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Thermal behaviour of γ-titanium phosphate–phenanthroline intercalation compound exchanged with silver and other transition metal ions[☆]

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Abstract

The layered composite γ-TiPO$_4$(H$_2$PO$_4$)phen$_{0.48}\cdot$1.5H$_2$O (phen = 1,10-phenanthroline) is able to exchange transition metal ions to give new intercalation compounds. The uptake of divalent cobalt, nickel and copper gives materials with interlayer distances unchanged in respect of the precursor, while with silver ions two new compounds are obtained with the interlayer spacing increased by about 3 Å. The silver materials also exchange Co(II), Ni(II) and Cu(II) and bimetallic intercalation compounds are thus obtained. All the new phases submitted to TG–DTA experiments show specific behaviour depending on the nature and amount of metal ion present in the solids. Silver has a catalytic effect on phenanthroline elimination with temperature, since the process is the more pronounced the higher the silver content. During exchange with cobalt the silver materials undergo a redox process and metallic silver is present in the solids as prepared. Ag^0 is no longer observable when the two compounds are heated above 500°C, a gain of weight of weight is detected in the TG curves, probably due to Ag$_2$O formation. The redox process presumably also occurs in the Ni–Ag derivatives since, as for the Co–Ag analogues, the compounds are dark-grey coloured. After elimination of phen, the thermal treatment leads to the formation of AgTi$_2$(PO$_4$)$_3$, transition metal–titanium double phosphates and pyrophosphates, processes always accompanied by exothermic effects in the DTA curves.

Keywords: Intercalation compounds; Layered composite; TG–DTA; Thermal behaviour; γ-Titanium phosphate–phenanthroline compounds; Transition metalions

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1. Introduction

Crystalline hydrogen phosphates of tetravalent metals can be obtained in two-layered structures, commonly denoted α [1] and γ [2], which correspond to two different series of compounds with chemical formulae $M^{IV}(HPO_4)_2 \cdot H_2O$ (M^{IV} = Zr, Ti, Sn) for the α materials (α-M^{IV}P) and $M^{IV}PO_4(H_2PO_4) \cdot 2H_2O$ (M^{IV} = Zr, Ti) for the γ compounds, (γ-M^{IV}P). They are all known ion-exchangers now increasingly appreciated and studied because, after suitable chemical and thermal treatment, they can be usefully employed in heterogeneous catalysis. As such [3, 4] or exchanged with transition metal ions (t.m.i.) [5] and conveniently calcined, these compounds have been employed in acid catalysis and in catalysed oxidation reactions [6]. Both α and γ phases have intercalating properties and a great variety of materials can be prepared by inserting polar molecules between the layers. Alcohols, glycols, organic bases, heterocycles, etc. [7, 8], have been intercalated and the resulting compounds possess interlayer distances greater than those of the precursors.

We have widely studied the intercalation of the aromatic diamines 2,2′-bipyridyl (bipy), 1,10-phenanthroline (phen) and 2,9-dimethyl-1,10-phenanthroline (dmp) in α-ZrP and γ-ZrP [8]. These two exchangers, the most investigated of the respective series, possess interlayer distances of 7.56 and 12.23 Å, respectively. We have demonstrated that the α- and γ-zirconium phosphate–diamine intercalation compounds are able to exchange t.m.i. which, in turn, have the possibility of forming, in-situ, between the layers, coordinated species with the previously intercalated diamines [8]. Some of these compounds have been used as catalysts in the oxidative dehydrogenation of aniline [9, 10] and in CO oxidation [11].

It was of obvious interest to extend such investigation to another layered ion-exchanger of the class, γ-$TiPO_4(H_2PO_4) \cdot 2H_2O$ (γ-TiP) [12], also having an expanded interlayer distance of 11.6 Å, the structure which has been recently proposed [13]. We have studied the intercalation properties of γ-TiP towards the above mentioned aromatic diamines [14, 15] and intercalated materials with a good degree of crystallinity and further increased interlayer distances have been obtained.

The present paper describes the thermal behaviour of the materials obtained from the γ-TiP–phenanthroline intercalation compound, after exchange with silver ions and divalent cobalt, nickel and copper, employing different experimental conditions. Mixed metal-containing compounds have also been prepared and thermally examined. This study is a necessary preliminary step before the submission of the materials for catalytic tests.

2. Experimental

2.1. Chemicals

Liquid $TiCl_4$, 85% aqueous H_3PO_4, divalent cobalt, nickel and copper acetates and silver nitrate were Erba RPE (analytical grade regent) products. 1,10-phenanthroline was Fluka Purissimum "pro analysi" (purity grade $>$ 99%). All were used as received.

2.2. Preparation of materials

2.2.1. γ-titanium phosphate

γ-$TiPO_4(H_2PO_4)\cdot 2H_2O$ (γ-TiP) was prepared hydrothermally according to the method of Allulli et al. [12]. Amorphous titanium phosphate was sealed in a Pyrex tube with 10 mol dm^{-3} H_3PO_4, charged into a hydrothermal bomb and heated in an oven at 300°C for 48 h. After cooling the solid was filtered, washed with water to pH 4 and air-dried at room temperature (r.t.).

2.2.2. Diamine γ-TiP intercalation compound

γ-$TiPO_4(H_2PO_4)phen_{0.48}\cdot 1.5H_2O$, γ-$TiPphen_{0.48}$ [14] was obtained by first pre-swelling γ-TiP with ethanol (1 g of γ-TiP + 100 mL anhydrous EtOH in contact for 24 h). The resulting γ-TiPEtOH intercalation compound, which possesses an interlayer distance of 15.7 Å, was then treated while still wet with 500 mL of a 0.01 mol dm^{-3} H_2O–EtOH (1:1) solution of phen for 4 d at 45°C. The solid was filtered, washed with ethanol and air-dried at r.t. γ-$TiPphen_{0.48}$ has an interlayer distance of 18.0 Å.

2.2.3. Monometallic intercalation compounds

The transition metal ion–γ-TiPphen intercalation compounds were prepared by ion-exchange, by equilibrating γ-$TiPphen_{0.48}$ with the appropriate salt solution (0.005 mol dm^{-3} for Co(II), Ni(II) and Cu(II) acetates and 0.01 mol dm^{-3} for Ag(I) nitrate). Two different solid/solution ratios were chosen. One series of materials was prepared by treating γ-$TiPphen_{0.48}$ (1 mmole) with a volume of t.m.i. solution containing 0.48 mmoles of metal ion, such that the amounts of phen in the solid and of t.m.i. in the solution were in a 1:1 molar ratio. The second series of materials was prepared by treating 1 mmole of γ-$TiPphen_{0.48}$ with a volume of t.m.i. solution containing an amount of t.m.i. (0.96 mmoles) double that of the phen in the solid, thus achieving a phen:t.m.i. = 1:2 molar ratio. All of the batches were thermostatted at 45°C for 7 d. The suspensions were then filtered, the solutions analysed for metal content and pH, and the solids were washed with distilled water and air-dried. The t.m.i. chemical analysis showed that the moles of metal ion taken up by γ-$TiPphen_{0.48}$ were always lower than those initially present in the contact solution. This is a feature already observed in these intercalation compounds [16]. For both series of compounds the uptake of Co(II), Ni(II) and Cu(II) ranged from 0.12–0.24 moles $mole^{-1}$ of γ-$TiPphen_{0.48}$. For the silver-exchanged materials, the first solid–solution condition leads to γ-$TiPO_4(H_{1.76}Ag_{0.24}PO_4)phen_{0.48}\cdot 2H_2O$, hereafter indicated as γ-$TiPphen_{0.48}Ag_{0.24}$, while the second gives γ-$TiPphen_{0.48}Ag_{0.35}$. A third silver-exchanged compound with formula γ-$TiPphen_{0.48}Ag_{0.48}$ has been obtained by adding to 1 mmole γ-$TiPphen_{0.48}$ a volume of Ag^+ such that the moles of silver ion (1.34 mmoles of Ag^+) were three times those of the phen in the solid. All of the three silver intercalation compounds possess the interlayer distance of 20.9 Å. The material formulations of some of the obtained compounds, synthetically expressed, are given in Table 1. Their interlayer distances are also reported.

Table 1
Chemical composition of some compounds obtained from γ-TiPphen$_{0.48}$

Compound[a]	Interlayer distance, d_{002} in Å
1) γ-Ti(PO$_4$)(H$_2$PO$_4$)phen$_{0.48}\cdot$1.5H$_2$O	17.7
2) γ-Ti(PO$_4$)(Co$_{0.12}$H$_{1.76}$PO$_4$)phen$_{0.48}\cdot$1.5H$_2$O	17.7
3) γ-Ti(PO$_4$)(Ni$_{0.14}$H$_{1.72}$PO$_4$)phen$_{0.48}\cdot$2H$_2$O	17.7
4) γ-Ti(PO$_4$)(Cu$_{0.24}$H$_{1.52}$PO$_4$)phen$_{0.48}\cdot$1.9H$_2$O	17.7
5) γ-Ti(PO$_4$)(Ag$_{0.24}$H$_{1.76}$PO$_4$)phen$_{0.48}\cdot$2H$_2$O	20.9
6) γ-Ti(PO$_4$)(Ag$_{0.48}$H$_{1.52}$PO$_4$)phen$_{0.48}\cdot$1.9H$_2$O	20.9

[a] The chemical formulae of the compounds will be briefly expressed in the text by γ-TiP then, in sequence, the phen and metallic content. Hydration water molecules will be omitted. As an example, compound 3 γ-TiPphen$_{0.48}$Ni$_{0.14}$

2.2.4. *Bimetallic intercalation compounds*

Bimetallic compounds were obtained by ion-exchange by equilibrating γ-TiPphen$_{0.48}$Ag$_{0.24}$ and γ-TiPphen$_{0.48}$Ag$_{0.48}$ with Co(II), Ni(II), Cu(II) acetate solutions. 1 mmole of γ-TiPphen$_{0.48}$Ag$_{0.24}$ or γ-TiPphen$_{0.48}$Ag$_{0.48}$ was treated with a volume of t.m.i. acetate solution such that the mequiv of metal ion in the liquid corresponded exactly to those of the hydrogen ions still exchangeable in the precursor (1.76 mequiv of exchangeable hydrogens in γ-TiPphen$_{0.48}$Ag$_{0.24}$ and 1.52 mequiv in γ-TiPphen$_{0.48}$ Ag$_{0.48}$). Temperature and contact time were as for the monometallic intercalation compounds. The material formulations and interlayer distances of some of the obtained compounds are given in Table 2, with the same abbreviations as in Table 1. The amounts of exchanged t.m.i. are higher than when silver is not present in the material. The interlayer distances remain those of the silver intercalation compounds.

2.3. *Physical measurements and chemical analyses*

The thermal curves were recorded on a simultaneous TG–DTA Stanton Redcroft 1500 thermoanalyzer, Pt crucibles, heating rate 8 K min^{-1}, ignition up to 1200°C to

Table 2
Chemical composition of some compounds obtained from γ-TiPphen$_{0.48}$Ag$_{0.24}$ and γ-tiPphen$_{0.48}$Ag$_{0.48}$

Compound[a]	Interlayer distances d_{002} in Å
1) γ-Ti(PO$_4$)(Ag$_{0.24}$Co$_{0.28}$H$_{1.1}$PO$_4$)phen$_{0.35}\cdot$4H$_2$O	20.9
2) γ-Ti(PO$_4$) Ag$_{0.24}$Ni$_{0.37}$H$_{1.02}$PO$_4$)phen$_{0.38}\cdot$4H$_2$O	20.9
3) γ-Ti(PO$_4$)(Ag$_{0.24}$Cu$_{0.50}$H$_{0.76}$PO$_4$)phen$_{0.41}\cdot$3.5H$_2$O	20.9
4) γ-Ti(PO$_4$)(Ag$_{0.48}$Co$_{0.25}$H$_{1.02}$PO$_4$)phen$_{0.18}\cdot$3.2H$_2$O	20.9
5) γ-Ti(PO$_4$)(Ag$_{0.48}$Ni$_{0.20}$H$_{1.12}$PO$_4$)phen$_{0.20}\cdot$3.4H$_2$O	20.9
6) γ-Ti(PO$_4$)(Ag$_{0.48}$Cu$_{0.51}$H$_{0.50}$PO$_4$)phen$_{0.23}\cdot$3.6H$_2$O	20.9

[a] The compounds will be formulated in the text with the same abbreviations as described in the footnote of Table 1

constant weight in an air flow. All the materials were submitted to X-ray diffraction analysis, especially by monitoring the d_{002} reflection (which is known to correspond to the interlayer distance for these ion-exchangers) and thus obtain information about the maintenance or not of the layered structure. The XRD were taken on a Philips diffractometer. Ni-filtered CuKα radiation was used, and measurements of 2θ were believed accurate to 0.05°.

Metal ions contents were determined by following the concentration changes in the supernatants by atomic absorption spectrometry using a G.B.C. 903 instrument. Water and phen content of the solids were determined from the TG curves.

3. Results and discussion

3.1. Monometallic intercalation compounds

3.1.1. X-ray diffraction analysis

In Fig. 1 are given the XRD patterns of γ-TiPphen$_{0.48}$ (a), γ-TiPphen$_{0.48}$Co$_{0.12}$ (b) and γ-TiPphen$_{0.48}$Ag$_{0.24}$ (c). γ-TiPphen$_{0.48}$ is a material with a very good degree of crystallinity and an interlayer distance of 18.0 Å, much larger than that of γ-TiP ($\Delta d = 6.4$ Å). The XRD pattern of the coderivative (b) (it is also the case for the nickel- and copper-based materials) is very similar to that of the precursor (a). The interlayer distance remains unchanged after cobalt insertion, only the material is less crystalline. By contrast, the Ag$^+$-exchanged compound (c) undergoes layer expansion on uptake of Ag$^+$ of about 3 Å in respect of the precursor (see Table 1) The XRD pattern indicates a high degree of crystallinity and shows an enhanced intensity of the d_{004} reflection relative of d_{002}. This feature gives an indication that silver ions have exchanged thoughout alternate layers, i.e. that the material is a stage 2-layered solid [17].

3.1.2. Thermal behaviour

γ-TiPphen$_{0.48}$

The TG–DTA curves of γ-TiPphen$_{0.48}$ are given in Fig. 2. The compound loses its water of hydration up to 250°C and correspondingly a series of small endothermic peaks are observed in the DTA curve. The main phen elimination takes place in two steps at 250–420°C and 420–650°C. These two thermal effects give an indication that the phen molecule interacts with the matrix into two different ways: the I.R. and U.V. spectra of the materials [15] show evidence of protonated phen, consequent to the interaction of the nitrogen atoms of phen with the $(HO)_2PO_2$ groups present in the interlayer region, but also of covalent hydration of the aromatic ring [18], C(H)–OH. The higher amount of phen loss occurs from 420–650°C and is accompained by a strong exothermic peak in the DTA curve. This step is the loss of that part of phen more tightly interacting with the host, i.e. the rings with the protonated nitrogens. The condensation of the dihydrogen phosphate groups to pyrophosphate also begins in this range of temperatures. In pure γ-TiP this process is accompanied by an endothermic effect. In a last step, between 750 and 900°C, the condensation process goes to

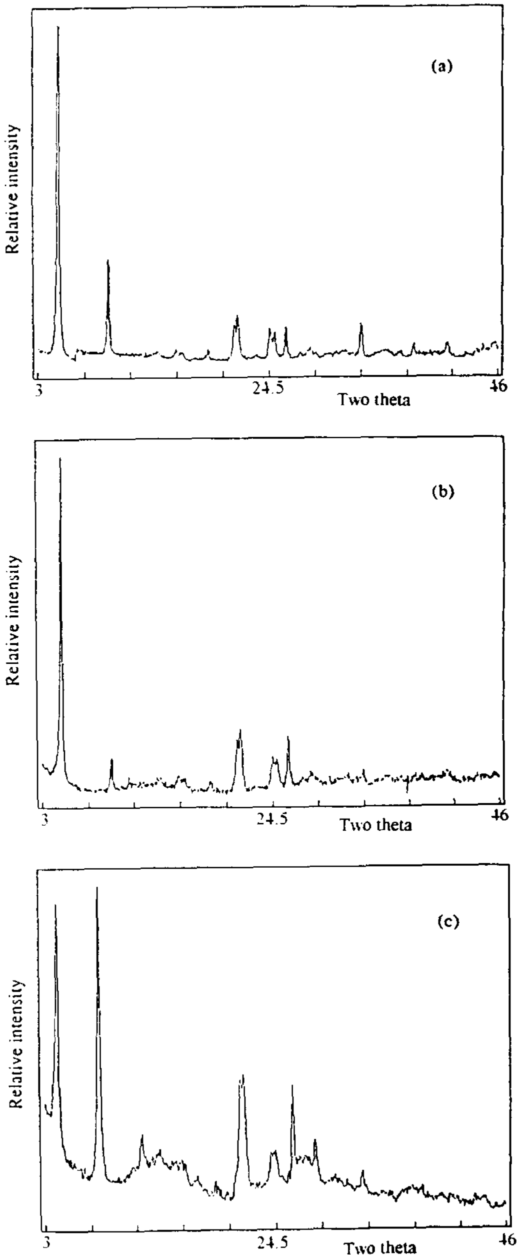

Fig. 1. X-ray diffraction patterns of γ-TiPphen$_{0.48}$ (a), γ-TiPphen$_{0.48}$Co$_{0.12}$ (b) and γ-TiPphen$_{0.48}$Ag$_{0.24}$ (c).

completion together with the loss of the carbonaceous residues of the diamine. At 880°C a small exothermic peak is observed in the DTA curve due to formation of cubic α-TiP_2O_7.

γ-$TiPphen_{0.48}$-t.m.i.(Co, Ni, Cu)

The TG–DTA curves of γ-$TiPphen_{0.4}Co_{0.12}$ are given in Fig. 2. They are very similar to those of γ-$TiPphen_{0.48}$ except that the last weight loss ends at a lower temperature and an exothermic reaction occurs from 730–830°C. This latter effect is connected with salt formation. The X-ray diffraction pattern of the Co-containing material calcined at 900°C shows the reflection of both α-TiP_2O_7 and $Co_2P_2O_7$, and the other reflections also present in the diagram could be related to a double phosphate of the type $CoTi(PO_4)_2$ by analogy with what occurs in the case of layered α-zirconium phosphate exchanged with the first row t.m.i. [19]. This behaviour is also shown by the Ni(II) and Cu(II) derivatives in the same range of temperatures.

γ-$TiPhen_{0.48}Ag_{0.24}$

The thermal behaviour of γ-$TiPphen_{0.48}Ag_{0.24}$ is shown in Fig. 2. It is different from both the precursor and the divalent t.m.i. derivatives. The main phen loss always occurs in two steps but in a higher amount than in the previous cases between 250 and 450°C, as if the presence of silver catalyses the organic combustion. Further, the last weight loss, related to the final dihydrogen phosphate condensation and carbonaceous residues now begins around 650°C. In the DTA curve the exothermic effect occurring from 700–850°C shows, at 820°C, a sharp and intense peak associated to the formation of cubic α-TiP_2O_7 and $AgTi_2(PO_4)_3$, both present in the solid heated at 950°C.

γ-$TiPphen_{0.48}Ag_{0.48}$

Concerning the thermal behaviour of γ-$TiPphen_{0.48}Ag_{0.48}$ (see Fig. 5a), the three steps in the TG curve are now contained in the range 250–650°C with a lowering of 250°C relative to that of γ-$TiPphen_{0.48}$. The presence of a higher amount of silver in the solid favours even more the elimination of phen in the first step of loss, and in the DTA, in correspondence of the third step, the thermal effect related to $AgTi_2(PO_4)_3$ formation is strongly anticipated at 650°C. This is evidentiated by an exothermic, well defined peak larger than that found for γ-$TiPphen_{0.48}Ag_{0.24}$. As expected the X-ray diffraction pattern of this material taken at 900°C, only shows the presence of $AgTi_2(PO_4)$; since the Ag:Ti molar ratio in the formula is 1:2, all of the titanium is involved in the formation of this salt.

3.2. *Bimetallic intercalation compounds derived from* γ-$TiPphen_{0.48}Ag_{0.24}$

3.2.1. *X-ray diffraction analysis*

The divalent cobalt, nickel and copper ions are exchanged in γ-$TiPphen_{0.48}Ag_{0.24}$ in a much higher amount than in γ-$TiPphen_{0.48}$ (see Table 2). The X-ray diffraction patterns of the as prepared solids containing more than 0.15–0.20 moles of t.m.i. $mole^{-1}$ of compound, account for materials slightly less crystalline than the precursor. The interlayer distance is maintained at 20.9 Å and, in the case of the Co(II) derivative, a small and sharp reflection at $2\theta = 38.1$ ($d = 2.37$ Å), characteristic of metallic silver

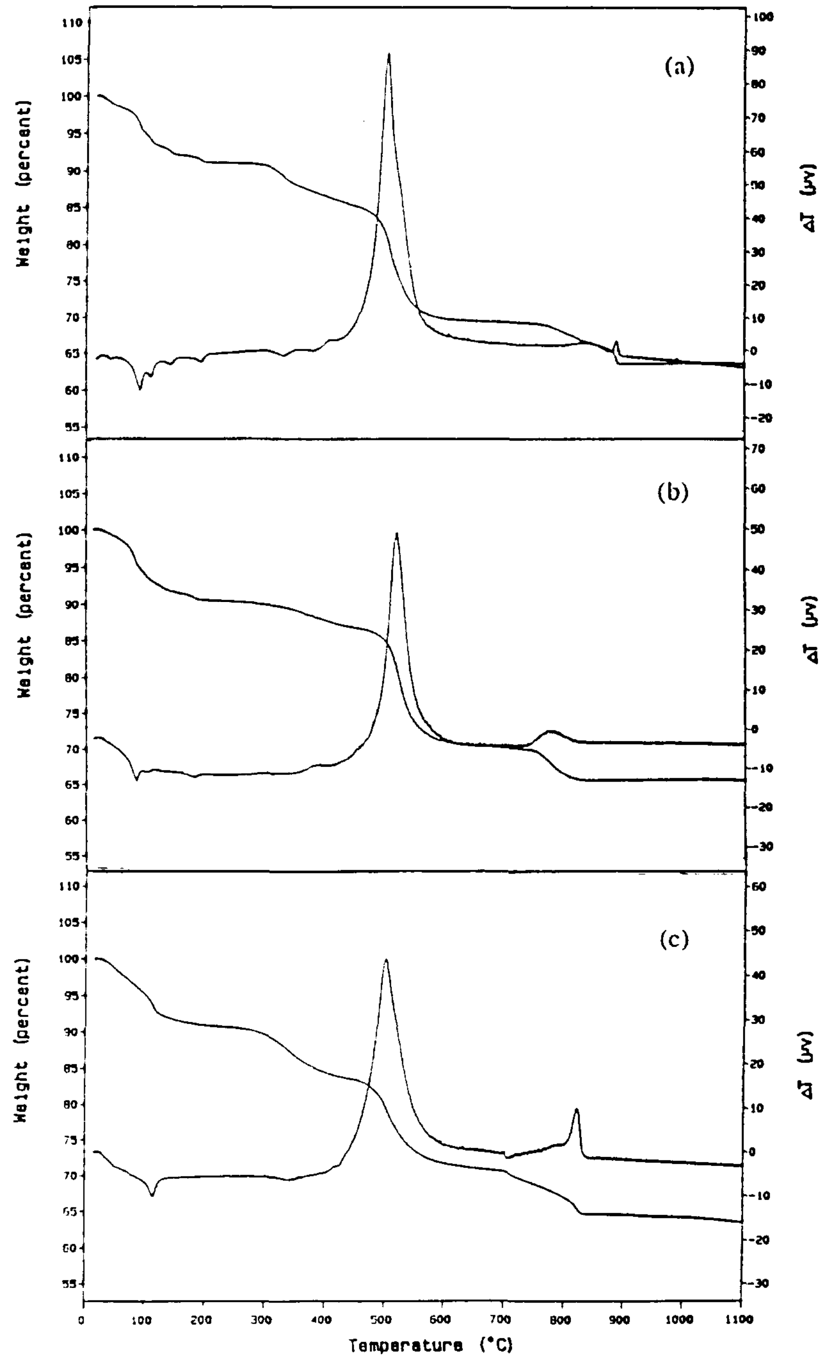

Fig. 2. TG–DTA curves of γ-TiPphen$_{0.48}$ (a), γ-TiPphen$_{0.48}$Co$_{0.12}$ (b) and γ-TiPphen$_{0.48}$Ag$_{0.24}$ (c).

Ag^0, is well evident. Although the Ni-based compound does not show the Ag^0 reflection in its X-ray pattern, presumably the reduction of Ag^+ also takes place in this material since both Co(II)- and Ni(II)-charged materials assume a grey–black colour during t.m.i. uptake. However, the nickel compound is less dark than the cobalt analogue, thus, the absence of the Ag^0 could either mean that, in the nickel material, the redox process occurs to a lower extent, or that Ag^0 is more finely dispersed in this solid than in the cobalt derivative. By contrast, the copper compound is light-blue coloured after exchange and the Ag^0 reflection is not present in the XRD pattern. Two tentative redox processes are here hypothesised for the Co- and Ni-exchanged solids. For cobalt, for example:

(1) $\gamma\text{-TiPphen}_{0.48}\text{Ag}_{0.24} + 0.88\text{Co}^{2+} \longrightarrow \gamma\text{-TiPphen}_{0.35}\text{Ag}_{0.24-x}\text{Co(II)}_{0.28-x/2}$
$\text{Co(III)}_{x/2} + x\text{Ag}^0 + 0.60\text{Co}^{2+} + 0.13\text{phen}$

(2) $\gamma\text{-TiPphen}_{0.48}\text{Ag}_{0.24} + 0.88\text{Co}^{2+} + x/2\text{H}_2\text{O} \longrightarrow \gamma\text{-TiPphen}_{0.35}\text{Ag}_{0.24-x}\text{H}_x$
$\text{Co}_{0.28} + x\text{Ag}^0\downarrow + x/4\text{O}_2\uparrow + 0.60\text{Co}^{2+} + 0.13\text{phen}$

It is difficult to give an explanation of the redox reactions happening in these materials. In fact, it is hazardous to take into account the Standard Reduction Potentials series, because the interlayer region, where exchange and redox processes and water molecule movements are occurring at the same time, is a rather constraining place, for which a solution-like situation is far from reality.

3.2.2. Thermal behaviour

In Fig. 3 are given the TG and DTA curves referring to $\gamma\text{-TiPphen}_{0.35}\text{Ag}_{0.24-x}\text{Co}_{0.28} + x\text{Ag}^0$ (a), $\gamma\text{-TiPphen}_{0.38}\text{Ag}_{0.24}\text{Ni}_{0.37}$ (b) and $\gamma\text{-TiPphen}_{0.41}\text{Ag}_{0.24}\text{Cu}_{0.50}$ (c). For all of the materials the TG curves show a continuous weight loss from 25 to 400°C corresponding to hydration and coordination water, and initial phen loss. The process is accompanied by small and successive endothermic effects in the DTA curves. Then the main elimination of phen occurs with its big exothermic peak in the DTA curves, the position of the maximum being 50°C lower for the copper derivative. Between 550 and 600°C, and only for the Co(II)- and Ni(II)-based intercalation compounds, a slight weight increment is observed in the TG curves; we believe this can be ascribed to the re-oxidation of Ag^0 to Ag^+ with O_2, since the X-ray pattern of the Co-charged material heated at 600°C no longer shows the Ag^0 reflection. Between 620 and 750°C for the Co and Ni derivatives and between 550 and 850°C for the Cu material, two distinct exothermic peaks are observed in the DTA curves. The first is related to the formation of $AgTi_2(PO_4)_3$ and the second to that of double salts of the type $MeTi(PO_4)_2$ or to $Me_2P_2O_7$, with Me = Co(II), Ni(II) and Cu(II). $\alpha\text{-TiP}_2\text{O}_7$ is not formed.

It is apparent from the chemical formulae of the three intercalation compounds that the amount of phen is less than in the precursor. This is due to elimination of the diamine by the incoming t.m.i; in order to exchange H^+ in the interlayer region it causes the deprotonation of the nitrogen of a more or less higher number of phen molecules from the dihydrogen phosphate groups. As a matter of fact, the elution of diamine has been observed in a few cases, such as that of dmp from $\alpha\text{-ZrPdmp}_{0.50}$ during exchange with Cu(II) [20] or that of phen from $\alpha\text{-ZrPhen}_{0.50}$ with Rh(III) [21]. The amount of phen no longer interacting with the matrix depends on the extent of t.m.i. exchange, and

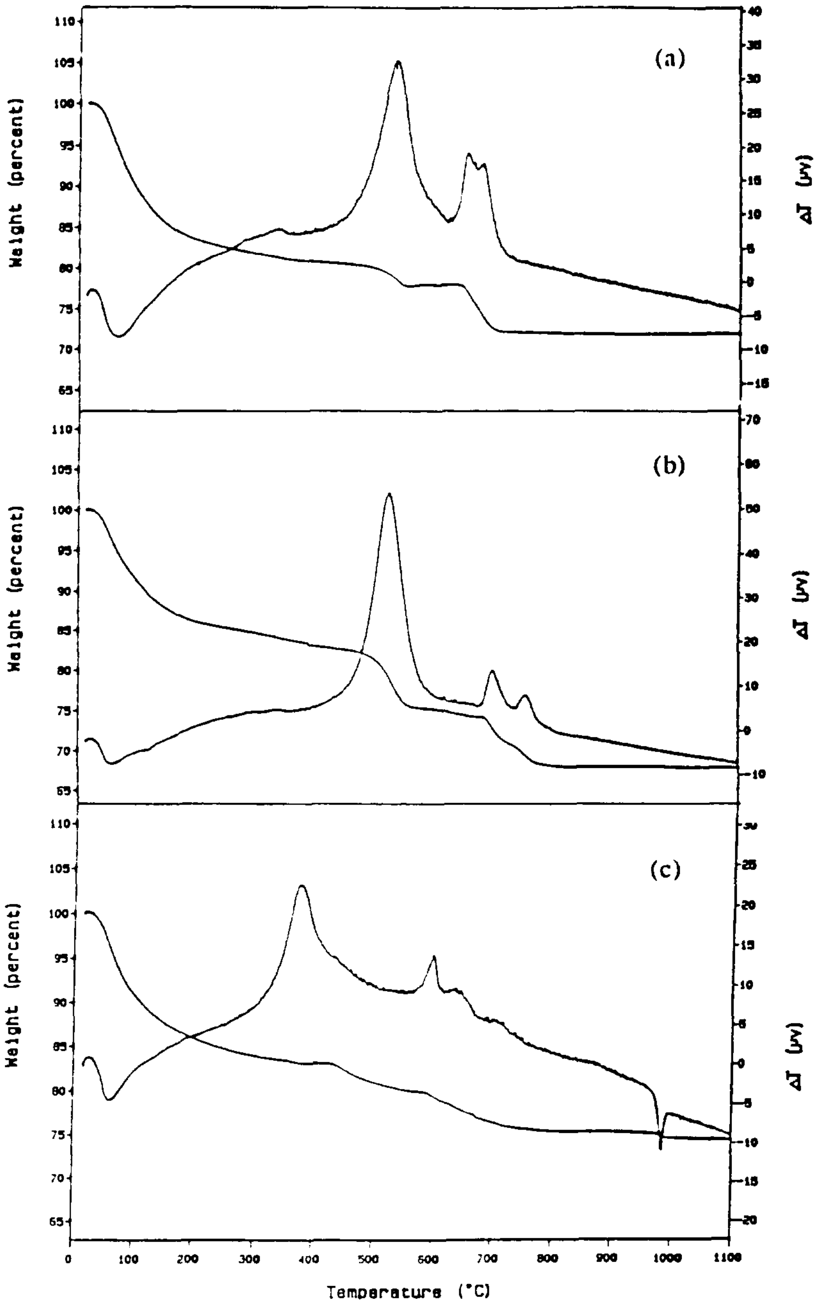

Fig. 3. TG–DTA curves of γ-TiPphen$_{0.35}$Ag$_{0.24}$Co$_{0.28}$ (a), γ-TiPphen$_{0.38}$Ag$_{0.24}$Ni$_{0.37}$ (b) and γ-TiPphen$_{0.41}$Ag$_{0.24}$Cu$_{0.50}$ (c).

if coordination compounds are not formed with the t.m.i. in the interlayer region, as instead is observed in most cases [8], the phen molecules leave the solids and go into solution. With the γ-TiPphen$_{0.48}$Ag$_{0.24}$ precursor about 15–25% of the initial amount of phen is elminated.

3.3. Bimetallic intercalation compounds derived from γ-TiPphen$_{0.48}$Ag$_{0.48}$

3.3.1. X-ray diffraction analysis

Another series of bimetallic intercalation compounds is obtained from γ-TiPhen$_{0.48}$Ag$_{0.48}$. In this case, however, there is greater elimination of phen (55–70%). In Fig. 4 are reported the X-ray diffraction patterns of γ-TiPphen$_{0.48}$Ag$_{0.48}$ (a) and γ-TiPphen$_{0.22}$Ag$_{0.48}$Co$_{0.25-x/2}$$+x$Ag^0 as prepared (r.t.) (b) and calcined at 900°C (c). For the precursor (a) the d_{002} and d_{004} reflections have about the same intensity. For the cobalt derivative at r.t. (b), the d_{004} reflection strongly decreases in intensity, while the peak corresponding to Ag^0 at $2\theta = 38.1$ ($d = 2.37$ Å) is well evident and more intense than in the corresponding compound with Ag$_{0.24}$ mentioned in the previous section. The material is grey–black as the nickel compound that, however, also is this case, does not show the presence of Ag^0 in its r.t. XRD. The peak of Ag^0 in the cobalt compound is no longer observable when the material is heated around 550°C. In the X-ray diffraction pattern of the material calcined at 900°C (c) the reflections of AgTi$_2$(PO$_4$)$_3$ and Co$_2$P$_2$O$_7$ are clearly evident. For the nickel derivatives at 900°C, AgTi$_2$(PO$_4$)$_3$ is also present, but clear reflections indicating a known nickel salt or oxide have not been distinguished.

The copper derivatives behave differently. The light blue materials are practically amorphous to X-ray diffraction analysis up to 900°C where AgTi$_2$(PO$_4$)$_3$ and CuP$_2$O$_7$ phases are clearly observed.

3.3.2. Thermal behaviour

In Fig. 5 are given the TG–DTA curves of γ-TiPphen$_{0.48}$Ag$_{0.48}$ (a), γ-TiPphen$_{0.20}$Ag$_{0.48}$Ni$_{0.20}$ (b) and γ-TiPphen$_{0.20}$Ag$_{0.48}$Cu$_{0.51}$ (c). For the Ni compound, but also for the Co derivative, the continuous weight loss due to the elimination of water of hydration and coordination and a small initial phen loss, is accompained, by an endothermic effect up to 400°C. The main elimination of phen which follows is noticeably diminshed because of the elution process, and, between 520 and 580°C, a small weight increment is observable, that, as previously, we ascribe to the re-oxidation of Ag^0 with formation of Ag$_2$O. At 680°C for the nickel material (620°C for the cobalt derivatives) a very sharp exothermic peak is observed due to formation of the nickel (or cobalt) and silver salts.

In the TG curve of the copper derivative (c) the elimination of hydration water ends at 320–330°C and is followed by two steps related to the phen combustion occurring, as previously observed for the monometallic copper materials, at about 100°C lower than for the cobalt and nickel derivatives. In correspondence with the formation of the salts, the DTA curves show a very sharp peak, like a “spike” between 530 and 550°C.

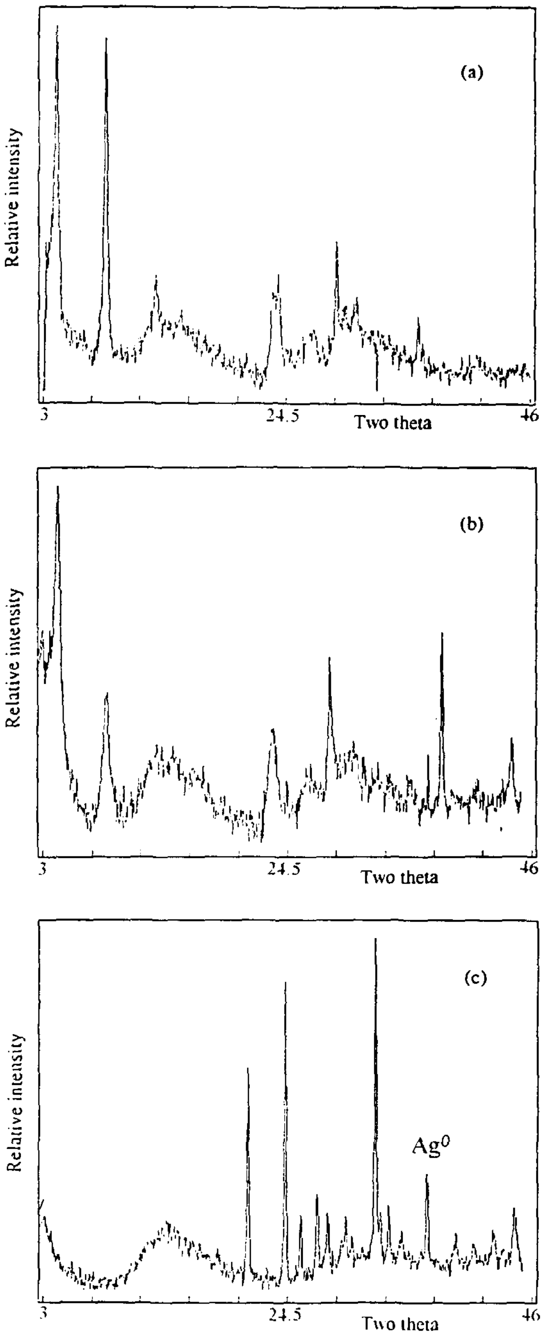

Fig. 4. X-ray diffraction patterns of γ-TiPphen$_{0.48}$Ag$_{0.48}$ (a), γ-TiPphen$_{0.18}$Ag$_{0.48}$Co$_{0.25}$ as prepared (b) and calcined at 900°C (c).

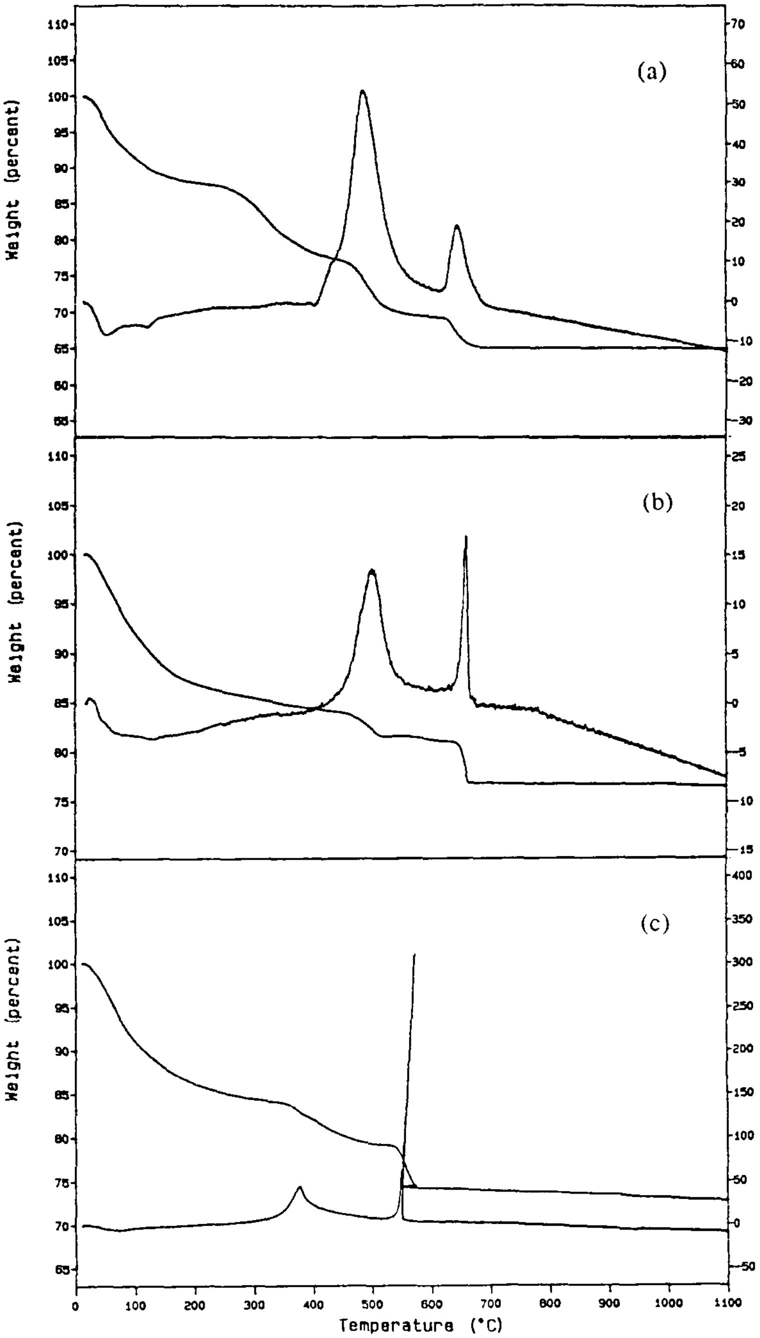

Fig. 5. TG–DTA curves of γ-TiPphen$_{0.48}$Ag$_{0.48}$ (a), γ-TiPphen$_{0.20}$Ag$_{0.48}$Ni$_{0.20}$ (b) and γ-TiPphen$_{0.23}$ Ag$_{0.48}$Cu$_{0.51}$ (c).

4. Conclusions

The intercalation compound γ-TiPphen$_{0.48}$ is able to exchange transition metal ions in its interlayer region through an H^+-t.m.i. process. The Co^{2+}, Ni^{2+} and Cu^{2+} derivatives are slightly less crystalline than the precursor. The interlayer distances of the new phases remain unchanged and no differences are observed in their thermal behaviour with respect to that of γ-TiPphen$_{0.48}$, except for the presence in the DTA curves of exothermic effects around 750–880°C corresponding to salt formation, obviously not observable in γ-TiPphen$_{0.48}$. In contrast, exchange with Ag^+ gives two well ordered materials γ-TiPphen$_{0.48}$Ag$_{0.24}$ and γ-TiPphen$_{0.48}$Ag$_{0.48}$ with an interlayer distance increased by about 3 Å relative to γ-TiPphen$_{0.48}$. Their thermal behaviour, different from that of the precursor, depend on the amount of silver in the materials. The elimination of the intercalated diamine, which takes place in three steps for all of the examined compounds, occurs in a range shortened by about 200°C for the material with the higher amount of silver. Calcination leads to the formation of $AgTi_2(PO_4)_3$ and eventually cubic α-TiP_2O_7.

The two silver materials exchange Co^{2+}, Ni^{2+} and Cu^{2+}. The process causes partial elimination of phen, higher in the compound richer in Ag^+. Two exothermic peaks are observed in the high temperature range of the respective DTA curves: the first is linked to the formation of $AgTi_2(PO_4)_3$ and the second to double titanium–t.m.i. phosphates or t.m.i. pyrophosphates. The exchange with Co^{2+} and Ni^{2+} immediately gives rise to dark-grey materials. The X-ray diffraction pattern of the co-derivative as prepared gives evidence of the presence of Ag^0 in the solid, indicating that a redox process has occurred during exchange. The TG curves of Co and Ni derivatives show, in the range 500–600°C, a weight increment corresponding to the Ag^0 re-oxidation with the probable formation of Ag_2O. The copper derivative, which is a light-blue coloured material, does not show this behaviour.

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