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Crystal structures of triphenyltellurium(IV) methylxanthate and isobutylxanthate — dependence on the steric influence of the alkyl group of the xanthate system

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Abstract

The crystal structures of $\text{Ph}_3\text{Te}(\mu\text{-S}_2\text{COMe})_2\text{TePh}_3$ (**1**) and $\text{Ph}_3\text{Te}(\text{S}_2\text{CO}^i\text{Bu})$ (**2**) have been determined by X-ray diffraction. The two xanthate ligands bridge the two tellurium atoms in triphenyltellurium(IV) methylxanthate. The coordination environment around each Te atom of **1** is a distorted octahedron. The three Te–C (phenyl) carbon atoms form one *fac* set and the two Te–S bonds along with the lone pair form the other. The Te–S bonds are long, suggesting that they are weak. The xanthate ligand in **2** is chelated with tellurium. The chelation of the $^i\text{BuOCS}_2^-$ skeleton is asymmetric and weak, the Te–S bond lengths being 3.535(4) and 3.123(4) Å. The change in the mode of coordination of the xanthate ligand arises from the greater steric influence of the ^iBu group.

Introduction

The crystal structures of tellurium(II and IV)-sulphur donor complexes show some unusual features [1–4]. We have recently shown from IR and NMR (^1H and ^{13}C) spectroscopic studies that in triphenyltellurium(IV) dithiocarbamates, xanthates, and dithiophosphates, the sulphur ligands are not chelated with tellurium [5]. Drake and Wong [6] determined the structure of triphenyltellurium(IV)-diisopropylidithiocarbamate and found that it has a centrosymmetric dimeric structure with long Te–S bonds. Recently we have observed [7] that triphenyltellurium(IV) ethylxanthate has two six-coordinated tellurium in the same molecule. Both the xanthate ligands in the dimer $[\text{Ph}_3\text{Te}(\text{S}_2\text{COEt})]_2$ ligate in the η^2 -mode and the other bridges the two tellurium atoms. We have now found that the structures of triphenyltellurium(IV) methylxanthate (**1**) and triphenyltellurium(IV)-*i*-butylxanthate (**2**) vary with the alkyl group of the xanthate ligand, probably owing to the difference in its steric effect. Thus **1** has a dimeric structure like that of triphenyl-

tellurium(IV)-alkyldithiocarbamates [6,8] whereas in **2** the xanthate ligand is chelated with tellurium to give a monomeric species as described below.

Experimental

Compounds **1** and **2** were made by a published method [5] and single crystals suitable for X-ray studies were grown from acetonitrile. X-Ray diffraction data were collected on an Enraf Nonius CAD-4 diffractometer. All crystallographic computations were performed with the SHELX-76 program [9]. Atomic scattering factors and anomalous dispersion factors were taken from the *International Tables for X-Ray Crystallography* [10]. Crystal data and details of the data collection and refinement are given in Table 1. Final coordinates of **1** and **2** are listed in Tables 2 and 3, respectively. Complete lists of bond lengths and angles, and tables of thermal parameters and structure factors are available from the authors.

Results and discussion

The molecular structure of triphenyltellurium(IV) methylxanthate with the numbering scheme is shown in Fig. 1. Selected bond lengths and bond angles are

Table 1

Crystal data and experimental details for $\text{Ph}_3\text{Te}(\text{S}_2\text{COMe})$ and $\text{Ph}_3\text{Te}(\text{S}_2\text{CO}^i\text{Bu})$

	$\text{Ph}_3\text{Te}(\text{S}_2\text{COMe})$	$\text{Ph}_3\text{Te}(\text{S}_2\text{CO}^i\text{Bu})$
Formula	$\text{C}_{40}\text{H}_{36}\text{O}_2\text{S}_4\text{Te}_2$	$\text{C}_{23}\text{H}_{24}\text{OS}_2\text{Te}$
Molecular weight	945.44	508.13
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	18.675(6)	10.413(5)
b (Å)	10.564(2)	10.633(5)
c (Å)	20.653(5)	11.928(8)
α (°)	90.00(2)	88.46(5)
β (°)	112.94(3)	66.61(5)
γ (°)	90.00(2)	71.20(5)
V (Å ³)	3752(2)	1140(1)
Z	4	2
D_m (g cm ⁻³)	1.464(5)	1.493(6)
D_c (g cm ⁻³)	1.452	1.487
$F(000)$	1840	508
$\mu(\text{Cu-K}\alpha)$ cm ⁻¹	142.0	117.4
$(\sin \theta / \lambda)_{\text{max}}$ (Å ⁻¹)	0.63	0.63
λ (Å)	1.541	1.541
Weighting scheme	$w = 1 / \sigma^2(F) + 0.007810F^2$	Unit weights
Total reflections	5859	4404
Unique reflections	5138	4050
Reflections used in refinement ($I \geq 2\sigma$)	4571	3869
S	1.19	2.35
No. of parameters	433	235
R, R_w	0.07, 0.08	0.09, 0.09

Table 2

Atomic coordinates and equivalent isotropic thermal parameters ($\times 10^4$) for non-hydrogen atoms in $\text{Ph}_3\text{Te}(\text{S}_2\text{COMe})$

Atom	x	y	z	U_{eq} (\AA^2)
Te1	0.6623(3)	0.0228(5)	0.6680(3)	382(3)
Te2	0.8393(3)	0.9828(5)	0.5817(3)	365(3)
S1	0.2335(1)	0.2333(2)	0.3140(1)	505(11)
S2	0.3031(1)	0.2090(2)	0.4702(1)	541(12)
S3	0.1939(1)	0.7107(2)	-0.2147(1)	561(12)
S4	0.2647(1)	0.7311(2)	-0.0583(1)	476(11)
O1	0.1731(4)	0.8946(5)	-0.1383(3)	577(33)
O2	0.3267(4)	0.3953(5)	0.3950(3)	597(33)
C1	0.4286(4)	0.1125(7)	0.3580(4)	430(40)
C2	0.4676(5)	0.1365(8)	0.4296(4)	474(43)
C3	0.5302(5)	0.2193(9)	0.4534(5)	524(48)
C4	0.5560(5)	0.2733(9)	0.4059(4)	566(49)
C5	0.5176(5)	0.2487(11)	0.3361(5)	682(56)
C6	0.4543(5)	0.1708(8)	0.3118(4)	569(49)
C7	0.2984(5)	-0.0115(7)	0.2187(4)	432(42)
C8	0.2767(5)	0.3945(8)	0.6854(4)	504(43)
C9	0.2486(5)	0.3947(10)	0.6119(4)	642(54)
C10	0.2389(6)	0.5040(10)	0.5753(5)	597(56)
C11	0.2604(5)	-0.1188(9)	0.1105(4)	631(51)
C12	0.2881(4)	-0.1203(7)	0.1827(3)	438(41)
C13	0.4181(5)	-0.1785(7)	0.3405(4)	406(40)
C14	0.5047(5)	0.3461(9)	0.1471(4)	544(49)
C15	0.4555(6)	0.2487(10)	0.1419(5)	619(56)
C16	0.4811(6)	0.1249(9)	0.1478(4)	531(51)
C17	0.4417(6)	-0.4000(9)	0.3399(5)	669(54)
C18	0.3918(6)	-0.3020(9)	0.3355(5)	603(52)
C19	0.0772(5)	0.3344(8)	-0.0917(4)	414(41)
C20	0.0015(5)	0.3591(9)	-0.1076(4)	471(44)
C21	-0.0512(6)	0.2627(9)	-0.1147(4)	541(49)
C22	-0.0256(6)	0.1391(8)	-0.1046(4)	618(53)
C23	0.0504(7)	0.1123(10)	-0.0882(5)	784(66)
C24	0.1035(6)	0.2087(8)	-0.0807(5)	578(52)
C25	0.2000(5)	0.4899(7)	0.0293(4)	390(41)
C26	0.1533(5)	0.4483(8)	0.0623(4)	540(47)
C27	0.1823(5)	0.4438(9)	0.1363(4)	548(47)
C28	0.2597(6)	0.4769(8)	0.1749(6)	567(55)
C29	0.3045(6)	0.5171(7)	0.1408(4)	508(49)
C30	0.2768(5)	0.5223(6)	0.0678(4)	416(41)
C31	0.0728(4)	0.6234(7)	-0.1077(3)	406(38)
C32	0.0315(5)	0.6424(7)	-0.1781(4)	454(41)
C33	0.0291(5)	0.2321(8)	0.7004(5)	526(46)
C34	0.0477(5)	0.2968(8)	0.6535(5)	577(54)
C35	0.0063(5)	0.2813(8)	0.5817(5)	622(52)
C36	0.0542(5)	0.6902(7)	-0.0592(4)	504(44)
C37	0.2904(4)	0.2838(7)	0.3949(4)	435(40)
C38	0.3747(9)	0.4494(11)	0.4620(6)	967(92)
C39	0.2069(5)	0.7849(7)	-0.1392(4)	433(40)
C40	0.1263(8)	0.9559(10)	-0.2028(6)	755(71)

Table 3

Atomic coordinates and equivalent isotropic thermal parameters ($\times 10^4$) for non-hydrogen atoms (in $\text{Ph}_3\text{Te}(\text{S}_2\text{CO}^i\text{Bu})$)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} (\AA^2)
Te1	0.2078(8)	-0.6590(7)	0.3561(6)	550(3)
S1	0.1858(3)	-0.6363(3)	0.6241(2)	690(15)
S2	-0.0876(3)	-0.6733(3)	0.6309(4)	942(21)
O1	0.0904(12)	-0.8144(9)	0.7320(9)	1138(67)
C1	0.2348(13)	-0.7081(11)	0.1719(11)	660(59)
C2	0.1047(17)	-0.6380(13)	0.1453(13)	861(80)
C3	0.1118(18)	-0.6689(15)	0.0347(15)	934(90)
C4	0.2392(20)	-0.7561(15)	-0.0571(14)	983(94)
C5	0.3668(18)	-0.8227(14)	-0.0297(14)	899(86)
C6	0.3567(14)	-0.7918(13)	0.0832(11)	674(65)
C7	0.4092(12)	-0.6083(12)	0.2964(10)	592(57)
C8	0.4450(15)	-0.5474(14)	0.1867(12)	869(77)
C9	0.5628(20)	-0.5073(18)	0.1517(16)	1176(111)
C10	0.6446(16)	-0.5234(17)	0.2274(14)	970(92)
C11	0.6046(14)	-0.5750(14)	0.3309(12)	805(74)
C12	0.4751(18)	-0.6156(14)	0.3722(11)	875(83)
C13	0.3053(12)	-0.8682(9)	0.3636(9)	544(50)
C14	0.2145(17)	-0.9431(13)	0.3845(15)	991(92)
C15	0.2691(24)	-1.0723(15)	0.3885(20)	1348(135)
C16	0.4142(22)	-1.1346(12)	0.3774(14)	932(95)
C17	0.5026(19)	-1.0600(14)	0.3584(14)	898(89)
C18	0.4543(14)	-0.9263(11)	0.3510(12)	700(66)
C19	0.0602(14)	-0.7117(10)	0.6672(11)	673(62)
C20	-0.0106(28)	-0.8901(21)	0.7795(22)	1570(158)
C21	-0.1097(32)	-0.8370(32)	0.8988(29)	1949(237)
C22	0.0883(54)	-1.0335(33)	0.7752(42)	3612(453)

listed in Tables 4 and 5, respectively. The phenyl rings have normal structures (bond lengths 1.304(8)–1.427(7) Å, bond angles 115.6(5)–123.0(4)°). In the discrete dimeric species, the two Te atoms are situated in a roughly distorted octahedral coordination environment. The three carbon atoms of the phenyl groups linked to Te constitute one *fac* set and two S atoms along with the lone pair form the other. The Te–S bond lengths in **1** are longer than expected for a single bond or observed for a three-centre four-electron Te–S bond [2]. However, the maximum difference between the two such bond lengths is less than that observed in the case of $\text{Ph}_3\text{Te}(\mu\text{-S}_2\text{CNEt}_2)_2\text{TePh}_3$ [8]. The CSS^- skeleton in **1** is also less asymmetric than that of dithiocarbamate analogues. The reason for both these observations is probably the poorer ligating ability of xanthates compared with dithiocarbamates. One of the C–O bond lengths is shorter than the other owing to conjugation with the adjacent C=S bond.

The molecular structure of **2** is shown in Fig. 2 along with the numbering scheme. The ligand $^i\text{BuOCS}_2^-$ is asymmetrically chelated with tellurium. Selected bond lengths and bond angles are given in Table 6. One of the two Te–S distances in **2** is much longer than the length of the Te–S bonds in **1**, but is less than the sum of van der Waal radii of Te and S (3.86 Å) [11]. However, the shorter Te–S bond length is also longer than single- and three-centre four-electron Te–S bonds [2].

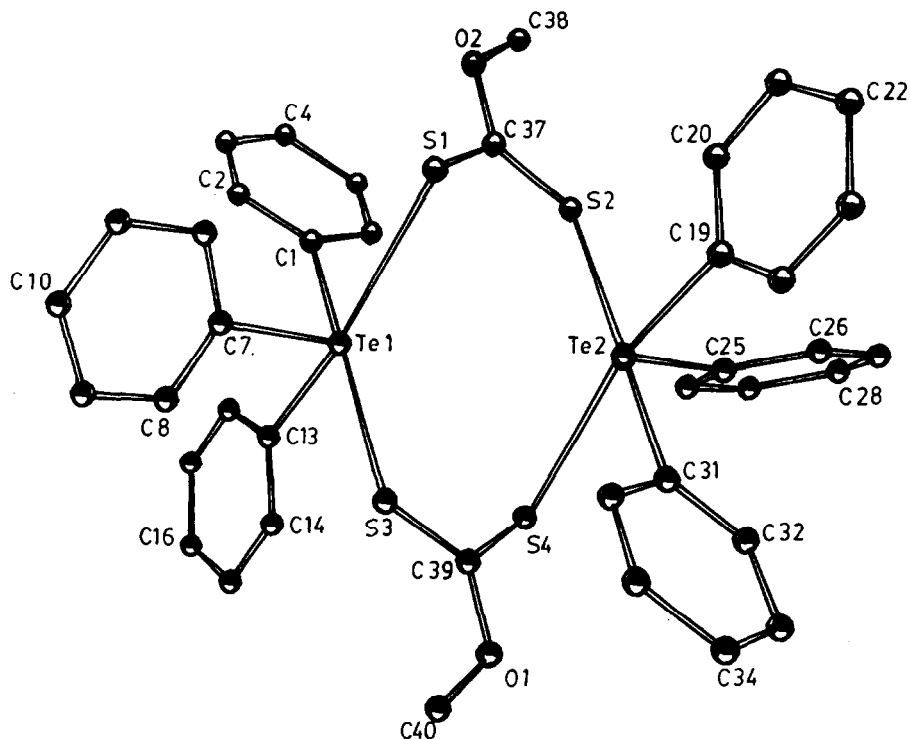


Fig. 1. Molecular structure of $\text{Ph}_3\text{Te}(\mu\text{-S}_2\text{COMe})_2\text{TePh}_3$ with atom labelling.

The tellurium atom in **2** is in a distorted octahedral environment formed by three carbon atoms of the phenyl group as one *fac* set, two S atoms and a lone pair as the other. The phenyl groups have normal geometries. The difference between two

Table 4

Selected bond lengths (Å) in $\text{Ph}_3\text{Te}(\mu\text{-S}_2\text{COMe})_2\text{TePh}_3$

Te(1)–S(1)	3.270(3)
Te(1)–S(3)	3.174(3)
Te(1)–C(1)	2.123(8)
Te(1)–C(7)	2.166(9)
Te(1)–C(13)	2.188(9)
Te(2)–S(2)	3.180(3)
Te(2)–S(4)	3.187(3)
Te(2)–C(19)	2.165(9)
Te(2)–C(25)	2.122(9)
Te(2)–C(31)	2.124(8)
S(1)–C(37)	1.681(8)
S(2)–C(37)	1.676(9)
S(4)–C(39)	1.697(7)
S(3)–C(39)	1.675(9)
O(1)–C(39)	1.324(10)
O(2)–C(37)	1.360(10)
O(1)–C(40)	1.417(10)
O(2)–C(38)	1.428(11)

Table 5

Selected bond angles (°) in $\text{Ph}_3\text{Te}(\mu\text{-S}_2\text{COMe})_2\text{TePh}_3$

S(1)–Te(1)–S(3)	95.0(1)
S(1)–Te(1)–C(1)	81.6(2)
S(1)–Te(1)–C(7)	84.0(3)
S(1)–Te(1)–C(13)	172.4(2)
S(3)–Te(1)–C(1)	175.9(2)
S(3)–Te(1)–C(7)	79.4(3)
S(3)–Te(1)–C(13)	91.6(2)
C(1)–Te(1)–C(7)	97.9(3)
C(1)–Te(1)–C(13)	91.7(3)
C(7)–Te(1)–C(13)	93.5(3)
S(2)–Te(2)–S(4)	95.3(1)
S(2)–Te(2)–C(19)	92.7(3)
S(2)–Te(2)–C(25)	76.4(3)
S(2)–Te(2)–C(31)	174.0(2)
S(4)–Te(2)–C(19)	169.9(3)
S(4)–Te(2)–C(25)	82.6(3)
S(4)–Te(2)–C(31)	80.1(2)
C(19)–Te(2)–C(25)	93.5(4)
C(19)–Te(2)–C(31)	91.4(3)
C(25)–Te(2)–C(31)	99.0(3)
S(1)–C(37)–S(2)	125.4(6)
S(3)–C(39)–S(4)	124.5(5)
O(1)–C(39)–S(3)	121.8(7)
O(1)–C(39)–S(4)	113.8(6)
O(2)–C(37)–S(1)	113.4(6)
O(2)–C(37)–S(2)	121.2(6)

C–S bond lengths in **1** and **2** is less than that for mono or anisobidentate dithiocarbamate ligands bonded to tellurium [4,12]. One carbon atom of the isobutyl group could not be accurately located owing to thermal motion. One of the two C–O bonds is shorter than the other owing to conjugation with the adjacent C=S double bond.

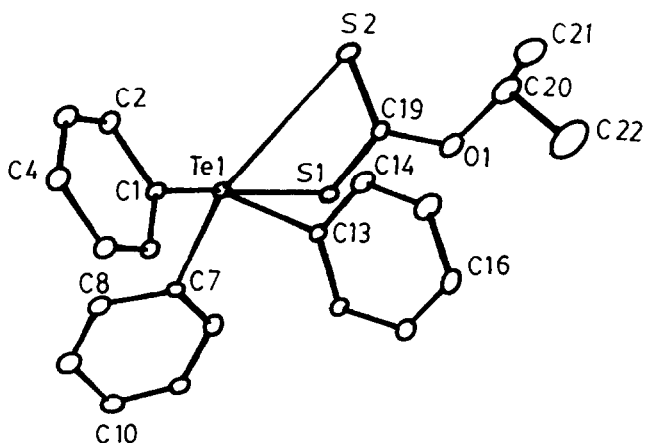
Fig. 2. Molecular structure of $\text{Ph}_3\text{Te}(\text{S}_2\text{CO}^i\text{Bu})$ with atom labelling.

Table 6

Selected bond lengths (Å) and angles (°) in $\text{Ph}_3\text{Te}(\text{S}_2\text{CO}^i\text{Bu})$

<i>Bond lengths</i> (Å)			
Te(1)–S(1)	3.123(4)	S(2)–C(19)	1.684(1)
Te(1)–S(2)	3.535(4)	O(1)–C(19)	1.347(1)
Te(1)–C(1)	2.157(12)	O(1)–C(20)	1.457(2)
Te(1)–C(17)	2.172(11)		
Te(1)–C(13)	2.142(10)		
S(1)–C(19)	1.656(12)		
<i>Bond angles</i> (°)			
S(1)–Te(1)–S(2)	89.8(1)	C(13)–Te(1)–S(1)	83.0(3)
C(1)–Te(1)–S(1)	172.9(3)	C(13)–Te(1)–S(2)	170.4(3)
C(1)–Te(1)–S(2)	97.3(3)	S(1)–C(19)–S(2)	125.4(6)
C(1)–Te(1)–C(7)	94.4(4)	S(1)–C(19)–O(1)	113.0(9)
C(1)–Te(1)–C(13)	88.4(4)	S(2)–C(19)–O(1)	121.6(9)
C(7)–Te(1)–C(13)	97.8(4)	C(19)–O(1)–C(20)	120.3(11)
C(7)–Te(1)–S(1)	87.4(3)	Te(1)–S(1)–C(19)	88.5(4)
C(7)–Te(1)–S(2)	75.3(3)	Te(1)–S(2)–C(19)	105.5(4)

The alkylxanthates of triphenyltelluronium ion show a progressive variation in structure when the alkyl group of the sulphur ligands is changed from methyl to isobutyl. The methylxanthate forms a dimeric species with Ph_3Te^+ , in which both the ligands are coordinated in a bridging mode (Fig. 1). Triphenyltellurium(IV) ethylxanthate also has a dimeric structure [7], but the two sulphur ligands coordinate in bridging mode and the η^2 -mode, resulting in the presence of two six-coordinated tellurium in the same molecule. In triphenyltellurium(IV) isobutylxanthate, the sulphur donor is asymmetrically chelated rather than forming the dimeric moiety. This is probably due to the greater steric hindrance by the isobutyl group to dimerization. The steric effect of the ethyl group is smaller than that of ^iBu but larger than that of Me and so an intermediate structure is found for the ethylxanthate of Ph_3Te^+ . However, the Te–S bonds are weak in both xanthates and dithiocarbamates of Ph_3Te^+ ion, and they all exhibit ionic behaviour in polar solvents.

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