$(PPh_3\text{-}C_3H_6\text{-}PPh_3)_{0.5}[NiPS_4]$ and $(PPh_3\text{-}C_2H_2\text{-}PPh_3)_{0.5}[NiPS_4]$: Two new compounds containing $[NiPS_4]^-$ chains

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From bowl-like $[Ni_3P_3S_{12}]^{3-}$ anions containing DMF–$KNiPS_4$ solutions, metathesis experiments were successfully carried out using bi-charged anisotropic organic species and led to two new amorphous $(PPh_3\text{-}C_3H_6\text{-}PPh_3)_{0.5}[NiPS_4]$ (**I**) and $(PPh_3\text{-}C_2H_2\text{-}PPh_3)_{0.5}[NiPS_4]$ (**II**) compounds. Thanks to solid state ^{31}P NMR, Raman and IR spectroscopies, it has been proved that **I** and **II** enclose $[NiPS_4]^-$ chains. Hence, $[Ni_3P_3S_{12}]^{3-}$ discrete entities can rearrange into chains similar to those observed in the pristine $KNiPS_4$ inorganic materials.

1 Introduction

Recently, several studies in solution have been carried out on $KNiPS_4$.[1,2] In the solid state, $KNiPS_4$ is composed of $1/_\infty[NiPS_4]^-$ infinite chains.[3] These chains are built upon $[MS_4]$ rectangles and $[PS_4]$ tetrahedra sharing edges. $KNiPS_4$ exfoliates in DMF or DMSO and the $1/_\infty[NiPS_4]^-$ chains undergo a solvent-induced auto-fragmentation with a reorganization into discrete crown-shaped $[Ni_3P_3S_{12}]^{3-}$ trinuclear entities.[1,2] From a structural point of view, in the $[Ni_3P_3S_{12}]^{3-}$ discrete anions, each $[NiS_4]$ polyhedron shares two edges with two $[PS_4]$ tetrahedra and two corners with two other $[NiS_4]$ rectangles. The breaking up of the chains into $[Ni_3P_3S_{12}]$ entities, corresponding to a shift from anisotropic to isotropic particles, was first evidenced by the loss of birefringence for the solution. Then, the exfoliation and fragmentation of the chains in solution have been studied by mass spectroscopy and ^{31}P NMR of the sols.[1,2]

Due to the occurrence of the anionic molecular $[Ni_3P_3S_{12}]^{3-}$ species in DMF solution, exchange reactions have been considered. For the first time, potassium cations have been exchanged by isotropic monovalent organic cations A, such as A = tetraphenyl phosphonium (PPh_4^+), tetramethyl ammonium ($(CH_3)_4N^+$) and tetraethyl ammonium ($(C_2H_5)_4N^+$) or slightly anisotropic methyl morpholinium ($[C_9N_1H_{22}]^+$), leading to $A_3[Ni_3P_3S_{12}]$ compounds with the stabilization, in the solid state, of crown-shaped $[Ni_3P_3S_{12}]^{3-}$ anions in all cases.[1,2] More recently, exchanges with single-charged anisotropic cations, such as *n*-hexyltrimethylammonium ($[CH_3\text{-}(CH_2)_5\text{-}N(CH_3)_3)]^+$) or dodecyltrimethylammonium ($[CH_3\text{-}(CH_2)_{11}\text{-}N(CH_3)_3]^+$), were performed with the help of a macrocyclic molecule, such as (222)-cryptand, leading also to the stabilization, in the solid state, of crown-shaped $[Ni_3P_3S_{12}]^{3-}$ anions.[4] The cyclic cryptand molecule, well known to selectively encapsulate cations of appropriate size,[5,6] is expected to increase the solubility of $KNiPS_4$ and the reactivity of the anion by complexing the cation and thus enhancing hopefully the reactivity of the phase in contact with a prospective solvent.

It has been observed that, when isotropic or anisotropic organic single-charged cations are introduced in the $KNiPS_4$–DMF solution, the discrete $[Ni_3P_3S_{12}]^{3-}$ entities, already present in solution, are maintained in the solid state. The anionic arrangement goes then from 1D with K^+ to 0D with A^+ isotropic or anisotropic cations. This is in accordance with the tendency that the larger the cation size and/or the higher the concentration of the counter cation, the lower the dimensionality of the covalent sub-network.[7–9]

In order to study the influence of the charge of the cation on the nickel thiophosphate anion arrangement, experiments have been performed by using bi-charged organic cations with two separated single-charges in substitution of K^+ in $KNiPS_4$. We then report the preparation of two new compounds, $(PPh_3\text{-}C_3H_6\text{-}PPh_3)_{0.5}[NiPS_4]$ (**I**) and $(PPh_3\text{-}C_2H_2\text{-}PPh_3)_{0.5}[NiPS_4]$ (**II**), by metathesis reactions between K^+ and these bi-charged cations with the help of a crown ether. The macrocyclic molecule used in this work, 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane), is very well adapted in complexing potassium ions ($r_{K^+} = 1.33$ Å) because of the suitable size of its cavity ($r = 1.45$ Å).

Surprisingly and contrary to the exchange with anisotropic cation,[4] we obtain the same amorphous and insoluble compounds with or without the help of the macrocyclic molecule. Since no attempts to crystallize the materials proved successful, several spectroscopic methods were used to determine the conformation of the anionic part of our phases. First, solid state ^{31}P NMR was performed on powder of **I** and **II** and the two spectra were compared with those of $KNiPS_4$ (**III**) and $(PPh_4)_3[Ni_3P_3S_{12}]$ (**IV**).[1,2] Then, infrared and Raman analysis of **I** and **II** were carried out. Regarding the large literature devoted to thiophosphate compounds, a vibrational approach

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clearly proved to be a suitable method to acquire information about the structure. In effect, a detailed spectroscopic study (Raman scattering and infrared absorption spectroscopies combined with valence force field calculations) with precisely defined length and constitution has already provided information not only about the molecular vibrations of these thiophosphates[10–12] but also about their electronic configuration. Indeed, the Raman and IR spectroscopies are highly sensitive to even small structural or electronic alterations: they are thus well adapted techniques within the scope of this structural study of our amorphous phases, for which the anionic arrangement is unknown. The assignment of the fundamental modes in the 50–650 cm^{-1} range will be proposed by comparison with the vibrational characteristics of the inorganic polymer anionic chain $1/_\infty[NiPS_4]^-$[10] and of the bowl-like structure of $[Ni_3P_3S_{12}]^{3-}$ anions[11] present in **III** and **IV** respectively.

2 Experimental section

2.1 Synthesis

All experiments were carried out under a dry nitrogen atmosphere.

$(PPh_3\text{-}C_3H_6\text{-}PPh_3)_{0.5}[NiPS_4]$ (I). 0.74 mmol of $KNiPS_4$, prepared as previously described,[3] and 1 mmol of 18-crown-6 was dissolved in 10 ml DMF (dimethylformamide) under magnetic stirring at 50 °C for one day. After filtration, 1.55 mmol of trimethylene bis(triphenylphosphonium) bromide was added to the solution and allowed to react for 1 hour. The precipitate, a brown powder, was washed with DMF and diethyl ether. The so-formed compound is air-stable and insoluble in DMF, acetonitrile, dichloromethane and chloroform. An EDXS (Energy Dispersive X-ray Spectroscopy) analysis of the heaviest elements by means of a Jeol microscope (PGT-IMIX-PTS equipped Jeol-JSM5800LV) yielded the elemental ratio $Ni_{1.0}$:$P_{1.9}$:$S_{3.9}$:$K_{0.0}$.

$(PPh_3\text{-}C_2H_2\text{-}PPh_3)_{0.5}[NiPS_4]$ (II). The synthesis was analogous to that of **I** except that 1 mmol of 1,2-vinylene bis(triphenylphosphonium) bromide was added in place of trimethylene bis(triphenylphosphonium) bromide. The compound, a brown powder, is also air-stable and also insoluble in DMF, acetonitrile, dichloromethane, chloroform. The EDXS analysis of the heaviest elements yielded the elemental ratio $Ni_{1.0}$:$P_{2.0}$:$S_{4.1}$:$K_{0.0}$.

2.2 NMR spectroscopy

Solid State ^{31}P NMR spectra were recorded on a Bruker DSX400 spectrometer operating at 9.4 T, using CP-MAS $\{^1H\}$–^{31}P excitation with a typical contact time of 1.5 ms and a 1 s recycle time. Spectra were simulated using the "dmfit" sofware package.[13]

2.3 Spectroscopic investigations

Infrared absorption spectra of the brown powders were collected with a Nicolet 20 SXC FTIR and a Nicolet 20 SF FTIR (far infrared). The data were recorded by transmission (KBr and polyethylene pellets technique) at room temperature. A 4 cm^{-1} spectral resolution was considered for all the IR experiments and the spectra were corrected from the substrate absorption.

The Raman scattering spectra were measured with several lines ranges from 457.9 to 1064 nm. Raman characteristics obtained with the excitation lines in the visible range (457.9 and 514.5 nm with an Argon ion laser and 676.4 nm with a Krypton laser) were recorded using a microscope on a multichannel Jobin-Yvon T64000 spectrometer connected to a nitrogen-cooled Charged Coupled Device (CCD) detector (resolution around 8 cm^{-1}). The scattering signal was collected with a back-scattering geometry under the microscope. In order to avoid the problems of degradation, the spectra were recorded with a power beam of about 1 mW. The laser beam was about 10 μm wide. The longest excitation wavelength used so far is 1064 nm. The Raman spectra excited at this near-infrared laser excitation (Nd:YAG laser) was measured on a Fourier Transform Raman spectrophotometer (RFS 100 Brucker).

3 Results and discussion

3.1 NMR spectroscopy

As **I** and **II** are amorphous, ^{31}P experiments were carried out on powders to determine whether they contain $1/_\infty[NiPS_4]^-$ fragments or $[Ni_3P_3S_{12}]^{3-}$ oligomers. ^{31}P NMR spectra of **III** and **IV** were used as references (Fig. 1) (the spectra of **I** and **II** being similar, only that of **I** is given).

From previous works,[1,2,14] it is known that the ^{31}P solid state NMR spectrum of $KNiPS_4$ exhibits only one resonance peak at $\delta = 119.7$ ppm characteristic of the crystallographically equivalent phosphorus atoms in the chain, whereas that of $(PPh_4)_3[Ni_3P_3S_{12}]$ exhibits six resonances lines at 111.5, 110.5, 108.0, 21.7, 18.8 and 18.2 ppm. The three first lines, very similar in intensity, have been assigned to the three crystallographically unequivalent P sites in the $[Ni_3P_3S_{12}]^{3-}$ anions while the three last peaks have been assigned to the three crystallographically unequivalent P sites in the tetraphenylphosphonium group. The asterisked peaks represent the rotation bands. It is noteworthy that the NMR signature of the trinuclear entity may be a little more intricate than the one observed in $(PPh_4)_3[Ni_3P_3S_{12}]$ as evidenced in $[K(222\text{-cryptand})_3]$-$[Ni_3P_3S_{12}]$ and $[CH_3(CH_2)_{11}N(CH_3)_3]_3[Ni_3P_3S_{12}]$[4] (*i.e.* a slight shift in frequency of the NMR signals, unequal peak intensity, and the possible appearance of a fourth peak whose origin remains unexplained).

The spectrum of **I** is composed of one wide peak at 22.9 ppm characteristic of the phosphorus contained in the $(PPh_3\text{-}C_3H_6\text{-}PPh_3)^{2+}$ cation and of a very broad band located between 131 and 102 ppm. The major contribution to this band is a line located at $\delta = 122$ ppm. This suggests the

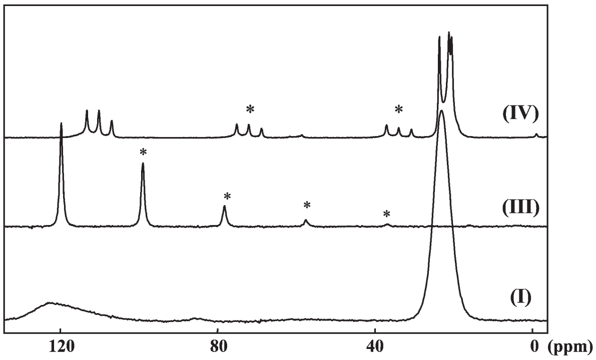

Fig. 1 Superposition of the $KNiPS_4$ (**III**), $(PPh_4)_3Ni_3P_3S_{12}$ (**IV**) and $(PPh_3\text{-}C_3H_6\text{-}PPh_3)_{0.5}[NiPS_4]$ (**I**) ^{31}P solid state NMR spectra (spectra are referenced to H_3PO_4 as the standard $\delta = 0$). $KNiPS_4$ spectrum presents one peak at 122 ppm corresponding to phosphorus atoms inside the chain. $(PPh_4)_3Ni_3P_3S_{12}$ presents three peaks at high chemical shift corresponding to the three phosphorus of $[Ni_3P_3S_{12}]^{3-}$ and three other peaks at low chemical shift corresponding to the three distinct phosphorus atoms of the $[(PPh_4)_3]^{3+}$ cations. The last spectrum present a large peak at low chemical shift corresponding to the phosphorus signal of the $(PPh_3\text{-}C_3H_6\text{-}PPh_3)^{2+}$ cations and a very large peak between $\delta = [131\text{–}102]$ indicative of the presence of $[Ni_nP_nS_{4n}]^{n-}$ fragments in **I**.

existence of $[NiPS_4]^-$ chains in this material. The broad character of this band in **I** (and **II**) could originate from the existence of a wide distribution of $[Ni_nP_nS_{4n}]^{n-}$ linear fragments with an increase of the relative strength of the signals of the terminal $[PS_4]$ tetrahedra with a shortening of the links. Such an assertion remains to be proved by mass spectroscopy but this would go along with the observed amorphous nature of the material observed by X-ray diffraction techniques. Nevertheless, ^{31}P solid state NMR experiments cannot rule out unambiguously the presence of $[Ni_3P_3S_{12}]^{3-}$ anions in **I** and **II**. In order to confirm the chain-like structure of the anionic part in these materials, IR and Raman investigations have been undertaken.

3.2 IR and Raman spectroscopy

We now describe the fundamental vibrational modes of **I** and **II** in the 50–800 cm^{-1} spectral domain. The assignment of the bands in the 800–3600 cm^{-1} frequency range is not discussed because either the experimental frequencies are combinations and overtones or they come from the organic part of the compounds. Indeed, many peaks in the 800–3200 cm^{-1} spectral region can be ascribed without ambiguity to the benzenoid, vinyl and alkyl stretching and bending modes.

In Figs. 2 and 3 are given the Raman spectra and the IR spectra of $(PPh_3\text{-}C_3H_6\text{-}PPh_3)_{0.5}[NiPS_4]$ (**I**), $(PPh_3\text{-}C_2H_2\text{-}PPh_3)_{0.5}[NiPS_4]$ (**II**), $(PPh_4)_3Ni_3P_3S_{12}$ (**IV**), $(PPh_4\text{-}C_3H_6\text{-}PPh_4)Br_2$ (**V**) and $(PPh_4\text{-}C_2H_2\text{-}PPh_4)Br_2$ (**VI**). For the Raman spectra, only data collected at 676.4 nm are discussed because the spectral patterns recorded with an exciting radiation of 457.9, 514.5, 676.4 or 1064 nm are practically the same. In fact, no frequency dispersion is observed, only the relative intensities vary from one wavelength to the other when going from 457.9 to 1064 nm.

For the sake of clarity, the most characteristic Raman and IR bands will be discussed separately and the notation established by C. Sourisseau *et al.*[10,11] will be adopted. The experimental frequencies are collected in Tables 1 and 2.

The 150–800 cm^{-1} spectral range turns to be of a particular interest because it corresponds to the domain of the *P–S* stretching and bending modes. Consequently, its study was supposed to yield information sufficient to determine the nature of the structural arrangement around the $[PS_4]$ tetrahedra and to address the question about the presence of inorganic polymer chain or bowl-like character of the $[Ni_3P_3S_{12}]^{3-}$ anions in compounds **I** and **II**.

Based on the spectroscopic investigations of $KNiPS_4$[10] and $(PPh_4)_3[Ni_3P_3S_{12}]$,[11] and a vibrational assignment by a complete force field lattice dynamic calculations for the former and valence force field calculations for an isolated $[Ni_3P_3S_{12}]^{3-}$ anions of C_{3v} symmetry for the latter, we can assign the different bands of **I** and **II** as follow. The Raman lines at 614, 432, 350, 300, 273 and 208 cm^{-1} could be associated either to the $\nu_3(F_2)\ PS_4^{3-}$, $\nu_1(A_1)\ PS_4^{3-}$, $\nu_4(F_2)\ PS_4^{3-}$, $\nu_4(F_2)\ PS_4^{3-}$, $\nu_2(E)\ PS_4^{3-}$, $T' + R'$ PS_4 vibrations of $1/_\infty[NiPS_4]^-$ chains or to the $\nu_3(F_2)\ PS_4^{3-}$ + mode PPH_3, $\nu_1(A_1)\ PS_4^{3-}$, $\nu_1(A_1)\ PS_4^{3-}$, $\nu_4(F_2)\ PS_4^{3-} + \nu\ NiS_4$, $\nu_4(F_2)\ PS_4^{3-} + \nu\ NiS_4$ and $\nu_2(E)\ PS_4^{3-} + \delta\ NiS_4$ + mode PPH_3 vibrations of discrete $[Ni_3P_3S_{12}]^{3-}$ anions by comparison with the compounds **III** and **IV** respectively (Table 1). Indeed, the equivalent modes appears at 608, 432, 348, 307, 264 and 209 cm^{-1} for **III** and at 614, 431, 351, 305, 282 and 212 cm^{-1} for **IV**. Unfortunately, no important difference has been noted between **I** and **II** and the Raman spectra of the $1/_\infty[NiPS_4]^-$ inorganic polymer anionic chain present in **III** and the bowl-like structure of $[Ni_3P_3S_{12}]^{3-}$ anions present in **IV**. Thus, the Raman spectroscopy turns out to be not a relevant technique to elucidate the nature of the structural arrangement of the mineral framework in **I** and **II**.

More interesting results come from infrared spectroscopy. Fig. 3 presents the infrared spectra of **I**, **II** and **IV**. Let us note that the data features of **I** and **II** with regards to those of the inorganic polymer anionic chains as $1/_\infty[NiPS_4]^-$ anions present in **III** are very similar[10] (Table 2). Hence, $KNiPS_4$ presents four main IR-bands observed at 600, 571, 355 and 266 cm^{-1}, while five bands are situated at 597, 561, 534, 350 and 268 cm^{-1} for **I** and at 600, 563, 526, 353 and 270 cm^{-1} for **II** (Fig. 3), the absorption band at about 530 cm^{-1} being assigned to the presence of triphenyl phosphonium groups in these materials. In contrast, the spectrum of the bowl-like structure of $[Ni_3P_3S_{12}]^{3-}$ is very different. Indeed, it presents five main bands at 651, 559, 524, 350 and 254 cm^{-1}, with two bands far away from those observed in **I** and **II** (Fig. 3). Consequently, these experimental IR results indicate that **I** and **II** are very likely to contain the $1/_\infty[NiPS_4]^-$ inorganic polymer anionic chain anions present in $KNiPS_4$ (**III**).

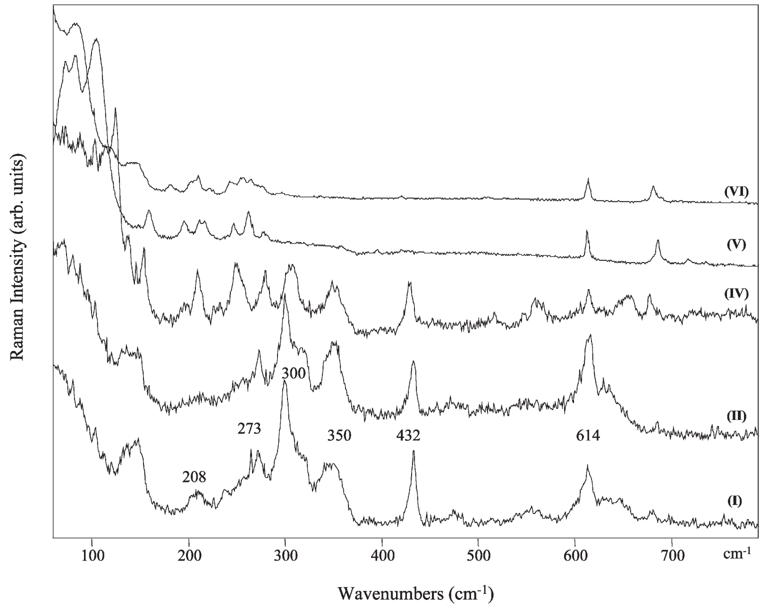

Fig. 2 Raman spectra of $(PPh_3\text{-}C_3H_6\text{-}PPh_3)_{0.5}[NiPS_4]$ (**I**), $(PPh_3\text{-}C_2H_2\text{-}PPh_3)_{0.5}[NiPS_4]$ (**II**), $(PPh_4)_3Ni_3P_3S_{12}$ (**IV**), $(PPh_4\text{-}C_3H_6\text{-}PPh_4)Br_2$ (**V**) and $(PPh_4\text{-}C_2H_2\text{-}PPh_4)Br_2$ (**VI**) collected with an exciting radiation of 676.4 nm.

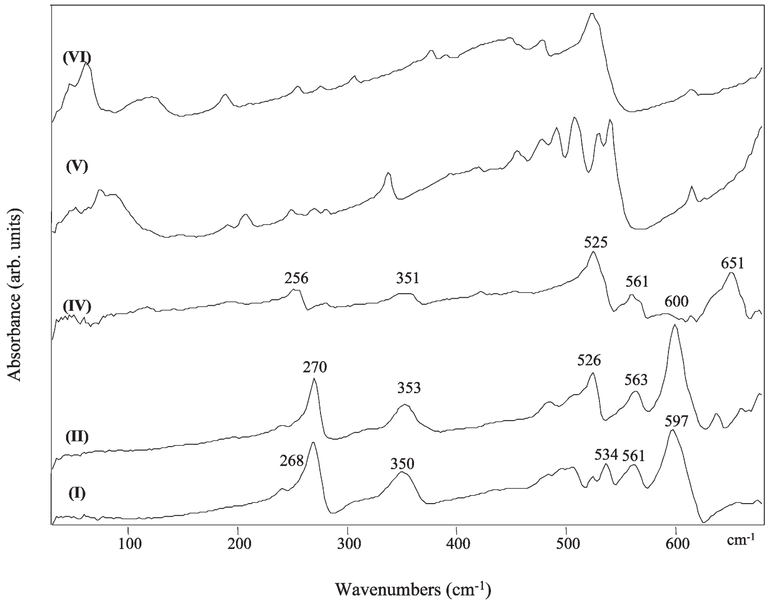

Fig. 3 IR spectra of $(PPh_3\text{-}C_3H_6\text{-}PPh_3)_{0.5}[NiPS_4]$ (**I**), $(PPh_3\text{-}C_2H_2\text{-}PPh_3)_{0.5}[NiPS_4]$ (**II**), $(PPh_4)_3Ni_3P_3S_{12}$ (**IV**), $(PPh_4\text{-}C_3H_6\text{-}PPh_4)Br_2$ (**V**) and $(PPh_4\text{-}C_2H_2\text{-}PPh_4)Br_2$ (**VI**).

Table 1 Raman band wavenumbers (cm^{-1}) observed in $(PPh_3\text{-}C_3H_6\text{-}PPh_3)_{0.5}[NiPS_4]$ (**I**) and$(PPh_3\text{-}C_2H_2\text{-}PPh_3)_{0.5}[NiPS_4]$ (**II**) compared to those observed in $KNiPS_4$ (**III**),[10] $(PPh_4)_3Ni_3P_3S_{12}$ (**IV**)[11] (tentative assignments of the bands in **III** and **IV** according to C. Sourisseau *et al.* are given in parentheses)

I and II	III	IV
614	608 ($\nu_3(F_2)$ PS_4^{3-})	614 ($\nu_3(F_2)$ PS_4^{3-} + mode PPH_4)
432	432 ($\nu_1(A_1)$ PS_4^{3-})	431 ($\nu_1(A_1)$ PS_4^{3-})
350	348 ($\nu_4(F_2)$ PS_4^{3-})	351 ($\nu_1(A_1)$ PS_4^{3-})
300	307 ($\nu_4(F_2)$ PS_4^{3-})	305 ($\nu_4(F_2)$ PS_4^{3-} + ν NiS_4)
273	264 ($\nu_2(E)$ PS_4^{3-})	282 ($\nu_4(F_2)$ PS_4^{3-} + ν NiS_4)
208	209 (T′ + R′ PS_4)	212 ($\nu_2(E)$ PS_4^{3-} + δ NiS_4 + mode PPH_4)

4 Conclusion

Our attempt to synthesis compounds containing bi-charged countercations has been successfully achieved. The exchange of a mono-charged K^+ cation by a bi-charged cation with two separated single-charges has been possible with the addition of an ABr_2 molecule (A = bi-charged cation) in a $KNiPS_4$/DMF-solution containing exclusively $[Ni_3P_3S_{12}]^{3-}$ trinuclear entities.[1,2] For both amorphous materials, ^{31}P solid state NMR, IR and Raman experiments revealed the presence of infinite $1/_\infty[NiPS_4]^-$ fragments with probably a wide length distribution. Hence, after a solvent induced cyclisation-fragmentation of the infinite $1/_\infty[NiPS_4]^-$ chains into discrete $[Ni_3P_3S_{12}]^{3-}$ anions in DMF, these ones react after evaporation in the presence of an organic dication to reconstruct the pristine chains. This result is in agreement with the experimental fact that the phases under study are disordered and thus amorphous and also insoluble in polar solvents. The amorphous nature of **I** and **II** makes sense if one considers that the materials are prepared at too low a temperature to allow for an ordering of the infinite $1/_\infty[NiPS_4]^-$ anions. These results are on line too with the fact that the drying of a solution of $KNiPS_4$ gives also an amorphous material thought to contain the infinite chains present in the crystallized pristine $KNiPS_4$ phase. It seems, then, that the dimensionality of the anionic part is less influenced by an increase of the charge of the counter-cation (*i.e.* the substitution of two potassium cations for one A^{2+} organic cation) than an increase of the size of the single-charged counter-cation (*i.e.* the substitution of K^+ for PPh_4^+ for instance). However, we may wonder if the dimensionality of the covalent network is influenced by the lone steric effect or if it may be influenced by the density of charge of the cation too. Experiments are at present under way in order to answer this question.

Table 2 Infrared band wavenumbers (cm^{-1}) observed in $(PPh_3\text{-}C_3H_6\text{-}PPh_3)_{0.5}[NiPS_4]$ (**I**), $(PPh_3\text{-}C_2H_2\text{-}PPh_3)_{0.5}[NiPS_4]$ (**II**) compared to those observed in $KNiPS_4$ (**III**),[10] $(PPh_4)_3Ni_3P_3S_{12}$ (**IV**)[11] (tentative assignments of the bands in **III** and **IV** according to C. Sourisseau *et al.* are given in parentheses)

I	II	III	IV
597	600	600 ($\nu_3(F_2)$ PS_4^{3-})	651 (mode PPh_4)
561	563	571 ($\nu_3(F_2)$ PS_4^{3-})	561 ($\nu_3(F_2)$ PS_4^{3-} + mode PPH_4)
526	526	—	525 (mode PPh_4)
350	353	355 ($\nu_4(F_2)$ PS_4^{3-} + ν NiS_4)	351 ($\nu_1(A_1)$ PS_4^{3-})
268	270	266 ($\nu_2(E)$ PS_4^{3-})	256 ($\nu_4(F_2)$ PS_4^{3-} + ν NiS_4)

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