

XPS Studies on the Host–Guest Interaction of 2,2′-Bipyridyl, 1,10-Phenanthroline and 2,9-Dimethyl-1,10-Phenanthroline Intercalated in α -Zirconium Phosphate

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Abstract. The host–guest interactions of 2,2′-bipyridyl, 1,10-phenanthroline and 2,9-dimethyl-1,10-phenanthroline intercalated between the layers of crystalline α -zirconium monohydrogen phosphate have been studied by X-ray photoelectron spectroscopy. Evidence that, on average, only one of the two nitrogen atoms of each aromatic diamine is protonated by the $\equiv\text{P}-\text{OH}$ groups of the host is given. The acid–base interaction is strongly reduced on dehydration of the materials. The role of the cointercalated water is discussed, together with the probable disposition of the guests within the interlayer region.

Key words. Zirconium phosphate, 2,2′-bipyridyl, 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline intercalation, host–guest interaction, X-ray photoelectron spectroscopy.

1. Introduction

The intercalation of organic ligands and their coordination compounds in layered inorganic materials is at present a very promising field of investigation because it offers an interesting way of preparing a great variety of composite materials and also of supporting compounds usually employed as homogeneous catalysts.

In the last few years we have commenced an investigation on the intercalating properties of α - and γ -zirconium and titanium bis-monohydrogen phosphates, known as synthetic inorganic ion-exchangers with a layered structure [1, 2]. Our attention is particularly focused on α -zirconium monohydrogen phosphate, α -Zr(HPO₄)₂·H₂O. This exchanger has an interlayer spacing of 7.6 Å. Crystallographic studies [3] showed that each layer consists of zirconium atoms lying nearly in a plane and bridged through tetrahedral PO₃-OH groups alternatively located above and below the plane of the zirconium atoms.

α -Zirconium hydrogen phosphate forms intercalation compounds with relatively large amines such as *N*-heterocycles [4–7], amino acids [4], and amino alcohols [8].

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These materials, which possess an almost doubled interlayer distance with respect to that of the host, exchange divalent transition metal ions (e.g. Cu, Co, Ni, Pd and Pt), which then coordinate to the ligands throughout the layers with a further increase of the interlayer distance [5–7, 9, 10].

Information on the 'bulk' features of all the materials has been obtained from chemical analyses, X-ray diffractometry, UV, visible and EPR spectroscopy. Thus each new phase has been characterized by its own chemical formula, X-ray diffraction pattern and type of coordination and geometry for the complex species intercalated between the layers of the zirconium phosphate.

One of the most important problems to be solved is the interaction of the polar sites of the guest molecules with those of the host, i.e. how different parameters such as the structure of the host, the kind and the strength of the polar groups that meet in the interlayer region, the steric hindrances, etc., can determine the stoichiometry of the intercalation compounds, the arrangement of the guests between the layers and, in the case of coordination compounds formed *in situ*, the complexity and stereochemistry of the species.

X-ray photoelectron spectroscopy (XPS) is particularly appropriate for obtaining such information, since it provides structural characterization and valuable information on the electronic charge density of the elements in a chemical compound [11].

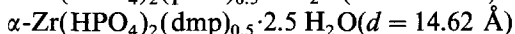
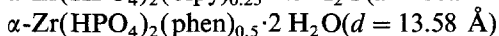
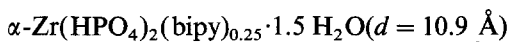
In this paper the 2,2'-bipyridyl (bipy), 1,10-phenanthroline (phen) and 2,9-dimethyl-1,10-phenanthroline (dmp) α -zirconium phosphate intercalation compounds have been studied by XPS in order to obtain a better knowledge of the interaction between the aromatic diamines and the $\equiv\text{P}-\text{OH}$ groups present in the interlayer region of the host, the arrangement of the guests and the part played by the water molecules cointercalated during the process.

2. Experimental

2.1. MATERIALS

The operating conditions adopted for the intercalation of bipy, phen and dmp between the layers of $\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ have been described in References [5, 6 and 7], respectively.

The materials under investigation have the following chemical formulae:



The data in parentheses represent the interlayer spacings of the intercalation compounds.

The anhydrous materials were obtained by heating the hydrated compounds at 150°C, according to the thermogravimetric measurements. The pure diamines and phen-HCl were supplied by Fluka. Other reagents were Merck 'pro analysi' products.

2.2. PHYSICAL MEASUREMENTS

X-ray photoelectron spectra were taken with a Vacuum Generator Ltd. ESCA 3 MK II Spectrometer using $AlK_{\alpha_{1,2}}$ excitation (1486.6 eV) at a residual pressure of 10^{-7} Pa.

Samples were dusted as a thin film onto a gold plate to minimize charging effects. Calibration was made by the $4f_{7/2}$ gold signal at 83.7 eV and sample charging was corrected by referencing to the $C1s$ line of contaminating oil-carbon, taken at 285.0 eV. The accuracy of the measured binding energies was estimated at ± 0.2 eV. Cooling of the samples to liquid N_2 temperature was performed to prevent possible secondary decomposition effects.

Peak deconvolution was performed with a Du Pont 310 curve resolver using a Gaussian shape fit. The area of the peaks were calculated by multiplying their height by their width at half height.

3. Results and Discussion

In Table I the core level binding energy values (in eV) of the elements present in the compounds under investigation and in those chosen as references are reported.

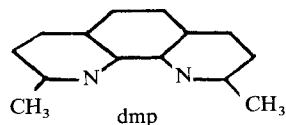
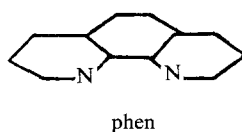
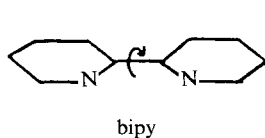
The binding energy value of the $P2p$ (133.3 ± 0.2 eV) is found to be constant along the series of the compounds and characteristic of the PO_4 group (cf. the value of 133.2 eV found for $Na_2HPO_4 \cdot H_2O$ [12]).

The binding energy value of the $Zr3d_{5/2}$ (183.0 ± 0.2 eV) indicates the typical formal oxidation state of +4 for zirconium [9].

The analysis of the $N1s$ spectra of the intercalation compounds shows that the binding energy values at 399.0–399.6 and 401.2–401.5 eV found for the hydrated and anhydrous bipy-, phen- and dmp-zirconium phosphate phases are exactly the

Table I. Binding energy values (eV) for the compounds analysed

Compound	$N1s$	$P2p$	$Zr3d_{5/2}$	N/NH
α -Zr(HPO_4) ₂ ·H ₂ O		133.2	182.9	
$Na_2HPO_4 \cdot H_2O$		133.2		
phen	399.2			
phen·HCl	399.2–401.3			1
α -Zr(HPO_4) ₂ phen _{0.5} ·2 H ₂ O	399.2–401.5	133.3	183.0	0.9–1.0
α -Zr(HPO_4) ₂ phen _{0.5}	399.2–401.5	133.3	183.0	1.3–1.4
dmp	398.8			
α -Zr(HPO_4) ₂ dmp _{0.5} ·2.5 H ₂ O	399.0–401.4	133.5	182.9	0.9–1.0
α -Zr(HPO_4) ₂ dmp _{0.5}	399.0–401.5	133.5	183.0	1.3–1.5
bipy	399.6			
α -Zr(HPO_4) ₂ bipy _{0.25} ·1.5 H ₂ O	399.4–401.2	133.3	182.9	0.6–0.8
α -Zr(HPO_4) ₂ bipy _{0.25}	399.6–401.4	133.5	183.1	1.3–1.5



same as those given in the literature for the diamines monohydrochlorides and to those found by us for phen·HCl [12]. In fact, by considering by XPS results obtained for phen·HCl [12], two binding energy values at 399.2 and 401.3 eV are found, the first being ascribed to the free nitrogen (see Table I for free phen) and the second to the nitrogen protonated by HCl).

As an example, Fig. 1 shows the N1s spectra of pure phen, phen monohydrochloride, the hydrated and anhydrous phen-zirconium phosphate intercalation compounds. From the figure it can be noted that the two areas obtained by deconvolution of the N1s spectrum of the hydrated phen-zirconium phosphate phase have about the same weight as those obtained for phen·HCl. This result gives two important indications: (i) between the layers some of the nitrogen atoms of the phen molecules are free (left area) and some are anchored to the host through a

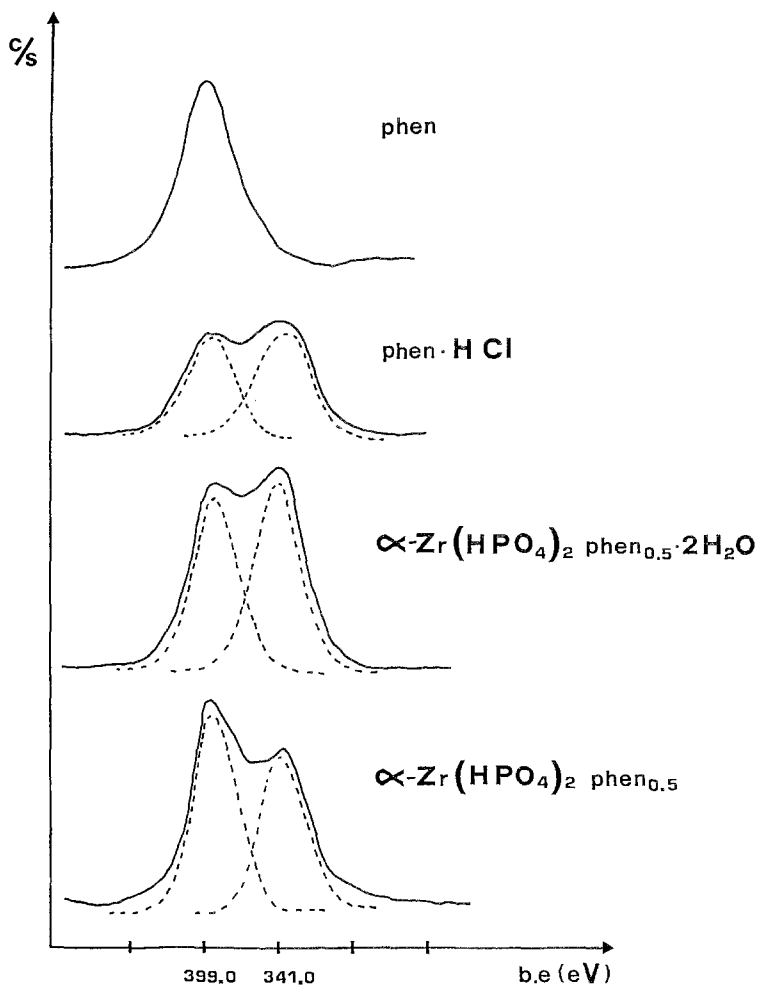


Fig. 1. Photoelectron spectra of the N1s levels of phen, phen·HCl, hydrated and anhydrous phen-zirconium phosphate.

protonation process with the $\equiv\text{P}-\text{OH}$ groups (right area); (ii) on average, only one of the two nitrogens of each phen molecule can interact with the acid sites of the intercalating agent. This behaviour is certainly a consequence of the 1,10-positions of the two nitrogens in the phenanthrenic skeleton of the phen molecule, whose separation is such that when one of them interacts directly with a $\equiv\text{P}-\text{OH}$ group in the interlayer region, the other does not find a second acid site at a distance suitable for its protonation (the $\equiv\text{P}-\text{OH}$ groups in layered α -zirconium phosphate are disposed in a hexagonal arrangement at a distance of 5.3 Å on each side of a layer [3]).

Some interesting features arise from the deconvolution of the $N1s$ spectra of all the hydrated and anhydrous intercalation compounds:

- (1) The value of the N/NH ratio (N refers to the area of the free nitrogen; NH to the area of the protonated nitrogen) found for the hydrated intercalation compounds is lower than that of the anhydrous materials (Table I). This feature is very interesting because it suggests that the cointercalated water takes part in the protonation of the diamines between the layers of α -zirconium phosphate.
- (2) The N/NH value found for the hydrated bipy-intercalation compound is lower than that found for the other two hydrated materials.
- (3) When the materials are dehydrated the N/NH ratio increases to an almost identical value for all the compounds.

As far as the lower N/NH value of hydrated bipy-zirconium phosphate is concerned, an explanation can be found by first recalling some general features of the intercalation of bases in $\alpha\text{-Zr}(\text{HPO}_4)_2\cdot\text{H}_2\text{O}$ and by comparing the intercalation of bipy, phen and dmp in this exchanger.

Generally, the alkyl monoamines (except methylamine) [13], mono- and di-*N*-heterocycles, such as pyridine [14], imidazole, benzimidazole, histamine [4], in their first step of intercalation between the layers of $\alpha\text{-Zr}(\text{HPO}_4)_2\cdot\text{H}_2\text{O}$, give phases having the lowest loading of amine and an interlayer distance ranging between 10.6 and 11.3 Å. The increment, when referred to the interlayer distance of pure zirconium monohydrogen phosphate (7.6 Å), is consistent with a monolayer of guest molecules lying parallel, or almost parallel, to the layers of the host structure. The differences in the composition and in the interlayer distance of these intercalation compounds is connected with the van der Waals volume of the different guests [4].

By considering the content of bipy per mole of exchanger in comparison with that of phen and dmp (0.25 moles of bipy per mole of host against 0.5 for phen and dmp), and the interlayer distances of the hydrated intercalation compounds (10.9, 13.58 and 14.62 Å for bipy, phen and dmp, respectively), it can be deduced that bipy lies parallel to the layers of zirconium phosphate, while phen and dmp must assume a slanted position. The position of the two bulkier diamines could be due to the presence of the additional aromatic ring, absent in bipy, which makes both phen and dmp more hydrophobic in character than bipy. Consequently, being less attracted by the hydrophilic host, phen and dmp are constrained to assume a straightened position.

Furthermore, it has been demonstrated from the reflectance spectra that bipy assumes a *trans* configuration between the layers of $\alpha\text{-Zr}(\text{HPO}_4)_2\cdot\text{H}_2\text{O}$ [5].

Consequently, the possibility of twisting the two pyridine rings and their nearly flat position, allow the bipy molecule to interact better via its nitrogens, directly or through the water molecules, with the $\equiv\text{P}-\text{OH}$ groups disposed in a regular array above and below each side of a layer. Thus bipy, being loosely packed, is able to protonate or form hydrogen bonds much more easily than phen or dmp and gives an N/NH ratio ranging between 0.6 and 0.8, while the other two diamines, because of their rigid phenanthrenic structure and their tight packing, move with difficulty and interact, on average, with only one nitrogen per molecule so that their N/NH ratio is close to 1.

The behaviour of all the compounds on dehydration is very interesting. A large decrease in the number of protonated nitrogens is observed, which is more pronounced for the bipy derivative (see Table). This finding indicates that, in the hydrated materials, the water molecules participate in the protonation of a noticeable fraction of the nitrogen atoms of the guests, probably acting as a bridge between the diamines and the $\equiv\text{P}-\text{OH}$ groups of the host. With the removal of the cointercalated water, the interaction between the basic groups and the acid sites is strongly reduced, the extent of the decrease depending on the conformation and the arrangement of the different diamines in the interlayer region.

Generally, when the α -zirconium phosphate exchanged or intercalated compounds are dehydrated, the loss of cointercalated water leads to the decrease of the interlayer spacing [15]. In the present case this behaviour is observed for phen and dmp-zirconium phosphate materials, for which the interlayer spacings decrease by ca. 1.1 Å becoming 12.45 [6] and 13.50 Å [7], respectively.

For the bipy analogue, the X-ray diffraction pattern of the dehydrated material shows the presence of two phases with interlayer distances of 11.62 and 7.45 Å, respectively [16]. Since the phase with the spacing of 7.45 Å is the well known anhydrous phase of α -zirconium hydrogen phosphate [17, 18], the phase with the spacing of 11.62 Å must be an anhydrous bipy-containing phase. A similar behaviour on dehydration was observed by Kijima in the case of the pyridine- α -zirconium phosphate [14] and by Casciola *et al.* [19] for the lowest loaded 1,8-octanediamine- α -zirconium phosphate sample.

If the larger interlayer distance value of the anhydrous bipy phase, in comparison with that of the hydrated material (10.9 Å), was due to a 'straightening out' of the bipy molecules in order to establish some new direct interactions of the nitrogen atoms with the $\equiv\text{P}-\text{OH}$ groups of the host, X-ray photoelectron spectroscopy should have given, for the anhydrous bipy material, an N/NH ratio of the same order as that of the hydrated compound and anyway lower than the obtained value of 1.3–1.5. But this is not the case, since the X-ray photoelectron results give approximately the same N/NH ratio for the three anhydrous intercalation materials. What is probably occurring on dehydration of the bipy hydrated phase is a 'solid state reaction' leading to the formation of a phase without bipy, the anhydrous α -zirconium phosphate '7.45 Å' phase, and an anhydrous bipy-zirconium phosphate phase necessarily richer in bipy than the initial hydrated phase. The higher content of bipy forces the diamine molecules to pass from an almost flat position to a more slanted one, so that the interlayer distance is now increased to 11.62 Å. The process could then be the following: the loss of the cointercalated water favours a higher mutual attraction between the bipy molecules

that, as a consequence, migrate within the interlayer region to form a more populated bipy phase. At the same time, crystals of pure anhydrous α -zirconium hydrogenphosphate are segregated.

4. Conclusions

The X-ray photoelectron spectroscopic investigation carried out on the hydrated and anhydrous bipy-, phen- and dmp-zirconium phosphate intercalation compounds, has permitted us to evaluate the extent of the *N*-protonation of the three aromatic diamines in the interlayer region of α -zirconium monohydrogen phosphate and to demonstrate the importance of the cointercalated water in favouring the protonation process.

The disposition of the different diamines between the layers of α -zirconium phosphate is certainly connected with the acid-base (host-guest) interactions, but, for a complete explanation of the structural arrangements observed in both the hydrated and anhydrous phases, other parameters, such as the flexibility and the hydrophobicity of the different intercalated molecules, must also be taken into account.

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