Structure of the First Polymeric *catena*-μ-Tris[oxalato(2−)-O^1,O^2;O^3,O^4]-dicopper Complex with Interlocked Helical Chains

Markku R. Sundberg,*[a] Raikko Kivekäs[a] and Jorma K. Koskimies[b]

[a] Division of Inorganic Chemistry, and [b] Division of Organic Chemistry, University of Helsinki, Vuorikatu 20, SF-00100 Helsinki, Finland

Oxidation of a mixture of copper(II), vitamin C and 2-diethylaminoethanol in the presence of H_2O_2 yielded a polymeric *catena*-μ-tris(oxalato)-copper(II) compound with the Cu^{II} ion surrounded by six oxygen atoms of three oxalate ions, each one starting a helical chain.

The addition of copper(II) to an ascorbic acid (vitamin C) solution has been shown to increase the biological effect against melanoma cells.[1] Also induced haemolysis of rat erythrocytes[2] and induction of DNA lesions in bacterial cells have been observed.[3] So far, attempts to synthesize a stable coordination compound of copper(II) and ascorbic acid have been unsuccessful. The ascorbic acid is very easily oxidized in alkaline solutions by molecular oxygen, *e.g.* to oxalic acid and L-threonic acid.[4] The decomposition product obtained by Norman *et al.* contained 1,2,3,4-tetrahydroxybutane-1,1-dicarboxylate anions coordinated to copper,[5] whereas in another experiment, disodium *catena*-bis(μ-oxalato)-cuprate(II) dihydrate was obtained by using molecular oxygen and ascorbic acid.[6] We decided to use hydrogen peroxide as oxidant under aerobic conditions to react with copper(II) ion and ascorbic acid. With the help of single-crystal X-ray analysis† the product was assigned as bis[diethyl-(2-hydroxyethyl)ammonium] *catena*-μ-tris[oxalato(2−)O^1,O^2;O^3,O^4]-dicuprate(II).

To the best of our knowledge, this is the first known structure in which the copper ion is surrounded by three coordinated oxalato groups (Fig. 1). Compounds are known in which there is six-coordination around the central Cu^{II} ion, but only three of the four oxygen atoms of the corresponding oxalate anions are coordinated.[6–8] In our compound, six oxygen atoms of the three oxalate ions are bonded to the copper ion forming a network of interlocked helical chains (Fig. 2). Formally, the asymmetric unit consists of the central copper ion, three halves of tetradentate oxalate anions and a partly disordered diethyl-(2-hydroxyethyl)ammonium cation.

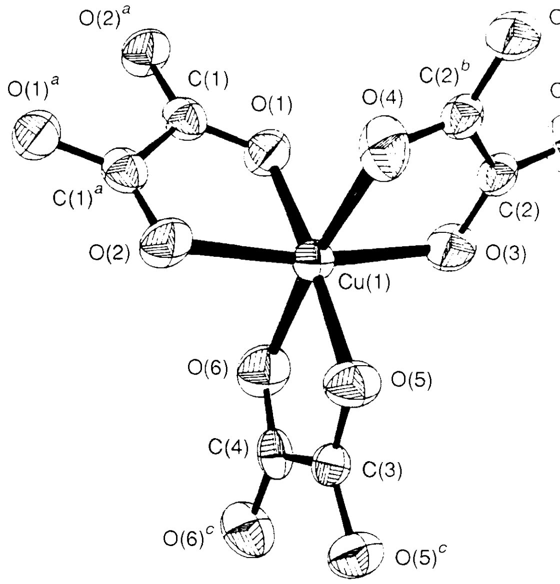

Fig. 1 ORTEP drawing with the labelling scheme for the central copper ion surrounded by three oxalate ions. The thermal ellipsoids are drawn at the 50% probability level. The bond lengths around the Cu^{II} ion are: Cu(1)–O(1) 2.002(5), Cu(1)–O(2) 2.090(5), Cu(1)–O(3) 2.120(5), Cu(1)–O(4) 2.145(5), Cu(1)–O(5) 1.989(5), Cu(1)–O(6) 2.146(5) Å. Each oxygen of the oxalate anions is connected to a copper atom, but only one copper is shown here to illustrate the tris(oxalato)copper(II) units. $a = ½ - x, ½ - y, -z$; $b = i - x, 1 - y, -z$; $c = 1 - x, y, ½ - z$.

---

† *Crystal data* for $C_9H_{16}CuNO_7$, $M = 313.66$, monoclinic, space group *C*2/*c*, $a = 14.297(3)$, $b = 10.472(2)$; $c = 18.539(3)$ Å, $\beta = 114.068(13)°$, $v = 2534.3(8)$ Å^3, $Z = 8$, $D_c = 1.64$ g cm^{-3}, $F(000) = 1296$, $\mu = 18.2$ cm^{-1}. Intensity data ($5° < 2\theta < 55°$, 2237 independent reflections) were recorded on a Nicolet P3 four-circle automatic diffractometer with Mo-Kα radiation ($\lambda = 0.71069$ Å). The structure was solved by direct methods (MULTAN78)[12] and refined by the XRAY76[13] program system. The final *R* was 0.051 for 1563 reflections with $I \geqslant 1.96\ \sigma(I)$ ($R_w = 0.047$, $1/\sigma^2$ weights). Atomic coordinates, bond length and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

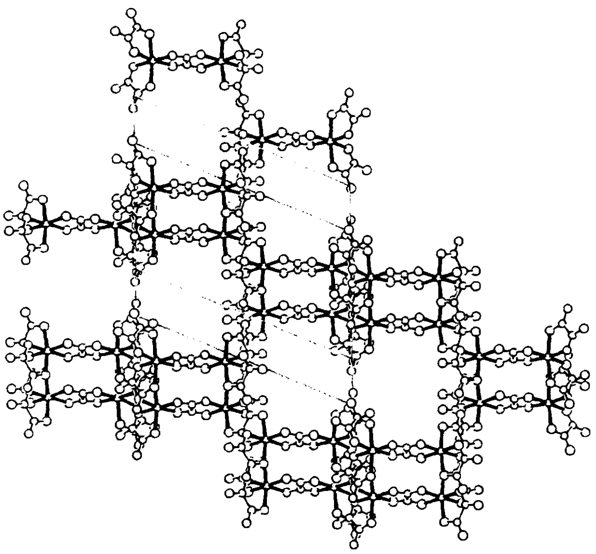

Fig. 2 A Pluto diagram illustrating the interlocked helical chains. The diethyl-(2-hydroxyethyl)ammonium cations are omitted for clarity.

Each oxalato anion acts as a bridge between two copper ions. Two of the oxalato ligands are situated across the centres of symmetry, and the carbon atoms of the third oxalate group occupy a two-fold axis. The partly disordered diethyl-(2-hydroxyethyl)ammonium cation is located in the channels of the three dimensional polymeric network.

The coordination sphere CuO_6 is clearly deformed, so that there is no symmetry around the central atom. After the deformations predicted by the Jahn–Teller theorem for an ideal CuO_6 polyhedron with O_h symmetry, there should be left at least either a centre of symmetry or two-fold symmetry axes.[9,10] However, if we shelve this argument and look at the Cu–O bond lengths only, we observe two short opposite bond lengths [to O(1) and O(5), approximately 2.00 Å] and four longer, equatorial bond lengths. This is quite contrary to the axial elongations observed so far for CuL_6 coordination spheres.

The sum of the bonds is 12.496 Å, which is very near to the ideal value of 12.48 Å calculated for Cu^{II}. The corresponding expected value for the sum is 11.34 Å, if the oxidation state of copper is assumed to be Cu^{III}. The ideal values have been obtained by using the crystal radii for Cu and O in ref. 11.

The magnetic moment at 281 K is *ca.* 1.8 μ_B, which corroborates our assumption about the oxidation state of copper. A detailed synthetic scheme and magnetic properties will be published in a later article.

Received, 19th November 1990; Com. 0/05184E

References

1 S. Bram, P. Froussard, M. Guichard, C. Jasmin, Y. Augery, F. Sinoussi-Barre and W. Wray, *Nature*, 1980, **284**, 629.

2 R. A. Loevstad, *Int. J. Biochem.*, 1984, **16**, 155.

3 M.-A. Van Sluys, R. Costa de Oliveria, I. Felzenschwalb, C. F. M. Menck and R. Alcantara-Gomes, *Carcinogenesis*, 1986, **7**, 197.

4 E. S. G. Barron, R. de Meio and F. W. Klemperer, *J. Biol. Chem.*, 1936, **112**, 625.

5 R. E. Norman, N. J. Rose and R. E. Stenkamp, *J. Chem. Soc., Dalton Trans.*, 1987, 2905.

6 P. Chananont, P. E. Nixon, J. M. Waters and T. N. Waters, *Acta Crystallogr., Sect. B*, 1980, **36**, 2145.

7 D. R. Bloomquist, J. J. Hansen, C. P. Landee, R. D. Willett and R. Buder, *Inorg. Chem.*, 1981, **20**, 3308.

8 R. Kivekäs and A. Pajunen, *Cryst. Struct. Commun.*, 1977, **6**, 477.

9 I. B. Bersuker, *The Jahn–Teller Effect and Vibronic Interactions in Modern Chemistry*, in the Series *Modern Inorganic Chemistry*, Series ed. J. P. Fackler, Jr., Plenum Press, New York, 1984, p. 18.

10 R. Englman, *The Jahn–Teller Effect in Molecules and Crystals*, Wiley, Bath, 1972, p. 217.

11 J. E. Huheey, *Inorganic Chemistry*, Harper & Row, New York, 1978, pp. 71–72.

12 P. Main, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declerq and M. Woolfson, MULTAN78. A Computer Program for the Automatic Solution of Crystal Structures, Universities of York, and Louvain, March 1978.

13 J. M. Stewart, P. A. Machin, C. W. Dickinson, H. L. Ammon, H. Heck and H. Flack, The XRAY76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.