Crystal and Molecular Structure of Bisaquabis(thiobenzoato)zinc(II)

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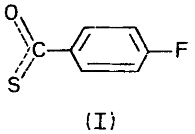
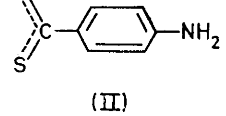
The crystal and molecular structure of the title compound has been determined from photographic *X*-ray data by the heavy-atom technique and refined by anisotropic least-squares methods to R 0.062 for 909 visually estimated reflections. Crystals are monoclinic, space group $C2$, with $Z = 2$, in a unit cell of dimensions: $a = 9.836$, $b = 6.809$, $c = 11.915$ Å, $\beta = 108°12'$.

The tetrahedral zinc environment consists of two water molecules and two monothiobenzoate groups bonding as unidentate ligands through sulphur, with a shortest Zn–S distance 2.278(2) Å.

THE large difference between di- and mono-thiobenzoatonickel(II) complexes in the mode by which the ligand bonds to the metal,[1-3] and questions arising from the properties of the two four-membered chelate rings structure of bis(dithiobenzoato)zinc(II),[4] induced us to undertake comparative structural studies on complexes of the same metal atom with mono- and di-thiobenzoate ligands, containing electron-attracting or -releasing substituents in the phenyl ring, *i.e.* (I) and (II).



(I)



(II)

We wished to provide information on the difference between sulphur and oxygen as donor atoms, and on factors involved in the formation of four-membered chelate rings. We report here the *X*-ray analysis of the zinc(II) thiobenzoate (mtb) complex $Zn(mtb)_2{\cdot}2H_2O$, (III).

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[1] M. Bonamico, G. Dessy, and V. Fares, *Chem. Comm.*, 1969, 324.

[2] G. A. Melson, P. T. Green, and R. F. Bryan, *Inorg. Chem.*, 1970, **9**, 1116.

[3] M. Bonamico, G. Dessy, and V. Fares, *Chem. Comm.*, 1969, 697.

[4] M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, *J.C.S. Dalton*, 1972, 2515.

TABLE 1

Co-ordinates ($\times 10^4$) and temperature factors,* with standard deviations in parentheses

	x/a	y/b	z/c	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Zn	0	0	0	44(1)	0	14(1)	69(3)	0	42(1)
S	−1 204(2)	1 527(3)	−1 725(2)	80(2)	−37(5)	4(2)	98(4)	6(3)	44(1)
O	838(5)	4 201(10)	−985(5)	53(5)	14(13)	2(7)	116(12)	16(12)	56(4)
O(W)	−1 463(5)	−2 024(10)	123(6)	40(4)	−29(14)	40(8)	138(14)	76(15)	90(5)
C(1)	−386(6)	3 792(11)	−1 652(6)	44(6)	−9(17)	26(8)	100(15)	0(13)	33(4)
C(2)	−1 208(7)	5 282(12)	−2 536(6)	58(6)	22(18)	10(8)	93(17)	−2(14)	38(4)
C(3)	−477(9)	6 436(13)	−3 109(6)	93(9)	−11(21)	21(10)	103(16)	40(16)	43(5)
C(4)	−1 242(10)	7 809(16)	−3 933(8)	118(11)	−29(25)	41(13)	130(19)	64(20)	61(6)
C(5)	−2 710(11)	8 019(15)	−4 179(8)	127(11)	16(26)	−28(12)	108(19)	48(20)	57(6)
C(6)	−3 389(9)	6 901(17)	−3 608(7)	85(9)	64(27)	19(12)	181(23)	19(23)	66(6)
C(7)	−2 701(7)	5 501(13)	−2 791(6)	51(6)	10(18)	9(9)	123(18)	25(16)	52(5)
H(3) †	580	6 289	−2 936						
H(4)	−725	8 656	−4 354						
H(5)	−3 251	8 998	−4 778						
H(6)	−4 443	7 084	−3 779						
H(7)	−3 245	4 664	−2 390						

* For non-hydrogen atoms, exponential coefficients b_{ij} as given here are defined by $T = \exp[10^{-4}(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$. † For H atoms anisotropic thermal parameters, B 3.0, see text.

EXPERIMENTAL

Preparation.—The compound was prepared according to the method of ref. 5 and crystallized from aqueous ethanol as monoclinic prisms, elongated along [$\bar{1}$10].

Crystal Data.—$C_{14}H_{14}O_4S_2Zn$, $M = 375.763$, Monoclinic, $a = 9.836 \pm 0.01$, $b = 6.809 \pm 0.01$, $c = 11.915 \pm 0.01$ Å, $\beta = 108°12' \pm 10'$, $U = 758$ Å^3, $D_m = 1.65 \pm 0.02$ (by flotation), $Z = 2$, $D_c = 1.647$, $F(000) = 379.30$, Cu-K_α radiation, $\lambda = 1.5418$ Å; μ(Cu-K_α) = 48.96 cm^{-1}. Space group $C2$ (C_2^3, No. 5) from systematic absences and structure determination.

A triclinic unit-cell, with the a', b', and c' axes coincident with the [110], [$\bar{1}$10], and [1$\bar{1}$2] directions, was defined in order to index six sets of multiple-film equi-inclination Weissenberg photographs taken about the b' axis ($h'0$–$5l'$), the relations between the monoclinic indices hkl and the triclinic ones $h'k'l'$ being: $h = h' - k'$; $k = h' + k'$; $l = k' + l'$.

Unit-cell dimensions were determined from the triclinic data by an improved version of Christ's method [6] from zero-layer Weissenberg film taken about the b' axis, and precession photographs taken about a' and c' axes, by use of reflections obtained with Cu-K_α and, where possible, Cu-$K_{\alpha 1}$ radiation ($\lambda = 1.54056$ Å).

Intensity Measurements and Data Reduction.—The intensities of 909 independent reflections above film background (*ca.* 26% of the total possible with Cu-K_α radiation) were estimated visually.

The triclinic data were corrected for Lorentz and polarization effects, and for spot extension.[7] No absorption or extinction corrections were applied. Initial scaling was based on the relative exposure-times of the different photographs. Independent layer-scales were refined during the isotropic phase of structure refinement.

Determination and Refinement of the Structure.—The structure was solved by the heavy-atom method which led to the location of all atoms except hydrogen. Positional and isotropic thermal parameters of the non-hydrogen atoms (B 3.0 Å^2 by Wilson's method) were refined by several cycles of full-matrix least-squares to R 0.103.

The hydrogen atoms of the phenyl group were then included at calculated positions, with a mean isotropic temperature factor of 4.0 Å^2. Further refinement of non-hydrogen atomic parameters reduced R to 0.101. A new scaling (see earlier) and the introduction of anisotropic thermal motion for all non-hydrogen atoms brought R to 0.062 in six cycles. Refinement was performed by use of anisotropic thermal parameters with a 9×9 block-diagonal approximation; the final shifts on the atomic parameters were all $< 0.2\sigma$. The weighting scheme $w = (a + bF_o + cF_o{}^2)^{-1}$ was used throughout refinement, with $a = 0.4$, $b = 1.0$, and $c = 0.015$.

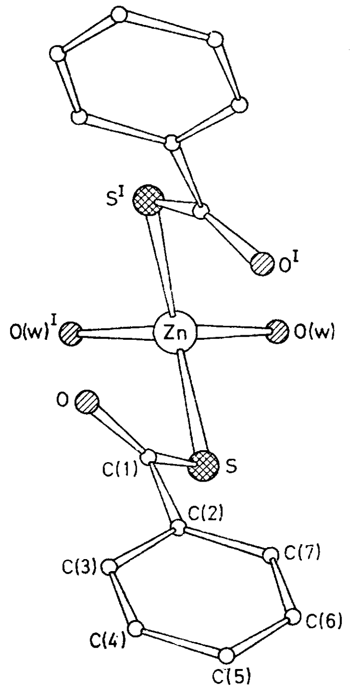

FIGURE 1 Projection of the molecule along the two-fold axis

Table 1 gives final parameters for the crystal-chemical unit. Observed and calculated structure factors, based on the final atomic parameters, are listed in Supplementary

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[5] V. V. Savant, J. Gopalakrishnan, and C. C. Patel, *Inorg. Chem.*, 1970, 748.

[6] G. Mazzone, A. Vaciago, and M. Bonamico, *Ricerca Sci.*, 1963, **33**, 1113.

[7] D. C. Phillips, *Acta Cryst.*, 1954, **7**, 746.

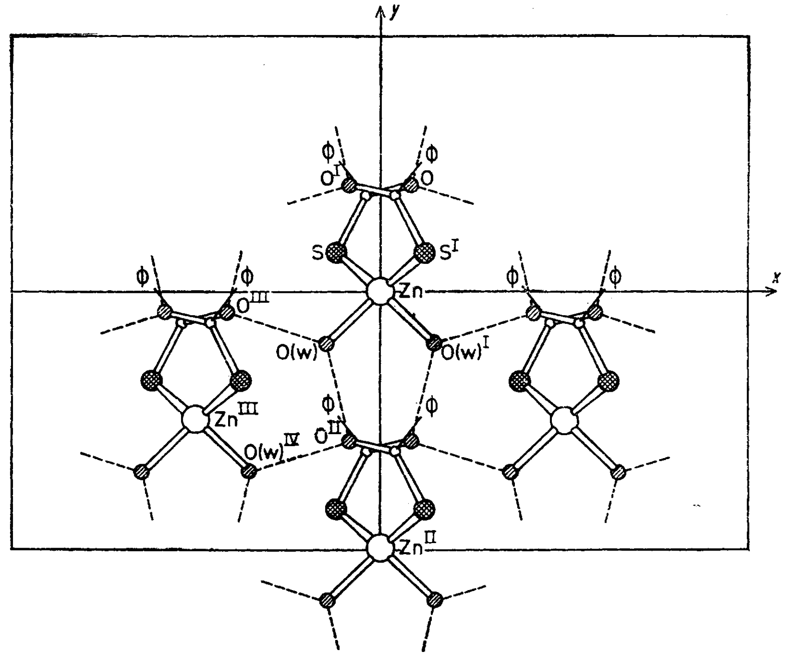

FIGURE 2 Partial projection of the structure along the *c* axis, on the (001) plane, showing the hydrogen-bond system. Roman numeral superscripts are defined in Table 2

Publication No. SUP 21502 (6 pp., 1 microfiche).* Bond distances and angles are listed in Table 2.

Calculations were carried out on a Univac 1108 Computer of Rome University. Intensity corrections, scaling, Wilson plot, Fourier syntheses, and interatomic distances and angles were calculated by use of the programs of ref. 8, and structure factors and least-square planes calculations, and least-squares refinement, by the programmes of ref. 9. Neutral atomic scattering factors, corrected for anomalous dispersion in the case of zinc and sulphur atoms, were taken from ref. 10.

TABLE 2

Main distances (Å) and angles (°), with standard deviation in parentheses

(*a*) Distances			
Zn–S	2.278(2)	C(1)–C(2)	1.50(1)
Zn–O	3.293(7)	C(2)–C(3)	1.38(1)
Zn–O(W)	2.031(6)	C(2)–C(7)	1.41(1)
O(W)–O^{II}	2.765(9)	C(3)–C(4)	1.39(1)
O(W)–O^{III}	2.701(9)	C(4)–C(5)	1.39(2)
C(1)–S	1.729(8)	C(5)–C(6)	1.33(2)
C(1)–O	1.250(7)	C(6)–C(7)	1.38(1)
(*b*) Angles			
S–Zn–O(W)	101.2(2)	O–C(1)–C(2)	119.7(7)
S–Zn–S^{I}	125.7(2)	C(1)–C(2)–C(3)	118.8(6)
S–Zn–O(W)^{I}	115.2(2)	C(1)–C(2)–C(7)	121.2(7)
O(W)–Zn–O(W)^{I}	94.5(2)	C(3)–C(2)–C(7)	120.1(7)
Zn–S–C(1)	105.0(2)	C(2)–C(3)–C(4)	118.7(8)
O^{II}–O(W)–O^{III}	122.6(5)	C(3)–C(4)–C(5)	121.0(10)
O(W)–O^{II}–O(W)^{IV}	92.0(5)	C(4)–C(5)–C(6)	119.2(9)
S–C(1)–O	124.9(6)	C(5)–C(6)–C(7)	122.8(9)
S–C(1)–C(2)	115.3(4)	C(2)–C(7)–C(7)	118.2(8)

Roman numeral superscripts refer to the following equivalent positions, relative to the reference molecule at x,y,z:

I $\bar{x}, y, \bar{z}$ III $x - \frac{1}{2}, y - \frac{1}{2}, z$
II $\bar{x}, y - 1, \bar{z}$ IV $\frac{1}{2} - x, y - \frac{1}{2}, \bar{z}$

DISCUSSION

Description of the Structure.—The molecule is illustrated in Figure 1, and Table 2 gives bond lengths and angles. The zinc atom lies on the symmetry axis of the cell, and the monothiobenzoate groups bond as unidentate ligands through sulphur. The co-ordination group around zinc is a distorted tetrahedron, and consists of two sulphur atoms from two equivalent ligand molecules, and two oxygen atoms from two equivalent water molecules.

The Zn–O bond length is 2.031(6) Å, longer than the sum (1.96 Å) of covalent radii[11] found in other tetrahedral zinc complexes, *e.g.* bis(thiourea)zinc acetate.[12]

The Zn–S distance [2.278(2) Å] is significantly shorter than either the sum of the covalent radii (2.35 Å)[11] or the short distances found in zinc dithiobenzoate and thiocarbamate complexes: 2.307(5) in Zn(SSCPh)$_2$ and 2.311(5) Å in Zn[SOCN(CH$_2$)$_5$]$_2$·(NC$_5$H$_{11}$)$_2$ (refs. 4 and 13).

This last-mentioned compound is very similar to (III). Both are monomeric, and the two ligand groups are unidentate through sulphur. The main difference between them regards the nature of the other two molecules in the co-ordination tetrahedron: piperidine in the first one, in the second water molecules, which take part in a close two-dimensional network of

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

[8] A. Domenicano and A. Vaciago, unpublished work.

[9] R. Spagna and J. B. Carruthers, unpublished work.

[10] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[11] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., 1960, Cornell University Press, Ithaca, New York.

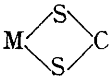
[12] L. Cavalca, G. Fava Gasparri, G. D. Andretti, and P. Damiano, *Acta Cryst.*, 1967, **22**, 90.

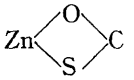
[13] C. G. Pierpont, D. L. Greene, and B. J. McCormick, *J.C.S. Chem. Comm.*, 1972, 960.

hydrogen bonds with the unco-ordinated oxygen atom of the thiocarboxylate groups (see Figure 2 and Table 2). We consider that the hydrogen bonds play an important role in determining the above-mentioned values for the Zn–O distance.

The C–S and C–O bond lengths [1.729(8) and 1.250(7) Å] are comparable to the values found in nickel(II) monothiobenzoate [2] [1.71(1) and 1.25(1) Å].

In addition, the C–C(Ph) distance [1.50(1) Å] and the lack of co-planarity between the phenyl rings and the thiocarboxylic groups show that the structure of the ligand is essentially the same in the two complexes, even if the mode of bonding to the metal is very different.

Comparison between the structures of zinc mono- and di-thiobenzoate [4] complexes shows that, as for the analogous nickel(II) complexes,[12] the substitution of an oxygen for sulphur atom results in a bridging (in this case *via* hydrogen bonds), instead of chelating, thiocarboxylate ligand. We have already discussed the main factors determining the existence of four-membered chelate rings of the type  in the structure of bis(dithiobenzoate)zinc(II).[4] Conjugation was one of the major factors. However, the monothiobenzoate ligand is not conjugated: the phenyl ring is not co-planar with the monothiocarboxylate group, the angle between them being 42.6(5)°.

This fact, together with the strong strain occurring in a chelate ring of the type  caused by the reduced dimensions of the oxygen atom and the tetrahedral geometry, could explain the unidentate character which the monothiocarboxylate group presents either in thiocarbamate or in thiobenzoate zinc tetrahedral complexes.

[5/566 *Received*, 24*th March*, 1975]