maximum deviation of 0·081 Å, the Cl atom and the CO group being located at *trans* positions.

The packing of the crystal is determined only by van der Waals interactions.

The bond lengths and angles are as expected for the triarylphosphine ligand. The Rh–C and Rh–P lengths are similar to those found by La Placa & Ibers (1965) in $Rh(CO)[P(Ph)_3]_3$; thus the F atoms have no influence on the Rh–P bond.

Most of the calculations were carried out with XRAY70 (Stewart, Kundell & Baldwin, 1970). Thanks are due to the staff of the Computing Center of JEN (Madrid) for the facilities provided on the Univac 1100/80 computer.

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Structure of the Rhombohedral Form (α Form) of Arsenious Methylxanthate,*[As(C₂H₃OS₂)₃]

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Abstract. $M_r = 396·4$, $R\bar{3}$, $a = 14·639$ (7), $c = 12·384$ (7) Å, $V = 2298$ (2) Å³, $Z = 6$, $D_x = 1·719$ Mg m⁻³, $\lambda(Mo\,K\alpha) = 0·71073$ Å, $\mu(Mo\,K\alpha) = 3·11$ mm⁻¹, $T = 298$ K, $F(000) = 1188$, $R = 0·035$ for 1227 unique reflections ($2\theta < 60°$). The structure is isostructural with that of arsenious ethylxanthate [Carrai & Gottardi (1960). *Z. Kristallogr.* **113**, 373–384]. The $As(S_2COCH_3)_3$ molecule is located on a threefold rotation axis passing through the As atom. Each As atom is coordinated with six S atoms in a distorted octahedral arrangement at distances of 2·298 (1) Å × 3 and 2·992 (1) Å × 3; the three shorter As–S bonds make an angle of 90·56 (3)° with each other. Difference electron density maps revealed sharp residual peaks of 0·35 e Å⁻³ on the shorter As–S bonds, indicating a $4p^3$-type covalent bond nature of the As atom. A pair of molecules approach closely with S···S contacts of 3·650 (2) Å × 6 to form a loosely bound dimeric unit.

Introduction. Metal xanthates, $M(S_2COR)_n$, where M = metal and R = alkyl, are an interesting group of metal complexes which show various kinds of S

coordination around metals. Although structural information on metal ethylxanthates and their higher homologues has been accumulated (Rao, 1971), no structures of methylxanthates have thus far been reported. Methylxanthates are the simplest among xanthate homologues and, therefore, are most suitable for a detailed study of the structural chemistry of xanthates. The present paper describes the crystal and molecular structure of the rhombohedral form (α form) of arsenious methylxanthate [abbreviated as $As(MeX)_3$ in the following]. It is designated as the α form because a monoclinic form (β form) has been found.

Experimental. Powder of $As(MeX)_3$ was precipitated by acidifying an aqueous solution of sodium arsenite and potassium methylxanthate until pH = 1·0 with HCl while cooling with ice. Recrystallization from an ether solution gave rhombohedral and prismatic colourless crystals; preliminary Weissenberg photographs showed that the former (α form) belong to the rhombohedral space group $R\bar{3}$ or $R3$, and the latter (β form) to the monoclinic space group $P2_1/a$. A parallelepiped with rhombohedral faces (edges 0·46 × 0·50 × 0·60 mm) was mounted on a Rigaku automated four-circle diffractometer; cell parameters determined with 42 reflections within the 2θ range 50 to 55° (Mo $K\alpha_1$,

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$\lambda = 0.70930$ Å); intensities measured with graphite-monochromated Mo $K\alpha$ radiation using the ω–2θ scan mode with a rate in ω of $2°$ min^{-1} up to $2\theta = 60°$; 2930 reflections (hkl and $h\bar{k}l$) with $F_o > 3\sigma (F_o)$ obtained and corrected for Lorentz, polarization and absorption effects; calculated transmission factors ranged from 0.221 to 0.352; equivalent reflections then averaged to give 1227 unique reflections; the space group was assumed to be $R\bar{3}$, which was confirmed by the structure analysis. Approximate positions of the As and S atoms were obtained from a Patterson map, and those of the O and C, and H atoms were found from Fourier and difference Fourier maps, respectively. The structure was refined by a block-diagonal least-squares method with anisotropic and isotropic temperature factors for the non-hydrogen and H atoms, respectively. The function minimized was $\sum w |F_o - F_c|^2$ with unit weights. Refinement converged to an R value of 0.035 for the observed reflections. The atomic scattering factors and the dispersion correction factors were taken from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic coordinates and anisotropic temperature factors are given in Tables 1 and 2, respectively.*

Molecular structure. The structure of arsenious methylxanthate is isostructural with that of arsenious ethylxanthate, $As(EtX)_3$ (Carrai & Gottardi, 1960),

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38306 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	B_{eq} or B (Å^2)
As	0	0	0.33406 (4)	4.0
S(1)	0.14868 (6)	0.07246 (6)	0.22799 (7)	4.8
S(2)	0.16535 (8)	0.21446 (7)	0.40786 (7)	5.5
O	0.3155 (2)	0.2398 (2)	0.2721 (2)	5.5
C(1)	0.2181 (2)	0.1852 (2)	0.3073 (2)	4.1
C(2)	0.3867 (3)	0.3386 (3)	0.3242 (3)	7.0
H(1)	0.400 (3)	0.322 (3)	0.402 (3)	7.6 (9)
H(2)	0.447 (3)	0.371 (3)	0.282 (3)	8.9 (11)
H(3)	0.357 (3)	0.385 (3)	0.329 (3)	8.8 (11)

Table 2. *Anisotropic temperature factors with e.s.d.'s in parentheses* ($\times 10^4$)

The temperature-factor expression is $\exp(-2\pi^2 \sum_i \sum_j h_i h_j a_i^* a_j^* U_{ij})$.

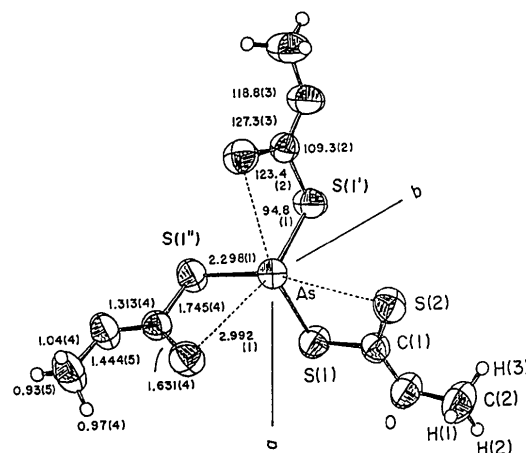|	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
As	501 (2)	501 (2)	523 (3)	250 (1)	0	0
S(1)	539 (4)	583 (4)	633 (5)	225 (4)	68 (3)	−101 (4)
S(2)	760 (6)	661 (5)	666 (5)	347 (5)	73 (4)	−102 (4)
O	543 (13)	621 (14)	764 (15)	161 (11)	54 (11)	−113 (11)
C(1)	532 (16)	504 (15)	523 (15)	262 (13)	−4 (12)	28 (12)
C(2)	677 (23)	728 (24)	942 (27)	128 (19)	−4 (21)	−215 (21)

Fig. 1. Structure of the Δ-As(MeX)$_3$ molecule viewed down the c axis. The thermal ellipsoids are at the 50% probability level. (Distances in Å, angles in degrees.)

Table 3. *Interatomic distances (Å) and angles (°) with e.s.d.'s in parentheses*

	As (MeX)$_3$ Present work	As (EtX)$_3$ Carrai & Gottardi (1960)
Bond distances and angles		
As–S(1)	2.298 (1)	2.28 (1)
As–S(2)	2.992 (1)	2.94 (1)
S(1)–C(1)	1.745 (4)	1.66 (4)
S(2)–C(1)	1.631 (4)	1.65 (4)
O–C(1)	1.313 (4)	1.31 (4)
O–C(2)	1.444 (5)	1.45 (3)
C(2)–H(1)	1.04 (4)	
C(2)–H(2)	0.93 (5)	
C(2)–H(3)	0.97 (4)	
S(1)–As–S(1')	90.56 (3)	92.0 (5)
As–S(1)–C(1)	94.8 (1)	92 (1)
S(1)–C(1)–S(2)	123.4 (2)	129 (3)
S(1)–C(1)–O	109.3 (2)	112 (3)
S(2)–C(1)–O	127.3 (3)	112 (3)
C(1)–O–C(2)	118.8 (3)	122 (4)

Shortest intermolecular distances in As(MeX)$_3$			
As···As	4.110 (1)		
S···S	3.650 (2)		
S···C	3.811 (5)	S···H	3.04 (4)
O···C	3.431 (5)	O···H	2.77 (4)
C···C	3.775 (6)	C···H	3.13 (4)

and also with antimonious ethylxanthate, $Sb(EtX)_3$ (Gottardi, 1961). An *ORTEP* drawing (Johnson, 1965) of an As(MeX)$_3$ molecule viewed down the c axis is shown in Fig. 1. The bond distances and angles are given in Table 3.

Since an As(MeX)$_3$ molecule is located on a threefold axis passing through the As atom, the three methylxanthate groups bonded to the As atom are symmetry related. The As atom is coordinated with six S atoms in a distorted octahedral arrangement with interatomic distances As–S (1) = 2.298 (1) Å × 3 and As···S (2) = 2.992 (1) Å × 3. The three shorter As–S bonds make an angle of 90.56 (3)° (almost rec-

tangular) with each other. The bond orders (Pauling, 1960) estimated from the As–S(1) and As···S(2) distances are 0·9 and 0·1, respectively; *i.e.* As–S(1) is a normal single bond, whereas As···S(2) is hardly a bond.

The methylxanthate group excluding the H atoms is planar within ±0·025 Å, and the As atom deviates from the least-squares plane by 0·29 (1) Å. The S(1)–C(1) and S(2)–C(1) distances correspond to bond orders of 1·2 and 1·8 respectively, while the C(1)–O and O–C(2) distances agree fairly well with the normal C(sp^2)–O and O–C(sp^3) distances of 1·34 and 1·43 Å, respectively. Thus, the bonding scheme in an As(MeX)$_3$ molecule can approximately be represented by the ideal formula:

$$\diagup \overset{S(2)}{\diagdown} \underset{S(1)}{\overset{}{\diagup}} As \diagdown C(1) - O - C(2)H_3.$$
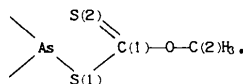
Such a clear distinction between the *M*–S and *M*···S bonds is a special feature of arsenious and antimonious xanthates; in xanthates of other metals, the distributions of the *M*–S distances are generally more complicated (Rao, 1971). Except for the alkyl ends, the molecular structure of As(MeX)$_3$ is essentially the same as that of As(EtX)$_3$ (Carrai & Gottardi, 1960), as compared in Table 3. However, a close comparison is difficult because of the lower accuracies of the latter results.

In order to investigate further the nature of the As–S bonds, a difference electron density map through the S(1)–As–S(1″) plane was calculated and is shown in Fig. 2; the S(2) and C(1) atoms also lie on the plane within ±0·1 Å. Sharp residual peaks of 0·35 e Å^{-3}, characteristic of covalent bonds, are seen on the shorter As–S(1) and As–S(1″) bonds; the contours on the latter bond are equivalent to those on the perpendicular section through the former bond because of symmetry. On the other hand, no well defined peak is found on the As···S(2) internuclear line. Thus, the electron distribution around the As atom is in good accord with the bond distances and bond orders mentioned above.
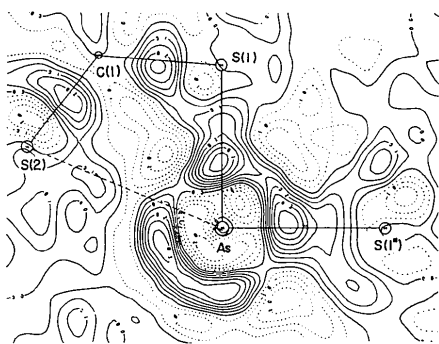
These observations together with the valence-electron configuration of an As atom ($4s^2 4p^3$) and the rectangular arrangements of the three shorter As–S bonds indicate that the bonding of the As atom is a p^3-type covalent one.

The observed anisotropic temperature factors of the non-hydrogen atoms (Table 2) were examined for rigid-body motion of the As(MeX)$_3$ molecule by the TLS treatment of Schomaker & Trueblood (1968). The assumption of a rigid body for a whole molecule is rather poor with a discrepancy index, R_{rigid} (= $\sum |U_{\text{obs}} - U_{\text{calc}}| / \sum |U_{\text{obs}}|$) of 0·123. In particular, the thermal motion of the C(1) atom is too small compared with those of the neighbouring atoms, as can be seen from the thermal ellipsoids of Fig. 1; similar trends have been noted also in related compounds such as zinc isopropylxanthate (Ito, 1972). If the C(1) atoms are omitted, the R_{rigid} value significantly improves to 0·078. The reason for the too-small motion of the C(1) atoms is not clear, but it may be found in a deviation of the atomic scattering factor (*i.e.* the electron density distribution) of the C(1) atom from that of the free C atom which was used for the structure refinement.

A loosely bound dimer. A pair of As(MeX)$_3$ molecules related by a centre of symmetry approach each other closely, as shown in Fig. 3. Short intermolecular contacts are the six S(2)···S(2)′ contacts of 3·650 (2) Å, which are a little shorter than the expected van der Waals contact of 3·70 Å (Pauling, 1960); on the other hand, the As···As′ distance of 4·110 (1) Å is a little longer than the sum (4·0 Å) of the van der Waals radii of As atoms. The As(MeX)$_3$ molecule of Fig. 1, which is the same as that depicted with open circles in Fig. 3, has a *Δ*-type distorted octahedral coordination of three bidendate methylxanthate ligands, whereas the partner molecule depicted with shaded circles has an enantiomorphic *Λ*-type coordination. Thus, a *Δ·Λ* pair of molecules bound with short S···S contacts constitute a loosely bound dimeric unit with 3̄ symmetry, and these dimers are stacked along the *c* axis forming a molecular column.
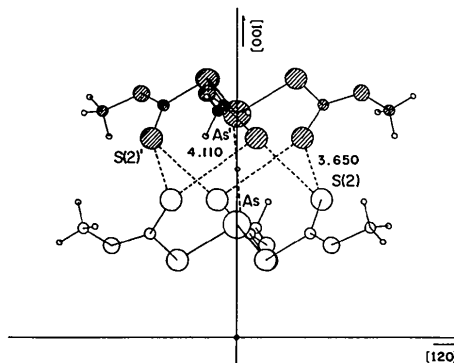

Fig. 2. Difference electron density map through the S(1)–As–S(1″) plane. Contours at 0·05 e Å^{-3}; negative contours dotted.

Fig. 3. Structure of a loosely bound dimer viewed down the *a* axis. The *Δ*-type molecule is depicted with open circles and the *Λ*-type one with shaded circles. (Distances are in Å.)
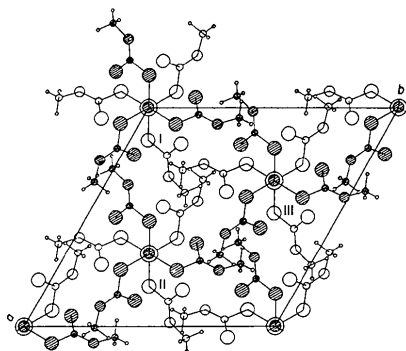
Fig. 4. Crystal structure viewed down the c axis. The molecular columns I, II and III are packed with van der Waals contacts.

The c-axis projection of the crystal structure is shown in Fig. 4, where the molecular columns I, II and III are related by translations; they are displaced by $\pm c/3$ along the columns and fill in the space with each other. Shortest intermolecular distances are summarized in Table 3.

The calculations were performed on a FACOM M200 computer of this Institute using the UNICS III program system (Sakurai & Kobayashi, 1979). The authors are grateful to Professor T. Shimozawa, Saitama University, for his encouragement throughout this work.

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2,2-Dimethyl-1,3-dithia-2-stannacyclopentane, C4H10S2Sn

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Abstract. $M_r = 240.93$, orthorhombic, $P2_12_12_1$, $a = 6.6906$ (2), $b = 9.2514$ (3), $c = 12.5897$ (4) Å, $V = 779.27$ (5) Å^3, $Z = 4$, $D_x = 2.053$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 34.5$ cm^{-1}, $F(000) = 464$, $T = 294$ K. Final $R = 0.022$ for 1982 observed reflections. The structure contains molecules with a five-membered SnS$_2$C$_2$ ring (envelope conformation), with a short intermolecular Sn$\cdots$S contact completing distorted trigonal bipyramidal coordination at tin. Sn–S = 2.415 (1), 2.474 (1), Sn$\cdots$S = 3.182 (1), Sn–CH$_3$ = 2.130 (3), S–C = 1.832 (4), CH$_2$–CH$_2$ = 1.509 (7) Å.

Introduction. 2,2-Dimethyl-1,3-dithia-2-stannacyclopentane, (CH$_3$)$_2$SnS(CH$_2$)$_2$S, is obtained by reaction of dichlorodimethyltin and 1,2-ethanedithiol (Wieber & Schimdt, 1963; Abel & Brady, 1965; Bernardi, Distefano, Modelli, Pietropaolo & Ricci, 1977). The present paper describes the crystal structure.

Experimental. Crystal dimensions 0.2 × 0.2 × 0.4 mm, CAD-4F diffractometer, Mo $K\alpha$ radiation (graphite monochromator), hkl, $0 < \theta \le 40.0°$, ω–(4/3)θ scans, ω scan angle (0.60 + 0.35 tan θ)° (extended by 25% on each side for background counts), scan speeds 1.18–10.06° min^{-1}, horizontal aperture (2.00 + tan θ) mm, vertical aperture 4 mm; intensity check reflections every hour (decrease of 1% over the whole period) and crystal orientation checked after every 100 reflections; cell parameters by least-squares fit to the sin θ values for 24 reflections with $40 \le 2\theta \le 52°$; intensities corrected for Lorentz and polarization effects and for absorption (Coppens, Leiserowitz & Rabinovich, 1965; Busing & Levy, 1967), transmission factors 0.456–0.590; of 2722 reflections measured, 1982 (73%) had $I \ge 3\sigma(I)$, where $\sigma^2(I) = S + 2B + [0.04(S-B)]^2$, S = scan count, B = time-averaged background count. Structure determined by Patterson and Fourier methods; refined by full-matrix least-squares techniques, finally with anisotropic thermal parameters; H atoms located on a difference map and included in refinement with isotropic temperature factors; function minimized $\sum w(|F_o| - |F_c|)^2$, with