	N(6)–N(7)–C(5)	112.6(12)
N(7)–C(5)–O(5)	110.7(11)	C(5)–N(7)–C(13)	108.9(12)
C(8)–C(7)–O(5)	108.5(12)	N(1)–N(8)–C(13)	112.1(12)
C(8)–C(7)–N(8)	114.2(13)	N(1)–N(8)–C(7)	112.9(12)
N(8)–C(7)–O(5)	110.0(13)	C(7)–N(8)–C(13)	110.9(13)
C(10)–C(9)–N(3)	113.7(12)	C(5)–O(5)–C(7)	110.3(12)
C(10)–C(9)–O(6)	109.9(12)	C(9)–O(6)–C(11)	111.2(12)
N(3)–C(9)–O(6)	110.5(11)	O(8)–Cl(1)–O(9)	111.7(15)
C(12)–C(11)–N(4)	110.9(12)	O(8)–Cl(1)–O(10)	110.7(16)
C(12)–C(11)–O(6)	111.0(12)	O(8)–Cl(1)–O(11)	112.5(15)
N(4)–C(11)–O(6)	112.0(11)	O(9)–Cl(1)–O(10)	106.6(17)
C(14)–C(13)–N(7)	110.0(12)	O(9)–Cl(1)–O(11)	109.5(16)
C(14)–C(13)–N(8)	112.6(12)	O(10)–Cl(1)–O(11)	105.6(17)

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1975, Index Issue.

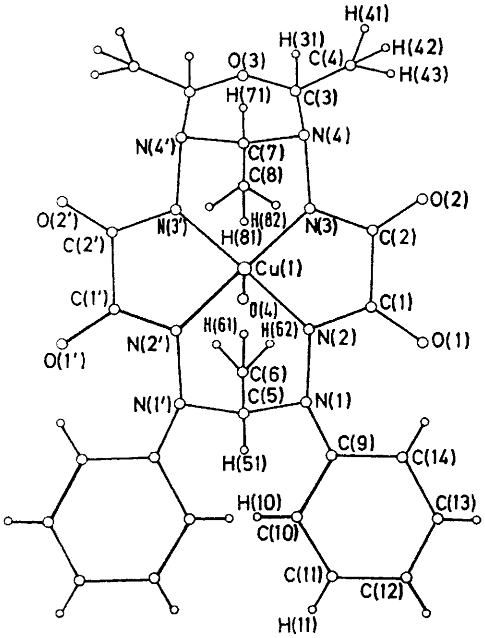

FIGURE 2 The numbering scheme for the cation of the green complex, (II). The ammonium nitrogen atom is N(5), and solvent oxygen atoms are O(5)—(11)

TABLE 4

Atomic positions, with standard deviations in parentheses, for (II)

Atom	x/a	y/b	z/c
Cu(1)	0.0	0.354 0(1)	0.0
N(1)	0.073 9(5)	0.528 0(6)	−0.001 2(10)
N(2)	0.084 3(6)	0.438 8(6)	−0.008 0(8)
N(3)	0.048 9(6)	0.272 8(6)	−0.019 4(7)
N(4)	0.047 8(7)	0.182 2(7)	−0.034 6(8)
C(1)	0.159 5(8)	0.406 6(9)	−0.022 6(8)
C(2)	0.158 9(8)	0.305 7(8)	−0.033 3(9)
C(3)	0.077 1(8)	0.130 1(9)	0.044 6(10)
C(4)	0.150 1(8)	0.145 9(12)	0.101 3(11)
C(5)	0.0	0.559 3(13)	−0.046 3(14)
C(6)	0.0	0.536 2(14)	−0.138 1(16)
C(7)	0.0	0.160 9(18)	−0.083 4(15)
C(8)	0.0	0.209 2(14)	−0.170 0(14)
C(9)	0.101 3(7)	0.567 1(9)	0.075 3(10)
C(10)	0.110 9(10)	0.659 2(11)	0.077 6(12)
C(11)	0.136 0(12)	0.698 6(11)	0.152 6(14)
C(12)	0.166 0(10)	0.649 1(13)	0.225 6(14)
C(13)	0.158 6(11)	0.563 0(13)	0.222 0(12)
C(14)	0.126 1(10)	0.521 0(11)	0.149 4(10)
O(1)	0.223 6(5)	0.448 0(6)	−0.031 2(7)
O(2)	0.222 6(6)	0.270 7(7)	−0.054 3(8)
O(3)	0.0	0.147 4(12)	0.100 4(11)
N(5)	0.143 8(11)	0.150 6(13)	0.357 4(12)
O(4)	0.0	0.315 8(10)	0.169 8(10)
O(5)	0.256 0(7)	0.105 7(8)	−0.119 4(7)
O(6)	0.146 5(10)	0.308 3(11)	0.260 0(11)
O(7)	0.142 2(13)	0.024 6(14)	−0.216 2(13)
O(8)	0.0	0.023(2)	0.229(2)
O(9)	0.150 5(15)	−0.080 2(16)	0.096 5(17)
O(10)	0.0	0.201(3)	0.429(3)
O(11)	0.0	−0.106(3)	0.034(2)

and chemical tests already outlined. The solvent atoms were also investigated crystallographically and structurally and that labelled N(5) was assigned as the nitrogen of the ammonium ion since it fitted a nitrogen scattering curve better than oxygen and since its interaction with the carbonyl oxygens of the anionic complex is not unexpected for a hydrogen-bonding cation.

The final stages of the refinement took into account the anomalous scattering of copper and converged at R 0.077 for a model described by the atom positions of Table 4. The numbering scheme is that of Figure 2. A model of the reverse polarity refined to 0.080. Bond lengths and angles are in Tables 5 and 6 respectively.

TABLE 5

Bond lengths (Å), with standard deviations in parentheses, for (II)

Cu(1)–N(2)	1.897(9)	C(1)–O(1)	1.23(2)
Cu(1)–N(3)	1.886(9)	C(2)–O(2)	1.22(2)
Cu(1)–O(4)	2.67(1)	C(3)–C(4)	1.50(2)
N(1)–N(2)	1.38(2)	C(3)–O(3)	1.55(2)
N(1)–C(5)	1.47(2)	C(5)–C(6)	1.45(3)
N(1)–C(9)	1.39(2)	C(7)–C(8)	1.52(3)
N(2)–C(1)	1.34(2)	C(9)–C(10)	1.42(2)
N(3)–C(2)	1.33(2)	C(10)–C(11)	1.36(3)
N(3)–N(4)	1.42(2)	C(11)–C(12)	1.44(3)
N(4)–C(3)	1.45(2)	C(12)–C(13)	1.33(3)
N(4)–C(7)	1.47(2)	C(13)–C(14)	1.39(2)
C(1)–C(2)	1.55(2)	C(14)–C(9)	1.40(2)

TABLE 6

Bond angles (°), with standard deviations in parentheses, for (II)

N(2)–Cu(1)–N(3)	84.7(6)	C(2)–C(1)–O(1)	120.4(12)
N(2)–Cu(1)–N(3′)	167.1(8)	C(1)–C(2)–O(2)	117.5(12)
N(2)–Cu(1)–N(2′)	93.1(5)	C(1)–C(2)–N(3)	111.5(10)
N(2)–Cu(1)–O(4)	102.3(6)	O(2)–C(2)–N(3)	131.0(11)
N(3)–Cu(1)–N(3′)	94.6(5)	N(4)–C(3)–C(4)	114.7(11)
N(3)–Cu(1)–O(4)	90.5(6)	N(4)–C(3)–O(3)	110.3(10)
N(2)–N(1)–C(5)	112.8(11)	O(3)–C(3)–C(4)	107.4(12)
N(2)–N(1)–C(9)	116.7(10)	N(1)–C(5)–C(6)	112.1(11)
C(5)–N(1)–C(9)	121.3(13)	N(1)–C(5)–N(1′)	110.3(9)
N(1)–N(2)–Cu(1)	125.7(5)	N(4)–C(7)–N(4′)	112.4(10)
Cu(1)–N(2)–C(1)	115.0(6)	N(4)–C(7)–C(8)	109.7(12)
N(1)–N(2)–C(1)	119.3(11)	N(1)–C(9)–C(10)	118.9(9)
Cu(1)–N(3)–C(2)	116.4(6)	N(1)–C(9)–C(14)	124.2(8)
Cu(1)–N(3)–N(4)	125.8(5)	C(14)–C(9)–C(10)	116.7(14)
C(2)–N(3)–N(4)	116.9(12)	C(9)–C(10)–C(11)	119.7(13)
N(3)–N(4)–C(7)	113.5(12)	C(10)–C(11)–C(12)	121.8(14)
N(3)–N(4)–C(3)	113.5(10)	C(11)–C(12)–C(13)	117.4(14)
C(3)–N(4)–C(7)	109.0(14)	C(12)–C(13)–C(14)	121.9(13)
N(2)–C(1)–O(1)	127.3(11)	C(13)–C(14)–C(9)	121.9(12)
N(2)–C(1)–C(2)	112.2(10)		

Primed atoms are at $\bar{x}, y, z$.

RESULTS

Description of the Structures.—(*a*) *Purple complex,* (I). As illustrated in the ORTEP diagram (Figure 3) the complex ion possesses a cage-like structure resulting from ring-closing reactions with acetaldehyde. The copper atom is five-co-ordinate, the exact geometry being that of a slightly distorted square pyramid with the base containing four nitrogen donor atoms and the apex a co-ordinated water molecule. A plane-of-best-fit [13] (Table 7) through the four basal donors shows that the metal atom is displaced towards the fifth position by 0.15 Å. The four nitrogen atoms themselves depart from planarity (χ^2 20.6) in that opposite pairs are displaced by 0.039 Å from their mean plane in a slight tetrahedral distortion.

The complex contains a macrocyclic ligand having some relationship to those of the cyclam family.[14] Thus it can be

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[13] V. Schomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Cryst.*, 1959, **12**, 600.

[14] B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, 1965, **4**, 1102.

described in terms of alternating five- and six-membered chelate rings but it has the added complication of the etheric bridges. An examination of the bond lengths and angles in the five-membered chelate rings containing the oxalate moiety shows that the carbon atoms are sp^2 hybridised and that the carbon–oxygen bond lengths [1.24(2), 1.26(2), 1.22(2), and 1.24(2) Å] are normal for carbonyl groups. The ligand is thus in the keto rather than the enolic form. The carbon–carbon distances [1.52(2) and 1.50(2) Å] suggest single bonds, and the carbon–nitrogen bonds [1.31(2), 1.33(2), 1.34(2), and 1.35(2) Å], although significantly shorter than those expected for single bonds, are similar to those in amides.[15] The four nitrogen–nitrogen lengths of the six-membered chelate rings [1.40(2), 1.41(2), 1.41(2), and 1.42(2) Å] reflect single bonds. The etheric rings bound into the six-membered chelate system are in the chair conformation (Table 8) with the methyl groups equatorial.

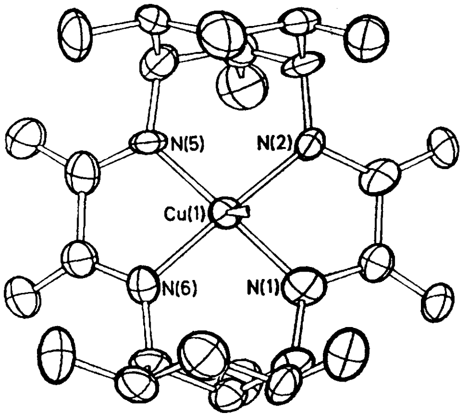

FIGURE 3 An ORTEP diagram of the cation of (I) (omitting hydrogen atoms and the co-ordinated oxygen)

TABLE 7

Planes of best fit for complex (I). Equations of planes, referred to an orthogonal set of axes, are in the form: $AX + BY + CZ - D = 0$ where A, B, and C are direction cosines.* Displacements (Å) of all atoms from the plane Å are in square brackets

Plane (i): Cu(1), N(1), N(2), N(5), N(6)

$$0.6856X + 0.7178Y - 0.1212Z - 1.738 = 0$$

[Cu(1) −0.016, N(1) 0.113, N(2) 0.163, N(5) 0.096, N(6) 0.159, O(7) −2.77, N(3) 0.152, N(4) 0.091, N(7) 0.171, N(8) 0.102]

Plane (ii): N(1), N(2), N(5), N(5)

$$0.6868X + 0.7156Y - 0.1263Z - 1.844 = 0$$

[N(1) −0.031, N(2) 0.028, N(5) 0.027, N(6) 0.027, Cu(1) −0.150]

Plane (iii): C(1), O(1), C(2), O(2)

$$0.0412X + 0.4859Y - 0.2369Z - 0.2365 = 0$$

[O(1) 0.001, O(2) −0.001, C(1) −0.003, C(2) 0.004]

Plane (iv): C(3), C(4), O(3), O(4)

$$-0.4401X - 0.8982Y - 0.0220Z + 2.6779 = 0$$

[C(4) 0.015, C(3) −0.015, O(3) 0.004, O(4) −0.004]

Plane (v): Cu(1), N(1), N(2), C(1), C(2)

$$0.7935X + 0.5760Y - 0.1965Z - 0.9082 = 0$$

[Cu(1) 0.003, N(1) −0.113, N(2) −0.103, C(1) 0.082, C(2) 0.102, O(1) 0.199, O(2) 0.214]

Plane (vi): Cu(1), N(5), N(6), C(3), C(4)

$$0.5563X + 0.8294Y - 0.0513Z - 2.414 = 0$$

[Cu(1) 0.003, N(5) −0.109, N(6) −0.102, C(3) 0.118, C(4) 0.090, O(3) 0.263, O(4) 0.274]

Plane (vii): N(3), N(4), C(9), C(11)

$$-0.1196X + 0.4881Y - 0.8646Z - 1.041 = 0$$

[C(9) 0.002, N(3) −0.001, N(4) 0.001, C(11) −0.002, C(12) 0.67, O(6) −0.64, C(15) 0.64]

Plane (viii): N(7), N(8), C(5), C(7)

$$-0.6458X - 0.0584Y - 0.7612Z + 5.241 = 0$$

[C(5) −0.008, C(7) 0.007, N(7) 0.005, N(8) −0.004, C(6) 0.701, C(13) −0.673, C(14) −0.827, O(5) 0.664, C(8) 0.705]

* The relationships between orthogonal and crystallographic axes are $X = x + z\cos\beta$, $Y = y$, and $Z = z\sin\beta$.

TABLE 8

Equations for least-squares planes for (II), defined in Table 7, with deviations (Å) of all atoms from the planes given in square brackets

Plane (i): N(2), N(2′), N(3), N(3′)

$$0.0093Y - 0.998Z - 0.5930 = 0$$

[Cu(1) −0.217, C(1) 0.19, C(2) 0.24, N(2) = N(2′) = N(3) = N(3′) 0.0, O(1) 0.36, O(2) 0.55, O(4) −2.85]

Plane (ii): N(2), N(2′), N(3), N(3′), Cu(1)

$$0.695Y - 0.998Z - 0.551 = 0$$

[N(2) = N(3) = N(2′) = N(3′) 0.04, Cu(1) −0.174]

Plane (iii): Cu (1),N(2), N(3), C(1), C(2)

$$0.166X + 0.076Y + 0.983Z - 0.408 = 0$$

[Cu(1) 0.007, N(2) 0.006, N(3) −0.02, C(1) −0.02, C(2) 0.02, O(1) −0.02, O(2) −0.15]

Plane (iv): C(1), C(2), O(1), O(2)

$$-0.221X + 0.128Y - 0.967Z - 0.541 = 0$$

[C(1) 0.02, C(2) −0.02, Cu(1) 0.151, O(1) −0.01, O(2) 0.01, N(3) −0.02, N(2) 0.14]

Plane (v): C(9)—(14)

$$-0.924X + 0.058Y + 0.377Z - 0.609 = 0$$

[C(9) 0.01, C(10) −0.04, C(11) 0.05, C(12) −0.02, C(13) −0.01, C(14) 0.02]

Plane (vi): C(7), N(4′), C(3), O(3)

$$-0.272X - 0.959Y - 0.078Z + 2.290 = 0$$

[C(7) 0.04, O(3) 0.01, C(3) −0.01, C(3′) 0.67, N(4′) −0.01, N(4) −0.67]

The carbon–nitrogen lengths of these rings are normal for single bonds and all angles have values close to the tetrahedral ones. However, as already mentioned, the carbon–oxygen bond lengths are long, although this is not without precedent.[16] Metal–donor distances are discussed later.

The packing of the constituent species into the crystal structure is shown in Figure 4. Inter- and (noteworthy) intra-molecular approaches less than the sum of van der Waals radii are listed in Table 9. Those thought to be hydrogen bonds, *i.e.* those with acceptable angle relationships, are noted. As expected for a structure containing so many potentially hydrogen-bonding centres, this interaction occurs extensively. Unfortunately, unequivocal location of the hydrogen atoms of the water molecules and ammonium ions did not prove possible, so that the hydrogen-bonding network can only be inferred. It seems clear, nonetheless, that all the oxygen atoms except O(8) and O(9) of the perchlorates, and all the ' solvent ' molecules (which includes the ammonium ions), are involved. In addition there are interactions with N(4) and N(7).

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[15] E. M. Ayerst and J. R. C. Duke, *Acta Cryst.*, 1954, **7**, 588.

[16] I. L. Karle and J. Karle, *J. Amer. Chem. Soc.*, 1966, **88**, 24.

TABLE 9

Hydrogen-bonding geometry for (I): distances (Å), angles (°)

O(1) ··· O(13)	2.70(2)	C(1)–O(1) ··· O(13)	138.0(7)
O(2) ··· O(16)	2.99(3)	C(2)–O(2) ··· O(16)	128.0(12)
O(3) ··· O(14)	2.81(2)	C(3)–O(3) ··· O(14)	129.3(8)
O(3) ··· O(17)	2.74(2)	C(3)–O(3) ··· O(17)	129.1(8)
		O(14) ··· O(3) ··· O(17)	99.7(7)
O(4) ··· O(12)	2.81(2)	C(4)–O(4) ··· O(12)	124.1(11)
O(4) ··· O(15)	2.89(2)	C(4)–O(4) ··· O(15)	137.2(12)
		O(12) ··· O(4) ··· O(15)	89.8(6)
O(5) ··· O(7)	2.87(2)	C(5)–O(5) ··· O(7)	115.0(9)
		C(7)–O(5) ··· O(7)	110.1(9)
O(6) ··· O(7)	2.99(2)	O(7) ··· O(6) ··· O(17)	112.2(7)
O(6) ··· O(17)	2.71(2)	C(9)–O(6) ··· O(7)	113.2(9)
		C(9)–O(6) ··· O(17)	109.1(10)
		C(11)–O(6) ··· O(7)	110.7(9)
		C(11)–O(6) ··· O(17)	99.7(10)
O(7) ··· O(5)	2.87(2)	O(5) ··· O(7) ··· O(6)	149.3(7)
O(7) ··· O(6)	2.99(2)	O(5) ··· O(7) ··· O(12)	101.8(7)
O(7) ··· O(12)	2.66(2)	O(5) ··· O(7) ··· O(13)	101.6(7)
O(7) ··· O(13)	2.79(2)	O(6) ··· O(7) ··· O(12)	97.3(6)
		O(6) ··· O(7) ··· O(13)	101.1(6)
		O(12) ··· O(7) ··· O(13)	92.9(6)
O(10) ··· O(18)	3.11(3)	Cl(1)–O(10) ··· O(18)	106.5(8)
O(11) ··· O(12)	2.98(3)	Cl(1)–O(11) ··· O(12)	119.6(9)
O(11) ··· O(18)	3.08(3)	Cl(1)–O(11) ··· O(18)	107.1(9)
		O(12) ··· O(11) ··· O(18)	118.5(7)
O(12) ··· O(4)	2.81(2)	O(4) ··· O(12) ··· O(7)	103.6(6)
O(12) ··· O(7)	2.66(2)	O(4) ··· O(12) ··· O(11)	121.3(7)
O(12) ··· O(11)	2.98(3)	O(7) ··· O(12) ··· O(11)	134.6(7)
O(12) ··· N(7)	3.20(2)	N(7) ··· O(12) ··· O(4)	53.8(3)
		N(7) ··· O(12) ··· O(7)	156.9(3)
		N(7) ··· O(12) ··· O(11)	68.5(5)
O(13) ··· O(1)	2.70(2)	O(1) ··· O(13) ··· O(7)	74.1(3)
O(13) ··· O(7)	2.79(2)	O(1) ··· O(13) ··· O(14)	113.9(5)
O(13) ··· O(14)	2.81(2)	O(1) ··· O(13) ··· O(15)	125.7(4)
O(13) ··· O(15)	2.82(2)	O(7) ··· O(13) ··· O(14)	121.5(7)
		O(7) ··· O(13) ··· O(15)	99.7(6)
		O(14) ··· O(13) ··· O(15)	114.6(8)
O(14) ··· O(3)	2.81(2)	O(3) ··· O(14) ··· O(13)	103.5(6)
O(14) ··· O(13)	2.81(2)	O(3) ··· O(14) ··· O(16)	91.6(6)
O(14) ··· O(16)	3.26(3)	O(3) ··· O(14) ··· O(18)	127.9(6)
O(14) ··· O(18)	2.86(3)	O(13) ··· O(14) ··· O(16)	99.5(7)
O(14) ··· N(4)	3.24(2)	O(13) ··· O(14) ··· O(18)	114.3(7)
		O(16) ··· O(14) ··· O(18)	114.8(7)
		N(4) ··· O(14) ··· O(3)	53.4(3)
		N(4) ··· O(14) ··· O(13)	155.0(3)
		N(4) ··· O(14) ··· O(16)	91.6(5)
		N(4) ··· O(14) ··· O(18)	80.3(4)
O(15) ··· O(4)	2.89(2)	O(4) ··· O(15) ··· O(13)	109.2(3)
O(15) ··· O(13)	2.82(2)	O(4) ··· O(15) ··· O(17)	119.1(4)
O(15) ··· O(17)	2.88(2)	O(4) ··· O(15) ··· O(18)	98.7(4)
O(15) ··· O(18)	2.86(2)	O(13) ··· O(15) ··· O(17)	91.6(6)
		O(13) ··· O(15) ··· O(18)	129.6(7)
		O(17) ··· O(15) ··· O(18)	110.6(7)
O(16) ··· O(2)	2.99(3)	O(2) ··· O(16) ··· O(14)	127.2(4)
O(16) ··· O(14)	3.26(3)	O(2) ··· O(16) ··· O(19)	105.2(11)
O(16) ··· O(19)	2.55(5)	O(2) ··· O(16) ··· O(20)	106.5(9)
O(16) ··· O(20)	2.45(5)	O(14) ··· O(16) ··· O(19)	127.3(12)
		O(14) ··· O(16) ··· O(20)	91.6(11)
		O(19) ··· O(16) ··· O(20)	76.2(14)
O(17) ··· O(3)	2.74(2)	O(3) ··· O(17) ··· O(4)	54.6(4)
		O(3) ··· O(17) ··· O(6)	122.2(6)
O(17) ··· O(4)	3.23(2)	O(3) ··· O(17) ··· O(15)	121.1(6)
O(17) ··· O(6)	2.71(2)	O(3) ··· O(17) ··· O(17′)	117.5(6)
O(17) ··· O(15)	2.88(2)	O(4) ··· O(17) ··· O(6)	85.3(5)
O(17) ··· O(17′)	3.10(2)	O(4) ··· O(17) ··· O(15)	169.4(7)
		O(4) ··· O(17) ··· O(17′)	103.8(5)
		O(6) ··· O(17) ··· O(15)	104.3(6)
		O(6) ··· O(17) ··· O(17′)	110.8(6)
		O(15) ··· O(17) ··· O(17′)	68.9(6)
O(18) ··· O(10)	3.11(3)	O(10) ··· O(18) ··· O(11)	40.8(6)
O(18) ··· O(11)	3.08(3)	O(10) ··· O(18) ··· O(14)	83.9(7)
O(18) ··· O(14)	2.86(3)	O(10) ··· O(18) ··· O(15)	127.5(8)
O(18) ··· O(15)	2.86(2)	O(11) ··· O(18) ··· O(14)	108.8(7)
		O(11) ··· O(18) ··· O(15)	118.4(7)
		O(14) ··· O(18) ··· O(15)	132.0(8)
O(19) ··· O(16)	2.55(5)	O(16) ··· O(19) ··· O(19′)	123.0(12)
O(19) ··· O(19′)	2.44(7)	O(16) ··· O(19) ··· O(20)	50.5(9)
O(19) ··· O(20)	3.09(6)	O(19′) ··· O(19) ··· O(20)	86.9(14)
O(20) ··· O(16)	2.45(5)	O(16) ··· O(20) ··· O(19)	53.3(11)
O(20) ··· O(19)	3.09(6)		
N(4) ··· O(14)	3.24(2)	C(11)–N(4) ··· O(14)	96.6(10)
		C(15)–N(4) ··· O(14)	114.4(10)
		N(5)–N(4) ··· O(14)	112.8(10)
N(7) ··· O(12)	3.20(2)	C(5)–N(7) ··· O(12)	110.7(10)
		C(13)–N(7) ··· O(12)	101.8(9)
		N(6)–N(7) ··· O(12)	108.8(10)

Primed atoms are at $1 - x, -y, -z$.

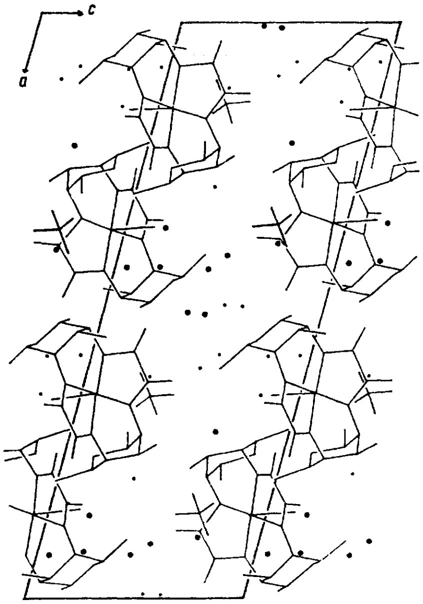

FIGURE 4 The contents of the unit cell of (I) projected down *b*. Dots represent water molecules or ammonium ions

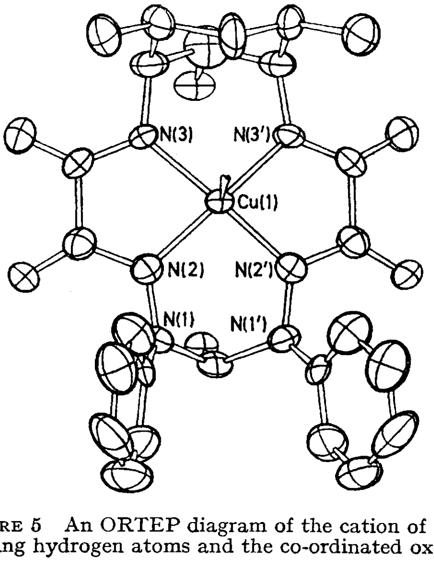

FIGURE 5 An ORTEP diagram of the cation of (II) (omitting hydrogen atoms and the co-ordinated oxygen)

The perchlorate group does not interact with the complex anion but bonds, weakly, to the solvent atoms O(12) and O(18) through two of its oxygens [O(10) ··· O(18) 3.11(3), O(11) ··· O(12) 2.98(3), O(11) ··· O(18) 3.08(3) Å]. It appears, therefore, to have mainly a space-filling role and its absence from *ca.* 25% of the structure is no doubt accommodated by extra water molecules and a slight rearrangement of the network. The apparent shortness of the calculated chlorine–oxygen bond lengths are undoubtedly an artefact of a significant degree of the vibrational disorder so often noticed in perchlorates.

(*b*) *Green complex*, (II). The complex anion is bisected by a crystallographic mirror plane which passes through the copper atom and carbons C(5)—(8), but its structure (Figure 5) is nevertheless very similar to that of (I). The coordination geometry is again square pyramidal with four nitrogen donors in the base and a water molecule at the apex. The basal donors are required to be coplanar by symmetry but the copper atom is displaced 0.17 Å towards the water molecule. The oxygens of the oxalate residues are in the keto-form as judged by bond lengths and angles, and their carbon–carbon distances [1.55(2) Å] indicate single bonds. The nitrogen–nitrogen distances [1.42(2) and 1.38(2) Å] also indicate single bonds (but see later). The overall *cis*-conformation, which brings the two phenyl groups together on the same six-membered chelate ring, allows the formation of one etheric ring. As with the purple complex it is in the chair conformation with the methyl substituents equatorial, and again it has long carbon–oxygen bonds [1.55(2) Å]. Otherwise the only bond length requiring comment is the 1.45(3) Å of C(5)—C(6). It is just acceptable on the 3σ test but in any event no chemical significance is read into its value. Selected planes of best fit are recorded in Table 8.

There are even more water molecules of crystallisation than in (I), and it can be seen from Figure 6 and confirmed from Table 10 that there is a large hydrogen-bonding network. Since the hydrogen atoms of the solvent molecules and the ammonium ion could not be located unequivocally from difference maps, this network cannot be discussed in detail. However, the ammonium ion, N(5), is surrounded by five atoms at hydrogen-bonding distances and it is supposed that a bifurcated bond involves N(5), O(1), and O(2).

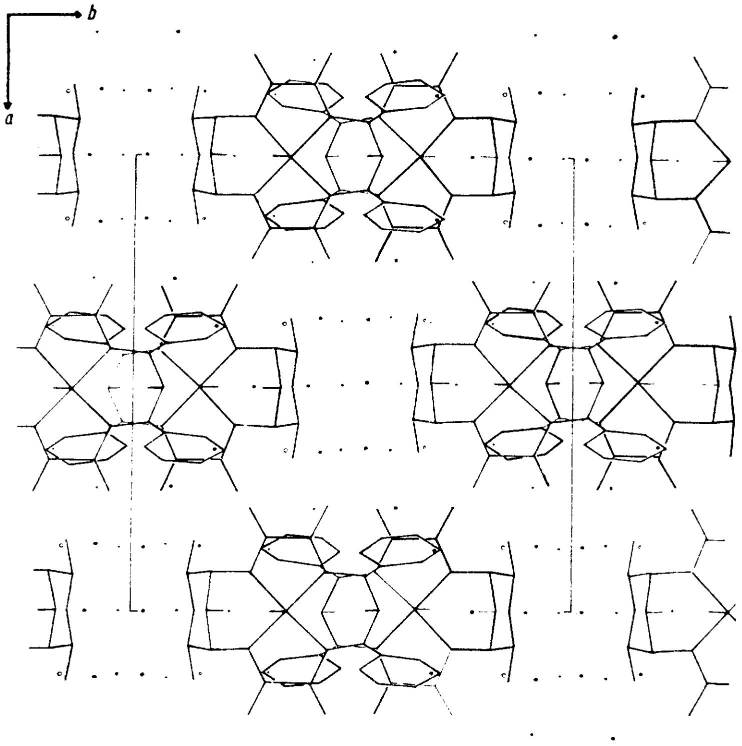

FIGURE 6 The contents of the unit cell of (II) projected down *c*. Dots represent water molecules or ammonium ions

DISCUSSION

In one respect the results of the analyses are quite clear in showing that dioxygen is not a ligand in these final reaction products. The analyses also clearly show that none of the suggested structures were correct. They do not, however, offer an obvious explanation for the role of molecular oxygen in the reaction sequences.

Although the presence of at least one etheric (1,3,5-oxadiazine) moiety and at least one bridging acetaldehyde residue in each compound was unexpected, this finding is not inexplicable. It is probable that the mechanism of reaction is the same as that suggested[17] for the formation of oxazolidene rings when bis(glycinato)copper(II)[18] and bis(*S*-serinato)copper(II)[17] react with acetaldehyde or formaldehyde. The ether bridge is thus envisaged as forming in the manner shown in Scheme 1 with the addition of the further acetaldehyde moiety following Scheme 2, a route in which the bonding angles defined by the first reaction preclude the condensation of two aldehydes. Neither of the ring closures

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[17] J. R. Brush, R. J. Magee, M. J. O'Connor, S. B. Teo, R. J. Geue, and M. R. Snow, *J. Amer. Chem. Soc.*, 1973, **95**, 2034.

[18] J. P. Aune, P. Maldonado, G. Larcheres, and M. Pierrot, *Chem. Comm.*, 1970, 1351.

requires the direct participation of molecular oxygen nor does an indirect role, resulting from the modification of the electronic effects of the co-ordination centre, seem likely for this molecule in view of the intervening nitrogen–nitrogen single bonds.

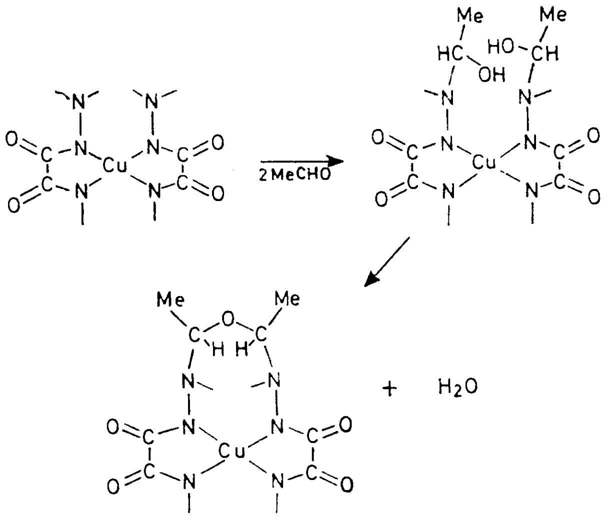
TABLE 10

Hydrogen-bonding geometry for (II): distances (Å), angles (°)

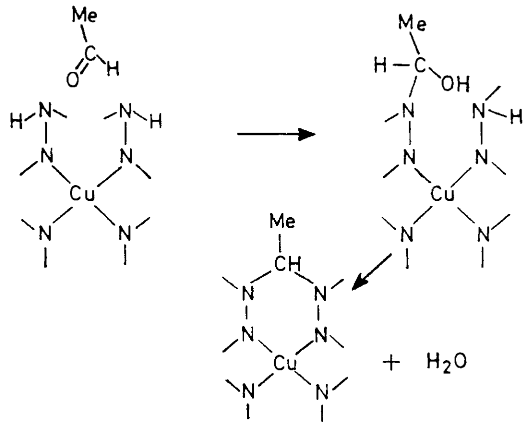
O(3) · · · O(4)	2.79 Å	C(3)–O(3) · · · O(4)	111.7(9)°
O(3) · · · O(8)	2.74(3)	C(3)–O(3) · · · O(8)	106.2(10)
		O(4) · · · O(3) · · · O(8)	111.6(9)
O(1) · · · O(5)	2.79(2)	C(1)–O(1) · · · O(5)	126.9(9)
O(1) · · · O(9)	2.87(3)	C(1)–O(1) · · · O(9)	117.3(10)
		O(5) · · · O(1) · · · O(9)	112.0(8)
O(2) · · · O(5)	2.77(2)	C(2)–O(2) · · · O(5)	131.0(10)
O(2) · · · N(5)	2.84(2)	C(2)–O(2) · · · N(5)	126.7(11)
		O(5) · · · O(2) · · · N(5)	93.7(8)
O(4) · · · O(6)	2.77(2)	Cu(1)–O(4) · · · O(6)	119.8(4)
O(4) · · · O(3)	2.79(2)	Cu(1)–O(4) · · · O(3)	80.2(3)
		O(6) · · · O(4) · · · O(3)	98.8(7)
		O(6) · · · O(4) · · · O(6′)	119.8(8)
O(5) · · · O(6)	2.77(2)	O(1) · · · O(5) · · · O(6)	131.7(6)
O(5) · · · O(7)	2.68(3)	O(1) · · · O(5) · · · O(7)	87.1(6)
O(5) · · · O(1)	2.79(2)	O(6) · · · O(5) · · · O(7)	104.4(7)
O(6) · · · O(4)	2.77(2)	O(4) · · · O(6) · · · O(5)	144.2(6)
O(6) · · · O(5)	2.77(2)	O(4) · · · O(6) · · · N(5)	106.5(7)
O(6) · · · N(5)	2.84(3)	O(5) · · · O(6) · · · N(5)	93.5(6)
O(7) · · · O(8)	2.58(4)	O(5) · · · O(7) · · · O(8)	159.4(8)
O(7) · · · O(5)	2.68(3)	O(8) · · · O(7) · · · N(5)	82.7(8)
O(7) · · · N(5)	2.91(3)	O(8) · · · O(7) · · · O(9)	79.0(8)
O(7) · · · O(9)	3.00(3)	O(5) · · · O(7) · · · N(5)	101.9(5)
		O(5) · · · O(7) · · · O(9)	111.5(7)
		N(5) · · · O(7) · · · O(9)	129.2(7)
O(8) · · · O(3)	2.74(3)	O(3) · · · O(8) · · · O(7)	115.6(7)
O(8) · · · O(7)	2.58(4)	O(7) · · · O(8) · · · O(7′)	128.8(8)
N(5) · · · O(2)	2.84(3)	O(2) · · · N(5) · · · O(6)	82.9(5)
N(5) · · · O(6)	2.84(3)	O(2) · · · N(5) · · · O(7)	125.7(6)
N(5) · · · O(7)	2.91(3)	O(2) · · · N(5) · · · O(10)	110.6(9)
N(5) · · · O(10)	2.71(5)	O(2) · · · N(5) · · · O(1)	54.2(3)
N(5) · · · O(1)	3.15(3)	O(6) · · · N(5) · · · O(7)	125.5(7)
		O(6) · · · N(5) · · · O(10)	89.1(9)
		O(6) · · · N(5) · · · O(1)	133.1(4)
		O(7) · · · N(5) · · · O(10)	114.4(10)
		O(7) · · · N(5) · · · O(1)	77.0(5)
		O(10) · · · N(5) · · · O(1)	121.0(8)
O(9) · · · O(1)	2.87(3)	O(1) · · · O(9) · · · O(7)	130.0(6)
O(9) · · · O(7)	3.00(3)	O(1) · · · O(9) · · · O(11)	115.9(9)
O(9) · · · O(11)	2.67(5)	O(7) · · · O(9) · · · O(11)	110.2(10)
O(10) · · · N(5)	2.71(5)	N(5) · · · O(10) · · · O(11)	96.3(11)
O(10) · · · O(11)	2.71(5)	N(5) · · · O(10) · · · N(5′)	120.5(7)
O(11) · · · O(9)	2.67(5)	O(9) · · · O(11) · · · O(9′)	134.3(9)
O(11) · · · O(10)	2.71(5)	O(9) · · · O(11) · · · O(10)	111.5(12)

Primed atoms are at $\bar{x}$, y, z.

Another feature of the complexes which remains to be explained is their intense electronic absorptions in the visible region of the spectrum. Again, the nitrogen–nitrogen distances suggest that no electronic effects will be transferred between the aldehyde moieties and the central metal even though the substitution of two phenyl groups for a bridging unit shifts the absorption from 18 550 cm^{-1} (540 nm) to 13 700 cm^{-1} (730 nm) and lowers ε from 29 500 $\text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}$ to 10 400. It is not appropriate to label these absorptions as *d–d* or charge-transfer; [19] however it is thought that bands of this intensity in the visible region are only to be expected if there are strongly reducing ligands present,[19] probably RS^- or N^-. It is also suggested that the bonding situation must allow the unpaired electron to be near the copper atom, but strongly delocalised and for an unusually low symmetry for the metal environment.[19] It will be seen that the first two of these requirements are met in the compounds under study since all the donor nitrogens are in the formal N^- state and, as we now demonstrate, there is structural evidence for a very strong metal–donor interaction. In the purple complex (I) the copper–nitrogen bond lengths average 1.863(7) Å [range 0.027 Å] and in the green complex (II) 1.892(6) Å [range 0.011 Å]. These can be compared with the 1.95 Å expected for a Cu–N(sp^2) bond [20] and the 1.93 Å observed in potassium bis(biureto)cuprate(II).[21] In both (I) and (II) the two copper–water bonds are long, implying strong in-plane bonding.[22] The chromophore appears to



SCHEME 1



SCHEME 2

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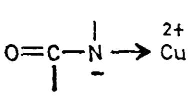
[19] G. Morpurgo and R. J. P. Williams, in 'Physiology and Biochemistry of Haemocyanins,' ed. F. Ghiretti, Academic Press, London, 1968.

[20] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York.

[21] H. C. Freeman, J. E. W. L. Smith, and J. C. Taylor, *Acta Cryst.*, 1961, **14**, 407.

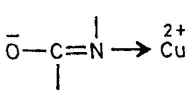
[22] E. N. Baker, D. Hall, and T. N. Waters, *J. Chem. Soc.* (*A*), 1970, 406.

be the O:C·N·Cu group in which the main canonical forms can be represented as (A)—(C).



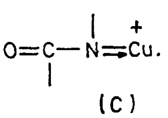
$\underset{|}{O{=}C}{-}\overset{|}{\underset{-}{N}}\rightarrow \overset{2+}{Cu}$

(A)



$\bar{O}{-}\underset{|}{C}{=}\overset{|}{N}\rightarrow \overset{2+}{Cu}$

(B)



$O{=}\underset{|}{C}{-}\overset{|}{N}\rightleftharpoons\overset{+}{Cu}.$

(C)

As indicated by bonding structure (C) there is a tendency towards reduction of the metal and we suggest, therefore, that the heterocyclic etheric rings are important to the stability of the complex ion, since they maintain the rigid tetragonal symmetry of the copper(II) state. They thus allow the presence of very strongly reducing ligands without reduction to the copper(I) state. It can then be surmised that molecular oxygen is necessary only to keep the metal oxidised before ring closure occurs. Indeed, in the presence of base (to form the imido-ion) and acetaldehyde it is possible, in the absence of air, to produce a white copper(I) compound.

Finally we note that the nitrogen–nitrogen bonds adjacent to the two phenyl groups in (II) are a little shorter [1.38(2) Å] than the other two bonds [1.42(2) Å] in the same molecule. The bonds in (I) are 1.40(2), 1.41(2), 1.41(2), and 1.42(2) Å. Statistical significance for the difference cannot be claimed, but if it is real it indicates that the reducing power of the associated donor-nitrogen atoms, and hence the colour of the complex, is not quite independent of the aromatic substituents.

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