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PAs_3S_3 Cage as a New Building Block in Copper Halide Coordination Polymers

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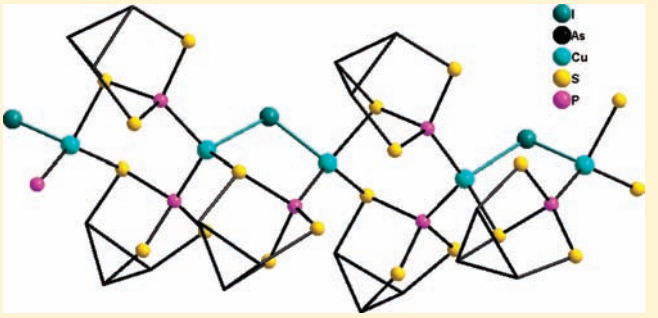
Supporting Information

ABSTRACT: First examples of the coordination chemistry of the PAs_3S_3 cage were obtained from solutions of $PAs_3S_3 \cdot W(CO)_5$ (**1**) in CH_2Cl_2 or CH_2Cl_2/toluene and CuX (X = Cl, Br, I) in MeCN through interdiffusion techniques. Crystals of $[Cu(PAs_3S_3)_4]X$ (**2**, X = Cl; **3**, X = Br) and $[(Cu_2I)(PAs_3S_3)_3]I$ (**4**) were obtained and characterized by Raman spectroscopy (**2**) and single-crystal X-ray crystallography. The solid-state structures reveal an unexpected coordination versatility of the PAs_3S_3 ligand: apical phosphorus and bridging sulfur atoms interact with copper, while As···X interactions determine the dimensionality of the frameworks. The structures of **2** and **3** contain tetrahedral $[(PAs_3S_3)_4Cu]^+$ cations as secondary building units (SBUs), which are arranged by interactions with Cl^- or Br^- anions into two- and three-dimensional substructures. These interpenetrate into a (2D + 3D) polycatenane. Compound **4** is built up by a one-dimensional $[(Cu_2I)(PAs_3S_3)_3]_n^{n+}$ ribbon with PAs_3S_3 cages as P,S-linkers. The As atoms of the exo PAs_3S_4 linkers interact with iodide counterions ($3.35 < d(As-I) < 3.59$ Å). The resulting two-dimensional layer is organized by weak As···I interactions ($d(As-I = 3.87$ Å) into a 3D network.



INTRODUCTION

As_4S_3 as well as P_4S_3 are cage molecules of the nortricyclane type.[1] The coordination behavior of P_4S_3 toward Lewis-acid compounds is already well established because of its better solubility in organic solvents.[2] Recently, we have shown that both compounds form structurally very different coordination polymers with copper halides.[3] Whereas P_4S_3 coordinates exclusively through its P atoms,[4] As_4S_3 interacts with copper through sulfur.[5] In the latter case formation of three-dimensional networks seems to be additionally supported by weak but significant As−X (X = Cl, Br, I) interactions. These differences cannot be explained by theoretical studies. Density functional theory calculations on P_4S_3[6] and As_4S_3 do not show significant differences in the energy and shape of HOMOs and LUMOs.[7]

A chemical approach for solution of this problem could be the investigation of the yet unknown coordination behavior[8] of mixed cages $P_nAs_{4-n}S_3$ ($n = 1-3$).[9] Of particular interest may be the PAs_3S_3 cage, because it combines the PS_3 building block of P_4S_3 and the As_3 basis of As_4S_3.[10] This similarity makes it an interesting ligand for the formation of coordination polymers with copper(I) halides. In this work we report on the formation of novel coordination polymers of PAs_3S_3 via participation of P and S coordination sites, while the As sites are blocked by intermolecular interactions with halide ions.

RESULTS AND DISCUSSION

1. Synthesis and Characterization of $PAs_3S_3 \cdot W(CO)_5$ (1). The high-temperature synthesis from the elements was reported to give PAs_3S_3 along with phosphorus-rich $P_nAs_{4-n}S_3$ ($n = 2-4$) compounds.[9a] We found that fusing together stoichiometric amounts of P, As, and S at 600 °C for 7 days followed by extremely slow cooling (1 °C/min) to room temperature gave yellow-orange PAs_3S_3 of spectroscopic purity. The ^{31}P NMR spectrum in CS_2 (δ = 104 ppm) is in agreement with formation of $P_{apical}As_3S_3$.[11] However, the ^{31}P MAS NMR spectrum reveals two singlets of equal intensity at δ = 106 and 113 ppm. The existence of two phosphorus resonances may be explained by a different orientation of the cage molecules in the crystal. This phenomenon was first described for β-P_4S_3[12] and was also found for P_4Se_3.[13] Because of the extremely low solubility of PAs_3S_3 in, e.g., toluene, CH_2Cl_2, and THF we investigated formation of an adduct with $W(CO)_5$. In analogy to the chemistry of As_4S_3, such an adduct should be much more soluble.[5]

Reaction of PAs_3S_3 with $W(CO)_5$THF in THF gave after filtration over SiO_2 $PAs_3S_3 \cdot W(CO)_5$ (**1**) as a yellow-orange powder in 52% yield. The IR spectrum reveals absorptions at 1935 and 2080 cm^{-1} which are characteristic of ν(CO) stretch

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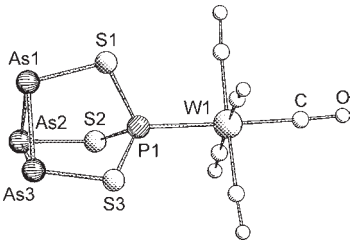
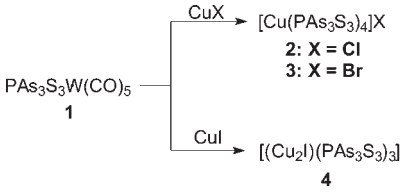


Figure 1. Molecular structure of $PAs_3S_3 \cdot W(CO)_5$ (**1**). Selected distances (Å): P1−S1 2.095(1), P1−S2 2.097(1), P1−S3 2.091(1), As1−S1 2.190(1), As2−S2 2.203(1), As3−S3 2.181(1), As1−As2 2.438(1), As1−As3 2.417(1), As2−As3 2.429(1), P1−W1 2.460(1).

Scheme 1. Diffusion Reactions of 1 (in toluene or/and CH_2Cl_2) with CuX (X = Cl, Br, I) (in MeCN)



vibrations typical of a $W(CO)_5$ fragment. The field desorption mass spectrum exhibits the parent ion at m/z = 675.6. The ^{31}P NMR spectrum in C_6D_6 shows a singlet at δ = 115.9 ppm. The observed $^1J_{P,W}$ coupling of 300 Hz is stronger than that in $P_4S_3 \cdot W(CO)_5$ (126 Hz).[14] The ^{31}P MAS NMR spectrum contains one signal at δ = 113.0 ppm and weak resonances at δ = 109 and −64.3 ppm indicating impurities of still unknown nature. The structure of **1** is composed of a PAs_3S_3 cage bearing a $W(CO)_5$ fragment at the apical P atom (Figure 1). There are no significant distortions within the cage compared to the free molecule.[10a] Only the As−S bonds are slightly lengthened by 0.02−0.04 Å. The packing in the crystal structure may be described by layers parallel to the *ab* plane but with an inverse orientation of the $W(CO)_5$ groups in neighbored layers (Figure S1, Supporting Information).

2. Synthesis and Characterization of Coordination Polymers. *2.1. Syntheses and Spectroscopic Data.* Layering of solutions of **1** in the respective solvent with solutions of copper(I) halides gave after complete interdiffusion yellow crystals (ca. 1% yield) of $[Cu(PAs_3S_3)_4]Cl$ (**2**), $[Cu(PAs_3S_3)_4]Br$ (**3**), and $[(Cu_2I)(PAs_3S_3)_3]I$ (**4**) (Scheme 1). The low yields may be explained by competitive formation of yellow, orange, or brown powders during the diffusion process. Formation of crystals is solvent dependent. Thus, **2** crystallizes from solutions of **1** in toluene, crystallization of **3** occurs when using a mixture of **1**, toluene, and CH_2Cl_2, and **4** requires dissolution of **1** in CH_2Cl_2. Variation of the stoichiometry and concentration did not affect the crystallization processes. Layering of saturated solutions of PAs_3S_3 in toluene, CH_2Cl_2, or CS_2 with CuX solutions gave in all cases immediate precipitation of powders at the phase border.

For the purpose of comparison, reaction of a hot saturated solution of PAs_3S_3 in toluene with CuCl in CH_3CN was studied. An orange microcrystalline material precipitated in nearly quantitative yield. The Raman spectrum of this material agrees fairly well with the spectrum of pure **2** (Figure S2, Supporting Information). Therefore, similar composition and structures for both products are very likely.

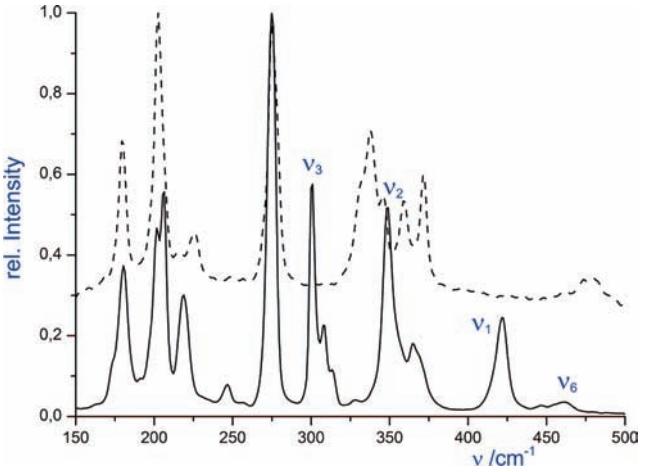


Figure 2. Raman spectra of PAs_3S_3 (—) and $[Cu(PAs_3S_3)_4]Cl$ (**2**) (---).

Table 1. Raman Frequencies [cm^{-1}] of PAs_3S_3 and $[Cu(PAs_3S_3)_4]Cl$ (2)

PAs_3S_3[15]	assignment[15]	PAs_3S_3[a]	**2**
183m	ν_{10} (E)	180m	179m
206s	ν_8 (E)	206s	202vs
223m	ν_9 (E)	218m	225w
243w		246w	247vw
277s	ν_4 (A_1)	274vs	274vs
312m	ν_3 (A_1)	307s	
354vs	ν_2 (A_1)	349s	337s, 346sh
		364sh	358w, 371 m
424mw	ν_1 (A_1)	421m	
464w	ν_6 (E)	461w,br	479w,br

[a] This work.

Raman spectra of PAs_3S_3 and **2** were measured (Figure 2). The comparison of both spectra shows that the frequencies ν_1, ν_3, and ν_6 of the free cage, which are assigned to vibrations of the apical PS_3 moiety,[15] are significantly affected, very likely by coordination to copper (Table 1). The mode ν_2 (symmetric As−S stretching) of the free cage is split into vibrations at 337, 346, 358, and 371 cm^{-1}. The interaction of the As_3 basis with the Cl^- anion is held responsible for this splitting (see below), although it is difficult to assign the vibrations. A similar influence of copper coordination on P_4S_3 Raman frequencies has been studied recently.[14]

2.2. Structures of $[Cu(PAs_3S_3)_4]X$ (X = Cl, Br). The structures of **2** and **3** are composed of pairs of $[(PAs_3S_3)_4Cu]^+$ cations and Cl^- or Br^- anions. The cations are built up of a central copper atom, which is tetrahedrally surrounded by four apical P atoms of PAs_3S_3 molecules (Figure 3). The Cu−P distances (2.23−2.27 Å) are in the same range as those observed for copper phosphides.[16]

The crystal structures of **2** (and isostructural **3**) were determined by interactions between As_3 basis atoms and Cl^- (Br^-) anions, Table 2. In the structure of **2** there are two different types **A** and **B** of $[(PAs_3S_3)_4Cu]^+$ cations, which are defined by the number of Cl^- anions interacting with PAs_3S_3 cages. In type **A**

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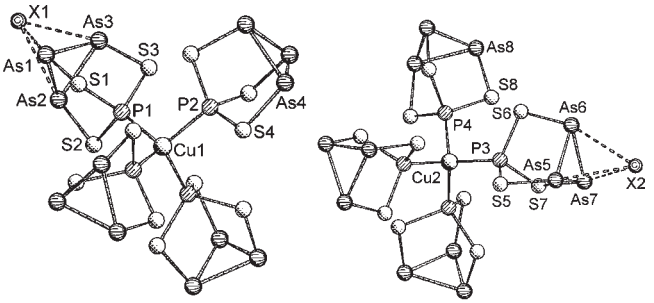

Figure 3. Structure of $[Cu(PAs_3S_3)_4]X$ (X = Cl, **2**, Br, **3**). The two different cations with the corresponding anions are shown.

Table 2. Selected Distances (Å) of $[Cu(PAs_3S_3)_4]X$ (X = Cl, 2, Br, 3)

	2	3
Cu1−P1	2.229(4)	2.225(3)
Cu1−P2	2.235(7)	2.240(5)
Cu2−P3	2.271(4)	2.291(2)
Cu2−P4	2.229(11)	2.237(7)
P1−S1	2.069(6)	2.072(4)
P1−S2	2.076(6)	2.066(4)
P1−S3	2.086(7)	2.068(5)
P2−S4	2.078(4)	2.074(3)
P3−S5	2.082(7)	2.061(5)
P3−S6	2.078(7)	2.065(5)
P3−S7	2.077(6)	2.067(4)
P4−S8	2.097(10)	2.075(8)
As1−S1	2.243(3)	2.233(6)
As2−S2	2.233(6)	2.220(5)
As3−S3	2.242(6)	2.232(5)
As4−S4	2.236(4)	2.230(3)
As5−S5	2.245(5)	2.256(4)
As6−S6	2.235(6)	2.239(4)
As7−S7	2.243(5)	2.256(4)
As8−S8	2.201(8)	2.210(6)
As1−As2	2.473(3)	2.474(2)
As1−As3	2.483(3)	2.482(2)
As2−As3	2.473(3)	2.466(2)
As4−As4a	2.496(3)	2.481(2)
As5−As6	2.471(4)	2.461(3)
As5−As7	2.476(3)	2.464(2)
As6−As7	2.464(3)	2.448(3)
As8−As8a	2.472(15)	2.457(10)

cations four PAs_3S_3 molecules are arranged arround one Cl^- anion with As···Cl distances between 3.14 and 3.18 Å (Figure 4), whereas in type **B** cations there are only three PAs_3S_3 molecules with As···Cl distances between 3.13 and 3.20 Å (Figure 5). The observed As···Cl distances are significantly shorter than the sum of the van der Waals radii of As and Cl. The corresponding As···Br distances in **3** range from 3.24 to 3.37 Å in both types of cations.

Two different substructures of different dimensionality follow from the different coordination pattern of Cl^- anions: Cation **A** interacts with four Cl^- anions of coordination number 12,

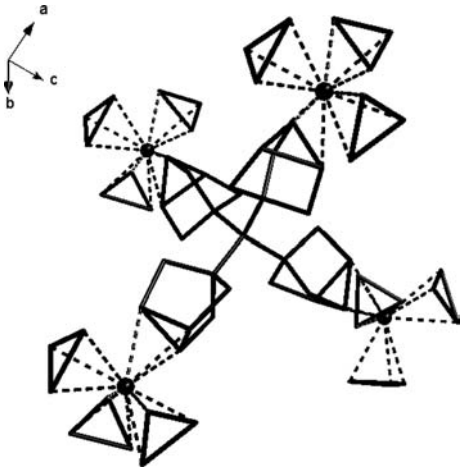

Figure 4. Section of the 3D network of **2** represented by cation **2A** and corresponding As···Cl interactions (---). Each Cl^- anion is surrounded by four PAs_3S_3 molecules, but only one of them is shown completely for the sake of clarity.

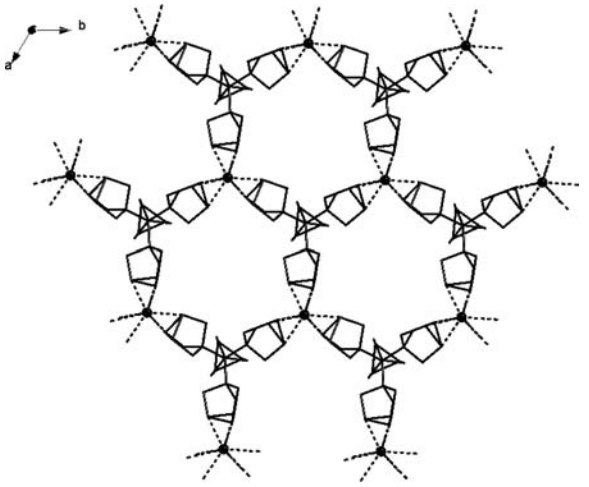

Figure 5. Section of the 2D network of **2** represented by cation **B** and corresponding As···Cl interactions (---).

leading to formation of a 3D network (Figure 4). In the second substructure cation **B** interacts with three Cl^- anions of coordination number 9, giving rise to a 2D network parallel to *ab*. The cage without interaction with Cl^- is oriented along *c*. A further characteristic of this cage is large thermal ellipsoids, which is in agreement with a possible motion in the crystal lattice (Figure 5). The two-dimensional layer possesses voids with an average diameter of ca. 10.7 Å. These voids are penetrated by the three-dimensional network, giving a polycatenated structure (Figure 6). Only a few examples of (2D + 3D) polycatenation of substructures of different dimensionality have been described in the literature.[17]

2.3. Structure of [(Cu$_2$I)(PAs$_3$S$_3$)$_3$]I. Compound **4** is a coordination polymer, which is composed of cationic $[(Cu_2I)(PAs_3S_3)_3]^+$ and anionic (I^-) building blocks (Figure 7). Cationic $[Cu_2I(\mu\text{-}PAs_3S_3)]^+$, which contains a rare example of a cationic copper halide building block,[18] functions as a secondary building unit (SBU). The resulting SBUs are P,S-linked by two cage molecules, giving rise to formation of a one-dimensional

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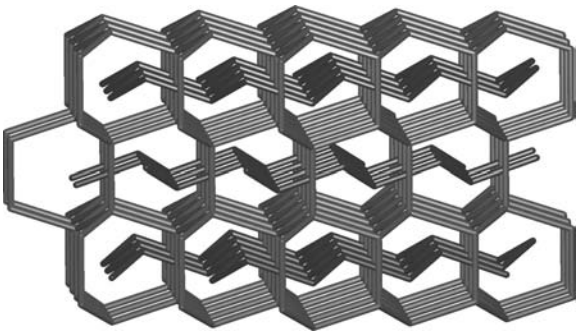

Figure 6. Schematic representation of the (2D + 3D) polycatenation of **2** (and **3**).

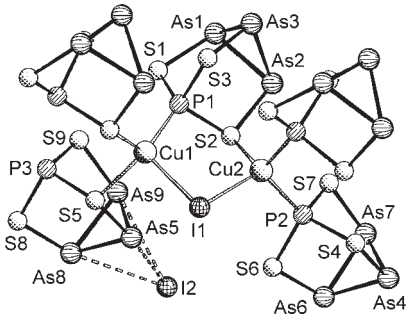

Figure 7. Section of the structure of $[(Cu_2I)(PAs_3S_3)_3]I$ (**4**).

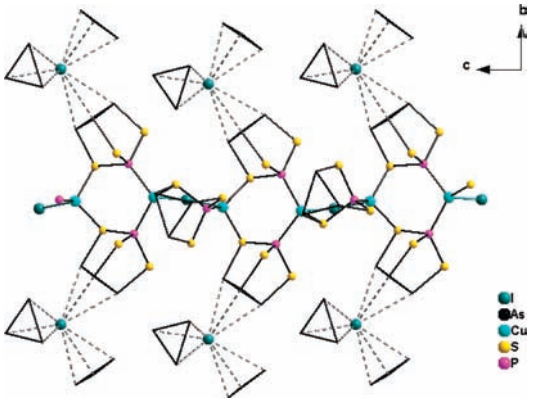

Figure 8. Section of the 1D-$(Cu_2I)(PAs_3S_3)_3$ ribbons with adjacent iodide counterions in **4** and As···I interactions < 3.6 Å (---). For the sake of clarity, the exo PAs_3S_3 cages are represented by triangles for the As_3 basis atoms.

$[(Cu_2I)(PAs_3S_3)_3]_n^{n+}$ ribbon (Figure 8). It is noteworthy that a P,S-coordination behavior of a P_4S_3-derived cage has been reported thus far only for Ag^+ compounds.[2g,12]

Coordination of Cu1 is achieved by two S atoms, one P atom, and one iodide ligand, while Cu2 bears iodide, one S atom, and two P atoms. The Cu−S and Cu−I distances are in the range typical of other P_4Q_3 (Q = S, Se) coordination polymers with copper(I) iodide,[4a] just as the Cu−P distances.[4,16] The distances P1−S2, P2−S4, and P3−S5 are slightly longer than the other P−S distances because of the bridging character of these atoms (Table 3). The As−S and As−As bonds are longer by

Table 3. Selected Distances (Å) of $[(Cu_2I)(PAs_3S_3)_3]I$ (4)

Cu1−I1	2.628(3)
Cu2−I1	2.577(3)
Cu1−P1	2.236(5)
Cu2−P2	2.266(4)
Cu2−P3	2.243(4)
Cu1−S4	2.329(4)
Cu1−S5	2.317(4)
Cu2−S2	2.351(4)
P1−S1	2.098(6)
P1−S2	2.112(5)
P1−S3	2.087(6)
P2−S4	2.104(5)
P2−S6	2.084(6)
P2−S7	2.090(5)
P3−S5	2.120(5)
P3−S8	2.086(6)
P3−S9	2.069(6)
As1−S1	2.257(4)
As2−S2	2.278(4)
As3−S3	2.250(5)
As4−S4	2.273(4)
As5−S5	2.278(4)
As6−S6	2.264(4)
As7−S7	2.246(4)
As8−S8	2.258(4)
As9−S9	2.255(4)
As1−As2	2.482(3)
As1−As3	2.465(3)
As2−As3	2.481(3)
As4−As6	2.480(2)
As4−As7	2.478(3)
As6−As7	2.476(3)
As5−As8	2.480(2)
As5−As9	2.477(3)
As8−As9	2.483(3)

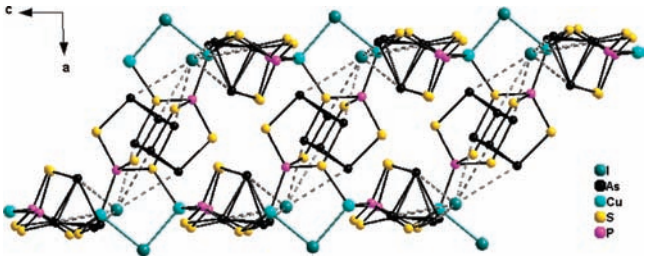

Figure 9. Two-dimensional arrangement of two planar substructures of **4**. As···I interactions (3.35 < *d* < 3.59 Å) are represented by dashed lines.

0.03−0.06 Å than those in free PAs_3S_3,[9a] probably as a consequence of weak interactions with the counterions (see below).

The exo As atoms As4−As9 of the 1D-$[(Cu_2I)(PAs_3S_3)_3]_n^{n+}$ ribbons interact with adjacent iodide counterions to form a layer within the *bc* plane (Figure 8). The corresponding As−I distances are between 3.35 and 3.59 Å. This is longer than

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covalent As−I bonds, e.g., 2.51 Å in AsI_3[19] or 3.05 Å in $As_6I_8^{2-}$,[20] but in the same range as weak interlayer As···I interactions in AsI_3 (d(As−I) = 3.5 Å).[19] Such weak interactions may be forced by electrostatic attractions as observed in $[Cp^*_2Fe_2As_2Se_2]I$ (d(As−I) = 3.24 Å).[21]

The atoms As1, As2, and As3 of the bridging SBUs coordinate to I2 in the same range, which gives pairs of mutually arranged layers of about 13 Å diameter (Figure 9). Slightly weaker As···I interactions (d = 3.87 Å) exist between I1 of each of the $[Cu_2I]^+$ units and two As atoms (As6, As8) of PAs_3S_3 molecules belonging to the next layer. These distances are still shorter than the sum of the van der Waals radii of As and I (4.15 Å). Finally, a 3D network is built up consisting of stacks of planar substructures parallel to the bc plane (Figure 10).

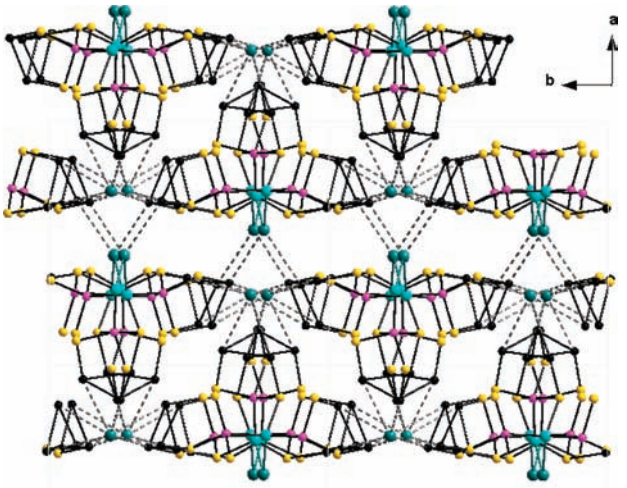

Figure 10. Stacks of planar substructures of **4**, organized by weak As···I interactions (d = 3.87 Å).

CONCLUSIONS

The first examples of coordination polymers from PAs_3S_3 or its metal carbonyl derivative $PAs_3S_3{\cdot}W(CO)_5$ (**1**) and copper halides were obtained by interdiffusion techniques between solvents of different polarity. The solid-state structures demonstrate an unexpected coordination behavior of the PAs_3S_3 building block exhibiting properties in between P_4S_3 and As_4S_3. Thus, coordination of apical phosphorus is reminiscent of that of P_4S_3, and weak but significant As···X interactions resemble those of As_4S_3. However, the role of sulfur, which serves for the first time as a coordination site toward copper, is unprecedented in the series of P_4Q_3 (Q = S, Se) cage molecules.

EXPERIMENTAL SECTION

General Methods. All manipulations were carried out under nitrogen using glovebox or Schlenk techniques. The Raman spectra were recorded on a Varian FTS 7000e spectrometer containing a FT Raman unit. Excitation of the microcrystalline samples was carried out with a Nd:YAG laser (λ = 1064 nm), and detection was performed with a liquid N_2-cooled Ge detector. ^{31}P MAS NMR spectra were recorded with a Bruker Avance 300 spectrometer using a double-resonance 2.5 mm MAS probe. The ^{31}P resonance was 121.495 MHz. All spectra were acquired at a MAS rotation frequency of 30 kHz, a 90° pulse length of 2.3 μs, and a relaxation delay of 450 s.

Table 4. Crystallographic Data of Compounds 1−4

	1	2	3	4
formula	$C_5As_3O_5PS_3W$	$As_{12}ClCuP_4S_{12}$	$As_{12}BrCuP_4S_{12}$	$As_9Cu_2I_2P_3S_9$
M_w	675.83	1506.76	1551.21	1436.72
crystal size [mm]	0.070 × 0.051 × 0.042	0.13 × 0.12 × 0.05	0.11 × 0.044 × 0.03	0.07 × 0.05 × 0.01
crystal system	orthorhombic	trigonal	trigonal	monoclinic
space group	*Pbcn*	*P*31*c*	*P*31*c*	$P2_1/c$
a [Å]	10.594(1)	13.314(1)	13.414(1)	12.020(1)
b [Å]	22.909(1)	13.314(1)	13.414(1)	13.774(1)
c [Å]	12.036(1)	21.172(1)	21.482(1)	15.895(1)
β [deg]				91.7(1)
γ [deg]		120.0	120.0	
V [Å^3]	2921.1(3)	3250.2(2)	3347.7(1)	2630.4(2)
Z	8	4	4	4
σ_{calcd} [g cm^{-3}]	3.073	3.079	3.078	3.628
μ [Cu Kα,mm^{-1}]	27.368	24.411	24.364	41.411
instrument	Oxf. Diff. Gemini Ultra	Oxf. Diff. Gemini Ultra	Oxf. Diff. SuperNova	Oxf. Diff. Gemini Ultra
T [K]	123	123	295	123
scan range	4.60 < Θ < 66.49	3.83 < Θ < 66.47	3.80 < Θ < 71.35	3.68 < Θ < 56.23
reflns collected	9111	8478	16 127	6840
unique obd [$I > 2\sigma(I)$]	2106	2739	4029	2579
params refined	163	182	182	226
abs corr	analytical	analytical	analytical	semiempirical
transmission	0.474/0.274	0.328/0.051	0.412/0.153	1.0000/0.2858
max/min residual density [e/Å^{-3}]	2.424/−2.224	1.518/−0.920	0.586/−0.603	2.581/−2.195
R_1, wR_2 ($I > 2\sigma$)	0.043, 0.136	0.046, 0.116	0.034, 0.095	0.057, 0.154
R_1, wR_2 (all data)	0.051, 0.142	0.047, 0.117	0.035, 0.096	0.073, 0.162

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Synthesis of PAs_3S_3[9a]. A 0.4 g (0.013 mmol) amount of red phosphorus, 2.9 g (0.039 mmol) of arsenic, and 1.2 g (0.039 mmol) of sulfur were heated in evacuated vials at 600 °C for 7 days. After very slow cooling (1 °C/min) to room temperature orange PAs_3S_3 is obtained quantitatively. ^{31}P MAS NMR (121 MHz): δ = 106 (s), 113 ppm (s).

$PAs_3S_3 \cdot W(CO)_5$. A 50 mL amount of a $W(CO)_5$THF solution (c = 0.028 mol·L^{-1}) was added to 350 mg (0.99 mmol) of PAs_3S_3. The resulting suspension was stirred for 18 h at room temperature. After evaporation of the solvent, the residue was dissolved in 25 mL of toluene and filtered over SiO_2 (column 15 × 3 cm). **1** was isolated as a yellow solid, which after washing with pentane was employed for the reactions. Recrystallization from 10 mL of toluene/pentane 2:1 at −24 °C gave material suitable for X-ray diffraction analysis. [$PAs_3S_3 \cdot W(CO)_5$] (**1**): Yield, 348 mg (52%); ^{31}P NMR (121 MHz, C_6D_6) δ = 115.9 ppm (s) ($J_{P,W}$ = 300 Hz); ^{31}P MAS NMR (121 MHz) δ = 113 ppm; FD MS (toluene) m/z = 675.6 (M^+); IR (KBr, cm^{-1}) 1935vs, 2080s [ν(CO)].

Syntheses of $[Cu(PAs_3S_3)_4]Cl$. *Method A.* A yellow solution of 40 mg (0.059 mmol) of **1** in 20 mL of toluene was layered with a solution of 15 mg (0.15 mmol) of CuCl in 15 mL of acetonitrile. A brown precipitate formed after 2 days; crystallization of yellow prisms started after 4 days. After decantation of the solvent the crystals were washed with toluene and pentane. The composition of the prisms was determined by X-ray diffraction analysis as $[Cu(PAs_3S_3)_4]Cl$ (**2**).

Method B. A 50 mg (0.14 mmol) amount of PAs_3S_3 was stirred for 1 h at 110 °C in 100 mL of toluene and then filtered. The hot filtrate was combined with a solution of 10 mg (0.1 mmol) of CuCl in 10 mL of acetonitrile. Immediately, a yellow-orange precipitate formed. Crystallization was completed after keeping the solution for 1 day at room temperature to give 45 mg of a microcrystalline powder, which was isolated by decantation of the solvent and washing with pentane. The product was examined Raman spectroscopically. $[Cu(PAs_3S_3)_4]Cl$ (**2**): Raman (cm^{-1}) 179m, 203s, 224w, 249vw, 278vs, 298vw, 337m, 347w, 357vw, 371 m, 480w,br. Anal. Calcd: S, 25.54. Found: S, 23.51.

$[Cu(PAs_3S_3)_4]Br$ (3). The solution of 25 mg (0.037 mmol) of **1** in a mixture of 30 mL of toluene/CH_2Cl_2 (v/v 2:1) was layered with a solution of 15 mg (0.1 mmol) of CuBr in 15 mL of acetonitrile. A yellow precipitate formed immediately at the phase border; yellow intergrown crystals formed after 3 days of diffusion. These were separated from yellow powder by decantation and washing with pentane. X-ray diffraction analysis showed them to have composition $[Cu(PAs_3S_3)_4]Br$ (**3**).

$[(Cu_2I)(PAs_3S_3)_3]I$ (4). A solution of 37 mg (0.055 mmol) of **1** in 25 mL of CH_2Cl_2 was layered with 36 mg (0.19 mmol) of CuI in 20 mL of acetonitrile. A yellow to orange precipitate formed immediately, and then very slowly intergrown yellow platelets crystallized. The reaction was finished after the initially yellow solution of **1** decolorized. After isolation and washing with pentane the crystals were determined to have composition $[(Cu_2I)(PAs_3S_3)_3]I$ (**4**).

X-ray Structure Determination of Compounds 1−4. Crystallographic data of the crystal structure determinations for **1**−**4** are given in Table 4. The structures were solved by direct methods (SIR-97 program)[22] and refined by full-matrix anisotropic least-squares (SHELXL97 program)[23] with all reflections. The examined crystal of compound **3** was a merohedral twin, the twin law was (−1 0 0, 0 −1 0, 0 0 1), and the ratio of the twin components was refined to 0.616(0.002) to 0.384.

■ ASSOCIATED CONTENT

Supporting Information. X-ray crystallographic data in CIF format, packing diagram of **1**, and Raman spectrum of microcrystalline **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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