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The Crystal and Molecular Structure of Anhydrous Zinc 8-Quinolinolate Complex, $[Zn(C_9H_6NO)_2]_4$†

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The molecular structure of an anhydrous zinc 8-quinolinolate obtained by sublimation has been determined by means of X-ray diffraction. The complex forms triclinic crystals; $a=11.858(1)$, $b=13.019(2)$, $c=10.834(1)$ Å, $\alpha=106.56(1)$, $\beta=109.00(1)$, and $\gamma=74.14(1)°$, space group $P\bar{1}$ (No. 2) with one $[Zn(C_9H_6NO)_2]_4$ molecule. The structure was solved by the heavy atom method and refined by the block-diagonal least-squares procedure to $R=0.043$ for 3320 non-zero reflections. The molecule is centrosymmetric and tetrameric; four $[Zn(C_9H_6NO)_2]$ units being connected by oxygen atoms of 8-quinolinolate ligands. Two types of bridging oxygen atoms were found. Two crystallographically independent zinc atoms take different geometries, hexa-, and penta-coordinations.

Many investigations have been carried out on the crystal structures of metal 8-quinolinolate complexes hitherto. Interesting weak intermolecular interactions have been found between metal and oxygen atoms of ligands in crystal structures of anhydrous copper 8-quinolinolates.[1-4]

The crystal structure of zinc 8-quinolinolate dihydrate has been determined by Merritt, Cady and Mundy,[5] redetermination of which has been carried out by Palenik.[6] Ogawa[7] reported a preliminary result of the X-ray studies on the solution-grown crystals of anhydrous zinc 8-quinolinolate; triclinic, $a=11.1$, $b=9.20$, $c=11.1$ Å, $\alpha=114.9$, $\beta=75.1$, $\gamma=90.8°$, and $Z=2$. This paper will deal with the crystal and molecular structure of an anhydrous zinc 8-quinolinolate recrystallized directly from the gas phase. Interestingly, 8-quinolinolate complexes of zinc were obtained by S. Ikeda and co-worker by the direct reaction of 8-quinolinol with zinc metal,[8] the study of which closely related to the dissolution of zinc and this fact promoted the present study.

Experimental

Anhydrous zinc 8-quinolinolate was prepared by drying the zinc 8-quinolinolate dihydrate above 130 °C under vacuum. The complex was sublimed at about 400 °C and recrystallized directly from the gas phase. Only few crystals with pale yellow color and small polyhedral shape were available for the X-ray experiment.

Crystal Data: $C_{72}H_{48}N_8O_8Zn_4$, M 1414.7, triclinic, space group $P\bar{1}$(No. 2), $a=11.858(1)$, $b=13.019(2)$, $c=10.834(1)$ Å, $\alpha=106.56(1)$, $\beta=109.00(1)$, and $\gamma=74.14(1)°$, $V=1485.3(3)$ Å^3, $D_c=1.581$ g cm^{-3} for $Z=1$.

Unit-cell dimensions were determined by the least-squares fit of 2θ values of higher order reflections using Mo $K\alpha$ radiation ($\lambda=0.71069$ Å). The unit-cell was first taken as a base-centered lattice, $A\bar{1}$ and later transformed to the reduced standard cell, $P\bar{1}$. The measurement of the crystal density was omitted because no extra crystal was available but for the X-ray experiment.

A Rigaku automated, four-circle diffractometer was used for the intensity data collection. The integrated intensities were measured by the $\theta-2\theta$ scan technique using zirconium-filtered Mo $K\alpha$ radiation. The peak scan of each reflection was started at an angle of $(2\theta-1.0)°$ with the scan width of $(2.0+0.7\tan\theta)°$ and the scan rate in 2θ was 2° min^{-1}. Backgrounds were measured for 10 s at both ends of a scan. During the X-ray experiment the intensity fluctuations of four standard reflections measured after every 50 reflections were within the error of counting statistics. A total of 3659 independent reflections were measured. The intensities were corrected for usual Lorentz and polarization effects but not for the absorption [μ(Mo $K\alpha$)=17.1 cm^{-1}]. The crystal used had approximate dimensions of 0.1×0.1×0.2 mm.

Structure Solution and Refinement

The structure was solved by the heavy atom method. The initial coordinates of two crystallographically independent zinc atoms in an asymmetric unit were easily determined from the three-dimensional Patterson map. Non-hydrogen atoms could be located by the subsequent Fourier synthesis. The structure was refined by the block-diagonal least-squares procedure (*HBLS* V),[9] the function minimized being $\sum w(\Delta F)^2$. At the initial stage of the refinement, the intensity data used were limited within a sphere of $(\sin\theta)/\lambda \leqq 0.481$ (2743 out of 3659 total reflections) and $w=1$. Four cycles of isotropic refinement gave the R value of 0.076. Further refinement with anisotropic temperature factor for zinc atoms gave the R of 0.062. Anisotropic temperature factors were then introduced for the other non-hydrogen atoms. Hydrogen atoms were located on the calculated positions, almost all of which were confirmed by the difference Fourier synthesis, and they were also included in the structure factor calculation but their atomic coordinates were fixed with equal temperature factors ($B=3.0$ Å^2). Four cycles of the refinement improved the R to 0.051. At this stage, all of the reflection data were included in the least-squares calculation and the positional and thermal parameters of hydrogen atoms were also refined using small damping factors (one-tenth of those of the heavy atoms). After several cycles of the refinements the R index converged to 0.043 for non-zero (0.052 for all)

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TABLE 1. FINAL ATOMIC COORDINATES[a] WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z	B_{eq}/Å^2
Zn(1)	0.09937(5)	0.39703(5)	−0.04956(6)	3.01
Zn(2)	0.28152(6)	0.20180(5)	0.09065(6)	3.02
O(1)	0.2787(3)	0.3157(3)	0.0029(4)	3.7
O(2)	−0.0760(3)	0.4829(3)	−0.1157(4)	3.7
O(3)	0.0874(3)	0.2698(3)	0.0349(4)	3.0
O(4)	0.4573(4)	0.1269(4)	0.1497(4)	4.2
N(1)	0.1911(4)	0.4750(4)	−0.1296(5)	3.7
N(2)	0.0333(4)	0.2996(4)	−0.2482(5)	3.5
N(3)	0.2146(4)	0.0662(4)	−0.0266(4)	3.1
N(4)	0.2953(4)	0.2321(4)	0.2913(5)	3.7
C(11)	0.1453(6)	0.5520(5)	−0.1991(7)	4.5
C(12)	0.2121(7)	0.5825(5)	−0.2638(7)	5.4
C(13)	0.3320(7)	0.5348(5)	−0.2500(7)	5.4
C(14)	0.5090(6)	0.3990(6)	−0.1548(7)	4.9
C(15)	0.5506(5)	0.3196(6)	−0.0824(7)	4.9
C(16)	0.4766(5)	0.2883(5)	−0.0280(6)	4.0
C(17)	0.3560(5)	0.3401(5)	−0.0444(6)	3.4
C(18)	0.3107(5)	0.4247(4)	−0.1171(5)	3.2
C(19)	0.3862(6)	0.4537(5)	−0.1741(6)	4.1
C(21)	0.0907(6)	0.2061(5)	−0.3093(6)	4.1
C(22)	0.0291(7)	0.1451(5)	−0.4293(7)	5.4
C(23)	−0.0919(7)	0.1799(5)	−0.4850(6)	5.0
C(24)	−0.2783(6)	0.3198(6)	−0.4725(7)	5.2
C(25)	−0.3312(6)	0.4162(6)	−0.4028(7)	5.2
C(26)	−0.2647(5)	0.4749(5)	−0.2827(6)	4.1
C(27)	−0.1438(5)	0.4360(5)	−0.2298(6)	3.5
C(28)	−0.0865(5)	0.3359(5)	−0.3030(5)	3.3
C(29)	−0.1539(6)	0.2785(5)	−0.4225(6)	4.2
C(31)	0.2814(5)	−0.0324(5)	−0.0556(6)	3.9
C(32)	0.2267(6)	−0.1218(5)	−0.1305(6)	4.2
C(33)	0.1037(5)	−0.1084(5)	−0.1758(6)	3.9
C(34)	−0.0966(5)	0.0194(5)	−0.1947(6)	4.2
C(35)	−0.1588(5)	0.1244(5)	−0.1633(6)	4.1
C(36)	−0.0991(5)	0.2106(5)	−0.0851(6)	3.8
C(37)	0.0254(5)	0.1919(4)	−0.0366(5)	3.0
C(38)	0.0910(5)	0.0835(4)	−0.0710(5)	3.0
C(39)	0.0310(5)	−0.0033(5)	−0.1474(5)	3.2
C(41)	0.2129(6)	0.2837(5)	0.3584(6)	4.3
C(42)	0.2358(7)	0.2876(6)	0.4959(7)	5.6
C(43)	0.3446(6)	0.2347(6)	0.5606(7)	5.3
C(44)	0.5493(6)	0.1202(6)	0.5531(6)	5.2
C(45)	0.6269(6)	0.0646(6)	0.4771(7)	5.3
C(46)	0.5995(5)	0.0650(5)	0.3425(6)	4.4
C(47)	0.4892(5)	0.1216(5)	0.2756(6)	3.9
C(48)	0.4045(5)	0.1795(5)	0.3549(5)	3.5
C(49)	0.4348(6)	0.1771(5)	0.4934(6)	4.2

a) Only those of non-hydrogen atoms with equivalent isotropic temperature factors, B_{eq}[12] are given. Those of hydrogen atoms are kept at the Chemical Society of Japan, Document No. 8525.

reflections (R_W=0.049). The weighting schemes used were $w=F_{wt}$ for $|F_o|=0$, $w=1.0$ for $|F_o| \leqq F_{max}$, and $w=(F_{max}/|F_o|)^{-2}$ for $F_{max}<|F_o|$, where F_{max}=70.0 and F_{wt}=0.2, respectively. Neutral atomic scattering factors used for non-hydrogen atoms were taken from International Tables for X-Ray Crystallography[10] and for hydrogen atoms from Stewart, Davidson, and Simpson.[11] The final atomic coordinates and thermal parameters of atoms in an asymmetric unit are listed in Table 1.††††

††††A list of observed and calculated structure facotrs and anisotropic thermal parameters are kept at the Chemical Society of Japan, Document No. 8525.

TABLE 2. BOND LENGTHS AND BOND ANGLES AROUND THE ZINC ATOMS[a] WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Bond lengths[l/Å]			
Zn(1)–O(1)	2.072(4)	Zn(2)–O(1)	1.965(4)
Zn(1)–O(2)	2.075(4)	Zn(2)–O(3)	2.176(4)
Zn(1)–O(2′)	2.053(4)	Zn(2)–O(4)	2.020(4)
Zn(1)–O(3)	2.163(4)		
Zn(1)–N(1)	2.165(5)	Zn(2)–N(3)	2.047(4)
Zn(1)–N(2)	2.178(5)	Zn(2)–N(4)	2.055(5)
Bond angles[ϕ/°]			
O(1)–Zn(1)–O(2)	174.5(2)	O(1)–Zn(2)–O(3)	79.2(2)
O(1)–Zn(1)–O(3)	77.3(2)	O(1)–Zn(2)–O(4)	106.9(2)
O(1)–Zn(1)–O(2′)	105.5(2)	O(3)–Zn(2)–O(4)	173.9(2)
O(2)–Zn(1)–O(3)	107.6(2)		
O(2)–Zn(1)–O(2′)	77.0(2)		
O(1)–Zn(1)–N(1)	77.2(2)	O(1)–Zn(2)–N(3)	118.0(2)
O(1)–Zn(1)–N(2)	101.1(2)	O(1)–Zn(2)–N(4)	122.4(2)
O(2)–Zn(1)–N(1)	97.7(2)	O(3)–Zn(2)–N(3)	78.9(2)
O(2)–Zn(1)–N(2)	76.9(2)	O(3)–Zn(2)–N(4)	94.7(2)
O(3)–Zn(1)–N(2)	88.8(2)	O(4)–Zn(2)–N(3)	97.6(2)
O(3)–Zn(1)–O(2′)	93.1(2)	O(4)–Zn(2)–N(4)	82.4(3)
N(1)–Zn(1)–N(2)	90.2(2)	N(3)–Zn(2)–N(4)	116.6(2)
N(1)–Zn(1)–O(2′)	99.4(2)		
N(1)–Zn(1)–O(3)	153.8(2)		
N(2)–Zn(1)–O(2′)	153.1(2)		
Zn(1)–O(1)–Zn(2)	106.7(2)	Zn(1)–O(2)–Zn(1′)	103.1(2)
Zn(1)–O(1)–C(17)	116.4(4)	Zn(1)–O(2)–C(27)	116.5(4)
Zn(2)–O(1)–C(17)	136.1(4)	Zn(1′)–O(2)–C(27)	138.4(4)
Zn(1)–O(3)–Zn(2)	96.6(2)	Zn(2)–O(4)–C(47)	111.7(4)
Zn(1)–O(3)–C(37)	122.3(4)		
Zn(2)–O(3)–C(37)	110.7(4)		

a) List of those in quinolinolate ligands is kept at the Chemical Society of Japan, Document No. 8525.

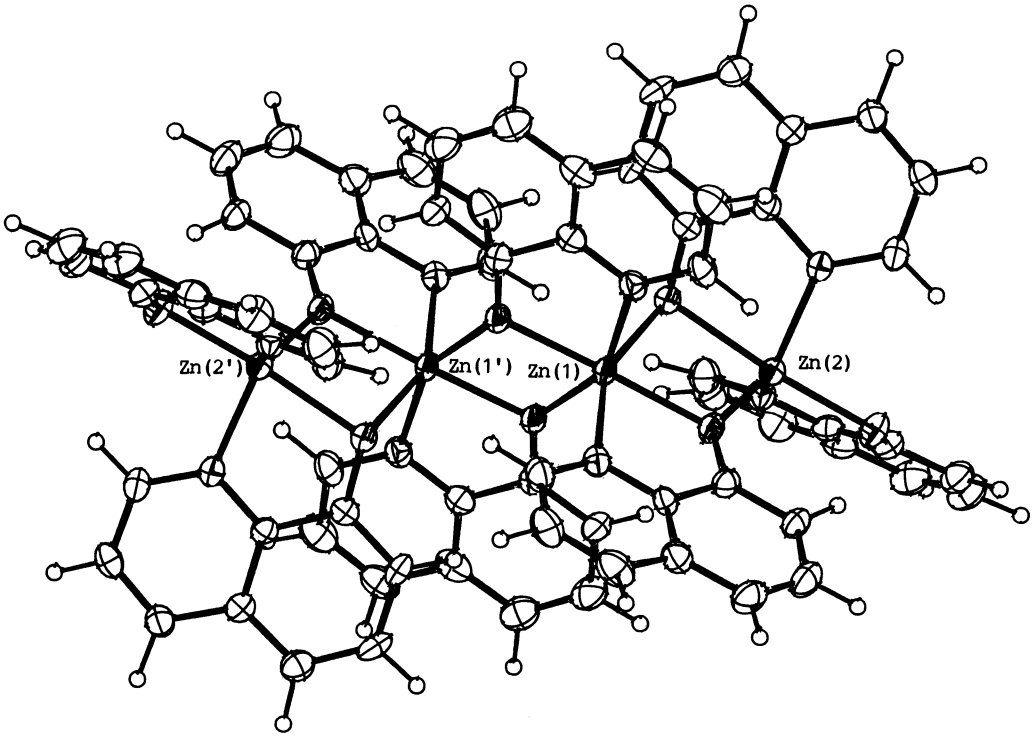
Results and Discussion

Molecular Structure. The molecular structure is shown in Fig. 1 with the numbering scheme of atoms in an asymmetric unit. The bond lengths and bond angles are listed in Table 2.

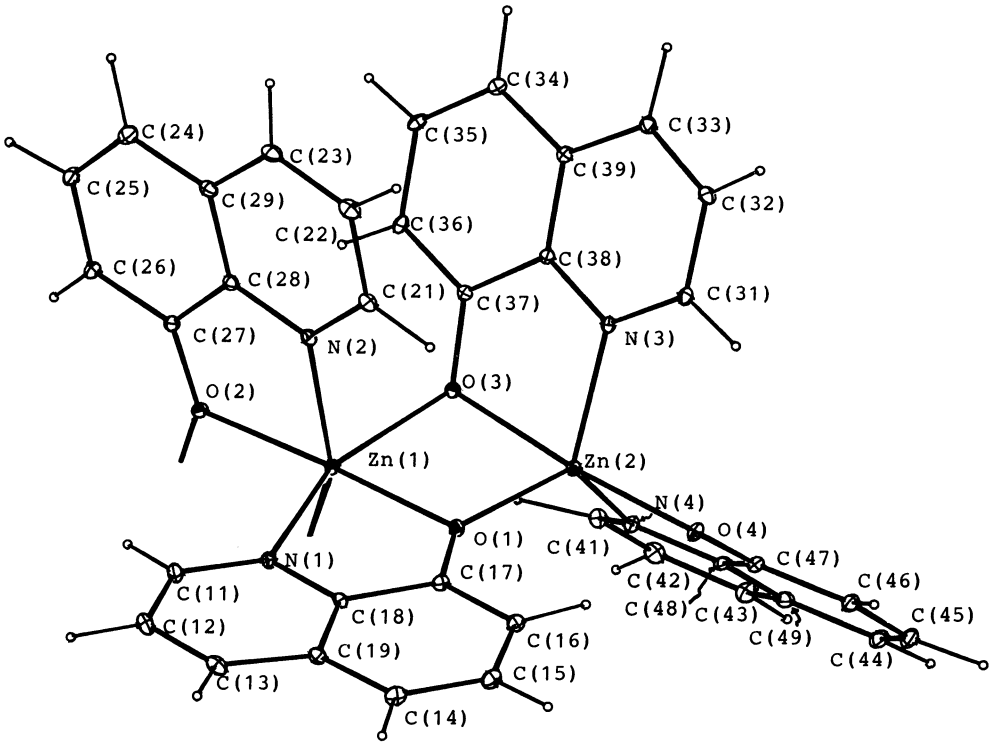
As seen in Fig. 1, two [$Zn(C_9H_6NO)_2$] units connected by two bridging oxygen atoms form an asymmetric unit. Two asymmetric units (x, y, z and $-x$, 1$-y$, $-z$) related by a center of symmetry, connected by two bridging oxygen atoms, make the whole molecule tetrameric.

Geometry Around the Zinc Atoms. Two crystallographically independent zinc atoms have different coordination geometries. The Zn(1) atom takes a hexa-coordination whereas the Zn(2) a penta-coordination.

The coordination geometry of the Zn(1) atom is octahedral but largely distorted. Bond lengths from the Zn(1) atom to the O(1), O(2), and O(2′) are equal [2.072(4), 2.075(4) and 2.053(4)Å]. These values are equal to the Zn–O bond length [2.066(15)Å] observed with the octahedrally coordinated zinc atom in the zinc 8-quinolinolate dihydrate.[6] But they are significantly shorter than the Zn(1)–O(3) length [2.163(4)Å]. Two Zn(1)–N bonds are equal in length [2.165(5) and 2.178(5) Å]. The O(1)–Zn(1)–O(2) angle is 174.5(2)°, which is close to 180°. But, the other two bond angles, N(1)–



(a)



(b)

Fig. 1. Molecular structure[13] of $[Zn(C_9H_6NO)_2]_4$.
(a) A perspective view.
Non-hydrogen atoms are drawn as thermal ellipsoids with 30% probability level and hydrogen atoms with $B=1.0$ Å^2.
(b) Numbering scheme of atoms in an asymmetric unit.

Zn(1)–O(3) [153.8(2)°] and N(2)–Zn(1)–O(2') [153.1(2)°] show large deviations from 180°. All of the other bond angles around the Zn(1) atom [between 77.0(2) and 107.6(2)°] deviate from 90°.

The geometry around the Zn(2) atom is distorted trigonal bipyramidal. The Zn(2) atom deviated by 0.20

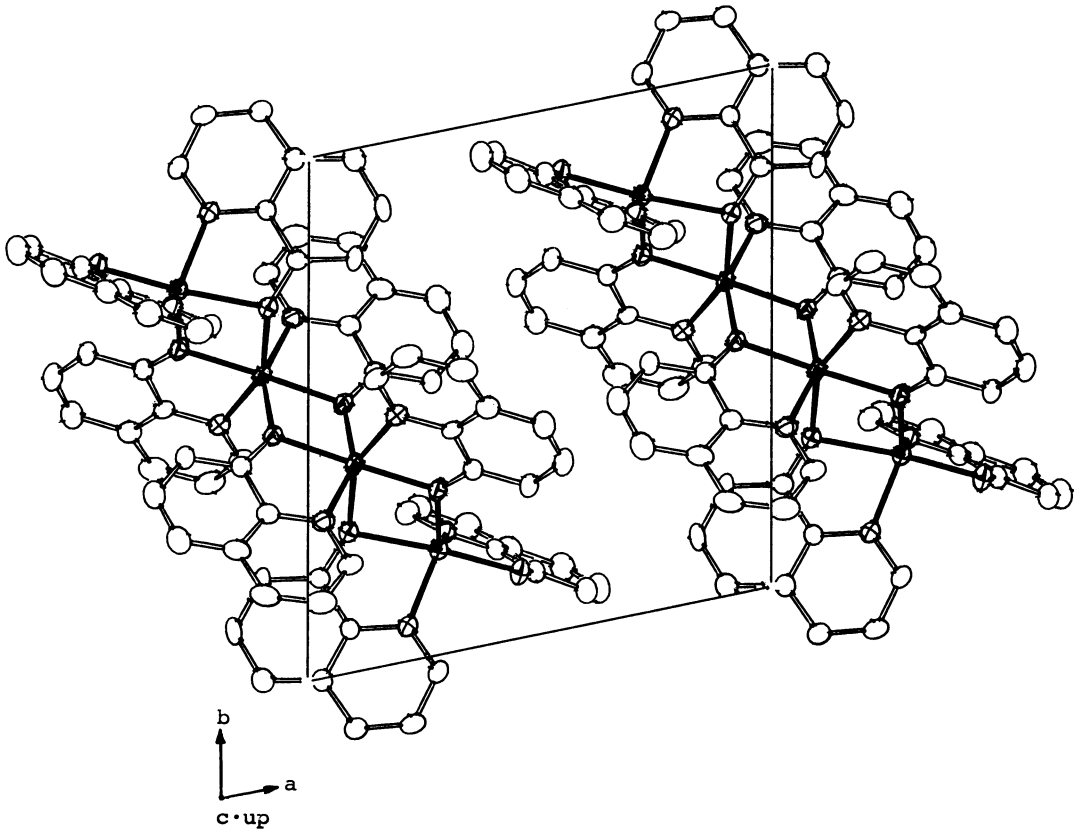


Fig. 2. Crystal structure[13] of $[Zn(C_9H_6NO)_2]_4$.
Non-hydrogen atoms are drawn as thermal ellipsoids with 30% probability level. Hydrogen atoms are omitted for clarity.

Å from the base plane defined by the O(1), N(3), and N(4) atoms. The O(3)-Zn(2)-O(4) angle is 173.9(2)°, three bond angles in the base plane are 116.6(2), 118.0(2), and 122.4(2)°, and the other angles are between 78.9(2) and 106.9(2)°. The Zn(2)-O(1) bond [1.965(4)Å] is the shortest among three Zn(2)-O bonds, and this is also the shortest Zn-O bond in the present complex. The Zn(2)-O(3) bond length [2.176(4)Å] is equal to the Zn(1)-O(3). These two are the longest Zn-O bonds and both involved with the O(3) atom. The sum of the three bond angles about the O(3) atom [329.6°] is largely deviated from 360°, whereas those about the O(1) [359.2°] and O(2) [358.0°] atoms are all equal to 360°. The Zn(2)-O(4) bond length is 2.020(4)Å, which is comparable to those of three Zn(1)-O bonds except the Zn(1)-O(3). The O(4) atom is the non-bridging oxygen atom at the apical position of the distorted trigonal bipyramid. Two Zn(2)-N bonds in the base plane [2.047(4) and 2.055(5)Å] are significantly shorter than the Zn(1)-N bonds which appeared in the geometry of the octahedrally coordinated Zn(1) atom.

Structure of the Quinolinolate Moieties. All of the corresponding bond lengths and bond angles in four quinolinolate moieties are equal within the limits of error.†††† The planarity of four quinolinolate moieties are slightly poor, they are planar within 0.08Å. These dimensions are similar to those of zinc 8-quinolinolate dihydrate[6] and β-copper 8-quinolinolate anhydride.[2]

†††† Bond lengths and bond angles in the quinolinolate moieties are also deposited at the Chemical Society of Japan, Document No. 8525.

TABLE 3. SHORT INTERMOLECULAR ATOMIC CONTACTS [*l*/Å] LESS THAN 3.6 Å WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

C(33)·····C(36)[a]	3.472(8)	key: a, $-x$, $-y$, $-z$
C(34)·····C(38)[a]	3.479(8)	b, x, y, $-1+z$
C(39)·····C(39)[a]	3.477(11)	c, $1-x$, $-y$, $1-z$
C(19)·····C(43)[b]	3.436(9)	d, $1-x$, $-y$, $-z$
C(44)·····C(44)[c]	3.399(14)	
C(44)·····C(45)[c]	3.480(10)	
C(45)·····C(49)[c]	3.538(10)	
O(4)·····C(31)[d]	3.378(7)	

Crystal Structure. Crystal structure projected along the c axis is depicted in Fig. 2. Several short interatomic contacts (less than 3.6Å) are observed (Table 3). Almost all of them are involved between carbon atoms of quinolinolate groups in adjacent molecules. The closest contact is observed between the O(4)(x, y, z) atom and C(31)($1-x$, $-y$, $-z$) [3.378(7)Å].

Calculations were mostly done on a NEAC 2200-700 computer at the Computation Center, Osaka University and at the final stage on an ACOS 850 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

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