are coplanar one thioamide group is out of this plane with S(1) in a position that tends to balance the coordination sphere.

The bite of the ligand leaves the Zn^{2+} ion in an exposed position. The smaller Cu^{2+} ion for which the average Cu—N bond length in CuKTS is 1·97 Å is more completely enclosed by the ligand than is the Zn^{2+} ion in ZnKTS where the Zn—N distances average 2·136 Å. This, along with inherently weaker Zn—ligand bonds, is a reason why the stability of ZnKTS [log K = 6·0 at pH = 7·4, Petering (1974)] is lower than that of CuKTS [log K = 18·6 at pH = 7·4, Petering (1974)].

The interatomic distances in the ligand are similar to those in related complexes. The weaker Zn—ligand binding leads to smaller perturbations in the KTS^{2-} ligand bonds than is observed in Cu complexes. In particular, the C—S bonds retain more of their double-bond character in ZnKTS than they do in CuKTS (1·746 Å) or in [benzil bis(thiosemicarbazonato)]copper(II) (1·755 Å) (Bushnell & Tsang, 1979).

The molecules are linked together in sheets within the plane of the KTS^{2-} ligands by a few weak hydrogen bonds in a pattern that is similar to that found in CuKTS (Fig. 3). Not all the amino H atoms form hydrogen bonds. One, H(1) of the amino group that is proximal to the side chain, is hydrogen bonded to N(5) of another molecule at a distance of 2·98 Å (cf. 2·96 Å in CuKTS). This is coupled with a N—H···S intermolecular interaction of 3·59 Å (Fig. 3) compared to a similar one of 3·70 Å in CuKTS. There appears to be a growing body of evidence that indicates that the hydrogen-bonding potential of the amino protons in these complexes is very low. This is consistent with the observation that a number of these complexes are

soluble in weakly polar solvents. Hydrogen bonds of the water molecules link molecules of the complex related by a center of symmetry in pairs $[O(w) \cdots N(2)]$ and within sheets $[O(w) \cdots O]$.

References

BUSHNELL, G. W. & TSANG, A. Y. M. (1979). Can. J. Chem. 57, 603–607.

CARRELL, H. L. (1975). ICRFMLS. Modification of UCLALS4. Program from The Institute for Cancer Research, Philadelphia, USA.

CARRELL, H. L. (1976). VIEW. Program from The Institute for Cancer Research, Philadelphia, USA.

CRIM, J. A., BUSKIRK, H. H. & PETERING, H. G. (1967). Cancer Res. 27, 1109–1114.

GABE, E. J., TAYLOR, M. R., GLUSKER, J. P., MINKIN, J. A. & PATTERSON, A. L. (1969). Acta Cryst. B25, 1620–1631.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72–98, 149–150. Birmingham: Kynoch Press.

PETERING, D. H. (1974). Biochem. Pharmacol. 23, 567–576.

RAE, A. D. (1965). Acta Cryst. 19, 683–684.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). J. Chem. Phys. 42, 3175–3187.

TAYLOR, M. R., GLUSKER, J. P., GABE, E. J. & MINKIN, J. A. (1974). Bioinorg. Chem. 3, 189–205.

The Structure of Disodium catena-Bis(μ-oxalato)-cuprate(II) Dihydrate

By Pongchan Chananont, Phillip E. Nixon, Joyce M. Waters and T. Neil Waters

Department of Chemistry, University of Auckland, Private Bag, Auckland, New Zealand

Abstract. $\{Na_2[Cu(C_2O_4)_2] \cdot 2H_2O\}_n$, $(C_4CuO_8^{2-})_n \cdot 2n$-$Na^+ \cdot 2nH_2O$, $M_r = 321 \cdot 6$; triclinic, $P\bar{1}$, $a = 3 \cdot 583$ (7), $b = 9 \cdot 649$ (6), $c = 7 \cdot 549$ (6) Å, $\alpha = 109 \cdot 07$ (1), $\beta = 76 \cdot 38$ (1), $\gamma = 103 \cdot 32$ (1)°, $V = 236$ Å^3; $D_m = 2 \cdot 25$, $Z = 1$, $D_c = 2 \cdot 26$ Mg m^{-3}. The final R value for 604 independent data is 0·052. The compound was produced as an unknown product during oxygenation reactions with cupric complexes. It is recorded for comparison with its ammonium and potassium analogues from which it differs in having the water molecules absent from the coordination sphere. The distorted octahedral geometry about each Cu atom is completed by the formation of oxalate bridges and by the sharing of individual oxygen donors.

Introduction. During studies of the interaction of copper(II) complexes with molecular oxygen it was noticed that after reduction with ascorbic acid a small

number of compounds showed striking colour changes on subsequent oxygenation and deposited a small quantity of deep-blue crystals. Infrared data suggested the presence of organic groups but characterization was unable to proceed because of the lack of material. In the belief that knowledge of the compound and its structure would help towards an ultimate description of reactions occurring on oxygenation we chose the one large crystal for an X-ray study. This grew from a solution of $Cu_2(L)Cl_4$ in dimethylformamide which had been reduced by ascorbic acid before oxygen addition. The ligand, L, was 1,8-diamino-4-methyl-3,6-dithia-octane and it, and the complex, were contaminated with a small amount of sodium perchlorate from preparative procedures. Intensity data were collected (Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å) from a crystal of approximate dimensions $0.4 \times 0.2 \times 0.03$ mm using the ω–2θ technique on a Hilger & Watts Y290 diffractometer. Reflexions were scanned over a 2θ range of $1.0°$ in $0.02°$ steps counting for 1 s at each. Backgrounds at both ends were counted for 15 s. Three reflexions were monitored at intervals but their intensities did not vary significantly. A total of 604 independent values for which $I > 3\sigma(I)$ were recorded and used in the subsequent analysis after treatment for Lorentz and polarization effects. A p value (Busing & Levy, 1957; Corfield, Doedens & Ibers, 1967) of 0.04 was used in the determination of individual standard deviations. Absorption corrections [μ(Mo $K\alpha$) = 25.4 mm^{-1}] were not applied.

Although the structure may be derived from the Patterson function with the benefit of hindsight we, in fact, used direct methods in which intensity values were modified before the application of *MULTAN* (Declercq, Germain, Lessinger, Main & Woolfson, 1974) procedures. The successfully interpreted E map showed that the substance was polymeric, based on a bis(oxalato)cuprate(II) unit with two further atoms in the asymmetric unit of the cell. These were eventually shown to fit the form factors for O (*i.e.* a water molecule is present) and Na and a subsequent check on their interactions with neighbouring atoms confirmed this. We thus found the compound to be disodium *catena*-bis(μ-oxalato)-cuprate(II) dihydrate. Least-squares refinement in which the thermal motion of all atoms of the complex ion was described aniso-tropically returned a final R factor of 0.052. The scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Atomic coordinates are listed in Table 1, and the calculated bond lengths and angles in Table 2. The atom-numbering scheme is that of Fig. 1.*

Table 1. *Atom coordinates*

$$U_{eq.} = (1/6\pi^2) \sum \sum \beta_{ij} \, \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	$U_{eq.}$ (Å^2)
Cu	0	0	0	0.01803
Na	0.118 (1)	0.4273 (4)	−0.2982 (5)	0.02738*
O(1)	0.269 (2)	0.3962 (7)	0.3436 (8)	0.02435
O(2)	0.464 (2)	0.1228 (7)	−0.0913 (8)	0.02458
O(3)	0.783 (2)	0.3562 (7)	0.0019 (9)	0.02886
O(4)	−0.029 (2)	0.1625 (7)	0.2322 (8)	0.02292
O(5)	−0.465 (2)	0.2456 (7)	−0.3952 (9)	0.03049*
C(1)	0.522 (3)	0.254 (1)	0.027 (1)	0.01756
C(2)	0.233 (3)	0.276 (1)	0.221 (1)	0.01901

$$* \ U_{eq.} = B/8\pi^2.$$

Table 2. *Calculated bond lengths* (Å) *and angles* (°)

Atoms at $x - 1, y, z$ are superscripted 1. Atoms at $-x, -y, -z$ are superscripted 2.

Cu–O(2)	1.932 (6)	O(2)^1–Cu–O(4)	85.0 (2)
Cu–O(2)^1	2.789 (6)	O(2)^1–Cu–O(2)^2	82.9 (2)
Cu–O(4)	1.933 (6)	O(2)^1–Cu–O(4)^2	95.0 (2)
O(1)–C(2)	1.227 (10)	O(2)–C(1)	1.293 (10)
O(2)–Cu–O(2)^1	97.14 (2)	O(3)–C(1)	1.224 (10)
O(2)–Cu–O(4)	85.66 (2)	O(4)–C(2)	1.280 (10)
O(2)–Cu–O(4)^2	94.34 (2)	C(1)–C(2)	1.564 (11)

Discussion. The compound presumably arises from a breakdown product of ascorbic acid; oxidation by molecular oxygen in the presence of copper is not unexpected. A knowledge of the structure establishes the identity of the species produced, one of the goals of the analysis, but it does not throw much light on the reactions occurring in solution. Regrettably, components of the original complex, $Cu_2(L)Cl_4$, are not included, except for the metal itself. The structure is reported for comparison with the similar compound $(NH_4)_2[Cu(oxalate)_2].2H_2O$ (Viswamitra, 1962*a*) and its isostructural K analogue (Viswamitra, 1962*b*).

The crystal structure of the Na salt contains a centrosymmetric Cu^{2+} ion bonded to two oxalate
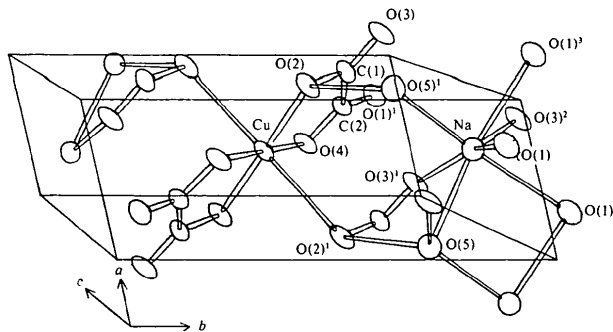

Fig. 1. The unit-cell contents and atom-numbering scheme. The origin is at Cu in the centre of the cell, the axes running in the directions specified.

groups. A double oxalate bridge is formed in both directions to the Cu atoms of adjacent unit cells along **a**, forming a spiralling polymeric chain with a planar CuO_4 coordination arrangement at each metal centre (see Fig. 2). The Cu atoms are also bridged by sharing two of the donor atoms, the six O atoms thus bonded to each metal ion completing a tetragonally distorted octahedral bonding geometry. The structure therefore differs from that of the K and NH_4 salts in which one Cu centre includes two water molecules in its distorted-octahedral coordination sphere and the other the free O atoms from the oxalate groups bound to the first centre. In the Na salt the water molecules remain uncoordinated.

Table 2 shows that in the Na salt the oxalate group is remarkably symmetrical. The in-plane Cu—O bonds are 1·932 and 1·933 Å and the associated bonds to carbon are 1·293 and 1·280 Å. The carbon bonds to the uncoordinated O atoms are shorter at 1·224 and 1·227 Å. Not surprisingly this bond distribution is similar to that seen in oxalic acid dihydrate (Kimura & Shibata, 1954).

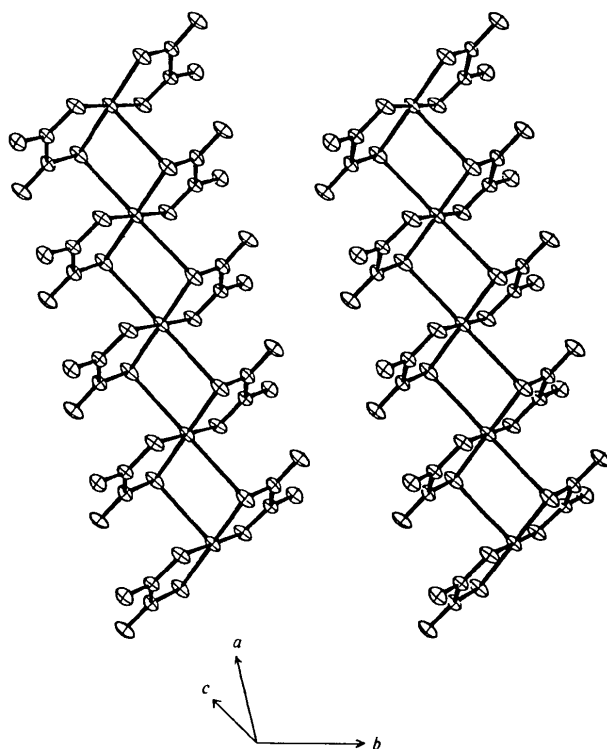It is presumed that the smaller size of the Na^+ ion is responsible for the structural differences from the K salt. The Na is surrounded by only seven O atoms at distances varying from 2·385 to 2·587 Å whereas K and NH_4 have eight. To a good approximation the coordination polyhedron can be described as a side-capped [by O(1)[1]] trigonal prism. The atoms involved are the uncoordinated O(1) and O(3) which make five contacts and the water molecules which make two. The angles around O(1), which makes three contacts with Na and also bonds to C(7), vary from 90·3 to 124·4° showing that the interactions are roughly along tetrahedral directions. Similarly the four contacts made by the water molecule [two to Na and one each to the coordinated O(2) and O(4)] vary from 88·0 to 128·3°. The distances of the two latter contacts are 2·845 and 2·834 Å and it can be inferred that these two interactions involve hydrogen bonding.

The apparent ease with which the coordination geometry around a cupric centre can be changed is well known. The effect is even seen within the one complex when crystalline isomers occur (Hall, Sheat & Waters, 1968; Martin & Waters, 1973) and can be thought to result from 'packing forces' or by solution effects prior to crystallization (Clark, Waters & Williams, 1976). The present instance affords an example where packing forces are more likely to be responsible, the change from eight coordination to seven coordination at the counter ion presumably requiring the new packing and different bonding to Cu.

Fig. 2. An *ORTEP* (Johnson, 1965) diagram showing the polymeric nature of the complex anion.

References

Busing, W. R. & Levy, H. A. (1957). *J. Chem. Phys.* **26**, 563–568.

Clark, G. R., Waters, T. N. & Williams, G. J. (1976). *J. Inorg. Nucl. Chem.* **39**, 1971–1975.

Corfield, P. W. R., Doedens, R. J. & Ibers, J. A. (1967). *Inorg. Chem.* **6**, 197–204.

Declercq, J.-P., Germain, G., Lessinger, L., Main, P. & Woolfson, M. M. (1974). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*, Univ. of York, England.

Hall, D., Sheat, S. V. & Waters, T. N. (1968). *J. Chem. Soc. A*, pp. 460–463.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Kimura, M. & Shibata, S. (1954). *Bull. Chem. Soc. Jpn*, **27**, 485–491.

Martin, D. W. & Waters, T. N. (1973). *J. Chem. Soc. Dalton Trans.* pp. 2440–2443.

Viswamitra, M. A. (1962a). *J. Chem. Phys.* **37**, 1408–1414.

Viswamitra, M. A. (1962b). *Z. Kristallogr.* **117**, 437–449.