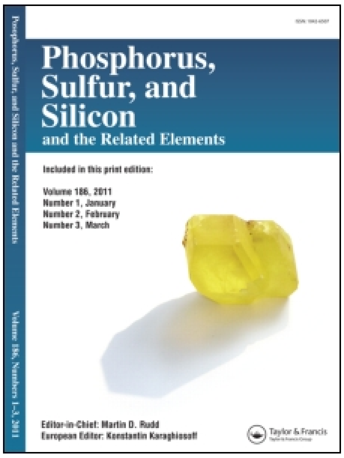

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SYNTHESIS AND CRYSTAL STRUCTURE OF TRIPHENYLTELLURIUM(IV)ETHYLXANTHATE: AN EXAMPLE OF ENHANCEMENT OF THE COORDINATION NUMBER OF TELLURIUM THROUGH LONG Te—S BONDS

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Triphenyltellurium(IV)ethylxanthate, [$Ph_3Te(S_2COEt)$], has been synthesized and its single crystal structure has been determined by X-ray diffraction. It has a dimeric structure in which each xanthate ligand forms an asymmetric chelate ring where one sulfur atom is involved in bridging the two tellurium atoms. The coordination environment around each tellurium atom is a very distorted octahedron constituted by two facial sets, one of three carbon atoms and the other of three sulfur atoms. The enhancement of coordination number of each tellurium from a value of five to six occurs through the formation of a long bridging Te—S bond (3.284(3), 3.703(3) Å). The four ν(Te—S) bands in the IR spectra of [$Ph_3Te(S_2COEt)$] occurring at 287, 280, 198 and 190 cm^{-1} are probably due to these tellurium-sulfur interactions.

Key words: Triphenyltellurium(IV)ethylxanthate; crystal structure; xanthate; tellurium.

INTRODUCTION

Our interest in the chemistry of tellurium(II and IV)-sulfur donor complexes is mainly due to the fact that tellurium(IV) dithiocarbamates find applications as accelerators in rubber vulcanization,[1,2] and many such derivatives have unique structural features[3–6] like hypervalent tellurium. Recently tellurium(IV) dithiocarbamates have been reported to be promising as stabilizers for polypropene.[7] Under our research programme[7,8] on tellurium(II and IV)-sulfur donor complexes and their applications in rubber technology, we have synthesized triphenyltellurium(IV)ethylxanthate and solved its crystal structure. Tellurium in this compound expands its coordination number to six through long Te—S bonds. The Far-IR spectra of [$Ph_3Te(S_2COEt)$] also reflect these Te—S interactions. The results of these investigations are the subject of this paper.

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RESULTS AND DISCUSSION

Crystal Structure of [$Ph_3Te(S_2COEt)$]

The molecular structure of triphenyltellurium(IV)ethylxanthate and the numbering scheme are shown in Figure 1. The selected bond lengths and bond angles are listed in Table III with e.s.d.'s in parentheses. In the solid state discrete dimeric species are present. The phenyl rings in the structure appear normal (bond lengths 1.338(16)–1.432(17) Å, bond angles 117.8(10)–121.8(15)°). The detailed information about them is available as supplementary material. Te—C bond lengths are also similar to those observed for dithiocarbamates[5] and other xanthates[20] of Ph_3Te^+. Both the tellurium atoms in the structure of $Ph_3Te(S_2COEt)$ are in a very distorted octahedral coordination environment formed by three carbon and three sulfur atoms. The carbon atoms form one facial set and sulfur atoms form the other. Each tellurium forms a chelate with a xanthate ligand which also coordinates through one of its sulfur atoms to the other tellurium atom. This results in two six coordinated tellurium atoms and two three coordinated sulfur atoms in the same molecule. In essence the structure of $Ph_3Te(S_2COEt)$ appears to represent an intermediate stage between the dimeric $Ph_3Te(S_2COMe)$[20] and monomeric $Ph_3Te(S_2CO(i\text{-}Bu))$,[20] further confirming the role of steric hindrance[20] erected by xanthate ligands in the structures of triphenyltellurium xanthates. The chelation of Te(2) is less asymmetrical than that of Te(1). The C—Te—C bond angles (92.5(4)–97.7(4)°) of the present structure are very close to the similar angles of $Ph_3Te(S_2CO(i\text{-}Bu/Me))$[20] and $Ph_3Te(S_2CN(i\text{-}Pr)_2)$.[5] This in conjunction with the S—Te—S bond angles of $Ph_3Te(S_2COEt)$ suggests that the lone pair is stereochemically active in this structure and is probably present between three Te—S bonds. Consequently the geometry of ligands around tellurium atoms becomes very distorted octahedral. In comparison to $Ph_3Te(S_2CO(i\text{-}Bu))$[20] the chelation of both these tellurium atoms

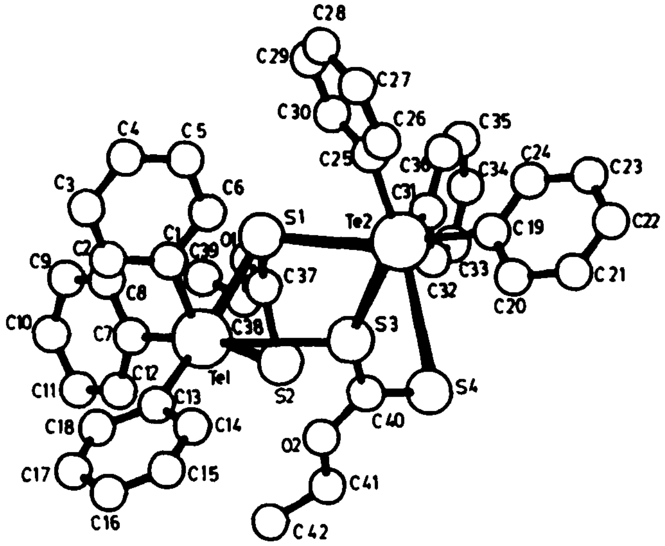

FIGURE 1 Structure of $Ph_3Te(S_2COEt)$.

TABLE I

Crystal data, details of intensity measurement and refinement of triphenyltellurium(IV)ethylxanthate

Formula	$C_{42}H_{40}S_4O_2Te_2$
Molecular weight	959.44
Crystal dimensions (mm^3)	2.00 × 1.00 × 0.09
Crystal system	Monoclinic
Space group	$P2_{1/c}$
a (Å)	15.310 (2)
b (Å)	12.385 (7)
c (Å)	21.433 (3)
α (°)	90.00 (0)
β (°)	96.18 (2)
τ (°)	90.00 (0)
V ($Å^3$)	4040.4 (24)
Z	4
D_c	1.565
F (000)	1904
2θ (°)	1-130
λ (Cu-K_α) (A)	1.5418
μ (cm^{-1})	114.702
Electron density in final difference map	($e/Å^3$)
Maximum	78.28
Minimum	−113.00
Measured reflections	5878
Unique reflections	5483
Agreement between equivalent reflections (R_{merge})	0.054
Reflections used in refinement [$I > 3\sigma(I)$]	5043
Weighting scheme	Unit weights
R	0.0523
R_w	0.0523

is more symmetrical. The difference between two C—S bond lengths of each xanthate ligand is not large; suggesting a high delocalization of the double bond as expected in its η^2 mode of bonding. The xanthate ligand bonded to Te(1) however exhibits somewhat greater difference between C—S bond length in comparison to the one bonded to Te(2). The comparison of present C—S bond lengths with those observed earlier for $Ph_3Te(S_2CO(i\text{-}Bu/Me))$[20] suggests that they are not much different whether the xanthate ligand is bridging or chelating. One C—O bond length of each xanthate ligand molecule is shorter than that of the other, due to partial

TABLE II

Final atomic coordinates and equivalent isotropic thermal parameters of non-hydrogen atoms (Estimated standard deviations are given in parentheses) of [$Ph_3Te(S_2COEt)$]

Atom	X/*a*	Y/*b*	Z/*c*	Ueq (Å^2)
Te1	0.7193(0)	−0.1260(0)	0.3614(0)	0.0397(3)
Te2	0.7989(0)	0.2401(0)	0.3984(0)	0.0395(3)
S1	0.6494(1)	0.0678(2)	0.4348(1)	0.0474(13)
S2	0.5660(2)	0.0679(3)	0.3026(1)	0.0724(23)
S3	0.9031(1)	0.0519(2)	0.3284(1)	0.0511(15)
S4	0.7928(2)	0.2076(3)	0.2471(1)	0.0656(20)
O1	0.4903(5)	0.1040(11)	0.4037(4)	0.0903(82)
O2	0.7949(4)	−0.0050(6)	0.2359(3)	0.0569(45)
C1	0.7821(6)	−0.1691(9)	0.4496(5)	0.0512(58)
C2	0.7849(7)	−0.2759(10)	0.4699(5)	0.0557(67)
C3	0.8248(9)	−0.3016(11)	0.5281(6)	0.0577(80)
C4	0.8627(7)	−0.2242(12)	0.5678(6)	0.0582(85)
C5	0.8629(7)	−0.1189(12)	0.5480(6)	0.0637(81)
C6	0.8220(6)	−0.0928(10)	0.4866(6)	0.0573(71)
C7	0.5953(6)	−0.1925(8)	0.3757(4)	0.0408(52)
C8	0.5657(6)	−0.1926(9)	0.4338(4)	0.0490(60)
C9	0.4814(6)	−0.2241(10)	0.4421(5)	0.0595(71)
C10	0.4268(7)	−0.2563(10)	0.3904(6)	0.0638(78)
C11	0.4537(7)	−0.2536(10)	0.3308(6)	0.0615(73)
C12	0.5387(6)	−0.2207(10)	0.3235(4)	0.0534(66)
C13	0.7678(6)	−0.2650(9)	0.3156(4)	0.0449(58)
C14	0.8456(7)	−0.2490(10)	0.2902(4)	0.0512(65)
C15	0.8813(8)	−0.3362(11)	0.2587(5)	0.0505(79)
C16	0.8382(9)	−0.4299(11)	0.2524(5)	0.0560(81)
C17	0.7615(9)	−0.4464(10)	0.2787(5)	0.0634(77)
C18	0.7257(8)	−0.3631(9)	0.3091(5)	0.0551(72)
C19	0.8965(6)	0.3608(8)	0.3870(4)	0.0406(57)
C20	0.9515(6)	0.3476(10)	0.3419(5)	0.0501(66)
C21	1.0137(7)	0.4274(10)	0.3332(6)	0.0539(77)
C22	1.0215(8)	0.5160(12)	0.3709(6)	0.0611(84)
C23	0.9658(9)	0.5298(12)	0.4166(7)	0.0857(97)
C24	0.9039(8)	0.4519(10)	0.4251(6)	0.0725(83)
C25	0.8438(6)	0.2178(8)	0.4940(4)	0.0418(52)
C26	0.9335(7)	0.2045(10)	0.5101(6)	0.0565(81)
C27	0.9660(8)	0.1798(11)	0.5718(6)	0.0616(83)
C28	0.9108(8)	0.1660(11)	0.6161(6)	0.0679(78)
C29	0.8226(7)	0.1753(10)	0.6010(4)	0.0614(69)
C30	0.7887(6)	0.1987(9)	0.5397(4)	0.0515(58)
C31	0.6960(6)	0.3490(8)	0.4104(5)	0.0446(57)
C32	0.6339(6)	0.3578(11)	0.3592(6)	0.0589(75)
C33	0.5648(9)	0.4300(12)	0.3612(8)	0.0698(105)
C34	0.5577(10)	0.4917(12)	0.4106(9)	0.0708(116)
C35	0.6189(9)	0.4849(11)	0.4629(8)	0.0722(102)
C36	0.6903(8)	0.4132(9)	0.4622(6)	0.0604(77)
C37	0.5650(7)	0.0814(8)	0.3790(4)	0.0483(57)
C38	0.4088(9)	0.1122(25)	0.3625(10)	0.1649(288)
C39	0.3460(11)	0.0796(23)	0.3909(9)	0.1928(255)
C40	0.8291(6)	0.0820(9)	0.2675(4)	0.0423(57)
C41	0.7294(9)	0.0079(13)	0.1831(5)	0.0794(97)
C42	0.6966(11)	−0.1010(14)	0.1639(7)	0.1166(130)

TABLE III

Selected bond lengths (Å) and bond angles (°) of [$Ph_3Te(S_2COEt)$]

Bond lengths	
Te(1) .... Te(2)	4.741(2)
Te(1) ---- S(1)	3.122(3)
Te(1) ---- S(2)	3.496(4)
Te(1) ---- S(3)	3.703(3)
Te(1) ---- S(4)	4.993
Te(2) ---- S(3)	3.279(3)
Te(2) ---- S(4)	3.259(3)
Te(2) ---- S(1)	3.284(3)
Te(2) ---- S(2)	4.461
Te(1) ---- C(1)	2.097(10)
Te(1) ---- C(7)	2.121(10)
Te(1) ---- C(13)	2.152(11)
Te(2) ---- C(19)	2.146(11)
Te(2) ---- C(25)	2.108(10)
Te(2) ---- C(31)	2.111(10)
C(37) ---- O(1)	1.341(14)
C(37) ---- S(1)	1.672(10)
C(37) ---- S(2)	1.647(10)
C(40) ---- O(2)	1.348(14)
C(40) ---- S(3)	1.675(9)
C(40) ---- S(4)	1.694(12)
C(38) ---- O(1)	1.452(19)
C(41) ---- O(2)	1.439(14)
Bond angles	
S(1) --- Te(1) --- S(2)	53.1(1)
S(1) --- Te(1) --- S(3)	87.0(1)
S(2) --- Te(1) --- S(3)	91.0(1)
S(1) --- Te(1) --- C(1)	83.7(3)
S(1) --- Te(1) --- C(7)	82.2(3)
S(1) --- Te(1) --- C(13)	176.7(3)
S(2) --- Te(1) --- C(1)	136.4(3)
S(2) --- Te(1) --- C(7)	75.1(3)
S(2) --- Te(1) --- C(13)	129.5(3)
S(3) --- Te(2) --- S(4)	54.5(1)
S(1) --- Te(2) --- S(3)	91.9(1)
S(1) --- Te(2) --- S(4)	102.1(1)
S(3) --- Te(2) --- C(25)	103.2(3)
S(3) --- Te(2) --- C(31)	156.4(3)
S(3) --- Te(2) --- C(19)	93.7(3)
S(4) --- Te(2) --- C(19)	85.3(3)
S(4) --- Te(2) --- C(25)	157.3(3)
S(4) --- Te(2) --- C(31)	105.0(3)
S(1) --- Te(2) --- C(19)	172.4(3)
S(1) --- Te(2) --- C(25)	81.2(3)
S(1) --- Te(2) --- C(31)	80.7(3)
S(3) --- C(40) --- S(4)	125.5(6)
S(3) --- C(40) --- O(2)	114.0(8)
S(4) --- C(40) --- O(2)	120.4(7)
C(40) -- O(2) ---- C(41)	120.5(10)
S(1) --- C(37) --- S(2)	127.7(7)
S(1) --- C(37) --- O(1)	111.4(7)
S(2) --- C(37) --- O(1)	120.9(8)
C(37) -- O(1) ---- C(38)	119.2(12)
C(1) --- Te(1) --- C(13)	93.5(4)
C(1) --- Te(1) --- C(7)	95.8(4)
C(7) --- Te(1) --- C(13)	96.5(4)
C(19) -- Te(2) --- C(31)	96.1(4)
C(25) -- Te(2) --- C(19)	92.5(4)
C(25) -- Te(2) --- C(31)	97.7(4)

delocalization of an oxygen lone pair of electrons. Similar observation has been made for other triphenyltellurium(IV)xanthates. The length of one of the two Te—S bonds bridging the two tellurium atoms is longer than that of the other, but shorter than sum of van der Waal's radii 3.86 Å[9] of Te and S. All Te—S bond lengths are longer than that of a single covalent Te—S bond length,[10] suggesting their weak nature. The shorter Te—S bond lengths (3.122(3)-3.284(3) Å) of $Ph_3Te(S_2COEt)$ are similar to those observed for $Ph_3Te(S_2CO(i\text{-}Bu))$[20] and $Ph_3Te(S_2CN(i\text{-}Pr)_2)$.[5]

Solution Behavior and IR Spectra of [$Ph_3Te(S_2COEt)$]

The Λ_M of [$Ph_3Te(S_2COEt)$] in DMSO and DMF at 25°C and concentration ≈1 mM were found to be 30 and 57 $ohm^{-1}\ cm^2\ mol^{-1}$. The expected values of a 1:1 electrolyte are 30 and 80 $ohm^{-1}\ cm^2\ mol^{-1}$ in the two solvents respectively. The comparison of two values suggest that association of Ph_3Te^+ with the xanthate anion in dilute solution is quite significant in DMF. Probably the dimer formation and two additional Te—S interactions, as revealed by the crystal structure in the solid state, do not completely vanish, even on dissolving [$Ph_3Te(S_2COEt)$] in solvents like DMF. Consequently, Λ_M is lower than the expected value for a 1:1 electrolyte. The molecular weight of [$Ph_3Te(S_2COEt)$] in $CHCl_3$ was found to be somewhat higher than the calculated value except at concentration below $20 \times 10^{-3}\ kg^{-1}$. This does not favour the ionic dissociation of [$Ph_3Te(S_2COEt)$] but can not be stretched to support the presence of associations similar to those found in the crystal structure. However, the Λ_M value in DMF as well as molecular weight both indicate significant association of Ph_3Te^+ and xanthate ion in solution.

The Far-IR spectra of [$Ph_3Te(S_2COEt)$] has four bands at 287, 280, 198 and 190 cm^{-1} which may be assigned to the Te—S interactions. The last two are very weak. The number of distinguishable types of Te—S bonds in solid [$Ph_3Te(S_2COEt)$] is also four. Thus there is a good agreement between IR spectra and crystal structure. The ν(CS), bands in IR spectra of [$Ph_3Te(S_2COEt)$] have been observed[11] at 1035 and 995. Since the two C—S bond lengths do not differ much, the assignment of ν(C—S) is not correct. The very weak band at 995 probably does not originate from ν(C—S). The ν(COC) and ν(CO) have been observed[11] at 1115 and 1080 cm^{-1} respectively in the IR spectra of [$Ph_3Te(S_2COEt)$]. Since one CO bond is affected by delocalization of the C═S bond, the bands at 1115 as well as 1087 cm^{-1} both have a contribution from ν(C—O). The first one may have a contribution from ν(C—O—C) too.

EXPERIMENTAL

Published methods were used to synthesize Ph_3TeCl[12] and ethylxanthate.[13] Tellurium was determined by a standard method.[14] The C, H and N analyses were carried out with a Perkin-Elmer elemental analyzer 240C. The ^1H NMR were recorded on a JEOL FX-100 FT-NMR spectrometer at 99.55 Hz. The FAR IR spectra in polyethylene were recorded on a Perkin Elmer 1700X FT-IR spectrometer. The conductivities in DMSO and DMF were measured with a Pye conductivity bridge. The molecular weights in $CHCl_3$ were determined with a Knauer Vapour Pressure Osmometer.

Synthesis of [$Ph_3Te(S_2COEt)$].[11] Ph_3TeCl (1.25 mmol) was dissolved in water and aqueous solution heated to 80-90°C. This hot solution was mixed with sodium ethyl xanthate (1.25 mmol) and the mixture stirred for 40 min, while maintaining the temperature around 80-90°C. The precipitate thus formed was filtered, dried and recrystallized from acetonitrile. Yield: ≈80%; m.p. 128-130°C.

Analyses: Found: C, 51.87; H, 3.99; Te, 27.05%. Calcd.: for $C_{21}H_{20}OS_2Te$: C, 52.54; H, 4.17; Te, 26.61%. NMR (^1H, $CDCl_3$, 25°C) δ: 1.33 (t, 3H, CH_3), 4.46 (q, 2H, OCH_2), 7.27–7.77 (m, 15H, ArH). Mol. wt.: Found, 491; Calcd., 479.6.

Crystal Structure of [*$Ph_3Te(S_2COEt)$*]. Single crystals of [$Ph_3Te(S_2COEt)$] suitable for X-ray work were grown from acetonitrile. X-ray diffraction data were collected on an Enraf Nonius CAD-4 diffractometer in ω-2θ scan mode with $1 \leq 2\theta \leq 140°$; h, $0 \rightarrow 11$, k, $0 \rightarrow 12$, l, $0 \rightarrow 15$ and CuK_α radiation. Data were corrected[15] for Lorentz polarization and absorption effects. A semiempirical Ψ-scan technique[13] was used to correct for absorption (the maximum and minimum correction factors were 0.85 and 0.35). The structures were solved by direct methods and refined by full matrix least square refinement procedure on $|F|$ for non hydrogen atoms with anisotropic thermal parameters using SHELX 86.[16] With SHELX 76,[17] hydrogen atoms located from a difference Fourier map, were given the isotropic thermal parameters of the atoms to which they were attached and were included in the structure factor calculation but not refined. The literature values of atomic scattering of hydrogen[18] and non-hydrogen atoms[19] were used. All calculations were performed on a MicroVAX II system. Experimental data of the crystal and refinement conditions are given in Table I. Final coordinates are listed in Table II. All reflections were given equal weight during refinement, thus weighing scheme was of unit weights.

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