Synthesis, Vibrational Spectra and Normal Coordinate Analysis of Cesium-Hexathiohypodiphosphate Cs₄P₂S₆

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The title compound has been prepared by elemental synthesis at high temperatures and also by reaction of Na₄P₂S₆·6H₂O with CsCl in aqueous solution. Both reaction products have closely related vibrational spectra which are assigned on the basis of a P₂S₆⁴⁻ anion with perturbed D₃h symmetry. A normal coordinate analysis has been performed using a force field with 4 initial force constants. The refined force field, potential energy distribution (PED), mean amplitudes of vibration and Coriolis coupling constants are given.

Keywords: Cesiumhexathiohypodiphosphate, Cs₄P₂S₆, Vibrational Spectra, Normal Coordinate Analysis

Introduction

Since their rediscovery in the mid-sixties [1–3] metal thiophosphodiphosphates, especially those with transition metal cations, have shown great prospect for future development [3–13] because of their interesting chemical and physical properties. Most notable are their chemical inertness and their ability to intercalate lithium [8] and metalloccenes [10, 14, 15]. Some of them are also noted for their nonlinear electrical and optical properties.

Common to all thiophosphodiphosphates is the spectroscopically relevant P₂S₆⁴⁻ complex anion in which two terminal PS₂-groups are joined through a P–P-bond. In recent publications contradictory assignments of the vibrational frequencies of thiophosphodiphosphates have been put forward [1, 13, 15–18]. A probable cause for these discrepancies could be seen in the existence of other thiophosphorous compounds which are formed in subsequent solid state reactions during annealing, laser irradiation or even self storage [19].

The extent of H₂O–P₂S₆⁴⁻ interactions like protonation and hydrolysis in crystal water containing salts and aqueous solutions is not clear. We have obtained Cs₄P₂S₆ in two ways: (i) by synthesis from the elements at high temperatures, (ii) by reaction of Na₄P₂S₆·6H₂O with CsCl in aqueous solution. The vibrational spectra of both products are nearly identical.

Experimental

The high temperature synthesis of Cs₄P₂S₆ was carried out in quartz glass crucibles in evacuated ampoules made of the same material, using a stoichiometrical mixture of the high purity elements. Cesium and the P/S mixture were kept in separate parts of the ampoule so that the formation reaction occurred in the gas phase during slow warm up (8–10 K/h). The cell was then kept at 1020 K for 12 hours and afterwards left to cool in the switched off furnace. Light yellow Cs₄P₂S₆ of spectroscopic purity was formed at the outer quartz wall.

From a saturated aqueous solution of Na₄P₂S₆·6H₂O (synthesized according to Falius [1]), twice recrystallized from water) and CsCl (10% excess CsCl relative to Na) at 310 K, large colorless platelets of Cs₄P₂S₆ are precipitated upon cooling to
room temperature. These were then twice recrystallized from diluted CsCl solution.

Raman spectra were recorded using a Coderg PH1 spectrometer and 647.1 nm/500 mW excitation from a Spectra Physics Krypton-ion-laser, model 165/01. The scattered light was collected perpendicular to the incident beam. The FIR spectra were obtained from Cs$_4$P$_2$S$_6$-PE pellets with a Bruker IFS 113 v FT spectrometer.

**Results**

The vibrational frequencies (cm$^{-1}$) of our Cs$_4$P$_2$S$_6$ samples with their intensities and assignment are compared in Table 1 with data from literature (Na$_4$P$_2$S$_6$•6H$_2$O [1, 15]). Polarization data were obtained from phosphorous-sulfide/Cs$_4$P$_2$S$_6$-melts [19]. The IR/FIR (a) and Raman (b) spectrum of Cs$_4$P$_2$S$_6$ are shown in Figure 1.

**Discussion and Normal Coordinate Analysis**

In hexathiohypodiphosphates the P$_2$S$_6^-$ complex anion is the spectroscopically relevant unit, which is isoelectronic with Si$_2$Cl$_6$ and has D$_{3d}$ symmetry. The normal modes of vibration are distributed among the symmetry species of the D$_{3d}$ point group according to [20]

$$I_{vib} = 3A_{1g}(RE) + A_{1u}(ia) + 2A_{2u}(IR) + 3E_g(RE) + 3E_u(IR).$$

2$A_{1g}$ + $A_{2u}$ + $E_g$ + $E_u$ are stretching vibrations, the remaining ones are deformations. The mutual exclusion rule is valid.

Our assignment of the P$_2$S$_6^-$ vibration frequencies (Table 1) is supported by polarization data obtained from cold saturated Na$_4$P$_2$S$_6$•6H$_2$O solutions ("free" P$_2$S$_6^-$ anion [17]) and Cs$_4$P$_2$S$_6$ melts [19]. Our experimental data and their assignment are in agreement with those published by Bürger and Falius [1], Kliche [13] and Mercier et al. [16] but opposed to those reported by Sourisseau et al. [15]. The differing vibrational frequencies are plausible when the synergetic formation reactions and possible equilibriations between different thiophosphates [19, 21] are considered. Of these,

$$\begin{align*}
P_2S_6^- + S &\rightleftharpoons P_2S_5^2^- + S^{2-} \\
P_2S_5^2- \rightleftharpoons P_2S_4^3- + PS_4^2-
\end{align*}$$

play a major role. It can be shown [19, 21] that alkali hexathiohypophosphates react in the solid state at room temperature (faster at higher temperatures) corresponding to the equilibria mentioned above. A series of vibrational frequencies found in [15] can be assigned accordingly to the anions P$_2$S$_5^2-$ and PS$_4^2-$ (cf. Table 1).

The Wilson-GF-matrix method [20] was used to model the vibrational behavior of the P$_2$S$_6^-$ anion. Bürger and Falius proceeded in the same way using Fadini’s “Kopplungsstufen” method [22] to solve the secular equations whereas we used a different iteration method [23].

The symmetry coordinates of the staggered X$_2$Y$_5$ (symmetry D$_{3d}$) model are easily constructed in the usual way [20]. The set employed here is practically identical with the one published elsewhere [24], with the exception that the redundancies were handled in a simpler way. The situation is explained by Table 2, where the types of valence coordinates used in the appropriate symmetry-adapted combination are specified.

![Fig. 1. IR/FIR (a) and Raman (b) spectrum of solid Cs$_4$P$_2$S$_6$ at room temperature.](image)
Table 1. Vibrational frequencies (cm\(^{-1}\)) of Cs\(_4\)P\(_2\)S\(_6\) with their intensity and polarization data and assignment compared with literature data (s = strong, m = medium, w = weak, v = very, sh = shoulder, p = polarized).

<table>
<thead>
<tr>
<th>Species Coordinate types</th>
<th>(\nu_1) (E(_{u}))</th>
<th>(\nu_2) (A(_{1g}))</th>
<th>(\nu_3) (E(_{g}))</th>
<th>(\nu_4) (E(_{g}))</th>
<th>(\nu_5) (E(_{u}))</th>
<th>(\nu_6) (A(_{2u}))</th>
<th>(\nu_7) (A(_{2u}))</th>
<th>(\nu_8) (E(_{g}))</th>
<th>(\nu_9) (E(_{u}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(_2)S(_6^2^-) wing; (^b) PS(_2^2^-) and/or S and Polysulfide bands, respectively; (^c) PS(_2^2^-) and/or P(_2)S(_5^2^-) mode; (^d) S and/or Polysulfide fundamentals; (^e) the mean values have been used for calculations.</td>
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The initial force field in form of a diagonal \(F\) matrix was set up using the following force constants (in mdyn/Å): \(f(P-S) = 2.40\), \(f(P-P) = 1.40\), \(f(SPP) = f(PS) = 0.25\) and \(f_T = 0.1\).

Already this simple initial force field yielded a quite good agreement with the experimental data (cf. Table 1, 3). The value obtained for the inactive \(A_{1u}\) torsion mode at 109 cm\(^{-1}\) seems reasonable. In Table 3 calculated frequencies (cm\(^{-1}\)) and the potential energy distribution (PED) data are listed [25].

The final force field in terms of symmetry coordinates was fitted exactly to the experimental frequencies and is given in Table 4. The PED values (Table 3) show that almost all Raman active fundamental modes of vibration are strongly coupled.

The conventional description of the normal modes of vibration is unsatisfactory. Especially the
Table 3. Calculated frequencies (cm$^{-1}$) of the P$_2$S$^-$ complex anion and the potential energy distribution (PED).

<table>
<thead>
<tr>
<th>Species</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>PED$^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A$_1g$</td>
<td>$v_1$</td>
<td>553</td>
<td>558</td>
<td>553</td>
</tr>
<tr>
<td></td>
<td>$v_2$</td>
<td>378</td>
<td>316</td>
<td>378</td>
</tr>
<tr>
<td></td>
<td>$v_3$</td>
<td>183</td>
<td>182</td>
<td>183</td>
</tr>
<tr>
<td>E$_g$</td>
<td>$v_7$</td>
<td>580</td>
<td>635</td>
<td>580</td>
</tr>
<tr>
<td></td>
<td>$v_8$</td>
<td>261</td>
<td>235</td>
<td>261</td>
</tr>
<tr>
<td></td>
<td>$v_9$</td>
<td>154</td>
<td>183</td>
<td>154</td>
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<tr>
<td>A$_2u$</td>
<td>$v_4$</td>
<td>109</td>
<td>109</td>
<td>109</td>
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<tr>
<td>E$_u$</td>
<td>$v_{10}$</td>
<td>588</td>
<td>586</td>
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<tr>
<td></td>
<td>$v_{11}$</td>
<td>227</td>
<td>227</td>
<td>227</td>
</tr>
<tr>
<td></td>
<td>$v_{12}$</td>
<td>141</td>
<td>141</td>
<td>141</td>
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</tbody>
</table>

$^a$: experimental Cs$_4$P$_2$S$_6$ frequencies, for the E$_g$ and E$_u$ frequencies mean values have been used; $b$: calculated frequencies from the initial force field; $c$: calculated from the final force field.

* Terms below 20 are omitted.
** Calculated value from the initial force field.

Table 4. Final symmetry force constants (mdyn/A) for P$_2$S$^-$.

<table>
<thead>
<tr>
<th></th>
<th>A$_1g$</th>
<th>E$_g$</th>
<th></th>
<th></th>
<th>A$_2u$</th>
<th>E$_u$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A$_1g$</td>
<td>3.08</td>
<td>2.03</td>
<td>0.12</td>
<td>0.34</td>
<td>0.33</td>
<td>0.84</td>
</tr>
<tr>
<td>E$_g$</td>
<td>2.27</td>
<td>0.22</td>
<td>0.10</td>
<td>0.22</td>
<td>0.09</td>
<td>0.23</td>
</tr>
</tbody>
</table>

$^a$: Parenthesized equilibrium distances in Å.

Among the Coriolis coupling constants the most important ones are the first-order constants. They are given in Table 5. In Table 6 the mean amplitudes of vibration at different temperatures are reported.

Acknowledgements

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