The Crystal Structures of Metal 8-Hydroxyquinolinate.
I. Copper 8-Hydroxyquinolinate*[1]

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In the course of recent developments in the valency theory and streochemistry of copper, it has been reported by Orgel and Dunitz1) that there are three types of environment about the cupric ion: (1) distorted octahedral with four short and two long bonds, (2) square coplanar, and (3) tetrahedral. The tetrahedral compounds, such as $Cu_2CsCl_4$2), are few in number, but, in the case of the cuprous ion, copper usually makes sp^3 (tetrahedral) bonds with surrounding ligands. A greater number of cupric compounds are of type 1 or 2. These types may be considered together as a single class, since we regard the planar compounds as a limiting case of 1, with the two opposite ligands with long bonds removed completely.

The crystal structure of copper 8-hydroxyquinolinate dihydrate has been determined by Kruh and Dwiggins3). It is isomorphous with the corresponding zinc salt, the crystal structure of which has been determined by Meritt et al.4) Moreover, since Liu and Bailar5) have found that, in zinc salt of 8-hydroxyquinoline-5-sulfonic acid, the coordination of the zinc is tetrahedral, it may be assumed that the same arrangement of the ligands will be found in the anhydrous zinc 8-hydroxyquinolinate. According to the results of the X-ray analysis of the corresponding anhydrous copper compound by Mundy6), the copper atoms are not arranged at the centers of symmetry, but in the general positions of the unit cell of the space group $P2_1/a$. Thus, he inferred that there is no reason why the copper complex should not be tetrahedral.

Since copper(II) shows a strong tendency toward a square planar coordination and since Mundy's analysis is not complete, it will be interesting to see which of the two possible structures is the actual arrangement in the anhydrous salt. The present paper deals with the structure analysis of copper 8-hydroxyquinolinate in more detail than Mundy provides. In connection with this substance, it has been determined by Ogawa that the anhydrous zinc 8-hydroxyquinolinate is triclinic, with two formula units in a cell of the dimensions $a=11.1$, $b=9.20$, $c=11.1$ Å, $\alpha=114.9°$, $\beta=75.1°$, $\gamma=90.8°$; the details of his research will be published elsewhere.

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1) L. E. Orgel and J. D. Dunitz, *Nature*, **179**, 462 (1957).

2) L. Helmholz and R. F. Kruh, *J. Am. Chem. Soc.*, **74**, 1176 (1952).

3) R. Kruh and C. W. Dwiggins, ibid., **77**, 806 (1955).

4) L. L. Meritt, Jr., R. T. Cady and B. W. Mundy, *Acta Cryst.*, **7**, 473 (1954).

5) J. C. I. Liu and J. C. Bailar, *J. Am. Chem. Soc.*, **73**, 5432 (1951).

6) B. W. Mundy, Ph. D. Dissertation, Indiana University (1948).

Experimental

The anhydrous copper 8-hydroxyquinolinate was prepared by heating, on the water bath, the hydrated precipitate obtained by mixing a solution of copper in acetic acid with an alcoholic solution of 8-hydroxyquinoline (oxine). Crystals of anhydrous copper 8-hydroxyquinolinate were grown by slow evaporation at about 45°C from a pyridine solution of the anhydrous compound. The crystals in the shape of rods or of hexagonal plates are colored dark brown. They were not always obtained in the form of rods however, and the axis of the rod was not always parallel to the direction of the b axis. In the present experiment, we used a rod crystal the axis of which was parallel to b, thus obtaining the Weissenberg *h0l* reflections, otherwise we used specimens cut along the b or c direction out of hexagonal tabular crystals with developed (100).

When anhydrous copper 8-hydroxyquinolinate is recrystallized from a pyridine solution, a green pyridine addition compound is also obtained at the same time[7]. In order to ascertain that the specimen is the desired anhydrous salt, we determined the nitrogen content of the specimen and took an X-ray diffraction powder pattern for comparison with the results reported by Sekido[8]. The analysis showed that the chemical formula of the specimen corresponded to $CuC_{18}H_{12}O_2N_2$, while the phase corresponded to the β-form of $Cu(oxine)_2$ designated by Sekido.

Using Ni-filtered Cu-K_α radiation, Weissenberg, Sauter, and oscillation photographs were taken about the b and c axes using the multiple-film technique. These photographs showed that the unit cell was monoclinic and that the cell dimensions were $a=23.66\pm0.04$, $b=8.72\pm0.01$, $c=15.30\pm0.02$Å, $\beta=117.5\pm0.5°$. The systematic absences of *hkl* reflections when $h+l$ is odd, of *h0l* reflections when both *h* and *l* are odd, and of *0k0* reflections when *k* is odd show that the space group is $C_{2h}^5-B2_1/a$. This space group expression is different from that given by Mundy, but this difference may be due to the difference in the selection of axes between our method and Moundy's. If we adopt the following lattice constants: $a=10.72$, $b=8.72$, $c=15.30$Å, and $\beta=98.0°$, the space group of this crystal becomes $P2_1/c$, but our present investigation is based on the space group $B2_1/a$.

The approximate density measured with a picnometer is 1.5 g. cm^{-3}, so that there are eight molecules in the unit cell (the calculated density 1.66 g. cm^{-3}). The intensities of integrated Weissenberg photographs of *hk0* and *h0l* layers were estimated visually by comparison with a calibrated scale of time exposures. Corrections for Lorentz and polarization factors were made in the usual way. No absorption corrections were made, since small crystals were used ($\mu=26.1$ cm^{-1} for Cu-K_α).

By the use of Wilson's method, the relative structure amplitudes were converted to the absolute scale by a comparison of the calculated average intensities $\sum f_j^2$ with those observed for five zones of the appropriate reciprocal lattice section; at the same time the values of the temperature factors were calculated to be 4.9Å^2 for (*h0l*) and 3.2Å^2 for (*hk0*).

Determination of Structure

As has been shown by Howells, Phillips and Rogers[9], there are remarkable differences among centric, acentric and hypercentric crystals as regards the distribution of the magnitudes of the structure factors. It is the necessary condition for the application of this method that there should be a sufficiently large number of equal atoms in general positions in the unit cell. In our case, however, there are eight heavy copper atoms in the cell, thus greatly influencing the structure factors, so the statistical method is not strictly applicable. Nevertheless, we applied this method to our crystal and guessed the structure to be a hypercentric one. From this we further inferred that there would be centers of symmetry in the unit cell besides the one in the molecule itself, so that the $Cu(oxine)_2$ molecule will not have a tetrahedral configuration, but a planar one (Fig. 1).

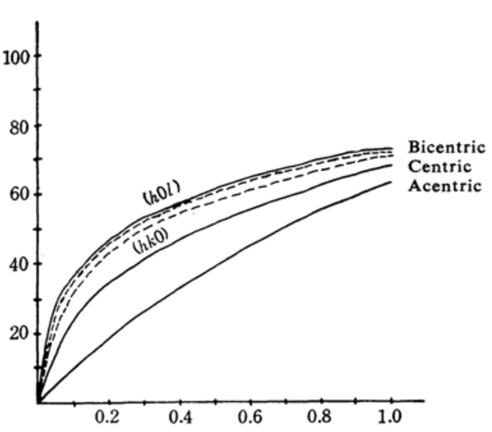

Fig. 1. Comparison of the experimental distribution N(z) for $Cu(oxine)_2$ (marked by dotted lines) with the theoretical distribution curves.

The sharpened Patterson synthesis of (*h0l*) and (*hk0*) projections showed that copper atoms were located at the positions with $x=0.061$, $y=0.118$, and $z=0.010$. In view of the short b axis, this synthesis was considered to proceed first with a projection on (010). On the basis of the above copper parameters, the values of the $F(h0l)$ for the copper atoms only were calculated. From a comparison of

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[7] Y. Nakatsuka, This Bulletin, **11**, 45 (1936).

[8] E. Sekido, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **78**, 1791 (1957).

[9] E. R. Howells, D. C. Phillips and Rogers, *Acta Cryst.*, **3**, 210 (1950); D. Rogers and A. J. C. Wilson, ibid., **6**, 439 (1953).

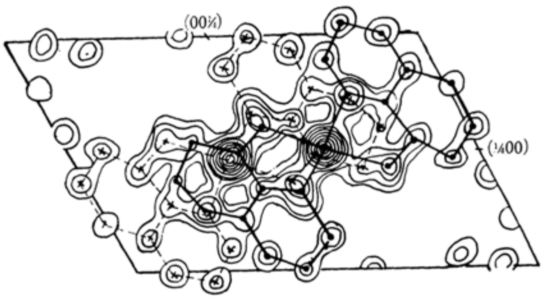

Fig. 2. Electron-density projection along the b axis.

them with the observed structure amplitudes of this compounds, it was possible to deduce the signs of about one-tenth of all the possible reflections $F(h0l)$ within the limiting sphere. In the following calculations, the atomic scattering factors of carbon, nitrogen, and oxygen given by McWeeny and that of copper listed in the Internationale Tabellen were adopted. The expressions for $F(h0l)$ and $F(hk0)$ of the space group $B2_1/a$ are given by:

$$F(h0l)=8\sum f_j \cos 2\pi(hx_j+lz_j)$$

$$F(hk0)=8\sum f_j \cos 2\pi hx_j\cdot\cos 2\pi ky_j$$

when k is even,

$$F(hk0)=-8\sum f_j \sin 2\pi hx_j\cdot\sin 2\pi ky_j$$

when k is odd.

Parameters were assigned to all the atoms in the initial projection on (010), using an assumed model of the 8-hydroxyquinoline molecule; these were refined as far as possible by successive Fourier syntheses of electron density. The x parameters finally obtained were incorporated into projections along the c axis. From the information derived from the preceding Patterson projection on (010), and from the fact that the intensity of the (420) reflection is strongest, we could determine the orientation of the 8-hydroxyquinoline molecule in the following way: The calculated copper contribution to the (420) reflection is almost zero, so that the structure factor (420) contributed from 8-hydroxyquinoline molecules must be large. This means that the plane of the oxine molecule must be nearly parallel to (420) or ($\bar{4}$20) through the positions of the copper atoms determined from Patterson projections. In this case, one cannot distinguish between the two-fold axes and the centers of symmetry in the (010) projection, so it was also not possible to decide the two alternatives in the (010) projection. Setting up two kinds of structure models projected on the (00l) plane, in each of which the origin of a unit cell was the two-fold screw axis or the center of symmetry, we found an approximate arrangement of the molecules by spacing the molecules so that they would not be too close together and so that the calculated intensity of the reflection of (420) would be very large in conformity with the obtained one. Then, calculating the three-dimensional structure factors $F(h1l)$, we ascertained that the crystal structure thus obtained gave a satisfactory agreement between the observed and calculated structure factors.

The refinement of the structure was accomplished by using the error synthesis method proposed by Bunn et al.[10] Also we partly adopted Booth's back-shift method as a correction for termination-of-series errors. In order to find the diffraction ripples in a Fourier summation due to copper atoms, which might overlap the positions of light atoms in projection, a Fourier synthesis was carried out using the calculated values of $F(h0l)$ for the copper atoms alone for the reflections included in the original summation; this was then compared with the original Fourier projection. In determining the exact positions of the peaks representing the light atoms, we allowed for these diffraction effects.

The coordinates that gave the best agreement between calculated and observed structure factors were chosen. The results are given in

TABLE I. THE COORDINATES OF THE ATOMS

Atom	x	y	z
Cu	0.0608	0.1200	0.0100
N	0.118	0.007	0.125
C(1)	0.114	−0.022	0.207
C(2)	0.158	−0.127	0.277
C(3)	0.205	−0.193	0.253
C(4)	0.253	−0.230	0.150
C(5)	0.258	−0.197	0.068
C(6)	0.217	−0.105	−0.008
C(7)	0.172	−0.032	0.022
C(8)	0.165	−0.060	0.107
C(9)	0.208	−0.163	0.168
O	0.125	0.063	−0.042
N′	0.004	0.250	−0.092
C′(1)	0.008	0.280	−0.180
C′(2)	−0.031	0.387	−0.245
C′(3)	−0.075	0.460	−0.217
C′(4)	−0.126	0.498	−0.123
C′(5)	−0.130	0.472	−0.028
C′(6)	−0.087	0.362	0.042
C′(7)	−0.043	0.285	0.017
C′(8)	−0.038	0.320	−0.067
C′(9)	−0.078	0.430	−0.130
O′	−0.002	0.180	0.058

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[10] D. Crowfoot, C. W. Bunn, B. W. Rogers-Low and A. Turner-Jones, "The X-Ray Crystallographic Investigation of the Structure of Penicillin" Princeton Univ. Press, Princeton, N. J. (1949), p. 310.

Table I, where x, y, and z are expressed in fractional coordinates, all referred to the monoclinic axial directions. They are also expressed in orthogonal coordinates x′, y′, and z′ referred to the a, b and c′ axes, where c′ is an axis perpendicular to the b and a axes. These orthogonal coordinates, not shown here, were used in calculating the interatomic distances and valency angles. They are derived from the monoclinic crystal coordinates by the relations $x'=x+z\cos\beta$, $y'=y$, and $z'=z\sin\beta$.

In electron-density projections on both (*hk*0) and (*h*0*l*), calculations of standard errors by Cruickshank's method were rendered impossible by the overlapping of the maxima which were present in this structure. Therefore, we adopted Luzzati's method as an indication of the accuracy of the given coordinates. The mean errors for *hk*0 and *h*0*l* reflections are 0.07 and 0.06 Å respectively. The fact that the values of *R* for *hk*0 reflections do not precisely follow the curve shown by Luzzati may be due to the absorption effect of the crystal. The mean disagreement factors, *R*, were as follows: $R(h0l)=0.18$, $R(hk0)=0.195$

Description and Discussion of the Structure

The interatomic distances and the bond angles calculated on the basis of the above parameter values are shown in Fig. 3. Each copper atom in the lattice is surrounded by two oxygen and two nitrogen atoms in a square configuration. These four atoms are coplanar with the copper atom, and in the direction perpendicular to the plane of this square there are no atoms within a distance of 3.0 Å from the copper atom, so that the electronic structure of the copper atom is a typical dsp² type.

Each 8-hydroxyquinoline radical is almost flat. Two plane equations for the two crystallographically different radicals coordinated with the same copper atom were determined. Within the range of experimental error, they are coplanar with a central copper atom and almost parallel to each other. The mean plane, containing two 8-hydroxyquinoline molecules with a copper atom, was found by the least-squares method to have the following equation:

$$0.268x'+0.465y'+0.256z'=1$$

The orientation of the molecule in the crystal can be expressed by the angles χ, ψ, and ω, which the molecular axes, L, M and their normal, make with the a, b and c axes. Axes L and M are taken to lie in the mean plane of the molecule and to be directed parallel to the C(8)—C(9) line and its normal respectively. The mean values of these angles are listed in Table II. These show also that the inclination of the molecular plane to the (010) plane is about 51.5°. The arrangement of the

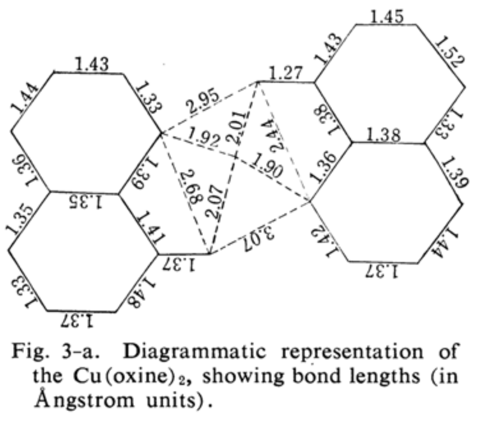

Fig. 3-a. Diagrammatic representation of the Cu(oxine)₂, showing bond lengths (in Ångstrom units).

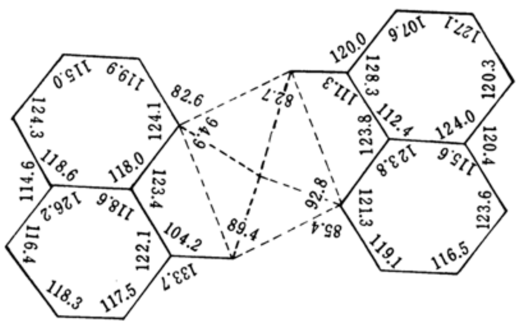

Fig. 3-b. Diagrammatic representation of the Cu(oxine)₂, showing bond angles (in degrees).

TABLE II. THE ANGLES BETWEEN THE MOLECULAR AXES AND THE CRYSTAL AXES

	χ	ψ	ω
L	68.2°	49.3°	49.2°
M	132.7°	58.6°	57.4°

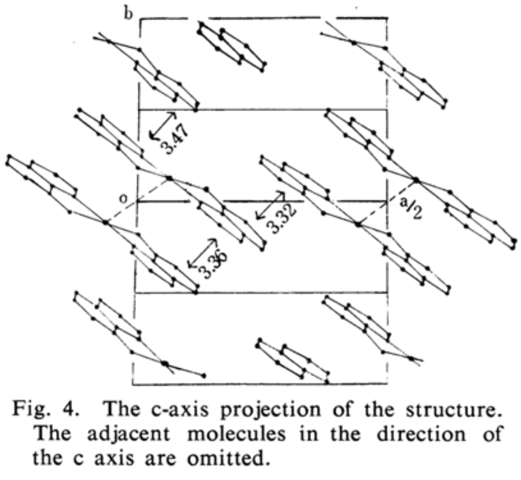

Fig. 4. The c-axis projection of the structure. The adjacent molecules in the direction of the c axis are omitted.

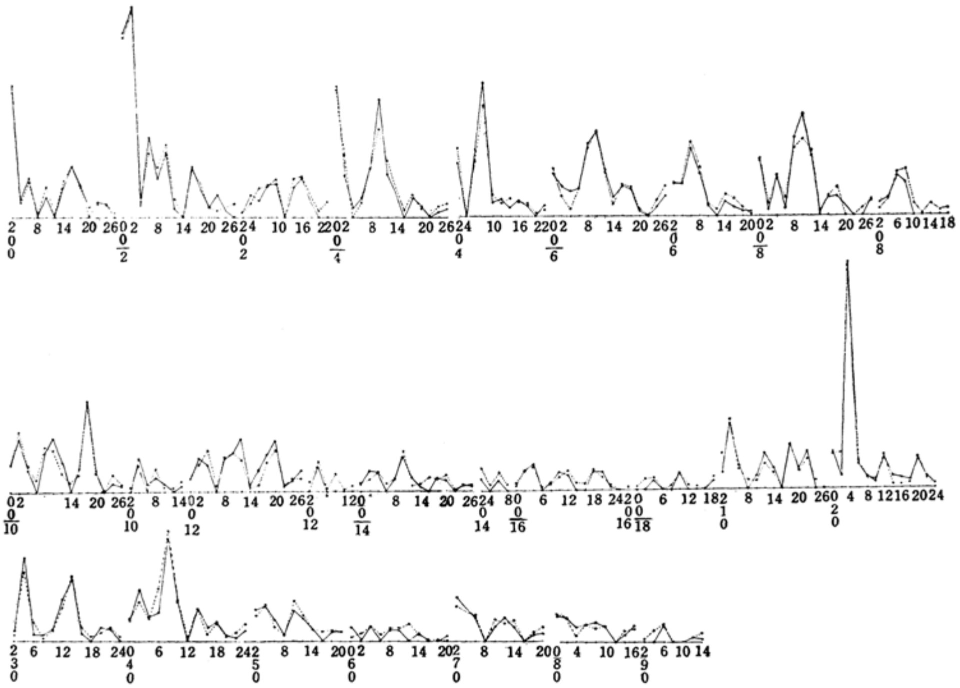

Fig. 5. Comparison of observed (solid lines) and calculated structure factors (dotted lines); $F(h0l)$ and $F(hk0)$.

molecules in the crystal will be clear from the projection in Fig. 4. The perpendicular distances between successive mean molecular planes are 3.36, 3.48 and 3.32 Å. These values are to be compared with the interplane spacing in graphite 3.41 Å, coronene 3.40 Å, or phthalocyanine 3.38 Å. The shortest Cu–Cu distance of 3.45 Å implies that the Cu–Cu bonds contribute to a union of the two chelate molecules, but not so strongly as in copper acetate dihydrate $Cu_2(CH_3COO)_4 \cdot 2H_2O$[11]. The possibility of the type of metal-metal interaction suggested here has also been shown in nickel dimethylglyoxime[12], in which the metal-metal interaction has been reported to have some relation with the solubility. In the copper 8-hydroxyquinolinate crystal, such dimeric molecules as $Cu_2(oxine)_4$ with the Cu–Cu distance of 3.45 Å, are juxtaposed to form layers in the direction of the b and [101] axes like brick walls. The binding forces between these layers may be due to the van der Waals interaction, while within the layers π-bond overlapping will contribute somewhat to the layer formation, as will the metal-metal bond and the van der Waals forces. Such a layer structure, with π-bond overlapping, has been found in quinhydrone[13], phenoquinone[14] and chloranil-hexamethylbenzene complexes[15], while the results of the measurement of the electric conductivity of $Cu(oxine)_2$ powder crystals seems to prove the partial overlap of molecular π-orbitals.

Summary

The crystal structure of anhydrous copper 8-hydroxyquinolinate has been determined by the two-dimensional Fourier method. It is monoclinic and has been shown to belong to the $B2_1/a$ space group, with eight molecules in a cell of the dimensions: $a=23.66$, $b=8.72$, $c=15.30$ Å and $\beta=117.5°$. A copper atom is surrounded by four atoms with Cu–N distances of 1.92 and 1.90 Å, and Cu–O distances of 2.01 and 2.07 Å. Two nitrogen and two oxygen atoms form a square and are coplanar with the copper atom. The closest approach of adjacent chelate molecules occurs along the b axis and in the [101] direction, where the interplanar distances are 3.36, 3.47, and 3.32 Å. These chelate molecules are grouped in pairs around the symmetry center at the point of origin with a Cu–Cu bond of 3.45 Å. The perpendicular distances between successive dimeric molecules given above are almost the same

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[11] J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.*, **6**, 227 (1953).

[12] L. E. Godycki and R. E. Rundle, ibid., **6**, 487 (1953).

[13] H. Matsuda, K. Osaki and I. Nitta, This Bulletin, **31**, 611 (1958).

[14] T. T. Harding and S. C. Wallwork, *Acta Cryst.*, **6**, 791 (1953).

[15] T. T. Harding and S. C. Wallwork, ibid., **8**, 787 (1955).

within the range of experimental error. A π-bond overlapping of molecules is considered to be a part of the binding forces between such layers. The metal-metal bond is presumably the same as that in nickel dimethylglyoxime.

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