

type. On this basis it could be suggested that the hydrogen bond within the H_5O_2^+ ion is of this type. It is, however, uncertain whether this is a sufficiently definitive test to eliminate the possibility that the bond is of the statistically symmetric double-potential type.

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The Crystal Structure of Zinc Isopropylxanthate

BY TETSUZO ITO

The Institute of Physical and Chemical Research, Rikagaku Kenkyusho, Wako-shi, Saitama 351, Japan

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The crystal structure of zinc isopropylxanthate, $\text{Zn}(\text{S}_2\text{COiso}-\text{C}_3\text{H}_7)_2$ has been determined. The final R value was 6.8%. The crystal is triclinic, space group $P\bar{1}$, with $a=10.915$ (3), $b=13.167$ (4), $c=10.393$ (2) Å, $\alpha=100.89$ (2), $\beta=100.42$ (2), $\gamma=101.33$ (7)°, $Z=4$. The four zinc isopropylxanthate

molecules in the unit cell are linked together by the $-\text{Zn}-\text{S}-\text{C}-\text{S}-\text{Zn}-$ bridges to form a tetramer with a 16-membered ring. The tetramer is centrosymmetric about the centre of the ring. Four isopropylxanthate groups (bridging groups) make up the ring formation, and each of the other four (chelating groups) coordinates to a zinc atom. The coordination of the four sulphur atoms about each zinc atom forms a distorted tetrahedron, the Zn-S distances ranging from 2.307 to 2.408 Å.

Introduction

Although the sulphur coordinations around a zinc atom in some zinc salts of dithioacids form distorted tetrahedra, in the crystalline state (Ito, Igarashi & Hagihara, 1969), the modes of molecular aggregations are varied as shown schematically in Fig. 1. In zinc ethylxanthate, $\text{Zn}(\text{EX})_2$ (Ikeda & Hagihara, 1966), the molecules aggregate into two-dimensional networks with 16-membered rings [Fig. 1(a)]. In zinc diethyldithiophosphate, $\text{Zn}(\text{EP})_2$ (Ito *et al.*, 1969), only one half

of the phosphate groups take part in bridge formation, forming infinite linear zigzag chains [Fig. 1(b)]. On the other hand, dimeric structures with an 8-membered ring [Fig. 1(c)] are reported for zinc diethyldithiocarbamate, $\text{Zn}(\text{EC})_2$ (Bonamico, Mazzone, Vaciago & Zambonelli, 1965), zinc dimethyldithiocarbamate, $\text{Zn}(\text{MC})_2$ (Klug, 1966) and zinc diisopropylidithiophosphate, $\text{Zn}(\text{isoPP})_2$ (Lawton & Kokotailo, 1969). In organic solvents, however, the $\text{Zn}(\text{EC})_2$ and $\text{Zn}(\text{EP})_2$ molecules are monomeric (Bonamico *et al.*, 1965; Ito *et al.*, 1969).

In order to study the effect of alkyl substitutions on the molecular structure, the crystal structure of zinc isopropylxanthate, $\text{Zn}(\text{isoPX})_2$, a higher homologue of $\text{Zn}(\text{EX})_2$, was investigated. The $\text{Zn}(\text{isoPX})_2$ molecules have been found to aggregate into tetramers with a 16-membered ring [Fig. 1(d)].

Experimental

Crystal data

Zinc(II) bis-(*O*-isopropylthiocarbonate),

$\text{Zn}(\text{S}_2\text{COiso-C}_3\text{H}_7)_2$; F.W. 335.61.

Triclinic prismatic along the *a* axis,

$a = 10.915(3)$, $b = 13.167(4)$, $c = 10.393(2)$ Å,

$\alpha = 100.89(2)$, $\beta = 100.42(2)$, $\gamma = 101.33(7)^\circ$,

$V = 1400.9(5)$ Å³.

$D_m = 1.58$ g.cm⁻³ (by flotation), $Z = 4$, $D_x = 1.59$ g.cm⁻³.

Space group $P\bar{1}$ or $P1$; $P\bar{1}$ was assumed.

$\text{Zn}(\text{isoPX})_2$ powder was precipitated by combining aqueous solutions of zinc chloride and potassium isopropylxanthate. Crystals were obtained by recrystallization of the powder from an ethanol solution. The cell parameters were determined from 24 high-angle reflexions recorded by the Straumanis method around the *a* and *b* axes. The space group was assumed to be the centric $P\bar{1}$; this was subsequently confirmed by the solution of the structure.

Intensity measurements

The intensities were measured with a diffractometer of the equi-inclination type, READ-1 (Sakurai, Ito & Iimura, 1970), around the *a* axis up to the 11th layer. Mo $K\alpha$ radiation was used with a graphite mono-

chromator. The crystal was rotated in the ω -scan mode with a scanning speed of 2° per minute. The crystal used measured 0.23 mm along the *a* axis with a cross section of 0.08 × 0.10 mm. Altogether 1550 independent reflexions were collected. These were corrected for Lorentz and polarization factors. No absorption or extinction corrections were applied. The relative scales of different layers were checked by the $h0l$ reflexions measured with a different crystal around the *b* axis;

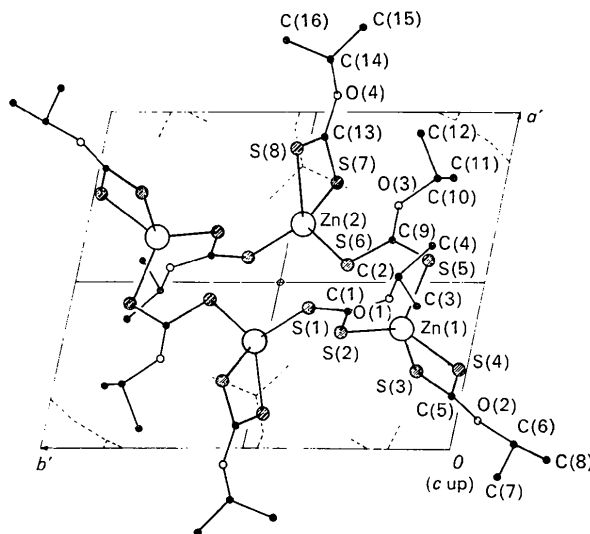


Fig. 2. Structure of $\text{Zn}(\text{isoPX})_2$, viewed along the *c* axis.

Table 1. Atomic coordinates of the non-hydrogen atoms with standard deviations ($\times 10^4$)

No.	Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
1	Zn(1)	3707 (3)	1841 (2)	4131 (3)
2	Zn(2)	6848 (3)	4673 (2)	2226 (3)
3	S(1)	4215 (7)	4092 (5)	8521 (7)
4	S(2)	3488 (7)	3342 (6)	5546 (6)
5	S(3)	2278 (6)	1230 (6)	2011 (7)
6	S(4)	2384 (6)	200 (5)	4305 (6)
7	S(5)	5717 (6)	1513 (5)	3987 (7)
8	S(6)	5500 (6)	3445 (5)	2968 (8)
9	S(7)	8021 (6)	4134 (5)	619 (7)
10	S(8)	8995 (6)	5312 (5)	3446 (7)
11	O(1)	4551 (14)	2329 (12)	7114 (16)
12	O(2)	806 (14)	-570 (11)	1887 (16)
13	O(3)	7338 (15)	2540 (13)	2818 (20)
14	O(4)	10425 (15)	4586 (12)	1805 (15)
15	C(1)	4101 (19)	3190 (16)	7028 (22)
16	C(2)	5202 (22)	2121 (16)	8351 (23)
17	C(3)	4254 (28)	1598 (24)	9095 (27)
18	C(4)	6127 (23)	1429 (24)	7929 (31)
19	C(5)	1736 (20)	193 (15)	2716 (25)
20	C(6)	236 (23)	-1558 (19)	2324 (26)
21	C(7)	-828 (29)	-1289 (22)	3011 (36)
22	C(8)	-279 (29)	-2422 (18)	1024 (26)
23	C(9)	6306 (19)	2476 (18)	3209 (23)
24	C(10)	8107 (19)	1684 (15)	2904 (27)
25	C(11)	8151 (35)	1266 (22)	1483 (29)
26	C(12)	9395 (31)	2313 (24)	3742 (36)
27	C(13)	9256 (20)	4682 (16)	1954 (23)
28	C(14)	11513 (20)	4941 (18)	2938 (26)
29	C(15)	12493 (24)	4304 (21)	2487 (29)
30	C(16)	12069 (23)	6105 (19)	3104 (23)

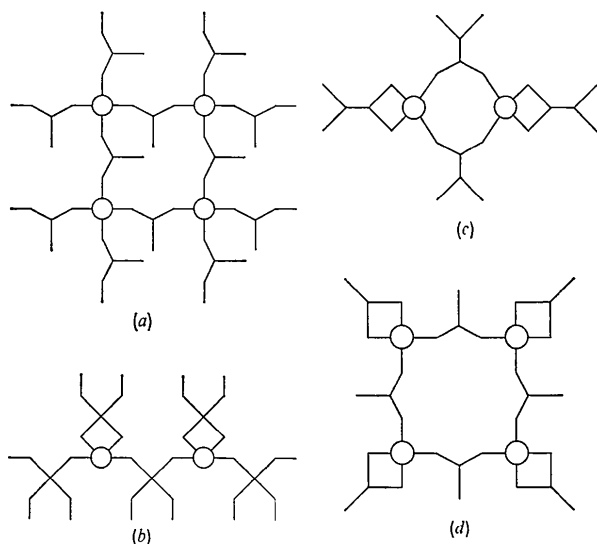


Fig. 1. Modes of molecular aggregation in zinc salts of dithioacids in the crystalline state: (a) two-dimensional networks in $\text{Zn}(\text{EX})_2$, (b) linear chains in $\text{Zn}(\text{EP})_2$, (c) dimers in $\text{Zn}(\text{EC})_2$, $\text{Zn}(\text{MC})_2$ and $\text{Zn}(\text{isoPP})_2$, (d) tetramers in $\text{Zn}(\text{isoPX})_2$.

their deviations from unity were found to be less than three per cent.

Determination of the structure

Patterson map

In the asymmetric unit of a three-dimensional Patterson map, two prominent peaks with peak values

of about $2000 \text{ e}^2 \cdot \text{\AA}^{-3}$ which corresponded to twofold Zn-Zn vectors, were observed. This indicated that the space group was probably $P\bar{1}$; with the space group $P1$, the four zinc atoms in the unit cell are all independent and no twofold Zn-Zn vectors were to be expected except for the case of accidental coincidence of vectors. Further analysis was, therefore, continued with the space group $P\bar{1}$. All thirty non-hydrogen

Table 2. Thermal parameters of the non-hydrogen atoms with standard deviations

The thermal parameters refer to the expression $T = \exp \{-10^{-3} \cdot 2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots)\}$.

The B_{eq} values are the equivalent isotropic temperature factors proposed by Hamilton (1959).

No.	Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B_{eq}
1	Zn(1)	41 (1)	37 (2)	44 (2)	10 (1)	12 (1)	6 (1)	3.2
2	Zn(2)	45 (2)	34 (2)	55 (2)	15 (1)	19 (1)	14 (1)	3.3
3	S(1)	72 (5)	44 (4)	39 (4)	27 (4)	0 (4)	2 (3)	4.1
4	S(2)	76 (4)	37 (4)	31 (4)	25 (3)	14 (4)	6 (3)	3.7
5	S(3)	59 (4)	36 (4)	56 (5)	0 (3)	7 (4)	23 (3)	4.0
6	S(4)	50 (4)	39 (4)	40 (4)	9 (3)	5 (3)	14 (3)	3.4
7	S(5)	49 (4)	39 (4)	69 (5)	17 (3)	23 (4)	25 (4)	3.8
8	S(6)	54 (4)	50 (5)	105 (6)	24 (4)	41 (4)	41 (4)	4.9
9	S(7)	48 (4)	46 (4)	50 (5)	8 (3)	3 (3)	-2 (4)	4.1
10	S(8)	57 (4)	59 (4)	44 (4)	20 (3)	9 (4)	6 (4)	4.2
11	O(1)	51 (10)	47 (10)	64 (12)	26 (8)	15 (9)	23 (9)	4.0
12	O(2)	58 (10)	37 (10)	53 (12)	5 (8)	20 (9)	2 (9)	3.9
13	O(3)	64 (11)	55 (12)	121 (17)	27 (9)	47 (12)	50 (12)	5.6
14	O(4)	67 (11)	60 (11)	51 (11)	38 (9)	24 (9)	23 (9)	4.2
15	C(1)	36 (12)	27 (13)	43 (15)	4 (10)	6 (12)	-2 (11)	3.0
16	C(2)	62 (16)	22 (13)	60 (17)	29 (12)	-20 (13)	4 (12)	4.0
17	C(3)	104 (23)	104 (25)	50 (19)	10 (19)	28 (17)	62 (18)	6.4
18	C(4)	36 (15)	102 (24)	99 (25)	29 (16)	21 (16)	19 (20)	6.1
19	C(5)	47 (14)	12 (11)	73 (19)	9 (10)	21 (13)	-23 (12)	3.7
20	C(6)	61 (16)	45 (16)	78 (20)	18 (13)	25 (15)	34 (15)	4.5
21	C(7)	101 (23)	55 (19)	121 (32)	9 (17)	38 (22)	20 (20)	7.3
22	C(8)	133 (25)	17 (13)	59 (19)	14 (14)	17 (18)	15 (13)	5.5
23	C(9)	33 (12)	56 (17)	48 (16)	15 (11)	17 (12)	31 (13)	3.3
24	C(10)	37 (13)	4 (11)	121 (23)	14 (9)	29 (14)	24 (13)	4.0
25	C(11)	186 (34)	69 (21)	55 (21)	104 (23)	-7 (21)	-8 (16)	7.9
26	C(12)	111 (26)	69 (22)	140 (34)	59 (20)	-24 (23)	-24 (22)	9.1
27	C(13)	55 (15)	29 (13)	58 (17)	13 (11)	48 (13)	26 (12)	3.2
28	C(14)	28 (13)	50 (17)	81 (20)	-2 (11)	3 (13)	22 (15)	4.3
29	C(15)	64 (17)	61 (18)	90 (23)	43 (15)	1 (16)	35 (17)	5.3
30	C(16)	65 (16)	47 (16)	36 (16)	6 (13)	-3 (13)	25 (13)	4.0

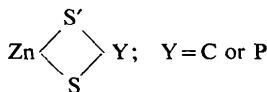
Table 3. Atomic coordinates ($\times 10^3$) and isotropic temperature factors (\AA^2) of the hydrogen atoms, and the C-H bond distances (\AA) with standard deviations

No.	Atom	x/a	y/b	z/c	B	r (C-H)
1	H(2,1)	608 (15)	296 (13)	885 (17)	2.4 (4.2)	1.26 (17)
2	H(3,1)	451 (12)	155 (10)	995 (14)	1.1 (3.1)	0.91 (14)
3	H(3,2)	376 (17)	94 (15)	825 (19)	5.5 (4.8)	1.08 (19)
4	H(4,1)	550 (18)	93 (15)	681 (19)	5.8 (5.2)	1.22 (20)
5	H(4,2)	683 (11)	196 (10)	755 (13)	-1.7 (2.8)	1.11 (13)
6	H(6,1)	100 (10)	-157 (9)	295 (11)	0.0 (2.4)	0.97 (12)
7	H(7,1)	-120 (17)	-207 (14)	321 (18)	3.4 (4.6)	1.10 (19)
8	H(7,2)	-42 (18)	-82 (16)	345 (20)	6.5 (5.4)	0.71 (21)
9	H(7,3)	-145 (20)	-124 (17)	220 (22)	8.2 (6.1)	1.00 (23)
10	H(8,1)	-50 (18)	-324 (15)	115 (19)	3.7 (5.1)	1.10 (20)
11	H(10,1)	757 (18)	115 (15)	309 (19)	5.2 (5.1)	0.90 (20)
12	H(11,1)	844 (13)	64 (11)	151 (14)	-0.1 (3.2)	0.94 (15)
13	H(11,2)	713 (23)	104 (19)	89 (24)	11.8 (7.3)	1.12 (25)
14	H(11,3)	845 (16)	205 (13)	115 (17)	3.4 (4.3)	1.16 (18)
15	H(12,1)	957 (19)	270 (16)	331 (21)	9.9 (5.6)	0.76 (22)
16	H(12,2)	922 (11)	257 (10)	495 (12)	-0.8 (2.7)	1.29 (13)
17	H(15,1)	1221 (18)	368 (15)	242 (19)	5.3 (5.6)	0.80 (20)
18	H(15,2)	1279 (22)	446 (19)	165 (24)	9.2 (7.1)	1.02 (25)
19	H(16,1)	1274 (20)	644 (17)	411 (21)	6.6 (5.8)	1.12 (22)
20	H(16,2)	1232 (10)	605 (8)	213 (11)	-2.5 (2.3)	1.09 (11)

Table 5. Bond distances and angles with standard deviations

				Average
Zn(1)—S(2)	2.311 (7) Å	Zn(2)—S(6)	2.307 (8) Å	2.309 Å
Zn(1)—S(5)	2.343 (8)	Zn(2)—S(1')	2.342 (8)	2.343
Zn(1)—S(3)	2.351 (7)	Zn(2)—S(8)	2.357 (7)	2.354
Zn(1)—S(4)	2.408 (7)	Zn(2)—S(7)	2.370 (8)	2.389
Bridging isopropylxanthate groups				
S(2)—C(1)	1.63 (2)	S(5)—C(9)	1.71 (3)	1.67
S(1)—C(1)	1.73 (2)	S(6)—C(9)	1.72 (3)	1.73
O(1)—C(1)	1.33 (3)	O(3)—C(9)	1.26 (3)	1.30
O(1)—C(2)	1.45 (3)	O(3)—C(10)	1.54 (3)	1.50
C(2)—C(3)	1.53 (4)	C(10)—C(11)	1.49 (4)	1.51
C(2)—C(4)	1.55 (4)	C(10)—C(12)	1.50 (3)	1.53
Chelating isopropylxanthate groups				
S(4)—C(5)	1.67 (3)	S(7)—C(13)	1.68 (2)	1.68
S(3)—C(5)	1.72 (2)	S(8)—C(13)	1.71 (2)	1.72
O(2)—C(5)	1.32 (2)	O(4)—C(13)	1.34 (3)	1.33
O(2)—C(6)	1.51 (3)	O(4)—C(14)	1.44 (3)	1.48
C(6)—C(7)	1.53 (4)	C(14)—C(16)	1.50 (3)	1.52
C(6)—C(8)	1.53 (3)	C(14)—C(15)	1.57 (4)	1.55
S(3)—Zn(1)—S(4)	76.7 (0.2)°	S(7)—Zn(2)—S(8)	77.1 (0.2)°	76.9°
S(4)—Zn(1)—S(5)	106.6 (0.3)	S(6)—Zn(2)—S(7)	121.5 (0.3)	114.1
S(3)—Zn(1)—S(5)	110.2 (0.3)	S(6)—Zn(2)—S(8)	118.1 (0.3)	114.2
S(2)—Zn(1)—S(4)	114.1 (0.3)	S(1')—Zn(2)—S(7)	107.6 (0.3)	110.8
S(2)—Zn(1)—S(3)	117.7 (0.3)	S(1')—Zn(2)—S(8)	117.7 (0.3)	117.7
S(2)—Zn(1)—S(5)	122.1 (0.2)	S(1')—Zn(2)—S(6)	111.0 (0.3)	116.6
Bridging isopropylxanthate groups				
Zn(2')—S(1)—C(1)	102.1 (0.8)	Zn(2)—S(6)—C(9)	105.8 (0.8)	104.0
Zn(1)—S(2)—C(1)	102.4 (0.8)	Zn(1)—S(5)—C(9)	101.5 (0.8)	102.0
S(1)—C(1)—S(2)	123.9 (1.4)	S(5)—C(9)—S(6)	119.9 (1.4)	121.9
S(1)—C(1)—O(1)	117.3 (1.7)	S(6)—C(9)—O(3)	116.4 (2.0)	116.9
S(2)—C(1)—O(1)	118.8 (1.6)	S(5)—C(9)—O(3)	123.6 (2.0)	121.2
C(1)—O(1)—C(2)	125.1 (1.7)	C(9)—O(3)—C(10)	121.3 (2.1)	123.2
O(1)—C(2)—C(4)	105.5 (2.0)	O(3)—C(10)—C(11)	103.9 (2.2)	104.7
O(1)—C(2)—C(3)	112.1 (1.9)	O(3)—C(10)—C(12)	103.0 (1.8)	107.6
C(3)—C(2)—C(4)	113.6 (2.3)	C(11)—C(10)—C(12)	112.1 (2.6)	112.9
Chelating isopropylxanthate groups				
Zn(1)—S(4)—C(5)	80.9 (0.7)	Zn(2)—S(7)—C(13)	81.4 (0.9)	81.2
Zn(1)—S(3)—C(5)	81.6 (0.7)	Zn(2)—S(8)—C(13)	81.1 (0.7)	81.4
S(3)—C(5)—S(4)	120.8 (1.1)	S(7)—C(13)—S(8)	120.2 (1.4)	120.5
S(3)—C(5)—O(2)	113.6 (1.8)	S(8)—C(13)—O(4)	122.3 (1.4)	118.0
S(4)—C(5)—O(2)	125.6 (1.8)	S(7)—C(13)—O(4)	117.4 (1.6)	121.5
C(5)—O(2)—C(6)	120.9 (1.8)	C(13)—O(4)—C(14)	120.8 (1.8)	120.9
O(2)—C(6)—C(8)	104.9 (2.1)	O(4)—C(14)—C(15)	103.4 (1.8)	104.2
O(2)—C(6)—C(7)	106.4 (2.1)	O(4)—C(14)—C(16)	109.1 (2.1)	107.8
C(7)—C(6)—C(8)	112.7 (2.1)	C(15)—C(14)—C(16)	108.9 (2.0)	110.8

Table 6. Structures of four-membered chelate rings



	Zn(isoPX) ₂		Zn(EC) ₂	Zn(MC) ₂	Zn(EP) ₂	Zn(isoPP) ₂
	Present work		Bonamico <i>et al.</i> (1965)	Klug (1966)	Ito <i>et al.</i> (1969)	Lawton <i>et al.</i> (1969)
Zn—S	2.351 (7) Å	2.357 (7) Å	2.355 (3) Å	2.333 (6) Å	2.351 (6) Å	2.351 (5) Å
Zn—S'	2.408 (7)	2.370 (8)	2.443 (3)	2.429 (6)	2.401 (7)	2.409 (5)
S—Y	1.72 (2)	1.71 (2)	1.73 (1)	1.75 (2)	1.987 (9)	1.984 (7)
S'—Y	1.67 (2)	1.68 (2)	1.72 (1)	1.70 (2)	1.973 (11)	1.968 (7)
S—Zn—S'	76.7 (0.2)°	76.9 (0.2)°	75.8 (0.2)°	76.4 (0.2)°	85.9 (0.2)°	85.5 (0.2)°
Zn—S—Y	81.6 (0.7)	81.1 (0.7)	84.5 (0.6)	84.0 (0.6)	82.5 (0.3)	82.6 (0.2)
Zn—S'—Y	80.9 (0.7)	81.4 (0.9)	81.9 (0.6)	82.0 (0.7)	81.5 (0.3)	81.4 (0.2)
S—Y—S'	120.8 (1.1)	120.2 (1.4)	117.5 (0.9)	117.3 (1.1)	109.7 (0.4)	109.7 (0.3)

chelate rings in $\text{Zn}(\text{isoPX})_2$ are similar to those observed in related crystals. They are compared in Table 6. It can be seen from the Table that one Zn-S distance in each chelate ring is significantly longer than the other except for the second ring in $\text{Zn}(\text{isoPX})_2$, in which the difference, 0.013 Å, between the two distances is hardly significant.

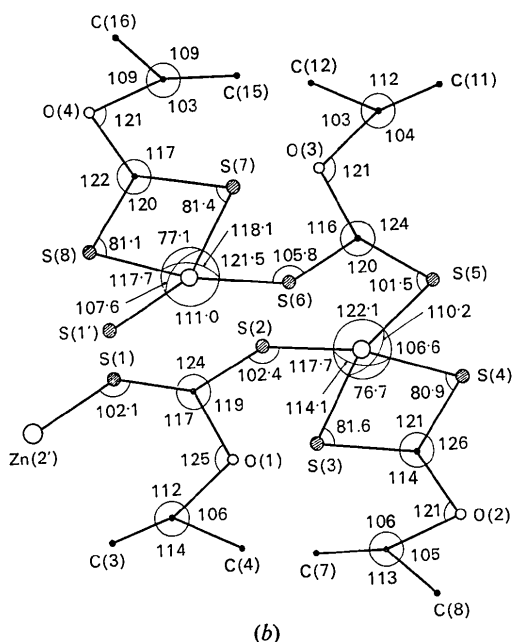
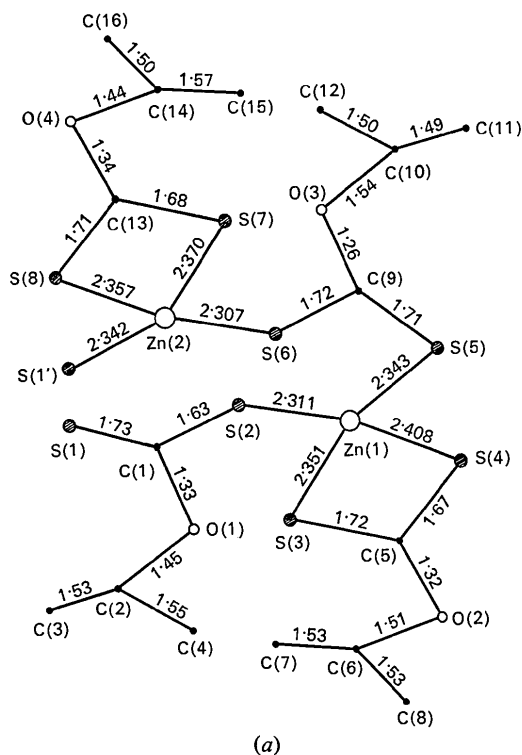


Fig. 3. (a) Bond distances (Å) and (b) bond angles (degrees) in $\text{Zn}(\text{isoPX})_2$.

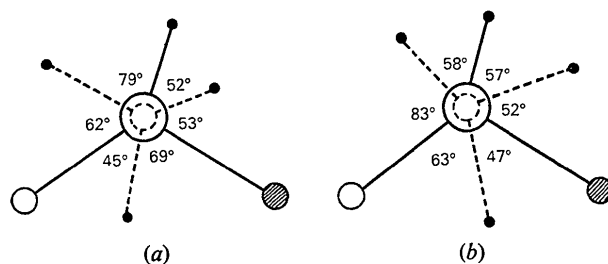


Fig. 4. Staggered configuration of methyl groups: (a) projection along C(6)-C(7), (b) projection along C(10)-C(11). The standard deviations of the dihedral angles involving one and two hydrogen atoms are about 5 and 8°, respectively.

Although the coordinations of the bridging and chelating isopropylxanthate groups about zinc atoms are different, the two xanthate groups have almost the same structure; the effect of different coordinations are limited within the coordination sphere of zinc atoms. All distances and angles in the xanthate groups can be regarded as normal compared with those in related crystals.

The isopropylxanthate groups are planar except for the methyl ends and hydrogen atoms; the maximum deviations of the dithiocarbonyl and tertiary carbon atoms from the planes defined by SSO are 0.02 and 0.13 Å, respectively. The zinc atoms are also located approximately on the planes, the maximum deviations being 0.30 Å.

It is interesting to note that all methyl hydrogen atoms that could be located in the present analysis take staggered configurations, typical examples of which are shown in Fig. 4.

Van der Waals contacts of tetramers

The closest distances between adjacent tetramers are summarized in Table 7. These values may be compared with the sums of van der Waals or ionic radii of atoms: $\text{S}\cdots\text{S}=3.70$, $\text{S}\cdots\text{C}=3.85$, $\text{C}\cdots\text{C}=4.00$ Å (Pauling,

Table 7. Van der Waals contacts of tetramers

The primes denote inversion at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

$\text{S}(1)\cdots\text{S}(1', +a)$	3.44 (1) Å
$\text{S}(6)\cdots\text{C}(15, -a)$	3.66 (3)
$\text{S}(4)\cdots\text{C}(4', -b)$	3.67 (3)
$\text{S}(2)\cdots\text{C}(15, -a)$	3.70 (3)
$\text{S}(7)\cdots\text{C}(2, -c)$	3.72 (2)
$\text{S}(4)\cdots\text{C}(7', -a-b)$	3.73 (4)
$\text{S}(8)\cdots\text{C}(12', +a)$	3.73 (3)
$\text{S}(7)\cdots\text{C}(16', +a)$	3.80 (3)
$\text{C}(4)\cdots\text{C}(5', -b)$	3.53 (4)
$\text{C}(9)\cdots\text{C}(16', +a)$	3.85 (3)
$\text{C}(3)\cdots\text{C}(7', -a-b)$	3.88 (4)
$\text{C}(4)\cdots\text{C}(16', +a)$	3.89 (4)
$\text{C}(1)\cdots\text{C}(7', -a-b)$	3.93 (4)
$\text{C}(4)\cdots\text{C}(6', -b)$	4.00 (4)

1960). The closest S...S distance of 3.44 Å is smaller than the expected value by 0.26 Å; such a short distance (3.38 Å) was also found in Zn(EX)₂ (Ikeda *et al.*, 1966). The closest C...C distance of 3.53 Å may be attributed to the small volume of the dithiocarbonic carbon atom. The other distances are normal. It can be seen from the Table that the sulphur-methyl and methyl-methyl contacts are most important in the structure.

The numerical calculations were performed on the FACOM270-30 computer of this Institute, with a universal crystallographic computation program system, UNICS (Sakurai, Ito, Iwasaki, Watanabe & Fukuhara, 1967).

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Studies on Flavin Derivatives. The Crystal and Molecular Structure of 5-Ethyl-3,7,8,10-tetramethylisoalloxazinium Perchlorate

BY ROLF NORRESTAM AND OVE TILLBERG

Institute of Inorganic and Physical Chemistry, University of Stockholm, S-104 05 Stockholm, Sweden

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The crystal structure of 5-ethyl-3,7,8,10-tetramethylisoalloxazinium perchlorate, C₁₆H₁₉ClN₄O₆, has been derived from three-dimensional X-ray diffractometer data. The unit cell is orthorhombic, space group *P*2₁2₁2₁, with the dimensions *a* = 7.768 (3), *b* = 13.255 (4) and *c* = 17.647 (6) Å. There are four formula units in the unit cell. The structure was determined by direct methods. Full-matrix least-squares refinement of the structural parameters gave an *R* value of 0.042 for the 1342 observed reflexions. The isoalloxazinium ring system is nearly planar. The packing of the molecules in the unit cell leads to several very short (2.8 to 3.0 Å) non-bonded C...O and N...O contacts.

Introduction

The structure determination of 5-ethyl-3,7,8,10-tetramethylisoalloxazinium perchlorate (ETIP) reported here is part of a series (Kierkegaard *et al.*, 1971) of structural investigations of flavin derivatives in different states of protonation and oxidation.

A schematic structural formula of ETIP is given in Fig. 1. ETIP is an example of a 5-alkylflavoquinonium ion. The significance of such ions in the catalysis of flavin enzymes has been discussed by Hemmerich, Ghisla, Hartman & Müller (1971).

Experimental

A blackish crystalline specimen of 5-ethyl-3,7,8,10-tetramethylisoalloxazinium perchlorate was kindly supplied by Dr S. Ghisla (University of Konstanz,

Germany). The crystals were examined by X-ray photographic methods (Guinier, oscillation and Weissenberg techniques). The photographs indicated orthorhombic symmetry and the systematic absences among the X-ray reflexions were consistent with the space group *P*2₁2₁2₁. The crystal finally selected had the dimensions 0.04 × 0.12 × 0.36 mm, with the prismatic axis along [011], and was mounted on a goniometer along the *a* axis. The cell parameters were obtained by least-squares refinement of diffractometer measurements with Cu *K*α radiation (*λ* = 1.54184 Å).

The crystal data are:

Composition of asymmetric unit = C₁₆H₁₉ClN₄O₆, *a* = 7.768 (3), *b* = 13.255 (4), *c* = 17.647 (6) Å, *V*₀ = 1817.0 Å³, *D*_c = 1.45 g.cm⁻³, *Z* = 4, μ(Cu *K*α) = 22.6 cm⁻¹, space group *P*2₁2₁2₁.

Three-dimensional X-ray intensity data were collected on a Siemens AED single-crystal diffractometer