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The Unexpected Versatility of P_4S_3 as a Building Block in Polymeric Copper Halide Networks: 2,3-P, 1,2,3-P and all-P Coordination

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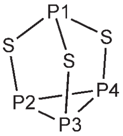
Abstract: Layering solutions of P_4S_3 in CH_2Cl_2 with solutions of CuCl or CuI in CH_3CN gives the coordination polymers $(P_4S_3)_3(CuCl)_7$ (**1**), $(P_4S_3)_2(CuCl)_3$ (**2**), $(P_4S_3)(CuI)$ (**3**) and $(P_4S_3)(CuI)_3$ (**4**), respectively, after slow diffusion. The yellow compounds were characterised by elemental analysis, ^{31}P magic-angle spinning (MAS) NMR spectroscopy and single-crystal X-ray crystallography. The solid-state structures demonstrate the unexpected ligand versatility of the P_4S_3 molecule, which interacts through two, three, or even all of the phosphorus atoms with copper according to the nature of the copper halide. Compound **1** has a three-dimensional network in which linear and cylindrical infinite CuCl subunits coexist with diatomic CuCl building blocks. For the first time, all four P atoms of the P_4S_3 cage are involved in coordination with metal atoms. The 3D structure of **2** contains stacks of P_4S_3 that are interconnected by slightly undulated and planar $[CuCl]_n$ ribbons. Compound **3** is a one-dimensional polymer composed of alternating $(CuI)_2$ rings and P_4S_3 bridges. The structure of **4** consists of undulated $[CuI]_n$ layers in which the P_4S_3 cage functions as a bridge within the layer, as well as a spacer between the layers. The ^{31}P MAS NMR spectra obtained are in good agreement with the solid-state structures obtained crystallographically. Thus, analytically pure **3** and **4** show singlet peaks that correspond to uncoordinated P and quartets owing to coupling with ^{63}Cu and ^{65}Cu, respectively, whereas that of **1** contains quartets according to all-P coordination. The spectrum of **2** was obtained from a sample that still contained 40% of **1**.

Keywords: copper halides · NMR spectroscopy · phosphorus · polymers · sulfur

Introduction

The ligand properties of tetraphosphorus trisulfide have been intensively studied over the past thirty years. The abundant availability of cage lone pairs made the molecule an attractive target for studying the addition of Lewis acidic metal fragments, preferentially in the apical P1 position.[1–5] The addition of four $Mo(CO)_5$ fragments has been postulated by Jean Riess on the basis of ^{31}P NMR spectroscopy, but a structural confirmation is still missing.[6] Only very recently has experimental proof been provided for the simultaneous contribution of the apical (P1) and one of the basal positions (P2). The successful coordination of suitably tailored Re, Ru and Rh complex fragments has shown that under appropriate conditions both types of phosphorus sites have comparable coordination properties.[7–9] By contrast, sulfur coordination is much more difficult and only one example has been described so far in which Ag^+ interacts simultaneously with S and P atoms of one cage or of different cage molecules.[10] The resulting 1D chains are the only example of coordination polymers that contain the P_4S_3 cage as a supramolecular building block.



Products of a polymeric nature were proposed for the insoluble precipitates obtained by treating P_4S_3 with Cu^I halides in polar solvents.[11] The stabilisation of P_4Q_3-derived cage molecules, for example, β-P_4Q_4 (Q: S,[12] Se[13]) in polymeric matrices of copper(I) iodide, has been achieved by solid-state techniques from the molten elements and CuI. It is striking that in these systems there was no indication of the formation of Cu coordination polymers that are composed of the P_4S_3 building block.

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In this work we report the formation of polymeric networks from Cu^I halides and P_4S_3 by interdiffusion techniques of different solutions and the participation of all four P atoms in coordination chemistry for the first time. The unexpected versatility of the cage ligand in multiple bridging modes has been demonstrated by structural and ^{31}P MAS NMR spectroscopic investigations.

Results

The CuCl/P_4S_3 system: Interdiffusion of solutions of P_4S_3 in CH_2Cl_2 and CuCl in CH_3CN (molar ratio 1:1) gave bright yellow needles of **1** in a yield of 73% after five days. The composition was determined to be $(P_4S_3)_3(CuCl)_7$ by single-crystal X-ray diffraction analysis and was confirmed by elemental analysis. Diffusion experiments were usually carried out in tubes 3 cm in diameter.

When the experiment was carried out in a narrow tube (diameter 0.8 cm, length 10 cm) and with a P_4S_3/CuCl ratio of 1:2, a mixture that contained predominantly transparent yellow platelets of **2** and bright yellow needles of **1** was obtained. The crystals were separated manually and identified by X-ray diffraction analysis. For compound **2** the composition $(P_4S_3)_2(CuCl)_3$ was determined. From ^{31}P MAS NMR spectroscopy (see below) the ratio of **1**/**2** was determined to be 2:3, which was confirmed by elemental analysis (sulfur).

*Crystal structure of $(P_4S_3)_3(CuCl)_7$ (**1**)*: Compound **1** crystallises in the trigonal space group *P*31*c*. The 3D polymeric network reveals stacks of P_4S_3 cages, which are interconnected by three types of differently coordinated copper atoms, along the *c* axis as its characteristic feature. Aside from planar ribbons (Cu1Cl1), there are hexagonal columns (Cu3Cl3), and, as a structural peculiarity, stacks of diatomic units (Cu2Cl2) that contain a threefold crystallographic axis. Stereochemical saturation of the corresponding copper atoms in the latter occurs by coordination of three P_4S_3 basal units (Figure 1).

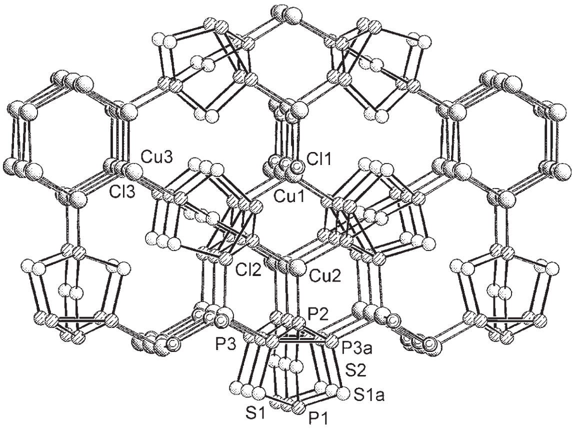

Figure 1. Section of the 3D structure of **1**. View down the *c* axis. A threefold crystallographic axis passes through the Cu2–Cl2 stacks.

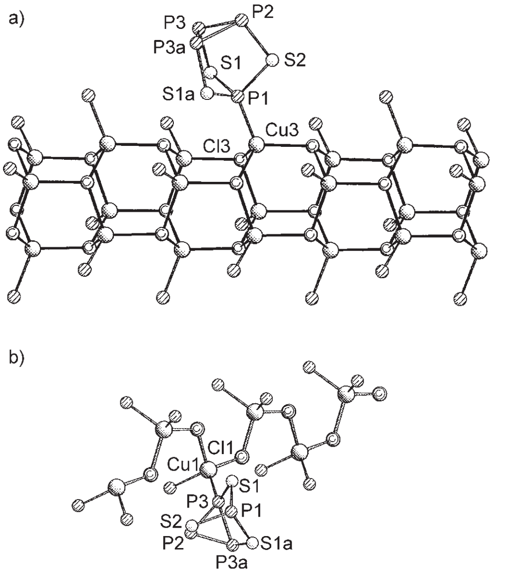

Figure 2. CuCl substructures of **1**: Hexagonal CuCl column with coordinated apical P atoms (a) and undulated CuCl chain with coordinated basal P atoms (b). In both cases only one complete P_4S_3 ligand is shown for clarity.

Compound **1** is the first example in which all four phosphorus atoms of the P_4S_3 cage coordinate to metal fragments. Whereas the basal phosphorus P2 is fixed at the central Cu2 atom, P3 and P4 are coordinated to two $[Cu1Cl1]_n$ chains. The apical phosphorus P1 is fixed at Cu3 of the hexagonal columns in a way that six ligands are distributed around the tube in a staggered conformation (Figure 2). The P–S distances do not differ much from those in uncoordinated P_4S_3.[14] However, it is striking that *d*(P3–P4) is longer than the other two P–P bond lengths by 0.06 Å (Table 1).

The unique character of the structure of **1** may be a consequence of the coexistence of linear and cylindrical infinite CuCl subunits with a diatomic building block. The hexagonal columns, which have a diameter of 4.5 Å, are composed of stacked chairlike six-membered CuCl rings (Figure 2), in which every other ring is rotated by 60°. Such an arrangement comes close to the wurtzite structure type, which has already been described for analogous CuI columns in $(CuI)_3P_4Q_4$ (Q: S,[12] Se[13b]). However, the formation of hexagonal CuCl tubes in supramolecular compounds seems to be rather atypical because four-membered rings or 1D ladders may be the preferred structural motifs.[15] The Cu atoms are surrounded by three Cl and only one P ligand, whereas the Cu atoms of the $[Cu1Cl1]_n$ chains bear two Cl and two P atoms. The bond parameters of the planar $[Cu1Cl1]_n$ chains of **1** are comparable to those of **2** (see below). The Cl1-Cu1-Cl1 angles are 102° in both compounds, the Cu1–Cl1 and Cu1–P4 distances are between 2.262(1) and 2.332(1) Å.

*Crystal structure of $(P_4S_3)_2(CuCl)_3$ (**2**)*: Compound **2** crystallises in the orthorhombic space group *Pmna*. As in the structure of **1** there are stacks of P_4S_3 cages, but instead they are along the *a* axis. The interconnection is effected by two different types of $[CuCl]_n$ ribbons through three phosphorus atoms P1, P2 and P4. The Cu atoms in the slightly undulated

Table 1. Selected distances [Å] of compounds **1**–**4** and comparison with P_4S_3.[16]

	P_4S_3	1	2	3	4
S1−P1	2.104	2.096(2)	2.094(1)	2.121(1)	2.107(2)
S1−P3		2.082(2)			
S1−P4	2.080		2.083(1)	2.097(1)	2.100(2)
S2−P1	2.089	2.100(2)	2.104(1)	2.126(1)	2.109(2)
S2−P2	2.082	2.081(2)	2.091(1)	2.115(1)	2.112(2)
S3−P1	2.089		2.107(1)		
S3−P3	2.082		2.097(1)		
P2−P3	2.219	2.238(2)	2.250(1)	2.276(1)	2.247(2)
P2−P4	2.219		2.214(1)	2.276(1)	2.247(2)
P3−P3a		2.293(2)			
P3−P4	2.233	2.293(2)	2.267(1)	2.232(1)	2.269(2)
P1−Cu1					2.247(2)
P1−Cu2			2.252(1)		
P1−Cu3		2.173(2)			
P2−Cu1			2.264(1)		
P2−Cu2		2.300(2)			
P3−Cu2					2.274(2)
P3−Cu1		2.331(2)		2.309(1)	
P4−Cu1			2.302(1)		
Cu1−Cl1		2.28(4)–2.332(1)	2.288(1)–2.332(1)		
Cu2−Cl2		2.271(2)	2.306(1)–2.312(1)		
Cu3−Cl3		2.318(2)–2.326(2)			
Cu1−I1				2.621(1)	2.621(1)
Cu1−I2					2.618(1)
Cu2−I1					2.634(1)
Cu2−I2					2.632(1)

$[Cu1Cl1]_n$ chains bear two P_4S_3 cages that are coordinated through the basal atoms P2 and P4. The third atom of the base (P3) remains uncoordinated (Figure 3). By contrast, the $[Cu2Cl2]_n$ chains are planar and each copper atom is fixed at the apical P1 atoms of two P_4S_3 molecules. Each Cu atom of both ribbons is tetrahedrally surrounded by two P and two Cl atoms. The Cu−Cl and Cu−P bond lengths range between 2.252(1) and 2.332(1) Å (Table 1). Similar CuCl sheets as those found in **1** or **2** are part of the structure of (μ_2-2-ethylpyrazin-*N*-*N*′)-(CuCl).[16] The P–S distances are close to those found in uncoordinated P_4S_3,[14] whereas a small elongation of the P–P distances within the P_3 base is observed (Table 1).

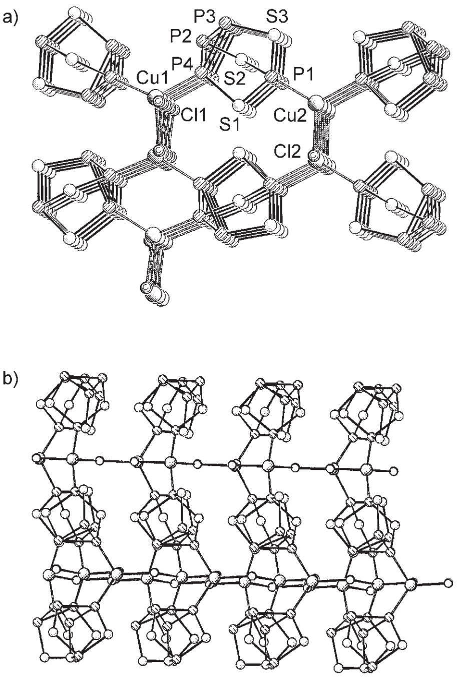

Figure 3. Sections of the 3D structure of **2**. View down the *a* axis (a); projection on the *ab* plain (b).

The CuI/P_4S_3 system: Layering a solution of P_4S_3 in CH_2Cl_2 with a solution of CuI in CH_3CN (molar ratio 1:3) gave a mixture of yellow transparent plates of the composition $(P_4S_3)(CuI)$ (**3**) and orange prisms of the composition $(P_4S_3)(CuI)_3$ (**4**) after four days. They were separated manually and their structures have been determined crystallographically. The ratio of the products is dependent on the concentrations of the starting material. Thus, decreasing the P_4S_3 concentration from 6 to 2.6 mmolL^{-1} and increasing the CuI concentration from 13.7 to 18 mmolL^{-1} gave analytically pure **3** in a yield of 81 %. On the other hand, further increasing the CuI concentration to 27 mmolL^{-1} resulted in the formation of analytically pure **4** in a yield of 80 %.

*Crystal structure of **3***: Compound **3** crystallises in the orthorhombic space group *Cmca*. Its structure is composed of linear chains, in which two P_4S_3 molecules serve as bridges for planar $Cu_2(\mu\text{-}I)_2$ rings through two phosphorus atoms (Figure 4). The resulting stacks are arranged in a zigzag manner along the *a* axis. The Cu atoms are found in a tetrahedral environment formed by the basal P atoms of two different P_4S_3 ligands and two I atoms. The Cu–Cu distances of 2.996(1) Å are indicative of a non-bonding interaction between these atoms. The bonding parameters of the coordinated P_4S_3 cages are slightly elongated when compared with those in the uncoordinated molecule. A similar structure was found for $(P_4S_3)(CuBr)$, which was obtained from P_4S_3 and CuBr. However, this compound is still contaminated by as yet unidentified side products.[17]

*Crystal structure of **4***: Compound **4** crystallises in the orthorhombic space group *Pnma*. The dominating structural feature is the undulated $[CuI]_n$ layers that are separated by P_4S_3 “spacers”, thus forming a three-dimensional lattice. The distance between the CuI layers is about 10 Å (Figure 5). Looking down the *c* axis one notices a seven-membered column that is formed by the bridging interaction of a P_4S_3 cage with two opposed Cu2 atoms of the CuI layer. Only P2

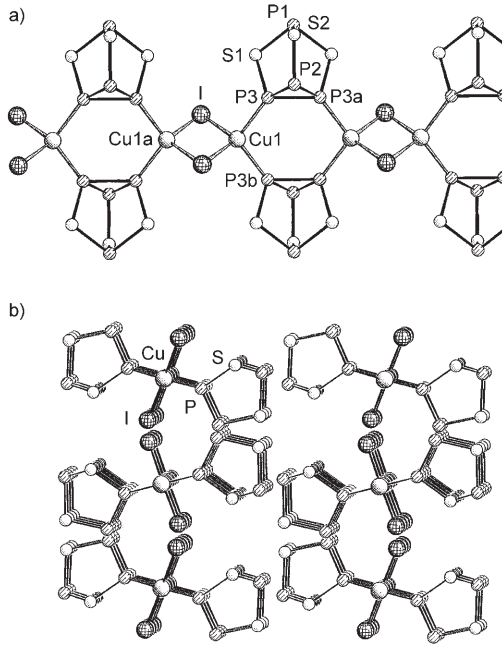

Figure 4. Sections of the structure of **3**. Side view of a single chain (a); projection of stacks down the *a* axis (b).

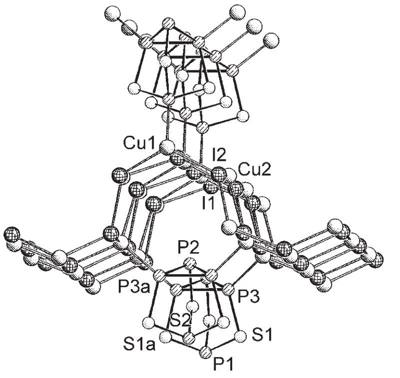

Figure 5. Section of the 3D structure of **4**; view down the *c* axis.

and P2a participate in the coordination, whereas the third basal phosphorus atom, P3, remains uncoordinated. The spacer function of P_4S_3 arises from the fact that the apical atom P1 coordinates to Cu1, which is part of the next column. The bond lengths P1−Cu1 (2.247 Å) are slightly shorter than those of P3−Cu2 (2.274 Å).

Another view of the undulated $[CuI]_n$ layers along the *b* axis reveals that the CuI substructure is composed of condensed hexagonal $[CuI]_n$ columns (Figure 6). The tetrahedral Cu atoms are surrounded by three I atoms and one P atom with average Cu−I bond lengths of 2.621(1) Å and angles that range from 104.9 to 117.8°. Interestingly, the P_3 base of the coordinated P_4S_3 molecules is tilted slightly towards the interior of the copper iodide column so that the P2 atom concerned is well protected from further coordination. Supramolecular compounds that contain condensed hexagonal CuI columns have only very recently been described.[18]

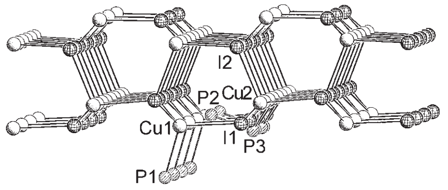

Figure 6. Projection of the CuI substructure of **4** down *b*. Condensed hexagonal $[CuI]_n$ columns form a two-dimensional layer; only selected P atoms of the coordinated P_4S_3 molecules are shown.

^{31}P MAS NMR spectroscopy: The coordination polymers are insoluble in common solvents, which prevents spectroscopic studies in solution. Therefore, ^{31}P MAS NMR spectroscopic studies have been carried out. The usefulness of this solid-state spectroscopy has already been demonstrated for several quarternary metal–phosphorus-chalcogenide systems.[12,13] Apart from structural information, this kind of spectroscopy should furthermore provide information on the homogeneity of the new compounds.

The ^{31}P MAS NMR spectrum of P_4S_3[19] exhibits a broad singlet at $\delta = 81.8$ ppm for the apical atom (P1) and another singlet at $\delta = -102.7$ ppm for the equivalent atoms of the P_3 base. ^2J(P,P) coupling constants cannot be detected. The assignment of the solid-state resonances follows from analogy of the chemical shifts with those of uncoordinated P_4S_3 in solution.

To establish a correlation between the solid-state structure and the ^{31}P MAS NMR spectroscopy results, spectra of well-defined compounds **1**, **3** and **4** and of the mixture of **1** and **2** were measured.

*^{31}P MAS NMR spectrum of **1***: The spectrum of **1** is shown in Figure 7. It exhibits a quartet at $\delta = 97.7$ ppm (J(Cu,P) = 1600 Hz) and a group of signals, which has been shown by simulation to be the result of the superposition of two quartets at $\delta = -55.0$ ppm (J(Cu,P) = 935 Hz) and $\delta = -63.1$ ppm (J(Cu,P) = 923 Hz) in a ratio of 1:2. The overall pattern is in agreement with the structure of **1** (Figures 1 and 2), in which all phosphorus atoms coordinate to Cu atoms and couple to the isotopes ^{63}Cu and ^{65}Cu ($I = 3/2$ for both isotopes), and it is also in agreement with the magnetic equivalence of P3 and P3a within the P_3 base.

*^{31}P MAS NMR spectrum of **2***: Compound **2** could not be prepared in a pure form because it is always contaminated by **1**. Thus, a typical sample obtained in a thin tube with a P_4S_3/CuCl ratio of 1:2 was examined. The resulting spectrum is shown in Figure 8. Simulation of the spectrum reveals distinct patterns that may be assigned to the structures of both **1** and **2**. Thus, a quartet at $\delta = 97.6$ ppm (P1) and quartets at $\delta = -56.5$ and -67.9 ppm agree well with the data obtained for pure **1**. The simulated data of **2** split into two sets of quartets at $\delta = 101.2$ (J(Cu,P) = 1040 Hz; (P1)) and $\delta = -77.5$ ppm (J(Cu,P) = 1040 Hz; (P2/P4)) and one singlet at

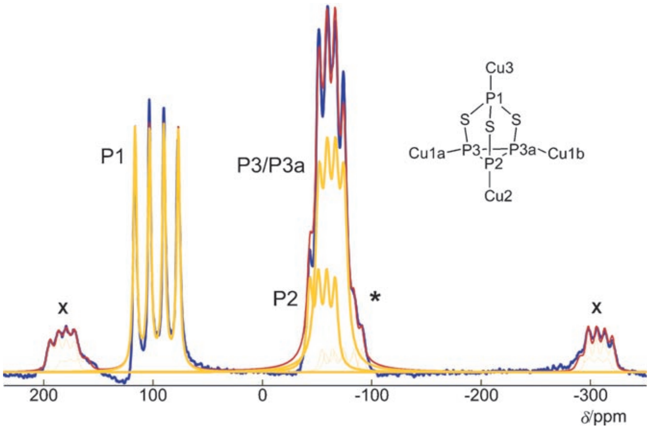

Figure 7. Experimental (blue) and simulated (yellow) ^{31}P MAS NMR spectrum of **1**. Spinning side bands are indicated by X, trace amounts of **2** are indicated by * and the superposed data is shown in red.

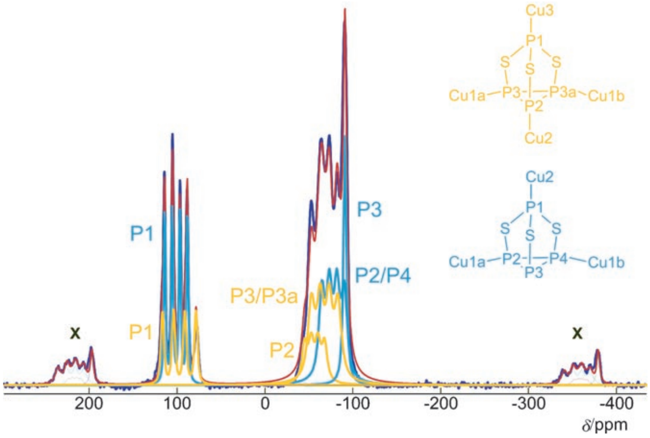

Figure 8. Experimental (dark blue) and simulated (yellow, pale blue) ^{31}P MAS NMR spectrum of a mixture of **1** and **2**. Spinning side bands are indicated by X and the superposed data is shown in red.

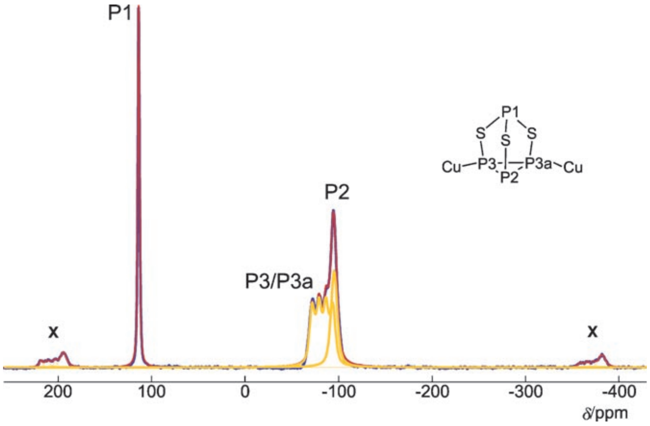

Figure 9. Experimental (blue) and simulated (yellow) ^{31}P MAS NMR spectrum of **3**. Spinning side bands are indicated by X and superposed data is shown in red.

$\delta = -91.1$ ppm (P3). The overall pattern is in agreement with Cu coordination of apical (P1) and two basal (P2,4) phosphorus atoms, whereas P2 of the base is uncoordinated. The calculated ratio of **1**/**2** of 2:3 corresponds to the analytically determined sulfur content (24.2 %) of a sample that contained 40 % of **1** and 60 % of **2**.

*^{31}P MAS NMR spectrum of **3***: The spectrum of **3** exhibits a singlet at $\delta = 113.8$ ppm and a group of superposed resonances at $\delta = -86$ ppm (Figure 9). The singlet, which is shifted 32 ppm downfield with respect to that of free P_4S_3, can be assigned to the uncoordinated apical atom P1. Simulation of the second group shows that it consists of a singlet at $\delta = -95.3$ ppm and a multiplet at $\delta = -82.8$ ppm. From the crystal structure of **3** (Figure 4) it is evident that one P atom of the base (P2) is not coordinated to Cu, whereas the other two P atoms (P3 and P3a) are bound to copper in a symmetrical environment such that they are magnetically equivalent. Owing to coupling with ^{63}Cu and ^{65}Cu, they appear as quartets with a simulated coupling constant of $J(\mathrm{Cu,P}) =$ 900 Hz. The observed pattern is also in agreement with the equivalence of the Cu1 and Cu1a copper sites.

*^{31}P MAS NMR spectrum of **4***: The solid-state ^{31}P NMR spectrum of **4** is depicted in Figure 10. X-ray crystallography (Figure 5) shows that **4** contains three types of P atoms, two of them bearing copper atoms. However, the spectrum exhibits only two groups of signals. The quartet at $\delta = 82.2$ ppm ($J(\mathrm{Cu,P}) = 1100$ Hz) may be assigned to the apical atom P1, which is high-field shifted by 31.6 ppm with respect to **3** as a result of Cu coordination. Simulation of the second signal reveals that it results from the superposition of a singlet at $\delta = -94.9$ ppm with a quartet at $\delta = -94.2$ ppm ($J(\mathrm{Cu,P}) = 698$ Hz). This pattern is in agreement with the nature of the P_3 base, which contains two magnetically equivalent atoms, P3 and P3a, integrated in the CuI network aside from the non-bonding P2 atom (Figure 6).

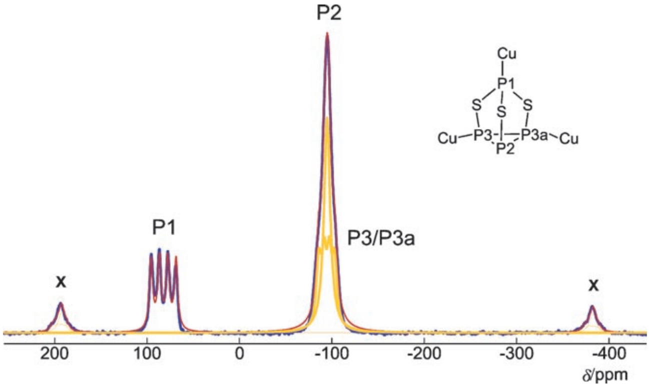

Figure 10. Experimental (blue) and simulated (yellow) ^{31}P MAS NMR spectrum of **4**. Spinning side bands are indicated by X and the superposed data is shown in red.

Conclusion

This study focuses on the preparation of coordination polymers from copper halides and P_4S_3 by interdiffusion techniques of solutions in CH_3CN and CH_2Cl_2, respectively. The solid-state structures demonstrate the unexpected versatility of P_4S_3 as a building block in the formation of the resulting networks as a function of the halogen used. Interaction of two, three, or for the first time, all of phosphorus atoms through their lone pairs with copper leads to CuHal (Hal: halogen) substructures, such as diatomic CuCl dumbbells, slightly distorted and planar $[CuCl]_n$ ribbons, hexagonal $[CuCl]_n$ columns, four-membered Cu_2I_2 rings and condensed hexagonal $[CuI]_n$ columns. The diffusion conditions may depend on the concentration of the starting materials, which on the other hand influences the product distribution.

As sulfur does not seem to play a direct role in the coordination in comparison with the results obtained with Ag^+, for example,[10] it may be appealing to extend these studies to As_4S_3, which is structurally closely related to P_4S_3. In this context it may be of interest that the assembly of $As_4S_4{\cdot}HgI_2$ dimers by melting together As, S and HgI_2 occurs through sulfur lone pairs.[20]

Experimental Section

General: All manipulations were carried out under nitrogen by using Schlenk techniques. Diffusion experiments were usually carried out in Schlenk tubes of 3.0 cm diameter unless described otherwise. A commercial sample of P_4S_3 (Riedel de Häen) was purified by boiling with water followed by subsequent recrystallisation from toluene. ^{31}P MAS NMR spectra were recorded by using a Bruker Advance 300 spectrometer by 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 35 kHz, a 90° pulse length of 2.3 μs and with a relaxation delay of 450 s. For simulation of the spectra the program DMFIT was used.[21]

Synthesis of 1: A solution of CuCl (9.0 mg, 0.091 mmol) in CH_3CN (10 mL; $c=9\,mmol\,L^{-1}$) was carefully layered over a solution of P_4S_3 (20 mg, 0.091 mmol) in CH_2Cl_2 (15 mL; $c=6\,mmol\,L^{-1}$). After five days the yellow needles of **1** that deposited were filtered, washed with CH_2Cl_2 and dried under vacuum (45 mg, 73 %). ^{31}P MAS NMR (300 MHz): $\delta=97.7$ (q, J(Cu,P) = 1600 Hz; P1), −56.5 (q, J(Cu,P) = 935 Hz; P2), −63.1 ppm (q, J(Cu,P) = 923 Hz; P3/P3a); elemental analysis calcd (%) for $Cl_7Cu_7P_{12}S_9$: S 21.33; found: S 21.47.

The CuCl/P$_4$S$_3$ system: A solution of CuCl (6.3 mg, 0.064 mmol) in CH_3CN (3 mL; $c=21\,mmol\,L^{-1}$) was layered over a solution of P_4S_3 (7.0 mg, 0.032 mmol) in CH_2Cl_2 (7 mL; $c=5\,mmol\,L^{-1}$) in a thin tube of 0.8 cm diameter. After two days the solvent was decanted and the deposited material was washed with CH_2Cl_2 and dried under vacuum. The crystalline mixture consisted of transparent yellow platelets of **2** contaminated with bright yellow needles of **1**. The crystals were separated manually and identified by X-ray diffraction analysis to be $(P_4S_3)_3(CuCl)_7$ (yellow needles; **1**) and $(P_4S_3)_2(CuCl)_3$ (yellow platelets; **2**).

The P$_4$S$_3$/CuI system: *Synthesis of 3*: A solution of CuI (52 mg, 0.27 mmol) in CH_3CN (15 mL; $c=18\,mmol\,L^{-1}$) was layered over a solution of P_4S_3 (20 mg, 0.09 mmol) in CH_2Cl_2 (35 mL; $c=2.6\,mmol\,L^{-1}$). After three days, bright-yellow, transparent plates of **3** crystallised, which were washed with CH_2Cl_2 and dried under vacuum (30 mg, 81 %); ^{31}P MAS NMR (300 MHz): $\delta=113.8$ (s; P1), −82.8 (q, J(Cu,P) = 900 Hz; P2/P2a), −95.3 ppm (s; P3); elemental analysis calcd (%) for $CuIP_4S_3$: S 23.43, I 30.91; found: S 23.49, I 30.99.

Synthesis of 4: A solution of CuI (52 mg, 0.27 mmol) in CH_3CN (10 mL; $c=27\,mmol\,L^{-1}$) was layered over a solution of P_4S_3 (20 mg, 0.09 mmol) in CH_2Cl_2 (30 mL; $c=3.0\,mmol\,L^{-1}$). Orange prisms of **4** crystallised after four days (57 mg, 80 %); ^{31}P MAS NMR (300 MHz): $\delta=82.2$ (q, J(Cu,P) = 1100 Hz; P1), −94.2 (q, J(Cu,P) = 698 Hz; P2/P2a), −94.9 ppm (s; P3); elemental analysis calcd (%) for $Cu_3I_3P_4S_3$ (791.4): calcd S 12.15, I 48.10; found: S 12.13, I 47.56.

Crystal structure determinations for 1–4: Crystallographic data for the crystal structure determinations for **1–4** are given in Table 2. The structures were solved by direct methods and refined by full-matrix least-squares (SHELXL97 program) with all reflections. Further details of the crystal-structure investigations may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository numbers CSD-418074 (**1**), -418075 (**2**), -418076 (**3**) and -418077 (**4**).

Table 2. Crystallographic data of **1–4**.

	1	**2**	**3**	**4**
formula	$Cl_7Cu_7P_{12}S_9$	$Cl_3Cu_3P_8S_6$	$CuIP_4S_3$	$Cu_3I_3P_4S_3$
M_w	1353.27	737.18	410.54	791.44
crystal size [mm^3]	0.18 × 0.04 × 0.04	0.12 × 0.11 × 0.03	0.26 × 0.16 × 0.02	0.23 × 0.20 × 0.17
crystal system	trigonal	orthorhombic	orthorhombic	orthorhombic
space group	*P63mc*	*Pnma*	*Cmca*	*Pnma*
a [Å]	16.556(2)	6.117(2)	7.845(1)	19.252(2)
b [Å]	16.556(2)	26.471(1)	21.773(2)	10.082(1)
c [Å]	6.121(1)	11.179(1)	10.305(2)	7.080(1)
V [Å^3]	1452.9(1)	1810.2(1)	1760.2(3)	1373.5(2)
Z	2	4	8	4
ρ_{cald} [g cm^{-3}]	3.093	2.705	3.098	3.827
μ [mm^{-1}]	23.850	21.211	7.338	12.222
λ (Cu$_{K\alpha}$ [Å])	1.54184	1.54184		
λ (Mo$_{K\alpha}$ [Å])			0.71073	0.71073
instrument	Oxford Diffraction Gemini Ultra		STOE-IPDS	
temperature [K]	123	123	123	123
scan range	$3.08<\theta<62.96$	$3.34<\theta<62.14$	$2.72<\theta<25.80$	$3.07<\theta<25.93$
reflns collected	23288	4871	8418	16194
reflns observed ($I>2s(I)$)	1521	1247	869	1336
parameters	106	94	48	67
absorption corr	semiempirical	semiempirical	analytical	analytical
transmission	1.0000/0.35413	1.0000/0.3012	0.4422/0.1945	0.2348/0.1408
residual density [e Å^{-3}]	0.951/−0.392	0.781/−0.437	1.626/−0.601	1.035/−0.932
R_1, wR_2 ($I>2\sigma$)	0.023, 0.068	0.026, 0.065	0.021, 0.056	0.025, 0.068
R_1, wR_2 (all data)	0.024, 0.068	0.030, 0.067	0.022, 0.057	0.027, 0.069

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