second tetragonal phase below room temperature. A sequence of phase transitions (Table 4) with decreasing temperature from tetragonal through orthorhombic and a second tetragonal phase to a monoclinic structure is reported for $(CH_3NH_3)_2CdCl_4$ and $(CH_3NH_3)_2MnCl_4$ (Heger *et al.*, 1975). The low temperature structure of tetrachlorocadmate (Chapuis *et al.*, 1976) is described in space group $B2_1/a$ allowing for a direct comparison with high temperature phases. The transformation of positional parameters from $B2_1/a$ to $P2_1/a$ reveals that the room temperature structure of $(CH_3NH_3)_2CuCl_4$ is isostructural to the low temperature phase of the tetrachlorocadmate. The low temperature form of $(CH_3NH_3)_2MnCl_4$ is reported to be monoclinic but no space group is given in the literature.

Support of this work by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

References

CHAPUIS, G., AREND, M. & KIND, R. (1975). *Phys. Status Solidi A*, **31**, 449–454.
CHAPUIS, G., KIND, R. & AREND, M. (1976). *Phys. Status Solidi A*, **36**, 285–295.
Enraf–Nonius (1982). *Structure Determination Package*. Enraf–Nonius, Delft.
HEGER, G., MULLEN, D. & KNORR, K. (1975). *Phys. Status Solidi A*, **31**, 455–462.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
KNORR, K., JAHN, J. R. & HEGER, G. (1974). *Solid State Commun.* **15**, 231–238.
STEIJGER, J. J. M., FRIKKEE, E., DE JONGH, L. J. & HUISKAMP, W. J. (1984*a*). *Physica B*, **123**, 284–290.
STEIJGER, J. J. M., FRIKKEE, E., DE JONGH, L. J. & HUISKAMP, W. J. (1984*b*). *Physica B*, **123**, 271–283.
STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. W. & HALL, S. R. (1972). The *XRAY* system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Acta Cryst. (1987). C**43**, 416–418

Trimethylbis[2-thenoato(1–)]antimony

BY H. PREUT, M. DOMAGALA AND F. HUBER

Universität Dortmund, Fachbereich Chemie, Postfach 500 500, *D*-4600 *Dortmund 50, Federal Republic of Germany*

(*Received* 12 *Febuary* 1986; *accepted* 22 *September* 1986)

Abstract. $[Sb(C_5H_3O_2S)_2(CH_3)_3]$, $M_r = 421{\cdot}1$, orthorhombic, *Pbca*, $a = 11{\cdot}197$ (7), $b = 26{\cdot}026$ (9), $c = 11{\cdot}224$ (7) Å, $V = 3270{\cdot}8$ Å^3, $Z = 8$, $D_x = 1{\cdot}710$ Mg m^{-3}, $\lambda(\text{Ag } K\alpha) = 0{\cdot}56083$ Å, $\mu = 1{\cdot}01$ mm^{-1}, $F(000) = 1664$, $T = 293$ (1) K. Final $R = 0{\cdot}039$ for 1555 unique observed X-ray diffractometer data and 174 variables. The thiophene ring with the atoms C(5) to C(8) and S(1) is disordered. The positions S(1) and C(6) have been refined with the scattering power of 0·5 S and 0·5 C. Sb is surrounded by three equatorial C(methyl) and two apical O atoms, one from each carboxylate group. The trigonal bipyramid is distorted by weak interaction with the second O of each carboxylate group, both approaching Sb to widen C(1)–Sb–C(2) to 125·11 (4)°.

Introduction. Only two X-ray diffraction studies of triorganoantimony dicarboxylates have been reported: diacetatotriphenylantimony (Sowerby, 1979) and bis(benzoato)triphenylantimony (Lebedev, Bochkova, Kuzubova, Kuz'min, Sharutin & Belov, 1982) have a distorted trigonal-bipyramidal arrangement of ligands around Sb, the covalently bonding O atoms of the essentially unidentate carboxylate groups being in apical positions. The distortion was explained by weak interaction between Sb and the carbonyl O atoms of each acetate ligand. In the following a first example of a structure of a trimethylantimony dicarboxylate as well as of a triorganoantimony derivative of a heterocylic carboxylic acid is described. One object of this study was to examine whether weak coordinative interaction occurs also in a trimethylantimony carboxylate and whether this is similarly accomplished by O atoms or by the heteroatom of the ring in the latter type of ligand as recently found in (2-furoato)trimethyllead (Preut, Röhm & Huber, 1986).

Experimental. Title compound prepared from $(CH_3)_3$-$Sb(OH)_2$ and 2-thenoic acid in chloroform. Crystals obtained from $CHCl_3$/petroleum ether (b.p. 313–333 K). Crystal size: 0·38 × 0·22 × 0·11 mm. $\omega/2\theta$ scan. Scan speed: 6·7° min^{-1} in θ. Nonius CAD-4 diffractometer, graphite-monochromated Ag $K\alpha$ radiation; lattice parameters from least-squares fit with 20 reflexions up to $2\theta = 25{\cdot}1°$; standard reflexions recorded every 2·5 h, only random deviations; 6938

0108-2701/87/030416-03$01.50

reflexions, $1 \leq \theta \leq 20°$, $(\sin\theta/\lambda)_{max} = 0{\cdot}61$ Å^{-1}, $0 \leq h \leq 13$, $0 \leq k \leq 13$, $-31 \leq l \leq 31$; after averaging 3095 unique reflexions, $R_{int} = 0{\cdot}026$, 1555 with $I > 3\sigma(I)$, Lorentz–polarization correction and absorption correction *via* ψ scans, max./min. transmission 1·00/0·88; systematic absences conform to space group *Pbca* (No. 61), structure solution *via* direct methods, ΔF syntheses and full-matrix least squares on F with 1555 reflexions; 174 refined parameters, anisotropic temperature factors for all non-H atoms and the disordered positions S(1*a*), S(1*b*), C(6*a*), C(6*b*), common isotropic temperature factor for all H atoms, H atoms in geometrically calculated positions (C—H 0·95 Å); $w^{-1} = [\sigma^2(I) + (0{\cdot}095F_o^2)^2]^{1/2}$, $S = 0{\cdot}87$, $R = 0{\cdot}039$, $wR = 0{\cdot}053$, max. $\Delta/\sigma = 0{\cdot}24$, largest peak in final ΔF map = $\pm 0{\cdot}7$ (2) e Å^{-3}; complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); programs: *SDP* (Frenz, 1981), *ORTEP*II (Johnson, 1976), *MULTAN*82 (Main *et al.*, 1982).

Discussion. The structure of the title compound is shown in Fig. 1. Positional parameters and equivalent values of the anisotropic temperature factors are given in Table 1,* bond lengths and angles in Table 2. As in diacetatotriphenylantimony (Sowerby, 1979) and bis(benzoato)triphenylantimony (Lebedev *et al.*, 1982) the coordination around the central Sb is a distorted trigonal bipyramid and there is an interaction between Sb and the second O of each carboxylate group. In the title compound these interactions are less pronounced than those in diacetatotriphenylantimony and bis(benzoato)triphenylantimony in which the corresponding Sb—O distances are 2·779 (4), and 2·70 (2), 2·81 (2) Å, respectively, whereas in the title compound these distances are markedly longer and the equatorial angle C(1)—Sb(1)—C(2) facing the weakly coordinating O atoms deviates distinctly less from 120° than does the corresponding angle in the two triphenylantimony dicarboxylates [diacetate: 148·2 (2); dibenzoate: 150 (1)°]. This can be correlated to reduced acceptor strength of Sb which is caused by the $+I$ effect of the methyl groups. The thiophene ring at C(4) shows orientational disorder. Interaction of the heteroatom in the ring of the carboxylate ligand with the central atom as observed in (2-furoato)trimethyllead (Preut *et al.*, 1986) does not occur.

* Lists of structure factors, anisotropic thermal parameters and H-atom positions have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43436 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

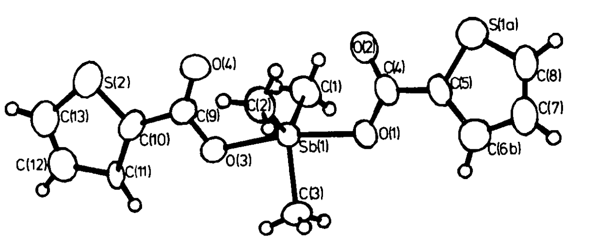


Fig. 1. General view of the molecule, showing atom numbering.

Table 1. *Fractional atomic coordinates and isotropic temperature factors* (Å$^2 \times 10^3$)

$$U_{eq} = (1/6\pi^2)\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}/U
Sb(1)	0·09690 (5)	0·06830 (2)	0·67351 (5)	37
S(2)	0·0822 (3)	−0·1292 (1)	0·8781 (3)	71
O(1)	0·1584 (6)	0·1411 (2)	0·6108 (6)	48
O(2)	0·3102 (7)	0·1385 (3)	0·7379 (6)	59
O(3)	0·0123 (6)	−0·0027 (2)	0·7135 (5)	43
O(4)	0·1622 (6)	−0·0228 (3)	0·8339 (6)	58
C(1)	0·0776 (9)	0·0941 (4)	0·8494 (8)	53
C(2)	0·2482 (9)	0·0317 (4)	0·6052 (9)	55
C(3)	−0·043 (1)	0·0781 (4)	0·5548 (8)	56
C(4)	0·2555 (8)	0·1597 (3)	0·6545 (7)	43
C(5)	0·2968 (8)	0·2075 (3)	0·6065 (8)	44
C(7)	0·329 (1)	0·2819 (4)	0·487 (1)	62
C(8)	0·413 (1)	0·2832 (4)	0·570 (1)	59
C(9)	0·0680 (8)	−0·0331 (4)	0·7858 (7)	41
C(10)	0·0086 (9)	−0·0839 (4)	0·7999 (7)	45
C(11)	−0·1123 (7)	−0·0984 (3)	0·7580 (7)	31
C(12)	−0·1226 (9)	−0·1521 (4)	0·805 (1)	64
C(13)	−0·032 (1)	−0·1710 (4)	0·8667 (9)	64
S(1*a*)	0·4155 (4)	0·2366 (2)	0·6668 (4)	60
C(6*a*)	0·398	0·240	0·646	65
S(1*b*)	0·2354 (4)	0·2338 (2)	0·4855 (4)	53
C(6*b*)	0·256	0·239	0·502	66

Positions S(1*a*), S(1*b*), C(6*a*) and C(6*b*) were isotropically refined and positions C(6*a*) and C(6*b*) fixed to S(1*a*) and S(1*b*) respectively.

Table 2. *Bond distances* (Å) *and bond angles* (°) *with standard deviations*

Sb(1)—C(1)	2·096 (9)	O(3)—C(9)	1·29 (1)
Sb(1)—C(2)	2·09 (1)	O(4)—C(9)	1·22 (1)
Sb(1)—C(3)	2·07 (1)	C(4)—C(5)	1·44 (1)
Sb(1)—O(1)	2·136 (6)	C(9)—C(10)	1·49 (1)
Sb(1)—O(2)	3·093 (7)	S(2)—C(10)	1·69 (1)
Sb(1)—O(3)	2·124 (6)	S(2)—C(13)	1·68 (1)
Sb(1)—O(4)	3·066 (7)	C(10)—C(11)	1·48 (1)
O(1)—C(4)	1·29 (1)	C(11)—C(12)	1·50 (1)
O(2)—C(4)	1·25 (1)	C(12)—C(13)	1·33 (2)
C(1)—Sb(1)—C(2)	125·1 (4)	Sb(1)—O(3)—C(9)	116·7 (5)
C(1)—Sb(1)—C(3)	119·3 (4)	O(3)—C(9)—O(4)	124·2 (8)
C(2)—Sb(1)—C(3)	115·6 (4)	O(1)—C(4)—C(5)	117·0 (7)
O(1)—Sb(1)—O(3)	170·1 (2)	O(2)—C(4)—C(5)	120·5 (8)
C(1)—Sb(1)—O(1)	93·4 (3)	O(3)—C(9)—C(10)	113·3 (7)
C(1)—Sb(1)—O(3)	91·9 (3)	O(4)—C(9)—C(10)	122·4 (8)
C(2)—Sb(1)—O(1)	91·3 (3)	C(9)—C(10)—C(11)	126·9 (8)
C(2)—Sb(1)—O(3)	92·5 (3)	C(9)—C(10)—S(2)	117·4 (7)
C(3)—Sb(1)—O(1)	85·5 (3)	C(10)—C(11)—C(12)	101·3 (7)
C(3)—Sb(1)—O(3)	84·6 (3)	C(11)—C(12)—C(13)	118·1 (9)
Sb(1)—O(1)—C(4)	118·6 (5)	C(12)—C(13)—S(2)	112·4 (8)
O(1)—C(4)—O(2)	122·4 (8)	C(13)—S(2)—C(10)	92·4 (5)
		S(2)—C(10)—C(11)	115·7 (6)

Financial support from the Fonds der Chemischen Industrie and the Minister für Wissenschaft und Forschung des Landes Nordrhein–Westfalen is gratefully acknowledged.

References

FRENZ, B. A. (1981). *Structure Determination Package*, 4th ed., version 18. Enraf–Nonius, Delft.
International Tables for X-ray Crystallography (1974). Vol. IV, Tables 2.2B and 2.3.1. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
LEBEDEV, V. A., BOCHKOVA, R. I., KUZUBOVA, L. F., KUZ'MIN, E. A., SHARUTIN, V. V. & BELOV, N. V. (1982). *Dokl. Akad. Nauk SSSR*, **265**, 332–335.
MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
PREUT, H., RÖHM, P. & HUBER, F. (1986). *Acta Cryst.* C**42**, 657–658.
SOWERBY, D. B. (1979). *J. Chem. Res.* (*S*), pp. 80–81; (*M*), pp. 1001–1028.

Acta Cryst. (1987). C**43**, 418–420

[1,2-Bis(dimethylphosphino)ethane]bis(cyclopentadienyl)dimethylthorium(IV) and [1,2-Bis(dimethylphosphino)ethane]dichlorobis(cyclopentadienyl)thorium(IV)

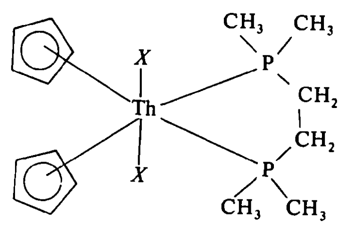
BY ALLAN ZALKIN, JOHN G. BRENNAN AND RICHARD A. ANDERSEN

Materials and Molecular Research Division, Lawrence Berkeley Laboratory and Department of Chemistry, University of California, Berkeley CA 94720, *USA*

(*Received* 13 *June* 1986; *accepted* 16 *September* 1986)

Abstract. $[Th(CH_3)_2(C_5H_5)_2(C_6H_{16}P_2)]$ (1), $M_r = 542{\cdot}44$, monoclinic, $P2_1/n$, $a = 18{\cdot}485$ (4), $b = 14{\cdot}118$ (4), $c = 8{\cdot}258$ (2) Å, $\beta = 91{\cdot}05$ (2)°, $V = 2154{\cdot}7$ Å^3, $Z = 4$, $D_x = 1{\cdot}672$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 73{\cdot}0$ cm^{-1}, $F(000) = 1040$, $T = 296$ K, $R = 0{\cdot}026$ for 2521 unique reflections with $F^2 > 2\sigma(F^2)$. Distances (Å) are: Th—C(Cp) 2·84 ± 0·03; Th—C(methyl) 2·562 (8), 2·583 (7); Th—P 3·146 (2), 3·147 (2); Th—Cp 2·59, 2·57. $[Th(C_5H_5)_2Cl_2(C_6H_{16}P_2)]$ (2), $M_r = 583{\cdot}28$, monoclinic, $P2_1/n$, $a = 18{\cdot}268$ (2), $b = 14{\cdot}237$ (6), $c = 7{\cdot}996$ (3) Å, $\beta = 92{\cdot}27$ (4)°, $V = 2078{\cdot}0$ Å^3, $Z = 4$, $D_x = 1{\cdot}864$ g cm^{-3}, λ(Mo $K\alpha$) = 0·70173 Å, $\mu = 78{\cdot}3$ cm^{-1}, $F(000) = 1104$, $T = 296$ K, $R = 0{\cdot}020$ for 2361 unique reflections with $I > \sigma(I)$. Distances (Å) are: Th—C(Cp) 2·80 ± 0·02; Th—Cl 2·707 (2), 2·708 (2); Th—P 3·121 (2), 3·122 (2); Th—Cp 2·56, 2·54. The structures of (1) and (2) are crystallographically isomorphous and were investigated to study their six-coordinate stereochemistry. The cyclopentadienyl rings are *trans* to the bidentate ligand.

Introduction. Compounds of the type $(C_5H_5)_2M(X)_2(L)$ where M is thorium or uranium, X is an anionic ligand such as halide or alkyl, and L is a neutral bidentate phosphine ligand were prepared in order to examine the details of inter- and intramolecular ligand exchange in solution. The stereochemistry of these six-coordinate compounds (defining the centroid of the cyclopentadienyl ring as occupying a coordination site) in the solid state was essential since two idealized geometries are possible for MX_2Y_2–(bidentate ligand), that is either the X ligands or the Y ligands are *trans* to the bidentate ligand. For comparison the X-ray structures of $(C_5H_5)_2Th(X)_2.[(CH_3)_2PCH_2CH_2P(CH_3)_2]$ where $X = Cl$, CH_3 (this paper) and where $X = CH_2C_6H_5$ (Zalkin, Brennan & Andersen, 1987) are described.



$X = CH_3$ or Cl

Experimental. The dimethyl complex (1) was made by the reaction of (2) with methyllithium at 228 K (Brennan, 1985). Colorless crystals suitable for X-ray studies were picked from the crystals obtained by crystallization from a toluene:pentane (1:4) solution at 203 K. The dichloro complex (2) was synthesized from the reaction of sodium cyclopentadienide with $ThCl_4.(CH_3)_2PCH_2CH_2P(CH_3)_2$ in a tetrahydrofuran solution at 203 K and crystallized from toluene. Crystals suitable for X-ray studies were grown from toluene:diethyl ether (6:4) at 253 K. The air-sensitive crystals were sealed inside quartz capillaries under

0108-2701/87/030418-03$01.50