# CRYSTAL STRUCTURE OF THE OXALATO-DIAMMINECOPPER(II)

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The crystal structure of $\alpha$-oxalato diamminecopper(II), $Cu(COO)_2(NH_3)_2$ was determined using the X-ray structure analysis. The space group is $Pn2_1a$, lattice parameters: $a = 6\cdot421$ (1) Å, $b = 7\cdot241$ (1) Å, $c = 11\cdot488$ (1) Å. Density $\varrho_0 = 1\cdot96$ g/cm³, $\varrho_c = 1\cdot97$ g/cm³ for four formula units in the unit cell. The crystal structure was solved by heavy-atom method using 372 independent, non-zero reflections, measured photometrically from Weissenberg photographs. Atomic coordinates and anisotropic temperature factor coefficients were refined by the least-squares method to the final R-factor value $0\cdot105$. The copper atom is coordinated in the plane by two ammonia molecules (1·93 Å) and by two oxygen atoms (2·02 Å; 2·05 Å) respectively. Two next oxygen atoms are in the distances 2·33 Å and 2·48 Å. The copper atom has an unsymmetrically distorted octahedral coordination. The planar oxalato group having a bridging function linkes polyhedra into the onedimensional chains, bonded by hydrogen bonds only. The structural possibilities for $\beta$ and $\gamma$ modifications are discussed.

The oxalato-diaminecopper(II) is known in several modifications[1-3]. The so-called $\alpha$-form crystallized from the system $Cu(COO)_2.0\cdot5\ H_2O—NH_3(H_2O)$. Another modification of the compound $Cu(COO)_2(NH_3)_2$ is formed by the decomposition of $Cu(COO)_2.(NH_3)_2.2\ H_2O$ or of $Cu(NH_3)_5(COO)_2$.

On the basis of electron reflectance spectra Hathaway and Tomlinson[3] report the existence of three modifications of composition $Cu(COO)_2(NH_3)_2$. According to them decomposition of the pentaminecopper(II) leads to a modification differing of that prepared by the decomposition of $Cu(COO)_2(NH_3)_2.2\ H_2O$, the so-called $\gamma$-modification. In studying the relationship between the conditions of preparation, the properties and the structure of the modifications, we occupied ourselves in the solution of the crystal structure of one of the modifications, namely of the complex $Cu(COO)_2(NH_3)_2$, conventionally called the $\alpha$-form. Short information of the structure analysis results is presented in paper[2], while this paper gives detailed data on the structure of the $\alpha$-modification.

### EXPERIMENTAL

*Preparation of the crystals.* The complex of the composition $Cu(COO)_2(NH_3)_2$ was prepared according to paper[1] by crystallization from aqueous solution. The light-blue crystals of prismatic shape are stable in the air; they are of following composition: (Mw = 185·6)

|            | Cu (%) | $C_2O_4^{2-}$ (%) | $(NH_3)$ (%) |
|------------|--------|-------------------|--------------|
| found      | 33·80  | 47·34             | 18·48        |
| calculated | 34·24  | 47·72             | 18·34        |

*Space group and unit cell*: The crystals of $Cu(COO)_2(NH_3)_2$ show orthorhombic symmetry. The Weissenberg pictures revealed that only those $F(hkl)$ are present, for which the conditions apply:

$$0kl \quad k + l = 2n \,; \quad hk0 \quad h = 2n \,.$$

These conditions yield two space groups $Pnma$ and $Pn2_1a$.

The lattice parameters were refined on the basis of experimental data obtained from the calibrated Guinier powder patterns of $Pb(NO_3)_2$ by the least squares method. The following values of the lattice parameters have been determined:

$$a = 6·421 \pm 0·001 \text{ Å}\,; \quad b = 7·241 \pm 0·001 \text{ Å}\,; \quad c = 11·488 \pm 0·001 \text{ Å}\,.$$

The volume of the unit cell is 534·18 $Å^3$. The density measured by flotation method was found to be 1·96 $g/cm^3$, the calculated value for four formula units in the basic cell is 1·97 $g/cm^3$.

The data of the powder diffractograms were established by photometric measurements of the Guinier figures.

*The process of solving the crystal structure.* The intensity data were collected using the Weissenberg method with $CuK_\alpha$ radiation. Four layers were taken along the growth axis (axis $b$), three layers along the $a$ axis, and in direction of the longest axis two layers were obtained. The intensities were evaluated photometrically. The experimental data were corrected for nonlinearity, for the splitting factor and for the Lorentz and polarization factors. The effect of absorption was neglected.

For the solution of the crystal structure 372 non-zero reflections were used. The site of the copper atom has been determined by the heavy atom method from the three-dimensional Patterson synthesis. The other atoms were found by the method of successive approximations. At the beginning the structure was solved in the centrosymmetric space group $Pnma$. According to the differential Fourier synthesis the final refinement was made in that of $Pn2_1a$. The co-ordinates of the atoms, the anisotropic temperature factor coefficients and the scale factors were refined by the least squares method using a program elaborated by Gantzel and coworkers[4] and modified by Lindgren. The final value of the R-factor defined as $\sum\|F_0| - |F_c\|/\sum|F_0|$ reached 0·105. In refining the structure the Cruickshank weighting scheme[5] was applied, where

$$\Delta w^2 = \text{const.} \quad \text{and} \quad w = (A + F_0 + CF_0^2)^{-1/2}\,.$$

The curves of the atomic factors were used for the calculations, in accordance with Ibers[6].

The refinement of the structure was accomplished by applying differential Fourier synthesis. The maximum electron densities in it reached the value of $1 \cdot 2 \, e/A^3$.

The refined coordinates of the symmetrically independent part of the atoms are listed in Table I and their anisotropic temperature factor coefficients in Table II. The standard deviations of the refined parameters are in parentheses. The interatomic distances are shown in Table III, while Table IV collects the observed and the calculated structure factors together with the bond angles.

TABLE I

The Coordinates of the Independent Atoms of the $Cu(COO)_2(NH_3)_2$ in Fractional Coordinates ($\times 10^4$)

Standard deviations are given in parentheses.

| Atom | $x/a$ | $y/b$ | $z/c$ |
|------|-------|-------|-------|
| Cu | 1 018 (2) | 2 500 (0) | 1 604 (2) |
| $O_1$ | 355 (30) | 7 334 (40) | 6 816 (11) |
| $O_2$ | 2 094 (24) | 2 229 (23) | 9 934 (14) |
| $O_3$ | 2 540 (29) | 2 338 (60) | 4 286 (17) |
| $O_4$ | −67 (30) | 2 778 (32) | 6 226 (51) |
| $C_1$ | 510 (44) | 2 539 (82) | 4 196 (19) |
| $C_2$ | 827 (41) | 7 410 (62) | 4 776 (16) |
| $N_1$ | 614 (35) | −280 (59) | 1 709 (22) |
| $N_2$ | 1 121 (35) | 5 079 (42) | 1 477 (15) |

TABLE II

The Anisotropic Individual Temperature Factor is Defined as: $\exp -(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)$

Standard Deviations are Given in Parentheses. Values are $\times 10^4$.

| Atom | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|------|----------|----------|----------|----------|----------|----------|
| Cu | 132 (11) | 92 (9) | 38 (2) | − 60 (36) | 16 (7) | 15 (11) |
| $O_1$ | 133 (33) | 60 (51) | 7 (7) | 279 (135) | − 6 (29) | 98 (45) |
| $O_2$ | 46 (40) | 17 (30) | 54 (11) | 138 (75) | 22 (35) | 38 (32) |
| $O_3$ | 37 (37) | 194 (70) | 86 (18) | −499 (160) | 27 (43) | 150 (71) |
| $O_4$ | 157 (51) | 33 (14) | 28 (11) | 14 (84) | 29 (40) | −30 (29) |
| $C_1$ | 109 (59) | 274 (107) | 24 (14) | −739 (299) | −30 (45) | 15 (84) |
| $C_2$ | 138 (62) | 63 (60) | 5 (9) | 506 (211) | 36 (37) | −20 (62) |
| $N_1$ | 12 (39) | 209 (98) | 23 (17) | −147 (151) | 135 (39) | 6 (69) |
| $N_2$ | 74 (58) | 39 (43) | 2 (12) | − 84 (147) | 95 (38) | −79 (40) |

**DISCUSSION**

The coordination of the central copper(II) in the structure of $Cu(COO)_2(NH_3)_2$ is one of the most common coordinations occurring in Cu(II) complexes. It has the shape of an unsymmetrically distorted, along the longest axis elongated bipyramid. The coordination number of copper(II) in this structure may be expressed as $4 + 1 + 1$.

The two shortest bonds Cu-ligand are formed by the central atom with the nitrogen atoms from the ammonia molecules (1·927 Å and 1·993 Å, respectively), somewhat longer bonds coordinate the copper(II) with the oxygen atoms from the two dif-

TABLE III

Distances (Å) with Standard Deviations in Parentheses ($\times 10^3$)

| Atoms | Value | Atoms | Value |
|---|---|---|---|
| | Distances in the copper(II) polyhedron[a] | | |
| $Cu-O_1$ | 2·01 (1) | $O_1-N_1$ | 2·57 (4) |
| $Cu-O_1'$ | 2·33 (2) | $O_1-N_1$ | 3·16 (3) |
| $Cu-O_2$ | 2·05 (1) | $O_1-N_2$ | 3·01 (3) |
| $Cu-O_3$ | 2·47 (1) | $O_1-N_2$ | 3·07 (3) |
| $Cu-N_1$ | 1·92 (4) | $O_2-O_3$ | 3·08 (2) |
| $Cu-N_2$ | 1·99 (3) | $O_2-N_1$ | 2·82 (3) |
| $O_1-O_1'$ | 3·56 (1) | $O_2-N_2$ | 2·85 (3) |
| $O_1-O_2$ | 2·71 (2) | $O_3-N_1$ | 2·98 (4) |
| $O_1-O_3$ | 2·24 (2) | $O_3-N_2$ | 3·18 (4) |
| $O_1'-O_3$ | 3·14 (2) | $N_1-N_2$ | 3·37 (5) |
| | Distances in the oxalic ion | | |
| $C_1-O_3$ | 1·28 (3) | $C_2-O_4$ | 1·29 (2) |
| $C_1-O_1$ | 1·30 (2) | $C_2-O_2$ | 1·33 (3) |
| $C_1-C_2$ | 1·48 (3) | | |
| | Intermolecular contacts | | |
| $O_1'-O_4$ | 3·36 (3) | $O_3''-N_2'$ | 3·18 (4) |
| $O_1-O_4$ | 3·53 (1) | $O_4-N_1'$ | 2·82 (3) |
| $O_2''-N_1''$ | 3·16 (3) | $O_4'-N_1''$ | 3·26 (3) |
| $O_2''-N_2''$ | 3·00 (3) | $O_4-N_2'$ | 3·31 (2) |
| $O_3-N_1''$ | 3·46 (4) | $O_4''-N_2''$ | 3·16 (3) |
| $O_3''-N_2''$ | 3·12 (3) | | |

[a] Nomenclature of atoms as in Fig. 2.

ferent oxalate groups $(2\cdot017$ and $2\cdot052$ Å) (Fig. 1). The oxygen atoms marked in Fig. 1 as $O_1$ and $O_2$ and the nitrogen atoms of the ammonia groups $NH_3$ and $NH_3'$ lay in a plane defined by the equation (in Å):

$$-0\cdot9180x + 0\cdot0582y - 0\cdot3913z = 1\cdot1137 . \qquad (1)$$

TABLE IV

Angles (Deg) with Standard Deviations in Parentheses

| Atoms | Value | Atoms | Value |
|---|---|---|---|
| | Angles in the copper(II) octahedra[a] | | |
| $O_1$—Cu—$O_1'$ | 110 (0·5) | $O_2$—Cu—$N_1$ | 90·4 (0·9) |
| $O_1$—Cu—$O_2$ | 170·1 (0·8) | $O_2$—Cu—$N_2$ | 90·0 (0·7) |
| $O_1$—Cu—$O_3$ | 88·2 (0·7) | $O_2$—Cu—$N_1$ | 84·3 (1·2) |
| $O_1$—Cu—$N_1$ | 81·5 (1·1) | $O_3$—Cu—$N_2$ | 90·0 (1·2) |
| $O_1$—Cu—$N_2$ | 97·5 (1·0) | $N_1$—Cu—$N_2$ | 174·2 (1·0) |
| $O_1'$—Cu—$O_2$ | 76·2 (0·6) | Cu—$O_1'$—Cu | 122·2 (0·7) |
| $O_1$—Cu—$O_3$ | 161·6 (0·6) | Cu—$O_1$—$C_1'$ | 126·9 (1·8) |
| $O_1$—Cu—$N_1$ | 95·5 (1·0) | Cu—$O_1'$—$C_1$ | 109·5 (1·5) |
| $O_1'$—Cu—$N_2$ | 90·2 (1·0) | Cu'—$O_3''$—$C_1'$ | 150·6 (1·6) |
| $O_2$—Cu—$O_3$ | 85·4 (0·6) | Cu—$O_2$—$C_2$ | 116·6 (1·3) |
| | Angles in the oxalic ion | | |
| $O_1'$—$C_1$—$O_3'$ | 120·3 (2·3) | $O_4$—$C_2'$—$O_2'''$ | 121·4 (2·2) |
| $O_1'$—$C_1$—$C_2$ | 116·5 (2·4) | $O_2$—$C_2$—$C_1$ | 119·0 (1·8) |
| $O_3$—$C_1$—$C_2$ | 120·1 (2·2) | $O_4$—$C_2'$—$C_1$ | 118·4 (2·5) |
| | Angles among intermolecular contacts | | |
| Cu—$O_1$—$O_4'''$ | 106·0 (1·0) | $C_2'$—$O_4$—$N_2'$ | 120·6 (2·1) |
| Cu—$O_1$—$O_4$ | 149·7 (0·9) | $C_2'$—$O_4''$—$N_2''$ | 104·5 (1·9) |
| Cu—$O_1'$—$O_4$ | 95·7 (0·9) | Cu''—$N_1''$—$O_2''$ | 129·7 (1·2) |
| Cu'—$O_2''$—$N_1''$ | 108·3 (0·8) | Cu''—$N_1''$—$O_3''$ | 113·4 (1·2) |
| Cu''—$O_2'$—$N_2'$ | 108·1 (0·7) | Cu'—$N_1'$—$O_4$ | 124·9 (1·4) |
| $C_1'$—$O_3''$—$N_1''$ | 113·2 (2·3) | Cu'—$N_1$—$O_4$ | 108·3 (1·1) |
| $C_1'$—$O_3''$—$N_2''$ | 111·8 (2·3) | Cu'—$N_2'$—$O_2'$ | 119·6 (1·0) |
| $C_1'$—$O_3''$—$N_2'$ | 132·7 (2·3) | Cu''—$N_2''$—$O_3''$ | 126·9 (1·1) |
| $C_2''$—$O_4$—$N_2'$ | 120·6 (2·1) | Cu'—$N_2'$—$O_4$ | 119·7 (0·8) |
| $C_2$—$O_4''$—$N_2''$ | 104·5 (1·9) | Cu''—$N_2''$—$O_4''$ | 129·4 (1·1) |

[a] Nomenclature of atoms as in Fig. 2.
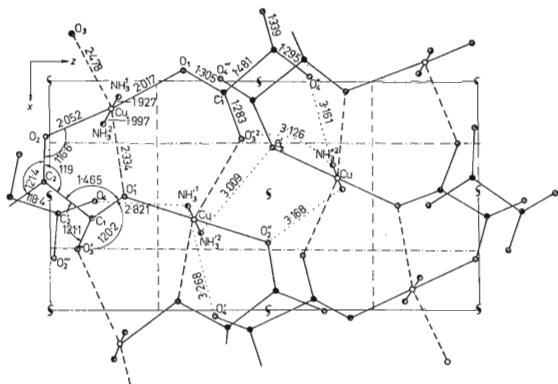
Fig. 1

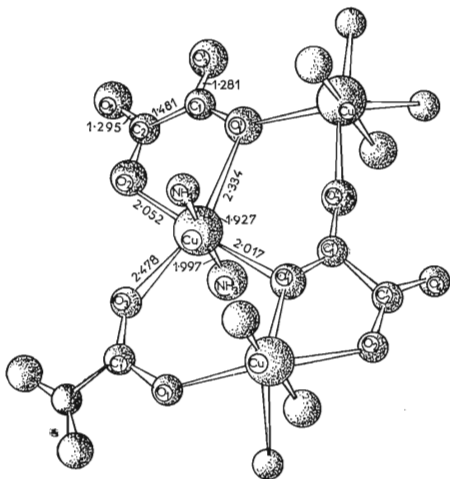Coordination of Copper(II) and Bonding of Octahedra in Crystals of $Cu(C_2O_4)(NH_3)_2$



Fig. 2

The Crystal Structure of the α Modification of $Cu(C_2O_4)(NH_3)_2$ along the $b$ Axis

The copper(II) is deviated out of this plane towards the atom $O_1$, which forms with the central atom a somewhat shorter chemical bond ($Cu$—$O_1$ = 2·334 Å). The deviation of the atoms from plane 1 are:

$$N_1 = -0.004 \text{ Å}; \quad N_2 = -0.004 \text{ Å}; \quad O_1 = +0.004 \text{ Å};$$

$$O_2 = +0.004 \text{ Å}; \quad Cu = -0.102 \text{ Å}.$$

The pyramidal coordination around the Cu(II) is completed by the oxygen atom $O_3$ ($Cu$—$O_3$ = 2·478 Å) to give a distorted bipyramid. This deviation of the central atom from the plane towards the nearer atom — marked in Fig. 1 as $O_1$ — is in accordance with the lower energy of the system.

The oxalate group coordinates three different copper atoms (Fig. 2). The oxygen atoms of the oxalate groups are from the crystallochemical point of view not equivalent. While the atom marked as $O_1$ forms one shorter bond $Cu$—$O_1$ (2·017 Å), its distances from the other Cu(II) atoms are 2·334 Å. Thus it has a bridging function. The angle $Cu$—$O_1'$—$Cu$ (Fig. 1) is 122·2°. The structure of $Cu(COO)_2(NH_2)_3$ shows along the slide plane $a$ the chain $...O_1$—$Cu$—$O_1$—$Cu....$. In this sense an interaction of the unpaired electrons of the Cu(II) atoms is possible. Thus the complex $\alpha$--$Cu(COO)_2(NH_3)_2$ may be expected to be antiferromagnetic.

The oxygen atom $O_2$ forms a short chemical bond to the copper atom (2·052 Å) and simultaneously it coordinates the molecule $NH_3$ by hydrogen bridges (3·009 Å). The third oxygen atom $O_3$ of the oxalate group forms a weak chemical bond only; the distance of $Cu$—$O_3$ is 2·478 Å. The oxygen atom marked as $O_4$ in the Fig. 1, does not coordinate copper(II) at all. The distance of $O_4$—$NH_3'1$ is 2·821 Å; $O_4''$—$NH_3''2$ equals 3·161 Å.

The different function of the oxygen atoms in the oxalate group does not essentially influence the interatomic distances in the group itself. The found bond lengths of $Cu$—$O$ (see Table III and Fig. 1) are equal within the standard deviations. The high coordination number of the oxalate group yields heavy steric requirements of this group, what could explain the deviation of the atoms from the plane arrangement. The plain going through the atoms of the oxalate group shows the form

$$-0.0875x + 0.9927y - 0.0828z = 1.3679$$

with the atom deviations: $C_1$ −0·079 Å, $C_2$ −0·056 Å, $O_1$ +0·061 Å, $O_2$ −0·067 Å, $O_3$ −0·104 Å, $O_4$ −0·087 Å.

As to its crystal structure the $\alpha$ $Cu(COO)_2(NH_3)_2$ consists of one-dimensional infinite formations parallel to the axis $x$ (see Fig. 1). These formations are mutually bonded only by hydrogen bonds between the atoms $O_2$ and $O_4$ on the one side, and the ammonia molecule, with its nitrogen marked on the other.

Based on the structure information of this complex as well as of other oxalato-copper(II) complexes, certain conclusions may be drawn on the substitution mechanism of the oxygen atoms by the ammonia molecules within the inner sphere of the complex, and also on the structure of the modifications. In $Cu(COO)_2(NH_3)_x$, where $x$ is equal to four or more, the ammonia molecules will be coordinated in short distances and in a plane (Fig. 3). The oxygen atoms of the oxalate groups will form
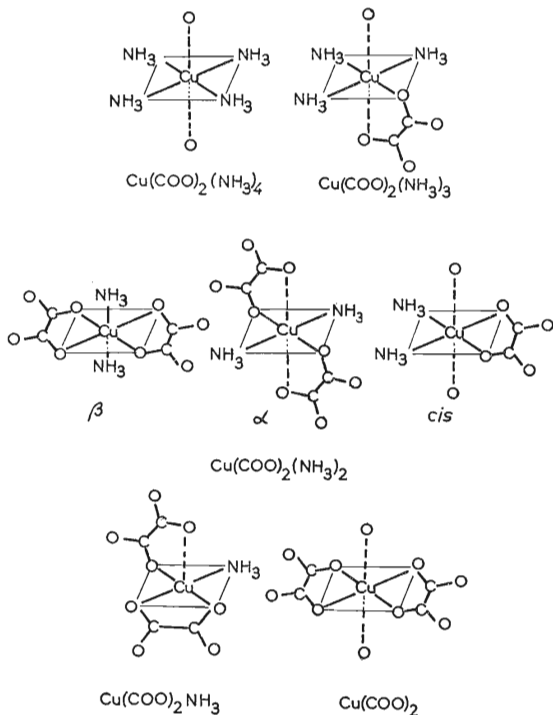


FIG. 3

Possible Coordination of Copper(II) and the Function of Oxalate Groups in Oxalate Copper(II) Complexes

at the most weak chemical bonds to the Cu(II) atom on the coordinate $z$ and complete so the planar coordination of Cu(II) to an elongated distorted (symmetrically or asymmetrically) octahedron. In decreasing the number of ammonia molecules in the formula of the oxalato complex their substitution will take place by the oxygen atoms of the oxalate groups.

More structural alternatives are possible for $Cu(COO)_2(NH_3)_2$ some of them are given in Fig. 3. In the $\alpha$-complex oxalate group is coordinated as a pseudochelate with one shorter and one longer bond Cu—O. The other possibility with the oxalate group in the function of a chelate and with two short Cu—O bonds leads to the formation of a *cis*-isomer Another possibility is the pentacoordinated copper(II) complex. These forms have, however, not yet been proved. $\beta$-$Cu(NH_3)_2(COO)_2$ might be formed by decomposition of $Cu(COO)_2(NH_3)_2 . 2 H_2O^2$.

Substitution of another ammonia molecule in the inner sphere of the $Cu(NH_3)_2.$ $.(COO)_2$ complex yields the compound of the composition $Cu(COO)_2(NH_3)_2$, where one of the oxalate groups forms[7] two short bonds Cu—O, and the other crystallographically independent group has the function of a pseudochelate with one shorter and one longer chemical bond of Cu—O. In the anhydrous copper(II) oxalate four short bonds Cu-ligand exist, formed by oxygen atoms. This may be a near oxalate bonding such as was observed for $Cu(COO)_2(NH_3)_2 . 2 H_2O$ with all the four bonds Cu—O being short.

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