Crystal Structure of Bis(dithiobenzoato)zinc(II): a Structure Containing Two Four-membered Chelate Rings

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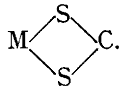
The crystal and molecular structure of the title compound has been determined from photographic X-ray data by Patterson and Fourier methods and refined by anisotropic least-squares methods to R 0·071 for 1200 observed reflections. The presence of two four-membered rings in the monomeric unit and the resulting severe distortion of the zinc co-ordination tetrahedron proves that conjugation on the whole ligand molecule is a determining factor in allowing such chelation to exist.

The crystals are triclinic, space group $P\bar{1}$ with $Z = 2$ in a unit cell of dimensions $a = 8·804 \pm 0·01$, $b = 8·123 \pm 0·01$, $c = 11·208 \pm 0·01$ Å, $\alpha = 87° 35' \pm 10'$, $\beta = 111° 2' \pm 10'$, $\gamma = 90° 32' \pm 10'$.

FOUR-MEMBERED chelate rings in metal complexes produce some strain on the metal co-ordination angles, and consequently an increase in bonding molecular orbital energy levels. The amount depends on two main factors: (*a*) the dimensions of the atoms in the ring and (*b*) the co-ordination geometry, the greatest strain being on the tetrahedral form. From our previous studies on transition-metal complexes with sulphur-containing bidentate ligands, conjugation on the ligand molecule seems to be an important factor in determining the existence of chelate rings of the type . This may be explained in terms of the repulsion between the electron pairs in the valence shell of the metal atom: such repulsion increases rapidly as the distances between the electron pairs decreases, so that the orbitals occupied by two of them begin to overlap to a significant extent.[1-3] Some degree of conjugation, causing electron delocalization and a compensating effect on the increase of the molecular orbital energy levels, could reduce the repulsion and allow distortion in the co-ordination geometry. In the tetrahedral zinc complexes with S_2C–R ligands, distortion is very large, the S–Zn–S′ angle being *ca.* 76°. Therefore, according to our interpretation, a high degree of conjugation in the ligand molecule would be necessary for chelation to occur. In agreement with this, in zinc *O*-ethyl dithiocarbonate,[4] there is unlikely to be conjugation in the ligand molecule and rings are not formed. Each zinc atom co-ordinates to four sulphur atoms of different ligands, which bridge two adjacent

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[1] R. J. Gillespie, *Canad. J. Chem.*, 1961, **39**, 318.

[2] R. J. Gillespie, *Canad. J. Chem.*, 1960, **38**, 818.

[3] R. J. Gillespie, *J. Amer. Chem. Soc.*, 1960, **82**, 5978.

[4] Takuro Ikeda and Hitosi Hagihara, *Acta Cryst.*, 1966, **21**, 919.

zinc atoms to complete a two-dimensional network. In zinc diethyl dithiocarbamate[5] and dimethyl dithiocarbamate[6] ($R = NEt_2$ and NMe_2), there is some conjugation in the ligand, and only one $S_2C{-}R$ group is chelated to the same zinc atom; the other bridges the zinc atoms of two neighbouring molecules, with formation of a binuclear complex. This strongly suggests that in a complex with a highly conjugated ligand, such as dithiobenzoate,[7,8] double chelation could occur. Since, to our knowledge, no zinc tetrahedral complexes with double chelation are known, the *X*-ray analysis of the title compound $Zn(S_2CPh)_2$ has been performed.

EXPERIMENTAL

Preparation.—The compound was prepared according to the method of Houben[9] and crystallized from CS_2 as red-orange needles, elongated along [010].

Crystal Data.—$C_{14}H_{10}S_4Zn$, $M = 371{\cdot}844$, Triclinic, $a = 8{\cdot}804 \pm 0{\cdot}01$, $b = 8{\cdot}123 \pm 0{\cdot}01$, $c = 11{\cdot}208 \pm 0{\cdot}01$ Å, $\alpha = 87° 35' \pm 10'$, $\beta = 111° 2' \pm 10'$, $\gamma = 90° 32' \pm 10'$, $U = 747$ Å^3, $D_m = 1{\cdot}65 \pm 0{\cdot}02$ (by flotation), $Z = 2$, $D_c = 1{\cdot}653$, $F(000) = 374{\cdot}99$. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = 71·7 cm^{-1}. Space group $P\bar{1}$ (C_i^1, No. 2) from the structure determination. The unit-cell dimensions were determined by a modified, improved version of Christ's method[10] from zero-layer Weissenberg film taken about the *b* axis, and precession photographs taken about the *a* and *c* axes, by use of reflections from Cu-K_α radiation and, if possible, from Cu-$K_{\alpha 1}$ radiation ($\lambda = 1{\cdot}54056$ Å).

TABLE 1

Co-ordinates (× 10⁴) 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	1647(2)	2518(2)	1217(2)	267(4)	49(6)	233(4)	230(5)	−24(4)	141(2)
S(1)	1300(4)	1060(5)	−610(3)	216(5)	−87(11)	210(8)	248(9)	−90(9)	151(4)
S(2)	4048(4)	3150(5)	789(3)	226(6)	−81(11)	171(8)	266(10)	−100(9)	143(4)
S(3)	1464(4)	1699(5)	3218(3)	268(6)	183(12)	192(8)	218(9)	48(8)	134(4)
S(4)	−344(5)	4221(5)	1382(3)	293(7)	192(12)	227(9)	252(10)	100(8)	135(4)
C(1)	3179(12)	1912(14)	−425(10)	138(16)	−5(30)	99(23)	126(27)	−3(25)	119(12)
C(8)	13(14)	3120(16)	2794(10)	209(20)	−7(38)	102(25)	167(29)	−21(27)	99(12)
				B/Å^2					
C(2)	3973(13)	1569(15)	−1328(10)	4·51(22)					
C(3)	3188(15)	658(18)	−2388(12)	5·73(27)					
C(4)	3955(16)	341(18)	−3247(12)	6·14(29)					
C(5)	5456(16)	990(19)	−3047(12)	6·14(29)					
C(6)	6299(16)	1924(19)	−2032(13)	6·43(30)					
C(7)	5550(15)	2180(18)	−1153(12)	5·53(26)					
C(9)	−944(13)	3431(15)	3614(10)	4·46(22)					
C(10)	−516(15)	2674(17)	4823(11)	5·52(26)					
C(11)	−1377(15)	2990(17)	5610(12)	5·54(26)					
C(12)	−2688(15)	3982(17)	5136(12)	5·56(26)					
C(13)	−3126(16)	4671(18)	3942(12)	6·05(28)					
C(14)	−2264(14)	4417(17)	3161(11)	5·37(25)					
H(3)	2070	227	−2538	6·00					
H(4)	3414	−352	−3999	6·00					
H(5)	5977	770	−3684	6·00					
H(6)	7391	2394	−1929	6·00					
H(7)	6139	2813	−376	6·00					
H(10)	428	1891	5132	6·00					
H(11)	−1034	2496	6500	6·00					
H(12)	−3348	4213	5674	6·00					
H(13)	−4115	5393	3615	6·00					
H(14)	−2607	4947	2283	6·00					

* Exponential coefficients b_{ij} as given here are defined by $T = \exp 10^{-4}(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)$.

Intensity Measurements and Data Reduction.—The intensities of 1200 independent reflections above film background (*ca.* 35% of the total possible with Cu-K_α radiation) were estimated visually from sets of multiple-film equi-inclination Weissenberg photographs taken about the *b* axis (6 layers *h*0—5*l*), from a needle-shape crystal (*ca.* 0·05 mm of radius).

The data were corrected for Lorentz and polarization effects, and for spot extension.[11] 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. The positional, and isotropic thermal parameters of the non-hydrogen atoms ($\bar{B} = 3{\cdot}5$ Å^2 by Wilson's method) were refined by several cycles of a full-matrix least-squares, the function minimized being $\Sigma w(|F_o| - k|F_c|)$.[2]

At this stage *R* was 0·146. The hydrogen atoms of the phenyl groups were then included at calculated positions, and with the average isotropic temperature factor of the atoms to which they were linked. Further refinement for non-hydrogen atomic parameters reduced *R* to 0·140. Refinement was then continued for non-hydrogen atoms, by use of isotropic thermal parameters for the carbon atoms of the phenyl groups, and anisotropic thermal parameters for all the other atoms. Convergence was achieved after five cycles with a final *R* of 0·071. The final shifts in the atomic parameters were all $< 0{\cdot}2\sigma$.

[5] M. Bonamico, G. Mazzone, A. Vaciago, and L. Zambonelli, *Acta Cryst.*, 1965, **19**, 898.

[6] H. P. Klug, *Acta Cryst.*, 1966, **21**, 536.

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

[8] M. Bonamico and G. Dessy, *Chem. Comm.*, 1968, 483.

[9] J. Houben, *Ber.*, 1906, **39**, 3225.

[10] G. Mazzone, A. Vaciago, and M. Bonamico, *Ricerca sci.*, 1963, **33** (II*A*), 1113.

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

The weighting scheme $w = (a + bF_o + cF_o^2)^{-1}$ was used throughout the refinement, with $a = 2{\cdot}0$, $b = 1{\cdot}0$, and $c = 0{\cdot}01$.

TABLE 2

Bond lengths (Å) and angles (°), with estimated standard deviations in parentheses

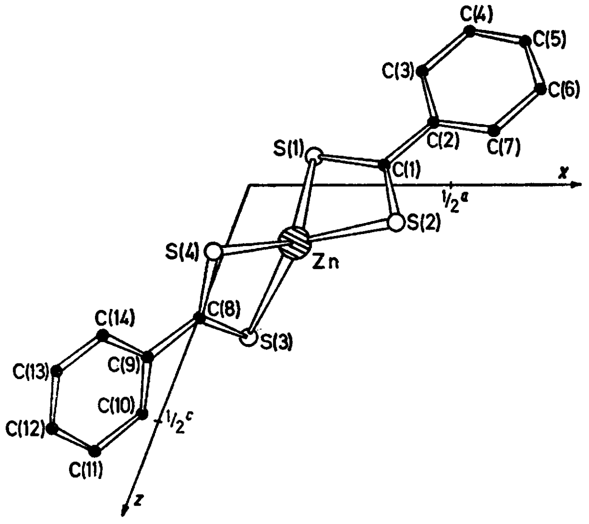
(*a*) Distances

Zn–S(1)	2·332(4)	C(3)–C(4)	1·39(2)
Zn–S(2)	2·377(4)	C(4)–C(5)	1·36(2)
Zn–S(3)	2·373(4)	C(5)–C(6)	1·37(2)
Zn–S(4)	2·307(5)	C(6)–C(7)	1·39(2)
S(1)–C(1)	1·73(1)	C(2)–C(7)	1·42(2)
S(2)–C(1)	1·67(1)	C(9)–C(10)	1·39(2)
S(3)–C(8)	1·65(1)	C(10)–C(11)	1·39(2)
S(4)–C(8)	1·71(1)	C(11)–C(12)	1·34(2)
C(1)–C(2)	1·46(2)	C(12)–C(13)	1·35(2)
C(8)–C(9)	1·48(2)	C(13)–C(14)	1·37(2)
C(2)–C(3)	1·38(2)	C(9)–C(14)	1·35(2)

(*b*) Angles

S(1)–Zn–S(2)	77·1(1)	C(1)–C(2)–C(3)	120(1)
S(1)–Zn–S(3)	131·8(2)	C(1)–C(2)–C(7)	121(1)
S(1)–Zn–S(4)	122·5(1)	C(8)–C(9)–C(10)	120(1)
Zn–S(1)–C(1)	82·0(4)	C(8)–C(9)–C(14)	119(1)
S(2)–Zn–S(3)	127·2(1)	C(2)–C(3)–C(4)	120(1)
S(2)–Zn–S(4)	130·6(2)	C(3)–C(2)–C(7)	119(1)
Zn–S(2)–C(1)	81·8(4)	C(3)–C(4)–C(5)	119(1)
S(3)–Zn–S(4)	76·1(2)	C(4)–C(5)–C(6)	124(2)
Zn–S(3)–C(8)	82·5(5)	C(5)–C(6)–C(7)	116(1)
Zn–S(4)–C(8)	83·4(5)	C(6)–C(7)–C(2)	122(1)
S(1)–C(1)–S(2)	119·0(8)	C(9)–C(10)–C(11)	121(1)
S(1)–C(1)–C(2)	120·2(8)	C(10)–C(9)–C(14)	120(1)
S(2)–C(1)–C(2)	120·8(8)	C(10)–C(11)–C(12)	118(1)
S(3)–C(8)–S(4)	117·9(8)	C(11)–C(12)–C(13)	121(1)
S(3)–C(8)–C(9)	120·9(8)	C(12)–C(13)–C(14)	122(1)
S(4)–C(8)–C(9)	121·2(9)	C(13)–C(14)–C(9)	118(1)

Table 1 gives the final atomic parameters for the crystal-chemical unit. Observed and calculated structure factors, based on the final atomic parameters, are listed in Supplementary Publication No. SUP 20500 (5 pp., 1 microfiche).* Bond distances and angles within the formula unit are listed in Table 2. A projection of the structure is shown in the Figure.



Calculations.—Calculations were carried out on a UNIVAC 1108 computer at Rome University. Intensity corrections, scaling, Wilson plot, Fourier syntheses, and interatomic distances and angles were calculated by use of programmes written by Domenicano and Vaciago.[12] For the structure-factors and least-squares planes calculations, and least-squares refinement, the programmes written by Spagna and Carruthers [13] were used. Neutral atomic scattering factors, corrected for anomalous dispersion in the case of zinc and sulphur atoms, were taken from ref. 14.

DISCUSSION

Description of the Structure.—The crystal structure consists of discrete monomeric units, the shortest intermolecular contacts being 3·47 Å between S(1) and the centrosymmetrically related one. Two dithiobenzoate groups chelate to the same zinc atom, thus forming two four-membered rings. The resultant effect on the configuration of the sulphur atoms about zinc is a high distortion from strict tetrahedral geometry. The six tetrahedral angles (Table 2) differ greatly from the ideal value of 109·5°: the S–Zn–S′ angles within the rings are reduced by ring closure to 76·1(2) and 77·1(1)°; consequently the external S–Zn–S″ angles increase from the expected 109·5° to a mean value of 128·0°, with a range between 122·5(1) and 131·8(2)°. The Zn–S distances vary from 2·307(5) to 2·377(4) Å, in agreement with the value of 2·35 Å calculated from the sum of the tetrahedral covalent radii of zinc and sulphur atoms.[15] The angles at the sulphur atoms (mean 82·4°) are in excellent agreement with the corresponding angles observed in zinc diethyl [5] and dimethyl [6] compounds. The mean sulphur–carbon bond length (1·69 Å) agrees well with those already reported for dithiolato-chelates.[16] The angles about the C(1) and C(8) carbon atoms are not significantly different from the expected value of 120°. Each of the two ligand molecules is planar, maximum and mean deviations of the ligand atoms and zinc atom from the plane of each ligand being 0·06 [for C(7)] and 0·03 Å for one ligand, and 0·16 [for S(4)] and 0·07 Å for the other. The C(1)–C(2) and C(8)–C(9) distances are 1·46(2) and 1·48(2) Å respectively. The planarity and the bond lengths indicate extensive conjugation on the whole ligand molecule.

As mentioned, the main reason for the investigation of the present structure was to check the possibility of a highly conjugated ligand giving double chelation in a tetrahedral zinc complex. The resultant structure proves that conjugation is an important factor in overcoming strain in chelation. If our explanation in terms of electron-pair repulsion is correct, the same effect could be produced by a dithiochelate ligand containing strong electron-attracting groups. Further work in this direction is planned.

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

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