Formation and Intercalation of Hexamethylenetetramine in the Layered Structure of α-Zirconium Phosphate

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The reaction of α-layered $Zr(NH_4PO_4)_2 \cdot H_2O$ with concentrated HCHO solutions gave a new solid phase which was characterized by elemental analysis, X-ray powder diffraction, IR spectroscopy and thermogravimetric determinations. The new phase possesses the same type of layered structure as the parent material but has an interlayer distance of 11.2 Å. Hexamethylenetetramine, methylamine, ammonia and water are accommodated in the interlayer region. Compounds having the same interlayer distance and similar composition were also obtained by direct intercalation of hexamethylenetetramine into the ethanolic intercalate of α-zirconium phosphate.

Direct intercalation of large weak bases into α-layered acid salts of tetravalent metals can hardly occur for steric reasons: in this connection it was recently reported that hexamethylenetetramine (HMTA) cannot be intercalated into α-tin phosphate.[1] However, the intercalation process can be facilitated using as a host material an intercalate of the acid salt having a large interlayer distance and containing weakly bonded species. This procedure was used to intercalate alkyldiamines in α-zirconium phosphate.[2]

Alternatively, the guest molecule could be synthesized in the host structure by reaction between a suitable solution and a suitable host material. In the present work α-Zr $(NH_4PO_4)_2 \cdot H_2O$ was chosen as a host material to investigate the possibility of forming HMTA in α-zirconium phosphate by reaction with formaldehyde.

Both the diammonium and the dihydrogen form of α-zirconium phosphate possess a common layered structure[3,4] built up by the packing of planar macroanions in which the zirconium atoms lie in a plane and are bridged by phosphate groups. Each zirconium is octahedrally coordinated by the oxygens of six different phosphates and each phosphate is bonded to three different zirconiums. Counterions and water molecules are placed in the interlayer region. The interlayer distance in the dihydrogen and diammonium forms is 7.56 and 9.36 Å, respectively.

The present paper reports the characterization of the solid phase obtained from the reaction between HCHO and α-Zr $(NH_4PO_4)_2 \cdot H_2O$ as well as the preparation and the characterization of the intercalation compounds of α-zirconium phosphate with hexamethylenetetramine $(CH_2)_6N_4$.

Experimental

Reaction of α-Zr$(NH_4PO_4)_2 \cdot H_2O$ with HCHO. The diammonium form of zirconium phosphate was obtained at room temperature by equilibrating under stirring, for three days, 5 g of α-Zr$(HPO_4)_2 \cdot H_2O$ with 200 ml of a solution 0.25 M in NH_3 and 0.25 M in NH_4Cl; α-zirconium phosphate was prepared according to the direct precipitation method.[5] After centrifugation, the solid was washed with water until constant conductivity of the washing water was obtained (6×10^{-5} S cm^{-1} at 25 °C).

3 g of α-Zr$(NH_4PO_4)_2 \cdot H_2O$ were suspended under stirring in 120 ml of 13 M HCHO for 4 days, at room temperature. The solid was washed three times with 3×200 ml of water, dried in air, and then stored at 75 % relative humidity (RH).

Intercalation of HMTA in α-Zr$(HPO_4)_2 \cdot xC_2H_5OH \cdot nH_2O$. The ethanolic intercalate of zirconium phosphate was prepared by treating α-ZrHNa$(PO_4)_2 \cdot 5H_2O$ with a solution of 0.3 M $HClO_4$ in ethanol.[2] After washing with ethanol (10 ml g^{-1} of solid) until constant conductivity of the washing solution was obtained (6×10^{-7} S cm^{-1} at 25 °C), the solid was partially dried in air and kept in a sealed container at ca. 5 °C (the fully dry material is not stable). Its interlayer distance was 10 Å. The content of Zr (2.56 mmol per g of solid) was calculated from the weight of the Zr pyrophosphate obtained by heating at 900 °C; the content of ethanol and water was not determined.

The intercalation of HMTA was carried out at room temperature. A weighed amount of the ethanolic intercalate was suspended under stirring, for 3 days, in a suitable volume of aqueous HMTA; the mass/volume ratio was such as to have 0.5 g of intercalate per 10 mmol of HMTA. After centrifugation the solid was washed twice with water (100 ml per 0.25 g each time), dried in air and stored at 75 % RH.

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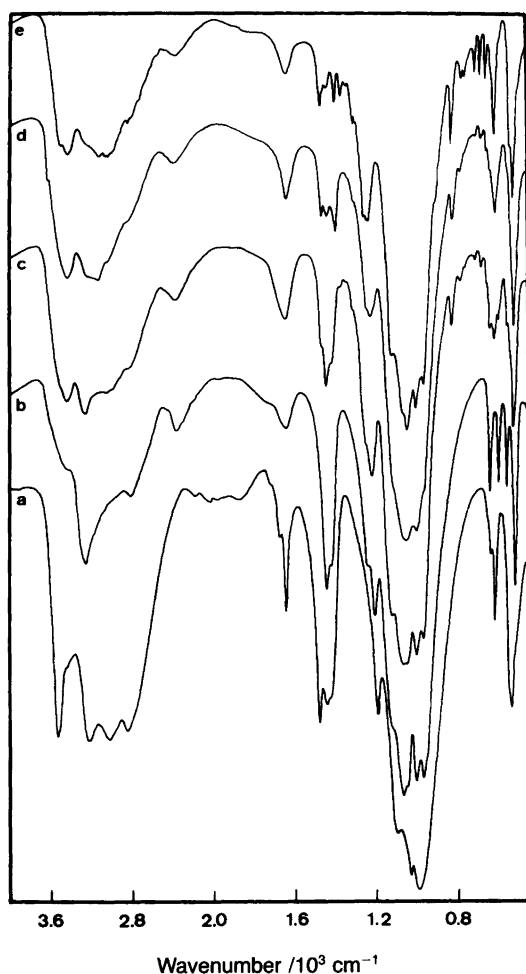‡ To whom correspondence should be addressed.

Fig. 1. IR spectra of α-Zr(NH₄PO₄)₂·H₂O not treated (a) and treated with HCHO at different concentrations: 0.4 M (b), 2 M (c) and 13 M (d). The spectrum of the intercalate prepared in 1 M HMTA (e) is also shown.

Analytical procedures. X-Ray powder patterns were recorded with a Guinier–Hägg camera using α-SiO₂ as an internal standard (a = 4.91309, c = 5.40462 Å,[6] λ(CuKα₁) = 1.54051 Å).[7] Thermogravimetric determinations were

carried out with a Setaram TGDTA92 apparatus. IR spectra were taken on KBr pellets using a Perkin Elmer 1720 Fourier-transform spectrometer. Mass spectra were recorded with a Varian MAT 311A mass spectrometer. Elemental analyses were carried out by Mr Preben Hansen at the Chemistry Department of Copenhagen University.

Results and discussion

HMTA formation in α-zirconium phosphate. Preliminary investigations were carried out by using aqueous solutions of 13 M formaldehyde and α-ZrHNH₄(PO₄)₂·H₂O and α-Zr(NH₄PO₄)₂·H₂O as host materials. The monoammonium form did not react, but the diammonium form was transformed into a new solid phase whose XRD powder pattern was characterized by a broad and intense reflection at 11.2 Å. Experiments were then performed with different HCHO concentrations; in all cases the volume of solution was such as to have at least 20 mmol of HCHO per mmol of NH₄⁺ in the solid phase. No reaction was observed for a concentration of 0.2 M, and only partial deammoniation, with formation of α-ZrHNH₄(PO₄)₂·H₂O, occurred in the range 0.4–1 M. The reaction with 2 M HCHO gave a mixture of the new phase and α-ZrHNH₄(PO₄)₂·H₂O. In the samples treated with HCHO concentrations ≥ 4 M only the new phase was present.

In Fig. 1 the IR spectra of the diammonium form treated with 0.4, 2 and 13 M HCHO are compared with the spectrum of the starting material. The reaction with more and more concentrated HCHO causes a progressive reduction of the bands at 3214, 3014, 2840, 1479 and 1441 cm⁻¹ which are associated with NH₄⁺ vibrations; in addition, the maximum of the absorption due to the stretching of the phosphate group shifts from 991 to 1050 cm⁻¹. (This is usually due to a change of tertiary phosphate groups to secondary groups.) A few weak absorptions appear between 613 and 828 cm⁻¹ as the new phase is formed.

The compound obtained in 13 M HCHO, hereafter called ZPFORM, was chosen for further investigation. The weight loss curve of a sample previously stored at 75 % RH
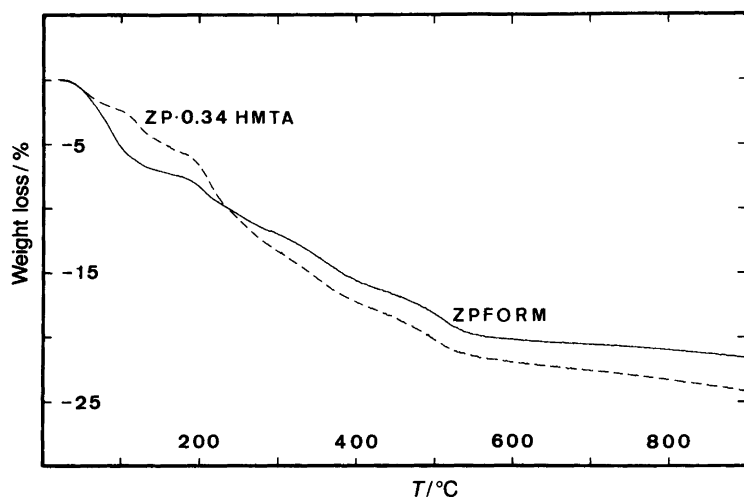

Fig. 2. Weight loss curves of ZPFORM and of the intercalate prepared in 1 M HMTA (ZP 0.34 HMTA). Heating rate 5°C min⁻¹.

is shown in Fig. 2. Heating the material to 900 °C causes a loss of 22 % in four ill defined steps, the last of which (between 400 and 500 °C) leads to the formation of zirconium pyrophosphate. Assuming that the loss observed below 150 °C (i.e. −7 %) is entirely due to crystallization water, an amount of 1.3 H₂O molecules per unit formula can be calculated, thus excluding the possibility that ZPFORM is a polyhydrated phase. Elemental microanalysis of a sample stored at 75 % RH revealed the presence of carbon (3.13 %), nitrogen (4.35 %) and hydrogen (2.20 %). Taking into account the Zr percentage obtained by weight loss, the ratio N/Zr turned out to be 1.06, appreciably lower than in the parent diammonium form. Therefore, a considerable deammoniation also occurs in concentrated HCHO solutions.

The X-ray powder pattern of ZPFORM, stored at 75 % RH, is listed in Table 1. The pattern shows broad lines (as is usually the case for intercalates). The reflection at $d = 2.69$ Å is almost in the same position as the (020) reflection in the parent diammonium form $[d(020) = b/2 = 2.689$ Å]. Considering that the length of the b axis of Zr $(NH_4PO_4)_2 \cdot H_2O$ is equal to the distance between two Zr atoms in the same layer, it can be suggested that the integrity of the α-layer is retained in ZPFORM.

In order to have information on the reactivity of the chemical species present in ZPFORM, the solid was treated with NH_3, KOH and HCl. The treatment with ammonia gave $Zr(NH_4PO_4)_2 \cdot H_2O$, thus further confirming that ZPFORM possesses a layered structure of the α-type; the reaction occurred both equilibrating ZPFORM with 1 M NH_3 (0.1 g + 20 ml) and exposing the solid to the vapour of a concentrated ammonia solution (2 days at room temperature in both cases). In the second experiment a large increase in the weight of the solid was observed (ca. 50 %) arising essentially from water uptake. Ammonia uptake cannot be higher than two molecules per Zr atom, corresponding to about 10 % of the formula weight of the

monohydrated diammonium form. However, no polyhydrated phase was detected by X-ray diffraction. This behaviour can be explained by ascribing the weight gain to the hydration of a non-volatile molecule which is deintercalated as a consequence of the ammonia uptake. To check this hypothesis, the solid was dried at 50 % RH and its X-ray pattern recorded: together with the lines of the diammonium form some extra lines were observed corresponding to the strongest reflections of the powder pattern of HMTA. To calculate the amount of deintercalated HMTA, a portion of the solid was heated to 900 °C and its weight loss determined (−25.6 %); another portion was washed with water to remove HMTA and stored at 50 % RH; its weight loss up to 900 °C was −20.6 %, as expected for the diammonium form (−20.9 %). The amount of HMTA originally present in ZPFORM, obtained on the basis of the two weight losses, turned out to be 0.16 molecules per Zr atom; the corresponding amount of nitrogen (0.64 N per Zr) is appreciably lower than that calculated from elemental analysis.

The treatment with 1 M KOH caused the evolution of a gas which gave a basic reaction on a pH indicator paper, thus indicating ammonia and/or volatile amines to be present. To detect the presence of amines, 1 g of ZPFORM was stirred with 10 ml of 1 M HCl for 2 days. After this treatment the solid phase was found to be converted into $\alpha\text{-}Zr(HPO_4)_2 \cdot H_2O$. The hydrochloric solution was heated at 75 °C to remove H_2O and HCHO arising from the hydrolysis of HMTA. The IR spectrum of the solid left showed a strong absorption at 1402 cm⁻¹, due to NH_4^+, and three absorptions at 1262, 1000 and 931 cm⁻¹ which are characteristic of methylammonium chloride. Elemental microanalysis of the solid gave a molar ratio C/N equal to 0.256. To know whether methylamine could be formed in the hydrolysis of HMTA, an amount of HMTA equal to that present in 1 g of ZPFORM was allowed to react with 10 ml of 1 M HCl for 2 days. The IR spectrum of the solid obtained after heating the solution at 75 °C showed only the presence of ammonium chloride. Therefore, it can be inferred that methylamine is present in ZPFORM, in an amount (calculated from the elemental analysis data) of 0.27 molecules per zirconium atom.

To obtain more detailed information on the composition of ZPFORM, thermolysis coupled with mass spectrometry was employed to monitor continuously the evolution of species with mass 17 (NH_3), 18 (H_2O) and 31 (CH_3NH_2) at temperatures up to 400 °C. This experiment clearly showed that water is lost below 150 °C, while ammonia and methylamine are evolved in the range 200–300 °C; these results explain the first two steps of the thermogravimetric curve. The amount of nitrogen present as ammonia in ZPFORM can be estimated by subtracting the amounts present in HMTA and CH_3NH_2 from the total nitrogen content, so that the following formula can be written for ZPFORM:

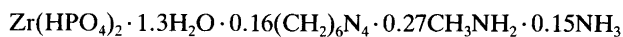$$Zr(HPO_4)_2 \cdot 1.3H_2O \cdot 0.16(CH_2)_6N_4 \cdot 0.27CH_3NH_2 \cdot 0.15NH_3$$

Table 1. d values (Å) for ZPFORM and HMTA intercalates prepared in 0.5 M HMTA. s = strong, m = medium, w = weak.

ZPFORM	HMTA intercalate before washing	HMTA intercalate washed and stored at 75 % RH
11.22 s	16.57 s	11.20 s
4.57 s	8.28 w	4.59 s
4.11 w	6.48 m	4.34 w
3.98 m	5.28 w	4.12 w
3.66 w	4.59 s	2.65 m
2.69 m	4.48 m	
2.64 w	4.43 m	
2.60 w	4.33 w	
	4.11 m	
	4.01 m	
	3.62 w	
	2.70 w	
	2.64 s	
	1.73 w	

The weight loss expected from this composition for pyrophosphate formation (-21.99%) is the same as that found experimentally (-22%). The calculated hydrogen percentage (2.45%) is slightly higher than that given by elemental microanalysis (2.20%). A disagreement is found for the calculated (4.34%) and observed (3.13%) carbon percentages owing to an incomplete combustion of the carbon. The ashes coming from elemental analysis are black, and their weight (79.7% of the initial weight) is higher than that expected from pyrophosphate formation (78%).

HMTA intercalation. Based on the above results it was thought of interest to try to intercalate HMTA into α-zirconium phosphate and compare the intercalation compounds thus obtained with ZPFORM. As mentioned in the introduction, the intercalation of a large weak base, like HMTA, is expected to be easier in a material containing weakly bonded molecules; to this purpose the ethanolic intercalate of α-zirconium phosphate was chosen as a starting material. The experiments were carried out at room temperature, using HMTA aqueous solutions with a concentration between 0.01 and 2.5 M (see Experimental section).

The intercalation of HMTA was observed over the whole concentration range. The X-ray pattern of unwashed intercalates obtained with HMTA concentrations ≤ 0.1 M showed the first reflection at $d = 11.2$ Å, while a new phase with a reflection at $d = 16.57$ Å was present at concentrations ≥ 0.5 M; a mixture of the two phases was found for 0.2 M HMTA. The phase with the first reflection at 16.57 Å turned out to be unstable in water, so that, after washing, all the intercalates were characterized by the same interlayer distance (11.2 Å) and very similar X-ray patterns. The X-ray patterns of intercalates prepared in 0.5 M HMTA, recorded before and after washing, are listed in Table 1. No further investigation was carried out on "the 16.57 Å phase".

The weight loss curves of the HMTA intercalates, washed with water and stored at 75 % RH, do not show any well defined step as in the case of ZPFORM; however,

assuming the crystallization water to be completely lost at 150 °C, a water content of 0.8–1 molecules per Zr atom was calculated for all the intercalates.

The HMTA content of the intercalates, determined by the same procedure used for ZPFORM, is shown in Fig. 3 as a function of the initial concentration of HMTA in solution. It can be seen that, in spite of the large difference in concentration (more than two orders of magnitude) only a relatively small change in the HMTA loading (from 0.20 to 0.34 molecules per Zr atom) is observed. The fact that the interlayer distance is independent of HMTA loading and that phases with loadings higher than 0.34 HMTA per Zr are not stable in water can be accounted for by simple structural considerations.

Solid HMTA has a body-centred cubic cell[8] with $a = 7.021$ Å at 20 °C; if the crystal structure is assumed to be built up by the packing of rigid spheres, a "radius" of 3.04 Å can be assigned to the HMTA molecule. The arrangement of PO_4 groups and Zr atoms in an α-layer is such as to create semicavities on both sides of the layer. Each semicavity is circumscribed by the hydroxyls of three phosphates belonging to the same side of the layer and closed by a phosphate on the opposite side. There are two semicavities per Zr atom. The hydroxyl baricentres occupy the vertices of an equilateral triangle inscribed in a circle with radius 3.06 Å. Thus, an HMTA molecule can be accommodated between two semicavities of adjacent layers. Fig. 4 shows a schematic arrangement of HMTA molecules in the semicavities of a layer corresponding to a loading of 0.33 HMTA molecules per Zr. Each HMTA molecule is surrounded by six empty cavities, but in each of them there is not room enough for an HMTA molecule. Loadings higher than 0.33 HMTA per Zr can be obtained by forming a bilayer, so that each HMTA molecule can interact with the hydroxyls of only one semicavity. This arrangement is expected to be less stable than that consisting of a single HMTA monolayer. On the other hand, it can be observed that any loading lower than 0.33 can be obtained by arranging HMTA in a monolayer of equally spaced molecules without changing the interlayer spacing.
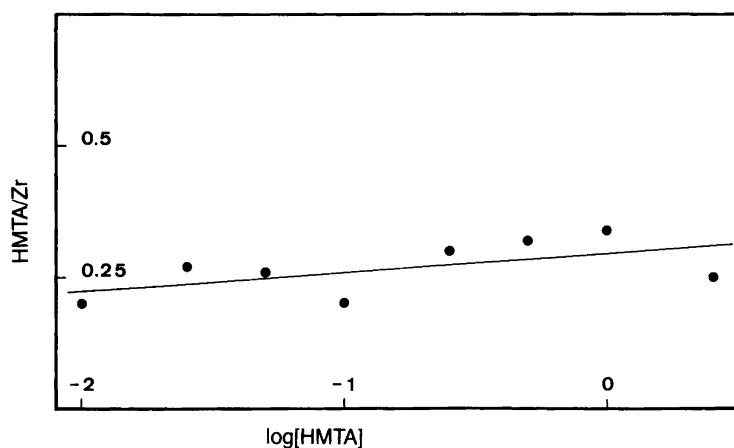

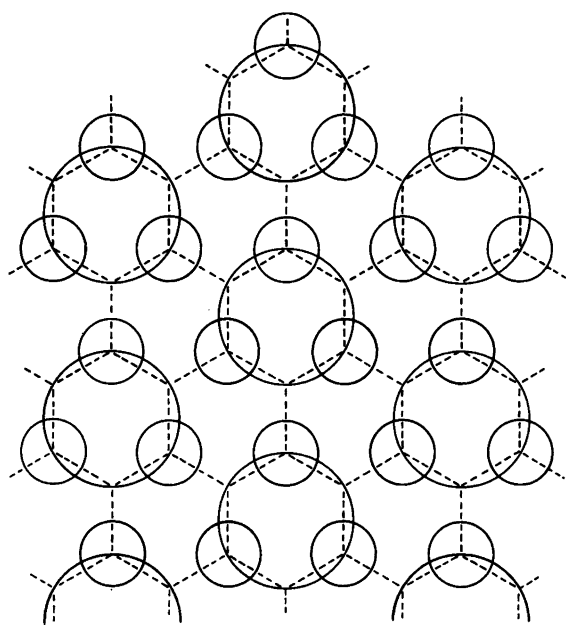*Fig. 3.* HMTA loading (molecules per Zr) of intercalates obtained at different HMTA concentrations.

Fig. 4. Schematic arrangement of HMTA molecules (large circles) in the semicavities of an α-layer corresponding to a loading of 0.33 molecules per Zr atom. Small circles represent the hydroxyls; dashed lines are the projection into the hydroxyl plane of the underlying P–O–Zr bonds.

Comparison of ZPFORM and HMTA intercalates. ZPFORM and the intercalates of zirconium phosphate with HMTA exhibit some common characteristics: the same interlayer distance, similar IR spectra (Fig. 1) and similar thermal behaviour (Fig. 2). Specifically, around 200 °C, both the thermogravimetric curves show a shoulder, which in the case of ZPFORM was ascribed to the loss of ammonia and methylamine. The presence of volatile bases could therefore be expected in the intercalates too, and the evolution of a basic gas was indeed observed from all of them after treatment with 1 M KOH. The intercalate prepared with 1 M HMTA was then analysed according to the procedure described for ZPFORM. The contents of ammonia and methylamine turned out to be 0.12 and 0.02 molecules per Zr atom, respectively. It was checked experimentally that HMTA is stable in neutral aqueous solutions, at least

for the time taken for the preparation of the intercalates. Thus, the monohydrogen phosphate acidity is to some extent responsible for the formation of ammonia and methylamine. Decomposition of HMTA could also be expected in the solid phase. On the other hand, if decomposition took place in the solid, it should have occurred to a large extent just after intercalation or during drying, since the composition of both ZPFORM and intercalates does not change appreciably over 2 months at least.

Conclusion

The reaction of concentrated aqueous HCHO with the diammonium form of α-zirconium phosphate leads to the formation of a compound containing HMTA, methylamine and ammonia. Similar compounds can also be obtained by direct intercalation of HMTA from aqueous solutions.

The presence of ammonia and methylamine in the compounds prepared by intercalation indicates that α-zirconium phosphate is sufficiently acidic to decompose HMTA. Further investigation is necessary to determine to which extent the methylamine contained in ZPFORM comes from the reaction of HCHO and NH_4^+ or from HMTA decomposition. In this connection it might be useful to study the composition of the formaldehyde solution after the reaction with the diammonium form of α-zirconium phosphate.

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