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Synthesis and Crystal Structure of Bis(diethyldithiocarbamato)iodophenyltellurium(IV), [PhTe(Et_2NCS_2)$_2$I]

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The title compound, **1**, was made by the reaction between [PhTe(Et_2NCS_2)$_3$] and I_2 in CH_2Cl_2. The yellow crystals are triclinic with $a = 10.124(3)$, $b = 13.762(5)$, $c = 17.592(6)$ Å, $\alpha = 83.61(2)$, $\beta = 82.62(2)$, $\gamma = 71.54(3)°$, $Z = 4$, space group $P\bar{1}$ and $R = 0.026$ for 9113 unique, observed reflections. There are two crystallographically independent molecules present, connected into pairs by weak intermolecular Te···S interactions of 3.598(1) and 3.832(1) Å. These weak intermolecular Te···S bonds are in a direction roughly *trans* to the phenyl group. The structure of the molecules is essentially pentagonal bipyramidal with the phenyl group and a sulfur atom of a neighbour molecule being axial, and the sulfurs of the bidentate ligands and iodine being in equatorial positions. Average Te–S, Te–I and Te–C bond lengths are 2.674, 3.126 and 2.153 Å, respectively. The roles of the secondary bonding and the lone pair of electrons on Te are discussed.

The present paper is part of a study of structures of tellurium(IV) complexes of the type [$ArTeL_{3-n}X_n$], where Ar is phenyl or substituted phenyl, X is a halogenide, L is a dialkyldithiocarbamate and $n = 0$, 1 or 2. Structures of complexes with $n = 0$ have been known for some time.[1,2] Recently the first structure of a complex with $n = 1$, [PhTeCl(Et_2NCS_2)$_3$], **2**, was published.[3] The related structure of [MeTe(Et_2NCS_2)$_2$I], **3**, is also known.[4]

These latter compounds are of the AB_6E type, where E denotes the Te^{IV} lone pair of electrons, and B the number of ligand atoms bonded to the central atom, A. They have pentagonal bipyramidal structures with Ph or CH_3 groups in one axial position and weak intermolecular contacts or a stereochemically active lone pair of electrons in the direction of the other. Making complexes similar to **2** with X = Br or I was difficult starting with $PhTeX_3$ and adding dithiocarbamates or alternately by substitutions in chloro complexes like **1**. However, a procedure based on additions of the free halogen, X_2, to [$ArTe(R_2NCS_2)_3$], gave the desired results.

Experimental

Synthesis. The complex [PhTe(Et_2NCS_2)$_2$I], **1**, was prepared as follows. To a solution of 0.1350 g (0.021 mmol) of PhTe(Et_2NCS_2)$_3$ dissolved in 5 ml CH_2Cl_2 was slowly added 0.0264 g (0.0104 mmol) of I_2 in 10 ml CCl_4 under stirring. The yellow precipitate was washed with ether and recrystallized from a 3:1 mixture of CH_2Cl_2 and ethanol. Yield 0.074 g of **1** corresponding to 56.2%, m.p. = 168 °C (dec.).

X-Ray data. Crystal data, intensity collection and structural refinement parameters are listed in Table 1. Three standard reflections were remeasured every 3 h for scaling purposes. No significant decrease in intensity was observed for these reflections. Intensities were corrected for absorption.

Structure determination. Space group $P\bar{1}$ was chosen on the basis of E statistics and later justified by the successful refinement. The structure was solved by direct methods and refined by least-squares methods. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were positioned by a special program and given isotropic temperature factors equal to 1.3 times those on the parent carbon atoms. They were refined with fixed C–H bond lengths of 0.95 Å. The intensities were corrected for absorption using an empirical method based on the ψ-scan procedure. No peaks above 0.55 e^- $Å^{-3}$ were found in the final difference map. There are two crystallographically independent molecules in the asymmetric unit. The function minimised is $\Sigma w(\Delta F)^2$. A weighting scheme with $w = 4F_0^2/\sigma(F_0^2)^2$, where $\sigma(F_0^2) = [\sigma(I)^2 + 0.03I)^2]^{1/2}$, was used. Computer pro-

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Table 1. Crystal and experimental data.

Compound	$[PhTe(Et_2NCS_2)_2I]$
Diffractometer	Enraf-Nonius CAD-4
Radiation	Mo*K*α
Wavelength/Å	0.710 69
Crystal system	Triclinic
a/Å	10.124(3)
b/Å	13.762(5)
c/Å	17.592(6)
α/°	83.61(2)
β/°	82.62(2)
γ/°	71.54(3)
V/Å^3	2299.2
Space group	$P\bar{1}$
Formula wt.	628.15
Z	4
D(calc)/g cm^{-3}	1.815
μ(Mo*K*α)/cm^{-1}	29.77
Crystal dimensions/mm	0.20×0.30×0.37
Scan mode; θ_{max}	ω; 28
Fudge factor, *p*	0.030
Scale factor	1.533
Temperature of intensity collection/°C	22
No. of independent measurements	11071
No. with $I > 2.0\sigma(I)$	9113
Transmission (max/min)	0.9994/0.6798
$R=\Sigma\|F_o-F_c\|/\Sigma F_o$	0.027
$R_w=[\Sigma_w(F_o-F_c)^2/\Sigma_w F_o^2]^{1/2}$	0.032
$S=[\Sigma_w(\Delta F)^2/(N-n)]^{1/2}$	1.347

grams used were supplied by Enraf-Nonius (SPD/VAX V3). Positional parameters, and selected bond lengths and angles are shown in Tables 2–4.

Supplementary material. Further details of the structural work are deposited with the Cambridge Crystallographic Data Centre, UK.

Results and discussion

The title compound, $[PhTe(Et_2NCS_2)_2I]$, **1**, was prepared according to the scheme

$$2[PhTe(Et_2NCS_2)_3] + I_2 = 2[PhTe(Et_2NCS_2)_2I] + Et_2NC(S)SS(S)CNEt_2$$

This redox method seems well suited to prepare species of the type $[ArTeL_2X]$, where L is a dialkyldithiocarbamate and X is halogen. A similar redox reaction has been used to prepare $[TeL_3I]$ and $[TeL_2I_2]$ by adding I_2 to $[TeL_4.]$.[5,6]

An extension of this reaction has been used to prepare mixed dihalide complexes according to the equation

$$2[MeOPhTe(Et_2NCS_2)_2I] + Br_2 = 2[MeOPhTe(Et_2NCS_2)BrI] + Et_2NC(S)SS(S)CNEt_2$$

The main product formed was $[MeOPhTe(Et_2NCS_2)_2(Br_{0.41}I_{0.59})]$, **4**,[7] but a small amount of $[MeOPhTe(Et_2NCS_2)(Br_{0.4}I_{0.6})_2]_2$ was also formed.[8]

Attempts to prepare dihalides using the reaction

$$[ArTe(R_2NCS_2)_3] + X_2 = [ArTe(R_2NCS_2)X_2] + R_2NC(S)SS(S)CNR_2 \quad (X = Br, I)$$

only yielded $[MeOPhTe(Et_2NCS_2)_2I]$, **5**,[7] and

Table 2. Positional parameters and their estimated standard deviations.

Atom	*x*	*y*	*z*	*B*/Å^2
I1	0.37347(2)	0.61230(2)	0.27507(1)	4.413(5)
I2	0.55143(2)	−0.08523(2)	0.29669(1)	4.249(5)
Te1	0.29162(2)	0.41934(1)	0.24221(1)	2.952(4)
Te2	0.63669(2)	0.11002(1)	0.23995(1)	2.795(4)
S1	0.25066(9)	0.41813(6)	0.39776(5)	3.87(2)
S2	0.25512(9)	0.24827(6)	0.30939(5)	4.17(2)
S3	0.2701(1)	0.31401(6)	0.13109(5)	4.26(2)
S4	0.32114(9)	0.51446(6)	0.10012(5)	3.74(2)
S5	0.60692(9)	0.11179(6)	0.39432(5)	3.72(2)
S6	0.64246(9)	0.28446(6)	0.28817(5)	3.78(2)
S7	0.6970(1)	0.21508(6)	0.11106(5)	4.27(2)
S8	0.68896(9)	0.00342(6)	0.11424(5)	4.09(2)
N1	0.2325(3)	0.2384(2)	0.4624(2)	4.26(6)
N2	0.2766(3)	0.4110(2)	−0.0083(2)	3.95(6)
N3	0.6054(3)	0.2899(2)	0.4404(2)	3.82(6)
N4	0.7600(3)	0.1082(2)	−0.0130(2)	4.37(7)
C1	0.2437(3)	0.2955(2)	0.3984(2)	3.50(7)
C2	0.2353(4)	0.1297(3)	0.4622(3)	6.1(1)
C3	0.0928(5)	0.1174(4)	0.4691(4)	9.8(2)
C4	0.2098(4)	0.2811(3)	0.5378(2)	5.33(9)
C5	0.0600(4)	0.3419(4)	0.5597(3)	6.9(1)
C6	0.2889(3)	0.4133(2)	0.0653(2)	3.47(6)
C7	0.2516(4)	0.3228(3)	−0.0389(2)	5.17(9)
C8	0.3862(5)	0.2471(3)	−0.0659(3)	7.7(1)
C9	0.2795(4)	0.4978(3)	−0.0643(2)	4.86(8)
C10	0.1353(5)	0.5701(3)	−0.0713(3)	6.4(1)
C11	0.0722(3)	0.5016(2)	0.2443(2)	3.09(6)
C12	0.0300(3)	0.6070(2)	0.2297(2)	3.63(7)
C13	−0.1117(3)	0.6611(3)	0.2322(2)	4.34(8)
C14	−0.2100(3)	0.6106(3)	0.2494(2)	4.77(9)
C15	−0.1683(3)	0.5066(3)	0.2615(2)	5.07(9)
C16	−0.0274(3)	0.4508(3)	0.2599(2)	4.52(8)
C17	0.6176(3)	0.2341(2)	0.3819(2)	3.28(6)
C18	0.6080(4)	0.3969(3)	0.4295(2)	5.17(9)
C19	0.7404(5)	0.4081(4)	0.4506(3)	7.5(1)
C20	0.5861(4)	0.2469(3)	0.5203(2)	4.87(9)
C21	0.7210(4)	0.1831(4)	0.5516(2)	6.0(1)
C22	0.7202(3)	0.1082(2)	0.0618(2)	3.60(7)
C23	0.7818(4)	0.1993(3)	−0.0580(2)	5.3(1)
C24	0.9301(5)	0.2001(4)	−0.0630(3)	6.9(1)
C25	0.7937(5)	0.0134(3)	−0.0537(2)	6.0(1)
C26	0.6668(5)	0.0051(4)	−0.0862(3)	7.7(1)
C27	0.8568(3)	0.0402(2)	0.2527(2)	3.15(6)
C28	0.9067(3)	−0.0636(3)	0.2697(2)	4.70(8)
C29	1.0483(4)	−0.1096(3)	0.2779(3)	5.8(1)
C30	1.1364(3)	−0.0520(4)	0.2694(2)	5.6(1)
C31	1.0864(3)	0.0516(3)	0.2525(3)	6.02(9)
C32	0.9459(4)	0.0990(3)	0.2441(2)	4.90(8)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as: $(4/3)[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$.

Table 3. Selected bond lengths (in Å) with standard deviations.

Molecule (a)		Molecule (b)	
Te1–I1	3.1513(3)	Te2–I2	3.1003(3)
Te1–S1	2.7134(9)	Te2–S5	2.6957(8)
Te1–S2	2.6258(8)	Te2–S6	2.6534(8)
Te1–S3	2.6286(9)	Te2–S7	2.6604(9)
Te1–S4	2.7164(8)	Te2–S8	2.6931(9)
Te1–C11	2.148(3)	Te2–C27	2.159(3)
Te1···S6′	3.598(1)	Te2···S2′	3.832(1)
C1–S1	1.710(3)	C17–S5	1.708(3)
C1–S2	1.738(3)	C17–S6	1.736(3)
C1–N1	1.313(4)	C17–N3	1.322(4)
C6–S3	1.731(3)	C22–S7	1.727(3)
C6–S4	1.718(3)	C22–S8	1.717(3)
C6–N2	1.320(4)	C22–N4	1.326(4)

Table 4. Selected bond angles (in °) with standard deviations.

Molecule (a)		Molecule (b)	
I1–Te1–S1	77.10(2)	I2–Te2–S5	76.11(2)
I1–Te1–S4	76.66(2)	I2–Te2–S8	75.86(2)
S1–Te1–S2	66.64(3)	S5–Te2–S6	66.68(3)
S2–Te1–S3	74.06(3)	S6–Te2–S7	76.45(3)
S3–Te1–S4	66.83(3)	S7–Te2–S8	66.46(3)
C11–Te1–I1	93.91(8)	C27–Te2–I2	95.70(8)
C11–Te1–S1	85.78(8)	C27–Te2–S5	85.06(8)
C11–Te1–S2	94.85(8)	C27–Te2–S6	90.96(8)
C11–Te1–S3	89.84(8)	C27–Te2–S7	90.54(9)
C11–Te1–S4	86.89(8)	C27–Te2–S8	85.27(8)
Te1–S1–C1	87.2(1)	Te2–S5–C17	87.6(1)
Te1–S2–C1	89.5(1)	Te2–S6–C17	88.4(1)
Te1–S3–C6	89.2(1)	Te2–S7–C22	88.8(1)
Te1–S4–C6	86.6(1)	Te2–S8–C22	87.9(1)
S1–C1–N1	122.4(3)	S5–C17–N3	122.3(3)
S2–C1–N1	121.0(3)	S6–C17–N3	120.4(2)
S1–C1–S2	116.6(2)	S5–C17–S6	117.2(2)
C3–C6–N2	120.8(3)	S7–C22–N4	121.0(3)
S4–C6–N2	122.0(3)	S8–C22–N4	122.2(3)
S3–C6–S4	117.2(2)	S7–C22–S8	116.8(2)
Te1–C11–C12	119.3(2)	Te2–C27–C28	119.1(2)
Te1–C11–C16	121.1(2)	Te2–C27–C32	120.7(3)
S6′···Te–C11	166.14(8)	S2′···Te2–C27	154.82(8)

[MeOPhTe(Me_2NCS_2)$_2$Br], **6**, the corresponding monohalides.[9] The dihalide is probably formed initially, as seen by the decolorization of the halogen, but only crystals of the monohalide could be isolated. This has also been found when adding $NaEt_2NCS_2$ to $PhTeCl_3$ in the ratio 1:1.[4]

However, the reaction of Ph_2Te_2 with I_2 and $NaEt_2NCS_2$ gave the diiodide, [PhTe(Et_2NCS_2)I_2].[8]

The two crystallographically independent molecules of [PhTe(Et_2NCS_2)$_2$I], **1**, are shown in Fig. 1. They are quite similar, their structures (excluding secondary bonds) are pentagonal pyramidal with the phenyl group being axial. The diethyldithiocarbamate ligands (except for methyl groups and H-atoms) are planar and nearly coplanar with the equatorial $TeIS_4$ plane (Table 5). One of the dithiolate ligands in both molecules has both methyl groups on the same side of the ligand plane, while the

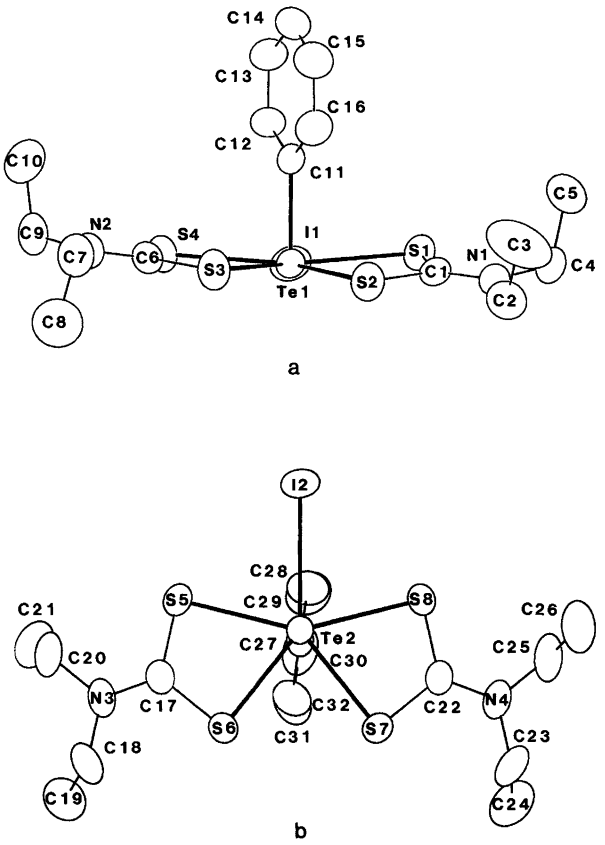

Fig. 1. The structure of the two crystallographically independent molecules of [PhTe(Et_2NCS_2)$_2$I], **1**. On top (a) as seen along the Te1–I1 bond. Below (b) as seen along the normal to the equatorial plane.

other has a methyl group on each side of this plane. This was also found for the analogous chloride complex, **2**. Another analogy with **2** is that the angle between the pseudo-mirror plane defined by CTeI (Table 5) and the phenyl group differs by 14–15° in the two molecules. This is the main structural deviation between the crystallographically independent molecules.

Other differences in distances and angles between these molecules are small. Also, the molecules of **1** have a similar structure to those of **4**–**6**. There are, however, great differences in secondary, intermolecular bonding in these complexes. Nevertheless, these secondary bonds are all in the direction of the vacant axial position in a pentagonal bipyramidal coordination sphere around Te.

Bonding in [PhTe(Et_2NCS_2)$_2$I], **1**. The diethyldithiocarbamate ligands are nearly isobidentate; average long and short C–S bonds are 1.713 and 1.732 Å, respectively. The corresponding Te–S bond lengths are accordingly long and short. The short Te–S bonds are those roughly *trans* (ca. 141.9°) to the halogen ligand, with an average Te–S bond length of 2.642 Å. A kind of *trans* influence relating the strength of these Te–S bonds to the strength of the Te–halogen bond has been found earlier in the similar chloride, **2**. To the Tel–I1 bond length of

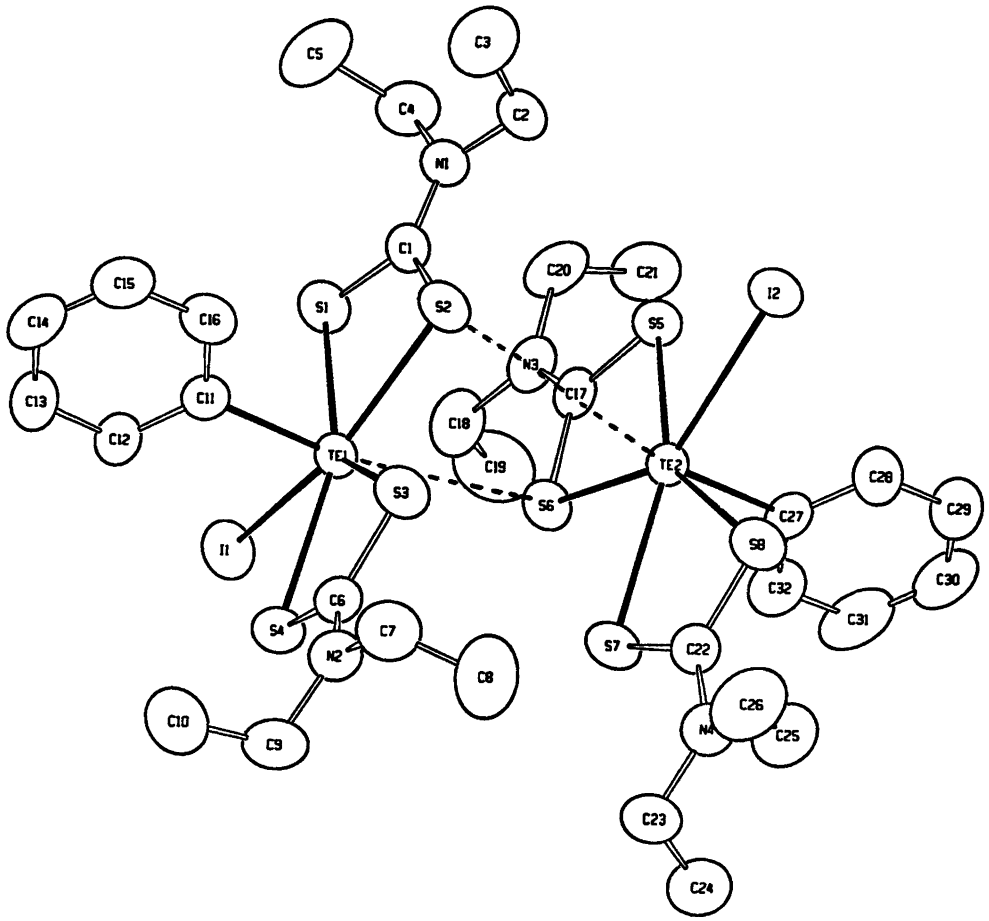

Fig. 2. A pair of molecules (a) and (b) connected by secondary bonds shown as dashed lines.

Table 5. Least-squares molecular planes.

Plane no.	Atoms included	Max. atomic dev. from plane/Å	Interplanar angle/°
1	Te1,I1,S1,S2,S3,S4	−0.245	1,2:89.31(6)
2	Te1,I1,C11	0	1,3:90.30(8)
3	C11–C16	−0.015	2,3:23.13(7)
4	Te2,I2,S5,S6,S7,S8	0.240	4,5:89.99(6)
5	Te2,I2,C27	0	4,6:89.71(9)
6	C27–C32	0.002	5,6:8.44(28)
			1,4:171.03(5)

3.1513(3) Å in molecule (a) there correspond '*trans*' Te–S2 and Te–S3 bond lengths of only 2.6258(9) and 2.6286(9) Å. To the shorter Te2–I2 bond length of 3.1003(3) Å in molecule (b), there correspond *trans* Te2–S6 and Te2–S7 bond lengths of 2.6534(8) and 2.6604(9) Å respectively. The average of all Te–S bond lengths in this study, except for the secondary bonds, is 2.6734 Å, as compared to the sum of the respective covalent radii of only 2.41 Å.[10] However, this value is normal for highly coordinated Te^{IV} complexes.[11] The Te–I and Te–S bond lengths in molecule (a) are very close to the corresponding bond lengths in **4–6**.[7,9] The axial Te-C bond length has an average value of 2.153 Å, which is normal for such compounds. Average C–S, C–N, N–C, C–C(Et) and C–C(Ph) bond lengths are normal at 1.723, 1.320, 1.476, 1.499 and 1.376 Å, respectively.

Molecular packing and secondary bonding. Two intermolecular, weak secondary Te···S bonds connect molecules of types (a) and (b) into (ab) pairs. They are Te1···S6 = 3.598(1) and Te2···S2 = 3.832(1) Å, and may be compared to the corresponding van der Waals contact of 3.86 Å.[13] These bonds, although very weak, are roughly in the direction of the empty axial position in a pentagonal bipyramidal geometry [angle C–Te···S is 166.1(1) and 154.8(1)°, respectively]. An interesting study of similar secondary bonding forming dimeric Te^{IV} species has recently been published.[12]

Table 6 shows a comparison between secondary bonding in five [ArTeL$_2$X] complexes with similar structures. The secondary bonds are all roughly in the direction of a missing axial ligand *trans* to aryl in the pentagonal bipyramidal structures. It can be seen that the relative strengths of the secondary bonding are Te···I > Te···Br > Te···S > Te···Cl > Te···C. Thus, the softer the ligand atom, the stronger it is bonded to the soft Te atom. With respect to Te···C, a π-interaction

Table 6. Secondary bridging in [ArTeL$_2$X] complexes (L=R$_2$NCS$_2$, X=halogen). The bridges knit the molecules into dimers; the first four dimers are centrosymmetric.

Complex	Secondary bridge bonds, Te–Y′/Å		Contraction/relative to van der Waals contacts/Å		Angle/ C(Aryl)–Te···Y′/°	Ref.
[PhTeCl(Et$_2$NCS$_2$)$_2$]	Te···S	3.739(1),3.705(1)	0.12,	0.15	161.8(1),162.3(1)	2
[MeOPhTeBrMe$_2$NCS$_2$)$_2$]	Te···C	3.751(3)	0.01		170.2(1)	9
[MeOPhTe(Et$_2$NCS$_2$)$_2$Br$_{0.41}$I$_{0.59}$]	Te···Br[I]	3.476(9),[3.558(4)]	0.43,	[0.48]	176.3(2),[174.9(1)]	7
[MeOPhTe(Et$_2$NCS$_2$)$_2$I]	Te···I	3.569(1)	0.47		176.8(1)	7
[PhTe(Et$_2$NCS$_2$)$_2$I]	Te···S	3.598(1),3.832(1)	0.26,	0.03	166.14(3),154.82(3)	This work

between Te and the π_{MO} in the NCS_2^- group of the ligand $Me_2NCS_2^-$ has been proposed.[9] It is somewhat surprising that the secondary bonding is so different in the two iodides: [PhTe(Et$_2$NCS$_2$)$_2$I] has Te···S bonds while [MeOPhTe(Et$_2$NCS$_2$)$_2$I] has Te···I bonds.[7] Because such bonding is very weak, packing effects probably play a role in determining the preferred type of secondary intermolecular bonds. From the table we can see that there is a trend towards increasing linearity of the C(aryl)–Te···S,X, C three-center system with increasing strength of the secondary bonding.

The lone pair of electrons on Te^{IV}. It is difficult to assess the stereochemical role of the lone pair in **1** and its analogs of the type [ArTe(L)$_2$X]. Without the secondary bonds, the lone pair of electrons would presumably occupy the vacant axial position in the pentagonal bipyramidal structure. However, in this position, the lone pair will screen the electronegative sulfur or halogen atom on a neighbouring molecule from the residual positive change on tellurium and thus prevent formation of the secondary interaction in the axial direction. Thus the lone pair is either stereochemically inert or it occupies a position roughly *trans* to the Te–C(aryl) bond, but located well to the side of the Te···S(X) secondary bond. The most likely direction is away from the bend in the C(aryl)–Te···S(X) system, which varies from 161.8 to 176.8 in these complexes.

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