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Silver(I) coordination by variants of the bis(diphenylphosphino)-amine chalcogenide ligand†

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Treatment of silver(I) bromide with the ligands $[Ph_2P(Se)HNP(E)Ph_2]$ (E = Se, S or O) and $[Ph_2P(Se)HNPPh_2]$ results in the formation of the salts $[\{HN(Ph_2PSe)_2\text{-}Se,Se'\}_2Ag]Br$, $[\{HN(Ph_2PSe)(Ph_2PS)\text{-}Se,S\}_2Ag]Br$, $[\{HN(Ph_2PSe)(Ph_2PO)\text{-}Se\}_2Ag]Br$ and $[\{HN(Ph_2PSe)(Ph_2P)\text{-}Se,P\}_2Ag]Br$, respectively. From analysis of spectroscopic data, it appears that the $[Ph_2P(Se)HNP(O)Ph_2]$ ligand is coordinated through selenium donors only. The ligand $[Ph_2P(Se)CH_2CH_2AsPh_2]$ forms a complex $[\{Ph_2P(Se)CH_2CH_2AsPh_2\}_2Ag]Br$. These products constitute the first examples of metal complexes bearing these ligands in the neutral form (protonated at the nitrogen atom). The structures of three of the complexes were determined and found to contain homoleptic, spirocyclic inorganic chelates associated with hydrogen-bonded, bridging counteranions. The compound $[\{HN(Ph_2PSe)(Ph_2PS)\text{-}Se,S\}_2Ag]Br$ underwent a transformation upon standing in solution through loss of a single $[Ph_2P(Se)HNP(S)Ph_2]$ ligand to provide a bromide-bridged, neutral complex $[\{HN(Ph_2PSe)(Ph_2PS)\text{-}Se,S\}AgBr]_2$.

Introduction

In its complexes, silver displays an ability to coordinate readily to both hard and soft donor centres. The versatility of the iminodiphosphine chalcogenide species $[R_2P(E)HNP(E)R_2]$ (E = O, S, Se or lone pair) renders them excellent ligands with which to probe the hard–soft behaviour of silver(I) centres. These ambidentate compounds remained largely neglected for many years after the synthesis of the first members of the ligand class in the 1960s.[1] Recently, interest has been renewed in their coordination abilities, mainly regarding the corresponding dichalcogenidodiphosphinoimide anions[2,3] which have found use in a number of diverse areas such as catalysis,[4] NMR shift reagents[5] and selective metal extractants.[6] The ligands with mixed chalcogen donors $[R_2P(O)HNP(E)R_2]$ (E = S or Se) were prepared more recently and their anions widely applied as ligands for metal centres.[7–10] A recent review covers some of the di-chalcogen and mixed ligands.[11] Bis(diphenylphosphino)-methane monoselenide is not readily available from dppm and selenium.[12] However, the discovery that the analogous amine monoselenide $[Ph_2P(Se)HNPPh_2]$ can be obtained from simple reaction of elemental selenium with the amine[13] has increasingly led to its use in the complexation of transition metals.

The homoleptic silver complexes reported here are, to our knowledge, the first examples with the neutral ligands $[Ph_2P(Se)HNP(E)Ph_2]$ (E = Se, S, O or lone pair) and $[Ph_2P(Se)CH_2CH_2AsPh_2]$. The ability to vary the 'softness' of these ligands through the choice of donor atoms enabled the coordination chemistry of monovalent silver with this class of chelating ligands to be explored. Additional impetus for this research was provided by the possibility that the amino proton could act as an intermolecular bridge in an analogous manner to that described in a recent report.[14]

Experimental

General information

The experiments were carried out routinely in air. NMR: JEOL GX 400 spectrometer using deuterated solvents with the usual standards at 25 °C. MS: Varian MAT311A instrument (FAB, *p*-nitrobenzyl alcohol). Silver bromide was obtained commercially and the ligands $[Ph_2P(Se)HNP(Se)Ph_2]$,[2] $[Ph_2P(Se)HNP(O)Ph_2]$,[10] $[Ph_2P(Se)HNPPh_2]$,[13] $[Ph_2P(Se)HNP(S)Ph_2]$[9] and $[Ph_2P(Se)CH_2CH_2AsPh_2]$[15] were prepared following literature procedures.

Syntheses

$[\{HN(Ph_2PSe)_2\text{-}Se,Se'\}_2Ag]Br$ (1). Silver bromide (17.3 mg, 0.092 mmol) and $[Ph_2P(Se)HNP(Se)Ph_2]$ (100.0 mg, 0.184 mmol) were stirred in acetone (30 mL) for 2 h. The solvent volume was reduced to *ca.* 5 mL and diethyl ether (20 mL) carefully added to precipitate the white product. This was washed with diethyl ether (10 mL) and pentane (10 mL) and dried. Yield: 88% (103 mg). MS (FAB) m/z = 1199, 5% $[M]^+$, 652, 22% $[M - HN(Ph_2PSe)_2]^+$. ^{31}P NMR (CD_2Cl_2–d^6-benzene 1 : 4): δ 51.8 (J_{PSe} = 745 Hz) ^1H NMR (CD_2Cl_2–d^6-benzene 1 : 4): δ 4.84 (s, 2 H, NH), 7.39, 7.88 (m, 40 H, C_6H_5) Anal. calculated for $C_{48}H_{42}AgBrN_2P_4Se_4$: C, 45.24; H, 3.32; N, 2.20%. Found: C, 44.98; H, 3.22; N, 1.93%.

$[\{HN(Ph_2PSe)(Ph_2PS)\text{-}Se,S\}_2Ag]Br$ (2). Silver bromide (19 mg, 0.10 mmol) and $[Ph_2P(Se)HNP(S)Ph_2]$ (100 mg, 0.20 mmol) were stirred in acetone (30 mL) for 5 h. The resulting solution was filtered through diatomaceous earth and the solvent volume reduced to *ca.* 5 mL causing a microcrystalline solid to precipitate. The white product was washed with cold acetone (25 mL) and pentane (20 mL) and dried. Yield: 62% (74 mg). Crystals were grown from CH_2Cl_2–pentane. MS (FAB) m/z = 1102, 6% $[M]^+$, 712, 8% $[M - HN(Ph_2P)_2]^+$, 604, 24% [M −

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† Electronic supplementary information (ESI) available: tables of crystal data. See http://www.rsc.org/suppdata/dt/b1/b105154g

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$Ph_2P(S)HNP(Se)Ph_2]^+$. ^{31}P NMR (CD_2Cl_2–d^6-acetone 1 : 4): δ 57.2 (d, $SPPh_2$, J_{PP} = 12.4 Hz), 50.9 (d, $SePPh_2$, J_{PP} = 12.4 Hz, J_{PSe} = 770 Hz) ^1H NMR (d^6-acetone): δ 4.81 (s, 2 H, NH), 7.43, 7.82 (m, 40 H, C_6H_5) Anal. calculated for $C_{48}H_{42}AgBrN_2P_4S_2Se_2{\cdot}0.25CH_2Cl_2$: C, 48.02; H, 3.56; N, 2.32%. Found: C, 48.20; H, 3.50; N, 1.77%. Solvent of crystallisation was established by integration of the ^1H NMR spectrum in d^6-dmso.

[{HN(Ph$_2$PSe)(Ph$_2$PS)-*Se,S*}AgBr]$_2$ (3). A crystallisation experiment intended to provide crystals of **2** from a layered mixture of acetone and pentane was found to yield single crystals of complex **3** instead. $C_{24}H_{21}AgBrP_2NSSe$ requires: C, 42.13; H, 3.09; N, 2.06%. Found: C, 42.33; H, 2.99, N, 1.93%.

[{HN(Ph$_2$PSe)(Ph$_2$P)-*Se,P*}$_2$Ag]Br (4). Silver bromide (20.3 mg, 0.108 mmol) and $[Ph_2P(Se)HNPPh_2]$ (100.0 mg, 0.216 mmol) were stirred in acetone (30 mL) for 2 h. The solvent volume was reduced to *ca.* 5 mL and diethyl ether (20 mL) carefully added to precipitate the white product. This was washed with diethyl ether (10 mL) and pentane (10 mL) and dried. Yield: 69% (83 mg). MS (FAB) *m*/*z* = 1037, 54% $[M]^+$, 651, 14% $[M - HN(Ph_2P)_2]^+$, 572, 90% $[M - HN(Ph_2PSe)(Ph_2P)]^+$. ^{31}P NMR (CD_2Cl_2–EtOH 1 : 5): δ 38.7 (dd, PPh_2, J_{PAgP} = 376 Hz, J_{PNP} = 80 Hz); 62.8 (d, $SePPh_2$, J_{PNP} = 80 Hz, J_{PSe} not resolved) ^1H NMR (d^4-methanol): δ 3.61 (m, 2 H, NH), 7.30–7.68 (m, 40 H, C_6H_5). Anal. calculated for $C_{48}H_{42}AgBrN_2P_4Se_2$: C, 51.64; H, 3.79; N, 2.51%. Found: C, 51.88; H, 3.78; N, 2.25%.

[{HN(Ph$_2$PSe)(Ph$_2$PO)-*Se*}$_2$Ag]Br (5). Silver bromide (19.6 mg, 0.104 mmol) and $[Ph_2P(Se)HNP(O)Ph_2]$ (100.0 mg, 0.208 mmol) were stirred in acetone (30 mL) for 2 h. The solvent volume was reduced to *ca.* 5 mL and pentane (20 mL) carefully added to precipitate the white product. This was washed with pentane (10 mL) and dried. Yield: 57% (68 mg). IR (KBr/Nujol): 1181 [ν(PO)] cm^{-1}. MS (FAB) *m*/*z* = 1070, 6% $[M]^+$, 589, 4% $[M - \text{ligand}]^+$. ^{31}P NMR (CD_2Cl_2): δ 21.8 (d, $OPPh_2$, J_{PP} = 20.0 Hz), 51.9 (d, $SePPh_2$, J_{PP} = 20.1 Hz, J_{PSe} not resolved). ^1H NMR (CD_2Cl_2): δ 4.96 (s, 2 H, NH), 7.34–7.49, 7.67, 7.93 (m, 40 H, C_6H_5). Anal. calculated for $C_{48}H_{42}AgBrN_2O_2P_4Se_2$: C, 50.20; H, 3.69; N, 2.44%. Found: C, 50.50; H, 3.93; N, 2.08%.

[{Ph$_2$P(Se)CH$_2$CH$_2$AsPh$_2$}$_2$Ag]Br (6). Silver bromide (19.6 mg, 0.104 mmol) and $[Ph_2P(Se)CH_2CH_2AsPh_2]$ (100 mg, 0.208 mmol) were stirred in acetone (30 mL) for 2 h. The solvent volume was reduced to *ca.* 5 mL and pentane (20 mL) carefully added to precipitate the white product. This was washed with pentane (10 mL) and dried. Yield: 30% (38 mg). MS (FAB) *m*/*z* = 1154, 10% $[M]^+$, 629, 100% $[M - Ph_2P(Se)CH_2CH_2AsPh_2]^+$. ^{31}P NMR (d^6-acetone): δ 39.1 (s, $SePPh_2$, J_{PSe} = 716 Hz). ^1H NMR (d^6-acetone): δ 3.25 (m, 2 H, CH_2), 7.33, 7.47, 7.86 (m, 40 H, C_6H_5). Anal. calculated for $C_{52}H_{48}AgAs_2BrP_2Se_2{\cdot}2CHCl_3$: C, 44.15; H, 3.43%. Found: C, 43.52; H, 3.10%. The complex was recrystallised from a chloroform–pentane mixture and yielded the chloroform bis-solvate as shown by integration of the ^1H NMR spectrum.

X-Ray crystallography

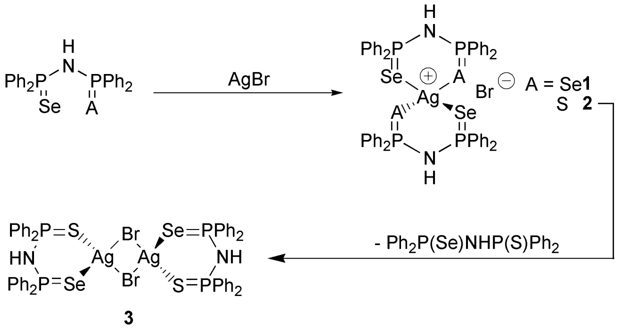
Specimens of suitable quality and size of compounds **1**, **3**, and **4** were mounted on the ends of quartz fibres in F06206R oil and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo-Kα radiation. The structures were solved by a combination of direct methods (SHELXS-97)[17a] and difference-Fourier syntheses and refined by full matrix least-squares calculations on F^2 (SHELXL-97).[17b] The thermal motion was treated anisotropically for all non-hydrogen atoms. All N–H atoms were located and included into the refinement isotropically (**3**, **4**) and with fixed isotropic contributions (**1**), respectively. All C–H atoms were calculated and allowed to ride on their parent atoms with fixed isotropic contributions. In the crystal of compound **3**, the S and Se atoms were disordered and refined accordingly. The crystal of compound **4** contained some additional solvent which could not be identified unambiguously and which was processed using the SQUEEZE procedure (PLATON).[17c] The volume occupied by the solvent is 218.5 Å^3, the number of electrons per unit cell deduced by SQUEEZE is 10. Further information on crystal data, data collection and structure refinement are summarised in Table 1. Important interatomic distances and angles are shown in the corresponding figure captions.

CCDC reference numbers 165867–165869.

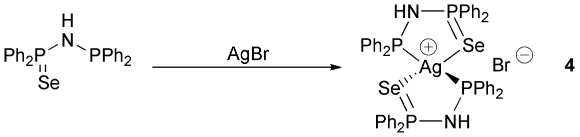
See http://www.rsc.org/suppdata/dt/b1/b105154g/ for crystallographic data in CIF or other electronic format.

Synthesis and characterisation of complexes

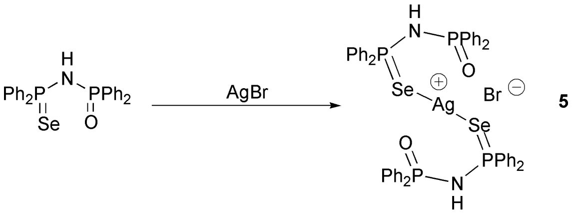
Acetone solutions of $[Ph_2P(Se)HNP(E)Ph_2]$ (E = Se, S, O or lone pair) and AgBr were allowed to react at room temperature to provide moderate to good yields of the complexes [{HN(Ph$_2$PSe)$_2$-*Se,Se′*}$_2$Ag]Br (**1**), [{HN(Ph$_2$PSe)(Ph$_2$PS)-*Se,S*}$_2$Ag]Br (**2**) [{HN(Ph$_2$PSe)(Ph$_2$P)-*Se,P*}$_2$Ag]Br (**4**) and [{HN(Ph$_2$PSe)(Ph$_2$PO)-*Se*}$_2$Ag]Br (**5**) (see Schemes 1–3).



Scheme 1 Preparation of the complexes **1** and **2** and the loss of $[Ph_2P(Se)HNP(S)Ph_2]$ ligand to form **3**.



Scheme 2 Preparation of complex **4**.



Scheme 3 Preparation of complex **5**.

The composition of the complexes **1**, **2**, **4** and **5** was elucidated from microanalysis and FAB mass spectrometric data. The latter technique provided *m*/*z* peaks for the molecular ions in each case along with peaks corresponding to the loss of an aminodiphosphine chalcogenide ligand ($[M - L]^+$). The fragmentations observed correlate well with the simulated isotope patterns. ^{31}P NMR spectroscopy also proved an invaluable tool in the determination of ligand geometry at the metal centre. In each complex, the phosphorus atom bearing selenium gave rise to a resonance at *ca.* 51 ppm with ^{31}P–^{77}Se coupling in the range 745–770 Hz. A large coupling between the two Ag-bound phosphorus atoms of 376 Hz (AA′BB′ spin system) is observed

Table 1 Crystal data, data collection, and structure refinement of compounds **1**, **3** and **4**

	1	**3**·2Me$_2$CO	**4**·1.5EtOH
Empirical formula	$C_{48}H_{42}AgBrN_2P_4Se_4$	$C_{54}H_{54}Ag_2Br_2N_2O_2P_4S_2Se_2$	$C_{51}H_{51}AgBrN_2O_{1.5}P_4Se_2$ [b]
M	1274.34	1484.47	1185.52
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	19.8727(2)	10.6362(1)	10.3900(1)
b/Å	19.9494(3)	10.8018(2)	17.3447(3)
c/Å	26.8027(3)	12.8637(2)	29.5465(5)
α/°	76.036(1)	97.776(1)	102.491(1)
β/°	72.849(1)	92.204(1)	98.362(1)
γ/°	72.363(1)	106.635(1)	92.744(1)
U/Å^3	9540.4(4)	1398.3(1)	5125.9(1)
ρ_{calc}/g cm^{-3}	1.774	1.763	1.536 [b]
Z	8	1	4
μ(Mo-Kα)/cm^{-1}	44.83	36.62	27.6
T/K	143	143	143
Measured reflections	245595	40038	116262
Unique reflections	39019 [$R_{int} = 0.114$]	5709 [$R_{int} = 0.044$]	19290 [$R_{int} = 0.044$]
Refined parameters	2182	320	1136
$R1$ [$I \geqslant 2\sigma(I)$]	0.0618	0.0279	0.0408
$wR2$	0.0991	0.0665	0.0857
Weighting scheme [a]	$a = 0.00$ $b = 44.96$	$a = 0.0220$ $b = 1.79$	$a = 0.0274$ $b = 12.28$
σ_{fin}(max/min)/e Å^{-3}	1.385/−1.048	0.483/−0.875	1.234/−0.962

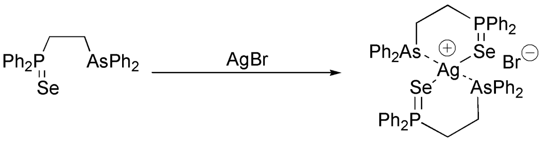
[a] $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$. [b] Data correspond to the given stoichiometry, although the crystal contains additional unidentified solvent (see Experimental section).

in the ^{31}P NMR spectrum of the product [{HN(Ph$_2$PSe)(Ph$_2$P)-*Se,P*}$_2$Ag]Br (**4**).

Single crystals were grown of the complexes **1** and **4**. The structural investigations confirmed the predicted composition and the tetrahedral coordination geometry at the silver atom of the compounds in addition to providing information on intermolecular interactions. These were found to take place through the bromide counteranions to form a chain motif. Attempts to obtain crystals of **2** from a layered mixture of acetone and pentane resulted instead in the crystallisation of a compound with an altogether different stoichiometry. The crystal lattice contains the dinuclear, neutral complex [{HN(Ph$_2$PSe)(Ph$_2$PS)-*Se,S*}AgBr]$_2$ (**3**) which displays bromide bridging and only one [Ph$_2$P(Se)HNP(S)Ph$_2$] ligand attached to each silver atom.

A diffraction study of compound **5** would have provided an unambiguous insight into the coordination properties of the mixed soft–hard donor combination of the [Ph$_2$P(Se)HN-P(O)Ph$_2$] ligand, providing an excellent comparison with the diselenide complex **1**. Despite repeated attempts, compound **5** failed to yield suitable single crystals for such a study, however, the spectroscopic data permit a plausible structural proposal to be made. The ^{31}P NMR chemical shift for Ph$_2$PO in the free ligand [Ph$_2$P(Se)HNP(O)Ph$_2$] appears at 21.0 ppm.[10] Woollins and co-workers reported that this resonance shifts downfield to 26.9–30.6 ppm in their platinum and palladium complexes, for which bidentate coordination has been structurally confirmed.[10] The ^{31}P NMR spectrum of compound **5** reveals a resonance at 21.8 ppm for the Ph$_2$PO group; almost unchanged with respect to that of the free ligand. The medium strength ν(PO) absorption at 1181 cm^{-1} observed for **5** in the solid state (KBr/Nujol) infrared spectrum is also in agreement with that found for the free ligand (1190 cm^{-1}). The platinum complexes described[10] exhibit ν(PO) absorptions in the lower frequency range 1055–1060 cm^{-1}. This clearly leads to the conclusion that in the silver complex, the ligand is coordinated in a monodentate fashion to give a linear complex bound solely through selenium.

The related ligand [Ph$_2$P(Se)CH$_2$CH$_2$AsPh$_2$] was prepared in order to examine the coordination abilities of an arsine functionality within the same system. The reaction proceeds in relatively low yield to provide the complex [{Ph$_2$P(Se)CH$_2$CH$_2$AsPh$_2$}2Ag]Br (**6**) (see Scheme 4). The composition was established through elemental analysis and FAB mass spectrometry (molecular ion at m/z = 1154, 10%). Unfortunately, no suitable crystals of sufficient quality were obtained of this complex in order for a structural study to be undertaken. Previous investigation of the coordination properties of arsine ligands in silver(I) complexes have provided a number of examples,[16] though the Ag–As coordination is relatively weak compared to that between silver and phosphorus. We were unable to find structurally characterised silver(I) examples of mixed-donor chelates containing arsenic in the literature. It is reasonable to propose that compound **6** adopts a geometry in which the silver is bound to both selenium and arsenic donor atoms, *i.e.* an analogue of compound **4**.



6

Scheme 4 Preparation of complex **6**.

Structural discussion

Crystals of compound **1** (obtained from slow diffusion of a dichloromethane–diethyl ether mixture) are triclinic and of space group $P\bar{1}$ with Z = 8. The large asymmetric unit thus contains four independent bromide anions together with complex cations which are all very similar in their basic structures and dimensions. One representative cation is shown in Fig. 1. Each silver atom is coordinated by the selenium atoms of two chelating ligands in a distorted tetrahedral geometry with Ag–Se bond lengths in the narrow range from 2.6237(8) to 2.7283(8) Å. Together with P–Se distances between 2.116(2) to 2.129(2) Å, these data suggest strong coordinative bonding of symmetrical ligands. The P–N distances in the chelate loops are indicative of P–N single bonding between the phosphorus atoms and non-deprotonated imino groups.

The imino protons of all four independent molecules were localised and refined in plausible positions. They are engaged in hydrogen bonding with the bromide counteranions to forms chains of alternating cations and anions. The N ··· Br distances are in the range 3.244 to 3.319 Å with H ··· Br contacts between 2.276 and 2.539 Å and N–H ··· Br angles between 165.9 and 176.1°. Two such hydrogen bonds originate from each bromide anion. The two non-equivalent chains resulting from

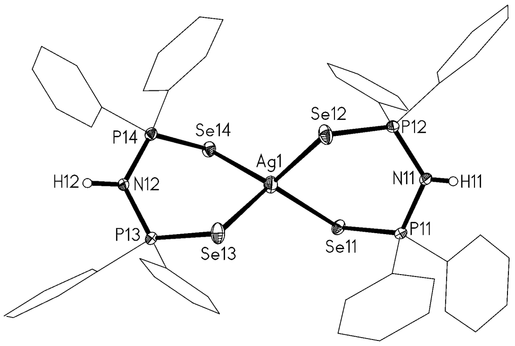


Fig. 1 Structure of one of the four independent cations in the unit cell of compound **1**. (ORTEP[18] for the heavy atoms with 50% probability ellipsoids; phenyl hydrogen atoms are omitted, phenyl groups are introduced schematically). Selected bond lengths (Å) and bond angles (°): Ag1–Se11 2.6571(8), Ag1–Se12 2.6747(8), Ag1–Se13 2.7141(9), Ag1–Se14 2.6393(8); P11–N11 1.679(5), P12–N11 1.685(5), P13–N12 1.679(5), P14–N12 1.685(5); P11–Se11 2.126(2), P12–Se12 2.116(2), P13–Se13 2.118(2), P14–Se14 2.122(2); Se11–Ag1–Se12 102.59(2), Se13–Ag1–Se14 108.88(2), P11–N11–P12 125.3(3), P13–N12–P14 127.9(3). The distances and angles in the other three cations (with silver atoms Ag2–Ag4) are similar. The monomers are connected through hydrogen bonds between H11 and H12 and the bromide anions Br1 and Br2. Monomers with Ag1 and Ag3 and Br1 and Br2 form an individual chain, as do monomers with Ag2 and Ag4 together with Br3 and Br4 (supplementary material).

these interactions run parallel and comprise the silver atoms Ag1 and Ag3 or Ag2 and Ag4, respectively. The chains are well separated with no discernible inter-strand phenyl stacking.

Compound **3** crystallises from acetone–pentane as a 1 : 2 solvate **3**·2Me$_2$CO (triclinic, space group $P\bar{1}$, Z = 1). The neutral dinuclear molecules reside on a centre of inversion located in the middle of the Ag$_2$Br$_2$ ring (Fig. 2). The bromine atoms are bridging the silver atoms to form a rhombus with distances Ag–Br 2.6987(3) and Ag–Br′ 2.7102(3) Å and angles Ag–Br–Ag′ 79.77(1) and Br–Ag–Br′ 100.23(1)°. Each silver atom is also chelated by a [Ph$_2$P(S)HNP(Se)Ph$_2$] ligand to give a six-membered ring very similar in its conformation to those in compound **1** (above). There is disorder in the sulfur and selenium positions which was resolved by a suitable model in the structure solution. Owing to this disorder, the Ag–S/Se and P–S/Se distances are not discussed in any detail here.

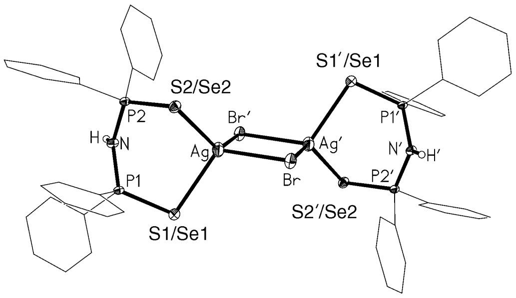


Fig. 2 Molecular structure of compound **3** in crystals of **3**·2Me$_2$CO (ORTEP for the heavy atoms with 50% probability ellipsoids; phenyl hydrogen atoms are omitted, phenyl groups are introduced schematically). The sulfur and selenium atoms are disordered. Selected bond lengths (Å) and angles (°): Ag–S1/Se1 2.6761(4), Ag–S2/Se2 2.6150(4); Ag–Br 2.6987(3), Ag–Br′ 2.7102(3), P1–N 1.679(2), P2–N 1.684(2); Ag–Br–Ag′ 79.77(1), Br–Ag–Br′ 100.23(1), P1–N–P2 128.3(1). The hydrogen atoms H(N) and H′(N′) form hydrogen bonds with the acetone molecules (supplementary material).

Both imino groups in compound **3** are found protonated with the hydrogen atoms forming discrete hydrogen bonds to the acetone solvent molecules. There are no further conspicuous intermolecular contacts.

Crystals of compound **4** (from slow diffusion of ethanol into diethyl ether) are triclinic, of space group $P\bar{1}$ with Z = 4, and contain three molecules of ethanol in the unit cell. The asymmetric unit thus contains two independent complex cations, two anions, and 1.5 equivalents of solvent. The two complex cations are structurally very similar. Fig. 3 shows one of the two cationic units. The silver atom is in a distorted tetrahedral environment bound by two neutral Se,P-chelating ligands. The hydrogen atoms of the imino groups have been located and their positions refined such that there can be no doubt about the nature of the ligands as neutral bidentate groups.

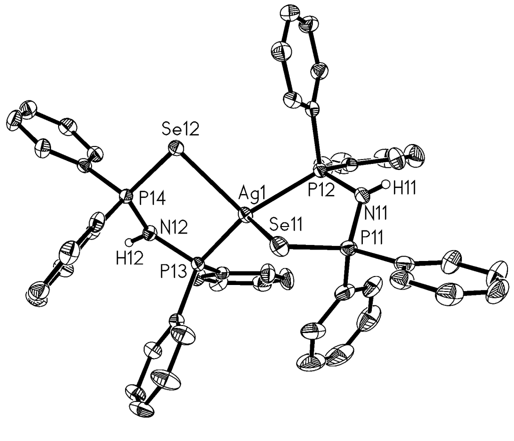


Fig. 3 One of the two independent cations in crystals of compound **4**·1.5EtOH (ORTEP, 50% probability ellipsoids; phenyl hydrogen atoms are omitted). Selected bond lengths (Å) and angles (°): Ag1–P12 2.4740(9), Ag1–P13 2.4453(9), Ag1–Se11 2.8050(5), Ag1–Se12 2.7008(4), P11–N11 1.653(3), P12–N11 1.704(3), P13–N12 1.710(3), P14–N12 1.674(3); Se11–Ag1–P12 88.12(2), Se12–Ag1–P13 91.99(2), P11–N11–P12 118.4(2), P13–N12–P14 120.3(2). The dimensions of the second cation (with Ag2) are similar.

The cations are arranged in strings with the bromide anions and ethanol molecules acting as bridging units (Fig. 4). The bromide anions are hydrogen-bonded to one imino group and the hydroxyl group of an ethanol molecule, which in turn entertains another hydrogen bond with the imino group of the following cation. The remaining interstitial molecule of ethanol per unit cell (one out of three) does not take part in the chain system. The dimensions of the N–H ··· Br hydrogen bonds are similar to those in compound **1**. Further details are given in the figure captions and have been deposited as supplementary material.

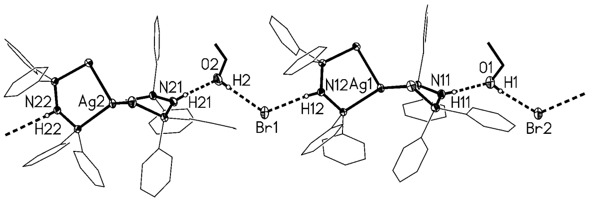


Fig. 4 Supramolecular catenation through hydrogen bonding between the components (two cations, two bromide anions and two ethanol molecules) in crystals of compound **4**. Selected bond lengths (Å), angles (°): N12–H12 0.836, Br1 ··· H12 2.586, N12 ··· Br1 3.437, N12–H12–Br1 172.9; O2–H2 0.724, Br1 ··· H2 2.508, O2 ··· Br1 3.232, O2–H2 ··· Br1 177.8.

Conclusion

In this work, the hitherto poorly-explored coordination chemistry of the neutral mixed-donor ligands Ph$_2$P(Se)HNP(E)PPh$_2$ (E = Se, S, O or lone pair) has been investigated with monovalent silver. This has confirmed that these ligands have a good complexation ability and do not require deprotonation in order to bind. The retention of the amine proton permits the complexes to form hydrogen-bonded, supramolecular chains either solely through their counteranions or through both counteranions and solvent molecules.

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