Crystal and Molecular Structure of Triaquazinc(II) Thiodiglycolate Monohydrate

By **Michael G. B. Drew,* David A. Rice,*** and **Christopher W. Timewell,** Department of Chemistry, University of Reading, Whiteknights, Reading RG6 2AD

Crystals of the title compound are orthorhombic, space group $P2_12_12_1$, with a = 7·589(7), b = 9·289(8), c = 14·168(11) Å, Z = 4. The structure was determined from Patterson and Fourier syntheses and refined by least-squares to R 0·041 for 1373 independent reflections measured on a diffractometer. The zinc atom has a distorted octahedral environment, being weakly bonded to a sulphur atom [2·601(2) Å] and five oxygen atoms, one from each of two carboxy-groups [2·029(5), 2·102(5) Å], the remainder from three mutually *cis* water molecules [2·050(5), 2·016(5), 2·098(5) Å]. The two five-membered rings are significantly non-planar. The molecule is considerably distorted from m symmetry, as is shown particularly by the ring conformations and dimensions involving zinc. There is extensive hydrogen bonding.

THE stability constants of the 1 : 1 metal(II) thiodiglycolic acid complexes follow the sequence: Cu > Ni > Zn.[1] This trend is also that of decreasing affinity of sulphur and an identical effect is seen in the stability constants for the 1 : 1 complexes of ethylene dithiodiacetic acid.[1] The only reported molecular and crystal structure of a thioether-containing carboxylic acid metal salt is that of diaquanickel(II) ethylenedithiodiacetate where the nickel–sulphur bond is 2·46 Å.[2] Accordingly we have determined the structure of triaquazinc(II) thiodiglycolate monohydrate to ascertain if this trend in stability constants is related to the length of the metal–sulphur bond and to aid in the assignment of structures of other divalent metal salts of the thioether-containing carboxylic acids.[3]

EXPERIMENTAL

Crystals were prepared by mixing an aqueous solution of thiodiglycolic acid with an excess of zinc hydroxide, and setting aside the filtrate.

Crystal Data.—$C_4H_{12}O_8SZn$, M = 285·6, Orthorhombic, a = 7·589(7), b = 9·289(8), c = 14·168(11) Å, U = 998·76 Å^3, D_c = 1·89, Z = 4, D_m = 1·89(1), $F(000)$ = 584. Mo-K_α radiation λ = 0·7107 Å, μ(Mo-K_α) = 28·3 cm^{-1}, Space group $P2_12_12_1$ from systematic absences: $h00$, $h = 2n + 1$, $0k0$, $k = 2n + 1$, $00l$, $l = 2n + 1$. Equivalent positions (non-standard) were: x, y, z; $\frac{1}{2} - x, \frac{1}{2} + y, -z$; $-x, \frac{1}{2} - y, \frac{1}{2} + z$; and $\frac{1}{2} + x, -y, \frac{1}{2} + z$.

A crystal with dimensions 0·20 × 0·18 × 0·40 mm was mounted with the (310) planes perpendicular to the instrument axis of a General Electric XRD 5 apparatus which was used to measure diffraction intensities and cell dimensions. The instrument was equipped with a manual goniostat, scintillation counter, and pulse-height discriminator. The stationary-crystal–stationary-counter method was used with a 4° take-off angle and a counting time of 10 s. Individual backgrounds were taken for those reflections whose counts were seriously affected by the streaking of other orders. For other reflections, backgrounds were taken from plots of background as a function of 2θ. Several standard reflections monitored during the course of the experiment, showed no significant changes in intensity. 1680 Independent reflections were measured for $2\theta < 60°$. No absorption or extinction corrections were applied. The standard deviations $\sigma(I)$ of the reflections were taken as $[I + 2E + (0{\cdot}03I)^2]^{\frac{1}{2}}$, where I is the intensity and E is the estimated background of the reflection. 1373 Reflections with $I > 3\sigma(I)$ were used in the subsequent refinement.

Structure Determination.—The structure was determined from Patterson and Fourier synthesis and refined by full-matrix least-squares. The weighting scheme, chosen to give average values of $w\Delta^2$ for groups of reflections independent of the values of F_0 and sin θ/λ, was $\sqrt{w} = 1$ for $F_0 < 25$ and $\sqrt{w} = 25/F_0$ for $F_0 > 25$. Calculations were made on an Atlas computer (at S.R.C., Chilton, Berkshire) with the programs described in ref. 4. Atomic scattering factors for zinc, sulphur, carbon, and oxygen were taken from ref. 5, as were the corrections for the real and imaginary parts of the anomalous dispersion for zinc and sulphur. The hydrogen scattering factors were taken from ref. 6. The anisotropic thermal parameter is defined as: exp $-2\pi^2\sum_i\sum_j (h_ih_jb_ib_jU_{ij})$, $i,j, = 1,2,3$, where b_i is the ith reciprocal cell dimension. The isotropic thermal parameter is defined as: $\exp(-8\pi^2U\sin^2\theta/\lambda^2)$. The zinc, sulphur, oxygen, and carbon atoms were refined anisotropically. Two models were refined, in which the effect of the imaginary part of the anomalous dispersion was reversed (*i.e.* with opposing signs for the z co-ordinate). The model with the lowest R value (0·049 *vs.* 0·060) was assumed to be correct. A difference-Fourier map was then calculated and the positions of 8 of the 12 hydrogen atoms were clearly observed in acceptable positions. These hydrogen atoms were included in the refinement. During several cycles, the hydrogen atom parameters did not converge and for subsequent cycles they were fixed at values which were means of those obtained in the last two cycles. Further refinement gave R 0·041. In the final cycle of refinement, all shifts were $<0{\cdot}05\sigma$ and none of the unobserved reflections showed any serious discrepancy. Final atomic co-ordinates and thermal parameters, together with standard deviations, are given in Tables 1 and 2. Final observed and calculated structure factors, together with intermolecular contacts <3·5 Å not listed in Table 4, are in Supplementary Publication SUP 21153 (7 pp., 1 microfiche).* Bond distances and angles are listed in Table 3.

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are supplied as full size copies).

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[2] J. Loub and J. Podlahova, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 409.

[3] C. W. Timewell, Ph.D. Thesis, University of Reading, 1972.

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TABLE 1

Final atomic co-ordinates ($\times 10^5$ for Zn and S, $\times 10^4$ for other atoms), with standard deviations in parentheses

Atom	*x*	*y*	*z*
Zn	14069(9)	27407(7)	09803(5)
S	−11876(22)	13659(16)	01883(11)
O(1)	3048(6)	4203(5)	1614(4)
O(2)	3177(6)	1870(5)	0086(3)
O(3)	1967(7)	0962(5)	1842(3)
O(4A)	−0579(6)	3433(6)	1825(3)
O(5A)	−3389(7)	3858(6)	2128(4)
C(1A)	−2172(9)	3303(7)	1639(5)
C(2A)	−2814(8)	2447(8)	0792(5)
O(4B)	0748(6)	4125(5)	−0139(3)
O(5B)	−0101(7)	4486(5)	−1616(3)
C(1B)	−0036(8)	3740(7)	−0872(4)
C(2B)	−0984(8)	2293(7)	−0914(5)
O(6)	5341(8)	1898(6)	3544(4)
H(O21)	3722	2506	−0340
H(O22)	3504	0643	0010
H(O31)	3197	0400	1831
H(O32)	1560	0956	2388
H(C2A1)	−3279	3153	0303
H(C2A2)	−3713	1844	0928
H(C2B1)	−2149	2379	−1237
H(C2B2)	0018	1749	−1396

Hydrogen atom parameters were fixed during the refinement. Their isotropic thermal parameters ($\times 10^3$) were: 90, 90, 114, 83, 45, 60, 69, and 88.

TABLE 2

Anisotropic thermal parameters (Å^2 $\times 10^3$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn	27·8(3)	26·7(3)	25·9(3)	02·5(3)	−00·6(3)	−01·0(3)
S	39·6(7)	24·2(6)	32·7(7)	−03·3(6)	00·6(7)	−01·2(5)
O(1)	34(2)	38(2)	52(3)	−03(2)	−03(2)	−16(2)
O(2)	48(3)	33(2)	41(2)	08(2)	14(2)	−01(2)
O(3)	45(2)	44(2)	32(2)	11(2)	07(2)	07(2)
O(4A)	30(2)	48(3)	38(2)	02(2)	00(2)	−12(2)
O(5A)	33(2)	52(3)	55(3)	−01(2)	05(2)	−22(2)
C(1A)	31(3)	35(2)	31(3)	01(3)	01(3)	−02(3)
C(2A)	28(3)	48(4)	39(3)	−05(3)	03(3)	−17(3)
O(4B)	43(2)	29(2)	32(2)	−07(2)	−11(2)	04(2)
O(5B)	49(3)	40(2)	30(2)	−09(2)	−06(2)	04(2)
C(1B)	31(3)	26(3)	27(3)	01(3)	01(3)	−02(3)
C(2B)	44(3)	32(3)	32(3)	−09(3)	−03(3)	−04(3)
O(6)	57(3)	58(3)	42(3)	02(3)	−03(3)	−06(2)

DISCUSSION

The structure (I) consists of discrete units of triaqua(thiodiglycolato)zinc(II), occupying general fourfold positions in the unit cell. The remaining uncoordinated water molecule is also in a general position.†

The molecule (I) is shown in Figure 1 together with the atomic numbering scheme, the two halves of the terdentate ligand being numbered A and B. The most noticeable points about the molecular structure are the long metal–sulphur bond, the differences in the Zn–O(carboxy) bond lengths and in the Zn–O(water) bond lengths, and the different ring conformations. Figure 1 shows that the zinc atom is six-co-ordinate, being bonded weakly to one sulphur atom [2·601(2) Å] and strongly to five oxygen atoms. Two of the oxygen atoms are from carboxy-groups [Zn–O(4A) 2·029(5), and, Zn–O(4B) 2·102(5) Å] and the remaining three from water molecules [Zn–O(1) 2·050(5), Zn–O(2) 2·016(5), and Zn–O(3) 2·098(5) Å].

TABLE 3

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

(*a*) Distances not involving hydrogen

Zn–S	2·601(2)	Zn–O(2)	2·016(5)
Zn–O(1)	2·050(5)	Zn–O(3)	2·098(5)
Zn–O(4A)	2·029(5)	Zn–O(4B)	2·102(4)
O(4A)–C(1A)	1·243(8)	O(4B)–C(1B)	1·248(7)
C(1A)–C(2A)	1·520(9)	C(1B)–C(2B)	1·526(9)
C(1A)–O(5A)	1·264(8)	C(1B)–O(5B)	1·263(9)
C(2A)–S	1·807(7)	C(2B)–S	1·790(7)

(*b*) Angles not involving hydrogen

S–Zn–O(1)	166·9(1)	O(1)–Zn–O(2)	97·8(2)
S–Zn–O(2)	92·1(1)	O(1)–Zn–O(3)	98·3(2)
S–Zn–O(3)	91·0(1)	O(2)–Zn–O(3)	85·1(2)
S–Zn–O(4A)	81·2(2)	S–Zn–O(4B)	78·2(1)
O(1)–Zn–O(4A)	89·0(2)	O(1)–Zn–O(4B)	94·0(2)
O(2)–Zn–O(4A)	173·1(2)	O(2)–Zn–O(4B)	86·0(2)
O(3)–Zn–O(4A)	93·2(2)	O(3)–Zn–O(4B)	165·7(2)
O(4A)–Zn–O(4B)	94·3(2)	C(2A)–S–C(2B)	101·8(3)
Zn–O(4A)–C(1A)	124·6(5)	Zn–O(4B)–C(1B)	124·4(5)
O(4A)–C(1A)–C(2A)	122·0(6)	O(4B)–C(1B)–C(2B)	120·6(5)
O(4A)–C(1A)–O(5A)	123·7(6)	O(4B)–C(1B)–O(5B)	123·8(6)
C(2A)–C(1A)–O(5A)	114·3(6)	C(2B)–C(1B)–O(5B)	115·6(5)
C(1A)–C(2A)–S	116·5(4)	C(1B)–C(2B)–S	115·5(4)
Zn–S–C(2A)	92·3(3)	Zn–S–C(2B)	94·3(4)

(*c*) Distances involving hydrogen *

C(2A)–H(C2A1)	1·02(7)	O(2)–H(O21)	0·94(5)
C(2A)–H(C2A2)	0·90(7)	O(2)–H(O22)	1·17(5)
C(2B)–H(C2B1)	1·00(7)	O(3)–H(O31)	1·07(5)
C(2B)–H(C2B2)	1·14(7)	O(3)–H(O32)	0·83(5)

(*c*) Angles involving hydrogen *

C(1A)–C(2A)–H(C2A1)	108(6)
C(1A)–C(2A)–H(C2A2)	113(6)
C(1B)–C(2B)–H(C2B1)	111(6)
C(1B)–C(2B)–H(C2B2)	96(6)
H(C2A1)–C(2A)–H(C2A2)	106(6)
H(C2B1)–C(2B)–H(C2B2)	110(6)
Zn–O(2)–H(O21)	116(4)
Zn–O(2)–H(O22)	126(3)
Zn–O(3)–H(O31)	123(4)
Zn–O(3)–H(O32)	118(3)
H(O21)–O(2)–H(O22)	117(5)
H(O31)–O(3)–H(O32)	110(5)

* Standard deviations are means of those obtained in the two last cycles of hydrogen-parameter refinement (see text).

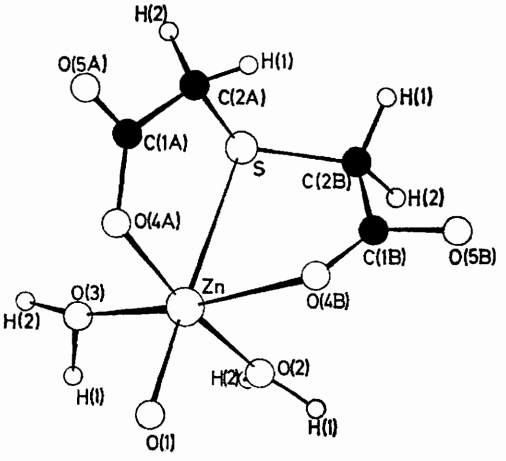

FIGURE 1 The molecule, showing the atom numbering system used

The wide range in Zn–O(water) and Zn–O(carboxy) bond distances is not unusual. For example, in the

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† The hazards involved in the prediction of structures from spectral data are well illustrated by O. Prochazkova, J. Podhakova, and J. Podlaka (*Coll. Czech. Chem. Comm.*, 1973, **38**, 1120), who predict a polymeric, oxygen-bonded, tetrahedral structure for this compound.

octahedral molecule, diaquadiglycolatozinc(II),[7] Zn–O(water) bond distances are 2·048 and 2·094, while Zn–O(carboxyl) distances are 2·056 and 2·104 Å. In $ZnCl_2,1\frac{1}{3}H_2O$, Zn–O is 2·02 and 2·03 Å;[8] in zinc picolinate tetrahedrate, Zn–O(water) is 2·18 Å and Zn–O(carboxyl) 2·08 Å;[9] in diaquabis(pyridyl-2-acetato)-zinc, Zn–O(water) is 2·212 and Zn–O(carboxy) 2·075 Å.[10] The relatively wide range of such distances, particularly for Zn–O(water) bonds, indicates that they are particularly sensitive to intermolecular hydrogen bonds which proliferate, particularly in the present structure and in that of diaquadiglycolatozinc(II).[7]

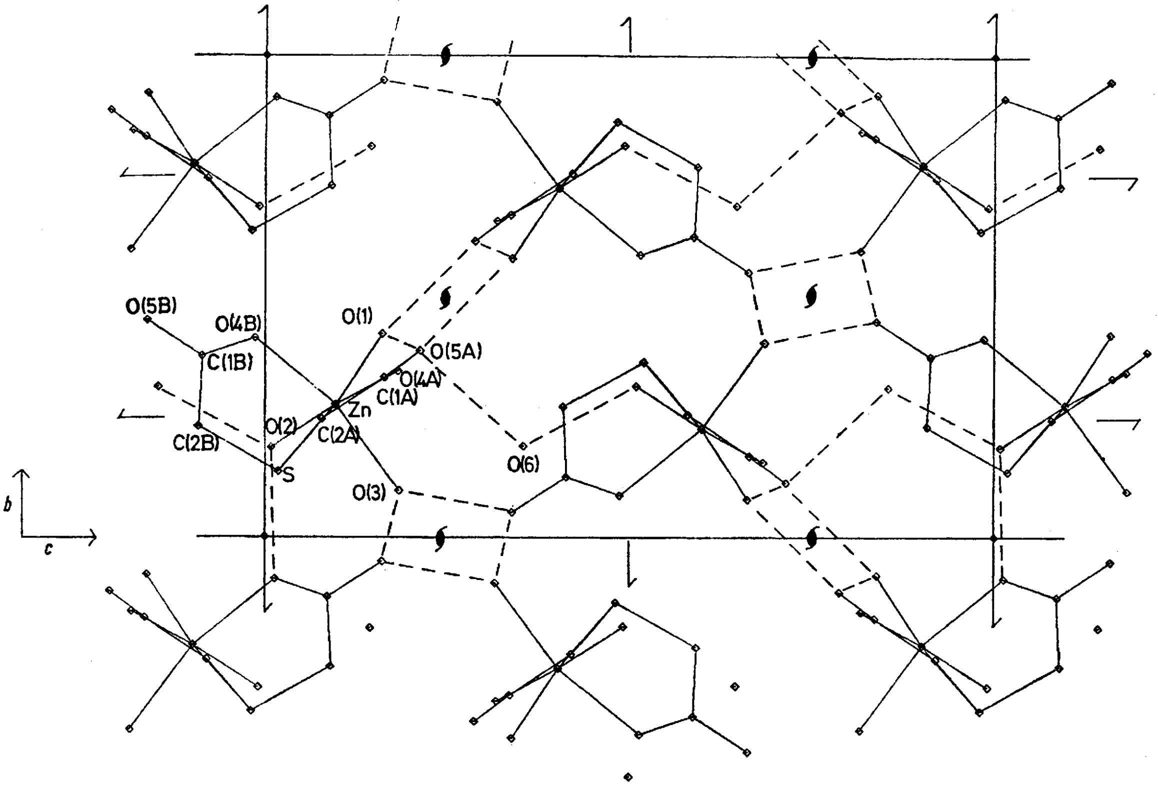

FIGURE 2 The unit cell in the *a* projection. Dotted lines represent postulated hydrogen bonds (see text)

The hydrogen bonding scheme in the unit cell is shown in Figure 2, which is the *a* projection of the unit cell. The dimensions involved in this scheme are listed in Table 4.

O(3) Acts as a proton donor to $O(5B^{V})$ and $O(5B^{III})$, the distances 2·64 and 2·76 Å being well within the range for such hydrogen bonds.[11] The positions of the hydrogen atoms H(O31) and H(O32) are compatible with this scheme, the O–H ··· O angles being 170(3) and 160(4)°. This series of hydrogen bonds forms an infinite spiral around the screw axis at $y = 0$, $z = \frac{1}{4}$. It can be postulated that O(1) acts as a proton donor to two carboxy-oxygen atoms for although the hydrogen atoms bonded to O(1) [and also those to O(6)] could not be located in the the difference-Fourier map, the $O(1) \cdots O(5A^{I})$ and $O(1) \cdots O(5A^{II})$ distances are 2·82 and 2·76 Å and the various angles are acceptable (see Table 4). This series of hydrogen bonds forms another pair of infinite spirals around the two screw axes at $y = \frac{1}{2}$, $z = \frac{1}{4}, \frac{3}{4}$. Thus all four screw axes parallel to *a* (cell dimension 7·589 Å) are encircled by strong hydrogen-bond infinite spirals which each involve a co-ordinated water molecule as a proton donor and a carboxy-oxygen atom as a proton acceptor. The formation of such spirals is probably the main factor in fixing the mode of packing in the unit cell. This type of packing leaves large gaps between molecules and it is not surprising that an additional water of crystallisation was necessary for the formation of this complex: in fact we were unable to prepare an anhydrous form.

Apart from these spirals, there is some additional hydrogen bonding in the unit cell (Table 4, and Figure 2). There is also one O ··· O intermolecular contact of 2·98 Å [$O(6) \cdots O(3^{VIII})$] which could represent a weak hydrogen bond.

In (I), the internal dimensions of the terdentate ligand are comparable to those found in an analysis of thiodiglycolic acid, which has crystallographically imposed *m* symmetry and is approximately planar, the planes of the two halves intersecting at 7·9°.[12] In (I) the three donor atoms of the acid are mutually *cis*. This arrange-

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TABLE 4

Intramolecular distances (Å) and angles (°) relevant to hydrogen bonds.* Standard deviations involving non-hydrogen atoms <0·01 Å and 1·0°

O(1) · · · O(5A$^{\mathrm{I}}$)	2·82
O(1) · · · O(5A$^{\mathrm{II}}$)	2·76
Zn–O(1) · · · O(5A$^{\mathrm{I}}$)	128
Zn–O(1) · · · O(5A$^{\mathrm{II}}$)	118
O(5A$^{\mathrm{I}}$) · · · O(1) · · · O(5A$^{\mathrm{II}}$)	107
O(2) · · · O(4B$^{\mathrm{III}}$)	2·68
O(2) · · · O(6$^{\mathrm{IV}}$)	2·71
Zn–O(2) · · · O(4B$^{\mathrm{III}}$)	125
Zn–O(2) · · · O(6$^{\mathrm{IV}}$)	128
O(4B$^{\mathrm{III}}$) · · · O(2) · · · O(6$^{\mathrm{IV}}$)	107
O(2)–H(O21) · · · O(6$^{\mathrm{IV}}$)	157(3)
O(2)–H(O22) · · · O(4B$^{\mathrm{III}}$)	165(3)
O(3) · · · O(5B$^{\mathrm{III}}$)	2·76
O(3) · · · O(5B$^{\mathrm{V}}$)	2·64
Zn–O(3) · · · O(5B$^{\mathrm{III}}$)	120
Zn–O(3) · · · O(5B$^{\mathrm{V}}$)	120
O(5B$^{\mathrm{III}}$) · · · O(3) · · · O(5B$^{\mathrm{V}}$)	119
O(3)–H(O31) · · · O(5B$^{\mathrm{III}}$)	170(3)
O(3)–H(O32) · · · O(5B$^{\mathrm{V}}$)	160(4)
O(6) · · · O(5A$^{\mathrm{I}}$)	2·88
O(5A$^{\mathrm{I}}$) · · · O(6) · · · O(2$^{\mathrm{VI}}$)	99
Zn–O(4B) · · · O(2$^{\mathrm{VIII}}$)	119
C(1B)–O(4B) · · · O(2$^{\mathrm{VIII}}$)	116
C(1B$^{\mathrm{III}}$)–O(5B$^{\mathrm{III}}$) · · · O(3)	110
C(1B$^{\mathrm{III}}$)–O(5B$^{\mathrm{III}}$) · · · O(3$^{\mathrm{VIII}}$)	129
O(3) · · · O(5B$^{\mathrm{III}}$) · · · O(3$^{\mathrm{VIII}}$)	116
C(1A$^{\mathrm{I}}$)–O(5A$^{\mathrm{I}}$) · · · O(1)	127
C(1A$^{\mathrm{I}}$)–O(5A$^{\mathrm{I}}$) · · · O(6)	112
C(1A$^{\mathrm{I}}$)–O(5A$^{\mathrm{I}}$) · · · O(1$^{\mathrm{IX}}$)	109
O(1) · · · O(5A$^{\mathrm{I}}$) · · · O(6)	86
O(1) · · · O(5A$^{\mathrm{I}}$) · · · O(1$^{\mathrm{IX}}$)	118
O(6) · · · O(5A$^{\mathrm{I}}$) · · · O(1$^{\mathrm{IX}}$)	95

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

I	$1 + x, y, z$	VI	$1 - x, \frac{1}{2} - y, \frac{1}{2} + z$
II	$\frac{1}{2} + x, 1 - y, \frac{1}{2} - z$	VII	$\frac{1}{2} - x, \frac{1}{2} + y, -z$
III	$\frac{1}{2} - x, -\frac{1}{2} + y, -z$	VIII	$\frac{1}{2} + x, -y, \frac{1}{2} - z$
IV	$1 - x, \frac{1}{2} - y, -\frac{1}{2} + z$	IX	$-\frac{1}{2} + x, 1 - y, \frac{1}{2} - z$
V	$-x, \frac{1}{2} - y, \frac{1}{2} + z$	X	$-\frac{1}{2} - x, \frac{1}{2} + y, -z$

ment is obligatory, given a long Zn–S bond, and the requirement that the C–S–C angle is *ca.* 100°. However, the analogous oxydiacetic acid H$_2$oda [= O(CH$_2$CO$_2$H)$_2$] is found to be approximately planar in complexes such as Ca(oda),5H$_2$O[13] and Na$_3$[M(oda)$_3$],2NaClO$_4$,6H$_2$O (M = Nd or Yt[14]). The C–S–C and S–C–C angles in (I) are larger than in the free acid (C–S–C 101·8 *vs.* 95·8°, C–C–S 116·5 and 115·5 *vs.* 111·9°) and this general increase is presumably due to the formation of the five-membered rings. In the present molecule, for parts (A) and (B), the two C(1)–O(4) bonds [1·243(8) and 1·248(7) Å] are only just shorter than the C(1)–O(5) bonds [1·264(8) and 1·263(9) Å] though this disparity may not be significant. The near equality of the C–O bonds is often found in carboxylates, indicating that the electrons are delocalised over the O–C–O groups.[10]

The internal dimensions of the two halves of the ligand are thus very similar in (I). As for the ring conformations, atoms C(1), C(2), O(4), and O(5) are planar in both parts of the molecule [planes (2) and (3), Table 5]. For both planes the Zn atom is on one side of the plane with the S(1) atom on the other. Planes (2) and (3) intersect at 81·4° and the respective O(4), Zn, S planes at angles of 11·9 (A) and 18·9° (B). Plane (2) is bent away from part (B) while plane (3) is bent towards part (A), as can be seen from the dihedral angles (Table 6). Particularly striking are the H(C2A1)–C(2A)–S–C(2B) and H(C2B1)–C(2B)–S–C(2A) dihedral angles (8·9 and −56·8° for the two rings). There are presumably other conformations of lower energy for the molecule in which this eclipsing of H(C2A1) with C(2B) does not occur [two examples are (*a*) if the five-membered rings (A) and (B) are planar; (*b*) if plane (2) is bent towards ring (B) and plane (3) is bent towards ring (A)], and this suggests that the actual conformation found for (I) may be due to hydrogen bonding in the crystal.

TABLE 5

Equations of least-square planes in the form $Ax + By + Cz = D$ where *x*, *y*, and *z* are orthogonal co-ordinates in Å. Distances (Å) of the relevant atoms from the planes are given in square brackets

	A	*B*	*C*	*D*
Plane (1): O(2), O(3), O(4A), O(4B)	0·673	0·610	0·416	2·685
[O(2) 0·05, O(3) −0·05, O(4A) 0·04, O(4B) −0·05, Zn 0·17, S −2·41, O(1) 2·21]				
Plane (2): O(4A), O(5A), C(1A), C(2A)	0·040	0·826	−0·563	1·160
[O(4A), O(5A), C(1A), C(2A) 0·00, S −0·30, Zn 0·20]				
Plane (3): O(4B), O(5B), C(1B), C(2B)	0·836	−0·436	−0·328	−1·130
[O(4B), O(5B), C(1B), C(2B) 0·00, S −0·27, Zn 0·46]				

TABLE 6

Ring dihedral angles (°)

	(A)	(B)
Zn–O(4)–C(1)–C(2)	7·0	15·1
O(4)–C(1)–C(2)–S	10·6	9·8
C(1)–C(2)–S–Zn	−16·4	−21·4
C(2)–S–Zn–O(4)	14·3	20·1
S–Zn–O(4)–C(1)	−14·4	−22·9
O(5)–C(1)–C(2)–H(C21)	71·7	−42·2
O(5)–C(1)–C(2)–H(C22)	−46·0	72·2
H(C21)–C(2)–S–C(2) *	8·9	−56·8

* Atom in the other ring to H[C(2)1].

The Zn–S bond [2·601(2) Å] is much longer than expected both from data on Zn–S bonds and from other octahedral M–S distances. We were unable to find comparative values for octahedral zinc but ranges of 2·29—2·41 Å have been found for zinc in a tetrahedral compound,[15] and in the distorted trigonal prismatic bis(*NN*-dimethyldithiocarbamato)pyridinezinc[16] Zn–S(eq) bonds are 2·328 and Zn–S(ax) 2·605 Å. Despite the long bond in (I) the C–S–C and Zn–S–C angles are

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not particularly different from those in other dialkyl sulphides.[17,18]

There are two possible explanations for the length of the Zn–S bond: that the ligand configuration would be unreasonably strained if the bond were short, or that zinc(II) has a low affinity for thioethers,[19] and therefore the molecule tends towards five-co-ordination. We have calculated the effect on the molecular conformation of shortening the Zn–S bond to 2·3 Å and the resulting dimensions are unexceptional, and we conclude that the second explanation is the more likely.

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