Synthesis, Vibrational Spectra and Normal Coordinate Analysis of Cesium-Hexathiohypodiphosphate $Cs_4P_2S_6$

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The title compound has been prepared by elemental synthesis at high temperatures and also by reaction of $Na_4P_2S_6 \cdot 6\,H_2O$ with CsCl in aqueous solution. Both reaction products have closely related vibrational spectra which are assigned on the basis of a $P_2S_6^{4-}$ anion with perturbed D_{3d} 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, $Cs_4P_2S_6$, Vibration Spectra, Normal Coordinate Analysis

Introduction

Since their rediscovery in the mid-sixties [1–3] metal thiohypodiphosphates, 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 metallocenes [10, 14, 15]. Some of them are also noted for their nonlinear electrical and optical properties.

Common to all thiohypodiphosphates is the spectroscopically relevant $P_2S_6^{4-}$ complex anion in which two terminal PS_3-groups are joined through a P–P-bond. In recent publications contradictory assignments of the vibrational frequencies of thiohypodiphosphates 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 $H_2O-P_2S_6^{4-}$ interactions like protonation and hydrolysis in crystal water containing salts and aqueous solutions is not clear. We have obtained $Cs_4P_2S_6$ in two ways: (i) by synthesis from the elements at high temperatures, (ii) by reaction of $Na_4P_2S_6 \cdot 6\,H_2O$ with CsCl in aqueous solution. The vibrational spectra of both products are nearly identical.

Experimental

The high temperature synthesis of $Cs_4P_2S_6$ 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 $Cs_4P_2S_6$ of spectroscopic purity was formed at the outer quartz wall.

From a saturated aqueous solution of $Na_4P_2S_6 \cdot 6\,H_2O$ (synthesized according to Falius [1], twice recrystallized from water) and CsCl (10% excess CsCl relative to Na) at 310 K, large colorless plateletts of $Cs_4P_2S_6$ are precipitated upon cooling to

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room temperature. These were then twice recrystallized from diluted CsCl solution.

Raman spectra were recorded using a Coderg PH 1 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 $Cs_4P_2S_6$-PE pellets with a Bruker IFS 113 v FT spectrometer.

Results

The vibrational frequencies (cm^{-1}) of our $Cs_4P_2S_6$ samples with their intensities and assignment are compared in Table 1 with data from literature ($Na_4P_2S_6 \cdot 6\,H_2O$ [1, 15]). Polarization data were obtained from phosphorous-sulfide/$Cs_4P_2S_6$-melts [19]. The IR/FIR (a) and Raman (b) spectrum of $Cs_4P_2S_6$ are shown in Figure 1.

Discussion and Normal Coordinate Analysis

In hexathiohypodiphosphates the $P_2S_6^{4-}$ complex anion is the spectroscopically relevant unit, which is isoelectronic with Si_2Cl_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]

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

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

Our assignment of the $P_2S_6^{4-}$ vibration frequencies (Table 1) is supported by polarization data obtained from cold saturated $Na_4P_2S_6 \cdot 6\,H_2O$ solutions ("free" $P_2S_6^{4-}$ anion [17]) and $Cs_4P_2S_6$ 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 equilibrations between different thiophosphates [19, 21] are considered. Of these,

$$P_2S_6^{4-} + S \rightleftharpoons P_2S_6^{2-} + S^{2-}$$

and

$$P_2S_6^{2-} \overset{S^{2-}}{\rightleftharpoons} P_2S_7^{4-} \overset{S^{2-}}{\rightleftharpoons} 2\,PS_4^{3-}$$

play a major role. It can be shown [19, 21] that alkali hexathiohypodiphosphates 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 $P_2S_6^{2-}$ and PS_4^{3-} (cf. Table 1).

The Wilson-GF-matrix method [20] was used to model the vibrational behavior of the $P_2S_6^{4-}$ 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_2Y_6 (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.

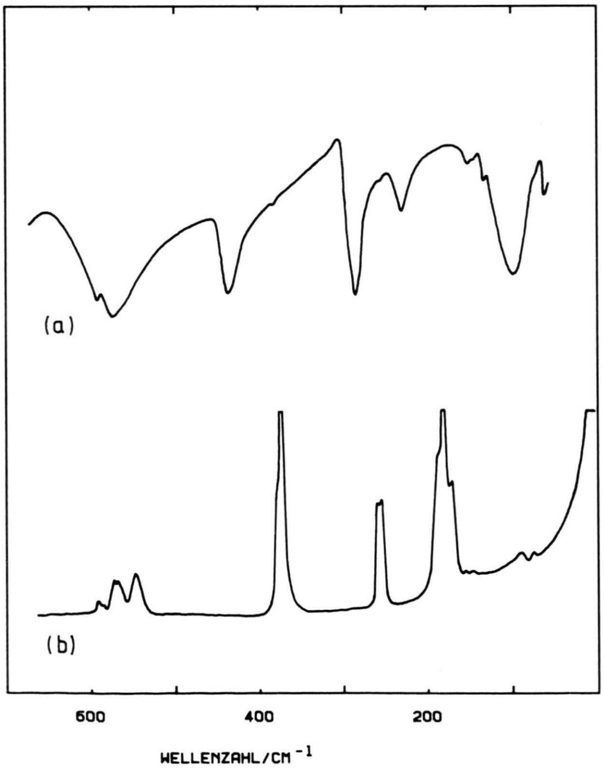

Fig. 1. IR/FIR (a) and Raman (b) spectrum of solid $Cs_4P_2S_6$ at room temperature.

Table 1. Vibrational frequencies (cm^{-1}) of $Cs_4P_2S_6$ with their intensity and polarization data and assignment compared with literature data (s = strong, m = medium, w = weak, v = very, sh = shoulder, p = polarized).

$Na_4P_2S_6 \cdot 6\,H_2O$ [1]		$Cs_4P_2S_6$		Assignment	$Na_4P_2S_6 \cdot 6\,H_2O$ [15]		Assignment [15]
Raman	FIR/IR	Raman	FIR/IR	D_{3d}	Raman	FIR/IR	D_{3d}
					21 s, 33 vs, 44 vw	29 vw, 40 vw	
		86 m	97 s	Lattice vibr.	59 w, 67 w, 90 vw	83 vw	
					100 vw	96 vw	ν_9 (E_u)
	87 w		130 w 152 w [e]	ν_{12} (E_u)			
169 w		152 vw 156 vw [e]		ν_q (E_g)	158 m [a]	154 w	ν_2 (A_{1g})
197 m		183 vs		ν_3 (A_{1g})	178 m [a] 200 s	182 vw 205 vw	ν_{12} (E_g)
	243 m		227 m	ν_{11} (E_u)	222 m [b]	220 vw 240 m	ν_8 (E_u)
259 s		259 s 263 s [e]		ν_8 (E_g)			
					264 s	265 vw	ν_{11} (E_g)
	302 s		284 s	ν_6 (A_{2u})		300 m	ν_6 (A_{2u})
374 vs		378 vs, p		ν_2 (A_{1g})	378 vs		ν_1 (A_{1g})
	380 vw				408 vw [c]	399 vw	
	444 s		440 s	ν_5 (A_{2u})	439 vw	443 m	ν_3 (A_{1g})
					475 vw [d] 482 vw [d]		
	489 vw					479 w 525 w	Libration (H_2O)
	528 vw						
557 s		553 s, p		ν_1 (A_{1g})	557 s		ν_{10} (E_g)
578 m		572 m		ν_7 (E_g)			
		588 w [e]			580 m	582 vs	ν_7 (E_u)
	585 s		578 m 598 s [e]	ν_{10} (E_u)		592 sh	
	606 sh					606 s	

[a] $P_2S_6^{2-}$ wing; [b] PS_4^{3-} and/or S and Polysulfide bands, respectively; [c] PS_4^{3-} and/or $P_2S_6^{2-}$ mode; [d] S and/or Polysulfide fundamentals; [e] the mean values have been used for calculations.

Table 2. Types of valence coordinates for the staggered X_2Y_6 molecular model with D_{3d} symmetry.

Species	Coordinate types [a]		
A_{1g}	d	r	α
E_g	r	α	β
A_{1u}	τ		
A_{2u}	r	β	
E_u	r	α	β

[a] d: P–P stretch; r: P–S stretch; α: SPS bend; β: PSS bend; τ: torsion.

The structure parameters were estimated from related compounds as 2.02 Å and 2.20 Å for the P–S and P–P bond lengths, respectively. They are in reasonable agreement with the recent data of $Pb_2P_2S_6$ [12]. The angles were assumed as tetrahedral.

The initial force field in form of a diagonal F matrix was set up using the following force constants (in mdyn/Å): $f_{(P-S)} = 2.40$, $f_{(P-P)} = 1.40$, $f_{(SPS)} = f_{(SPP)} = 0.25$ and $f_\tau = 0.1$.

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 $P_2S_6^{4-}$ complex anion and the potential energy distribution (PED).

Species		*a*	*b*	*c*	PED*
A_{1g}	ν_1	553	558	553	$61d + 44r + 41\alpha$
	ν_2	378	316	378	$59r$
	ν_3	183	132	183	$49\alpha + 31d$
E_g	ν_7	580	635	580	$80r + 24\beta$
	ν_8	261	235	261	$29\beta + 25\alpha + 21r$
	ν_9	154	183	154	$74\alpha + 54\beta$
A_{1u}	ν_4	–	109	109**	100τ
A_{2u}	ν_5	440	452	440	$79r + 29\beta$
	ν_6	284	266	284	$72\beta + 22r$
E_u	ν_{10}	588	586	588	$84r$
	ν_{11}	227	244	227	90α
	ν_{12}	141	128	141	101β

a: experimental $Cs_4P_2S_6$ 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/Å) for $P_2S_6^{4-}$.

A_{1g}	3.08			E_g	2.27		
	0.34	2.03			−0.10	0.22	
	0.12	−0.33	0.84		0.09	−0.05	0.23
A_{1u}	0.10						
A_{2u}	2.39			E_u	2.37		
	0.09	0.57			0.04	0.31	
					0.01	−0.05	0.33

ν_1 and ν_2 modes cannot be attributed to pure P−P resp. PS_3 stretchings. This has already been pointed out by Bürger and Falius [1]. The same is true for the assignment of the $P_2O_6^{4-}$ frequencies [26].

The final force field (Table 4) was used to calculate different "molecular" constants of $P_2S_6^{4-}$ [25].

Table 5. Mean amplitudes of vibration (Å) of $P_2S_6^{4-}$.

Distance type[a]	Mean amplitude		
	$T = 0$	298 K	773 K
P−S (2.02)	0.0452	0.0500	0.0692
P−P (2.20)	0.0475	0.0550	0.0781
S ... S (3.30)	0.0615	0.0840	0.1285
P ... S (3.45)	0.0597	0.0840	0.1286
S ... S (4.03)	0.0796	0.1340	0.2115
S ... S (5.20)	0.0627	0.0885	0.1361

[a] Parenthesized equilibrium distances in Å.

Table 6. The most important Coriolis coupling constants of the $P_2S_6^{4-}$ complex anion.

$E_g \times E_g$	ζ_7	0.837
	ζ_8	− 0.448
	ζ_9	− 0.050
$E_u \times E_u$	ζ_{10}	0.803
	ζ_{11}	− 0.843
	ζ_{12}	0.039

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.

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