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The Crystal Structure of Lead n-butylxanthate. I. Disordered Structure

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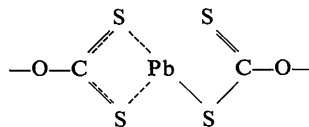
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Lead n-butylxanthate, $\text{Pb}(\text{SSCOC}_4\text{H}_9)_2$, crystallizes into ordered and disordered structures. The disordered crystal is monoclinic with $a = 36.87 \pm 0.25$, $b = 4.58 \pm 0.11$, $c = 10.71 \pm 0.09$ Å; $\beta = 112.0 \pm 0.6^\circ$; the space group is $C2/c$ and $Z = 4$. The ordered crystal is also monoclinic. Its cell dimensions are the same as those of the disordered crystal except that the b axis is quadruplicated. A three-dimensional X-ray structure analysis was carried out with the disordered crystal by the split atom method. The asymmetric molecule of $\text{Pb}(\text{SSCOC}_4\text{H}_9)_2$ is found to distribute about the twofold rotation axis with the multiplicity 0.5, satisfying the conditions of the space group $C2/c$.

The lead atom is bonded to one xanthate group with Pb-S distances of 2.82 ± 0.04 and 2.77 ± 0.09 Å and to the other with 2.76 ± 0.06 and 3.03 ± 0.08 Å. The two xanthate groups are bonded to the lead atom with S-Pb-S bond angles $91.7 \pm 1.5^\circ$ and $93.7 \pm 2.2^\circ$. These results suggest the following type of bonding between lead atom and the dithiocarbonic ends of the xanthate groups:



Introduction

In an analysis of lead ethylxanthate crystal by X-ray diffraction (Hagihara & Yamashita, 1966) a molecule of lead ethylxanthate, $\text{Pb}(\text{SSCOC}_2\text{H}_5)_2$, has been found to form an asymmetric unit of the structure. The four sulphur atoms of the dithiocarbonic ends of the two ethylxanthate groups are coordinated to the lead atom without any symmetry relations. The Pb-S distances have been found to be 2.74 and 2.84 Å for one xanthate group and 2.79 and 2.95 Å for the other, all ± 0.03 Å. Within each branch of the molecule consisting of a lead atom and one xanthate group, the difference be-

tween the Pb-S distances was concluded to be significant. In order to ascertain whether such a type of bonding of the lead atom with the dithiocarbonic sulphur atoms exists also in the other alkylxanthates, the structure analysis of lead n-butylxanthate crystal has been carried out.

Experimental

Preparation of the crystals

Lead n-butylxanthate powder was obtained as a white precipitate when an aqueous solution of purified potassium n-butylxanthate was added slowly to an

aqueous solution of lead nitrate. The powder was dissolved in acetone or ethyl alcohol, and colourless single crystals were obtained by slow evaporation of the solvent. The crystal from acetone solution had a leaflet shape less than 0.1 mm thick. The crystal from alcohol solution was a thin needle a few millimetres long.

Stability of the crystal

The crystal was not so stable in air at room temperature as crystals of lead ethylxanthate, which merely showed weak lead sulphide rings in an X-ray diffraction photograph even after being kept in a desiccator for more than two years. The crystal began to show a brownish colour within a few weeks after its preparation. When a crystal was kept in a desiccator for several months, its colour deepened gradually until a black metallic lustre was developed. X-ray examination revealed the decomposition product to be randomly oriented lead sulphide crystallites.

Ordered and disordered state

Preliminary X-ray diffraction examination showed the crystal to be monoclinic. From a rotation photograph as shown in Fig. 1(a) the length of the b axis was determined to be about 4.5 Å. However, the crystals prepared from both acetone and alcohol solutions often showed additional sharp diffraction spots corresponding to a cell with quadruplicated b axis. Fig. 1(b) shows an example in which sharp spots are observed on the $K=1/4, 3/4, 5/4$ and $7/4$ layers. On the $K=2/4$ and $6/4$ layers they are observed only faintly in a few numbers. The relative intensities of reflexions on these layers with respect to those on the zero or first layer were variable, depending on the still uncontrollable conditions of preparation. Furthermore, diffuse reflexions were always observed on layers corresponding to the quadruplicated b axis even when sharp reflexions were not observed at all on these extra layers. Fig. 1(c) shows an example of the diffuse reflexions.

On the basis of this evidence the crystal with sharp reflexions on the $K=n/4$ ($n=0,1,2,\dots$) layers has been interpreted to be in the ordered state, while the one with only diffuse reflexions on the $K=n/4$ ($n=1,3,5,\dots$) layers is in a partially ordered state, and the one with sharp reflexions only on the $K=n/4$ ($n=0,4,8,\dots$) in the disordered state. Because at room temperature it was easier to obtain disordered crystals repeatedly and an ordered crystal had a tendency to transform gradually into a partially ordered or disordered crystal during prolonged X-ray exposure at room temperatures, the analysis of the disordered crystal was carried out first.

Crystal data

The accurate determination of the cell constants was difficult with the present crystal because the reflexion intensities decreased rapidly with increasing value of $\sin \theta$. Only few reflexions with well resolved $K\alpha_1$ and $K\alpha_2$ were obtained in a limited region of reciprocal

space. The error was particularly large for the b axis, along which the crystal was preferentially elongated. The monoclinic cell has the dimensions:

$$a = 36.87 \pm 0.25, \quad b = 4.58 \pm 0.11, \quad c = 10.71 \pm 0.09 \text{ \AA};$$

$$\beta = 112.0^\circ \pm 0.6^\circ.$$

The systematic extinctions indicated the space group Cc or $C2/c$. Four molecules of $\text{Pb}(\text{SSCO}_4\text{H}_9)_2$ per unit cell give a calculated density of 1.835 g.cm^{-3} , which is to be compared with the measured value 1.72 g.cm^{-3} (flotation). The linear absorption coefficient μ was calculated to be 205 cm^{-1} .

Intensity measurement

A series of Weissenberg photographs of the $K=0, 1, 2, 3$ and 4 layers of a b -axis oriented needle crystal and $L=0$ layer of a c -axis oriented leaflet crystal were taken at room temperature with filtered $\text{Cu } K\alpha$ radiation by the equi-inclination method. The needle crystal had a cross section of $0.2 \times 0.1 \text{ mm}$ and the leaflet crystal $0.5 \times 0.1 \text{ mm}$. The intensities of the 835 observed reflexions were measured by visual comparison with a standard scale. In order to minimize the number of unobserved reflexions in the calculation a limit was set for the $\sin \theta$ value at 0.67, by inspecting the diffraction photographs. For reflexions with $\sin \theta \geq 0.67$ only observed ones were used. For those with $\sin \theta < 0.67$ unobserved ones were given intensity values half the minimum intensity in each layer photograph. They were 54 in total. The intensities of the 889 observed and unobserved reflexions were corrected for the Lorentz and polarization factors. Absorption correction was made by a graphical method for the $h0l$ and $hk0$ reflexions. Corrections for the extinction effects were considered at the final stage of the refinement for the 200, 400 and 600 reflexions.

Determination of the structure

The (010) Patterson projection was calculated with 145 $h0l$ reflexions observed. Mainly owing to the overwhelmingly strong Pb–Pb vector, the contours about the origin were nearly elliptical, and two Pb–S and one Pb–O peaks were observed distinctly in the asymmetric area of the projection. The direction of the alkyl group in the molecule was also well defined. On the assumption that the S–Pb–S bond angle is nearly 98.2° , a value obtained with lead ethylxanthate, the space group of the crystal was assumed as a starting point of the analysis to be $C2/c$. If the molecule in the crystal did not possess a twofold rotation axis about the lead atom parallel to the b axis, the two Pb–S peaks and one Pb–O peak should have been separated into three or four peaks in the former case, and two peaks in the latter case, because of the added centre of symmetry in the Patterson functions. With $C2/c$ and without further extinctions the four lead atoms should occupy special positions; $(000; \frac{1}{2}\frac{1}{2}0) + 0y\frac{1}{4}; 0\bar{y}\frac{3}{4}$. The y coord-

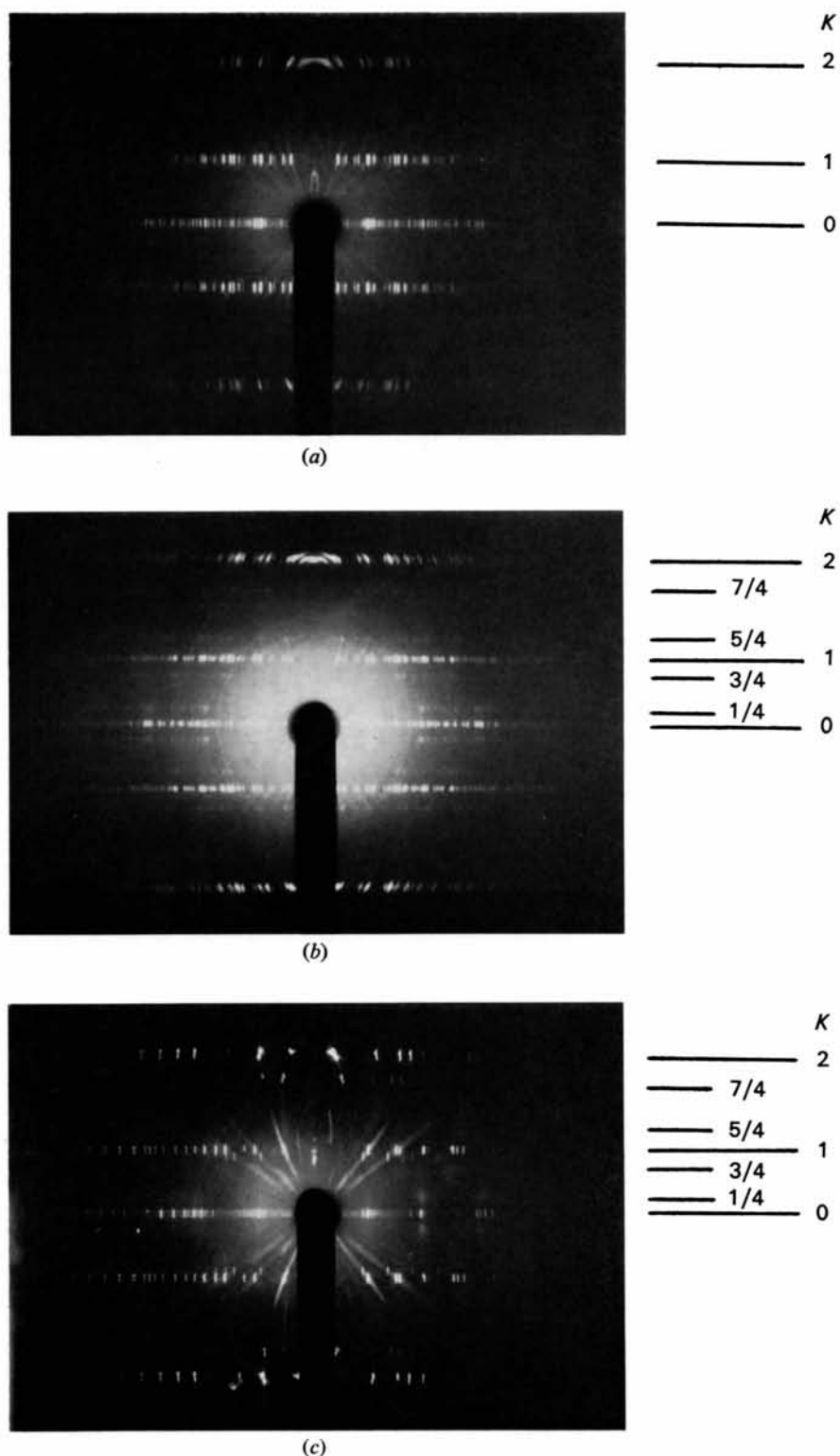


Fig. 1. X-ray diffraction patterns of lead n-butylxanthate crystals, $\text{Pb}(\text{SSCOC}_4\text{H}_9)_2$. (a) A rotation photograph of a disordered crystal, (b) a rotation photograph of an ordered crystal, and (c) an oscillation photograph of a partially ordered crystal, all about the b axis.

dinate of the lead atom was determined from the (001) Patterson projection calculated with 55 $hk0$ reflexions observed.

A three-dimensional Fourier synthesis was carried out with the phases calculated on the basis of the coordinates of the lead atom. Successive refinements were carried out as usual. Starting from an R value of 44%, three cycles of least-squares refinement with isotropic temperature factors were carried out. The R value was, however, improved only to 37% at $B=8.2$ for the lead atom. The difference Fourier synthesis showed that further improvements were not promising even on introduction of anisotropic temperature factors.

By taking account of the two observed facts that the present crystal had features of a disordered crystal and the origin of the Patterson projections showed nearly elliptical contours, a split atom method was applied

at this stage to the lead atom, this atom being split into two halves. The magnitude of the split was first determined from the shape of the origin of the Patterson projections. A Fourier synthesis was carried out, and then each of the other atoms was also split into two halves from observation of the map obtained. With 889 reflexions of equal weight three cycles of the least-squares refinement were applied to the split atoms. The R value improved to 17.2% for the total reflexions used, and to 16.8% for the 835 observed reflexions only. The result of the final Fourier synthesis is shown in Fig. 2. These calculations were carried out by ERFR-2 (Sly, Shoemaker & Van den Hende, 1962) and ERBR-1 (Van den Hende, 1961). Atomic scattering values were those adopted in the program.

By comparing the atomic distances between these split atoms with those which have already been found

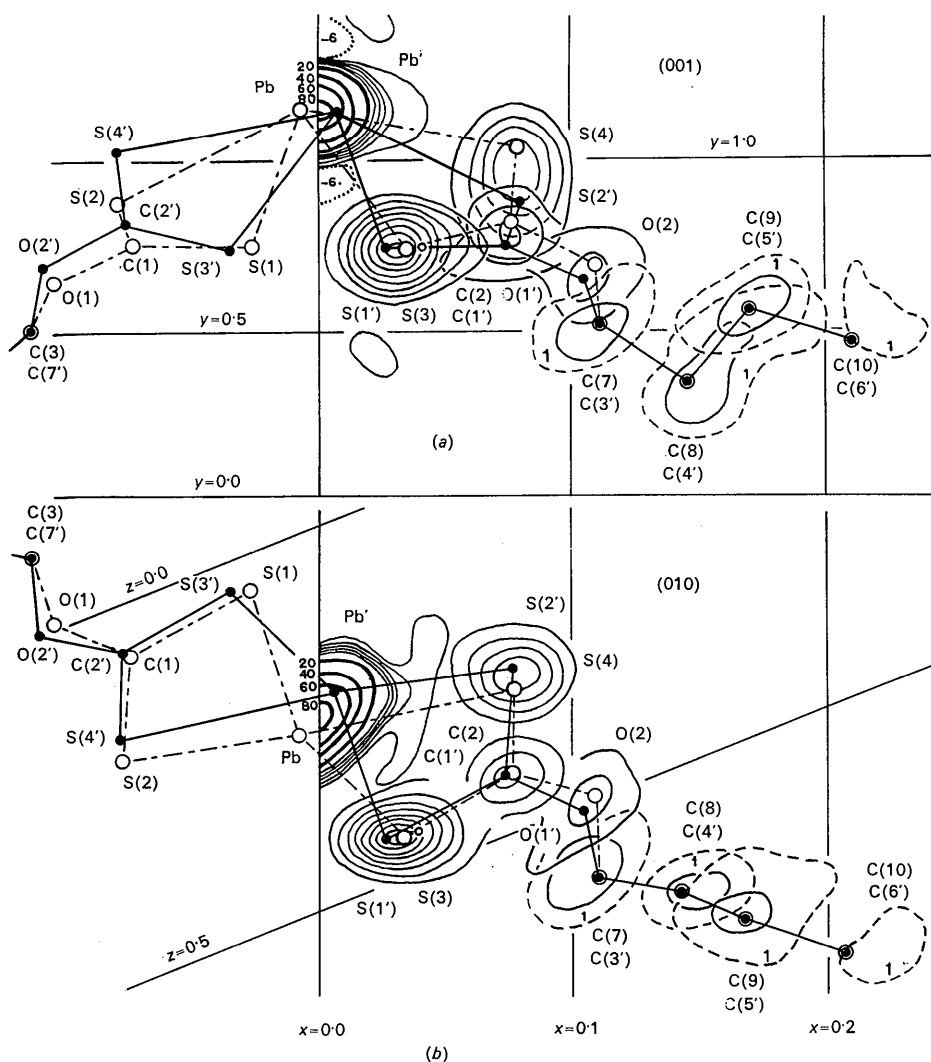


Fig. 2. Sections of electron density contours through the maximum density regions in the three-dimensional Fourier synthesis of the lead *n*-butylxanthate crystal in the disordered state: (a) parallel to (001), and (b) parallel to (010). Contours are drawn at intervals of $2 \text{ e.}\text{\AA}^{-3}$ except for the lead atom and the $1 \text{ e.}\text{\AA}^{-3}$ contours of the carbon atoms belonging to the *n*-butyl groups. Small open circles indicate the positions of the S(3) atom, which were determined directly from the least-squares refinement.

for lead ethylxanthate, the split atoms were resolved into two lead n-butylxanthate molecules, each with the multiplicity of 0.5. As Fig.2 shows, they are arrayed

about the twofold rotation axis, satisfying the conditions for the space group $C2/c$. In this tentative calculation the distance S(3)–S(4) came out to be 2.73

Table 1. Atomic parameters of lead n-butylxanthate, $Pb(SSCOC_4H_9)_2$, in the disordered state

All the atoms have multiplicity 0.5.

	x_i	x_i/a_i	$\sigma(x_i)$ (Å)	B (Å ²)	$ \Delta x_i /\sigma(x_i)$	ΔB
Pb	x	−0.0067	0.008	6.16	0.55	0.04
	y	0.1525	0.008		0.01	
	z	0.2656	0.008		0.29	
S(1)	x	−0.026	0.05	4.8	0.40	−0.4
	y	0.743	0.04		0.04	
	z	0.053	0.04		0.21	
S(2)	x	−0.078	0.09	9.9	0.07	0.4
	y	0.872	0.09		0.07	
	z	0.212	0.09		0.12	
S(3)	x	0.035	0.06	7.4	0.94	−0.0
	y	0.739	0.06		0.05	
	z	0.451	0.06		0.03	
S(4)	x	0.078	0.08	8.7	0.19	−0.3
	y	0.024	0.08		0.10	
	z	0.314	0.08		0.06	
C(1)	x	−0.074	0.18	6.5	0.12	0.9
	y	0.74	0.17		0.16	
	z	0.076	0.18		0.06	
C(2)	x	0.076	0.18	5.3	0.32	−0.4
	y	0.80	0.17		0.06	
	z	0.424	0.18		0.13	
O(1)	x	−0.104	0.19	9.7	0.05	0.8
	y	0.64	0.19		0.05	
	z	−0.010	0.20		0.06	
O(2)	x	0.108	0.19	10.0	0.26	1.3
	y	0.69	0.19		0.09	
	z	0.495	0.20		0.18	
C(3)	x	−0.110	0.18	5.3	0.32	−0.4
	y	0.50				
	z	−0.10				
C(4)	x	−0.140	0.18	5.3	0.32	−0.4
	y	0.32				
	z	−0.16				
C(5)	x	−0.168	0.18	5.3	0.32	−0.4
	y	0.55				
	z	−0.23				
C(6)	x	−0.205	0.18	5.3	0.32	−0.4
	y	0.45				
	z	−0.33				
C(7)	x	0.110	0.18	5.3	0.32	−0.4
	y	0.50				
	z	0.60				
C(8)	x	0.140	0.18	5.3	0.32	−0.4
	y	0.32				
	z	0.66				
C(9)	x	0.168	0.18	5.3	0.32	−0.4
	y	0.55				
	z	0.73				
C(10)	x	0.205	0.18	5.3	0.32	−0.4
	y	0.45				
	z	0.83				

From C(3) to C(10);
 $\sigma(x) = 0.3 \text{ \AA}$
 $\sigma(y) = 0.3$, $B = 10 \text{ \AA}^2$.
 $\sigma(z) = 0.3$

± 0.10 Å, a value much smaller than the corresponding values 2.94–3.00 Å found for the other metal xanthates (Carrai & Gottardi, 1960; Gottardi, 1961; Hagihara & Yamashita, 1966; Ikeda & Hagihara, 1966). In order to minimize this discrepancy the X coordinate of the S(3) atom was changed from the value determined by the least-squares refinement. The displacement amounting to 0.20 Å was observed in the Fourier map as seen in Fig. 2. As a result the Pb–S(3) distance changed from 2.82 to 2.76 Å, both ± 0.06 Å. As to the carbon atoms belonging to the *n*-butyl groups, the B factors came out to be around 10 and their contours in the Fourier map were so diffuse that their atomic positions were determined only approximately without considering the splitting.

With the new coordinates of the S(3) and of the carbon atoms the F_c values were again calculated. The R value for the over-all reflexions came out to be 18.9%, while that for the observed reflexions alone 18.5%. They were larger by 1.7% than the corresponding values obtained directly from the least-squares refinement with all the atoms split formally into two halves.

The final atomic coordinates, the standard deviations in Å, B factors, the displacement of coordinates in terms of the standard deviation and ΔB in the final cycle of refinement are listed in Table 1. The comparison of the observed and calculated structure factors, F_o and F_c respectively, is shown in Table 2. Atomic distances and bond angles of a resolved molecule of lead *n*-butylxanthate are shown in Fig. 3 and with the standard deviations in Table 3.

Discussion

The configuration of the four sulphur atoms belonging to two *n*-butylxanthate groups which are bonded to a lead atom is shown in Fig. 4. The corresponding configuration in the case of lead ethylxanthate has been shown in Fig. 5 of the previous paper (Hagihara & Yamashita, 1966). Although the configuration as a whole shows a close similarity in both cases, there are important differences. With lead ethylxanthate the difference in the interatomic distances between Pb–S(1) and Pb–S(2) was 0.10 Å and that between Pb–S(3) and Pb–S(4) was 0.16 Å, both with $\sigma = 0.04$ Å. These dif-

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

Distances		Angles	
Pb—S(1)	2.83 ± 0.04 Å	S(1)—Pb—S(2)	65.8 ± 2.0°
Pb—S(2)	2.77 ± 0.09	S(1)—Pb—S(3)	91.7 ± 1.5
Pb—S(3)	2.76 ± 0.06	S(2)—Pb—S(3)	93.7 ± 2.2
Pb—S(4)	3.03 ± 0.08	S(3)—Pb—S(4)	58.6 ± 2.0
S(1)—S(2)	3.04 ± 0.10	S(4)—Pb—S(2)	141.2 ± 2.6
S(3)—S(4)	2.85 ± 0.10	S(4)—Pb—S(1)	86.8 ± 1.7
S(2)—S(3)	4.04 ± 0.11	Pb—S(1)—C(1)	82 ± 7
S(4)—S(1)	4.02 ± 0.09	Pb—S(2)—C(1)	88 ± 7
C(1)—S(1)	1.86 ± 0.19	Pb—S(3)—C(2)	93 ± 7
C(1)—S(2)	1.62 ± 0.20	Pb—S(4)—C(2)	85 ± 7
C(2)—S(3)	1.66 ± 0.19	S(1)—C(1)—S(2)	122 ± 11
C(2)—S(4)	1.58 ± 0.20	S(3)—C(2)—S(4)	123 ± 11
C(1)—O(1)	1.25 ± 0.26	S(1)—C(1)—O(1)	122 ± 16
C(2)—O(2)	1.25 ± 0.26	S(2)—C(1)—O(1)	117 ± 16
O(1)—C(3)	1.37 ± 0.35	S(3)—C(2)—O(2)	123 ± 16
O(2)—C(7)	1.41 ± 0.35	S(4)—C(2)—O(2)	115 ± 16
C(3)—C(4)	1.34 ± 0.42	C(1)—O(1)—C(3)	112 ± 20
C(7)—C(8)		C(2)—O(2)—C(7)	120 ± 20
C(4)—C(5)		O(1)—C(3)—C(4)	109 ± 25
C(8)—C(9)		O(2)—C(7)—C(8)	124 ± 25
C(5)—C(6)	1.46 ± 0.42	C(3)—C(4)—C(5)	96 ± 25
C(9)—C(10)		C(7)—C(8)—C(9)	
		C(4)—C(5)—C(6)	
		C(8)—C(9)—C(10)	

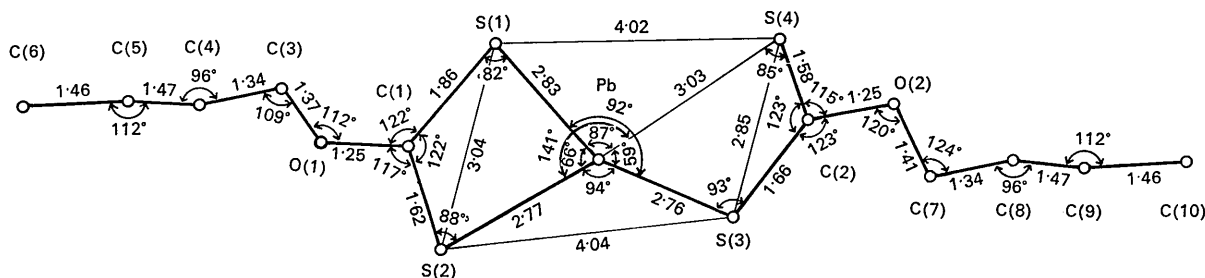


Fig. 3. Interatomic distances and bond angles in a molecule of lead *n*-butylxanthate analyzed from the disordered crystal.

ferences were found to be significant by Cruickshank's criterion (see *e.g.*, Lipson & Cochran, 1953). With lead *n*-butylxanthate, in which $\sigma=0.10$ Å for the Pb-S distance, the difference between Pb-S(1) and Pb-S(2), 0.05 Å, is not significant, while that between Pb-S(3) and Pb-S(4), 0.27 Å is significant. Pb-S(1) and Pb-S(2) are equal in length within the limit of error, while the lengths of Pb-S(3) and Pb-S(4) are different. The bond angles for the shortest Pb-S bonds at the lead atom are also all different. With lead ethylxanthate the bond angle S(1)-Pb-S(3) was $98.2^\circ \pm 0.9^\circ$, while with lead *n*-butylxanthate the two corresponding bond angles, S(1)-Pb-S(3) and S(2)-Pb-S(3), are $91.7 \pm 1.5^\circ$ and $93.7 \pm 2.2^\circ$, respectively. They are equal to each other within the limit of error but different from the S-Pb-S bond angle in the case of lead ethylxanthate.

The characteristic features of these configurations are interpreted as follows. In the case of lead ethylxanthate the configuration is determined by the following conditions: first, the two shortest Pb-S bonds, namely, Pb-S(1) and Pb-S(3), make a bond angle of 98.2° about the lead atom, secondly, S(2) and S(3) atoms come into van der Waals contact at the distance of 3.77 Å, and, thirdly, the Pb-S(4) distance will be 2.95 Å, which is nearest to the sum of the ionic radii of the divalent lead and sulphur ions, 3.05 Å, of the four Pb-S distances. These conditions are realized by the rotations of the molecular segments around the C-S and Pb-S single bonds as discussed in the previous paper (Hagihara & Yamashita, 1966). In lead *n*-butylxanthate the configuration is determined by the following conditions: first, the Pb-S(3) bond is directed almost normal to each of the Pb-S(1) and Pb-S(2) bonds, and secondly the Pb-S(4) distance will be 3.03 Å, which is the same as the sum of the ionic radii of the divalent lead and sulphur ions, 3.05 Å. The distances between sulphur atoms belonging to different xanthate groups, S(2)-S(3) and S(1)-S(4), are 4.04 ± 0.11 and 4.02 ± 0.09 Å, respectively. They are larger than the van der Waals distance between two sulphur atoms, 3.7 Å, indicating that the configuration is not affected by the van der Waals contact of these sulphur atoms. The bonding property of the lead atom with the dithiocarbonic sulphur atoms is shown schematically in Fig. 4 with thick continuous and broken lines.

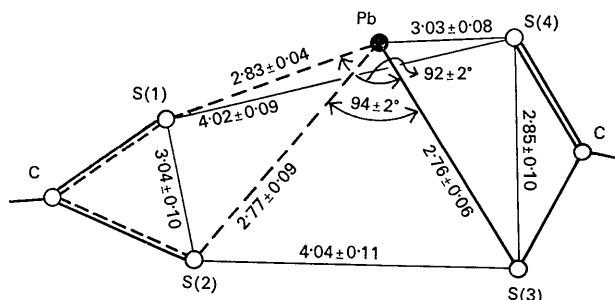


Fig. 4. Configuration of the four dithiocarbonic sulphur atoms about the lead atom in the lead *n*-butylxanthate crystal, $\text{Pb}(\text{SSCO}_4\text{H}_9)_2$.

Recently, the type of configuration of a lead atom and four atoms in a dithiocarbonic group, which is similar to the case of lead *n*-butylxanthate, has been revealed in the case of the lead isopropylxanthate precipitated from pyridine solution. The structure of this crystal will be reported shortly. The intermolecular relations in the lead *n*-butylxanthate crystal will be discussed in an analysis of the structure of the ordered crystal.

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