Bismuth(III) Complexes with Sulfur and Selenium Donor Ligands: Synthesis and Crystal Structures of $BiCl_3\cdot Pr^n{}_2P(S)P(S)Pr^n{}_2$ and $[(Me_2N)_3PSeSeP(NMe_2)_3]^{2+}[(BiCl_4)_2]_n{}^{2n-}$ †

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Direct addition of bismuth(III) chloride and tetra-*n*-propyldiphosphane disulfide gave bright yellow crystals of the 1:1 adduct $BiCl_3\cdot Pr^n{}_2P(S)P(S)Pr^n{}_2$. An X-ray crystallographic investigation reveals a halide-bridged dimeric structure in which each bismuth atom is surrounded by an essentially octahedral arrangement of four chlorine [two terminal, Bi–Cl 2.500(5), 2.516(5), and two bridging, Bi–Cl 2.653(4), 3.015(5) Å] and two sulfur atoms [Bi–S 2.857(4), 2.973(4) Å]. Each of the two ligand molecules is involved in bidentate (*S,S'*) chelation to a bismuth atom to form a five-membered ring. Crystals are monoclinic, space group $P2_1/n$, with a = 10.127(6), b = 16.057(6), c = 13.843(6) Å, β = 93.3(1)°, Z = 4. The reaction of $BiCl_3$ and tris(dimethylamino)phosphane selenide in acetonitrile gave the yellow crystalline salt $[(Me_2N)_3PSeSeP(NMe_2)_3]^{2+}[(BiCl_4)_2]_n{}^{2n-}$ as identified by a crystal structure determination. Formation of the unusual cation follows from air oxidation of the organophosphine selenide in the presence of $BiCl_3$. The Se–Se bond distance is 2.309(5) Å and the torsion angle P–Se–Se–P is −112.4(4)°. For the anion, linkage of dimeric $(BiCl_4)_2$ units *via* further halide bridging results in an infinite chain structure of edge-shared octahedra. Crystals are triclinic, space group $P\bar{1}$ with a = 7.386(6), b = 12.813(8), c = 18.919(8) Å, α = 76.0(1), β = 78.9(1), γ = 73.2(1)° and Z = 2.

The co-ordination chemistry of the bismuth(III) halides involving Group 16 (O, S, Se) donor ligands has been extensively studied.[1] Despite the fact that adducts of various stoichiometries based on uni- and multi-dentate ligand systems have been reported, a dearth of structural information hangs like a pall of uncertainty over this area of bismuth chemistry. In those cases where X-ray structural identification of product(s) has been successful[2] the ability of Bi^{III} to assume high-co-ordination geometries in both anionic and cationic frameworks and the variable stereochemical demands of the associated lone pair of electrons[3] emerge as characteristic traits, *e.g.* $BiCl_3\cdot 3tu$[2a] (tu = thiourea) has the ionic structure $[Bi(tu)_6][Bi\{(tu)_{1.5}Cl_{1.5}\}Cl_3]_2$, $[\{Bi(tu)(pcdt)_2Cl\}_2]$[2f] [pcdt = pyrrolidine-1-carbodithioate anion $(C_4H_8NCS_2)$] involves a seven-co-ordinate pentagonal-bipyramidal metal geometry, $BiCl_3\cdot$15-crown-5[2n] (15-crown-5 = 1,4,7,10,13-pentaoxacyclopentadecane) has a half-sandwich structure with the metal in an eight-co-ordinate environment, $BiCl_3\cdot$18-crown-6[2g,h] (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane) and $BiCl_3\cdot[18]aneS_6$[2i] ($[18]aneS_6$ = 1,4,7,10,13,16-hexathiacyclooctadecane) similarly feature a nine-co-ordinate metal geometry.

In this report we describe the formation and structural chemistry of the products obtained from the reactions of $BiCl_3$ and the potential bidentate sulfur donor $Pr^n{}_2P(S)P(S)Pr^n{}_2$ and the monodentate selenium donor $Se{=}P(NMe_2)_3$. A limited number of transition-metal complexes involving the tetramethyl and tetraethyl derivatives of the sulfur compound have been prepared and characterised, *e.g.* Cu^I,[4] Cu^{II},[5] Rh^I and Ir^I,[6] but none with the organoselenide.

Experimental

Manipulations were carried out under a dinitrogen atmosphere using Schlenk techniques and/or a standard dry-box. All solvents were stored over CaH_2 and distilled under a dinitrogen atmosphere immediately prior to use. Bismuth trichloride was used as supplied commercially (Aldrich). The compound $Se{=}P(NMe_2)_3$ was prepared as described in ref. 7. The IR spectra were recorded on a Perkin-Elmer 580B spectrometer with samples as Nujol mulls placed between CsI plates, ^1H (400 MHz) and ^{31}P (161.9 MHz) NMR spectra on a Brüker WH400 spectrometer. The $CDCl_3$, CD_3COCD_3 and CD_3CN NMR solvents were dried over 4 Å molecular sieves prior to use. Elemental analyses were carried out by Medac Ltd., Brunel University, Uxbridge, Middlesex.

Preparation of the Compounds.—(*a*) $Pr^n{}_2P(S)P(S)Pr^n{}_2$. This compound was prepared by an anomalous Grignard reaction following a modification of the literature procedure.[8] Thiophosphoryl chloride (5.49 g, 0.032 mol) was added dropwise over a period of 2 h to a stirred, chilled (0 °C) solution of *n*-propylmagnesium chloride (10.0 g, 0.097 mol). The resulting solution was allowed to warm to room temperature and then heated at reflux under an atmosphere of dinitrogen for 2 h. Following cooling to 0 °C this solution was poured into a beaker containing crushed ice and concentrated sulfuric acid (100 cm³). On standing for 12 h a white solid separated out which was filtered off, washed with diethyl ether (3 × 25 cm³) and then dried *in vacuo* with pumping. Yield 7.35 g (77%). Recrystallisation from toluene–ethanol (1:1) gave white needle crystals of the product of suitable quality for X-ray diffraction studies, m.p. 142–143 °C (Found: C, 48.40; H, 9.55. $C_{12}H_{28}P_2S_2$ requires C, 48.30; H, 9.45%). $\delta_H(CDCl_3)$ 1.05 (t, CH_3, 12 H), 1.59–1.80 (m, CH_2, 8 H) and 1.96–2.24 (m, CH_2, 8 H); $\delta_P(CDCl_3)$ 46.94 (s, $\equiv P{=}S$). IR $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 1034, 903, 853, 584 and 412.

(*b*) $BiCl_3\cdot Pr^n{}_2P(S)P(S)Pr^n{}_2$ **1**. A solution of tetra-*n*-propyl-

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

diphosphane disulfide (0.095 g, 0.030 mmol) in acetonitrile (30 cm^3) was added dropwise to a stirred, chilled (0 °C) solution of bismuth trichloride (0.10 g, 0.032 mmol) in acetonitrile (35 cm^3). The resulting mixture was stirred for 24 h at room temperature and then filtered under dinitrogen to give a clear light yellow solution. Slow removal of solvent *in vacuo* resulted in a concentrated solution (*ca.* 15 cm^3) from which small, pale yellow, cube crystals deposited on cooling in a refrigerator. Yield 0.18 g (91%), m.p. 136–137 °C (Found: C, 23.20; H, 4.70; Cl, 17.10. $C_{24}H_{56}Bi_2Cl_6P_4S_4$ requires C, 23.50; H, 4.60; Cl, 17.35%). $\delta_H(CDCl_3)$ 1.07 (t, CH_3, 12 H), 1.61–1.80 (m, CH_2, 8 H) and 2.20–2.28 (m, CH_2, 8 H); $\delta_P(CDCl_3)$ 52.61 (s, ≡P=S). IR $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 1155, 1062, 973, 899, 845, 739, 722, 593, 557, 533, 515 (ligand), 377 and 255 (BiCl).

(*c*) $[(Me_2N)_3PSeSeP(NMe_2)_3][Bi_2Cl_8]$ **2**. A solution of tris(dimethylamino)phosphane selenide (0.0768 g, 0.031 mmol) in acetonitrile (25 cm^3) was added dropwise to a stirred, chilled (0 °C) solution of bismuth trichloride (0.10 g, 0.032 mmol) in acetonitrile (30 cm^3). The resulting mixture was stirred at room temperature for 24 h and filtered under dinitrogen to give a clear yellow solution. This solution was concentrated to *ca.* 15 cm^3 by gradual removal of solvent *in vacuo* and placed in the refrigerator overnight to give bright yellow cube crystals of the product. Yield 0.15 g (85%), m.p. 180–183 °C (Found: C, 12.00; H, 3.00; Cl, 23.85; N, 7.00. $C_{12}H_{36}Bi_2Cl_8N_6P_2Se_2$ requires C, 12.15; H, 3.05; Cl, 23.90; N, 7.10%. $\delta_H(CD_3COCD_3)$ 2.65 (s, NCH_3, 3 H) and 2.61 (s, NCH_3, 3 H); $\delta_P(CD_3COCD_3)$ 83.04 (s, ≡P–Se–). IR $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 1169, 1063, 990, 749, 739, 665, 513 (ligand), 335 and 272 (BiCl).

X-Ray Crystallography.—Crystal data are given in Table 1, together with refinement details. Data for both crystals were collected with Mo-Kα radiation using the MAR research image plate system. The crystals were positioned at 75 mm from the image plate in random orientations. Ninety frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program.[9] Both structures were solved using direct methods with the SHELX 86 program.[10] In compound **1** the Bi, Cl, P and S atoms were refined with anisotropic thermal parameters; the remaining atoms with isotropic thermal parameters. The methylene hydrogen atoms were included in calculated positions with a common thermal parameter. The methyl hydrogen atoms were refined as rigid groups each with a different refineable thermal parameter. In **2** the Bi, Cl, Se and P atoms were refined anisotropically and the N and C atoms isotropically. The methyl hydrogen atoms were refined as rigid groups each with a different refineable thermal parameter. An empirical absorption correction was supplied using DIFABS.[11]

Both structures were refined using SHELXL.[12] All calculations were carried out on a Silicon Graphics R4000 workstation at the University of Reading. The final coordinates for compounds **1** and **2** are given in Tables 2 and 3 and important dimensions in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The two bismuth(III) compounds, $BiCl_3{\cdot}Pr^n{}_2P(S)P(S)Pr^n{}_2$ **1** and $[(Me_2N)_3PSeSeP(NMe_2)_3]^{2+}[(BiCl_4)_2]_n{}^{2n-}$ **2** were obtained following reaction of the tervalent metal chloride with the corresponding diphosphorus compound in acetonitrile solution. Both these products are bright yellow crystalline solids which show limited solubility in the common organic solvents and must be handled under an inert atmosphere of dinitrogen to curb decomposition *via* air/moisture hydrolysis reactions. The IR spectra show band patterns in the 1200–600 cm^{-1} range characteristic of the corresponding diphosphorus parent and intense broad bands in the low energy region at 377, 255 (**1**), 335, 272 (**2**) cm^{-1} assigned to ν(Bi–Cl).[13] For **1** the ligand ν(P=S) band at 584 cm^{-1} is shifted 27 cm^{-1} to lower energy following sulfur co-ordination to the metal,[14]

Table 1 Crystal data and structure refinement for compounds **1** and **2***

	1	2
Empirical formula	$C_{24}H_{56}Bi_2Cl_6P_4S_4$	$C_{12}H_{36}Bi_2Cl_8N_6P_2Se_2$
M	613.73	1185.89
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	10.127(6)	7.386(6)
b/Å	16.057(6)	12.813(8)
c/Å	13.843(6)	18.919(8)
α/°	(90)	76.0(1)
β/°	93.3(1)	78.9(1)
γ/°	(90)	73.2(1)
U/Å^3	2247.2	1649.0
Z	4	2
D_c/Mg m^{-3}	1.814	2.388
μ/mm^{-1}	8.521	13.625
F(000)	1184	1100
Crystal size/mm	0.2 × 0.2 × 0.3	0.2 × 0.2 × 0.15
θ/° range for data collection	1.94–24.87	1.84–24.93
hkl ranges	0–11, −18 to 18, −16 to 16	0–8, −13 to 14, −21 to 22
No. reflections measured	10 634	7350
Independent reflections (R_{int})	3596 (0.049)	4240 (0.026)
% of independent reflections measured	93.6	85.6
Data/parameters	3596/190	4240/226
Weighting scheme parameters	$a = 0.08, b = 34.6$	$a = 0.12, b = 48.6$
Goodness-of-fit on F^2	1.138	1.225
Final R indices [$I > 3\sigma(I)$]	2417 data, $R1 = 0.037$	3217 data, $R1 = 0.072$
R indices (all data)	$R1 = 0.0854$, $wR2 = 0.1620$	$R1 = 0.1238$, $wR2 = 0.3008$
Largest difference peak and hole, e Å^{-3}	1.154, −1.595	2.600, −3.223

* Details in common: 293(2) K; λ(Mo-Kα) 0.7107 Å; full-matrix least-squares refinement on F^2; $w = 1/[\sigma^2(F_o{}^2) + (aP)^2 + bP]$, $P = [\max(F_o{}^2, 0) + 2F_c{}^2]/3$.

Table 2 Atomic coordinates (× 10^4) for compound **1**

Atom	*x*	*y*	*z*
Bi(1)	584(1)	9 549(1)	6 391(1)
S(1)	1 912(4)	8 207(2)	5 329(3)
S(2)	−416(4)	8 236(3)	7 535(3)
P(3)	−90(5)	7 216(3)	6 790(3)
P(4)	1 906(5)	7 285(3)	6 252(3)
Cl(1)	1 531(4)	10 676(3)	5 212(3)
Cl(2)	−660(6)	10 579(3)	7 365(4)
Cl(3)	2 552(5)	9 647(3)	7 561(4)
C(41)	2 977(17)	7 399(11)	7 305(12)
C(42)	4 338(20)	7 686(13)	7 109(15)
C(43)	5 170(22)	7 906(14)	8 014(16)
C(51)	2 080(24)	6 277(14)	5 672(17)
C(52)	3 128(33)	6 170(20)	5 092(24)
C(53)	3 026(29)	5 325(18)	4 533(20)
C(61)	−1 156(17)	7 106(12)	5 719(13)
C(62)	−2 615(19)	7 217(13)	5 861(14)
C(63)	−3 431(21)	7 204(13)	4 927(15)
C(71)	−176(31)	6 296(18)	7 484(21)
C(72)	−655(43)	6 210(26)	8 231(30)
C(73)	−724(27)	5 393(17)	8 815(20)

Table 3 Atomic coordinates (× 10^4) for compound **2**

Atom	*x*	*y*	*z*
Bi(1)	2 905(2)	9 093(1)	65(1)
Cl(11)	1 797(15)	7 549(7)	960(5)
Cl(12)	5 153(13)	7 720(7)	−652(4)
Cl(13)	122(14)	9 354(7)	−778(5)
Cl(14)	5 371(15)	9 088(8)	916(5)
Bi(2)	17 064(2)	5 907(1)	−5 065(1)
Cl(21)	16 278(15)	4 366(7)	−5 769(5)
Cl(22)	20 391(16)	5 912(8)	−5 916(5)
Cl(23)	15 302(15)	7 436(7)	−5 949(5)
Cl(24)	17 225(16)	7 290(7)	−4 340(5)
Se(3)	13 583(5)	6 751(2)	−2 790(2)
Se(4)	12 544(5)	8 247(2)	−2 206(2)
P(4)	10 693(11)	9 452(6)	−3 005(4)
N(41)	11 530(36)	9 495(19)	−3 828(13)
C(42)	12 756(65)	10 219(35)	−4 254(24)
C(43)	11 554(46)	8 629(24)	−4 234(16)
N(44)	10 479(40)	10 593(21)	−2 744(14)
C(45)	11 937(57)	10 917(31)	−2 481(21)
C(46)	8 716(62)	11 441(33)	−2 736(24)
N(47)	8 701(42)	9 158(22)	−2 911(15)
C(48)	7 731(42)	8 841(23)	−2 182(15)
C(49)	7 441(53)	9 488(28)	−3 456(19)
P(3)	12 150(12)	5 545(6)	−2 000(4)
N(31)	9 945(40)	5 849(21)	−2 100(14)
C(32)	8 551(59)	5 513(33)	−1 554(22)
C(33)	9 305(43)	6 161(23)	−2 818(15)
N(34)	13 314(33)	4 421(17)	−2 262(12)
C(35)	15 309(56)	4 148(32)	−2 511(22)
C(36)	12 385(67)	3 521(35)	−2 167(25)
N(37)	12 221(39)	5 500(20)	−1 154(14)
C(38)	10 927(47)	6 388(25)	−770(17)
C(39)	13 751(60)	4 793(33)	−790(23)

cf. [Rh(cod){$Et_2P(S)P(S)Et_2$}]ClO_4[6] (cod = cycloocta-1,5-diene) $\nu(P{=}S)_{\text{co-ordinated}}$ 545 cm^{-1} and for **2** the strong ν(P=Se) stretching frequency (530 cm^{-1}) disappears. The ^1H NMR spectra of **1** and **2** corroborate the presence of ligand molecules but are uninformative in terms of binding patterns; the corresponding ^{31}P NMR spectra which consist of single resonances δ 52.61 (**1**) and 83.04 (**2**) located *ca.* 6 ppm downfield with respect to those of the parent diphosphorus compounds, merely serve to confirm the conservation and equivalence of pentavalent phosphorus atoms in both compounds. As perhaps might be anticipated, the only real measure of the identity of these intended 'adducts' comes from the X-ray diffraction studies.

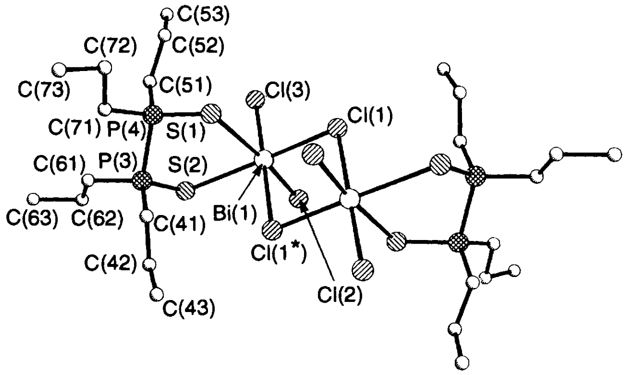

Fig. 1 Molecular structure of [$BiCl_3\cdot Pr^n{}_2P(S)P(S)Pr^n{}_2$]$_2$ **1** with atom labelling

The structure of compound **1** has been established as a halide-bridged dimeric unit [Bi_2Cl_6(bidentate ligand)$_2$] based on edge–edge fusion of two octahedra, see Fig. 1 with the atom numbering scheme. The structure is centrosymmetric with each of the bismuth atoms in a distorted-octahedral environment bonded unequally to two bridging chlorine atoms [2.653(4), 3.015(5) Å], two terminal chlorine atoms [2.500(5), 2.516(5) Å] and two sulfur atoms from the bidentate ligand [2.857(4), 2.973(4) Å]. There are precedents for this dimeric arrangement in which the bismuth(III) co-ordination sphere comprises four halogen atoms and two mutually *cis* donor atoms, *e.g.* [$Bi_2Br_6(PMe_3)_4$] and [$Bi_2Br_6(PMe_2Ph)_2(OPMe_2Ph)_2$][15] and [$Bi_2I_6(OPPh_3)_4$][16] but with the subtle distinction that the ligands involved are monodentate. As in **1**, the core Bi_2X_2 units (X = halide) in all these examples are asymmetric. At the outset of this work the crystal structure of the potentially bidentate $Pr^n{}_2P(S)P(S)Pr^n{}_2$ was undertaken to reveal a non-eclipsed (*anti*) ethane-like conformation with crystallographic *i* symmetry [P–P 2.215(2), P–S 1.951(2) Å]. During the preparation of this manuscript the ligand structure was published independently by Sillanpää *et al.*[17] [P–P 2.220(1), P–S 1.953(1) Å]. The tetramethyl[18] and the tetraethyl[19] analogues adopt a similar *anti* rotational configuration. What is clear is that formation of **1** entails a ligand conformational change *anti* → *gauche* thereby facilitating *S,S′* bidentate chelation. A similar situation has been noted by Cotton *et al.*[4b] in the structure of [Cu{$Me_2P(S)P(S)Me_2$}$_2$][$CuCl_2$] [P–P 2.217(2), P–S 1.973(2), 1.995(2) Å] where each of the tetramethyldiphosphane disulfide ligands adopts a *gauche* rotational configuration for its *S,S′* bidentate role. Again the tetraethyldiphosphane disulfide ligand is found to be bidentate in [Rh(cod){$Et_2P(S)P(S)Et_2$}]ClO_4[6] [P–P 2.215(6), P–S 2.001(4), 1.972(4) Å]. In contrast the copper(II) compound [$CuCl_2${$Me_2P(S)P(S)Me_2$}][5] incorporates the tetramethyldiphosphane disulfide ligand with retention of its *anti* rotational conformation such that each sulfur atom is bonded to a separate copper(II) centre in a chain structure [P–P 2.220(8), P–S 1.995(9), 1.991(9) Å]. The dimensions of the chelated tetra-*n*-propyldiphosphane disulfide ligand in **1** [P–P 2.197(7), P–S 1.956(5), 1.974(6) Å], which fit into the general pattern observed in these similar complexes (above), show a slight lengthening of the P–S bond distances but no real or significant change in the P–P backbone following co-ordination to Bi^{III}. The ligand 'bite' angle S–Bi–S 85.67(12)° closely approaches the ideal (90°).

The structure of compound **2** consists of discrete [$(Me_2N)_3PSeSeP(NMe_2)_3$]$^{2+}$ cations, see Fig. 2 with atom labelling, and two independent but equivalent two-dimensional polymeric anionic chains [$(BiCl_4)_2$]$_n{}^{2n-}$ of which one is shown in Fig. 3. A search of the Cambridge Crystallographic Data Base reveals no comparable cations in the literature; indeed there are very few instances of P–Se–Se–P linkages in any format. One example, the neutral compound $Et_2P(S)SeSeP(S)Et_2$,[20] maintains a pyramidal environment of both of the phosphorus(V) centres, Se–P–C 106.9(13)°, with Se–Se 2.334(12), P–Se 2.275(11) Å, and

Table 4 Important dimensions in compounds **1** and **2** (bond lengths in Å and angles in °)

Compound **1**			
Bi(1)–Cl(3)	2.500(5)	Bi(1)–S(2)	2.857(4)
Bi(1)–Cl(2)	2.516(5)	Bi(1)–S(1)	2.973(4)
Bi(1)–Cl(1)	2.653(4)	Bi(1)–Cl(1^{I})	3.015(5)
Cl(3)–Bi(1)–Cl(2)	90.9(2)	Cl(1)–Bi(1)–S(1)	90.00(14)
Cl(3)–Bi(1)–Cl(1)	93.0(2)	S(2)–Bi(1)–S(1)	85.67(12)
Cl(2)–Bi(1)–Cl(1)	95.2(2)	Cl(3)–Bi(1)–Cl(1^{I})	172.0(2)
Cl(3)–Bi(1)–S(2)	89.0(2)	Cl(2)–Bi(1)–Cl(1^{I})	96.7(2)
Cl(2)–Bi(1)–S(2)	89.1(2)	Cl(1)–Bi(1)–Cl(1^{I})	84.03(13)
Cl(1)–Bi(1)–S(2)	175.24(13)	S(2)–Bi(1)–Cl(1^{I})	93.45(12)
Cl(3)–Bi(1)–S(1)	89.9(2)	S(1)–Bi(1)–Cl(1^{I})	82.64(13)
Cl(2)–Bi(1)–S(1)	174.6(2)	Bi(1)–Cl(1)–Bi(1^{I})	95.97(13)
S(1)–P(4)	1.956(5)	P(3)–P(4)	2.197(7)
S(2)–P(3)	1.974(6)		
S(2)–P(3)–P(4)	108.7(3)	P(3)–S(2)–Bi(1)	104.3(2)
P(4)–S(1)–Bi(1)	101.9(2)	S(1)–P(4)–P(3)	107.3(3)
S(2)–P(3)–P(4)–S(1)	−65.5(3)		
Compound **2**			
Polymeric anion			
Bi(1)–Cl(11)	2.497(9)	Bi(2)–Cl(23)	2.474(9)
Bi(1)–Cl(12)	2.508(9)	Bi(2)–Cl(24)	2.528(9)
Bi(1)–Cl(14)	2.651(10)	Bi(2)–Cl(22)	2.667(11)
Bi(1)–Cl(13)	2.736(9)	Bi(2)–Cl(21^{IV})	2.726(10)
Bi(1)–Cl(13^{II})	2.889(10)	Bi(2)–Cl(21)	2.870(8)
Bi(1)–Cl(14^{III})	3.035(10)	Bi(2)–Cl(22^{V})	3.023(10)
Cl(11)–Bi(1)–Cl(12)	90.2(3)	Cl(23)–Bi(2)–Cl(24)	90.2(3)
Cl(11)–Bi(1)–Cl(14)	91.9(3)	Cl(23)–Bi(2)–Cl(22)	92.2(3)
Cl(12)–Bi(1)–Cl(14)	96.2(3)	Cl(24)–Bi(2)–Cl(22)	96.1(3)
Cl(11)–Bi(1)–Cl(13)	90.9(3)	Cl(23)–Bi(2)–Cl(21^{IV})	90.7(3)
Cl(12)–Bi(1)–Cl(13)	90.4(3)	Cl(24)–Bi(2)–Cl(21^{IV})	90.7(3)
Cl(14)–Bi(1)–Cl(13)	172.9(3)	Cl(22)–Bi(2)–Cl(21^{IV})	172.5(3)
Cl(11)–Bi(1)–Cl(13^{II})	88.3(3)	Cl(23)–Bi(2)–Cl(21)	88.2(3)
Cl(12)–Bi(1)–Cl(13^{II})	171.4(3)	Cl(24)–Bi(2)–Cl(21)	170.9(3)
Cl(14)–Bi(1)–Cl(13^{II})	92.3(3)	Cl(22)–Bi(2)–Cl(21)	92.8(3)
Cl(13)–Bi(1)–Cl(13^{II})	81.2(3)	Cl(21^{IV})–Bi(2)–Cl(21)	80.4(3)
Cl(11)–Bi(1)–Cl(14^{III})	173.3(3)	Cl(23)–Bi(2)–Cl(22^{V})	173.8(3)
Cl(12)–Bi(1)–Cl(14^{III})	89.3(3)	Cl(24)–Bi(2)–Cl(22^{V})	89.4(3)
Cl(14)–Bi(1)–Cl(14^{III})	81.2(3)	Cl(22)–Bi(2)–Cl(22^{V})	81.6(3)
Cl(13)–Bi(1)–Cl(14^{III})	95.8(3)	Cl(21^{IV})–Bi(2)–Cl(22^{V})	95.5(3)
Cl(13^{II})–Bi(1)–Cl(14^{III})	93.2(3)	Cl(21)–Bi(2)–Cl(22^{V})	93.1(3)
Bi(1)–Cl(13)–Bi(1^{II})	98.8(3)	Bi(2^{IV})–Cl(21)–Bi(2)	99.6(3)
Bi(1)–Cl(14)–Bi(1^{III})	98.5(3)	Bi(2)–Cl(22)–Bi(2^{V})	98.4(3)
Cation			
Se(3)–P(3)	2.227(8)	Se(4)–P(4)	2.234(8)
Se(3)–Se(4)	2.309(5)		
P(3)–Se(3)–Se(4)	100.1(2)	P(4)–Se(4)–Se(3)	99.9(2)
P(3)–Se(3)–Se(4)–P(4)	−112.4(4)		

Symmetry transformations used to generate equivalent atoms: I $-x, -y+2, -z+1$; II $-x, -y+2, -z$; III $-x+1, -y+2, -z$; IV $-x+3, -y+1, -z-1$; V $-x+4, -y+1, -z-1$.

a P–Se–Se–P torsion angle of 104.5°; the dimensions of the dication of compound **2** show a close similarity with Se–Se 2.309(5), Se–P 2.227(8), 2.234(8) Å and a P–Se–Se–P torsion angle of −112.4(4)°. For comparison the parent $(Me_2N)_3P{=}Se$[21] has a P=Se bond distance 2.120(1) Å as a reflection of the multiple (double) bond linkage.

The formation of the bismuthate(III) salt **2** rather than the anticipated adduct $BiCl_3{\cdot}2Se{=}P(NMe_2)_3$ came as an initial surprise. The cation is derived from the diphosphorus parent most probably *via* the free radical $(Me_2N)_3P{=}Se^{\bullet +}$ followed by rapid coupling *viz.*, $2(Me_2N)_3P{=}Se \longrightarrow [(Me_2N)_3P^+{-}Se{-}Se{-}P^+(NMe_2)_3] + 2e$. Presumably this ligand rearrangement follows from air oxidation in the presence of bismuth(III) chloride but we have as yet been unable to identify any reduction product [although possible, bismuth(I) species seem highly unlikely?]. Slinkard and Meek[22] have observed a similar oxidation of the analogous sulfur ligand $(Me_2N)_3P{=}S$ to the phosphorus(V)–sulfur cation $[(Me_2N)_3PSSP(NMe_2)_3]^{2+}$ in the presence of Cu^{II} or bromine. The equivalent oxygen dication $[(Me_2N)_3POOP(NMe_2)_3]^{2+}$ is unknown in line with the expected trend Se ≫ S ≫ O for ease of oxidation of $(Me_2N)_3$-P=E (E = O, S or Se).

For the anion, dimeric $(BiCl_4)_2$ units are linked by further halide bridging to give separate infinite chains of edge-sharing

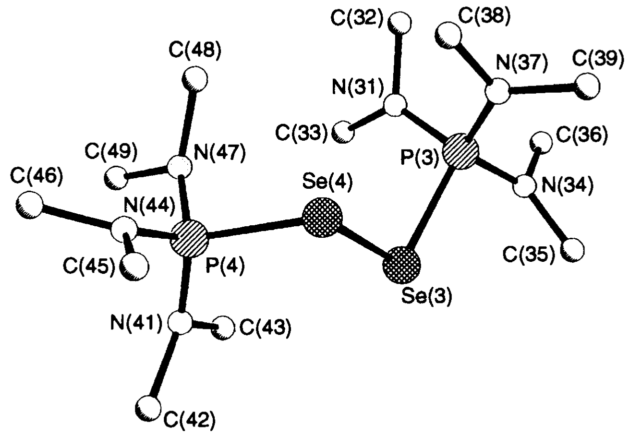

Fig. 2 A view of the $[(Me_2N)_3PSeSeP(NMe_2)_3]^{2+}$ cation in compound **2** with atom labelling

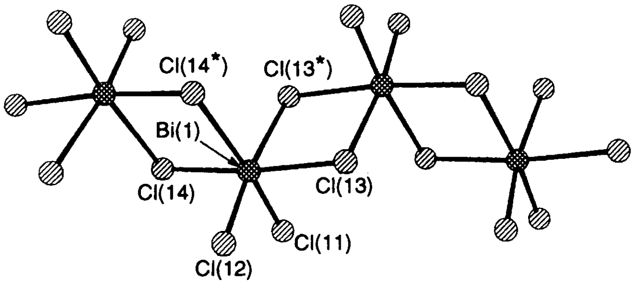

Fig. 3 A view of the halide-bridged polymeric $[(BiCl_4)_2]_n{}^{2n-}$ anion in compound **2** with atom labelling

octahedra with no glimmer of evidence of lone-pair stereochemical activity. Within each chain there are two terminal Bi–Cl bonds, 2.497(9), 2.508(9) and 2.474(9), 2.528(9) Å and four bridging Bi–Cl linkages 2.65(1)–3.04(1) and 2.67(1)–3.02(1) Å around each metal centre. Such $[(BiCl_4)_2]_n{}^{2n-}$ chains have been observed before notably in $[Fe(\eta^5\text{-}C_5H_5)_2][BiCl_4]$ [23] where the independent Bi–Cl terminal distances are 2.50(1) and 2.52(1) Å and the Bi–Cl bridging distances lie in the range 2.70–3.10(1) Å. This six-co-ordinate chain structure involving bridging halogen atoms is fairly commonplace in the wider context of condensed $[MX_4]^-$ anions of Group 15 where M = As,[24] Sb,[25] or Bi.[26]

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