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Novel Coordination Modes for E_4S_3 Cage Molecules (E = P, As) in Unprecedented Quaternary $As_4S_3(CuCl)_n$ (n = 1,2) Solid-State Phases

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First examples of the coordination chemistry of the As_4S_3 cage were obtained from solutions of $As_4S_3{\cdot}M(CO)_5$ (M = Cr, W) in CH_2Cl_2 and $CuCl_n$ in CH_3CN (n = 1) or CH_3OH (n = 2) through interdiffusion techniques. The compounds $(As_4S_3)(CuCl)_n$ (**1**: n = 1; **2**: n = 2) exhibit Cu coordination exclusively through the sulfur bridges. The crystal structure of **1** contains a saw-like $^1_\infty$[CuCl] backbone to which As_4S_3 cages are alternately fixed on both sides through two of their sulfur atoms. The crystal structure of **2** is built up of sheets, in which As_4S_3 molecules are connected by folded four-membered Cu_2Cl_2 rings through all sulfur atoms. Comparative Raman spectra of As_4S_3 and **1** indicate significant interactions between the cage S atoms and Cu.

Introduction

The coordination chemistry of P_4S_3, a molecule belonging to the nortricyclane cage type, has been the goal of intense efforts for more than 30 years.[1] Despite the abundant availability of cage lone pairs on all heteroatoms, the simultaneous coordination of more than one Lewis acidic complex fragment has been reported only in 2002 by Peruzzini et al.[2] Nearly at the same time the formation of P,S-coordinated polymers was found by using Ag[WCA] (WCA = weak coordinating anions).[3] Recently, coordination of all phosphorus atoms of the cage has been realized in the quaternary solid-state compound $(P_4S_3)_3(CuCl)_7$, which is the result of the interaction of solutions of P_4S_3 and CuCl in different solvents by diffusion techniques.[4]

The coordination chemistry of the heavier homologue of P_4S_3, As_4S_3, might be considered as much more frustrating. Only a few reactions of the As_4S_3 cage with transition-metal complexes have been described,[5] very likely because of the poor solubility of the cage in organic solvents. Apart from cage fragmentation, only one example of an insertion of a metal fragment into basal As–As bonds has been described, for example, $[(C_5Me_4Et)Co(CO)(\eta^2\text{-}As_4S_3)]$.[5c] A similar chemistry is characteristic of the structurally related As_4S_4 cage compound, which was preferentially used for the synthesis of complexes containing mixed As/S ligands.[1b,1c,6]

In this paper we report on first examples of the coordination chemistry of the As_4S_3 cage. The synthesis of various $As_4S_3(CuCl)_n$ solid-state phases (n = 1,2) proceeds through interdiffusion of solutions of $As_4S_3{\cdot}M(CO)_5$ (M = Cr, W) and $CuCl_n$ (n = 1,2) in CH_2Cl_2 and CH_3CN, respectively. The key for the preparation of the novel compounds may be the addition of a bulky organometallic reagent to the cage, which increases the solubility of As_4S_3 in a manner that it allows the controlled formation of solid-state phases from solutions of a potentially insoluble binary arsenic sulfur phase.

Results and Discussion

Interdiffusion of solutions of CuCl in CH_3CN and $As_4S_3{\cdot}Cr(CO)_5$ in CH_2Cl_2 (molar ratio 2:1) gave fine yellow needles of **1** in 40% yield. The composition As_4S_3CuCl was determined by single-crystal X-ray diffraction and was confirmed by elemental analysis. A similar yield (32%) was obtained when starting from $As_4S_3{\cdot}W(CO)_5$.[7] No hint for the fate of the $M(CO)_5$ fragments was found, but the importance of the $M(CO)_5$ fragments for the reaction follows from control experiments, in which saturated solutions of As_4S_3 in CH_2Cl_2 gave only some crystals of **1** in irreproducible yields under analogous conditions.

The crystal structure of **1**[8] is composed of one-dimensional chains, in which As_4S_3 cages are alternately fixed on both sides of a saw-like $^1_\infty$[CuCl] backbone through two of their sulfur atoms (Figure 1). The resulting chains are packed along the c axis into parallel sheets, in which opposite layers are held together by attractive As–Cl interactions in the range between 3.14 and 3.30 Å. The resulting structural motif is that of a hexagonal rod packing (Figure 2). The Cu–S bond lengths are comparable to those observed in covalent copper containing sulfide clusters or ternary copper chalcogenides.[9] Accordingly, the As_4S_3 cage is slightly distorted as shown by the distances As1–S2 and As1–S2a, which are 0.035 Å longer than that in the free

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cage.[10] The other bonds are shorter (As1–S1, As3–S1) or are not affected. The slight stretching of some of the cage bonds indicates significant interactions between the cage S atoms and the $^{1}_{\infty}$[CuCl] chain. This fact is supported by comparing the Raman frequencies of freshly prepared As_4S_3 and **1** (Figure 3, Table 1).[11] It is striking that among the observed frequencies those arising from As–S vibrations are significantly more affected than those arising from the As_3 basis.

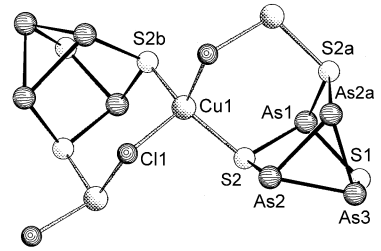


Figure 1. Repetitive structural unit of **1**. Important distances [Å] and angles [°]: As2–As2a 2.482(2), As2–As3 2.473(1), As1–S1 2.238(2), As1–S2 2.265(2), As2–S2 2.248(2), As3–S1 2.234(2), Cu1–Cl1 2.363(2), Cu1–S2 2.286(2); S2–Cu1–S2b 102.2.

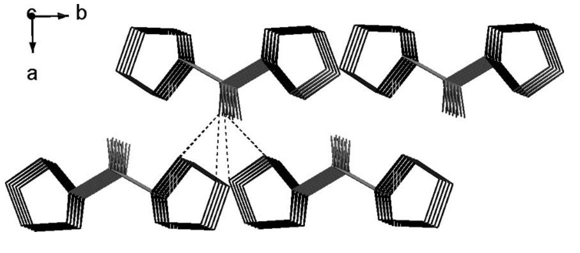


Figure 2. Section of the 1D structure of **1**. The perspective view along the *c* axis illustrates the hexagonal rod packing. As_4S_3 cages are black; the type of As···Cl interactions is indicated by dotted lines.

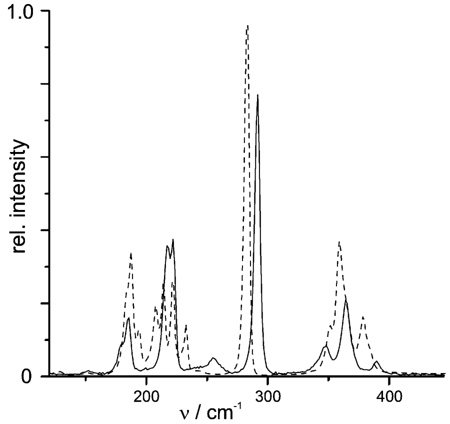


Figure 3. Raman spectra of As_4S_3 (---) and As_4S_3CuCl (—; He-Ne laser, λ = 632.78 nm, CCD detector; T = 25 °C); the assignment of frequencies is given in Table 1.

The coordinative flexibility of copper(II)[12] encouraged us to investigate the reactions of $CuCl_2$ and $As_4S_3{\cdot}M(CO)_5$ solutions in CH_2Cl_2 under various conditions. No reaction was observed when $CuCl_2$ was dissolved in CH_3CN. However, when $CuCl_2$ was dissolved in CH_3OH and then layered with $As_4S_3{\cdot}W(CO)_5$ in CH_2Cl_2 (molar ratio 5:1) fine yellow platelets of **2** formed in 14% yield along with a fine precipitate of still-unknown nature. The use of $As_4S_3{\cdot}Cr(CO)_5$ only gave a few crystals of **2**. The identity of this material with **2** was checked by crystallographic methods. The composition $As_4S_3(CuCl)_2$ was determined by single-crystal X-ray diffraction and was confirmed by elemental analysis. These data are consistent with the loss of the $M(CO)_5$ fragment during reaction and reduction of Cu^{II} to Cu^{I}.

Table 1. Comparison of the Raman frequencies for β-As_4S_3 and As_4S_3CuCl (all frequencies in cm^{-1}).

Assignment	β-As_4S_3[a]	**1**[b]
ν_9, $\delta(As_{basal}–S)$	187 (s)	185 (m)
ν_8, $\nu(As_3)$	213 (m)	217 (s)
ν_8', $\nu(As_3)$	221 (m)	222 (s)
ν_4, $\delta(As_{apical}–S)$	232 (m)	254 (w, br.)
ν_3, $\nu(As_{basal}–S)$	282 (vs)	292 (vs)
ν_1, $\nu(As_3)$	358 (s)	364 (m)
ν_6, $\nu(As_{basal}–S)$	378 (m)	390 (w)

[a] Based on ref.[11] [b] Tentative assignment.

The crystal structure of **2**[8] is built up of sheets, in which As_4S_3 molecules are connected by folded four-membered Cu_2Cl_2 rings (Figure 4). Contrary to the structure of **1**, all sulfur atoms are involved in the coordination of four Cu subunits thus forming a two-dimensional network (Figure 5). The S1 atom contributes both lone pairs to Cu coordination. A slight elongation of the cage along the pseudo-

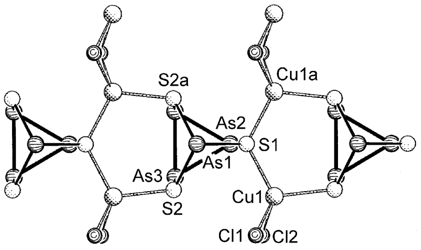


Figure 4. Repetitive structural unit of **2**. Important distances [Å] and angles [°]: As2–As3 2.465(2), As3–As3a 2.492(2), As1–S1 2.289(2), As1–S2 2.247(2), As2–S1 2.268(2), As3–S2 2.255(2), Cu1–S1 2.277(2), Cu1–S2b 2.323(2), Cu1–Cl1 2.297(2), Cu1–Cl2 2.480(2); Cu1–S1–Cu1a 121.9(1).

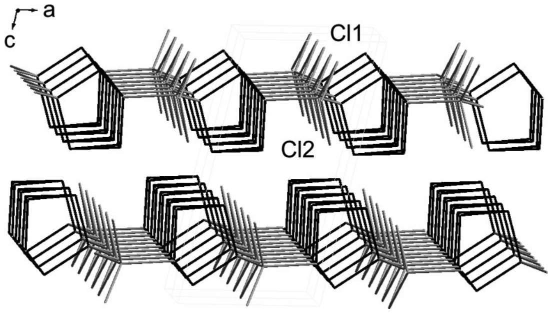
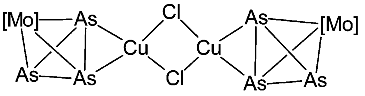


Figure 5. Section of the 2D structure of **2**. View along the *b* axis; the As_4S_3 cages are shown in black, the positions of outer and inner Cl bridges are symbolized by Cl1 and Cl2, respectively.

threefold axis between 0.04 (As2–S1) and 0.06 Å (As1–S1) relative to both dimorphite modifications[10] is observed. The As–As and Cu–S bond lengths are of the same order as those in **1**. The organization into pairs of parallel sheets in the solid-state structure may be forced by attractive As–Cl interactions. Thus, the inner wingtips of the Cu_2Cl_2 rings (Cl2) point towards the center of opposite As_3 cage bases, whereas the outer Cl bridges (Cl1) have no counterpart. The average distances As(2,3)···Cl2 are 3.16 Å. This fact is also reflected by a significantly longer Cu–Cl2 bond length relative compared to that of Cu–Cl1 (Δd = 0.2 Å).

Compounds **1** and **2** are missing links in the coordination chemistry of E_4S_3 cage molecules for the coordination of two and three sulfur bridges, respectively, to different (Cu-Hal)$_n$ substructures is also unprecedented for P_4S_3. Whereas up to four P atoms may be involved in the coordination of the latter, it is not clear why As atoms do not participate in coordination. Trivalent organoarsine compounds as well as trivalent phosphorus compounds have lone pairs so that coordination polymers from As-containing donor ligands and copper halides are known.[13] A previously published crystal-structure determination of $As_4S_3{\cdot}Cr(CO)_5$ showed the carbonyl fragment to be fixed at the apical As position.[1c]

The particular and unpredictable coordination behavior of polyarsa compounds is illustrated by the metallatetrahedrane complex $[C_5Me_5Mo(CO)_2(\eta^3\text{-}As_3)]$. This compound gives with CuCl $[\{Cp^*(CO)_2MoAs_3\}_2(Cu_2Cl_2)]$ (**3**),[14] in which π interactions between the *cyclo*-As_3 moiety and Cu^I have been proposed. Theoretical studies of the P_4S_3 cage have shown that energy differences between basal and apical coordination modes are small and that the participation of sulfur lone pairs may not be impossible.[2a] From our results it appears that Cu^I combines σ and d_π capabilities able to render the as-yet-unknown S coordination of the cage possible. A preliminary study of the nature of lone pairs of As_4S_3 on the B3LYP level does not yet reveal any substantial differences in comparison to P_4S_3.[15] Further calculations are in progress.



3 [Mo] = $C_5Me_5Mo(CO)_2$

Completely different synthetic approaches are represented by a high-temperature route, in which arsenic, sulfur, and a d^{10} metal halide are melted together,[16] and by the solvothermal reaction of a binary cage like As_4S_4 and $HgBr_2$ in CS_2 at 160 °C.[17] In both cases, the quaternary compounds $As_4S_4{\cdot}HgHal_2$ (Hal = Br, I) are formed as molecular adducts, in which the d^{10} ion is very weakly coordinated to the sulfur bridges of the main group cage.

Conclusions

The first examples of the novel S-only coordination mode of the intact As_4S_3 cage are presented, and this extends the chemistry of mixed cage molecules of the type E_4S_3 (E = P, As) and related compounds. The synthesis of various $As_4S_3(CuCl)_n$ phases (n = 1,2) proceeds through interdiffusion of solutions of $As_4S_3{\cdot}M(CO)_5$ (M = Cr, W) and $CuCl_n$ (n = 1,2) in different solvents at ambient temperature. The addition of a bulky organometallic reagent to the cage increases the solubility of As_4S_3 in a manner that it allows the controlled formation of quaternary solid-state phases from solutions of a potentially insoluble binary arsenic sulfur phase and CuCl. In a more general context, our results open new perspectives on the use of organometallic E_mS_n ligand complexes and their inorganic cage precursors in supramolecular chemistry.[18]

Experimental Section

General: All manipulations were carried out under a nitrogen atmosphere by using Schlenk techniques (tube diameter in diffusion experiments 3 cm). As_4S_3 was obtained by melting together the elements in stoichiometric amounts and subsequent Soxhlet extraction of the crude product with boiling toluene. After crystallization at –20 °C, β-As_4S_3 was obtained as proved by powder diffraction X-ray analysis.[10]

As_4S_3CuCl (1): A solution of CuCl (20 mg, 0.2 mmol) in CH_3CN (20 mL) was carefully layered over a yellow solution of $As_4S_3{\cdot}Cr(CO)_5$[7] (61 mg, 0.1 mmol) in CH_2Cl_2 (35 mL). After 12 h, crystallization of fine yellow needles of As_4S_3CuCl began at the phase border and was complete after the end of the diffusion process. The product was separated, washed with pentane, and then dried to give pure **1** (20 mg, 40%). As_4ClCuS_3 (494.9): calcd. Cl 7.16, S 19.44; found Cl 7.45, S 19.53.

$As_4S_3(CuCl)_2$ (2): A green solution of $CuCl_2$ (64 mg, 0.48 mmol) in CH_3OH (25 mL) was carefully layered over an orange solution of $As_4S_3{\cdot}W(CO)_5$[7] (40 mg, 0.095 mmol) in CH_2Cl_2 (40 mL). During the diffusion process a fine yellow precipitate and yellow platelets separated at the phase border. The crystals were isolated and washed with pentane to give pure **2** (8 mg, 0.013 mmol, 14%). $As_4Cl_2Cu_2S_3$ (593.9): calcd. S 16.20; found S 16.50.

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[7] As$_4$S$_3$·M(CO)$_5$ adducts (M = Cr, W) were obtained by stirring suspensions of β-As$_4$S$_3$ (250 mg) in thf (25 mL) for 18 h with M(CO)$_5$thf (1.5 equiv.). After chromatography on SiO$_2$ (toluene) and evaporation of the solvent dark-yellow powders are obtained (30–35% yield), which still contain small amounts of M(CO)$_6$ according to IR spectroscopy. IR (KBr, M = Cr): $\tilde{\nu}$ = 2074 (m) [ν(CO)], 1937 (s) [ν(CO)] cm^{-1}. IR (KBr, M = W): $\tilde{\nu}$ = 2080 (m) [ν(CO)], 1937 (s) [ν(CO)] cm^{-1}.

[8] Crystal structure analyses: Data were collected with an Oxford Diffraction Gemini Ultra diffractometer (Cu-K_α-radiation) at 123 K. The structures were solved by direct methods and refined by full-matrix least-squares (SHELXL97 program) with all reflections. Data for **1**: Yellow needles, $0.08 \times 0.03 \times 0.01$ mm, orthorhombic, *Pb*cm, a = 10.861(1) Å, b = 11.002(1) Å, c = 7.192(1) Å. V = 859.41(3) Å^3, Z = 4, $\rho_{\text{calcd.}}$ = 3.825 g cm^{-3}, θ = 4.07–62.04°, μ = 29.685 mm^{-1}, 4591 measured reflections, 737 independent reflections (R_{int} = 0.0677), 661 observed reflections [$I > 2\sigma(I)$], 48 refined parameters, R_1 = 0.0463, wR_2 = 0.109, residual electron density 1.577/–1.327 e Å^{-3}. Data for **2**: Yellow plates, $0.18 \times 0.11 \times 0.02$ mm, monoclinic, $P2_1/m$, a = 6.156(1) Å, b = 6.925(1) Å, c = 11.765(1) Å, β = 103.1(0)°. V = 488.60(3) Å^3, Z = 2, $\rho_{\text{calcd.}}$ = 4.037 g cm^{-3}, θ = 3.86–66.76°, μ = 30.901 mm^{-1}, 1960 measured reflections, 913 independent reflections (R_{int} = 0.0381), 803 observed reflections [$I > 2\sigma(I)$], 58 refined parameters, R_1 = 0.0438, wR_2 = 0.105, residual electron density 1.428/–0.968 e Å^{-3}. Further details of the crystal-structure investigation(s) may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number(s) CSD-419754 (for **1**) and -419755 (for **2**).

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