

The Crystal Structure of Metal Diethyldithiophosphates I. Zinc Diethyldithiophosphate

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The crystal structure of zinc diethyldithiophosphate, $\text{Zn}[\text{S}_2\text{P}(\text{OC}_2\text{H}_5)_2]_2$ has been determined. The final R value obtained by the anisotropic least-squares method was 7.9%. The crystal is monoclinic, space group $P2_1/a$, with $a = 12.084$ (0.003), $b = 19.840$ (0.006), $c = 8.463$ (0.005) Å, $\beta = 113.99$ (0.03)°, $Z = 4$. One dithiophosphate group is coordinated to a single zinc atom by its two sulphur ends, while the other, also by its two sulphur ends, bridges two different zinc atoms related by a -glide. Thus the formula unit does not exist as a monomer in the crystal, but infinite linear zigzag chains (polymers) are formed along the a axis. These chains are stacked laterally with methyl-sulphur, methyl-methyl and methyl-oxygen van der Waals contacts. The coordination of the four sulphur atoms about each zinc atom is distorted tetrahedral, the Zn-S distances ranging from 2.337 to 2.401 Å.

Introduction

Knowledge of the crystal structure of heavy-metal salts of collector anions is an important basis for understanding the flotation mechanism. In this connection crystal structure analyses of the following heavy metal xanthates have been undertaken to date: lead ethylxanthate (Hagihara & Yamashita, 1966), zinc ethylxanthate (Ikeda & Hagihara, 1966) and lead *n*-butylxanthate (Hagihara, Watanabe & Yamashita, 1968).

The present paper describes the crystal and molecular structure of zinc(II) bis(*O,O'*-diethyldithiophosphate), $\text{Zn}[\text{S}_2\text{P}(\text{OC}_2\text{H}_5)_2]_2$, a zinc salt of diethyldithiophosphoric acid. The sodium salt of this acid is a major component of Aerofloat 208, one of the most commonly used collectors in the flotation of sulphide minerals. Another point of interest is the coordination chemistry of the zinc atom surrounded by sulphur atoms. Since crystal structure data on related crystals are now available, the structure data of zinc diethyldithiophosphate can be compared with them.

Experimental

Crystal data

Zinc(II)bis(*O,O'*-diethyldithiophosphate),

$\text{Zn}[\text{S}_2\text{P}(\text{OC}_2\text{H}_5)_2]_2$; F.W. = 435.55.

Monoclinic prismatic along c (twinned) and fibrous along a ,

$a = 12.084$ (0.003)†, $b = 19.840$ (0.006), $c = 8.463$ (0.005) Å, $\beta = 113.99$ (0.03)°, $V = 1853.8$ (1.3) Å³.

$D_{\text{obs}} = 1.55$ g.cm⁻³ by flotation, $Z = 4$, $D_{\text{calc}} = 1.56$ g.cm⁻³.

Space group $P2_1/a$ from systematic absences.

Zinc diethyldithiophosphate powder was precipitated by combining concentrated aqueous solutions of

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† Throughout this paper, the figures in parentheses are the estimated standard deviations.

zinc sulphate and sodium diethyldithiophosphate in a molar ratio of 1:2. Crystals were obtained by slow evaporation of an acetone solution of the precipitate at room temperature. Most of the crystals were prismatic along c and some were fibrous along a . All the prisms along c examined showed twinning in various ratios of the twin components. The twin axis was c with a rotation of 180°. The cell parameters were determined from 24 high angle reflexions recorded by Straumanis' method around the a and c axes. The wavelengths used were 1.54051 and 1.54433 Å for Cu $K\alpha_1$ and α_2 radiations respectively.

Intensity measurements

Sets of multiple-film equi-inclination Weissenberg photographs were taken by the use of an integrating cassette around the a (0 to 2nd layers) and c (0 to 7th layers) axes with Ni-filtered Cu $K\alpha$ radiation. The cross sections of the crystals used for the measurements were about 0.01₅ × 0.02 and 0.04 × 0.06₅ mm for the a and c axes respectively. The specimen aligned along c showed a partial twinning, the ratio of the two components being 1:0.146 as estimated from the intensities of 25 pairs of equivalent reflexions. The intensities of 11 reflexions in the 1st and 6th layers (marked with asterisks in Table 3) were corrected for overlap of the minor twin component; the magnitudes of the corrections were about 10% of the original values. The peak intensities of the integrated spots were measured with a microphotometer and a total of 1294 independent reflexions (31% of those possible with Cu $K\alpha$ radiation) were collected. The intensities were corrected for Lorentz and polarization factors and for spot extensions. No absorption or extinction corrections were applied.

Determination of the structure

Patterson function

From a three-dimensional Patterson function, approximate coordinates of zinc, sulphur and phosphorus atoms were found. A Wilson plot to place the observed

structure factors on an approximate absolute scale facilitated the above analysis. All the nineteen non-hydrogen atoms were located by the usual procedures of the heavy atom method. The R value at this stage was 25%.

Least-squares refinement

The structure was then refined by full-matrix least squares. Unit weights were given to all reflexions. The hydrogen atoms were neglected.* Three cycles of isotropic refinement reduced the R value to 16%. An additional three cycles of anisotropic refinement reduced R to a final value of 7.9% (based on the observed reflexions only). The parameter shifts in the final cycle of the refinement were less than the corresponding estimated standard deviations.

The final atomic coordinates and thermal parameters are given in Tables 1 and 2 respectively. The numbering of the atoms is included in Fig. 1. The observed and calculated structure factors are compared in Table 3. A correction for anomalous dispersion was applied to the zinc, sulphur and phosphorus atoms (imaginary

parts ignored). The atomic scattering factors and the dispersion correction factors were taken from *International Tables for X-ray Crystallography* (1962). Among a total of about 2900 zero-intensity and unobserved reflexions within the Cu $K\alpha$ sphere, only twenty unobserved ones have F_c values greater than 20.0; the average value of the F_c values of the remaining reflexions is 5.2. The twenty reflexions mentioned above are included in Table 3 with their F_c values only.

Table 1. Final atomic coordinates with standard deviations ($\times 10^4$)

	x/a	y/b	z/c
Zn	1330 (2)	1702 (1)	3420 (3)
S(1)	4217 (3)	3318 (3)	1901 (6)
S(2)	1916 (3)	2458 (3)	1787 (6)
S(3)	2125 (4)	1752 (3)	6455 (6)
S(4)	2143 (5)	580 (3)	3807 (10)
P(1)	3708 (3)	2579 (2)	3053 (6)
P(2)	2789 (5)	856 (3)	6258 (10)
O(1)	4090 (9)	2708 (6)	5041 (14)
O(2)	4425 (9)	1900 (6)	3227 (16)
O(3)	4198 (16)	817 (11)	7209 (35)
O(4)	2547 (17)	310 (10)	7513 (27)
C(1)	3711 (18)	3333 (11)	5659 (29)
C(2)	4257 (19)	3288 (13)	7574 (28)
C(3)	4243 (20)	1486 (12)	1673 (32)
C(4)	5069 (20)	894 (11)	2293 (33)
C(5)	5083 (32)	1257 (20)	7378 (63)
C(6)	6194 (23)	1146 (19)	7897 (44)
C(7)	1321 (25)	179 (15)	7427 (47)
C(8)	1305 (28)	174 (16)	9073 (39)

Table 2. Final thermal parameters with standard deviations

The U_{ij} as given here are defined by:†

$$T = \exp \{ -10^{-4} \cdot 2\pi^2 (U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots) \}.$$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn	360 (11)	769 (17)	795 (17)	-15 (12)	281 (11)	-17 (16)
Bridging diethyldithiophosphate group						
S(1)	316 (18)	754 (33)	766 (31)	57 (23)	225 (20)	135 (30)
S(2)	271 (19)	1193 (46)	728 (33)	-43 (25)	158 (20)	97 (33)
P(1)	293 (19)	623 (32)	585 (29)	34 (20)	176 (20)	52 (26)
O(1)	474 (67)	809 (97)	542 (76)	129 (63)	212 (60)	141 (70)
O(2)	459 (65)	470 (79)	823 (91)	64 (55)	282 (64)	69 (66)
C(1)	821 (140)	593 (144)	1120 (174)	125 (126)	507 (128)	-26 (143)
C(2)	1084 (163)	1271 (198)	641 (157)	-149 (162)	577 (136)	-142 (163)
C(3)	970 (166)	868 (184)	1068 (195)	-71 (131)	552 (151)	-387 (150)
C(4)	973 (175)	583 (148)	1329 (205)	279 (131)	382 (155)	-83 (151)
Chelating diethyldithiophosphate group						
S(3)	599 (26)	894 (38)	773 (34)	-50 (28)	251 (25)	20 (33)
S(4)	860 (39)	824 (42)	1499 (63)	255 (33)	554 (42)	19 (42)
P(2)	520 (31)	931 (47)	1408 (61)	94 (32)	286 (35)	263 (45)
O(3)	539 (110)	1509 (196)	3050 (299)	311 (119)	356 (152)	264 (194)
O(4)	1092 (146)	1412 (179)	1852 (211)	435 (132)	305 (141)	693 (160)
C(5)	906 (286)	2318 (399)	3194 (558)	-146 (270)	907 (360)	1187 (405)
C(6)	470 (157)	2085 (353)	1937 (327)	91 (194)	108 (201)	-396 (287)
C(7)	675 (198)	931 (242)	2030 (327)	-284 (171)	68 (214)	93 (247)
C(8)	1891 (293)	1477 (280)	906 (229)	-250 (209)	637 (219)	-305 (206)

† The mean-square amplitude in a given direction \mathbf{p} (unit vector) is given by $\langle u_p^2 \rangle = \tilde{p} U p$, where \tilde{p} and p are the row and column matrices with elements defined by $\mathbf{p} = p_1(\mathbf{a}^*/a^*) + p_2(\mathbf{b}^*/b^*) + p_3(\mathbf{c}^*/c^*)$; in particular, U_{11} , U_{22} and U_{33} are the mean-square amplitudes (in 10^{-4} \AA^2 units) along the a^* , b^* and c^* axes respectively. The parameters U_{ij} multiplied by the factor 0.0079 ($= 10^{-4} \cdot 8\pi^2$), are comparable with the ordinary Debye factor, B .

Table 3 (cont.)

-11	12	-16	0	14	10	-3	72	-71	-6	47	46	-5	21	-14	H	6	6	H	12	6	H	4	7	-4	14	-11
-9	13	16	7	9	-13	-1	29	28	-4	44	-40	-4	39	-39	-14	14	17	-10	12	13	-14	10	12	0	11	-8
-6	23	-23	H	15	4	0	20	17	-5	17	-15	-4	40	44	-10	19	-20	-8	13	14	-10	29	-27	H	13	7
-7	19	18							-1	14	18	-1	17	22	-8	36	37	-7	17	-14	-9	30	28	H	13	7
-5	24	25	-7	16	14				2	26	26	0	20	-19	-7	12	15	-8	19	-21	-6	28	27	-10	11	-13
-3	75	-54	-4	26	30	H	3	5	-11	15	-18	-3	34	-34	-6	25	-28	0	23	23	-5	31	-27	-4	14	17
1	42	47	-2	13	20				6			5	17	-21	-2	18	-18	0	15	13	-4	11	-15	0	15	-16
H	10	4																								
-13	23	-27	H	16	4	-7	24	19	-14	14	15	-13	25	-28	-13	25	-28	H	7	6	H	14	6	H	14	7
-10	13	14	-7	20	24	-5	41	-33	-10	23	-21	-12	13	17	-10	17	-15	-9	21	20	H	7	6	H	14	7
-9	16	19	-5	13	-16	-6	9	11	-6	24	22	-7	15	18	-6	31	27	-14	13	-14	H	15	6	H	5	7
-7	28	28	-2	13	-15	-3	25	24	-4	38	-42	-5	15	-14	-4	26	26	-10	39	44	-9	14	-13	-6	17	-18
-4	31	-31	-1	16	19	-2	40	-38	-2	26	-30	-4	23	25	-3	13	18	-6	25	-28	-5	13	19	-4	11	-11
-3	32	-33	2	12	14	-1	16	-17	0	27	27	-1	14	-17	0	58	-55	-8	16	20	-4	13	-12	-2	19	20
-1	33	35	3	12	-13	0	20	-19	1	15	13	1	15	17	1	32	-29	-2	12	15	1	12	-12	H	6	7
1	35	-39	H	17	4	2	40	34	2	44	49	5	17	-21	2	18	19	0	13	-15	0	17	-18	H	0	7
7	18	19				5												4	19	18	-14	15	-18	-1	11	12
H	11	4																								
-12	20	-24	H	18	4	-12	14	-12	-14	9	-12	-8	18	21	-11	13	13	-14	20	-23	-14	15	-18	H	0	8
-8	41	43	-2	18	21	-10	31	29	-7	48	46	-8	17	-15	-9	40	-44	-8	17	-15	-12	16	19	-6	32	-33
-7	25	-25				-8	13	-13	-6	16	-18	-6	25	26	-6	21	-21	-7	21	-24	H	1	7	-6	13	13
-4	32	-38	H	0	5	-7	46	-55	-5	25	-29	-4	15	-15	-5	32	32	-3	17	18	-4	24	-23	H	7	7
-3	37	42				-5	80	75	-3	33	-36	-6	15	-15	-3	39	36	1	19	-22	H	1	7	-6	13	13
-2	20	24	-14	14	20	-4	38	35	0	20	-20	-1	15	14	-3	27	33	2	17	-14	-12	16	18	-2	18	-24
1	21	-27	1	21	-27	-3	31	26	1	24	26	1	24	26	1	24	26	-3	17	18	-10	32	-30	H	8	7
-3	22	-25	-6	83	-73	-2	17	-16	5	14	-13	H	15	5	-3	19	20	-6	26	20	H	8	7	-4	42	46
3	18	-20	-4	28	26	0	33	-30	0	20	-20	-5	13	18	H	4	6	-10	19	-20	-4	42	46	-10	20	-18
4	13	-12	4	13	-12	4	13	-12	4	13	-12	4	13	-12	4	13	-12	4	13	-12	-2	26	-19	-6	26	29
8		20				6	16	9	6	16	9	6	16	9	6	16	9	6	16	9	0	36	-37	-5	18	21
H	12	4				6	16	9	6	16	9	6	16	9	6	16	9	6	16	9	2	11	13	-1	13	-15
-8	13	-15	H	1	5				-13	16	-20	-10	21	24	-9	21	23	-10	14	15	-6	18	21	0	15	16
-4	28	27	-14	11	-12	-12	13	16	-10	21	20	-5	14	20	-9	19	21	-3	20	28	H	2	7	H	9	7
-1	15	16	-9	26	-24	-14	18	-21	0	19	14	-2	20	20	-2	20	20	-13	12	13	-11	13	-17	-6	-	23
0	27	-25	-8	25	19	-10	28	23	1	25	-26	-1	21	-18	-1	21	-18	H	10	6	-6	23	-19	-5	16	18
4	16	-18	-6	13	7	-9	30	-31	4	18	18	H	0	6	2	16	-19	-13	12	19	-5	29	31	-3	13	-15
H	13	4				-7	24	-19	5	17	21	H	0	6				-10	13	13	-3	14	15	H	10	7
-12	13	19	-2	43	39	-6	12	-8	H	10	5	-12	26	-24	-14	13	15	-9	19	-17	-11	12	-14	-11	11	11
-5	42	-43	0	54	51	-9	13	29	-8	31	33	-10	32	33	-12	13	14	-11	12	-14	-4	23	25	-5	17	-18
-4	30	32	4	13	-15	-2	23	26	-7	27	-33	-8	68	-60	-10	46	-50	0	13	-13	-8	14	-15	-1	14	18
-2	19	-21	H	2	1	6	6	5	-4	23	-24	2	24	-22	-9	27	28	1	19	24	-13	15	16	-12	19	-16
4	16	17				-3	44	47	-3	44	47	H	1	6	-6	32	33	H	11	6	-11	16	-18	-11	13	13
H	14	4				-2	13	13	-2	13	13	-2	13	13	-2	13	13	-4	28	-17	-9	13	11	-10	17	17
-11	10	16	-7	41	37	-14	16	17	3	18	-19	-16	16	-18	-3	20	-24	-8	14	-15	-3	13	-12	-4	17	-20
-6	16	17	-4	44	36	-12	17	19	5	14	13	-10	17	17	2	22	23	-4	13	14	-1	12	12	0	15	15
-5	24	-25	-10	23	-26	-10	23	-26	-8	37	-33	H	11	5	-8	27	23	1	14	13	0	19	18	H	12	7
-1	20	-23	-4	37	-31	-8	37	-31																		

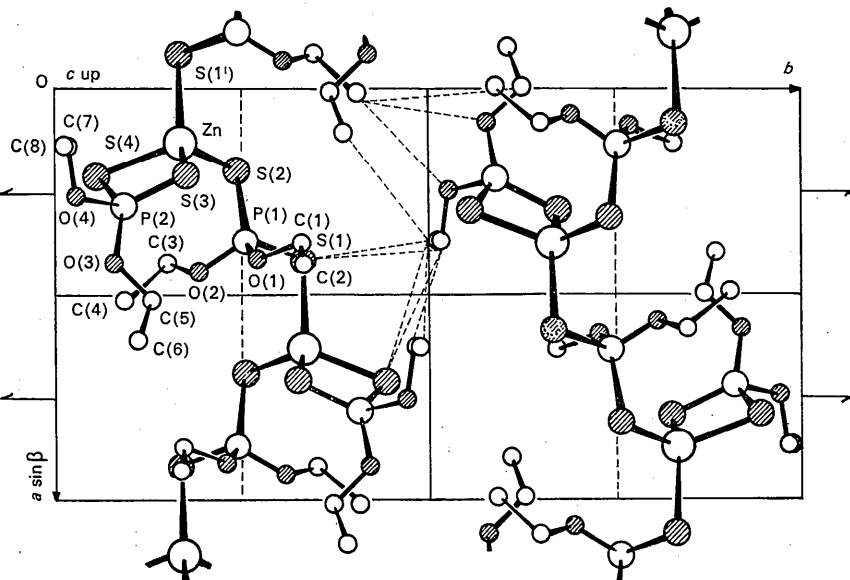


Fig. 1. Atomic arrangements in the unit cell of zinc diethyldithiophosphate, viewed along the c axis. The broken lines indicate the van der Waals contacts along the b axis between the adjacent chains (*cf.* Table 5).

other (the bridging group) bridges with two sulphur ends, S(1) and S(2), two zinc atoms, Zn and Zn', related by a glide. Thus, the formula unit does not exist as a monomer; instead, infinite linear zigzag chains (polymers) are formed along the a axis. These chains are stacked laterally along the b and c axes with van

der Waals contacts of methyl-sulphur, methyl-methyl and methyl-oxygen.

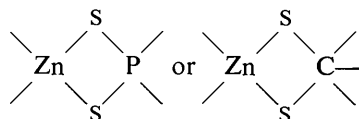
This linear zigzag chain structure is unique among related crystals so far investigated. In zinc ethylxanthate (ZnEX) (Ikeda & Hagihara, 1966) each zinc atom is bound to four sulphur atoms in a slightly distorted tet-

rahedral arrangement, whereas each xanthate group bridges, with its two sulphur ends, two neighbouring zinc atoms along the *b* or *c* axis, forming a two-dimensional network. In zinc(II) bis(diethyldithiocarbamate) (ZnEC) (Bonamico, Mazzone, Vaciego & Zambonelli, 1965) each zinc atom is coordinated with five sulphur atoms, one displaced some way from the other four, in a distorted trigonal bipyramidal arrangement through a dimerization of the molecules. A similar dimeric structure is reported for zinc dimethyldithiocarbamate (ZnMC) (Klug, 1966), where each zinc atom is bound to four sulphur atoms in a distorted tetrahedral arrangement.

Bond distances and bond angles

The bond distances and angles are given in Table 4 and are also shown in Fig. 2. Except those associated with the atom C(5), all of them can be regarded as normal compared with available data. The four Zn-S distances in the tetrahedron, 2.337, 2.345, 2.351 and 2.401(0.006) Å, fall in the range 2.312 to 2.443 Å found in the structures mentioned above, and are in agreement with the sum (2.35 Å) of the tetrahedral covalent bond radii of zinc and sulphur atoms (Pauling, 1960).* The difference, 0.057 Å, between the shorter distances

(average 2.344 Å) and the longest one, Zn-S(4) = 2.401 Å, is statistically significant. The same characteristic feature that one of the two Zn-S distances in a four-membered chelate ring,



is significantly longer than the shorter three, has been observed both in ZnEC and in ZnMC. In ZnEX, where no such chelate ring exists, the four Zn-S distances do not differ from one another by so much, varying only from 2.337 to 2.369 Å. Among the six tetrahedral angles around a zinc atom, the angle S(3)-Zn-S(4) = 85.9(0.2)° is smaller than the ideal value, 109.5°, by 23.6°, apparently as a result of the ring formation. The corresponding angles in ZnEC and ZnMC are 75°47' and 75.37° respectively. In ZnEX, however, the maximum deviation from the ideal value is only 6.9°.

The fifth Zn-S distance of 2.815 Å in ZnEC, one of the two axial coordination distances in the trigonal bipyramid interpretation, is far longer than the other four (2.331, 2.355, 2.383 and 2.443 Å) and even longer than the sum (2.59 Å) of the ionic radius of Zn²⁺ and the van der Waals radius of sulphur. Therefore, as was pointed out by Klug (1966), the distorted tetrahedron interpretation which ignores the fifth coordi-

* The atomic radii used in the following discussion are all taken from this reference.

Table 4. Bond distances and angles with standard deviations

Bond distances			
Zn-S(1')	2.345 (0.004) Å	O(1)-C(1)	1.49 (0.03) Å
Zn-S(2)	2.337 (0.007)	O(2)-C(3)	1.49 (0.03)
Zn-S(3)	2.351 (0.006)	O(3)-C(5)	1.34 (0.05)
Zn-S(4)	2.401 (0.007)	O(4)-C(7)	1.48 (0.04)
S(1)-P(1)	1.992 (0.007)	C(1)-C(2)	1.48 (0.03)
S(2)-P(1)	2.001 (0.005)	C(3)-C(4)	1.49 (0.03)
S(3)-P(2)	1.987 (0.009)	C(5)-C(6)	1.25 (0.05)
S(4)-P(2)	1.973 (0.011)	C(7)-C(8)	1.40 (0.06)
P(1)-O(1)	1.57 (0.01)		
P(1)-O(2)	1.57 (0.01)		
P(2)-O(3)	1.56 (0.02)		
P(2)-O(4)	1.62 (0.02)		
Bond angles			
S(1')-Zn-S(2)	102.2 (0.2)°	S(3)-P(2)-S(4)	109.7 (0.4)°
S(1')-Zn-S(3)	118.0 (0.2)	S(3)-P(2)-O(3)	113.2 (0.9)
S(1')-Zn-S(4)	110.7 (0.2)	S(3)-P(2)-O(4)	110.8 (0.9)
S(2)-Zn-S(3)	122.1 (0.2)	S(4)-P(2)-O(3)	114.3 (1.2)
S(2)-Zn-S(4)	118.0 (0.3)	S(4)-P(2)-O(4)	113.8 (0.8)
S(3)-Zn-S(4)	85.9 (0.2)	O(3)-P(2)-O(4)	94.5 (1.2)
Zn'-S(1)-P(1)	101.8 (0.2)	P(1)-O(1)-C(1)	120.8 (1.1)
Zn-S(2)-P(1)	106.4 (0.3)	P(1)-O(2)-C(3)	120.7 (1.1)
Zn-S(3)-P(2)	82.5 (0.3)	P(2)-O(3)-C(5)	132.6 (2.3)
Zn-S(4)-P(2)	81.5 (0.3)	P(2)-O(4)-C(7)	121.9 (1.7)
S(1)-P(1)-S(2)	108.0 (0.3)	O(1)-C(1)-C(2)	105.7 (1.7)
S(1)-P(1)-O(1)	112.9 (0.5)	O(2)-C(3)-C(4)	106.7 (1.7)
S(1)-P(1)-O(2)	114.0 (0.6)	O(3)-C(5)-C(6)	128.2 (3.6)
S(2)-P(1)-O(1)	112.0 (0.5)	O(4)-C(7)-C(8)	111.8 (2.4)
S(2)-P(1)-O(2)	112.5 (0.5)		
O(1)-P(1)-O(2)	97.4 (0.7)		

nation seems more reasonable than the trigonal bipyramidal one. From this point of view, the sulphur coordinations around a zinc atom in ZnEX, ZnEC, ZnMC and the present ZnEP can be summarized by a common principle, *i.e.* the tetrahedral coordination of sulphur atoms around a zinc atom, the distortion from the ideal tetrahedron being governed by the structure of the ligand groups. However, introduction of non-sulphur atoms in the ligands may completely change the coordination. Some examples of five coordination around a zinc atom are quoted by Bonamico *et al.* (1966).

The four S-P distances, 2.001, 1.992, 1.987 and 1.973 (0.008) Å, lie between the S-P single- and double-bond distances (1.94 and 2.14 Å, respectively). The sequence of their magnitudes is consistent with that of the Zn-S distances; the shorter the S-P distance, the longer the corresponding Zn-S distance and *vice versa*. Each phosphorus atom is bound to two sulphur and two oxygen atoms, and the arrangements around the central phosphorus atoms, P(1) and P(2), are also distorted tetrahedral. The deviations of the angles, O-P-O = 97.5 and 94.5 (1.0)°, from the ideal tetrahedral value are probably a result of the volume of the oxygen atom being less than that of the sulphur atom. A similar tetrahedral structure around a phosphorus atom has been reported in potassium dimethyldithiophosphate, $\text{KS}_2\text{P}(\text{OCH}_3)_2$ (Coppens, MacGillavry, Hovenkamp & Douwes, 1962).

The bond distances $\text{O}(3)\text{-C}(5) = 1.34$ and $\text{C}(5)\text{-C}(6) = 1.25$ Å are exceptionally short and the bond angles, $\text{P}(2)\text{-O}(3)\text{-C}(5) = 132.6^\circ$ and $\text{O}(3)\text{-C}(5)\text{-C}(6) = 128.2^\circ$ are exceptionally large. These anomalies may have been caused by some errors such as those in the correction for the overlap of the minor twin component, or by some positional disorder of the atom C(5) and of its environment.

Thermal parameters

The thermal parameters of ZnEP (Table 2) have several characteristic features. First, the mean-square amplitudes along the a^* axis (U_{11}) are generally smaller than those along the b^* and c^* axes (U_{22} and U_{33} respectively); this is reasonable for the infinite chain structure along the a axis. Secondly, the thermal parameters of the bridging diethyldithiophosphate group are generally smaller than the corresponding parameters of the chelating group; the thermal motions of the bridging group are suppressed by the chain formation. Thirdly, attempts to interpret the thermal parameters in terms of the rigid-body vibrations of the whole chain (Cruickshank, 1961) proved to be unsuccessful. The average discrepancies between the observed and the calculated amplitudes were greater than the average standard deviations in the observed amplitudes.

Van der Waals contacts between chains

The closest distances between adjacent chains are summarized in Table 5, and are also included in Figs. 1

and 3 for the b and c axis directions respectively. The symmetry related contacts are omitted. The even-numbered carbon atoms belong to methyl groups, while those with odd-numbers belong to methylene groups. All the distances can be regarded as normal compared

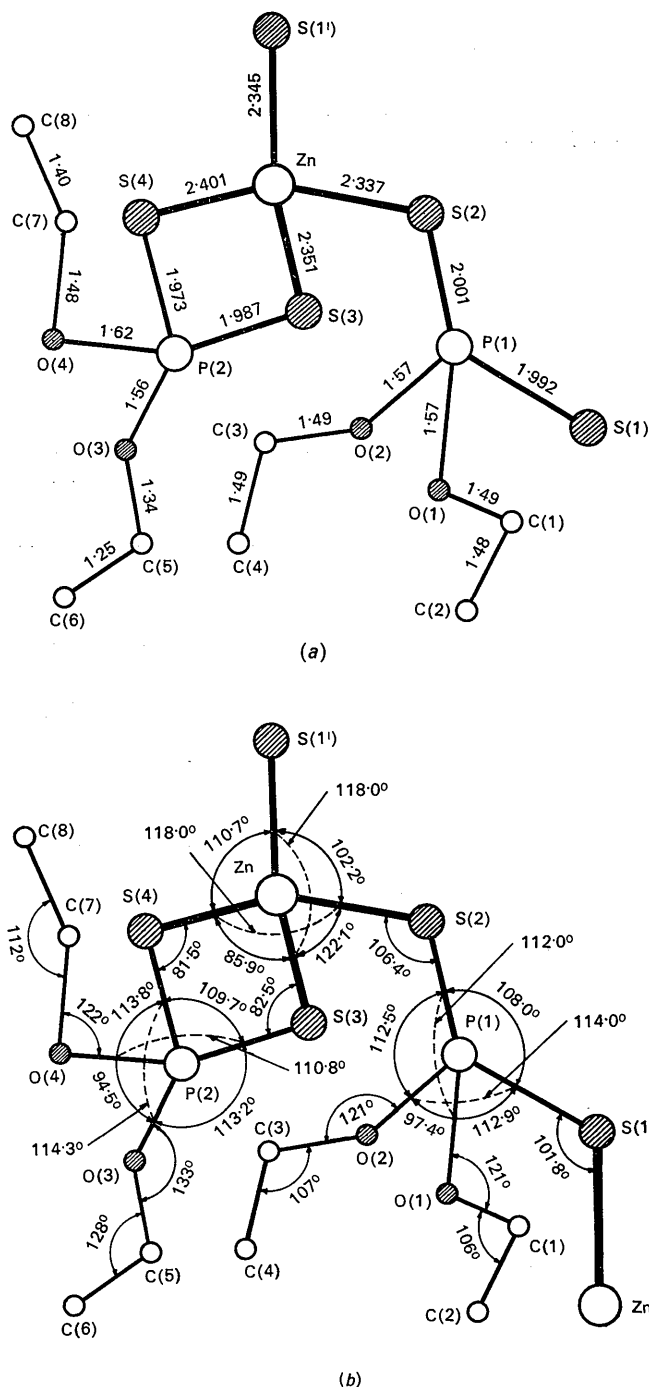


Fig. 2. (a) Bond distances (Å) and (b) bond angles in zinc diethyldithiophosphate.

Table 5. *Van der Waals contacts between adjacent chains*

Figures in parentheses are the standard deviations ($\times 10^2$).
 Notation: unprimed ... (x, y, z) ; single-primed ... $(\frac{1}{2} + x, \frac{1}{2} - y, z)$; double-primed ... $(\frac{1}{2} - x, \frac{1}{2} + y, 1 - z)$.

Along <i>b</i> axis		Along <i>c</i> axis	
S(1) ····· C(8'')	3·77 (3) Å	S(1) ····· C(2, - <i>c</i>)	3·68 (3) Å
S(1) ····· C(7'')	3·83 (3)	S(4) ····· C(8, - <i>c</i>)	3·80 (3)
S(4') ····· C(7'')	4·16 (3)	S(1) ····· C(6', - <i>a</i> - <i>c</i>)	3·99 (3)
S(4') ····· C(8'')	4·16 (3)	S(2') ····· C(2, - <i>c</i>)	3·99 (2)
O(3'') ····· C(4', - <i>a</i>)	3·49 (3)	S(2) ····· C(6', - <i>a</i> - <i>c</i>)	4·11 (4)
O(4'') ····· C(4', - <i>a</i>)	3·69 (3)	S(3, - <i>c</i>) ····· C(3)	4·14 (2)
C(6', - <i>a</i>) ····· C(8'', + <i>c</i>)	4·03 (4)	C(3) ····· C(5, - <i>c</i>)	4·18 (6)
C(7') ····· C(7'')	4·11 (4)	C(3) ····· C(8, - <i>c</i>)	4·23 (4)
C(8') ····· C(8'', + <i>c</i>)	4·11 (6)	C(4) ····· C(5, - <i>c</i>)	4·23 (6)
C(4', - <i>a</i>) ····· C(5'')	4·29 (4)		

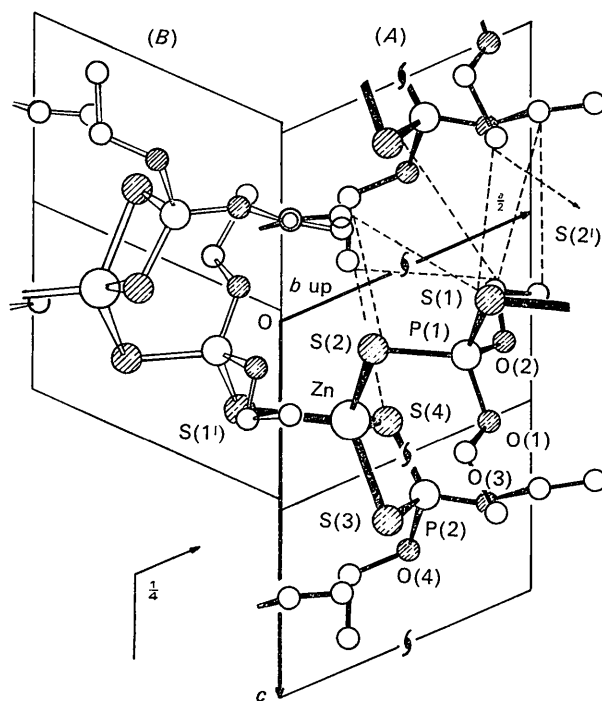


Fig. 3. Model of a twin boundary in zinc diethyldithiophosphate, as seen along the *b* axis. The twin component (B) is obtained from (A) by a rotation of 180° around the *c* axis (the twin operation) with a subsequent translation, $\Delta z = -0.53$. The molecular chains which are related by 2_1 symmetry to those shown in the Figure are omitted. The broken lines indicate the van der Waals contacts along the *c* axis between the adjacent chains (*cf.* Table 5).

with the expected values: S...C = 3.85, O...C = 3.40 and C...C = 4.00 Å (Pauling, 1960). It should be noted that sulphur-methyl and sulphur-methylene contacts are important in this structure.

According to a preliminary molecular weight determination, zinc diethyldithiophosphate is monomeric in

chloroform solution, *i.e.* the formula unit,



behaves as a molecular unit in the solution. It can be inferred, therefore, that polymerization takes place through the Zn-S bond formation in the course of crystal growth. If we assume that the coordinates of the sulphur atom S(1') are not affected by the twinning, a model of the twin boundary can be conceived as shown in Fig. 3. In this model, the bond angle of S(1') is distorted from the original value (101.8°) to 109.5° .

Crystal structure analyses on lead and copper diethyldithiophosphates are now being undertaken in our laboratory.

The main part of the calculations was performed on the HITAC 5020 computer of the computer centre of the University of Tokyo and on the OKITAC 5090H computer of this Institute, with a universal crystallographic computation program system, UNICS (Sakurai, Ito, Iwasaki, Watanabe & Fukuhara, 1967). This work was supported in part by a Scientific Research Grant of the Ministry of Education.

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