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The Structure of Coordination Compounds. III. A Refinement of the Structure of Zinc 8-Hydroxyquinolinate Dihydrate

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The crystal structure of zinc 8-hydroxyquinolinate dihydrate, $Zn(C_9H_6ON)_2.2H_2O$, which was originally determined by Merritt, Cady & Mundy in 1954 has been refined by least-squares methods. The coordinates and individual anisotropic thermal parameters for all atoms, except the hydrogen atoms, were refined. The full matrix was computed for each least-squares cycle.

The bond distances in the hydroxyquinoline group have undergone significant changes. The results are compared with the structures of β-copper 8-hydroxyquinolinate and 2,2′-biquinolyl.

Introduction

After the completion of a structural study of the β form of anhydrous copper 8-hydroxyquinolinate (Palenik, 1964), we wished to compare our results with other compounds containing similar groups. The crystal structure of zinc 8-hydroxyquinolinate dihydrate was originally determined by Merritt, Cady & Mundy (1954) (MCM). However, the structure was not completely refined, even though the authors had carefully collected three-dimensional data. Since the data were readily available, we decided to complete the refinement of this structure so that a valid comparison of the two salts could be made.

Refinement procedure

The space group of the zinc salt reported by MCM is $P2_1/a$. The unit cell was transformed to the space group $P2_1/c$, since the necessary programs had been assembled for the latter space group. The pertinent crystal data reported by MCM are given below for the setting $P2_1/c$.

$$a_0=13\cdot16,\ b_0=5\cdot42,\ c_0=11\cdot28\ \text{Å};\ \beta=106°\ 18'\ .$$

The density measured by MCM is 1·682 g.cm^{-3}, while the value calculated for two molecules per unit cell is 1·676 g.cm^{-3}.

The present refinement was carried out by least-squares using the observed amplitudes of MCM. A total of nine cycles of least squares was carried out, the full matrix being computed for each cycle. The weighting scheme employed for each cycle was:

$$\text{if } F(\text{obs}) \leq 15\cdot0 \quad \sqrt{w}=1\cdot0$$
$$\text{if } F(\text{obs}) > 15\cdot0 \quad \sqrt{w}=15\cdot0/F(\text{obs})$$

where the original scale of MCM was retained for the observed amplitudes.

The scattering factor for zinc was corrected for dispersion by subtracting the value of 1·7 electrons

Table 1. *Summation of positional parameters from previous work* (MCM), *and the present study* (PS) *and standard deviations in the present study*

All values have been multiplied by 10^4

Atom		*X*	*Y*	*Z*
C(1)	MCM	1940	2860	1580
	PS	1972	2896	1588
	σ	0007	0016	0008
C(2)	MCM	3010	3260	2040
	PS	3057	3315	2046
	σ	0008	0018	0008
C(3)	MCM	3720	1750	1670
	PS	3742	1818	1679
	σ	0007	0018	0008
C(4)	MCM	3360	−0220	0820
	PS	3351	−0120	0826
	σ	0006	0017	0007
C(5)	MCM	3960	−1680	0370
	PS	3987	−1745	0372
	σ	0007	0019	0008
C(6)	MCM	3500	−3540	−0490
	PS	3540	−3505	−0471
	σ	0007	0020	0009
C(7)	MCM	2440	−3770	−0910
	PS	2449	−3805	−0893
	σ	0007	0019	0008
C(8)	MCM	1780	−2300	−0480
	PS	1769	−2287	−0486
	σ	0006	0016	0007
C(9)	MCM	2250	−0420	0410
	PS	2232	−0391	0408
	σ	0006	0014	0007
N	MCM	1560	1040	0790
	PS	1574	1087	0800
	σ	0005	0013	0006
O(1)	MCM	0760	−2380	−0880
	PS	0733	−2512	−0866
	σ	0005	0011	0005
O(2)	MCM	0020	−2660	1560
	PS	0024	−2750	1517
	σ	0006	0012	0006
Zn	MCM	0000	0000	0000
	PS	0000	0000	0000

given by Dauben & Templeton (1955) from the neutral zinc curve given by Freeman & Watson (1961). The oxygen and nitrogen scattering factors were taken from Hoerni & Ibers (1954) and carbon–graphite and hydrogen from McWeeny (1951).

The refinement was initiated with MCM's final positional parameters which are reproduced in Table 1. An isotropic B of 2·23 was used for the initial least-squares cycle and anisotropic thermal parameters were refined in subsequent cycles. Three least-squares cycles dropped the residual R from 24·1% to 13·7% and the sum of the squares of the weighted residuals from 14560·4 to 4541·5. At this point a careful survey of the observed and calculated values of the structure amplitudes revealed five reflections that were in poor agreement. Four of the five reflections appeared to be in error by $\sqrt{10}$, a reasonable error. Since neither the films nor the original intensity data were available, the five reflections were arbitrarily changed. These five reflections are listed in Table 2 together with the values calculated after three cycles and the adjusted values. Three additional least-squares cycles were computed. At this point the shifts were all smaller than the standard deviations computed from the inverse matrix. The value of R was 13·1%.

Table 2. *List of structure amplitudes changed from previous values of* MCM

hkl	F(obs)* MCM	F(calc)†	F(obs)‡ PS
$24\bar{2}$	37·2	3·5	3·7
640	38·1	18·1	12·1
10,4,0	41·6	17·0	13·2
11,4,0	37·3	13·5	11·8
12,4,0	31·5	11·2	10·0

* Value reported by MCM.
† Value calculated after 3 least-squares cycles.
‡ Corrected value.

An attempt was made to locate the hydrogen atoms. There was some doubt as to whether this effort was warranted because of the accuracy of the data. A difference Fourier synthesis was calculated with the last set of parameters from the least-squares refinement. The hydrogen atoms were assumed to lie on an extension of the cross-ring vector at a distance of 1 Å from the appropriate carbon atom. The six hydrogen atoms on the quinoline ring all fell near or on positive areas in the difference Fourier map. The ring hydrogen positions were then adjusted to correspond to the positive peaks in the difference Fourier synthesis. Of the two hydrogen atoms on the water molecule, only one could be located with even a small degree of confidence. The second hydrogen was assumed to be 1 Å away from the oxygen. Of the two positions which would give the oxygen tetrahedral configuration, one position oriented the hydrogen atom toward another oxygen atom. This configuration was assumed to be correct.

Three additional least-squares cycles were computed. The contribution of the hydrogen atoms was calculated, but the atoms were not refined. No significant changes were produced in the parameters of the heavier atoms. Thus, the refinement was terminated.

Results and discussion

The final position parameters and their standard deviations computed from the inverse matrix are summarized in Table 1. The final coordinates of MCM were transformed to correspond to the new settings and are included for comparison in Table 1. The difference between the two sets of parameters is undoubtedly due to the diagonal approximation used by MCM and to the small number of least-squares cycles computed with this approximation.

The present refinement utilized anisotropic thermal parameters. The thermal parameters and their standard deviations are given in Table 3.

The parameter shifts have changed the bond distances and angles reported by MCM. In Table 4 the pertinent intramolecular bond distances and angles have been collected for the two sets of parameters. The distances and angles in the molecule, with the exception of the water molecule, are illustrated in Fig. 1.

The zinc–hydroxyl oxygen bond distance of 2·066 Å is 0·033 Å shorter than the zinc–nitrogen distance of

Table 3. *Anisotropic thermal parameters*

The temperature factor was of the form

$$T_i = \exp\{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)\}$$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	0042	0204	0038	0008	−0011	−0019
σ	0005	0030	0006	0020	0009	0024
C(2)	0047	0234	0051	−0084	0005	−0028
σ	0006	0031	0007	0022	0010	0026
C(3)	0039	0270	0049	−0046	−0003	0003
σ	0005	0033	0007	0021	0010	0027
C(4)	0034	0261	0034	−0010	0014	0036
	0005	0031	0006	0021	0008	0025
C(5)	0027	0331	0053	0029	0032	0036
σ	0005	0036	0007	0021	0009	0028
C(6)	0038	0347	0056	0064	0028	−0009
σ	0005	0040	0008	0024	0010	0029
C(7)	0044	0308	0048	0052	0026	0003
σ	0006	0036	0007	0024	0011	0028
C(8)	0032	0232	0028	−0010	0019	0015
σ	0005	0029	0005	0019	0008	0022.
C(9)	0028	0187	0027	−0010	0008	0030
σ	0004	0027	0005	0017	0008	0021
N	0034	0168	0041	−0020	0009	0003
	0004	0022	0005	0015	0007	0019
O(1)	0034	0234	0045	−0021	0004	−0051
σ	0004	0021	0005	0014	0006	0017
O(2)	0073	0222	0045	−0043	0007	−0002
σ	0005	0022	0005	0018	0008	0018
Zn	0022	0229	0035	−0003	0008	−0048
σ	0001	0006	0001	0003	0001	0004

2·099 Å. The inequality of the metal–oxygen and metal–nitrogen bond distances has been discussed previously by the author (Palenik, 1964). There are few precise values of either the zinc–oxygen or zinc–nitrogen bond distance reported in the literature for comparison with the present values. The values for the zinc–oxygen bond distance were summarized by Klug, Alexander & Sumner (1958) and also by Lippert & Truter (1960). The distances reported for the zinc–oxygen bond distance range from 2·05 Å to 2·18 Å, and the distance of 2·066 Å found in the present study is not unreasonable. Fewer values for the zinc–nitrogen bond distance are available, but this distance can be expected to be slightly longer than the corresponding metal–oxygen distance.

The distance of 2·263 Å from the water molecule to the zinc atom is longer than is usually found for a zinc–oxygen bond. As MCM pointed out, the compound is easily dehydrated, suggesting a weak zinc–water bond.

A comparison of the bond distances and angles of the hydroxyquinolinate group in the zinc and copper salts is very interesting. The average distances in anhydrous β-copper 8-hydroxyquinolinate are illustrated in Fig. 2. The structure of 8-hydroxyquinoline has not been reported in the literature, but the dimensions of 2,2′-biquinolyl reported by Datta (1959) are also illustrated in Fig. 2.

Table 4. *Intramolecular distances and angles for the two parameter sets*

Bond	Distance*	
	MCM	PS
Zn–O(1)	2·05 Å	2·066 Å
Zn–O(2)	2·27	2·263
Zn–N	2·06	2·099
N–C(1)	1·33	1·328
C(1)–C(2)	1·38	1·394
C(2)–C(3)	1·40	1·361
C(3)–C(4)	1·42	1·420
C(4)–C(5)	1·32	1·407
C(5)–C(6)	1·41	1·359
C(6)–C(7)	1·34	1·388
C(7)–C(8)	1·37	1·386
C(8)–C(9)	1·44	1·448
C(9)–C(4)	1·40	1·423
C(9)–N	1·37	1·342
C(8)–O(1)	1·29	1·314

Atoms	Angle	
	MCM	PS
O(1)–Zn–N	79·8°	81·5°
O(1)–Zn–O(2)	94·6	90·8
N–Zn–O(2)	92·7	93·3
Zn–N–C(9)	111·8	109·9
N–C(1)–C(2)	120·9	122·6
C(1)–C(2)–C(3)	119·9	119·1
C(2)–C(3)–C(4)	121·1	120·2
C(3)–C(4)–C(9)	113·5	116·4
C(4)–C(9)–N	125·1	122·2
C(9)–C(4)–C(5)	121·0	118·8
C(4)–C(5)–C(6)	120·1	120·6
C(5)–C(6)–C(7)	120·6	121·7
C(6)–C(7)–C(8)	121·6	121·2
C(7)–C(8)–C(9)	117·4	117·8
C(8)–C(9)–C(4)	118·8	119·9
C(8)–O(1)–Zn	114·3	111·3
C(9)–C(8)–O(1)	117·4	119·3

* The probable error in the light atom–light atom distances is 0·06–0·08 Å for MCM and 0·015 Å for PS.

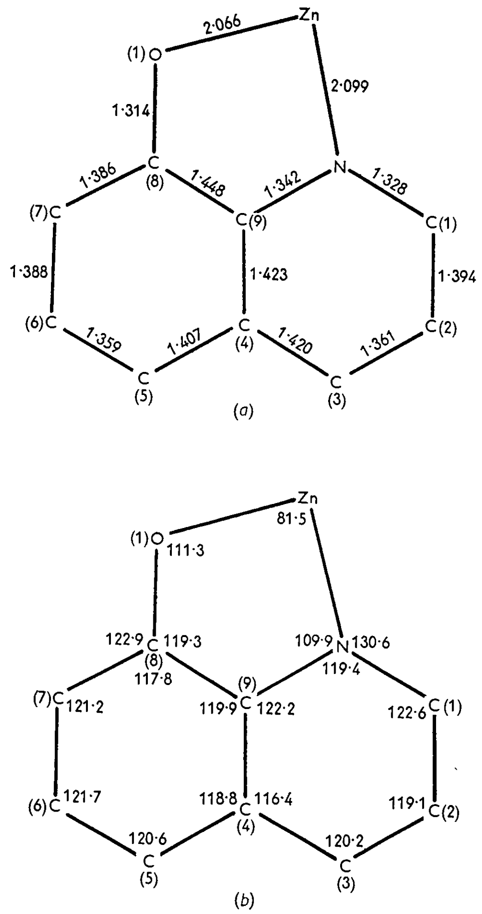

Fig. 1. Distances and angles in the zinc 8-hydroxyquinolinate portion of the molecules.

The dimensions of the hydroxyquinoline group in the two metal salts are surprisingly similar. The standard deviation between chemically equivalent bonds is 0·017 Å. The largest difference is 0·047 Å between the distances C(6)–C(7) in the two salts. By the criterion proposed by Cruickshank & Robertson (1953), $t_0 = 2{\cdot}66$, this difference is on the border of significance. However, the three values of this bond distance observed in the two determinations, 1·388, 1·424 and 1·446 Å, give an average value of 1·419. None of the three bond distances differs significantly from this mean value.

It appears that the hydroxyquinoline group has identical dimensions in the two salts. This result is somewhat surprising since the two metal atoms have different configurations. The dimensions are also similar to those found in 2,2′-biquinolyl by Datta (1959).

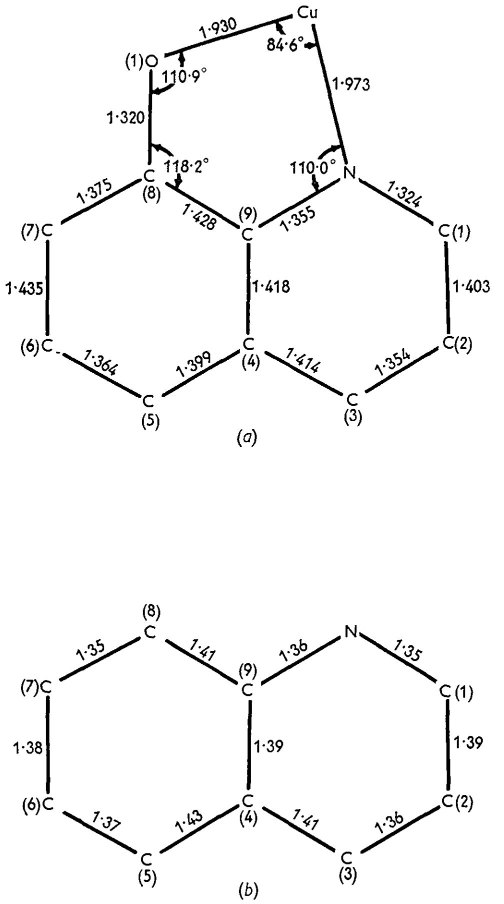

Fig. 2. Distances and angles in β-copper 8-hydroxyquinolinate and 2,2′-biquinolyl.

Table 5. *Least-squares planes*

Atom	I†	II†	III†
C(1)	010	009	023
C(2)	020	020	022
C(3)	−002	−001	−008
C(4)	−013	−013	−017
C(5)	−013	−013	−025
C(6)	013	013	004
C(7)	012	010	013
C(8)	005	003	015
C(9)	−015	−016	−008
N	−016	−017	−001
O(1)	006	003	026
Zn	−075	−078	−045

Plane	Direction cosines with respect to *a*	*b*	*c**	Distance from origin	Description of plane
I	1874	6299	−7537	0·075	Quinoline group only C(1)–C(9), N
II	1881	6301	−7534	0·078	Hydroxyquinoline group C(1)–C(9), N, O(1)
III	1794	6308	−7549	0·045	Zinc and hydroxy-quinoline, C(1)–C(9), N, O(1), Zn

† Deviation from the specified plane × 10^3.

Table 6. *Intermolecular distances*

X_i-X_j	Molecule	Distance*
O(2)–C(7)	$B(0\bar{1}0)$	3·646 Å
O(2)–C(8)	$B(0\bar{1}0)$	3·552
O(2)–O(1)	$B(0\bar{1}0)$	2·777
C(5)–C(5)	$B(100)$	3·556
C(2)–C(6)	$C(000)$	3·894
C(2)–C(7)	$C(000)$	3·992
C(2)–C(6)	$C(0\bar{1}0)$	3·748
C(3)–C(6)	$C(0\bar{1}0)$	3·756
C(1)–C(7)	$C(0\bar{1}0)$	3·519
C(2)–C(7)	$C(0\bar{1}0)$	3·614
C(3)–C(7)	$C(0\bar{1}0)$	3·959
N–C(7)	$C(0\bar{1}0)$	3·790
O(2)–C(7)	$C(0\bar{1}0)$	3·768
O(2)–C(8)	$C(0\bar{1}0)$	3·514
O(2)–O(1)	$C(0\bar{1}0)$	2·839
C(1)–O(2)	$D(000)$	3·840
O(2)–O(2)	$D(000)$	3·514
C(3)–C(5)	$D(100)$	3·876

* X_i is in molecule *A* and X_j in the molecule specified after X_j. The molecules are located as follows:

A	x, y, z	*C*	$x, \frac{1}{2}-y, \frac{1}{2}+z$
B	$\bar{x}, \bar{y}, \bar{z}$	*D*	$\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$

The numerals after the molecular designation give the unit cell translations in the order *a*, *b*, *c*.

The indication is that there is little change in the 8-hydroxyquinoline molecule resulting from complex formation. It would be interesting to compare the hydroxyquinoline configuration in the two metal salts with a strictly ionic case such as the potassium or sodium salt.

A number of least-squares planes were computed by the method of Schomaker, Waser, Marsh & Bergman (1959), and the data are presented in Table 5. The hydroxyquinoline group is planar, but the zinc atom is displaced from this plane. In the copper salt, the copper atom is also displaced from the plane of the hydroxyquinoline molecule. In the zinc salt this displacement is difficult to explain since d^2Sp^3 hybridization of the zinc atom presumably would lead to a planar configuration.

A projection of several molecules on the (010) plane is illustrated in Fig. 3. The intermolecular distances less than 4·0 Å were computed and some of the pertinent distances are given in Table 6. The closest intermolecular approach is between the coordinated water of one molecule and the hydroxyl oxygen of another molecule. The two different oxygen–oxygen contacts are 2·777 and 2·839 Å. The zinc–oxygen (water)–oxygen (hydroxyl) angles of 133·2 and 118.8° are larger than 109°. However, the possibility of the existence of a hydrogen bond is not eliminated. Therefore, the statement of MCM that 'these distances eliminate the possibility of hydrogen bonds' may not be valid.

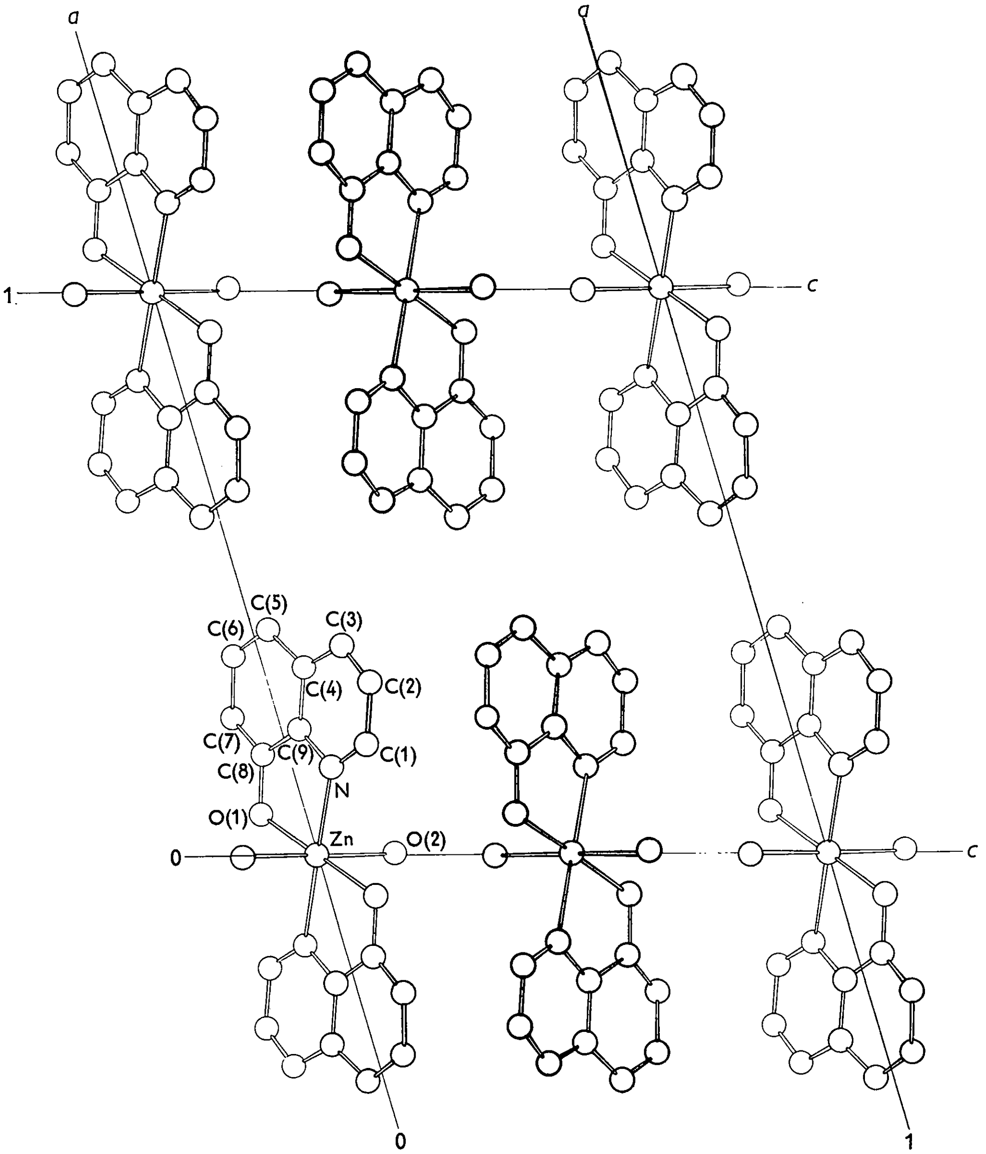

Fig. 3. Projection of the zinc 8-hydroxyquinolinate dihydrate structure on the (010) plane.

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