Crystal Structure of a Tetrahedral Zinc(II) Complex of a 1,3-Dithiolate: Bis(*O*-ethyl thioacetothioacetato)zinc(II)

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The crystal and molecular structure of the title compound [Zn(*O*-Etsacsac)$_2$] has been determined by *X*-ray diffraction methods. Crystals are monoclinic, a = 22·769(3), b = 5·2615(3), c = 14·907(3) Å, and β = 106·33(1)° with space group $C2/c$ and Z = 4. The structure was solved by Patterson and Fourier methods and refined by a least-squares method to R 0·054 for 1480 independent reflections, collected on a diffractometer. The crystals are composed of discrete monomeric molecules. Each zinc atom is bonded to two ligand groups, which are related by a two-fold axis, with four sulphur atoms approximately tetrahedrally arranged about the metal atom. The Zn–S bond lengths are *ca.* 2·30 Å. The bond distances in the chelate ring indicate aromatic character with a lone pair on the ethoxy-oxygen being involved in the delocalization.

UNTIL recently, 1,3-dithiolate complexes have been restricted to the dithioacetylacetonate derivatives of Group VIII transition elements. This is due mainly to the difficult preparative procedure necessitated by the fact that the free ligand cannot be isolated.[1] Hendrickson and Martin [2] have used the self-condensation of *O*-ethyl thioacetate to prepare *O*-ethyl thioacetatothioacetate (1-ethoxy-3-mercaptobut-2-ene-1-thione), abbreviated as *O*-EtsacsacH, and with this ligand, have synthesized complexes of the type [M(*O*-Etsacsac)$_2$] (where M = Zn, Cd, Hg, Ni, Pd, and Pt). We report here the crystal structure of (I), bis(*O*-ethyl thioacetothioacetato)zinc(II).[3]

EXPERIMENTAL

Data Collection.—Pale yellow needle crystals separated from a solution of (I) in light petroleum which was allowed to evaporate slowly.

Weissenberg photographs, taken about the b (the needle direction) and c axes, showed that the crystals were monoclinic with the systematic extinctions indicating the space group to be either $C2/c$ or Cc; [4] a satisfactory solution was obtained by use of $C2/c$. Crystal data were obtained by use of a Siemens automatic single-crystal diffractometer with cell dimensions derived from the θ values measured for 12 high-angle reflections and refined by a least-squares procedure.[5]

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[1] R. L. Martin and I. M. Stewart, *Nature*, 1966, **210**, 522.

[2] A. R. Hendrickson and R. L. Martin, *Austral. J. Chem.*, 1972, **25**, 257; *Inorg. Chem.*, 1973, **12**, 2582.

[3] R. Beckett and B. F. Hoskins, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 679.

[4] 'International Tables for *X*-Ray Crystallography,' vol. I, Kynoch Press, Birmingham, 1952.

[5] W. R. Busing, R. D. Ellison, H. A. Levy, S. P. King, and R. T. Roseberry, Oak Ridge National Laboratory, Report ORNL 4143, 1968.

A crystal with dimensions 0·12 × 0·40 × 0·20 mm was mounted with the crystallographic b axis along the θ axis of the diffractometer and data collected by the five values θ—2θ scan method,[6] to a Bragg angle of 70°. During data collection, the check reflection was found to decrease gradually in intensity and finally diminished to *ca.* 90% of its initial value. The remeasurement of several other reflections showed a similar decrease and, since the compound was somewhat volatile, this reduction in intensity was probably due to a gradual decrease of the crystal volume. The intensity data were scaled according to the variation in the check reflection.

A total of 2052 unique reflections were recorded, of which 1480 were considered to be observed on the basis of the 3σ criterion. Corrections were made for Lorentz, polarization, and absorption [7] factors, but not for extinction.

Crystal Data.—$C_{12}H_{18}O_2S_4Zn$, $M = 387{\cdot}8$, Monoclinic, $a = 22{\cdot}769(3)$, $b = 5{\cdot}2615(3)$, $c = 14{\cdot}907(3)$ Å, $\beta = 106{\cdot}33(2)°$, $U = 1713{\cdot}8$ Å^3, $D_m = 1{\cdot}49$, $Z = 4$, $D_c = 1{\cdot}503$ g cm^{-3}. Space group $C2/c$ (C^6_{2h}, No. 15). Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = 63·6 cm^{-1}. Single-crystal oscillation and Weissenberg photographs, Siemens automatic diffractometer, absorption corrections applied.

Structure Determination.—If it is assumed that the space group is $C2/c$ the zinc atoms must lie on special positions, probably of the type $(0,y,\frac{1}{4})$, *etc.* A solution to the Patterson function gave zinc and sulphur positions, with the zinc atom situated on a crystallographic two-fold axis and the sulphur atoms arranged tetrahedrally around it. The remaining non-hydrogen atom positions were obtained from a three-dimensional electron-density map phased by use of the zinc and sulphur positions.

TABLE 1

Final atomic co-ordinates and thermal parameters * (Å^2 × 10^4), with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn	0·00000(0)	0·03605(12)	0·25000(0)	268(4)	494(4)	428(4)	0(0)	81(3)	0(1)
S(1)	0·02905(4)	−0·21706(18)	0·14121(6)	306(4)	601(6)	472(5)	−1(3)	36(4)	−132(4)
S(2)	0·08618(4)	0·25390(16)	0·32320(6)	349(4)	472(5)	492(5)	−50(3)	94(4)	−92(3)
O	0·13357(12)	−0·41151(51)	0·13557(18)	408(12)	530(13)	459(13)	−3(11)	147(10)	−117(10)
C(1)	0·10569(15)	−0·24439(60)	0·17846(22)	341(13)	416(16)	379(15)	−9(12)	119(12)	−4(12)
C(2)	0·14974(14)	−0·10741(75)	0·24821(23)	279(12)	557(19)	433(16)	−19(14)	72(12)	−37(15)
C(3)	0·14695(14)	0·09170(70)	0·30562(21)	284(12)	516(18)	353(15)	−32(13)	63(11)	25(13)
C(4)	0·20744(18)	0·1935(10)	0·36563(32)	315(15)	839(30)	724(26)	−97(18)	5(17)	−245(23)
C(5)	0·09768(20)	−0·57536(76)	0·06233(26)	546(19)	546(20)	438(18)	−66(17)	129(16)	−127(15)
C(6)	0·14219(25)	−0·73984(87)	0·03176(32)	789(27)	604(24)	619(23)	−12(21)	361(23)	−125(19)
H(1)	0·1909	−0·1299	0·2369	282	548	440	−20	79	−43
H(2)	0·0777	−0·5195	0·0178	546	528	475	−70	155	−148
H(3)	0·0660	−0·6891	0·0861	546	528	475	−70	155	−148

* The temperature factor expression is $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + 2U_{12}hkab + \ldots etc.)]$.

Refinement was achieved by the full-matrix least-squares method minimizing the function $\Sigma w\Delta^2$, where Δ is $\Sigma w(|F_o| - |F_c|)$, w being the weight applied to each reflection.

The data were weighted according to the scheme of ref. 8, so that each reflection was assigned a weight according to the equation: $w = [\sigma_{cs}^2 + 0{\cdot}005F_o^2 + 0{\cdot}0001 \sum_{i=1}^{m} f_i^2]^{-1}$.

Anisotropic temperature factors were used and refinement was continued until all parameters had converged.

A difference Fourier map computed at this stage revealed the positions of the hydrogen atoms attached to C(2) and C(5), but no peaks were found near the methyl carbon atoms [C(4) and C(6)]. The hydrogen atoms found were included in the refinement with an arbitrary temperature factor equal to that of the carbon to which they are attached. Two cycles varying only the hydrogen positional co-ordinates followed by two cycles varying all the other atom parameters resulted in convergence of $\Sigma w\Delta^2$ and the parameters, with a final R 0·054 and weighted residual R' 0·081.

Final co-ordinates and temperature factor parameters are given in Table 1. The scattering factors for zinc(II), sulphur, oxygen, carbon, and hydrogen were taken from ref. 9, the zinc and sulphur values being corrected for the effects of anomalous dispersion.[10] Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21256 (7 pp., 1 microfiche).*

RESULTS AND DISCUSSION

The crystal structure of (I) consists of molecular units situated along two-fold crystallographic axes of the type $(0,y,\frac{1}{4})$. There are no abnormally short intermolecular distances, the shortest contact between non-hydrogen atoms being 3·52 Å between a sulphur [S(2)] of one molecule of centre $(0,y,\frac{1}{4})$ and a ring carbon [C(1)] of a neighbouring molecule centred at $(0,1 + y,\frac{1}{4})$. The usual van der Waals distance between these atoms is *ca.* 3·53 Å.[11]

The packing of the molecules in the unit cell is illustrated in Figures 1 and 2, and the molecular geometry and labelling of atoms is given in Figure 3. Bond lengths and bond angles are listed in Tables 2 and 3.

The fact that (I) is monomeric, whereas bis(acetylacetonato)zinc(II),[12] as well as zinc(II) derivatives of many

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[6] W. Hopper, *Angew. Chem. Internat. Edn.*, 1965, **6**, 508; 'Automatic Single-Crystal Diffractometer AED According to W. Hoppe,' users' manual for Siemens Automated Diffractometer.

[7] G. W. Cox, personal communication; W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.

[8] R. C. G. Killean, *Acta Cryst.*, 1967, **23**, 54, 1109; D. F. Grant, R. C. G. Killean, and J. L. Lawerence, *Acta Cryst.*, 1969, **B25**, 374.

[9] Ref. **4**, Vol. III, p. 201, *et seq.*

[10] Ref. 9, p. 214.

[11] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, p. 260; A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

[12] M. J. Bennett, F. A. Cotton, R. Eiss, and R. C. Elder, *Nature*, 1967, **213**, 174.

bidentate sulphur chelates, have been found to be polymeric in the solid state, is in agreement with the trends found for dithioacetylacetonate derivatives of other bivalent metals. Thus, the cobalt(II)[13] and nickel(II)[14] derivatives of acetylacetone are polymeric, but the corresponding dithioacetylacetonates have simple monomeric structures.[15]

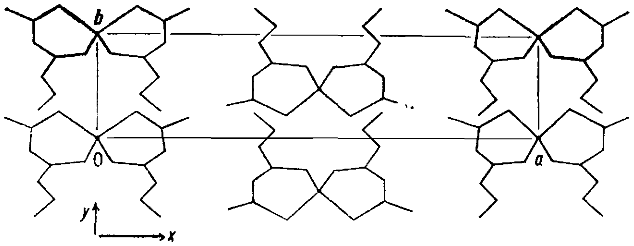

FIGURE 1 Projection of the crystal structure of (I) on the (001) plane

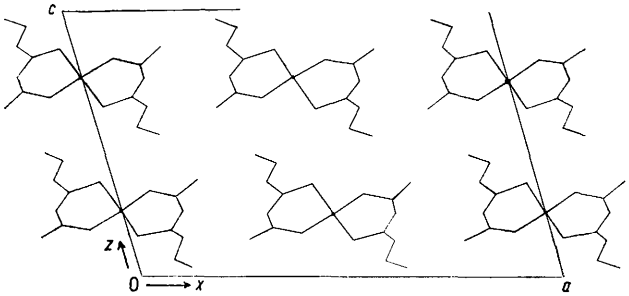

FIGURE 2 Projection of the crystal structure on the (010) plane

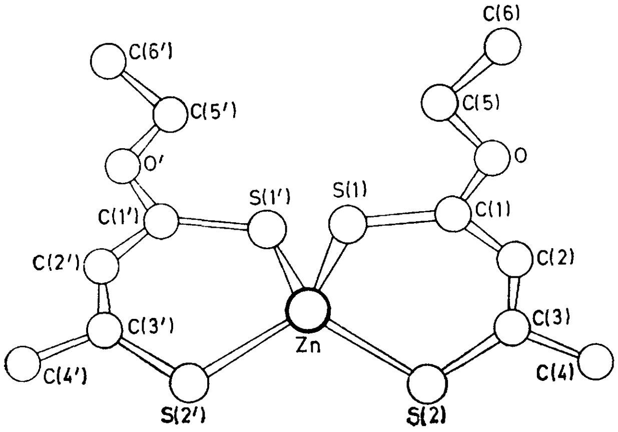

FIGURE 3 The molecular structure and labelling of the atoms

The Metal Environment.—Each zinc atom is surrounded by two *O*-ethyl thioacetothioacetate ligands, which are related by a two-fold axis with the four sulphur atoms approximately tetrahedrally arranged about the metal atom. A distortion from tetrahedral stereochemistry is seen by the decrease in the intraligand S(1)–Zn–S(2) angle from 109·5 to 104·38(3)°, and a substantial increase in the interligand S(2)–Zn–S(2') angle to 119·33(6)°.

The two independent Zn–S distances [2·333(1) and 2·270(1) Å] are in agreement with previously reported distances which usually fall in the range 2·2—2·5 Å,[16] and the difference of 0·063 Å is significant, the longer distance being associated with the sulphur closest to the ethoxy-group. There does not appear to be any simple explanation for this, but the introduction of a π-donor substituent asymmetrically on the ligand, as here, could cause such a perturbation to the bond lengths. A similar effect is observed in the structure of bis(ethylacetoacetato)copper(II).[17]

The Ligand.—The chelate rings in (I) possess similar features to those in metal complexes of the related ligand dithioacetylacetone.[15,18] Thus the entire ligand moiety in (I) is essentially planar with the zinc atom lying 0·470 Å out of this plane. This corresponds to a dihedral angle of 19·5° between the plane through the ligand, and that through atoms S(1), Zn, and S(2).

TABLE 2

Bond lengths (Å) in (I)

Zn–S(1)	2·333(1)	C(2)–C(3)	1·366(5)
Zn–S(2)	2·270(1)	C(3)–C(4)	1·514(5)
S(1)–C(1)	1·682(4)	C(5)–C(6)	1·498(6)
S(2)–C(3)	1·707(4)	C(2)–H(1)	1·00
C(1)–O	1·337(4)	C(5)–H(2)	0·75
C(5)–O	1·459(5)	C(5)–H(3)	1·07
C(1)–C(2)	1·421(5)		

TABLE 3

Bond angles (°) in (I)

S(1)–Zn–S(2)	104·28(3)	C(2)–C(1)–O	110·2(3)
S(1)–Zn–S(1')	110·39(6)	C(2)–C(3)–C(4)	116·5(3)
S(1)–Zn–S(2')	109·26(3)	C(1)–O–C(5)	120·3(3)
S(2)–Zn–S(2')	119·33(3)	O–C(5)–C(6)	106·8(4)
Zn–S(1)–C(1)	106·9(1)	C(1)–C(2)–H(1)	108·5
Zn–S(2)–C(3)	107·6(1)	C(3)–C(2)–H(1)	113·9
S(1)–C(1)–C(2)	130·6(3)	O–C(5)–H(2)	120·7
S(2)–C(3)–C(2)	131·5(3)	O–C(5)–H(3)	111·4
C(1)–C(2)–C(3)	134·4(3)	C(6)–C(5)–H(2)	104·4
S(1)–C(1)–O	119·1(3)	C(6)–C(5)–H(3)	110·8
S(2)–C(3)–C(4)	112·0(3)	H(2)–C(5)–H(3)	102·4

The C–C and C–S bond lengths in the chelate ring are in the range expected for a delocalized system[19] but, in addition, the short C(1)–O distance [1·337(4) Å] suggests that a lone pair on the oxygen atom is also involved in the delocalization. This is supported by the fact that the

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[13] F. A. Cotton and R. C. Elder, *J. Amer. Chem. Soc.*, 1965, **4**, 1145.

[14] G. J. Bullen, R. Mason, and P. Pauling, *Inorg. Chem.*, 1965, **4**, 456.

[15] R. Beckett and B. F. Hoskins, *Chem. Comm.*, 1967, 909; *J.C.S. Dalton*, 1974, 622.

[16] I. D. Brown, C. P. Weiss, and K. K. Wu, 'Bond Index to the Determinations of Inorganic Crystal Structures,' McMaster University, Hamilton, Ontario, 1969, 1970, and 1971.

[17] G. A. Barclay and A. Cooper, *J. Chem. Soc.*, 1965, 3746.

[18] R. Beckett and B. F. Hoskins, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 683; R. Beckett, G. A. Heath, B. F. Hoskins, B. P. Kelly, R. L. Martin, I. A. G. Roos, and P. L. Weickhardt, *ibid.*, 1970, **6**, 257; R. Beckett, Ph.D. Thesis, University of Melbourne, 1972, p. 46.

[19] *Chem. Soc. Special Publ.*, No. 11, 1958, and No. 18, 1965.

ethoxy-group atoms oxygen and C(5) are coplanar with the rest of the ligand, and the angle C(1)–O–C(5) is 120·3(3)°.

Although the bond lengths in the chelate rings are similar to those observed in analogous systems,[15,18] there are significant differences between almost chemically equivalent bond lengths. Thus the C(1)–C(2) and C(2)–C(3) bond lengths differ considerably [1·421(5) and 1·366(6) Å] and there is a small, but nevertheless significant, difference in the S(1)–C(1) and S(2)–C(3) distances [1·682(4) and 1·707(4) Å]. The mean C–C and C–S distances found for the chelate rings of dithioacetylacetonate complexes are 1·385 and 1·681 Å. Similar trends have been reported for the ligand bond lengths in bis(ethylacetoacetato)copper(II).[17]

An explanation for most of these observations in the bond lengths can be given in terms of a simple mesomeric effect if, in addition to the two canonical structures usually considered in these complexes, there is a significant contribution to the structure of a third canonical form: $CH_3{\cdot}C(S^-){:}CH{\cdot}C(S^-){:}O^+Et$.

The ligand ' bite ' [S(1)–S(2) 3·63 Å] is less than required (3·88 Å) to span the regular tetrahedral positions of the zinc atom, but is much greater than that expected (2·40 Å) if the normal valency requirements of the carbon atoms of the chelate ring were the only determining factor. This appears to be due to a balance of several factors. The repulsion between the sulphur atoms, which have a van der Waals distance of *ca.* 3·52 Å,[11] and the strain in the S(1)–Zn–S(2) angle tend to increase the ' bite ' from 2·40 Å, whereas the internal C–C–C and C–C–S angles of the chelate ring, which are larger than expected for sp^2 hybridized atoms, would tend to decrease the ' bite ' from 3·88 Å.

Two of the hydrogen atoms have fairly normal C–H bond lengths (1·07 and 1·00 Å), but the third, H(2), attached to C(5), is 0·75 Å, which is unreasonably short. This anomaly is also reflected in the bond angles involving this hydrogen atom. However, hydrogen-atom positions obtained by *X*-ray methods are often subject to rather large systematic errors,[20] accentuated in this case because of the simple treatment of their thermal motion.[21]

We thank the Australian Research Grants Committee for financial support.

[4/1510 *Received, 22nd July,* 1974]

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