JOURNAL OF SOLID STATE CHEMISTRY 49, 379–384 (1983)

The Crystal and Molecular Structure of Bis(*ortho*-aminobenzoato)zinc(II), $Zn(H_2NC_6H_4COO)_2$

SHARON M. BOUDREAU AND ROBERT A. BOUDREAU

Department of Chemistry, Wheaton College, Norton, Massachusetts 02766

AND HELMUT M. HAENDLER*

*Department of Chemistry, University of New Hampshire,
Durham, New Hampshire 03824*

Received February 23, 1983; in revised form June 10, 1983

Bis(*ortho*-aminobenzoato)zinc(II), $Zn(H_2NC_6H_4COO)_2$, is monoclinic, space group $P2_1c$, with a = 13.938(2) Å, b = 5.207(1) Å, c = 9.346(1) Å, β = 108.37°, Z = 2. The structure was solved by direct and Fourier methods and refined to a final R of 0.047 based on 1198 observable reflections. The zinc is octahedrally coordinated, with four equatorial positions occupied by two amino nitrogen atoms and two carboxylate oxygen atoms such that both the nitrogen and oxygen atoms are in *trans* positions. The axial positions are occupied by two carbonyl oxygen atoms belonging to two other ligands not associated with the equatorial sites. The extreme insolubility of the compound may be accounted for not only by the two-dimensional polymeric network of carboxylate bridges between zinc atoms in the (100) plane, but also by the presence of hydrogen bonding between ligand molecules.

Introduction

ortho-Aminobenzoic acid (anthranilic acid) is an important precursor to tryptophan, one of the biologically important α-amino acids. The acid forms stable, highly insoluble compounds with a variety of divalent and trivalent metals. Some of these have potential use as anti-inflammatory agents, hydrogenation catalysts, and components of adhesives and films. Complete crystallographic structure determinations have been carried out on $Cu(H_2NC_6H_4COO)_2$ (*1*) and on the only known hydrate of the series, $Y(H_2NC_6H_4COO)_3 \cdot H_2O$ (*2*). A recent paper has reported nitrogen-14 nuclear quadrupole resonance studies of a number of these metal complexes (*3*). Because of the biological importance of zinc, and the similarity exhibited by the powder diffraction patterns of the copper and zinc complexes, we found it appropriate to characterize the coordination in zinc anthranilate. The d^9 copper complex shows distorted octahedral coordination due to the Jahn–Teller effect, but one would expect the zinc complex to approach a more regular octahedral configuration. This has been substantiated by the structure determination.

Experimental

Single crystals of $Zn(H_2NC_6H_4COO)_2$, comparable in quality to our copper and yt-

---

* To whom correspondence should be addressed.

0022-4596/83 $3.00

TABLE I

CRYSTALLOGRAPHIC DATA

Symmetry	Monoclinic
Cell dimensions	$a = 13.938(2)$ Å
	$b = 5.207(1)$ Å
	$c = 9.346(1)$ Å
	$\beta = 108.37(1)°$
Cell volume	643.7(2) $Å^3$
Formula weight	337.6
Z	2
Density (X-ray)	1.74 g/cm^3
Density (measured)	1.746 g/cm^3
Absorption coefficient, μ	19.8 cm^{-1}
Systematic absences	$h0l$: $l = 2n + 1$
	$0k0$: $k = 2n + 1$
Space group	$P2_1/c$ (No. 14)
$F(000)$	344

trium complexes, were grown by reactive diffusion (*4*) between solutions of zinc acetate and sodium anthranilate. These crystals were flat parallelepipeds, with a light tan color. Preliminary photographic studies using Weissenberg and precession techniques indicated monoclinic, $P2_1/c$ symmetry, with systematic absences of $h0l$ with $l = 2n + 1$ and $0k0$ with $k = 2n + 1$. This centrosymmetric space group was further confirmed by intensity statistics. The density was determined pycnometrically with an aqueous soap solution of known density and corresponds to that for two formula units per unit cell. The crystallographic data are given in Table I.

Intensity measurements were made at room temperature using a computer-controlled four-circle Nicolet autodiffractometer with graphite monochromated Mo$K\alpha$ radiation. The crystal used for the data collection was a flat parallelepiped with dimensions 0.45 × 0.50 × 0.04 mm and was oriented with its longest dimension nearly parallel to the phi axis of the diffractometer. Intensities of all 1489 independent reflections with $2\theta \leq 55°$ were measured using the θ–2θ scan technique. The scan was between 2θ settings 1.2° above and below the calculated Mo$K\alpha$ doublet values (λ = 0.70930 and 0.71359 Å) for each reflection. Background counts, each lasting one-fourth the total scan time, were taken at both ends of the scan range.

The hemisphere recorded was that with $\pm h + k \pm l$. Scan rates of 4°/min were used for those reflections having $3.00 \leq 2\theta \leq 43.0°$, and scanning rates of 2.0/min for $43.0 \leq 2\theta \leq 55.0°$. Six standard reflections were measured every 300 reflections to ensure that the crystal retained its alignment and that it did not deteriorate in the incident beam. There was no indication of either. Of the 1489 reflections measured, 193 were classified as unobserved, with a ratio of estimated standard deviation to observed intensity greater than 0.33. Although normal Lorentz and polarization effects corrections were accounted for, no extinction or absorption corrections were made (μ = 19.8 cm^{-1}).

Structure Determination and Refinement

The structure was solved by direct methods, utilizing the computer program DIRDIF (*5–7*). Initially, block-diagonal least-squares refinement with isotropic temperature factors for 11 nonhydrogen atoms gave an R factor of 0.17, which was lowered to 0.064 after four cycles. An additional five cycles of refinement with anisotropic temperature factors reduced R to 0.052. A differential synthesis shifted the coordinates slightly, resulting in $R = 0.050$.

A difference Fourier calculation revealed the positions of the four hydrogen atoms of the benzene ring. The hydrogen atoms of the amino groups showed broad, ill-defined peaks on the map and were therefore assigned positions from a structural model. Additional refinement using least-squares calculations with anisotropic thermal parameters for nonhydrogen atoms and isotropic thermal parameters for hydrogen atoms reduced R to a final value of 0.047

based on 1198 reflections. The remaining 98 reflections were very weak ($F_{calc.} < 5.0$) and were rejected by the refinement program. In the final cycle, the ratio of the largest shift to the standard deviation in the coordinate was less than 0.33. An error analysis revealed no systematic errors as a function of either $\sin^2\theta$ or F_{obs}. In addition, the error analysis indicated that of the 1296 observed reflections, 1272 had $||F_{obs}| - |F_{calc}||/|F_{obs}|$ less than three times the final R value.

In the block diagonal least-squares refinement, the function minimized was $\Sigma W(|F_o| - |F_c|)^2$, $W = 1/\sigma^2(|F_o|)$. The atomic scattering factors for the nonhydrogen atoms were those tabulated by Hanson (*8*), and the hydrogen scattering factors were taken from Stewart (*9*). No anomalous dispersion correction for zinc was made. The values of the final positional and thermal parameters, along with estimated standard deviations, are tabulated in Table II. A listing of calculated and observed structure factors is available from the authors.

TABLE IIA

FINAL POSITIONAL AND THERMAL PARAMETERS: POSITIONAL PARAMETERS[a,b]

Atom	x	y	z
Zn	0.0000	0.0000	0.0000
O(1)	−0.0295(3)	0.3058(7)	0.2980(4)
O(2)	−0.1111(3)	0.2289(8)	0.0558(4)
N(1)	−0.1164(3)	0.7608(8)	0.3713(5)
C(1)	−0.1077(4)	0.3136(9)	0.1835(5)
C(2)	−0.2049(4)	0.4224(10)	0.1965(6)
C(3)	−0.2074(4)	0.6314(10)	0.2900(6)
C(4)	−0.2996(4)	0.7097(12)	0.3044(7)
C(5)	−0.3884(5)	0.5803(14)	0.2275(8)
C(6)	−0.3863(5)	0.3755(14)	0.1338(8)
C(7)	−0.2950(4)	0.2974(12)	0.1178(7)
H(1)	−0.125(4)	0.905(12)	0.405(6)
H(2)	−0.096(4)	0.807(11)	0.298(6)
H(4)	−0.310(6)	0.846(17)	0.352(9)
H(5)	−0.450(6)	0.632(16)	0.240(9)
H(6)	−0.449(5)	0.257(15)	0.086(8)
H(7)	−0.294(5)	0.152(14)	0.069(7)

[a] The anisotropic thermal parameter is defined as $f = f_o \exp[-2\pi^2 (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

[b] Estimated standard deviations are given in parentheses; x, y, and z are fractional coordinates.

TABLE IIB

FINAL POSITIONAL AND THERMAL PARAMETERS: ANISOTROPIC THERMAL PARAMETERS (× 10^4 Å^2)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn	430(7)	284(7)	287(7)	9(7)	96(5)	10(10)
O(1)	507(14)	373(34)	378(33)	51(30)	127(28)	−25(4)
O(2)	553(37)	545(39)	456(35)	81(33)	169(29)	−108(32)
N(1)	518(42)	302(39)	461(42)	24(56)	165(33)	−6(22)
C(1)	467(14)	240(37)	322(42)	−19(68)	118(36)	14(37)
C(2)	460(47)	360(47)	418(45)	39(38)	132(38)	−10(18)
C(3)	537(51)	372(48)	368(45)	58(40)	184(40)	51(39)
C(4)	605(56)	600(59)	688(60)	153(50)	275(48)	−42(48)
C(5)	519(58)	936(79)	932(72)	166(18)	252(74)	80(63)
C(6)	514(58)	835(73)	944(74)	−55(55)	140(28)	−54(28)
C(7)	556(54)	559(58)	619(58)	−69(49)	101(45)	−63(41)

Results and Discussion

A projection of the molecule drawn with ORTEP is shown in Fig. 1. Bond distances and angles found in bis(*ortho*-aminobenzoato)zinc(II) are tabulated in Table III. The coordination around the zinc atom is close to that of a regular octahedron. Each ligand of the *ortho*-aminobenzoate group acts as a tridentate ligand, but the three sites of attachment on the ligand are not associated with the same zinc atom. The zinc atom is coordinated equatorially with two amino nitrogen atoms, N(1), and two carboxylate oxygen atoms, O(1), with both nitrogen and oxygen atoms in *trans* positions. Two carbonyl oxygen atoms, O(2), each belonging to a different ligand, complete the octahedral arrangement by occupying axial positions. As a result, four *ortho*-aminobenzoate residues are associated with each zinc. This carboxylate bridging leads to a two-dimensional polymeric network coincident with the (100) plane.

Hydrogen bonding between the amino nitrogen N(1) and an adjacent carbonyl oxygen O(2) provides additional crosslinking in

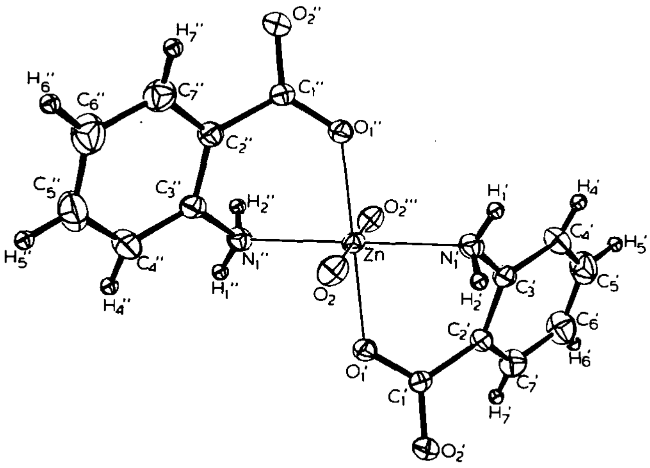

FIG. 1. ORTEP drawing of zinc anthranilate coordination.

the molecule, leading to further stabilization. This networking has also been reported in zinc acetate dihydrate (*10*) and zinc lactate trihydrate (*11*). The N(1) · · · O(2) distance (3.16 Å) and the N(1)–H(1) · · · O(2) angle (163.8°) are well within the range found for hydrogen bonds between amine groups and oxygen (2.57–3.22 Å). What is perhaps of greater interest is the possibility that a second hydrogen bond exists between N(1) and the oxygen atom O(1) bound to the zinc atom. The N(1)–O(1) distance (2.95 Å) and the N(1)–H(2) · · · O(1) angle (146.9°) also lie within the reported range. This is also consistent with the similarity of the two C–O distances in the carbonyl group, C(1)–O(1) = 1.264 Å and C(1)–O(2) = 1.258 Å, indicating equivalent pi delocalization between these bonds.

Comparison of the equatorial Zn–O and Zn–N geometry shows a slight deviation from perfect planar symmetry, (O(1)–Zn–N(1) = 84.3°, Table IIIB). Comparison of the equatorial Zn–O (2.066 Å) bond with the axial Zn–O bond (2.145 Å) shows that there is no significant Jahn–Teller distortion, in contrast to that found in the copper complex, with its long Cu–O axial distance (2.415 Å).

Reported distances for zinc–oxygen bonds range from 1.97 to 2.26 Å and zinc–nitrogen bond distances vary from 1.99 to 2.15 Å. These are consistent with the values reported here. Table IV gives a comparison of bond distances reported for some *trans* octahedral zinc complexes. The bond distances for Zn–O and Zn–N in zinc-8-hydroxyquinolinate dihydrate (*15*) are very similar to those in zinc anthranilate. The bond distances and angles of the *ortho*-aminobenzoate ligand in zinc and copper complexes are very similar despite the dif-

TABLE IIIA

BOND DISTANCES AND ANGLES: DISTANCES (Å)[a]

Bond	Distance	Bond	Distance
Zn–O(1)	2.066(3)	C(5)–C(6)	1.386(10)
Zn · · · O(2)[b]	2.145(4)	C(6)–C(7)	1.389(10)
Zn–N(1)	2.166(4)	C(7)–C(2)	1.399(8)
C(1)–O(1)	1.264(6)	N(1)–H(1)	0.84(6)
C(1)–O(2)	1.258(6)	N(1)–H(2)	0.86(6)
C(1)–C(2)	1.509(8)	C(4)–H(4)	0.87(9)
C(2)–C(3)	1.403(7)	C(5)–H(5)	0.94(8)
C(3)–N(1)	1.426(7)	C(6)–H(6)	1.05(8)
C(3)–C(4)	1.395(9)	C(7)–H(7)	0.88(7)
C(4)–C(5)	1.393(9)		

TABLE IIIB

BOND DISTANCES AND ANGLES: ANGLES (°)[a]

Bond	Angle	Bond	Angle
O(1)–Zn–N(1)	84.3(2)°	C(3)–C(4)–C(5)	120.3(6)°
O(1)–Zn · · · O(2)[b]	90.0(1)	C(4)–C(5)–C(6)	120.4(6)
O(2) · · · Zn–N(1)	89.3(2)	C(5)–C(6)–C(7)	119.7(6)
Zn–O(1)–C(1)	128.9(3)	C(6)–C(7)–C(2)	120.5(6)
O(1)–C(1)–O(2)	123.8(5)	H(1)–N(1)–H(2)	100(5)
O(1)–C(1)–C(2)	120.0(4)	C(3)–C(4)–H(4)	126(6)
O(2)–C(1)–C(2)	116.2(4)	C(5)–C(4)–H(4)	114(6)
C(1)–C(2)–C(3)	122.7(5)	C(4)–C(5)–H(5)	120(5)
C(1)–C(2)–C(7)	117.6(5)	C(6)–C(5)–H(5)	120(5)
C(3)–C(2)–C(7)	119.6(5)	C(5)–C(6)–H(6)	123(4)
C(2)–C(3)–N(1)	120.4(5)	C(7)–C(6)–H(6)	117(4)
C(4)–C(3)–N(1)	120.2(5)	C(6)–C(7)–H(7)	118(5)
C(2)–C(3)–C(4)	119.4(5)	C(2)–C(7)–H(7)	121(5)

[a] Estimated standard deviations are given in parentheses and are calculated from those derived for the positional parameters.

[b] The dotted line represents a bond between a zinc atom and the carbonyl oxygen of a ligand attached to a different zinc atom.

ferent coordination in each compound, whereas the average C–C distance in the aromatic ring is somewhat greater in the yttrium complex.

The types of coordination encountered in the three complexes studied so far are not unexpected, but the modes of attachment are different. The *ortho*-aminobenzoate group functions as a bridging bidentate ligand in the yttrium compound, but becomes bridging tridentate when complexed with the zinc or copper. Both nitrogen and oxygen atoms are active in bonding in the latter, but only oxygen atoms are bonded to the yttrium in the seven-coordinate capped octahedron. In all cases the bonding is unique in that each carbonyl oxygen O(2) comes from a different ligand. The shorter Zn–O(2) distance controls the regular octahedral configuration, whereas the longer Cu–O(2) bond gives rise to a distorted octahedron. Although the Zn–O axial and equatorial bonds are not as different as the corresponding Cu–O bonds, they are inequivalent. This could be attributed to differences in Zn–O–C strain or to the effect of hydrogen bonding between the nitrogen atom and the carbonyl oxygen. In the seven-coordinate yttrium complex the severe distortion results in C–O bond distances of different lengths, indicating unequal *pi* delocalization, quite different from the equivalent delocalization in the carbonyl groups of both zinc and copper complexes.

Extensive crosslinking of hydrogen bonds between the amino nitrogen N(1) and an adjacent carbonyl oxygen O(2) has been found in the structure of copper anthranilate, as well. Although the data set was not sufficient to locate all hydrogen atoms in the yttrium complex, there is evidence of

TABLE IV

BOND DISTANCES FOR *trans* OCTAHEDRAL COMPLEXES[a]

Compound	Bond distances (Å)						Atoms						Reference
	M–a	*M–b*	*M–c*	*M–d*	*M–e*	*M–f*	*a*	*b*	*c*	*d*	*e*	*f*	
$Zn(OC(NH_2)NHNH_2)Cl_2$	2.85	2.59	1.97	2.07	2.06	1.99	Cl	Cl	O	N	O	N	(*12*)
$Zn(OOC–CO–NH_2) \cdot 2H_2O$	2.09	2.09	2.15	2.04	2.15	2.04	O	O	O	O	O	O	(*13*)
$Zn(CH_3CHOHCOO)_2 \cdot 3H_2O$	2.07	2.04	2.15	2.09	2.19	2.08	O	O	O	O	O	O	(*11*)
$(Zn(N_2H_4)_2)Cl_2$	2.58	2.58	2.15	2.15	2.15	2.15	Cl	Cl	N	N	N	N	(*14*)
$Zn(CH_3COO)_2 \cdot 2H_2O$	2.14	2.14	2.17	2.18	2.17	2.18	O	O	O	O	O	O	(*10*)
$Zn(C_9H_6ON)_2 \cdot 2H_2O$	2.26	2.26	2.07	2.10	2.07	2.10	O	O	O	N	O	N	(*15*)
$Zn(H_2NC_6H_4COO)_2$	2.15	2.15	2.07	2.17	2.07	2.17	O	O	O	N	O	N	[b]
$Cu(H_2NC_6H_4COO)_2$	2.42	2.42	1.97	2.02	1.97	2.02	O	O	O	N	O	N	(*1*)

[a] Atoms *a* and *b* are axial, while atoms *f–M–d* and *e–M–c* are *trans* equatorial, respectively.

[b] This work.

some hydrogen bonding. Perhaps this networking, in addition to the polymeric parallel chains found in the compounds of the series, may be a source for their extreme insolubility.[1]

The powder diffraction patterns of the nickel and cobalt complexes with *ortho*-aminobenzoic acid are identical to that of the zinc complex, suggesting that the three compounds are isostructural. Investigations of lanthanum anthranilate, belonging to a hexagonal space group, are currently in progress.

Acknowledgment

We thank Wheaton College for financial support and the University of New Hampshire for the use of computing facilities. Intensity data and the ORTEP plot were supplied by Dr. Cynthia Day, Crystalytics Company, Lincoln, Nebr. Dr. F. R. Ahmed's National Research Council of Canada programs were used for refinement.

References

1. B. A. Lange and H. M. Haendler, *J. Solid State Chem.* **15,** 325 (1975).
2. S. M. Boudreau and H. M. Haendler, *J. Solid State Chem.* **36,** 190 (1981).
3. D. Andre d'Avignon and T. L. Brown, *Inorg. Chem.* **21,** 3041 (1982).
4. S. A. Martin and H. M. Haendler, *J. Appl. Crystallogr.* **11,** 62 (1978).
5. P. T. Beurskens and J. H. Noordik, *Acta Crystallogr. Sect. A* **27,** 187 (1971).
6. R. O. Gould and Th. E. M. van den Hark and P. T. Beurskens, *Acta Crystallogr. Sect. A* **31,** 813 (1975).
7. Th. E. M. van den Hark, P. Prick, and P. T. Beurskens, *Acta Crystallogr. Sect. A* **32,** 816 (1976).
8. H. P. Hanson, F. Herman, J. D. Lee, and S. Skillman, *Acta Crystallogr.* **17,** 1040 (1964).
9. R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.* **42,** 3175 (1965).
10. J. N. van Niekerk, F. R. L. Schoening, and J. H. Talbot, *Acta Crystallogr.* **6,** 720 (1953).
11. K. D. Singh, S. C. Jain, T. D. Sakore, and A. B. Biswas, *Acta Crystallogr. Sect. B* **31,** 990 (1975).
12. M. Nardelli, G. F. Gasparri, P. Boldrini, and G. G. Battistini, *Acta Crystallogr.* **19,** 491 (1965).
13. A. Braibanti, M. A. Pellinghelli, A. Tiripicchio, and M. Tiripicchio Camellini, *Acta Crystallogr. Sect. B* **27,** 1240 (1971).
14. A. Ferrai, A. Braibanti, and G. Bigliardi, *Acta Crystallogr.* **16,** 498 (1963).
15. G. Palenik, *Acta Crystallogr.* **17,** 696 (1964).

---

[1] The comparison to the structure of copper anthranilate is more obvious if the zinc atom is placed at 0, ½, ½. The figures in Ref. (*2*) are then directly comparable to those for the zinc complex.