Intercalation from the liquid phase of *n*-alkylamines (*n* = 1–6) and cyclic amines in α-hafnium phosphate

Marta Suárez, M. Luz Rodríguez, Ricardo Llavona, Luisa M. Barcina, Ana Vega and Julio Rodríguez*

Departamento de Química Orgánica e Inorgánica, Facultad de Química, Universidad de Oviedo, 33071 Oviedo, Spain

The intercalation behaviour from the liquid phase of *n*-alkylamines (*n* = 1–6) and the cyclic amines aniline, benzylamine, cyclohexylamine, piperidine and pyridine in α-hafnium phosphate $Hf(HPO_4)_2 \cdot H_2O$ has been studied. The composition of the intercalation compounds was determined and the arrangement of the amines in the interlayer region as mono-(pyridine) or bi-molecular films (the remaining amines) is discussed from data obtained from X-ray diffraction, IR spectroscopy and chemical and thermal analysis.

α-Hafnium hydrogenphosphate monohydrate $Hf(HPO_4)_2 \cdot H_2O$ (α-HfP) is a layered compound which crystallizes in the monoclinic symmetry with cell constants $a = 901.42(1)$, $b = 525.66(5)$, $c = 1547.68(2)$ pm, $\beta = 101.66°$ and space group $P2_1/c$.[1] The layers consist of metal atoms lying slightly above and below the mean plane and bridged by phosphate groups from above and below. The water molecule sits inside the cavity near its center forming a hydrogen-bonding network with the phosphate groups as illustrated in Fig. 1.[2] The interlayer distance is 760 pm and the thickness of the layer calculated as the shorter distance between the baricenter of the oxygen of P–OH groups present in the opposite sides of one layer is 630 pm. The free area associated with each P–OH group is 23.7×10^4 pm². This compound should exhibit ion-exchange and intercalation properties very similar to those of α-ZrP since they are isomorphous[3] and the replacement of the tetravalent metal atom does not appreciably modify the acid strength of the phosphate group. Both compounds can readily intercalate basic organic molecules in addition to exchanging ions.[4]

The chemistry of metal(IV) phosphates with an α-type layered structure has grown considerably and a large number of compounds with a variety of organic groups has been prepared.[5–8] Extensive information has been compiled in recent reviews and books.[9–13]

Interest in the intercalation reactions of α-zirconium phosphate and in the preparation of intercalation compounds with particular properties, such as proton conductivity and catalysis, has led to the preparation of several intercalation compounds with alkylamines, aromatic and heterocyclic bases.[12] Nevertheless, α-HfP has scarcely been investigated. Only ion exchange toward Li[14] and K[15] and intercalation from the vapour phase of some alkylamines[16] has been previously reported.

This paper describes the intercalation behaviour from the liquid phase of *n*-alkylamines (methyl, ethyl, propyl, butyl, pentyl and hexyl) and cyclic amines (aniline, benzylamine, cyclohexylamine, piperidine and pyridine) in α-HfP. X-Ray diffraction, IR spectroscopy and thermal and elemental analysis of the intercalated species allow their composition and the possible arrangement of the amines in the interlayer region to be discussed.

Experimental

Preparations

Crystalline α-HfP was prepared by refluxing newly formed amorphous hafnium phosphate in 12 mol dm⁻³ H_3PO_4 at the boiling point for more than 210 h.[15] The gel was obtained by precipitation of a solution of $HfCl_4$ in aqueous HCl with dilute
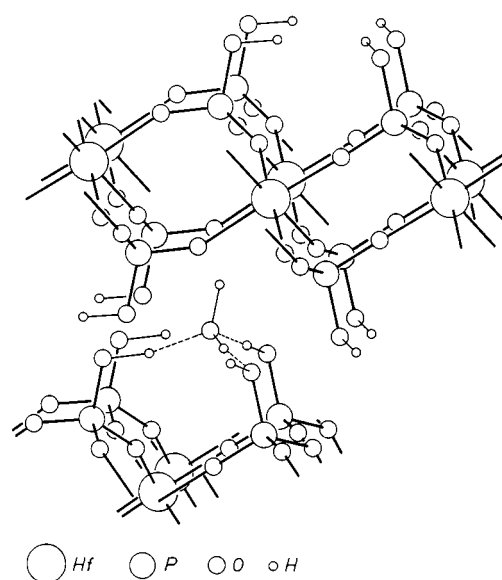

Fig. 1 Cavities in the structure of α-$Hf(HPO_4)_2 \cdot H_2O$

H_3PO_4. The solid was washed with deionized water until pH 3.5, dried at 50 °C and ground to a particle size of less than 0.03 mm. The totally substituted ammonium phase of α-HfP was obtained by equilibrating α-HfP for 48 h with a mixture of NH_3 (aq) (0.1 mol dm⁻³) and NH_4Cl (aq) (0.1 mol dm⁻³) in a ratio of 250 cm³ : 1 g. The resulting crystallites were identified by means of X-ray diffractometry, IR spectroscopy and chemical and thermal analysis (TG).

Intercalation procedure

The compound α-HfP (200 mg) was placed in contact with a portion (20 cm³) of the pure amine $C_nH_{2n+1}NH_2$ (*n* = 1–6) and the five mentioned cyclic amines and shaken for 48 h at 25 °C following the batch method. After equilibration, the solids were separated by centrifugation, dried in air at 50 °C and stored over a solution of 50% H_2SO_4. The solid phase was analyzed by means of X-ray power diffraction, IR spectroscopy and chemical and thermal analysis.

Analytical procedures

Quantitative analysis of hafnium was performed gravimetrically.[17] Microanalytical data (C, H, N) were obtained with a Perkin-Elmer, model 2400 elemental analyzer. The TG curves were taken with a Mettler TA 4000 (TG 50) thermoanalyzer at a

Table 1 Microanalytical data (C and N) and experimental weight loss at 800 °C for the intercalated compounds with linear amines and those calculated (in parentheses) from the formulae

Compound	Analysis (%)		Weight loss (%)
	C	N	
α-Hf(HPO$_4$)$_2$·3CH$_3$NH$_2$·H$_2$O	7.60	8.70	26.95
	(7.48)	(8.72)	(26.79)
α-Hf(HPO$_4$)$_2$·2C$_2$H$_5$NH$_2$·H$_2$O	10.10	5.81	26.45
	(10.03)	(5.85)	(26.33)
α-Hf(HPO$_4$)$_2$·2C$_3$H$_7$NH$_2$·H$_2$O	14.31	5.56	30.52
	(14.22)	(5.53)	(30.40)
α-Hf(HPO$_4$)$_2$·2C$_4$H$_9$NH$_2$·H$_2$O	17.84	5.32	34.16
	(17.96)	(5.24)	(34.05)
α-Hf(HPO$_4$)$_2$·2C$_5$H$_{11}$NH$_2$·H$_2$O	21.21	5.06	37.50
	(21.33)	(4.98)	(37.33)
α-Hf(HPO$_4$)$_2$·2C$_6$H$_{13}$NH$_2$·H$_2$O	24.27	4.75	40.35
	(24.39)	(4.74)	(40.30)

Table 2 Interlayer distances and inclination angles of linear amine–α-HfP intercalates

Amine	d/Å	α/°
Ethyl	13.5	56.8
Propyl	17.0	90.0
Butyl	18.6	67.0
Pentyl	21.0	67.7
Hexyl	23.2	66.3
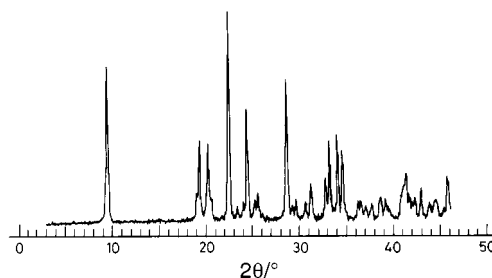
Fig. 3 X-Ray diffraction pattern of Hf(NH$_4$)$_2$(PO$_4$)$_2$·H$_2$O
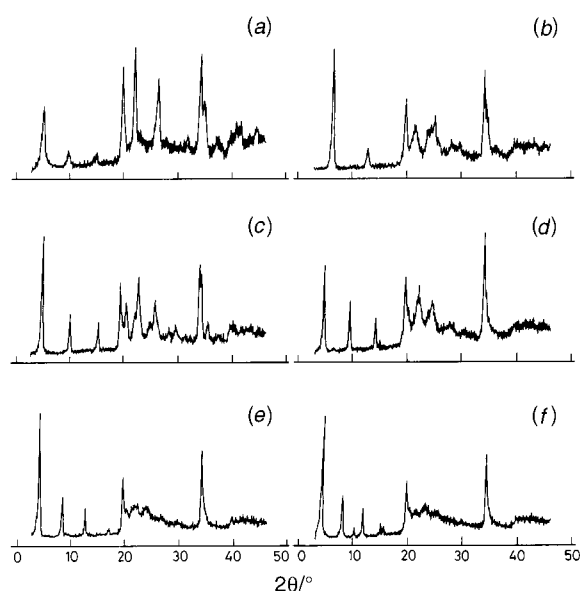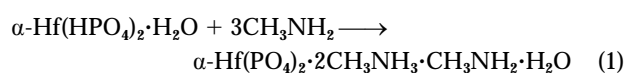

Fig. 2 X-Ray diffraction patterns of the *n*-alkylamine intercalates: (*a*) methylamine, (*b*) ethylamine, (*c*) propylamine, (*d*) butylamine, (*e*) pentylamine and (*f*) hexylamine
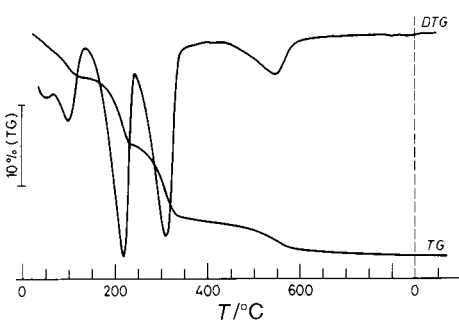
Fig. 4 The TG and DTG of the ethylamine intercalate of α-HfP

heating rate of 5 °C min^{-1} in an atmosphere of nitrogen. X-Ray diffraction patterns were recorded at room temperature on a computer-controlled Philips PW 1729/1720 diffractometer with Cu-Kα radiation ($\lambda = 1.5418$ Å).

Results and Discussion

Alkylamine intercalation

Elemental analysis and the total weight loss at 800 °C enabled the composition of the intercalates to be determined (Table 1). There is a good agreement between the theoretical and experimental values. All the crystal sites available for intercalation are occupied and phases of composition α-HfP·2RNH$_2$·H$_2$O are formed (except in the methylamine case), consistent with a bilayered disposition of the amine molecules between the α-HfP layers. When the intercalated amine is methylamine the intercalation process may be represented by equation (1).

$$\alpha\text{-Hf(HPO}_4)_2\cdot\text{H}_2\text{O} + 3\text{CH}_3\text{NH}_2 \longrightarrow$$
$$\alpha\text{-Hf(PO}_4)_2\cdot2\text{CH}_3\text{NH}_3\cdot\text{CH}_3\text{NH}_2\cdot\text{H}_2\text{O} \quad (1)$$

X-Ray patterns of the intercalated solids (Fig. 2) show that the compounds are crystalline and maintain the lamellar structure. Their interlayer distances are always higher than that of the α-HfP (7.6 Å) (Table 2).

The fully saturated ammonium phase of α-HfP was obtained in order to determine its interlayer distance. The process occurs in a single stage and leads to the formation of the phase Hf(NH$_4$)$_2$(PO$_4$)$_2$·H$_2$O with an interlayer distance of 9.25 Å (Fig. 3). Taking into account this value and that the increment of the alkyl-chain length is estimated as 1.27 Å for each additional carbon atom,[5] the inclination angle of the intercalated molecules with respect to the layer plane can easily be determined: $\sin^{-1}(d_{002} - 9.25/2\cdot n_c\cdot1.27)$. The results are shown in Table 2.

Thermal analysis (TG) was performed for the intercalated compounds from room temperature to 900 °C. The curves show comparable shapes. At least four well defined steps of weight loss can be observed except in the methylamine case. The first includes surface and crystal water. Loss of amine occurs in two equal steps, one for each mol of amine, in the range ≈175–350 °C. At higher temperatures (≈600 °C) the transformation of hydrogenphosphate groups into pyrophosphate takes place. As an example, Fig. 4 shows the TG and DTG of the ethylamine intercalate.

In the methylamine case the first loss takes place at <100 °C and is due to the crystallization water. The amine is lost in three steps between 150 and 400 °C and the loss of structural water occurs at ≈600 °C. The results of thermal analysis concur in all cases with the formula proposed from elemental analysis.

Infrared spectra of the intercalation compounds are very similar and the amine protonation is reflected by the presence of a band at 1560 cm^{-1}. The band at 1250 cm^{-1} assigned to the out-of-plane deformation of the P–O–H group and diagnostic of the presence of a monohydrogenphosphate group was never detected, indicating that the protonation of the amines is total.

The bilayered arrangement can be explained since there is just room for one alkyl chain in the upright position for every P–OH group (the cross-sectional area of a *trans-trans* alkyl

Table 3 Microanalytical data (C and N) and experimental weight loss at 800 °C for the intercalated compounds with cyclic amines and those calculated (in parentheses) from the formulae

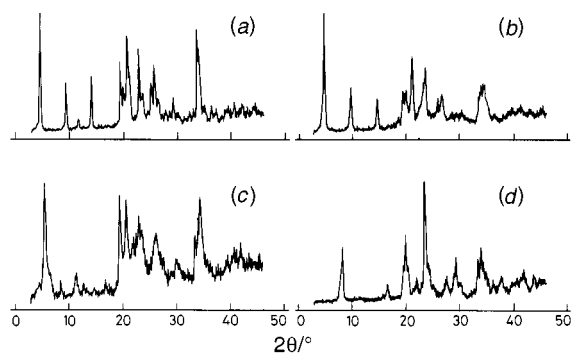| Compound	Analysis (%)		Weight loss (%)
	C	N	
α-Hf(HPO$_4$)$_2$·2C$_7$H$_7$NH$_2$·H$_2$O	28.21	4.59	41.62
	(27.88)	(4.64)	(41.49)
α-Hf(HPO$_4$)$_2$·2C$_6$H$_{11}$NH$_2$·H$_2$O	23.65	4.62	38.91
	(23.82)	(4.63)	(38.71)
α-Hf(HPO$_4$)$_2$·2C$_5$H$_{11}$N·H$_2$O	21.73	4.97	37.01
	(21.48)	(5.01)	(36.88)
α-Hf(HPO$_4$)$_2$·C$_5$H$_5$N·H$_2$O	12.77	3.05	24.75
	(12.83)	(2.99)	(24.60)

Fig. 5 X-Ray diffraction patterns of cyclic amine intercalates: (*a*) benzylamine, (*b*) cyclohexylamine, (*c*) piperidine and (*d*) pyridine

chain, 18.6×10^4 pm^2, is comparable to the free area surrounding each phosphate group, 23.7×10^4 pm^2), intercalated amines cannot interpenetrate the film already present and an ordered bilayer is obtained.[18]

Cyclic amines

Except for aniline, X-ray diffraction patterns of the cyclic amines–α-HfP intercalates (Fig. 5) show the formation of pure phases (the peak corresponding to α-HfP is never detected), the interlayer distances being: 18.7 (benzylamine), 15.4 (piperidine), 18.0 (cyclohexylamine) and 11.1 Å (pyridine). When the intercalated amine is aniline a reflection at 18.2 Å appears but the peak corresponding to α-HfP remains with a marked intensity.

Table 3 shows the corresponding formula determined from elemental analysis. In the aniline case the stoichiometry was estimated approximately also from the relative intensity of the reflection corresponding to the interlayer distance, giving the composition $0.25[\text{Hf(HPO}_4)_2\cdot2\text{C}_6\text{H}_5\text{NH}_2\cdot\text{H}_2\text{O}]\cdot0.75\alpha$-HfP from the values of the total weight loss (18.96%) and elemental analysis (C, 8.27; N, 1.61%).

Thermal analysis shows the loss of crystallization water at <100 °C, the amine is desorbed in one to four steps in the range 150–350 °C and the condensation water is lost between 550 and 600 °C. The TG and DTG curves for intercalated pyridine can be seen in Fig. 6.

The IR spectra presents the characteristic bands of the protonated amines. In the aniline case, despite the fact that only 25% intercalation takes place, an absorption at 2927 cm^{-1} and shoulder at 2870 cm^{-1} can be observed, characteristic of the stretching vibrations ν_{asym} and ν_{sym}, respectively of the NH$_3^+$ group, and a band at 1250 cm^{-1} corresponding to P–O–H is clearly observed, corresponding to partial amine saturation.
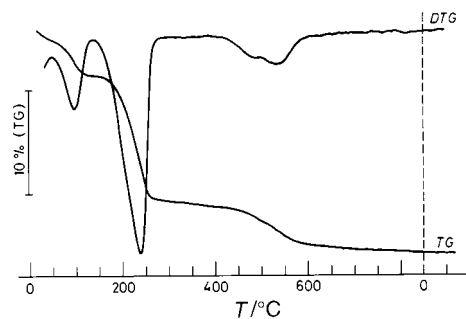

Fig. 6 The TG and DTG of the pyridine–α-HfP intercalate

This band disappears for the rest of the amines indicating that protonation and saturation are complete.

These facts are in agreement with the behaviour reported previously[12] for intercalates of this type: when the guest molecule contains a NH$_2$ group (aniline, benzylamine, cyclohexylamine, piperidine) which upon protonation gives rise to a sp^3-hybridized NH$_3^+$ group, giving a good fit to the hexagonal arrangement of the P–OH on the layer, the intercalation compound contains 2 mol of amine per mol of Hf and the guests are arranged in a bilayered fashion, while molecules containing a sp^2-hybridized N (pyridine) give rise to compounds containing 1 mol of amine per mol of Hf.

References

1 Y. Nakai, K. Imai, T. Kawashima, K. Ohsmi, F. Irumi and Y. Tomita, *Anal. Sci.*, 1990, **6**, 689.
2 M. A. Salvadó, P. Pertierra, S. García-Granda, J. R. García, J. Rodríguez and M. T. Fernandez-Díaz, *Acta Crystallogr., Sect. B*, 1996, **52**, 896.
3 J. M. Troup and A. Clearfield, *Inorg. Chem.*, 1977, **16**, 3311.
4 A. Clearfield, *Comments Inorg. Chem.*, 1990, **10**, 89.
5 A. Clearfield, *Inorganic Ion Exchange Materials*, ed. A. Clearfield, CRC Press, Boca Raton, FL, 1982, vol. 1, pp. 2–74.
6 G. Alberti and U. Costantino, *Intercalation Chemistry*, eds. M. S. Whittingham and A. J. Jacobson, Academic Press, New York, 1982, pp. 147–180.
7 A. Espina, J. B. Parra, J. R. García, J. A. Pajares and J. Rodríguez, *J. Mater. Chem. Phys.*, 1993, **35**, 250.
8 F. Menéndez, A. Espina, C. Trobajo, J. R. García and J. Rodríguez, *J. Incl. Phenom. Mol. Recog. Chem.*, 1993, **15**, 215.
9 G. Alberti, C. Dionigi, S. Murcia-Mascarós and R. Vivani, *Crystallography of Supramolecular Compounds*, ed. G. Tsoucaris, Kluwer, Dordrecht, 1996, pp. 143–157.
10 G. Alberti and U. Costantino, *Inclusion Compounds*, eds. J. L. Atwood, J. E. D. Davies and D. D. MacNicol, Oxford University Press, London, 1991, p. 5.
11 A. Clearfield, *Progress in Intercalation Research*, eds. W. Muller-Warmuty and R. Schollhorn, Kluwer, Dordrecht, 1994, pp. 223–271.
12 A. Clearfield and U. Costantino, *Comprehensive Supramolecular Chemistry*, eds. G. Alberti and T. Bein, Pergamon, New York, 1996, vol. 7, p. 107.
13 J. R. García, R. Llavona, M. Suárez and J. Rodríguez, *J. Trends. Inorg. Chem.*, 1993, **3**, 209.
14 I. Tomita, K. Magani, H. Watanabe, K. Suzuki and T. Nakamura, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 3183.
15 I. Tomita, M. Banju, K. Noguchi and T. Nakamura, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 3281.
16 M. L. Rodríguez, M. Suárez, J. R. García and J. Rodríguez, *Solid State Ionics*, 1993, **63**, 488.
17 M. Kolthoff, E. B. Sandell, E. J. Meehan and S. Bruckenstein, *Quantitative Chemical Analysis*, Nigar, Buenos Aires, 1972.
18 U. Costantino, *Inorganic Ion Exchange Materials*, ed. A. Clearfield, CRC Press, Boca Raton, FL, 1982, vol. 3, pp. 111–132.