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The Crystal and Molecular Structure of Zinc Complex of 2-Chlorobenzoic Acid. I. The Crystal and Molecular Structure of Bis(2-chlorobenzoato)zinc(II)

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The crystal of bis(2-chlorobenzoato)zinc(II) is monoclinic, space group $P2_1/c$, $a=7.284$, $b=10.480$, $c=19.091$ Å, $\beta=95.59°$, and $Z=4$. The structure was solved by usual heavy atom method and refined to the final R-value of 0.052. In the crystalline state, the complex forms a chain. Each zinc atom is bonded to four oxygen atoms from four different ligands.

Benzoic acid is able to react with metal ion to produce metal complexes in a similar way to aliphatic carboxylic acid, *e.g.*, those in copper(II) formate and copper(II) acetate. We have intended to investigate the influence of chlorine atom at ortho-position on the complex formation between zinc ion and 2-chlorobenzoate ion. Ferguson and Sim determined the crystal structure of 2-chlorobenzoic acid which consists of centrosymmetrically hydrogen-bonded dimers.[1] They found that the steric repulsion between carbonyl group and chlorine atom causes to allow the rotation of carboxyl group about the exocyclic C-C bond, and the chlorine atom and the exocyclic carbon atom are slightly displaced out of the plane of the benzene ring.

In the course of the synthesis of mefenamic acid used as an anti-inflammation drug, a derivative of anthranilic acid, we noticed that zinc complex of 2-chlorobenzoic acid crystallized in two different forms, prismatic and hexagonal pillar-shaped. One of these with a 1:2 ratio of zinc and 2-chlorobenzoic acid, was inactive for the following condensation reaction with 2,3-xylidine and only the other with a 2:3 ratio was reactive.[2] These two complexes could be separated by application of a solvent effect.

The present paper deals with the crystal structure of bis(2-chlorobenzoato)zinc(II), an inactive form of the two different complexes. We will present the structure analysis of the other form of the zinc complex in the following paper.

Experimental

Adding two-molar sodium 2-chlorobenzoate to one-molar zinc chloride in aqueous or methanol solution at room temperature, the white precipitate of zinc complex appeared after a few seconds, which was filtrated, washed several times with water and dissolved in anhydrous acetone. After a few days, transparent prismatic crystals were grown up to a proper size (0.2×0.1×0.1 mm) for X-ray investigation.

The cell dimensions were first determined from Weissenberg and precession photographs and were refined by remeasurement on a diffractometer. According to the systematic absences of reflection, $h0l$ with $l=2n+1$, and $0k0$ with $k=2n+1$, the crystal belongs to the space group of $P2_1/c$. The density was measured by flotation method in a carbon tetrachloride and ethylene dibromide mixture. The crystallographic data are listed in Table 1. The intensity data were

TABLE 1. CRYSTAL DATA OF BIS(2-CHLOROBENZOATO)ZINC
$C_{14}H_8O_4Cl_2Zn$: M.W=376.5

Crystal system: monoclinic
Cell constants: $a=7.284\pm0.005$ Å
$b=10.480\pm0.004$ Å
$c=19.091\pm0.008$ Å
$\beta=95.59\pm0.05$ °
$U=1448.05$ Å^3
Space group: $P2_1/c$
Z: 4
Density (obsd): $D_m=1.729\pm0.002$ g/cm^3
(calcd): $D_x=1.726$ g/cm^3

TABLE 2. THE FINAL FRACTIONAL COORDINATES WITH THEIR STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z	Atom	x	y	z
Zn	0.2484 (1)	0.0349 (1)	0.4869 (1)	CB2	0.7892 (11)	0.5261 (7)	0.5937 (4)
ClA	0.9250 (3)	0.0502 (2)	0.3322 (1)	CB3	0.9527 (13)	0.5796 (8)	0.6239 (5)
ClB	0.5849 (3)	0.3433 (2)	0.5281 (1)	CB4	1.1160 (11)	0.5133 (9)	0.6254 (4)
OA1	0.6340 (7)	0.0020 (5)	0.4197 (2)	CB5	1.1154 (10)	0.3922 (8)	0.5963 (4)
OA2	0.3773 (6)	0.1148 (5)	0.4142 (2)	CB6	0.9526 (9)	0.3356 (6)	0.5678 (3)
OB1	0.8399 (6)	0.1249 (4)	0.5525 (2)	CB7	0.9635 (9)	0.2030 (7)	0.5391 (3)
OB2	1.0996 (7)	0.1783 (4)	0.5068 (3)	HA1	0.898 (10)	0.196 (8)	0.217 (4)
CA1	0.7410 (9)	0.1434 (7)	0.2975 (3)	HA2	0.658 (11)	0.337 (8)	0.161 (4)
CA2	0.7730 (10)	0.2118 (8)	0.2374 (4)	HA3	0.346 (11)	0.360 (8)	0.215 (4)
CA3	0.6374 (12)	0.2852 (8)	0.2062 (4)	HA4	0.313 (9)	0.226 (7)	0.311 (3)
CA4	0.4666 (12)	0.2936 (8)	0.2316 (4)	HB1	0.655 (11)	0.579 (8)	0.600 (4)
CA5	0.4362 (10)	0.2266 (7)	0.2919 (3)	HB2	0.953 (13)	0.674 (9)	0.649 (5)
CA6	0.5719 (8)	0.1503 (6)	0.3259 (3)	HB3	1.259 (12)	0.545 (9)	0.644 (4)
CA7	0.5256 (9)	0.0830 (6)	0.3916 (3)	HB4	1.241 (11)	0.338 (8)	0.595 (4)
CB1	0.7937 (9)	0.4051 (6)	0.5667 (4)				

collected on a Rigaku-Denki four-circle diffractometer with Cu-$K\alpha$ radiation using the ω-2θ scan technique. A total of 1520 independent reflections in the range of $\sin\theta/\lambda \leq 0.53$ Å^{-1} were collected. The observed structure factors were converted into absolute values by Wilson's statistics. No absorption correction was applied.

Structure Determination and Refinement

The structure was solved by the usual heavy atom method. By successive Fourier synthesis, the positional parameters of all non-hydrogen atoms were determined (R-value, $R=\sum||F_o|-|F_c||/\sum|F_o|=0.183$). Further refinements were carried out by the block-diagonal least-squares method with isotropic temperature factors ($R=0.122$) and then anisotropic ones ($R=0.062$). A difference Fourier synthesis calculated at this stage revealed the positions of all eight hydrogen atoms with reasonable peak heights. The final refinement including the hydrogen atoms with isotropic temperature factor ($B=3.9$ Å^2) reduced the R-value to 0.052 (0.046 except $|F_o|=0$). The final atomic coordinats and temperature factors together with their estimated standard deviations are given in Table 2 and 3. The observed and calculated structure factors are listed in Table 4.3) The atomic scattering factors employed were those listed in the International Tables for X-ray Crystallography.4) All the numerical calculations were carried out on the NEAC 2200-700 in the Computation Center of Osaka University, using the UNICS programs.5)

TABLE 3. THE FINAL TEMPERATURE FACTORS AND THEIR STANDARD DEVIATIONS ($\times 10^4$)

The anisotropic temperature factors are in the form of $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	141(2)	65(1)	22(0)	27(2)	45(1)	6(1)
ClA	168(4)	163(3)	40(1)	55(6)	25(3)	19(2)
ClB	202(5)	109(2)	61(1)	67(5)	−53(3)	−21(3)
OA1	294(14)	109(6)	20(1)	89(15)	45(7)	22(5)
OA2	189(11)	124(6)	26(2)	−5(14)	74(7)	26(5)
OB1	220(12)	74(5)	33(2)	−5(13)	52(7)	−12(5)
OB2	228(13)	75(5)	35(2)	79(14)	88(8)	19(5)
CA1	167(16)	90(8)	20(2)	−10(18)	18(9)	−4(7)
CA2	225(19)	121(10)	29(3)	4(23)	73(11)	5(8)
CA3	341(24)	142(11)	24(3)	10(27)	78(12)	35(9)
CA4	325(24)	115(10)	31(3)	92(25)	30(13)	29(9)
CA5	237(18)	93(8)	21(2)	72(20)	48(10)	34(7)
CA6	153(14)	50(7)	14(2)	−20(15)	33(8)	0(5)
CA7	170(15)	74(7)	17(2)	−24(17)	3(9)	−9(6)
CB1	194(17)	56(7)	31(3)	35(18)	8(10)	−14(7)
CB2	254(20)	86(9)	39(3)	70(22)	21(12)	−21(8)
CB3	373(26)	92(10)	50(4)	−11(26)	49(16)	−52(10)
CB4	248(21)	141(11)	42(3)	−87(26)	41(13)	−45(10)
CB5	198(18)	112(10)	36(3)	6(22)	48(11)	−21(9)
CB6	183(16)	58(7)	19(2)	16(17)	29(9)	−11(6)
CB7	166(15)	92(8)	17(2)	28(18)	19(9)	13(7)

TABLE 5. THE BOND LENGTHS (Å) AND ANGLES (°), WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

From To	Length	From To	Length	From To	Length
Zn-OA1	1.940(5) Å	Zn-OA2′a)	1.939(5) Å	CA2-HA1	1.04(8) Å
Zn-OB1	1.922(5)	Zn-OB2″a)	1.912(5)	CA3-HA2	1.04(8)
ClA-CA1	1.737(7)	ClB-CB1	1.748(7)	CA4-HA3	1.14(9)
OA1-CA7	1.245(8)	OB1-CB7	1.260(8)	CA5-HA4	1.01(7)
OA2-CA7	1.247(8)	OB2-CB7	1.245(9)	CB2-HB1	1.14(8)
CA1-CA2	1.391(11)	CB1-CB2	1.372(11)	CB3-HB2	1.10(10)
CA1-CA6	1.396(9)	CB1-CB6	1.366(10)	CB4-HB3	1.12(9)
CA2-CA3	1.345(12)	CB2-CB3	1.389(12)	CB5-HB4	1.08(9)
CA3-CA4	1.380(13)	CB3-CB4	1.376(13)		
CA4-CA5	1.384(11)	CB4-CB5	1.386(12)		
CA5-CA6	1.383(9)	CB5-CB6	1.388(10)		
CA6-CA7	1.505(9)	CB6-CB7	1.499(10)		

	Angle		Angle
OA1-An-OA2′	122.8(2)°	OA1-Zn-OB1	106.6(2)°
OA1-Zn-OB2″	100.5(2)	OA2′-Zn-OB1	105.2(2)
OA2′-Zn-OB2″	97.3(2)	OB2″-Zn-OB1	126.0(2)
ClA-CA1-CA2	114.8(6)	ClB-CB1-CB2	116.7(6)
ClA-CA1-CA6	123.9(5)	ClB-CB1-CB6	120.7(5)
CA2-CA1-CA6	121.3(6)	CB2-CB1-CB6	122.5(7)
CA1-CA2-CA3	119.0(7)	CB1-CB2-CB3	118.6(7)
CA2-CA3-CA4	122.0(8)	CB2-CB3-CB4	120.6(8)
CA3-CA4-CA5	118.8(8)	CB3-CB4-CB5	119.0(8)
CA4-CA5-CA6	121.3(7)	CB4-CB5-CB6	121.1(7)
CA1-CA6-CA5	117.6(6)	CB1-CB6-CB5	118.0(6)
CA1-CA6-CA7	125.3(6)	CB1-CB6-CB7	124.2(6)
CA5-CA6-CA7	117.1(6)	CB5-CB6-CB7	117.7(6)
OA1-CA7-OA2	124.5(6)	OB1-CB7-OB2	125.7(6)
OA1-CA7-CA6	119.6(6)	OB1-CB7-CB6	117.6(6)
OA2-CA7-CA6	115.8(6)	OB2-CB7-CB6	116.5(6)

The bond angles involving the hydrogen atoms were all nearly 120±9° (E.S.D≅5°)

a) The coordinates of the single and double primed atoms are obtained by the translational operations of $(1-x, -y, 1-z)$ and $(2-x, -y, 1-z)$ from that of original atoms (x,y,z).

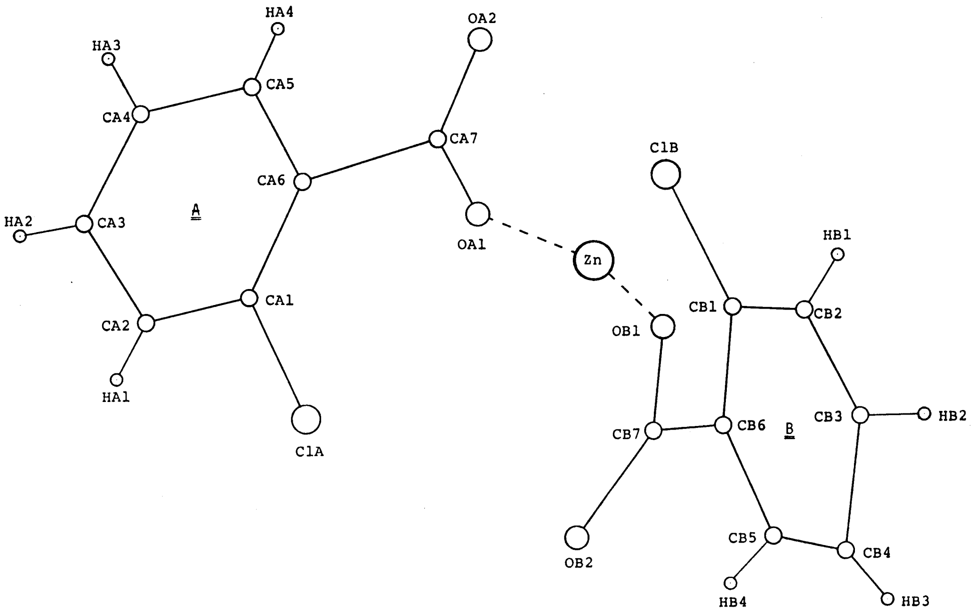

Fig. 1. The atomic numbering scheme of bis(2-chlorobenzoato)zinc(II).

Results and Discussion

The numbering of each atom is represented in Fig. 1. The bond lengths and angles are listed in Table 5, which indicate no significant differences between two independent benzoate ligands. Two C–O bond lengths in carboxyl group range from 1.24 to 1.26 Å which represent the double-bond character, while C_6–C_7 bonds (1.499 and 1.505 Å) are almost pure single-bond which allows the rotation of carboxyl group. The torsion angles between the plane of carboxyl group and that of benzene ring are 9° for ligand A and 41° for ligand B. Such twisting between carboxyl group and the benzene ring plane was also found in the crystal structure of 2-chlorobenzoic acid (14°)[1] and 2-chloro-5-nitrobenzoic acid (23°).[6]

The four carboxyl oxygen atoms coordinate tetrahedrally to each zinc atom as shown in Fig. 2. It is

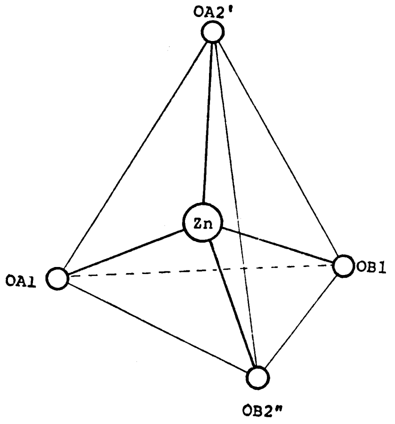

Fig. 2. The coordination of zinc atom.
About the single and double primed atoms, refer to the footnote in Table 5.

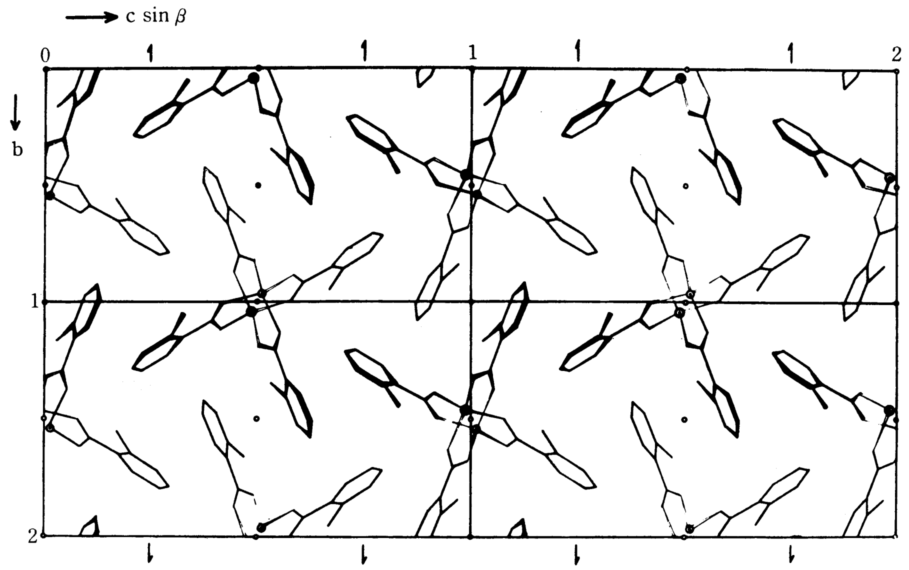

Fig. 3a. The view of the structure looking down the a-axis.

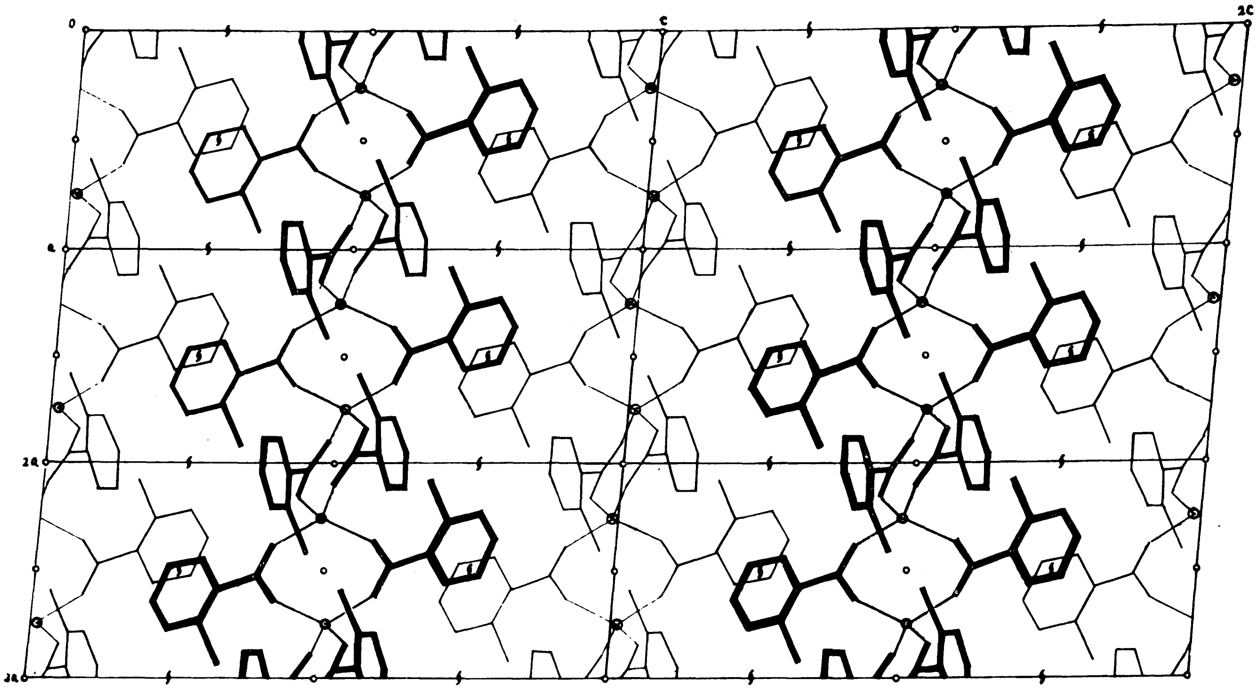

Fig. 3b. The view of the structure looking down the b-axis.

very interesting that four coordinated carboxyl oxygen atoms consist of O_1 of A and B, and O_2 of next neighboring A and B. That is to say, carboxyl oxygen atoms (O_1 and O_2) connect two adjacent zinc atoms to form the infinite chain extending in the direction of the a-axis. The stable coordination number of zinc atom is usually four or six; the former is found in zinc oxyacetate,[7] zinc salicylate dihydrate,[8] di(L-histidino)zinc dihydrate,[9] di(histidino)zinc pentahydrate[10] and the latter in zinc acetate dihydrate,[11] zinc 8-hydroxyquinolate dihydrate.[12] In this crystal, four oxygen atoms coordinate tetrahedrally to the central zinc atom and this sort of coordination may be more stable than that of the pentaligand zinc complex described in the following paper. The arrangements of molecules in the a- and b-axes projections are shown in Fig. 3(a) and 3(b), respectively. Looking down through the a-axis, the plane of each benzene ring sticks out with rotation angle of about 90°. The orientations of the ligands within two chains related by c-glide plane differ by 45° around the a-axis, and therefore, the arrangement of the infinite chains in the [011] direction looks like +×+×+×········· when viewed along the a-axis. Each chain contacts with normal van der Waals distances.

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