Oxidation of a One-Dimensional Coordination Polymer and Synthesis of the Macrocyclic Silver Complex $[Ag_{12}(PhS_2P{-}PS_2Ph)_6(dppeS)_6]$

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Keywords: Silver / Chalcogenides / Macrocycle / P ligands / S ligands

The cluster chemistry with functionalised trimethylsilyl reagents was investigated. The oxidation of the one-dimensional coordination polymer $1/_\infty[\{Ag_2(PhS_2P–PS_2Ph)dppe\}{\cdot}dppe]_\infty$ leads to the formation of $[Ag_{12}(PhS_2P–PS_2Ph)_6(dppeS)_6]$ (dppeS = $Ph_2P(CH_2)_2P(S)Ph_2$). The dianionic ligand $[PhPS_2–PS_2Ph]^{2-}$ could possibly give rise to a new class of macrocyclic transition-metal chalcogenides.

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 $[Ag_{262}S_{100}(StBu)_{62}(dppb)_6]$ [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 (X = 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 $P(S)(SSiMe_3)_3$ 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 $P(S)(SSiMe_3)_3$ cannot be used as a source of $[PS_4]^{3-}$ anions. Instead a hexathiodiphosphonato tetraanion $[S_3P{-}PS_3]^{4-}$ is formed in reactions with late transition metal salts and this indicates that $P(S)(SSiMe_3)_3$ possibly undergoes disproportionation into $[(Me_3SiS)_2(S)P{-}P(S)(SSiMe_3)_2]$, elemental sulfur and $S(SiMe_3)_2$.[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 $PhP(S)(SSiMe_3)_2$, 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 $[PhS_2P{-}PS_2Ph]^{2-}$ generated in the reaction.

Results and Discussion

By the reaction of AgOAc with dppe [dppe = 1,2-bis(diphenylphosphanyl)ethane] and $PhP(S)(SSiMe_3)_2$ (Scheme 1), the one-dimensional coordination polymer $1/_\infty[\{Ag_2(PhS_2P{-}PS_2Ph)dppe\}{\cdot}dppe]_\infty$ (**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 $P(S)(SSiMe_3)_3$, the formation of a P−P bond was observed in reactions of AgOAc with $PhP(S)(SSiMe_3)_2$. In the solid-state structure of **1**, the dianion $[PhS_2P{-}PS_2Ph]^{2-}$ 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 $[Ag_2(dppe)(PhS_2P{-}PS_2Ph)]$ 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)°] are similar to those observed in a bis(diphenylphosphanyl)methane adduct of a silver thiocarboxylate {S−Ag−S [99.67(5)°]}.[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 $[PhS_2P{-}PS_2Ph]^{2-}$ ligand is 50.2(4)°. A change of this torsion angle means alternative orientations of the S-donor centres in the ligand $[PhS_2P{-}PS_2Ph]^{2-}$, 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 $[Cu_6(P_2S_6)Cl_2(PPh_3)_6]$.[2b] X-ray structures of the closest related complexes of **1**,

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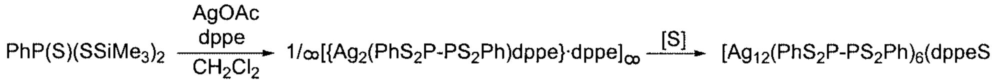
DOI: 10.1002/ejic.200400738



$$PhP(S)(SSiMe_3)_2 \xrightarrow[CH_2Cl_2]{AgOAc,\ dppe} \underset{\mathbf{1}}{1/\infty[\{Ag_2(PhS_2P\text{-}PS_2Ph)dppe\}\cdot dppe]_\infty} \xrightarrow{[S]} \underset{\mathbf{2}}{[Ag_{12}(PhS_2P\text{-}PS_2Ph)_6(dppeS)_6]}$$

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

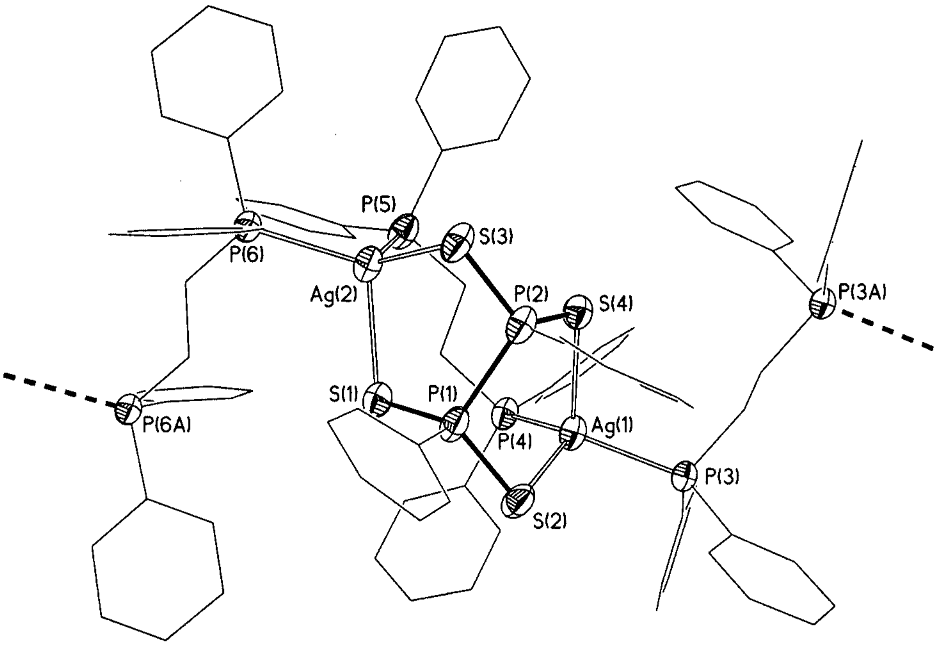


Figure 1. Structure of a dppe-bridged $[\{PhPS_2\}_2Ag_2\cdot dppe]$ unit in polymeric **1** (ellipsoids at 50%; connections to adjacent units are indicated; H atoms are omitted); selected bond lengths (Å) and angles (°): Ag−S 2.556(2)−2.631(2), Ag−P 2.475(2)−2.510(2), P−S 1.981(2)−1.992(2), P(1)−P(2) 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)

$[M_2(PhS_2P{-}PS_2Ph)]$ (M = Li, 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 δ = 84.4 and 81.2 ppm. A similar value (δ = 85.4 ppm) is observed in the ^{31}P NMR spectrum of $[Li_2(PhS_2P{-}PS_2Ph)]$.[6b] The P−P bond formation during the preparation of **1** could be rationalized by the disproportion of $PhP(S)(SSiMe_3)_2$ into $[Ph(S)(SSiMe_3)P{-}P(S)(SSiMe_3)Ph]$, which instantly reacts with AgOAc, elemental sulfur and $S(SiMe_3)_2$. The dppe ligands present in solution were oxidised to $Ph_2P(CH_2)_2P(S)Ph_2$ ($\delta_{P=S}$ = 45.6 ppm, $^3J_{P,P}$ = 58 Hz).[7] In **1**, the P^{III} centres of the dppe ligands and $Ph_2P(CH_2)_2P(S)Ph_2$ are identified by a broad singlet resonance (δ = 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 $[PhS_2P{-}PS_2Ph]^{2-}$ dianion we tried to synthesise the postulated intermediate diphenyltetrathiodiphosphonic acid trimethylsilyl ester $[Ph(S)(SSiMe_3)P{-}P(S)(SSiMe_3)Ph]$ in the absence of AgOAc by the reaction of $PhP(S)(SSiMe_3)_2$ 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 $[Ag_{12}(PhS_2P{-}PS_2Ph)_6(dppeS)_6]$ (**2**) [dppeS = $Ph_2P(CH_2)_2P(S)Ph_2$] (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)°] and forms a twelve-membered $[AgS]_6$ 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-

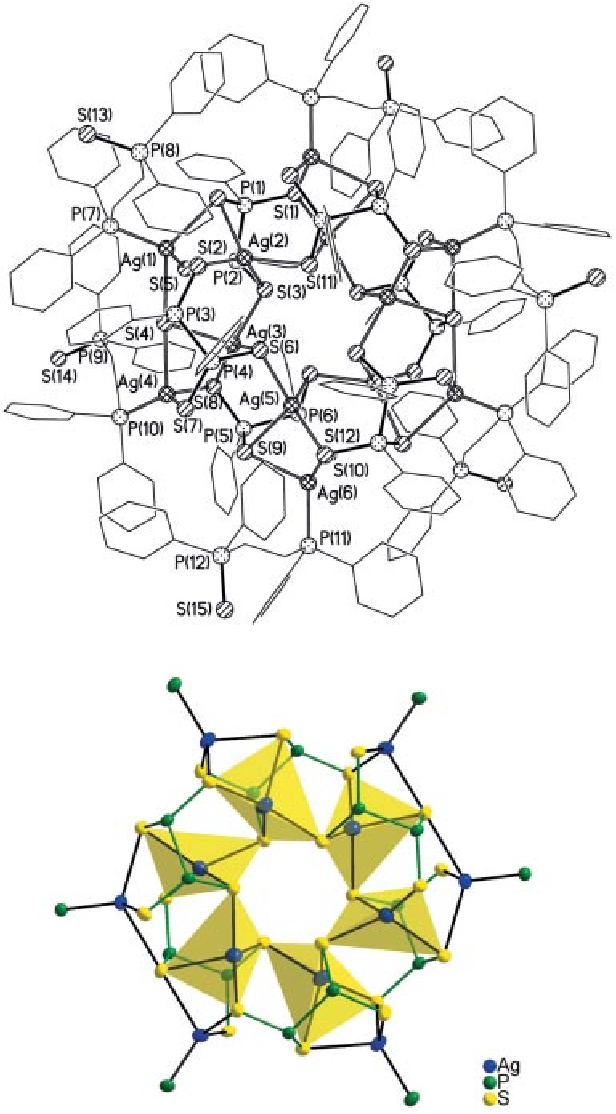


Figure 2. Molecular structure of **2** (H atoms are omitted) and structure of the core of **2** (C atoms and peripheral P and S atoms are omitted; ellipsoids at 50%;); selected ranges of bond lengths (Å) and angles (°): Ag−S 2.535(3)−2.952(4), Ag−P 2.430(3)−2.449(3), P−P 2.261(4)−2.275(5), P−S 1.988(4)−2.020(4), 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 AgS_4 tetrahedra, whilst Ag(4) and Ag(6) are located over the edges of the central AgS_4 units. One S atom of each $[PhS_2P-PS_2Ph]^{2-}$ ligand is not part of the $[Ag_6S_{18}]$ 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 $[PhS_2P-PS_2Ph]^{2-}$ ligand in **2** can be observed in the ^{31}P NMR spectrum (AB spin system; two doublet resonances at $\delta = 82.0$ 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 $[PhS_2P-PS_2Ph]^{2-}$ 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, MS_4 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: $PhP(S)(SSiMe_3)_2$ (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. ^{31}P NMR (101.256 MHz, $CDCl_3$, 25 °C, 65%H_3PO_4) $\delta = 84.4$, 81.2 (s, PhS_2P-PS_2Ph), 0.8 ppm (br. s, Ph_2P-), an additional resonance was observed at $\delta = 45.0$ ppm (d, $^3J_{P,P} = 60$ Hz, $Ph_2P(CH_2)_2\mathit{P}(S)Ph_2$]. $C_{384}H_{348}Ag_{12}P_{36}S_{24}$: 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 CH_2Cl_2). M.p. 166−168 °C (decomposition into brown melt >172 °C). ^{31}P NMR (121.485 MHz, $CDCl_3$, 25 °C, 65% H_3PO_4): $\delta = 93.2$, 89.4 (s, PhS_2P-PS_2Ph), 82.0 and 79.4 (dd, $^1J_{P,P} = 56$ Hz, PhS_2P-PS_2Ph), 45.2 [br. m, $Ph_2P(CH_2)_2\mathit{P}(S)Ph_2$], 28.3 ppm [m, $^3J_{P,P} = 59$ Hz, $Ph_2\mathit{P}(CH_2)_2P(S)Ph_2$] coupling to $^{107/109}Ag$ could not be identified unequivocally, $Ph_2\mathit{P}(CH_2)_2P(S)Ph_2$. 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) $[dppe^+]$. $C_{228}H_{204}Ag_{12}P_{24}S_{30}$ (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 ($\lambda = 0.71073$ 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 1·8C_7H_{16}·6CH_2Cl_2: $C_{384}H_{348}Ag_{12}P_{36}S_{24}$ (eight heptane and six CH_2Cl_2 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) Å^3; T = 197(2) K; $F(000)$ = 14568; $D_{calcd.}$ = 1.392 gcm^{-3}. 59537 reflections collected, of which 19049 were unique (R_{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 2·18CH_2Cl_2: $C_{228}H_{204}Ag_{12}P_{24}S_{30}$ (eighteen CH_2Cl_2 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; α = 96.20(3), β = 114.11(3), γ = 108.83(3)°; V = 7419(3) Å^3; T = 130(2) K; $F(000)$ = 3732; $D_{calcd.}$ = 1.672 gcm^{-3}. 43858 reflections measured, of which 24516 were unique (R_{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].

Acknowledgments

We gratefully acknowledge the DFG (Zentrum für funktionelle Nanostrukturen) and the Fonds der Chemischen Industrie for financial support. Thanks are also due to Dr. O. Fuhr (Forschungszentrum Karlsruhe) for recording MALDI-TOF spectra.

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Received September 2, 2004