X-ray Spectroscopic Characterization of Cu²⁺-Phenanthroline Complexes Intercalated in α-Zirconium Phosphate

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Abstract. X-ray photoelectron spectroscopy provides evidence that when $[Cu(phen)_2]^{2+}$ (phen = 1,10-phenanthroline) is diffused between the layers of α-zirconium phosphate, the complex species does not remain intact after intercalation, but some Cu—N bonds are broken, replaced with Cu—O bonds and the released nitrogen atoms can now interact with the PO_3-OH groups of the host. XPS also provides evidence for coordination of the Cu^{2+} ions when they are diffused by ion exchange in the phenanthroline–α-zirconium phosphate intercalation compound. Although Cu^{2+} and phen are in a 1 : 1 molar ratio in the interlayer region of the host, so that a 1 : 1 coordination could be expected between the two species, the characteristic peaks of the uncoordinated phenanthroline, even though at a low intensity, are still present. The differences between the two Cu(II)-intercalation compounds are discussed.

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

1. Introduction

In our investigations on the intercalating properties of the layered inorganic ion exchangers α- and γ-zirconium acid phosphate: $\alpha\text{-}Zr(HPO_4)_2 \cdot H_2O$ [1] and $\gamma\text{-}Zr(HPO_4)_2 \cdot 2\,H_2O$ [2, 3], we have recently demonstrated that coordination compounds can be formed between the layers of these materials [4–8].

The large aromatic diamines 2,2′-bipyridyl, 1,10-phenanthroline and 2,9-dimethyl-1,10-phenanthroline intercalated between the layers of α-[4–7] and γ-zirconium phosphate [8], are indeed able to coordinate *in situ* transition metal ions such as: Cu(II), Ni(II), Co(II), Pd(II) and Pt(II) [4–8]. Various compounds were obtained which were characterized by their own chemical formula and X-ray diffraction patterns. 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 [4–8].

Since these compounds behave as catalysts [9, 10], information on the chemical and physical state of their surface is also of great interest. Particularly appropriate for obtaining such information is X-ray photoelectron spectroscopy (XPS), which

provides structural characterization and valuable information on the electronic charge density of the elements in a chemical compound [11]. Thus we firstly submitted to X-ray photoelectron spectroscopic investigation the compounds that α-zirconium phosphate forms with the above-mentioned diamines, obtaining very important results on the host–guest interaction [12], and then, with the same technique, we studied the intercalation compounds that phenanthroline–α-zirconium phosphate forms with Co^{2+} ions [13]. The XPS results confirmed the formation of Co^{2+}–phen complex species between the layers of the exchanger, but only from the XPS data was it possible to reveal that, especially at low Co^{2+} loadings, the coordination process is more pronounced in the most external layers of the crystallites and that, even when the ratio $[Co^{2+}] : [phen] = 1 : 1$ is reached in the material, ca. 15% of the total phenanthroline remains uncoordinated [13].

In this paper we report the XPS results regarding the Cu^{2+}-phenanthroline–α-zirconium phosphate intercalation compound, $\alpha\text{-ZrH}[\text{Cu-Phen}]_{0.5}(PO_4)_2 \cdot 3\,H_2O$, in which the 1 : 1 Cu-phen species is formed between the layers of the exchanger. A comparison is made with the compound $\alpha\text{-ZrH}_{1.60}[\text{Cu(Phen)}_2]_{0.2}(PO_4) \cdot 3\,H_2O$, obtained by directly inserting the complex $[\text{Cu(phen)}_2]^{2+}$ in the interlayer region of the α-zirconium phosphate.

2. Experimental

2.1. MATERIALS

The compounds listed in Table I were of the highest purity commercially available (compounds 6 and 8) or were prepared according to the literature (compounds 1, 2 and 4 [5], compound 5 [14], compound 7 [15]). Compound 3 was prepared by contacting at room temperature 1 mmol of the metastable ethanolic form of α-zirconium acid phosphate, $\alpha\text{-Zr(HPO}_4)_2 \cdot 2\,\text{EtOH}$ ($d = 14.20\,\text{Å}$) [16] with 100 mL of a $5\,\text{mmol dm}^{-3}\,Cu^{2+}$ acetate solution. A contact time of 24 h at 25°C was

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

Compound	P_{2p}	$Zr_{2p3/2}$	N_{1s}			$Cu_{2p3/2}$	ΔE^*
1. $\alpha\text{-ZrH}[\text{Cu(phen)}]_{0.5}(PO_4)_2 \cdot 3\,H_2O$ ($d = 15.77\,\text{Å}$)	133.5	183.3	399.1	399.6	400.7	934.6	8–8.6
2. $\alpha\text{-ZrH}_{1.6}[\text{Cu(phen)}_2]_{0.20}(PO_4)_2 \cdot 3\,H_2O$ ($d = 14.24\,\text{Å}$)	133.5	183.3		399.5	400.7	934.5	8–8.8
3. $\alpha\text{-ZrHCu}_{0.5}(PO_4)_2 \cdot 4\,H_2O$ ($d = 9.6\,\text{Å}$)	133.4	183.3				935.0	8.6
4. $\alpha\text{-Zr(HPO}_4)_2(\text{phen})_{0.5} \cdot 2H_2O$ ($d = 13.58\,\text{Å}$)	133.3	183.1	399.1		400.9		
5. $\alpha\text{-Zr(HPO}_4)_2 \cdot H_2O$ ($d = 7.6\,\text{Å}$)	133.4	182.9					
6. Phenanthroline			399.1				
7. $[\text{Cu(phen)}_2](ClO_4)_2$				399.5		934.4	8.2
8. CuO						934.5	8.6

For the compounds 1–5 the interlayer spacings (d in Å) are also given.
*ΔE = Energy separation (eV) of the satellite lines from the $Cu_{2p3/2}$ peak.

required in order for Cu^{2+} to be completely taken up by the solid. The material was then filtered off, washed with distilled water and air dried. XRD patterns were taken on the wet and dried samples. The water content was determined thermogravimetrically.

2.2. PHYSICAL MEASUREMENTS

X-ray diffraction patterns were recorded on a Philips diffractometer using Ni-filtered Cu-K_α radiation (2θ angles accurate to $\pm 0.05°$).

For the TG-DTA measurements a Mettler 2000 C simultaneous thermoanalyzer was employed.

X-ray photoelectron spectra were taken with a Vacuum Generator Ltd. ESCALAB spectrometer (Servizio Esca, Research Area of Rome, CNR) 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 a gold plate to minimize charging effects. Calibration was made using the $4f_{7/2}$ gold signal at 83.7 eV and sample charging was corrected by referencing to the $C 1s$ 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 nitrogen temperature was performed as a precaution against possible secondary decomposition effects.

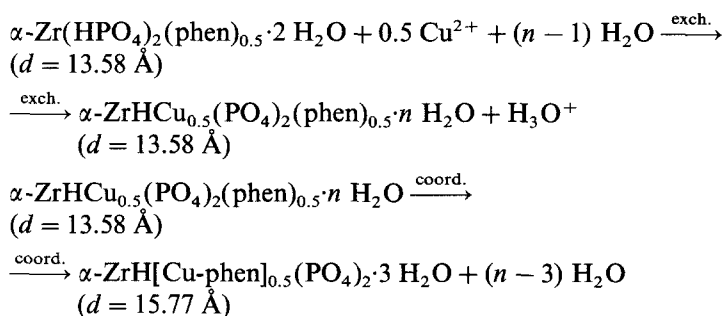Peak deconvolution was performed with a Du Pont 310 curve resolver using a Gaussian shape fit.

3. Results and Discussion

Before describing the results, it is helpful to recall the similarities and the differences that characterize the compounds under investigation.
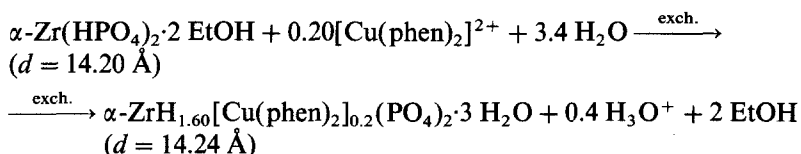
For both compounds **1** and **2**, Cu(II) (either as Cu^{2+} or $[Cu(phen)_2]^{2+}$) is inserted between the layers of the α-zirconium phosphate by an ion exchange process with the hydrogen ions of the PO_3-OH groups present in the interlayer region of the host [5]. The differences are in the reagent species that lead to different final compounds.

In the case of compound **1**, Cu^{2+} ions (as acetate) are first exchanged in the very stable phenanthroline−α-zirconium phosphate intercalation compound, α-$Zr(HPO_4)_2(phen)_{0.5}\cdot 2 H_2O$, (the batch method is used such that $[Cu^{2+}$ in the solution] : [intercalated phen] = 1 : 1) and subsequently coordinated to ligand throughout the layers. This latter process occurs with expansion of the interlayer spacing to allow an optimal orientation of the Cu-phen complex species formed *in situ* [5].

The reaction may be represented by the following scheme:

$$\alpha\text{-}Zr(HPO_4)_2(phen)_{0.5}\cdot 2 H_2O + 0.5\, Cu^{2+} + (n-1)\, H_2O \xrightarrow{\text{exch.}}$$
$$(d = 13.58\ \text{Å})$$

$$\xrightarrow{\text{exch.}} \alpha\text{-}ZrHCu_{0.5}(PO_4)_2(phen)_{0.5}\cdot n\, H_2O + H_3O^+$$
$$(d = 13.58\ \text{Å})$$

$$\alpha\text{-}ZrHCu_{0.5}(PO_4)_2(phen)_{0.5}\cdot n\, H_2O \xrightarrow{\text{coord.}}$$
$$(d = 13.58\ \text{Å})$$

$$\xrightarrow{\text{coord.}} \alpha\text{-}ZrH[Cu\text{-}phen]_{0.5}(PO_4)_2\cdot 3 H_2O + (n-3)\, H_2O$$
$$(d = 15.77\ \text{Å})$$

For compound **2** the complex species $[Cu(phen)_2]^{2+}$ is exchanged as such in the metastable diethanolic α-zirconium phosphate intercalation compound, α-$Zr(HPO_4)_2 \cdot 2$ EtOH according to the reaction scheme:

$$\alpha\text{-}Zr(HPO_4)_2 \cdot 2 \text{ EtOH} + 0.20[Cu(phen)_2]^{2+} + 3.4 \text{ H}_2\text{O} \xrightarrow{\text{exch.}}$$
$(d = 14.20 \text{ Å})$

$$\xrightarrow{\text{exch.}} \alpha\text{-}ZrH_{1.60}[Cu(phen)_2]_{0.2}(PO_4)_2 \cdot 3 \text{ H}_2\text{O} + 0.4 \text{ H}_3\text{O}^+ + 2 \text{ EtOH}$$
$(d = 14.24 \text{ Å})$

Compound **2** is at the maximum uptake of $[Cu(phen)_2]^{2+}$, no further complex can be intercalated.

Table I reports the core level binding energy values (in eV) of the elements present in the compounds under investigation (compounds **1** and **2**) and those chosen as references.

The binding energy value of P $2p$ (133.3 eV $\pm$ 0.2 eV) is found to be constant along the series of the compounds and characteristic of the PO_4^{3-} group [17].

The binding energy value of Zr $3d_{5/2}$ (183.1 $\pm$ 0.2 eV) indicates the typical formal oxidation state of (4+) for the Zr atoms [13].

The XPS results for the nitrogen of the compounds under investigation are shown in Table I. In Figure 1 the N $1s$ XPS spectra for compounds **1** and **2** together with those of compounds **4**, **6** and **7**, useful for the interpretation of compounds **1** and **2**, are reported.

Free phenanthroline (compound **6**) shows a single peak at 399.1 eV while α-Zr $(HPO_4)_2(phen)_{0.5} \cdot 2 H_2O$ (compound **4**) also shows a second peak at 400.9 eV. It has been demonstrated from previous XPS results [12] that the latter peak is attributable to a protonated nitrogen and that, on average, only one of the two nitrogen atoms of each phenanthroline molecule intercalated in the zirconium phosphate, is protonated by the PO_3-OH groups of the host. This can also be deduced by deconvolution of the N $1s$ XPS spectrum of compound **4** in Figure 1, where free nitrogen (399.1 eV) and protonated nitrogen (400.9 eV) are in an almost 1 : 1 intensity ratio [12].

In $[Cu(phen)_2](ClO_4)_2$ (compound **7**), in which all the phenanthroline nitrogens are coordinated to the copper, only one binding energy value at 399.5 eV is found. This value is more positive with respect to that at 399.1 eV of the free ligand (compound **6**) because of the decrease of the electronic charge density consequent upon the coordination effect.

The N $1s$ spectra of compounds **1** and **2** are very different from each other and in comparison with compounds **4**, **6**, and **7**. The analysis of the N $1s$ spectra of compound **1** gives three binding energy values at 399.1, 399.6 and 400.7 eV respectively, as was also found in the case of the Co^{2+}-phen-α-zirconium phosphate compounds [13]. The first value is coincident with the N $1s$ binding energy value found for the free ligand phenanthroline (399.1 eV) (see compound **6**). The second is very similar to that at 399.5 eV of the coordinated nitrogen in the complex $[Cu(phen)_2](ClO_4)_2$ (399.5 eV). The third binding energy value of N $1s$ at 400.7 eV is close to one of the two values found in α-$Zr(HPO_4)_2 (phen)_{0.5} \cdot 2 H_2O$ (compound **4**) and corresponds to a protonated nitrogen.
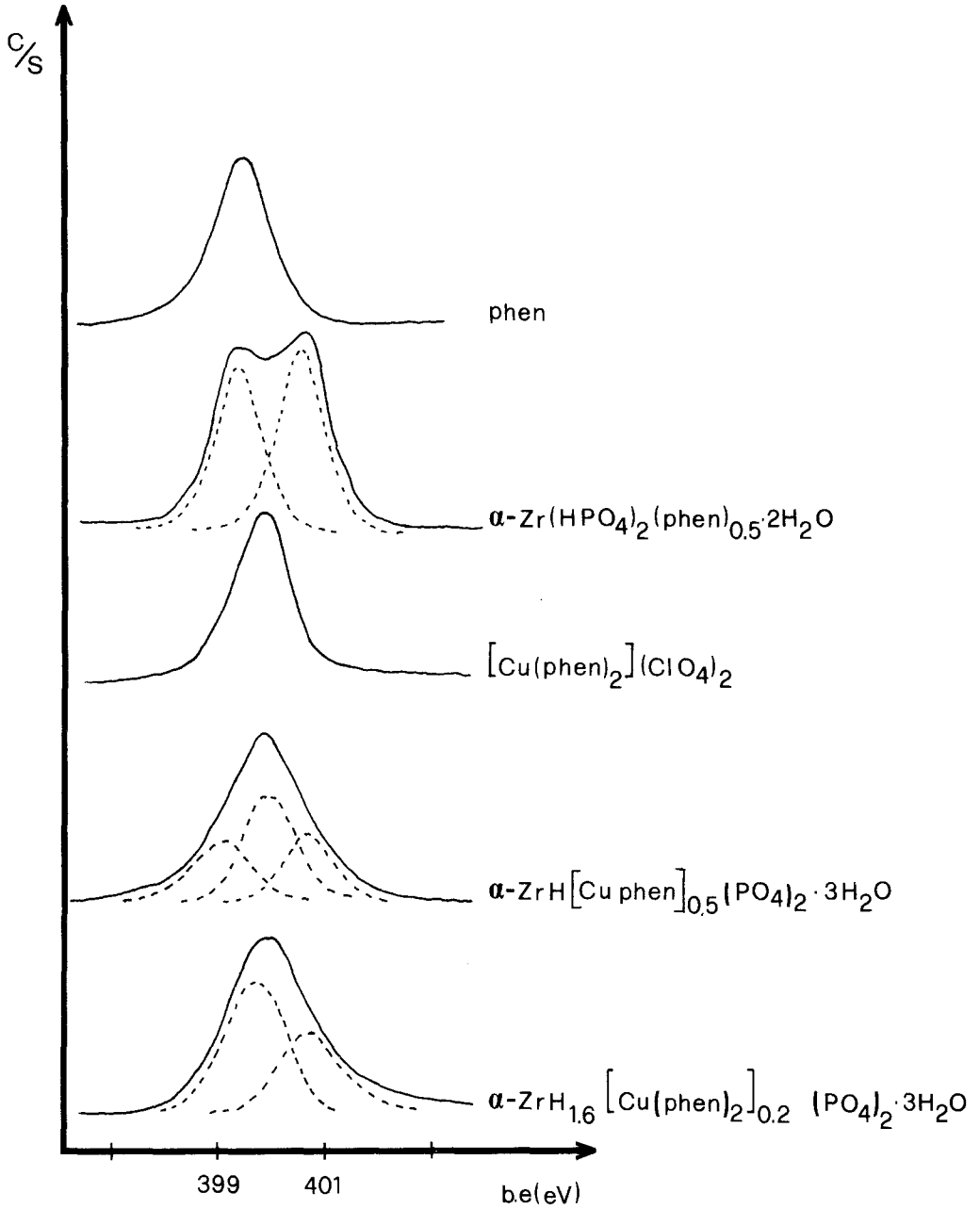
Fig. 1. Photoelectron spectra of the N_{1s} level.

The value at 399.6 eV clearly confirms that in compound **1** the copper ion is coordinated to the nitrogen, but the other two values (399.1 and 400.7 eV) are also meaningful in that they indicate that not all the phenanthroline present between the layers is coordinated to the copper ions. In fact the binding energy values at 399.1 and 400.7 eV are practically coincident with those obtained by deconvolution of the photoelectronic N $1s$ spectra of $Zr(HPO_4)_2(phen)_{0.5} \cdot 2H_2O$. The fact that in compound **1** some of the nitrogen atoms of the phenanthroline are free (399.1 eV) and some (400.7 eV) are anchored to the host through a protonation process with the PO_3-OH groups, indicates that the *in situ* coordination process between Cu^{2+} and the ligand, although present in a 1 : 1 ratio in the interlayer region of the host, does not go to completion.

The N $1s$ spectra of compound **2**, α-$ZrH_{1.6}[Cu(phen)_2]_{0.2}(PO_4)_2 \cdot 3H_2O$, shows only two binding energy values at 399.5 and 400.7 eV. The first binding energy value is similar to that of $[Cu(phen)_2](ClO_4)_2$ (399.5 eV); the second value (400.9 eV) is attributable to a protonated nitrogen (400.7 eV) (see Table I).

The binding energy value at 399.5 eV confirms that in compound **2** the Cu^{2+} ion is coordinated to the nitrogen, but the other value at 400.7 eV can only be explained by supposing that during the diffusion of $[Cu(phen)_2]^{2+}$ in the interlayer region some Cu—N bonds of the complex are broken and the nitrogen atoms of phenanthroline can now interact with the PO_3-OH groups of the host.
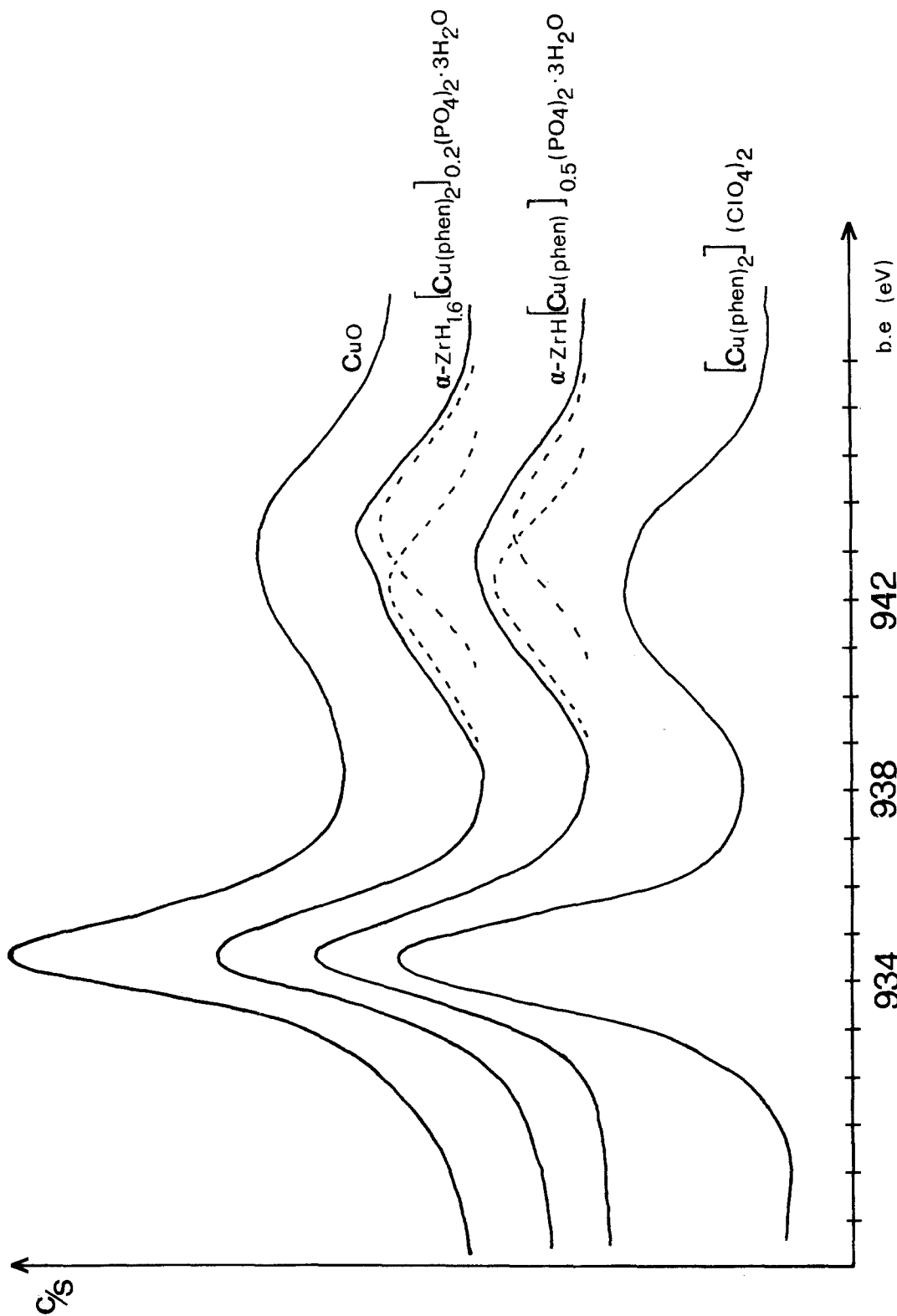
The Cu $2p_{3/2}$ photoelectron spectra of the Cu-containing compounds are reported in Figure 2.

The Cu $2p_{3/2}$ spectra of all the copper-containing compounds show a broad main $2p_{3/2}$ peak accompanied by the shake-up lines, which are typical for Cu(II) compounds. It is known that paramagnetic $3d$ transition metal ions present strong satellite lines of the $2p$ core levels and that the major component of the satellite structure can be attributed to the electron shake-up process [18, 19]. The shake-up process, in which the core level photoionization is accompanied by the excitation of valence electrons (multielectron-process), can give rise to several satellite peaks depending on the nature of the virtual orbitals to which the valence electrons are promoted.

The satellite structure can be generally attributed to a monopole charge transfer transition and it changes with the ground state configuration of the metal and depends on the ligand. The number of satellite peaks and their energy separation can be generally attributed to processes involving $L \rightarrow M$ charge transfer, and depends on the chemical nature of the different coordination geometries. However, Cu(II) is different in that it has been suggested that in the case of satellites seen in spectra of this ion, these are more likely to be due to processes involving $M \rightarrow L$ charge excitation, as the core ionized 'ground state' has a completed $3d$ shell due to an influx of electrons from the ligand. This is despite the fact that the ground state electronic structure of neutral Cu(II) compounds is characterized by a vacant spin orbital [20].

Therefore Larsson has suggested that in core level spectra of Cu(II) compounds the main peak corresponds closely to a d^{10} configuration which should not show any satellite structure, whereas the satellite corresponds to a d^9 configuration [19].

The Cu $2p_{3/2}$ binding energy values of all the compounds are similar (934.7 ± 0.2 eV) along the series, but the shape of each spectrum shows a peculiar

Fig. 2. Photoelectron spectra of Cu2$p_{3/2}$ level.

satellite structure (Figure 2). In compounds 1 and 2 a very broad and complex structure ont he high energy side of the Cu $2p_{3/2}$ peak can be observed, which by deconvolution gives rise to two satellite peaks with energy separation values ΔE from the main peak of 8.0 eV and 8.6–8.8 eV respectively. The first value of $\Delta E = 8.0$ eV, which is also found for [Cu(phen)$_2$](ClO$_4$)$_2$ (see Table I), can be attributed to the [CuN$_4$O$_2$] chromophore and the other one ($\Delta E = 8.6$–8.8 eV) is similar to the value found for CuO and α-ZrHCu$_{0.5}$(PO$_4$)$_2$·4 H$_2$O($\Delta E = 8.6$ eV), when copper is only surrounded by oxygen atoms (see Table I and [21]). In compound 2 the intensity of this second satellite peak ($\Delta E = 8.8$ eV) is higher than that of compound 1 and this could mean that in compound 2 a major contribution of oxygenated ligand could be present and that Cu^{2+} interacts more than in compound 1 with the oxygen atoms present in the interlayer region of the host. This result indicates that when [Cu(phen)$_2$]$^{2+}$ is inserted between the layers of α-zirconium phosphate, it anchors to the host by ion-exchange with the hydrogen of the PO$_3$-OH groups, but it also undergoes a change in the coordination in the sense that some of the four nitrogen atoms, initially bonded to Cu^{2+}, detach from the metal ion, protonate with the PO$_3$-OH groups abundantly present in the interlayer region of the host and are substituted in the coordination to Cu(II) with oxygen coming from water molecules. These results are in agreement with what was previously found for the N $1s$ spectra of compound 2. Here, besides the N $1s$ binding energy value at 399.5 eV, indicative of coordinated nitrogen atoms, the N $1s$ binding energy value observed at 400.7 eV, absent in pure [Cu(phen)$_2$]$^{2+}$ (see Table I and Figure 1), means that some other reactions occur leading to the nitrogen protonation when the complex species diffuses between the layers of the α-zirconium phosphate.

Further confirmation that Cu^{2+} coordination in compounds 1 and 2 is different, is obtained by examining the shape and the intensity of the satellite peaks of the two compounds, in comparison with [Cu(phen)$_2$](ClO$_4$)$_2$, where only the [CuN$_4$O$_2$] chromophore is present, and with CuO. In compound 1 the intensity of the satellite line at $\Delta E = 8$ eV is lower than in compound 7, so that the intensity ratio [$I_{Cu\,2p3/2}/I_{sat}$] is 1.27, while in the complex [Cu(phen)$_2$](ClO$_4$)$_2$ this intensity ratio is 0.82. These values suggested that the main peak Cu $2p_{3/2}$ of compound 1 is composed of a species of copper containing mixed nitrogen and oxygen ligands and another bonded to the oxygen ligand only.

In compound 2 the intensity ratio [$I_{Cu\,2p3/2}/I_{sat}$] of the satellite line at $\Delta E = 8.0$ eV is 1.73; the intensity of the satellite line at $\Delta E = 8.8$ eV, attributable to the [CuO] chromophore, is higher both with respect to the value of the satellite line at $\Delta E = 8.0$ eV and to the intensity of the corresponding satellite line at $\Delta E = 8.6$ eV of compound 1, thus confirming the change of the ligands when [Cu(phen)$_2$]$^{2+}$ is inserted between the layers of the zirconium phosphate.

4. Conclusions

The XPS studies carried out on Cu-phen intercalation compounds with α-Zr(HPO$_4$)$_2$·H$_2$O have given interesting results which confirm the different nature of the compounds examined owing to their different preparative methods.

The analysis of N 1s spectra of α-ZrH[Cuphen]$_{0.5}$(PO$_4$)·3 H$_2$O (complex formed *in situ*) gives three binding energy values: the first (399.1 eV) is coincident with the N 1s binding energy value of the free ligand phenanthroline, the second (399.5 eV) is very similar to the value of the coordinated nitrogen in the complex [Cu(phen)$_2$](ClO$_4$)$_2$ and the third (400.7 eV) is close to the value of a protonated nitrogen. This gives evidence for coordination of the Cu(II) ions, when they are diffused in the phenanthroline–α-zirconium phosphate intercalation compound.

The N 1s spectra of α-ZrH$_{1.6}$[Cu(phen)$_2$]$_{0.2}$(PO$_4$)$_2$·3 H$_2$O contains two peaks: the first (399.5 eV) corresponds to a coordinated nitrogen and the other (400.7 eV) to a protonated nitrogen. This means that, when the complex [Cu(phen)$_2$]$^{2+}$ is directly inserted between the layers of α-zirconium phosphate, the complex species does not remain intact after intercalation, but some Cu—N bonds are broken, replaced with Cu—O bonds and the released nitrogen atoms are linked to the host through the PO$_3$-OH groups.

Acknowledgements

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