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Oxygen substitution of the hexathiodiphosphate(IV) ion in aqueous solution

Eric Prouzet,*[a] Mikiko Fukatani,[b] Mohamed Barj[c] and Pascal Janvier[d]

[a] *Laboratoire des Matériaux et Procédés Membranaires, CNRS UMR 5635, E.N.S.C.M., 8 rue de l'Ecole Normale, F-34296 Montpellier Cedex 5, France. E-mail: prouzet@cit.enscm.fr*
[b] *Chiyoda Corp. 31-37 Tsurumichuo 4-chome, Tsurumi-ku, Yokohama 230, Japan*
[c] *Laboratoire de Spectroscopie Infrarouge et Raman (LASIR, CNRS UPR 2631), USTL Bat. C5, F-59655 Villeneuve d'Ascq Cedex, France*
[d] *Laboratoire de Synthèse Organique, CNRS UMR 6513, Faculté des Sciences et Techniques, BP 92208, 2 rue de la Houssinière, F-44322 Nantes Cedex 3, France*

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Phosphorus-31 NMR and Raman analyses have been performed in order to check the stability of the hexathiodiphosphate(IV) anion $[P_2S_6]^{4-}$ in aqueous solutions. This anion appears to be better stabilized in basic media than in acidic ones. Moreover, a gentle oxidation by a diluted solution of hydrogen peroxide allowed a partial substitution of sulfur by oxygen atoms that leads to mono- and di-substituted anions, respectively, $[P_2S_5O]^{4-}$ and $[P_2S_4O_2]^{4-}$, with a total yield of 72% conversion, compared with the initial hexathiodiphosphate anion.

1 Introduction

The divalent transition metal thiophosphates $M^{II}PS_3$ (M = Mn, Co, Fe, Ni or Zn) or $M^{I}_{1/2}M'^{III}_{1/2}PS_3$ compounds (M = Ag or Cu and M′ = V, Cr or In) obtained by heterosubstitution of the divalent metal constitute a large family of generally layer compounds that exhibit varied structural behaviours leading to a wide field of intercalation compounds with specific properties.[1–8] All these compounds are usually synthesized by classical solid state chemistry processes where elements are mixed in stoichiometric proportions and heated around 700 °C for days in an evacuated sealed tube. However, for almost ten years, it has been shown that similar phases can be obtained through a soft chemistry process with room temperature reactions in water between transition metal salts and the $[P_2S_6]^{4-}$ ion provided by dissolution of either $Li_4P_2S_6$ or $Na_4P_2S_6$ salts. The compounds $NiPS_3$ and $FePS_3$[9–13] were first synthesized and this family was recently increased by the synthesis of $Sn_2P_2S_6$[14] and $CuInP_2S_6$.[15] Unexpectedly, the hexathiodiphosphate $[P_2S_6]^{4-}$ ion is rather stable in water if specific conditions are observed, but varying the synthesis parameters can lead either to the breakage of this molecule or to obtaining oxothiophosphates like $NiPS_2O$.[16] As some syntheses require pH adjustment, we undertook ^{31}P NMR and Raman studies in order to see how far the $[P_2S_6]^{4-}$ ion preserves its integrity when dissolved in water at various pH. Our second aim was also to draw the limits of the partial substitution of sulfur by oxygen, in order to obtain new precursors for the synthesis of metal oxothiophosphates. Similar studies were previously reported on hexaoxodithio- or hexaoxotrithio-tetraphosphates,[17] oxothiophosphates $P_4O_{10-n}S_n$ ($n = 2$–9) with adamantane-like structures,[18] or hydridopentathiodiphosphate(III) $[P_2HS_5]^{3-}$.[19] However, until now, only monooxopentathiodiphosphate(IV) was obtained, as a minor reaction product in a mixture of thio- and oxothio-di- and tri-phosphates.[20]

2 Experimental

The salt $Li_4P_2S_6$ was prepared by heating at 450 °C in an evacuated sealed tube for 24 h a mixture of Li_2S, phosphorus and sulfur in the molar proportion 1 : 1 : 2. A white powder was obtained and aqueous solutions of 4 Li^+, $P_2S_6^{4-}$ were prepared by dissolution in deoxygenated deionized water in a cooling ice-bath followed by filtration. Such lithium thiodiphosphates in aqueous solution are yellowish.

Non-decoupled ^{31}P NMR analyses were performed on a AC 200 Bruker Fourier transform spectrometer equipped with a QNP. The spectrometer frequency was 81.01 MHz (offset 3 kHz), the sweep width 29411.76 Hz. Each recording was obtained by averaging 500 scans. The solutions were placed in 5 mm diameter tubes with, as external reference, a capillary tube containing a standard solution of 10% $(CH_3O)_3P$ in 90% of $(CD_3)_2CO$ $\{\delta[(CH_3O)_3P]\ 140\}$. All the chemical shifts were recalibrated by referring to H_3PO_4 (85%), as usual. Data treatment was performed by WIN-NMR 1D code.

The Raman spectra were recorded in the 100–600 cm^{-1} range with a T.800 CODERG spectrometer using an argon laser ($\lambda = 488$ nm).

3 Results and discussion

3.1 Stability with pH

In order to set the domain range of stability of the $[P_2S_6]^{4-}$ anion, we first undertook pH measurements of 0.23 mol l^{-1} solutions that had been prepared by dissolution of $Li_4P_2S_6$ in water, then acidified or basified by hydrochloric acid or lithium hydroxide, respectively. Measurements were performed after a week (Fig. 1). Both show that this salt exhibits an amphoteric behaviour that counterbalances the initial pH, but highest and lowest pH clearly lead to the total destruction of the compound (a solid precipitates). After a week all solutions with an initial pH between 2 and 12 gave final solutions with a pH close to 7. According to previous NMR results,[12,21] the ^{31}P NMR spectrum of the $[P_2S_6]^{4-}$ anion exhibits a single peak at $\delta \approx 108.4$, which can disappear upon slight acidification since NMR analyses showed that a final pH equal to 6.9 leads to the full destruction of this ion, marked by the disappearance of the peak. Thus, both acidic conditions and too long a period in solution induce a breaking of the molecule.

Stability under basic conditions was then explored through ^{31}P NMR analyses performed on more concentrated solutions

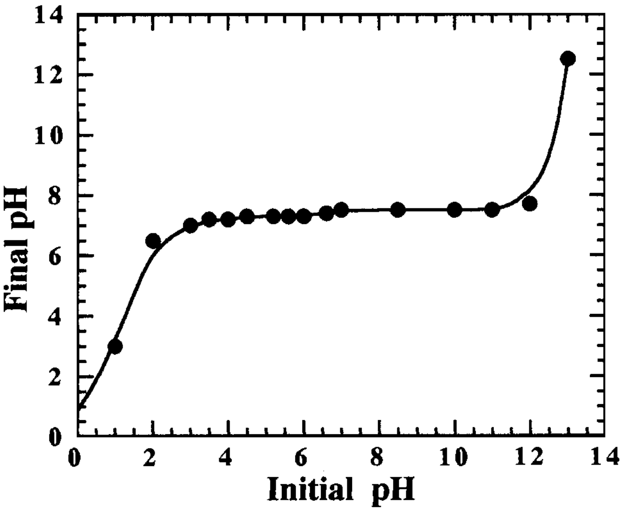

Fig. 1 Final pH of seven day old aqueous solutions of $Li_4P_2S_6$, *versus* the initial pH. This compound exhibits a tendency to counterbalance the initial pH toward a neutral one.

only allowed to stand for a shorter time: spectra were recorded for 24 h old (0.5 mol l^{-1}) solutions of $Li_4P_2S_6$. In this study, solutions were basified by adding lithium hydroxide with LiOH : $Li_4P_2S_6$ molar ratios equal to 0, 0.3, 0.5 and 1 : 1, respectively. After 24 h, the pH was equal to 10 for the first one and 14 for the others. The $[P_2S_6]^{4-}$ anion characteristic peak remains upon addition of LiOH, although two small new peaks appear at about δ 31 and 61. Finally, for the highest amount of LiOH added, another singlet at δ 85 and a doublet (δ 95.8 and 96.6) arise. However, these additional peaks exhibit low intensity, and do not correspond to more than 5% of the total phosphorus population in solution. This confirms that the $[P_2S_6]^{4-}$ anion is much more stable in basic media whereas it is readily destroyed in acidic solutions.

Twenty-four hour solutions, either acidified or basified by nitric acid or lithium hydroxide, were also analyzed by Raman scattering spectroscopy. The observed Raman spectra for the different pH conditions are compared in Fig. 2 and their attributions on the basis of $[P_2S_6]^{4-}$ vibrational modes are proposed in Table 1.

In the 200–600 cm^{-1} region one observes that only the spectrum in pure water (initial pH 5.5) is very similar to the spectra obtained for $Na_4P_2S_6$ aqueous solutions or in the solid state for $Na_4P_2S_6$,[22,23] $Li_4P_2S_6$[24] and MPS_3 compounds[25] where $[P_2S_6]^{4-}$ anions have been identified. It principally exhibits three significant components at 551 (medium), 376 (strong) and 260 (weak) cm^{-1}, which are discussed below. On the other hand, when both initial or acidic conditions have been applied, additional Raman peaks appear, mainly at 530, 352 and 222 cm^{-1}, whereas the peak at 376 cm^{-1} vanishes. These bands are probably due to the presence of partially oxygen substituted $[P_2S_6]^{4-}$ units.

For isolated $[P_2S_6]^{4-}$ units (D_{3d} point group), the vibrational selection rules predict six Raman active modes (3 A_{1g} and 3 E_g).[26] The strongest polarized (A_{1g} mode) peak located at 376 cm^{-1} is confidently assigned to the $\nu_{sym}(PS_3)$ symmetric stretching mode.[25] The high frequency component around 550 cm^{-1} and its shoulder around 560 cm^{-1} are attributed to the $\nu_d(PS_3)$ antisymmetric degenerate E_g stretchings. The ν(P–P) stretching A_{1g} mode could also be located in this spectral region.[24,25,27] This assignment of vibrational modes is in accord with the results of valence force field calculations performed for isolated $[P_2S_6]^{4-}$ units[24] and MPX_3[25] crystals, and also with lattice dynamic calculations on MPX_3.[27]

3.2 Sulfur substitution

We attempted in different ways (air bubbling, $HgCl_2$ oxidation) to substitute sulfur atoms by oxygen. This substitution was finally achieved by slowly adding a 4% solution of hydrogen peroxide (prepared from a 30% Aldrich solution). Several solutions with H_2O_2 : P_2S_6 molar ratios between 0 and 4 : 1 were prepared by adding dropwise the hydrogen peroxide to a 0.5 mol l^{-1} solution of $Li_4P_2S_6$ previously basified at pH 14 with lithium hydroxide. Addition of hydrogen peroxide is exothermic and must be carefully undertaken in a cooling ice-bath if one wants to avoid the whole destruction of the molecule. The initial basification was induced once preliminary observations had shown that hydrogen peroxide addition was followed by a further acidification of the solution. Since $[P_2S_6]^{4-}$ ions have been shown to be unstable under acidic conditions, this allowed us to add H_2O_2 whilst remaining in the stability region of the hexathiodiphosphate anion. An example of a ^{31}P NMR spectrum of the 24 h old solutions is displayed in Fig. 3 and observed chemical shifts and assignments are given in Table 2.

Table 1 Raman spectra lines of 24 h old aqueous solutions of $Li_4P_2S_6$ in cm^{-1}, and their comparison with literature data (v = very, s = strong, m = medium, w = weak, P = polarized)

Number and symmetry (D_{3d})[22]	Solid $Li_4P_2S_6$[21]	$Na_4P_2S_6$ in solution[23]	$Li_4P_2S_6$ in water (this study)
$\nu_d(PS_3)$, $\nu_{10}(E_g)$	571w	575w	561(sh)
ν(P–P), $\nu_3(A_{1g})$	547m	548m	551m
	495w		
$\nu_{sym}(PS_3)$, $\nu_1(A_{1g})$	382vs	372vs	376vs (P)
			352w
	283m		
$\delta_d(PS_3)$, $\nu_{11}(E_g)$	255s	258s	260w
$\rho_r(PS_3)$, $\nu_{12}(E_g)$	186s	180 (sh)	120–225 (br) (P)
or $\delta_s(PS_3)$, $\nu_2(A_{1g})$	98w		

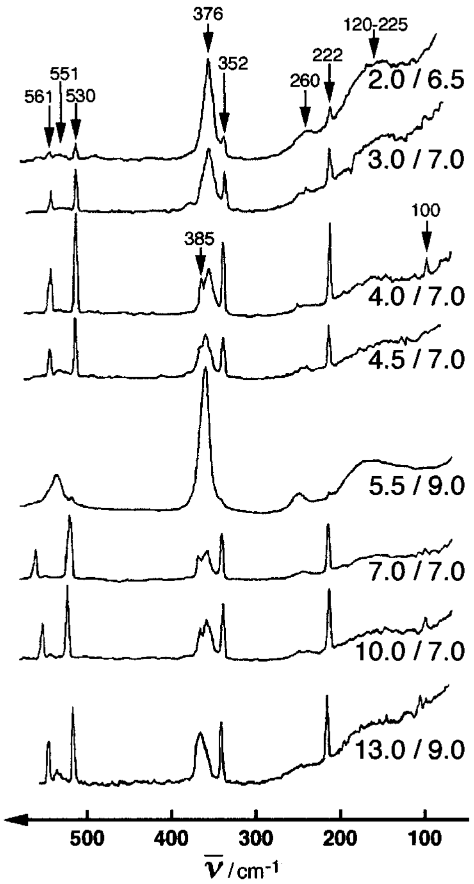

Fig. 2 Raman scattering spectra of 24 h old aqueous solutions of $Li_4P_2S_6$ initially acidified or basified by nitric acid or lithium hydroxide, respectively. Initial pH values are given together with and final pH at the measurement time, separated by solidi. Only the pure water solution (initial pH 5.5) exhibits the expected peaks at 120–225, 260, 376 and 551 cm^{-1} whereas these peaks vanished upon acidification or basification.

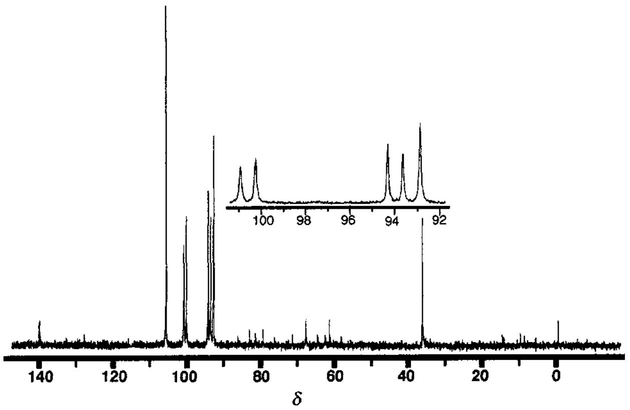

Fig. 3 ^{31}P NMR spectra of 24 h old aqueous solutions of $Li_4P_2S_6$, partially substituted by addition of hydrogen peroxide ($H_2O_2:Li_4P_2S_6$ molar ratio = 4:1). inset: the δ 92–102 region.

Table 2 ^{31}P NMR chemical shifts (in ppm with reference to H_3PO_4), J_{P-P}/Hz and respective percentage populations (in square brackets) of 24 h old parent ($P_2S_6^{4-}$, 4 Li^+) solution and partially substituted ions after hydrogen peroxide addition

$H_2O_2:Li_4P_2S_6$	PS_3–PS_3	PS_3–PS_2O	OS_2P–PS_2O
0	108.6 [100]		
0.1	108.3 [92]	99.7–96.4 (J = 65) [7]	90.1 [1]
0.5	108.0 [88]	98.2–94.2 (J = 62) [10]	90.6 [2]
1.0	105.6 [84]	99.7–93.7 (J = 56) [13]	91.8 [3]
1.5	105.8 [48]	100.6–94.1 (J = 52) [38]	92.8 [14]
4.0	105.7 [28]	100.6–94 (J = 55.0) [52]	92.9 [20]

After addition of hydrogen peroxide new peaks appear in the NMR spectra. There are two doublets at δ 100.6 and 94, respectively, with the same 55 Hz coupling for both. There are also two single peaks, at δ 93 and 35. The latter peak can be assigned to the $[SPO_3]^{3-}$ anion, resulting from the breaking of the pristine molecule. Chemical shifts for the $[PS_{4-x}O_x]^{3-}$ ions have been shown to decrease with increasing oxygen substitution, since they give the values δ 87, 86, 62, 32 and 0, respectively when x varies from 0 to 4.[28] The same trend can be applied to the oxothiodiphosphate anions $[P_2S_{6-x}O_x]^{4-}$ and one can conclude that both the doublets at δ 100.6 and 94 correspond to the oxopentathiodiphosphate anion $[P_2S_5O]^{4-}$ with chemical shifts assigned to the PS_3 and PS_2O parts, respectively, since the two phosphorus atoms are no longer equivalent. This is confirmed by the same J_{P-P} coupling of 55 Hz. The single peak at δ 93 is thus due to the symmetrical dioxotetrathiodiphosphate ion $[P_2S_4O_2]^{4-}$. Small peaks in the δ 60–80 region show that minor by-products are also obtained, surely resulting from the breaking of the P–P bond. The respective populations of $[P_2S_6]^{4-}$, $[P_2S_5O]^{4-}$ and $[P_2S_4O_2]^{4-}$ ions are given in Table 2. Hydrogen peroxide appears to be a good substitution agent since, for the $H_2O_2:P_2S_6$ molar ratio equal to 4:1, one obtains up to 72% substitution including mono- or di-substituted ions, without significant destruction of the molecule (no precipitate is observed). Besides, it appears that the second substitution always occurs in a symmetrical way, with the formation of the $[PS_2O–PS_2O]^{4-}$ ion. Further substitution seems not to be readily achievable without losing the integrity of the phosphorus–phosphorus bond as demonstrated by a noticeable amount of $[SPO_3]^{3-}$ ions (δ 35) and finally H_3PO_4 (δ 0) when full oxidation has been achieved through further addition of H_2O_2.

4 Conclusion

The $[P_2S_6]^{4-}$ anion is a fundamental unit for the synthesis of a wide family of metal thiophosphates by soft chemistry processes. Our study has shown that, when dissolved in water, it keeps its integrity if it is stored in basic aqueous media, though the storage time can hardly extend beyond 2 d. This stability allowed us to carry out a partial substitution of sulfur ligands by oxygen. Both monosubstituted oxopentathiodiphosphate(IV) and disubstituted dioxotetrathiodiphosphate(IV) ions have been obtained with relative proportions up to 52 and 20%, respectively. This process opens a new field for the synthesis of oxothiophosphate compounds similar to the $NiPS_2O$ compound previously synthesized.[16]

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