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The crystal structure of triphenyl(*N*,*N*-diisopropyldithiocarbamato)tellurium(IV), an unusual dimeric structure

John E. Drake and Maria L.Y. Wong

Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario N9B 3P4 (Canada)

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Abstract

The crystal structure determination of $Ph_3Te[S_2CN(i\text{-}Pr)_2]$ indicates a most unusual dimeric structure in which the ligand can be considered as acting as a bridge with very long Te–S bonds. The crystals are triclinic in space group $P\bar{1}$ with cell parameters *a* 12.101(3) Å, *b* 8.728(2) Å, *c* 12.301(2) Å, α 80.88(2)°, β 102.60(2)°, γ 106.21(2)°, *V* 1210.9(5) $Å^3$, $Z = 2$, $R = 0.0267$, $R_w = 0.0340$. The immediate environment about each tellurium atom can be described as that of a distorted octahedron. The three Te–C (phenyl) bonds are mutually *cis* with two long Te–S bonds of similar length and a lone pair completing the octahedron.

Introduction

Organotellurium(IV) dithiocarbamates have been the target of several structural studies. The tris-substituted species can be exemplified by $PhTe[S_2CNEt_2]_3$, which is described as having a distorted pentagonal, bipyramidal configuration [1]. The five equatorial and nearly co-planar Te–S bonds have lengths ranging from 2.606(3) to 2.816(3) Å while the 'axial' Te–S bond is 3.228(4) Å. Thus two of the dithiocarbamates are bidentate and one is anisobidentate. In bis-substituted species, as exemplified by $MeTe[S_2CNEt_2]_2I$ [2], $Ph_2Te[S_2CNEt_2]_2$ [3] and $Ph_2Te[S_2CNMe_2]_2$ [4], both bidentate and anisobidentate ligands have been found but not in the same molecule. Thus in $MeTe[S_2CNEt_2]_2I$ [2], the four Te–S atoms of the bidentate ligands, along with the iodine, form a pentagonal plane about tellurium with Te–S distances ranging from 2.618(1) to 2.725(1) Å. By contrast to these two bidentate ligands, in both modifications reported for $Ph_2Te[S_2CNEt_2]_2$ [3], the ligands are anisobidentate with one Te–S bond being in the range 2.6179(4) to 2.6303(9) Å and the other in the range 3.1103(9) to 3.1999(1) Å. Similar results are reported for $Ph_2Te[S_2CNMe_2]_2$ [4] in which the two anisobidentate ligands both have Te–S bonds of 2.621(1) and 3.186(2) Å.

We report herein the structure of $Ph_3Te[S_2CN(i\text{-}Pr)_2]$, which was crystallized from a solution in which an attempt was being made to prepare $Ph_2Te[S_2CN(i\text{-}Pr)_2]_2$. Recently, a preprint by Singh and Basumatary [5] was sent to us by the authors in which they reported on the preparations of $Ph_3Te[S_2CNR_2]$ species, where RR′ = Me_2, HMe, Et_2, $(C_2H_4OH)_2$, and $(CH_2)_2O(CH_2)_2$, by reaction of Ph_3TeCl with the appropriate sodium salts, NaS_2CNR_2. Our crystals of $Ph_3Te[S_2CN(i\text{-}Pr)_2]$ resulted from the reaction of impurities of Ph_3TeCl with NaS_2CNR_2 in very similar conditions to those described in detail elsewhere [5].

It seemed appropriate to report these results as soon as possible as a follow up to the preparative paper particularly as the dithiocarbamate is bonded in a different manner to that so far described for $PhTe(S\text{–}S)_3$ and $Ph_2Te(S\text{–}S)_2$ species. While those examined have all been monomeric, $Ph_3Te[S_2CN(i\text{-}Pr)_2]$ is in fact dimeric with two dithiocarbamate bridging groups.

Experimental

X-ray diffraction data were collected on a Syntex $P2_1$ diffractometer by the procedure already described in detail [6]. Intensity data were collected using the

Table 1

Final fractional coordinates and isotopic thermal parameters for non-hydrogen atoms of $Ph_3Te[S_2CN(i\text{-}PR)_2]$ with standard deviations in parentheses

Atom	x	y	z	U_{eq} ($Å^2 \times 10^3$)
Te1	0.09796(2)	−0.06577(3)	−0.09411(2)	35.90(3)
S1	0.2195(1)	0.1200(1)	0.1121(1)	48.89(9)
S2	0.0583(1)	−0.1759(1)	0.1924(1)	45.74(8)
N1	0.2761(3)	−0.0628(4)	0.2996(2)	50.6(3)
C1	0.1932(3)	−0.0415(4)	0.2103(3)	40.4(3)
C2	0.2571(4)	−0.2089(6)	0.3806(3)	68.0(4)
C3	0.2538(5)	−0.1686(7)	0.4965(4)	95.7(7)
C4	0.3440(5)	−0.3054(9)	0.3838(4)	100.3(7)
C5	0.3903(3)	0.0559(6)	0.3273(3)	66.1(4)
C6	0.3774(4)	0.2154(6)	0.3512(4)	85.1(6)
C7	0.4716(4)	0.0750(8)	0.2455(4)	89.2(6)
C8	0.2209(2)	−0.2063(3)	−0.0256(2)	43.1(3)
C9	0.1756(2)	−0.3538(3)	0.0319(2)	52.0(4)
C10	0.2483(2)	−0.4547(3)	0.0809(2)	68.2(6)
C11	0.3664(2)	−0.4080(3)	0.0723(2)	72.6(6)
C12	0.4117(2)	−0.2605(3)	0.0148(2)	67.3(5)
C13	0.3390(2)	−0.1596(3)	−0.0342(2)	55.2(3)
C14	0.0360(3)	−0.1896(3)	−0.2435(2)	44.7(3)
C15	−0.0220(3)	−0.1146(3)	−0.3386(2)	67.3(5)
C16	−0.0682(3)	−0.1939(3)	−0.4348(2)	74.5(6)
C17	−0.0564(3)	−0.3481(3)	−0.4358(2)	74.4(5)
C18	0.0016(3)	−0.4231(3)	−0.3407(2)	83.3(6)
C19	0.0478(3)	−0.3438(3)	−0.2445(2)	66.0(4)
C20	0.2120(2)	0.1263(3)	−0.1759(2)	37.8(3)
C21	0.2307(2)	0.2813(3)	−0.1478(2)	52.2(3)
C22	0.2992(2)	0.4110(3)	−0.2052(2)	65.2(5)
C23	0.3492(2)	0.3856(3)	−0.2906(2)	75.7(5)
C24	0.3305(2)	0.2305(3)	−0.3187(2)	67.4(5)
C25	0.2619(2)	0.1009(3)	−0.2613(2)	34.4(4)

coupled $\theta/2\theta$ method to a maximum Bragg angle of 27.5° using Mo-K_α radiation (highly oriented graphite monochromator (λ 0.71069 Å)). The crystal was sealed in a capillary and mounted along the largest dimension. A unique set of data in the shell defined by $15° < 2\theta < 30°$ was collected and a set of 35 strong reflections was chosen to form the basis for the determination of the accurate orientation matrix and cell parameters given below. The appropriate space group was used and later assumed correct because of successful refinement of the data. During data collection, the intensities of three monitor reflections measured after every 200 reflections decreased by less than 2% and the appropriate scaling factor was applied. The data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied. The minimum and maximum absorption correction factors were 0.957 and 0.968 respectively.

Crystallographic data. $Ph_3Te[S_2CN(i\text{-}Pr)_2]$: $C_{28}H_{29}N_2S_4Te$, M_r 535.24, triclinic, space group $P\bar{1}$, a 12.101(3), b 8.728(2), c 12.301(2) Å, α 80.88(2), β 102.60(2) γ 106.21(2)°, crystal dimensions 0.31 × 0.35 × 0.38 mm; V 1210.9(5) Å^3, $Z = 2$, D_e 1.47 g cm^{-3}, D_c 1.51 g cm^{-3}, collected data $4.5° < \theta < 45°$, μ 12.97 cm^{-1}; 3375 $(+h, \pm k, \pm l)$ reflections measured; 2769 $(I > 3\sigma I)$ unique data used.

The data for the single crystal of $Ph_3Te[S_2CN(i\text{-}Pr)_2]$ showed no symmetry, other than that required by Friedel's law, and therefore the triclinic space group $P\bar{1}$ (C_i^1, No. 2) was assumed. The position of the tellurium atom was determined from a three-dimensional Patterson synthesis, while the other non-hydrogen atoms were

Table 2

Interatomic distances (Å) and bond angles (°) in $Ph_3Te[S_2CN(i\text{-}Pr)_2]$

Te–S1	3.095(1)	S1–Te–C8	83.1(1)
Te–S2	3.604(1)	S1–Te–C14	172.4(1)
Te–C8	2.139(2)	S1–Te–C20	82.5(1)
Te–C14	2.163(2)	C8–Te–C14	92.5(1)
Te–C20	2.122(2)	C8–Te–C20	97.3(1)
		C14–Te–C20	92.0(1)
S1–C1	1.711(4)		
S2–C1	1.718(3)	C1–S1–Te	96.1(1)
N1–C1	1.344(4)	C1–N1–C2	121.1(3)
N1–C2	1.486(5)	C1–N1–C5	124.0(3)
N1–C5	1.486(5)	C2–N1–C5	114.9(3)
C2–C3	1.532(7)	S1–C1–S2	118.5(2)
C2–C4	1.510(7)	S1–C1–N1	120.8(3)
C5–C6	1.523(7)	S2–C1–N1	120.7(3)
C5–C7	1.515(6)		
		N1–C2–C3	111.5(4)
		N1–C2–C4	111.6(4)
		N1–C5–C6	112.9(4)
		N1–C5–C7	114.0(4)
		C3–C2–C4	113.1(4)
		C6–C5–C7	113.1(4)
Te–S2′	3.145(1)	S2′–Te–S1	92.6(1)
Te–S1′	3.698(2)	S2′–Te–C8	173.6(1)
Te–Te′	4.130(1)	S2′–Te–C14	91.5(1)
		S2′–Te–C20	76.8(1)

[a] Prime: symmetry position $-x$, $-y$, $-z$.

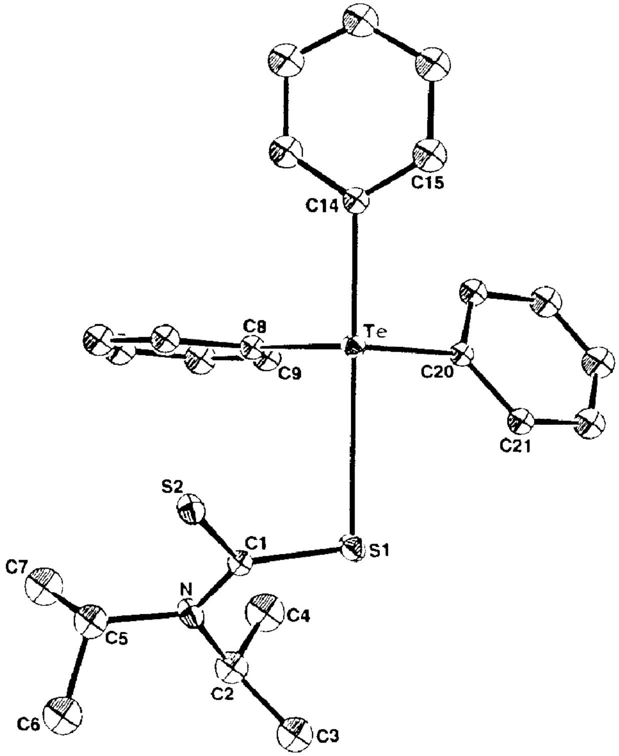

Fig. 1. ORTEP plot of the asymmetric unit of $Ph_3Te[S_2CN(i\text{-}Pr)_2]$. The atoms are drawn with 20% probability ellipsoids. Hydrogen atoms are omitted for clarity.

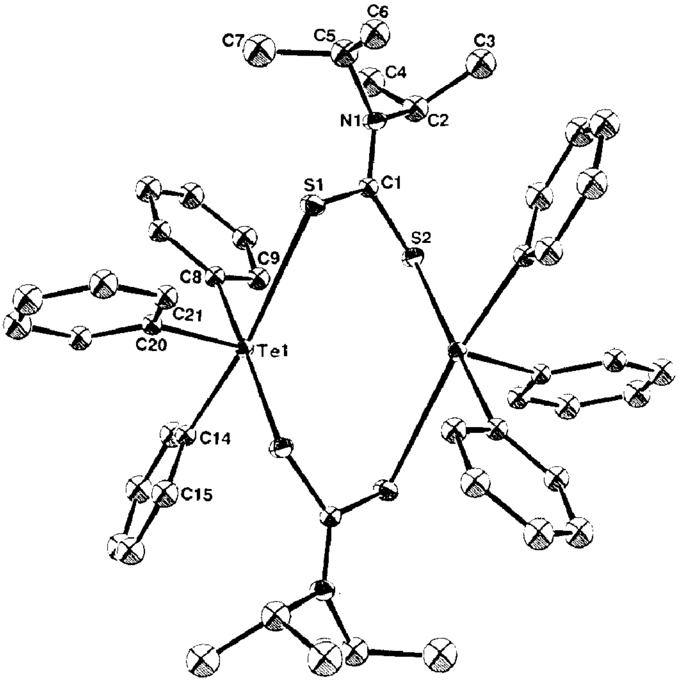

Fig. 2. ORTEP plot of the dimeric unit of $\{Ph_3Te[S_2CN(i\text{-}Pr)_2]\}_2$. The atoms are drawn with 20% probability ellipsoids. Hydrogen atoms are omitted for clarity.

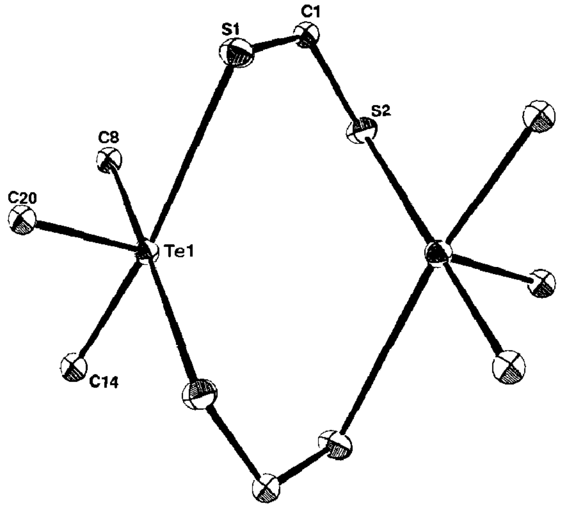

Fig. 3. ORTEP plot of the core atoms in the bridging unit of $Ph_3Te[S_2CN(i\text{-}Pr)_2]$.

located from subsequent difference maps. The structure was refined by using a full-matrix least-squares refinement procedure, with anisotropic temperature factors assigned to all non-hydrogen atoms. From 226 variables and 2769 unique reflections, convergence occurred with $R = 0.0267$ and $R_w = 0.0340$, where the weighting scheme $w = 1.2739[\sigma^2(F) + 0.000001F^2]^{-1}$ was used. The phenyl rings were refined as hexagonal groups with C–C bond distances set a 1.395 Å and C–C–C angles at 120.0 °. Their corresponding hydrogen atoms were also included in the refinement at their geometrically estimated positions, with C–H set at 0.95 Å. The remaining hydrogen atoms for the other alkyl groups were also included with C–H again set at 0.95 Å. The final refinement cycle showed that the greatest residual electron density peaks, 0.620 and 0.542 $eÅ^{-3}$ are 1.09 and 1.00 Å respectively from the Te atom. The programs used during structural analysis include local version of CHECK (check standard reflections) [7], PROC (data reduction) [7], SHELX (Fourier synthesis and structural refinement) [8], XANADU (crystallographic calculations) [9] and ORTEP (thermal elipsoid plotting program) [10]. Table 1 lists the final fractional coordinates and thermal parameters for the non-hydrogen atoms and selected bond distances and angles are shown in Table 2; ORTEP drawings of the molecular structure, the bridging system and the core atoms of the dimeric unit are shown in Figs. 1–3. Tables of anisotropic thermal parameters of non-hydrogen atoms, final fractional coordinates and thermal parameters of hydrogen atoms and observed and calculated structure factors can be obtained from the authors on request.

Results and discussion

An ORTEP diagram of the single molecule of $Ph_3Te[S_2CN(i\text{-}Pr)_2]$ showing the numbering scheme is displayed in Fig. 1. This gives no indication of the bridge and indeed the four atoms closest to the tellurium atom, C8, C14, C20 and S1, together with the supposed lone electron pair appear to provide the typical approximate trigonal bipyramidal environment. The two Te–C(phenyl) bonds in the equatorial plane have an average bond length of 2.14(2) Å which is very close to that of the two Te–C bonds (2.136(5) Å) in $Ph_2TeCl[S_2CN(i\text{-}Pr)_2]$, as is the C8–Te–C20 bond angle of 97.3(1)° compared to 96.0(2)° in the chloro derivative [4].

The angles between the carbon atom of the phenyl group in the axial position and the two carbon (phenyl) atoms in the equatorial plane are close to 90° as expected with C14–Te–C8 at 92.5(1) and C14–Te–C20 and 92.0(1)°. In $Ph_2TeCl[S_2CN(i\text{-}Pr)_2]$, the Te–Cl (axial) bond of 2.661(2) Å is considerably longer than the Te–S (axial) bond of 2.484(2) Å [4]. This lengthening may be associated with the fact that it is the chlorine atom that appears to provide the link to the nearest molecule. The Te–S1 bond in $Ph_3Te[S_2CN(i\text{-}Pr)_2]$ is considerably longer at 3.095(1) Å. The dithiocarbamate group as a whole provides the link to the next molecule and it is notable that the S2–Te′ (or Te–S2′) bond length is only slightly longer at 3.145(1) Å. In other words the dithiocarbamate group is a bridge so that $Ph_3Te[S_2CN(i\text{-}Pr)_2]$ is better considered as a dimeric unit as is shown in the ORTEP plot of the dimeric unit in Fig. 2 and the core geometry emphasizing the bridging system in Fig. 3. The environment about each tellurium atom is now better described as that of a distorted octahedron, with the three Te–C (phenyl) carbon atoms forming one *fac* set and the two long Te–S bonds along with the lone pair forming the other. The longest of the Te–C bonds (Te–C14) is 2.163(2) Å and is essentially *trans* to the shorter of the Te–S bond (Te–S1 3.095(1) Å). The angle C14–Te–S1 is 172.4(1)°. The Te–C bond of intermediate length (Te–C8) is 2.139(2) Å and is *trans* to the longer Te–S2′ bond of 3.145(1) Å. The C8–Te–S2′ angle is 173.6°. The shortest bond, Te–C(20) is 2.122(2)Å and it is *trans* to the assumed lone pair.

The dithionate bridge is remarkably symmetric, suggesting total delocalization. Both C–S bonds are equivalent 1.718(3) and 1.711(4) Å which is close to the value of 1.721(9) and 1.722(9) for one of the bidentate ligands in $PhTe[S_2CNEt_2]_3$ [1]. Mono- or aniso-bidentate ligands normally contain short and long C–S bonds as exemplified by 1.67(1) and 1.73(2) Å in $PhTe[S_2CNEt_2]_3$ 1.678(5) and 1.738(5) Å in $Ph_2Te[S_2CNMe_2]_2$, 1.690(2) and 1.758(2) Å in the *C2/c* modification of $Ph_2Te[S_2CNEt_2]_2$ [3], and 1.660(6) and 1.788(6) Å in $Ph_2TeCl[S_2CN(i\text{-}Pr)_2]$ [4]. The partial double C–N bond of 1.344(5) Å is very similar to that reported for the above compounds as is the value for the C–N single bonds of 1.486(5) Å. These bond lengths appear to be very similar whether the ligands are monodentate or anisobidentate [1–4], truly bidentate [2], or bridging as in this case. A final comparison is of particular interest. The structure of the sodium salt, $Na[S_2CNMe_2] \cdot 2H_2O$, has been determined [11]. The dithiocarbamate ion, by contrast to the bridge in this case, shows short and long C–S bonds of 1.709(2) and 1.736(2) Å, the average of the two being slightly longer than those in the bridge. The C–N bond lengths are slightly shorter than in the bridge; 1.465(4) and 1.460(4) Å for the C–N single bonds and 1.335(3) Å for the partial double bond. The S_2CN skeleton in both the ion and the bridge is co-planar.

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