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OCTAHEDRAL COORDINATION COMPLEXES OF TELLURIUM TETRACHLORIDE

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Abstract—The reaction between $TeCl_4$ and two equivalents of $OPPh_3$ affords crystals of the coordination complex $[TeCl_4(OPPh_3)_2]$, which has been characterized by X-ray crystallography. The coordination geometry around the tellurium centre is close to regular octahedral, with little evidence of any lone pair stereochemical activity, and the oxygen donor atoms are *cis*. A similar reaction involving the chelating ligand $dppmS_2$ $[Ph_2P(S)CH_2P(S)Ph_2]$ afforded the complex $[TeCl_4(dppmS_2)]$, which was also characterized by X-ray crystallography and found to be similar in most respects to the $OPPh_3$ complex. However, large thermal ellipsoids associated with the two chlorines *trans* to the sulphur atoms are interpreted in terms of the onset of lone pair stereochemical activity. Attempted preparations of a 4-picoline adduct of $TeCl_4$ and an $SPPh_3$ adduct of $SeCl_4$ resulted in the complexes [4-picolinium]$_2[TeCl_6]$ and $[Ph_3PSH]_2[Se_2Cl_6]$ respectively, both of which were characterized by X-ray crystallography.

In a series of recent papers we have described the results of structural studies for a range of cationic, neutral and anionic coordination complexes of Sb^{III} and Bi^{III} halides;[1-7] in particular, we have been interested in octahedral complexes and the extent to which the lone pair of electrons is stereochemically active as judged by observed distortions from an idealized or regular geometry. One class of compound which we have considered in some detail may be represented by the general formula $[EX_4(L)_2]^-$, where E = Sb or Bi, X = halide and L is a neutral two-electron donor ligand,[3,7] examples being $[H(py)_2][SbI_4(dmpe)]$ (**1**)[3] (py = pyridine, dmpe = 1,2-dimethylphosphinoethane) and $[Ph_4P][BiI_4(PMe_2Ph)_2]$ (**2**).[7] In both **1** and **2**, the ligands (L) are *cis* (constrained as such in **1** because of the chelating nature of dmpe) and the observed distortions from an idealized octahedral geometry have been rationalized both in terms of a lone pair localization along or towards one edge of the coordination octahedron and in terms of a reaction coordinate analysis, points to which we will refer in more detail later.

In order to broaden the scope of $[EX_4(L)_2]$ complexes (hereafter type **A**) studied, we turned our attention to the isoelectronic neutral Te^{IV} species, previous structurally characterized examples of which are rare. The first such complexes reported were $[TeX_4(tmt)_2]$ (**3**: X = Cl; **4**: X = Br; tmt = tetramethylthiourea), described by Husebye and George,[8,9] in which the thiourea ligands are *trans*, and the only subsequent examples of which we are aware are $[TeCl_4(L)_2]$ (**5**: L = benzothiazolethione-*S*;[10] **6**: L = benzimidazolethione-*S*[11]), in which the sulphur donor ligands are also

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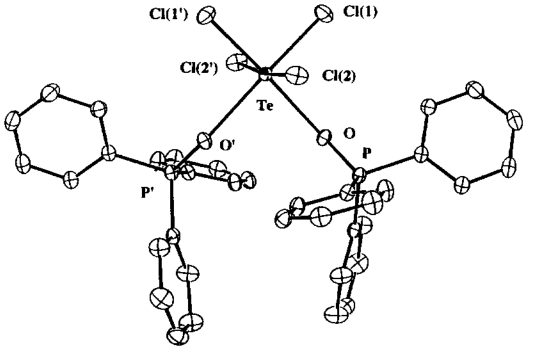


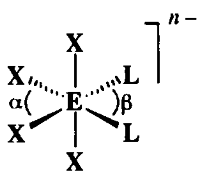
Fig. 1. The molecular structure of **7** showing the atom numbering scheme. Thermal ellipsoids are drawn at the 20% level. Primed atoms are related to unprimed atoms by the symmetry operation $(-x, y, 1/2-z)$.

trans. Herein, we describe our own results in this area and comment in general on structures of the type $[EX_4(L)_2]^{n-}$ (E = Sb, Bi, $n = 1$; E = Te, $n = 0$).

RESULTS AND DISCUSSION

The reaction between $TeCl_4$ and two equivalents of $OPPh_3$ afforded, after work-up and crystallization, yellow crystals of the complex $[TeCl_4(OPPh_3)_2]$ (**7**), the structure of which was established by X-ray crystallography. A view of the molecular structure is shown in Fig. 1, with selected bond lengths and angles given in Table 1. The coordination geometry around the tellurium centre in **7** is octahedral with *cis* $OPPh_3$ ligands (the molecule resides on a crystallographic two-fold axis). Furthermore, it is clear from a consideration of the bond angles subtended at the tellurium centre that the coordination geometry is close to that of a regular octahedron, the only significant deviation being associated with the two axial chlorines Cl(2) and Cl(2′) [defining the Cl(1), Cl(1′), O(1), O(1′) plane as the equatorial plane] such that these are tipped away from the bulky $OPPh_3$ ligands. The stereochemical influence of the Te^{IV} lone pair is therefore negligible, at least as far as any angular distortions are concerned. If we consider the bond lengths, the equatorial Te—Cl distances [Te—Cl(1) 2.373(1)] are similar to but slightly shorter than the corresponding axial Te—Cl bonds [Te—Cl(2) 2.488(1) Å], both of which may be compared with a value for the terminal Te—Cl bonds in tetrameric $TeCl_4$ of 2.31 Å; the Te—O bonds [Te—O 2.466(3) Å] are intermediate in length and indicative of a significant Te—O interaction.

If we compare the structure of **7** with the antimony and bismuth complexes **1** and **2** described in refs 3 and 7, any angular distortion as a result of the presence of the lone pair is clearly much less. Moreover, in terms of the double nucleophilic substitution reaction coordinate analysis, described in ref. 7, in which the two equatorial iodines (in general, halides) are substituted, as iodide (halide), by the two ligands (L), we may identify the structure of **7** as being close to the symmetrical intermediate **B** shown below (and in Scheme 1 in ref. 7), in which both the iodines (halides) and the ligands are substantially bonded to the element (E) centre with little distortion as a result of the lone pair. Thus, at one extreme of the reaction, the equatorial halides are becoming substituted as evidenced by the fact that the angle α is $>90°$ and the equatorial E—X bonds are long, whereas at the other extreme, the angle β is $>90°$ with long E—L bonds.



B

X = halide; E = Sb, Bi, $n = 1$; E = Te, $n = 0$

Table 1. Selected bond lengths (Å) and angles (°) for **7**[a]

Te—Cl(1)	2.373(1)	Te—Cl(2)	2.488(1)
Te—O	2.466(3)	P—O	1.505(3)
Cl(1)—Te—Cl(1′)	92.4(1)	Cl(1)—Te—Cl(2)	88.3(1)
Cl(1)—Te—Cl(2′)	87.0(1)	Cl(1)—Te—O	90.5(1)
Cl(1)—Te—O′	175.3(1)	Cl(2)—Te—Cl(2′)	173.1(1)
Cl(2)—Te—O	89.5(1)	Cl(2)—Te—O′	95.5(1)
O—Te—O′	86.7(2)	Te—O—P	142.4(2)

[a] Primed atoms are related to unprimed atoms by the symmetry operation $(-x, y, 1/2-z)$.

Comparison with the structures of **3** and **4** is also interesting. The structures of **3** and **4** originally described in ref. 8 also have geometries close to regular octahedral, but in contrast to **7** are centrosymmetric and thus have a *trans* geometry with respect to the tmt ligands. Interestingly, crystals of **3** were subsequently re-examined several years later[9] and found to have undergone a structural change, from orthorhombic to monoclinic, resulting in a noticeable angular distortion at the tellurium centre, as illustrated in Scheme 1. The widening of one of the S—Te—Cl angles was also associated with a lengthening of the corresponding Te—S and Te—Cl bonds, and the suggestion was made that the lone pair was becoming localized along the octahedral edge associated with the long Te—Cl and Te—S bonds, i.e. the Cl···S edge. In terms of any reaction coordinate analysis, this is equivalent to a complex $[TeCl_4(tmt)_2]$ transforming to a $[TeCl_3(tmt)]^+$ cation with a substituted chloride anion and neutral tmt ligand.

The structures of **5**[10] and **6**[11] show no significant deviations from regular octahedral geometry and also have *trans* geometries similar to **3** and **4** but in contrast to **7** which is, therefore, the first example of a type **A** tellurium complex with *cis* ligands. The factors affecting whether a *cis* or *trans* configuration is adopted in structures of this type are not clear, although we note that in a range of antimony and bismuth complexes described and referenced in refs 1–7, there are no examples where two ligands occur *trans* to each other. Some calculations on model compounds would be useful here, as we have also suggested in relation to the occurrence of *cis* and *trans* isomers in the related $[EX_4(L)_2]^{n-}$ compounds, where E is an element from group 13 or 14 (E = Ga, In, $n = 1$; E = Ge, Sn, $n = 0$) and no lone pair is present.[12]

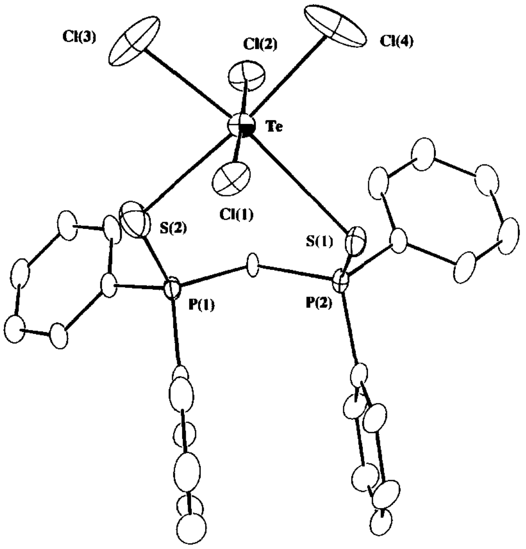
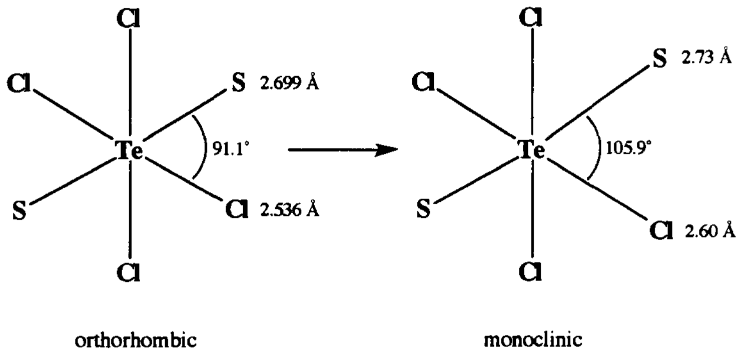


Fig. 2. The molecular structure of **8** showing the atom numbering scheme. Thermal ellipsoids are drawn at the 20% level.

Another example of a tellurium complex of type **A** was obtained from the reaction between $TeCl_4$ and the diphosphine–disulphide ligand $Ph_2P(S)CH_2P(S)Ph_2$ (hereafter $dppmS_2$), which afforded yellow crystals of $[TeCl_4(dppmS_2)]$ (**8**). The structure was established by X-ray crystallography, the results of which are shown in Fig. 2, with selected bond lengths and angles given in Table 2. The coordination geometry around the tellurium centre is very similar to that in **7**, the *cis* ligand configuration being constrained in this instance by the chelating nature of the ligand, with no angles deviating from idealized values by more than a few degrees. Also as with **7**, the axial Te—Cl distances (av. 2.501 Å) are longer than the equatorial Te—Cl distances (av. 2.374 Å), although the $dppmS_2$ ligand is somewhat asymmetrically bound, with Te—S distances of 2.891(3) and 2.633(4) Å; there is probably little significance in this, although the longer Te—S(1) distance is associated with a slightly shorter *trans* Te—Cl bond [Te—Cl(3) 2.362(4) vs Te—Cl(4) 2.386(4) Å].

The most notable feature concerning the structure of **8** is the thermal ellipsoids associated with



Scheme 1.

Table 2. Selected bond lengths (Å) and angles (°) for **8**

Te—Cl(1)	2.466(3)	Te—Cl(2)	2.537(3)
Te—Cl(3)	2.362(4)	Te—Cl(4)	2.386(4)
Te—S(1)	2.891(3)	Te—S(2)	2.633(4)
S(1)—P(2)	1.984(4)	S(2)—P(1)	1.950(4)
Cl(1)—Te—Cl(2)	178.2(2)	Cl(1)—Te—Cl(3)	89.6(2)
Cl(1)—Te—Cl(4)	91.2(2)	Cl(1)—Te—S(1)	83.5(1)
Cl(1)—Te—S(2)	87.6(2)	Cl(2)—Te—Cl(3)	89.1(2)
Cl(2)—Te—Cl(4)	90.0(2)	Cl(2)—Te—S(1)	97.7(1)
Cl(2)—Te—S(2)	91.1(2)	Cl(3)—Te—Cl(4)	93.3(3)
Cl(3)—Te—S(1)	170.7(2)	Cl(3)—Te—S(2)	81.6(2)
Cl(4)—Te—S(1)	93.2(2)	Cl(4)—Te—S(2)	174.7(2)
S(1)—Te—S(2)	91.8(1)	Te—S(1)—P(2)	109.3(2)
Te—S(2)—P(1)	111.7(2)		

the chlorines Cl(3) and Cl(4). It is clear from Fig. 2 that these are considerably larger than those of the other elements in the primary tellurium coordination sphere and, furthermore, that the major axis of the ellipsoids lie in the equatorial plane, i.e. the plane defined by the atoms Te, S(1), S(2), Cl(3) and Cl(4). We may assume that this feature is associated with a low energy bending vibration for the Cl(3)—Te—Cl(4) unit, which is interesting in view of the nature of geometry distortions associated with lone pair stereochemical activity.* As discussed in ref. 6, distortions from idealized O_h symmetry, for systems with the electron count relevant here, are expected to be of T_{1u} symmetry, which may be manifest either as an asymmetric lengthening and shortening of two *trans* bonds (C_{4v}), an opening of the angle between and/or lengthening of two *cis* bonds (C_{2v}) or an opening of the angle between and/or lengthening of three *fac* bonds (C_{3v}). These are associated with lone pair localizations towards a vertex, edge or face of the octahedron, respectively. In the case of the second example where an edge localization is important, we may consider the trend from a regular octahedron to one in which there is a considerable widening of one bond angle and lengthening of the corresponding bonds (as found in **1** for example) as the result of a progressive second order Jahn–Teller distortion. In molecular orbital terms, the magnitude of any distortion will depend on the extent of orbital mixing in the O_h reference structure (usually between the a_{1g} HOMO and the t_{1u} LUMO), the greater the mixing, the greater the distortion. At an intermediate stage of mixing, the effect is not sufficient to result in a static ground state distortion, but can result instead in a low energy bending mode of T_{1u} symmetry associated with a pair of *cis* bonds. This may well be the origin of the large thermal ellipsoids for Cl(3) and Cl(4) in **8** such that, although the actual symmetry is reduced here from O_h to C_{2v} (idealized), the lone pair is starting to become localized in the region of the Cl(3)···Cl(4) edge.

Examples of dppmS_2 as a ligand are not common and **8** is the first example for a *p*-block element complex. Crystallographically characterized examples from *d*-block chemistry are found in refs 13–15.

In attempting to prepare a bis 4-picoline adduct of $TeCl_4$, the only crystals of X-ray quality which we were able to isolate were of a presumed hydrolysis product, [4-picolinium]$_2$[$TeCl_6$] (**9**), containing the $[TeCl_6]^{2-}$ dianion and picolinium cations. The structure was determined by X-ray crystallography and a view of the $[TeCl_6]^{2-}$ anion is shown in Fig. 3; selected bond lengths and angles are given in Table 3. The dianion resides on a crystallographic centre of inversion and, as is evident from Table 3, is very close to a regular octahedral geometry. A considerable number of structures are known in which the $[TeCl_6]^{2-}$ dianion is present and, in the majority of cases, undistorted or only very slightly distorted structures are observed. In fact, for anions which reside on a crystallographic centre of inversion, as in **9**, no significant distortions are observed, but for anions in crystallographically general positions, C_{2v} distortions have been found in some cases. A number of examples of $[TeCl_6]^{2-}$ structures

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* The possibility that the origin of the elongated thermal ellipsoids associated with Cl(3) and Cl(4) is an artefact of the structure refinement is considered unlikely since it is only these ellipsoids that are unusual.

Table 3. Selected bond lengths (Å) and angles (°) for **9**[a]

Te—Cl(1)	2.560(1)	Te—Cl(2)	2.524(1)
Te—Cl(3)	2.530(1)		
Cl(1)—Te—Cl(1′)	180.0	Cl(1)—Te—Cl(2)	90.9(1)
Cl(1)—Te—Cl(2′)	89.1(1)	Cl(1)—Te—Cl(3)	89.2(1)
Cl(1)—Te—Cl(3′)	90.8(1)	Cl(2)—Te—Cl(2′)	180.0
Cl(2)—Te—Cl(3)	90.5(1)	Cl(2)—Te—Cl(3′)	89.5(1)
		Cl(3)—Te—Cl(3′)	180.0

[a] Primed atoms are related to unprimed atoms by the symmetry operation $(-x, -y, -z)$.

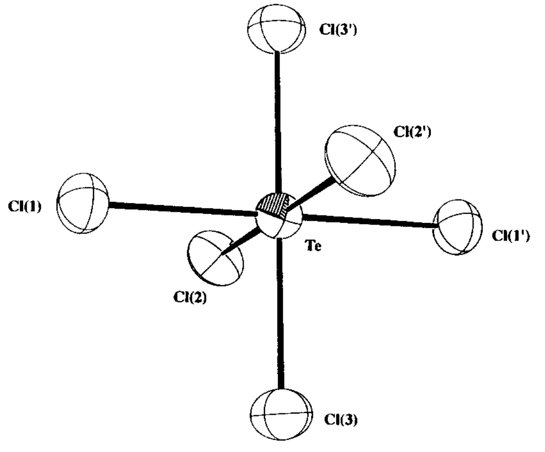

Fig. 3. The molecular structure of the $[TeCl_6]^{2-}$ anion in **9** showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% level. Primed atoms are related to unprimed atoms by the symmetry operation $(-x, -y, -z)$.

and a discussion of the factors affecting any distortions have been presented by Abriel and coworkers.[16]*

In seeking to extend this work to analogous selenium complexes, we carried out reactions between $SeCl_4$ and both $OPPh_3$ and $SPPh_3$. The results of the former are described in the Experimental section dealing with the preparation of **7**. Analytical data were consistent with the formulation $[SeCl_4(OPPh_3)_2]$, as was a unit cell volume determination on an apparently well formed crystal, but a poor quality data set was insufficient for a full structure determination to be carried out. The reaction between $SeCl_4$ and two equivalents of $SPPh_3$ afforded a small number of crystals of a compound characterized as $[Ph_3PSH]_2[Se_2Cl_6]$ (**10**) by X-ray crystallography. A view of the $[Se_2Cl_6]^{2-}$ dianion is shown in Fig. 4, with selected bond lengths and angles given in Table 4. Clearly, a degree of hydrolysis and reduction from Se^{IV} to Se^{II} has resulted in the formation of **10** and we will do little here except to report the results of the structure. It is worth reporting since only three previous examples of this dinuclear Se^{II} anion have been reported, namely $[Se_3N_3]_2[Se_2Cl_6]$ (**11**),[17] $[Ph_4P]_2[Se_2Cl_6]$ (**12**)[18] and $[Me_3SiN(H)PMe_3]_2[Se_2Cl_6]$ (**13**).[19] The structure of the $[Se_2Cl_6]^{2-}$ dianion in **10** is planar (crystallographically centrosymmetric), with each selenium in a square planar coordination environment. The terminal Se—Cl bond lengths are 2.288(2) and 2.238(2) Å, whereas the bridging chlorines have somewhat longer bonds and are slightly asymmetrically bonded [Se—Cl(1) 2.631(2), Se—Cl(1′) 2.833, difference 0.202 Å]. The metric parameters for the anions in **11**–**13** are similar in all respects and all are analogous to the solid-state structure of the isoelectronic I_2Cl_6. In all cases, the angles at each selenium (iodine) are such that the terminal

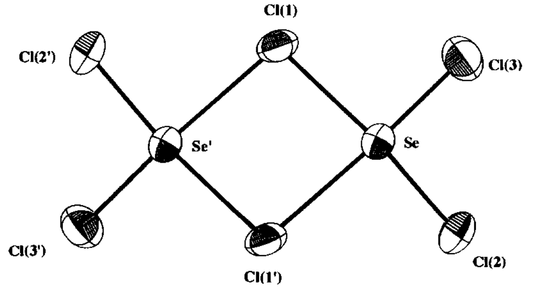

Fig. 4. The molecular structure of the $[Se_2Cl_6]^{2-}$ anion in **10** showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% level. Primed atoms are related to unprimed atoms by the symmetry operation $(2-x, -y, -z)$.

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* Distortions from regular octahedral geometry in $[TeCl_6]^{2-}$ dianions have sometimes been associated with hydrogen bonding interactions involving the chlorine atoms.[16] In **9**, however, there are no unusually short N—H···Cl distances; the shortest H···Cl distance is 2.57 Å.

Table 4. Selected bond lengths (Å) and angles (°) for **10**[a]

Se—Cl(1)	2.631(2)	Se—Cl(1′)	2.833(2)
Se—Cl(2)	2.288(2)	Se—Cl(3)	2.238(2)
Cl(1)—Se—Cl(1′)	84.7(1)	Cl(1)—Se—Cl(2)	174.2(1)
Cl(1)—Se—Cl(3)	92.1(1)	Cl(1)—Se—Cl(2′)	89.5(1)
Cl(1)—Se—Cl(3′)	176.2(1)	Cl(2)—Se—Cl(3)	93.7(1)
Se—Cl(1)—Se′	95.3(1)		

[a] Primed atoms are related to unprimed atoms by the symmetry operation $(2-x, -y, -z)$.

chlorines subtend an angle of >90°, whilst the bridging chlorines subtend an angle of <90°.

EXPERIMENTAL

General considerations

All experiments were performed under an atmosphere of dry, oxygen-free dinitrogen using standard Schlenk techniques. All solvents were dried and distilled over appropriate drying agents immediately prior to use. Microanalytical data were obtained at the University of Newcastle. $TeCl_4$, $SeCl_4$ and other reagents were procured commercially and used without further purification. The compound dppm S_2 was prepared from dppm ($Ph_2PCH_2PPh_2$) and S_8 in toluene as a yellow solid whereas dppm O_2 was prepared from dppm and a 3% solution of H_2O_2 in acetone.

Preparations

$[TeCl_4(OPPh_3)_2]$ (**7**). A sample of $TeCl_4$ (0.182 g, 0.676 mmol) was dissolved in thf (6 cm^3), affording a pale yellow solution to which a solution of $OPPh_3$ (0.376 g, 1.351 mmol) in thf (6 cm^3) was added at room temperature, resulting in a darkening of the yellow colour. After stirring for 30 min, hexane (25 cm^3) was added as an overlayer and solvent diffusion at room temperature over a period of days afforded yellow crystals of **7** (0.360 g, 65%), one of which was used for X-ray crystallography. Found C, 52.9; H, 3.5. $C_{36}H_{30}Cl_4O_2P_2Te$ requires C, 52.4; H, 3.7%.

The analogous yellow crystalline selenium compound $[SeCl_4(OPPh_3)_2]$ was prepared similarly. Found C, 55.6; H, 3.9. $C_{36}H_{30}Cl_4O_2P_2Se$ requires C, 55.6; H, 3.9%. An attempted X-ray crystallographic study was thwarted as a result of a poorly diffracting crystal, although a unit cell volume determination was consistent with the anticipated formula.

$[TeCl_4(dppmS_2)]$ (**8**). A sample of $TeCl_4$ (0.100 g, 0.371 mmol) was dissolved in thf (6 cm^3), affording a pale yellow solution to which a solution of $dppmS_2$ (0.166 g, 0.371 mmol) in thf (6 cm^3) was added at room temperature, resulting in a darkening of the yellow colour. After stirring for 30 min, hexane (25 cm^3) was added as an overlayer and solvent diffusion at room temperature over a period of days afforded yellow crystals of **8** (0.188 g, 71%), although these were not suitable for X-ray crystallography. X-ray quality crystals were obtained by recrystallization from MeCN–Et_2O mixtures and these were found to contain MeCN molecules of crystallization. Found: C, 41.9; H, 3.2; N, 1.7. $C_{27}H_{25}Cl_4NP_2S_2Te$ requires C, 42.8; H, 3.3; N, 1.9%.

The analogous yellow crystalline $dppmO_2$ compound $[TeCl_4(dppmO_2)]$ was prepared similarly. Found: C, 45.9; H, 3.6. $C_{25}H_{22}Cl_4O_2P_2Te$ requires C, 46.0; H, 4.0%. An attempted X-ray crystallographic study was thwarted as a result of a poorly diffracting crystal.

$[C_6NH_8]_2[TeCl_6]$ (**9**). A sample of $TeCl_4$ (0.277 g, 1.028 mmol) was dissolved in thf (6 cm^3), affording a pale yellow solution to which a sample of 4-picoline (0.2 cm^3, 2.055 mmol) was added at room temperature, resulting in a darkening of the yellow colour. After stirring for 30 min, hexane (25 cm^3) was added as an overlayer and solvent diffusion at room temperature over a period of days afforded a mixture of a brown solid and a yellow crystalline solid. The yellow crystals were dissolved in CH_3CN (8 cm^3), affording a yellow solution to which ether (20 cm^3) was added as an overlayer. Solvent diffusion over a period of a few days resulted in yellow crystals of **9** (0.036 g, 10%), one of which was used for X-ray crystallography. Found C, 27.4; H, 2.9; N, 5.2. $C_{12}H_{16}Cl_6N_2Te$ requires C, 27.7; H, 3.1; N, 5.3%.

$[Ph_3PSH]_2[Se_2Cl_6]$ (**10**). A sample of $SeCl_4$ (0.150 g, 0.679 mmol) was dissolved in thf (3 cm^3), affording a pale yellow solution to which Ph_3PS (0.400 g, 1.359 mmol) was added as a solution in thf (5 cm^3), resulting in the immediate formation of a yellow

Table 5. Crystallographic and structure solution data for compounds 7, **8**, **9** and **10**

	7	**8**·MeCN	**9**	**10**
Compound formula	$C_{36}H_{30}Cl_4O_2P_2Te$	$C_{25}H_{22}Cl_4P_2S_2Te.C_2H_3N$	$C_{12}H_{16}Cl_6N_2Te$	$C_{36}H_{32}Cl_6P_2S_2Se_2$
M_r	826.0	759.0	528.6	961.4
Space group	$C2/c$	$P\bar{1}$	$P2_1/a$	$P2_1/n$
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
a (Å)	17.224(2)	11.552(2)	7.2489(4)	12.9932(8)
b (Å)	12.424(1)	11.731(2)	16.8886(8)	11.7125(10)
c (Å)	17.127(2)	13.670(2)	8.7900(5)	13.1654(9)
α (°)		81.66(1)		
β (°)	104.65(1)	82.74(1)	113.579(4)	92.706(5)
γ (°)		63.35(1)		
V (Å^3)	3545.9(7)	1598.4(4)	986.26(9)	2001.3(2)
θ range for cell (°)	$17.3 < \theta < 20.6$	$17.6 < \theta < 20.7$	$17.7 < \theta < 21.0$	$17.5 < \theta < 20.9$
Z	4	2	2	2
D_{calc} (g cm^{-3})	1.55	1.57	1.78	1.60
F(000)	1648	752	512	960
μ(Mo-K_α) (cm^{-1})	12.64	15.12	23.26	24.38
T (K)	298	298	298	293
Scan mode	θ–2θ	θ–2θ	θ–2θ	θ–2θ
θ range (°)	$2 < \theta < 25$	$2 < \theta < 25$	$2.4 < \theta < 25$	$2.2 < \theta < 25$
Crystal size (mm)	0.4 × 0.3 × 0.25	0.4 × 0.3 × 0.25	0.3 × 0.2 × 0.22	0.3 × 0.33 × 0.33
Range of transmission coefficients	0.83–1.07	0.68–1.38	0.79–1.23	0.83–1.17
No. of data collected	3397	5877	1928	3868
No. of unique data	3121	5615	1737	3506
hkl range	0 to 20, −14 to 0, −20 to 20	−13 to 13, −13 to 13, 0 to 15	−7 to 8, 0 to 20, −10 to 0	0 to 15, −13 to 0, −15 to 15
R_{merge}	0.025	0.021	0.026	0.018
Observability criterion	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 2\sigma(I)$
No. of data in refinement	2565	4100	1514	2291
No. of refined parameters	219	262	129	181
Final R	0.029	0.064	0.024	0.044
Final R_w	0.037	0.081	0.032	0.043
Goodness of fit, S	1.61	3.31	1.71	3.7
Largest remaining feature in electron density map (e Å^{-3})	+0.47 (max), −0.55 (min)	+1.15 (max), −1.37 (min)	+0.51 (max), −0.52 (min)	+0.44 (max), −0.53 (min)
Shift/e.s.d. in last cycle	0.09 (max), 0.006 (av.)	0.04 (max), 0.009 (av.)	0.025 (max), 0.002 (av.)	0.0018 (max), 0.0095 (av.)

crystalline solid. CH_3CN (6 cm^3) was then added and, on heating, all of the solid dissolved. Et_2O (20 cm^3) was then added as an overlayer, once the solution had cooled to room temperature, and solvent diffusion at room temperature over a period of days afforded a small crop of dark orange crystals of **10**, one of which was used for X-ray crystallography. Found C, 44.9; H, 2.9. $C_{36}H_{32}Cl_6P_2S_2Se_2$ requires C, 45.0; H, 3.4%.

X-ray crystallography

Crystallographic data and details of the data collection procedures and structure refinement for all structures are presented in Table 5. The following section deals with the structure of **7**; data for **8**, where different, are given in square brackets [ ], data for **9** in braces { }, data for **10** in double square brackets [[ ]]. Data were collected on an Enraf–Nonius Turbo-CAD4 diffractometer, running under CAD4-Express software, and with graphite monochromated X-radiation ($\lambda = 0.71069$ Å). Accurate unit cell parameters were determined by refinement of setting angles of 25 reflections. Standard reflections were measured every 2 h during data collection, and a 10% [5%] {no significant variation} [[75%]] decrease in intensities was noted and a linear correction applied [[interpolated correction]]. Corrections were applied for Lorentz-polarization and absorption (DIFABS[20]) effects. The structure was solved for the tellurium atom [Te, Cl, S and P atoms] {Te and Cl atoms} [[Se, Cl, P and S atoms]] by heavy atom methods (SHELX86[21]). Subsequent difference syntheses gave all other atomic positions [a molecule of MeCN was found in difference Fourier maps but positional parameters could not be successfully refined; in the final cycles of refinement, the positional parameters of this molecule were fixed at the positions determined from the difference map, but their isotropic thermal parameters were allowed to refine]. All non-hydrogen atoms were allowed anisotropic thermal motion [except those associated with the MeCN molecule]. Hydrogen atoms were included at calculated positions (C—H 0.96 Å), but were allowed freely refined isotropic thermal parameters. [Hydrogen atoms, apart from the MeCN, were assigned fixed isotropic thermal parameters 1.2 times that of the attached carbon atom; the phenyl groups were refined as rigid groups with idealized geometry, C—C 1.395 Å.] {Hydrogen atoms were allowed unconstrained refinement of positional and thermal parameters.} [[Hydrogen atoms were assigned fixed isotropic thermal parameters 1.2 times that of the attached carbon atom. The S—H hydrogen was neither located nor refined. The phenyl groups were refined as rigid groups with idealized geometry, C—C 1.395 Å.]] Refinement was by full matrix least-squares, with the function $\Sigma w(|F_o|-|F_c|)^2$ minimized, and with the weighting scheme $w = [\sigma^2(F_o)]^{-1}$ used and judged satisfactory. $\sigma(F_o)$ was estimated from counting statistics. Neutral atom scattering factors were taken from ref. 22 with corrections for anomalous dispersion. All calculations were carried out on a Micro VAX 3600 [[DEC alpha-3000]] computer using the Glasgow GX suite of programs[23] or SHELXS86[21] for structure solution.

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