Coordination Chemistry Reviews 254 (2010) 2078–2085

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

# Novel aspects in the coordination chemistry of mixed group 15/16 cage molecules

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## Contents

ARTICLE INFO

*Article history:*
Received 12 February 2010
Accepted 3 April 2010
Available online 14 April 2010

*Keywords:*
Pnicogen
Chalcogen
Coordination polymer
Synthesis
Crystal structure

ABSTRACT

Cage molecules with mixed group 15 ($E = P, As$) and group 16 elements ($Q = S, Se$) are versatile ligands in coordination chemistry. The introduction of solid-state techniques allows one to extend the coordination flexibility of the cage molecules and to realize new coordination modes. The use of $P_4S_3$ or $As_4S_3$ as building blocks in copper(I) halide networks has initiated a new kind of "soft" solid-state chemistry, in which solutions of binary inorganic cage molecules are transferred into one-, two- or three-dimensional polymers. This strategy has been stimulated by the existence of competitive phosphorus, arsenic and sulfur coordination sites in the cage molecules.

## 1. Introduction

Cage molecules composed of mixed group 15 ($E = P, As$) and group 16 elements ($Q = S, Se$), e.g. $E_4Q_3$, $E_4Q_4$ (Scheme 1), represent a small but important class of inorganic compounds, which exhibit a pronounced reactivity towards Lewis-acidic metal fragments. The reactivity behavior may be roughly divided into two classes: (i) coordination of the intact cage via cage lone pairs and (ii) fragmentation reactions of the cage caused by the instability of preformed primary complexes or adducts.

The addition of Lewis-acidic metal fragments to the apical position of $P_4S_3$ is, from a historical point of view, the most intensively studied reaction type since more than 30 years [1–6]. The basal and apical P atoms were predicted as early as in 1977 to exhibit comparable coordination properties [7]. Insertion reactions in P–P bonds of the $P_3$ basis were also observed [8,9]. Due to the relatively good solubility of $P_4S_3$ in organic solvents, which decreases in the order $P_4S_3 > P_4Se_3 > As_4S_3 \approx As_4S_4$ there are only a few examples concerning $P_4Se_3$ [3,5,10] and one for $As_4S_3$ [11]. For these reasons the number of complexes bearing the intact cage molecule has been limited for a long time.

Modern research aspects focus on the use of as many as possible cage lone pairs of the intact cage molecule by Lewis-acidic metal ions or metal halides, e.g. $Ag^+$ or CuX ($X = Cl, Br, I$). It is the intention of this review to show that the coordination polymers obtained are at the borderline of molecular and solid-state chemistry. Accordingly, solid-state techniques also provide access to related compounds and it is one of the objectives of this article

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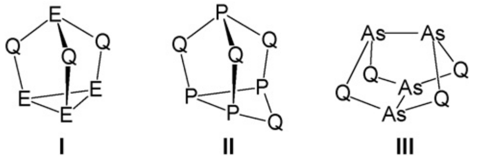
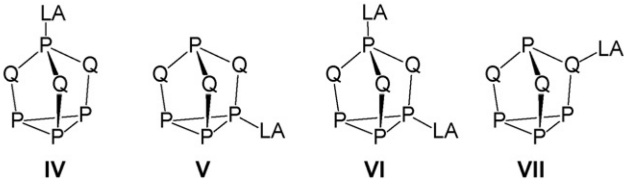
doi:10.1016/j.ccr.2010.04.004



**Scheme 1.** Representative examples of group 15/16 cage molecules (E = P, As; Q = S, Se): $E_4Q_3$ (**I**), β-$P_4Q_4$ (**II**), $As_4Q_4$ (**III**).



**Scheme 2.** Potential coordination sites at the $P_4Q_3$ cage (Q = S, Se; LA = Lewis-acidic fragment).

to point out relationships and differences between “conventional” coordination chemistry and solid-state chemistry. In this context the question has to be put whether unsaturated metal centers coordinate to both the pnicogen and the chalcogen atoms or whether there is a preference for one element type.

## 2. Complexes with Lewis-acidic metal fragments

### 2.1. $P_4S_3$ and $P_4Se_3$ derived compounds

The coordination chemistry of $P_4S_3$ is part of several reviews and it is mostly focussed on addition reactions at the apical and basal phosphorus (**IV** and **V**; Scheme 2) or on fragmentation reactions [6,8]. The first crystal structure of a $P_4S_3$ adduct was that of $Mo(CO)_5(P_4S_3)$ published by Cordes [1]. An extension to other group VI metal carbonyls was tried, but with contradictory results. Thus, the addition of four $Mo(CO)_5$ fragments to the cage has been postulated by Riess on the basis of $^{31}P$ NMR spectra, but a structural confirmation is still missing [6]. Recently it has been shown that 16-electron Re, Ru or Rh fragments allow the realization of simultaneous apical and basal coordination (**VI**) [10,12]. Only one example has been reported for the participation of sulfur lone pairs (**VII**) [13].

Because of apparent contradictions in the literature we have re-investigated the reaction of $P_4S_3$ with $W(CO)_5THF$ (THF = tetrahydrofuran). A slight excess of $W(CO)_5THF$ produces $W(CO)_5(P_4S_3)$ (**1**), spectroscopic data of which are in agreement with those described by Riess [6]. The reaction with four equivalents of $W(CO)_5THF$ gives $\{W(CO)_5\}_2(\mu_2\text{-}P_4S_3)$ (**2**) after chromatography, whereas a larger excess produces a mixture of several compounds from which some crystals of $\{W(CO)_5\}_4(\mu_4\text{-}P_4S_3)\cdot W(CO)_6$ (**3**) were isolated and characterized by X-ray diffraction analyses. The structures of **1**–**3** are shown in Fig. 1. In all cases the $W(CO)_5$ fragments occupy the phosphorus sites of the cage. A comparison of cage bonds of **1**–**3** with those of the free cage [14] reveals that there is only little deformation [$\Delta(d)$ = 0.006–0.025 Å] upon coordination even of four $W(CO)_5$ fragments. As in the free cage molecule the $P_{apical}$–S bonds are longer than the $P_{basal}$–S ones by 0.01–0.026 Å.

Weak 1:1 donor–acceptor adducts are formed in the reactions of $P_4Q_3$ (Q = S, Se) with $BX_3$ (X = Br, I). Density functional calculations on the B3LYP level have predicted similar energies for apical (**IV**) and basal (**V**) coordination modes, whereas thermodynamics should slightly favor the formation of basal adducts in the gas phase [5]. Because of the weak nature of the P–B bonding the compounds only exist in the solid-state. Concomitantly, there are significant structural changes upon passing from gas phase into solid-state. Therefore, small intermolecular effects in the solid-state seem to be responsible for the structural diversity in these adducts. The structures of $(ap\text{-}P_4S_3)BX_3$ and $(bas\text{-}P_4Se_3)BI_3$ were solved by X-ray powder diffraction and solid-state $^{31}P$ MAS NMR spectroscopy and were compared with that of $P_4Se_3\cdot NbCl_5$ (**7**, Scheme 4).

The simultaneous coordination at basal and apical phosphorus has been realized by means of the cation $[(triphos)Re(CO)_2]^+$ [triphos = $MeC(CH_2PPh_2)_3$]. Theoretical and spectroscopic studies provided proof for the formation of $[\{(triphos)Re(CO)_2\}_2(\mu\text{-}P_4S_3)]^{2+}$ dication, which contains the first example of an intact $P_4S_3$ molecule bridging two transition metal fragments [10]. No thermodynamic reason has been found for the preference of one coordination mode over the other, and from a theoretical analysis of electronic properties of the free cage the participation of sulfur lone pairs has not been excluded. Other examples including the similar chemistry of $P_4Se_3$ adducts followed [12], but the first crystal structure of a basal–apical adduct was that of $[\{(C_5H_5)Ru(PPh_3)_2\}_2(\mu\text{-}P_4S_3)][CF_3SO_3]_2$ (**4**) published in 2007 [15]. The central structural feature of **4** is closely related to that of **2**. Interestingly, in **4** a similar lengthening as in **2** of one of the P–P bonds [$\Delta(d)$ = +0.06 Å] of the $P_3$ basis is found.

A new strategy in the coordination chemistry of $P_4S_3$ employs the use of Ag(I) salts with weakly coordinating anions of the type $[Al(OR^F)_4]^-$ ($OR^F$ = poly- or perfluorinated alkoxide) [13]. Depending on the size of the anion the structure of the cations so formed are dimeric or polymeric. Whereas smaller aluminates form polymeric species, that with the largest anion forms the dimeric

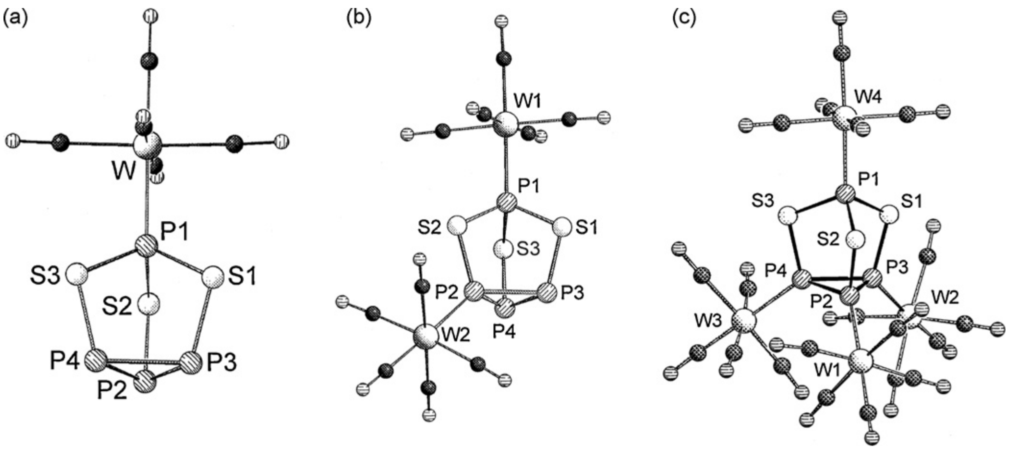
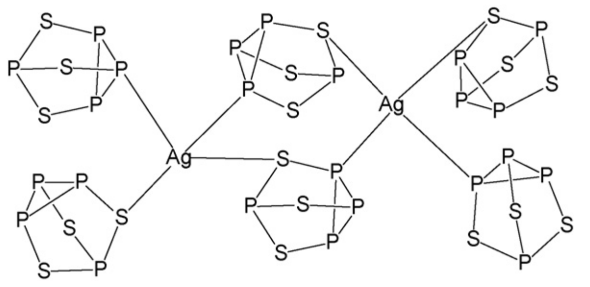
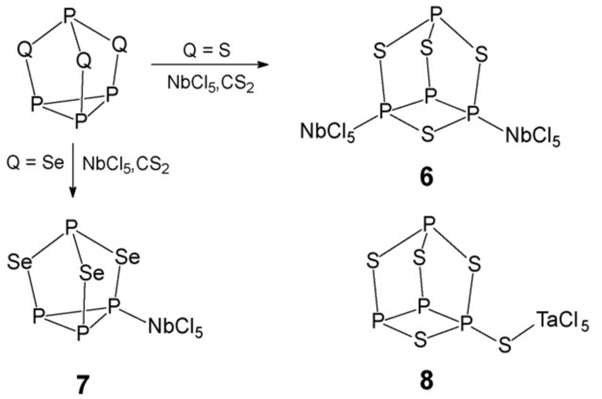


**Fig. 1.** Molecular structures of (a) $W(CO)_5(P_4S_3)$ (**1**), (b) $\{W(CO)_5\}_2(\mu_2\text{-}P_4S_3)$ (**2**) and (c) $\{W(CO)_5\}_4(\mu_4\text{-}P_4S_3)\cdot W(CO)_6$ (**3**; $W(CO)_6$ omitted).



**Scheme 3.** Structure of the $[Ag_2(P_4S_3)_6]^{2+}$ dication (**5**) in $[Ag_2(P_4S_3)_6][(\{(CF_3)_3CO\}_3Al)_2F]_2$ [13].



**Scheme 4.**

$[Ag_2(P_4S_3)_6]^{2+}$ dication (**5**) (Scheme 3). The structure of **5** is characterized by Ag atoms surrounded by four $P_4S_3$ molecules. The two bridging ligands coordinate through one P atom of the basis and one S atom, while the terminal cages coordinate either through sulfur or basal phosphorus. The anion–cation interactions are very weak, as are the bonds between $Ag^+$ and the respective main groups atoms. In consequence this and the other adducts exhibit a highly dynamic behavior in solution.

Another type of Lewis-acidic metal fragment is represented by $NbCl_5$. Its reaction with $P_4S_3$ gives β-$P_4S_4(NbCl_5)_2$ (**6**) in 3% yield (Scheme 4) [16]. The surprising insertion of a sulfur atom in one of the P–P bonds of the basis might have its reason in the use of $CS_2$ as solvent. The preparation of **6** directly from β-$P_4S_4$ has failed so far because of the tendency of the latter to decompose in solution. Blachnik et al. reported that $P_4Se_3$ forms the mono-adduct **7** in the analogous reaction (Scheme 4). A more systematic investigation of the reaction of $P_4Q_3$ and $M_2Cl_{10}$ confirms the formation of $(MCl_5)_2$(β-$P_4Q_4$) (M = Nb, Ta; Q = S, Se) [17], which are isostructural with **6**. Geometrical parameters and Raman spectroscopy reveal the adduct character of the products.

An extension of this chemistry includes the adduct formation from other sulfur rich compounds like α-$P_4S_5$, β-$P_4S_5$, and β-$P_4S_6$, and $NbCl_5$ or $TaCl_5$ units [18]. Their coordination to the cage molecules occurs via basal phosphorus sites. Coordination through sulfur is only possible for terminal sulfur sites like in (α-$P_4S_5$)($TaCl_5$) (**8**). The regioselectivity of adduct formation was investigated by *ab initio* electronic structure calculations. This study is able to confirm the experimentally obtained structures as the energetically favored products [18].

### *2.2. Solution chemistry of $As_4S_n$ cages (n = 3, 4)*

The mineral character of $As_4S_3$ and $As_4S_4$, respectively, is among others expressed by the poor solubility of these compounds in organic solvents. This problem can be reduced by heating their solutions. On the other hand, such a procedure increases the reactivity of the employed organometallic [11] or Lewis-acidic [8] complexes or complex fragments, giving rise to the extrusion of small homo- or heteroatomic ligands from the respective cage.

The few examples in which intact cage molecules serve as ligands are represented by $(C_5Me_4Et)Co(CO)(\eta^2\text{-}As_4S_3)$ (**9**; Fig. 2a) and $(C_5Me_4Et)Co(CO)(\eta^2\text{-}As_4S_4)$ (**10**; Fig. 2b). Both compounds are insertion products of $(C_5Me_4Et)Co(CO)$ fragments in As–As bonds of the respective cage molecules. They are formed in poor yields for the preferred reaction products arise from cage fragmentation and ligand recombination processes [19]. The insertion character is reflected by widening of As–As distances to 3.251(4) in **9** and 3.714(6) Å in **10**.

Dark-yellow powders of composition $M(CO)_5(As_4S_3)$ (M = Cr, W) can be synthesized from $M(CO)_5THF$ and $As_4S_3$ in tetrahydrofuran (THF) [20]. The coordination of metal carbonyl fragments increases the solubility considerably, but crystals of $Cr(CO)_5(As_4S_3)$ (**11**) were obtained only fortuitously [11]. The molecular structure of **11** (Fig. 3) shows the $Cr(CO)_5$ fragment to be fixed at the apical As atom. The apical As–S distances differ by ca. −0.02 Å compared to the free cage, the basal ones by ca. +0.02 Å.

The coordination chemistry of $As_4S_4$ in solution is less straightforward. The reaction of $M(CO)_5THF$ (M = Cr, W) with $As_4S_4$ in THF has been studied in our laboratory. According to these studies the presence of light and a donor solvent seems to facilitate the reaction, which on the other hand does not give well-defined products. The observations may be compatible with the behavior of mineral α-$As_4S_4$ in strong bases [21] and the slow transformation of solid

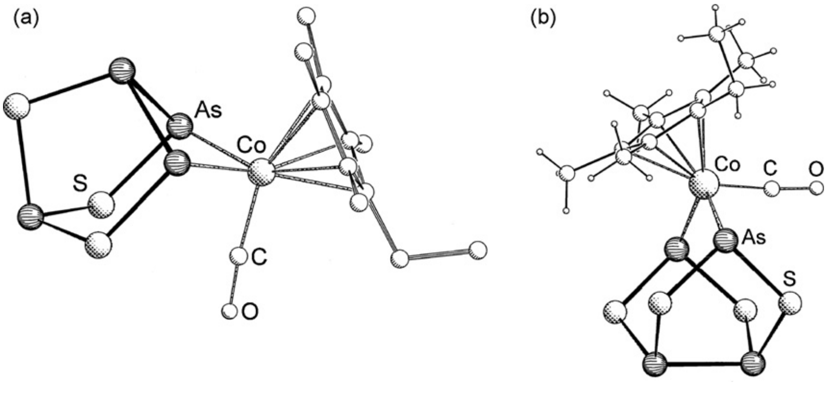


**Fig. 2.** Molecular structures of (a) $\{(C_5Me_4Et)Co(CO)\}(\eta^2\text{-}As_4S_3)$ (**9**) and (b) $\{(C_5Me_4Et)Co(CO)\}(\eta^2\text{-}As_4S_4)$ (**10**) [19].

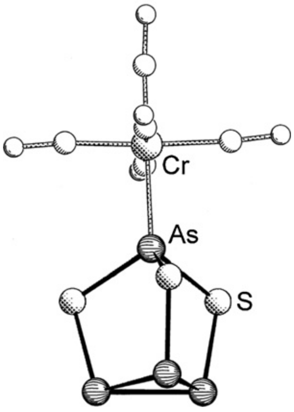


**Fig. 3.** Molecular structure of $Cr(CO)_5(As_4S_3)$ (**11**).

samples into pararealgar and $As_4S_5$ under the influence of daylight [22].

## 3. Solid-state reactions

### 3.1. The copper iodide matrix

Copper(I) halides are a useful tool for the synthesis of neutral or low-charged phosphorus polymers [23]. Thus, the preparation of new phosphorus polymers from the elements and CuX (X = Br, I) at 500 °C has been ascribed to the stabilization effect of a copper halide matrix [24]. The extension of these solid-state techniques to the synthesis of phosphorus chalcogenides produces the adducts β-$P_4Q_4(CuI)_3$ (Q = S: **12-S** [25]; Q = Se: **12-Se** [26]). In these compounds β-$P_4Q_4$ cage molecules are linked by hexagonal columns of CuI (Fig. 4). Three of the four phosphorus atoms are connected with copper, which could be confirmed by solid-state MAS NMR spectroscopy ($^{31}P$, $^{63}Cu$, $^{65}Cu$) and the respective $^{31}P$–$^{63/65}Cu$ coupling patterns. The $\delta(^{31}P)$ values of the coordinated P atoms are shifted upfield between 30 and 90 ppm compared to the chemical shift of the free P atom of the basis [25]. The $^{31}P$ NMR spectra of β-$P_4S_4$ have been reported whereas a crystal structure analysis has not.

The $P_4S_4$ cage in **12-S** exhibits similar metric parameters as those in the adduct **6**. Weak interactions between the metal and the cage atoms have been postulated on the basis of $^{31}P$ MAS NMR [27] and Raman spectra [28]. It is striking that coordination polymers comprising the $P_4S_3$ building block were not found among the products formed by the high temperature method. Furthermore, this method cannot be applied to CuCl and CuBr because of the formation of the corresponding phosphorus trihalides.

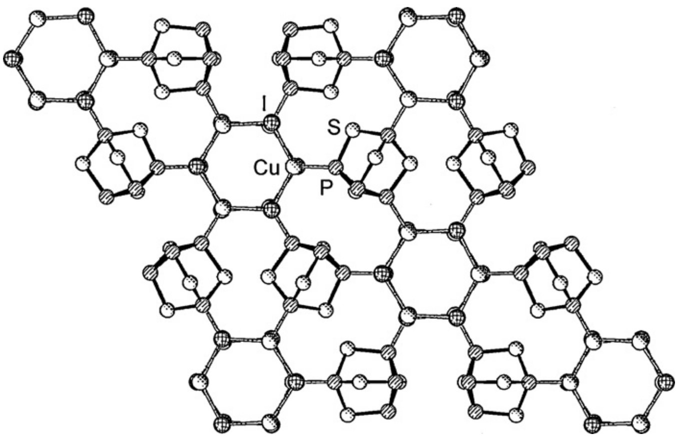


**Fig. 4.** Section of the crystal structure of β-$P_4S_4(CuI)_3$ (**12-S**); projection on the *ab* plane [25].

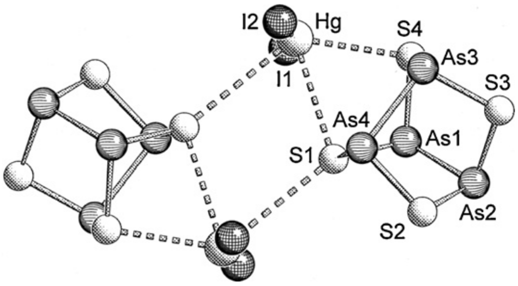


**Fig. 5.** Structure of $(As_4S_4)_2(HgI_2)_2$ (**13**) [30].

### 3.2. Adduct formation from $As_4S_4$ and $HgX_2$ (X = Br, I)

It has already been mentioned that the reaction of $As_4S_n$ ($n$ = 3, 4) with transition metal complexes in solution ends up with fragmentation of the cage molecules [11]. High temperature syntheses in analogy to Section 3.1 result in the formation of compounds the structures of which correspond to the minerals enargite, $Cu_3AsS_4$, and lautite, CuAsS, as the most stable products [29]. The formation of As/S cage molecules has not been observed.

However, if one turns to $HgI_2$ instead of CuI, elemental arsenic and sulfur give orange crystals of $(As_4S_4)_2(HgI_2)_2$ (**13**) at 400 °C, followed by annealing at 200 °C [30]. The crystal structure contains dimeric units in which two $As_4S_4$ cradles are bridged by nearly linear $HgI_2$ units. Weak bonding interactions are found between Hg and S1 (3.236 Å) and Hg and S4 (2.984 Å). Coordination to the second cage results in Hg–S distances of (3.59 Å) (Fig. 5). In spite of the weak character of the Hg–S interactions the formation of **13** seems to be thermodynamically controlled [30]. A similar situation has been found in $(As_4S_4)_2(HgBr_2)_3$ (**14**) [29]. Although the stoichiometry of **14** is different from that in **13** the building principle of weakly bound $HgBr_2$ units as bridges between two $As_4S_4$ cages is comparable.

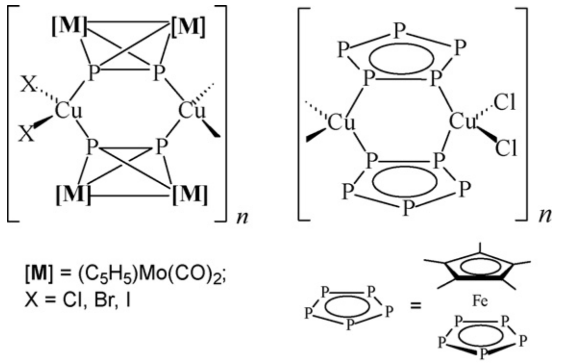
## 4. Formation of copper(I) halide containing networks in solution

### 4.1. From phosphines to cage molecules

Organophosphorus ligands L form supramolecular assemblies with copper(I) halides. Examples include differently substituted tertiary phosphines (as well as arsines) and phosphites giving $Cu_4X_4L_4$ cubane tetramers [31] as the most frequent structural motif or stepped cubanes [32]. $Cu_6X_6$ aggregates are able to adopt a ring-like structure [33] or that of a capped adamantane derived cage [34]. Further examples are listed in the review of Peng et al. [35].

Organometallic complexes with $E_n$ ligands (E = P, As, Sb) represent another versatile class of building blocks in Cu(I), Ag(I) and CuX (X = Cl, Br, I) coordination chemistry [36]. By this way oligomers and polymers have been formed starting from organometallic $P_n$-ligand complexes, like $[(C_5H_5)_2Mo_2(CO)_4P_2]$ and $[Cp^*FeP_5]$ (Scheme 5) [37,38]. The formation of spherical aggregates from $[Cp^*FeP_5]$ and CuCl under carefully controlled diffusion conditions is an exciting aspect in the chemistry of spherical nanoclusters [39]. Many of these compounds exhibit dynamic behavior in solution as a consequence of dissociation–association equilibria [36].

While the reaction of $P_4$ with CuX is affected by redox processes, $P_4$ derived cage molecules with adamantane structure merit attention. Although the latter should exhibit excellent donor properties



**Scheme 5.** Building principle of one-dimensional polymeric structures generated from $[(C_5H_5)_2Mo_2(CO)_4P_2]$ and $[Cp^*FeP_5]$, respectively, and various copper halides [36].

only the reaction of $P_4(NMe)_6$ with CuI has been reported [40]. The related P,N-bifunctional 1,3,5-triaza-7-phosphaadamantane exhibits a rich coordination chemistry [41], but the first examples of polymers containing copper halide have only been reported very recently [42]. Surprisingly little is known about the coordination properties of bifunctional P,S ligands except those of the cage molecules which are the subject of this work.

### 4.2. $P_4S_3$ containing polymers

A first attempt to react $P_4S_3$ with Cu(I) halides in polar solvents led to the formation of insoluble precipitates, which were proposed to be of polymeric nature [43]. However, if interdiffusion techniques were applied a series of new quaternary solid-state phases formed in kinetically controlled reactions. In detail, solutions of the respective copper(I) halide in $CH_3CN$ are carefully layered over the solution of the cage molecule in $CH_2Cl_2$ or toluene. The solvent may play a crucial role for the composition of the product as does the concentration of the CuX solution. The latter controls the diffusion rate and, consequently, the selectivity of the reaction. The yields vary from some percent up to 80% depending on the system. A limiting factor may be the relatively low solubility of the cage molecules employed or their derivatives [44]. All $P_4S_3$ containing copper halide polymers are listed in Table 1, the corresponding structural motifs are summarized in Fig. 9.

The polymers $(P_4S_3)(CuX)$ (**15**) belong to the one-dimensional structural type. Linear chains are composed of planar $Cu_2X_2$ four-membered rings (X = Br, I) and bridging cage molecules (Fig. 6), which provide two of their basal P atoms as donor sites [44,45]. The resulting chains are stacked along the *a* axis with no significant intermolecular contacts between the chains. If one compares bonding parameters of **15** or the following compounds with those of $P_4S_3$ [14] or the $W(CO)_5$ adducts **1**–**3** [46] they are a little bit longer. On the other hand, the distance P3–P3a in the $P_3$ triangle of **15-I** is shorter by 0.044 Å than the two other P–P bonds.

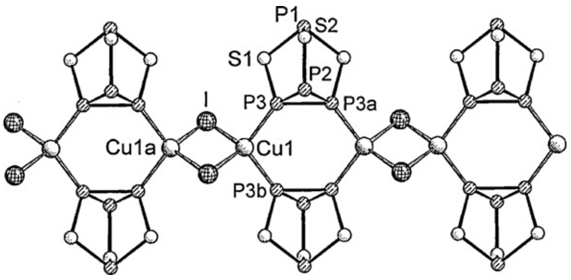


**Fig. 6.** Section of the crystal structure of 1D-$(P_4S_3)(CuI)$ (**15-I**).

Whereas it is difficult to find out uniform structural trends, $^{31}P$ MAS NMR spectra of the compounds presented in Table 1 confirm the integration of the $P_4S_3$ molecule in the corresponding copper halide network. The $^{31}P$ resonances of **15**–**18** are shifted to lower field with respect to $P_4S_3$ by 0.4–22.3 (apical) and 7.4–49.9 (basal) ppm. Contrary to **12-S** and **12-Se** the deshielding of P atoms by Cu(I) sites suggests that $P_4S_3$ behaves in these compounds as a weak Lewis base. The degree of interaction between the cage molecule and the copper halide framework has also been investigated by Raman spectroscopy [47]. Assignments of the vibrational modes of **1**, **15-I**, and **16-I** have been obtained through density functional theory calculations in the solid-state using the CRYSTAL06 code.

The structures of the three-dimensional compounds $(P_4S_3)(CuX)_3$ **16-Br** and **16-I** are of the same type, i.e., in **16-I** undulated $(CuI)_n$ layers are linked by $P_4S_3$ molecules acting as tridentate ligands (Fig. 7). Two atoms of the $P_3$ basis form columns upon connecting two fused six-membered $Cu_3I_3$ ring-subunits of one and the same layer, while the apical atom P1 coordinates to Cu1, which is part of the seven-membered column of the next sheet [44,45]. In an alternative view one may describe the CuBr or CuI substructures to consist of condensed hexagonal columns **f** (Fig. 9). Compounds that contain similar hexagonal $(CuX)_n$ columns are still extremely rare [35,48].

A three-dimensional structure, which is composed of three different structural motifs is found in $(P_4S_3)_3(CuCl)_7$ (**17-Cl**) and $(P_4S_3)_3(CuBr)_7$ (**17-Br**) (Table 1). Both compounds form selectively in the respective reactions, while **17-I** is unknown. The structure of **17-Cl** comprises hexagonal $(CuCl)_n$ columns **g**, castellated $(CuCl)_n$ chains **c** and stacks of diatomic CuCl units **a** (Fig. 9), that are part of a threefold crystallographic axis. The various components are linked by $P_4S_3$ as a tetradentate ligand (Fig. 8). Compound **17-Br** is isostructural. The resulting frameworks are unique in the coordination chemistry of copper(I) halides. While $(CuCl)_n$ columns have

**Table 1**
Classification of copper halide polymers of $E_4Q_n$ ($n = 3, 4$).

| Formula | Dimensionality | Linker position[a] | CuX motif | Reference |
|---|---|---|---|---|
| $(P_4S_3)_2(CuCl)_3$ (**18**) | 2-D | 1-P, 2-P, 3-P | **c**, **d** | [44] |
| $(P_4S_3)_3(CuCl)_7$ (**17-Cl**) | 3-D | 1-P, 2-P, 3-P, 4-P | **a**, **c**, **g** | [44] |
| $(P_4S_3)(CuBr)$ (**15-Br**) | 1-D | 2-P, 3-P | **b** | [45] |
| $(P_4S_3)(CuBr)_3$ (**16-Br**) | 3-D | 1-P, 2-P, 3-P | **f** | [45] |
| $(P_4S_3)_3(CuBr)_7$ (**17-Br**) | 3-D | 1-P, 2-P, 3-P, 4-P | **a**, **c**, **g** | [45] |
| $(P_4S_3)(CuI)$ (**15-I**) | 1-D | 2-P, 3-P | **b** | [44] |
| $(P_4S_3)(CuI)_3$ (**16-I**) | 3-D | 1-P, 2-P, 3-P | **f** | [44] |
| $(As_4S_3)(CuCl)$ (**19**) | 1-D | 1-S, 2-S | **e** | [20] |
| $(As_4S_3)(CuCl)_2$ (**20**) | 2-D | 1-S, 2-S, 3-S | **b**[b] | [20] |
| $(\beta\text{-}P_4S_4)(CuI)_3$ (**12-S**) | 3-D | 1-P, 2-P, 3-P | **g** | [25] |
| $(\beta\text{-}P_4Se_4)(CuI)_3$ (**12-Se**) | 3-D | 1-P, 2-P, 3-P | **g** | [25] |

[a] Position 1-P is defined as apical phosphorus.
[b] Butterfly.

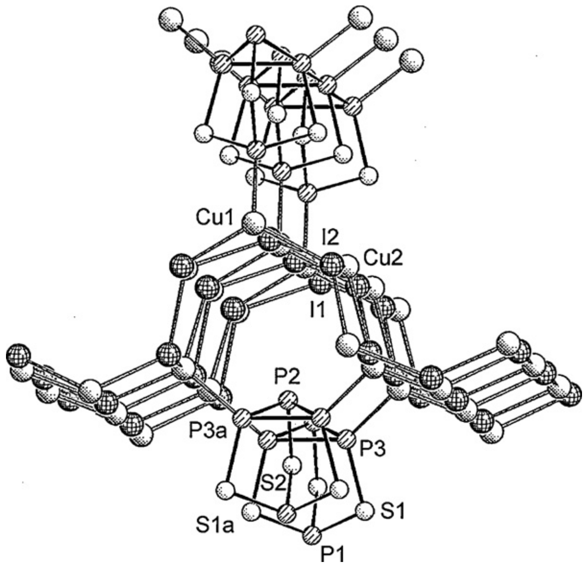


**Fig. 7.** Section of the crystal structure of 3D-$(P_4S_3)(CuI)_3$ (**16-I**).

not been reported thus far, $(CuBr)_n$ columns **g** have been described in $[Cu_3Br_3(tri)]_n$ (tri = 1,3,5-triazine) and $[Cu_2Br_2(tri)]_n$ along with castellated $(CuBr)_n$ chains **c**. In both cases triazine molecules serve as linkers [49]. One may speculate that the spherical geometry of the $P_4S_3$ cage compared to the planar tridentate N-donor ligand makes the difference.

### 4.3. $As_4S_3$ containing polymers

From the observation that the apical As atom seems to be the preferred coordination site of $Cr(CO)_5$ (Fig. 3) one may conclude that the $As_4S_3$ molecule exhibits electronic properties similar to those of $P_4S_3$. However, the reaction of $As_4S_3$ with CuCl under diffusion conditions gives $(As_4S_3)(CuCl)$ (**19**) and $(As_4S_3)(CuCl)_2$ (**20**). In these polymers the novel sulfur-only coordination mode of the $As_4S_3$ cage is derived (Fig. 10) [20]. Better yields are obtained when employing $M(CO)_5(As_4S_3)$ (M = Cr, W) instead of the free cage.

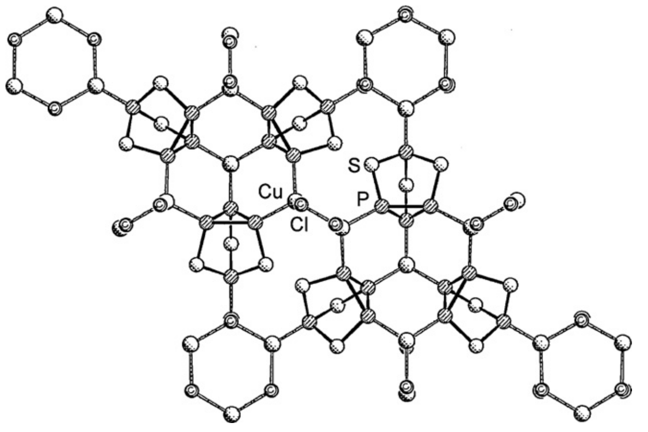


**Fig. 8.** Section of the crystal structure of 3D-$(P_4S_3)_3(CuCl)_7$ (**17-Cl**); projection on the *ab* plane.

The crystal structure of **19** contains the sawlike $(CuCl)_n$ backbone **e** bearing the cage molecules alternately on both sides (Fig. 10a). The crystal structure of **20** is built up of sheets, in which all sulfur atoms of the $As_4S_3$ cages are linked by folded $Cu_2Cl_2$ rings (Fig. 10b). Crystallographic data reveal a slight stretching of As–S bonds indicating significant Cu–S interactions. This observation is supported by comparing the Raman frequencies of $As_4S_3$ and **19**, which are significantly affected for the As–S vibrations. This behavior contrasts that of the β-$P_4Q_4$ derivatives **12** or $As_4S_4$ containing compounds **13** and **14**, which are clearly adducts with weak metal–sulfur interactions [25,26,29,30].

A comparison of qualitative MO data of $P_4S_3$ [10] and $As_4S_3$ [50] cannot explain the different coordination behavior of both cage types. It is striking, however, that in both structures attractive As–Cl interactions in the range between 3.14 and 3.40 Å are observed, while the sum of van der Waals radii is 3.81 Å. These interactions may be responsible for the organization into two-dimensional (**19**) (Fig. 11) or three-dimensional (**20**) networks (Fig. 12). They may also compensate the energy gain provided by "conventional" coordination of copper through basal arsenic.

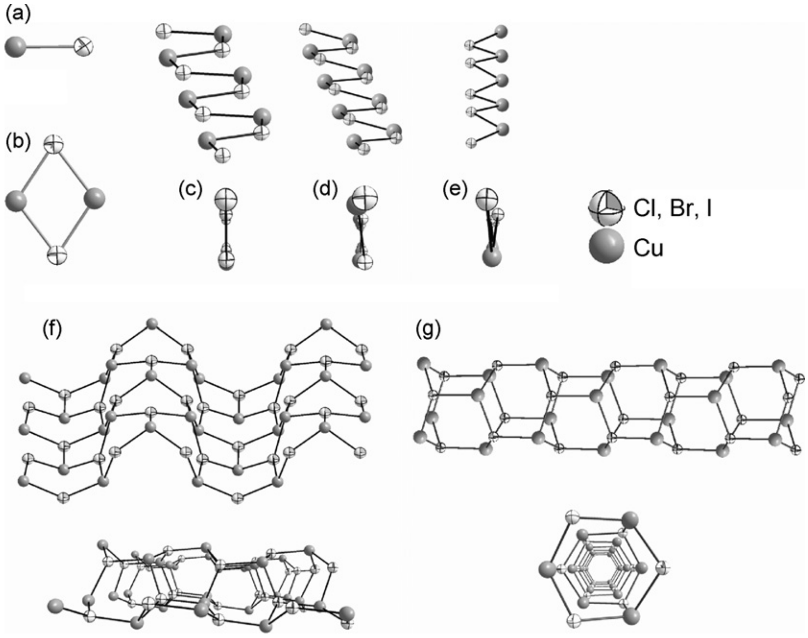


**Fig. 9.** Structural motifs of copper(I) halide substructures in **12** and **15**–**20**.

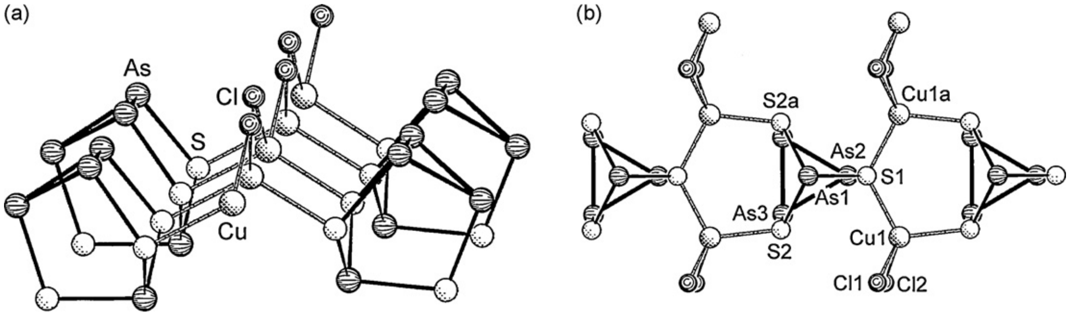


**Fig. 10.** (a) Section of the structure of $(As_4S_3)(CuCl)$ (**19**); (b) section of the structure of $(As_4S_3)(CuCl)_2$ (**20**).

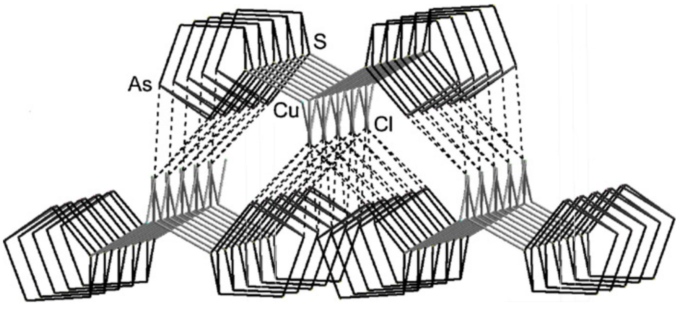


**Fig. 11.** Section of the crystal structure of **19**; As–Cl interactions are indicated by dotted lines.

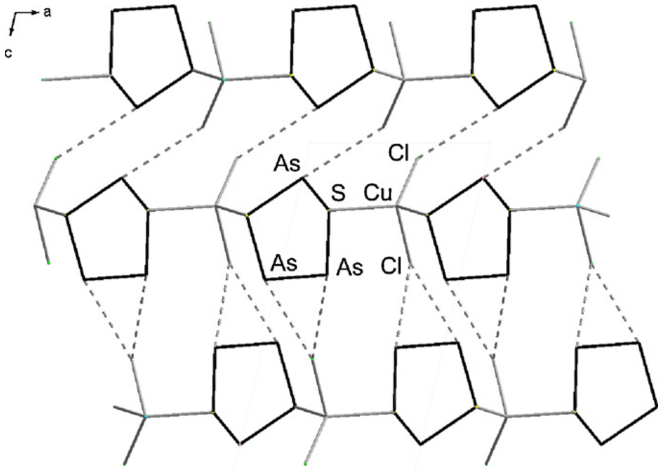


**Fig. 12.** Representation of the three-dimensional lattice of **20** viewed down the *b* axis; As–Cl interactions are indicated by dotted lines.

## 5. Summary

New developments in the coordination chemistry of mixed group 15/16 cage molecules are summarized. The formation of complexes with Lewis-acidic metal fragments has been an exclusive research subject for decades with a particular focus on $P_4S_3$. An extension to β-$P_4Q_4$ (Q = S, Se) containing copper iodide networks can be achieved by fusing together the elements and copper(I) iodide. Application of solid-state techniques was also successful for the synthesis of adducts of $As_4S_4$ with $HgBr_2$ or $HgI_2$. The advantage of this method is thermodynamic control, which allows the stabilization of unprecedented structures and new coordination modes. Application of interdiffusion techniques opens new perspectives in solid-state chemistry of $E_4S_3$ (E = P, As) cage molecules. Coordination polymers of an impressing structural variability are obtained from solutions of inorganic ligands and copper(I) halides, though in different solvents, Whereas all-P coordination has been found for $P_4S_3$, all-S coordination has been realized in $As_4S_3$ derived compounds. However, mixed forms, in which a metal center interacts with both phosphorus and sulfur are so far only found in $Ag^+$ containing compounds. A supramolecular chemistry on the basis of other metal cations or halides remains still a challenge. New hybrid materials may be constructed by the simultaneous use of mixed E15/16 cage molecules and organic N- or P-donor ligands. Copper(I) halide networks with N,P ligands [51] or N,S functional groups [52] are already known. P,S-bifunctional organometallic tripledecker complexes with the *cyclo*-$P_{5-n}S_n$ ($n$ = 1, 3) middle deck as additional linkers along with $P_4S_3$ are an optional choice [53].

## Acknowledgements

I wish to thank my co-workers, who are cited in the literature section for their valuable contributions and Prof. Dr. M. Scheer for his generous support. I am also grateful to the Deutsche Forschungsgemeinschaft for financial support.

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