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Vibration Spectrum and Normal Coordinate Analysis of the Pyrothiophosphates $Na_4P_2S_7$, $Na_2FeP_2S_7$, and $Ag_4P_2S_7$

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ABSTRACT

$Na_4P_2S_7$, $Na_2FeP_2S_7$, and $Ag_4P_2S_7$ were prepared by elemental synthesis at high temperatures and were characterized by vibration spectra and differential thermal analysis (DTA). A normal coordinate analysis was performed for $P_2S_7^{4-}$. Additional vibration frequencies indicate the presence of the decathiotriphosphate anion $P_3S_{10}^{5-}$. The formation of higher thiophosphates of the type $P_nS_{3n+1}^{(n+2)-}$ with $n \geq 4$ cannot be excluded.

INTRODUCTION

In metal sulphide–phosphorus sulphide systems, coupled Lewis acid–base and redox reactions take place at elevated temperatures [1, 2]. Thiophosphate species with pentavalent phosphorus dominate in such systems with stoichiometry $PS_3^- : S^{2-} = 1:0 - 1:1$ as coupled Lewis acid–base equilibria, according to

$$P_2S_6^{2-} \rightleftharpoons 2\,PS_3^- \overset{S^{2-}}{\rightleftharpoons} P_2S_7^{4-} \overset{S^{2-}}{\rightleftharpoons} 2\,PS_4^{3-} \tag{1}$$

A more general formulation can be written as

$$n(PS_3^-) + S^{2-} \rightleftharpoons P_nS_{3n+1}^{(n+2)^-} \tag{2}$$

Therefore, the existence of higher thiophosphates must be considered. The $P_2S_6^{2-}$ dimer and the PS_3^- monomer [3–6] as well as the PS_4^{3-} anion [7, 8] are well characterized. The $P_2S_7^{4-}$ anion could be obtained as a connecting link in crystalline $Ag_4P_2S_7$ [9].

The kind of thiophosphate species formed is not only dependent on stoichiometry of element mixtures for high temperature syntheses but is also dependent on the cation and its oxidation state against sulfur. Univalent cations are able to compose the thiophosphates with $P_2S_6^{2-}$, $P_2S_7^{4-}$, and PS_4^{3-} groups. Trivalent cations form almost complete orthothiophosphates of the type Me(III)PS_4. Di- and tetravalent cations (preferably from 3d metals) form hypothiophosphates of the types Me_2(II)P_2S_6 and Me(IV)P_2S_6, respectively. Under certain conditions different cations with differing oxidation states can react to a thiophosphate type according to the sum of their oxidation states, e.g., Tl(I)Sn(II)PS_4 and Cs(I)Eu(II)PS_4 [5, 8]. In this context $Na_2FeP_2S_7$ could be obtained. There is an evident similarity between thiophosphates and isoelectronic $AlCl_3$–Cl^- systems (e.g. PS_4^{3-}-$AlCl_4^-$). This leads to the discussion of $P_3S_{10}^{5-}$ species and $P_nS_{3n+1}^{(n+2)^-}$ ($n \geq 4$) homologues.

EXPERIMENTAL

The title compounds were prepared using high temperature element synthesis of stoichiometric amounts in evacuated quartz ampoules. To avoid a violent reaction of sodium with sulfur, phosphorus, and phosphorus sulphides, the elements were inserted separately into the reaction ampoules (Figure 1) so that a slow reaction could then proceed through the gas phase. After tempering for several hours at 100°C the temperature was slowly in-

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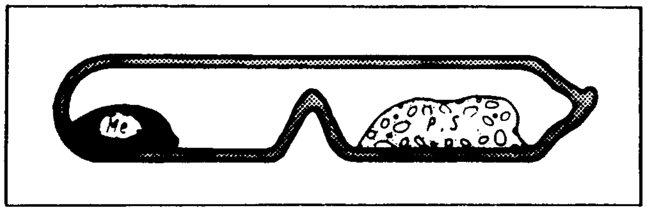


FIGURE 1 Quartz ampoule for preparation of alkali thiophosphates.

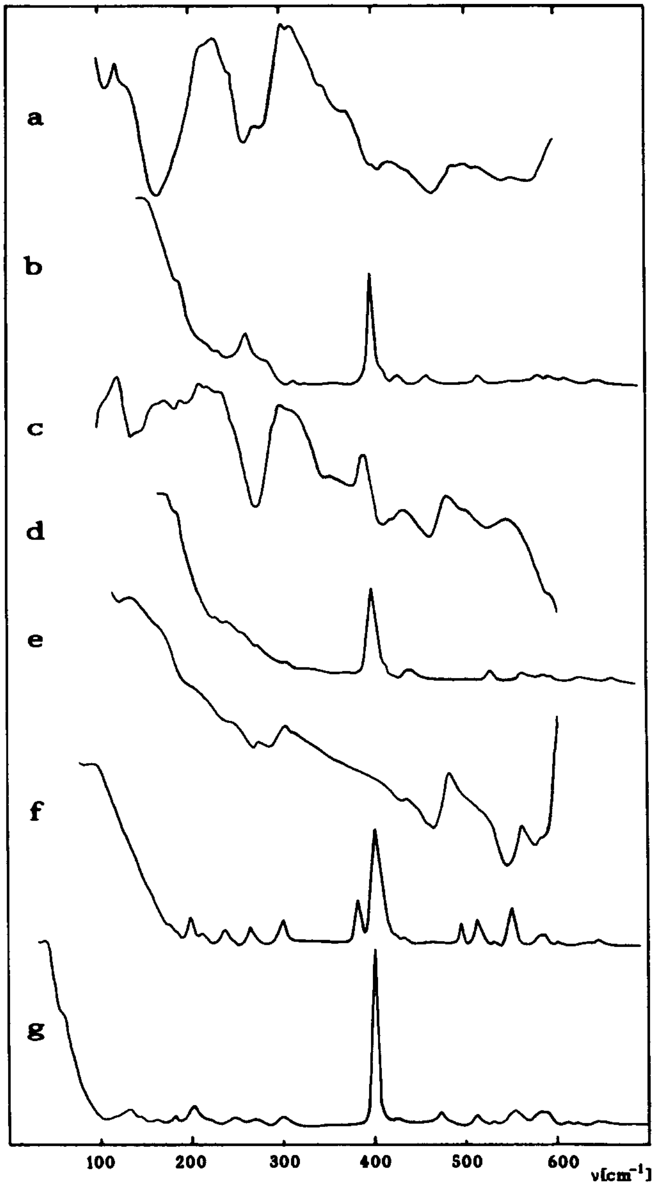


FIGURE 2 Vibration spectra of the title compounds. a. $Na_4P_2S_7$, IR/FIR, 20°C; b. $Na_4P_2S_7$, RE, 20°C; c. $Na_2FeP_2S_7$, IR/FIR, 20°C; d. $Na_2FeP_2S_7$, RE, 20°C; e. $Ag_4P_2S_7$, IR/FIR, 20°C; f. $Ag_4P_2S_7$, RE, −196°C; g. $Ag_4P_2S_7$, RE, 20°C.

creased (20°C/h) to 900°C. The molten reaction mixture was kept at 900°C for 6 h, then was cooled down in a linear temperature gradient of 35°C/h (24 h). The $Na_4P_2S_7$ charge yielded a homogeneous white product, which decomposed by moisture to H_2S and unidentified phosphates. $Na_2FeP_2S_7$ was obtained as an orange-colored homogeneous product, which also decomposed by moisture with a peculiar foaming of the substance and H_2S odor. $Ag_4P_2S_7$ was obtained as a pale yellow homogeneous crystalline cake out of a stoichiometric mixture by heating to 900°C (5 h), 10 h reaction time at this temperature, and cooling slowly (35°C/h). $Ag_4P_2S_7$ is not decomposed by moisture.

The Raman spectra were recorded with a Coderg PH1 spectrometer and Laser light excitation (Krypton–Ion–Laser, Spectra Physics 165/01; 647.1 nm). The registration of the Raman scattering was carried out perpendicular to the incident Laser beam. Function and modified sample compartment of the spectrograph used have already been published [10, 11]. The infrared (FIR/IR) spectra were obtained from thiophosphate–PE pellets with a Beckman FS 720 interferometer. DTA data have been determined with self-built equipment (Quartz glass reference, ±5°C at 1000°C).

RESULTS

Infrared and Raman spectra of the title compounds are shown in Figure 2. The vibrational frequencies (cm^{-1}) are summarized in Table 1 along with their intensities and assignment. Raman melt spectra could not be obtained because of an intense red glow and dark coloring.

DISCUSSION AND NORMAL COORDINATE ANALYSIS

The $P_2S_7^{4-}$ group with C_{2v} symmetry is the relevant vibration spectroscopical unit in pyrothiophosphates of the title compounds. In $Ag_4P_2S_7$ this unit is characterized by X-ray structure determination [9]. $P_2S_7^{4-}$ is isoelectronic with $Al_2Cl_7^-$. A point group analysis of $P_2S_7^{4-}$ based on the C_{2v} model (Figure 3) gives the following results:

$$\Gamma_{vib}\,(C_{2v}) = 7A_1(IR,RE) + 4A_2(RE) + 4B_1(IR,RE) + 6B_2(IR,RE) \qquad (3)$$

It is difficult to assign all 21 vibration bands without polarization data; therefore, a vibrational analysis was carried out. The assignment of the $P_2S_7^{4-}$ vibration bands is based on their positions in the stretching, bridge, and deformation regions known from similar thiophosphates and phosphorus sulphides. Furthermore, the selection rule and the band intensities are taken as arguments. Only the $P_2S_7^{4-}$ spectrum was found experimentally in the title compounds; thus, site symmetry splitting could not be applied.

In the Na_2S–P_4S_{10} system, solid and molten samples of $Na_4P_2S_7$ stoichiometry were prepared and characterized by Raman spectroscopy [12]. These Raman spectra are dominated by a very strong band at 399 cm^{-1} in agreement with the $Na_4P_2S_7$ spectrum shown in Figure 2b.

TABLE 1 Raman and FIR/IR Frequencies (cm^{-1}) of the Title Compounds with Intensities and Their Assignment.

$Na_4P_2S_7$		*$Na_2FeP_2S_7$*		*$Ag_4P_2S_7$*			Assignment (C_{2v})
RE	*FIR/IR*	*RE*	*FIR/IR*	*RE*	*$RE_{(-196°C)}$*	*FIR/IR*	
	112 m		107 w				$\nu_{15}(B_1)$
	134 w		134 m	122 vw		113 vw	$\nu_6(A_1)$
	146 vw		146 vw	135 m		128 m	$\nu_{21}(B_2)$
	166 vs		168 vw	168 vw	170 w		$\nu_{10}(A_2)$
183 m	185 vw	183 w	182 m	185 m	185 w	167 m	$\nu_5(A_1)$
215 vw	210 vw		216 vw	203 s	200 s	198 w	$\nu_{20}(B_2)$
230 vw		232 m	221 vw	218 w	220 m		$\nu_{19}(B_2)$
248 wsh	246 vw	248 m	246 vw	247 mb	245 m	239 w	$\nu_{14}(B_1)$
260 s	263 s	262 w			250 wsh		$\nu_9(A_2)$
280 m	282 m	278 m	273 vs	273 m	270 m	268 m	$\nu_4(A_1)$
310 vw	310 w	303 m	309 w	300 m	300 m	287 m	$\nu_{13}(B_1)$
	344 w		348 m				
	368 w		372 m	377 vw	375 s		
398 vs	399 vw	404 vs	409 w	399 vs	399 vs		$\nu_3(A_1)$
410 msh	408 w	418 wsh		415 wsh	415 wsh		
435 s	443 vw	427 wsh	424 vw	435 w	435 vw	431 m	$\nu_{18}(B_2)$
462 s	467 m	458 s	461 s	477 s	480 m	466 s	$\nu_{17}(B_2)$
524 s	518 vw	529 s	524 m	516 s	520 m	506 vw	$\nu_2(A_1)$
540 vw	540 vw	565 w	564 vw	555 s	555 s	547 s	
583 w	576 s	584 w	592 vw	582 wb	580 mb	576 m	$\nu_{16}(B_2)$
595 w		595 w		590 wb	590 mb	585 vw	$\nu_1(A_1)$
610 w		633 m		602 vw	602 w		$\nu_{12}(B_1)$
650 m		668 m		651 vw	651 vw		$\nu_8(A_2)$

s = strong, m = medium, w = weak, v = very, sh = shoulder, b = broad

In context with the vibration spectra of niobium phosphorus sulphides, $Ag_4P_2S_7$ vibration frequencies have been given for comparison [13]. These spectral data differ from the $Ag_4P_2S_7$ frequencies summarized in Table 1. According to the key frequencies of the known thiophosphates [1–8, 14–18], the $Ag_4P_2S_7$ spectrum of Queignec et al. [13] shows that neither $Ag_2P_2S_6$, $Ag_4P_2S_6$, and sulfur nor $Ag_4P_2S_7$, with its characteristic 399 cm^{-1} Raman band, are present. Therefore, it appears that Ag_3PS_4 and other thiophosphate species are components of the investigated sample. Indeed the $Ag_4P_2S_7$ vibration frequencies of Queignec et al. [13] are contrary to those of $Na_4P_2S_7$ [12] and the data of Table 1, but we consider that spectrum [13] to be an independent indication for the existence of higher thiophosphate species of the type $P_nS_{3n+1}^{(n+2)-}$ discussed below.

Structural Parameters

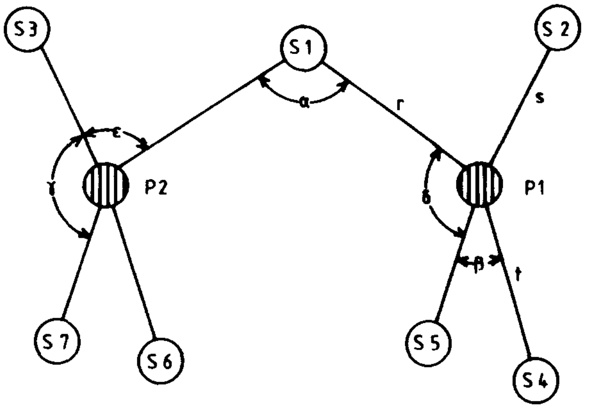
All structural parameters used (mean values) were taken from the crystal structure determination of $Ag_4P_2S_7$ [9], and are summarized in Table 2 and designated in Figure 3.

TABLE 2 Structural Parameters (Mean Values) Used for Vibrational Analysis (Distances in Å, Angles in °) [9].

P1–S1	2.125 Å
P1–S2	2.030 Å
P1–S4	2.031 Å
∢ P1–S1–P2	113.4°
∢ S4–P1–S5	114.2°
∢ S2–P1–S4	112.1°
∢ S1–P1–S4	110.0°

Atomic weights: P: 30.9738 S: 32.064

FIGURE 3 The $P_2S_7^{4-}$ molecular model with C_{2v} symmetry and designation of the valence coordinates.



Valence and Symmetry Coordinates

Valence and symmetry coordinates of $Al_2Cl_7^-$ from Rytter [19] were applied for vibrational analysis of $P_2S_7^{4-}$. The valence coordinates contain the changes of bond lengths, angles, and both torsions, which are defined by

$$\tau_1 = \tau_{P2-S1-P1-S2} \quad \text{and} \quad \tau_2 = \tau_{P1-S1-P2-S3} \qquad (4)$$

Of the 6 angles with P1 as the origin of coordinates (analogous to P2), only 5 are variable independently. A set of 21 independent valence coordinates results in accordance with the number of expected frequencies. Table 3 lists the valence coordinates in the particular symmetry species used for the construction of the set of symmetry coordinates.

TABLE 3 Types of Valence Coordinates Used for the Construction of the Symmetry Coordinates (See Figure 3 and Ref. 19).

Species	*Valence Coordinates*
A_1	$r, s, t, \alpha, \gamma, \delta, \epsilon$
A_2	t, γ, δ, τ
B_1	t, γ, δ, τ
B_2	$r, s, t, \gamma, \delta, \epsilon$

Normal Coordinate Analysis

Frequencies and force constants were calculated using the model of the general valence force field, which considers only forces between chemically bonded atoms. Initially a simple force field using valence coordinates was assumed, using force constant estimates qualitatively evolved from compounds such as $P_2S_6^{2-}$ [20]. The title ion contains the following numerical parameters (in mdyn/Å): $f_r = 1.7$, $f_s = f_t = 2.5$, $f_\varphi = 0.2$ ($\varphi = \alpha, \beta, \epsilon$), $f_\varphi = 0.3$ ($\varphi = \gamma, \delta$), $f_\tau = 0.12$ and $f_{ww} = 0.3$ for all interactions with common atoms.

The initial force constant matrix in terms of the symmetry coordinates was calculated with the T transformation [21, 22] according to Equation 5:

$$F = T' \cdot f \cdot T \qquad (5)$$

Its diagonal elements are summarized in Table 4. The eigenvalue matrix Λ is obtained by solving the problem [22] $G \cdot F \cdot L = L \cdot \Lambda$, and is used to calculate the frequencies. As shown in Table 5 these data agree very well with the experimental frequencies, so that their faithful assignment can be made together with qualitative considerations. The substitution of the calculated frequencies by the observed frequencies gave the final force field in terms of symmetry coordinates with receipt of the L matrix. Its diagonal elements are also listed in Table 4. The unobserved frequencies $\nu_7(A_1)$, $\nu_{11}(A_2)$, and $\nu_{15}(B_1)$ are calculated values.

TABLE 4 Symmetry Force Constants (mdyn/Å) for the $P_2S_7^{4-}$ Ion (Normalization Based on Ref. 19). a. Initial Force Field; b. Final Force Field.

Species	*Symmetry Coordinate*	a	b
A_1	$S_1(r)$	2.00	1.96
	$S_2(s)$	2.50	2.41
	$S_3(t)$	2.80	2.73
	$S_4(\alpha)$	0.20	0.19
	$S_5(\gamma)$	0.60	0.44
	$S_6(\delta)$	0.55	0.45
	$S_7(\epsilon)$	0.30	0.27
A_2	$S_8(t)$	2.20	2.22
	$S_9(\gamma)$	0.30	0.28
	$S_{10}(\delta)$	0.30	0.30
	$S_{11}(\tau)$	0.12	0.12
B_1	$S_{12}(t)$	2.20	2.17
	$S_{13}(\gamma)$	0.30	0.29
	$S_{14}(\delta)$	0.30	0.28
	$S_{15}(\tau)$	0.12	0.12
B_2	$S_{16}(r)$	1.40	1.37
	$S_{17}(s)$	2.50	2.53
	$S_{18}(t)$	2.80	2.85
	$S_{19}(\gamma)$	0.60	0.54
	$S_{20}(\delta)$	0.55	0.49
	$S_{21}(\epsilon)$	0.30	0.27

TABLE 5 Calculated and Observed Frequencies (cm^{-1}) of the $P_2S_7^{4-}$ Ion. a. Calculated from the Initial Force Field; b. Experimental Frequencies of $Ag_4P_2S_7$.

		Vibration frequencies		
Species		a	b[b]	*PED terms*[a]
A_1	ν_1	596	588	$54s + 30t$
	ν_2	498	511	$42r + 20s + 19t$
	ν_3	405	399	$49t + 24r$
	ν_4	284	269	$72\delta + 22s + 22\alpha + 19\gamma$
	ν_5	211	176	62γ
	ν_6	124	118	$84\epsilon + 27r + 21\gamma$
	ν_7	66	66[c]	$66\alpha + 22\delta + 15\epsilon$
A_2	ν_8	629	651	$63t$
	ν_9	260	243	$36\gamma + 34t + 17\tau$
	ν_{10}	168	168	$77\delta + 18\gamma$
	ν_{11}	58	58[c]	$73\tau + 15\gamma$
B_1	ν_{12}	603	602	$73t$
	ν_{13}	313	294	$63\delta + 34\tau$
	ν_{14}	247	243	$70\gamma + 20t$
	ν_{15}	101	101[c]	$60\tau + 21\delta + 15\gamma$
B_2	ν_{16}	571	579	$66s + 31t$
	ν_{17}	483	472	$54r + 31t + 28\delta$
	ν_{18}	423	433	$34t + 23r$
	ν_{19}	225	208	$94\gamma + 39\epsilon + 21\delta + 19r$
	ν_{20}	211	201	$27\gamma + 19\epsilon$
	ν_{21}	144	132	$81\delta + 70\epsilon$

[a] PED terms below 15 are omitted.

[b] The observed frequencies are FIR/IR and Raman mean values.

[c] Unobserved frequencies estimated by the authors.

Potential Energy Distribution (PED)

PED terms calculated from the final force field are summarized in Table 5 [23]. By use of those PED terms the vibrational coupling in a species can be discerned. There are mostly coupled vibrations in $P_2S_7^{4-}$, with only a few exceptions. Vibrations that are mainly dependent of one symmetry coordinate are $\nu_5(A_1)$, $\nu_8(A_2)$, and $\nu_{12}(B_1)$. Weak coupling has been found for $\nu_{10}(A_2)$, $\nu_{11}(A_2)$, and $\nu_{14}(B_1)$. These vibrations can still be considered sufficiently characteristic. The $\nu_1(A_1)$ and $\nu_{16}(B_2)$ vibrations must originate from terminal bonds. All the other vibrations cannot be regarded as characteristic.

Mean Amplitudes of Vibration

The mean amplitudes of vibration calculated from the final force field are given in Table 6 for all distances in $P_2S_7^{4-}$ at three temperatures [24]. Comparison with published data [1, 20] shows agreement for similar bonds.

TABLE 6 Mean Amplitudes of Vibration (Å Units) for All Distances and Three Temperatures.

Distances	*T = 0 K*	*298 K*	*773.15 K*
P1–S1	0.050	0.060	0.086
P1–S2	0.045	0.050	0.070
P1–S4	0.045	0.050	0.069
P1···P2	0.060	0.101	0.158
S4···S5	0.064	0.093	0.143
S2···S4	0.062	0.085	0.130
S1···S4	0.062	0.089	0.137
S1···S2	0.068	0.108	0.169
P2···S2	0.068	0.110	0.172
P2···S4	0.078	0.144	0.228
S4···S6	0.118	0.219	0.345
S4···S7	0.075	0.146	0.231
S3···S4	0.083	0.155	0.246
S2···S3	0.086	0.164	0.261

Thermal Behavior of the Title Compounds

The differential–thermo–analytical (DTA) measurements of the pyrothiophosphates investigated gave differing curves. $Na_2FeP_2S_7$ shows only one distinct DTA effect at 439 ± 5°C, which is attributed to its melting point. $Na_4P_2S_7$ yields two thermal effects at 340°C and 415°C, in accordance with the Na_2S–P_4S_{10} phase diagram [25]. These effects are caused by the peritectic $Na_4P_2S_7$ decomposition (343°C and 420°C [25]). The $Ag_4P_2S_7$ DTA curvature is complex and shows five thermal effects. In the Ag_2S–P_4S_{10} phase diagram [26, 27], four effects can be assigned to phase changes and to the melting/crystallization temperature at 568 ± 5°C(575 ± 5°C [27]).

Decathiotriphosphate $P_3S_{10}^{5-}$ and $P_nS_{3n+1}^{(n+2)-}$ Homologues

Since PS_3^- ions exist in the equilibrium system of thiophosphates at higher temperatures according to $P_2S_6^{2-} \rightleftharpoons 2PS_3^-$, these ions can equilibrate with $P_2S_7^{4-}$ to $P_3S_{10}^{5-}$ and $P_nS_{3n+1}^{(n+2)-}$ species. This equilibration is indicated by the change in the $Ag_4P_2S_7$ Raman spectrum over a period of several weeks, in which time a new strong Raman band around 375 cm^{-1} is observed (cf. Table 1). The Raman frequency near 550 cm^{-1} can also be interpreted as an indication for the $P_3S_{10}^{5-}$ ion.

A high temperature synthesis of an $Ag_5P_3S_{10}$ stoichiometry charge yielded a crystalline homogeneous brown product similar to the $Ag_4P_2S_7$ compound (900°C, slow cooling). The Raman spectrum can be interpreted as being unrestricted by a mixture of $Ag_2P_2S_6$ and $Ag_4P_2S_7$. Using the Ag_2S–P_4S_{10} phase diagram [26], the $Ag_5P_3S_{10}$ sample was tempered in a temperature gradient of 400–420°C for four days. Four partly separated solid regions were formed with different colorings (orange, yellow-brown, pale yellow, and brown). The three phases previously mentioned could be identified safely as $Ag_2P_2S_6/Ag_4P_2S_7$ mixtures and $Ag_4P_2S_7$, respectively. The brown phase produced at 420°C is noteworthy. The Raman band around 375 cm^{-1} appears to be intense beside the main band of $P_2S_7^{4-}$ at 399 cm^{-1}. Raman bands of phosphorus sulphides [28] are not present in the spectrum. Traces of sulfur and/or polysulphides [29–31] cannot be excluded definitively. Therefore, two possible interpretations must be considered:

1. The $P_2S_6^{4-}$ ion was produced by the redox reaction

   $$P_2S_6^{2-} + S^{2-} \rightleftharpoons P_2S_6^{4-} + S \qquad (6),$$

   and the Raman frequency at 375 cm^{-1} arises from $P_2S_6^{4-}$ with its characteristic band around 370–380 cm^{-1} [1, 14–16].

2. On the other hand, $P_2S_7^{4-}$ and $P_2S_6^{2-}$ (PS_3^-) can equilibrate to $P_3S_{10}^{5-}$ and $P_nS_{3n+1}^{(n+2)-}$ homologues with $n \geq 4$. The previously mentioned 375-cm^{-1} Raman band can also originate from the $P_3S_{10}^{5-}$ and $P_nS_{3n+1}^{(n+2)-}$ species, which may be present in a mixture together with $P_2S_7^{4-}$ and $P_2S_6^{2-}$.

Vibrational analysis for the $P_3S_{10}^{5-}$ group with C_{2v} symmetry yields 33 Raman active vibrations expected to be close to the $P_2S_7^{4-}$ frequencies. In the isoelectronic $Al_2Cl_7^-$–$AlCl_3$ system Rytter et al. [32] and Dymek et al. [33] found only a few more vibrational bands for $Al_3Cl_{10}^-$. This can be explained by noting that vibrations of the smallest units of the oligomers create adequate vibration bands. The

$Ag_4P_2S_7$ vibration spectrum of Queignec et al. [13] as well as the spectral data presented indicate that the existence of $P_3S_{10}^{5-}$ and $P_nS_{3n+1}^{(n+2)-}$ species in the $Ag_2S–P_4S_{10}$ system can not be ruled out.

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