

Oxidation of a One-Dimensional Coordination Polymer and Synthesis of the Macrocyclic Silver Complex $[\text{Ag}_{12}(\text{PhS}_2\text{P}-\text{PS}_2\text{Ph})_6(\text{dppeS})_6]$

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The cluster chemistry with functionalised trimethylsilyl reagents was investigated. The oxidation of the one-dimensional coordination polymer $1/\infty[\{\text{Ag}_2(\text{PhS}_2\text{P}-\text{PS}_2\text{Ph})\cdot\text{dppe}\}]_\infty$ leads to the formation of $[\text{Ag}_{12}(\text{PhS}_2\text{P}-\text{PS}_2\text{Ph})_6(\text{dppeS})_6]$ ($\text{dppeS} = \text{Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{S})\text{Ph}_2$). The dian-

ionic ligand $[\text{PhPS}_2-\text{PS}_2\text{Ph}]^{2-}$ could possibly give rise to a new class of macrocyclic transition-metal chalcogenides.

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Introduction

Over the last few years we have been investigating the syntheses, structures and properties of a variety of silver-chalcogen clusters including the phosphane-stabilised nanoparticle $[\text{Ag}_{262}\text{S}_{100}(\text{tBu})_{62}(\text{dppb})_6]$ [$\text{dppb} = 1,4$ -bis(diphenylphosphanyl)butane], which can be regarded as the largest ligand-protected silver sulfide complex characterised so far.^[1] The general synthetic route to these species involves the reaction of AgX ($\text{X} = \text{halide, carboxylate}$) salts with tertiary phosphanes and subsequent reaction with trimethylsilyl chalcogenides.^[1] Recently, we continued with earlier work where we investigated the potential of reactions between the sulfur-functionalised phosphane $\text{P}(\text{S})(\text{SSiMe}_3)_3$ and late transition metal salts for the building up of transition metal clusters with functionalised phosphane ligands.^[2] A discovery made during these investigations was that $\text{P}(\text{S})(\text{SSiMe}_3)_3$ cannot be used as a source of $[\text{PS}_4]^{3-}$ anions. Instead a hexathiodiphosphonato tetraanion $[\text{S}_3\text{P}-\text{PS}_3]^{4-}$ is formed in reactions with late transition metal salts and this indicates that $\text{P}(\text{S})(\text{SSiMe}_3)_3$ possibly undergoes disproportionation into $[(\text{Me}_3\text{SiS})_2(\text{S})\text{P}-\text{P}(\text{S})(\text{SSiMe}_3)_2]$, elemental sulfur and $\text{S}(\text{SiMe}_3)_2$.^[2d,2e] This reactivity prompted us to prepare new families of metal aggregates, which are accessible by the reaction of Ag_2S with P_2S_5 or by heating mixtures of elemental Ag, P and S.^[3,4] Research in this area was motivated by the interest in sulfide-based glasses and their use as solid electrolytes.^[3] For a wet-chemistry approach to these compounds, however, the use of solubilising organic groups is particularly promising. We therefore chose the related silylated reagent $\text{PhP}(\text{S})(\text{SSiMe}_3)_2$, tertiary phosphanes and silver acetate (AgOAc) as starting materials. Here we wish to report the

first result of these efforts and demonstrate the versatility of the P–S ligand $[\text{PhS}_2\text{P}-\text{PS}_2\text{Ph}]^{2-}$ generated in the reaction.

Results and Discussion

By the reaction of AgOAc with dppe [$\text{dppe} = 1,2$ -bis(diphenylphosphanyl)ethane] and $\text{PhP}(\text{S})(\text{SSiMe}_3)_2$ (Scheme 1), the one-dimensional coordination polymer $1/\infty[\{\text{Ag}_2(\text{PhS}_2\text{P}-\text{PS}_2\text{Ph})\cdot\text{dppe}\}]_\infty$ (**1**) was obtained, and it was characterised by X-ray crystallography and ^{31}P NMR spectroscopy (Figure 1).

Analogous to the previously described reaction of $\text{P}(\text{S})(\text{SSiMe}_3)_3$, the formation of a P–P bond was observed in reactions of AgOAc with $\text{PhP}(\text{S})(\text{SSiMe}_3)_2$. In the solid-state structure of **1**, the dianion $[\text{PhS}_2\text{P}-\text{PS}_2\text{Ph}]^{2-}$ and one molecule of the neutral phosphane ligand dppe hold together a tricyclic arrangement of two tetrahedrally coordinated Ag^+ ions. An additional molecule of dppe completes the coordination sphere of the Ag atoms and acts as a bridging ligand between the $[\text{Ag}_2(\text{dppe})(\text{PhS}_2\text{P}-\text{PS}_2\text{Ph})]$ units (Figure 1). Bond lengths in **1** are within the range of commonly observed values.^[4] S–Ag–S bond angles in **1** [$96.20(5)$ and $96.88(5)^\circ$] are similar to those observed in a bis(diphenylphosphanyl)methane adduct of a silver thiocarboxylate $\{\text{S}-\text{Ag}-\text{S} [99.67(5)^\circ]\}$.^[5] It is worth noting that each S atom in **1** (coordination number: 2) coordinates one Ag atom only, and the C–P–P–C torsion angle in the $[\text{PhS}_2\text{P}-\text{PS}_2\text{Ph}]^{2-}$ ligand is $50.2(4)^\circ$. A change of this torsion angle means alternative orientations of the S-donor centres in the ligand $[\text{PhS}_2\text{P}-\text{PS}_2\text{Ph}]^{2-}$, and this might therefore result in different coordination modes of this ligand. Higher coordination numbers for the S-donor centres were found in the related complex $[\text{Cu}_6(\text{P}_2\text{S}_6)\text{Cl}_2(\text{PPh}_3)_6]$.^[2b] X-ray structures of the closest related complexes of **1**,

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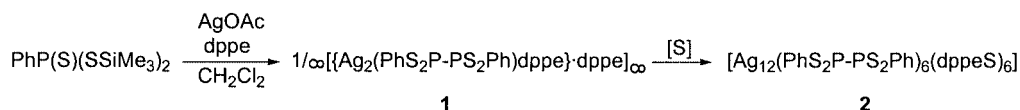
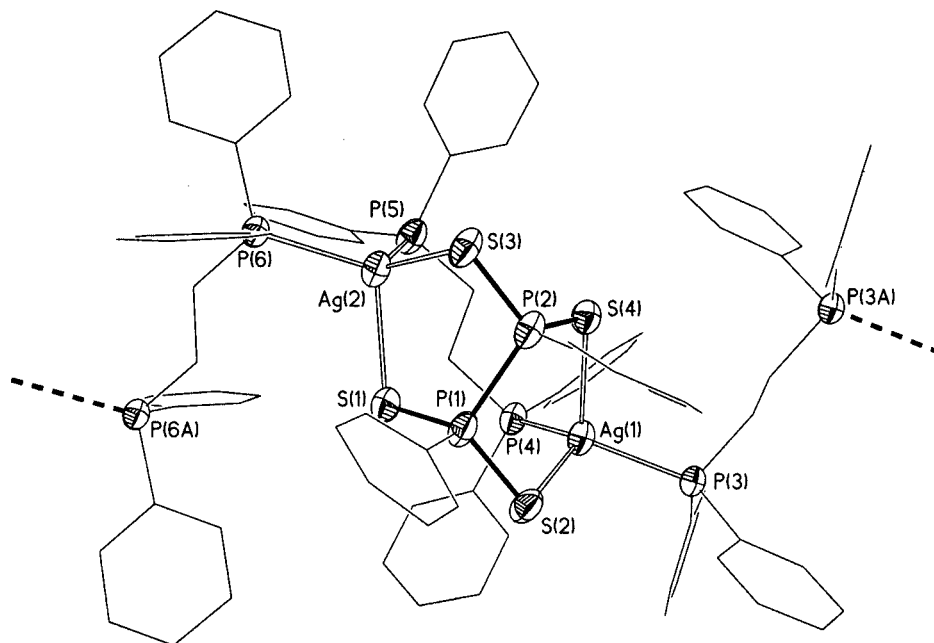

 Scheme 1. Synthesis of **1** and oxidation leading to the formation of **2**


Figure 1. Structure of a dppe-bridged $[\{\text{PhPS}_2\}_2\text{Ag}_2\cdot\text{dppe}]$ unit in polymeric **1** (ellipsoids at 50%; connections to adjacent units are indicated; H atoms are omitted); selected bond lengths (Å) and angles ($^\circ$): Ag–S 2.556(2)–2.631(2), Ag–P 2.475(2)–2.510(2), P–S 1.981(2)–1.992(2), P(1)–P(2) 2.262(3); C–P(1)–P(2)–C 50.2(4), S(2)–Ag(1)–S(4) 96.88(5), S(3)–Ag(2)–S(1) 96.20(5), S–Ag–P 103.89(6)–117.66(6), P–P–S 108.1(1)–108.8(1), S(1)–P(1)–S(2) 117.3(1), S(4)–P(2)–S(3) 116.0(1)

$[\text{M}_2(\text{PhS}_2\text{P-PS}_2\text{Ph})]$ ($\text{M} = \text{Li}, \text{K}$), have to the best of our knowledge not yet been determined.^[6]

In solutions of **1**, two species, possibly rotamers, containing P–P bonds are present, which show two singlet resonances at $\delta = 84.4$ and 81.2 ppm. A similar value ($\delta = 85.4$ ppm) is observed in the ^{31}P NMR spectrum of $[\text{Li}_2(\text{PhS}_2\text{P-PS}_2\text{Ph})]$.^[6b] The P–P bond formation during the preparation of **1** could be rationalized by the disproportion of $\text{PhP(S)(SSiMe}_3)_2$ into $[\text{Ph(S)(SSiMe}_3)\text{P-P(S)(SSiMe}_3)\text{Ph}]$, which instantly reacts with AgOAc, elemental sulfur and $\text{S(SiMe}_3)_2$. The dppe ligands present in solution were oxidised to $\text{Ph}_2\text{P(CH}_2)_2\text{P(S)Ph}_2$ ($\delta_{\text{P-S}} = 45.6$ ppm, $^3J_{\text{P-P}} = 58$ Hz).^[7] In **1**, the P^{III} centres of the dppe ligands and $\text{Ph}_2\text{P(CH}_2)_2\text{P(S)Ph}_2$ are identified by a broad singlet resonance ($\delta = 0.6$ ppm) (P–Ag coupling has not been resolved).^[7,5] In order to gain further mechanistic insight and to understand the formation of the $[\text{PhS}_2\text{P-PS}_2\text{Ph}]^{2-}$ dianion we tried to synthesise the postulated intermediate diphenyltetrahydriodiphosphonic acid trimethylsilyl ester $[\text{Ph(S)(SSiMe}_3)\text{P-P(S)(SSiMe}_3)\text{Ph}]$ in the absence of AgOAc by the reaction of $\text{PhP(S)(SSiMe}_3)_2$ with dppe. However, these attempts failed, and this indicates that P–P bond formation only occurs in the presence of AgOAc.

Storage of a reaction mixture containing crystals of **1** at room temperature for approximately three weeks produced colourless crystals of $[\text{Ag}_{12}(\text{PhS}_2\text{P-PS}_2\text{Ph})_6(\text{dppeS})_6]$ (**2**) [$\text{dppeS} = \text{Ph}_2\text{P(CH}_2)_2\text{P(S)Ph}_2$] (Scheme 1). Initially, this was realised because the amount of crystalline precipitate in the reaction mixtures containing crystals of **1** increased, and a closer look revealed that only crystalline blocks of **2** were present. Further experiments have shown that **2** can also be obtained by filtering off crystals of **1** and storage of the filtrate for several weeks. Mixtures of both **1** and **2** were not observed. An X-ray analysis of **2** confirms the results from the ^{31}P NMR spectra, in which indication for the formation of dppeS is found. As a consequence, oxidation-induced fragmentation of polymeric arrangements of **1** gives rise to the macrocyclic complex **2** (Figure 2).

Complex **2** crystallizes in the space group $P\bar{1}$ with the inversion centre located in the middle of the molecule. Complex **2** is constructed from six corner-sharing distorted AgS_4 tetrahedra [Ag-S 2.553(3)–2.767(3) Å, S-Ag-S 89.4(1)–139.9(1) $^\circ$] and forms a twelve-membered $[\text{AgS}_6]_6$ ring (Figure 2). The six S atoms of the ring are located on the corners of an octahedron with nonbonding S–S distances of about 3.64–4.04 Å. In the periphery, Ag(1) is co-

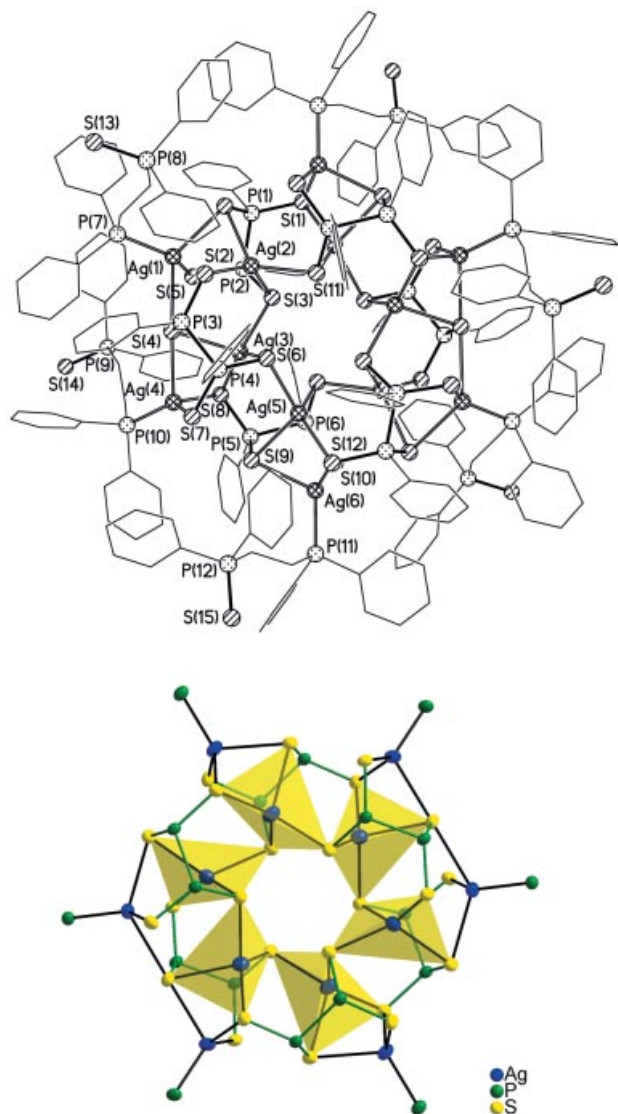


Figure 2. Molecular structure of **2** (H atoms are omitted) and structure of the core of **2** (C atoms and peripheral P and S atoms are omitted; ellipsoids at 50%; selected ranges of bond lengths (Å) and angles (°): Ag–S 2.535(3)–2.952(4), Ag–P 2.430(3)–2.449(3), P–P 2.261(4)–2.275(5), P–S 1.988(4)–2.020(4), P–S_{dppeS} 1.955(5)–1.966(4); S–Ag–S 87.5(1)–139.9(1), S–Ag–P 91.1(1)–132.6(1), P–P–S 104.1(2)–110.7(2), S–P–S 119.1(2)–120.0(2)

ordinated by S atoms of two different AgS₄ tetrahedra, whilst Ag(4) and Ag(6) are located over the edges of the central AgS₄ units. One S atom of each [PhS₂P–PS₂Ph]^{2–} ligand is not part of the [Ag₆S₁₈] core and completes the tetrahedral coordination sphere of the outer Ag atoms, together with one P atom of the monodentate dppeS ligands (Figure 2). Signals for the chemically non-equivalent P atoms in the [PhS₂P–PS₂Ph]^{2–} ligand in **2** can be observed in the ³¹P NMR spectrum (AB spin system; two doublet resonances at δ = 82.0 and 79.4 ppm, ¹J_{P,P} = 56 Hz). In the Maldi TOF-MS the ions [Ag(dppeS)]⁺, [dppe]⁺ and [dppeS]⁺ were detected. The coordination numbers of the S atoms in **2** are greater than those in the solid-state structure of **1**, and also the C–P–P–C torsion angle in **2**

[55.45(5)–58.59(5)°] is about 5–8° wider than that observed in **1**.

Conclusion

The ability of the [PhS₂P–PS₂Ph]^{2–} ligand to coordinate in a variety of modes is demonstrated. Slight changes in the C–P–P–C torsion angle should allow access to a range of new coordination modes with different arrangements of polyhedral building blocks, for example, MS₄ tetrahedra (M = Cu, Ag).^[8] Further reactions currently under investigation include metathesis reactions of **1** with metal halides and the oxidation of **1** with elemental sulfur.

Experimental Section

General Remarks: All operations were carried out under purified nitrogen. Dichloromethane was refluxed over calcium hydride, heptane was dried with Na/benzophenone and freshly distilled. AgOAc and dppe were purchased from Aldrich and used without further purification. PhP(S)(SSiMe)₂ was prepared by a published method.^[9]

1: PhP(S)(SSiMe₃)₂ (0.50 g, 1.44 mmol) was added to a pale yellow solution of AgOAc (0.24 g, 1.44 mmol) and dppe (0.57 g, 1.44 mmol) in dichloromethane (20 mL) at –40 °C. The solution instantly became colourless, and the mixture was stirred for 2 h and then warmed up to –10 °C. The reaction was kept at 0 °C for two days. The solvent was then reduced to about 15 mL. Upon addition of heptane (approximately 0.7 mL), a colourless precipitate was formed, which redissolved when the mixture was shaken. After storage of the solution at 0 °C for three weeks, colourless cuboctahedral crystals of **1** were isolated. ³¹P NMR (101.256 MHz, CDCl₃, 25 °C, 65% H₃PO₄) δ = 84.4, 81.2 (s, PhS₂P–PS₂Ph), 0.8 ppm (br. s, Ph₂P–), an additional resonance was observed at δ = 45.0 ppm (d, ³J_{P,P} = 60 Hz, Ph₂P(CH₂)₂P(S)Ph₂). C₃₈₄H₃₄₈Ag₁₂P₃₆S₂₄: calcd. C 56.65, H 4.31; found C 57.03, H 3.92.

2: After formation of **1** (this was checked by determination of unit-cell dimensions of a small sample), the reaction was stored for four more weeks at 0 °C, and only blocks of **2** were isolated. Yield 0.41 g, 58% (based on AgOAc supplied; **2**, excluding lattice-bound CH₂Cl₂). M.p. 166–168 °C (decomposition into brown melt >172 °C). ³¹P NMR (121.485 MHz, CDCl₃, 25 °C, 65% H₃PO₄): δ = 93.2, 89.4 (s, PhS₂P–PS₂Ph), 82.0 and 79.4 (dd, ¹J_{P,P} = 56 Hz, PhS₂P–PS₂Ph), 45.2 [br. m, Ph₂P(CH₂)₂P(S)Ph₂], 28.3 ppm [m, ³J_{P,P} = 59 Hz, Ph₂P(CH₂)₂P(S)Ph₂] coupling to ^{107/109}Ag could not be identified unequivocally, Ph₂P(CH₂)₂P(S)Ph₂. IR (CsI, Nujol): $\tilde{\nu}$ = 1439 (P–Ph), 690, 612 (P=S), 579, 508, 466 cm^{–1} (tentatively assigned as P–P and P–S). MS (Maldi TOF), *m/z* (%) = 538.39 (30) [dppeSAg⁺], 430.61 (100) [dppeS⁺], 398.69 (8) [dppe⁺]. C₂₂₈H₂₀₄Ag₁₂P₂₄S₃₀ (5943.7): calcd. C 46.07, H 3.46; found C 46.05, H 3.50.

X-ray Crystallography: Data were collected with a STOE STADI 4 diffractometer equipped with a CCD detector (**1**) and with a Stoe IPDS II diffractometer (**2**) using graphite-monochromated Mo-*K*_α radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares on *F*² (all data) with the SHELXTL program package.^[10] Hydrogen atoms were placed in calculated positions, non-hydrogen atoms were assigned

anisotropic thermal parameters, atoms of lattice-bound solvent molecules were refined with isotropic thermal parameters. In order to identify further possible by-products unit-cell dimensions of crystals from different samples were repeatedly determined, and in each case, at first **1** and then **2**, were obtained as the only products that we were able to characterise.

Crystal Data for 1·8C₇H₁₆·6CH₂Cl₂: C₃₈₄H₃₄₈Ag₁₂P₃₆S₂₄ (eight heptane and six CH₂Cl₂ solvent molecules per formula unit), $M = 8141.93$; trigonal, space group $R\bar{3}$; $Z = 3$; $a = b = 31.214(4)$, $c = 40.099(8)$ Å; $V = 33835(10)$ Å³; $T = 197(2)$ K; $F(000) = 14568$; $D_{\text{calcd.}} = 1.392$ g cm⁻³. 59537 reflections collected, of which 19049 were unique ($R_{\text{int}} = 0.0615$). 771 parameters; final $wR_2 = 0.2367$ (all data); $R_1 = 0.0727$ [$I > 2\sigma(I)$]; largest difference peak and hole 2.834, -0.947 e·Å⁻³.

Crystal Data for 2·18CH₂Cl₂: C₂₂₈H₂₀₄Ag₁₂P₂₄S₃₀ (eighteen CH₂Cl₂ solvent molecules per formula unit) $M = 5943.83$; triclinic, space group $P\bar{1}$; $Z = 1$; $a = 19.281(4)$, $b = 20.329(4)$, $c = 22.806(5)$ Å; $\alpha = 96.20(3)$, $\beta = 114.11(3)$, $\gamma = 108.83(3)^\circ$; $V = 7419(3)$ Å³; $T = 130(2)$ K; $F(000) = 3732$; $D_{\text{calcd.}} = 1.672$ g cm⁻³. 43858 reflections measured, of which 24516 were unique ($R_{\text{int}} = 0.0860$). 1432 parameters; final $wR_2 = 0.2395$ (all data); $R_1 = 0.0859$ [$I > 2\sigma(I)$]; largest difference peak and hole 2.457, -2.055 e·Å⁻³.

CCDC-243898 and CCDC-243899 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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