Vibrational Study of a Polycrystalline Sample of the New Chromium Thiophosphate $CrP_3S_{9.25}$

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A vibrational study of $CrP_3S_{9.25}$ was undertaken in order to confirm the substitution of some S^{2-} anions by $(S_2)^{2-}$ pairs as focused by a X-ray single-crystal analysis. Comparison between the infrared and Raman spectra allowed us to assign the main vibrational bands. Very similar spectra were observed for $Ag_2P_2S_6$ and $CrP_3S_{9.25}$ in the 100–600 cm^{-1} range, allowing confident internal vibrational mode assignments of the $(P_2S_6)^{2-}$ anions. An assignment to the $(S_2)^{2-}$ group stretching mode in $CrP_3S_{9.25}$ is mainly suggested from Raman results. The 491 cm^{-1} signal attributed to this vibration led to a S–S distance estimate of 2.10 Å, in good agreement with the crystal structure determination (2.07 Å). © 1994 Academic Press, Inc.

I. INTRODUCTION

A recent structural study (1) established the crystal structure of a new thiophosphate of a transition metal, $CrP_3S_{9.25}$. Many difficulties were encountered in solving this structure. In effect, a first series of refinements involving the stoichiometric composition CrP_3S_9 and implying classical S^{2-} anions led to acceptable results, with a correct charge balance $Cr^{3+}P_3^{5+}S_9^{2-}$ and fair agreement with the semiquantitative element analyses. Although some Atomic Displacement Parameters (ADP) were rather high, they could be accounted for by the interlocked nature of the structure. Some degree of freedom could in effect be envisioned among the three independent structure-forming rings.

A somewhat better refinement result was, however, achieved through partial substitution of some S^{2-} sulfur anions by $(S_2)^{2-}$ disulfide groups. Occurrence of such $(S_n)^{2-}$ groups was found to take place in several MPS compounds like PV_2S_{10} (2), $Nb_4P_2S_{21}$ (3), Nb_2PS_{10} (4), or $Ta_4P_4S_{29}$ (5). While improving the results with a meaningfully better reliability factor and with more acceptable atomic displacement parameters, this substitution allowed the maintenance of the phase charge balance $Cr^{3+}P_3^{5+}(S^{2-})_{8.75}(S_2)^{2-}_{0.25}$. The substitution was found to

take place randomly on specific sites of the structure. By comparing the unsubstituted (CrP_3S_9) and the substituted phase ($CrP_3S_{9.25}$), it was found that such atomic replacement alleviated some stress within the structure. Occurrence of such $(S_2)^{2-}$ groups was thus not to be attributed to some kind of internal redox mechanism as is the case in the MS_2 series, in agreement with the anionic/cationic electronic band competition. Because there are few disulfide groups within the structure, and in spite of the meaningfulness of the refinement data following their introduction, it was thought important to check their presence in the phase. In effect, the idea of substituting S^{2-} by $(S^2)^{2-}$ groups was an a priori one and deserved further checking and evidencing.

This is why a complete infrared and Raman vibrational study was undertaken on the phase to determine the occurrence of the characteristic stretching mode of the $(S_2)^{2-}$ group, a rather well-identified anion among inorganic solid-state sulfides (6). This article reports the successful assignment of the vibrational spectra of $CrP_3S_{9.25}$, in particular by comparison with $(P_2S_6)^{2-}$ anion-containing phases like $Tl_2P_2S_6$ and $Ag_2P_2S_6$, and the confirmation of the correctness of the structure determination.

II. EXPERIMENTAL

$CrP_3S_{9.25}$ was prepared as described in (1). To obtain an amount of phase large enough for a classical infrared and Raman powder study and since the phase cannot be obtained in the pure state, single crystals were sorted out with a pincer from the synthesis batch. In effect, among other impurities and along with the studied phase, the preparation tubes contained some amount of $CrPS_4$. Because the morphology of this latter compound and that of the phase under study are very different, a clear separation of the two materials could be safely achieved. The powdered $CrP_3S_{9.25}$ samples obtained were reasonably assumed to be of a pure phase.

The infrared spectra of $Ag_2P_2S_6$ and $CrP_3S_{9.25}$ polycrystalline compounds at 300 K were recorded as nujol mulls

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(using Si or polyethylene optical windows) on the Per-kin–Elmer 983G spectrometer (1000–180 cm^{-1}) and on the Nicolet 20F FTIR instrument (650–30 cm^{-1}). The Raman spectra were recorded from polycrystalline pow-ders not only for the chromium phase, but also for a phase containing the same $(P_2S_6)^{2-}$ anionic unit, i.e., $Ag_2P_2S_6$. In that case, a triple monochromator Dilor Z24 was used with the exciting red line $\lambda = 647.1$ nm of a Spectra-Physics 164 Kr$^+$ laser, with $P_o = 40$–50 mW. This was chosen because of the yellow color of the sample. In the case of $CrP_3S_{9.25}$, a spectrograph with multichannel detection including 1024 photodiodes (OMARS 89 from Dilor) and excitation of the green line $\lambda = 514.5$ nm of a Ar$^+$ Spectra-Physics 164 laser was used in a Raman microspectrometer mounting. This was performed with a 100× objective, in relation to the very pure microscopic grains of the phase. A very weak power was focused on the sample (a few mW) in order to avoid any thermal or photochemical degradation that can easily be detected by the occurrence of the well-known characteristic Raman lines of the elementary sulfur S_8 and polysulfides (it is to be recalled that $CrP_3S_{9.25}$ is prepared at a rather low temperature (1)). Finally, the recordings made on different grains have shown to be identical, with no signal attributed either to S_8 (7) or to $CrPS_4$.[2] Infrared and Raman spectra of $Tl_2P_2S_6$, $Ag_2P_2S_6$, and $CrP_3S_{9.25}$ are gathered in Figs. 1, 2, and 3, respectively.

III. CRYSTAL STRUCTURE AND SELECTION RULES

Let us briefly recall the main structural features of $CrP_3S_{9.25}$. With 208 atoms per cell, the structure is rather complex. Neglecting the partial and random substitution of some S^{2-} anions by $(S_2)^{2-}$ groups, the phase can be seen as made up of (CrP_3S_{12}) basic units. These are made of one (CrS_6) octahedron sharing three edges with three (PS_4) tetrahedra (Fig. 4). All the (CrP_3S_{12}) units are inter-connected through the three available tetrahedron edges, i.e., to other (PS_4) tetrahedra, to form connecting $(P_2S_6)^{2-}$ biprisms. These bondings yield three interlocked net-works, one of them being partly represented in Fig. 5. To better model the structure, one sulfur position (S5) (Fig. 6) corresponding to two sulfur atoms shared by two adjacent (PS_4) tetrahedra had to be substituted by some $(S_2)^{2-}$ pairs. This led to a better refinement (1) (although some ADP remained high) and to some local rearrangement of the network as shown in Fig. 6. This substitution and the subsequent twist of the $(P_2S_6)^{2-}$ groups were attributed to an alleviation of the stress of the groups. According to (1), the new thiophosphate crystallizes in the orthorhom-bic symmetry, in the space group F_{ddd} or D_{2h}^{24}, with a

FIG. 1. (a) Infrared (in % of transmittance) and (b) Raman spectra (20–800 cm^{-1}) of the $Tl_2P_2S_6$ solid compound at 300 K, according to Ref. (7).
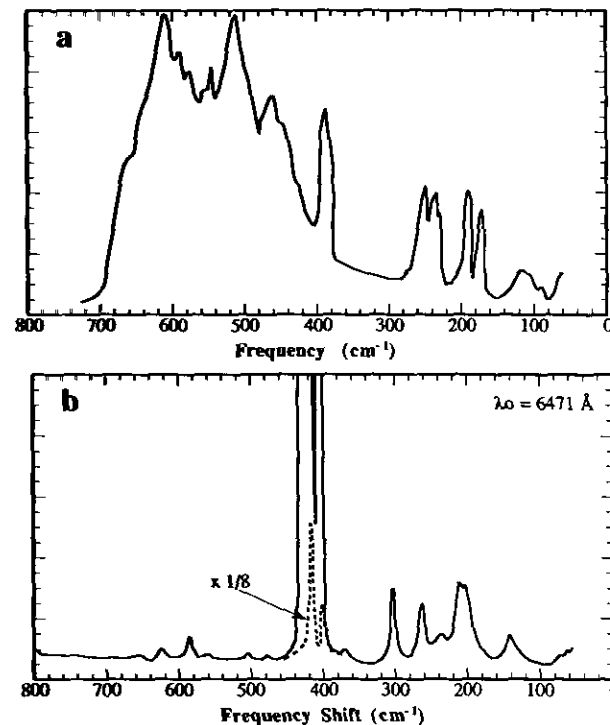
FIG. 2. (a) Infrared (in absorbance) and (b) Raman spectra (10–800 cm^{-1}) of the $Ag_2P_2S_6$ solid compound at 300 K.

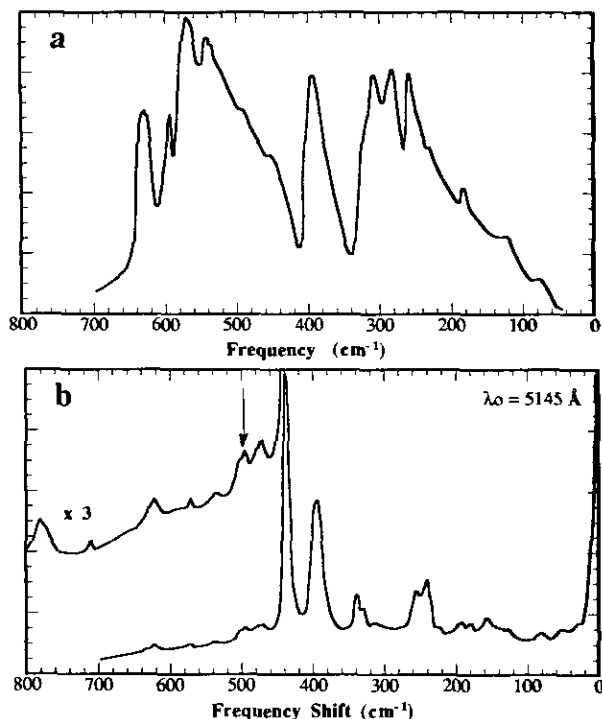[2] The $CrPS_4$ compound is characterized by a single intense Raman band at 426 cm^{-1}.

FIG. 3. (a) Infrared (in absorbance) and (b) Raman spectra (10–800 cm^{-1}) of the $CrP_3S_{9.25}$ solid compound at 300 K. Arrows indicate bands assigned to the $\nu(S-S)^{2-}$ stretching mode.

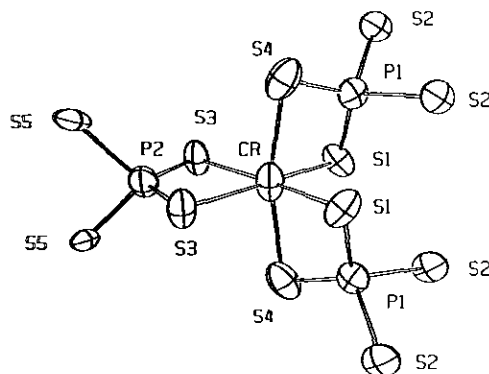FIG. 4. CrP_3S_{12} unit made of (CrS_6) octahedra sharing three opposite edges with three (PS_4) tetrahedra.

number of molecular weight of $Z = 16$ per cell; that is, $Z' = 4$ per spectroscopic primitive cell.

In a first approximation, with taking into account the partial substitution of the S^{2-} anions by the $(S_2)^{2-}$ groups, one can decompose this structure assuming some ionic character as follows:

$$4 \, [CrP_3S_9] \Leftrightarrow 4 \, (Cr^{3+}) + 6 \, (P_2S_6)^{2-}.$$
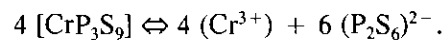
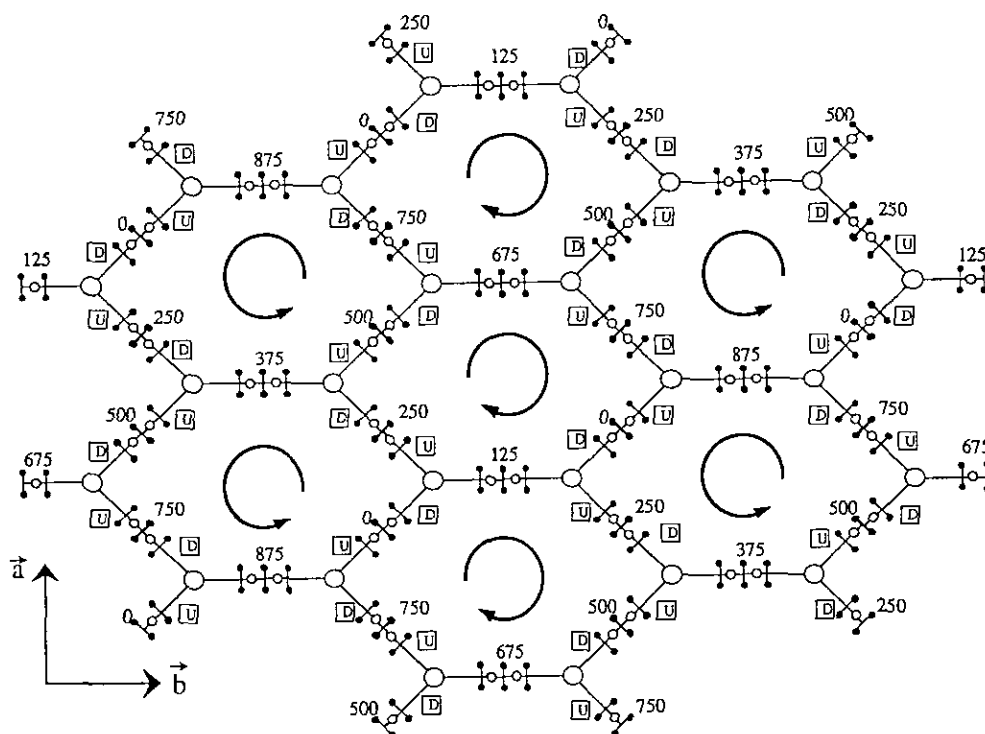With Cr^{3+} ions in C_2^y (16f) sites, these will give rise to low-frequency modes of translational and distortion

FIG. 5. One of the three interlocked networks built from the cluster of Fig. 4, constituting the $CrP_3S_{9.25}$ structure. Numbers represent fractional heights ($\times 1000$) of the (P_2S_6) groups.
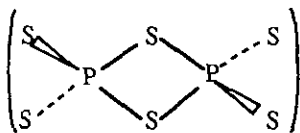
types:

$$\Gamma^{C_{2v}}_{site} = \qquad 1A \qquad + \qquad 2B$$

$$\Gamma^{D_{2h}}_{crystal} = 1A_g + (1A_u) + 1B_{2g} + 1B_{2u} + 2B_{1g} + \underline{2B_{1u}} + 2B_{3g} + \underline{2B_{3u}}$$
(in)

One obtains six Raman-active modes (italic symbols) and five infrared-active modes (underlined symbols) (in, inactive). Possible coincidences may be expected between the infrared and Raman band wavenumbers.

The $(P_2S_6)^{2-}$ anionic groups represented in space as

are of the Al_2Cl_6 type with a D_{2h} internal symmetry. One finds a first family with P_2 and $\tau = 0.5$ in a $(8a)D_2$ site (i.e., two anions per primitive cell).

A second family corresponds to P_1 and $\tau = 1.0$ in a $(16c)$ C_i site (i.e., four anions per primitive cell). According to (8), it is possible to determine the 18 fundamental vibrations of an Al_2Cl_6-type group (with conservation of the notations and numberings of the vibrations as shown in Table 1 which indicates the frequencies) and to establish the following correlation diagrams.

First family:

$$\Gamma^{D_{2h}}_{anion} = 4A_g + (1A_u) + 2B_{1g} + 3B_{1u} + 2B_{2g} + 2B_{2u} + 1B_{3g} + 3B_{3u}$$

$$\Gamma^{D_2}_{site} = \qquad 5A \qquad + \qquad 5B_1 \qquad + \qquad 4B_2 \qquad + \qquad 4B_3$$

internal modes:

$$\Gamma^{D_{2h}}_{crystal} = (5A_g + (5A_u)) + (5B_{1g} + 5B_{1u}) + (4B_{2g} + 4B_{2u}) + (4B_{3g} + 4B_{3u})$$
(in)

external modes:

$$\Gamma^{D_{2h}}_{rot} = \qquad\qquad 1 \quad\quad 1 \quad\quad 1 \quad\quad 1 \quad\quad 1 \quad\quad 1$$

$$\Gamma^{D_{2h}}_{transl} = \qquad\qquad 1 \quad\quad 1 \quad\quad 1 \quad\quad 1 \quad\quad 1 \quad\quad 1$$

Eighteen Raman-active internal modes plus $3R'$ and $3T'$ are thus expected, as well 13 infrared-active internal modes plus $3R'$ and $3T'$. Indeed, there may again be possible coincidences between Raman and infrared signals.

Second family:
$(P_2S_6)^{2-}$ anions in the C_i $(16c)$ site:

$$\Gamma^{D_{2h}}_{anion} = 4A_g + 2B_{1g} + 2B_{2g} + 1B_{3g} + (1A_u) + 3B_{1u} + 2B_{2u} + 3B_{3u}$$

$$\Gamma^{C_i}_{site} = \qquad\qquad 9A_g \qquad\qquad + \qquad\qquad 9A_u$$

internal modes:

$$\Gamma^{D_{2h}}_{crystal} = (9A_g + 9B_{1g} + 9B_{2g} + 9B_{3g}) + ((9A_u) + 9B_{1u} + 9B_{2u} + 9B_{3u})$$
(in)

external modes:

$$\Gamma^{D_{2h}}_{rot} = \quad 3 \qquad 3 \qquad 3 \qquad 3$$

$$\Gamma_{transl} = \qquad\qquad\qquad\qquad (3) \qquad 3 \qquad 3 \qquad 3$$
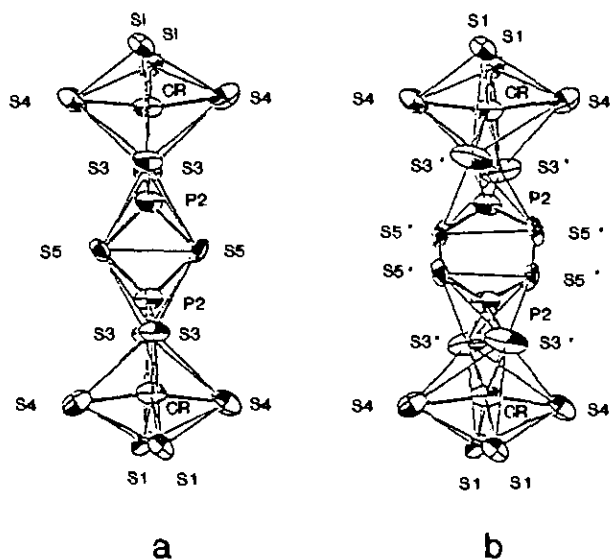(in)

FIG. 6. View of the thiophosphate group (a) without the substitution of the two S5 sulfurs and (b) with the substitution of the two S5 sulfurs by two pairs (S5') giving a (P$_2$S$_8$) group.

Thirty-six Raman-active internal modes are thus expected with 12R', and 27 infrared-active internal modes with 9T', with a mutual exclusion between Raman and infrared responses.

Three acoustic modes with zero frequencies (at the Brillouin zone center, $k = 0$) still must be subtracted from these modes, and, a priori, they can be substracted from the T' modes of anions, which are much heavier than the cations. This implies that one expects rather complex spectral patterns because of the two families of (P$_2$S$_6$)$^{2-}$ anions, crystallographically different or nonequivalent.

Compounds with similar anions like Tl$_2$P$_2$S$_6$ (9, 10) and Ag$_2$P$_2$S$_6$ (11), with much more simple cells, may be of great help (see below) for studying CrP$_3$S$_{9.25}$.

Finally, the occurrence of (S$_2$)$^{2-}$ pairs in substitution will introduce extra infrared signals that will be difficult to localize because the ν_a[PS$_2$(b)] (b; bridging) bands are expected to be very intense (see Table 1). In Raman, for which the spectral zone is more favorable, the ν(S–S)$^{2-}$ mode is expected to appear in the 480–520 cm^{-1} region according to the Steudel empirical relation (6, 12).

IV. THEORETICAL FORECAST FOR THE PHASES Tl$_2$P$_2$S$_6$ AND Ag$_2$P$_2$S$_6$

IV.1. Tl$_2$P$_2$S$_6$

The crystal structure and vibrational spectra of Tl$_2$P$_2$S$_6$ have already been studied by Brockner et al. (9, 10). The symmetry is orthorhombic, with the space group $I_{mmm}(D_{2h}^{25})$ and $Z = 2$ formula weights per unit cell, i.e., $Z' = 1$ per primitive spectroscopic cell.

This corresponds to 2 Tl$^+$ ions in site 4e (C_{2v}^x) and one (P$_2$S$_6$)$^{2-}$ anion in site 2a (D_{2h}). Hence the following modes can be classified.

(T') Cations Tl$^+$:

$$\Gamma_{site}^{C_{2v}^x} = 1A_1 \quad + \quad 1B_1 \quad + \quad 1B_2$$

$$\Gamma_{crystal}^{D_{2h}} = (1A_g + 1B_{3u}) + (1B_{1g} + 1B_{2u}) + (1B_{2g} + 1B_{1u})$$

One thus expects three low-frequency modes, active in Raman, plus 3 infrared-active low frequencies (with nonexclusion).

Anions (P$_2$S$_6$)$^{2-}$:

internal modes:	$\Gamma_{site} = \Gamma_{crystal}^{D_{2h}} = (4A_g + 2B_{1g} + 2B_{2g} + 1B_{3g}) + ((1A_u) + 3B_{1u} + 2B_{2u} + 3B_{3u})$		
			(in)
external modes:	$\Gamma_{rot}^{D_{2h}} =$	1	1	1
	$\Gamma_{transl}^{D_{2h}} =$				1	1	1

The correlation is straightforward both for the internal and external modes because of the type of site D_{2h} (2a).

One thus expects nine Raman-active internal modes–plus 3R'—and eight infrared-active internal modes—plus 3T'. A perfect exclusion between the Raman and infrared wavenumbers is expected for the internal modes of the anion and the three acoustic modes (translation of the whole molecules) with a zero frequency (1B$_{1u}$ + 1B$_{2u}$ + 1B$_{3u}$) will have to be eliminated.

IV.2. Ag$_2$P$_2$S$_6$

The structure of this phase was published by Toffoli et al. (11), and its vibrational study was performed recently (13). Ag$_2$P$_2$S$_6$ crystallizes in the monoclinic symmetry with the B_2/m space group (C_{2h}^3), with $Z = 2$ per unit cell, i.e., $Z' = 1$ per primitive spectroscopic cell. The Ag$^+$ ions are in the 4g site (C_2^z) and the (P$_2$S$_6$)$^{2-}$ anions are in site 2c (C_{2h}).

TABLE 1
Infrared and Raman Band Wavenumbers (cm^{-1}) and Proposed Assignments in Tl$_2$P$_2$S$_6$, Ag$_2$P$_2$S$_6$, and CrP$_3$S$_{9.25}$ Solid Compounds at 300 K

Tl$_2$P$_2$S$_6$ (Ref (6))		Ag$_2$P$_2$S$_6$ (This work)		CrP$_3$S$_{9.25}$ (This work)		Assignements for the (P$_2$S$_6$)$^{2-}$ anions (D$_{2h}$ symmetry)
IR	Raman	IR	Raman	IR	Raman	
			795 vw			$2 \times 398 = 2\nu_2 = 796\ cm^{-1}$
			786 vw			
					779 m	$2 \times 392 = 2\nu_2 = 784\ cm^{-1}$
	731 w					$2 \times 366 = 2\nu_2 = 732\ cm^{-1}$
					708 vw	$2\nu_2 - 78 = 706\ cm^{-1}$
665 w						
	645 w	644 s	641 vw	629 s ⊗	626 vw	$\nu_{17}+\nu_{18}=395+247=642\ cm^{-1}$
	612 vw		612 w		616 w	ν_{11} (B$_{2g}$)
		592 m		592 s ⊗	591 vw	ν_1 (A$_g$) and ν_8 (B$_{1u}$)
	592 ms		577 m			
		580 ms		567 vs ⊗	567 vw	
			554 w			$\nu_3+\nu_7 = 299+259 = 558\ cm^{-1}$
540 w		542 s		541 s	533 vw	$\nu_9+\nu_{18}=283+259=542\ cm^{-1}$
530 ms		520 vs		520 sh		with ν_{16} (B$_{3u}$)
	492 w		498 w		498 w	$\nu_6 + 75\ (78) = 493\ (498)\ cm^{-1}$
—		—		490 sh ⊗	491 m	ν (S-S)$^{2-}$
			474 vw			
480 m		466 s		465 sh ⊗	466 vw	ν_{13} (B$_{2u}$)
		454 sh		450 s		
420 mw		428 sh				ν_6 (B$_{1g}$)
	415 vs		418 vs		432 vs	
392 ms		395 ms		393 vs		ν_{17} (B$_{3u}$)
	366 m		398 s		392 s	ν_2 (A$_g$)
360 vw	360 vw		362 vw		—	$\nu_{17} - 32 = 392 - 32 = 360\ cm^{-1}$
345 ms		—			—	Impurity (Tl$_3$PS$_4$?)
				325 sh	334 m / 324 m	$\nu_7 + 78 = 253+78 = 331\ cm^{-1}$
	304 s		299 m	307 s ⊗	306 vw	ν_3 (A$_g$)
282 m		262 m		283 s		ν_9 (B$_{1u}$) with ν_{18} (B$_{3u}$)
249 ms		247 m		259 s		
	244 s		259 m / 233 w		253 m / 236 m	ν_7 (B$_{1g}$)
226 vs		226 vw		226 sh	226 vw	ν_{14} (B$_{2u}$)
218 vw	219 vw	210 ms			—	$\nu_{18} + 31 = 184 + 31 = 215\ cm^{-1}$
	196 m		206 m		188 w	ν_{15} (B$_{3g}$) with ν_4 (A$_g$)
	175 vs		200 m		176 w	
189 ms		184 ms		183 m		ν_{18} (B$_{3u}$)
	159 s		143 m		156 m / 148 sh / 131 vw	ν_{12} (B$_{2g}$)
122 m		120 m		124 w ⊗	121 vw	ν_5 (A$_u$)
		90 sh				
	75 s		75 w		78 mw	External modes with $\underline{T}$ $\underline{M}^+$ or Cr^{3+} (and ν_{10}(B$_{1u}$) ?)
		60 m	62 w			
	48 s		50 s		48 mw	
			41 w			
		31 vw	32 m			
	29 s		22 m		25 mw	

Note. ⊗, Coincidences between Raman and infrared wavenumbers. vw, Very weak; w, weak; m, medium; ms (mw), medium strong (weak); s, strong, vs, very strong; sh, shoulder.

Hence the following correlations must be applied. (T') Cations Ag$^+$:

$$\Gamma_{site}^{C_2^i} = \quad 1A \quad + \quad 2B$$

$$\Gamma_{crystal}^{C_{2h}} = \overbrace{(1A_g + 1A_u)} + \overbrace{(2B_g + 2B_u)}$$

Three active Raman and three active infrared models are expected (with possible coincidences). Anion $(P_2S_6)^{2-}$:

$$\Gamma_{anion}^{D_{2h}} = \underbrace{4A_g + 2B_{1g}} + \underbrace{2B_{2g} + 1B_{3g}} + \underbrace{1A_u + 3B_{1u}} + \underbrace{2B_{2u} + 3B_{3u}}$$

internal
modes:
$$\Gamma_{site}^{C_{2h}} = \Gamma_{crystal}^{C_{2h}} = \quad 6A_g \quad + \quad 3B_g \quad + \quad 4A_u \quad + \quad 5B_u$$

external
modes:
$$\begin{cases} \Gamma_{rot} = \quad 1 \quad\quad 2 \\ \\ \Gamma_{transl} = \quad\quad\quad\quad\quad\quad 1 \quad\quad 2 \end{cases}$$

$$\underbrace{}_{Raman} \quad \underbrace{}_{Infrared}$$

In this case, one thus expects a perfect exclusion between the infrared and Raman active modes. After substraction of the acoustic modes, one finds for the complete structure

$$\Gamma_{Total}^{C_{2h}} = \underset{\substack{15\ Raman \\ modes}}{(8A_g + 7B_g)} + \underset{\substack{12\ infrared \\ modes}}{(5A_u + 7B_u)}$$

V. EXPERIMENTAL RESULTS AND DISCUSSION

The Raman and infrared spectra are reported in Figs. 1, 2, and 3. They originate from Ref. (9) for Tl$_2$P$_2$S$_6$,

(13) for Ag$_2$P$_2$S$_6$, and from this work, respectively. The wavenumbers and corresponding assignments are gathered in Table 1, in which the assignments have been completed and sometimes modified as compared to the original work of Brockner *et al.* (9).

It is to be noted that the spectra of Ag$_2$P$_2$S$_6$ and CrP$_3$S$_{9.25}$, obtained as indicated in Section II (recording range, 20–900 cm^{-1}), are of very good quality and present striking similarities in the spectral responses between 100 and 600 cm^{-1}. The majority of the observed bands are thus to be assigned to internal modes of the $(P_2S_6)^{2-}$ anions of D_{2h} symmetry exhibiting terminal PS$_2$ groups (PS$_2$(t)) and bridging PS$_2$ groups (PS$_2$(b)). We have used the following numbering for these 18 vibrations:

$A_g : \nu1 = \nu_S[PS_2(t)]; \nu2 = \nu_S[PS_2(b)]; \nu3 = \delta[PS_2(t)]; \nu = \delta$

$A_u : \nu5 = $ twist [PS$_2$]

$B_{1g} : \nu6 = \nu_a[PS_2(b)]; \nu7 = $ wag[PS$_2$]

$B_{1u} : \nu8 = \nu_a[PS_2(t)]; \nu9 = $ rock[PS$_2$]; $\nu10 = \tau_{inversion}$

$B_{2g} : \nu11 = \nu_a[PS_2(t)]; \nu12 = $ rock[PS$_2$]

$B_{2u} : \nu13 = \nu_a[PS_2(b)]; \nu14 = $ wag[PS$_2$]

$B_{3g} : \nu15 = $ twist[PS$_2$]

$B_{3u} : \nu16 = \nu_S[PS_2(t)]; \nu17 = \nu_S[PS_2(b]; \nu18 = \delta[PS_2(t)].$

In addition, many lines with weak intensities could be assigned to overtones or combinations. In particular the Raman signals around 730–790 cm^{-1} could be assigned to the first overtone of a mode at 366, 398, and 392 cm^{-1} in $Tl_2P_2S_6$, $Ag_2P_2S_6$, and $CrP_3S_{9.25}$, respectively. This led us to invert the assignments of the $\nu2$ (A_g) and $\nu6$ (B_{1g}) modes, because the enhancement of a totally symmetrical mode is more likely to occur under near-resonant Raman conditions.

Finally, contrary to the results observed with $Tl_2P_2S_6$ and $Ag_2P_2S_6$, it is believed possible to note a few infrared and Raman coincidences on the anion internal modes (noted $\otimes$ in Table 1). This is due to the first family of $(P_2S_6)^{2-}$ anions on D_2 sites and/or to the structural distortions involved by the partial substitution of some S^{2-} anions by $(S_2)^{2-}$ groups.

The presence of additional signals attributable to $\nu(S-S)^{2-}$ modes around 500 cm^{-1} is very delicate, possibly illusory in infrared. This is because of the occurrence of the very strong bands due to the $\nu16(B_{3u})$ and $\nu13(B_{2u})$ modes and of combinations in this region. In Raman, the spectral region is much clearer, in spite of a weak intensity combination at 492, 498, and 499 cm^{-1} in $Tl_2P_2S_6$, $Ag_2P_2S_6$, and $CrP_3S_{9.25}$ ($\nu6 + 75$ and $\nu6 + 78$). There remains then the only medium intensity signal at 491 cm^{-1} assignable to this vibration. The empirical Steudel relation (6)

$$\nu\,(S-S)^{2-}(cm^{-1}) = \frac{2.57 - d(S-S)(\text{Å})}{9.17 \times 10^{-4}}$$

yields a value of $d(S-S) \simeq 2.10$ Å for the $(S_2)^{2-}$ pairs, in good agreement with the diffraction study (2.07 Å). The agreement may be considered satisfactory since one cannot exclude possible vibrational couplings, in particular with $\nu1(Ag)$ and $\nu2(Ag)$.

VI. CONCLUSION

In this comparative vibrational (infrared and Raman) study of several compounds presenting similar $(P_2S_6)^{2-}$ groups, we have been able to confidently assign the internal vibrations of this anion. It has been difficult to detect the occurrence of the substituting $(S_2)^{2-}$ groups in $CrP_3S_{9.25}$, although a band in the Raman spectrum at 491 cm^{-1} can be attributed to the stretching vibration of such a unit. It yields an estimate of the $d(S-S)$ value (2.10 Å) in good agreement with previous diffraction data (1).

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