XPS Characterization of γ-Zirconium Phosphate and of Some of Its Intercalation Compounds. A Comparison with the α-Zirconium Phosphate Analogues

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Abstract. An X-ray photoelectron spectroscopic investigation of γ-Zr $(HPO_4)_2 \cdot 2 H_2O$ and its intercalation compounds with 1,10-phenanthroline, Co^{2+}-phenanthroline and Cu^{2+}-phenanthroline is described. The analysis of the $N1s$ spectra of the compound containing only phenanthroline clearly shows that, on average, more than one nitrogen atom of the diamine interacts with the acid groups of the host, giving protonated species. XPS also provides evidence of the coordination of Co^{2+} and Cu^{2+} ions after their diffusion in the phenanthroline-γ-zirconium phosphate intercalation compound. They form mixed N- and O-coordinated species with the diamine and the oxygens of the interlayer region, but the presence of the characteristic peaks of uncoordinated phenanthroline, even at low intensity, shows that the diamine molecules anchored to the host are still present.

A comparison is made with the analogous derivatives of α-Zr $(HPO_4)_2 \cdot H_2O$ and the differences between the two series of compounds are discussed.

Key words. γ-zirconium phosphate, phenanthroline intercalation, Co(II)–1,10-phenanthroline complex intercalation, Cu(II)–1,10-phenanthroline complex intercalation, *in-situ* coordination, host–guest interaction, X-ray photoelectron spectroscopy.

1. Introduction

Alpha- and gamma-zirconium phosphates, α-Zr$(HPO_4)_2 \cdot H_2O$ [1] and γ-Zr $(HPO_4)_2 \cdot 2 H_2O$ [2] respectively, are crystalline, insoluble, ion-exchangers with a layered structure [1, 2]. Although the structure of the γ-form is not yet known, the different interlayer spacings of the two compounds, $d = 7.6$ Å for the α form and $d = 12.27$ Å for the γ-form, account for a different structure of the α and γ layers, the latter being seemingly more compact [3]. Both materials possess intercalating properties so that various kinds of polar organic molecules can be accommodated in the interlayer region giving a great variety of compounds [4], in which the guests are bound to the inorganic host with a strength depending on the nature of the

organic molecule: ionic interactions for alkyl and aryl amines [5], weak bonds for alcohols and glycols [5], or both for aminoalcohols and aminoacids [6].

In previous papers [7–10] it was shown that bulky aromatic diamines such as 2,2′-bipyridyl (bipy), 1,10-phenanthroline (phen) and 2,9-dimethyl-1,10-phenanthroline (dmp) can be inserted between the layers of α- and γ-zirconium phosphate giving well ordered, non-stoichiometric organic–inorganic compounds with an expansion of the interlayer spacing.

Transition metal ions such as Co(II), Ni(II), Cu(II), Pd(II), Pt(II), Rh(III), etc., inserted into such compounds by ion-exchange, can be subsequently coordinated to the ligand throughout the layers, the process generally occurring with further expansion of the interlayer distance to allow an optimum orientation of the complex formed *in-situ* [7–12]. Various compounds were obtained which were characterized by their chemical formula and X-ray diffraction pattern, whereas UV, visible and EPR spectroscopy provided information on the type of coordination and geometry of the complex species formed in the interlayer region of the exchangers. Some of these compounds behave as catalysts [12–14] and a great contribution in explaining the mechanism of action of these materials was obtained by analysing the chemical and physical state of the outermost part of the solids before and after their use in catalyzed reactions using X-ray photoelectron spectroscopy (XPS) [12–14]. It is well known, in fact, that XPS provides structural characterization and valuable information on the electronic charge density of the elements on the surface of a chemical compound [15].

With XPS it has been possible to give an evaluation of the host–guest interaction between the above mentioned aromatic diamines and α-zirconium phosphate [16, 17] and, in the case of phenanthroline–α-zirconium phosphate containing Co^{2+} [16] and Cu^{2+} [18], to quantify the extent of the *in-situ* complex formation occurring in the first 20–30 Å from the surface of the solid, taking account of the fact that XPS is a surface analysis technique and that the situation in the bulk could be different. Also, due to the surface heterogeneity of this polycrystalline compound, the information obtained by this technique could be the average of different situations.

The present paper describes the results of an XPS investigation on the host–guest interaction in the compound obtained by intercalating phenanthroline into γ-zirconium phosphate, γ-$Zr(HPO_4)_2(phen)_{0.5} \cdot 3\,H_2O$, and in its Co^{2+} and Cu^{2+} derivatives, γ-$ZrH_{1.56}[Co_{0.22}(phen)_{0.5}](PO_4)_2 \cdot 3\,H_2O$ and γ-$ZrH_{1.2}[Cu_{0.4}(phen)_{0.5}](PO_4)_2 \cdot 2\,H_2O$, respectively. A comparison is made with the XPS results obtained from the corresponding α-analogues, in an attempt to test whether XPS spectroscopy could give any information about the structure of the gamma compounds.
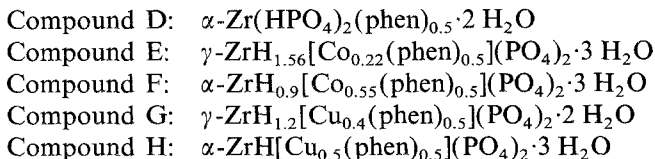
2. Experimental

2.1. MATERIALS

The materials submitted to XPS analysis in this paper are:

> Compound A: γ-$Zr(HPO_4)_2 \cdot 2\,H_2O$
> Compound B: α-$Zr(HPO_4)_2 \cdot H_2O$
> Compound C: γ-$Zr(HPO_4)_2(phen)_{0.5} \cdot 3\,H_2O$

Compound D: α-Zr(HPO$_4$)$_2$(phen)$_{0.5}$·2 H$_2$O
Compound E: γ-ZrH$_{1.56}$[Co$_{0.22}$(phen)$_{0.5}$](PO$_4$)$_2$·3 H$_2$O
Compound F: α-ZrH$_{0.9}$[Co$_{0.55}$(phen)$_{0.5}$](PO$_4$)$_2$·3 H$_2$O
Compound G: γ-ZrH$_{1.2}$[Cu$_{0.4}$(phen)$_{0.5}$](PO$_4$)$_2$·2 H$_2$O
Compound H: α-ZrH[Cu$_{0.5}$(phen)$_{0.5}$](PO$_4$)$_2$·3 H$_2$O

The compounds listed above, except compound E, were prepared according to literature methods (compound A [3], compound B [19], compound C and G [10], compounds D, F and H [8]). Their purity was checked by the usual chemical and physical methods [7]. Compound E was prepared by contacting compound C (1 mmole) with a 5 mmol/dm^{-3} Co^{2+} acetate solution (100 mL) for 10 days at 45°C. The solid was then filtered, washed with distilled water and air dried. X-ray diffraction patterns were taken on wet and dried samples. The uptake of Co^{2+} from solution was obtained by monitoring the concentration change in the supernatant liquid *via* AA spectrophotometry. The water and organic ligand content was determined thermogravimetrically.

2.2. XPS MEASUREMENTS

X-ray photoelectron spectra were taken with a Vacuum Generator Ltd. ESCALAB 5 MK2 spectrometer using Al$_{k_{\alpha 1.2}}$ excitation (1486.6 eV) at a residual pressure of 10^{-9} Pa.

Samples were dusted as a thin film onto gold or steel plates to minimize charging effects. The binding energy calibration was made with respect to the $4f_{7/2}$ gold line at 83.7 eV and sample charging was corrected by referencing to the 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 nitrogen temperature was performed as a precaution against possible secondary decomposition effects owing to the source.

The spectra were usually recorded in the fixed analyser transmission (FAT) mode at 20 eV. The collection and the fit of the XPS spectra were made by a DEC PDP 11/24 data system, described previously [20].

3. Results and Discussion

Table I reports the core binding energy values (BE in eV) of the compounds examined. The binding energy value of Zr3$d_{5/2}$ (183.0 $\pm$ 0.2 eV) agrees with the values found in the literature for the formal oxidation state of 4+ for zirconium [16, 17]. The binding energy value of P2p (133.6 $\pm$ 0.2 eV) is found to be constant along the series of compounds, except compounds A and B (see Table I), and it is characteristic of the PO$_4^{3-}$ group [16, 17].

3.1. γ-Zr(HPO$_4$)$_2$·2 H$_2$O AND THE α-COMPOUND

It is noticeable that in γ-zirconium phosphate (compound A) and in α-zirconium phosphate (compound B), the BE values of the Zr3$d_{5/2}$ and P2p lines are higher than the corresponding values of the other compounds reported in Table I. The

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

Compound	P_{2p}	$Zr_{3d5/2}$	N_{1s}			$M_{2p3/2}$	ΔE
(A) γ-Zr(HPO$_4$)$_2$·2 H$_2$O	134.6	183.8					
(B) α-Zr(HPO$_4$)$_2$·H$_2$O	134.5	184					
(C) γ-Zr(HPO$_4$)$_2$(phen)$_{0.5}$·3 H$_2$O	133.6	183.2	399.2		401.1		
(D) α-Zr(HPO$_4$)$_2$(phen)$_{0.5}$·2 H$_2$O	133.6	183	399.0		400.8		
(E) γ-ZrH$_{1.56}$[Co$_{0.22}$(phen)$_{0.5}$](PO$_4$)$_2$·3 H$_2$O	133.4	182.9	399.0	399.5	401.1	780.8	4.8–8.4[a] 5.4–8.6[b]
(F) α-ZrH$_{0.9}$[Co$_{0.55}$(phen)$_{0.5}$](PO$_4$)$_2$·3 H$_2$O	133.6	183	398.9	399.5	400.8	781.0	4.8–8.4[a] 5.1–8.6[b]
(G) γ-ZrH$_{1.2}$[Cu$_{0.4}$(phen)$_{0.5}$](PO$_4$)$_2$·2 H$_2$O	133.6	183	398.9	399.5	401.0	934.3	8–8.8
(H) α-ZrH[Cu$_{0.5}$(phen)$_{0.5}$](PO$_4$)$_2$·3 H$_2$O	133.8	183.2	399.0	399.7	400.8	934.4	8–8.6

$M_{2p3/2}$ = Co$_{2p3/2}$ or Cu$_{2p3/2}$.

ΔE = Energy separation (eV) of satellite lines from $M_{2p3/2}$ peak.

[a] In Figure 3 as ■.

[b] In Figure 3 as ▼.

decrease of the values in the other compounds is attributable to a decrease of the positive charge on the Zr and P atoms owing to the interaction of the phenanthroline with the phosphate groups.

It is known that the alpha and gamma forms of the zirconium phosphate are structurally different. The layers of α-Zr(HPO$_4$)$_2 \cdot$ H$_2$O consist of zirconium atoms lying nearly in a plane, with each zirconium linked to six different phosphate groups. In turn, the phosphate groups, located alternatively above and below the zirconium plane, share three oxygens with three different zirconium atoms whereas the fourth oxygen bears a proton exchangeable by other counterions [21]. The packing of the layers is such that the distance between two adjacent zirconium planes is 7.6 Å [21].

The structure of γ-Zr(HPO$_4$)$_2 \cdot$2 H$_2$O is still not known because no single crystals large enough for X-ray structural analysis have been obtained. However two models of the layers of γ-zirconium phosphate are available in the literature. The first, based on partial XRD results [2, 3], suggests that in the γ form the PO$_3$—OH groups are packed much closer than in α-zirconium phosphate, and the pendant $\geqslant$P—OH groups point directly towards one another in the interlayer region, different from the α form where there is a certain co-penetration between the $\geqslant$ P—OH groups belonging to two adjacent layers [21]. As a consequence, the γ form has a more expanded structure and, in fact, the interlayer distance is 12.27 Å [2, 3].

The second model, proposed by Clayden [22], suggests, on the basis of high resolution ^{31}P magic angle spinning (m.a.s.) NMR spectroscopy, that two chemically different phosphate groups in equal proportions are present in γ-zirconium phosphate: one, a PO$_4$ group, with the four oxygens linked to four different zirconium atoms, and the other, a PO$_2$—(OH)$_2$ group, with two framework oxygens linked to two zirconium atoms, whereas the other two bear the exchangeable protons. An alternate arrangement of the two types of phosphate groups along each layer should thus give rise to a stacking of the layers such that, even with the second structural possibility, the more hydrophilic $>$P—(OH)$_2$ groups belonging to two adjacent layers should point directly towards one another and hence justify a more open structure for γ-zirconium phosphate.

Turning to the XPS investigation, taking account of the Clayden suggestions, the presence of two chemically different phosphate groups in equal amount between the layers of γ-zirconium phosphate should ideally give rise to two distinct P2p peaks, or more probably to a broad P2p peak that should be resolved into two components with the same area. Unfortunately, as can be seen in Figure 1 and in Table I, the P2p peaks of compounds A and B are practically identical in shape and position (134.5 $\pm$ 0.2 eV) thus making it difficult to deconvolute the peak of the γ form: the full width at half maximum (FWHM) (2.2–2.3 eV) of the γ form is equal to that of the α form (2.2–2.3 eV), where only a single phosphorus species is present. Supposing that this occurs because the water molecules present in the interlayer region diminish the differences between the two types of phosphate groups, the P2p spectrum of the anhydrous γ-zirconium phosphate was repeated by decreasing the pass energy values from 20 eV to 5 eV to improve the photoelectron peak resolution. Notwithstanding this, the P2p peak remains single and the FWHM for all the pass energy values used is identical to that of the hydrated compound
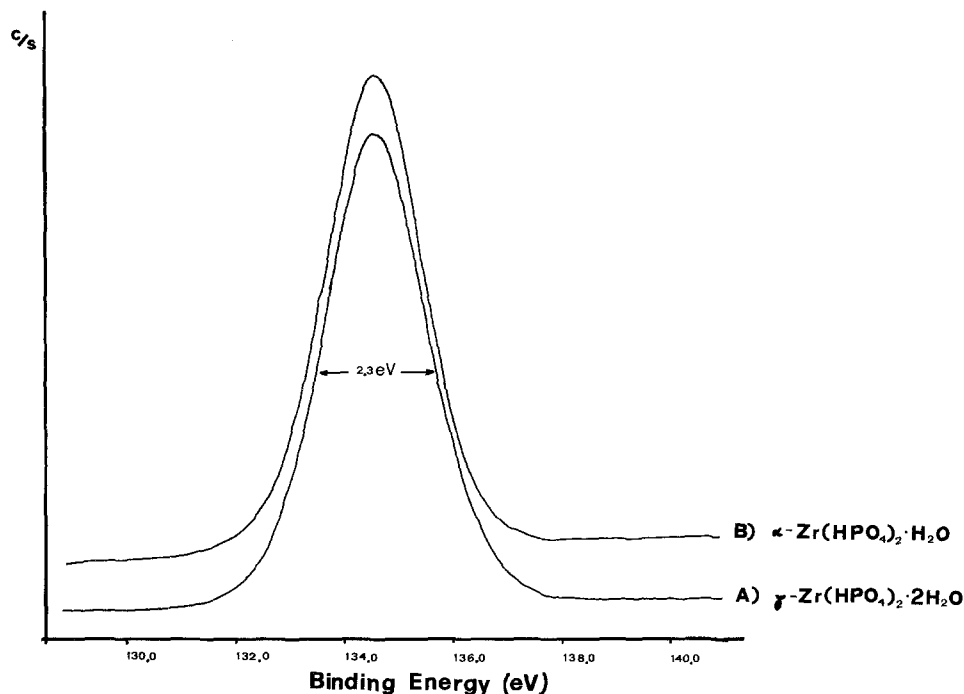
Fig. 1. P2p photoelectron spectra for the compounds: (A) γ-Zr(HPO$_4$)$_2$·2 H$_2$O; (B) α-Zr(HPO$_4$)$_2$·H$_2$O.

obtained at 20 eV (2.3 eV). This means that the two phosphorus atoms in the γ form have such a small difference in their electronic charge density that the consequent difference in binding energy is limited by the instrumental resolution.

3.2. γ-Zr(HPO$_4$)$_2$(phen)$_{0.5}$·3 H$_2$O AND THE α-COMPOUND

Table I presents the XPS data for the elements present in compound C and compound D, the latter for comparison [16, 17].

The analysis of the $N1s$ spectra of these compounds (Figure 2) gives two BE values in both α and γ-zirconium phosphate. As previously demonstrated [16, 17], the first value at 399.0 $\pm$ 0.2 eV is attributable to a free nitrogen atom and the second value at 401.0 $\pm$ 0.2 eV to a protonated nitrogen atom of the diamine. Thus, in compound C, the phenanthroline interacts with the host by a partial protonation of its nitrogen atoms with the acid groups present in the interlayer region, but to a larger extent than in compound D. In fact, by labelling with N the area referring to the free nitrogen and with NH that corresponding to the protonated one, it can be seen that the value of the N/NH peak area ratio calculated from Figure 2 falls in the range 0.6–0.7 for compound C, while this peak area ratio is almost equal to 1 for compound D.
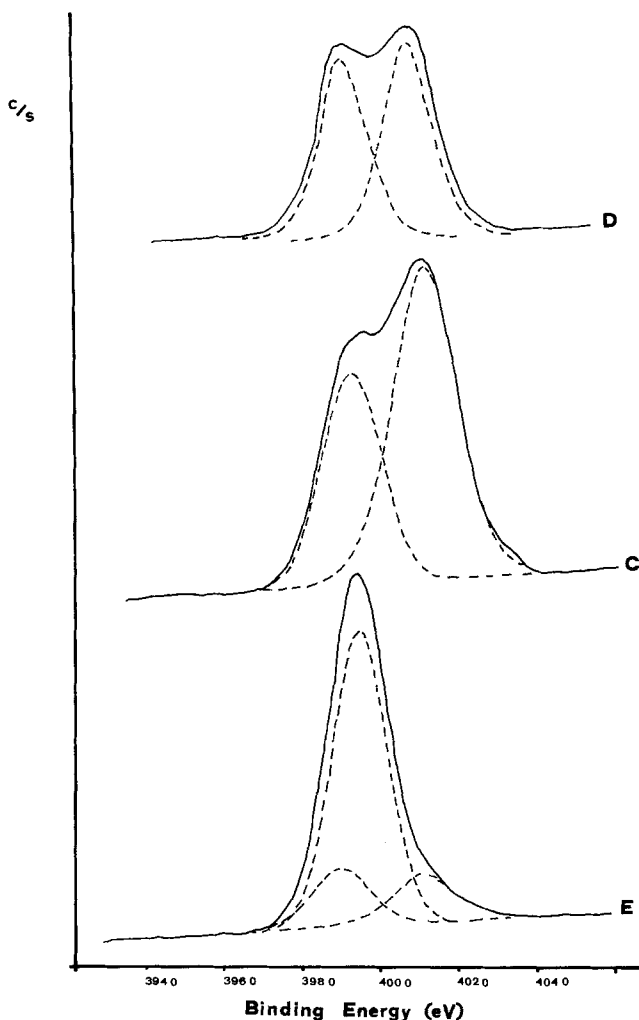
Fig. 2. $N1s$ photoelectron spectra for the compounds: (D) α-Zr(HPO$_4$)$_2$(phen)$_{0.5}$·2 H$_2$O; (C) γ-Zr(HPO$_4$)$_2$(phen)$_{0.5}$·3 H$_2$O; (E) γ-ZrH$_{1.56}$[Co$_{0.22}$(phen)$_{0.5}$](PO$_4$)$_2$·3 H$_2$O.

The value of the N/NH peak area ratio, *ca.* 1 for compound D, means that between the layers of the α form, on average, only one of the two nitrogens of each phen molecule is anchored to the host through a protonation process with an acid site, the other nitrogen remains free: the 1,10 position of the two nitrogens in the phenanthrenic skeleton of the diamine is such that only one of them interacts directly with a $\geqslant$ P—OH group, the other does not find a second acid site at a distance suitable for its protonation [17].

For compound C the value of the N/NH peak area ratio (0.6–0.7) indicates that, in contrast with compound D, some of the phen molecules have both nitrogens protonated. Taking into account that the amount of intercalated phen per mole of

host is the same for both γ- and α-zirconium phosphate and that the increase of the interlayer distance on intercalation of the diamine is very similar ($\Delta d = 6.6$ and 7.0 Å, respectively), the two different N/NH peak area ratio values could be attributable to a different distribution, and/or a different nature of the acid groups in the interlayer region, such that, in the case of γ-zirconium phosphate, a higher protonation of the aromatic diamine could be achieved.

3.3. γ-ZrH$_{1.56}$[Co$_{0.22}$(phen)$_{0.5}$](PO$_4$)$_2$·3 H$_2$O AND THE α-COMPOUND

The insertion of Co^{2+} into compound C gives rise to compound E. The corresponding XPS data are reported in Table I together with those of compound F [16] for comparison.

In Figure 3 the Co$2p_{3/2}$ XPS spectra for compounds E and F are reported. The spectra are practically the same in both compounds: a main peak at 781.0 ± 0.2 eV and a satellite structure is observed (see Table I and Figure 3), which is typical of the presence of the high spin Co^{2+} species [23]. This satellite line is placed on the high energy side of the main peak (781.0 eV) and it arises from an electron shake-up process [24–25].

The presence of this satellite structure is very important for distinguishing the Co^{2+} species from other cobalt species [23] and the number of satellite peaks and
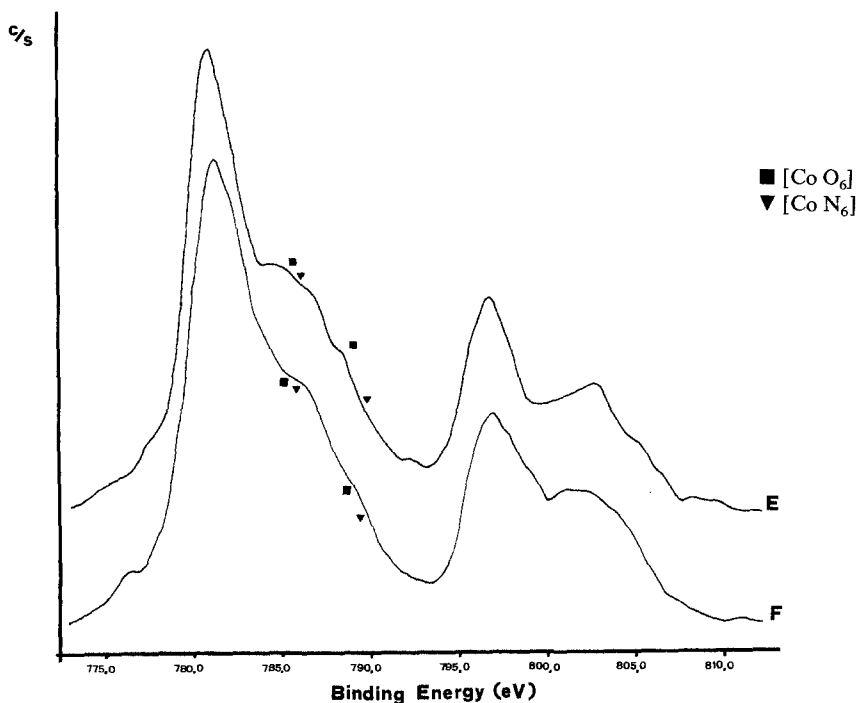

Fig. 3.   Co$2p_{3/2}$ photoelectron spectra for the compounds: (E) γ-ZrH$_{1.56}$[Co$_{0.22}$(phen)$_{0.5}$](PO$_4$)$_2$·3 H$_2$O; (F) α-ZrH$_{0.9}$[Co$_{0.55}$(phen)$_{0.5}$](PO$_4$)$_2$·3 H$_2$O.

their energy separation from the main peak are due to the chemical nature of the ligands and to the different coordination geometries of the compounds.

Deconvolution of the satellite structure was attempted and four satellite peaks, which can be separated into two pairs were resolved: the first, with an energy separation ΔE around 4.8 and 8.4 eV (see Table I) from the main peak, is close to that of $Co(OH)_2$ ($\Delta E = 4.6$, 8.1 eV) and the other pair, with ΔE values of 5.1–5.4 and 8.6 eV (see Table I), corresponds to that of the complex $[Co(phen)_3]Cl_2$ ($\Delta E = 5.3$, 8.6 eV) [16].

The presence of two pairs of satellite lines similar to those of $[CoN_6]$ and $[CoO_6]$ octahedral species are consistent with the presence of either mixed N- and O-, or only N- or O-coordinated high spin Co^{2+} species in compound E and F for comparison [16]. The coordination geometry will probably be distorted, owing to steric constraints imposed by the interlayer region.

The $N1s$ spectrum of compound E is very close to that of compound F and for these compounds the analysis gives three binding energy values located at 399.0 eV, 399.5 eV and 401.1 eV (Table I and Figure 2).

The first and the third values are practically coincident with those obtained by deconvolution of the N1s spectra of compounds C and D (Table I and Figure 2) and they correspond to a free and protonated nitrogen respectively.

The second value (399.5 eV) is very close to that of the coordinated nitrogen in the complex $[Co(phen)_3]Cl_2$ (399.8 eV) [16].

The presence of the peak at 399.5 eV confirms that some nitrogens of the phen molecules are coordinated to the cobalt ion, but the other two peaks at 399.0 eV and 401.1 eV indicate that in compound E, as for compound F [16], not all the phenanthroline present between the layers is coordinated to the Co^{2+} ions, but anchored to the host.

The extent of the coordinated phen molecules is much higher than that of the simply anchored phen. In fact, in compound E the percentage of metal-coordinated nitrogen (obtained as the ratio between the peak area of the coordinated N1s line and the total area of the N1s peak) is 72%. This means that the amount of coordinated phen in compound E is similar to that of compound F (84%) [16].

Since the amount of phen in the two compounds is the same and in compound E the cobalt content is nearly half that of compound F (see the stoichiometric formulae of compounds E and F in Table I) both $Co2p_{3/2}$ and N1s spectra seem to account for a complex species with two phen molecules coordinated to a Co^{2+} ion, i.e. a $[CoN_4O_2]$ chromophore, instead of a hypothetical $[CoN_2O_4]$ chromophore obtained for compound F from ESR [8] data.

It must be pointed out that here we have compared compounds E and F containing the maximum amount of cobalt ions that each of the parent compounds C and D could assume. This choice was made in order to obtain information on the way the α and γ structure can affect the coordination process. For the α derivative containing about the same amount of cobalt ions as compound E [16], with formula α-$ZrH_{1.64}[Co_{0.18}(phen)_{0.5}](PO_4)_2 \cdot 2\,H_2O$, the XPS data have given [16] a percentage of coordinated nitrogen of $ca.$ 40% and the $Co2p_{3/2}$ spectrum has a satellite structure similar to that of compound F, suggesting for this compound the presence of a $[CoN_2O_4]$ chromophore between the layers of the host, i.e. a 1 : 1

metal–ligand coordination even when the ligand, in high excess, could have formed a 'bis' complex species.

3.4. γ-ZrH$_{1.2}$[Cu$_{0.4}$(phen)$_{0.5}$](PO$_4$)$_2\cdot$2 H$_2$O AND THE α-COMPOUND

Finally the XPS data of compound G, obtained by inserting Cu^{2+} ions into compound C, and of compound H, the corresponding α derivative, are compared in Table I.

The N1s spectrum of compound G has been deconvoluted into three peaks, as found for compound H [18], located at 398.9 eV, 399.5 eV and 401.0 eV. These three binding energy values (see Table I and [18]), correspond to a free (398.9 eV), a metal-coordinated (399.5 eV) and a protonated (401.0 eV) nitrogen, respectively, giving exactly the same situation as that found for the cobalt compounds E and F (Table I). This means that in this case too the phen molecules are in part coordinated to the Cu^{2+} ions and in part anchored to the host through the protonation process with acid groups.

The percentage of diamine coordinated to the metal is 59% in compound G and 73% in compound H and this agrees with the lower quantity of metal in the γ form (10% lower). Taking into account the difference in the metal content and the fact that both materials contain the same amount of phen per mole of compound, it
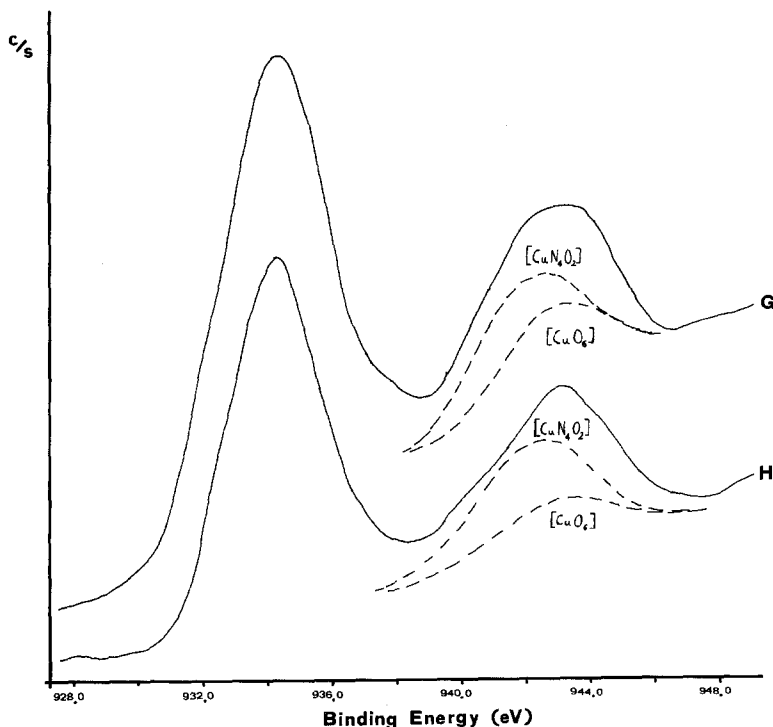

Fig. 4.   Cu2$p_{3/2}$ photoelectron spectra for the compounds: (G) γ-ZrH$_{1.2}$[Cu$_{0.4}$(phen)$_{0.5}$](PO$_4$)$_2\cdot$2 H$_2$O; (H) α-ZrH[Cu$_{0.5}$(phen)$_{0.5}$](PO$_4$)$_2\cdot$3 H$_2$O.

follows that in compound G the percentage of the diamine anchored to the host, calculated from the peak area, is higher than in compound H.

Figure 4 presents the $Cu2p_{3/2}$ spectra of compound G and of compound H for comparison [18]. The spectra, in both cases, comprise a main peak located at 934.4 ± 0.2 eV and a satellite structure due to an electron shake-up process that is typical for Cu(II) compounds [26–28]. The presence of shake-up lines is crucial in distinguishing the Cu(II) species from Cu(I) and Cu(0), which do not have the satellite line [23].

In compound G, as previously observed in compound H [18], the fitting of the satellite structure gives rise to two satellite peaks at 8 eV and 8.6–8.8 eV from the main peak. The first value ($\Delta E = 8$ eV), which is also found for $[Cu(phen)_2](ClO_4)_2$ [18], can be attributed to the $[CuN_4O_2]$ chromophore and the second value ($\Delta E = 8.6$–8.8 eV) is similar to that found for CuO, i.e. when copper is only surrounded by oxygen atoms [26–28].

These results mean that in the interlayer region of compound G, as previously found in the case of compound H [18], the Cu^{2+} taken up, in part coordinates to the phen and in part remains simply exchanged and surrounded by the oxygen atoms supplied by the phosphate groups and the water molecules also present between the layers of the host.

In compound G the peak intensity of the first satellite peak ($\Delta E = 8$ eV) is lower than the corresponding value obtained in compound H, whereas the peak intensity of the second satellite line ($\Delta E = 8.6$–8.8 eV) is higher than in compound H. This could mean that in compound G a major contribution of oxygenated ligand could be coordinated and hence that copper interacts more than in compound H with the oxygen atoms present in the interlayer region.

4. Conclusion

The X-ray photoelectron spectroscopic investigation applied to the phen-γ-zirconium phosphate intercalation compound has shown that the host–guest interaction of the diamine in γ-zirconium phosphate occurs with the same mechanism as in the α-zirconium phosphate, i.e. by means of the protonation of nitrogen atoms of the diamine with the hydrogen bearing phosphate groups (PO_3—OH or PO_2—$(OH)_2$, ?) present in the interlayer region of the host. But, in contrast to the α-zirconium phosphate compound, where each phen molecule interacts, on average, with only one of its two nitrogen atoms, in the γ-zirconium phosphate compound about 20% of the phen molecules are linked to the host with both their nitrogens.

X-ray photoelectron spectroscopy has given evidence that in the Co(II) and Cu(II) derivatives of phen-γ-zirconium phosphate, an *in-situ* metal–phen complex formation between the layers of the host takes place.

In the case of the Co(II) compound (compound E), a careful examination of the satellite structure of the $Co2p_{3/2}$ spectra has indicated that high-spin mixed N- and O-coordinated Co(II) is present and, in particular, a $[CoN_4O_2]$ chromophore is proposed, instead of a $[CoN_2O_4]$ chromophore as suggested for the α analogue (compound F).

The peculiar satellite structure of the $Cu2p_{3/2}$ peak for Cu(II)–phen–γ-zirconium phosphate (compound G), also accounts for a $[CuN_4O_2]$ chromophore, but it also

indicates that copper surrounded only by oxygen atoms is also present. The same features were found for compound H, but in this compound, as suggested by the shape of the satellite line, the full oxygenated chromophore is present to a minor extent.

The N1s spectra of compounds E and G confirm the complex formation between the layers of the γ-zirconium phosphate compound, since for both compounds an N1s peak corresponding to the coordinated nitrogen is found. But the presence of two N1s peaks referring to free and protonated nitrogens, even with low peak intensities, accounts for some uncoordinated phen molecules, in part linked to the host.

Acknowledgements

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