

Phosphorus Vacancies and Intercalation in Lamellar NiPS₃

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New intercalation compounds of NiPS₃ are described, in which the electrical charge of guest cations is counterbalanced by a deficit of P^{IV} atoms.

The MPS₃ lamellar materials have been shown in the last ten years to have an original and versatile chemical reactivity. NiPS₃ and FePS₃ are efficient cathodic materials in rechargeable lithium batteries because of their ability to insert Li⁺ cations reversibly, this process being accompanied by a reduction of the M²⁺ cations to the M⁰ oxidation state.¹ Several members of the family (M = Mn, Zn, Fe, Cd, but not Ni) readily insert various cations under mild conditions (*e.g.* alkali metal, organometallics, and ammonium cations in aqueous solution) through an ion exchange mechanism based on the removal of M²⁺ ions from the slabs.² This process, unique in intercalation chemistry, is based on the occurrence of a heterogeneous equilibrium between the solid MPS₃ and the solvated M²⁺ and P₂S₆⁴⁻ ions, a feature of which suggests that the MPS₃ materials behave as polynuclear co-ordination complexes.³ In an attempt to extend this chemistry to NiPS₃, we have found that this material undergoes a complex two step reaction which leads eventually to novel intercalation compounds in which the positive charge of the guest cations is counterbalanced by an equivalent deficit of P^{IV} atoms.

Treating NiPS₃ with aqueous solutions of Na₂S or NaOH (*ca.* 0.5 M, for 12 h to 2 days) yielded a dark powder, which was washed with aqueous NaCl (0.1 M) until neutral (the material tends to disperse in pure water), followed by methanol, and finally dried in air. The X-ray pattern of the material (1) exhibits a series of sharp 00*l* reflections, and the value of the interlamellar distance (12.2 Å) demonstrates the presence of guest Na⁺ ions solvated by a bilayer of water molecules. On the basis of elemental (except for oxygen) and thermogravimetric analyses, an overall composition NiPS₃Na_x(H₂O)_y or NiPS₃(NaOH)_x(H₂O)_y can be written for (1), with *y* ≈ 4 and *x* varying between *ca.* 0.4 and *ca.* 0.8, depending on the reaction time.

In a second step, the intercalate (1) was treated overnight at room temperature with *ca.* 0.5M aqueous solutions of cobalticinium chloride, dibenzenechromium iodide, chromium nitrate, and with a saturated solution of copper bromide in acetonitrile; the dark powders obtained were washed with water (MeCN in the case of the copper compound), then with methanol, and finally dried *in vacuo* at *ca.* 80 °C. According to the elemental analysis data, all materials have a composition

of the type NiP_{1-x}S₃(G)_{4x/n}(H₂O)_y, where *n* represents the positive charge of the guest cations Gⁿ⁺. Detailed compositions are given in Table 1 which show that a small fraction of the sodium cations initially present in (1) may still exist in the final materials.

The X-ray diffraction pattern of materials (2) and (3) exhibits a series of sharp 00*l* reflections, which lead to interlamellar distances consistent with the van der Waals size of the guest species (Table 1). In contrast, materials (4) and (5) essentially display a rather broad intense reflection corresponding to an interlamellar distance close to that of pure NiPS₃. The i.r. spectra of (4) and (5) exhibit the intense characteristic ν(PS₃) asymmetric stretching band at *ca.* 570 cm⁻¹. In contrast, the ν(PS₃) band in the spectra of (2) and (3) appears to be split into three components at 610, 575, and 550 cm⁻¹ exactly as in the intercalation compound synthesized from the direct reaction of cobaltocene with NiPS₃.⁴ The spectra of (2) and (3) also display bands characteristic of the organometallic guests.

The EXAFS spectra at the nickel K-edge of materials (4), (5), and of NiPS₃ have been recorded (Figure 1). The curves appear almost indistinguishable, a feature which strongly

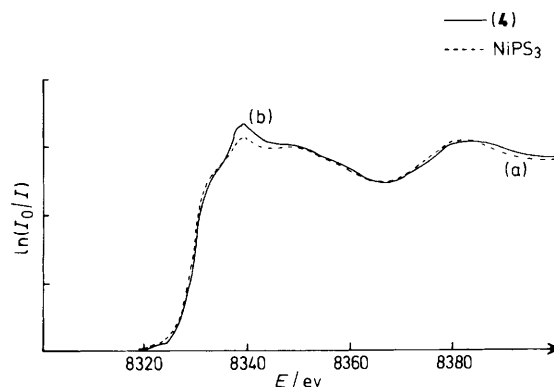


Figure 1. Comparison of the EXAFS spectra at the nickel K-edge (a) of NiPS₃ and (b) of (4). The spectrum of (5) is almost identical to that of (4) and is not shown for clarity.

Table 1. Materials obtained by reaction of the sodium intercalate (1) with various salts.

Salt exchanged with (1)	Composition ^a		Interlamellar distance/Å
Co(C ₅ H ₅) ₂ Cl aq.	NiP _{0.90} S ₃ [Co(C ₅ H ₅) ₂] _{0.36} Na _{0.03} (H ₂ O) _{0.5}	(2)	11.9
Cr(C ₆ H ₆) ₂ I aq.	NiP _{0.92} S ₃ [Cr(C ₆ H ₆) ₂] _{0.31} Na _{0.09} (H ₂ O) _{0.7}	(3)	12.4
Cr(H ₂ O) ₆ NO ₃ aq.	NiP _{0.89} S ₃ Cr _{0.12} Na _{0.09} (H ₂ O) _{1.0}	(4)	6.36
CuBr/MeCN	NiP _{0.90} S ₃ Cu _{0.34} Na _{0.06} (H ₂ O) _{0.6}	(5)	6.5

^a All formulae were obtained from full elemental analysis except for oxygen.

suggests that the nickel atoms have very similar electronic and geometrical structures in these materials.⁵ Therefore, no redox process involving nickel appears to occur during any stage of the synthesis, in contrast to the chemistry involved in the synthesis of the Li_xNiPS₃ materials.¹

Preliminary experiments have shown that lithium can also undergo electrochemical insertion into materials (4) and (5). At least four moles of Li per mole of Ni can be inserted and we have checked that the reversibility of the process is good throughout the composition range between one and two moles of Li per mole of Ni, which is the operational range for pure NiPS₃. In addition to their possible technological interest, these features confirm the lamellar character of materials (4) and (5).

The mechanism responsible for the loss of P^{IV} atoms is not yet clear. Preliminary EXAFS spectra at the nickel K-edge of the sodium intercalate (1) indicate that the Ni^{III} cations easily de-coordinate from the P₂S₆ ligands, a process which facilitates subsequent hydrolysis of the latter. Indeed, the i.r.

spectrum of (1) shows a broad band of moderate intensity in the range from 1000 to 1100 cm⁻¹ which reveals the presence of the phosphate. The latter would then be eliminated from the solid during the second step of the synthesis. Further studies are underway to explore the new synthetic possibilities offered by this controlled modification of NiPS₃.

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