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The Crystal Structure of Zinc 8-Hydroxyquinolinate Dihydrate*

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The crystal structure of zinc 8-hydroxyquinolinate dihydrate, $Zn(C_9H_6ON)_2 . 2H_2O$, has been determined by single-crystal methods. The unit cell is monoclinic with $a = 11{\cdot}28$, $b = 5{\cdot}42$, $c = 13{\cdot}16$ Å, $\beta = 106° 18'$. The space group is $P2_1/a$–C_{2h}^5 and there are two molecules per unit cell.

Atomic positions were determined by electron-density projections and were refined by a three-dimensional Fourier electron-density synthesis and by the method of least squares. Structure factors were obtained from visually estimated intensities on Weissenberg photographs taken with Cu $K\alpha$ radiation.

The molecule, with the exception of the water molecules, is essentially planar. Including the water molecules, there is a sort of distorted octahedral arrangement of bonds around the central zinc ion.

$$Zn–O = 2{\cdot}05 \text{ Å}, \quad Zn–N = 2{\cdot}06 \text{ Å}, \quad Zn–OH_2 = 2{\cdot}27 \text{ Å}.$$

Introduction

This report is the second in a series from these Laboratories dealing with the crystal structure of organic reagents of analytical importance and the complexes they form with metallic ions. The first report (Merritt & Lanterman, 1952) concerned the structure of dimethylglyoxime. Unlike dimethylglyoxime, which is quite selective in its action, 8-hydroxyquinoline reacts with a large number of different ions.

Experimental technique, unit cell and space group

Single crystals of zinc 8-hydroxyquinolinate dihydrate are quite difficult to prepare. The zinc salt is precipitated from an acetic acid solution by addition of a slight excess of a 5% solution of 8-hydroxyquinoline in 12% acetic acid and subsequent neutralization with dilute ammonium hydroxide. The precipitate consists of very small crystals which give a powder pattern identical with that of powdered single dihydrate crystals. This finely crystalline precipitate is washed thoroughly with hot water to remove any excess 8-hydroxyquinoline and then is dissolved in pyridine. Water is added to the pyridine solution, kept at about 80° C., until a precipitate begins to form. The precipitate is redissolved by adding a little pyridine and the whole solution is cooled slowly, in an oven, to room temperature. Cooling over a period of two or three days yields crystals of usable size; most crystals, however, are lamellar twins, twinning plane (001). Only rarely does one find a good single crystal. The crystals are pale yellow and translucent. The refractive indices were determined by the usual immersion methods to be

$$\alpha = 1{\cdot}650 \pm 0{\cdot}002, \quad \beta = 1{\cdot}78 \pm 0{\cdot}02, \quad \gamma = > 1{\cdot}82;$$

sign of refraction: negative.

So few well-formed single crystals were available that the orientation of the indicatrix was not thoroughly established; however, $b = \gamma$.

The unit-cell dimensions were obtained from oscillation photographs and from Weissenberg photographs employing the method of ω separations (Buerger, 1942). The results are

$$a = 11{\cdot}28, \quad b = 5{\cdot}42, \quad c = 13{\cdot}16 \text{ Å}, \quad \beta = 106° 18'.$$

The density by the flotation method is 1·682 g.cm.$^{-3}$, which gives 1·98, i.e. 2, molecules per unit cell. By an unusual coincidence in this crystal, pointed out by Hughes (1950), there exists a good check on the consistency of the values of a, c and β. On Weissenberg photographs of twinned crystals rotated about the [010] axis, every third layer where $h = 0$, 6 or 12 consists of single spots, whereas otherwise the spots are doublets. Only when all of the spots begin to be resolved into $K\alpha_1$ and $K\alpha_2$ doublets are these spots on every third layer resolved into three or four spots. This indicates that the reciprocal lattice moves $2c^*$ in going $6a^*$, so that, using the values of a and c found previously:

$$\cos\beta = c^*/3a^* = a/3c, \tag{1}$$

and

$$\beta = 106° 36'. \tag{2}$$

This value of β checks well with that found above.

Complete sets of equi-inclination Weissenberg photographs about the [100] and [010] axes were taken for intensity estimation. The crystals used were roughly

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1 mm. in length along the rotation axis by 0·2 mm. in diameter. No corrections for absorption were made. Copper $K\alpha$ radiation filtered through nickel was employed, and relative intensities were estimated visually by comparison with a standard intensity strip prepared by making a series of timed exposures of the (202) reflection. The multiple-film technique of Robertson (1943) was employed, using four sheets of Eastman No-Screen X-ray film and a factor of 3·7 for the decrease in intensity on passage of the beam through one layer of film. The usual corrections for the Lorentz and polarization factors, the oblique penetration of the film by the X-rays for non-equatorial layer photographs, and the relative time factor of Cox & Shaw (1930) were applied. The zero-layer Weissenberg film about [100] was taken as the standard film, and by cross calibration all intensities were reduced to this common level. Relative F_o values were calculated.

Systematic absences were noted for $h0l$ when h is odd and for $0k0$ when k is odd with the single exception that an extremely weak reflection was observed at the place where (010) should occur. This spot has a peculiar striated shape unlike the other true reflections and, also, it appears only on the upper half of the film. If this is a true reflection then the space group could be $P2/a$ or P/a. The external morphology of the crystal shows a twofold axis of symmetry which would fix the space group as $P2/a$. However, it is impossible to pack the required two molecules satisfactorily in the unit cell in this space group with the short b axis existing in this crystal. Therefore it appears certain that the correct space group is $P2_1/a$–C_{2h}^5 and that the very weak (010) reflection is most probably due to simultaneous reflection, i.e. a Renninger spot (Renninger, 1937). Since there are only two zinc atoms in one unit cell, these atoms must be located at symmetry centers.

Determination of atomic positions

A trial structure is easily obtained by a Patterson projection on (010) or by an electron-density projection with all signs of ($h0l$) taken as positive. Structure factors, F_{h0l}, were calculated from this trial structure. Atomic scattering factors were taken from the *Internationale Tabellen* with corrections applied to those for zinc due to dispersion of the K electrons (James, 1950). Since the zinc atom contributes to all of the 182 terms of this zone, nearly all signs are positive. Actually the signs of 154 terms appeared to be definitely fixed so that they could be included in the next Fourier synthesis. Three projections served to refine the x and z parameters. Only a very few of the weaker terms changed sign in the process of refinement. The third projection on (010) is shown in Fig. 1(*a*). For comparison purposes the final structure is shown as if projected on (010) in Fig. 1(*b*).

After each projection, a temperature and scale factor was determined by the method of least squares,

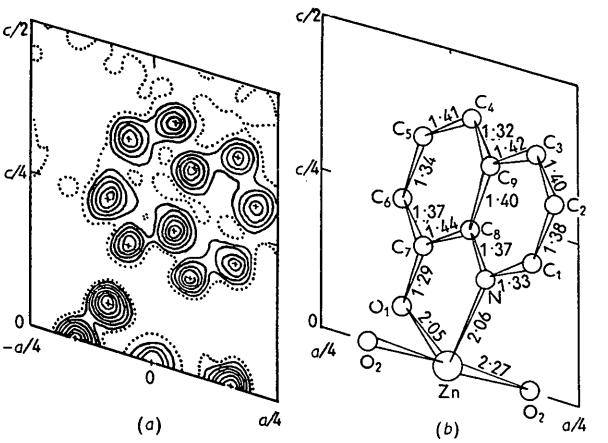

Fig. 1. (*a*) Fourier electron-density projection of asymmetric unit of zinc 8-hydroxyquinolinate dihydrate upon [010]. Contour interval 1 e.Å^{-2} except near origin, where contours are at 5 e.Å^{-2}. The dotted contour = 1 e.Å^{-2}. Crosses represent ultimate centers of the atoms. (*b*) Zinc 8-hydroxyquinolinate dihydrate as seen projected upon [010]. Numbers represent actual bond distances in Angström units.

using the following equation to represent the relationship between F_o and F_c:

$$k|F_o| = |F_c| \exp\left[-B\,(\sin\theta/\lambda)^2\right]. \qquad (3)$$

The value of $R = \Sigma|F_o - F_c| \div \Sigma|F_o|$ decreased from 0·81 to 0·18 and 0·164 during the process of these refinements. Centers of peaks were determined by the method of Carpenter & Donohue (1950). After the x and z parameters were established by the projection on (010) an estimate of the tilt of the molecule was made by measuring the bond lengths in the benzene and pyridine rings, in projection, and comparing these lengths with the expected values. It was estimated that the molecule was tilted about 49° around an axis nearly perpendicular to [100] and lying in the (010) plane. From this information the y parameters were estimated and the structure factors for all reflections were calculated. By trial and error it was discovered that better agreement between $|F_o|$ and $|F_c|$ could be obtained if the angle of tilt were increased to 50°. At this point it was decided to carry out the refinement with a three-dimensional Fourier synthesis, since ordinary projections along [100] or [001] would not show many resolved atoms.

Slight corrections were obtained from the three-dimensional density function. It appears that the molecule is tilted about 50·5° around an axis inclined 94° to [100] which also makes a slight angle of $3\frac{3}{4}$° with the (010) plane.

A least-squares refinement of the parameters according to the method of Hughes (1941) completed the structure determination. All of the 1636 reflections within the region investigated were included in this treatment. Only the diagonal and $x_i z_i$ terms were used in solving the normal equations. The final corrections from the least-squares method averaged

0·025 Å per parameter with a maximum of 0·10 Å in the z parameter of the C_1 atom. Final parameters for the atoms are given in Table 1 and final values of F_o

Table 1. *Atomic parameters of zinc 8-hydroxyquinolinate dihydrate*

Atom	x/a	y/b	z/c
C_1	0·158	0·286	0·194
C_2	0·204	0·326	0·301
C_3	0·167	0·175	0·372
C_4	0·037	0·832	0·396
C_5	0·951	0·646	0·350
C_6	0·909	0·623	0·244
C_7	0·952	0·770	0·178
C_8	0·041	0·958	0·225
C_9	0·082	0·978	0·336
O_1	0·912	0·762	0·076
O_2	0·156	0·734	0·002
N_1	0·079	0·104	0·156
Zn	0·000	0·000	0·000

and F_c in Table 2.* The final value of B, the exponent in the temperature-factor expression, was $2{\cdot}23\times10^{-16}$ cm.^{2}.

There are 213 unobserved reflections. If those for which F_c is below the minimum observable value for the region of the film in which the reflection should occur are not counted, but those for which F_c would indicate the reflection should have been observed are taken at the minimum observable value of F_o, then R turns out to be 0·226. If these 213 reflections are left out altogether R would be 0·219.

The Fourier calculations of the density functions, structure factors and least-squares refinement were carried out with the aid of I.B.M. machines (Donohue & Schomaker, 1949; Shaffer, Schomaker & Pauling, 1946).

Discussion of structure

The dimensions of a single asymmetric unit are presented in Fig. 1(*b*) and Table 3. Because of the presence of a heavy atom in the structure the positions of the lighter atoms cannot be fixed as accurately as desired. It seems probable that errors in bond distances between light atoms may be as high as 0·06–0·08 Å judging by the bond lengths in the benzene and pyridine ring, and little weight should be placed on the irregularities in the bond lengths in these rings. The lengths of the bonds around the zinc atom, which are the most interesting in this crystal, are undoubtedly more precise, owing to the exact knowledge of the position of the zinc ion, and should not be in error by more than about 0·03–0·04 Å.

Table 3. *Interatomic distances and angles in zinc 8-hydroxyquinolinate dihydrate crystal*

Bond	Distance	Bonds	Angle
Zn–O_1	2·05 Å	O_1–Zn–N	79·8°
Zn–N	2·06	O_1–Zn–O_2	94·6
Zn–O_2	2·27	N–Zn–O_2	92·7
N–C_1	1·33	Zn–N–C_8	111·8
C_1–C_2	1·38	N–C_8–C_7	116·1
C_2–C_3	1·40	C_8–C_7–O_1	117·4
C_3–C_9	1·42	C_7–O_1–Zn	114·3
C_8–C_9	1·40	N–C_1–C_2	120·9
C_8–N	1·37	C_1–C_2–C_3	119·9
C_4–C_9	1·32	C_2–C_3–C_9	121·1
C_4–C_5	1·41	C_3–C_9–C_8	113·5
C_5–C_6	1·34	C_9–C_8–N	125·1
C_6–C_7	1·37	C_8–N–C_1	119·0
C_7–C_8	1·44	C_7–C_8–C_9	118·8
C_7–O_1	1·29	C_8–C_9–C_4	121·0
		C_9–C_4–C_5	120·1
		C_4–C_5–C_6	120·6
		C_5–C_6–C_7	121·6
		C_6–C_7–C_8	117·8
		C_6–C_7–O_1	124·4
		Zn–N–C_1	128·9
		C_3–C_9–C_4	125·6

It would appear that the major distortions in bond angles which results from formation of the five-membered ring are in the angles around the zinc ion and around the nitrogen atom. The Zn–N–C_8 angle has been decreased significantly from the expected angle of 120°.

The arrangement around the zinc atom is that of a distorted octahedron. This is shown schematically in Fig. 2. The bond angle of 79·8° between the oxygen, zinc and nitrogen atoms of the main part of the molecule probably represents a sort of compromise due to the rigid structure of the organic chelating molecule and the inability to approach closer to the zinc atom without causing too short bonds and too great a negative charge upon the zinc atom. A somewhat similar distorted octahedral arrangement is found in

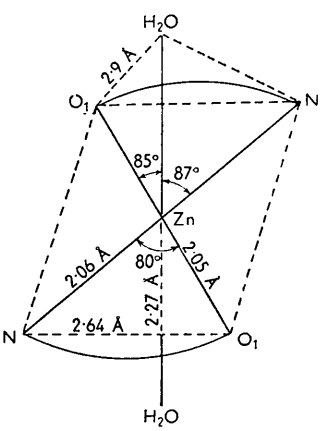

Fig. 2. Schematic diagram showing distorted octahedral arrangement of bonds around central zinc atom in zinc 8-hydroxyquinolinate dihydrate.

* Table 2, containing F_o and F_c values for about 1,500 reflections, has been withdrawn and is deposited as Document No. 4208 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C., U.S.A. A copy may be secured by citing the Document number and by remitting \$2·50 for photoprints, or \$1·75 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress. A copy may also be obtained from the author.

nickel glycine dihydrate (Stosick, 1945). If the ligands were free to move as necessary, then a more regular octahedral structure would be expected, such as was observed by Tang & Sturdivant (1952) in manganese chloride dihydrate–hexamethylene diamine complex.

The zinc atom has a closed third electron shell and therefore the bonding of the six groups must be through use of the $4s$, $4p^3$ and $4d^2$ orbits. This would be similar to the case of the above mentioned manganese complex where magnetic susceptibility measurements have shown five unpaired electrons. There is undoubtedly considerable ionic character in these bonds.

From the normal covalent radii ascribed to oxygen (0·66 Å) and to nitrogen (0·70 Å) and the Zn–O and Zn–N bond distances in this crystal, it appears that the octahedral covalent radius of the zinc atom is about 1·38 Å. Pauling (1945) lists 1·31 Å as the tetrahedral covalent radius of zinc. The increase of about 0·07 Å seems reasonable if the unstable $4d$ orbitals are involved at all.

The water molecules are much less firmly attached to the zinc atom than is the organic molecule, as shown by the greater $Zn–O_2$ distance and confirmed by the fact that the compound loses these water molecules on drying above 135° C. The anhydrous complex is undoubtedly tetrahedral since Liu & Bailar (1951) have been able to resolve the anhydrous zinc complex of 8-hydroxyquinoline-5-sulfonic acid into optically active isomers. Mundy (1948) has shown that the copper 8-hydroxyquinolinate complex exists in two forms, an anhydrous form with space group $P2_1/a$ and four atoms per unit cell, and a dihydrate isomorphous with the zinc complex. According to this observation, there is no reason why the anhydrous form, at least of the copper complex, should not be tetrahedral. It is interesting to note that the resolved compounds of Liu & Bailar are easily racemized on standing in water; this might indicate that they pick up two molecules and revert to the structure shown in this report.

The molecules in zinc 8-hydroxyquinolinate dihydrate show no unusually close approaches. The smallest intermolecular distance is 3·45 Å between adjacent water molecules. The closest approach of carbon atoms is 3·47 Å. These distances eliminate the possibility of hydrogen bonding and indicate that molecular binding in the crystal is mainly through van der Waals forces.

The hydrogen atoms, which altogether contribute 8% of the scattering matter of the unit cell, were neglected entirely in this determination. Inclusion of the hydrogens would probably improve slightly the agreement between observed and calculated structure factors. It is also probable that an anisotropic temperature factor would materially improve the agreement. A root-mean-square displacement of the atoms of 0·17 Å is indicated from the value of B in the temperature-factor expression.

The atoms of the 8-hydroxyquinoline molecules and the zinc atom all lie in a plane within the limits of experimental error, except, perhaps, for the oxygen atom O_1, which seems to be about 0·10 Å below the least-squares best plane. If the five-membered ring alone is considered, none of the atoms in this ring is more than 0·05 Å from a plane. The equation of the least-squares best plane for the whole asymmetric unit in terms of the unit cell vectors is

$$a-0{\cdot}3994b-0{\cdot}2554c = 0\,. \qquad (4)$$

The average deviation of atoms from this plane is 0·03 Å and the maximum deviation is 0·10 Å for the oxygen atom O_1.

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