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Compounds of γ-zirconium hydrogen phosphate with cadmium ions
Synthesis, thermal behavior and X-ray characterization

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Abstract

The materials obtained by exchanging Cd^{2+} ions into γ-zirconium phosphate and γ-zirconium phosphate-L materials (L = organic diamines) have been investigated. The kinetic uptake of the Cd^{2+} ions by the starting materials, the thermal behavior and the structural characterization of the obtained compounds has also been examined.

γ-Zirconium phosphate intercalated with CdS particles has also been prepared and characterized. Its property to exchange further cadmium ions, and thus, insert more CdS particles between the layers of the exchanger has been investigated.

Keywords: Ion exchange; Intercalation compounds; Layered composite; Thermal behavior; X-ray diffraction

1. Introduction

Inorganic ion-exchangers with a layered structure belonging to the class of acid phosphates of the tetravalent elements ($Me(IV)H_2P_2O_8 \cdot nH_2O$; Me = Zr, Ti, Sn; $n = 1, 2, \ldots$) have been the object of interest due to their peculiar ability both to exchange transition metal ions (t.m.i.'s) [1–3] and to intercalate polar molecules inserted between the layers [4,5]. Some intercalation compounds can in turn exchange and co-ordinate t.m.i. in order to obtain 'in situ' formed complexes [6,7]. The materials thus obtained can be utilized in heterogeneous catalysis [8–10] instead of the materials generally used in homogeneous catalysis. The main interest in producing these materials is to obtain either catalysts or catalyst precursors to be used in different processes (e.g. petrochemical, oxidative dehydrogenation, carbonylation) or materials for gas separation and ionic conduction.

We have already studied α- and γ-zirconium phosphate (α-$Zr(HPO_4)_2 \cdot H_2O$ (α-ZrP) and γ-$Zr(PO_4)(H_2PO_4) \cdot 2H_2O$ (γ-ZrP)) and γ-titanium phosphate (γ-$Ti(PO_4)(H_2PO_4) \cdot 2H_2O$ (γ-TiP)) intercalated with diamines (L) such as 2,2′-bipyridyl (bipy), 1,10-phenanthroline (phen) and 2,9-dimethyl-1,10-phenanthroline (dmp) and exchanged with ions of the first [5] and the second [11,12] rows of t.m.i. of known catalytic interest. We recently studied the cadmium-exchanged material [13] following the studies of Cao et al. [14] and the cadmium sulfide particles intercalate into γ-zirconium phosphate, for their potential capacity as catalysts and semiconductors [15–17].

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In this paper, we have continued our research on cadmium ions exchanged into γ-ZrP to determine the kinetic uptake of this host when behaving as an ion-exchanger and as material previously intercalated with the above-mentioned diamines. We have sought to define the composition and the stability of these obtained compounds by studying their thermal behavior and structural phases. In terms of physical properties and potential applications, encapsulation in the pores of zeolites is one of the best methods for the formation of semiconductor clusters. The choice of zeolites, crystalline aluminosilicate systems containing regular three-dimensional channels or cavities with molecular dimensions, provides constrained systems that are able to produce semiconductors with defined particle size. Following this line of research, we have continued the study of CdS particles intercalated into γ-zirconium phosphate [13] to define the influencing parameters and the best conditions to obtain the matrix hosting CdS particles.

2. Experimental

2.1. Chemicals

The cadmium acetate dihydrate, iron sulfide, hydrochloride acid and the diamines were from Aldrich. All other reagents were Merck pro analyze products. Crystalline γ-zirconium phosphate were prepared and stored as previously described [18]. The diamine intercalation compounds (γ-ZrPL): γ-$Zr(PO_4)(H_2PO_4)bipy_{0.48}\cdot 1.07H_2O$ (γ-$ZrPbipy_{0.48}$); γ-$Zr(PO_4)(H_2PO_4)phen_{0.49}\cdot 2.58H_2O$ (γ-$ZrPphen_{0.49}$); γ-$Zr(PO_4)(H_2PO_4)dmp_{0.45}\cdot 3.11H_2O$ (γ-$ZrPdmp_{0.45}$) were prepared as previously described [19]. The cadmium γ-ZrP materials were prepared by the batch procedure at 45°C, at different set time intervals. The fully-exchanged cadmium form was prepared as reported in the literature [13]. The cadmium intercalation compounds were obtained by two methods: (1) by ion exchange by equilibrating the diamine intercalation compounds with Cd^{2+} acetate solution; all the batches were thermostated at 45°C, at several set time intervals; the suspensions were then filtered, the solutions analyzed for metal content and final pH, and the solids were washed with distilled water and air dried; (2) by hydrothermal synthesis, by putting a sample of γ-ZrPL phase sealed in a Pyrex tube with cadmium acetate solution; the tube was put into a hydrothermal bomb and heated for 72 h in an oven at 80°C; the cadmium sulfide intercalation into γ-ZrP was carried out by flowing anhydrous H_2S over the cadmium zirconium phosphate material, as reported in the literature [13].

2.2. Physical measurements and chemical analysis

Cadmium ions were determined on a GBC 903 A.A. spectrophotometer by following the concentration change in the supernatant solutions before and after contact with the exchanger. Phosphates were determined colorimetrically. The contents of water and the diamines were determined with a simultaneous TG-DTA Stanton Redcroft 1500 thermoanalyzer, Pt crucibles, at a heating rate of 10°C min^{-1}, and ignition up to 1100°C to constant weight in an airflow.

X-ray powder diffraction was used to follow the phase changes undergone by the materials. A Philips diffractometer (model PW 1130/00) was used with Ni-filtered Cu Kα radiation ($\lambda = 1.541$ Å); the measurements of 2θ are believed to be accurate to 0.05°. The content of sulfur, carbon, nitrogen and hydrogen in the materials was determined with a Fisions 1108 microanalyser.

3. Results and discussion

3.1. Cadmium uptake by γ-ZrP

Samples of 1 mmol of γ-ZrP were contacted, at 45°C, with volumes of 20 ml of 5×10^{-2} mol dm^{-3} cadmium acetate solution, at different set time intervals, so as to obtain the fully-exchanged cadmium zirconium phase. We did not obtain a fully-exchanged compound even by prolonging the time of contact between the exchanger and the cadmium solution (3 weeks). Table 1 reports the chemical composition of the obtained materials with their interlayer distance d according to contact time. As we can observe in Table 1, the maximum cadmium content is 0.65 mol mol^{-1} exchanger (from 3 days until 3 weeks). The ion uptake is very fast for short contact times between exchanger and cadmium solution. As previously reported [13] with a renewed batch contact

Table 1
Chemical composition and interlayer distance of the obtained compounds

Materials obtained from γ-Zr(PO$_4$)(H$_2$PO$_4$)$\cdot$2H$_2$O; $d = 12.26$ Å	d (Å)	Time (h)
γ-ZrCd$_{0.46}$(PO$_4$)(H$_{1.08}$PO$_4$)$\cdot$2.85H$_2$O	12.35–6.39–5.81	1
γ-ZrCd$_{0.53}$(PO$_4$)(H$_{0.94}$PO$_4$)$\cdot$2.88H$_2$O	12.35–6.37–5.81	3
γ-ZrCd$_{0.55}$(PO$_4$)(H$_{0.90}$PO$_4$)$\cdot$2.90H$_2$O	12.35–6.21–5.81	6
γ-ZrCd$_{0.60}$(PO$_4$)(H$_{0.80}$PO$_4$)$\cdot$2.95H$_2$O	6.21–5.81	24
γ-ZrCd$_{0.65}$(PO$_4$)(H$_{0.70}$PO$_4$)$\cdot$3.01H$_2$O	6.21–5.81	72
γ-ZrCd$_{0.65}$(PO$_4$)(H$_{0.70}$PO$_4$)$\cdot$3.01H$_2$O	6.21–5.81	504
γ-ZrCd(PO$_4$)$_2$$\cdot$4H$_2$O[a]	6.21	

[a] Renewed batch contact of γ-ZrP and cadmium acetate solution.

of γ-ZrP and cadmium acetate solution, the fully-exchanged cadmium zirconium phosphate material was obtained with a chemical composition of γ-ZrCd(PO$_4$)$_2$$\cdot$4H$_2$O ($\gamma$-ZrPCd$\cdot$4H$_2$O).

3.2. Cadmium uptake by γ-ZrPbipy$_{0.48}$, γ-ZrPphen$_{0.49}$ and γ-ZrPdmp$_{0.45}$

Samples of 1 mmol of γ-ZrP-diamine were contacted with an amount of 5×10^{-2} mol dm^{-3} cadmium acetate solution such that [Cd^{2+}]:[intercalated diamine]=1:1. The 1:1 molar ratio was chosen in order to favor the 1:1=CdL (L = bipy, phen, dmp) complex species between the layers of the exchanger. Table 2 reports the chemical composition of the cadmium obtained materials and their interlayer distance according to contact time. The precursors γ-ZrPL behave in a different way when they exchange cadmium ions. The uptake speed of the cadmium ions for the γ-ZrPL-derived materials is in the order dmp $>$ bipy $>$ phen and the total amount of the exchanged cadmium ions, in the order bipy $>$ dmp $>$ phen. The bipy ligand has less steric hindrance than that of phen and dmp, but the interlayer distance

Table 2
Chemical composition and interlayer distance of the obtained compounds

Obtained compounds	d (Å)	Time (h)
Materials obtained from γ-Zr(PO$_4$)(H$_2$PO$_4$)bipy$_{0.48}$$\cdot$1.07H$_2$O; $d = 14.05$ Å		
γ-ZrCd$_{0.13}$(PO$_4$)(H$_{1.74}$PO$_4$)bipy$_{0.48}$$\cdot$1.07H$_2$O	14.46–16.36	1
γ-ZrCd$_{0.17}$(PO$_4$)(H$_{1.66}$PO$_4$)bipy$_{0.45}$$\cdot$1.07H$_2$O	14.46–16.36	3
γ-ZrCd$_{0.20}$(PO$_4$)(H$_{1.60}$PO$_4$)bipy$_{0.45}$$\cdot$1.07H$_2$O	14.73–16.36	6
γ-ZrCd$_{0.25}$(PO$_4$)(H$_{1.50}$PO$_4$)bipy$_{0.45}$$\cdot$1.15H$_2$O	15.24–16.36	24
γ-ZrCd$_{0.30}$(PO$_4$)(H$_{1.40}$PO$_4$)bipy$_{0.44}$$\cdot$1.41H$_2$O	16.52	72
γ-ZrCd$_{0.34}$(PO$_4$)(H$_{1.32}$PO$_4$)bipy$_{0.44}$$\cdot$1.53H$_2$O	16.52	144
Materials obtained from γ-Zr(PO$_4$)(H$_2$PO$_4$)phen$_{0.49}$$\cdot$2.58H$_2$O; $d = 18.37$ Å		
γ-ZrCd$_{0.08}$(PO$_4$)(H$_{1.84}$PO$_4$)phen$_{0.49}$$\cdot$2.58H$_2$O	18.60	1
γ-ZrCd$_{0.11}$(PO$_4$)(H$_{1.78}$PO$_4$)phen$_{0.48}$$\cdot$2.50H$_2$O	18.60	3
γ-ZrCd$_{0.12}$(PO$_4$)(H$_{1.76}$PO$_4$)phen$_{0.48}$$\cdot$2.50H$_2$O	18.60	6
γ-ZrCd$_{0.13}$(PO$_4$)(H$_{1.74}$PO$_4$)phen$_{0.48}$$\cdot$2.50H$_2$O	18.60	24
γ-ZrCd$_{0.14}$(PO$_4$)(H$_{1.72}$PO$_4$)phen$_{0.48}$$\cdot$2.54H$_2$O	18.60	72
γ-ZrCd$_{0.16}$(PO$_4$)(H$_{1.68}$PO$_4$)phen$_{0.48}$$\cdot$2.56H$_2$O	18.60	144
Materials obtained from γ-Zr(PO$_4$)(H$_2$PO$_4$)dmp$_{0.45}$$\cdot$3.11H$_2$O; $d = 19.84$ Å		
γ-ZrCd$_{0.20}$(PO$_4$)(H$_{1.60}$PO$_4$)dmp$_{0.45}$$\cdot$3.11H$_2$O	19.21	1
γ-ZrCd$_{0.22}$(PO$_4$)(H$_{1.56}$PO$_4$)dmp$_{0.45}$$\cdot$3.11H$_2$O	19.21	3
γ-ZrCd$_{0.24}$(PO$_4$)(H$_{1.52}$PO$_4$)dmp$_{0.45}$$\cdot$3.11H$_2$O	19.21	6
γ-ZrCd$_{0.26}$(PO$_4$)(H$_{1.48}$PO$_4$)dmp$_{0.41}$$\cdot$2.52H$_2$O	19.21	24
γ-ZrCd$_{0.27}$(PO$_4$)(H$_{1.46}$PO$_4$)dmp$_{0.41}$$\cdot$2.33H$_2$O	19.21	72
γ-ZrCd$_{0.27}$(PO$_4$)(H$_{1.46}$PO$_4$)dmp$_{0.41}$$\cdot$3.11H$_2$O	19.21	144

d of γ-ZrPbipy$_{0.48}$ (14.05 Å) is smaller by ~4–5 Å than those of γ-ZrPphen$_{0.49}$ (18.37 Å) and γ-ZrPdmp$_{0.45}$ (19.84 Å). That explains both the different cadmium uptake and speed of the bipy and dmp diamines intercalated in the γ-ZrP. The dmp ligand, with two –CH$_3$– groups, is bulkier than phen, but γ-ZrPdmp$_{0.45}$ seems to exchange more ions and to do so faster than γ-ZrPphen$_{0.49}$. We do not know why γ-ZrPdmp$_{0.45}$ behaves differently from γ-ZrPphen$_{0.49}$. Perhaps it could be due to both the different affinity of the two mentioned diamines with regard to cadmium ions and the higher *d* of the starting materials (19.84 versus 18.37 Å, respectively, for γ-ZrPdmp$_{0.45}$ and γ-ZrPphen$_{0.49}$). As previously observed in Table 1, the Cd^{2+} ion uptake is fast when there are no intercalated diamines in the γ-ZrP exchanger. In fact, as far as γ-ZrPbipy$_{0.48}$ we observe that, after 6 days of batch contact between this intercalated material and cadmium acetate solution, we have an uptake almost the same as that observed for γ-ZrP after 1 h of batch contact (see Table 1). This behavior is due to the γ-ZrP being less crowded (or less steric hindered) between the layers with respect to the γ-ZrPbipy$_{0.48}$ and not due to the interlayer distance *d* (12.26 and 14.05 Å, respectively). Concerning the cadmium uptake by γ-ZrPdmp$_{0.45}$, we also observe that the ion uptake is very fast (with respect to γ-ZrPbipy$_{0.48}$ and γ-ZrPphen$_{0.49}$). After 1 h of batch contact between the exchanger and the cadmium solution, the uptake is already almost completed. Prolonged batch contact time between γ-zirconium phosphate diamines and cadmium acetate solution does not increase the ion uptake, nor does a higher temperature for the experiment (60°C). Increasing the volumes of the cadmium solution, so as to have a ratio [Cd^{2+}]:[intercalated diamine] = 2:1, does not notably change the cadmium uptake. In this latter case, we obtained 0.40 Cd^{2+} mol mol^{-1} γ-ZrPbipy$_{0.48}$, 0.20 Cd^{2+} mol mol^{-1} γ-ZrPphen$_{0.49}$ and 0.29 Cd^{2+} mol mol^{-1} γ-ZrPdmp$_{0.45}$. As we can note, it is only in the case of γ-ZrPbipy$_{0.48}$ that we could obtain an almost [Cd^{2+}]:[L] = 1:1 ratio inside the exchanger (0.40 Cd^{2+}:0.48 phen). None of the obtained materials shows marked diamine elution. We note diamine elution by ~10% both for the derivatives of γ-ZrPbipy$_{0.48}$ and γ-ZrPdmp$_{0.45}$ [12]. With respect to the other t.m.i.'s, γ-ZrPL intercalation compounds [19], we observed that the cadmium ion uptake behavior is similar to the one observed for the platinum ion [12]. We attempted to improve the Cd^{2+} uptake into the γ-ZrPL and to obtain the CdL complex by performing the experiment with hydrothermal synthesis. We did not obtain a marked difference in the cadmium uptake with respect to the batch method. The ions uptake was 0.38 Cd^{2+} mol mol^{-1} γ-ZrPbipy$_{0.48}$, 0.18 Cd^{2+} mol mol^{-1} γ-ZrPphen$_{0.49}$ and 0.32 Cd^{2+} mol mol^{-1} γ-ZrPdmp$_{0.45}$. So we can conclude that it is only for the material derived from γ-ZrPbipy$_{0.48}$ that we can obtain an almost [Cd^{2+}]:[L] = 1:1 ratio inside the exchanger.

3.3. Thermal behavior and X-ray diffraction (XRD) of γ-ZrPCd and γ-ZrPLCd

Fig. 1 shows the simultaneous TG-DTA curves of the materials containing cadmium, derived from γ-ZrP, obtained at various set time intervals. For the materials obtained after a batch contact of 1, 3 and 6 h, we obtain three losses between 25 and 190°C due to the coordination and lattice water. There is a step between 190 and 220°C. The last loss, ranging between 220 and 900°C (in two to three steps) is related to the condensation water of the orthophosphates groups. For the samples derived from cadmium uptake in 24, 72 and 504 h, the TG curves show three losses between 25 and 200°C due to the loss of the coordination and lattice water. The fourth loss, between 200 and 900°C, overlaps and is a continuous and slow process; this is due to the residual coordination water and the condensation water of the orthophosphate groups going to form pyrophosphate groups. The DTA curves show in correspondence (for materials with a batch contact of 1, 3 and 6 h) endothermic peaks at 80–120–150 (sharpened) and 380°C (broadened) related to the water loss. All the not fully cadmium exchanged materials show an exothermic peak at 850°C due to the transition phase of layered L-pyrophosphate to α-cubic pyrophosphate transition phase. Fig. 2 shows the TG-DTA curves of the cadmium materials derived from γ-ZrPbipy$_{0.48}$, γ-ZrPphen$_{0.49}$ and γ-ZrPdmp$_{0.45}$ (all materials with maximum cadmium content) in comparison with those of their precursors. The DTA curve of the γ-ZrPbipy$_{0.48}$ cadmium materials shows an endothermic peak at 180°C related to the dehydration and coordination water loss; two well-defined exothermic peaks

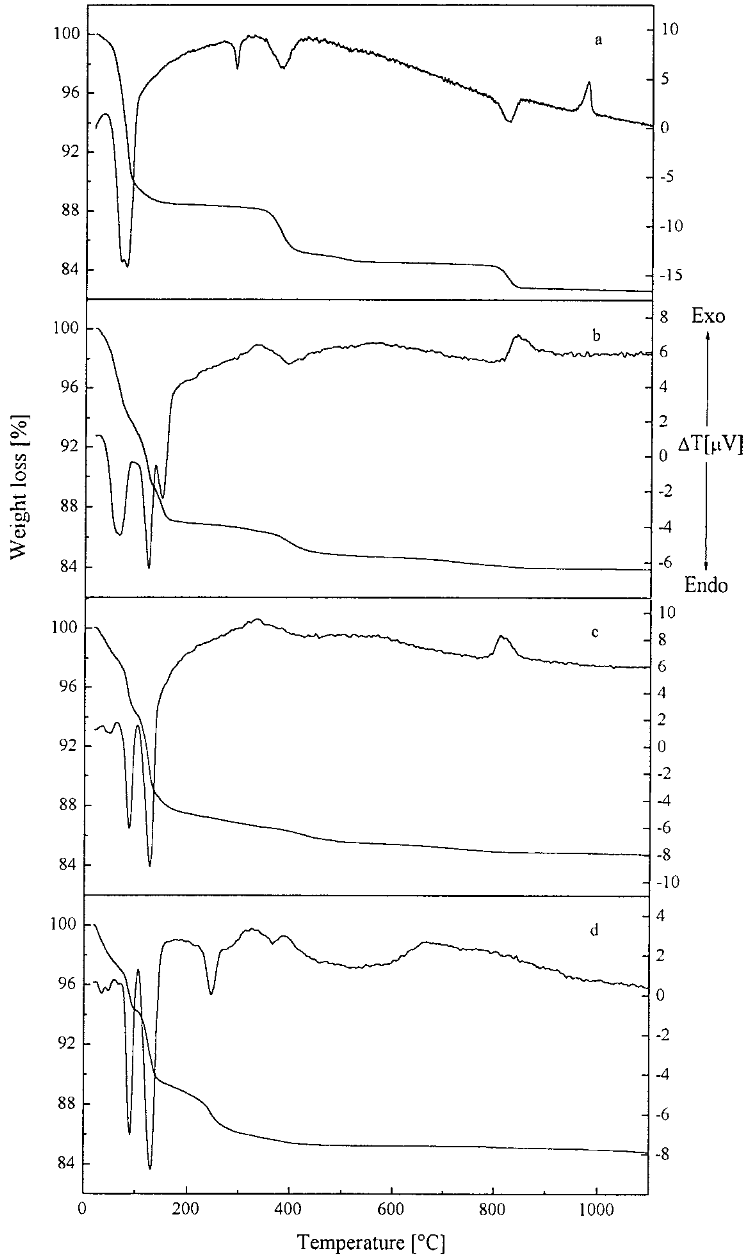

Fig. 1. TG-DTA curves of the (a) γ-$Zr(PO_4)(H_2PO_4)\cdot 2H_2O$, (b) γ-$ZrCd_{0.46}(PO_4)(H_{1.08}PO_4)\cdot 2.85H_2O$, (c) γ-$ZrCd_{0.60}(PO_4)(H_{0.80}PO_4)\cdot 2.95H_2O$ and (d) γ-$ZrCd(PO_4)_2\cdot 4H_2O$.

at 420–580°C (related to the ligand decomposition) and one sharpened peak at 860°C related to the pyrophosphate phase formation. The TG curve is in agreement with that of DTA: in correspondence with the endothermic or exothermic peaks, we note more or less pronounced water and ligand losses. For the γ-$ZrPphen_{0.49}$ cadmium material, the TG-DTA curves are very similar to those of its precursor. In the DTA curve of the cadmium material, two small exothermic peaks at 320 and 480°C are present with respect to that

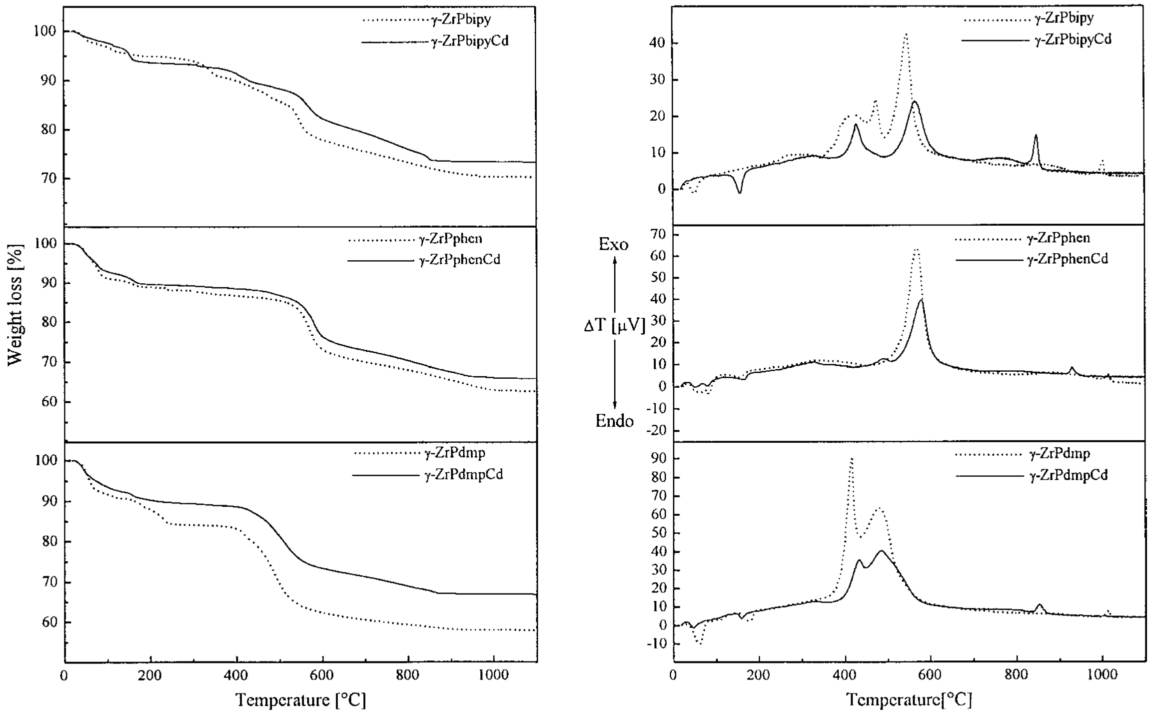

Fig. 2. TG-DTA curves of the cadmium zirconium phosphate intercalated materials in comparison with their precursors.

of its precursor; the exothermic peak related to the pyrophosphate phase formation is at 920°C. As regards γ-ZrPdmp$_{0.45}$ exchanged with cadmium ions, we do not find any marked difference between this material and its precursor. The only difference, which we observe, is the intensity inversion of the two exothermic peaks at 420–480°C and the exothermic peak at 860°C (as previously seen for the other intercalated cadmium compounds). In conclusion, we can state that, in all three cases, γ-ZrPbipy$_{0.48}$, γ-ZrPphen$_{0.49}$ and γ-ZrPdmp$_{0.45}$ cadmium materials show that the pyrophosphate phase formation happens at higher temperatures than those of either its precursor or other t.m.i.'s γ-ZrPL intercalation compounds [19].

The XRD of γ-ZrPCd (Fig. 3) shows one phase with $d = 6.21$ Å only when the cadmium content inside the exchanger is >0.65 mol mol^{-1} exchanger [13]. For the cadmium values of $\leq$0.65 mol mol^{-1} exchanger, two or three phases are present (Table 1). At a Cd^{2+} content of less than half the ion-exchange capacity, the first XRD reflection referred to the starting γ-ZrP phase is still present (in this case, the value is 12.35 Å). For the fully-exchanged form, the first reflection that we observe on XRD is $d = 6.21$ Å. We think that this value is too small to be related to the interlayer distance d of Cd^{2+} ions inside the exchanger. May be, the reflection was missing, due to the different arrangement of the Cd^{2+} between the layers. But we can state that the cadmium zirconium phosphate material obtained is still layered (even if this compound is less crystalline than the γ-ZrP precursor). This was confirmed by contacting the γ-ZrPCd·4H$_2$O with HCl (5×10^{-2} mol dm^{-3}), and the result, γ-ZrP again obtained, shows the maintenance of the layered structure.

For the cadmium intercalation compounds, the interlayer distance d increases only in the case of the material derived from ZrPbipy$_{0.48}$ and the cadmium content ranges between 0.32 and 0.34 Cd^{2+} mol mol^{-1} exchanger (16.52 versus 14.05 Å, respectively). For all the other materials listed in Table 2, there is no variation of the d values. For the cadmium zirconium phosphate intercalation

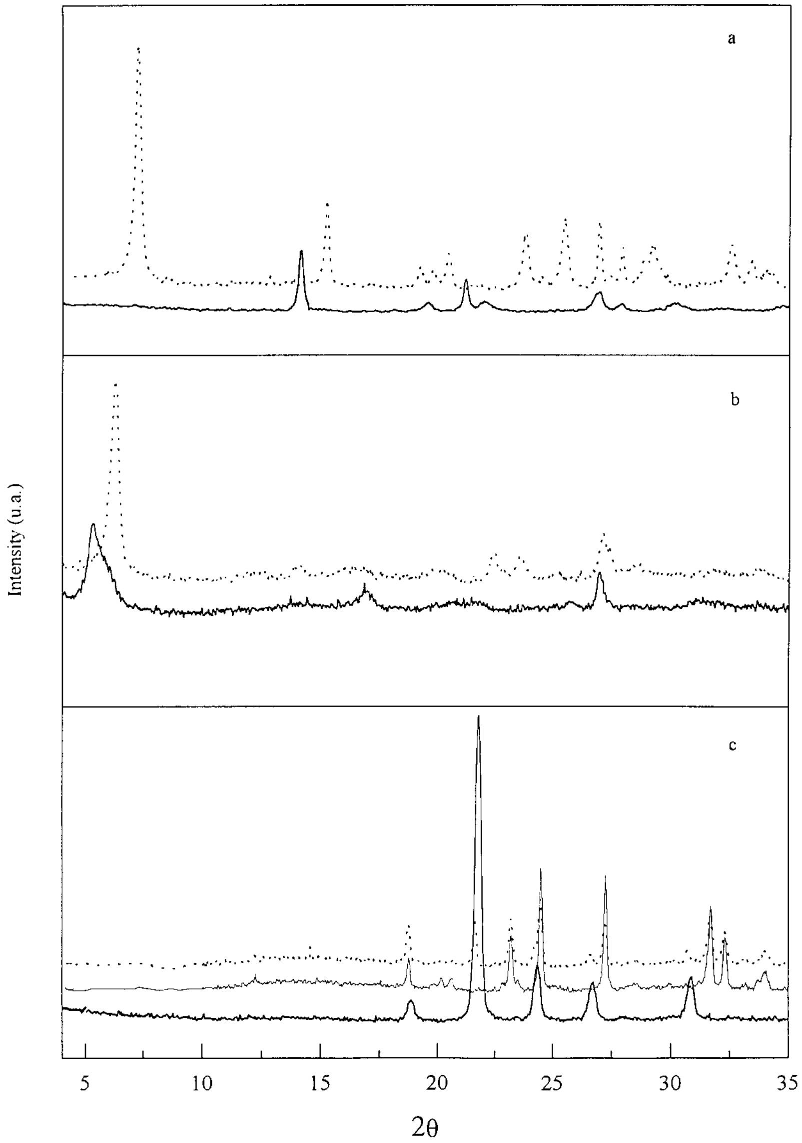

Fig. 3. XRD of the (a) γ-$Zr(PO_4)(H_2PO_4)\cdot 2H_2O$ (dotted line) in comparison with γ-$ZrCd(PO_4)_2\cdot 4H_2O$ (dark line), (b) γ-$Zr(PO_4)(H_2PO_4)$-$bipy_{0.48}\cdot 1.07H_2O$ (dotted line) in comparison with γ-$ZrCd_{0.34}(PO_4)(H_{1.32}PO_4)bipy_{0.44}\cdot 1.53H_2O$ (dark line), (c) γ-$ZrCd_{0.46}(PO_4)(H_{1.08}$-$PO_4)\cdot 2.85H_2O$ at 1100°C (dotted line) in comparison with γ-$ZrCd_{0.34}(PO_4)(H_{1.32}PO_4)bipy_{0.44}\cdot 1.53H_2O$ at 1100°C (dark line) and (d) $CdZr(PO_4)_2$ (dotted line) in comparison with ZrP_2O_7 α-cubic pyrophosphate (dark line).

compounds and for the not fully-exchanged cadmium zirconium phosphate materials, the XRD performed at 1100°C shows that, in the diffractograms, both pyrophosphate and cadmium double phosphate are present. In fact, as reported in the literature [20], the anhydrous phases rearrange to form double zirconium phosphates $MeZr(PO_4)_2$ (Me = Cu, Ni, Co) with the consequent loss of the layered structure. The XRD confirms this and shows that the compounds have *d*-line spacing very similar to those of $CaZr(PO_4)_2$ [21]. As expected, the compound is no longer an ion-exchanger. In Fig. 3, the XRD of some cadmium materials at r.t. and at 1100°C are reported.

3.4. Cadmium sulfide intercalated into γ-ZrP

Anhydrous H_2S was flowed for several set times (1–30 h), at r.t., over a sample of 1 mmol of γ-ZrPCd·$4H_2O$. We performed the experiments by flowing the H_2S either over the hydrated cadmium zirconium material or over partial anhydrous or fully anhydrous material. The obtained materials showed that the best condition to obtain a significant number of cadmium sulfide particles was to flow, for prolonged time (~30 h), the H_2S gas over the anhydrous (at 330°C) cadmium zirconium phosphate material to avoid the presence of water, taking into account the fact that the fully-exchanged cadmium phase contains four water molecules, between its layers, that could hinder the S^{2-} ions from combining with the cadmium ions already exchanged in γ-ZrP, to give CdS particles. γ-ZrPCd has a strong chemical affinity towards accepting S^{2-} ions. When the gas is flowed over the white cadmium material, its color suddenly changes to yellow, which grows more and more intense as the time of the H_2S flow increases. The chemical composition of the obtained material, after 30 h of H_2S flow, is $\gamma\text{-Zr(CdS)}_{0.74}\text{Cd}_{0.26}(\text{PO}_4)(\text{H}_{1.48}\text{PO}_4)\cdot 2.3\text{H}_2\text{O}$ (γ-ZrPCdS).

3.5. Thermal behavior and XRD of cadmium sulfide materials

Fig. 4 shows the XRD diffractograms of the obtained γ-ZrPCdS materials at various times of H_2S gas flow. As we can observe, the diffractogram of the final product (Fig. 4d) has a layered structure maintained almost equal (light amorphous) to that of the precursor γ-zirconium phosphate. We can explain the CdS formation as follows: as the H_2S gas flows over the cadmium zirconium phosphate material, the S^{2-} ions combine with the cadmium ions already exchanged in γ-ZrP, to give CdS particles. However, the free charge left by the Cd^{2+} can be replaced by the H^+ ions of the H_2S gas as given in the following scheme:

$$\gamma\text{-ZrCd(PO}_4)_2\cdot 4\text{H}_2\text{O} + \text{H}_2\text{S} \rightarrow \gamma\text{-Zr(CdS)}_{0.74}\text{Cd}_{0.26}(\text{PO}_4)(\text{H}_{1.48}\text{PO}_4)\cdot 2.3\text{H}_2\text{O}$$

The CdS particles stay stable intercalated into the host lattice. Votinsky et al. [22] list several types of interaction between the guest molecules and the host lattice. We presume that there are weak van der Waals' forces between the lattice of zirconium phosphate and CdS molecules, which are, however, strong enough to maintain the intercalated material stable up to 220°C. The 'reversion' to the hydrogen phase suggested the re-use of the obtained γ-ZrPCdS material as starting ion-exchanger of cadmium ions and then to expose it to H_2S gas to obtain other CdS particles inside the 'new' exchanger, even though not all the cadmium ions present in the starting materials combine with the incoming H_2S gas.

A sample of 1 mmol of γ-ZrPCdS was contacted with some amount of 5×10^{-2} mol dm^{-3} cadmium acetate solution, in batch, at 45°C, for a week. The filtered solution was analyzed for cadmium content; the powder material, after air drying, was subjected to the H_2S gas. We repeated this experiment (batch contact with Cd^{2+} solution and H_2S gas always flowing over the same material) for a total of three times. From chemical analysis (Cd^{2+} and S^{2-} uptake), we found that the materials obtained after one, two and three cycles have the supposed chemical composition reported in Table 3. We observe that the first γ-ZrPCdS obtained (one cycle) has an ion-exchange property enabling it to take other Cd^{2+} ions which replace the H^+ of the phosphate groups formed with H_2S gas (see before). We can perform repeated cycles of Cd^{2+} ion exchange and of H_2S flowing gas (e.g. in our case for three times) to increase the CdS into γ-zirconium phosphate. At the end of the cycles, we obtain ~1.38 mol CdS/mol γ-ZrP. When we perform the Cd^{2+} ion exchange over γ-ZrPCdS, we obtain from the XRD diffractogram the γ-ZrPCd·$4H_2O$ phase (less crystalline than that of the starting original phase). When the H_2S gas is flowing over this new cadmium-enriched material, we obtain the γ-ZrP phase from the XRD diffractogram.

Table 3
Chemical composition of the obtained compounds from γ-ZrPCdS at various cycles

Materials	Cycles
$\gamma\text{-Zr(CdS)}_{0.74}\text{Cd}_{0.26}(\text{PO}_4)(\text{H}_{1.48}\text{PO}_4)\cdot 2.3\text{H}_2\text{O}$	1
$\gamma\text{-Zr(CdS)}_{0.91}\text{Cd}_{0.19}(\text{PO}_4)(\text{H}_{1.62}\text{PO}_4)\cdot 2.16\text{H}_2\text{O}$	2
$\gamma\text{-Zr(CdS)}_{1.38}\text{Cd}_{0.18}(\text{PO}_4)(\text{H}_{1.34}\text{PO}_4)\cdot 1.79\text{H}_2\text{O}$	3

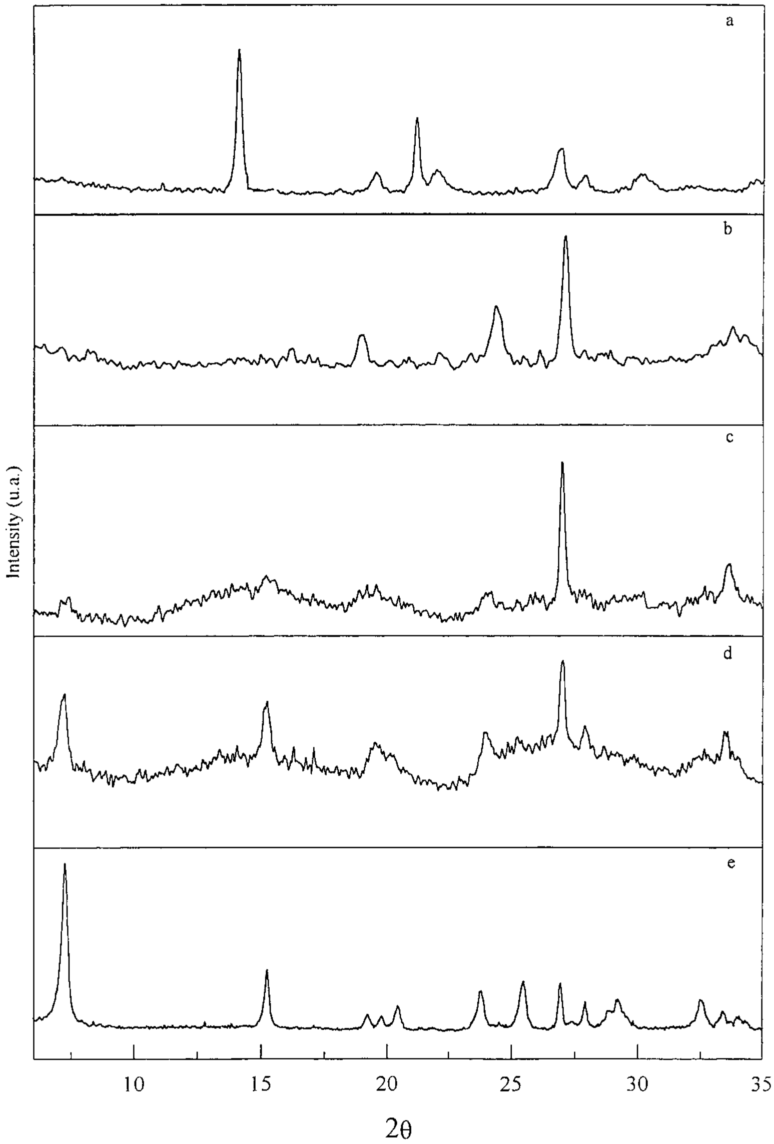

Fig. 4. XRD patterns of the (a) γ-$ZrCd(PO_4)_2·4H_2O$; γ-ZrPCdS obtained at various interval set times of H_2S gas flow: (b) 6 h, (c) 15 h, (d) 30 h; (e) γ-$Zr(PO_4)(H_2PO_4)·2H_2O$.

In Fig. 5, the TG-DTA curves of the three listed materials are reported. As we can observe in the TG curves, all three materials quickly show water loss between 25 and 120°C; then there is a step and consequent losses between 280 and 500°C (first cycle), 280 and 600°C (second cycle), 280 and 1100°C (third cycle). The DTA curves are in agreement with endothermic peaks at 80°C. The exothermic peaks at 320 and 380°C (first cycle), at 350 and 420°C (second cycle), and at 350–400–590°C (third cycle) are related to the S^{2-} loss (likely due to CdS differently linked between the zirconium phosphate layers). The S^{2-} loss is confirmed both by the microanalysis measurements, which show a decreasing sulfur content in the γ-ZrPCdS materials calcined at 350 and 450°C, and by observing the color of the calcined materials which becomes (at 350°C) a lighter shade of yellow and (at 450°C) white [13]. The XRD

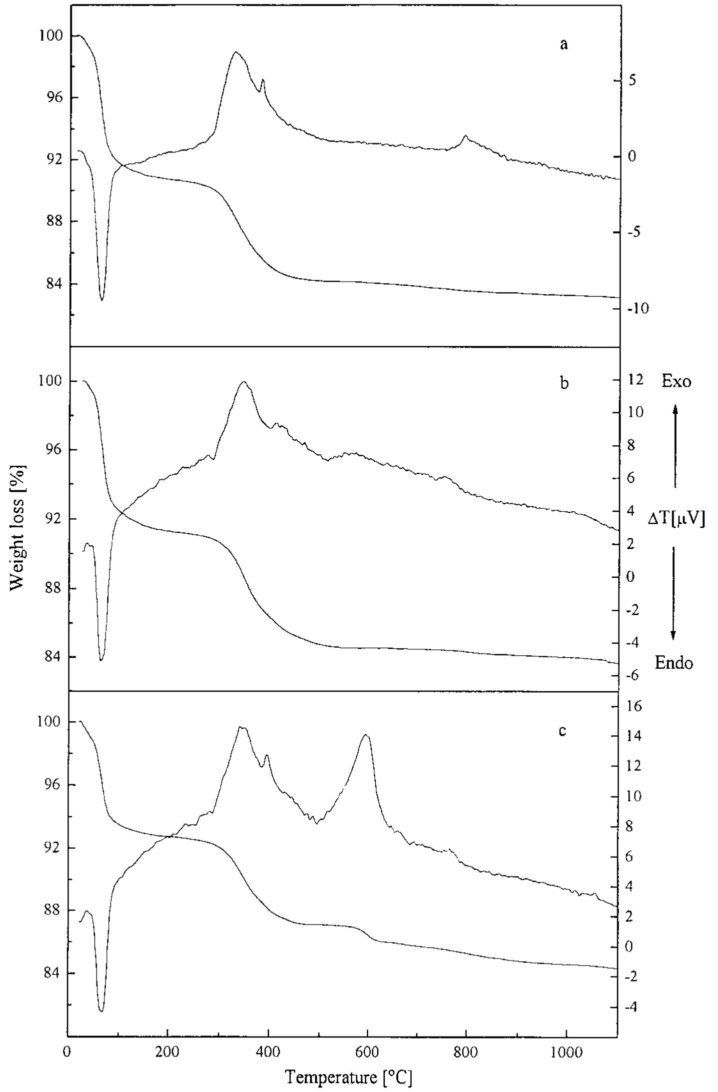

Fig. 5. TG-DTA curves of the cadmium sulfide intercalated materials obtained at various cycles: (a) one cycle; (b) two cycles; (a) three cycles.

performed on the γ-ZrPCdS materials heated to 1100°C shows the reflections due to the cadmium zirconium double phosphate phase as we saw for the γ-ZrPCd heated at the same temperature (see Fig. 3d).

4. Conclusions

Cadmium ions can be inserted between the layers of γ-ZrP and γ-ZrPL aromatic diamine by ion exchange, at 45°C. The uptake speed of the ions for the γ-ZrPL derived materials is in the order dmp > bipy > phen and the total amount of the exchanged ions, in the order bipy > dmp > phen. The interlayer distance of the γ-ZrPCd is smaller than the one of the precursor. The distance increases in the case of the material derived from γ-ZrPbipy$_{0.48}$. The TG-DTA curves of all cadmium materials show losses between 25 and 200°C due to the coordination and lattice water. The losses between 400 and 520°C of the γ-ZrPL derived materials are related to the ligand combustion (exothermic peaks in DTA curves).

When anhydrous H_2S is flowed over the white γ-ZrPCd, its color suddenly changes to yellow because the S^{2-} ions combine with the cadmium ions, already exchanged in γ-ZrP, to give CdS particles. The diffractogram of the final γ-ZrPCdS shows a layered structure, almost equal to that of the precursor. The 'reversion' to the hydrogen phase suggested the re-use of the obtained γ-ZrPCdS material as starting ion-exchanger of cadmium ions and then to expose it to H_2S flow. After three cycles, more CdS particles in the 'new' exchanger have been obtained. The TG-DTA curves of the γ-ZrPCdS material show water loss between 25 and 120°C. The losses between 280 and 590°C (strong exothermic peaks) are related to the S^{2-} loss, likely due to CdS differently linked between the zirconium phosphate layers.

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References

[1] A. Clearfield, J.M. Kalnins, J. Inorg. Nucl. Chem. 38 (1976) 849.

[2] S. Allulli, C. Ferragina, A. La Ginestra, M.A. Massucci, N. Tomassini, J. Chem. Soc., Dalton Trans. (1977) 1879.

[3] L. Alagna, A.A.G. Tomlinson, C. Ferragina, A. La Ginestra, J. Chem. Soc., Dalton Trans. (1981) 2376.

[4] G. Alberti, U. Costantino, Inclusion Compounds, University Press, New York, 1982, Chapter 5, p. 136.

[5] C. Ferragina, M.A. Massucci, A.A.G. Tomlinson, P. Patrono, A. La Ginestra, P. Cafarelli, Pillared Layered Structures, Elsevier, Amsterdam, 1990, p. 127.

[6] C. Ferragina, A. Frezza, A. La Ginestra, M.A. Massucci, P. Patrono, Expanded Clays and Other Microporous Solids, New York, 1992, p. 263.

[7] G. Mattogno, C. Ferragina, A. La Ginestra, M.A. Massucci, P. Patrono, J. Electron Spectrosc. Relat. Phenom. 46 (1988) 285.

[8] C. Ferragina, A. La Ginestra, M.A. Massucci, P. Patrono, P. Giannoccaro, F. Nobile, G. Moro, J. Mol. Catal. 53 (1989) 349.

[9] M. Lenarda, R.L. Ganzerla, R. Zanoni, J. Mol. Catal. 78 (1993) 339.

[10] P. Giannoccaro, S. Doronzo, C. Ferragina, Heterogeneous Catalysis and Fine Chemicals, Vol. IV, Elsevier, Amsterdam, 1997, p. 633.

[11] C. Ferragina, P. Cafarelli, R. Di Rocco, Mater. Res. Bull. 33 (1998) 305.

[12] C. Ferragina, P. Cafarelli, J. Thermal Anal. 53 (1998) 189.

[13] C. Ferragina, R. Di Rocco, Mater. Res. Bull. 34 (1999) 1981.

[14] G. Cao, V.M. Lynch, L.N. Yacullo, Chem. Mater. 5 (1993) 1000.

[15] L. Brus, J. Phys. Chem. 90 (1986) 2555.

[16] T. Bein, Supramolecular Architecture, American Chemical Society, Washington, DC, 1992, p. 274.

[17] Y. Wang, N. Herron, J. Phys. Chem. 91 (1987) 257.

[18] S. Yamanaka, M. Tanaka, J. Inorg. Nucl. Chem. 41 (1979) 45.

[19] C. Ferragina, M.A. Massucci, A.A.G. Tomlinson, J. Chem. Soc., Dalton Trans. (1990) 1191.

[20] S. Allulli, C. Ferragina, A. La Ginestra, M.A Massucci, N. Tomassini, A.A.G. Tomlinson, J. Chem. Soc. (1976) 2115.

[21] C. Bettinali, A. La Ginestra, M. Valigi, Atti Accad. Naz. Lincei, Sez. VIII, Vol. 88, 1962, p. 472.

[22] J. Votinsky, J. Kalousova, L. Benes, J. Incl. Phenom. 14 (1992) 19.