Structures, spectroscopic studies and solid-state thermal transformations of coordination polymers from P₄Se₃ and CuX (X=Cl, Br, I)

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A R T I C L E  I N F O

Article history:
Received 22 February 2011
Received in revised form 2 May 2011
Accepted 8 May 2011
Available online 14 May 2011

Keywords:
Phosphorus
Coordination polymers
Solid-state NMR spectroscopy
Raman spectra

1. Introduction

Cage molecules like P₄Q₃ (Q=S, Se) represent a small but important class of inorganic compounds. The P₄S₃ molecule exhibits a rich coordination chemistry towards Lewis-acidic metal fragments, although addition reactions are mostly focussed at the apical and/or basal phosphorus [1]. Due to relatively poor solubility of P₄Se₃ in organic solvents there are only a few examples for P₄Se₃ [2]. Attempts to synthesize new solid-state materials containing P₄Se₃ and (CuI)n aggregates from copper(I) halides and the molten elements gave (CuI)₂(P₄Q₄) (Q=S [3], Se [4,5]), while CuCl and CuBr led to decomposition reactions. We have recently found that P₄S₃ may be introduced in copper(I) halide networks by applying interdiffusion techniques from solutions of different polarity [6]. Because of the poorly developed coordination chemistry of P₄Se₃ we decided to systematically extend this work onto P₄Se₃ and CuX (X=Cl, Br, I). Herein we report the crystal structures and spectroscopic properties of the products, the calculation of Raman frequencies by DFT methods in the crystalline phase, their correlation with measured spectra and the thermally induced transformation of selected compounds.

2. Experimental

2.1. General procedure

All manipulations were carried out under nitrogen by Schlenk techniques. The diffusion experiments were carried out in Schlenk tubes of 3.0 cm diameter. P₄Se₃ was synthesized by melting red phosphorus and gray selenium in a molar ratio of 4 to 3 under a nitrogen-atmosphere, followed by extraction with CH₂Cl₂ in a Soxhlet apparatus and recrystallization from CH₂Cl₂ [7].

2.2. Syntheses

(CuCl)₃(P₄Se₃) (1): A solution of CuCl (25 mg, 0.249 mmol) in CH₃CN (5 ml, c=49.8 mmol l⁻¹) was layered over a solution of P₄Se₃ (30 mg, 0.083 mmol) in CH₂Cl₂ (30 ml, c=2.8 mmol l⁻¹). After diffusion transparent yellow needles of 1 crystallized and were washed with CH₂Cl₂ and dried under vacuum. Anal. Calcd. for ClCuP₄Se₃ (459.76): Cl 7.74; Found: Cl 7.71%. ³¹P MAS NMR ( δ, ppm): 72.0 (s), 35.8 (m, Jₚ-Cu = 896 Hz), -51.7 (m, Jₚ-Cu = 896 Hz), -84.2 (s).

(CuBr)₃(P₄Se₃)₂ (2): A procedure similar to that for 1 was used with CuBr (36 mg, 0.249 mmol) in CH₂CN (5 ml, c=49.8 mmol l⁻¹) and P₄Se₃ (30 mg, 0.083 mmol) in CH₂Cl₂ (30 ml, c=2.8 mmol l⁻¹). Yield 78 mg (82%). ³¹P MAS NMR ( δ, ppm): 59.0 (m, Jₚ-Cu = 900 Hz), -57.7 (m, Jₚ-Cu = 1094 Hz), -68.1 (s), -69.8 (m, Jₚ-Cu = 910 Hz).

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(CuI)P4Se3 (20 mg, 0.055 mmol) in CH2Cl2 (25 mL, c=2.2 mmol l−1). Yield 50 mg (70%).31P MAS NMR (δ, ppm): 52.5 (m, 1JPCu=880 Hz), −68.3 (s), −76.1 (m, 1JPCu=800 Hz), −101.1 (m, 1JPCu=780 Hz). Increasing the CuI concentration results in the cocrystallization of small amounts of red (Cu1)P4Se3.  

2.3. Crystal structure determination

Crystallographic data of the crystal structure determinations for 1–5 are given in Table 1 and Table S1. 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, http://www.fiz-karlsruhe.de/ecid/Internet/en/DB/jcd/depot_anforderung.html) on quoting the deposition numbers CSD-422534 (1), -422535 (2), -422536 (3), -422537 (3), -422538 (3).

2.4. Differential thermal analysis (DTA and TG)

The DTA analyses were carried out on a Setaram TMA 92 (16.18). In each case 10–20 mg of the substances were fused into evacuated silica glass vials (diameter 0.1 cm, length 0.8 cm) and then the heat flow was recorded. The temperature range from 25 °C to 800 °C was monitored for each sample in two heating and cooling cycles (10 °C/min). Then, the thermal behavior of a new sample at the first irreversible peak was investigated. After the DTA experiment the samples were examined microscopically and by X-ray diffraction.

The TG-analyses were carried out in open Al2O3-cups under nitrogen-atmosphere in a temperature range of 25–600 °C with a heating rate of 10 °C/min.

2.5. Raman spectra

The Raman spectra were recorded on a Varian FTS 7000e spectrometer containing a FT Raman unit. The excitation of the microcrystalline samples was carried out with a Nd:YAG laser (λ=1064 nm) and the detection was performed with a liquid N2 cooled Ge detector.

2.6. 31P MAS NMR spectra

31P MAS NMR spectra were recorded with a Bruker Avance 300 spectrometer using a double resonance 2.5 mm MAS probe. The 31P 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 with a relaxation delay of 450 s. For spectrum simulation the program DMFIT was used [8].

2.7. Density functional theory (DFT) calculations

The calculations were performed within the framework of DFT theory as implemented in the LCAO-code CRYSTAL06 [9,10]. The electronic structure is calculated from Gaussian type local basis sets. Raman frequencies were calculated from the vibrational spectra at the gamma point [11]. Exchange and correlation were treated as described by the B3LYP functional for all results presented in this paper. All electron basis sets were used for Cu (0.28, 0.4), and Se (0.21, 1.09), valence basis sets for P (0.23, 0.49), S (0.22, 0.45), Cl (0.21, 0.38), Br (0.21, 0.36) and I (0.22, 0.33) with respective optimized coefficients for outer (sp, d) functions [12]. The calculations were converged to total energy ΔE<10−8 H applying k-point shrinking factors of 4 to 8 and Anderson mixing (see [9]).

3. Results and discussion

3.1. Preparations

Layering of solutions of P8Se8 in CH2Cl2 with a solution of the respective copper halide CuX in CH3CN (molar ratio 1:3 to 1:4) gave for X=Cl after 3 d transparent yellow needles and fine hairs of CuClP4Se3 (1) in 83% yield. The composition was confirmed by single crystal X-ray diffraction, X-ray powder diffractometry and elemental analysis (CI).

When the experiment was carried out with CuBr yellow-orange platelets of CuBr3P4Se8 (2) crystallized in 82% yield.
The composition of 2 was determined by X-ray diffraction analysis, while the homogeneity was determined by means of $^{31}$P MAS NMR spectroscopy (Scheme 1).

The analogous experiment with CuI gave a mixture of orange-red plates of (CuI)$_3$(P$_4$Se$_3$)$_2$ (3) and thin red prisms of (CuI)P$_4$Se$_3$ (4), which were both examined by X-ray diffraction analysis. Decreasing the concentration of CuI in acetonitrile results in a nearly selective formation of 3, the purity of which has been established by $^{31}$P MAS NMR spectroscopy.

### 3.2. Crystal structure analysis

Compound 1 crystallizes in the monoclinic space group P2$_1$/c. The structure is composed of slightly distorted castellated [CuCl]$_n$ chains along the c axis, which are connected by two P$_4$Se$_3$ molecules via their phosphorus basis atoms P2 and P4 to give a two-dimensional layer (Fig. 1). The third atom of the P$_3$ basis (P3) and the apical atom P1 do not coordinate. The P–Se distances within the P$_4$Se$_3$ cage are comparable within experimental error with those of the free cage [13], while the distance P2–P4 is shorter by 0.03 and 0.04 Å, respectively, than the other two P–P bonds of the P$_3$ basis. The copper atoms are tetrahedrally surrounded by two Cl and two P atoms. The observed Cu–Cl (2.276(3) Å) and Cu–P distances (2.283(3) Å mean) are typical of copper halides and phosphides [5]. Similar [CuCl]$_n$ chains are, e.g., part of the structure of [(CuCl)($\mu_2$-2-ethylpyrazine-N-N)] [14].

Compound 2 crystallizes in the orthorhombic space group Pnma. The structure contains two different types of castellated [CuBr]$_n$ chains, which are bridged by P$_4$Se$_3$ cages (Fig. 2). While [Cu$_1$–Br$_1$]$_n$ is planar, [Cu$_2$–Br$_2$]$_n$ is distorted along the a axis by 17°. As in the structure of 1 the basal atoms P2 and P4 connect two neighboring non-planar chains via Cu$_2$. The apical atoms P1, however, coordinate to planar chains via Cu1. The result is a 3D network, which is isostructural with (CuCl)$_3$(P$_4$S$_3$)$_2$ [6a]. The Cu–Br distances range from 2.408(1) to 2.448(1) Å and the Cu–P distances from 2.261(1) to 2.267(1) Å. Each copper atom of the respective chains is tetrahedrally surrounded by two P and two Br atoms with angles between 103.6(1) and 117.9(1)°. The distance P3–P4 is slightly longer by 0.03 Å than the other two ones within the P$_3$ basis. [CuBr$_n$] chains similar to that in 1 and 2 have been found in coordination polymers of the type [(CuBr)$_2$(triazine)] [15].

Compound 3 crystallizes in the orthorhombic space group Pnma. The structure is built up of castellated [CuI]$_n$ chains with each copper (Cu$_2$) bearing a pair of apically (P1) coordinated P$_4$Se$_3$ cages. The backsides of the cages are bridged by planar Cu$_2$I$_2$ four-membered rings while the third basal P atom (P4) remains uncoordinated. As a result an unprecedented three-dimensional structure is formed (Fig. 3). The bond parameters of the P$_4$Se$_3$ cage behave similarly to those of 1 and 2.

Compound (CuI)P$_4$Se$_3$ (4) crystallizes in the orthorhombic space group Cmca. Like its isostructural analog (CuI)P$_4$S$_3$ [6] the structure is a one-dimensional polymer containing planar (CuI)$_2$ four-membered rings bridged by P$_4$Se$_3$ units (Fig. S1). The atoms P1 (apical) and P2 (basal) are not coordinated.
A comparison of the crystal structures found in the $\alpha$-P$_4$Se$_3$/CuX system (X=Cl, Br, I) with those of P$_3$S$_4$/CuX polymers reveals as common features copper halide substructures consisting of planar Cu$_4$X$_4$ four-membered rings (X=Br, I) and/or castellated [CuX]$_n$ chains. As a result one-dimensional ribbons (4), or two- (1) and three-dimensional networks (2, 3) are formed, which are new structure types in the case of 1 and 3. It is striking that no hexagonal (CuX)$_n$ substructures are formed, which seem to be typical of P$_3$S$_4$ containing polymers [6].

3.3. $^{31}$P MAS NMR spectroscopy

More structural informations on the polymers 1-4 may be obtained by solid-state $^{31}$P MAS NMR spectroscopy and by comparison with the spectrum of $\alpha$-P$_4$Se$_3$, which was also recorded. For the latter resonance signals for the apical P atom at $\delta=81.2$ and 77.2 ppm and for the basal P atoms at $\delta=-67.0$ ppm were found with an approximate $^{31}$P$_{\text{apical}}$: $^{31}$P$_{\text{basal}}$ integral ratio of 1:3 (Fig. S2). The splitting of the signal of the apical P atom into two singlets may be explained by the packing of the cage molecules in the unit cell [13]. A similar splitting was reported for $\alpha$-P$_4$S$_3$ [16].

The $^{31}$P MAS NMR spectrum of 1 exhibits two groups of signals centered at $\delta=57$ and $-60$ ppm (Fig. 4). The singlet at $\delta=72.0$ ppm may be assigned to apical P1. The broad signal at $\delta=-60$ ppm has been shown by simulation to be the result of the superposition of one singlet at $\delta=-84.2$ ppm and two multiplets at $\delta=-35.8$ ($J_{P,Cu}=886$ Hz) and $-51.7$ ppm ($J_{P,Cu}=986$ Hz). The latter indicate coupling of magnetically inequivalent basis atoms P2 and P4 with 63/65Cu, whereas the singlet may be assigned to the uncoordinated atom P3 of the P3 basis. $^{31}$P–$^{77}$Se coupling was not observed.

The $^{31}$P MAS NMR spectrum of 2 exhibits two groups of signals (Fig. 5). Simulation of the spectrum reveals a multiplet at $\delta=59.0$ ppm ($J_{P,Cu}=900$ Hz), a singlet at $\delta=-68.1$ ppm and two multiplets at $\delta=-57.7$ ppm ($J_{P,Cu}=1094$ Hz) and $\delta=-69.8$ ppm ($J_{P,Cu}=910$ Hz), respectively. The overall pattern is in agreement with the structure of 2 (Fig. 2). The magnetic inequivalence of the atoms P2 and P4 indicates that the symmetry of the free cage (C$_{3v}$) is lowered by coordination (C$_3$).

According to X-ray powder diffraction compound 3 is contaminated by compound 4. A nearly pure sample of 3 was obtained employing a low concentration of Cu in acetonitrile. The resulting $^{31}$P MAS NMR spectrum shows two groups of signals (Fig. 6). Simulation of the spectrum reveals a multiplet at $\delta=52.5$ ppm ($J_{P,Cu}=880$ Hz). The high field signal splits into two multiplets (copper coordination of P2 and P3) at $\delta=-76.1$ ppm ($J_{P,Cu}=800$ Hz) and $-101.1$ ppm ($J_{P,Cu}=780$ Hz), respectively, and a singlet at $\delta=-68.3$ ppm. The latter may be assigned to P4 of the P3 basis. Overall, the spectrum of 3 is in agreement with the crystal structure and it is similar to that of 2 inspite of different CuX substructures.

The $^{31}$P MAS NMR spectrum of a mixture of 3 and 4 allows a clear identification of an additional singlet at $\delta=91.3$ ppm, which may be assigned to the apical P atom of 4. The other resonances of 4 are superposed by those of 3. It is striking that the resonance of the apical P atom is downfield shifted compared to $\alpha$-P$_4$Se$_3$ (Table 2). A similar effect was observed for the apical resonances of the isosctructural polymers (CuX)P$_3$S$_3$ (X=Br, I) [6]. Ab initio calculations have shown that possible explanations have to take into account electronic effects rather than steric arguments [17].

A detailed $^{31}$P MAS NMR spectroscopic investigation of (CuI)$_3$(k-P$_4$Q$_4$) polymers (Q=S, Se) has been published recently [4]. In all cases it was found that the coordination of Cu(I) at phosphorus gave rise to a high field shift of the resonance signal by about 50 ppm compared to the free cage molecule, whereas the signals of uncoordinated P atoms were only slightly affected. These effects were explained by Cu–P back donation and electronic perturbations by Cu$^+$ complexation, which are predominantly local and mostly confined to the directly Cu-bonded
A similar but less pronounced trend is found for the chemical shifts of $1-3$, except the resonances of P2/P4 (1), P2 (2) and the apical P atom of 4 (Table 2).

### 3.4. Theoretical and Raman spectroscopic investigations

Recently, we have studied the nature of the interaction between $P_4S_3$ and copper(I) halides in periodic structures by density functional theory (DFT) calculations. The use of the program package CRYSTAL06 [9] allowed to consider the influence of packing effects and intermolecular forces in the condensed phase. The DFT approach was successfully applied to calculate vibrational frequencies as stated by comparison with Raman spectra [17].

Computational studies of frequencies of crystalline $P_4Se_3$ were carried out using the same basis set for phosphorus as in the computation of the Raman modes of $P_4S_3$. The basis set of selenium was optimized by calculation of the cage geometry and by correlation of calculated and measured Raman modes. The visualization of the vibration modes by the program Jmol [18] allowed unambiguous assignment. The calculated P–P distances of the P$_3$ basis deviate by 2%, while the other calculated distances come close to the experimental values [13]. The Raman modes and the corresponding vibrational assignments of $P_4Se_3$ have already been calculated for the gas phase (Table 3) [19]. Computational studies of frequencies of crystalline $P_4Se_3$ show a better agreement with experimental Raman shifts. The introduction of scaling factors is not necessary.

A comparison of experimental Raman spectra of $P_4Se_3$ and 1 is shown in Fig. 7. The observed Raman modes $n_1$, $n_2$ and $n_3$ may be assigned to the vibrations P–Se–P wag, P–Se–P bend and Se–P stretch. The intense $n_4$, $n_5$ and $n_6$ modes, which are all typical of the free cage were split into a couple of Raman active frequencies.

Fig. 6. $^{31}P$ MAS NMR spectrum of 3: (a) experimental spectrum; (b) simulated spectrum; (c) simulated spectrum showing individual components. Spinning side bands are marked by the symbol $\times$.

Table 2

<table>
<thead>
<tr>
<th>$P_{\text{apical}}$</th>
<th>$P_{\text{basal}}$</th>
<th>$^{31}P$–$^{63/65}\text{Cu}$ in $J$ (Hz) of $P_4Se_3$ and compounds 1–4.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g$–$P_4Se_3$</td>
<td>81.2, 77.2</td>
<td>–67</td>
</tr>
<tr>
<td>(CuCl)$_2$P$_4$Se$_3$ (1)</td>
<td>72.0</td>
<td>–35.8 (9 8 6), –51.7 (8 9 6), –84.2</td>
</tr>
<tr>
<td>(CuBr)$_2$P$_4$Se$_3$ (2)</td>
<td>59.0 (900)</td>
<td>–57.7 (10 9 4), –68.1, –69.8 (910)</td>
</tr>
<tr>
<td>(CuI)$_2$P$_4$Se$_3$ (3)</td>
<td>52.5 (880)</td>
<td>–68.3, –76.1 (800), –101.1 (780)</td>
</tr>
<tr>
<td>(CuI)P$_4$Se$_3$ (4)</td>
<td>91.3</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Superposed multiplet.

Table 3

Comparison of Raman shifts (cm$^{-1}$) of $P_4Se_3$ calculated in the gas phase and in the condensed phase (CRYSTAL06) and of 1 and 3 with experimental shifts.

<table>
<thead>
<tr>
<th>$P_4Se_3$</th>
<th>1</th>
<th>3</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>SQM-method$^a$</td>
<td>DFT/B3LYP$^b$</td>
<td>Exp. Raman shift</td>
<td>Calc.</td>
</tr>
<tr>
<td>168</td>
<td>161</td>
<td>131</td>
<td>152</td>
</tr>
<tr>
<td>269</td>
<td>187</td>
<td>209</td>
<td>211</td>
</tr>
<tr>
<td>404</td>
<td>286</td>
<td>317</td>
<td>–</td>
</tr>
<tr>
<td>442</td>
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<td>355</td>
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</tr>
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<td>484</td>
<td>380</td>
<td>397</td>
<td>–</td>
</tr>
<tr>
<td>561</td>
<td>468</td>
<td>477</td>
<td>476</td>
</tr>
</tbody>
</table>

$^a$ Scaled quantum mechanical calculations [19].

$^b$ Condensed phase, this work.
between 320 and 420 cm\(^{-1}\) as a consequence of symmetry reduction. The frequencies \(v_1\), \(v_2\) and \(v_6\) are also affected by coordination as shown by significant shifts to higher wave numbers when compared to free \(P_2Se_3\) (Table 3).

The Raman spectrum of 3 (Fig. 8) is similar to that of 1. This implies that the modes \(v_1\), \(v_2\) and \(v_6\) exhibit nearly the same red shift with respect to \(P_2Se_3\) (Table 3). The frequencies between 330 and 420 cm\(^{-1}\) are difficult to assign except the mode \(v_4\) at 353 cm\(^{-1}\), which can be assigned to symmetrical P-Se-P stretch. This vibration is not affected by Cu coordination of the cage, while \(v_5\) is shifted by 18 cm\(^{-1}\) to red.

### 3.5. Investigation of thermally induced solid-state transformation reactions

#### 3.5.1. Thermal conversion of (CuCl)\(_3\)(P\(_2\)Se\(_3\)) \((1)\) and (CuBr)\(_3\)(P\(_2\)Se\(_3\))\(_2\) \((2)\)

The preparation of (CuCl)\(_3\)(β-P\(_2\)Q\(_4\)) (Q = S, Se) was carried out at high temperatures starting from the elements and CuI [3]. Therefore, it seems interesting to investigate the thermal behavior of compounds with already preformed building blocks like in 1 or 2, which are both available in pure form. For comparison purposes the thermal behavior of previously prepared (CuI)\(_3\)P\(_4\)S\(_3\) [6a] has also been studied.

The TG spectrum of 1 is in agreement with the formation of PCl\(_3\) as a decomposition product. The corresponding DTA diagram of 1 shows two irreversible endothermic peaks at 221 and 255 °C, respectively. Therefore, 150 mg of pure 1 were sealed in a silica glass vial and annealed at 230 °C for three days. After slow cooling of the sample red-brown prisms were obtained, which were analyzed by single crystal X-ray diffraction and \(^{31}\)P MAS NMR spectroscopy. According to these studies an optically homogenous product of composition (CuCl)\(_3\)(P\(_2\)Se\(_3\))\(_2\) \((5)\) has formed. The compound is isostructural with 2, but with two kinds of [CuCl]\(_n\) chains instead of [CuBr]\(_n\) chains (Fig. S3, Tables S1 and S2). This implies release of P\(_2\)Se\(_3\) and a structural reorganization from two- to three-dimensional network.

The \(^{31}\)P MAS NMR spectrum of 5 proves the homogeneity of the sample and it is in agreement with the crystal structure (Fig. 9). It shows a multiplet at \(\delta = 55.3\) ppm \((J_{PCu} = 945\) Hz), which may be assigned to apical P1 of the cage and a group of signals, which is composed of two multiplets at \(\delta = -56.0\) \((J_{PCu} = 1081\) Hz) and -74.4 ppm \((J_{PCu} = 751\) Hz). These indicate magnetic inequivalence of P2 and P4. The singlet at \(\delta = -68.3\) ppm comes from the uncoordinated basal atom P3.

Annealing of (CuBr)\(_3\)(P\(_2\)Se\(_3\))\(_2\) \((2)\) at 320 °C for 3 d gave a dark shining product. X-ray diffraction experiments showed it to be amorphous and \(^{31}\)P NMR MAS spectroscopy could not be applied successfully.

#### 3.5.2. Thermal conversion of (Cul)\(_3\)P\(_4\)S\(_3\)

For the purpose of comparison the DTA diagram of (Cul)\(_3\)P\(_4\)S\(_3\) [6a] has been recorded. On heating the compound in a DTA
experiment between 25 and 800 °C an irreversible peak at 297 °C and a reversible endothermic peak at 374 °C were observed (Fig. 10). To get further insight into this thermal reaction 250 mg of the pure compound were sealed in an ampoule and annealed for 11 d at 371 °C. After slow cooling black shining crystals and yellow platelets were found by microscopic investigation.

An X-ray diffraction analysis of the black microcrystals gave cell data, which were identical with those of Cu₆PS₅I [20]. This compound is a member of the argyrodite family Cu₆PQ₅X (Q=S, Se; X=Cl, Br, I), which can be directly synthesized from the elements and the appropriate copper halide. The yellow crystals were determined as Cu₆PS₄, in which tetrathiophosphate ions coordinate at copper cations in a tetrahedral manner [21]. The ³¹P MAS NMR spectrum reveals two multiplets at δ=145.4 ppm (J_P,Cu=1212 Hz) and δ=118.2 ppm (J_P,Cu=1217 Hz) and one singlet at δ=84.1 ppm (Fig. S4). This pattern is in good agreement with that of (CuI)₃P₄S₄ [3a]. Unfortunately, a crystallographic evidence for this compound could not be found. On the other hand, the resonances of Cu₃PS₄ and of Cu₆PS₅I (δ=78.3 ppm, taken from a freshly prepared sample) may be covered by the signal at 84.1 ppm.

4. Conclusions

The formation and structural characterization of coordination polymers from P₄Se₃ and copper(I) halide building blocks from solution has been described. The results extend the poorly developed coordination chemistry of the P₄Se₃ cage and even differences are found compared to the structures of related CuX polymers containing P₄S₃ units as linkers. For the first time the thermal behavior of selected (CuX)₉[P₄Q₃]ₙ coordination polymers has been studied showing unexpected thermally induced transformations in the solid-state.

Supporting Information

Structure of 4 (Fig. S1), ³¹P MAS NMR spectrum of x-P₄Se₃ (Fig. S2); structure of 5 (Fig. S3), ³¹P MAS NMR spectrum of annealed (CuI)₃(P₄S₄) (Fig. S4) and crystallographic data of 5 (Tables S1 and S2).

Acknowledgment

This work was supported by the Deutsche Forschungsgemeinschaft (Wa 486/11-1 and We 4284/1-1). We gratefully acknowledge continuous support by Prof. Dr. M. Scheer. R.W. thanks Prof. R. Dovesi for fruitful discussions. We also thank Dr. M. Schlosser for recording the Raman spectra.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2011.05.011.

References