Isomerism of Oxalatodiamminecopper(II) Complex

By J. GARAJ

(Department of Inorganic Chemistry, Slovak Technical University, Bratislava, Czechoslovakia and Department of Inorganic Chemistry, Chalmers' Technical University and University of Gothenburg, Gothenburg, Sweden)*

IN the literature are reported different modifications of copper(II) compounds,[1] though discussions of structural differences between such materials are rare.[2] Structural studies are often complicated by the normally small energetical differences between the two forms. Thus, some of these copper(II) compounds undergo spontaneous isomerisation. In addition, there is usually difficulty in the preparation of crystals of the individual modifications suitable for structure analysis.

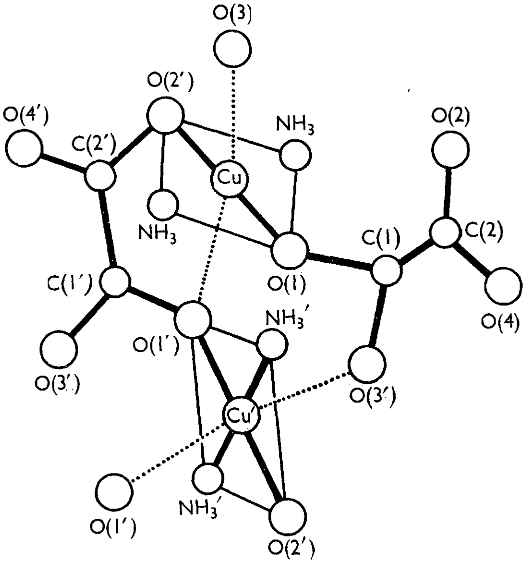

FIGURE 1. *Environment of the copper atom in the α-form of* $Cu(CO_2)_2(NH_3)_2$ *and bonding of oxalate ion. Lengths*: Cu–O(1) = 2·02, Cu–O(2) = 2·05, Cu–O(3) = 2·48, Cu–O(1′) = 2·93, Cu–NH_3 = 1·93 *and* 1·99 Å. *Estimated standard deviations in bond lengths are* ±0·03 Å. *Angles*: O(1)–Cu–NH_3 = 81·5 *and* 97·5, O(2)–Cu–NH_3 = 90·0 *and* 90·4, O(3)–Cu–NH_3 = 84·3 *and* 90·3, O(3)–Cu–O(2) = 84·5, O(3)–Cu–O(1) = 88·2, O(1)–Cu–NH_3 = 90·2 *and* 97·5, O(1)–Cu–O(3) = 161·6, O(1)–Cu–O(1) = 110·0. *Standard deviations in angles are* ±0·7.

The complex of the chemical formula $Cu(CO_2)_2(NH_3)_2$ is known in two forms.[3] The α-$Cu(CO_2)_2(NH_3)_2$, which crystallises from aqueous solutions, is more stable than the β-form. The latter is formed in the decomposition of the complex $Cu(CO_2)_2(NH_3)_5$ and changes into the α-modification at 100°. The structural nature of the isomerism has been investigated by X-ray analysis of α-$Cu(CO_2)_2(NH_3)_2$ and comparison with the known structure of $Cu(CO_2)_2(NH_3)_2,2H_2O$.[4]

Crystal data for α-$Cu(CO_2)_2(NH_3)_2$: $C_2H_6O_4N_2Cu$, M 185·63, orthorhombic, a = 6·421 ± 0·001, b = 7·241 ± 0·001, c = 11·488 ± 0·002 Å, U = 534·18 Å^3, D_m = 1·96 g.cm.$^{-3}$ (by flotation), Z = 4, D_c = 1·97 g.cm.$^{-3}$. Space group $Pn2_1a$ (C^9_{2v}, No. 33).

Three-dimensional intensity data were recorded by equi-inclination Weissenberg photography, using Cu-K_α radiation, and estimated photometrically.

The structure has been solved by the heavy-atom method on the basis of a three-dimensional Patterson synthesis. The atomic positions, anisotropic temperature parameters and scale factors have been refined by the least-square full-matrix method, using 372 independent non-zero reflections. The R-value, based on the observed structure amplitudes only, is 0·109. A schematic representation of the atomic arrangement around the copper(II) atoms, together with the bonding of the oxalate groups, is given in Figure 1.

In α-$Cu(CO_2)_2(NH_3)_2$ the copper(II) is approximately octahedrally co-ordinated and the coordination number of the central atom may be expressed as 2 + 2 + 1 + 1. There are two nitrogen atoms (at distances 1·93 and 1·99 Å) and two oxygen atoms (with bond lengths 2·02, 2·05 Å), in the plane. The next two oxygen atoms are at distances 2·33 and 2·48 Å respectively. The planar oxalate groups form bridges between the copper(II) polyhedra.

The other modification of $Cu(CO_2)_2(NH_3)_2$ could not be prepared in the form of single crystals. It was noticed, however, that this compound is also formed by the decomposition of $Cu(CO_2)_2(NH_3)_2,2H_2O$, which occurs readily at room temperature. The structure of the above-mentioned dihydrate is known.[4] Preliminary structural results for $Cu(CO_2)_2(NH_3)_2,2H_2O$ obtained from three projections show that the copper atom in this compound has a compressed octahedral ligand configuration with two shorter copper–nitrogen bonds (1·98 Å) and two pairs of longer copper–oxygen bonds (2·10 and 2·15 Å).

From the structure of $Cu(CO_2)_2(NH_3)_2,2H_2O$, it is possible to draw some conclusions concerning the co-ordination of the copper atom and also the function of the oxalate groups in β-$Cu(CO_2)_2(NH_3)_2$. In the dihydrate, the water molecules are not in the copper co-ordination sphere but are held by hydrogen bonds between parallel chains of copper(II) octahedra. It is therefore assumed that dehydration of this crystalline material will not bring about any essential changes in the ligand configuration. The ligand bonding will, of course, be affected, but only to a slight extent.

On the basis of this assumption, in both modifications of oxalatodiamminecopper(II), the metal atom is co-ordinated by two molecules of ammonia in a *trans*-position, and four oxygen atoms. The difference between the two forms lies in the functions of the oxalate group in the structures and also in the detailed configurations of the copper(II) atoms (see Figures 1 and 2).

This work has been supported by the Swedish Natural Council and by the Chalmers Institute of Technology, which has supplied a grant to cover the costs of the computer work carried out at the Gothenburg Universities' Computing Centre. I thank Dr. A. Jelen for revising the English text.

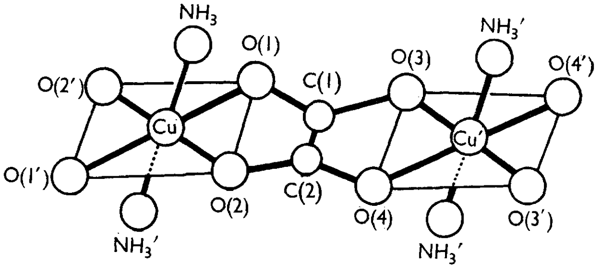

FIGURE 2. *The assumed co-ordination of the copper atom and function of the oxalate group in* β-$Cu(CO_2)_2(NH_3)_2$.

(*Received, May* 17*th*, 1968; *Com.* 624.)

---

[1] (a) J. Gazo, K. Seratorova and M. Serator, *Chem. Zvesti*, 1959, **13**, 5; (b) H. Langfelderova, V. Kabeshova, J. Garaj, and J. Gazo, *Z. Chem.*, 1960, **6**, 32; (c) M. Kato, H. B. Jonassen, and J. C. Faning, *Chem. Rev.*, 1964, **64**, 99; (d) S. C. Wallwork and W. E. Addison, *J. Chem. Soc.*, 1965, 2925.

[2] (a) F. Hanic and I. A. Cakajdova, *Acta Cryst.*, 1958, **11**, 610; (b) F. Hanic, *ibid.*, 1959, **12**, 739; (c) L. Zsoldos, *Magyar Fiz. Folyoirat*, 1962, **10**, 189; (d) G. A. Barclay and H. L. Kennard, *J. Chem. Soc.*, 1961, 5244; (e) F. Hanic, D. Shtempelova, and K. Hanicova, *Acta Cryst.*, 1964, **17**, 633; (f) D. Hall, A. J. McKinnon, and T. N. Waters, *J. Chem. Soc.*, 1965, 425; (g) R. D. Gillard, R. Mason, N. C. Payne, and G. B. Robertson, *Chem. Comm.*, 1966, 155.

[3] Gmelins Handbuch der anorganischen Chemie, Kupfer System No. 60, Teil B, Lf. 2, Verlag Chemie, Weinheim Bergstrasse, 1961, 732.

[4] V. Kabeshova and J. Garaj, unpublished results.