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## Synthesis of $[\text{Fe}(o\text{-phen})_3]_{1.5}[\text{Ni}_3\text{P}_3\text{S}_{12}]$ , a new heterobimetallic material containing trinuclear $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$ complex

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Dedicated to Prof. Francis Sécheresse on the occasion of his 60th anniversary

### Abstract

The exfoliation process of  $1/\infty[\text{NiPS}_4]^-$  chains containing  $\text{KNiPS}_4$  compound in DMF solution with 18-crown-6 ether has been performed. The ion-exchange of  $\text{K}^+$  by  $[\text{Fe}(o\text{-phen})_3]^{2+}$  in solution led to the formation of  $[\text{Fe}(o\text{-phen})_3]_{1.5}[\text{Ni}_3\text{P}_3\text{S}_{12}]$  (**1**) where the occurrence of discrete ring-shaped  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$  anionic entities was evidenced by  $^{31}\text{P}$  NMR MAS spectroscopy. This result shows the influence of the counteranions on the structural organization of the inorganic component. Hence, in contact with on-site bicharged  $[\text{Fe}(o\text{-phen})_3]^{2+}$  counteranions,  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$  anions are maintained in solid state, while the reconstruction of infinite  $1/\infty[\text{NiPS}_4]^-$  chains from  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$  discrete species is triggered with organic cations such as  $(\text{C}_6\text{H}_5)_3\text{-P}^+(\text{CH}_2)_3\text{-P}^+(\text{C}_6\text{H}_5)_3$  and  $(\text{C}_6\text{H}_5)_3\text{-P}^+\text{-CH=CH-P}^+(\text{C}_6\text{H}_5)_3$ . **To cite this article: I. Collin et al., C. R. Chimie 8 (2005).** © 2005 Académie des sciences. Published by Elsevier SAS. All rights reserved.

### Résumé

L'exfoliation du matériau  $\text{KNiPS}_4$  dans le DMF a été réalisée en présence d'éther couronne et a conduit à la fragmentation des chaînes infinies  $1/\infty[\text{NiPS}_4]^-$  et à la formation d'entités trinucéaires cycliques  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$ . La réactivité de cette nouvelle espèce est fortement dépendante de la nature du contre-cation en présence. Ainsi, lorsque les ions  $\text{K}^+$  sont substitués par des dications organiques tels que  $(\text{C}_6\text{H}_5)_3\text{-P}^+(\text{CH}_2)_3\text{-P}^+(\text{C}_6\text{H}_5)_3$  et  $(\text{C}_6\text{H}_5)_3\text{-P}^+\text{-CH=CH-P}^+(\text{C}_6\text{H}_5)_3$ , les entités  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$  se recombinent pour former des chaînes  $1/\infty[\text{NiPS}_4]^-$ . À l'opposé, la métathèse des ions  $\text{K}^+$  par le complexe  $[\text{Fe}(o\text{-phen})_3]^{2+}$  a conduit au composé  $[\text{Fe}(o\text{-phen})_3]_{1.5}[\text{Ni}_3\text{P}_3\text{S}_{12}]$  (**1**), dans lequel la présence des entités  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$  a été caractérisée par spectroscopie RMN MAS du  $^{31}\text{P}$ . **Pour citer cet article : I. Collin et al., C. R. Chimie 8 (2005).** © 2005 Académie des sciences. Published by Elsevier SAS. All rights reserved.

**Keywords:** Exfoliation process; Metathesis reaction;  $1/\infty[\text{NiPS}_4]^-$ ;  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$ ;  $[\text{Fe}(o\text{-phen})_3]^{2+}$

**Mots clés:** Exfoliation; Métathèse;  $1/\infty[\text{NiPS}_4]^-$ ;  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$ ;  $[\text{Fe}(o\text{-phen})_3]^{2+}$

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## 1. Introduction

Alkali metal containing low dimensional chalcogenide compounds may exhibit very fascinating chemical reactivity in solution. Hence,  $\text{LiMo}_3\text{Se}_3$  inorganic material containing infinite  $1/\infty[\text{Mo}_3\text{Se}_3]^-$  chains is soluble in highly polar organic solvents such as dimethylsulfoxide (DMSO) and *N*-methylformamide (NMF) to form colloidal solutions [1]. Many studies including optical microscope under polarized light measurements have confirmed the lyotropic nematic phase

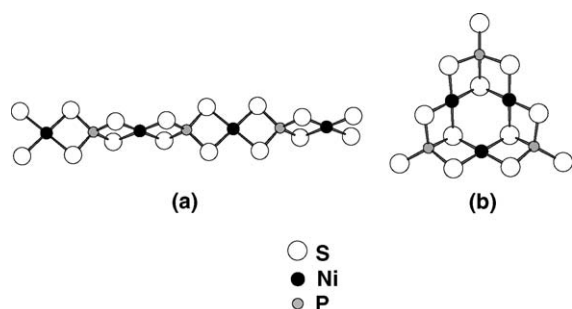


Fig. 1. (a) Infinite  $1/\infty[\text{NiPS}_4]^-$  chains in  $\text{KNiPS}_4$ . (b) View of discrete  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$  complex along its pseudofold axis.

behavior of  $\text{LiMo}_3\text{Se}_3$  in NMF solution [2,3]. More recently, the two isostructural materials  $\text{KNiPS}_4$  [4] and  $\text{KPdPS}_4$  [5] have been synthesized. Both compounds enclose infinite  $1/\infty[\text{MPS}_4]^-$  chains built upon  $[\text{MS}_4]$  squares and  $[\text{PS}_4]$  tetrahedra sharing edges, and are soluble in polar and donor organic solvents. Optical microscopy under polarized light and transmission electron microscopy studies have been shown that  $\text{KPdPS}_4/\text{DMF}$  solutions exhibit a fluid complex behavior due to the maintaining of spaghetti chains in solution [6,7]. At the opposite, the irreversible loss of the transient birefringence of few hours aged  $\text{KNiPS}_4/\text{DMF}$  solutions have been highlighted [6].  $^{31}\text{P}$  NMR spectroscopy [6] and mass spectrometry [7] have revealed that the infinite  $1/\infty[\text{NiPS}_4]^-$  chains are subjected to a solvent-induced fragmentation/cyclisation process in solution that leads to discrete crown-shaped  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$  entities (Figs. 1 and 2). Both the 0D and 1D species containing nickel thiophosphates have been characterized in solid state and in solution. These studies evidenced that  $^{31}\text{P}$  NMR spectroscopy is very well adapted in detecting the presence of  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$  anions and infinite  $1/\infty[\text{NiPS}_4]^-$  chains: the later exhibits one

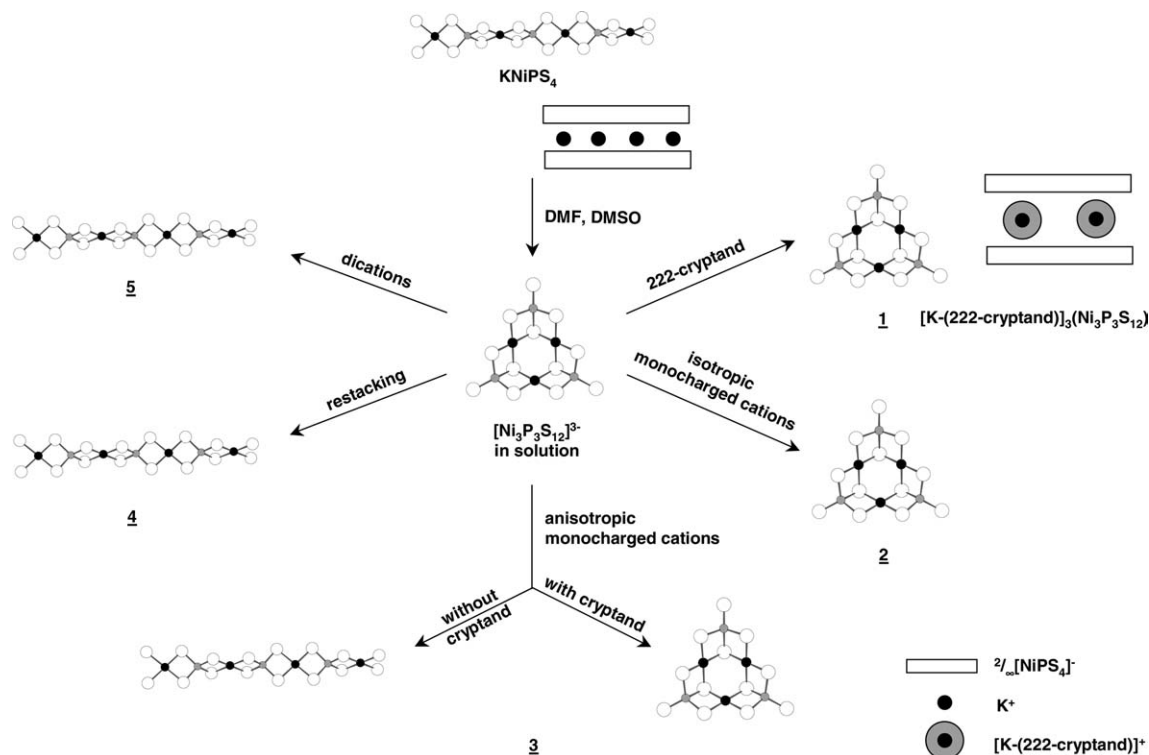


Fig. 2. Scheme showing the versatile reactivity of  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$  complex in DMF solution. See text for explanations.

characteristic resonance peak located at 119.6 ppm in solid state and at 122 ppm in DMF solution, whereas  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$  species give rise to a sharp or a broad resonance peak at about 114 ppm for solution and solid NMR measurements, respectively (in the solid state, the broad peak may sometimes be decomposed in three, four or more contributions versus the three dimensional packing of the  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$  anions and the symmetry operations at work) [6–8].

It is now clear that several parameters may control the exfoliation of  $\text{KNiPS}_4$  in solution. Hence, the kinetic of the cyclisation-fragmentation of the infinite  $1/\infty[\text{NiPS}_4]^-$  chains into  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$  discrete entities strongly depends on the  $\text{KNiPS}_4$  precursor concentration, the temperature, the possible use of a macrocyclic molecule, and of course, the nature of the solvent (polar organic solvent with high dielectric constant will favor dissolution). The same applies to the reactivity of  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$  anions in solution. Hence, under the influence of the organic counteranions used to exchange  $\text{K}^+$  for instance, the stabilization of the discrete anionic  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$  species in solid state can be achieved or  $1/\infty[\text{NiPS}_4]^-$  chains can be reconstructed. In Fig. 2 is illustrated the versatile behavior of  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$  in solution.

**1** – The use of organic cryptands allows a better solubilization of  $\text{KNiPS}_4$  by complexing the alkali cations and promoting the metathesis reactions. In this way, the reactivity of macrocyclic molecule 4,7,13,16,21,24-hexaoxa-1,10-diazobicyclo[8.8.8]hexacosane (222-cryptand) (specially suitable for the complexation of  $\text{K}^+$  ions) towards  $\text{KNiPS}_4/\text{DMF}$  solution leads to the formation of the  $[\text{K}-(222\text{-cryptand})]_3[\text{Ni}_3\text{P}_3\text{S}_{12}]$  compound characterized in the solid state by X-ray diffraction [8]. In this material,  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$  containing infinite  $2/\infty[\text{NiPS}_4]^-$  layers are well-separated by the cryptands-encapsulated  $\text{K}^+$  ions. On this geometrical point of view, the  $[\text{K}-(222\text{-cryptand})]_3[\text{Ni}_3\text{P}_3\text{S}_{12}]$  structural arrangement reminds the one of  $\text{KNiPS}_4$  where  $1/\infty[\text{NiPS}_4]^-$  chains are condensed in infinite slabs.

**2** –  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$  anions can be also stabilized in the solid state by replacing  $\text{K}^+$  ions by isotropic organic counter-cations such as tetraalkylammonium  $\text{NR}_4^+$  ( $\text{R} = \text{Me}, \text{Et}, \text{Bu}$ ) or tetraphenylphosphonium ( $\text{PPh}_4^+$ ) [6,7]. As for  $[\text{K}-(222\text{-cryptand})]_3[\text{Ni}_3\text{P}_3\text{S}_{12}]$ , this may be related to the classical steric effect observed in inorganic materials [9–11]: the dimensionality of the anionic framework decreases from (1D)  $1/\infty[\text{NiPS}_4]^-$

chains to (0D)  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$  complexes when the size of the monovalent counteranions increases.

**3** – When the exchange of  $\text{K}^+$  by monovalent anisotropic cations such as hexyltrimethylammonium  $[\text{CH}_3(\text{CH}_2)_5\text{N}(\text{CH}_3)_3]^+$  and dodecyltrimethylammonium  $[\text{CH}_3(\text{CH}_2)_{11}\text{N}(\text{CH}_3)_3]^+$  ions is performed with the help of 222-cryptand, the  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$  entities are stabilized in the solid state, whereas without macrocyclic molecule, the anionic complexes shift to the restacking of the  $1/\infty[\text{NiPS}_4]^-$  chains [8]. This surprising versatile behavior of  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$  is still unexplained but the polymerization of crowns into infinite chains was already observed with temperature in liquid-crystalline films containing  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$  entities and charged double-tail dialkylammonium surfactants (the reverse process occurs by dissolution) [12].

**4** – The restacking of the chains is also observed when the concentration of trinuclear complex increases. The drying of a  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}/\text{DMF}$  solution gives rise to an amorphous material [13].  $^{31}\text{P}$  solid state NMR spectrum of this compound have shown a lone broadline located at  $\delta = 121$  ppm, characteristic of the presence of  $1/\infty[\text{NiPS}_4]^-$  polymer. This broadening, more emphasized in the restacked materials than in the  $\text{KNiPS}_4$  pristine material (Fig. 3), may be due to possible factors such as the amorphous state of the material, residual  $^{31}\text{P}-^1\text{H}$  dipolar interactions with trapped solvent molecules or the occurrence of  $[\text{Ni}_n\text{P}_n\text{S}_{4n}]^{n-}$  linear fragments with a wide length distribution. So far,

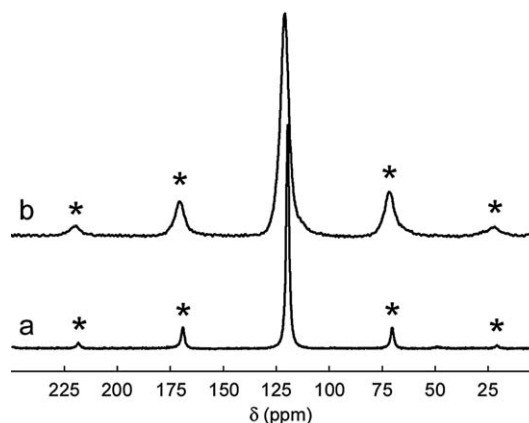


Fig. 3.  $^{31}\text{P}$  MAS NMR spectra recorded at 300 K of crystallized  $\text{KNiPS}_4$  (a) and restacked material obtained from the drying of  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}/\text{DMF}$  solution (b) (asterisks denote spinning side bands). The  $\text{KNiPS}_4$  spectrum presents one peak located around 119.6 ppm for (a) and 121.0 ppm for (b), corresponding to the phosphorus atoms inside the chain.

the mechanism leading to the reconstruction of the polymeric chains from the discrete trinuclear complexes remains mysterious. However, it appears that the concentration in minerals plays a major role in this reversible process.

**5** – In contrast to the ion-exchange process with monovalent organic cations, the reactivity of  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$ /DMF solution towards large sized bi-charged organic cations such as trimethylene bis(triphenylphosphonium)  $((\text{C}_6\text{H}_5)_3\text{-P}^+(\text{CH}_2)_3\text{-P}^+(\text{C}_6\text{H}_5)_3)$  or 1,2-vinylene bis(triphenylphosphonium)  $((\text{C}_6\text{H}_5)_3\text{-P}^+\text{-CH=CH-P}^+(\text{C}_6\text{H}_5)_3)$  yields the reconstruction of  $1/\infty[\text{NiPS}_4]^-$  chains in the solid state. This has been proven by  $^{31}\text{P}$ -NMR, Raman and IR spectroscopies [14]. At first sight, this behavior is in disagreement with the expectation that the higher the size of the counter-cations, the lower the dimensionality of the anionic framework. However, in the present case, it appears that the steric effect of the organic cations may be counter-balanced by a charge effect, i.e. the higher charge of the organic ions goes along with a lesser concentration in counter-cation. Nevertheless, the positive charge of the aforementioned organic bi-cations is localized around the two, well-separated phosphorus atoms, and the organic cations may be then described to some extents as the condensation of two mono-charged cations. Hence, as the influence of the charge density of the dication on the reactivity remains unknown, it remains questionable whether the restacking of  $1/\infty[\text{NiPS}_4]^-$  chains is due to a charge effect or a steric effect of the cations. To unravel this question, the ion-exchange of  $\text{K}^+$  with localized bi-charged cations such as  $[\text{Fe}(o\text{-phen})_3]^{2+}$  has been performed. We report here the synthesis of  $[\text{Fe}(o\text{-phen})_3]_{1.5}[\text{Ni}_3\text{P}_3\text{S}_{12}]$  (**1**), a new heterobimetallic compound.

## 2. Experimental section

### 2.1. Chemicals

All manipulations were carried out under the oxygen-free dry nitrogen atmosphere using standard Schlenk techniques. All commercial solvents were used as received. 1,10-Phenanthroline·H<sub>2</sub>O (puriss 99%), FeSO<sub>4</sub>·7H<sub>2</sub>O (puriss 98%), NaBF<sub>4</sub> (puriss 99%) and 18-crown-6 ether (puriss 98%) were purchased from Aldrich. KNiPS<sub>4</sub> was prepared as previously described [15].

### 2.2. NMR spectroscopy

Solid state NMR experiments were performed at room temperature on a Bruker Avance 500 MHz operating at 202.4 MHz for  $^{31}\text{P}$ , using a 4-mm double-bearing Bruker probehead.  $^{31}\text{P}$  MAS spectra of KNiPS<sub>4</sub> were acquired at 10 kHz and a repetition time of 10 s.  $^{31}\text{P}$  MAS spectrum of  $[\text{Fe}(o\text{-phen})_3]_{1.5}[\text{Ni}_3\text{P}_3\text{S}_{12}]$  (**1**) was acquired at 15 kHz with a repetition time of 20 s. Except for crystallized KNiPS<sub>4</sub>,  $^1\text{H}$  decoupling was systematically used during acquisition. Spectra were referenced to H<sub>3</sub>PO<sub>4</sub>.

### 2.3. Synthesis of $(\text{BF}_4)_2[\text{Fe}(o\text{-phen})_3]$

FeSO<sub>4</sub>·7H<sub>2</sub>O (278 mg, 1 mmol) and FeSO<sub>4</sub> enriched in  $^{57}\text{Fe}$  (31 mg, 0.2 mmol) were dissolved in 20 ml of water. 1,10-Phenanthroline·H<sub>2</sub>O (793 mg – 4 mmol) was added and the resulting dark-red solution was stirred for few minutes. NaBF<sub>4</sub> (550 mg – 5 mmol) was added and the solution was placed in an ice-bath leading to the formation of a red solid. The powder was isolated by filtration and dried under vacuum (yield: 80%).

### 2.4. Synthesis of $[\text{Fe}(o\text{-phen})_3]_{1.5}[\text{Ni}_3\text{P}_3\text{S}_{12}]$ (**1**)

KNiPS<sub>4</sub> (216 mg – 0.84 mmol) and 18-crown-6 ether (1,4,7,10,13,16-hexaoxacyclooctadecane) (0.204 mg – 0.85 mmol) was dissolved in 15 ml of DMF and the red-dark solution was stirring at 50 °C for 15 h.  $(\text{BF}_4)_2[\text{Fe}(o\text{-phen})_3]$  is then added to the solution leading to the formation of a air-stable red solid. The solution was filtered and the powder was washed with ethanol and acetone (yield: 65%). 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  $\text{Ni}_{2.8}/\text{P}_{3.0}/\text{S}_{11.5}/\text{Fe}_{1.5}$  in good agreement with the  $[\text{Fe}(o\text{-phen})_3]_{1.5}[\text{Ni}_3\text{P}_3\text{S}_{12}]$  title composition.

## 3. Results and discussion

Fe<sup>2+</sup> cations react with three equivalent of 1,10-phenanthroline in aqueous solution to give a red octahedral low spin tris(phenanthroline) iron (II) complex. Addition of bi-charged  $[\text{Fe}(o\text{-phen})_3]^{2+}$  cation to KNiPS<sub>4</sub>/DMF solution leads to the formation of  $[\text{Fe}(o\text{-phen})_3]_{1.5}[\text{Ni}_3\text{P}_3\text{S}_{12}]$ .

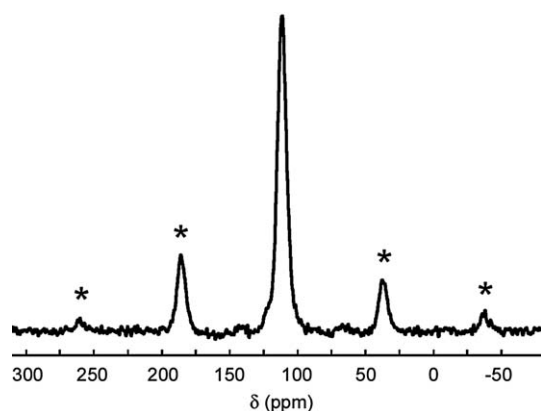


Fig. 4.  $^{31}\text{P}$  MAS NMR spectrum of  $[\text{Fe}(\text{o-phen})_3]_{1.5}[\text{Ni}_3\text{P}_3\text{S}_{12}]$  (**1**) recorded at 300 K. (asterisks denote spinning side bands). The signal of the phosphorus atoms of the  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$  complexes in **1** is located at  $\delta = 112$  ppm.

$\text{phen})_3]_{1.5}[\text{Ni}_3\text{P}_3\text{S}_{12}]$  (**1**) that precipitates as a red solid. The metathesis of  $\text{K}^+$  ions by  $[\text{Fe}(\text{o-phen})_3]^{2+}$  complexes is performed with the presence of 18-crown-6 ether to ensuring a better separation of charge in solution and also to increase anion's reactivity. The red powder of **1** is amorphous and no crystal suitable for X-ray diffraction characterization was obtained. The +2 oxidation state of Fe and its low spin configuration in **1** was confirmed by Mössbauer spectroscopy<sup>1</sup>.  $^{31}\text{P}$  NMR measurements were carried out to determine whether **1** contains  $1/\infty[\text{NiPS}_4]^-$  chains or  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$  entities. The  $^{31}\text{P}$  MAS NMR spectrum is shown on Fig. 4. It reveals the presence of a peak located at  $\delta = 112$  ppm. By comparison with the spectrum of  $(\text{PPh}_4)_3[\text{Ni}_3\text{P}_3\text{S}_{12}]$ , [6] this signal has been undoubtedly attributed to the phosphorus atoms of  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$  anions. No signal of the  $1/\infty[\text{NiPS}_4]^-$  chains at  $\delta = 119.6$  ppm appears. Contrary to the ion-exchange process with bi-charged organic cations such as trimethylene bis(triphenylphosphonium) or 1,2-vinylene bis(triphenylphosphonium) that led to  $1/\infty[\text{NiPS}_4]^-$  polymer, the substitution of  $\text{K}^+$  counterions by localized bi-charged cations such as  $[\text{Fe}(\text{o-phen})_3]^{2+}$  complexes allows the stabilization of  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$  crown-shaped anions both in solution and solid state. Consequently, the restacking of infinite  $1/\infty[\text{NiPS}_4]^-$  chains in

$(\text{PPh}_3-\text{C}_3\text{H}_6-\text{PPh}_3)_{0.5}[\text{NiPS}_4]$  and  $(\text{PPh}_3-\text{C}_2\text{H}_2-\text{PPh}_3)_{0.5}[\text{NiPS}_4]$  is not only due to a pure charge effect such as it was proposed initially but has to deal probably with the charge density distribution on the organic cations.

#### 4. Conclusions

The versatile behavior of the  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$  complexes towards organic and inorganic cations in DMF solution has again been highlighted. The mechanism of dissolution/restacking of the  $(1\text{D}) 1/\infty[\text{NiPS}_4]^-$  including the systematic formation of  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$  anions versus any other  $[\text{Ni}_x\text{P}_x\text{S}_{4x}]^{x-}$  ( $x > 3$ ) is still unknown. The stabilization of discrete trinuclear entities or infinite  $1/\infty[\text{NiPS}_4]^-$  chains in solid state from the evaporation of  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$  anions containing solution cannot be only explained in term of a steric effect or a charge effect of the counteranions.

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<sup>1</sup> Mössbauer spectra of  $[\text{Fe}(\text{o-phen})_3]_{1.5}[\text{Ni}_3\text{P}_3\text{S}_{12}]$  (**1**) have shown that the  $^{57}\text{Fe}$  signal is not perturbed by the trinuclear  $[\text{Ni}_3\text{P}_3\text{S}_{12}]^{3-}$  complexes, showing very weak interactions between anionic and cationic fragments in the network.