Cs$_4$P$_2$Se$_{10}$: A new compound discovered with the application of solid-state and high temperature NMR

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Abstract

The new compound Cs$_4$P$_2$Se$_{10}$ was serendipitously produced in high purity during a high-temperature synthesis done in a nuclear magnetic resonance (NMR) spectrometer. $^{31}$P magic angle spinning (MAS) NMR of the products of the synthesis revealed that the dominant phosphorus-containing product had a chemical shift of $-52.8$ ppm that could not be assigned to any known compound. Deep reddish brown well-formed plate-like crystals were isolated from the NMR reaction ampoule and the structure was solved with X-ray diffraction. Cs$_4$P$_2$Se$_{10}$ has the triclinic space group $P\overline{1}$ with $a = 7.3587(11)$ Å, $b = 7.4546(11)$ Å, $c = 10.1420(15)$ Å, $\alpha = 85.938(2)^\circ$, $\beta = 88.055(2)^\circ$, and $\gamma = 85.609(2)^\circ$ and contains the $[P_2Se_{10}]^{4-}$ anion. To our knowledge, this is the first compound containing this anion that is composed of two tetrahedral (PSe$_4$) units connected by a diselenide linkage. It was also possible to form a glass by quenching the melt in ice water, and Cs$_4$P$_2$Se$_{10}$ was recovered upon annealing. The static $^{31}$P NMR spectrum at $350\, ^\circ\mathrm{C}$ contained a single peak with a $-35$ ppm chemical shift and a $\sim 7$ ppm peak width. This study highlights the potential of solid-state and high-temperature NMR for aiding discovery of new compounds and for probing the species that exist at high temperature.

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Keywords: NMR; Solid state; High temperature; Chalcogenides; Metal selenophosphates; Phosphorus; $^{31}$P

1. Introduction

Chalcophosphates are compounds with oxidized phosphorus and at least one P–Q bond, where Q = S, Se, or Te. These compounds exhibit an impressively rich structural diversity because of the large number of stable $[P_xQ_y]^{z-}$ building blocks that can be stabilized and the variety of binding modes in which they can engage [1]. They are important in the areas of catalysis, ceramics, glasses, and molecular sieves [2–4]. Previously, solid-state nuclear magnetic resonance (NMR) has been useful in providing structural information about chalcophosphate materials [5–10]. Most notably, in selenophosphate materials there is a general correlation between the chemical shifts (CSs) of anions and the presence or absence of a P–P bond. Compounds containing a P–P bond resonate between 25 and 95 ppm whereas those that do not contain a P–P bond resonate between $-115$ and 5 ppm [11]. Additionally, the spectral intensity of a peak in an NMR spectrum is proportional to the number of nuclei that have the corresponding chemical environment [12]. Therefore, NMR spectroscopy is a useful tool to evaluate phase purity in cases where competing compounds have the same NMR-active nucleus.

There is little experimental data about the species that exist at high temperature although it has been proposed that different $[P_xQ_y]^{z-}$ anions exist in the melt in various equilibria [1]. Since there is $^{31}$P chemical shift discrimination between P–P and non-P–P bonded selenophosphate species in room temperature solids, in situ $^{31}$P NMR studies

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of high-temperature syntheses can potentially provide information about the identity of $^{31}$P-containing species that exist at high temperature. The known compound Cs$_4$P$_2$Se$_9$ [13] was initially chosen for a high-temperature NMR study because: (1) the synthesis temperature could be reached by our NMR probe; (2) the compound contained the interesting Se-bridged [P$_2$Se$_9^+$] anion; and (3) the compound melts congruently which suggests that spectra of subsequent high-temperature remelts should be similar to one another and that some correlation can be made between the remelt spectra and the spectrum of the solid compound.

In this paper, we present the new compound Cs$_4$P$_2$Se$_{10}$ which was discovered following high-temperature in situ NMR synthesis intended to produce Cs$_4$P$_2$Se$_9$. Room temperature solid-state $^{31}$P NMR spectra of the synthetic products clearly showed that Cs$_4$P$_2$Se$_9$ was not the dominant crystalline product and the structure of Cs$_4$P$_2$Se$_{10}$ was subsequently solved with X-ray diffraction of single crystals obtained from the NMR synthesis. Synthetic conditions were varied to ascertain the important factors leading to dominant Cs$_4$P$_2$Se$_9$ or Cs$_4$P$_2$Se$_{10}$ products and high-temperature $^{31}$P NMR spectra of synthetic melts were obtained and analyzed.

2. Experimental section

2.1. Sample preparation

Chemicals were used as obtained unless otherwise noted: phosphorous (MCB Reagents, Gibbstown, NJ, amorphous red), selenium shot (Tellurex Inc., Traverse City, MI, 99.999%), cesium metal, (Aldrich Chemical Co., Inc., St. Louis, MO). Phosphorous was freeze dried and Cs$_2$Se was prepared by a modified literature preparation [14,15]. P$_2$Se$_5$ was prepared by combining a stoichiometric amount of the elements in a pyrex ampoule, flame-sealing at a reduced pressure of 100 mTorr, then heating to 300 °C over 6 h, holding there for 6 h, and then quenching in air. Manipulations of all starting materials were performed under a nitrogen atmosphere in a dry box (Vacuum Atmospheres Inc.).

The synthesis that produced Cs$_4$P$_2$Se$_{10}$ as the dominant P-containing product was performed by combining Cs$_2$Se (0.186 g, 0.53 mmol), P$_2$Se$_5$ (0.124 g, 0.27 mmol), and Se (0.032 g, 0.41 mmol) in a fused silica ampoule. This ampoule was subsequently sealed under a reduced pressure of ~100 mTorr and allowed to react in a furnace. The sample was heated to 700 °C over 12 h, held at 700 °C for 12 h, and then cooled to room temperature over 12 h. The room temperature $^{31}$P NMR spectrum had a dominant isotropic peak at 22.0 ppm and integration of all the spectral peaks indicated that Cs$_4$P$_2$Se$_9$ was >90% of the reaction mixture.

![Figure 1](image-url) Fig. 1. Ambient temperature $^{31}$P MAS NMR spectra of the final products of: (A) a “Cs$_4$P$_2$Se$_{10}$” reaction stoichiometry indicating Cs$_4$P$_2$Se$_{10}$ as the dominant $^{31}$P-containing species at −22.0 ppm; (B) a “Cs$_4$P$_2$Se$_9$” reaction stoichiometry indicating Cs$_4$P$_2$Se$_9$ as the dominant $^{31}$P-containing species at −39.9 ppm, and (C) a “Cs$_4$P$_2$Se$_9$” reaction stoichiometry that produced Cs$_4$P$_2$Se$_9$ and Cs$_4$P$_2$Se$_{10}$ in a ~3:5 ratio. Panel D displays the static $^{31}$P NMR spectrum of a 350 °C melt of the products in C. The peak with a chemical shift of −22.0 ppm in panels B and C was not assigned and the peak at −99.8 ppm in panel B was not assigned. For spectra A–C, the spinning frequency was 14 kHz and spinning sidebands are grouped with $^{31}$P. The spinning frequency was 14 kHz and spinning sidebands are grouped with $^{31}$P.
### 31P-containing compounds (Fig. 1B). There were also peaks at \( \pm 22.0 \) and \( \pm 99.8 \) ppm that accounted for the remainder of the spectral intensity but were not assigned. The powder X-ray diffraction pattern contained only peaks that corresponded to Cs8P12Se9.

Vitrification of the mixture with “Cs8P12Se9” stoichiometry was accomplished by sealing a sample portion in a fused silica ampoule under a reduced pressure of \( \sim 100 \) mTorr, flame heating until molten, and then rapidly quenching in ice water. Complete vitrification was confirmed by powder X-ray diffraction.

### 2.2. Crystallographic studies

Intensity data for single crystals of Cs8P12Se10 were collected on a Bruker SMART platform CCD diffractometer using MoKx radiation operating at 40 kV and 40 mA (Table 1). A full sphere of data was collected and individual frames were acquired with a 10 s exposure time and a 0.3° rotation. The SMART software was used for data collection, and SAINt software was used for data extraction and reduction. An analytical absorption correction to the data was performed and direct methods were used to solve and refine the structures with the SHELXTL [16] software package.

Powder X-ray diffraction was performed with a Rigaku-Denki RW400F2 (Rotaflex) diffractometer equipped with a CuKx rotating anode operating at 45 kV and 100 mA with a 2°/min scan rate.

### 2.3. NMR spectroscopy

Room temperature 31P NMR spectra were collected on a 9.4 T spectrometer (Varian Infinity Plus) using a magic angle spinning (MAS) probe (Varian Chemagnetics) and served as an analytical tool to assess the phase purity of P-containing compounds. Samples were spun at 7–14 kHz in zirconia rotors of 4 mm outer diameter and a \( \sim 50 \) µL sample volume. Bloch decay spectra were taken with a 4.6 µs π/2 pulse calibrated using H3PO4 which also served as a chemical shift reference at 0 ppm. Four scans were summed with a 5000 s recycle delay. The longitudinal relaxation time of Cs8P12Se10 at ambient temperature was determined by fitting the signal intensity as a function of relaxation delay to an exponential buildup function [5].

High-temperature 31P NMR spectra were collected on a 9.4 T spectrometer (Varian Infinity Plus) using a static probe (Doty Scientific) with a 5.5 µs π/2 pulse calibrated at room temperature using H3PO4 which also served as a chemical shift reference at 0 ppm. Several hundred to several thousand scans were averaged with recycle delays ranging from 0.1 to 10 s. Sample temperatures ranging from 250 to 600 °C were reached at a rate of 10 °C/min and were allowed to equilibrate for \( \sim 5 \) min before data collection.

All NMR spectra were processed with line broadening and baseline correction.

### 2.4. Differential thermal analysis (DTA)

DTA was performed on a Shimadzu DTA-50 thermal analyzer. Sample portions (~30 mg) were sealed under a reduced pressure of \( \sim 80 \) mTorr in fused silica, and an equivalent mass of Al2O3 in a similarly prepared ampoule served as a reference. The sample was heated to 600 °C at a rate of 10 °C/min and then cooled at a rate of 10 °C/min back to room temperature. The residues after DTA were analyzed by powder X-ray diffraction.

### 3. Results and discussion

#### 3.1. Identification and structure description of Cs8P12Se10

The initial goal of synthesizing Cs8P12Se9 in a sealed tube in the NMR spectrometer was to obtain high-temperature 31P NMR spectra and to identify species present in the synthetic melt. After one of the syntheses was complete, the room temperature 31P NMR spectrum contained a dominant peak at \( \pm 52.8 \) ppm in addition to the \( \sim 39.9 \) ppm shift of Cs8P12Se9 [11]. The \( \pm 52.8 \) ppm peak could not be assigned to any known compound. Single deep reddish brown crystals were isolated, screened using X-ray diffraction, and the structure of Cs8P12Se10 was subsequently solved. A summary of the details of the refinement are displayed in Table 1. All of the peaks in the powder X-ray diffraction pattern of the sample prepared using the optimized synthetic method corresponded either to the calculated Cs8P12Se10 pattern or to elemental Se. The 31P NMR peak at \( \pm 52.8 \) ppm was therefore assigned to Cs8P12Se10.

Cs8P12Se10 has the molecular anion \([P2Se10]^{4-}\) which is composed of two PSe4 tetrahedra that are connected by two central selenium atoms thus forming a tetrathiolefinic fragment (Fig. 2A). The PSe4 tetrahedron is distorted with the Se–P–Se angles ranging from 92.14° to 116.67° [10]. The lengths of the P–Se bonds are typical and range from 2.159(2) to 2.312(2) Å. Tables 2 and 3 contain the atomic

| Table 1 Crystallographic data for Cs8P12Se10 |
|-----------------|-----------------|-----------------|-----------------|
| **Formula**     | **Cs8P12Se10**  | **d_\text{calc}** (g/cm³) | **4.153**       |
| FW              | 1383.18         | 23.113           |                 |
| Space group     | P-1             | 0.71073          |                 |
| \(a\) (Å)       | 7.5386(11)      | 298              |                 |
| \(b\) (Å)       | 7.4569(11)      | 56.6             |                 |
| \(c\) (Å)       | 10.1420(15)     | 0.0395           |                 |
| \(\alpha\) (deg)| 85.938(2)       | 0.0716           |                 |
| \(\beta\) (deg)| 88.055(2)       | 0.0687           |                 |
| \(\gamma\) (deg)| 85.609(2)     | 0.0789           |                 |
| \(V\) (Å³)     | 553.10(14)      |                  |                 |
| **Z**           | 1               |                  |                 |

\(a = \Sigma(F_d - |F_c|)/\Sigma F_d, \ R_w = (\Sigma |F_d - |F_c||^2/\Sigma |F_c|^2)^{1/2}.\)
and thermal parameters, and selected bond lengths and angles, respectively.

The Se-Se contacts range from 2.3125(13) to 2.4045(19) Å, a large range of bond lengths. This unusual behavior could be explained by the dihedral angles [17] around the bonds Se(4)–Se(5) and Se(5)–Se(5) of −83.78(1)° and 180.00(1)°, respectively. It is noteworthy that the Se(5)–Se(5) bond is shared by two planar structural moieties, namely Se(4)–Se(5)–Se(5)–Se(4) and Se(2)–Se(5)–Se(5)–Se(2) to give maximized lone pair repulsion in Se atoms and one of the longest Se–Se distances reported for a selenophosphate ligand. Compar-able or even longer Se–Se distances have been found in the disulfide bonds of 89.6° and 0°. In Cs₄P₂Se₁₀, only one anionic conformation is present with a dihedral angle about the central diselenide bond of 180° (vide supra). Additionally, there is positional disorder of the S atoms in Cs₄P₂S₁₀, and this is not evident for the Se atoms in Cs₄P₂Se₁₀.

3.2. Differential thermal analysis (DTA)

For the glass with “Cs₄P₂Se₁₆” stoichiometry, the first DTA heating cycle indicated an exothermic crystallization event centered at ~160 °C and broad endothermic melting features centered at 315 °C. The subsequent cooling cycle contained exothermic crystallization features that were centered near 275 °C. Subsequent DTA cycles were similar to the first cycle except that they did not contain the initial crystallization peak near 160 °C. Possible assignments of the DTA features are: (1) 160 °C exothermic feature, glass to crystal phase transition of Cs₄P₂Se₁₀ and Se; (2) 315 °C endothermic feature/275 °C exothermic features, melting/crystallization of Cs₄P₂Se₁₀ and Se.

The assignment of the 160 °C feature is supported by several arguments. First, the feature is exothermic and is only observed during the first heating cycle as would be expected for a transition from a metastable glass to a thermodynamically stable crystal. Second, annealing the glass near the putative glass to crystal transition temperature resulted in formation of a mixture of crystalline materials that were predominantly Cs₄P₂Se₁₀ and Se. ³¹P solid state NMR and powder X-ray diffraction were the methods used to analyze the annealed material. The glass to crystal transition temperature of the Cs₄P₂Se₁₆ glass is

![Diagram of Cs₄P₂Se₁₀](image)

Table 2: Fractional atomic coordinates and anisotropic thermal parameters for Cs₄P₂Se₁₀ with standard deviations in parentheses.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U₁₁</th>
<th>U₁₂</th>
<th>U₁₃</th>
<th>U₂₂</th>
<th>U₂₃</th>
<th>U₁₃</th>
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<td>0.0178(3)</td>
<td>0.0206(3)</td>
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<td>0.0010(2)</td>
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<td>Cs2</td>
<td>0.1943(1)</td>
<td>-0.1431(1)</td>
<td>1.3603(1)</td>
<td>0.0272(4)</td>
<td>0.0328(4)</td>
<td>0.0192(3)</td>
<td>0.0120(3)</td>
<td>-0.0038(3)</td>
<td>-0.0012(3)</td>
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<tr>
<td>Se1</td>
<td>0.2682(1)</td>
<td>0.7719(1)</td>
<td>0.9946(1)</td>
<td>0.0180(5)</td>
<td>0.0190(5)</td>
<td>0.0110(4)</td>
<td>-0.0009(4)</td>
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<td>0.0003(4)</td>
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<tr>
<td>Se2</td>
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<td>0.0372(1)</td>
<td>0.6737(1)</td>
<td>0.0256(5)</td>
<td>0.0139(5)</td>
<td>0.0173(5)</td>
<td>-0.0040(4)</td>
<td>0.0014(4)</td>
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<td>Se3</td>
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<td>0.6635(1)</td>
<td>0.7046(1)</td>
<td>0.0154(5)</td>
<td>0.0231(5)</td>
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<td>-0.0028(4)</td>
<td>-0.0000(4)</td>
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<tr>
<td>Se4</td>
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<td>0.5897(1)</td>
<td>0.7599(1)</td>
<td>0.0156(5)</td>
<td>0.0206(5)</td>
<td>0.0115(4)</td>
<td>0.0031(4)</td>
<td>-0.0017(4)</td>
<td>-0.0033(4)</td>
<td></td>
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<tr>
<td>Se5</td>
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<td>-0.6057(1)</td>
<td>1.4616(1)</td>
<td>0.0216(5)</td>
<td>0.0191(5)</td>
<td>0.0150(5)</td>
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<td>0.0041(4)</td>
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<tr>
<td>P</td>
<td>0.2533(3)</td>
<td>0.7841(3)</td>
<td>0.7789(2)</td>
<td>0.0122(11)</td>
<td>0.0126(11)</td>
<td>0.0112(11)</td>
<td>0.0005(8)</td>
<td>0.0007(9)</td>
<td>-0.0002(9)</td>
<td></td>
</tr>
</tbody>
</table>
lower than the corresponding temperatures that have been observed for glasses that form related metal selenophosphate compounds [22,24,25]. Materials with a reversible glass to crystal phase transition have potential use in data storage applications [22,26–30], and further characterization of the phase change properties of Cs₄P₂Se₁₀ may be of technological relevance.

3.3. Competition between Cs₄P₂Se₉ and Cs₄P₂Se₁₀

Analysis of the products of furnace reactions done with different stoichiometries showed that reaction stoichiometry had a significant effect on the Cs₄P₂Se₁₀:Cs₄P₂Se₉ final product ratio. Reduction by one equivalent of Se relative to Cs₄P₂Se₉, i.e. “Cs₄P₂Se₈” reaction stoichiometry, produced Cs₄P₂Se₉ as the dominant ³¹P-containing product with no Cs₄P₂Se₁₀. Fig. 1B. Syntheses with increased Se relative to Cs₄P₂Se₁₀, i.e. “Cs₄P₂Se₁₀+x” with 1 < x < 5 reaction stoichiometries, resulted in mixtures of Cs₄P₂Se₉ and Cs₄P₂Se₁₀. A representative spectrum of the products of the reaction where x = 2 is displayed in Fig. 1C. For the “Cs₄P₂Se₁₀” reaction stoichiometry, Cs₄P₂Se₁₀ was the only P-containing compound (Fig. 1A). The Fig. 1B,C spectra also had small peaks at ~22.0 and ~99.8 ppm that accounted for <10% of the total ³¹P signal intensity. To our knowledge, these shifts do not correspond to the measured ³¹P shifts of any known cesium selenophosphate compound. The related compound Cs₄P₂Se₁₀

<table>
<thead>
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<th>Table 3</th>
<th>Selected bond lengths (Å) and angles (deg) for Cs₄P₂Se₆ with standard uncertainties in parentheses</th>
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<tr>
<td>Cs₁–Se₂</td>
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<tr>
<td>Cs₁–Se₁</td>
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<tr>
<td>Cs₁–Se₄</td>
<td>3.6769(11)</td>
</tr>
<tr>
<td>Cs₁–Se₅</td>
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<tr>
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<td>2.215(2)</td>
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<tr>
<td>Se₁–P</td>
<td>2.218(2)</td>
</tr>
<tr>
<td>Se₁–P</td>
<td>2.221(2)</td>
</tr>
</tbody>
</table>

(i) – x, 1+y, 2+z; (ii) 1–x, 1+y, 2+z; (iii) x, 1+y, 2+z; (iv) x, 1+y, 2+z; (v) x, 1+y, 2+z; (vi) x, 1+y, 2+z; (vii) x, 1+y, 2+z; (viii) x, 1+y, 2+z; (ix) x, 1+y, 2+z.
was synthesized with the “Cs₅P₂S₁₀₅” reaction stoichiometry and although there was excess S, the as-yet unknown compound Cs₅P₂S₉ was not produced [21].

The literature preparation of Cs₅P₂Se₉ was done with the “Cs₅P₂Se₁₃₂₄” reaction stoichiometry that contained an excess of both Cs and Se relative to Cs₅P₂Se₉ [13]. Although an excess of elemental Se in the present study was found to favor the production of Cs₅P₂Se₁₀, this effect appeared to be counteracted in the literature preparation by an increased Se²⁻/Se ratio that was a result of the excess Cs₂Se. The Se²⁻/Se ratio correlates with the negative charge/Se atom ratio in the melt and increasing these ratios might reasonably favor selenophosphate anions with shorter Se chains [31].

Experiments were also done to understand the effect of the length of the heating/cooling profile on the Cs₅P₂Se₁₀/Cs₅P₂Se₉ crystalline product ratio. The 600 °C furnace syntheses were done with a “Cs₅P₂Se₁₂” reaction stoichiometry and the heating/cooling profile length was varied between 18 and 54 h. For all profile lengths, the final product distribution showed that Cs₅P₂Se₁₀ was more abundant than Cs₅P₂Se₉ but there was a general trend towards smaller Cs₅P₂Se₁₀/Cs₅P₂Se₉ ratios with longer heating/cooling profiles. This effect may provide some explanation for the discovery of Cs₅P₂Se₁₀ under the relatively short 6h heating/cooling profile of the initial NMR syntheses.

3.4. ³¹P room temperature and high-temperature NMR spectroscopy

A Herzfeld–Berger analysis [32] of a room temperature ³¹P NMR spectrum of Cs₅P₂Se₁₀ taken at 7 kHz spinning frequency indicated δ₁₁, δ₂₂, and δ₃₃ chemical shift anisotropy (CSA) principal values of 50, −41, and −167 ppm, respectively, [33] and similar values were obtained at 12 kHz spinning frequency. The δ₁₁−δ₃₃ CSA principal value difference of ~215 ppm was comparable to that of Cs₅P₂Se₉ (~180 ppm) and other compounds with [P₂Se₉]⁴⁻ anions containing (Se-Se)ₙ linkages [11]. The longitudinal relaxation time T₁ of Cs₅P₂Se₁₀ was 2100 ± 600 s and was comparable to the T₁ values of other metal selenophosphate compounds [5]. For both Cs₅P₂Se₉ and Cs₅P₂Se₁₀ peaks, splittings were observed corresponding to P-Se spin–spin coupling with coupling constant of ~270 Hz.

The high-temperature ³¹P NMR spectra of the melts of syntheses that produced Cs₅P₂Se₁₀ or Cs₅P₂Se₁₀/Cs₅P₂Se₉ mixtures contained one peak. Fig. 1D displays a representative spectrum of a 350 °C melt formed from Cs₅P₂Se₉/Cs₅P₂Se₁₀ products in a 3:5 ratio (Fig. 1C). Spectra obtained at a given temperature were independent of both the direction of the temperature ramp and the thermal history of the sample.

Although analysis of these spectra is not yet complete, some general spectral interpretation is presented. The ~35 ppm shift at 350 °C was consistent with room temperature chemical shifts of compounds with non-P–P bonded selenophosphate anions and suggested that the P-containing high-temperature species did not contain P–P bonds [11]. The high temperature shift was more positive than the crystalline Cs₅P₂Se₉ or Cs₅P₂Se₁₀ shifts observed at room temperature perhaps because of the loss of defined Cs⁺ ion coordination. An alternate interpretation is that the ³¹P-containing species at high-temperature were neither the [P₂Se₉]⁴⁻ nor the [P₂Se₁₀]⁴⁻ anions. At room temperature, the shifts of Cs₅P₂Se₉ and Cs₅P₂Se₁₀ differ by 13 ppm and it might be expected that if both [P₂Se₉]⁴⁻ and [P₂Se₁₀]⁴⁻ anions existed in high concentrations at high temperature, two peaks would be observed in the high-temperature spectrum. However, only one peak was observed in all of the melts. The presence of two peaks in the room temperature spectrum but only one peak in the high-temperature spectrum (Fig. 1C,D) shows that there is not a clear NMR correlation between speciation in the crystalline products and speciation in the high-temperature melt. It is possible that fast chemical exchange at high temperature prevented observation of discrete chemical shifts for the different species; however, such chemical exchange was not obvious. The final product spectra indicated an increase in the Cs₅P₂Se₁₀/Cs₅P₂Se₉ ratio with increasing Se but there was no clear trend of the ³¹P chemical shift in the high-temperature melts as a function of Se stoichiometry. For a single temperature, the overall chemical shift variation in the melts as a function of stoichiometry was less than 10 ppm. In the future, spectra could be obtained at lower temperatures and broader linewidths at these temperatures would provide evidence for chemical exchange.

The peak widths of the ³¹P NMR spectra at 350 °C were typically ~7 ppm or ~1 kHz which was less than the CSA magnitudes of Cs₅P₂Se₁₀ (~215 ppm, 35 kHz) and Cs₅P₂Se₉ (~180 ppm, 30 kHz) [11]. The relative sharpness of the line at high temperature indicated that most of the anisotropy had been averaged out by random tumbling. Therefore, the frequency of motion must be >30 kHz, or have a rotational correlation time of <5 μs/rad [34]. In the context of the Stokes–Einstein–Debye equation for a sphere tumbling in a liquid, this correlation time τ is proportional to the viscosity η and is inversely proportional to the sphere volume V:

\[ \tau = \frac{\eta}{k_B T V}, \]

where \(k_B\) is the Boltzmann constant and \(T\) is temperature in K units [35]. Using a known \(T\) and estimated \(\tau\), Eq. (1) could be used to calculate either \(\eta\) or \(V\) given a value for the complementary property. Although neither \(\eta\) nor \(V\) in selenophosphate melts is known with certainty, there is some information to assess these quantities: (1) flame-heated melts readily flow when the sample tube is inverted; and (2) the P-containing species are likely small molecular rather than large polymeric species because the final crystalline products contain discrete [P₂Se₉]⁻ or
[P₂Se₁₀]₄⁻ anions. In the next paragraph, (1) \( V \) is estimated from the dimensions of the [P₂Se₁₀]₄⁻ anion; (2) \( \eta \) is calculated using this value of \( V \); and (3) comparison is made between this calculated \( \eta \) and visual assessment of the melt viscosity. This approach tests whether a viscosity calculated with the assumption of small P-containing anions is close to the viscosity estimated from visual observation of the melts.

The radius of the [P₂Se₁₀]₄⁻ anion was estimated to be \( r \approx 8 \text{Å} \) from the longest Se–Se distance within a single [P₂Se₁₀]₄⁻ anion and the Se²⁻ ionic radius. Using \( V = 4\pi r^3/3 \), \( T = 1000 \text{K} \) (estimated temperature of flame-heated melt), and \( \tau = 5 \mu s \), Eq. (1) yielded \( \eta \approx 15 \text{Pa's} \) which is comparable to the viscosity of honey at room temperature[36] or glycerol at 0 °C [37]. This calculated \( \eta \) is likely an upper limit because \( \tau = 5 \mu s \) is an upper limit and because the P-containing anions might be smaller than [P₂Se₁₀]₄⁻, e.g. [PSe₄]³⁻ with corresponding smaller \( V \). Despite these caveats, there is general consistency between the calculated \( \eta \) and visual observation of the melt viscosity. The approach therefore yields qualitative support for the existence of small P-containing species [22]. For comparative purposes, the viscosity of liquid Se at 350 °C is 0.07 Pa’s [38].

4. Concluding remarks

The in situ NMR synthesis targeting Cs₄P₂Se₉ led to the discovery of Cs₄P₂Se₁₀ which can be formed with excess Se and a rapid heating/cooling profile. The Cs₄P₂Se₁₀ structure contained the novel discrete molecular anion [P₂Se₁₀]₄⁻. The chemically related compound Cs₄P₂S₁₀ is non-isomorphic, and it is possible that there are multiple polymorphs of both the thio- and seleno-compounds. The optimum Cs₄P₂Se₁₀ synthesis was performed in the high-temperature NMR probe with an excess of Se relative to Cs₄P₂Se₁₀ and with a ~6 h heating/cooling profile. The Cs₄P₂Se₁₀:Cs₄P₂Se₉ final product ratio from furnace syntheses was dependent on stoichiometry and on the length of the heating/cooling profile. Cs₄P₂Se₉ and Cs₄P₂Se₁₀ were favored with Se-starved and Se-rich stoichiometries and with long and short heating/cooling profiles, respectively.

Room temperature ³¹P NMR spectra provided a facile means of evaluating the relative amounts of the P-containing compounds made in furnace and NMR syntheses. In addition, some of these spectra presented in the paper have peaks that have not yet been assigned to known crystalline compounds. Careful screening of crystals from these reactions may therefore result in new compound identification.

The high-temperature static ³¹P NMR spectra of the synthetic melts contained one relatively narrow peak that may be the result of a rapidly tumbling selenophosphate anion that does not contain P–P bonds, i.e. a P²⁺ species. Future time-dependent studies of high-temperature spectra may provide information about reaction rates. As illustrated by the discovery of Cs₄P₂Se₁₀, future high-temperature NMR syntheses may also aid discovery of new compounds.

5. Supplemental data

A DTA plot and a ³¹P NMR spectrum with 7 kHz MAS frequency are included. Further details of the Cs₄P₂Se₁₀ crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: +49 7247 808 666; email: crysdata@fiz.karlsruhe.de) on quoting the depository number CSD 418434.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2007.08.002.

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Supplemental Data

Cs₄P₂Se₁₀: A New Compound Discovered with the Application of Solid State and High Temperature NMR

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Figure S1. Differential thermal analysis (DTA) of a mixture with “Cs₄P₂Se₁₀” stoichiometry that was quenched rapidly from the melt. The displayed plot is for the first heating/cooling cycle of this mixture. The interpretation of this plot relied on the powder X-ray diffraction pattern obtained following several heating/cooling cycles. This pattern indicated that Cs₄P₂Se₁₀ and elemental Se were the major crystalline products. In the displayed plot, the peak centered at ~160 °C is assigned to the glass to crystalline transition of Cs₄P₂Se₁₀ and Se, the peak centered at at ~315 °C is assigned to the melting of this mixture, and the peak centered at 277 °C is assigned to the subsequent recrystallization. The exothermic peak centered at ~160 °C was not observed for the second and subsequent heating/cooling cycles likely because the cooling rate was slow enough that crystalline rather than glassy material was formed. Thermal events due to pure Se were not observed perhaps because of insufficient Se or because of comelting/cocrystallization of Se with Cs₄P₂Se₁₀.
Figure S2. Room temperature $^{31}$P NMR spectrum of a reaction that resulted in a mixture of Cs$_4$P$_2$Se$_{10}$ and Cs$_4$P$_2$Se$_9$. The MAS frequency was 7 kHz. The intensities of peaks corresponding to Cs$_4$P$_2$Se$_{10}$ were used for the determination of CSA principal values of this compound.