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Synthesis and crystal structures of tellurium complexes containing imidophosphinate ligands

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The synthesis of TeL_2 complexes for a variety of imidophosphinate ligands $[R_2(E)PNP(E)R'_2]^-$ (E = S or Se) is described. The crystal structures of five examples are reported. Generally the complexes adopt square planar geometries but in one case [R = Et, R′ = OPh] two-coordinate geometry is observed. It appears that electronic effects are more important in controlling geometry than steric effects. Two examples of five-coordinate $TeL(C_6H_4OCH_3)Cl_2$ complexes have also been prepared and structurally characterised.

The coordination chemistry of $[R_2(E)PNP(E')R_2]^-$ (E = S or Se) ligands has been widely investigated and reviewed.[1–9] The first substantial investigation into the coordination chemistry of $[HN\{P(S)Ph_2\}_2]$ was reported in 1978 and since that time this ligand, in particular, has been coordinated with alkali metals and many of the transition metals[8] though, with the exception of tin, main group coordination chemistry has been largely ignored. Work in which $R_2P(E)NP(E)R_2$ systems have been complexed to tellurium containing species have yielded a few complexes with a variety of geometries around the Te centre.[10–13] It is interesting to note the ability of Te^{II} to adopt two- or four-coordinate geometries. The availability of sterically and electronically tunable S/Se donor ligands led us to investigate the coordination chemistry of a range of imidophosphinate ligands with sulfur or selenium donors with tellurium. The new compounds have been characterised spectroscopically and in several cases by X-ray crystallography.

Experimental

General

Infrared spectra were recorded from KBr discs on a Perkin-Elmer system 2000 spectrometer; ^{31}P NMR spectra on a JEOL FX90Q operating at 36.21 MHz; ^1H, ^{13}C and ^{31}P NMR spectra on Bruker instruments operating at 250, 62.9 and 101.3 MHz respectively and referenced to TMS or 85% H_3PO_4. Fast atom bombardment mass spectra were obtained by the Swansea mass spectrometery service.

Syntheses

$TeCl_3(C_6H_4OCH_3)$ and $Te(tu)_4Cl_2{\cdot}2H_2O$ were synthesised by literature methods.[14,15] The ligands, $^iPr_2P(S)NHP(S)^iPr_2$, $Et_2P(S)NHP(S)(OPh)_2$, $(C_6H_{11})_2P(S)NHP(S)(C_6H_{11})_2$, $(EtO)_2P(S)NHP(S)(OPh)_2$, $Et_2P(S)NHP(S)Ph_2$, $^iPr_2P(S)NHP(S)Ph_2$ and $^iPr_2P(Se)NHP(Se)^iPr_2$ were prepared using modifications of standard synthetic procedures.[9,16,17]

$Te[N(^iPr_2PS)_2]_2$ 1. KO^{t}Bu (0.037 g, 0.319 mmol) and $^iPr_2P(S)NHP(S)^iPr_2$ (0.1 g, 0.319 mmol) were stirred in methanol (10 ml) and $Te(tu)_4Cl_2{\cdot}2H_2O$ (0.087 g 0.160 mmol) in 5 ml of methanol was added. The yellow-orange solution was stirred for 30 min. The product, a yellow precipitate, was collected by filtration. Yield 0.115 g, 0.153 mmol, 96%. Microanalysis calculated for $C_{24}H_{56}N_2P_4S_4Te$: C 38.3; H 7.5; N 3.7. Observed: C 38.1; H 7.2; N 3.4%. ^{31}P-$\{^1H\}$ NMR ($CDCl_3$): δ 58.7. FTIR (KBr disc, cm^{-1}): ν(PNP) 1232 (s), 768 (m); ν(PS) 535 (w). FAB +ve MS: *m*/*z* 751 corresponds to $Te[N(^iPr_2PS)_2]_2$.

$Te[N(\{C_6H_{11}\}_2PS)_2]_2$ 2. KO^{t}Bu (0.037 g, 0.317 mmol) and $(C_6H_{11})_2P(S)NHP(S)(C_6H_{11})_2$ (0.15 g, 0.317 mmol) were stirred in methanol (10 ml) and $Te(tu)_4Cl_2{\cdot}2H_2O$ (0.085 g 0.159 mmol) in 5 ml of methanol was added. The yellow solution was stirred for 30 min. The product, a yellow precipitate, was collected by filtration. Yield 0.115 g, 0.108 mmol, 67%. Microanalysis calculated for $C_{48}H_{88}N_2P_4S_4Te$: C 53.8; H 8.2; N 2.6. Observed: C 53.4; H 8.4; N 2.5%. ^{31}P-$\{^1H\}$ NMR ($CDCl_3$): δ 51.9. FTIR (KBr disc, cm^{-1}): ν(PNP) 1247 (s), 746 (w); ν(PS) 549 (w). FAB +ve MS: *m*/*z* 1071 corresponds to $Te[N(\{C_6H_{11}\}_2PS)_2]_2$.

$Te[Et_2P(S)NP(S)(OPh)_2]_2$ 3. KO^{t}Bu (0.043 g, 0.388 mmol) and $Et_2P(S)NHP(S)(OPh)_2$ (0.15 g, 0.388 mmol) were stirred in methanol (10 ml) and $Te(tu)_4Cl_2{\cdot}2H_2O$ (0.104 g 0.194 mmol) in 5 ml of methanol was added. The yellow-orange solution was stirred for 2 h. The volume of solvent was reduced *in vacuo* to approximately $\frac{1}{4}$. The solution was then cooled in a freezer overnight. The product, a bright yellow precipitate, was collected by filtration. Yield 0.072 g, 0.081 mmol, 41%. Microanalysis calculated for $C_{32}H_{40}N_2P_4S_4O_4Te$: C 42.8; H 4.5; N 3.1. Observed: C 42.4; H 4.6; N 3.1%. ^{31}P-$\{^1H\}$ NMR ($CDCl_3$): δ 55.1, 43.7, $^2J(^{31}P–^{31}P)$ unresolved. FTIR (KBr disc, cm^{-1}): ν(PNP) 1187 (s), 773 (m); ν(PS) 665 (m), 581 (m). FAB +ve MS: *m*/*z* 897 corresponds to $Te[Et_2P(S)NP(S)(OPh)_2]_2$.

$Te[^iPr_2P(S)NP(S)Ph_2]_2$ 4. KO^{t}Bu (0.044 g, 0.392 mmol) and $Ph_2P(S)NHP(S)^iPr_2$ (0.15 g, 0.392 mmol) were stirred in methanol (10 ml) and $Te(tu)_4Cl_2{\cdot}2H_2O$ (0.106 g 0.196 mmol) in 5 ml of methanol was added. The yellow-orange solution was stirred for 2 h. The volume of solvent was reduced *in vacuo* to approximately $\frac{1}{4}$. The solution was then cooled in a freezer overnight. The product, a yellow precipitate, was collected by filtration. Yield 0.085 g, 0.096 mmol, 49%. Microanalysis calculated for $C_{36}H_{48}N_2P_4S_4Te$: C 48.6; H 5.4; N 3.1. Observed: C 48.1; H 5.3; N 3.2%. Two isomers present. ^{31}P-$\{^1H\}$ NMR ($CDCl_3$): δ 64.3, 63.7, 32.7, 31.8, $^2J(^{31}P–^{31}P)$ 22.5 Hz. FTIR (KBr disc, cm^{-1}): ν(PNP) 1232 (s), 777 (m); ν(PS) 520 (s). FAB +ve MS: *m*/*z* 889 corresponds to $Te[^iPr_2P(S)NP(S)Ph_2]_2$.

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Te[$Et_2P(S)NP(S)Ph_2$]$_2$ 5. KO^{t}Bu (0.040 g, 0.425 mmol) and $Et_2P(S)NHP(S)Ph_2$ (0.15 g, 0.425 mmol) were stirred in methanol (10 ml) and $Te(tu)_4Cl_2\cdot 2H_2O$ (0.114 g, 0.212 mmol) in 5 ml of methanol was added. The yellow solution was stirred for 2 h. The volume of solvent was reduced *in vacuo* to approximately $\frac{1}{4}$. The solution was then cooled in a freezer overnight. The product, a yellow precipitate, was collected by filtration. Yield 0.095 g, 0.114 mmol, 65%. Microanalysis calculated for $C_{32}H_{40}N_2P_4S_4Te$: C 46.2; H 4.8; N 3.3. Observed: C 45.7; H 4.9; N 2.8%. Two isomers present. ^{31}P-{^1H} NMR ($CDCl_3$): δ 53.7, 53.3, 33.9, 32.7, $^2J(^{31}P–^{31}P)$ unresolved. FTIR (KBr disc, cm^{-1}): ν(PNP) 1250 (s), 753 (m); ν(PS) 653 (w), 558 (w). FAB +ve MS: *m*/*z* 834 corresponds to Te[$Et_2P(S)NP(S)Ph_2$]$_2$.

Te[$(EtO)_2P(S)NP(S)(OPh)_2$]$_2$ 6. KO^{t}Bu (0.028 g, 0.240 mmol) and $(EtO)_2P(S)NHP(S)(OPh)_2$ (0.10 g, 0.239 mmol) were stirred in methanol (10 ml) and $Te(tu)_4Cl_2\cdot 2H_2O$ (0.065 g 0.120 mmol) in 5 ml of methanol was added. The yellow-orange solution was stirred for 2 h. The volume of solvent was reduced *in vacuo* to approximately 1/2. The product, a bright yellow precipitate, was collected by filtration. Yield 0.082 g, 0.085 mmol, 72%. Microanalysis calculated for $C_{32}H_{40}N_2P_4S_4O_8Te$: C 39.9; H 4.2; N 2.9. Observed: C 40.0; H 4.3; N 1.8%. ^{31}P-{^1H} NMR ($CDCl_3$): δ 65.0, 43.0, $^2J(^{31}P–^{31}P)$ unresolved. FTIR (KBr disc, cm^{-1}): ν(PNP) 1184 (s), 768 (m); ν(PS) 553 (w). FAB +ve MS: *m*/*z* 542 corresponds to Te$(EtO)_2P(S)NP(S)(OPh)_2$.

Te[N(^{i}Pr_2PSe)$_2$]$_2$ 7. KO^{t}Bu (0.043 g, 0.369 mmol) and ^{i}Pr_2-P(Se)NHP(Se)^iPr_2 (0.15 g, 0.369 mmol) were stirred in methanol (10 ml) and $Te(tu)_4Cl_2\cdot 2H_2O$ (0.099 g 0.185 mmol) in 5 ml of methanol was added. The yellow-orange solution was stirred for 3 h. The volume of solvent was reduced *in vacuo* to approximately $\frac{1}{4}$. The product, a yellow precipitate, was collected by filtration. Yield 0.107 g, 0.114 mmol, 62%. Microanalysis calculated for $C_{24}H_{56}N_2P_4Se_4Te$: C 30.7; H 5.9; N 2.9. Observed: C 30.3; H 5.9; N 2.9%. ^{31}P-{^1H} NMR ($CDCl_3$): δ 58.7, $^1J(^{77}Se–^{31}P)$ 528 Hz. FTIR (KBr disc, cm^{-1}): ν(PNP) 1231 (s), 761 (w); ν(PSe) 484 (s). FAB +ve MS: *m*/*z* 534 corresponds to TeN(^{i}Pr_2PS)$_2$.

Te($C_6H_4OCH_3$)[N(^{i}Pr_2PS)$_2$]Cl_2 8. KO^{t}Bu (0.054 g, 0.482 mmol) and ^{i}$Pr_2P(S)NHP(S)^iPr_2$ (0.15 g, 0.480 mmol) were stirred in methanol (10 ml) and $TeCl_3(C_6H_4OCH_3)$ (0.162 g 0.480 mmol) in 3 ml of methanol was added. The yellow solution was stirred for 30 min. The product, a bright yellow precipitate, was collected by filtration. Yield 0.215 g, 0.348 mmol, 73%. Microanalysis calculated for $C_{19}H_{35}NP_2S_2TeCl_2O$: C 36.9; H 5.8; N 2.2. Observed: C 36.7; H 5.4; N 1.3%. ^{31}P-{^1H} NMR ($CDCl_3$): δ 62.0. FTIR (KBr disc, cm^{-1}): ν(PNP) 1236 (s), 761 (m); ν(PS) 523 (w), ν(TeS) 325 (w). FAB +ve MS: *m*/*z* 584 corresponds to $CH_3OC_6H_4Te[N(^iPr_2PS)_2](Cl)_2 - Cl$.

Te($C_6H_4OCH_3$)[^{i}Pr_2P(S)NP(S)Ph_2](Cl)$_2$ 9. KO^{t}Bu (0.044 g, 0.393 mmol) and ^{i}$Pr_2P(S)NHP(S)Ph_2$ (0.15 g, 0.393 mmol) were stirred in methanol (5 ml) and $TeCl_3(C_6H_4OCH_3)$ (0.134 g, 0.393 mmol) in 3 ml of methanol was added. The yellow solution was stirred for 20 min. The product, a yellow precipitate, was collected by filtration. Yield 0.085 g, 0.124 mmol, 32%. Microanalysis calculated for $C_{25}H_{31}NP_2S_2TeCl_2O$: C 43.7; H 4.5; N 2.0. Observed: C 42.5; H 4.5; N 1.8%. ^{31}P-{^1H} NMR ($CDCl_3$): δ 69.2, 34.5, $^2J(^{31}P–^{31}P)$ 24.9 Hz. FTIR (KBr disc, cm^{-1}): ν(PNP) 1255 (s), 780 (w); ν(PS) 569 (m), ν(TeS) 379 (w). FAB +ve MS: *m*/*z* 651 corresponds to $CH_3OC_6H_4Te[^iPr_2P(S)NP(S)Ph_2]$-$(Cl)_2 - Cl$.

Crystallography

Details of the data collections and refinements are summarised in Table 1. Data were collected at room temperature using Mo radiation with a SMART system. Intensities were corrected

Table 1 Details of the crystal data and refinements

Compound	**1**	**2**·1.5$CHCl_3$	**3**	**4**	**7**	**8**	**9**
Empirical formula	$C_{24}H_{56}N_2P_4S_4Te$	$C_{49.5}H_{89.5}Cl_{4.5}N_2P_4S_4Te$	$C_{32}H_{40}N_2O_4P_4S_4Te$	$C_{36}H_{48}N_2P_4S_4Te$	$C_{24}H_{56}N_2P_4Se_4Te$	$C_{19}H_{35}Cl_2NOP_2S_2Te$	$C_{25}H_{31}Cl_2NOP_2S_2Te$
Formula weight	752.43	1251.998	896.38	888.48	940.03	618.04	686.07
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P\bar{1}$	$C2/c$	$P2_1/c$	$P2_1/c$	$P2_1$	$P2_12_12_1$
a/Å	10.4727(2)	10.4307(3)	22.7944(11)	9.7171(7)	10.4104(7)	9.1666(3)	13.4268(2)
b/Å	14.5022(3)	12.75430(10)	11.8286(5)	11.9430(8)	14.7541(11)	11.1730(4)	14.0714(4)
c/Å	11.9760(2)	14.4033(3)	30.2546(14)	18.4530(11)	12.1815(8)	13.5041(4)	15.05035(4)
α/°		114.9400(10)					
β/°	100.1450(10)	108.6960(10)	103.0180(10)	104.162(2)	98.739(2)	100.1440(10)	
γ/°		89.7000(10)					
V/Å^3	1790.44(6)	1623.86(6)	7957.8(6)	2076.4(2)	1849.3(2)	1361.45(8)	2929.14(12)
Z	2	1	8	2	2	2	4
D_c/g cm^{-3}	1.396	1.278	1.498	1.421	1.688	1.508	1.556
μ/mm^{-1}	1.260	0.900	1.157	1.099	4.931	1.571	1.469
Measured reflections	7664	4623	5721	2974	2660	3692	4216
Independent observed, reflections ($I > 2.0\sigma(I)$)	2332	3454	3895	1530	1955	3599	2666
Final *R*1/w*R*2	0.0368/0.0882	0.0545/0.1305	0.0323/0.0599	0.0474/0.0765	0.0249/0.0425	0.0232/0.0599	0.0573/0.1119

Table 2 Selected bond lengths (Å) and angles (°) for **1**, **2**, **3**, **4** and **7**

	1	**2**	**3**	**4**	**7** (S = Se)
Te(1)–S(1)	2.6730(6)	2.6971(12)	2.5267(11)	2.678(2)	2.8152(4)
Te(1)–S(2)	2.6978(6)	2.6820(13)	2.91	2.684(2)	2.7941(4)
Te(1)–S(3)			2.5131(12)		
Te(1)–S(4)			2.90		
S(1)–P(1)	2.0354(8)	2.046(2)	2.046(2)	2.022(2)	2.1944(10)
S(3)–P(3)			2.053(2)		
P(1)–N(1)	1.583(2)	1.584(4)	1.580(3)	1.589(5)	1.579(3)
P(3)–N(3)			1.567(3)		
N(1)–P(2)	1.584(2)	1.594(4)	1.558(3)	1.593(5)	1.588(3)
N(3)–P(4)			1.576(3)		
P(2)–S(2)	2.0363(8)	2.045(2)	1.962(2)	2.032(2)	2.1888(11)
P(4)–S(4)			1.968(2)		
S(1)–Te(1)–S(2)	87.21(2)	90.67(4)		85.69(6)	87.159(12)
Te(1)–S(1)–P(1)	100.84(3)	101.11(6)	103.7(5)	94.72(9)	98.15(3)
S(1)–P(1)–N(1)	118.66(7)	117.7(2)	117.57(12)	119.8(2)	118.98(12)
P(1)–N(1)–P(2)	142.93(12)	145.3(3)	142.2(2)	138.8(8)	145.1(2)
N(1)–P(2)–S(2)	117.04(7)	118.7(2)	120.98(13)	118.9(2)	116.90(12)
P(2)–S(2)–Te(1)	96.27(3)	102.98(6)		101.51(9)	93.22(3)

for Lorentz-polarisation and for absorption. The structures were solved by the heavy atom method or by direct methods. The positions of the hydrogen atoms were idealised. Refinements were by full-matrix least squares based on F^2 using SHELXTL.[18] The chirality of **9** was established by the Flack parameter (−0.06(4)).

CCDC reference number 186/1793.

See http://www.rsc.org/suppdata/dt/a9/a907336a/ for crystallographic files in .cif format.

Results and discussion

$Te(tu)_4Cl_2$ was reacted in a 1:2 molar ratio with a number of imidophosphinates $R_2P(E)NHP(E)R'_2$, to give the desired bis(imidophosphinate) complexes **1**–**7** (eqn. (1)). Reactions were

$$Te(tu)_4Cl_2{\cdot}2H_2O + 2HL \xrightarrow[MeOH]{2K^tBuO} TeL_2 \qquad (1)$$

carried out in methanol with K^{t}BuO used as the base to deprotonate the ligand.

The desired products were deposited as yellow solids after refrigeration overnight. Significant yields (41–96%) of high purity materials were isolated by this route. The materials are stable in the solid state when stored under argon with the exclusion of daylight. Satisfactory elemental analyses, IR spectra, ^{1}H and ^{31}P NMR spectra and FAB +ve mass spectra were obtained for each complex.

The ^{31}P NMR spectra of **1** and **2** contain a single peak (as predicted for a symmetric ligand) at δ 58.7 and 51.9 respectively with the characteristic downfield shift of *ca.* 30 ppm which results from deprotonation of the free ligand.[7] Their IR spectra are also indicative of a complex in which the ligand is deprotonated and consistent with delocalisation around an SNPNSM ring; *e.g.* the ν(P–S) vibration in **1** (535 cm^{-1}) reflects a reduced P–S bond relative to the free ligand (ν(P=S) 646 cm^{-1}), whilst the ν(PNP) vibration in **1** (1232 cm^{-1}) indicates an increase in P–N bond order over the free ligand (ν(PNP) = 960 cm^{-1}).

The complexes formed with unsymmetrical ligands $R_2P(S)NHP(S)R'_2$ offer the potential for the formation of *cis* and *trans* isomers (if the tellurium adopts a square planar geometry). The ^{31}P NMR spectrum of **4** is consistent with the production of both species and clearly shows two sets of doublets with very similar $^2J(^{31}P–^{31}P)$ couplings of 22.5 Hz. The free ligand has a higher $^2J(^{31}P–^{31}P)$ coupling of 30.8 Hz, which probably reflects the change in P–N–P angle/electronic delocalisation between the 'free ligand' and the complexed anions.

The solid-state structures of **1**, **2** and the (preferentially crystallized) *trans* isomer of **4** show (Table 2, Fig. 1) that the TeS_2P_2N rings adopt pseudo-chairlike conformations similar to those reported for some Pt(II) and Pd(II) complexes.[8] In all three complexes the S–P–N–P–S ligand is approximately planar and inclined to the coordination plane by 113, 119 and 110° for **1**, **2** and **4** respectively.

The room temperature ^{31}P NMR spectrum for **3** contains two broad peaks at δ 55.1 and 43.7. This suggests some sort of fluxional process within the complex, variable temperature experiments resulted in decomposition of the complex. The IR spectrum of **3** suggests both P=S (665 cm^{-1}) and P–S (581 cm^{-1}) bonds are present in the solid state.

Recent work suggests the presence of long range S···Te contacts in a number of mixed chalcogen containing systems.[19–21] The solid state structure of **3** (Fig. 2) reveals two-cordinate or 'pseudo-four-coordinate' behaviour; the Te(1)–S(1) and Te(1)–S(3) distances are 2.5267(11) and 2.5131(12) Å respectively with the Te(1)–S(2) and Te(1)–S(4) contacts being considerably longer (≈2.9 Å). The bond lengths in the SPNPS ring of **3** suggest that the negative charge is localised on the tellurium bound sulfur; P(4)–S(4) is 1.968(2) Å, typical for P=S while the bonded P(1)–S(1) is longer at 2.046(2) Å indicating a bond order lower than 2. Including all four sulfur atoms the geometry about tellurium is distorted square planar. The two pendant sulfur atoms are attached to the OPh substituted phosphorus atoms whilst the coordinated sulfur atoms are closest to Et substituents. The OPh groups are not as sterically demanding as the cyclohexyl substituents in **2** which is four-coordinate. It can be concluded that the electronic nature of the R groups is more significant in affecting coordination number/fluxionality in these complexes than the steric requirements of the phosphorus substituents.

Compounds **5** (R = Et, R′ = Ph) and **6** (R = OPh, R′ = OEt) display similar NMR properties to those of **3** and we were able to observe ν(P=S) (653 cm^{-1}) and ν(P–S) (558 cm^{-1}) bands in the IR spectrum for **5** but only one ν(P–S) vibration (553 cm^{-1}) for **6**, though crystals suitable for X-ray diffraction studies could not be obtained in these cases.

A tellurium complex of the selenium donor ligand $NH(^iPr_2PSe)_2]_2$ was synthesised to assess the influence of the donor atom type on structure. This complex was readily prepared but found to be very light sensitive. The ^{31}P NMR spectrum for **7** indicates the presence of only one phosphorus containing species, which was characterised as the bis chelate complex TeL_2. The IR spectrum shows one ν(P–Se) band at 484 cm^{-1} which compares well with related diselenoimidophosphinate systems where the ligand is deprotonated at the amine.[11]

The solid state structure of **7** (Fig. 3) is similar in most

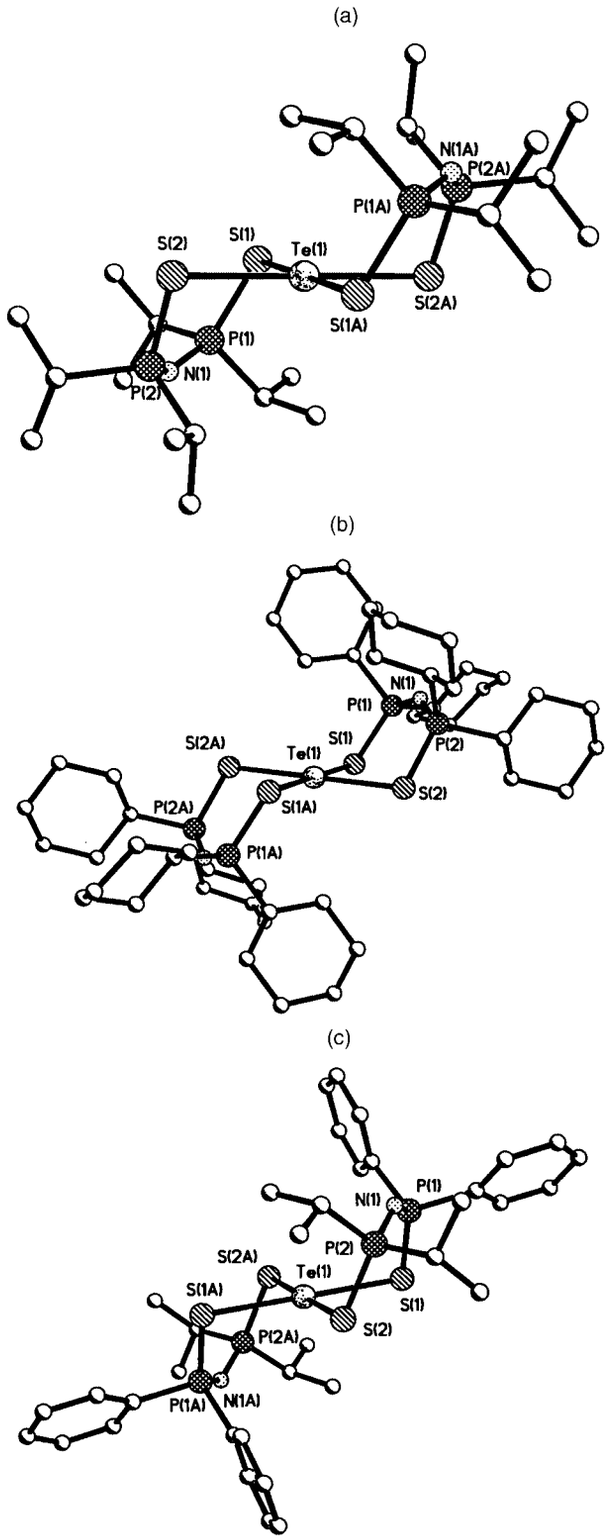

Fig. 1 Solid state structures of (a) **1**, (b) **2** and (c) *trans* isomer of **4**.

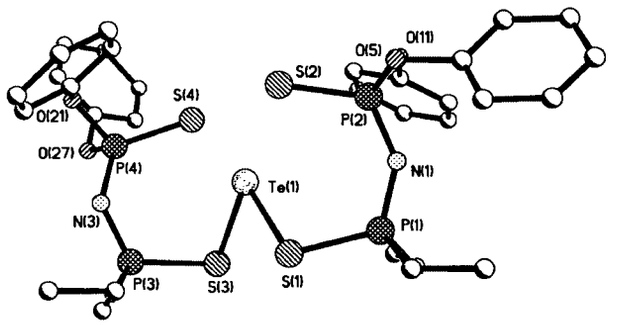

Fig. 2 Solid state structure of **3**.

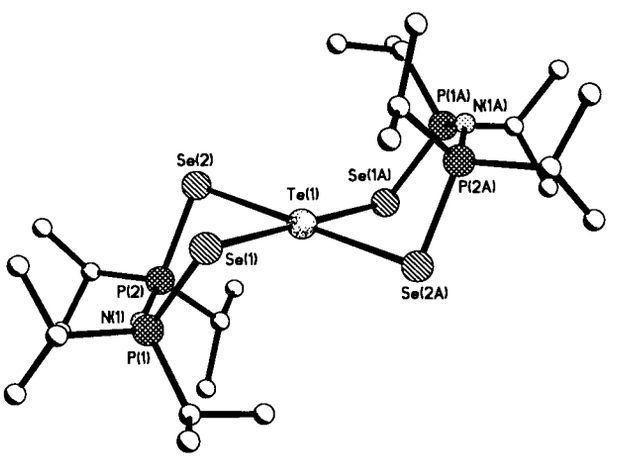

Fig. 3 Solid state structure of **7**.

Table 3 Selected bond lengths (Å) and angles (°) for **8** and **9**

	8	**9**
Te(1)–S(1)	2.5987(10)	2.669(3)
Te(1)–S(2)	2.6227(10)	2.603(3)
Te(1)–Cl(1)	2.5501(11)	2.505(3)
Te(1)–Cl(2)	2.5293(11)	2.510(3)
Te(1)–C(13)	2.134(4)	2.147(11)
S(1)–P(1)	2.0615(14)	2.029(4)
P(1)–N(1)	1.580(3)	1.558(9)
N(1)–P(2)	1.580(3)	1.599(9)
P(2)–S(2)	2.041(2)	2.015(4)
S(1)–Te(1)–S(2)	89.94(4)	91.39(12)
S(1)–Te(1)–C(13)	87.81(12)	84.4(3)
Cl(1)–Te(1)–Cl(2)	91.42(4)	91.23(14)
Cl(1)–Te(1)–C(13)	88.40(12)	89.2(3)
Te(1)–S(1)–P(1)	98.28(4)	93.50(13)
S(1)–P(1)–N(1)	115.74(14)	117.9(4)
P(1)–N(1)–P(2)	144.3(2)	139.0(6)
N(1)–P(2)–S(2)	115.25(14)	117.2(4)
P(2)–S(2)–Te(1)	97.97(5)	98.5(2)

respects to those formed with sulfur donor ligands. The tellurium is square planar and the $TeSe_2P_2N$ rings again adopt the pseudo chair conformations (the Se–P–N–P–Se ligand is inclined by 110° to the coordination plane). The ^{31}P NMR spectrum of **7** consists of one sharp peak with Se satellites, indicating that the complex is stable in solution.

A number of Te_2L_2 dimer species have been reported in the literature,[10] where L = $Ph_2P(S)NHP(S)Ph_2$. Here $TeCl_3(C_6H_4OCH_3)$ was reacted in a 1:1 molar ratio with the deprotonated imidophosphinate ligands in attempts to investigate the generality of the reaction, however substitution of a chloride ligand by a bidentate imidophosphinate ligand according eqn. (2) occurs instead. Satisfactory ^1H NMR spectra and elemental analyses were obtained for these compounds. The FAB +ve mass spectra for both **8** and **9** do not show the parent ion peaks, but peaks due to the loss of one, then two chlorides in each case.

$$TeCl_3(C_6H_4OCH_3) + HL \xrightarrow[MeOH]{K^tBuO} TeLCl_2(C_6H_4OCH_3) \quad (2)$$

The ^{31}P NMR spectrum of **8** is a singlet at δ 62.0 consistent with deprotonation of the ligand. Compound **9** gives a characteristic pair of doublets [$^2J(^{31}P–^{31}P) = 24.9$ Hz] indicating the presence of only one phosphorus containing species whilst the anticipated dimer structure has two potential isomeric forms.

Single crystal X-ray diffraction experiments identified **8** and **9** (Table 3, Fig. 4) as five-coordinate tellurium(IV) species with square based pyramidal geometry about the tellurium atom. The TeS_2Cl_2 geometry is very near to perfect square planar in

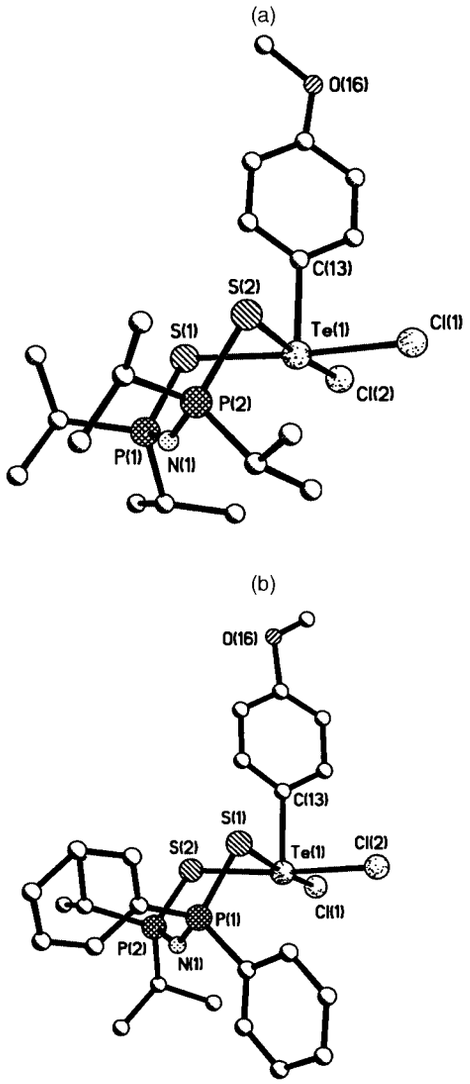

Fig. 4 Solid state structure of (a) **8** and (b) **9**.

both structures with the S–P–N–P–S ligand backbone being almost planar and inclined by 109 and 108° in **8** and **9** respectively. The phenyl ring of the $CH_3OC_6H_4$ group is perpendicular to the TeS_2Cl_2 plane and bisects the S(1)–Te(1)–S(2) plane. The OCH_3 substituent has the opportunity to occupy two sites *i.e.* on the same side as (**8**) or opposite side to (**9**) the chloride ligands. There are no significant intermolecular interactions in the structure of **8** but there is a weak O(16)···Cl(2′) interaction [3.61 Å] in ion **9**.

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