Crystal Structure of [*NN'*-Tetramethylenebis(thioacetylacetoniminato)-(2—)]zinc

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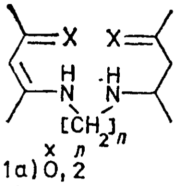
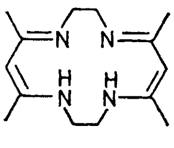
The title compound crystallises in space group *C*2/*c*, with *a* = 12·286(10), *b* = 11·970(10), *c* = 12·608(10) Å, β= 120·67(5)°, and *Z* = 4. The structure was solved by the heavy-atom method from diffractometer data and refined by least-squares methods to *R* 0·097 for 1056 reflections. The structure consists of discrete molecules lying on the two-fold rotation axes, and the ligand is folded to give pseudo-tetrahedral co-ordination about the zinc atom.

THE co-ordination chemistry of *NN'*-ethylenebis(acetylacetonimine) (Ia) has been studied extensively, and crystal structures have been determined for copper,[1] cobalt,[2] and vanadyl [3] complexes. The sulphur analogue (1b) described recently by Cummings and co-workers,[4] is of interest in relation to models of biological oxygen-carriers,[5] and has also been used as an intermediate in the synthesis of the macrocycle (3).[6] We were independently investigating that route to macrocycles and, being particularly interested in more flexible structures with more than two bridging carbon atoms, we prepared homologues of the thione with *n* = 3, 4, and 6.[7] Our observations of the reactivity of these substances will be reported separately. In this paper we describe the crystal structure of the zinc complex (4) of *NN'*-tetramethylenebis(thioacetylacetonimine) (2b). This structure was examined to confirm the monomeric nature of the complex, to determine the stereochemistry around the zinc atom, and to obtain bond lengths and angles for the co-ordinated ligand (2b).



X n
(1a) O, 2
(1b) S, 2
(2a) O, 4
(2b) S, 4



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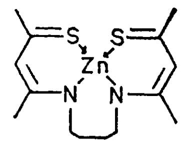

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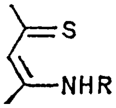

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The ligand (2b) was prepared from the oxygen analogue (2a) (obtained by a known route [8]) by reaction with triethyloxonium tetrafluoroborate followed by sodium hydrogensulphide. The procedure was identical to that used[4] to prepare the thione (1b), and earlier[9] in the preparation of a series of thiones (5). The zinc complex was readily obtained by reaction of the ligand with zinc acetate in methanol.

EXPERIMENTAL

Preparation of Compounds.—NN'-*Tetramethylenebis*(*thioacetylacetonimine*) (2b).—A solution of triethyloxonium tetrafluoroborate (16 g, 0·08 mol) in dry dichloromethane (50 ml) was added dropwise under nitrogen to a stirred solution of *NN'*-tetramethylenebis(acetylacetonimine) [8] (2a) (10 g, 0·04 mol) in dry dichloromethane (100 ml). After 20 min a solution of sodium hydrogensulphide (prepared by saturating with hydrogen sulphide a solution of 0·08 mol sodium ethoxide in 50 ml ethanol) was added. The orange mixture was stirred for 15 min, filtered to removo sodium tetrafluoroborate, and the filtrate was evaporated to dryness to give the crude product. After recrystallisation from acetone the *imine* (6·1 g, 55%) was obtained as fine yellow needles, m.p. 160 °C (Found: C, 59·1; H, 8·4; N, 10·1. $C_{14}H_{24}N_2S_2$ requires C, 59·1; H, 8·5; N, 9·9%); $\lambda_{max.}$ (MeOH) 242 (ε 9200), 361 (ε 42 100) nm.

NN'-*Tetramethylenebis*(*thioacetylacetoniminato*)*zinc* (4).—A saturated solution of the ligand (2b) (1 g) in methanol was added with stirring to a filtered saturated solution of $Zn(OAc)_2,H_2O$ (1 g) in methanol. Crystals began to grow at once. After 24 h the product was filtered off and recrystallised from benzene to give the *zinc complex* (1 g, 80%) as colourless needles, m.p. 230 °C (Found: C, 48·4; H, 6·6; N, 7·9. $C_{14}H_{22}N_2S_2Zn$ requires C, 48·3; H, 6·4; N, 8·05%); $\lambda_{max.}$ (MeOH) 346 (ε 13 300) nm.

Crystallographic Measurements.—The systematic absences and approximate lattice constants were determined from Weissenberg and rotation photographs, and accurate lattice constants were then obtained by the least-squares method from measurements with a Stoe two-circle diffractometer. Relative intensities were measured on the diffractometer by use of a truncated needle of size 0·15 × 0·15 × 0·30 mm mounted along *b*. Four octants were measured for layers *h*0—9*l* by the θ—2θ scan technique, and the intensities of equivalent reflections were averaged giving 1056 independent reflections with 2θ < 120°. Structure factors were calculated in the usual way after application of Lorentz and polarisation corrections, and approximate scale and overall temperature factors were found by Wilson's method. No absorption correction was made.

Crystal Data.—$C_{14}H_{22}N_2S_2Zn$, M = 347·7, Monoclinic, a = 12·286(10), b = 11·970(10), c = 12·608(10) Å, β = 120·67(5)°, U = 1595 Å^3, D_m = 1·44 g cm^{-3} (by flotation), Z = 4, D_c = 1·45 g cm^{-3}, $F(000)$ = 720. Space-group *C*2/*c* (C^6_{2h}, No. 15) or *Cc* (C^4_s, No. 9) from systematic absences; *C*2/*c* requires the molecule to lie at a special position. A centre of symmetry was suggested by the statistics of the normalised structure factors. Cu-K_α radiation, λ = 1·5418 Å; μ(Cu-K_α) = 44·3 cm^{-1}.

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[1] D. Hall, A. D. Rae, and T. N. Waters, *J. Chem. Soc.*, 1963, 5897; G. R. Clark, D. Hall, and T. N. Waters, *J. Chem. Soc.* (*A*), 1968, 223; G. R. Clark, D. Hall, and T. N. Waters, *ibid.*, 1969, 823; E. N. Baker, D. Hall, and T. N. Waters, *ibid.*, 1970, 396.

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[8] R. J. Hovey, J. J. O'Connell, and A. E. Martell, *J. Amer. Chem. Soc.*, 1959, **81**, 3189.

[9] D. H. Gerlach and R. H. Holm, *J. Amer. Chem. Soc.*, 1969, **91**, 3457.

Structure Analysis.—The structure was solved by the heavy-atom method assuming the space group $C2/c$. Initially data were limited to $\sin\theta/\lambda < 0{\cdot}4$. Three cycles of Fourier and structure-factor calculations gave all the non-hydrogen atoms, and then R was reduced from 0·54 to 0·165 by least-squares refinement with isotropic temperature parameters and unit weights. Refinement was continued for all the data with anisotropic temperature parameters. After seven cycles the maximum shift-to-error was 0·05, and R was 0·097. The weighting scheme was $\sqrt{w} = 10/F_{\text{rel}}$ if $F_{\text{rel}} > 40$, and $\sqrt{w} = 0{\cdot}25$ otherwise. This scheme gave a satisfactory distribution of $\langle w\Delta^2\rangle$. A difference synthesis gave values of $-1{\cdot}8$ to $1{\cdot}2$ eÅ^{-3} between the zinc and sulphur atoms, but otherwise there were no features $> \mp 0{\cdot}4$ eÅ^{-3}. Hydrogen atoms were not located and were not included in any calculation. The success of the refinement confirms the space group as $C2/c$. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21179 (8 pp., 1 microfiche).†

The structure was solved by use of the '*X*-Ray '67' system of programs [10a] on an ICL 4/70 computer at University College, Cardiff. The least-squares refinement (full-matrix method, based on F) was carried out on a CDC 7600 computer at London University by use of program CRYLSQ in '*X*-Ray '72.' [10b] Figure 1 was produced by the program ORTEP.[11] Other programs were written locally. Scattering factors (for neutral atoms) were taken from ref. 12*a*, with dispersion corrections [12b] for zinc and sulphur. No reflections were rejected as being unobserved.

RESULTS AND DISCUSSION

The structure consists of discrete molecules each lying on a two-fold rotation axis which passes through the zinc atom. The ligand is folded to give pseudo-tetrahedral co-ordination about the metal atom.

TABLE 1

Final atomic fractional co-ordinates, with estimated standard deviations in parentheses

	x	y	z
Zn(1)	0·0000	0·0578(1)	0·2500
S(1)	0·1857(2)	−0·0332(2)	0·3727(2)
N(1)	0·0000(5)	0·1646(5)	0·3718(5)
C(1)	0·2936(7)	−0·0983(7)	0·6101(6)
C(2)	0·2033(6)	−0·0160(7)	0·5174(5)
C(3)	0·1489(6)	0·0623(6)	0·5550(6)
C(4)	0·0655(6)	0·1529(6)	0·4937(6)
C(5)	0·0553(8)	0·2358(8)	0·5778(7)
C(6)	−0·0816(6)	0·2632(6)	0·3172(7)
C(7)	−0·0079(7)	0·3618(7)	0·3082(7)

Final positional and thermal parameters are listed in Tables 1 and 2, together with the estimated standard deviations taken from the least-squares calculations. Parameters for the atoms with primed numbers are related by symmetry to those with unprimed numbers and are not given. Numbering of the atoms is indicated in Figure 1 which shows one molecule viewed along the

TABLE 2

Thermal parameters * (Å^2 × 10^4), with estimated standard deviations in parentheses

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn(1)	459(8)	422(12)	257(7)	0	93(6)	0
S(1)	706(13)	740(17)	323(10)	308(10)	200(9)	38(8)
N(1)	353(27)	408(41)	310(27)	29(22)	101(22)	28(22)
C(1)	542(42)	427(55)	360(35)	27(34)	112(30)	1(32)
C(2)	372(34)	489(51)	326(33)	−34(29)	146(27)	−46(29)
C(3)	391(38)	519(61)	270(33)	−39(28)	86(28)	−9(26)
C(4)	297(31)	489(51)	374(35)	−45(28)	119(26)	−81(29)
C(5)	566(45)	691(67)	473(41)	101(39)	221(36)	−149(37)
C(6)	408(37)	334(51)	580(42)	73(29)	200(32)	26(32)
C(7)	545(42)	332(51)	610(46)	21(32)	244(35)	2(34)

* In the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

TABLE 3

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

(*a*) Distances			
Zn(1)–S(1)	2·277(3)	S(1)–C(2)	1·74(1)
Zn(1)–N(1)	1·997(6)	N(1)–C(4)	1·33(1)
		N(1)–C(6)	1·47(1)
C(1)–C(2)	1·50(1)		
C(2)–C(3)	1·37(1)	C(6)–C(7)	1·53(1)
C(3)–C(4)	1·42(1)	C(7)–C(7′)	1·575(20)
C(4)–C(5)	1·50(1)		
(*b*) Angles			
S(1)–Zn(1)–N(1)	100·2(2)	S(1)–C(2)–C(1)	112·8(6)
S(1)–Zn(1)–S(1′)	122·8(1)	S(1)–C(2)–C(3)	128·6(5)
S(1)–Zn(1)–N(1′)	115·8(2)	C(1)–C(2)–C(3)	118·6(7)
N(1)–Zn(1)–N(1′)	100·5(3)		
		C(2)–C(3)–C(4)	132·8(7)
Zn(1)–S(1)–C(2)	101·6(3)		
		N(1)–C(4)–C(3)	123·5(7)
Zn(1)–N(1)–C(4)	125·8(5)	N(1)–C(4)–C(5)	121·8(6)
Zn(1)–N(1)–C(6)	114·8(4)	C(3)–C(4)–C(5)	114·6(6)
C(4)–N(1)–C(6)	119·4(7)		
		N(1)–C(6)–C(7)	111·5(6)
		C(6)–C(7)–C(7′)	115·4(9)

TABLE 4

Equations * of least-squares planes, and, in square brackets, deviations (Å) of atoms from the planes

Plane (1): S(1), N(1), C(1)—(5); χ^2 1754

$$-0{\cdot}74970X - 0{\cdot}60551Y + 0{\cdot}26704Z = -0{\cdot}10758$$

[S(1) −0·18, N(1) 0·17, C(1) 0·06, C(2) 0·01, C(3) 0·09, C(4) 0·03, C(5) −0·19, Zn(1) 0·53]

Plane (2): S(1), C(1)—(3); χ^2 2·2

$$-0{\cdot}76284X - 0{\cdot}62518Y + 0{\cdot}16501Z = -0{\cdot}66269$$

[S(1) −0·003, C(1) −0·003, C(2) 0·01, C(3) −0·004, Zn(1) 0·75]

Plane (3): N(1), C(3)—(5); χ^2 0·1

$$-0{\cdot}75378X - 0{\cdot}52538Y + 0{\cdot}39471Z = 0{\cdot}81431$$

[N(1) 0·001, C(3) 0·001, C(4) −0·002, C(5) 0·001, Zn(1) 0·07]

* In the form $lX + mY + nZ = p$, where X, Y, and Z are orthogonal co-ordinates defined by: $X = ax \sin\beta$, $Y = by$, $Z = cz + ax\cos\beta$

TABLE 5

Intermolecular contacts (Å)

C(5) $\cdots$ C(1$'^{\text{I}}$)	3·93	C(5) $\cdots$ C(1$^{\text{II}}$)	3·97
C(3) $\cdots$ N(1$'^{\text{III}}$)	3·65	C(1) $\cdots$ C(7$'^{\text{IV}}$)	3·64
C(3) $\cdots$ C(3$'^{\text{III}}$)	3·52	C(7) $\cdots$ C(2$'^{\text{IV}}$)	3·72
C(3) $\cdots$ C(4$'^{\text{III}}$)	3·51	C(1) $\cdots$ C(7$^{\text{IV}}$)	3·74
C(4) $\cdots$ C(2$'^{\text{III}}$)	3·62		

Roman numeral superscripts refer to the following equivalent positions:

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

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† See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

[10] The *X*-Ray System, Computer Science Center, University of Maryland, (a) version of November 1967, Report TR 67 58; (*b*) version of July 1972, Report TR 72 192.

[11] ORTEP, Report ORNL 3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

[12] 'International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1968, (*a*) p. 202; (*b*) p. 214.

*a** axis. The packing in the unit cell is illustrated in Figure 2, the structure being viewed down the *b* axis. Tables 3 and 4 show the molecular geometry and Table 5 the intermolecular contacts, all of which are reasonable.

The Zn–S bond length (2·277 Å) is similar to those (2·27 and 2·33 Å) in bis-(*O*-ethyl thioacetothioacetato)-zinc where the zinc atom is tetrahedrally co-ordinated by a conjugated thione ligand.[13] The zinc atom lies 0·53 Å from the mean ligand plane. A similar deviation (0·47 Å) is seen in bis-(*O*-ethyl thioacetothioacetato)-zinc,[13] though in the tetrahedral bis(dipivalatomethanido)zinc the metal atom lies exactly in the ligand plane.[14]

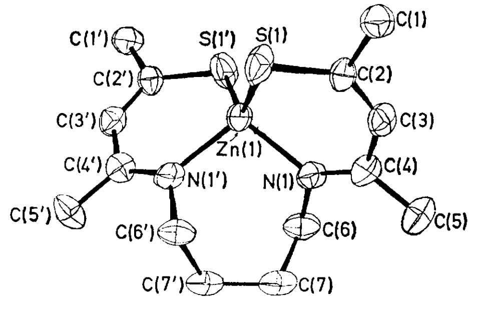


FIGURE 1 The molecule viewed along the *a** axis, with thermal ellipsoids scaled to 50% probability

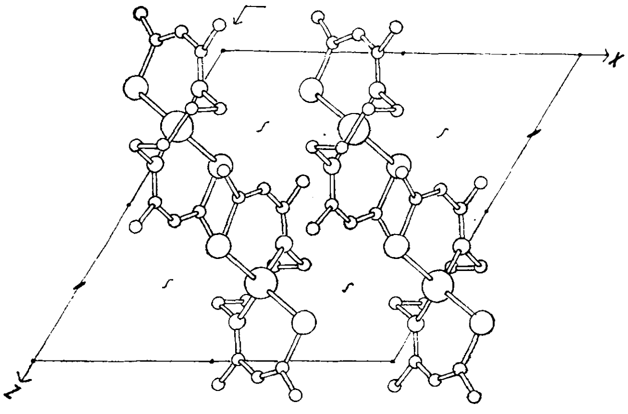


FIGURE 2 The unit cell viewed down the *b* axis

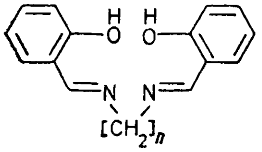
It is surprising that the conjugated part of the ligand is itself not quite planar. Table 4 shows significant deviations of the atoms from the mean plane. The distortion can be described as a rotation about the C(2)–C(3) or the C(3)–C(4) bond. Atoms S(1) and C(1)—(3) are almost planar (χ^2 2·2), and atoms N(1) and C(3)—(5) are accurately so (χ^2 0·1). The angle between the planes defined by these groups of atoms is 14·4°.

The C–S bond length (1·74 Å) is typical of co-ordinated conjugated thiones. It compares with the bond lengths in iron(III) (1·70 and 1·72 Å),[15a] nickel(II) (1·69 Å),[15b] and cobalt(II) (1·72 Å)[15b] complexes of dithioacetylacetone, and with those (1·71 and 1·68 Å) in bis-(*O*-ethyl thioacetothioacetato)zinc.[13]

The C(2)–C(3) and C(3)–C(4) bond lengths are significantly different, and are identical to the mean values (1·37 and 1·42 Å) for the corresponding bonds in several complexes of (1a).[16] These facts suggest that the replacement of oxygen by sulphur has little effect on the electron distribution in the conjugated part of the molecule, except in the C–S bond.

The C(2)–C(3)–C(4) angle is large (132·8°) for an *sp*^{2} hybridised carbon atom, but is similar to the values (128·7—131·5°) for the complexes of dithioacetylacetone.[15] Values for the corresponding angle in complexes of the oxygen ligand (1a) are 122—126°.[1-3] The widening of the angle is presumably due to the long C–S and sulphur–metal bonds.

In complexes of quadridentate ligands of types (1) and (2) with $n = 2$, the ligand is constrained to be planar or approximately so. For $n > 2$ there is more flexibility and the geometry may be planar, tetrahedral, or intermediate. The variation in geometry with the length of the bridging group has been studied by spectroscopic and magnetic methods for related complexes of divalent metals with ligands (6) derived from salicylaldehyde. When $n = 4$, nickel forms a square-planar complex,[17a] whereas zinc,[17b] beryllium,[17c] and cobalt[17d] form pseudo-tetrahedral structures. The folding of a tetramethylene chain to give planar co-ordination is seen in the crystal structure of the macrocyclic complex (7).[18] In the present structure the tetramethylene chain is folded to give pseudo-tetrahedral co-ordination. The angle between the mean ligand plane [plane (1) in Table 4] and the symmetry-related plane involving primed atoms is 74·5°. This structure is a further example of the tendency of zinc to assume tetrahedral geometry if sterically feasible.[19] The slight non-planarity of the conjugated atoms of the ligand (see



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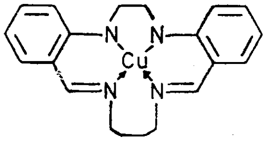

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earlier) appears to be a compromise between planar ligand and tetrahedral zinc; neither condition is fully satisfied. A longer central chain could probably accommodate both conditions.

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