

On the Nature of Sandwiched Chromium Complexes in Exchanged α -Zirconium Phosphate

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Layered α -zirconium hydrogenphosphate monohydrate was prepared by direct precipitation, exchanged with n-propylamine and then by chromium aquacomplexes. The solids were characterized by X-ray diffraction, mass spectrometry, infrared and UV-Visible spectroscopy. The results suggest that monomer complexes form extended, hydrogen bonded, sandwiched monolayers in the interlayer space.

Keywords: layered zirconium phosphate, intercalation, chromium aquacomplexes

1. Introduction

Layered phosphates such as $Zr(HPO_4)_2 \cdot H_2O$, or α -ZrP, have important applications as ion-exchangers, heterogeneous catalysts and ionic conductors^{1,2}. These materials readily undergo cationic exchange after interlayer separation by alkylamines. In particular, the perspective of increasing the layer separation by oxide intercalation, and ultimately produce stable, porous materials after thermal processing has stimulated a variety of studies in the field^{3,4}.

Exchange of α -ZrP with small cations such as Li^+ , Na^+ , Ag^+ , Tl^+ , Cu^+ and Ca^{2+} is a fast process. Direct proton substitution by larger, highly hydrated cations such as Cr^{3+} requires a higher activation energy to expand the interlayer region and occurs more slowly at ambient temperature⁵. In these cases, intercalation has proven more effective by starting from sodium or n-alkylamines exchanged materials³. Different phases were thus obtained upon varying the loading, and using Cr^{3+} aqua, amine or ethylenediamine complexes. In all cases, however, the interlayer distance fell in the range below 11 Å⁶⁻⁸.

Only intercalation of amine exfoliated α -ZrP using Cr^{3+} or mixed Fe/Cr^{3+} , Ga/Cr^{3+} and Al/Cr^{3+} polyhydroxy acetates was reported to increase the interlayer space between 13.0 and 39.0 Å, as a function of metal loading and resulted in porous materials with high specific area after calcination⁹⁻¹³. The presence of octahedral Cr^{3+} within the layers, and sometimes Cr^{6+} , was indicated by UV-Visible spectroscopy. These materials are finding applications as catalysts for oxidation

reactions of small alkanes, alkenes, aromatics or alcohols^{10,13}.

The exchange reaction is topotactic in nature, and it is currently assumed that the topology of the layers remains identical to that of the original α -ZrP precursor. However, highly disordered crystals are produced after ion insertion, with probably an irregular stacking sequence of the layers, and X-ray diffraction data cannot be used to provide structural information^{3,14,15}. Through XAS data, it was however reported that flat dimers (12 Å phase) closed trimers (17 Å phase) or open tetramers (34 Å phase), depending upon the chromium loading, stabilize the interlayer space in the precursor when Cr polyhydroxy acetates are used for intercalation¹⁶.

In the present work, we have applied UV-Visible spectroscopy to analyze the structure of solids intercalated with chromium aquacomplexes. Oligomer-containing solutions were prepared by dissolving the freshly precipitated hydroxide in dilute nitric acid or adding triethylamine to aqueous solutions of the salt. A structural model is proposed which justifies the failure of expansion of the interlayer space.

2. Experimental

α -Zirconium hydrogenphosphate was precipitated, by dissolving zirconyl chloride, $ZrOCl_2 \cdot 8H_2O$ (Vetec) in (40%) hydrofluoric acid (Merck), then adding concentrated phosphoric acid (Vetec) and allowing the solution to evaporate on water bath at about 80-90 °C; the solution was pre-

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pared with 5.5 g of salt dissolved in 80 ml; 4 ml hydrofluoric acid and 46 ml of H_3PO_4 were added with stirring¹⁷. α -ZrP (1.000 g) was exfoliated using an 0.1 M n-propylamine (Merck) solution (70 ml), corresponding to 7 meq of n-propylamine/g α -ZrP; the suspension was stirred magnetically for 24 h, filtered and the solid was washed with water and dried at 50 °C for 16 h¹⁴. Two methods were used for exchange by chromium aquacomplexes. In the first method, the hydroxide was precipitated from aqueous solutions of the chloride 0.1 M by addition of sodium hydroxide 0.3 M, separated and dissolved in aqueous nitric acid solution using the amount corresponding to the theoretical hydrolysis degree, $Z = [OH^-]/[Cr^{3+}] = 2$. In the second method, triethylamine was added to aqueous solution of the chloride with a cation:triethylamine ratio of 1:1. In both cases, the chromium concentration in solution was 0.1 M. N-propylamine exchanged ZrP was added to the solution with 10 meq Cr^{3+} /g α -ZrP; the suspension was stirred for 24 h, filtered and the resulting solid was washed with water and dried at 50 °C for 16 h. The solids were further calcinated for 2 h at 300 °C under air.

Four solids were obtained and named ZrP(x, T) where $x = h$ when the precursor was the hydroxide or $x = t$ when triethylamine was used. T indicates the temperature of the thermal treatment (T = 50 °C or T = 300 °C).

Thermal decomposition of dried sample was followed by mass spectrometry in the range 25-300 °C using a Balzers OMNISTAR mass spectrometer. The sample was heated at a rate of 10 °C/min and Ar was used as a carrier gas. Fourier-transform infrared spectra were performed in the region 4000-400 cm^{-1} with a Nicolet, MAGNA 760 apparatus; KBr pressed discs were used. X-Ray diffraction patterns were recorded in the region $2^\circ \leq 2\theta \leq 60^\circ$, step size 0.02° with a PHILIPS PW 1820 automatic powder diffractometer using $CuK\alpha$ radiation, current 40 mA, tension 40 kV and graphite monochromator. UV-Visible spectra were recorded in the region 200-900 nm using a Varian, CARY 5 spectrometer equipped with a Harrick diffuse reflectance accessory with Praying Mantis geometry. Barium sulfate was used as a reference. Atomic absorption spectrometry was realized on a Perkin Elmer 1100B and elemental CHN analysis was performed using a Perkin Elmer 2400 apparatus.

3. Results and Discussion

X-ray diffraction patterns of precipitated α -ZrP, Fig. 1a, indicated that a well crystallized material was obtained, in agreement with published data. Chemical analysis confirmed the stoichiometry of the phase, with 38.19 wt.% ZrO₂, 51.46 wt.% P₂O₅ and 10.22 wt. H₂O (theoretical values: 40.19 wt.%, 47.12 wt. and 11.97 wt.% respectively). The FTIR spectrum is shown in Fig. 2a, and the attribution of the bands is given in Table 1 according to the literature¹⁸⁻²⁰.

In particular the splitting of crystallization water band $\nu_{as}(OH)$ at 3592 cm^{-1} and 3509 cm^{-1} is clear in the spectrum. According to the literature, these bands are modified after exchange reactions.

The X-ray diffraction pattern in Fig. 1b shows that, after intercalation by n-propylamine, materials with lower crystallinity were obtained with interlayer distance of 17.26 and 16.36 Å. These values agree with literature reports and

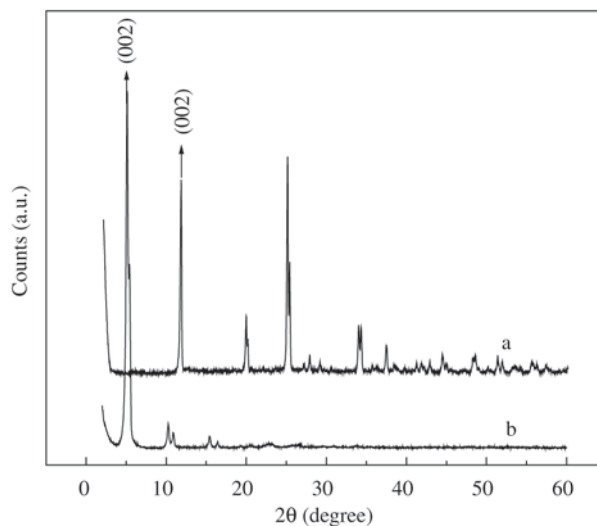


Figure 1. a) X-ray diffraction patterns of α -ZrP; b) α -ZrP/n-propylamine dried at 50 °C.

Table 1. Bands attributions in FTIR spectra of alpha-zirconium phosphate and zirconium phosphate exfoliated with n-propylamine dried at 50 °C.

Assignment	α -ZrP (cm^{-1})	α -ZrP/n-propylamine (cm^{-1})
$\nu_{as}(OH)$	3592	—
$\nu_{as}(OH)$	3509	—
$\nu_s(NH-OH)$	—	3416
$\nu(POH)$	3353	—
$\nu_s(OH)$	3139	—
$2\delta(N-H)$	—	2968-2937
$\nu_s(C-H)$	—	2881
$\nu(POH)$	2300	—
$\nu(POH)$	2100	—
$\delta_{as}(OH)$	1611	1636
$\delta((CNH)_{in}-NH_2)$	—	1557-1395
$\nu_{in}(POH)$	1252	—
$\delta(CNH)$	—	1209
$\nu_s(PO_4)$	1130-964	1132-976
$\delta_{out}(POH)$	600	610
$\delta(PO_4)$	530	542

indicate effective insertion of the amine into the interlayer space²¹. The corresponding FTIR spectrum reported in Fig. 2b, and attributed in Table 1, shows clearly the characteristic vibration bands from the amine and the phosphate group. The bands at 610 and 542 cm^{-1} attributed to deformation modes of PO_4 , however, are slightly shifted in relation to those of the precursor, probably due to the presence of n-propylamine^{2,22}. The results obtained by chemical analysis (viz. 15.55 wt.% C, 4.16 wt.% H and 6.12 wt.% N),

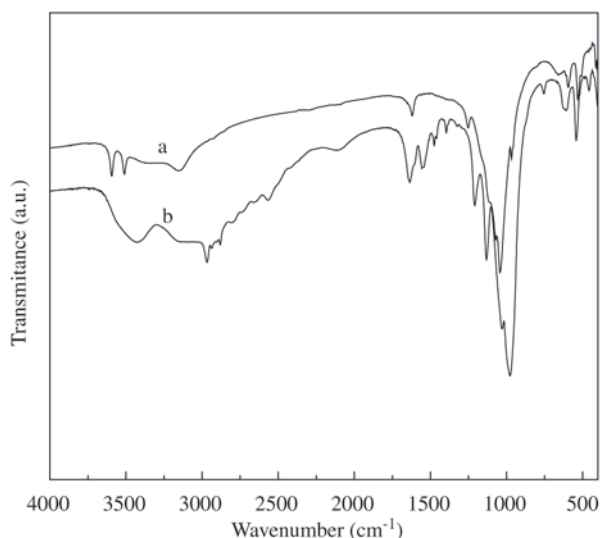


Figure 2. a) Infrared spectra of α -ZrP; b) α -ZrP/n-propylamine; dried at 50 °C.

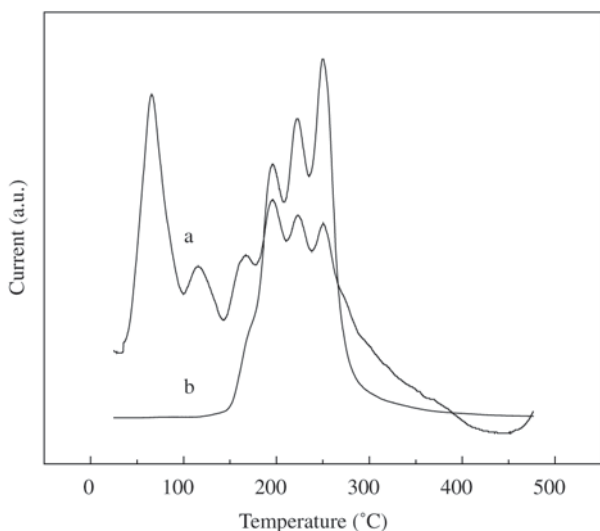


Figure 3. a) Decomposition mass spectra of α -ZrP/n-propylamine dried at 50 °C water; b) n-propylamine.

indicate that the exchange corresponded to 90% of the total exchange capacity of α -ZrP.

Figure 3 shows the mass spectra corresponding to the removal of water and n-propylamine intercalated in α -ZrP between 25 and 300 °C. Water alone is first eliminated up to 120 °C, probably adsorbed water as suggested earlier²³, then n-propylamine and water evolve simultaneously in four steps between 170 and 260 °C. The reaction appears to be complete at 300 °C, which led to choose this temperature for sample calcination.

Chemical analysis after exchange indicated Cr and water contents of 13.5 wt.0% and 26 wt.% respectively, corresponding to a ratio $\text{Cr}/\text{Zr} \cong 0.84$ for material prepared from the hydroxide precursor.

Figure 4 compares the FTIR spectra of α -ZrP exchanged with Cr(III) for both preparation methods, after drying and calcination. Only weak bands from residual n-propylamine are observed in the exchanged solid, but no new band from triethylamine. Moreover, the spectra of exchanged materials show a broad band near 3420 cm^{-1} which is characteristic of intercalated solids¹⁸. The same features were observed in the case of materials prepared from hydroxides. These results confirm the efficiency of both intercalation methods. In particular, the absence of intercalation of triethylamine was expected from steric hindrance.

X-ray diffraction patterns of α -ZrP intercalated with Cr(III) are shown in Fig. 5. Dried materials display broad patterns which are characteristic of transition metal ions-intercalated compounds with low crystallinity, but a few sharp lines are also observed in superposition; these could be attributed to residual amine-intercalated phases, in agree-

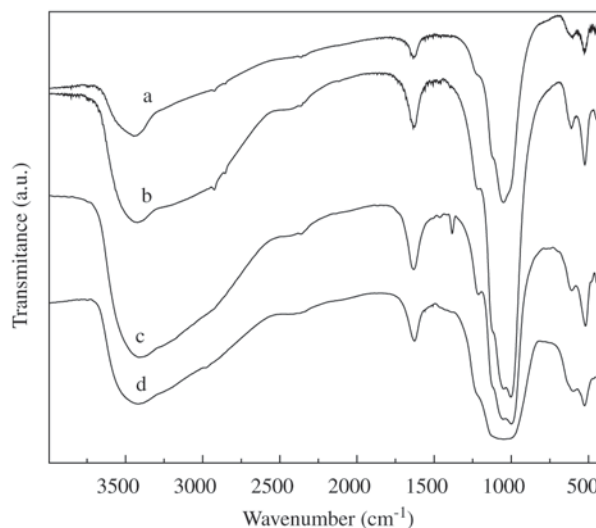


Figure 4. a) Infrared spectra ZrP(t, 300); b) ZrP(t, 50), c), ZrP(h, 50), d) ZrP(h, 300).

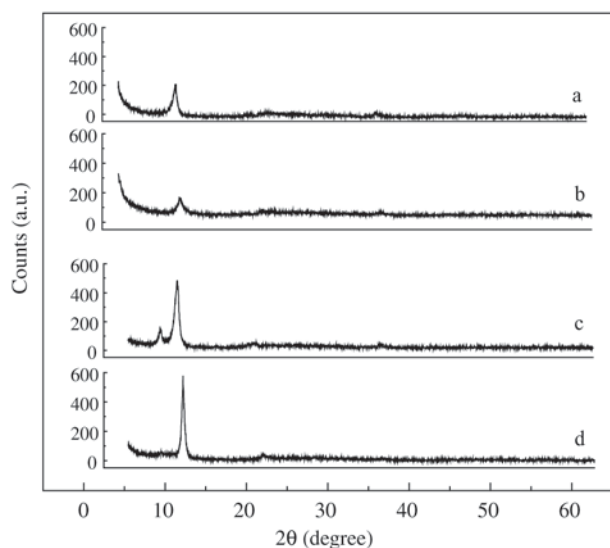


Figure 5. X-ray diffraction patterns of a) ZrP(h, 50); b) ZrP(h, 300), c), ZrP(t, 50), d) ZrP(t, 300).

ment with FTIR spectra. Only broad bands are observed after calcination for 2 h at 300 °C, which were attributed to chromium intercalated compounds. The corresponding interplanar distances obtained from X-ray diffraction patterns of these solids are listed in Table 2. A comparison between dried solids shows interlayer distances of 9.8 Å, equal for materials prepared by both methods, and in agreement with values cited in the literature²⁴. The increment of 2.24 Å in relation to the interlayer separation in the hydrate $Zr(HPO_4)_2 \cdot H_2O$ together with chemical analysis and FTIR results confirms chromium insertion within the interlayer space but suggests that not more than one cationic layer was intercalated. After calcination, the interlayer distances decreased to values of 9 Å for both samples.

Figure 6 shows UV-visible spectra of α -ZrP intercalated with Cr(III) in comparison with the spectrum of chromium hydroxide dried at 50 °C and the spectrum of chromium solution obtained after hydrolysis of the hydroxide. The spectra obtained from dried intercalated solids using both preparation methods are similar, only a lower intensity was obtained for the sample exchanged using triethylamine, suggesting that lower chromium content was attained by this method. With exception of ZrP(h, 300), all compounds present two bands in the ranges of 400-450 and 550-600 nm which can be assigned respectively to ${}^4T_{1g} \leftarrow {}^4A_{2g}$ and ${}^4T_{2g} \leftarrow {}^4A_{2g}$ d-d transitions of octahedral chromium aquacomplexes²⁵. The bands observed at 423 and 586 nm for chromium in aqueous solution are characteristic of oligomeric species, probably the trimer, tetramer or hexamer complexes, as expected from the hydrolysis degree²⁶. It is

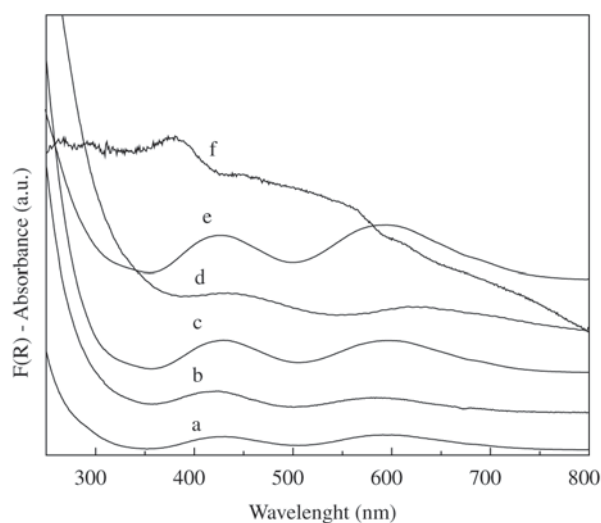


Figure 6. a) UV-Visible spectra of chromium solution; b), ZrP(t, 50); c), ZrP(h, 50); d), ZrP(t, 300); e) chromium hydroxide; f) ZrP(h, 300).

Table 2. Interplanar distances of alpha-zirconium phosphate intercalated with Cr(III), dried at 50 °C and calcined at 300 °C/2 h.

ZrPCr(h, 50)	ZrPCr(h, 300)	ZrPCr(t, 50)	ZrPCr(t, 300)
d(Å)	d(Å)	d(Å)	d(Å)
9.71	9.28	12.77	8.99
4.87	4.50	9.80	4.53
4.35	4.25	4.82	3.45
2.65	2.64	3.10	2.63
2.00	2.00	2.64	—

interesting to note, however, that equilibrium was reached as soon as chromium hydroxide was hydrolyzed, as opposed to solutions prepared by addition of base to the monomer. The bands corresponding to chromium hydroxide are seen at 427 and 593 nm. Dried intercalated solids show two bands near 429 and 594 nm. It is currently admitted that d-d transition bands shift towards the lower energy region in proportion as chromium species form an extended structure; the position of the bands of the pentaquahydroxy complex $[Cr(OH)(OH)_5]^{2+}$, which are seen at 430 and 590 nm following^{26,27}, and of chromium hydroxide indicate that the correlation is not straightforward, since the latter compound is built from hydrogen bonded monomeric $[Cr(OH)_3(H_2O)_3]$ complexes²⁸. The experimental data rather suggest that the partial charge on the chromium atom should be considered to be responsible for the shift.

The intensity ratios (ϵ_1/ϵ_2) between the two bands are listed in Table 3. Some authors have suggested that higher values were to be assigned to condensed chromium com-

Table 3. Band features in electronic spectra of Cr(III) intercalated solids dried at 50 °C and reference samples.

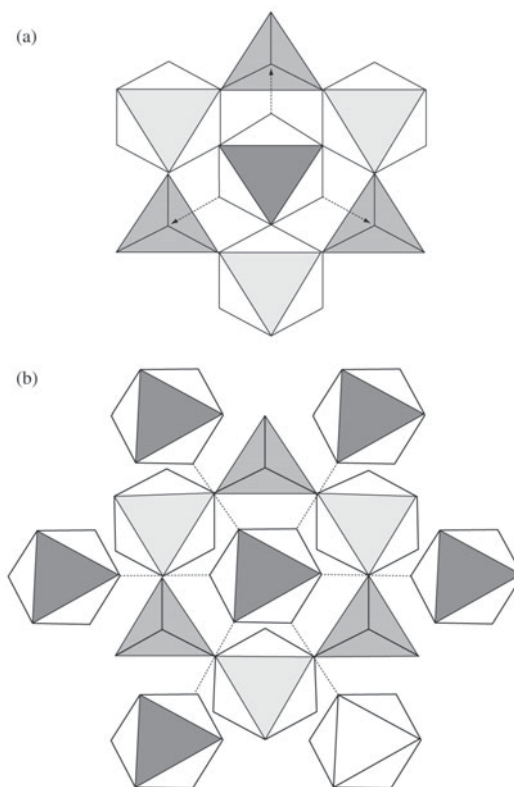
Sample	Absorption (nm)		Intensity Ratio (ϵ_1/ϵ_2)
	(ϵ_1)	(ϵ_2)	
ZrPCr(h, 50)	432	600	1.03
ZrPCr(t, 50)	432	602	1.07
Chromium Hydroxide	427	594	0.81
Original Solution	423	585	1.48

plexes. Indeed, absorption ratios of 1.17-1.18 characterize the monomer and dimer, 1.95 the tetramer, and 1.5-1.6 the pentamer and hexamer²⁶. In comparison, a small value was obtained in this work for chromium hydroxide whereas the value of 1.75 was given by the literature for the pentaquahydroxy complex. Accordingly, the intensity ratio alone does not provide a satisfactory criterion to characterize polymerization degrees of chromium complexes.

The comparison of the position of the bands suggest therefore that chromium within the interlayer space of α -ZrP forms an extended structure, based on monomer complexes, comparable to chromium hydroxide. This interpretation is in agreement with the interlayer distance obtained from X-ray diffraction patterns. Chemical analysis results, on the other hand, suggest the exchange of the two protons of α -ZrP by one chromium ion. This leads us to propose that chromium enters the interlayer space as the monomer $[\text{Cr}(\text{OH})(\text{OH}_2)_5]^{2+}$ and forms an extended, hydrogen bonded structure.

The electronic spectrum of the solid exchanged from hydroxide after calcination is less definite and presents stronger absorption in the high energy region, suggesting that temperature induces some polymerization to chromium oxide. A strong band at 250 nm suggests also the presence of some Cr(VI) ion. This was not observed in the case of the solid α -ZrP(t, 300), probably because of the lower chromium content.

The crystal cell of α -Zr $(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ (α -ZrP) is pseudo-hexagonal with $a = 9.076 \text{ \AA}$, $b = 5.298 \text{ \AA}$, $c = 15.414 \text{ \AA}$ and $\beta = 101.71^\circ$ and belongs to space group P21/c²⁹. Zirconium atoms in octahedral coordination lie in the ab plane, bridged by phosphate groups so that the phosphorus atoms occupy the centers of alternate triangles distributed above and below the zirconium planes, forming the layers. POH groups are oriented perpendicular to the layer. The interlayer distance is 7.56 \AA with a layer thickness of 6.30 \AA ¹³. Successive layers are shifted by 1/3 in the a direction and 2/3 in the b direction, so that six POH groups, three from each side of two consecutive layers, form a cavity with local D_{3d} symmetry. This cavity is closed with two zirconium atoms located on the C_3 axis, respectively below and above the basal faces of the triangular antiprism. One such cavity is present per

**Figure 7.** Polyhedral representation of alpha-zirconium phosphate intercalated with chromium (III). The monomers may be linked by hydrogen bonds to the six phosphate groups (a) or within themselves (b) (see text).

unit formula of α -ZrP and is occupied by the water molecule, linked by hydrogen bonds to POH groups^{3,15,30}.

Based on the previous results, we suggest that $[\text{Cr}(\text{OH})(\text{OH}_2)_5]^{2+}$ complexes occupy and expand normally to the layer the zeolitic type cavities in the interlayer space of α -ZrP, while forming an extended structure comparable with that of chromium hydroxide. An hexagonal layer structure was proposed for the latter compound with lattice parameter $a = 5.28 \text{ \AA}$ ³¹ equal to the pseudo-hexagonal parameter cell of α -ZrP; this allows the two-dimensional matching of the sandwiched chromium structure with the layers of the host. Figure 7 shows two proposals for the structure of α -ZrP intercalated with Cr(III). Only one side of the layer *i.e.* half of the cavity of α -ZrP formed by one six-members ring, has been represented with the phosphate groups above the zirconium octahedrons marked by light shaded faces. Chromium octahedrons, drawn with black faces stand above phosphate groups in the center of the cage and may be linked by hydrogen bonds to the six phosphate groups forming the cavity, as in model (7a) or within them-

selves as in model (7b) and in a similar fashion to chromium hydroxide.

4. Conclusion

Layered α -zirconium hydrogenphosphate monohydrate was intercalated with chromium aquacomplexes. Two methods were compared for cation exchange; chromium hydroxide was hydrolyzed with dilute acid or triethylamine was added to an aqueous solution of a chromium salt before addition of the n-propylamine exchanged ZrP. Both processes led to the intercalation of the same species. Electronic spectra suggested that the monomer complex $[\text{Cr}(\text{OH})(\text{OH}_2)_5]^{2+}$, forms an extended, hydrogen bonded sandwiched monolayer, comparable to chromium hydroxide, in preference to oligomer insertion, which prevents a larger expansion of the interlayer space. The chromium content was higher when the hydroxide was used as a precursor. The materials kept their interlayer distances after calcination at 300 °C; however, chromium excess led to some polymerization of chromium oxide. The question arises of whether this polymerization occurs within the interlayer space or not.

Acknowledgments

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