Reactions of P/S-containing proligands with coinage metal salts: a new route to polynuclear complexes with unusual structural types†‡

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The reactions of P/S-precursors with coinage metal alkoxides and carboxylates offer new perspectives for the synthesis of complex metal aggregates.

Various synthetic approaches to metal complexes containing P/S and P/Se ligands have been developed and it is hoped that their application will lead to materials with novel features.[1,2] Recent progress made on the synthesis and application of more readily available metal phosphonates clearly stimulated these efforts,[3] and has led to growing interest in the coordination chemistry of related P/S metal complexes. The formal replacement of oxygen atoms of $[RPO_3]^{2-}$ anions with other functional groups *e.g.*, RO, RS, S, *etc.* has so far produced a large number of novel metal complexes and very recent work is now directed towards the development of metal complexes containing [P/Se]-anions.[4–9]

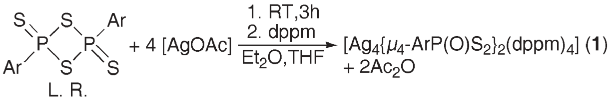
In a contribution to the area, reactions of metal alkoxides and carboxylates with Lawesson's reagent[10] (L.R.) $[ArP(S)(\mu\text{-}S)]_2$ were performed, producing selectively metal complexes containing $[ArS_2P\text{–}O\text{–}PS_2Ar]^{2-}$, $[ArPOS_2]^{2-}$ or $[ArPS_3]^{2-}$ anions (Ar = 4-anisyl).[11,12] The results from these investigations prompted us to attempt the synthesis of larger cluster complexes *via* the fragmentation of P–S bonds in sulfur-analogs to phosphorus or phosphonous acid anhydrides. For this purpose metal salts with oxygen-containing anions, *e.g.*, metal carboxylates and alkoxides were chosen and it was hoped that the strong P–O bond *vs* the weaker P–S bond would provide the thermodynamic driving force for the planned investigations.

This novel approach to P–S containing ligand systems is illustrated by the following two reaction types. At first the reaction of AgOAc with L.R. was investigated. Initially, a grey precipitate is formed when the reaction is performed in THF. The infra-red spectrum of this insoluble precipitate showed the presence of a carboxylate band at 1777 cm^{-1} and P–S vibrations at *ca.* 530 cm^{-1}. Mass spectrometric investigations (FAB) of the precipitate failed but elemental analysis points towards the composition $[ArP(SAg)_2(OAc)_2]$. The solid residue dissolved upon addition of the tertiary phosphine dppm. Slow diffusion of chilled (0 °C) diethyl ether into the filtered reaction mixture within a double Schlenck tube produced crystals of $[Ag_4\{\mu_4\text{-}ArP(O)S_2\}_2(dppm)_4]$ (**1**) (Ar = 4-anisyl) (Scheme 1).

In the solid state **1** exists as a dimer of $[Ag_2\{ArP(O)S_2\}(dppm)_2]$ units (Fig. 1). Both $[ArP(O)S_2]^{2-}$ anions in **1** are coordinated to the four Ag atoms forming an adamantane-like core of P, S and Ag atoms in which the remaining coordination sites at Ag atoms are occupied by dppm ligands. Bond lengths and angles in **1** are similar to those observed in $[Ag_{12}(PhS_2P\text{–}PS_2Ph)_6(dppeS)_6]$ [dppeS = $Ph_2PCH_2CH_2\text{–}P(S)Ph_2$].[13]

The synthesis of **1** demonstrates that previously reported reactions of metal carboxylates (Fe, Ni, Cu) with Lawesson's reagent are potentially applicable to an even broader variety of metal carboxylates resulting in the formation of metal complexes containing $[ArP(O)S_2]^{2-}$ ligands.

In a separate attempt PPh_3 was used to dissolve the precipitate obtained from the reaction of L. R. and AgOAc. X-ray analysis of



Scheme 1 Synthesis of **1** (Ar = 4-anisyl; dppm = 1,2-Bis(diphenylphosphino)methane).

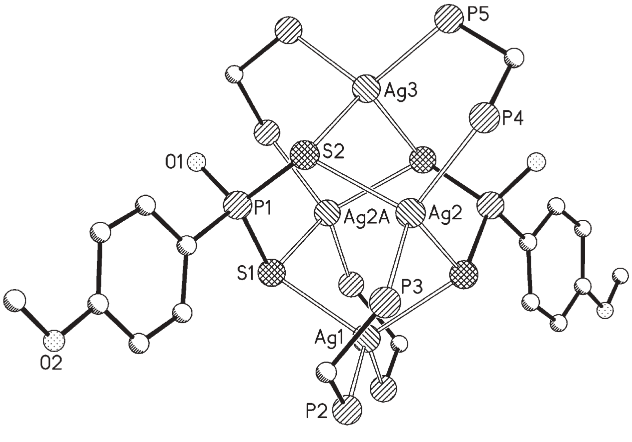


Fig. 1 Molecular structure of **1** in the solid state (Ph groups of dppm ligands are omitted). Selected bond lengths [Å] and angles [deg.]: Ag–S 2.5603(7)–2.5889(6), Ag–P 2.5102(7)–2.5499(7), P(1)–S(1) 2.0533(9), P(1)–S(2) 2.0521(9), P(1)–O(1) 1.5038(18), S(2)–P(1)–S(1) 116.00(4), S–Ag–S 109.65(3)–114.58(2), S–Ag–P 102.20(2)–111.55(2), P–Ag–P 113.01(4)–118.23(3).

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† This paper is dedicated to Ron Snaith.

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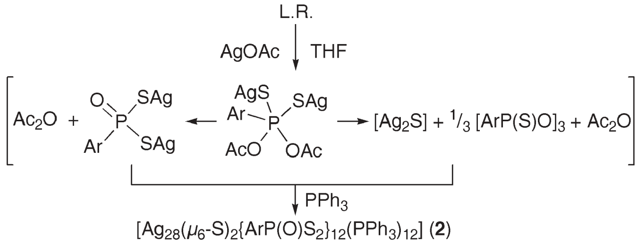
the orange product of this reaction gave to our surprise $[Ag_{28}(\mu_6\text{-}S)_2\{ArP(O)S_2\}_{12}(PPh_3)_{12}]$ **2**, the largest cluster so far containing $[ArP(O)S_2]^{2-}$ ligands (Scheme 2).

The key structural features of **2** are the two central μ_6-S atoms (Ag–S(1) distances 2.4729(17)–2.764(3) Å) coordinating the 10 inner Ag atoms. This arrangement is surrounded by an outer layer of 12 $[ArP(O)S_2]^{2-}$ ligands and the remaining 18 Ag atoms. A closer look at the structure of **2** (Fig. 2) reveals a variety of coordination modes of $[ArP(O)S_2]^{2-}$ ligands, which coordinate Ag^+ ions *via* S- and O-donor centres or just *via* S atoms.[14]

Whilst tripodal $[ArP(O)S_2]^{2-}$ ligands tend to form cage complexes with metal ions such as **1**, sulfido ligands tend to form large three-dimensional arrangements with Ag^+ ions (*e.g.*, $[Ag_{344}S_{124}(S^tBu)_{96}]$).[15] The longest nonbonding distances between symmetry-related Ag atoms in the core of **2** are 1.3 nm. The composition and molecular architecture of **2** reflect the features of both ligand types and also the phenomenon of disordered Ag positions characteristic for larger Ag–S clusters [Ag(1) is disordered over three positions with the occupancy Ag(1) : Ag(1A) : Ag(1B) of 60 : 20 : 20; the inversion center in **2** generates the other three Ag atoms] (Fig. 3). This illustrates the difficulties involved in the structure determination of larger Ag–S clusters, where Ag–S cores are sometimes treated as ionic liquids and average compositions have to be estimated on the basis of atomic volumes and charge-balance.[15]



Scheme 2 Synthesis of **2**.

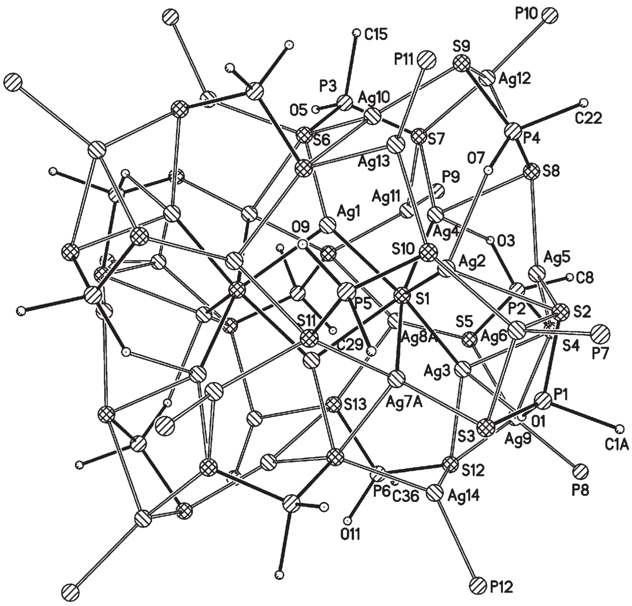


Fig. 2 Molecular structure of **2** in the solid state (disordered components and phenyl groups were omitted; only α-C atoms of 4-anisyl- substituents are displayed). Selected ranges of bond lengths [Å]: Ag–S 2.212(3)–2.925(2), Ag–P 2.4077(19)–2.4153(16), Ag–O 2.426(5)–2.503(4), P–S 2.037(3)–2.087(2), P–O 1.489(4)–1.506(4), Ag···Ag 2.7632(3)–3.3670(18).

The generation of both S^{2-} and $[ArP(O)S_2]^{2-}$ ligands in the course of the reaction between AgOAc and L. R. is observed for the first time. The occurrence of two different anions could be explained by competing decomposition reactions of $[ArP(SAg)_2(OAc)_2]$ in the presence of tertiary phosphines (Scheme 2).

Based on these results a number of metal carboxylates and alkoxides were reacted with different P–S ligand precursors. Initially we focused on P_4S_{10}, the second reaction type described here. It is well-known that the alcoholysis of P_4S_{10} is an important chemical process but reactions with coinage metal alkoxides or carboxylates have to the best of our knowledge not been described.[16] P_4S_{10} is, like L. R., a strong sulfur transfer reagent and reactions with metal salts often give amorphous precipitates of metal sulfides. The reaction of $[CuO^tBu]$ with P_4S_{10}, however, gave $[Cu_3\{PS_2(OPS_2O^tBu)_2\}(PPh_3)_4]$ (**3**), the first example of a sulfur-substituted triphosphatediester complex (Scheme 3).

The formation of **3** proceeds *via* alkoxide-induced cage-fragmentation of P_4S_{10} (Scheme 3). In the solid state the $[PS_2(OPS_2O^tBu)_2]^{3-}$ anion chelates three Cu^+ ions. The conformation of the anion is fixed by Cu(1), which is coordinated to S(3–5). Cu(2,3) are coordinated by S atoms of the central dithiophosphato group and the peripheral S atoms S(2,6). The tetrahedral [Cu(1) and Cu(3)] and trigonal [Cu(2)] coordination spheres are completed by triphenylphosphine ligands (Fig. 4).

The thermal instability of **3** and the insolubility of amorphous by-products (*e.g.*, $[Cu_3PS_4]$) once formed, prevented a more detailed reaction study. The formation of P–O–P bonds in **3** is likely to occur *via* ether elimination connecting–P–O^{t}Bu groups to –P–O–P– structural motifs.[11]

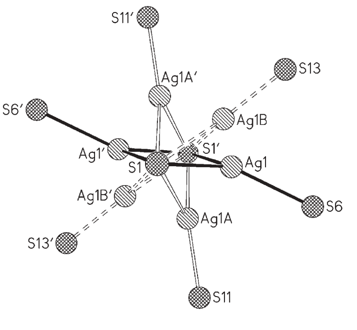
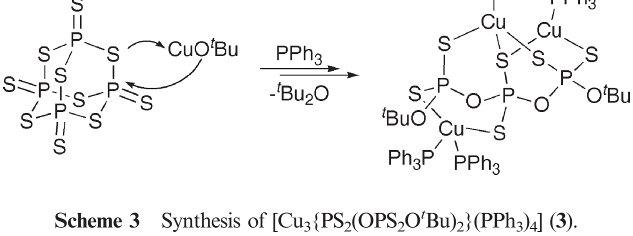


Fig. 3 The threefold disorder of Ag(1) (and symmetry equivalents, labelled ′) within the central eight S atoms.



Scheme 3 Synthesis of $[Cu_3\{PS_2(OPS_2O^tBu)_2\}(PPh_3)_4]$ (**3**).

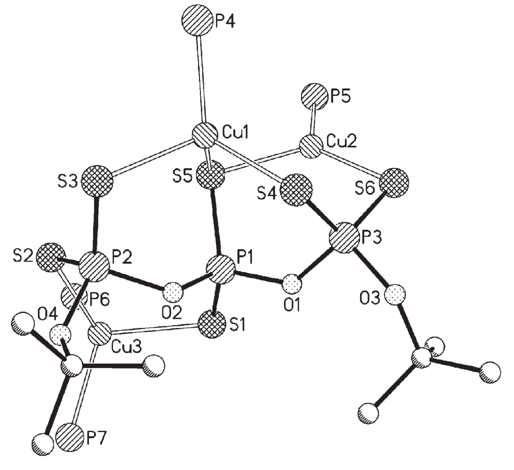


Fig. 4 Molecular structure of **3** in the solid state (Ph groups of PPh_3 ligands P(4–7) are omitted). Selected bond lengths [Å] and angles [deg.]: Cu–P 2.2139(9)–2.2981(8), Cu–S 2.2334(9)–2.4223(8), P(1)–O(1) 1.605(2), P(1)–O(2) 1.601(2), P(2)–O(2) 1.653(2), P(2)–O(4) 1.622(2), P(3)–O(1) 1.645(2), P(3)–O(3) 1.585(3), P–S 1.9611(11)–2.0155(11), S–P–S 116.30(5)–118.75(6), O(2)–P(1)–O(1) 99.37(11), O(4)–P(2)–O(2) 101.05(12), O(3)–P(3)–O(1) 101.34(12).

The results presented here offer a new approach to the coordination chemistry of P–S based ligands with applications in the synthesis of larger aggregates. The oxophilicity of phosphorus and the thiophilicity of coinage metal atoms allows facile transformation of readily available precursors, *e.g.*, L.R., P_4S_{10} into elaborate molecular architectures. Particularly unsubstituted P/S-precursors could, when functionalised with a range of metals, lead to the development of novel materials. Current work focuses on these aspects and in-depth DFT-studies of the disorder in **2** as well as the determination of physical properties of **2** (to be published in a full paper). The work was funded by the DFG (Center for Functional Nanostructures). A. R. thanks Prof. Fenske for his support.

Notes and references

§ *Crystal data for* **1**: $C_{114}H_{102}Ag_4O_4P_{10}S_4 \cdot 2Et_2O \cdot 2thf$, M = 2697.82, monoclinic, a = 25.1473(9), b = 20.5188(4), c = 26.3469(10) Å, β = 113.361(3)°, U = 12480.4(7) Å^3, T = 100(2) K, space group $C2/c$ (no. 15), Z = 4, μ(Mo–Kα) = 0.869 mm^{-1}, 48861 reflections measured, 13531 unique (R_{int} = 0.0361) which were used in all calculations. wR_2 (all data) = 0.1050, R_1 = 0.0378 $\{I > 2\sigma(I)\}$. Atoms of lattice-bound solvent (H atoms not added) were refined with isotropic thermal parameters. One disordered overlay of thf and Et_2O per asymmetric unit could not be refined, and was corrected for using the *squeeze* option in PLATON,[17] (39 e$^-$ corrected per a.u.). *Crystal data for* **2**: $C_{300}H_{264}Ag_{28}O_{24}P_{24}S_{26} \cdot 2Et_2O \cdot 13thf$ M = 9935.90, triclinic, a = 22.8410(6), b = 23.4102(7), c = 23.8337(6) Å, α = 118.290(2), β = 96.031(2), γ = 113.295(2)°, U = 9609.6(5) Å^3, T = 100(3) K, space group $P\bar{1}$ (no. 2), Z = 1, μ(Mo–Kα) = 1.692 mm^{-1}, 77691 reflections measured, 39248 unique (R_{int} = 0.0458) which were used in all calculations. wR_2 (all data) = 0.1945, R_1 = 0.0630 $\{I > 2\sigma(I)\}$. Disordered components were refined with isotropic thermal parameters. Most of the solvent could be located and refined; the presence of three further thf molecules per cluster was dealt with using *squeeze*[17] (corrected for 113 e−). *Crystal data for* **3**: $C_{80}H_{78}Cu_3O_4P_7S_6 \cdot 6(C_7H_8)$, M = 2256.00, triclinic, a = 14.0332(4), b = 16.4359(5), c = 26.1064(8) Å, α = 106.226(2), β = 102.598(2), γ = 91.228(3)°, U = 5620.5(3) Å^3, T = 100(3) K, space group $P\bar{1}$ (no. 2), Z = 2, μ(Mo–Kα) = 0.826 mm^{-1}, 45184 reflections measured, 22875 unique (R_{int} = 0.0389) which were used in all calculations. wR_2 (all data) = 0.1118, R_1 = 0.0446 $\{I > 2\sigma(I)\}$. All structures solved by direct methods and refined using SHELXTL[18] with anisotropic thermal parameters for heavy atoms unless stated. CCDC 283238–283240. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b512473e

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