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31P solid-state nuclear magnetic resonance (NMR) spectra of 12 metal-containing selenophosphates have been examined to distinguish between the \([P_2Se_6]^{4−}\), \([PSe_4]^{3−}\), \([P_2Se_7]^{4−}\), and \([P_2Se_9]^{4−}\) anions. There is a general correlation between the chemical shifts (CSs) of anions and the presence of a P–P bond. The \([P_2Se_6]^{4−}\) and \([P_2Se_7]^{4−}\) anions both contain a P–P bond and resonate between 25 and 95 ppm whereas the \([PSe_4]^{3−}\), \([P_2Se_7]^{4−}\), and \([P_2Se_9]^{4−}\) anions do not contain a P–P bond and resonate between −115 and −30 ppm. The chemical shift anisotropies (CSAs) of compounds containing \([PSe_4]^{3−}\) anions are less than 80 ppm, which is significantly smaller than the CSAs of any of the other anions (range: 135–275 ppm). The smaller CSAs of the \([PSe_4]^{3−}\) anion are likely due to the unique local tetrahedral symmetry of this anion. Spin–lattice relaxation times (\(T_1\)) have been determined for the solid compounds and vary between 20 and 3000 s. Unlike the CS, \(T_1\) does not appear to correlate with P–P bonding. 31P NMR is also shown to be a good method for impurity detection and identification in the solid compounds. The results of this study suggest that 31P NMR will be a useful tool for anion identification and quantitation in high-temperature melts.

Introduction

Chalcophosphates are compounds with oxidized phosphorus and at least one P–Q bond, where Q = S or Se. To date, no examples with Q = Te exist in the literature. These compounds exhibit an impressively rich structural diversity because of the large number of stable \([P,Q]^{m−}\) building blocks that can be stabilized and the variety of binding modes in which they can engage. Thio- and selenophosphates are still a relatively small group of compounds compared to the huge class of oxophosphates. The latter are important in the areas of catalysis, ceramics, glasses, and molecular sieves. Many thio- and selenophosphates however also exhibit promising and unique properties such as intercalation chemistry, ion-exchange, and magnetic and optical phenomena.

Among the first chalcophosphate compounds to be studied were the M_{12}P{eq}_{2}Q_{6} class (M = divalent metal) which features the ethane-like \([P_2Q_6]^{4−}\) ligand as well as M_{12}P{eq}_{4}Q_{5} and M_{12}P{eq}_{4}Q_{5} with \([PQ_4]^{3−}\) ligands (M = monovalent or trivalent metal). Various other examples of \([P,Q]^{m−}\)-containing materials also exist. Interesting properties and uses exhibited by some \([P,Q]^{m−}\)-containing compounds are the following: ferroelectric properties for use in memory devices (Sn_{2}P_{2}Se_{6}, CuInP_{2}S_{6}); nonlinear optical properties (Mn_{2}P_{2}S_{6}, \text{2e photoconductivity (In}_{1.33}P_{2}Se_{6}); cathode material in secondary lithium batteries. Although many chalcophosphate compounds have been synthesized using the traditional high temperature solid-state synthesis routes, more recent developments have employed solvothermal conditions and aqueous solutions. These approaches have led to the discovery of new compounds with unique properties.

Notes

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method in which the corresponding metals and chalcophosphate phases are combined stoichiometrically at high temperature, there was also a crucial role for poly(chalcophosphate) fluxes. In flux methodology, molten salts generate low-melting \([P_2 Q_6]^{4-}\) ligands which then react with metal ions. Because of the low temperature, thermodynamically stable phases can be avoided and metastable or kinetically stable phases can be made.

There has been one NMR study of flux composition by Eckert et al. In a Li–P–Se melt at \(T > 370^\circ C\), the high-temperature \(31P\) NMR spectrum provided evidence for the existence of the stable phases \(Li_2P_6Se_6\) and \(Li_2PSe_6\). NMR spectra of the solid products showed that \(Li_2P_6Se_6\) contains the \([P_6Se_6]^{3-}\) unit, while \(Li_2PSe_6\) contains \([PSe_6]^{3-}\) and Se\(^{-2}\) units. There have been additional \(31P\) NMR studies of ternary phases of crystalline solid products formed from direct combination of \(M + P + Se\) (\(M = Cu, Ag, Cd, Hg, Pb, Sn, Ca, and In\)), and it was reported that the \(M–P–Se\) system has much less structural anion variety compared to the ternary sulfide systems. In these direct combination melts, high-temperature NMR data were consistent with the presence of only two anions, \([P_2Se_6]^{4-}\) and \([PSe_6]^{3-}\). Eckert et al. have also studied pure \(P–S\) and \(P–Se\) glasses with high-temperature \(31P\) and \(77Se\) NMR.

Given the plethora of new chalcophosphate phases discovered in the past decade, and the variety of novel structural types, bonding modes, and chalcophosphate anions, it would be particularly desirable to study the NMR properties of these types, bonding modes, and chalcophosphate anions, it would yield considerable new insights in understanding and characterizing chalcophosphate compounds. Here we present the first solid state \(31P\) NMR investigations of several recently discovered phases containing known anions such as \([P_2Se_6]^{4-}\) (\(K_2CdP_2Se_6\)), and \(Rb_2CdPSe_6\) \(Rb_2PSe_4\) (KpbPSe\(_4\), RbPbPSe\(_4\), \(Kp(PSe_4)\)) which contain poly(chalcophosphate) ligands. In the more recent investigations, we have used the high-temperature NMR method in which the corresponding metals and chalcophosphate phases are combined stoichiometrically at high temperature.

**Experimental Section**

**Synthesis.** \(P_2Se_6\) was prepared by reacting stoichiometric amounts of the elements in an evacuated Pyrex tube at 300 °C for 1 day, followed by a cool-down to 50 °C over 2 h. Purity was assessed by X-ray powder diffraction analysis.

\(Ag_2P_2Se_6\), \(Pb_2P_2Se_6\), and \(Cu_2PSe_4\) were prepared by reacting stoichiometric amounts of the metal (\(Ag, Pb, Cu\)) with \(P_2Se_6\) and elemental Se. The reaction took place in an evacuated quartz tube at 600 °C for 1 day followed by a cool-down to 50 °C over 12 h.

KpbPSe\(_4\) and RbPbPSe\(_4\) were prepared from stoichiometric amounts of the alkali selenide \(K_2Se\) or \(Rb_2Se\), Pb metal, \(P_2Se_6\), and elemental Se. The reactants were heated in an evacuated quartz tube at 600 °C for 1 day and cooled to 50 °C over 12 h.

\(K_2CuP_2Se_10\) was prepared from 0.3 mmol of Cu, 0.9 mmol of P, 0.3 mmol of \(K_2Se\), and 2.4 mmol of Se. The reactants were heated at 570 °C for 2 days followed by cooling at 21 °C/h. The residual flux was removed with \(N,N\)-dimethylformamide. After the remaining solid was washed with diethyl ether, dark irregularly shaped crystals were obtained which were stable in air and water.

\(Kp(PSe_4)\) was prepared as orange crystals from 0.15 mmol of Pb, 0.225 mmol of \(P_2Se_6\), 0.6 mmol of \(K_2Se\), and 1.5 mmol of Se. The reactants were heated at 500 °C for 3 days followed by cooling at 10 °C/h.

\(RbTeTiPSe_5\) was synthesized from 0.45 mmol of \(P_2Se_6\), 1.20 mmol of \(Cs_2Se\), and 3.0 mmol of Se. The reactants were sealed under vacuum in a Pyrex tube and heated to 490 °C for 4 days followed by cooling to 150 °C at 10 °C/h. The product crystals were red and were sensitive to air and water.

\(RbTeTi_PSe_5\) was synthesized from a mixture of 0.2 mmol of Ti, 0.4 mmol of \(P_2Se_6\), 0.4 mmol of \(Rb_2Se\), and 2 mmol of Se. The reactants were sealed under vacuum in a Pyrex tube and heated according to the same heating profile as \(Cs_2P_2Se_6\). The residual flux was removed with \(N,N\)-dimethylformamide. After the remaining solid was washed with ether, black crystals were formed, which were stable in air and water. The original goal of this synthesis was to make \(RbTePSe_5\), but powder X-ray diffraction on the whole sample and elemental analysis on selected crystals showed that \(Rb_2Te_3P_2Se_5\) was the only crystalline product.

**Physical Measurements.** (a) Elemental Analysis. The elemental compositions of selected crystals of \(Rb_2Te_3P_2Se_5\) and \(K_2CuP_2PSe_4\) were confirmed by semi-quantitative elemental analysis using energy dispersive spectroscopy (EDS) on a JEOL 6400 scanning electron microscope equipped with a Tracor Noran detector.

(b) Powder-X-ray Diffraction. Powder X-ray diffraction (PXRD) analyses were performed using an INEL CPS 120 powder diffractometer with graphite-monochromatized Cu K\(\alpha\) radiation. To assess sample purity, we visually compared the experimental powder diffraction pattern to a pattern calculated from a single-
crystal structure. Visual inspection using a light microscope was also performed to assess the crystallinity of the sample.

(c) NMR. The room-temperature solid-state NMR measurements of these compounds were taken on a 9.4 T NMR spectrometer (Varian Infinity Plus) using a double resonance magic angle spinning (MAS) probe. Samples were spun at frequencies between 7 and 15 kHz using zirconia rotors of 4 mm outer diameter and 50 μL sample volume. Bloch decay spectra were taken with the excitation/detection channel tuned to 31P at 161.39 MHz, a 4.5 μs 90° pulse (calibrated to ±0.1 μs with 85% H3PO4), and a relaxation delay between 5 and 15000 s. Each spectrum was processed with ≤100 Hz line broadening and up to a 10th order polynomial baseline correction. The spectra were referenced using 85% H3PO4 at 0 ppm. If the relaxation delay prior to pulsing is comparable to or longer than 31P longitudinal relaxation time, a high signal-to-noise spectrum can be obtained with one scan on ~100 mg of material.

Best-fit chemical shift anisotropy (CSA) principal values were calculated with a Herzfeld—Berger computer program whose inputs were the 31P NMR and spinning frequencies and the experimental peak intensities of the isotropic resonance and the spinning sidebands. For compounds containing the [P2Se6]4−, [P2Se10]5−, or [P2Se8]4− anion, there were typically four spinning sidebands in a spectrum, and for compounds containing the [P2Se6]4− or [PSe4]3− anion, there were typically two spinning sidebands in a spectrum.

To quantitatively evaluate uncertainties in CSA principal values, spectra for each compound were typically taken at two or more spinning frequencies and the CSA principal value analysis was done at each frequency. Uncertainty was also evaluated by doing analyses with spectral intensities changed by amounts comparable to the spectral noise. Comparison of the principal values derived from the different analyses showed that the greatest variation of a best-fit principal value was ~20 ppm.

We also calculated an overall CSA value by taking the difference between the two extreme CSA principal values. This overall CSA gives the approximate range of 31P CSs which would be observed in the static powder pattern, i.e., for consideration of all possible orientations of the selenophosphate unit cell relative to the magnetic field direction. The CSA is also a measure of the shielding field range for the 31P. When analyses were compared between spectra taken at different spinning frequencies or between spectra whose peak intensities were changed by amounts comparable to the spectral noise, the greatest variation of CSA was ~20 ppm.

Each compound 31P longitudinal relaxation time (T1) was determined by fitting the following equation:

\[ S(r) = S_0 (1 - e^{-r/T_1}) \]  

Here r is the relaxation delay time before pulsing, S(r) is the integrated signal intensity (sum of isotropic peak and spinning sidebands), and S0 is a fitting parameter representing the signal intensity at infinite r. Before each r, the magnetization was nulled with a 90° pulse and subsequent rapid transverse dephasing. For each compound, there were typically at least two data sets and the experimental T1 uncertainty was calculated from the variation in best-fit T1 values among the different data sets. This variation was generally larger than the fitting uncertainty in the T1 value of a single data set.

Results and Discussion

Figure 1 summarizes the structural schemes for the different selenophosphate anions examined in this paper. 31P solid-state NMR spectra are presented in Figure 2, and the measured chemical shifts (CSs), CSA principal values, CSAs, and T1 values are presented in Table 1. Figure 3 displays an experimental Rb2CdP2Se6 spectrum as well as a simulated stick spectrum calculated from its best-fit CSA principal values. The agreement between intensities in the experimental and simulated spectra is a qualitative illustration of the accuracy of the principal value analysis. Figure 4 displays examples of experimental and best-fit buildup curves which were used to derive T1 values. In general, there was good agreement between the experimental and fitted curves. Finally, it is noted that, in some spectra, there were resolved spectral splittings due to scalar (spin−spin) couplings which are isotropic and not averaged by MAS. For K2Cu2P4−2Se10, Ag2PSe6, K2PbPSe6, K2Pb(PSe4)2, and Cs2P2−Se9, the splittings were due to 31P−7Se scalar couplings while, for Ag2PSe6, the splittings were due to 31P−31P scalar couplings.

Figure 2. $^{31}$P solid-state MAS NMR spectra of selenophosphate compounds. Each spectrum represents a single Bloch decay acquired after a delay time much longer than the $^{31}$P $T_1$ of the compound. Each spectrum was processed with $\leq 100$ Hz line broadening and up to a 10th order polynomial baseline correction. Chemical shift referencing was done using 85% H$_3$PO$_4$ at 0 ppm. The isotropic peaks are indicated by asterisks (*), and spinning sidebands are marked as “ssb”. (a) Pb$_2$P$_2$Se$_6$. The isotropic peak is at 29.1 ppm, the spinning frequency is 12 kHz, and the delay time is 10000 s. (b) Rb$_2$CdP$_2$Se$_6$. The isotropic peak is at 62.0 ppm, the spinning frequency is 12 kHz, and the delay time is 300 s. (c) K$_2$CdP$_2$Se$_6$. The isotropic peak is at 63.3 ppm, the spinning frequency is 12 kHz, and the delay time is 300 s. (d) Ag$_2$P$_2$Se$_6$. The spinning frequency is 12 kHz, and the delay time is 15000 s. There are isotropic peaks at 77.6 and 91.8 ppm which represent the averages of doublets whose splitting is due to P–P $J$-coupling. For Ag$_2$P$_2$Se$_6$, the two P atoms in the [P$_2$Se$_6$]$^{4-}$ anion are crystallographically and magnetically inequivalent and this is reflected in the observation of two CSs. The peak at $-51.9$ ppm corresponds to Ag$_7$PSe$_6$, which cocrystallizes as an impurity with Ag$_2$P$_2$Se$_6$. (e) K$_2$Cu$_2$P$_4$Se$_{10}$. The isotropic peak is at $-83.3$ ppm, the spinning frequency is 12 kHz, and the delay time is 10000 s. (f) Cu$_3$PSe$_4$. The isotropic peak is at $-83.3$ ppm, the spinning frequency is 12 kHz, and the delay time is 10000 s. (g) RbPbPSe$_4$. The isotropic peak is at $-74.9$ ppm, the spinning frequency is 12 kHz, and the delay time is 15000 s. Some impurity phases can also be seen in the NMR spectrum. (h) KPbPSe$_4$. The isotropic peak is at $-74.3$ ppm, the spinning frequency is 12 kHz, and the delay time is 5500 s. Some impurity phases can also be seen in the NMR spectrum. (i) K$_4$Pb(PSe$_4$)$_2$. The isotropic peak is at $-113.2$ ppm, the spinning frequency is 12 kHz, and the pulse delay is 6000 s. (j) Cs$_4$P$_2$Se$_9$. The isotropic peak is at $-39.9$ ppm, the spinning frequency is 9 kHz, and the pulse delay is 4200 s. (k) Rb$_4$Ti$_2$P$_6$Se$_{25}$. The isotropic peaks are at $-34.6$, $-47.6$, and $-67.7$ ppm, the spinning frequency is 12 kHz, and the delay time is 6000 s. The first two peaks correspond to the two [P$_2$Se$_6$]$^{4-}$ units, and the last peak corresponds to the [P$_2$Se$_7$]$^{4-}$ unit.
similarities help to explain the observation that the CS of K$_2$Cu$_2$P$_4$Se$_{10}$, the resolved P atom resolved P atom the CSAs found for compounds with [P$_2$Se$_6$]$_4^-$ anions. Cu$_3$PSe$_4$, has a wurtzite-related normal tetrahedral structure, but the $^{31}$P NMR spectrum has only a single peak. Two crystallographically inequivalent P atoms in its crystal unit cell and a single CS. The CSA of K$_2$Cu$_2$P$_4$Se$_{10}$ (138 ppm) is also close to those found for compounds containing [P$_2$Se$_6$]$_4^-$ anions. As a ligand, it possesses eight terminal Se sites available for coordination (cf. Figure 1e). K$_2$Cu$_2$P$_4$Se$_{10}$ has the form Ag$_7$(PSe$_4$)$_3$. The CS of the [PSe$_4$]$_3^-$ anion was discovered in K$_2$Cu$_2$P$_4$Se$_{10}$ and it essentially derives from the fusion of two [PSe$_4$]$_3^-$ units followed by the elimination of two Se$^{2-}$ anions. As a ligand, it possesses eight terminal Se sites available for coordination (cf. Figure 1e). K$_2$Cu$_2$P$_4$Se$_{10}$ has the form Ag$_7$(PSe$_4$)$_3$, and its CS is distinct from those found for compounds containing [P$_2$Se$_6$]$_4^-$ units.

Table 1. $^{31}$P Chemical Shift (CS), Chemical Shift Anisotropy (CSA), and $T_1$ Measurements for Metal Selenophosphates

<table>
<thead>
<tr>
<th>selenophosphate</th>
<th>anion type</th>
<th>CS (ppm)$^a$</th>
<th>$\delta_{11}$</th>
<th>$\delta_{22}$</th>
<th>$\delta_{33}$</th>
<th>CSA (ppm)$^c$</th>
<th>$T_1$ (s)$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbP$_2$Se$_6$</td>
<td>P$_2$Se$_6^-$</td>
<td>29.1</td>
<td>97</td>
<td>49</td>
<td>−59</td>
<td>156</td>
<td>1700 (100)</td>
</tr>
<tr>
<td>Rb$_2$Cd$_2$P$_4$Se$_6$</td>
<td>P$_2$Se$_6^-$</td>
<td>62.0</td>
<td>161</td>
<td>93</td>
<td>−69</td>
<td>230</td>
<td>80 (5)</td>
</tr>
<tr>
<td>K$_2$CdP$_2$Se$_6$</td>
<td>P$_2$Se$_6^-$</td>
<td>63.3</td>
<td>155</td>
<td>101</td>
<td>−66</td>
<td>221</td>
<td>23 (2)</td>
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<tr>
<td>Ag$_2$P$_2$Se$_6$</td>
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<td>152</td>
<td>73</td>
<td>7</td>
<td>145</td>
<td>3000 (200)</td>
</tr>
<tr>
<td>K$_2$Cu$_2$P$<em>4$Se$</em>{10}$</td>
<td>P$_2$Se$_4^-$</td>
<td>91.8</td>
<td>166</td>
<td>106</td>
<td>3</td>
<td>164</td>
<td></td>
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<tr>
<td>Ag$_2$P$_4$Se$_6$</td>
<td>P$_2$Se$_4^-$</td>
<td>55.7</td>
<td>126</td>
<td>53</td>
<td>−12</td>
<td>138</td>
<td>1050 (100)</td>
</tr>
<tr>
<td>Cu$_3$PSe$_4$</td>
<td>P$_2$Se$_4^-$</td>
<td>−51.9</td>
<td>nd$^b$</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>1500 (50)</td>
</tr>
<tr>
<td>RbPbP$_2$Se$_4$</td>
<td>P$_2$Se$_4^-$</td>
<td>−83.3</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>300 (10)</td>
</tr>
<tr>
<td>RbPbP$_2$Se$_4$</td>
<td>P$_2$Se$_4^-$</td>
<td>−74.9</td>
<td>−50</td>
<td>−61</td>
<td>−114</td>
<td>64</td>
<td>970 (75)</td>
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<tr>
<td>K$_2$Pb$_2$P$_6$Se$_2$</td>
<td>P$_2$Se$_4^-$</td>
<td>−74.3</td>
<td>−53</td>
<td>−54</td>
<td>−118</td>
<td>65</td>
<td>1080 (100)</td>
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<td>P$_2$Se$_4^-$</td>
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<td>−113</td>
<td>−147</td>
<td>67</td>
<td>1250 (100)</td>
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<td>Cs$_4$P$_2$Se$_9$</td>
<td>P$_2$Se$_4^-$</td>
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<td>60</td>
<td>−59</td>
<td>−121</td>
<td>181</td>
<td>800 (200)</td>
</tr>
<tr>
<td>Rb$_4$Ti$_2$P$<em>6$Se$</em>{25}$</td>
<td>P$_2$Se$_4^-$</td>
<td>−34.6</td>
<td>100</td>
<td>−30</td>
<td>−174</td>
<td>274</td>
<td>540 (50)</td>
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<tr>
<td>P$_2$Se$_4^-$</td>
<td>P$_2$Se$_4^-$</td>
<td>−47.6</td>
<td>52</td>
<td>−66</td>
<td>−129</td>
<td>181</td>
<td>630 (40)</td>
</tr>
<tr>
<td>Cs$_4$P$_2$Se$_9$</td>
<td>P$_2$Se$_4^-$</td>
<td>−67.7</td>
<td>11</td>
<td>−65</td>
<td>−149</td>
<td>160</td>
<td>690 (50)</td>
</tr>
</tbody>
</table>

$^a$ Uncertainties are $\sim \pm 0.5$ ppm. $^b$ Maximum uncertainties are $\sim \pm 20$ ppm. $^c$ CSA = $\delta_{11} - \delta_{33}$, i.e., the approximate overall width of the static CS powder pattern. Maximum CSA uncertainties are $\sim \pm 20$ ppm. $^d$ Uncertainties are given in parentheses. $^e$ CS assignments were based on ref 23b. $^f$ nd = not determined because of negligible spinning sideband intensity.

which is assigned to a 20% Ag$_2$P$_4$Se$_6$ impurity.$^{22}$ Ag$_2$P$_4$Se$_6$ has the form Ag$_7$(PSe$_4^-$)$_3$(Se$_2^{2-})_2$, and its CS is distinct from those found for compounds containing [P$_2$Se$_6$]$_4^-$ units.

[PCSe$_4$]$_3^-$ anion. The unique [PCSe$_4$]$_3^-$ anion was discovered in K$_2$Cu$_2$P$_4$Se$_{10}$ and it essentially derives from the fusion of two [PCSe$_4$]$_3^-$ units followed by the elimination of two Se$^{2-}$ anions. As a ligand, it possesses eight terminal Se sites available for coordination (cf. Figure 1e). K$_2$Cu$_2$P$_4$Se$_{10}$ has two crystallographically inequivalent P atoms in its crystal structure, but the $^{31}$P NMR spectrum has only a single peak at 55.7 ppm. To understand this apparent discrepancy, the environments around the two P atoms were visually examined in the crystal structure. It was observed that the local interatomic bond distances and angles were substantially the same for the two atoms, which results in chemically and magnetically equivalent P atoms. The [PCSe$_4$]$_3^-$ anion is similar to the [PCSe$_4$]$_4^-$ anion in that it contains P–P bonds and tetravalent P. These structural similarities help to explain the observation that the CS of K$_2$Cu$_2$P$_4$Se$_{10}$ (55.7 ppm) is within the CS range of [PCSe$_4$]$_4^-$ anions. The CSA of K$_2$Cu$_2$P$_4$Se$_{10}$ (138 ppm) is also close to the CSAs found for compounds with [PCSe$_4$]$_4^-$ anions. In K$_2$Cu$_2$P$_4$Se$_{10}$ the resolved P–Se scalar coupling is 694 Hz.

[PCSe$_4$]$_3^-$ anion. The $^{31}$P CSs of selenophosphates containing [PCSe$_4$]$_3^-$ units occur upfield in the −115 to −50 ppm range. Their CSAs are <80 ppm, which is significantly smaller than those observed for [PCSe$_4$]$_4^-$ anions, and likely reflects the high tetrahedral symmetry of [PCSe$_4$]$_3^-$ units. One of the compounds, Cu$_3$PSe$_4$, has a wurtzite-related normal tetrahedral structure with crystallographically equivalent P atoms in its unit cell and a single CS.$^{11}$ Two of the compounds, K$_2$PbP$_2$Se$_4$ and RbPbP$_2$Se$_4$, have the same orthorhombic crystal structure with crystallographically equivalent P atoms in their unit cells. This leads to a single CS for each compound which differ by only 0.6 ppm. Both K$_2$PbP$_2$Se$_4$ and RbPbP$_2$Se$_4$ exhibit a resolved P–Se scalar coupling of 435 Hz. K$_2$PbP$_2$Se$_4$ has a structure consisting of two [PCSe$_4$]$_3^-$ ligands which bridge adjacent Pb atoms. All P atoms are crystallographically equivalent, leading to a single CS and a resolved P–Se scalar coupling of 432 Hz. The P–Se scalar coupling of Ag$_7$P$_2$Se$_6$ is 490 Hz.

[PCSe$_4$]$_3^-$ anion. Two compounds, Cs$_4$P$_2$Se$_9$ and Rb$_4$Ti$_2$P$_6$Se$_{25}$, contain the [PCSe$_4$]$_3^-$ anion. This ligand is structurally composed of two Se-sharing [PCSe$_4$]$_3^-$ subunits. Thus, it is reasonable that the CSs observed for this ligand (−50 to −35 ppm) are close to the CS range observed for compounds containing single [PCSe$_4$]$_3^-$ anions. The CSAs of [PCSe$_4$]$_3^-$ anions are comparable to those observed for [PCSe$_4$]$_4^-$ anions and are significantly larger than those observed for [PCSe$_4$]$_4^-$ anions. The latter finding likely reflects the lower symmetry of [PCSe$_4$]$_4^-$ units relative to tetrahedral [PCSe$_4$]$_3^-$ units. In Cs$_4$P$_2$Se$_9$, the resolved P–Se scalar coupling is 530 Hz.

[PCSe$_4$]$_3^-$ anion. Rb$_4$Ti$_2$P$_6$Se$_{25}$ also contains the [PCSe$_4$]$_3^-$ ligand, which is structurally composed of two [PCSe$_4$]$_3^-$ sharing a common Se. The CS of the [PCSe$_4$]$_3^-$ anion is −67.7 ppm and is within the CS range of [PCSe$_4$]$_4^-$ anions. The CSA of the [PCSe$_4$]$_4^-$ anion is comparable to those of [PCSe$_4$]$_4^-$ and...
As shown in the figure, there is a correlation between the 5a displays all of the measured CSs on a single ppm scale. There is a correlation between the presence of a P—P bond and a downfield CS. The [P2Se4]4− and [P4Se10]4− compounds have positive CSs while the [PSe4]3−, [PSe6]3−, and [PSe9]4− compounds have negative CSs. It may also be that the [P3Se7]4− CSs are somewhat downfield of the [PSe4]3− and [PSe7]4− CSs.

For a given anion type, isostructural compounds which only differed in alkali metal ion had 31P CSs within 2 ppm of each other and CSAs within 10 ppm of each other (e.g., Rb2CdP2Se6/K2CdP2Se6 and RbPbPSe4/KPbPSe4). Thus, the CSs and CSAs appear to have only minor dependence on substitution of a metal ion within the same group. By contrast, K,Pb(PSe4)2 has the same elements and anion type ([PSe4]3−) as KPbPSe4 but their CSs differ by 39 ppm. All of these observations are probably reasonable because the electronic structure around 31P and thus the corresponding CSs and CSAs should largely depend on local molecular structure.

Figure 5b displays all of the measured CSAs on a single ppm scale. The [PSe4]3− CSAs are significantly smaller than those of other ligands, presumably because of the unique tetrahedral symmetry of the [PSe4]3− anion. For compounds containing [PSe4]3− anions, the smallest CSAs were found for Pb2P2Se6 and Ag2P2Se6. This may be due to the presence of one cation type in these solids as compared to two cation types in Rb2CdP2Se6 and K2CdP2Se6.

The T1 values for compounds with [P2Se7]4− and [P2Se9]4− units were clustered between 600 and 800 s, while those for compounds with [PSe4]3− units ranged between 20 and 3000 s and those for compounds with [PSe6]3− units ranged between 300 and 1500 s. Similar to the CS and CSA, isostructural pairs such as Rb2CdP2Se6/K2CdP2Se6 and Rb-PbPSe4/KPbPSe4 exhibit T1 values which are close to one another. However, unlike the CS, T1 does not appear to correlate with P—P bonding. There may be a variety of interactions which contribute to 31P relaxation, including homo- and heteronuclear dipolar couplings. The experimental correlation between 1/T1 and the square of the dipolar coupling is at most qualitative, not quantitative, so there are likely other factors which affect relaxation. As one example, although none of the compounds are paramagnetic per se, there could be small quantities of trapped paramagnetic impurities or defects which contribute to relaxation. To test this hypothesis, we resynthesized the fast-relaxing Rb2CdP2Se6 with the idea that paramagnetic reactant concentrations could vary between reactant batches and, thus, produce different T1 values in the final product. The T1 value for the resynthesized Rb2CdP2Se6 is 70 s, which is close to but not the same as its value in the first synthesis. In future studies, we will attempt to detect paramagnetic impurities using electron spin resonance.

Interestingly, repeated attempts to synthesize pure Ag_4P_2Se_6 always yielded \(~20\%\) Ag_7PSe_6 impurity. This was the case even when the reaction was carried out using the Ag_4P_2Se_6 stoichiometry. These results suggest that an equilibrium exists between [P_2Se_6]^4− and [PSe_4]^3− under the 600 °C synthesis melt conditions and that the equilibrium constant is close to 1. Future high-temperature NMR studies will determine the conditions which favor formation of Ag_4P_2Se_6 or Ag_7PSe_6 and will follow up on work by Eckert et al., which showed the presence of [P_2Se_6]^4− and [PSe_4]^3− units in M−P−Se melts (M = Li, Ag).11

Our data show other examples of the utility of NMR in analyzing the products of a selenophosphate synthesis. For example, for Figure 2k, the intention of the synthesis was to produce RbTiPSe_6 using a procedure and stoichiometry analogous to that employed for KTiPSe_5.20 The NMR spectrum revealed that a pure product was formed, but it was Rb_2Ti_2P_6Se_35 rather than the intended compound. In the RbPhPSe_6 synthesis, impurities are clearly present in the spectrum (cf. Figure 2g) but their chemical identification has not yet been done. Finally, for spectra from some failed syntheses, broad signals were observed which indicate glass rather than crystalline product formation.

In summary, the main result of this study is that the 31P CS is correlated with the presence of P−P bonding in selenophosphate compounds. There are nonoverlapping CS ranges of compounds with P−P bonds (20−100 ppm) and compounds without P−P bonds (<120 to ~30 ppm). Thus, in future high-temperature studies of metal−selenophosphate melts, the 31P CS should be useful in ligand identification. It may also be possible to use the CS to distinguish between similar ions in a melt, such as [P_2Se_7]^4− and [P_2Se_9]^4− anions. CSA measurements demonstrated that the CSs of compounds containing [PSe_4]^3− units were significantly smaller than those of compounds containing any other ion. These other compounds include those with complex ions such as [P_2Se_6]^4− and [P_2Se_9]^4− which are bridged forms of dimeric [PSe_4]^3−. These CSA observations are most reasonably explained by the tetrahedral symmetry which is unique to [PSe_4]^3− units. The T_1 values of the selenophosphate compounds varied between 20 and 3000 s, but there was no clear correlation with P−P bonding. Finally, 31P NMR was shown to be a useful tool for impurity detection and identification in selenophosphate syntheses.

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