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The Crystal Structure of Zinc Ethylxanthate

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Zinc ethylxanthate, $Zn(SSCOC_2H_5)_2$, is monoclinic with $a=18{\cdot}278\pm0{\cdot}014$, $b=5{\cdot}700\pm0{\cdot}003$, $c=11{\cdot}381\pm0{\cdot}012$ Å; $\beta=101{\cdot}47°\pm0{\cdot}10°$, and space group $P2_1/c$. The unit cell contains four formula units. A three-dimensional X-ray structure analysis has shown that each zinc atom is tetrahedrally coordinated to four sulphur atoms belonging to different xanthate groups at distances 2·362, 2·337, 2·364 and 2·369 Å, all approximately within ±0·010 Å. The bonds are directed to the corners of a slightly distorted tetrahedron. Each xanthate group, in turn, bridges two zinc atoms with its dithiocarbonic end in the *y*- or *z*-axis direction to complete a two-dimensional network consisting of the zinc atoms and $-\mathrm{S}-\overset{|}{\mathrm{C}}-\mathrm{S}-$ atom groups. Zn–S–C bond angles are 104·9, 105·1, 105·5 and 114·8°, all ±1·0°. The xanthate group is almost planar. The ethyl group, bonded with the dithiocarbonic carbon atom through an oxygen atom, protrudes on both sides of the network in the ±*x*-axis direction. The methyl ends of the ethyl groups belonging to successive sheets of the two-dimensional network come into van der Waals contact through twofold screw axes.

Introduction

In the technical process of froth flotation, sulphide minerals are separated from the gangue minerals or from each other by their difference in wettability by water. With the galena(PbS)–zincblende(ZnS) system, for instance, their separation is made possible by soaking the powders in aqueous ethylxanthate solution. Galena reacts readily with the solution to develop a hydrophobic property on its surface, while zincblende remains hydrophilic in the same solution. In order to make the zincblende surface sufficiently hydrophobic for the purpose, a pretreatment of its particles with a dilute aqueous solution containing Cu^{2+} ion is necessary before the reaction with xanthate solution. Cu^{2+} ions in the solution activate the zincblende surface, while Zn^{2+} ions do not.

In these reactions it is supposed that a small amount of heavy metal cations, either dissolved from the mineral surfaces or added purposely to the solution, reacts with xanthate anions to produce molecular or crystalline aggregates of the heavy metal xanthate at the mineral surface. The above mentioned behavior of galena and activated zincblende in the xanthate solution suggests that the formation of a molecular or crystalline aggregate of lead and copper xanthates at mineral surfaces is effective for endowing galena and zincblende surfaces respectively with the hydrophobic property, while the formation of similar aggregates of zinc xanthate has no such effect on zincblende surfaces. In order to elucidate these differences from the viewpoint of the molecular and crystalline structure of heavy metal xanthates, it was decided to determine the crystal structure of zinc ethylxanthate, $Zn(SSCOC_2H_5)_2$, for comparison with the structure of lead ethylxanthate crystal which has been determined previously (Hagihara & Yamashita, 1966).

Experimental

Zinc ethylxanthate powder was prepared from the white precipitate obtained on titration of aqueous solutions of purified potassium ethylxanthate and zinc chloride. The precipitate was filtered and dehydrated in a vacuum desiccator. The powder obtained was dissolved in ethyl alcohol. Single crystals of zinc ethylxanthate were collected from the precipitate obtained by the slow evaporation of the solution. The crystals were usually thin rectangular plates in shape. They often showed a needle-like appearance as a result of elongation along one of the edges of the plate. The crystal was stable in air at room temperatures.

From preliminary Weissenberg photographs taken with Cu *Kα* radiation, the crystal was found to be monoclinic, with the *b* axis along the shorter edge of the rectangular plate. An accurate determination of the dimensions of the monoclinic cell was done with high purity silicon powder coated on the crystal surface as a reference material. With the use of values $\lambda = 1{\cdot}5418$ Å for Cu *Kα* and $a = 5{\cdot}4306$ Å for silicon, we obtained

$$a = 18{\cdot}278 \pm 0{\cdot}014,\ b = 5{\cdot}700 \pm 0{\cdot}003,$$
$$c = 11{\cdot}381 \pm 0{\cdot}012\ \text{Å};\ \beta = 101{\cdot}47^\circ \pm 0{\cdot}10^\circ.$$

The systematic extinctions indicated the space group $P2_1/c$. Four formula units of $Zn(SSCOC_2H_5)_2$ per unit cell give a calculated density of 1·758 g.cm^{-3}. The linear absorption coefficient μ was calculated to be 94 cm^{-1}. The crystal specimen used was of the dimensions $0{\cdot}01_3 \times 0{\cdot}19 \times 0{\cdot}27$ mm.

A series of multiple film Weissenberg photographs of the $k = 0$, 1, 2 and 3 layers of a *b*-axis oriented crystal were taken at room temperatures with filtered Cu *Kα* radiation by the equi-inclination method. The intensities of 1548 independent reflexions (about 60% of the ones which may be covered with Cu *Kα* radiation) were measured by the microphotometer method, and also by the visual method for weaker reflexions. Of these reflexions, 521 were too weak to give measured values. They were given numerical values corresponding to half the minimum value of the observed intensities in each layer photograph. The measured intensities ranged from 1300 to 1. The intensities were corrected for the Lorentz and polarization factors. No absorption correction was made.

Determination of the structure

From a three-dimensional Patterson function calculated with 800 fairly strong reflexions by the program ERFR-2 (Sly, Shoemaker & Van den Hende, 1962), the coordinates of zinc and sulphur atoms were determined approximately. Based on the *xz* coordinates of zinc and sulphur atoms thus determined, several trials were made in order to find the electron density projection on (010) which is reasonable in shape and height of the electron density contours and in conformity with

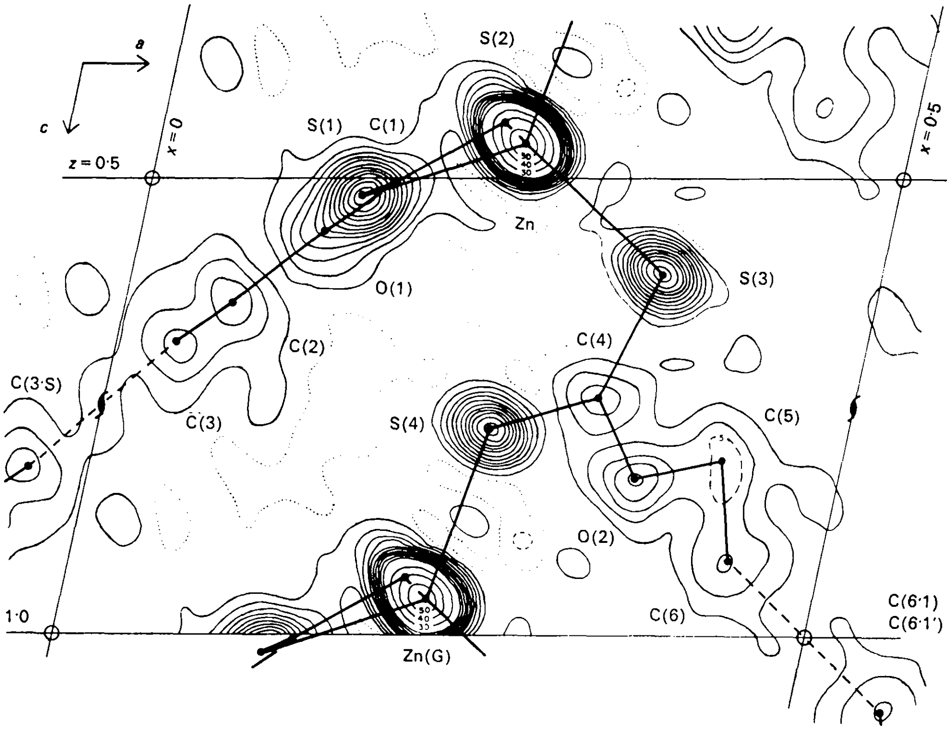

Fig. 1. (010) electron-density projection, with contours at intervals of 2 e.Å^{-2} except for the zinc atom.

the configuration of the ethylxanthate group already determined for lead ethylxanthate crystal (Hagihara, Sakurai & Ikeda, 1964; Hagihara & Yamashita, 1966). By applying the successive procedure, the *xz* coordinates of zinc, sulphur, oxygen and carbon atoms were refined. Fig. 1, which is the final (010) projection, reveals the most important feature of the structure, that each of the two sulphur atoms belonging to a xanthate group is bonded to a different zinc atom, *i.e.* S(3) in Fig. 1 is bonded with the Zn atom, but S(4) with the Zn(*G*) atom. Such a configuration is quite different from that in lead ethylxanthate. The *R* value at this stage was 0·16.

With this projection, and information obtained from the Patterson functions, a tetrahedral configuration of four sulphur atoms around the zinc atom was confirmed, and their *xyz* coordinates were determined. By a three-dimensional Fourier synthesis phased on the contribution of these atoms, the *y* coordinates of oxygen and carbon atoms were also determined. In this synthesis a negative electron density region amounting to -5 e.Å^{-3} at the minimum appeared between Zn and S(2) atoms. However, since this region disappeared in the difference Fourier synthesis, it was attributed to the diffraction effect of zinc and sulphur atoms due to series termination, particularly that for the $k=3$ layer reflexions. The above computations were carried out by the programs XTL–FC and XTL–FS (Ikeda, 1965). Atomic scattering values used were those adopted in *International Tables for X-ray Crystallography* (1962).

Least squares refinement. A three-dimensional least-squares refinement program, XTL-LS (Ikeda, 1965), was applied to the 1548 reflexions, of which the 521 very weak ones were given the weight 0·2. The overall *R* value was improved from 0·38 at the initial stage of three-dimensional Fourier synthesis to 0·20 in the final stage of the refinement. Incidentally, it amounted

Table 1. *Atomic parameters of zinc ethylxanthate*, $Zn(SSCOC_2H_5)_2$

	x_i	x_i/a_i	$\sigma(x_i)$ (Å)	B (Å^2)	$\sigma(B)$	$\lvert\Delta x_i\rvert/\sigma(x_i)$	$\lvert\Delta B\rvert/\sigma(B)$
Zn	x	0·2425	0·0034 Å	3·60	0·09	0·05	0·27
	y	0·2694	0·0040			0·04	
	z	0·4638	0·0032			0·05	
S(1)	x	0·1416	0·0074	4·10	0·16	0·11	0·42
	y	0·0674	0·0085			0·01	
	z	0·5189	0·0073			0·18	
S(2)	x	0·2255	0·0075	4·35	0·16	0·19	0·36
	y	−0·3265	0·0086			0·26	
	z	0·4363	0·0073			0·19	
S(3)	x	0·3526	0·0072	4·04	0·16	0·15	0·03
	y	0·1799	0·0084			0·50	
	z	0·6043	0·0070			0·07	
S(4)	x	0·2598	0·0073	3·86	0·15	0·03	0·26
	y	0·3582	0·0081			0·10	
	z	0·7731	0·0070			0·04	
O(1)	x	0·1224	0·018	4·1	0·4	0·17	0·5
	y	−0·3852	0·019			0·01	
	z	0·5580	0·017			0·06	
O(2)	x	0·3627	0·020	5·1	0·4	0·03	0·3
	y	0·0476	0·021			0·23	
	z	0·8288	0·019			0·12	
C(1)	x	0·1606	0·024	3·6	0·5	0·02	0·7
	y	−0·2061	0·028			0·06	
	z	0·5070	0·024			0·08	
C(2)	x	0·0714	0·027	4·1	0·5	0·13	0·2
	y	−0·2879	0·030			0·09	
	z	0·6360	0·025			0·01	
C(3)	x	0·0390	0·031	5·2	0·7	0·02	0·1
	y	−0·5137	0·034			0·35	
	z	0·6803	0·030			0·07	
C(4)	x	0·3277	0·027	4·5	0·6	0·19	0·2
	y	0·1831	0·031			0·47	
	z	0·7401	0·027			0·07	
C(5)	x	0·4188	0·037	7·2	0·6	0·10	0·2
	y	−0·1305	0·038			0·19	
	z	0·8078	0·036			0·22	
C(6)	x	0·4355	0·037	7·1	0·9	0·06	0·1
	y	−0·2795	0·040			0·31	
	z	0·9185	0·035			0·05	

to 0·16 omitting the above mentioned 521 reflexions.

The final atomic coordinates, temperature factors, their standard deviations in Å, and the parameter shifts as fractions of the standard deviation in the final cycle of refinement are tabulated in Table 1.

The observed and calculated structure factors (FO and FC respectively) are shown in Table 2. Atom distances and bond angles are shown in Fig. 2 and with standard deviations in Table 3. The configuration of atoms in the structure is shown in Fig. 3.

Discussion

Figs. 2 and 3 show that each zinc atom is surrounded by four sulphur atoms arranged almost tetrahedrally around it. Each sulphur atom belongs to a different xanthate group. Each xanthate group, in turn, bridges two adjacent zinc atoms in such a way that the bonding $-S(1)-\overset{|}{C}(1)-S(2)-$ bridges zinc atoms in the *y* direction and the bonding -S(3)-C(4)-S(4)- bridges them in the *z* direction. The ethyl groups protrude outwards on both sides of the network consisting of zinc atoms and $-S-\overset{|}{C}-S-$ atom groups. The sheets bounded by the methyl ends of the ethyl groups are piled up in the *x* direction through twofold screw axes. The methyl ends belonging to successive sheets come into van der Waals contact. The external shape of the crystal, being thin in the *a*-axis direction and extended in the *b*- and *c*-axis directions, is in conformity with this structure. The structure here found is quite different from that of lead ethylxanthate crystal (Hagihara & Yamashita, 1966), in which the lead ethylxanthate molecule represented by $Pb(SSCOC_2H_5)_2$ is an entity which builds a

Table 2. *Observed* (FO) *and calculated* (FC) *structure factors*

Asterisks denote unobserved reflexions

H	L	FO	FC
	k=0		
1	0	10	19
2	0	118	-226
3	0*	2	-10
4	0	24	26
5	0	30	32
6	0	78	-90
7	0	35	-36
8	0	116	136
9	0	65	56
10	0	128	-148
11	0	46	-46
12	0	50	46
13	0*	5	12
14	0*	6	6
15	0	17	-16
16	0	14	13
17	0	16	17
18	0	27	-25
19	0*	5	-12
20	0	11	11
21	0	5	3
22	0	4	-1
-22	2*	4	-10
-21	2	24	22
-20	2	13	13
-19	2	35	-34
-18	2*	5	-5
-17	2	18	24
-16	2*	6	13
-15	2	12	-13
-14	2	17	-18
-13	2	33	35
-12	2	27	32
-11	2	55	-57
-10	2	75	-79
- 9	2	40	54
- 8	2	71	87
- 7	2	59	64
- 6	2	28	-41
- 5	2	83	-82
- 4	2	99	96
- 3	2	30	-29
- 2	2	57	-64
- 1	2	24	22
0	2	122	134
1	2	102	119
2	2	125	-130
3	2	211	-239
4	2	75	-75
5	2	115	132
6	2*	3	-7
7	2	45	-61
8	2	51	60
9	2	49	55
10	2	38	-28
11	2	65	-72
12	2*	5	-17
13	2	70	72
14	2	30	37
15	2	40	-43
16	2*	6	-5
17	2	25	26
18	2	19	-12
19	2	13	-18
20	2	5	3
21	2	4	13
-22	4	9	-15
-21	4	18	14
-20	4	26	25
-19	4*	5	-7
-18	4	23	-26
-17	4*	6	-12
-16	4	51	45
-15	4	30	28
-14	4	91	-82
-13	4*	5	-3
-12	4	83	89
-11	4	22	-27
-10	4	91	-91
- 9	4*	5	-6
- 8	4	114	107
- 7	4	101	92
- 6	4	116	-104
- 5	4	159	-154
- 4	4	102	98
- 3	4	28	33
- 2	4	134	-133
- 1	4	13	12
0	4	85	85
1	4	64	67
2	4	72	-74
3	4	148	-163
4	4	36	34
5	4	95	108
6	4*	5	11
7	4	30	38
8	4	17	17
9	4*	5	-8
10	4*	5	2
11	4	45	46
12	4*	6	-11
13	4	41	41
14	4*	6	8
15	4	12	-7
16	4*	5	-4
17	4*	5	-17
18	4*	5	3
19	4*	5	4
20	4*	4	-8
-21	6*	5	3
-20	6*	5	7
-19	6*	5	7
-18	6	49	-31
-17	6	17	-20
-16	6	39	30
-15	6*	6	8
-14	6	13	-16
-13	6*	6	-12
-12	6*	6	-4
-11	6	56	46
-10	6*	5	-9
- 9	6	99	-84
- 8	6	61	51
- 7	6	109	101
- 6	6	51	-40
- 5	6	97	-96
- 4	6	28	-29
- 3	6	77	69
- 2	6	81	74
- 1	6	79	-66
0	6	17	-12
1	6	116	123
2	6	13	-11
3	6	111	-109
4	6	18	-24
5	6	91	86
6	6	52	62
7	6	37	-33
8	6	32	-42
9	6	28	10
10	6*	6	0
11	6	42	-52
12	6*	6	-3
13	6	36	37
14	6	14	13
15	6	15	-11
16	6*	5	-14
17	6*	5	6
18	6*	4	5
-21	8	15	-10
-20	8	24	18
-19	8	14	14
-18	8	46	-32
-17	8	25	-19
-16	8	46	33
-15	8	36	30
-14	8	15	-12
-13	8	32	-24
-12	8	15	14
-11	8	60	40
-10	8	30	-26
- 9	8	66	-50
- 8	8	56	42
- 7	8	44	35
- 6	8	13	-10
- 5	8	38	-35
- 4	8	49	-40
- 3	8	47	40
- 2	8	52	45
- 1	8	32	-23
0	8*	5	-8
1	8	27	22
2	8	32	-27
3	8	14	-17
4	8	12	-20
5	8*	6	-10
6	8	59	61
7	8*	6	1
8	8	32	-42
9	8*	6	-3
10	8*	6	0
11	8*	6	1
12	8*	5	8
13	8*	5	6
14	8	12	16
15	8*	4	6
16	8	15	-20
-20	10*	2	6
-19	10	16	13
-18	10*	4	-4
-17	10	19	-15
-16	10	12	-9
-15	10	53	33
-14	10	25	23
-13	10	65	-47
-12	10	25	-18
-11	10	43	29
-10	10*	6	5
- 9	10	42	-31
- 8	10	31	-20
- 7	10	54	39
- 6	10	57	39
- 5	10	66	-48
- 4	10	61	-47
- 3	10	68	48
- 2	10	25	29
- 1	10	25	-18
0	10	13	-14
1	10*	6	0
2	10	27	19
3	10	32	-24
4	10	29	-25
5	10	49	35
6	10	25	27
7	10	22	-14
8	10*	5	-7
9	10*	5	1
10	10*	5	-3
11	10*	5	3
12	10*	5	1
13	10*	6	8
-16	12	10	-6
-15	12	25	17
-14	12*	5	7
-13	12	17	-15
-12	12*	5	-9
-11	12*	5	-1
-10	12	11	10
- 9	12	23	11
- 8	12	25	-14
- 7	12*	5	7
- 6	12	33	26
- 5	12	13	-9
- 4	12	27	-24
- 3	12*	5	-2
- 2	12	16	17
- 1	12	19	16
0	12	18	-13
1	12	24	-19
2	12	22	14
3	12*	5	5
4	12	22	-16
6	12	15	16
7	12*	4	4
8	12	10	-12
9	12*	2	-13
-10	14	26	20
- 9	14	11	-5
- 8	14	15	-12
- 7	14	25	12
- 6	14*	4	3
- 5	14	18	-11
- 4	14*	4	-8
- 3	14*	4	-5
- 2	14	11	11
- 1	14*	4	7
0	14	15	-10
1	14*	3	1
2	14*	2	4
	k=1		
1	0	108	-126
2	0	50	80
3	0	110	128
4	0	61	-67
5	0	9	-14
6	0	15	-17
7	0	60	63
8	0	19	21
9	0	107	-112
10	0*	5	7
11	0	69	67
12	0*	6	-16
13	0	33	-40
14	0*	6	8
15	0	19	25
16	0*	7	4
17	0	24	-29
18	0*	7	-9
19	0	27	34
20	0*	6	11
-20	1*	6	-7
-19	1*	6	-7
-18	1*	7	3
-17	1	16	15
-16	1	18	17
-15	1	31	-32
-14	1	23	-30
-13	1	15	14
-12	1*	6	1
-11	1*	5	-2
-10	1	11	14
- 9	1	23	26
- 8	1	30	33
- 7	1	49	-50
- 6	1	53	-74
- 5	1	78	84
- 4	1	76	68
- 3	1*	7	-6
- 2	1	53	52
- 1	1	12	-16
0	1*	1	4
1	1	11	12
2	1	52	-57
3	1	42	46
4	1	23	31
5	1	30	-40
6	1	18	-24
7	1	20	-30
8	1	30	-30
9	1	16	16
10	1	24	30
11	1*	6	-4
12	1*	6	-10
13	1*	6	-13
14	1*	7	-6
15	1*	7	0
16	1*	7	-6
17	1*	7	11
18	1	14	17
19	1*	6	0
-20	2	20	-20
-19	2	22	-20
-18	2	15	15
-17	2	12	19
-16	2*	7	8
-15	2*	7	-3
-14	2	22	-16
-13	2	24	28
-12	2*	6	-5
-11	2	27	-32
-10	2*	5	13
- 9	2*	5	8
- 8	2	12	13
- 7	2	22	-25
- 6	2	30	-30
- 5	2	14	-2
- 4	2	33	35
- 3	2	35	-43
- 2	2	14	-15
- 1	2	54	66
0	2	15	-13
1	2	57	51
2	2	14	-10
3	2*	3	0
4	2	52	52
5	2	52	-62
6	2	61	-65
7	2	38	53
8	2	26	32
9	2	48	-57
10	2	14	-16
11	2	14	22
12	2	30	37
13	2*	6	1
14	2	41	-44
15	2*	7	15
16	2	31	39
17	2	18	-22
18	2	24	-26
19	2*	6	16
-20	3*	6	-3
-19	3*	6	8
-18	3*	7	12
-17	3*	7	10
-16	3*	6	4
-15	3	15	-10
-14	3	26	-22
-13	3*	6	-7
-12	3	14	16
-11	3	31	37
-10	3	12	21
- 9	3	11	-17
- 8	3*	5	5
- 7	3*	4	-4
- 6	3	62	-57
- 5	3	35	-33
- 4	3	62	60
- 3	3	62	58
- 2	3	38	-33
- 1	3	73	-72
0	3	50	-44
1	3	31	33
2	3	31	-34
3	3	35	-38
4	3	47	50
5	3*	4	12
6	3	12	-13
7	3	23	-35
8	3*	5	-3
9	3	34	48
10	3*	6	11
11	3*	6	-6
12	3	14	11
13	3*	7	-6
14	3*	15	-14
15	3*	6	5
16	3*	6	5
17	3*	6	8
18	3*	6	5
-20	4*	6	-3
-19	4	15	-15
-18	4	14	-13
-17	4	31	34
-16	4	39	38
-15	4	33	-38
-14	4	34	-34
-13	4	31	38
-12	4*	6	-9
-11	4	50	-51
-10	4	11	12
- 9	4	22	26
- 8	4	27	31
- 7	4	30	-37
- 6	4	57	-53
- 5	4	98	86
- 4	4	23	27
- 3	4	89	-80
- 2	4	20	16
- 1	4	85	80
0	4*	4	-2
1	4	37	-45
2	4	49	-41
3	4	53	45
4	4	22	24
5	4	83	-88
6	4	9	-2
7	4	52	63
8	4*	6	14
9	4	12	-19
10	4	18	-20
11	4*	6	10
12	4	37	42
13	4	16	-14
14	4	24	-32
15	4	15	14
16	4	12	8
17	4*	6	-6
-20	5	16	12
-19	5*	6	-1
-18	5*	6	-2
-17	5	24	21
-16	5*	7	-4
-15	5	27	-27
-14	5	15	-16
-13	5*	6	-11
-12	5	28	30
-11	5	24	22
-10	5	20	-17
- 9	5*	5	9
- 8	5	15	-16
- 7	5	66	-54
- 6	5*	5	-5
- 5	5*	5	13
- 4	5	8	7
- 3	5	71	58
- 2	5*	4	0
- 1	5	39	36
0	5*	4	-11
1	5	30	-25
2	5	43	49
3	5	34	35
4	5	16	-16
5	5	15	20
6	5*	5	11
7	5	12	-18
8	5*	6	-14
9	5*	6	5
10	5	14	22
11	5*	7	10
12	5	18	-23
13	5*	7	-13
14	5*	7	8
15	5*	6	-5
16	5*	6	-2
-19	6*	6	-4
-18	6	15	-14
-17	6	19	15
-16	6	18	15
-15	6	14	-16

crystalline assembly through the van der Waals contact between the sulphur atoms and between the methyl ends in ethyl groups.

The bond distances between zinc and sulphur atoms, Zn–S(1), Zn–S(2′), Zn–S(3) and Zn–S(4*G*), are the same according to Cruickshank's criterion for significance levels (*e.g.* Lipson & Cochran, 1953). Their mean value, 2·358 Å, is equal to the sum of the tetrahedral covalent radii of zinc and sulphur atoms, 2·35 Å (*e.g.* Pauling, 1960).

Of the six bond angles about the zinc atom, S(1)–Zn–S(3), S(3)–Zn–S(4*G*) and S(4*G*)–Zn–S(1) are equal or almost equal to the tetrahedral angle of 109·5°, the difference in all cases being less than 2°. On the other hand, the bond angles S(2′)–Zn–S(1), S(2′)–Zn–S(3) and S(2′)–Zn–S(4*G*) deviate much more from the tetrahedral angle as seen in Table 3. These deviations are due to the deviation of S(2′) from the apex of the regular tetrahedron formed by the four sulphur atoms around the zinc atom. S(2′) is displaced towards S(4*G*), making the bond angle S(2′)–Zn–S(4*G*) 102·6°. In order to ascertain whether this deviation of S(2′) atom is real or is due to the misplacement of S(2′) at the start of the least-squares refinement, the process was again applied, starting with S(2′) at the corner of a regular tetrahedron defined as above. After four cycles of re-

Table 2 (*cont.*)

H	L	FO	FC
-14	6	14	-14
-13	6	26	-22
-12	6*	6	8
-11	6	35	28
-10	6	22	-23
- 9	6	12	12
- 8	6	71	59
- 7	6	31	-32
- 6	6	38	-38
- 5	6	23	26
- 4	6	14	13
- 3	6*	5	4
- 2	6	46	-39
- 1	6	11	-10
0	6	80	62
1	6*	5	-13
2	6	95	-89
3	6	13	23
4	6	75	66
5	6	16	-22
6	6	31	-33
7	6*	6	6
8	6	47	56
9	6*	6	7
10	6	46	-61
11	6	14	-4
12	6	30	43
13	6*	7	1
14	6	20	-32
15	6*	6	-6
-20	7*	5	4
-19	7	11	9
-18	7*	6	3
-17	7	15	-12
-16	7*	7	-2
-15	7*	7	1
-14	7	16	-18
-13	7	14	-10
-12	7	31	27
-11	7	54	38
-10	7*	6	0
- 9	7	30	-28
- 8	7	18	-17
- 7	7	12	11
- 6	7*	6	-1
- 5	7	11	-8
- 4	7	46	40
- 3	7	43	41
- 2	7	12	-11
- 1	7	41	-41
0	7*	6	-14
1	7*	6	5
2	7*	6	9
3	7	14	15
4	7*	6	1
5	7*	6	0
6	7	15	-18
7	7	22	-23
8	7*	7	5
9	7*	7	2
10	7*	7	-1
11	7*	7	10
12	7*	7	-1
13	7*	6	-9
14	7*	6	-4
15	7*	5	3
-19	8	9	-12
-18	8*	6	-9
-17	8	22	21
-16	8*	6	8
-15	8	14	-15
-14	8	12	-14
-13	8*	7	1
-12	8	22	24
-11	8*	7	-5
-10	8*	6	-8
- 9	8	50	37
- 8	8*	6	5
- 7	8	54	-43
- 6	8	15	-17
- 5	8	11	10
- 4	8	11	10
- 3	8	11	8
- 2	8	46	-37
- 1	8*	6	13
0	8	57	46
1	8	31	-34
2	8	15	-18
3	8*	6	13
4	8*	6	15
5	8	15	18
6	8*	7	-15
7	8	24	-24
8	8	24	25
9	8*	7	14
10	8	24	-33
11	8*	6	-9
12	8*	6	11
13	8*	6	14
14	8*	5	0
15	8	11	-18
-17	9*	6	-3
-16	9*	6	-6
-15	9*	6	-1
-14	9*	6	-5
-13	9*	7	8
-12	9*	7	12
-11	9*	7	5
-10	9	20	13
- 9	9	15	-16
- 8	9	47	-36
- 7	9*	7	-1
- 6	9	15	15
- 5	9*	7	11
- 4	9*	6	7
- 3	9*	6	-7
- 2	9*	6	3
- 1	9*	6	-10
0	9	46	-43
1	9*	7	3
2	9	31	34
3	9*	7	4
4	9*	7	-1
5	9	11	-8
6	9	11	-7
7	9*	7	3
8	9*	6	-8
9	9*	6	5
10	9	14	19
11	9*	5	0
12	9*	5	-6
-17	10*	5	0
-16	10	12	11
-15	10*	6	7
-14	10	18	-23
-13	10	12	-11
-12	10	37	30
-11	10*	7	5
-10	10	30	-21
- 9	10*	7	2
- 8	10*	7	9
- 7	10*	7	1
- 6	10	43	-37
- 5	10	19	-13
- 4	10	20	55
- 3	10	18	14
- 2	10	47	-38
- 1	10*	7	-3
0	10	34	33
1	10	14	7
2	10	24	-28
3	10	27	-23
4	10	27	31
5	10	27	26
6	10	30	-36
7	10	12	-15
8	10	18	21
9	10*	6	6
10	10*	5	-10
11	10*	5	-11
12	10	11	7
-17	11	16	-10
-16	11*	4	-2
-15	11*	5	0
-14	11*	5	-1
-13	11*	6	-2
-12	11*	6	4
-11	11	15	11
-10	11*	6	-4
- 9	11	23	-18
- 8	11*	7	-8
- 7	11*	7	3
- 6	11*	7	6
- 5	11	14	12
- 4	11	12	10
- 3	11*	7	-2
- 2	11*	7	-9
- 1	11*	7	-10
0	11*	6	0
1	11*	6	4
2	11*	6	7
3	11	12	14
4	11*	6	6
5	11*	6	-10
6	11*	6	-11
7	11*	5	1
8	11*	5	5
9	11*	5	3
10	11	8	1
-14	12	19	-16
-13	12*	5	4
-12	12*	5	7
-11	12*	5	1
-10	12*	6	0
- 9	12*	6	-7
- 8	12*	6	0
- 7	12	14	9
- 6	12	14	-12
- 5	12	12	-8
- 4	12	28	25
- 3	12	11	12
- 2	12*	6	-9
- 1	12	12	-16
0	12	12	-4
1	12	16	18
2	12*	6	-4
3	12	22	-24
4	12*	5	7
5	12	12	21
6	12*	5	-3
7	12*	4	-15
8	12	7	-3
-14	13	11	3
-13	13*	3	5
-12	13*	4	-4
-11	13*	4	4
-10	13*	5	4
- 9	13*	5	-6
- 8	13*	5	-6
- 7	13*	5	-3
- 6	13	15	12
- 5	13	15	13
- 4	13	14	-7
- 3	13*	5	-5
- 2	13	11	1
- 1	13	11	-9
0	13*	5	-4
1	13*	5	6
- 9	14	14	-15
- 8	14	16	13
- 7	14	8	8
- 6	14	18	-14
- 5	14*	4	-3
- 4	14*	4	10
- 3	14*	4	9
- 2	14*	3	-5
- 1	14	14	-19
0	14	5	1
1	14	11	16
K=2			
0	0	107	-125
1	0	21	27
2	0	81	113
3	0*	2	-1
4	0	81	-95
5	0	27	-25
6	0	82	82
7	0	55	55
8	0	34	-33
9	0	43	-43
10	0	43	47
11	0*	5	9
12	0	53	-35
13	0	20	-20
14	0	15	20
15	0	27	24
16	0	13	-11
17	0	20	-25
18	0*	5	2
19	0	11	12
20	0*	4	-5
-21	1*	3	9
-20	1*	4	1
-19	1	11	-9
-18	1*	5	-5
-17	1	14	14
-16	1*	6	-7
-15	1	25	-28
-14	1	25	24
-13	1	31	32
-12	1*	5	-4
-11	1*	5	-2
-10	1	33	-28
- 9	1*	4	-7
- 8	1	8	5
- 7	1	14	-16
- 6	1	55	65
- 5	1	23	26
- 4	1	63	-69
- 3	1*	2	1
- 2	1	7	-1
- 1	1	49	-66
0	1*	1	-4
1	1	40	58
2	1	55	58
3	1	36	45
4	1	64	-70
5	1	38	-48
6	1	32	46
7	1	31	-38
8	1	18	-25
9	1	38	41
10	1	19	24
11	1*	5	2
12	1	11	-19
13	1	20	-23
14	1*	5	3
15	1	13	13
16	1*	5	2
17	1	11	9
18	1*	5	3
-22	2	11	13
-21	2*	4	-6
-20	2	17	-16
-19	2*	5	11
-18	2*	5	3
-17	2	21	-24
-16	2	12	-12
-15	2	19	21
-14	2	36	36
-13	2*	5	-2
-12	2	59	-52
-11	2*	5	6
-10	2	71	73
- 9	2	8	-11
- 8	2	19	-25
- 7	2	16	21
- 6	2	52	50
- 5	2	24	25
- 4	2	120	-119
- 3	2	56	-56
- 2	2	91	101
- 1	2	34	36
0	2	71	-78
1	2	17	-19
2	2	20	25
3	2	50	49
4	2	34	-34
5	2	95	-109
6	2	50	64
7	2	51	71
8	2	32	-44
9	2	27	-35
10	2*	5	-1
11	2	12	13
12	2*	5	0
13	2	25	-30
14	2*	6	7
15	2	45	46
16	2*	5	-4
17	2	17	-22
-22	3	8	-7
-21	3*	4	-1
-20	3	17	17
-19	3*	5	0
-18	3	9	-17
-17	3*	6	2
-16	3*	6	8
-15	3*	6	6
-14	3*	5	-5
-13	3*	5	-6
-12	3	24	31
-11	3*	5	2
-10	3	46	-58
- 9	3	26	-22
- 8	3	38	40
- 7	3	17	17
- 6	3	8	-4
- 5	3	13	15
- 4	3	12	-11
- 3	3	17	-13
- 2	3	49	-48
- 1	3*	3	3
0	3	65	65
1	3	6	-10
2	3	19	21
3	3	38	34
4	3	31	-28
5	3	58	-59
6	3	24	-24
7	3	20	28
8	3	24	39
9	3*	5	-7
10	3	13	-19
11	3	30	41
12	3*	5	-3
13	3	40	-45
14	3*	6	0
15	3	12	18
16	3*	5	15
-22	4	14	15
-21	4*	3	-4
-20	4	11	-12
-19	4*	5	-2
-18	4*	5	11
-17	4*	6	7
-16	4	19	-24
-15	4*	6	6
-14	4	68	61
-13	4*	5	-2
-12	4	59	-57
-11	4	12	-18
-10	4	40	38
- 9	4	28	29
- 8	4	58	-50
- 7	4	46	-47
- 6	4	50	46
- 5	4	31	29
- 4	4	98	-95
- 3	4	55	-49
- 2	4	59	60
- 1	4	78	78
0	4	21	-18
1	4	69	-68
2	4	45	35
3	4	51	49
4	4	24	-28
5	4	49	-51
6	4	23	23
7	4	40	49
8	4*	5	5
9	4	26	-31
10	4	12	-15
11	4	26	27
12	4*	6	5
13	4	15	-17
14	4*	6	8
15	4*	5	20
-21	5	12	11
-20	5*	4	4
-19	5	9	-7
-18	5*	5	9
-17	5*	5	-6
-16	5	12	-15
-15	5	12	11
-14	5	12	7
-13	5*	5	-6
-12	5*	5	2
-11	5	13	-16
-10	5*	5	3
- 9	5*	5	12
- 8	5	53	-43
- 7	5	49	39
- 6	5	71	62
- 5	5	37	-36
- 4	5	25	-25
- 3	5	12	-13
- 2	5*	4	5
- 1	5	19	17
0	5*	4	-6
1	5	9	7
2	5	33	39
3	5	14	-17
4	5	42	-43
5	5*	4	1
6	5	14	-15
7	5	11	14
8	5	26	31
9	5*	5	3
10	5*	5	1
11	5	13	-14
12	5*	6	-8
13	5*	6	5
14	5*	5	-11
-20	6	12	-12
-19	6	13	-12
-18	6	12	13
-17	6	13	11
-16	6	13	-20
-15	6	11	-7
-14	6	28	30
-13	6*	6	4
-12	6	43	-34
-11	6	49	-42
-10	6*	5	7
- 9	6	79	64
- 8	6	12	-14
- 7	6	64	-54
- 6	6	38	35
- 5	6	63	49
- 4	6	27	-25
- 3	6	32	-28
- 2	6	9	11
- 1	6	71	67
0	6	34	36
1	6	85	-83
2	6	11	-15
3	6	53	51
4	6	9	-12
5	6	30	-33
6	6*	5	-3
7	6	25	30
8	6	15	23
9	6	19	-30
10	6	19	-26
11	6	21	24
12	6*	6	6
13	6	13	-14
14	6*	5	1
-20	7	12	10
-19	7	8	6
-18	7	9	-9
-17	7	14	-13
-16	7*	5	9
-15	7*	6	3
-14	7	9	-13
-13	7	14	15
-12	7*	5	8
-11	7	11	-11
-10	7*	5	-4
- 9	7*	5	0
- 8	7	13	16
- 7	7*	5	4
- 6	7	12	-12
- 5	7	12	12
- 4	7	12	12
- 3	7	65	-53
- 2	7	25	-20
- 1	7	68	53
0	7	12	10
1	7	12	-15
2	7*	5	-9
3	7*	5	5
4	7	11	14
5	7	18	-27
6	7	19	-22
7	7	26	37
8	7	21	27
9	7	13	-16
10	7*	6	-9
11	7*	5	-2
12	7*	5	-3
13	7*	5	-1
-20	8	14	-13
-19	8	25	-18
-18	8	14	12
-17	8	15	11
-16	8*	5	-9
-15	8*	5	-10
-14	8*	6	9
-13	8	25	25
-12	8	17	-15
-11	8	52	-41
-10	8	23	21
- 9	8	72	51
- 8	8*	5	0
- 7	8	23	-10
- 6	8*	5	-10
- 5	8	25	21
- 4	8	15	16
- 3	8	58	-49

finement, however, the *xyz* parameter of S(2′) converged again to the value corresponding to the distorted tetrahedron as above.

The distances S(2′)–S(4*G*) and S(1)–S(4), 3·67 and 3·65 Å, between sulphur atoms belonging to different xanthate groups shown in Fig. 2 and Table 3, are almost the same as the distance of the van der Waals contact of spherical sulphur atoms, 3·6–3·7 Å. However, S(2)–S(4*G*), 3·38 ± 0·01 Å, is a little shorter than the above value, and this may be a result of the distortion of the spherical shape of sulphur atoms, due to their bondings with carbon and zinc atoms which permit a closer approach of S(2) and S(4*G*) (*e.g.* Pauling, 1960). The smallest effective radius for a sulphur atom in the van der Waals bonding cited in Landolt–Börnstein is 1·63 Å, *i.e.* 3·26 Å in interatomic distance (Landolt–Börnstein, 1955).

Of the bond angles of four sulphur atoms connecting a zinc atom and a xanthate group, the bond angles at Zn–S(3)–C(4), Zn–S(4)–C(4) and Zn–S(1)–C(1) are the same within the error limit, the mean value being 105·2°. The bond angle at Zn–S(2)–C(1), however, is 114·8° ± 1·0°. It seems that the large allowance for the variation in the bond angles of sulphur atoms has resulted in the comparatively simple monoclinic structure of the crystal with the *b* axis as short as 5·70 Å. The bond angle Zn–S–C in dichlorobisthioureazinc, 108·6° ± 0·7°, is comparable to the above values (Kunchur & Truter, 1958).

Table 2 (*cont.*)

H	L	FO	FC
-2	8*	5	-11
-1	8	51	43
0	8*	5	3
1	8	39	-37
2	8	13	-19
3	8*	5	6
4	8	19	19
5	8*	6	-4
6	8	20	-19
7	8	21	22
8	8	12	18
9	8	12	-18
10	8	11	-14
11	8*	5	5
12	8*	5	9
-19	9	14	8
-18	9*	3	2
-17	9	14	-10
-16	9	9	-6
-15	9*	5	1
-14	9	20	13
-13	9*	5	7
-12	9	21	-14
-11	9*	6	1
-10	9	17	11
-9	9	19	-16
-8	9*	6	-1
-7	9*	6	9
-6	9*	6	-3
-5	9*	5	5
-4	9	13	-13
-3	9*	5	-7
-2	9	12	11
-1	9	13	-9
0	9	13	15
1	9	32	25
2	9	24	-23
3	9	22	-15
4	9	13	14
5	9*	6	0
6	9*	6	-5
7	9*	5	-2
8	9	8	6
9	9*	5	18
10	9*	5	-12
11	9	21	-23
-17	10	18	13
-16	10	11	6
-15	10	11	-12
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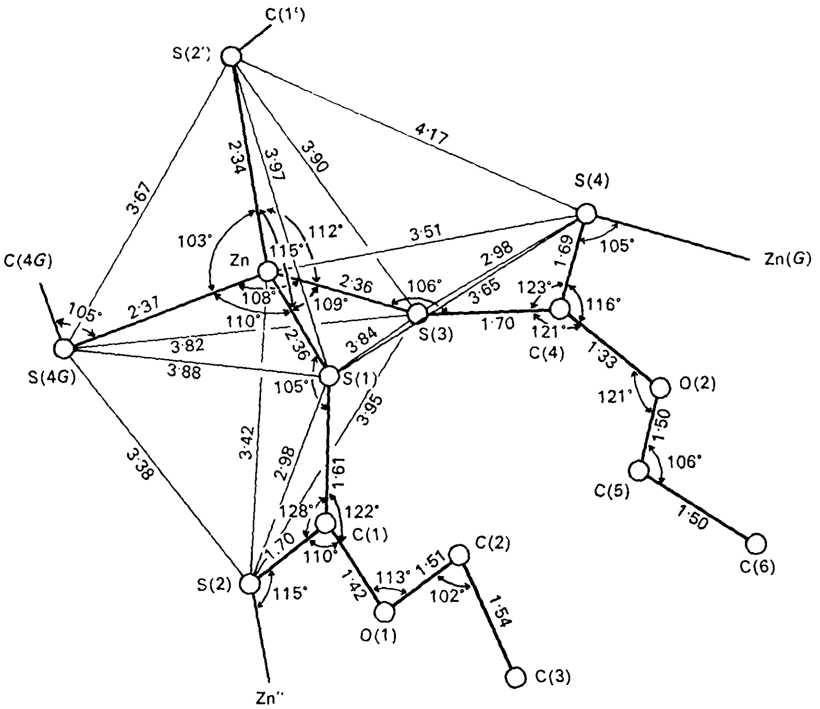

Fig. 2. Atom distances and bond angles in zinc ethylxanthate crystal.

Table 3. *Atom distances, bond angles and their standard deviations*

Atom distances	
Zn—S(1)	2·362 ± 0·009 Å
Zn—S(2')	2·337 ± 0·010
Zn—S(3)	2·364 ± 0·012
Zn—S(4G)	2·369 ± 0·008
Zn—S(2)	3·420 ± 0·011
Zn—S(4)	3·508 ± 0·009
S(1)—S(3)	3·840 ± 0·011
S(3)—S(4G)	3·820 ± 0·011
S(4G)-S(1)	3·883 ± 0·012
S(2')—S(4G)	3·673 ± 0·012
S(2')—S(1)	3·968 ± 0·013
S(2')—S(3)	3·899 ± 0·011
S(2)—S(3)	3·952 ± 0·011
S(2)—S(4G)	3·381 ± 0·013
S(1)—S(4)	3·647 ± 0·011
S(1)—S(2)	2·975 ± 0·012
S(1)—C(1)	1·61 ± 0·03
S(2)—C(1)	1·70 ± 0·03
C(1)—O(1)	1·42 ± 0·03
O(1)—C(2)	1·51 ± 0·03
C(2)—C(3)	1·54 ± 0·05
S(3)—S(4)	2·983 ± 0·012
S(3)—C(4)	1·70 ± 0·03
S(4)—C(4)	1·69 ± 0·03
C(4)—O(2)	1·33 ± 0·03
O(2)—C(5)	1·50 ± 0·04
C(5)—C(6)	1·50 ± 0·06
C(3)—C(3·S)	3·68 ± 0·06
C(6)—C(6·1)	3·69 ± 0·07
C(6)—C(6·1')	4·17 ± 0·08

Bond angles	
S(1)-Zn—S(3)	108·7 ± 0·3°
S(1)-Zn—S(4G)	110·3 ± 0·3
S(1)-Zn—S(2')	115·2 ± 0·3
S(3)-Zn—S(4G)	107·6 ± 0·3
S(3)-Zn—S(2')	112·1 ± 0·3
S(2')-Zn—S(4G)	102·6 ± 0·3
Zn—S(1)-C(1)	104·9 ± 1·0
C(1)-S(2)-Zn''	114·8 ± 1·0
S(1)-C(1)-S(2)	127·7 ± 1·8
S(1)-C(1)-O(1)	121·9 ± 2·0
S(2)-C(1)-O(1)	110·3 ± 1·9
C(1)-O(1)-C(2)	112·7 ± 2·0
O(1)-C(2)-C(3)	102·0 ± 3·2
Zn—S(3)-C(4)	105·5 ± 1·0
C(4)-S(4)-Zn(G)	105·1 ± 1·2
S(3)-C(4)-S(4)	123·4 ± 1·6
S(3)-C(4)-O(2)	120·7 ± 2·3
S(4)-C(4)—O(2)	116·0 ± 2·0
C(4)-O(2)-C(5)	121·0 ± 2·4
O(2)-C(5)-C(6)	106·4 ± 3·9

Recently the crystal and molecular structure of zinc diethyldithiocarbamate, $[(C_2H_5)_2NCS_2]_2Zn$, has been determined (Bonamico, Mazzone, Vaciago & Zambonelli, 1965). The crystal is composed of the dimeric complex consisting of the monomer of the above formula unit in such a way that each zinc atom is five-coordinated with Zn–S distances $2{\cdot}35_5$, $2{\cdot}33_1$, $2{\cdot}38_3$, $2{\cdot}44_3$ and $2{\cdot}81_5$ Å. Of these, the four shorter bonds are directed to the corners of a considerably distorted tetrahedron. The structure surrounding a zinc atom found for zinc ethylxanthate by the present analysis is much simpler; in it each zinc atom is tetrahedrally coordinated to four sulphur atoms at distances 2·34, 2·36, 2·36 and 2·37 Å, all ±0·01 Å, and the bonds are directed to the corners of a slightly distorted tetrahedron. Such a difference in the configuration of sulphur atoms around a zinc atom between zinc diethyldithiocarbamate and zinc ethylxanthate is supposed to be due to the steric hindrance of the large $(C_2H_5)_2N$ atom groups which occurs in the former when a continuous network of tetrahedrally bonded zinc atoms and $-\mathrm{S}-\overset{|}{\mathrm{C}}-\mathrm{S}-$ atom groups, as in the latter, is formed. The bond angle Zn–S–C ranges from 78° to 94° in the case of zinc diethyldithiocarbamate.

The sulphur–carbon bond lengths were found to be 1·61, 1·69, 1·70 and 1·70 Å, all ±0·03 Å. The latter three agree with the sulphur–carbon distance already reported (Bonamico *et al.*, 1965; other references are quoted therein). The first, corresponding to S(1)–C(1), is shorter than the other three by 0·08–0·09 Å, although this difference is not definitely significant by Cruickshank's criterion (*e.g.* Lipson & Cochran, 1953).

Each xanthate group takes almost a planar configuration as shown in Fig. 4. The deviation of C(2) and C(3) atoms and that of C(6) atom from each plane defined by two sulphur and one oxygen atom may be explained by the rotation of the ethyl group around the O–C single bond as shown in Fig. 4. However, this interpretation should not be taken as final because of the inaccuracy in the atomic positions of carbon atoms due to the presence of zinc atoms in the structure. The situation is seen in the electron density contours in Fig. 1 and also in the large *B* values for C(3), C(5) and C(6) in Table 1. For the same reason the atomic distances between methyl ends of the ethyl groups, C(3)–C(3·S), C(6)–C(6·1) and C(6)–C(6·1′) in Table 3, are to be taken as being substantially in conformity with the distance of van der Waals contact, 4·0 Å.

The result that zinc atoms are bonded with the sulphur atoms of the xanthate groups by tetrahedral covalent bonds forming a two-dimensional network of atoms is of particular interest in interpreting the action of xanthate on zincblende surfaces. Such a bonding property will hinder the adsorption of each isolated xanthic cation, or zinc xanthate molecule or molecular ion to the atom sites of the zincblende surface, and, accordingly, will be inactive in developing the hydrophobic property on it. When the concentration of zinc anions in the solution is increased, zinc xanthate crystallites will be precipitated. However, the side planes of the thin platelike crystallites are bounded by the methyl ends of the alkyl groups, and they will lack the ability for strong adhesion to the mineral surfaces. Xanthates are, therefore, concluded to be inactive in endowing zincblende surfaces with the hydrophobic property, in contrast with the case of the galena–xanthate system (Hagihara, Sakurai & Ikeda, 1964), as is experienced in flotation practice.

The present analysis was initiated at Kobayasi Institute of Physical Research, Kobubunzi, Tokyo.

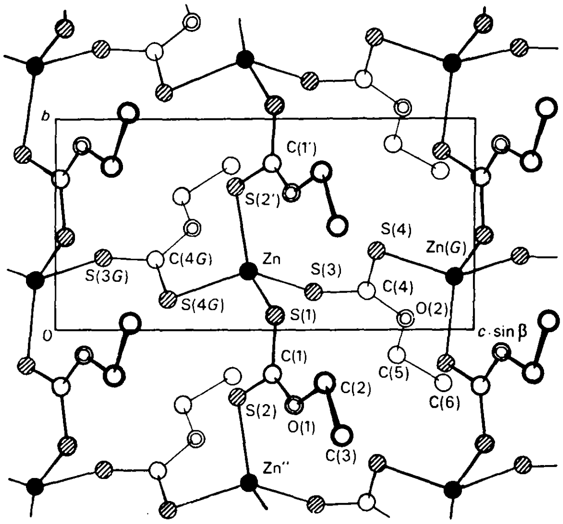

Fig. 3. Configuration of atoms in zinc ethylxanthate crystal, within the sectional layer, 0 < x < 0·5, viewed along the *x*-axis.

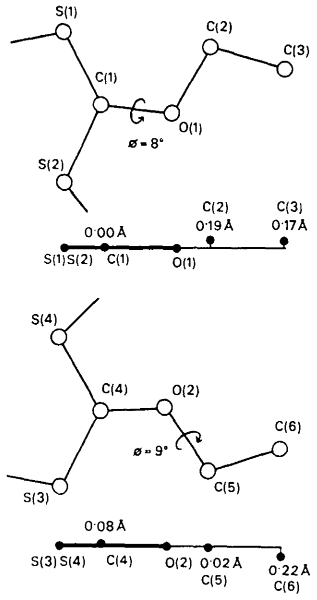

Fig. 4. Nearly planar configuration of atoms in the ethylxanthate groups in zinc ethylxanthate crystal.

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The Crystal and Molecular Structure of 1,5-Dihydroxyanthraquinone

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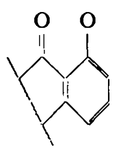
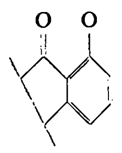
Crystals of 1,5-dihydroxyanthraquinone are monoclinic with two molecules in a unit cell of dimensions $a=15\cdot755$, $b=5\cdot308$, $c=6\cdot003$ Å, $\beta=93°37'$, space group $P2_1/a$. The structure was solved by Fourier methods and refined in three dimensions with anisotropic thermal parameters, using differential syntheses. The final R value was 13·3 % and the mean coordinate standard deviation 0·004 Å. The molecule forms a strong asymmetric intramolecular hydrogen bond. Electron delocalization across the quinonoid ring, as gauged by the structural parameters, appears minimal. The molecular packing is tight.

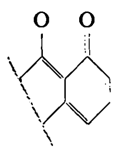
The hydroxyanthraquinones offer an interesting problem in hydrogen bonding, in that when substituted in the α position they can form intramolecular bonds, but in the β position intermolecular bonds only. The melting points of the former compounds are characteristically lower (Table 1), although 1,5-dihydroxyanthraquinone is an exception. Various spectroscopic investigations have been reported (Peters & Sumner, 1953; Hadzi & Sheppard, 1954; Bloom, Briggs & Cleverley, 1959). The spectra of the α-substituted compounds confirm the formation of an intramolecular bond, and are interpreted in terms of contributing structures, such as (I), (II), and (III).



(I)



(II)



(III)

The spectra are consistent with a strong hydrogen bond, but the proton is thought to be asymmetrically placed between the two oxygen atoms and firmly attached to only one of them. The possibility of occasional proton tunnelling between two potential minima in the bond could not, however, be excluded.

Table 1. *Melting points of some anthraquinone derivatives*

Derivative	m.p.
1-Hydroxy	190°C
2-Hydroxy	302
1,8-Dihydroxy	191
1,4-Dihydroxy	194
1,5-Dihydroxy	280
1,2-Dihydroxy	290
2,6-Dihydroxy	>330

The present three-dimensional crystallographic study of 1,5-dihydroxythraquinone was undertaken to provide information on the over-all structure of the molecule, to attempt to describe further the extent and influence of hydrogen bonding upon the structure, and to explain the abnormal melting point of these crystals.

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