The Crystal and Molecular Structure of Zinc Complex of 2-Chlorobenzoic Acid. II. The Crystal and Molecular Structure of μ_3-Hydroxo-tri-μ-(2-chlorobenzoato)dizinc(II) Dihydrate

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$C_{21}H_{12}O_6Cl_3Zn_2OH \cdot 2H_2O$ crystallizes in the monoclinic space group $P2_1/c$: $a = 12.779$, $b = 23.732$, $c = 14.749$ Å, $\beta = 147.98°$, and $Z = 4$. The structure was determined by the usual heavy atom method and refined to $R = 0.039$. The complex forms polymeric complex chains in the crystalline state. The ligands around two independent zinc atoms form an unusual trigonal bipyramid and an octahedron, respectively; the coordination geometry apparently differs from that found in the crystal structure of bis(2-chlorobenzoato) zinc(II). The correlation between coordination geometry and catalytic action of zinc atom is also discussed.

Two different forms of zinc complex of 2-chlorobenzoic acid were found.[1] In this paper, we report the detailed crystal and molecular structure of the second crystal, a reactive form, as regards the coordination around central zinc atom differing from that in the first crystal, an inactive form. From the results, a mechanism for complex formation and catalytic reactivity of zinc atom is discussed.

Experimental

The complex was prepared by mixing three-molar sodium 2-chlorobenzoate and two-molar zinc chloride in aqueous or acetone-aqueous solution at room temperature. By recrystallization from a mixed solvent of acetone and water 9: 1 ratio, a hexagonal pillar-shaped single crystal was obtained, which was cut to approximately $0.12 \times 0.11 \times 0.55$ mm for X-ray study. The density was measured by the flotation method in a carbon tetrachloride and ethylene dibromide mixture. The cell dimensions were obtained on a Rigaku-Denki four-circle diffractometer with Cu*Kα* radiation (Table 1). From the systematic absence of reflections ($h0l$: $l = 2n+1$, $0k0$: $k = 2n+1$), the space group was determined to be $P2_1/c$. The intensity data were collected on the diffractometer with Cu*Kα* radiation

TABLE 1. CRYSTAL DATA OF μ_3-HYDROXO-TRI-μ-(2-CHLOROBENZOATO)DIZINC DIHYDRATE
$C_{21}H_{17}O_9Cl_3Zn_2$: M.W. = 650.5

Crystal system:	monoclinic
Cell constants:	$a = 12.779 \pm 0.004$ Å
	$b = 23.732 \pm 0.006$ Å
	$c = 14.749 \pm 0.006$ Å
	$\beta = 147.98 \pm 0.04°$
	$U = 2371.40$ Å^3
Space group:	$P2_1/c$
Z :	4
Density (obsd):	$D_m = 1.825 \pm 0.002$ g/cm^3
(calcd):	$D_x = 1.830$ g/cm^3

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

Atom	*x*	*y*	*z*
Zn 1	0.0724(1)	0.0610(0)	0.0472(1)
Zn 2	0.5506(1)	0.0217(0)	0.6373(1)
ClA	0.3172(3)	0.2286(1)	0.3674(3)
ClB	0.8671(3)	0.0597(1)	0.4674(2)
ClC	0.2814(3)	0.1599(1)	0.6225(3)
O A1	0.2949(6)	0.1155(2)	0.2583(5)
O A2	0.5078(6)	0.0550(2)	0.4755(5)
O B1	0.4845(7)	0.0162(2)	0.2671(6)
O B2	0.2029(6)	0.0651(2)	0.0293(5)
O C1	0.5524(6)	0.1010(2)	0.6874(5)
O C2	0.8741(6)	0.1110(2)	0.9654(5)
OW1	0.2178(6)	0.0219(2)	0.4091(5)
OW2	0.1497(6)	−0.0091(2)	0.1689(5)
OW3	0.0486(8)	0.1240(2)	0.2614(7)
C A1	0.5623(10)	0.2064(3)	0.5179(8)
C A2	0.7147(12)	0.2483(3)	0.6269(10)
C A3	0.9121(12)	0.2338(3)	0.7513(10)
C A4	0.9661(11)	0.1781(3)	0.7774(10)
C A5	0.8135(10)	0.1374(3)	0.6682(9)
C A6	0.6105(9)	0.1505(3)	0.5355(8)
C A7	0.4555(9)	0.1045(2)	0.4122(8)
C B1	0.6834(10)	0.0648(3)	0.2517(8)
C B2	0.7565(11)	0.0778(3)	0,2233(10)
C B3	0.6214(13)	0.0839(4)	0.0572(12)
C B4	0.4148(12)	0.0775(4)	−0.0777(10)
C B5	0.3453(11)	0.0658(3)	−0.0438(9)
C B6	0.4770(10)	0.0585(3)	0.1207(8)
C B7	0.3825(10)	0.0455(3)	0.1409(8)
C C1	0.4718(10)	0.2065(3)	0.7276(8)
C C2	0.4431(12)	0.2648(3)	0.7239(10)
C C3	0.5971(13)	0.3021(3)	0.8103(10)
C C4	0.7669(14)	0.2849(2)	0.9014(12)
C C5	0.8023(11)	0.2276(3)	0.9103(10)
C C6	0.6506(9)	0.1879(3)	0.8194(8)
C C7	0.6924(10)	0.1285(3)	0.8216(8)
H A1	0.686 (12)	0.288 (4)	0.622 (11)
H A2	1.052 (11)	0.264 (3)	0.860 (10)
H A3	1.126 (12)	0.168 (3)	0.881 (10)
H A4	0.844 (11)	0.102 (3)	0.668 (9)
H B1	0.920 (10)	0.085 (3)	0.334 (9)
H B2	0.654 (12)	0.099 (3)	0.016 (10)
H B3	0.314 (12)	0.082 (3)	−0.202 (10)
H B4	0.207 (11)	0.056 (3)	−0.124 (9)
H C1	0.307 (12)	0.280 (3)	0.654 (10)
H C2	0.584 (13)	0.348 (4)	0.823 (12)
H C3	0.876 (14)	0.316 (4)	0.963 (12)
H C4	0.919 (11)	0.219 (3)	0.979 (10)
HW1	0.171 (11)	0.047 (3)	0.377 (10)
HW2	0.167 (12)	−0.012 (4)	0.235 (11)
HW3	0.044 (13)	0.126 (4)	0.216 (11)

using the ω-2θ scan technique. A total of 2472 independent reflections were collected in the range $\sin\theta/\lambda \leqq 0.55$ Å^{-1}. A Wilson plot was then made to place the observed intensities on an absolute scale. No correction was made for absorption.

Structure Determination and Refinement

The structure was solved by application of the usual heavy atom method. Except for three water molecules, all the positions of thirty-two nonhydrogen atoms were determined by the first Fourier synthesis with phases based on zinc and chlorine atoms. The coordinates of oxygen atoms in three water molecules were then found (R=0.26). After several cycles of block-diagonal least-squares refinement, a difference Fourier synthesis was carried out in order to determine the location of hydrogen atoms. Twelve hydrogen atoms bound to carbon atoms and three hydrogen atoms (HW1, HW2, and HW3, see Fig. 1) attached to water molecules were satisfactorily located at proper positions with reasonable peak heights. Only one hydrogen atom peak was found around the water oxygen atom OW2, almost on the line connecting OW1 and OW2 to form a hydrogen bond. However, the positions of the remaining two hydrogen atoms bound to the oxygen atoms (OW1 and OW3) were obscure, and were omitted in further refinement. The final least-squares refinement including fifteen hydrogen atoms with isotropic temperature factors (B=2.0~7.0 Å^2) reduced the R-value to 0.041. The final atomic parameters with their estimated standard deviations except those for the two undetectable hydrogen atoms are given in Tables 2 and 3. The observed and calculated structure factors are listed in Table 4.[2] The atomic scattering factors and all the numerical calculation procedures were the same as given previously.[1]

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 1	107(2)	6(0)	81(1)	0(1)	148(3)	0(1)
Zn 2	113(2)	7(0)	76(1)	0(1)	147(3)	1(1)
ClA	270(6)	10(0)	222(4)	15(2)	411(9)	2(2)
ClB	161(5)	24(0)	129(3)	−12(2)	220(8)	1(2)
ClC	194(5)	22(0)	196(4)	6(2)	333(9)	2(2)
O A1	119(11)	7(1)	70(7)	−3(5)	122(17)	2(4)
O A2	153(11)	6(1)	73(7)	−8(5)	178(17)	−5(4)
O B1	193(13)	15(1)	148(9)	16(6)	301(21)	25(5)
O B2	114(11)	16(1)	94(8)	11(5)	167(18)	17(5)
O C1	182(12)	7(1)	104(8)	3(5)	255(19)	−10(4)
O C2	144(12)	12(1)	107(9)	30(5)	181(19)	−1(5)
OW1	142(12)	13(1)	104(8)	8(5)	191(18)	4(5)
OW2	110(10)	7(1)	55(7)	−4(4)	123(16)	0(4)
OW3	289(16)	18(1)	216(11)	27(7)	457(25)	22(6)
C A1	196(19)	11(1)	106(13)	−13(8)	237(30)	−7(7)
C A2	321(25)	9(1)	168(16)	−40(10)	387(38)	−22(8)
C A3	236(23)	15(2)	140(15)	64(10)	264(35)	−34(8)
C A4	183(21)	16(2)	143(15)	−39(10)	228(33)	−15(8)
C A5	160(19)	12(1)	120(13)	−18(8)	211(30)	−6(7)
C A6	142(17)	8(1)	92(12)	−16(7)	191(27)	−6(6)
C A7	144(17)	7(1)	107(12)	−7(7)	216(27)	−7(6)
C B1	153(18)	13(1)	106(13)	0(8)	216(28)	−2(7)
C B2	209(21)	19(2)	180(16)	−17(10)	348(35)	−10(8)
C B3	354(28)	22(2)	291(21)	−21(12)	601(47)	−3(10)
C B4	268(24)	30(2)	180(17)	−13(12)	391(38)	8(10)
C B5	203(20)	21(2)	148(15)	−18(10)	308(33)	−2(8)
C B6	176(18)	10(1)	111(12)	0(8)	249(28)	0(7)
C B7	178(18)	9(1)	114(13)	−27(8)	250(29)	−18(6)
C C1	175(19)	11(1)	110(13)	25(8)	233(29)	11(7)
C C2	271(24)	21(2)	158(15)	59(11)	366(37)	31(9)
C C3	350(27)	10(2)	210(18)	21(10)	472(41)	9(8)
C C4	374(29)	11(2)	272(21)	−13(11)	550(46)	−19(9)
C C5	227(22)	12(2)	188(16)	−1(9)	348(36)	−11(8)
C C6	147(17)	9(1)	93(12)	10(7)	191(27)	2(6)
C C7	172(18)	8(1)	132(13)	8(8)	270(29)	2(7)

Results and Discussion

Numbering of molecule is made by use of two letters and two numbers. The first letter corresponds to the kind of atom, and the second to one of the three independent 2-chlorobenzoic acid ligands (A, B and C) or water molecule (W). The first number corresponds to the

TABLE 5. BONDLENGTHS WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

(a) Zn–O lengths

From To	Unit$^{a)}$	Length	From To	Unit$^{a)}$	Length
Zn1–O A1	1	2.110(9) Å	Zn2–O A2	1	2.113(9) Å
Zn1–O B1	1	1.998(9)	Zn2–O A2	2	2.138(9)
Zn1–O C2	3	2.013(10)	Zn2–O B2	2	2·007(10)
Zn1–O W2	1	1.986(8)	Zn2–O C1	1	2.011(10)
Zn1–O W2	4	2.093(8)	Zn2–O W1	1	2.266(9)
			Zn2–O W2	2	2.101(8)

(b) Other lengths

From To	Length	From To	Length
Cl A–C A1	1.793(14) Å	C lB–C B1	1.727(13) Å
O A1–C A7	1.238(14)	O B1–C B7	1.238(15)
O A2–C A7	1.279(14)	O B2–C B7	1.283(14)
C A1–C A2	1.427(20)	C B1–C B2	1.343(19)
C A1–C A6	1.400(18)	C B1–C B6	1.439(17)
C A2–C A3	1.414(22)	C B2–C B3	1.353(22)
C A3–C A4	1.384(21)	C B3–C B4	1.428(23)
C A4–C A5	1.416(19)	C B4–C B5	1.367(21)
C A5–C A6	1.430(17)	C B5–C B6	1.352(19)
C A6–C A7	1.521(17)	C B6–C B7	1.500(17)
C A2–H A1	1.01 (16)	C B2–H B1	1.13 (13)
C A3–H A2	1.19 (15)	C B3–H B2	1.04 (15)
C A4–H A3	1.13 (15)	C B4–H B3	1.02 (15)
C A5–H A4	0.91 (14)	C B5–H B4	1.01 (13)
OW1–HW1	0.68 (14)	OW2–HW2	0.81 (16)
Cl C–C C1	1.775(13)	C C5–C C6	1.426(19)
O C1–C C7	1.240(15)	C C6–C C7	1.498(17)
O C2–C C7	1.308(15)	C C2–H C1	1.08 (13)
C C1–C C2	1.420(20)	C C3–H C2	1.14 (17)
C C1–C C6	1.414(17)	C C4–H C3	1.08 (18)
C C2–C C3	1.380(22)	C C5–H C4	0.86 (14)
C C3–C C4	1.375(24)	OW3–HW3	0.63 (16)
C C4–C C5	1.405(23)		

a) *cf.* Unit No. in Table 7.

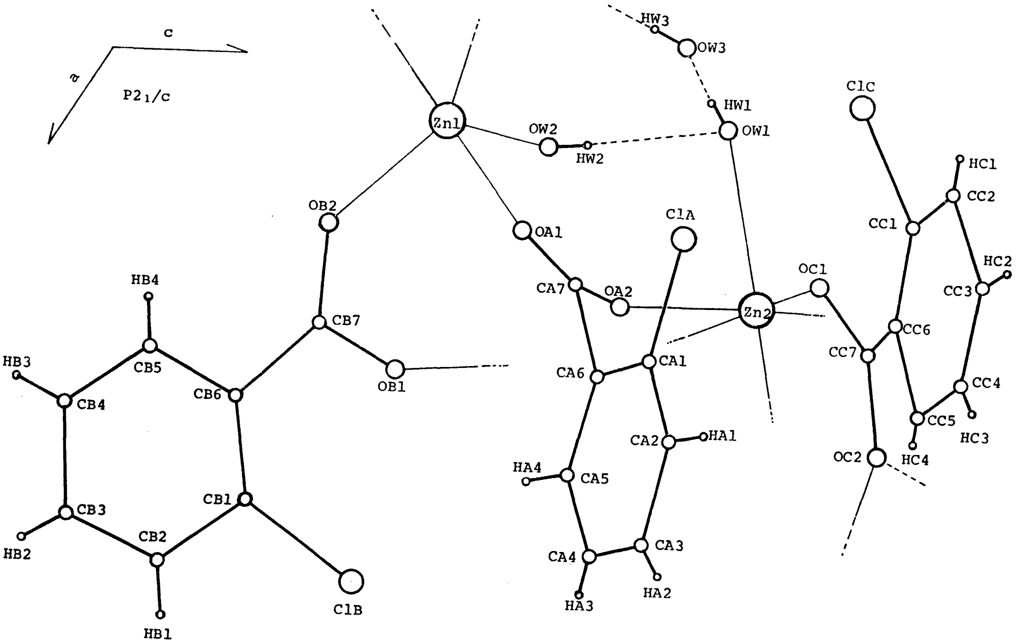

Fig. 1. Schematic drawing around two kinds of zinc ions.

TABLE 6. BOND ANGLES WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES.

	Angle		Angle		Angle
ClA–CA1–CA2	118.5(10)°	ClB–CB1–CB2	111.9(10)°	ClC–CC1–CC2	117.1(10)°
ClA–CA1–CA6	122.5(10)	ClB–CB1–CB6	123.1(9)	ClC–CC1–CC6	123.1(10)
CA2–CA1–CA6	119.0(12)	CB2–CB1–CB6	125.0(12)	CC2–CC1–CC6	119.7(12)
CA1–CA2–CA3	121.5(14)	CB1–CB2–CB3	115.6(14)	CC1–CC2–CC3	118.8(14)
CA2–CA3–CA4	120.9(14)	CB2–CB3–CB4	121.6(15)	CC2–CC3–CC4	122.5(15)
CA3–CA4–CA5	117.0(13)	CB3–CB4–CB5	121.2(14)	CC3–CC4–CC5	120.5(15)
CA4–CA5–CA6	124.0(12)	CB4–CB5–CB6	118.5(13)	CC4–CC5–CC6	118.6(13)
CA1–CA6–CA5	117.6(11)	CB1–CB6–CB5	118.0(12)	CC1–CC6–CC5	119.9(11)
CA1–CA6–CA7	122.8(11)	CB1–CB6–CB7	128.6(11)	CC1–CC6–CC7	124.8(11)
CA5–CA6–CA7	119.4(10)	CB5–CB6–CB7	113.4(11)	CC5–CC6–CC7	115.2(11)
OA1–CA7–OA2	124.0(11)	OB1–CB7–OB2	127.1(11)	OC1–CC7–OC2	126.6(11)
OA1–CA7–CA6	119.6(10)	OB1–CB7–CB6	114.5(11)	OC1–CC7–CC6	117.0(11)
OA2–CA7–CA6	116.2(10)	OB2–CB7–CB6	118.4(10)	OC2–CC7–CC6	116.4(10)
CA1–CA2–HA1	121(9)	CB1–CB2–HB1	120(7)	CC1–CC2–HC1	121(9)
CA3–CA2–HA1	118(9)	CB3–CB2–HB1	124(7)	CC3–CC2–HC1	120(9)
CA2–CA3–HA2	126(7)	CB2–CB3–HB2	124(8)	CC2–CC3–HC2	122(9)
CA4–CA3–HA2	112(7)	CB4–CB3–HB2	114(8)	CC4–CC3–HC2	115(9)
CA3–CA4–HA3	118(8)	CB3–CB4–HB3	120(9)	CC3–CC4–HC3	119(9)
CA5–CA4–HA3	125(8)	CB5–CB4–HB3	118(9)	CC5–CC4–HC3	120(9)
CA4–CA5–HA4	116(9)	CB4–CB5–HB4	130(8)	CC4–CC5–HC4	116(10)
CA6–CA5–HA4	118(9)	CB6–CB5–HB4	111(8)	CC6–CC5–HC4	125(10)

individual atom number in a ligand and the second one to the unit number (Table 7), those corresponding to unit No. 1 being omitted (Fig. 1).

The bond lengths and angles are listed in Tables 5 and 6 with their estimated standard deviations. Two of the exocyclic bond angles increase from the normal value of 120° to 122.5° and 122.8° for A, to 123.1° and 128.6° for B, and to 123.1° and 124.8° for C. This might be due to repulsion between the adjacent chlorine atom and carboxyl group. The dihedral angles between carboxyl plane and benzene-ring plane in three independent 2-chlorobenzoic acid ligands are 35° for A, 30° for B and 35° for C, whereas the values in bis(2-chlorobenzoato)zinc(II) are 9° and 41°,[1] and 23° in 2-chloro-5-nitrobenzoic acid.[3]

The coordination geometry around two independent zinc atoms is of interest. Zn1 is surrounded by five ligands to form a distorted trigonal bipyramid, and Zn2 by six ligands to form a distorted octahedron (Fig. 2 and Table 7). Zn1 shifts by 0.015 Å toward OA1 from the trigonal plane formed by OC2, OB1 and OW2, and the directions of two bonds, Zn1–OW2-4 and Zn1–OA1, deviate by 9.2° and 6.6° from the normal to the trigonal plane, respectively. Similarly, the bonds, Zn2–OW1

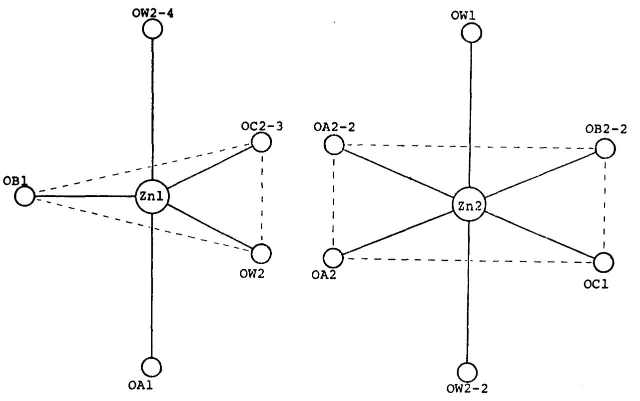

Fig. 2. The coordinations of zinc atoms.

TABLE 7. BOND ANGLES AROUND TWO INDEPENDENT ZINC ATOMS

Atom Unit Atom Unit	Angle
O B1 1–Zn1–O W2 4	91.6(3)°
O W2 4–Zn1–O C2 3	92.8(4)
O C2 3–Zn1–O W2 1	116.8(4)
O B1 1–Zn1–O C2 3	133.4(4)
O W2 4–Zn1–O W2 1	83.0(3)
O A1 1–Zn1–O C2 3	88.0(4)
O A1 1–Zn1–O W2 4	176.8(3)
O B1 1–Zn1–O W2 1	109.6(4)
O A1 1–Zn1–O B1 1	85.7(4)
O A1 1–Zn1–O W2 1	99.4(3)
O W1 1–Zn2–O W2 2	170.5(3)
O W1 1–Zn2–O A2 2	82.8(3)
O W1 1–Zn2–O B2 2	78.2(4)
O W1 1–Zn2–O A2 1	87.8(3)
O W1 1–Zn2–O C1 1	88.3(4)
O W2 2–Zn2–O A2 2	87.7(3)
O W2 2–Zn2–O B2 2	102.5(4)
O W2 2–Zn2–O C1 1	101.1(4)
O W2 2–Zn2–O A2 1	90.5(3)
O C1 1–Zn2–O B2 2	96.3(4)
O C1 1–Zn2–O A2 1	88.3(4)
O A2 2–Zn2–O A2 1	81.5(3)
O A2 2–Zn2–O B2 2	91.5(4)

The coordinates of Zn1 and Zn2 are those belongoing to unit No. 1

Unit No. 1	($0.0+x$, $0.0+y$, $0.0+z$)
Unit No. 2	($1.0-x$, $0.0-y$, $1.0-z$)
Unit No. 3	($-1.0+x$, $0.0+y$, $-1.0+z$)
Unit No. 4	($0.0-x$, $0.0-y$, $0.0-z$)

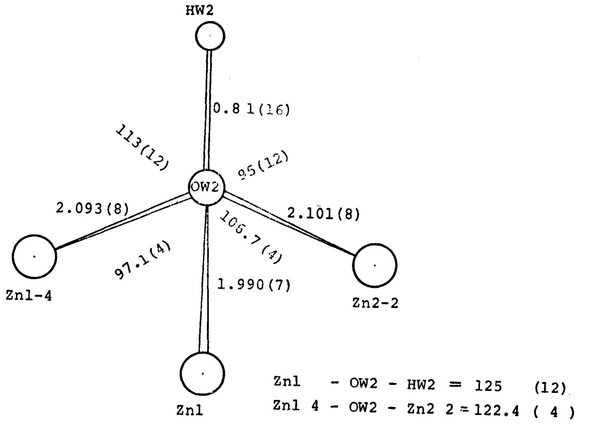

Fig. 3. The coordination of the hydroxyl oxygen atom. Bond distances are in Å and angles are in degree.

and Zn2-OW2-2, deviate by 5.5° and 8.8° from the least-squares plane consisting of OA2, OA2-2, OB2-2, and OC1. These unusual coordinations, especially a distorted trigonal bipyramidal coordination, which is probably the first case in zinc complexes,** might give important information on catalytic function of the zinc atom. The interatomic distances between adjacent zinc atoms are 3.06 Å for Zn1 to Zn1-4, 3.22 Å for Zn2 to Zn2-2, and 3.28 Å for Zn1 to Zn2-2. The values are much smaller than those in bis(2-chlorobenzoato)-zinc(II), 3.77 Å.[1] From density measurement, it seems that three water molecules are involved in an asymmetric unit. However, the difference Fourier map indicates that one of these water molecules should be of anionic form, OH^-, that is, only one peak for hydrogen atom around OW2 was found. This is reasonable for the balance of charge in crystal, provided that four units of positive charge are supplied by $2Zn^{2+}$ and four units of negative charge by three $C_6H_4ClCOO^-$ and one OH^- ions. This was confirmed by counting the number of OH-proton in NMR spectra. As shown in Fig. 3, OW2 coordinates to three neighboring zinc atoms, Zn1, Zn1-4 and Zn2-2, and the OH^- (*i.e.*, OW2-HW2) bond directs to one remaining apex of tetrahedron to form a hydrogen bond with OW1 (2.94 Å). Two water molecules participate in hydrogen bonding of OW1-HW1···OW3 (2.70 Å) and OW3-HW3···OC2 (2.77 Å), but the remaining two hydrogen atoms bound to OW1 and OW3 do not take part in hydrogen-bond formation, their positions being obscure. The molecular arrangements projected along the a- and b-axes are given in Figs. 4(a) and 4(b), respectively. They show the formation of a complicated infinite chain through coordinations and hydrogen bonds.

In comparison with the coordination geometry around two independent zinc atoms, the infrared spectra reported previously and herewith were measured by KBr disk technique. As in the case of metal complex of acetic acid, the zinc complex of 2-chlorobenzoic acid has characteristic strong absorption bands associated with the stretching of carboxyl group; for this complex, the bands appear at 1610 cm^{-1} and 1545 cm^{-1} for ν_{as} (OCO), and 1410 cm^{-1} and 1375 cm^{-1} for ν_s(OCO), while the corresponding bands of bis(2-chlorobenzoato)-zinc(II) appear at 1540 cm^{-1} for ν_{as}(OCO) and at 1410 cm^{-1} for ν_s(OCO). The splitting of bands in this complex supports the X-ray evidence of the antisymmetrical chelation around two independent zinc atoms, Zn1 and Zn2.

The difference in the coordination geometry of the two zinc complexes of 2-chlorobenzoic acid described in the present and previous papers might be strongly

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** M. Bonamico *et al.* report that the coordination geometry around the zinc atom is considered to be a distorted trigonal bipyramidal in the crystal structure of zinc diethyldithiocarbamate.[4]

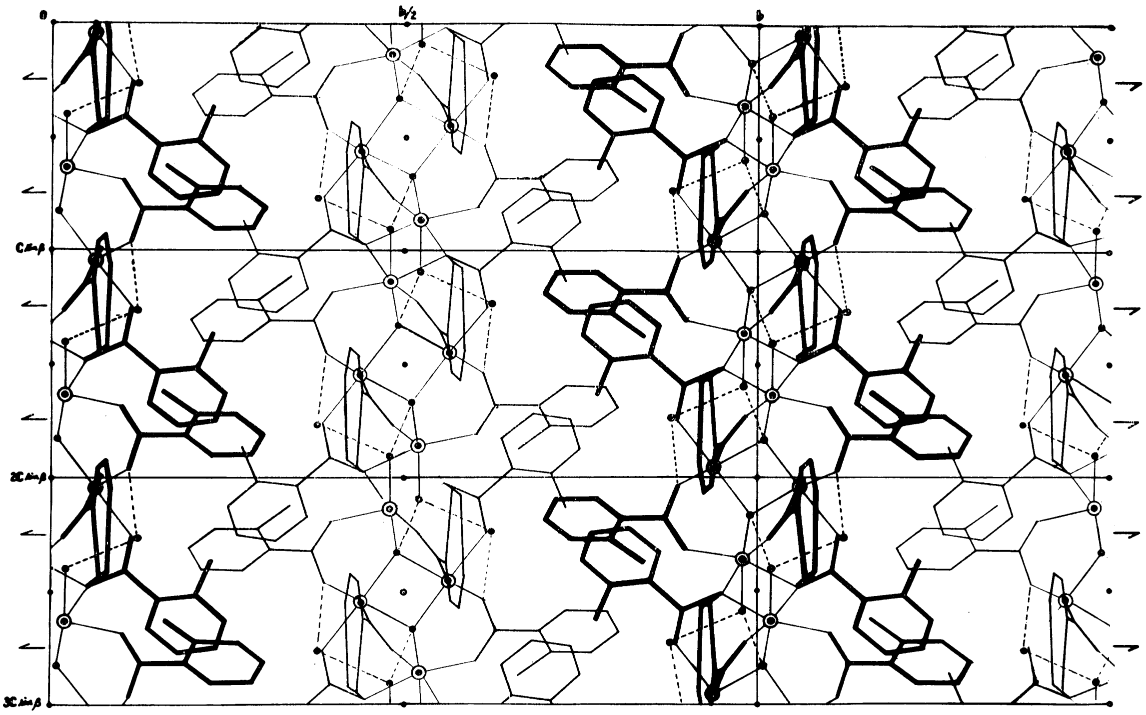

Fig. 4(a). The view of the structure looking down the a-axis.

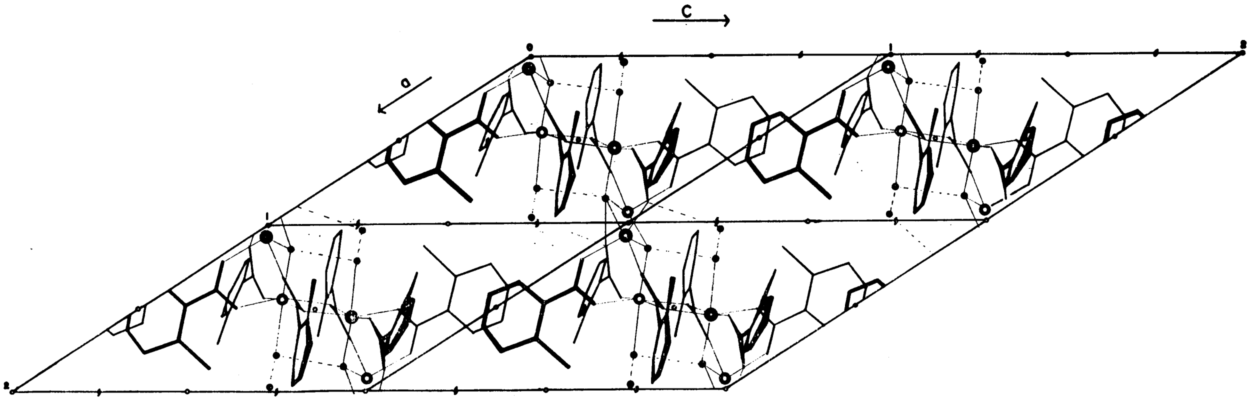

Fig. 4(b). The view of the structure looking down the b-axis.

correlated with the difference in their catalytic actions, *i.e.*, the former is active but the latter is inactive for the following condensation reaction with 2,3-xylidine. The distorted trigonal bipramidal coordination around the zinc atom found in this crystal is probably the first example as a zinc complex so far determined by the X-ray method. By the difference thermal analysis, it was confirmed that two water molecules disappeared at 60—70 °C and 140 °C, respectively, but the remaining OH^- ion was tightly bound to zinc atoms even at the condensation reaction temperature, 170—180 °C (Fig. 3). The overall coordination geometry might be retained at the condensation reaction except two water molecules. At the first step of the condensation reaction, it seems that a reactive group, the amino group of 2,3-xylidine, is fixed by coordination to the zinc atom, and the other reactive atom, the chlorine atom attached at C-2 position of benzoic acid, adjoins the amino group as much as possible. Let us suppose that the amino-nitogen of 2,3-xylidine coordinates to Zn2 in place of OW1 on addition of 2,3-xylidine to the non-aqueous solution of this complex. The nearest chlorine atom to OW1 is ClB-2 in the molecule B of 2-chlorobenzoic acid coordinated to Zn1-2 with a distance of 3.42 Å. The reaction mechanism is still obscure, but probably these amino groups and the chlorine atom react to synthesize mefenamic acid.

References

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