# Crystal Structures of Two Trinuclear Schiff-base Copper(II) Complexes

By **Joel M. Epstein,** Department of Physics, University of Western Australia, Nedlands, 6009 Western Australia
**Brian N. Figgis, Allan H. White,*** and **Anthony C. Willis,** Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, 6009 Western Australia

The crystal structures of (I), $[\{Cu(es)\}_2Cu(H_2O)_2][ClO_4]_2,H_2O$, [es = *NN'*-ethylenebis(salicylaldimine)] and (II) $[\{Cu(eha)\}_2Cu(H_2O)][ClO_4]_2$, [eha = *NN'*-ethylenebis-(*o*-hydroxyacetophenimine)], have been determined by single-crystal *X*-ray diffraction by use of diffractometer data, and refined by least-squares to *R* (I) 5·9 (3226, all reflections) and (II) 7·4% (2015 observed reflections).

Crystal data: (I), monoclinic, space group $P2_1/n$, $a$ = 15·488(2), $b$ = 21·883(4), $c$ = 10·884(1) Å, $\beta$ = 94·28(1)°, $Z$ = 4; (II), orthorhombic, space group *Pbca*, $a$ = 26·884(4), $b$ = 19·093(4), $c$ = 15·740(2) Å, $Z$ = 8.

In both these complexes, a pair of Cu(es) and Cu(eha) chelate complexes act as bidentate ligands to the central copper atom, bonding through the oxygen atoms which act as bridges. In (I), the central copper atom has appreciably longer Cu–O bonds owing to its higher co-ordination number of 6, the pair of Cu(es) ' ligands ' effectively occupying ' *cis* ' positions in a Jahn–Teller distorted configuration [Cu–O 2·324, 2·050, 2·025, and 2·328(6) Å], the remaining pair of equatorial co-ordination sites being filled by water molecules [$Cu-OH_2$ 1·950 and 2·000(6) Å]. Cu–Cu–Cu is 97·3(4)° and Cu ··· Cu 3·052 and 2·993(2) Å. In (II), the water molecule occupies an equatorial site in a trigonal bipyramidal configuration on the central copper [$Cu-OH_2$ 2·18(2) Å], the Cu(eha) ' ligands ' bridging axial and equatorial sites [Cu–O 1·98, 1·93, 1·95, and 2·06(1) Å]. Cu–Cu–Cu is 156·2(4)° and Cu ··· Cu 2·950 and 2·975(5) Å. In both complexes, the perchlorate ions could not be precisely located owing to very high thermal motion in the lattice. The large change caused in the Cu–Cu–Cu angle is probably not the reason for the remarkably different magnetic behaviour of the two complexes. The reason for the steric difference between the two structures is not clear, and the system appears to give another example of the extreme sensitivity of complexes of this type to display polymorphism in response to subtle differences in crystal-packing and hydrogen-bonding forces.

THE Schiff-base derivative, *NN'*-ethylenebis(salicylaldimine), (es), forms the copper complex Cu(es) by co-ordination through the nitrogen and oxygen atoms. Cu(es) can then further act as a bidentate ligand by bridging to a further copper atom by way of the oxygen atoms.[1] Thus it reacts with copper(II) perchlorate to form (I) $[\{Cu(es)\}_2Cu(H_2O)_2][ClO_4]_2,H_2O$. It has been shown that the magnetic properties of the parent (I;

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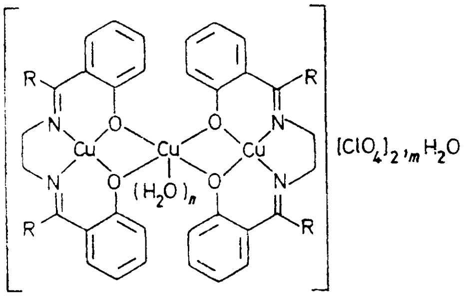
[1] S. J. Gruber, C. M. Harris, and E. Sinn, *J. Inorg. Nuclear Chem.*, 1968, **30**, 1805.

R = H) are radically different from those of its alkyl-substituted derivatives.[2] Since it seemed possible that steric effects might cause this by provoking a change in co-ordination type of the central copper atom as suggested by Gruber *et al.*,[1] crystal-structure determinations of (I) and the methyl-substituted complex $[\{Cu(eha)\}_2Cu(H_2O)][ClO_4]_2$ * were undertaken, suitable crystals being obtained from previously prepared samples.[2]



(I) R=H, $n=2$, $m=1$
(II) R=Me, $n=1$, $m=0$

EXPERIMENTAL

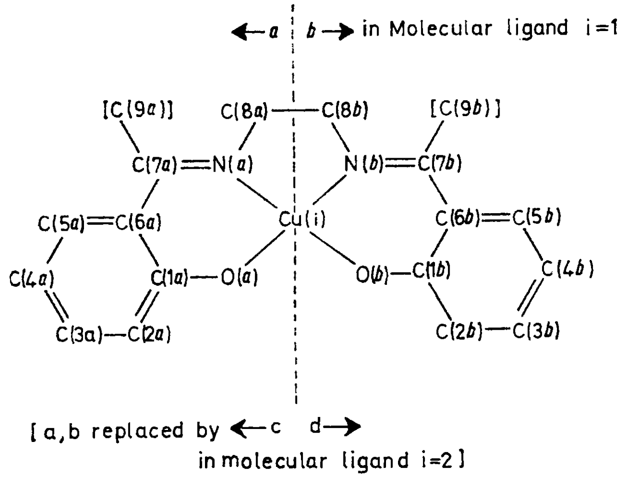
Single crystals were selected as prisms of axial dimensions (I) 0·10 × 0·07 × 0·07 mm and (II) 0·07 × 0·17 × 0·15 mm. In both cases, cell dimensions were obtained by a least-squares fit of the angular parameters of 15 reflections centred in the counter of a Syntex P$\bar{1}$ four-circle diffractometer. Unique data sets in the range $2\theta < 100°$ (Cu-$K_\alpha$ radiation, Ni-filtered, $\lambda = 1·5418$ Å) were collected by use of a $2\theta$-$\theta$ scan; for (I), 3226 independent reflections were obtained, all of which were employed in the structure solution and refinement with unit weights. For (II), 3000 independent reflections were obtained; these were much weaker than those for (I), and solution and refinement was carried out on a data set restricted by the criterion $|I_o| > 3\sigma(I_o)$, using unit weights. All data processing and computation was carried out on a CDC 6200 computer at the University of Western Australia, using a local adaption of the '*X*-Ray '72' computing system.[3] All data were corrected for absorption and both structures solved (by direct methods) and refined in this system.

*Crystal Data.*—(I), $C_{32}H_{34}Cl_2Cu_3N_4O_{15}$, $M = 976·1$, Monoclinic, $a = 15·488(2)$, $b = 21·883(4)$, $c = 10·884(1)$ Å, $\beta = 94·28(1)°$, $U = 3678(1)$ Å$^3$, $D_m = 1·72$, $Z = 4$, $D_c = 1·76$, $F(000) = 2100$. $\mu$(Cu-$K_\alpha$) = 40·8 cm$^{-1}$. Space group $P2_1/n$ ($C^5_{2h}$, No. 14).[4]

(II), $C_{36}H_{38}Cl_2Cu_3N_4O_{13}$, $M = 996·2$, Orthorhombic, $a = 26·884(4)$, $b = 19·093(4)$, $c = 15·740(2)$ Å, $U = 8079(2)$ Å$^3$, $D_m = 1·64$, $Z = 8$, $D_c = 1·67$, $F(000) = 4296$. $\mu$(Cu-$K_\alpha$) = 36·8 cm$^{-1}$. Space group *Pbca* ($D^{15}_{2h}$, No. 61).[5]

Scattering factors used were for the neutral atoms,[6] those for Cu and Cl [7] being corrected for the effects of anomalous dispersion ($\Delta f'$, $\Delta f''$).[8] Refinement of the structures by least squares was carried out by refining the copper atoms and their immediate oxygen and nitrogen atom environment as a single matrix, the other non-hydrogen atoms being refined as 9 + 9 blocks, anisotropic thermal parameters being of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*]$ throughout. For (I), hydrogen atoms were located geometrically or in difference-Fourier syntheses and their positional parameters also refined, the thermal parameters being constrained at $U$ 0·10 Å$^2$. For (II), this was not possible and hydrogen atoms were simply located and included in the refinement assuming C–H 1·00 Å and C–C–H 109 or 120°. In both structures, the perchlorate ions presented considerable difficulty, since they were undergoing very high thermal motion. In (I), a difference-Fourier synthesis showed perchlorate (f) to be disordered, occupying a trigonal bipyramidal type of electron distribution; oxygen O(4f) was therefore refined as two halves with fixed population parameters of 0·5, the anisotropy of the other three oxygens being very high along this axis. In (II), perchlorate (f) was very diffuse and it was not possible to find a satisfactory model which reproduced its behaviour in a sensible way; this is reflected in the O(2)–Cl–O(3) angle of 150°. The structure was refined to convergence, when all parameter shifts were $<0·2\sigma$ and the residuals were $R$ 0·059 (I) and 0·074 (II), and $R'$ was 0·056 (I) and 0·087 (II) $\{R' = [\Sigma(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{\frac{1}{2}}\}$.

Structure factors and hydrogen atom parameters are given in Supplementary Publication No. SUP 21058 (26 pp., 1 microfiche),† and co-ordinates, and distances and angles in Tables 1 and 2. In the Tables and description of the structure, each molecule which bonds to the central atom is called a ligand, *i.e.* Cu(es) and Cu(eha), and are numbered as shown:



DISCUSSION

In each complex (Figures 1 and 2), the asymmetric unit comprises a dipositive trinuclear cation together with two perchlorate anions and, in (I), a lattice water

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* This complex was reported in the literature as being the dihydrate,[1] a formulation which the structure determination does not support.

† For details of Supplementary Publications, see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

[2] B. N. Figgis and D. J. Martin, *J.C.S. Dalton*, 1972, 2174.

[3] *X*-Ray system of programs, version of June 1972, Technical Report TR 192, of the Computer Science Centre, University of Maryland, U.S.A.

[4] 'International Tables for *X*-ray Crystallography,' vol. I, Kynoch Press, Birmingham, 2nd edn., 1965, p. 99.

[5] Ref. 4, p. 150.

[6] Ref. 4, vol. III, 1969, p. 202 ff.

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

[8] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

TABLE 1

Atomic fractional cell and anisotropic thermal parameters for non-hydrogen atoms, with least-squares estimated standard deviations in parentheses

(*a*) (I) $[\{Cu(es)\}_2Cu(H_2O)_2][ClO_4]_2,H_2O$

| Atom | $10^5x$ | $10^5y$ | $10^5z$ | $10^3U_{11}$ | $10^3U_{22}$ | $10^3U_{33}$ | $10^3U_{12}$ | $10^3U_{13}$ | $10^3U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Cu(1) | 65339(8) | 16642(5) | 5912(1) | 56(1) | 30(1) | 73(1) | −1(1) | 10(1) | 9(1) |
| Cu(2) | 86068(8) | 18092(5) | 3192(1) | 60(1) | 33(1) | 80(1) | 9(1) | −1(1) | 7(1) |
| Cu(3) | 74827(8) | 26475(5) | 4548(1) | 55(1) | 26(1) | 76(1) | 1(1) | 5(1) | 5(1) |
| (i) Ligand (ab) | | | | | | | | | |
| | $10^4x$ | $10^4y$ | $10^4z$ | | | | | | |
| O(a) | 6187(3) | 2469(2) | 5435(5) | 55(4) | 30(3) | 87(4) | 4(3) | 8(3) | 16(3) |
| O(b) | 7689(3) | 1961(2) | 5817(5) | 52(4) | 29(3) | 85(4) | 0(3) | 12(3) | 14(3) |
| N(a) | 5389(4) | 1362(2) | 5949(6) | 61(5) | 34(4) | 66(5) | −4(3) | −4(4) | −1(3) |
| N(b) | 6894(5) | 0842(3) | 6315(7) | 69(5) | 26(4) | 101(6) | 0(3) | 18(4) | 17(4) |
| C(1a) | 5392(5) | 2677(4) | 5344(8) | 63(6) | 37(5) | 66(6) | 12(4) | −5(5) | 2(4) |
| C(2a) | 5228(6) | 3292(4) | 4979(9) | 77(7) | 51(6) | 90(7) | 15(5) | 18(6) | 12(5) |
| C(3a) | 4419(6) | 3533(4) | 491(1) | 78(7) | 55(6) | 107(8) | 26(5) | 7(6) | 2(6) |
| C(4a) | 3722(7) | 3203(4) | 520(1) | 83(7) | 68(7) | 94(8) | 23(6) | −14(6) | 1(6) |
| C(5a) | 3840(6) | 2605(5) | 5545(9) | 53(6) | 78(7) | 88(7) | 6(5) | −7(5) | −3(6) |
| C(6a) | 4655(6) | 2323(4) | 5608(8) | 66(6) | 43(5) | 68(6) | −2(5) | −5(5) | 3(5) |
| C(7a) | 4706(5) | 1678(4) | 5885(9) | 48(5) | 59(6) | 81(7) | −7(4) | −5(5) | −4(5) |
| C(8a) | 5366(6) | 0691(4) | 611(1) | 71(7) | 38(5) | 160(11) | −17(5) | −8(7) | 15(6) |
| C(1b) | 8414(5) | 1657(3) | 6158(7) | 51(5) | 33(4) | 57(5) | 5(4) | 6(4) | 0(4) |
| C(2b) | 9200(5) | 1965(4) | 6211(8) | 57(6) | 44(5) | 73(6) | 6(4) | 1(5) | 7(5) |
| C(3b) | 9984(6) | 1673(4) | 6514(9) | 57(6) | 59(6) | 107(8) | −8(5) | −6(6) | −13(6) |
| C(4b) | 9977(6) | 1056(4) | 6829(9) | 64(6) | 49(6) | 107(8) | 10(5) | −18(6) | −14(5) |
| C(5b) | 9222(6) | 0755(4) | 6816(9) | 75(7) | 41(5) | 84(7) | 11(5) | −10(5) | −1(5) |
| C(6b) | 8426(5) | 1033(4) | 6492(8) | 54(5) | 41(5) | 73(6) | 10(4) | 4(5) | −9(4) |
| C(7b) | 7662(6) | 0667(3) | 6513(9) | 66(6) | 30(5) | 84(7) | 14(4) | 9(5) | −2(4) |
| C(8b) | 6150(7) | 0433(4) | 638(2) | 78(8) | 26(6) | 402(25) | −8(6) | 64(12) | 48(9) |
| (ii) Ligand (cd) | | | | | | | | | |
| O(c) | 7396(4) | 2008(2) | 3200(5) | 58(4) | 35(2) | 78(4) | 5(7) | −4(3) | −7(2) |
| O(d) | 8780(4) | 2647(2) | 3597(6) | 68(4) | 30(3) | 100(5) | 4(3) | −4(4) | −13(3) |
| N(c) | 8414(5) | 0946(3) | 3013(7) | 68(5) | 25(4) | 104(6) | 5(3) | 6(4) | −1(4) |
| N(d) | 9799(5) | 1610(3) | 3227(7) | 68(5) | 38(4) | 83(6) | 5(4) | −12(4) | 3(4) |
| C(1c) | 6730(5) | 1621(4) | 2958(7) | 58(5) | 44(5) | 48(5) | 0(4) | 10(4) | 1(4) |
| C(2c) | 5897(6) | 1844(4) | 2837(8) | 59(6) | 58(6) | 67(6) | 6(5) | 3(5) | −2(5) |
| C(3c) | 5186(6) | 1473(4) | 2573(9) | 58(6) | 75(7) | 91(8) | 6(5) | −2(5) | 9(6) |
| C(4c) | 5322(6) | 0848(4) | 2280(9) | 79(7) | 60(6) | 84(7) | −26(5) | −8(6) | 9(5) |
| C(5c) | 6137(6) | 0622(4) | 2487(9) | 75(7) | 54(6) | 77(7) | 1(5) | −4(5) | 7(5) |
| C(6c) | 6850(5) | 0989(4) | 2738(8) | 56(5) | 40(5) | 69(6) | −7(4) | −2(5) | 2(4) |
| C(7c) | 7690(6) | 0691(4) | 2835(8) | 87(7) | 37(5) | 67(6) | −5(5) | 14(5) | −6(4) |
| C(8c) | 9224(7) | 0600(4) | 312(1) | 84(8) | 36(6) | 250(16) | 31(6) | 9(9) | −6(8) |
| C(1d) | 9538(6) | 2921(4) | 3786(9) | 68(6) | 50(5) | 75(7) | −19(5) | −12(5) | 1(5) |
| C(2d) | 9536(7) | 3547(4) | 4087(9) | 94(8) | 40(5) | 79(7) | −16(5) | 3(6) | −11(5) |
| C(3d) | (1·)0308(7) | 3848(4) | 4323(9) | 100(8) | 56(6) | 79(7) | −18(6) | −7(6) | −1(5) |
| C(4d) | (1·)1082(7) | 3568(5) | 428(1) | 83(8) | 80(8) | 108(9) | −24(6) | −20(7) | 14(7) |
| C(5d) | (1·)1110(7) | 2954(5) | 396(1) | 72(2) | 85(7) | 106(9) | −1(6) | −24(6) | 10(7) |
| C(6d) | (1·)0335(6) | 2622(4) | 3739(9) | 60(6) | 62(6) | 89(7) | 0(5) | −16(5) | 9(5) |
| C(7d) | (1·)0435(6) | 1979(4) | 3435(9) | 67(7) | 66(6) | 86(7) | 16(5) | −7(6) | 2(6) |
| C(8d) | 9983(7) | 0962(4) | 299(1) | 76(7) | 58(6) | 138(10) | 15(6) | −3(7) | −20(7) |
| (iii) Perchlorate (e) | | | | | | | | | |
| Cl(e) | 2403(2) | 0936(1) | 5355(3) | 63(2) | 60(1) | 107(2) | −1(1) | 0(1) | −5(1) |
| O(1e) | 1694(5) | 0545(4) | 5193(9) | 78(5) | 105(6) | 207(9) | −31(5) | −10(6) | −20(6) |
| O(2e) | 2120(6) | 1529(3) | 5692(9) | 133(7) | 59(5) | 182(9) | 11(5) | 29(6) | −3(5) |
| O(3e) | 2969(6) | 0735(4) | 632(1) | 107(1) | 135(8) | 266(13) | −39(6) | −66(8) | 92(8) |
| O(4e) | 2835(8) | 0987(5) | 4337(9) | 254(13) | 146(8) | 130(8) | −54(8) | 113(8) | −45(7) |
| (iv) Perchlorate (f) | | | | | | | | | |
| Cl(f) | 7163(3) | 4775(1) | 5231(3) | 204(4) | 39(1) | 98(2) | 9(2) | 25(2) | −2(1) |
| O(1f) | 698(1) | 4463(5) | 621(1) | 426(21) | 117(8) | 116(8) | −39(11) | 18(11) | 15(7) |
| O(2f) | 706(1) | 4495(4) | 4151(8) | 420(19) | 58(5) | 105(7) | 5(8) | 40(9) | −21(5) |
| O(3f) | 7208(7) | 5378(3) | 5237(9) | 198(10) | 38(4) | 179(9) | −11(5) | 4(7) | −14(5) |
| O(4f1) | 616(2) | 486(1) | 512(4) | 229(31) | 114(19) | 590(66) | 25(2) | 69(4) | −22(29) |
| O(4f2) | 806(1) | 462(1) | 555(2) | 124(17) | 183(21) | 262(28) | 93(16) | −35(17) | −8(19) |
| (v) Water molecules | | | | | | | | | |
| O(1) | 7829(4) | 3241(3) | 5828(6) | 84(5) | 43(3) | 89(5) | −2(3) | 3(4) | 2(3) |
| O(2) | 7058(4) | 3299(2) | 3365(6) | 72(4) | 35(3) | 81(4) | 9(2) | 11(2) | 0(2) |
| O(3) | 7942(7) | 2920(4) | 8089(8) | 208(11) | 129(8) | 101(7) | 9(7) | 0(7) | −13(6) |

TABLE 1 (*Continued*)

(*b*) (II) $[\{Cu(eha)\}_2Cu(H_2O)]\ [ClO_4]_2$

| Atom | $10^4x$ | $10^4y$ | $10^4z$ | $10^3U_{11}$ | $10^3U_{22}$ | $10^3U_{33}$ | $10^3U_{12}$ | $10^3U_{13}$ | $10^3U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Cu(1) | 1121(1) | 3934(2) | 1523(2) | 54(2) | 55(2) | 53(2) | 2(2) | −3(2) | −9(2) |
| Cu(2) | 1221(1) | 5941(2) | 4282(2) | 54(2) | 64(2) | 53(2) | −10(2) | 0(2) | −4(2) |
| Cu(3) | 1397(1) | 4902(2) | 2906(2) | 83(2) | 56(2) | 51(2) | −15(2) | −9(2) | 0(2) |
| (i) Ligand (ab) | | | | | | | | | |
| O(a) | 1019(5) | 4873(7) | 1829(8) | 68(10) | 54(9) | 46(9) | 11(8) | −14(7) | −8(8) |
| O(b) | 1371(5) | 3915(7) | 2644(9) | 67(9) | 60(9) | 71(11) | −9(9) | −23(9) | 4(9) |
| N(a) | 0970(6) | 407(1) | 036(1) | 52(11) | 88(15) | 54(13) | −3(12) | 24(10) | −10(12) |
| N(b) | 1282(6) | 299(1) | 128(1) | 38(11) | 73(13) | 69(14) | −2(10) | 8(9) | −4(11) |
| C(1a) | 0749(7) | 532(1) | 139(1) | 35(13) | 68(16) | 60(15) | −15(11) | 2(12) | −17(13) |
| C(2a) | 0540(8) | 589(1) | 179(1) | 62(16) | 89(20) | 71(18) | 15(15) | −9(13) | −8(16) |
| C(3a) | 0274(9) | 640(1) | 138(1) | 77(19) | 84(20) | 140(27) | 17(16) | −29(18) | −45(20) |
| C(4a) | 0219(9) | 637(1) | 050(2) | 75(19) | 66(18) | 166(31) | 4(15) | −25(19) | 57(20) |
| C(5a) | 0400(8) | 579(1) | 006(2) | 59(16) | 86(20) | 108(22) | −27(14) | −4(16) | 11(18) |
| C(6a) | 0678(8) | 527(1) | 051(1) | 65(15) | 45(14) | 75(18) | −12(12) | −2(13) | 20(13) |
| C(7a) | 0844(8) | 465(1) | 000(1) | 53(15) | 112(21) | 44(15) | −33(15) | −7(12) | −6(15) |
| C(8a) | 1134(9) | 346(1) | −013(1) | 61(17) | 114(21) | 59(17) | 19(15) | 13(14) | −19(16) |
| C(9a) | 086(1) | 470(2) | −096(2) | 154(28) | 124(26) | 64(19) | −48(23) | 2(19) | 14(19) |
| C(1b) | 1610(7) | 334(1) | 303(1) | 33(12) | 61(15) | 77(17) | −8(11) | 3(12) | 14(14) |
| C(2b) | 1804(8) | 349(1) | 387(1) | 60(16) | 100(20) | 65(17) | −14(15) | −18(14) | 8(16) |
| C(3b) | 2078(9) | 297(2) | 423(2) | 60(17) | 139(25) | 86(21) | 2(17) | −8(16) | 38(20) |
| C(4b) | 2132(7) | 232(2) | 389(2) | 25(13) | 127(25) | 134(25) | 4(15) | −1(15) | 51(21) |
| C(5b) | 1909(8) | 220(1) | 313(2) | 48(14) | 58(17) | 150(27) | 9(12) | 28(16) | 55(18) |
| C(6b) | 1637(7) | 268(1) | 263(2) | 36(12) | 51(15) | 89(19) | −4(11) | 17(12) | 4(14) |
| C(7b) | 1431(7) | 251(1) | 181(1) | 47(13) | 52(14) | 84(19) | −4(12) | 17(13) | 3(13) |
| C(8b) | 1089(8) | 284(1) | 044(2) | 43(14) | 84(18) | 93(19) | 5(13) | 19(14) | −51(16) |
| C(9b) | 139(1) | 174(1) | 158(2) | 83(19) | 59(18) | 172(30) | −22(15) | −8(21) | −2(20) |
| (ii) Ligand (cd) | | | | | | | | | |
| O(c) | 1420(5) | 5905(7) | 3132(9) | 78(9) | 64(9) | 45(11) | −18(9) | 9(9) | 0(9) |
| O(d) | 1077(5) | 4987(7) | 4094(8) | 64(9) | 64(9) | 49(9) | −16(8) | 9(8) | 4(8) |
| N(c) | 1344(6) | 6934(9) | 436(1) | 35(10) | 71(13) | 50(11) | −10(9) | −3(9) | −23(10) |
| N(d) | 1020(6) | 5932(9) | 544(1) | 57(12) | 59(12) | 61(13) | 2(11) | −6(10) | −23(11) |
| C(1c) | 1642(7) | 642(1) | 268(1) | 36(12) | 52(14) | 64(16) | −10(11) | −22(11) | 27(13) |
| C(2c) | 1845(8) | 621(1) | 190(1) | 69(16) | 71(18) | 75(19) | −12(14) | 12(14) | 18(15) |
| C(3c) | 2074(9) | 669(1) | 139(1) | 95(19) | 72(18) | 53(17) | −1(15) | −2(15) | 8(14) |
| C(4c) | 2133(7) | 738(1) | 168(2) | 40(14) | 120(23) | 86(20) | −1(15) | −4(14) | 51(18) |
| C(5c) | 1936(7) | 758(1) | 244(2) | 42(14) | 60(16) | 128(24) | −3(13) | −20(15) | 36(16) |
| C(6c) | 1681(8) | 711(1) | 298(1) | 42(12) | 44(13) | 69(16) | −4(11) | −15(12) | 19(13) |
| C(7c) | 1487(7) | 736(1) | 377(1) | 46(13) | 73(17) | 52(15) | −12(12) | 3(11) | 1(13) |
| C(8c) | 146(1) | 815(1) | 395(2) | 94(20) | 37(15) | 140(25) | −6(4) | 14(18) | −38(16) |
| C(9c) | 1165(8) | 717(1) | 517(2) | 63(17) | 65(17) | 102(20) | −1(14) | 0(15) | −7(16) |
| C(1d) | 0763(7) | 461(1) | 459(1) | 38(12) | 54(14) | 49(14) | 4(11) | −6(11) | 7(12) |
| C(2d) | 0543(8) | 400(1) | 422(2) | 52(14) | 58(15) | 90(19) | −3(13) | −10(13) | −2(16) |
| C(3d) | 0217(7) | 359(1) | 472(2) | 29(13) | 61(16) | 141(25) | −3(12) | 7(14) | 40(17) |
| C(4d) | 0126(9) | 381(1) | 553(2) | 75(17) | 96(20) | 76(19) | 19(15) | 29(14) | 68(17) |
| C(5d) | 0325(9) | 435(1) | 589(2) | 93(20) | 69(18) | 95(22) | −3(15) | −10(17) | 23(17) |
| C(6d) | 0657(7) | 480(1) | 544(1) | 55(14) | 57(15) | 57(16) | 8(12) | −4(12) | 46(13) |
| C(7d) | 0847(7) | 542(1) | 586(2) | 34(13) | 59(16) | 113(21) | 8(12) | −12(14) | 13(16) |
| C(8d) | 1203(9) | 657(1) | 583(1) | 81(18) | 98(20) | 57(16) | 3(16) | 1(15) | −23(15) |
| C(9d) | 079(1) | 541(1) | 684(1) | 152(28) | 124(26) | 38(17) | 39(22) | 8(16) | −4(16) |
| (iii) Perchlorate (e) | | | | | | | | | |
| Cl(e) | 0019(2) | 8019(3) | 2907(4) | 68(4) | 91(5) | 82(4) | 5(4) | 16(4) | 5(4) |
| O(1e) | −0333(7) | 755(2) | 263(2) | 77(14) | 238(27) | 239(20) | −34(17) | 21(17) | −138(25) |
| O(2e) | −0180(7) | 8676(9) | 310(1) | 108(14) | 93(14) | 124(17) | 34(12) | 8(13) | −11(12) |
| O(3e) | 0392(9) | 805(1) | 235(2) | 187(23) | 113(17) | 250(30) | −20(17) | 159(23) | 9(20) |
| O(4e) | 018(1) | 773(1) | 362(2) | 245(30) | 117(21) | 209(28) | 8(20) | −47(25) | 44(21) |
| (iv) Perchlorate (f) | | | | | | | | | |
| Cl(f) | 2513(4) | 5389(5) | 525(1) | 118(7) | 106(7) | 448(21) | −5(6) | −169(10) | 22(11) |
| O(1f) | 218(1) | 488(2) | 559(3) | 218(33) | 227(36) | 557(76) | −102(29) | −159(41) | 109(46) |
| O(2f) | 284(1) | 499(2) | 521(3) | 146(24) | 270(28) | 544(69) | 113(27) | 7(34) | 122(44) |
| O(3f) | 2212(9) | 570(2) | 492(2) | 138(21) | 283(36) | 182(27) | 88(22) | −8(19) | 34(26) |
| O(4f) | 273(2) | 571(2) | 579(3) | 377(56) | 209(37) | 500(74) | −93(36) | −218(53) | −47(42) |
| (v) Water molecule | | | | | | | | | |
| O(1) | 2206(7) | 4855(9) | 293(1) | 124(15) | 99(15) | 148(18) | −55(13) | −46(15) | 54(15) |

molecule, the remaining water molecule(s) being co-ordinated to the central copper atom, Cu(3). The stereochemistries of the two cations provide a further remarkable example of the ease with which seemingly trivial changes in substituent, solvent, or physical conditions can provoke drastic changes in crystal form and co-ordination environment with accompanying parallel changes in the physical properties of the species (see *e.g.* the previous studies of copper [9] and palladium [10] with related ligands).

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[9] F. J. Llewellyn and T. N. Waters, *J. Chem. Soc.*, 1960, 2639.

[10] P. C. Jain and E. C. Lingafelter, *Acta Cryst.*, 1967, **23**, 127.

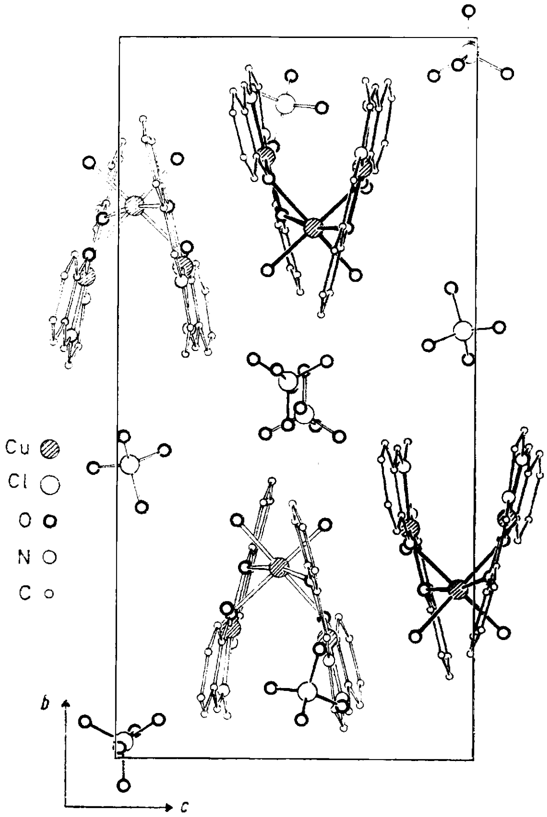


FIGURE 1 Unit-cell contents of (I) viewed down *a*

TABLE 2

Interatomic distances (Å) and angles (°), with least-squares estimated standard deviations in parentheses. Parameters for (II) are given below the corresponding entries for (I)

(*a*) Distances

| | i = a | b | c | d |
|---|---|---|---|---|
| Cu(1)–O(i) | 1·901(5) | 1·913(5) | | |
| | 1·88(1) | 1·89(1) | | |
| Cu(2)–O(i) | | | 1·925(6) | 1·900(5) |
| | | | 1·89(1) | 1·89(1) |
| Cu(1)–N(i) | 1·896(7) | 1·924(7) | | |
| | 1·90(2) | 1·90(2) | | |
| Cu(2)–N(i) | | | 1·919(6) | 1·895(7) |
| | | | 1·93(2) | 1·90(2) |
| Cu(3)–O(i) | 2·324(6) | 2·050(5) | 2·025(6) | 2·328(6) |
| | 1·98(1) | 1·93(1) | 1·95(1) | 2·06(1) |
| O(i)–C(1i) | 1·31(1) | 1·33(1) | 1·35(1) | 1·32(1) |
| | 1·32(2) | 1·41(3) | 1·36(2) | 1·35(2) |
| C(1i)–C(2i) | 1·42(1) | 1·39(1) | 1·38(1) | 1·41(1) |
| | 1·38(3) | 1·44(3) | 1·40(3) | 1·42(3) |
| C(2i)–C(3i) | 1·36(1) | 1·39(1) | 1·38(1) | 1·37(1) |
| | 1·36(3) | 1·36(4) | 1·37(3) | 1·42(4) |
| C(3i)–C(4i) | 1·36(1) | 1·39(1) | 1·40(1) | 1·35(1) |
| | 1·39(4) | 1·35(4) | 1·39(4) | 1·38(4) |
| C(4i)–C(5i) | 1·37(1) | 1·34(1) | 1·35(1) | 1·39(1) |
| | 1·39(4) | 1·37(4) | 1·37(4) | 1·30(4) |
| C(5i)–C(6i) | 1·40(1) | 1·40(1) | 1·38(1) | 1·41(1) |
| | 1·43(3) | 1·42(3) | 1·41(3) | 1·42(3) |
| C(6i)–C(1i) | 1·43(1) | 1·41(1) | 1·42(1) | 1·40(1) |
| | 1·40(3) | 1·41(3) | 1·41(3) | 1·42(3) |
| C(6i)–C(7i) | 1·44(1) | 1·43(1) | 1·45(1) | 1·46(1) |
| | 1·49(3) | 1·45(3) | 1·42(3) | 1·45(3) |
| C(7i)–N(i) | 1·26(1) | 1·25(1) | 1·26(1) | 1·28(1) |
| | 1·28(3) | 1·28(3) | 1·29(3) | 1·27(3) |
| N(i)–C(8i) | 1·48(1) | 1·47(1) | 1·46(1) | 1·47(1) |
| | 1·46(3) | 1·45(3) | 1·43(3) | 1·46(3) |
| C(9i)–C(7i) | 1·51(3) | 1·51(3) | 1·53(3) | 1·54(3) |

TABLE 2 (*Continued*)

(*b*) Angles

| | i = a | b | c | d |
|---|---|---|---|---|
| O(1)–Cu(3)–O(i) | 90·9(2) | 89·2(2) | 167·9(2) | 96·8(2) |
| | 121·7(7) | 90·0(7) | 90·3(7) | 113·8(7) |
| O(2)–Cu(3)–O(i) | 97·7(2) | 169·7(2) | 91·4(2) | 88·1(2) |
| O(i)–Cu(1)–N(i) | 94·8(3) | 94·2(3) | | |
| | 94·7(7) | 94·9(7) | | |
| O(i)–Cu(2)–N(i) | | | 94·5(3) | 95·6(3) |
| | | | 92·7(7) | 94·8(7) |
| Cu(3)–O(i)–Cu(1) | 92·0(2) | 100·7(2) | | |
| | 99·9(6) | 101·2(7) | | |
| Cu(3)–O(i)–Cu(2) | | | 98·5(2) | 89·6(2) |
| | | | 101·6(7) | 97·6(7) |
| O(i)–C(1i)–C(2i) | 120·0(8) | 123·2(7) | 119·6(7) | 124·0(3) |
| | 119(2) | 112(2) | 115(2) | 117(2) |
| O(i)–C(1i)–C(6i) | 123·8(7) | 119·1(7) | 122·6(7) | 117·4(8) |
| | 123(2) | 122(2) | 122(2) | 122(2) |
| Cu(2i)–C(1i)–C(6i) | 116·2(8) | 117·7(7) | 117·7(7) | 118·6(8) |
| | 117(2) | 124(2) | 123(1) | 120(2) |
| C(1i)–C(2i)–C(3i) | 122·0(9) | 122·2(8) | 122·5(8) | 119·6(9) |
| | 123(2) | 116(2) | 119(2) | 119(2) |
| C(2i)–C(3i)–C(4i) | 121·8(9) | 118·9(8) | 118·6(8) | 122·6(9) |
| | 120(2) | 123(2) | 120(2) | 117(2) |
| C(3i)–C(4i)–C(5i) | 118·8(9) | 119·7(8) | 119·5(9) | 119·5(9) |
| | 119(2) | 118(2) | 120(2) | 125(2) |
| C(4i)–C(5i)–C(6i) | 122·3(9) | 122·8(8) | 122·3(8) | 120·1(9) |
| | 120(2) | 126(2) | 123(2) | 122(2) |
| C(5i)–C(6i)–C(1i) | 118·8(8) | 123·4(7) | 123·7(7) | 124·6(8) |
| | 120(2) | 126(2) | 115(2) | 124(2) |
| C(5i)–C(6i)–C(7i) | 118·3(8) | 117·9(7) | 117·0(7) | 115·8(8) |
| | 116(2) | 112(2) | 120(2) | 119(2) |
| C(1i)–C(6i)–C(7i) | 122·8(8) | 118·7(7) | 119·2(8) | 119·6(9) |
| | 123(2) | 122(2) | 125(2) | 124(2) |
| C(6i)–C(7i)–N(i) | 125·4(8) | 127·0(7) | 126·7(7) | 123·8(8) |
| | 121(2) | 121(2) | 122(2) | 122(2) |
| C(7i)–N(i)–C(8i) | 121·5(7) | 123·0(7) | 122·2(7) | 118·7(8) |
| | 122(2) | 123(2) | 123(2) | 124(2) |
| N(i)–C(8i)–C(8i) | 114·2(8) | 115·6(9) | 114·2(8) | 110·2(9) |
| | 107(2) | 111(2) | 110(2) | 108(2) |
| Cu(1)–N(i)–C(7i) | 126·1(6) | 125·5(6) | | |
| | 127(1) | 128(1) | | |
| Cu(2)–N(i)–C(7i) | | | 125·7(6) | 126·5(6) |
| | | | 128(1) | 127(1) |
| Cu(1)–N(i)–C(8i) | 112·4(5) | 111·5(6) | | |
| | 109(1) | 107(1) | | |
| Cu(2)–N(i)–C(8i) | | | 112·1(6) | 114·8(6) |
| | | | 108(1) | 107(1) |
| C(9i)–C(7i)–C(6i) | 119(2) | 118(2) | 120(2) | 115(2) |
| C(9i)–C(7i)–N(i) | 119(2) | 121(2) | 118(2) | 122(2) |

| | | | |
|---|---|---|---|
| Cu(3)–O(1) | 1·950(6) | Cu(3)–O(2) | 2·000(6) |
| | 2·18(2) | | |
| O(1)–Cu(3)–O(2) | 92·6(2) | | |
| Cu(3)–Cu(1) | 3·053(2) | Cu(3)–Cu(2) | 2·993(2) |
| | 2·950(5) | | 2·975(5) |
| Cu(1)–Cu(3)–Cu(2) | 97·3(4) | | |
| | 156·2(2) | | |
| O(a)–Cu(3)–O(b) | 72·1(2) | O(c)–Cu(3)–O(d) | 71·9(2) |
| | 76·7(6) | | 76·8(6) |
| O(a)–Cu(3)–O(d) | 170·2(2) | O(b)–Cu(3)–O(c) | 88·9(2) |
| | 124·4(6) | | 178·0(6) |
| O(a)–Cu(3)–O(c) | 99·9(2) | O(b)–Cu(3)–O(d) | 101·7(2) |
| | 101·5(6) | | 104·8(6) |
| O(a)–Cu(1)–O(b) | 85·3(2) | O(c)–Cu(2)–O(d) | 84·3(2) |
| | 80·2(6) | | 82·7(6) |
| O(a)–Cu(1)–N(b) | 177·3(3) | O(b)–Cu(1)–N(a) | 178·0(3) |
| | 174·2(7) | | 169·2(2) |
| O(c)–Cu(2)–N(d) | 178·6(3) | O(d)–Cu(2)–N(c) | 172·4(2) |
| | 177·4(7) | | 174·2(7) |
| N(a)–Cu(1)–N(b) | 85·7(3) | N(c)–Cu(2)–N(d) | 85·4(3) |
| | 89·5(8) | | 89·9(7) |
| C(8a)–C(8b) | 1·35(2) | C(8c)–C(8d) | 1·43(2) |
| | 1·50(3) | | 1·54(3) |

TABLE 2 (*Continued*)

Perchlorates

| | i = e | f |
|---|---|---|
| Cl(i)–O(1i) | 1·393(8) | 1·31(1) |
| | 1·37(2) | 1·42(4) |
| Cl(i)–O(2i) | 1·425(8) | 1·32(1) |
| | 1·40(2) | 1·17(3) |
| Cl(i)–O(3i) | 1·39(1) | 1·32(1) |
| | 1·34(3) | 1·13(3) |
| Cl(i)–O(4i) | 1·34(1) | 1·55/1·45(3) |
| | 1·32(3) | 1·21(5) |
| O(1i)–Cl(i)–O(2i) | 109·7(5) | 117·4(7) |
| | 113(1) | 92(2) |
| O(1i)–Cl(i)–O(3i) | 110·4(6) | 122·1(7) |
| | 110(2) | 95(2) |
| O(1i)–Cl(i)–O(4i) | 112·5(6) | 81·2/86·9(16) |
| | 103(2) | 113(3) |
| O(2i)–Cl(i)–O(3i) | 106·5(6) | 117·9(6) |
| | 113(1) | 150(3) |
| O(2i)–Cl(i)–O(4i) | 108·5(6) | 86·3/98·3(12) |
| | 108(1) | 90(3) |
| O(3i)–Cl(i)–O(4i) | 109·0(7) | 86·3/100·9(10) |
| | 109(2) | 114(2) |
| O(4f1)–Cl(f)–O(4f2) | 168·1(17) | |

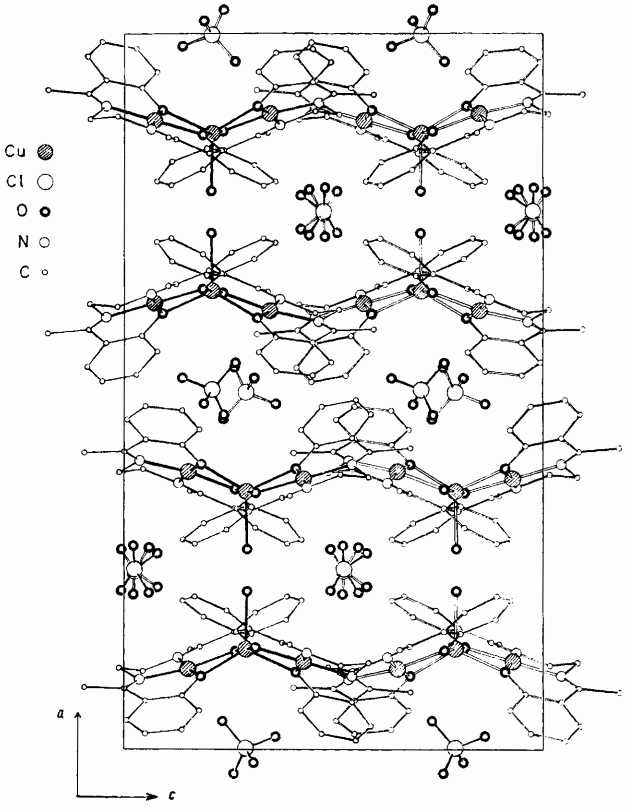


FIGURE 2 Unit-cell contents of (II) viewed down *b*

In both (I) and (II), the pair of ligand complex molecules co-ordinate to the central copper atom *via* the oxygen atoms so that an isosceles triangle of copper atoms is formed in each case, with an obtuse apical angle at Cu(3). Because of the different co-ordination geometries adopted by Cu(3) in each case, strikingly different cationic conformations are found. In (II), the central copper atom adopts a skewed five-co-ordinate trigonal bipyramid co-ordination, the water molecule O(1) co-ordinating in an equatorial site together with an

TABLE 3

(*a*) Equations of least-squares planes for selected cationic fragments in the form $pX + qY + rZ = s$; $\sigma$ is the estimated standard deviation of the defining atoms in Å. Atomic deviations (Å) are given in square brackets. Values for (I) are given first followed by those for (II) italicized.

Plane (*a*): O(a), C(1)—(7a)

| *p* | *q* | *r* | *s* | $\sigma$ |
|---|---|---|---|---|
| 0·0530 | 0·2625 | 0·9635 | 7·5405 | 0·04 |
| *0·8445* | *0·5064* | *−0·1740* | *6·4701* | *0·04* |

[O(a) 0·05, *0·05*; (C1a) 0·00, *−0·01*; C(2a) −0·04, *−0·04*; C(3a) −0·04, *−0·04*; C(4a) 0·02, *0·05*; C(5a) 0·05, *0·02*; C(6a) 0·02, *0·02*; C(7a) −0·06, *−0·06*; N(a) −0·12, *−0·43*; Cu(1) 0·11, *−0·54*; Cu(3) −0·67, *0·64*; Cu(2) −2·47, *0·87*; C(9a) —, *0·29*]

Plane (*b*): O(b), C(1)—(7b)

| *p* | *q* | *r* | *s* | $\sigma$ |
|---|---|---|---|---|
| −0·1578 | 0·2499 | 0·9553 | 5·3183 | 0·01 |
| *0·8483* | *0·2864* | *−0·4454* | *3·3725* | *0·03* |

[O(b) −0·02, *0·04*; C(1b) 0·00, *0·00*; C(2b) 0·03, *−0·06*; C(3b) 0·00, *0·02*; C(4b) −0·01, *0·03*; C(5b) 0·00, *−0·01*; C(6b) 0·00, *−0·02*; C(7b) 0·01, *0·00*; N(b) 0·09, *0·28*; Cu(1) 0·20, *0·27*; Cu(3) −0·92, *0·46*; Cu(2) −3·08, *−0·34*; C(9b) —, *−0·36*]

Plane (*c*): O(c), C(1)—(7c)

| *p* | *q* | *r* | *s* | $\sigma$ |
|---|---|---|---|---|
| −0·1444 | −0·1635 | 0·9760 | 1·0632 | 0·01 |
| *0·8658* | *−0·2264* | *0·4461* | *2·9357* | *0·01* |

[O(c) −0·01, *0·01*; C(1c) 0·02, *−0·01*; C(2c) −0·00, *0·00*; C(3c) 0·01, *0·01*; C(4c) −0·01, *0·02*; C(5c) 0·01, *−0·02*; C(6c) −0·02, *0·01*; C(7c) 0·01, *−0·01*; N(c) −0·06, *0·26*; Cu(2) −0·22, *0·34*; Cu(3) 1·19, *0·24*; Cu(1) 3·21, *−0·96*; C(9c) —, *0·31*]

Plane (*d*): O(d), C(1)—(7d)

| *p* | *q* | *r* | *s* | $\sigma$ |
|---|---|---|---|---|
| −0·0704 | −0·2323 | 0·9701 | 1·4938 | 0·01 |
| *0·7732* | *−0·5468* | *0·3213* | *−0·9075* | *0·01* |

[O(d) 0·01, *0·01*; C(1d) −0·01, *0·00*; C(2d) 0·00, *−0·01*; C(3d) 0·00, *0·00*; C(4d) 0·01, *−0·01*; C(5d) 0·00, *0·02*; C(6d) 0·00, *0·02*; C(7d) 0·00, *−0·02*; N(d) 0·04, *−0·41*; Cu(2) 0·03, *−0·59*; Cu(3) 1·16, *0·16*; Cu(1) 3·21, *−0·10*; C(9d) —, *0·36*]

Plane (*e*): Cu(1) N(a,b), O(a,b)

| *p* | *q* | *r* | *s* | $\sigma$ |
|---|---|---|---|---|
| −0·0513 | 0·2451 | 0·9681 | 6·5795 | 0·02 |
| *0·9350* | *0·2433* | *−0·2581* | *4·1149* | *0·07* |

[Cu(1) 0·03, *−0·09*; N(a) 0·00, *0·07*; N(b) −0·01, *−0·03*; O(a) −0·01, *−0·03*; O(b) 0·00, *0·07*; Cu(3) −0·96, *0·49*; O(c) −2·71, *0·94*; O(d) −2·06, *−0·75*; C(1a) 0·07, −0·32; C(7a) 0·15, *0·17*; C(1b) 0·14, *0·25*; C(7b) 0·04, *−0·09*]

Plane (*f*): Cu(2), N(c,d), O(c,d)

| *p* | *q* | *r* | *s* | $\sigma$ |
|---|---|---|---|---|
| −0·0455 | −0·1614 | 0·9858 | 2·2419 | 0·06 |
| *0·9368* | *−0·2114* | *0·2789* | *2·5370* | *0·03* |

[Cu(2) −0·06, *0·02*; N(c) 0·06, *−0·04*; N(d) −0·074, *0·03*; O(c) −0·04, *0·03*; O(d) 0·07, *−0·04*; Cu(3) 1·18, *0·28*; O(a) 2·29, *−1·13*; O(b) 2·77, *0·50*; C(1c) −0·11; *0·18*; C(7c) 0·02, *−0·11*; C(1d) 0·12, *−0·46*; C(7d) 0·12, *−0·02*]

Plane (*g*): Equatorial plane about Cu(3) in (I) [Cu(3), O(1,2,b and c]

| *p* | *q* | *r* | *s* | $\sigma$ |
|---|---|---|---|---|
| 0·9744 | 0·0648 | −0·2155 | 10·25 | 0·19 |

[Cu(3) −0·01, O(1) 0·20, O(2) −0·19, O(b) −0·19, O(c) 0·19]

Plane (*h*): Equatorial plane about Cu(3) in (II) [Cu(3), O(1,a,d)]

| *p* | *q* | *r* | *s* | $\sigma$ |
|---|---|---|---|---|
| 0·0443 | 0·9970 | −0·0629 | 9·215 | 0·00 |

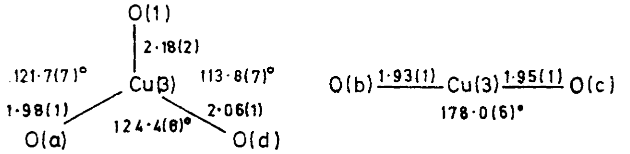
No atom deviation $>0·005$ Å.

(*b*) Angles between the normals to the planes (°)

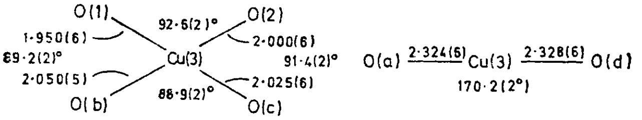
| | (*a*) | (*b*) | (*c*) | (*d*) | (*e*) |
|---|---|---|---|---|---|
| (*b*) | 12·1(*20·1*) | | | | |
| (*c*) | 27·2(*57·4*) | 23·9(*61·9*) | | | |
| (*d*) | 29·5(*71·3*) | 28·4(*69·1*) | 5·8(*20·5*) | | |
| (*e*) | 6·1(*16·7*) | 6·2(*12·1*) | 24·2(*50·3*) | 27·6(*59·5*) | |
| (*f*) | 25·2(*50·5*) | 24·7(*52·4*) | 5·7(*10·5*) | 4·4(*21·6*) | 23·5(*41·2*) |

* For (I) $X = ax + cz\cos\beta$, $Y = by$, $Z = cz\sin\beta$; for (II) $X = ax$, $Y = by$, $Z = cz$.

oxygen atom from each ligand yielding a tolerably flat Cu(3),O(1),O(a),O(d) equatorial plane [Table 3, plane (*h*)] in spite of irregular differences in the co-ordination angles and distances. The axial distances are appreciably shorter than the equatorial; as a result of the four-membered ring geometries entailed by the complex, the O(b)–Cu(3)–O(c) axis is skewed in the plane normal to the O(1)–Cu(3) bond so that O(1)–Cu(3)–O(b) and O(1)–Cu(3)–O(c) are 90·0 and 90·3(7)° still, while O(b)–Cu(3)–O(a) and O(c)–Cu(3)–O(d) are reduced to 76·7 and 76·8(6)°. As a consequence the cation is chiral and exists as the racemate in the centrosymmetric unit cell. The Cu(1) ··· Cu(3) and Cu(2) ··· Cu(3) distances are almost equal [2·950 and 2·975(5) Å]; Cu(1) ··· Cu(2) is 5·798(5) Å and Cu(1) ··· Cu(3) ··· Cu(2) 156·2(2)°.



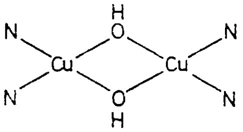
In (I), the central copper atom adopts a Jahn–Teller distorted octahedral geometry, the two molecular ligands adopting a *cis*-configuration, each bridging an axial and an equatorial position with two equatorial water molecules. The equatorial geometry is somewhat irregular and the plane somewhat distorted [Table 3, plane (*g*)]. The axial distances are somewhat larger, as expected, and not collinear. The greater irregularity in the co-ordination is presumably a consequence of the four-membered ring geometry of the ligands and also of the bond lengths which are generally greater than those in (II) by virtue of the axial co-ordination of the ligand molecules; O(a)–Cu(3)–O(b) and O(c)–Cu(3)–O(d) are reduced to 72·1 and 71·9(2)° in this complex. As a consequence of the *cis*-co-ordination geometry, this cation is also chiral and the centrosymmetric crystal a racemate; the Cu(3) ··· Cu(1) and Cu(3) ··· Cu(2) distances are longer than in (II) [3·053(2) and 2·993(2) Å] but the Cu(1) ··· Cu(2) distance is considerably shorter [4·537(2) Å] and Cu(1) ··· Cu(3) ··· Cu(2) reduced to 97·3(4)°.



Within the ligand molecules, the Cu(1,2) environments adopt a variety of configurations: in (I), the Cu(1) environment is a good approximation to a plane, no deviation being >0·03 Å [Cu(1)]; the Cu(2) environment displays the common slight tetrahedral distortion, alternate atoms being out of the plane by ~±0·05—0·07 Å. In (II), the same is true for the environments of both copper atoms. In the ligand molecules in both complexes, the Cu(1,2) atom and the nearby $-CH_2-CH_2-$ bridges act as the focii of folds whereby the two highly conjugated halves of each ligand molecule become non-coplanar to varying degrees, probably determined largely by crystal packing. Bond lengths and angles within the ligands are typical; the peripheral interatomic distances are somewhat shortened by thermal motion effects, no correction having been applied.

The structural information yielded by this study only partly provides an explanation for the differences between the behaviour of the magnetic susceptibilities of the two compounds as a function of temperature. Previous work [1,2] has shown that the magnetic exchange integral for (I) (*J ca.* $-40$ cm$^{-1}$) is a good deal smaller in absolute magnitude than for (II) (*J* $-190$ cm$^{-1}$). It also showed that the behaviour of (I) at low temperatures cannot be accounted for on the basis of three interacting $S = \frac{1}{2}$ species with exchange between the central atom and its neighbours but not between extreme members. The model suffices for (II) and some related compounds.[1,11]

The features of the structures which are most obviously relevant for the magnetic exchange is the angle Cu(1) ··· Cu(3) ··· Cu(2) and the various angles Cu(1)–O(a)–Cu(3), Cu(1)–O(b)–Cu(3), Cu(2)–O(c)–Cu(3), and Cu(2)–O(d)–Cu(3). However, the interpretation of the magnetic susceptibility data indicates that the exchange between the extreme copper(II) ions of the triad is negligible. Therefore, although the Cu(1)–Cu(3)–Cu(2) angle differs markedly between the two compounds, this is probably not relevant. The other angles vary quite appreciably within each structure, but the average values are distinctly different being 95·3° for (I) and 100·0° for (II). This difference may be responsible for the lower exchange integral found in (I). A study of a series of binuclear copper(II) complexes with two hydroxide bridging groups and nitrogen donor ligands in other positions, *i.e.* the system:



has shown the exchange integral to be a linear function of the Cu–O–Cu angle.[12] The value of *J* is zero at 97·7° and decreases at the rate of 44 cm$^{-1}$ deg$^{-1}$ so that it is negative above that value for the angle. If a similar type of relationship holds for the present compounds, it would account for the decrease in the absolute magnitude of *J* in (I) relative to that in (II). If exactly the same parameters described the relationship, *J* would be positive for (I). However, with the different ligands and stereochemistry about the copper(II) ions and with –O– bridging rather than $OH^-$ groups in the present structures relative to the systems examined earlier, it might well be that the exchange integral takes on its zero value at a slightly different angle. Again, taking

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[11] E. Sinn and C. M. Harris, *Co-ordination Chem. Rev.*, 1969, **4**, 403.

[12] K. T. McGregor, N. T. Watkins, D. L. Lewis, R. F. Drake, D. J. Hodgson, and W. E. Hatfield, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 423.

the differences between the mean Cu–O–Cu angles and the exchange integrals, the rate of change in $J$ is $-32$ cm$^{-1}$ deg$^{-1}$, a value as close as might be expected to that for the other system.

The magnetic susceptibility of (I) is described by the exchange model only down to *ca.* 100 K. Below that temperature, the susceptibility is higher than predicted by the theory which works well for a number of closely related compounds. The present structure determination of the compound does nothing to aid the explanation of the effect. The behaviour of the susceptibility can be accounted for by the assumption that *ca.* 25% of the copper(II) ion is present as a monomer and that the exchange integral is rather larger than was deduced.* It might be possible that an incompletely representative crystal was chosen for the structural work and that the bulk material contains other types of crystal. However there is no evidence to suggest this possibility and the satisfactory analyses obtained[1,2] make it seem unlikely.

[3/2552 *Received, 20th March,* 1974]

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* In ref. 2, the right-hand side of equation (1) should be multiplied by 1/3; this equation is not as, suggested in ref. 2, a corrected form of equation (1) in ref. 5, which refers to a different system.[13]

[13] E. Sinn, personal communication.