Synthesis, Structures and Theoretical Investigation of $[Cu_4(P_2S_6)(PPh_3)_4]$, $[Cu_6(P_2S_6)Cl_2(PPh_3)_6]$, and $[Au_4(P_2S_6)(PPh_3)_4]$

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 65th birthday

Abstract: The silylated derivative of thiophosphoric acid $(S)P(SSiMe_3)_3$ is used as a convenient starting compound for the synthesis of multinuclear Cu and Au cluster complexes. $(S)P(SSiMe_3)_3$ reacts with $CuCl/PPh_3$ and $[AuClPPh_3]$ to give the following compounds: $[Cu_4(P_2S_6)(PPh_3)_4]$ (**1**), $[Cu_6(P_2S_6)Cl_2(PPh_3)_6]$ (**2**) and $[Au_4(P_2S_6)(PPh_3)_4]$ (**3**). According to X-ray structure determination, these compounds contain $P_2S_6^{4-}$ ions, in which S atoms act as ligands for Cu^+ and Au^+ ions. Although **1** and **3** have the same stoichiometry, bonding of the metal ions to the P_2S_6 skeleton displays small but remarkable differences. Au is twofold coordinated, whereas Cu shows a threefold coordination. Ab initio calculations have been carried out to rationalise these structural differences. The theoretical treatment of the corresponding Ag compound indicates the latter to be less stable.

Keywords: ab initio calculations · cluster compounds · copper · gold · thiophosphate

Introduction

Metal salts of thiophosphates or mixed Group 15/16 cluster anions display an astonishing structural variety, as described in a recent review.[1] Of particular interest for this work are the PQ_4^{3-} and the $P_2Q_6^{4-}$ anions (Q = S, Se). For example, PQ_4^{3-} is found as a transition metal complex $[Pd(PQ_4)_2]^{4-}$, in compounds with the formula $M_4[Pd(PQ_4)_2]$ (M = K, Cs), with square planar coordination at the transition metal centre.[2] In the double salt $Cs_{10}Pd(PSe_4)_4$,[2] additional PSe_4^{3-} ions that do not coordinate to a transition metal atom were observed. PS_4^{3-} anions are also able to build infinite chains, such as $[NiPS_4]_n^{n-}$ with square planar coordination of Ni, for example, in $KNiPS_4$.[3]

Recently, Batail et al. reported the synthesis of $(PPh_4)_3[(NiPS_4)_3]$.[4] This complex is obtained by the reaction of $KNiPS_4$ and PPh_4Br in DMF. It consists of cyclic $[(NiPS_4)_3]^{3-}$ anions, which are formed by cleavage of the $[NiPS_4]^-$ chains in the starting material. Similar chains are formed by $P_2Se_6^{4-}$ in $(PPh_4)[In(P_2Se_6)]$.[5] Fragments of these chains are found in $Cs_5[In(P_2S_6)_2]$,[6] which contains $[In(P_2S_6)_2]^{5-}$ anions. In the compounds $Fe_2P_2S_6$ and $Fe_2P_2Se_6$,[6] the chalcogen atoms form double layers. The iron atoms and the pairs of phosphorus atoms are situated in the octahedral holes of the chalcogen sublattice and form P_2Q_6 units. These compounds are usually obtained by solid-state reactions of the metals with P and Q.

For several years we have been investigating the synthesis of transition metal clusters with S, Se, Te, P and As as bridging ligands.[7] Phosphine complexes of transition metal (pseudo)-halides are treated with silyl derivatives of Group 15 and Group 16 elements. The driving force of these reactions is the formation of Me_3SiX (X = halide, acetate). For example the reaction of CuCl and PEt_3 with $P(SiMe_3)_3$ forms the cluster complex $[Cu_{96}P_{30}\{P(SiMe_3)_2\}_6(PEt_3)_{18}]$.[8] We now report analogous reactions with the compound $(S)P(SSiMe_3)_3$.[9]

The following compounds have been synthesised and characterised by X-ray structure determination: $[Cu_4(P_2S_6)(PPh_3)_4]$ (**1**), $[Cu_6(P_2S_6)Cl_2(PPh_3)_6]$ (**2**) and $[Au_4(P_2S_6)(PPh_3)_4]$ (**3**). We were also able to sythesise the following compounds: $[Pd_2PS_4(PEt_3)_4]Cl$, $[Pd_2PS_4Cl(PEt_3)_3]$, $[Pd_3(PS_4)(PS_3)(PEt_3)_4]$ and $[Pd_6(PS_4)_4(PPh_3)_6]$.[10]

In this paper we focus only on the three coinage metal compounds **1**, **2**, and **3**. Ab initio calculations at HF, MP2 and DFT levels have been carried out for **1** and **2** in order to rationalise the different structural features of these compounds better. Since experimental attempts to synthesise the corresponding Ag cluster have not been successful so far, we also treated the hypothetical Ag analogue.

Results and Discussion

Synthesis of compounds and discussion of structures:[11] $(S)P(SSiMe_3)_3$ reacts with solutions of CuCl and PPh_3 or

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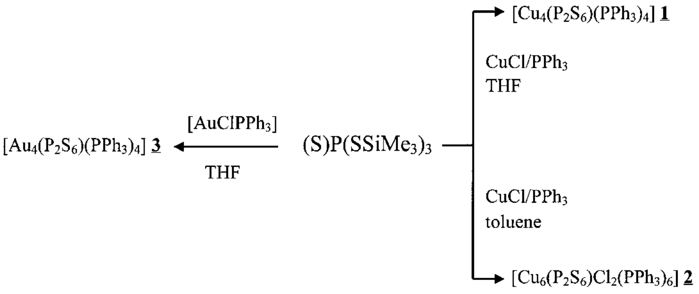
[AuClPPh$_3$] in THF or toluene to form the cluster complexes **1**–**3** (Scheme 1). The reactions proceed under elimination of Me$_3$SiCl to give colourless or light yellowish solutions. From these solutions the complexes **1**–**3** can be obtained as crystalline products suitable for X-ray analysis.



Scheme 1. Reaction scheme for the reported thiophosphate clusters.

Compound **1** (Figure 1) crystallises in the monoclinic spacegroup $C2/c$ with eight molecules per unit cell. The central bridging unit of the complex **1** emerges as $P_2S_6^{4-}$, which has evidently been formed from (S)P(SSiMe$_3$)$_3$ during reaction. The fragment of the molecule that is built by Cu, P and S atoms has approximately C_i symmetry with a P–P bond length of 223.4(2) pm. This is the expected length for a P–P single bond and has also been observed in other compounds that contain $P_2S_6^{4-}$ ions, for example, K$_2$PdP$_2$S$_6$.[2] The P–P bond length in the latter compound amounts to 220.5(8) pm and the P–S bond lengths lie in the range from 195.8 pm for nonbridging sulphur atoms to 211.0(8) pm for sulphur atoms that bridge metal centres. The P–S bond lengths found in compound **1** (201.2–205.9(4) pm) correspond well with those values.

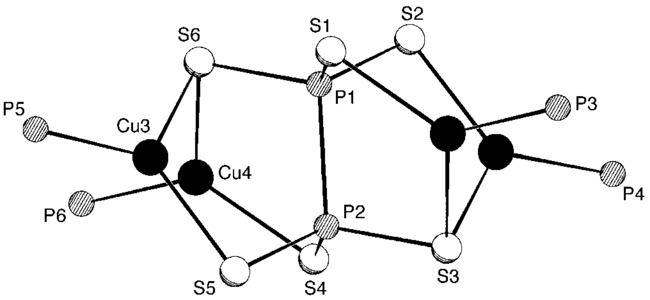


Figure 1. Molecular structure of **1**, phenyl groups are omitted; selected bond lengths [pm] and angles [°]: P1–P2 223.4(2), P1–S1 201.3(4), P1–S2 201.5(2), P1–S6 205.9(3), P2–S3 205.8(4), P2–S4 201.2(4), P2–S5 201.6(2), S1–Cu1 226.9(4), S2–Cu2 225.1(3), S3–Cu1 230.5(3), S3–Cu2 230.8(2), S5–Cu3 224.8(3), S4–Cu4 227.3(3), S6–Cu3 231.2(2), S6–Cu4 230.1(3), Cu1–Cu2 313.0, Cu3–Cu4 311.0, Cu–P(average) 220.8; S1-Cu1-P3 125.3(1), S2-Cu2-P4 123.3(1), S3-Cu1-P3 121.8(1), S3-Cu2-P4 122.9(1), S5-Cu3-P5 125.1(1), S4-Cu4-P6 126.4(1), S6-Cu3-P5 121.0(1), S6-Cu4-P6 120.8(1), S-P-S(average) 113.4, P-P-S(average) 105.0.

Abstract in German: *Das silylierte Derivat der Thiophosphorsäure (S)P(SSiMe$_3$)$_3$ ist eine geeignete Ausgangsverbindung zur Synthese von mehrkernigen Clusterkomplexen der Elemente Cu und Au. Durch Reaktion von (S)P(SSiMe$_3$)$_3$ mit CuCl und PPh$_3$ bzw. [AuClPPh$_3$] sind folgende Verbindungen zugänglich: [Cu$_4$(P$_2$S$_6$)(PPh$_3$)$_4$]* ***1****, [Cu$_6$(P$_2$S$_6$)Cl$_2$(PPh$_3$)$_6$]* ***2*** *und [Au$_4$(P$_2$S$_6$)(PPh$_3$)$_4$]* ***3****. Nach der Kristallstrukturanalyse liegen in* ***1*****–*****3*** *$P_2S_6^{4-}$-Ionen vor, deren S-Atome als Liganden für die daran gebundenen Cu$^+$- oder Au$^+$-Ionen wirken. Trotz gleicher Stöchiometrie von* ***1*** *und* ***3*** *weisen die Bindungen der Metallionen an das P$_2$S$_6$-Gerüst kleine, aber bemerkenswerte Unterschiede auf. Um diese Unterschiede besser zu verstehen, wurden ab initio-Rechnungen durchgeführt. Die theoretische Behandlung des entsprechenden Ag-Clusters ergab für diesen eine geringere Stabilität.*

The sulphur centres of the $P_2S_6^{4-}$ unit are bound to four copper atoms. The copper atom charge can be estimated as +1. As the Cu atoms are additionally coordinated by a phosphorous atom of a PPh$_3$ ligand, they have a distorted trigonal-planar environment of two sulphur atoms and one phosphorous atom.

For the sulphur atoms, different bonding modes are observed. S1, S2, S4 and S5 bind to one copper and one phosphorous atom each, whereas S3 and S6 are bound to one phosphorous and two copper atoms each. The variation of the bonding modes can be seen in the different P–S and Cu–S bond lengths. For S1, S2, S4 and S5 that bind to Cu1, Cu2, Cu3 and Cu4, respectively, short P–S bond lengths (201.2–201.6(2) pm) and relatively short Cu–S bond lengths (224.8–227.2(2) pm) are observed.

As expected, the situation for the μ_3-bridging atoms S3 and S6 is different. The P–S and Cu–S distances are elongated by about 4.0 pm relative to the above mentioned values (P1–S6 205.9(3); P2–S3 205.8(3); S3–Cu 230.5–230.8(2); S6–Cu 230.1–231.1(2) pm). Nevertheless, the overall Cu–S bond lengths in the molecule correspond to the values that have been found in other Cu–S clusters.[7e]

As a result of the molecular symmetry in **1** two "short" Cu–Cu contacts are observed. The distances of these contacts (Cu1–Cu2 313.0; Cu3–Cu4 311.0(2) pm) are definitely longer than the sum of the van der Waals radii for copper (280 pm).[12] The other Cu–Cu distances are above 487 pm and thus no evidence for d^{10}–d^{10} interactions between the d^{10} centres can be seen.

The cluster complex **2** (Figure 2) is the product of the reaction of (S)P(SSiMe$_3$)$_3$ with CuCl and PPh$_3$ in toluene. The influence of the solvent on the product formed has not yet been clearly investigated. Formation of compound **1** has not been observed under these reaction conditions. Nevertheless, one can imagine that **1** and **2** exist in solution as an equilibrium.

Compound **2** crystallises in the triclinic space group $P\bar{1}$ with one cluster molecule and two THF molecules per unit cell. The cluster molecule diplays an inversion centre. In contrast to the bonding situation in **1** all sulphur atoms of the central $P_2S_6^{4-}$ unit act as μ_2-bridges to two copper atoms. The two remaining sites of the distorted tetrahedral coordination sphere of each metal atom are taken by one μ_3-bridging Cl atom and one phosphorous atom from a PPh$_3$ ligand. As in compound **1**, copper atoms can be given the formal charge +1.

The P–S and P–P bond lengths in the $P_2S_6^{4-}$ ligand (P1–P1A 224.1(1); P–S 201.9–202.8(1) pm) are comparable with those observed in **1**. As a result of the overall threefold

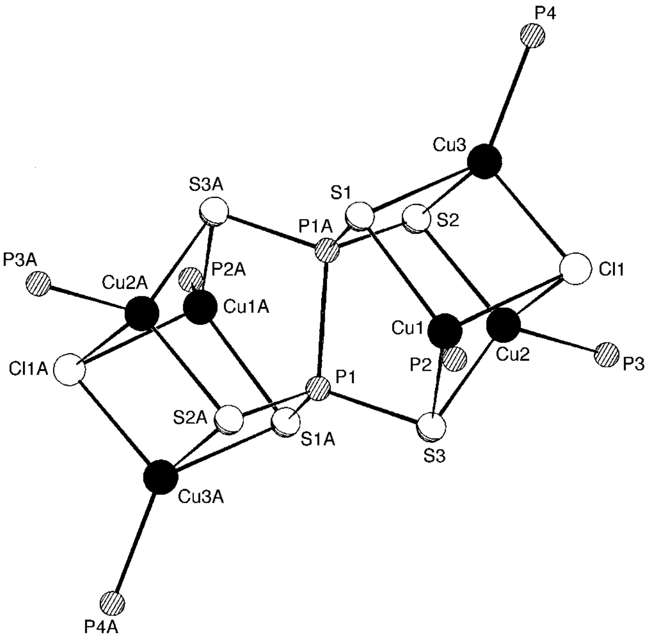


Figure 2. Molecular structure of **2**, phenyl groups are omitted; selected bond lengths [pm] and angles [°]: P1–P1A 224.1(1), P1A–S1 201.9(1), P1A–S2 202.8(1), P1–S3 202.4(1), S1–Cu1 235.3(1), S1–Cu3 254.0(1), S2–Cu2 231.6(1), S2–Cu3 243.0(2), S3–Cu1 232.0(2), S3–Cu2 234.8(1), Cu1–Cl1 249.0(1), Cu2–Cl1 254.4(2), Cu3–Cl1 239.7(1), Cu–P(average) 221.0, Cu1–Cu2 305.3(1), Cu1–Cu3 322.9(2), Cu2-Cu3 297.9(2); S1-Cu1-S3 111.5(1), S2-Cu2-S3 110.6(1), S1-Cu3-S2 83.6(1), S1-Cu1-P2 110.0(1), S2-Cu2-P3 117.3(1), S3-Cu1-P2 126.4(1), S3-Cu2-P3 122.5(1), S1-Cu3-P4 124.9(1), S1-Cu3-Cl1 97.8(1), S2-Cu3-Cl1 104.6(1), P4-Cu3-Cl1 115.8(1), Cu1-Cu2-Cu3 64.7(1), Cu2-Cu3-Cu1 51.3(1), S1-P1A-S2 110.0(1), S3-P1-S1A 113.8(1), S3-P1-S2A 113.9(1).

coordination of the sulphur atoms and the additional Cl ligand binding to the copper atoms, a slight lengthening of the Cu–S bond lengths to 232.0–235.2(1) pm can be observed. Similar to compound **1**, the Cu–Cu distances in **2** (297.9–305.3(1) pm) are too large for any Cu–Cu interactions.

Compound **3** (Figure 3) is obtained in an analogous way to **1** by the reaction of [AuClPPh$_3$] with (S)P(SSiMe$_3$)$_3$ in THF. Compound **3** crystallises in the monoclinic space group $P2_1/c$ with four molecules per unit cell. Similar to **1**, compound **3** is a four-core metal cluster that has C_i symmetry. The four gold centres are nearly linearly coordinated by four of the six sulphur atoms of the central $P_2S_6{}^{4-}$ unit (S1, S1A, S2 and S2A) and the phosphorous atoms of the PPh$_3$ ligands (P2, P2A, P3 and P3A).

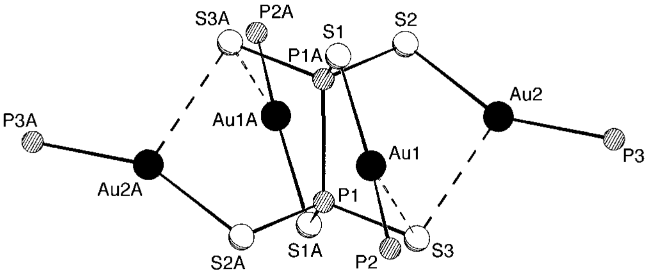


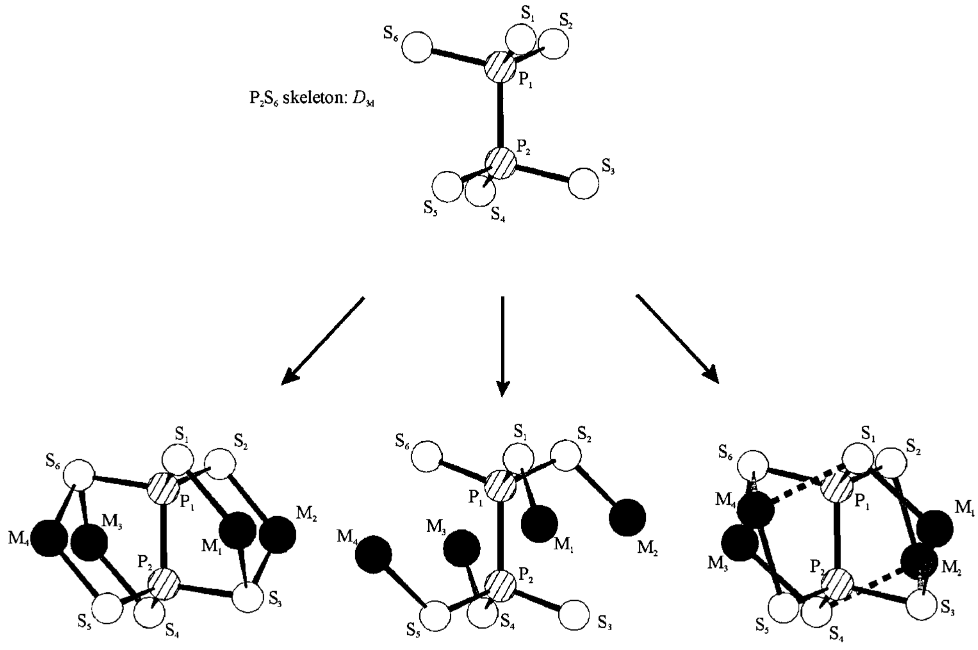
Figure 3. Molecular structure of **3**, phenyl groups are omitted; selected bond lengths [pm] and angles [°]: P1–P1A 226.6(4), P1A–S1 204.4(3), P1A–S2 202.9(4), P1–S3 199.5(3), Au1–S1 233.1(2), Au2–S2 233.8(2), Au1–P2 225.5(2), Au2–P3 225.6(2), Au1–Au2 417.0(3), Au1–Au2A 502.9(3); S1-Au1-P2 159.3(1), S2-Au2-P3 154.2(1), S1-P1A-S2 112.8(2), S3-P1-S1A 112.4(1), S3-P1-S2A 110.8(1).

Nevertheless, one observes that the coordination mode deviates strikingly from the ideal 180° angle (S1–Au1–P2 159.2(1), S2–Au2–P3 154.2(1)°), which would be expected for Au$^+$. This deviation might be caused by an additional but weak Au$\cdots$S interaction between S3 and Au1 or Au2; this is clearly shown in the variation of the Au–S bond lengths (S1–Au1 233.1(2); S2–Au2 233.8(2); S3–Au1 295.2(3); S3–Au2 283.1(3) pm). The values found for the Au1–S1 and the Au2–S2 bond lengths correspond to Au–S single bonds and show good accordance to values for Au–S single bonds found in literature, for example in [Ph$_3$PAu]$_2$S-(CH$_2$)$_5$S[AuPPh$_3$]$_2{}^{2+}$.[13a]

The somewhat stronger interaction of Au2 with S3 and thus the approach towards a (distorted) trigonal coordination sphere is in agreement with the slightly smaller S2–Au2–P3 angle compared with S1–Au1–P2. The μ_3-bridging tendency of S3 can also be seen in the different P–S distances (P1–S1 204.4(3); P1–S2 202.9(4); P1A–S3 199.5(3) pm). The bond P1A–S3 possesses at least partial double-bond character. A similar bonding situation has recently been reported by Laguna et al. in [Au$_2$(μ-C$_3$S$_5$){P(p-C$_6$H$_4$OCH$_3$)$_3$}$_2$].[13b]

From the comparison of the structural differences of **3** and **1**, the Au–Au bond lengths in compound **3** are very long (Au1–Au2 417.1(1); Au1–Au2A 502.9(1) pm). Thus d^{10}–d^{10} interactions can be ruled out. The observation of no Au$\cdots$Au interactions results possibly from the very rigid geometry of the central $P_2S_6{}^{4-}$ unit (P–P bond, P–P–S and S–P–S angles nearly unchanged in **1**–**3**) and the preferred twofold coordination of Au$^+$. Examples for gold clusters with relatively short Au–Au distances are: [Ag{[Au(μ-N^3, C^2-bzim)]$_3$}$_2$]BF$_4$ · CH$_2$Cl$_2$ with an Au$\cdots$Au-contact of 326.8(2) pm and [Au(AuCl)(AuPPh$_3$)$_8$]$^+$, which is a "true" gold cluster with an average gold oxidation state smaller than +1 in which short Au–Au bonds (263.7(1)–265.3(1) pm) and longer Au$\cdots$Au contacts (299.9–350.9(1) pm) can be observed.[14]

Quantum chemical investigations: For a closer investigation of the stability and bonding situation we carried out quantum chemical calculations for both the Cu and the Au cluster and additionally for a—hypothetical—Ag cluster of the same stoichiometry on the MP2 level. DFT methods were used for a pre-optimisation of the structural parameters; additionally HF calculations were performed to investigate effects of MP2 correction. We considered three different structure types shown in Figure 4. They all have a P$_2$S$_6$ skeleton of (approximately) D_{3d} symmetry, but differ in the coordination of metal atoms. In type I all metal atoms are bonded to two sulphur atoms; type II is a more open structure in which each metal atom is coordinated to just one sulphur atom. For both types the symmetry is C_{2h} at most, for which the σ_h plane is spanned by P$_1$, P$_2$ and S$_3$. The type I and type II structures can be converted into each other; both structures may exist as local minima, but it is also possible that only a single minimum exists. In the type III structure two of the metal atoms (M$_1$ and M$_3$) are bonded to two sulphur atoms like in type I; the others are closely coordinated to just one atom, but—different from type II—non-negligible contacts to two further sulphur atoms



TYPE I: C_{2h} (P_1, P_2, $S_3 \in \sigma_h$) TYPE II: C_{2h} (P_1, P_2, $S_3 \in \sigma_h$) TYPE III: C_{2h} (P_1, P_2, $S_2 \in \sigma_h$)

Figure 4. The three different structure types considered in the quantum chemical calculations.

exist. Type III also has C_{2h} symmetry, but here the σ_h plane is defined by P_1, P_2 and S_2; M_1 and M_3 are on the S_2 axis. A conversion from III to I or II within C_{2h} symmetry is therefore forbidden. For a bonding dominated by ionic interactions one would expect type III to have the lowest energy: M_1 and M_3 have contact to two anionic sulphur atoms, and M_2 and M_4 have contact to three. Furthermore, large PPh_3 ligands are more easily accommodated in type III than in I or II. Nevertheless, the Cu cluster is of the type I, and the Au cluster of the type II. The present calculations were done to investigate the effects that favour type I or type II structures and to find out whether the corresponding Ag cluster is possibly of lower stability.

Calculation of cluster cores without ligand covering: For all three coin metals we did an optimisation of the structure parameters for type I and type III at HF, MP2 and DFT levels. In order to avoid transitions between these two types we fixed the symmetry to C_{2h} in both cases as described above. Optimisations starting from type II always resulted in type I.

A comparison of the energies of the optimised structures, shown in Table 1, reveals the following picture. At the MP2 and DFT levels type I is always favoured. At the HF level type I is significantly preferred only for Au. For Cu type I and type III are nearly isoenergetic (energy difference less than 1 kJ mol^{-1}), and for Ag one observes a slightly lower energy for type III than for type I. This indicates that the reasons leading to a preference of structure I for Au are different from those for the two other coin metals. Hence, the stability of structure I, for the cases of Cu and Ag, is due to effects of electron correlation, which are accounted for only in DFT and MP2. Au prefers a (linear) twofold coordination that results from relativistic effects[15] which are already included in the HF treatment. This coordination is more closely realised in type I than in type III.

Table 1. Energy differences E(III) – E(I) and E(III) – E(II) [mHartree][a] for the Cu, Ag and Au compounds at HF, DFT and MP2 levels.

	ligand free			PH_3		
	HF	MP2	DFT	HF	MP2	DFT
Cu	+0.4	+15.5	+17.8	−1.2	+1.0	+2.4
Ag	−1.8	+4.4	+4.4	< 0[b]	< 0[b]	−1.9
Au	+11.2	+38.2	+23.6	> 0[c]	> 0[c]	> 0[c]

[a] 1 mHartree = 2.63 kJ mol^{-1}. [b] The optimisation started in type I converged to type III. [c] The optimisation started in type III converged to type II.

The computed structure parameters are shown in Table 2. The P_2S_6 skeleton is—except of the P–P bond length—not much influenced by the kind of the metal atom or by the method of calculation. The values for M–S distances are as expected; they increase from Cu to Ag and decrease from Ag to Au. Electron correlation reduces the equilibrium distance by 15–20 pm. The M–M distances are much more influenced by electron correlation. They are very much (65–95 pm) shorter in the MP2 than in the HF equilibrium geometry. Despite the fact, that at least for DFT and MP2, in type I the M–M distances are quite similar to those in the bulk metal, no indication for a metal–metal chemical bonding can be detected; attractive dispersive d^{10}–d^{10} interactions are present, of course. The relatively great variation of the P–P distance indicates a rather weak bond that is influenced by coulomb repulsion (e.g., of the positively charged phosphor atoms). This effect is greater for the (more ionic) Ag than for the Cu compound. The further increase when Ag is replaced by Au may be again a consequence of the preferred linear coordination of Au. This implies a larger S_1–M_1–S_3 angle and a longer P–P bond, since the P–P–S angles are rigid. We note

Table 2. Structure parameters [pm] in C_{2h} symmetry of the ligand-free cluster.

			Type I			Type III	
		HF	MP2	DFT	HF	MP2	DFT
$M_1–S_1$	Cu	236.8	217.7	222.4	239.2	219.3	222.8
	Ag	259.6	240.2	245.0	260.2	241.9	246.3
	Au	248.1	233.2	241.5	251.9	235.0	243.8
$M_2–S_2$[a]	Cu	236.8	217.7	222.4	244.2	224.2	226.3
	Ag	259.6	240.2	245.0	266.2	247.7	251.6
	Au	248.1	233.2	241.5	247.0	321.6	241.4
$M_2–S_3$	Cu	241.5	220.1	224.0	264.9	244.6	249.4
	Ag	264.3	243.8	249.0	285.9	268.2	273.5
	Au	259.1	239.5	248.5	306.7	285.1	287.9
$M_1–M_2$	Cu	363.5	268.2	261.3	409.5	346.4	343.6
	Ag	430.3	320.3	329.2	452.2	397.5	400.5
	Au	370.5	304.1	318.4	440.2	377.7	391.3
$S_1–M_1–S_3$	Cu	115.0	136.5	138.6	115.1	135.7	137.4
	Ag	107.8	124.0	124.3	105.2	122.1	123.7
	Au	111.9	131.8	128.9	112.8	133.2	129.8
P–P	Cu	231.5	234.0	243.3	230.8	234.5	245.5
	Ag	233.7	244.5	254.2	233.0	241.2	252.4
	Au	239.1	253.3	261.0	237.3	252.4	261.5

[a] In type I $M_2–S_2$ is equivalent to $M_1–S_1$ by symmetry.

that DFT, although it does not explicitly account for correlation effects of dispersion type, shows similar values for structure parameters and relative energies compared with MP2, whereas HF has turned out to be a less adequate method for the description of these systems. Thus we will not refer to HF results in the subsequent discussion.

Clusters covered by the model ligand PH_3: MP2 and DFT treatments for these model systems lead to similar results. The symmetry was lowered to C_i, which is the common subgroup for all three types. For this choice the direction of the M–P bonds and the orientation of the ligands bonded to "neighbouring" metal atoms (M_1 and M_2 in type I and type II) are not restricted by symmetry requirements. The energies of the optimised structures are also shown in Table 1. Type I is preferred for Cu; additionally the less favoured type III structure was found as a stationary point with only a few $kJ\,mol^{-1}$ higher energy. In all probability these stationary points are local minima in C_i symmetry, since the relaxation procedure employed was designed to locate minima. Type III is preferred for Ag; for DFT calculations type I is found as a stationary point in addition. The tendency for a preference of type III in case of Ag may be rationalised by the fact, that type III is more ionic, and bonds to PH_3 are enhanced. For both metals optimisations, carried out with DFT, starting from type II result in type I. For Au an optimisation starting from type I as well as from type III converges in type II. This is again in line with the preferred linear coordination specific for Au. The angle S–M–P (cf. Table 3) also indicates this: for Cu and Ag it is about 120°, for Au it amounts to about 170°. Moreover relativistic effects lead to a shorter metal–ligand distance for Au compared with Ag; this is well known.[15, 16] The metal–metal distances are too large to allow for pronounced aureophilic type attractions.

Table 3. Ligand-covered clusters: selected bond lengths [pm], angles [°] and bond energies [mHartree] for $L = PH_3$, PPh_3 at the DFT and MP2 levels.

		PH_3		PPh_3		
		DFT	MP2	DFT	MP2[b]	Exptl.
bond energy[a]	Cu	123.3	142.0	183.0	262.5	–
	Ag	117.5	136.1	151.4	232.0	–
	Au	153.0	188.3	201.9	335.0	–
$M_1–S_1$	Cu (type I)	228.1	222.2	234.1	228.2	226.9
	Ag (type III)	252.2	246.1	254.0	247.9	–
	Au (type II)	236.5	230.6	237.8	232.1	233.1
$M_2–S_2$	Cu	228.1	222.2	230.2	224.3	225.1
	Ag	254.7	247.7	257.3	250.3	–
	Au	236.8	231.1	240.8	234.9	233.8
$M_1–S_3$	Cu	229.7	225.8	230.7	226.8	230.5
	Ag	252.8	246.8	252.9	246.9	–
	Au	303.7	309.5	308.8	310.6	295.2
$M_2–S_3$	Cu	229.7	225.8	232.8	229.1	230.8
	Ag	278.7	272.2	281.0	274.7	–
	Au	307.4	309.2	297.2	303.0	283.1
$M_2–S_4$[c]	Ag	278.7	272.2	275.5	269.2	–
$M_1–M_2$	Cu	283.7	328.0	278.0	322.3	313.3
	Ag	433.0	425.5	434.1	426.6	–
	Au	438.8	403.9	451.7	416.8	417.1
P–P	Cu	233.2	225.6	232.9	225.3	223.4
	Ag	237.3	231.2	235.9	229.8	–
	Au	241.3	236.3	236.1	231.4	226.6
M–P	Cu	223.7	219.8	223.9–225.6	220.0–221.7	220.5–221.4
	Ag	240.7–243.2	237.9–240.1	241.3–243.1	238.5–240.0	–
	Au	230.7–231.3	224.9–225.4	232.2–232.4	226.4–226.5	225.5–225.6
$\alpha_{S1\text{-}M1\text{-}P}$	Cu	117.3	120.2	114.2	117.1	125.3
	Ag	126.9	126.8	124.1	124.0	–
	Au	169.7	175.5	164.5	170.3	159.3
$\alpha_{S2\text{-}M2\text{-}P}$	Cu	118.0	121.1	115.5	118.6	123.3
	Au	167.5	174.2	156.4	163.1	154.2

[a] cf. Equation (2). [b] Distances estimated from DFT [cf. Eq. (1)], bond energy calculated on the MP2 level for the DFT equilibrium geometry. [c] Symmetry non-redundant only for type III.

Clusters covered by the ligand PPh_3: The model ligands were exchanged by the PPh_3 ligands. Starting from the DFT equilibrium structure of the PH_3-covered clusters an optimisation of the structure parameters was carried out at the DFT level. The DFT results are qualitatively the same as for the model ligand-covered clusters as far as comparable and are in agreement with the experimental data, as shown in Table 3. For bond lengths the errors are amount to 10 pm (for the Cu and Au compounds), and for metal–metal distances the errors amount to -35 pm for Cu and to $+35$ pm for Au. This large deviation is not surprising, since these distances are too large for a pronounced interaction of any type and consequently no preference for a specific distance. We have performed an empirical correction of selected DFT structure parameters in the following way. Since DFT and MP2 showed close agreement with relatively systematic deviations in bond lengths in all previous calculations, we simply added Δr [Eq. (1)] of the PH_3-covered systems to the values of the structure parameters of the PPh_3-covered systems. The results obtained in this way agree better with the experimental data. For bond lengths the errors are 1–5 pm (for Cu and Au) and for the metal–metal distances the errors amount to 10 pm for Cu; for the Au–Au distance the corrected value is the same as obtained in the experiment.

$$\Delta r = r(\mathrm{DFT}) - r(\mathrm{MP2}) \qquad (1)$$

Finally the sum of the bond energy of the four PPh_3 ligands was calculated [Eq. (2)]. As can be seen from Table 3 this quantity is smaller for Ag than for Au or Cu. The stabilisation

$$E_\mathrm{B} = -[E\{\mathrm{P_2S_6(MPPh_3)_4}\} - E(\mathrm{P_2S_6M_4}) - 4E(\mathrm{PPh_3})] \qquad (2)$$

effect of the protective ligand shell is thus less pronounced for the Ag compound. This may help to rationalise why the synthesis of this cluster was not yet successful.

Experimental Section

Technical details of computation: All calculations were carried out with the program package TURBOMOLE. DFT and MP2 calculations were done in the RI approximation.[17–19] For the DFT calculations basis sets of the SVP type (split valence plus one polarisation function) were used for all elements except of H, for which an SV basis turned out to be sufficient.[20–22] For the MP2 calculations we used TZVP basis sets[20] (triple zeta valence plus one polarisation function) for P and S, SVP basis sets[20] for H and TZVPP basis sets[19] (triple zeta plus 1p1f) for the metal atoms. Trial calculations for M_2 and MCl showed these basis sets to be sufficiently flexible (deviations from the experimental values ca. +1 pm); only in case of Cu another f function ($\eta = 1.0$) had to be added (deviation for Cu_2: +3 pm). In all RI treatments auxiliary basis sets corresponding to the MO basis sets were used,[17, 19, 21] augmented by two h sets ($\eta = 2.5$, 1.0) for Cu. Core electrons were accounted for by ECP (effective core potential) of type ECP-28 for Ag and ECP-60 for Au; these include the description of dominant relativistic effects.[22] Computational effort of the MP2 calculations was reduced by excluding the inner shells (P,S: 1s–2p, Cu: up to 3s, Ag: up to 4s, Au: up to 5s) from the correlation treatment. For consistency the HF calculations were done with the same basis sets as the MP2 calculations.

Synthesis

Compound 1: A colourless solution of CuCl (0.20 g, 2.0 mmol) and PPh_3 (1.57 g, 6.0 mmol) in THF (20 mL) was added to a solution of $(S)P(SSiMe_3)_3$ (0.25 g, 0.66 mmol) in THF. After stirring for 10 minutes at room temperature the obtained yellow solution was stored at 0 °C. Within 10 days colourless crystals of **1** precipitated out of the solution.

Compound 2: A solution of $(S)P(SSiMe_3)_3$ (0.18 g , 0.46 mmol) in toluene (5 mL) was added to a suspension of CuCl (0.14 g, 1.4 mmol) and PPh_3 (0.37 g, 1.4 mmol) in toluene (15 mL). After stirring for 5 minutes, a clear orange solution was obtained, from which a colourless solid precipitated within 1 h. This solid was dissolved in THF (5 mL). After two weeks colourless crystals of **2** were formed.

Compound 3: A colourless solution of $AuCl(PPh_3)$ (0.08 g, 0.16 mmol) in THF (15 mL) was treated with a solution of $(S)P(SSiMe_3)_3$ (0.03 g, 0.08 mmol) in benzene at room temperature. The resulting pale yellow solution was exposed to daylight at room temperature. As a result, the solution colour changed to yellow and within 1 week and colourless crystals of **3** were formed.

Crystal structure analysis: A STOE IPDS diffractometer with $\mathrm{Mo}_{K\alpha}$ radiation ($\lambda = 71.073$ pm) was used at $T = 213$ K. Data collection, structure solution (SHELXS 86 and 97) and refinement (SHELXL 97) parameters of **1**–**3** are described below. An absorption correction on the datasets was carried out by means of the programm HABITUS (STOE, Darmstadt).

Compound 1: $a = 2455.5(5)$, $b = 2428.5(5)$, $c = 2383.8(5)$ pm; $\beta = 92.38(3)^\circ$; $V = 14185(5) \times 10^6$ pm^3; monoclinic, $C2/c$; $Z = 8$; $\mu(\mathrm{Mo}_{K\alpha}) = 1.540$ mm^{-1}; $2\theta_{max} = 48^\circ$; 14113 reflections, 7942 independent reflections, 3915 [$I > 2\sigma(I)$] reflections observed, 793 parameters (Cu, P, S and C refined anisotropically, H calculated for idealised positions); R_1 [$I > 2\sigma(I)$] = 0.0480; wR_2 [$I > 2\sigma(I)$] = 0.1115; GooF = 1.034

Compound 2·2THF: $a = 1358.4(3)$, $b = 1553.7(3)$, $c = 1595.2(3)$ pm; $\alpha = 110.71(3)^\circ$, $\beta = 93.49(3)^\circ$, $\gamma = 115.50(3)^\circ$; $V = 2750.4(10) \times 10^6$ pm^3; triclinic, $P\bar{1}$; $Z = 1$; $\mu(\mathrm{Mo}_{K\alpha}) = 1.468$ mm^{-1}; $2\theta_{max} = 56^\circ$; 13845 reflections, 10263 independent reflections, 9276 [$I > 2\sigma(I)$] reflections observed, 606 parameters (Cu, Cl, P, S, C refined anisotropically, H calculated for idealised positions, THF solvent molecule refined isotropically); R_1 [$I > 2\sigma(I)$] = 0.0458; wR_2 [$I > 2\sigma(I)$] = 0.1285; GooF = 1.066

Compound 3: $a = 2402.0(5)$, $b = 1741.6(4)$, $c = 1731.2(4)$ pm; $\beta = 91.37(3)^\circ$; $V = 7240(2) \times 10^6$ pm^3; monoclinic, $P2_1/c$; $Z = 4$; $\mu(\mathrm{Mo}_{K\alpha}) = 8.426$ mm^{-1}; $2\theta_{max} = 56^\circ$; 22141 reflections, 12751 independent reflections, 9812 [$I > 2\sigma(I)$] reflections observed, 793 parameters (Au, P, S, C refined anisotropically, H calculated for idealised positions); R_1 [$I > 2\sigma(I)$] = 0.0497; wR_2 [$I > 2\sigma(I)$] = 0.1177; GooF = 1.013.

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[11] For X-ray structure analysis see Experimental Section. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-118789 for (**1**), CCDC-118790 for (**2**) and CCDC-118791 for (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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