

Table 3. Lengths (Å) and angles (°) between Na and O neighbouring atoms

Na...O(1)	2.399 (2)	Na...O(4) <sup>m</sup>	2.384 (2)
Na...O(4)	2.474 (2)	Na...O(1) <sup>m</sup>	2.663 (2)
Na...O(2) <sup>y</sup>	2.472 (2)	Na...O(2) <sup>y</sup>	2.469 (1)
O(1)...Na...O(4)	83.7 (1)	O(4)...Na...O(2) <sup>y</sup>	83.5 (1)
O(1)...Na...O(2) <sup>y</sup>	107.5 (1)	O(2) <sup>y</sup> ...Na...O(4) <sup>m</sup>	88.7 (1)
O(1)...Na...O(4) <sup>m</sup>	160.5 (1)	O(2) <sup>y</sup> ...Na...O(1) <sup>m</sup>	74.6 (1)
O(1)...Na...O(1) <sup>m</sup>	117.9 (1)	O(2) <sup>y</sup> ...Na...O(2) <sup>y</sup>	121.3 (1)
O(1)...Na...O(2) <sup>y</sup>	79.0 (1)	O(4) <sup>m</sup> ...Na...O(1) <sup>m</sup>	76.2 (1)
O(4)...Na...O(2) <sup>y</sup>	153.9 (1)	O(4) <sup>m</sup> ...Na...O(2) <sup>y</sup>	83.4 (1)
O(4)...Na...O(4) <sup>m</sup>	86.1 (1)	O(1) <sup>m</sup> ...Na...O(2) <sup>y</sup>	154.0 (1)
O(4)...Na...O(1) <sup>m</sup>	79.3 (1)		

Symmetry code: (i)  $1-x, 1-y, 1-z$ ; (ii)  $1-x, -y, 1-z$ ;  
(iii)  $x, \frac{1}{2}-y, \frac{1}{2}+z$ ; (iv)  $1-x, -\frac{1}{2}-y, \frac{1}{2}-z$ .

of 0.39 and 0.27 e Å<sup>-3</sup> at a distance of about 0.8 Å from the S atom. These peaks and holes are located between the S—O bonds. In order to take this, and also the ionic character of Na<sup>+</sup> and SO<sub>3</sub><sup>-</sup>, into account the refinements were made with the atomic scattering factors of Na<sup>+</sup> and SO<sub>3</sub><sup>-</sup>. Several possibilities have been considered: first, the atomic scattering factors of neutral atoms were used, then electron partial charges were localized on different O atoms of the SO<sub>3</sub><sup>-</sup> ion. In all cases, however, no significant improvement in the reliability factor occurred. It seems that further improvements can be achieved by the use in calculations of non-spherical atomic scattering factors for atoms of the sulfonate ion.

An analysis of the anisotropic temperature factors (Schomaker & Trueblood, 1968), calculated from *SHELX76* for heavy atoms of the *m*-XS molecule, shows that the whole molecule cannot be treated as a rigid body. This fact can be explained by the possibility of rotation of the SO<sub>3</sub> group around the C(1)—S axis, independently of the rest of the molecule. Such a first rigid-body analysis has been made

without O atoms and a second one with the C(1)—SO<sub>3</sub> group. Eigenvalues and eigenvectors are almost equal for the two calculations, except for the eigenvalues  $L_1$ :  $T_1 = 0.0358$ ,  $T_2 = 0.0255$ ,  $T_3 = 0.0149$  Å<sup>2</sup>,  $L_1 = 44.3$ ,  $L_2 = 14.2$  and  $L_3 = 13.5$  deg<sup>2</sup> for the *m*-XS molecule without O atoms; for the C(1)—SO<sub>3</sub> group they are  $T_1 = 0.0336$ ,  $T_2 = 0.0230$ ,  $T_3 = 0.0175$  Å<sup>2</sup>,  $L_1 = 65.2$ ,  $L_2 = 15.7$  and  $L_3 = 16.6$  deg<sup>2</sup>.  $L_1$  in both cases is the mean-square rotational vibration around the C(4)—C(1)—S axis and, as expected, this rotational vibration is greater for the sulfonate group (65.2 deg<sup>2</sup>) than for the rest of the molecule (44.3 deg<sup>2</sup>). This thermal rotational vibration, which corresponds to the 'easy' direction (e.g. the smallest inertia moment), is about three times greater than the rotational vibrations around the two other directions.

This work was partially supported by the Polish Academy of Sciences within the Program CPBP 01.12.

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*Acta Cryst.* (1992). **C48**, 615–618

## Structure of a Zinc 3-Methylantranilate Complex: (2-Amino-3-methylbenzoato)hydrozinc(II)

BY SHARON M. BOUDREAU AND HELMUT M. HAENDLER

*Department of Chemistry, University of New Hampshire, Durham, New Hampshire 03824-3598, USA*

(Received 15 April 1991; accepted 10 September 1991)

**Abstract.** [Zn(OH)(C<sub>8</sub>H<sub>8</sub>NO<sub>2</sub>)],  $M_r = 232.5$ , monoclinic,  $P2_1/c$ ,  $a = 14.512$  (1),  $b = 5.260$  (1),  $c = 11.774$  (2) Å,  $\beta = 111.01$  (2)°,  $V = 839.0$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.84$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54056$  Å,  $\mu =$

$3.9$  mm<sup>-1</sup>,  $F(000) = 472$ ,  $T = 293$  (1) K,  $R = 0.037$  for 1053 reflections. The coordination of the Zn atom is tetrahedral. Each aminomethylbenzoate radical acts as a bridging ligand between two Zn

atoms. Each Zn atom is bonded to a carboxyl O atom and a hydroxyl group, to an N atom of another ligand, and to a second hydroxyl group of a Zn atom associated with a third asymmetric unit. The effect is to produce a spiral arrangement of OH—Zn—OH—Zn in the solid. The Zn bond distances are Zn—O(1) = 1.968 (4), Zn—O(2) = 1.933 (4), Zn—O(2)\* = 1.947 (4) and Zn—N\* = 2.103 (5) Å (an asterisk indicates an atom in the adjacent asymmetric unit).

**Introduction.** The structure analysis of the title compound is a continuation of the investigation of a variety of highly stable and insoluble complexes of divalent and trivalent metal atoms and anthranilic acid (*ortho*-aminobenzoic acid) and related acids with a carboxylate O atom and an N atom in *ortho* position. The structures of copper (Lange & Haendler, 1975), yttrium (Boudreau & Haendler, 1981) and zinc anthranilate (Boudreau, Boudreau & Haendler, 1983), copper methylanthranilate (Boudreau & Haendler, 1986), and copper quinaldinate (Haendler, 1986) have been determined. Some of these have potential use as anti-inflammatory agents, hydrogenation catalysts, and components of films and adhesives. Introduction of a methyl group into the anthranilic acid has affected structure and packing. Zinc anthranilate exhibits a regular octahedral configuration. The hydroxo methyl analog shows a slightly distorted tetrahedral configuration and a spiral OH—Zn—OH—Zn arrangement.

**Experimental.** Single crystals were prepared by diffusion of aqueous solutions of zinc nitrate and sodium 2-amino-3-methylbenzoate in a 1:2 ratio over a period of six weeks (Martin & Haendler, 1978). The expected bis complex was not formed. Analysis calculated for Zn(OH)C<sub>8</sub>H<sub>8</sub>NO<sub>2</sub>: C 41.32; N 6.02; H 3.90; found: C 41.79; N 6.12; H 4.10%.

The crystal used was a colorless rectangular parallelepiped, 0.02 × 0.20 × 0.40 mm. Nicolet four-circle diffractometer, graphite-monochromated Cu K $\alpha$  radiation. 15 reflections ( $2\theta > 45^\circ$ ) for measurement of lattice parameters at 293 (1) K. Empirical absorption correction, using  $\psi$  scan with four reflections, range  $21.4 < 2\theta < 72.3^\circ$ , transmission factors 0.602–1.000. Maximum  $\sin\theta/\lambda = 0.565 \text{ \AA}^{-1}$ ,  $h$  0 to 16,  $k$  0 to 5,  $l$  –13 to 12. Six check reflections, frequency 300, no indication of deterioration or alignment changes. 1266 reflections were measured, 1053 observed with  $I > 2.5\sigma(I)$ . No further cell reduction observed.

The Zn atom was located on a Patterson map and the remainder of the structure solved with the VAX version of the *DIRDIF* system (Beurskens *et al.*, 1985). Least-squares full-matrix refinement on  $F$ , isotropic and anisotropic thermal parameters. Posi-

tions of the ring H atoms were calculated; remaining H atoms were located by superposition of a Dreiding model on a scaled unit-cell projection, or on a difference Fourier map, with further refinement. Data did not permit unambiguous location of the H atom of the hydroxide. Final full-matrix refinement, with 1053 reflections, anomalous dispersion for Zn, O and N, fixed H positions and  $B = 5.0 \text{ \AA}^2$  for H atoms, converged at  $R = 0.037$ ,  $w = 1/\sigma^2(F_o)$ ,  $wR = 0.045$ ,  $(\Delta/\sigma)_{\text{max}} = 0.019$  exclusive of H shifts.  $S = 2.44$  with 158 variables. Final difference map showed maximum and minimum peaks of 0.590 and  $-0.520 \text{ e \AA}^{-3}$ . No systematic errors as functions of  $\sin^2\theta$  or  $F_o$ ; no significant correlations. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, p. 149). The National Research Council of Canada programs (Ahmed, 1973) and *NRCVAX* (Gabe, Lee & Le Page, 1985) were used for the computations; *ORTEPII* (Johnson, 1976) for the thermal-ellipsoid plot.

**Discussion.** The final positional parameters are given in Table 1,\* and principal bond distances and angles in Table 2. Fig. 1 shows a projection of the unit cell onto the *ac* plane; Fig. 2 is a thermal-ellipsoid plot. The coordination around the Zn atom is tetrahedral. The aminomethylbenzoate ligand acts as a bridging bidentate ligand coordinating through amino N atoms and carboxylate O atoms, each ligand bridging two Zn atoms. A carboxylate O atom from one ligand, an N atom of another ligand, a hydroxyl group, and a second hydroxyl group of a Zn atom associated with a third asymmetric unit provide the sites of attachment. The Fourier map indicated two possible H positions in the OH group. The best results were obtained when both were included with occupancy factor 0.5, but H(4) was selected for inclusion because of its position: the H(4)—O(2)—Zn angle is  $100 (6)^\circ$  as contrasted to  $77 (4)^\circ$  for the H(3)—O(2)—Zn angle; there is the suggestion of a hydrogen bond with H(4) between O(2) and O(3); the O(2)—O(3) distance is 2.963 Å, and the O(2)—H(4)—O(3) angle is  $169^\circ$ , which is not the case with H(3).

The Zn—O and Zn—N distances are comparable to values reported for the representative tetrahedral zinc complexes listed in Table 3. Values for the Zn—N distances (range 2.04–2.069 Å) are slightly longer than the metal–oxygen distances (range 1.95–

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, ring-bond distances and angles not in Table 2, and planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54646 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final positional parameters and equivalent Debye-Waller factors

$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$B_{eq} (\text{\AA}^2)$
Zn	0.42337 (6)	0.45311 (15)	0.22281 (7)	2.01 (4)
O(1)	0.3109 (3)	0.3923 (8)	0.2754 (4)	2.77 (20)
O(2)	0.5315 (3)	0.6464 (8)	0.3339 (4)	2.14 (19)
O(3)	0.4217 (3)	0.1619 (10)	0.4150 (4)	3.30 (22)
N	0.3623 (4)	-0.1514 (11)	0.5576 (4)	1.99 (23)
C(1)	0.3352 (4)	0.2315 (12)	0.3617 (5)	2.01 (26)
C(2)	0.2515 (4)	0.1271 (12)	0.3958 (5)	2.01 (26)
C(3)	0.2654 (4)	-0.0667 (12)	0.4838 (5)	1.80 (24)
C(4)	0.1830 (4)	-0.1712 (12)	0.5039 (5)	2.26 (27)
C(5)	0.0904 (5)	-0.0823 (14)	0.4359 (6)	2.98 (32)
C(6)	0.0763 (5)	0.1113 (14)	0.3523 (6)	3.00 (32)
C(7)	0.1561 (4)	0.2133 (13)	0.3317 (5)	2.42 (29)
C(8)	0.1970 (6)	-0.3785 (16)	0.5975 (7)	3.18 (36)

Table 2. Selected bond distances (Å) and angles (°)

The dotted line between atoms represents a bond between atoms in different asymmetric units.

Zn—O(1)	1.968 (4)	C(4)—C(5)	1.376 (9)
Zn—O(2)	1.933 (4)	C(5)—C(6)	1.380 (10)
Zn—O(2)	1.947 (4)	C(6)—C(7)	1.374 (9)
Zn...N	2.103 (4)	C(7)—C(2)	1.394 (8)
C(1)—O(1)	1.271 (7)	N—H(1)	0.89 (6)
C(1)—O(3)	1.240 (7)	N—H(2)	0.82 (7)
C(1)—C(2)	1.513 (8)	C(8)—H(81)	0.97 (9)
C(2)—C(3)	1.415 (8)	C(8)—H(82)	0.86 (6)
C(3)—C(4)	1.411 (8)	C(8)—H(83)	0.92 (10)
C(3)—N	1.433 (8)	O(2)—H(4)	0.84 (9)
C(4)—C(8)	1.511 (11)		
O(1)—Zn...N	104.5 (2)	O(3)—C(1)—C(2)	121.5 (5)
O(1)—Zn—O(2)	115.9 (2)	C(3)—C(4)—C(8)	120.2 (6)
O(1)—Zn...O(2)	113.1 (2)	C(1)—C(2)—C(3)	122.6 (5)
O(2)—Zn...N	109.6 (2)	C(1)—C(2)—C(7)	118.3 (5)
Zn—O(1)—C(1)	109.6 (4)	C(2)—C(3)—N	121.3 (5)
Zn—O(2)...Zn	119.7 (2)	H(1)—N—H(2)	109 (6)
O(2)—Zn...O(2)	112.1 (2)	C(4)—C(8)—H(81)	109 (5)
		C(3)—N—H(1)	109 (4)

2.019 Å). In octahedrally coordinated zinc anthranilate the Zn—O distances are 2.066 (3) and 2.145 (4) Å and the Zn—N distance is 2.166 (4) Å.

The structure of the title compound appears to be related to the reported early structure of  $\text{Zn}(\text{OH})_2$  (Corey & Wyckoff, 1933). The most stable lattice, the  $\epsilon$ - $\text{Zn}(\text{OH})_2$ , has each atom of Zn surrounded by four OH groups at the vertices of a tetrahedron. The tetrahedra are arranged tip to tip and form a zigzag chain in the *b* direction. The Zn—O distance of 1.95 Å is close to that reported here and the O—Zn—O spirals in the [010] direction may be related to the OH—Zn—OH system. The compound can be considered a one-dimensional polymer in the *c* direction, and this may be the source of the compound's insolubility.

Zinc anthranilate also has a bridging network, but the *ortho*-aminobenzoate ligand acts as a tridentate ligand, resulting in octahedral coordination. The three sites of attachment on the ligand were not associated with the same Zn atom. The Cu methyl

analog exhibits a different bridging bidentate ligand where the carboxylate O atoms and the amino N atoms from four different ligands are involved. A square-planar coordination results.

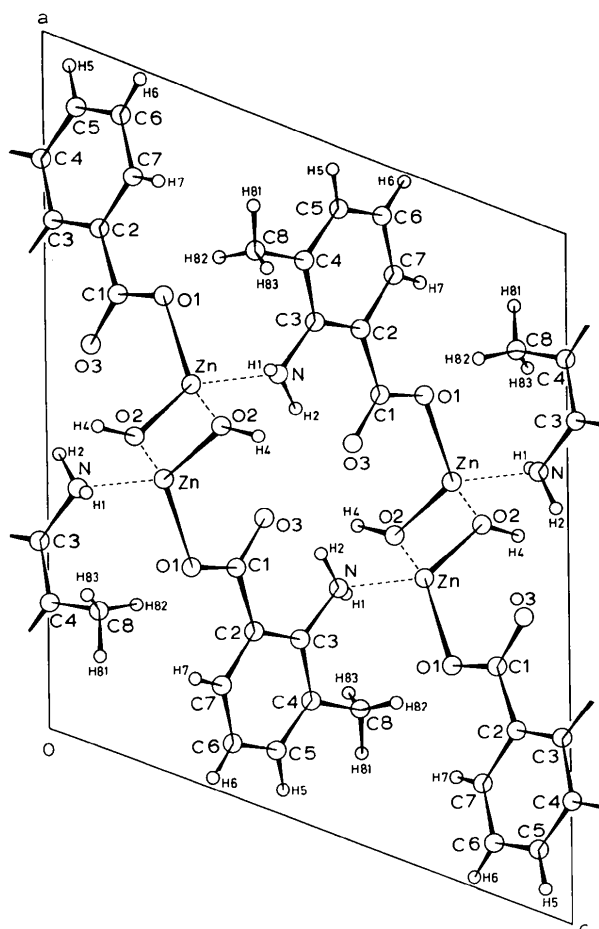


Fig. 1. Projection of the unit cell of (2-amino-3-methylbenzoato)-hydroxozinc(II) on the *ac* plane.

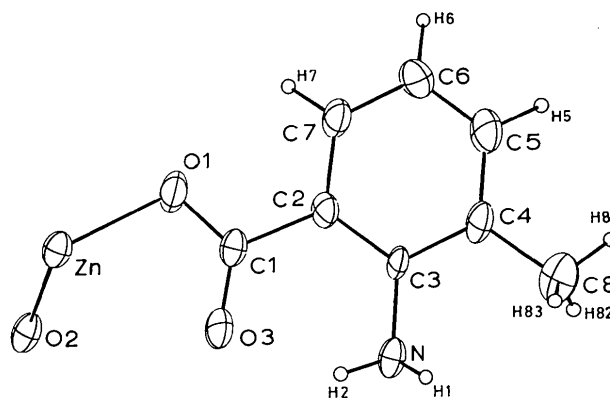


Fig. 2. Thermal-ellipsoid plot of (2-amino-3-methylbenzoato)-hydroxozinc(II).

Table 3. Zn—O and Zn—N distances (Å) in tetrahedral Zn complexes

	Zn—N	Zn—O	
(2-Amino-3-methylbenzoato)hydroxozinc(II)	2.103 (4)	1.968 (4) 1.933 (4) 1.947 (4)	This work
Zinc dicyanide-2,9-dimethyl-1,10-phenanthroline	2.069		Monge, Martínez-Ripoll & García-Blanco (1977)
Dichlorobis(4-vinylpyridine)zinc(II)	2.040		Steffen & Palenik (1977)
catena-Dichloro- $\mu$ -(9-methyladenine)-zinc(II)	2.040		McCall & Taylor (1976)
Zinc hydroxide nitrate		1.95	Stählin & Oswald (1970)
Bis(2,6-dimethyl-4H-pyran-4-one)-dinitratozinc		1.979	Brown & Lewis (1984)
Dichlorobis(antipyrine)zinc		1.997 (4) 2.019 (6)	Cingi, Guastini, Musatti & Nardelli (1972)
Bis(thiourea)zinc acetate		1.973 (6) 1.954 (8)	Cavalca, Gasparri, Andreotti & Domiano (1967)

The authors wish to acknowledge the receipt of a grant from Wheaton College, Norton, MA, that made possible the collection of intensity data by Dr Cynthia S. Day, Crystalytics Company, Lincoln, Nebraska, and a grant from the University of New Hampshire Research Office that provided for the use of the services of the University Computation Center.

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*Acta Cryst.* (1992). **C48**, 618–620

## A Monomeric Cyclopentadienyl Indium Complex. Structure of $[\eta^5$ -(Diphenylphosphino)tetramethylcyclopentadienyl]indium(I)

BY HERBERT SCHUMANN, TAHEREH GHODSI AND LOTHAR ESSER

*Institut für Anorganische und Analytische Chemie der Technischen Universität Berlin, Straße des 17. Juni 135, W-1000 Berlin 12, Germany*

(Received 2 July 1991; accepted 2 September 1991)

**Abstract.**  $C_{21}H_{22}InP$ ,  $M_r = 420.20$ , monoclinic,  $P2_1/c$ ,  $a = 11.6680$  (8),  $b = 10.589$  (1),  $c = 15.097$  (3) Å,  $\beta = 99.754$  (9)°,  $V = 1838.3$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.52$  Mg m<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu = 1.35$  mm<sup>-1</sup>,  $F(000) = 848$ ,  $T = 150$  K. The structure was refined to  $R(F) = 0.030$  for 3411 unique observed reflections. The formation of a polymeric structure containing zigzag chains of alternating cyclopentadienyl rings and In atoms is not observed. The In atom is only  $\eta^5$  bound to the cyclopentadienyl ring

[average In—C(ring) = 2.694 (3) Å], and undergoes interactions neither with the lone pair of the P atom [In...P = 3.703 (1) Å] nor with other In atoms [In...In = 5.929 (1) Å].

**Introduction.** In recent years, ring-substituted cyclopentadienyl complexes of low-valent Group 13 element complexes have been subject to considerable structural (Beachley, Bloom, Churchill, Faegri, Fettinger, Pazik & Vitoriano, 1989; Schumann,