

Synthesis, crystal structure and intercalation behaviour of hafnium phosphate dihydrogenphosphate dihydrate

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A highly crystalline compound $\text{Hf}(\text{PO}_4)(\text{H}_2\text{PO}_4)\cdot 2\text{H}_2\text{O}$ (γ -HfP) has been prepared *via* the partially substituted γ -HfP sodium phase, by the reflux method. Its crystalline structure was solved by X-ray powder diffractometry: monoclinic, space group $P2_1$, $a = 5.3499(3)$, $b = 6.5949(4)$, $c = 12.3939(8)$ Å, $\beta = 98.594(5)^\circ$ and $Z = 2$. The final agreement factors are: $R_{\text{wp}} = 0.054$, $R_{\text{exp}} = 0.031$ and $R_f = 0.033$. The compound is isostructural with γ -ZrP and has a layered structure built from PO_4 tetrahedra and HfO_6 octahedra stacked along the [001] direction. Its intercalation behaviour with *n*-alkylamines ($n = 1-6$) and cyclic amines (aniline, benzylamine, cyclohexylamine, piperidine and pyridine) was studied. The intercalation solids obtained present expanded interlayer distances and a general composition $\text{Hf}(\text{PO}_4)(\text{H}_2\text{PO}_4)\cdot x\text{amine}\cdot \text{H}_2\text{O}$ where x varies from 0.8 to 2.

Many layered phosphates of tetravalent metals have been synthesized and characterized. At present, two different structure types exist referred to as α and γ , both forms containing two phosphorus atoms per one atom of Group IV element. The difference between them is that α form has only one type of functional group HPO_4 and their formula can be represented as $\text{M}(\text{HPO}_4)_2\cdot \text{H}_2\text{O}$ (α -MP)¹ whereas in the corresponding γ phases half of the phosphorus atoms exist in the form of H_2PO_4 and the rest in the form of PO_4 groups, hence the formula is $\text{M}(\text{PO}_4)(\text{H}_2\text{PO}_4)\cdot 2\text{H}_2\text{O}$ (γ -MP).^{2,3}

These layered phosphates have received considerable attention in the last decades due to their properties: high thermal and chemical stability, resistance to oxidation, selectivity to certain ions, *etc.*, which allows their use as ion exchangers and adsorbents, molecular sieves, catalysts, ion and proton conductors and convenient matrices for chemical modification.⁴⁻⁷

A large number of phases can be obtained by partial or total exchange of the protons of the α or γ layers with other cations as well as by intercalation of polar molecules in the interlayer region.⁸⁻¹¹ The intercalation results in modification of the interlayer space giving rise to compounds which constitute a rich family of new materials with finely regulated porous structure adequate to be used as molecular sieves and precursors in pillaring reactions owing to its stability in aqueous medium, suitable interlayer distance and moderate affinity of the intercalated species toward the host active centers. Extensive information on the chemistry of Group IV metal phosphates with α - and γ -type structure has been compiled in recent reviews and books.¹²⁻¹⁴

While there are phosphates of the α variety for several metals (Ti, Zr, Hf, Ge, Sn and Pb) the structures and properties of which have been widely studied,¹⁵⁻¹⁷ only two γ -type polyvalent metal phosphates are known and studied in detail: γ -ZrP and -TiP.^{18,19} Their crystalline structures were solved by a powder diffraction method.^{17,20,21}

The structure of the α variety of hafnium phosphate was also determined²² and some properties of ion exchange and intercalation have been studied.²³⁻²⁵ Recently the location of the water molecules in the lattice has also been published.²⁶ The γ variety of hafnium phosphate was unknown.

In this paper the synthesis, crystal structure and intercalation behaviour of γ -HfP are reported and discussed.

Experimental

Synthesis

Some attempts to prepare γ -HfP following the method used by Alberti *et al.*²⁷ in the preparation of γ -TiP and several experiments carried out hydrothermally with different concentrations (from 12 to 17 M H_3PO_4), temperatures (from 120 to 200 °C) and reaction times (from 6 to 24 h) were not successful and the α variety which is thermodynamically the more stable phase was always obtained.

The compound γ -HfP was made following the reflux method used by Clearfield and Kalnins²⁸ for γ -ZrP: sodium dihydrogenphosphate monohydrate (81.4 g) was mixed with 2 M phosphoric acid (35.2 cm³) (≈ 7 M in $\text{NaH}_2\text{PO}_4\cdot \text{H}_2\text{O}$). This mixture was heated to boiling with stirring and then a 1 M $\text{HfOCl}_2\cdot 18\text{H}_2\text{O}$ (twice recrystallized from HCl) aqueous solution (30 cm³) was added dropwise. Boiling under reflux was continued for 3 weeks. The solid was separated by centrifugation and washed with 4 M HCl (until Na^+ ions were eliminated), 0.2 M H_3PO_4 (until free of chlorides) and deionized water (until pH 4) and dried in air.

Analytical procedures

The phosphorus and hafnium concentrations in the solid were determined by dissolving a weighted amount of γ -HfP in HF (aq) and by using a SpectraSpec DCP-AEC spectrometer. X-Ray powder diffraction patterns were obtained on a Philips model PW 1729/1720 diffractometer using $\text{Cu-K}\alpha$ radiation. Thermal analysis (TG) was performed by a Mettler TA4000 (TG 50) thermoanalyzer at a heating rate of 5 °C min⁻¹ in an atmosphere of nitrogen. Elemental analyses (C, N, H) of the intercalated solids were obtained with a Perkin-Elmer model 2400 elemental analyzer. Phosphorus in the equilibrium solution was analyzed spectrophotometrically by the molybdate method using a Spectronic GenesysTM 5.

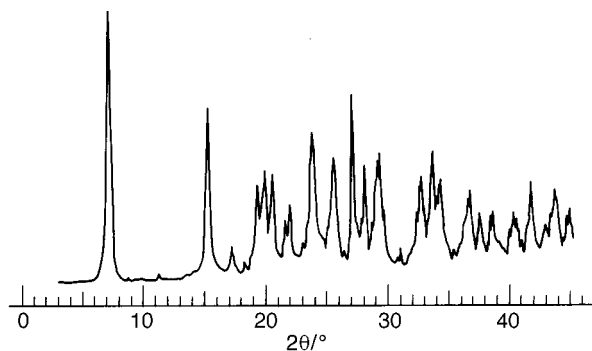
Structure solution

A sample of $\text{Hf}(\text{PO}_4)(\text{H}_2\text{PO}_4)\cdot 2\text{H}_2\text{O}$ (γ -HfP) was finely ground using an agate mortar and side-loaded on a flat sample holder in order to minimize the preferred orientation effects. Step-

Table 1 Crystal data for γ phases (space group $P2_1$)

| | γ -HfP | γ -ZrP ^a | γ -TiP ^b |
|------------------|---------------|----------------------------|----------------------------|
| $a/\text{\AA}$ | 5.3499(3) | 5.3825(2) | 5.186(1) |
| $b/\text{\AA}$ | 6.5949(4) | 6.6337(1) | 6.3505(8) |
| $c/\text{\AA}$ | 12.3939(8) | 12.4102(4) | 11.865(3) |
| β° | 98.594(5) | 98.687(2) | 102.52(3) |
| $U/\text{\AA}^3$ | 432.37 | 438.03 | 381.47 |

^a Data taken from ref. 20. ^b Data taken from ref. 21.

**Fig. 1** The X-ray pattern of γ -HfP

scanned X-ray powder data were collected by means of a Philips computer-automated diffractometer operating at 40 kV and 30 mA with a copper target and graphite-monochromated radiation. Data were collected in the range $3 < 2\theta < 110^\circ$ with a step size of 0.02° and a count time of 10 s per step.

The position of fifteen low-angle unambiguously characterized reflections were extracted from the data and indexed by trial-and-error methods implemented in the program TREOR²⁹ with a monoclinic cell and figures of merit $M_{15} = 36$ ³⁰ and $F_{15} = 26(0.0102, 57)$.³¹ Crystal data of γ -HfP are compared with those of other γ -phosphates in Table 1.

Owing to the similarities of the crystal data, the structural parameters of γ -ZrP²⁰ were used as the initial values for the Rietveld refinement using the program FULLPROF.³² After the initial refinement of the scale, background, profile and cell parameters, the atomic positions were refined using soft constraints only for the P–O distances [1.53(1) Å]. All the atoms were refined with a common isotropic thermal parameter. No corrections were made for anomalous dispersion or absorption. A correction for preferred orientation along [001] was included.³³ The [001] reflection appears isolated at 7.2° showing a strong asymmetry and being affected by the background fall off at low angles. Hence the zone below 12° was excluded for the refinement.

CCDC reference number 186/770.

Intercalation procedures

The γ -HfP was equilibrated during 6 d with pure *n*-alkylamines ($n = 1$ –6) and cyclic amines (aniline, benzylamine, cyclohexylamine, piperidine and pyridine) at 25°C following the batch method. The solid was present in the solution in an approximate ratio of 1 g : 100 cm³. The solids were separated by centrifugation, dried at 50°C for 24 h and characterized by X-ray diffraction and thermal and elemental analysis.

Results and Discussion

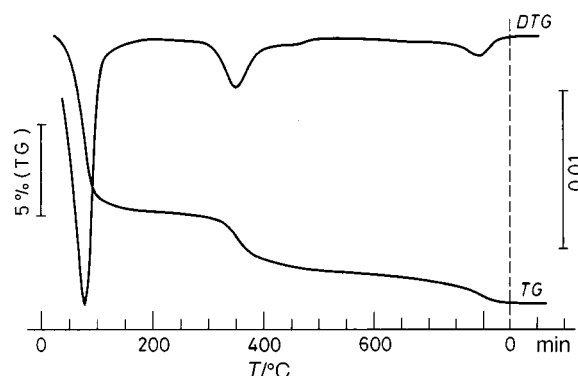
A well crystallized product was obtained by the described procedure. Elemental analysis of the solid indicated 15.32% P and 43.62% Hf in good agreement with the theoretical values (15.24% P and 43.91% Hf) deduced from the formula $\text{Hf}(\text{PO}_4)(\text{H}_2\text{PO}_4)\cdot 2\text{H}_2\text{O}$.

The X-ray diffraction pattern (Fig. 1) shows that the new γ -HfP phase presents an interlayer distance of 12.1 Å similar to

Table 2 Crystallographic data for $\text{Hf}(\text{PO}_4)(\text{H}_2\text{PO}_4)\cdot 2\text{H}_2\text{O}$

| | |
|------------------------------|---------------------------------------|
| Empirical formula | $\text{H}_6\text{HfO}_{10}\text{P}_2$ |
| M | 406.48 |
| Crystal system | Monoclinic |
| Space group | $P2_1$ |
| $D/\text{g cm}^{-3}$ | 3.12 |
| Z | 2 |
| No. contributing reflections | 596 ($K\alpha$ doublets) |
| No. geometric constraints | 8 |
| No. parameters | 54 |
| R_{wp} | 0.054 |
| R_{exp} | 0.031 |
| R_F | 0.033 |
| χ^2 | 3.11 |

$R_{\text{wp}} = [\sum_i w_i (y_{i,\text{obs}} - y_{i,\text{calc}})^2 / \sum_i w_i (y_{i,\text{obs}})^2]^{1/2}$, $R_F = \sum_k [(I_{k,\text{obs}})^{1/2} - (I_{k,\text{calc}})^{1/2}] / \sum_k (I_{k,\text{obs}})^{1/2}$, $R_{\text{exp}} = R_{\text{wp}} / (\chi^2)^{1/2}$, $\chi^2 = \sum_i [w_i (y_{i,\text{obs}} - y_{i,\text{calc}})^2 / (N_{\text{obs}} - N_{\text{var}})]$, where N_{obs} , N_{var} = number of observations and variables.

**Fig. 2** The TG curve of γ -HfP

that of the other γ -phosphates of tetravalent metals (γ -ZrP 12.2 Å and γ -TiP 11.6 Å).

The TG curve (Fig. 2) clearly shows three mass-loss steps. The first step takes place between room temperature and 100°C (8.92% weight loss) and corresponds to the loss of crystallization water molecules (8.86% theoretical weight loss). The two following steps occur at 350 and 750°C (4.34% weight loss) and were a result of the condensation of the hydrogenphosphate groups to α - HfP_2O_7 (4.43% theoretical weight loss). The process occurs in two steps due to the formation of an intermediate phosphate/pyrophosphate phase in a similar way as in the γ -TiP case, explaining the high temperature at which the condensation process takes place.³⁴

Thermal treatment of the γ -HfP phase leads to the formation of three phases: β -HfP ($d = 9.3$ Å, heating temperature 200°C), a hafnium phosphate pyrophosphate phase with lamellar structure ($d = 8.2$ Å, 450°C) and hafnium pyrophosphate (800°C). This is in good agreement with the results deduced from the TG curve.

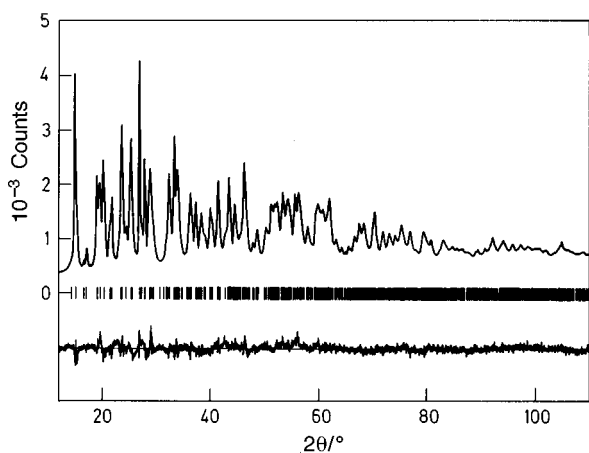
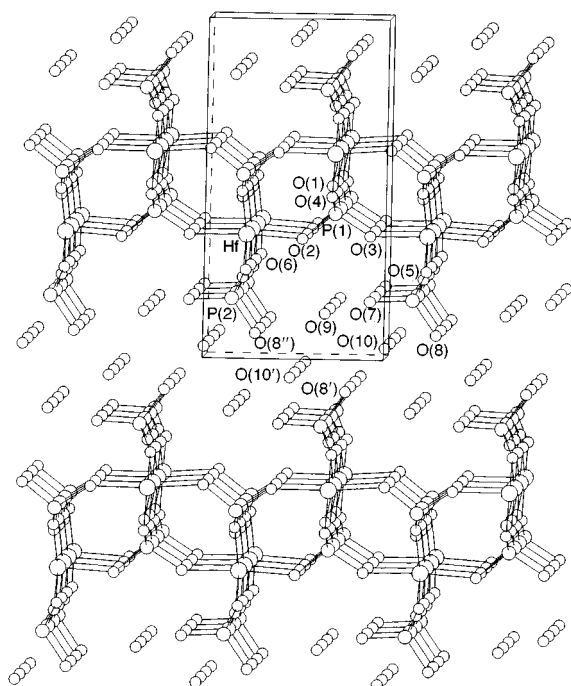
A summary of crystallographic data is given in Table 2, final positional parameters in Table 3, and bond lengths and angles in Table 4. The final Rietveld refinement plot is shown in Fig. 3. The structure is shown in Fig. 4.

Initially a pseudo-Voigt profile-shape function was used in the refinement; although the refinement progressed well the peak shape was not correctly described. A close examination of peak width showed that an anisotropic broadening along the c axis was present. In order to account for this effect a Thompson–Cox–Hastings pseudo-Voigt function³⁵ was used. A Lorentzian broadening along [001] was chosen. This led to an improvement of the reliability factors. The quality of the refinement is clearly limited in this case by the presence of a severe peak broadening due to strain/size effects.

The unit cell of γ -HfP is similar to that of γ -ZrP, being slightly contracted in the three directions. Accordingly the inter-

Table 3 Atomic positional parameters for $\text{Hf}(\text{PO}_4)(\text{H}_2\text{PO}_4)\cdot 2\text{H}_2\text{O}$

| Atom | <i>x</i> | <i>y</i> | <i>z</i> |
|-------|-----------|----------|-----------|
| Hf | 0.8026(4) | 0.25 | 0.1258(2) |
| P(1) | 0.244(1) | 0.240(1) | 0.9395(5) |
| P(2) | 0.370(1) | 0.187(1) | 0.3089(5) |
| O(1) | 0.054(3) | 0.216(5) | 0.018(1) |
| O(2) | 0.201(9) | 0.059(4) | 0.863(3) |
| O(3) | 0.21(1) | 0.434(3) | 0.873(3) |
| O(4) | 0.520(2) | 0.228(7) | 0.993(1) |
| O(5) | 0.089(2) | 0.225(7) | 0.258(1) |
| O(6) | 0.543(4) | 0.255(7) | 0.227(1) |
| O(7) | 0.368(5) | 0.952(1) | 0.315(2) |
| O(8) | 0.398(4) | 0.318(3) | 0.4127(9) |
| O(9) | 0.185(3) | 0.190(3) | 0.641(1) |
| O(10) | 0.123(4) | 0.524(3) | 0.539(2) |

**Fig. 3** Rietveld refinement pattern of $\gamma\text{-HfP}$. Points correspond to observed data, the solid line is the calculated profile. Vertical lines below upper curve show the positions of allowed reflections and a difference curve, on the same scale, is plotted at the bottom of the pattern.**Fig. 4** Perspective plot of the crystal structure down the *a* axis. The *c* axis is vertical and the *b* axis horizontal. For clarity atoms are labelled in different asymmetric units than shown in Table 3

layer distance was found to be approximately equal in the two compounds. Since $\gamma\text{-HfP}$ and $\gamma\text{-ZrP}$ are isostructural, $\gamma\text{-HfP}$ has a layered structure built from PO_4 tetrahedra and HfO_6

Table 4 Bond lengths (\AA) and angles ($^\circ$) for $\text{Hf}(\text{PO}_4)(\text{H}_2\text{PO}_4)\cdot 2\text{H}_2\text{O}$

| | | | |
|----------------|----------|----------------|----------|
| Hf–O(1) | 2.04(2) | P(1)–O(2) | 1.52(3) |
| Hf–O(2) | 2.04(3) | P(1)–O(3) | 1.52(3) |
| Hf–O(3) | 2.08(2) | P(1)–O(4) | 1.53(1) |
| Hf–O(4) | 2.06(1) | P(2)–O(5) | 1.56(1) |
| Hf–O(5) | 2.07(1) | P(2)–O(6) | 1.54(2) |
| Hf–O(6) | 2.01(2) | P(2)–O(7) | 1.55(1) |
| P(1)–O(1) | 1.52(2) | P(2)–O(8) | 1.54(2) |
| O(9)···O(8') | 3.32(2) | O(9)···O(7) | 2.93(3) |
| O(9)···O(8'') | 3.45(3) | O(10)···O(7) | 3.07(3) |
| O(9)···O(10) | 2.54(3) | O(10)···O(8) | 3.20(3) |
| O(9)···O(10') | 2.79(3) | O(10)···O(8') | 2.67(3) |
| O(1)–Hf–O(6) | 174.2(6) | O(1)–P(1)–O(4) | 114.1(8) |
| O(1)–Hf–O(5) | 91.3(6) | O(1)–P(1)–O(3) | 113(2) |
| O(1)–Hf–O(4) | 87.1(6) | O(1)–P(1)–O(2) | 106(2) |
| O(1)–Hf–O(3) | 85(1) | O(7)–P(2)–O(8) | 121.5(9) |
| O(1)–Hf–O(2) | 100(1) | O(6)–P(2)–O(8) | 113.0(9) |
| O(2)–Hf–O(6) | 86(2) | O(6)–P(2)–O(7) | 109(1) |
| O(2)–Hf–O(5) | 92(2) | O(5)–P(2)–O(8) | 103(1) |
| O(2)–Hf–O(4) | 96(2) | O(5)–P(2)–O(7) | 100(1) |
| O(2)–Hf–O(3) | 175(1) | O(5)–P(2)–O(6) | 108.7(9) |
| O(3)–Hf–O(6) | 90(2) | Hf–O(1)–P(1) | 168(1) |
| O(3)–Hf–O(5) | 86(2) | Hf–O(2)–P(1) | 138(2) |
| O(3)–Hf–O(4) | 86(1) | Hf–O(3)–P(1) | 147(2) |
| O(4)–Hf–O(6) | 90.3(6) | Hf–O(4)–P(1) | 152.7(8) |
| O(4)–Hf–O(5) | 171.5(5) | Hf–O(5)–P(2) | 152.6(8) |
| O(5)–Hf–O(6) | 90.5(6) | Hf–O(6)–P(2) | 161(1) |
| O(2)–P(1)–O(4) | 106(2) | | |
| O(2)–P(1)–O(3) | 109(1) | | |
| O(3)–P(1)–O(4) | 109(2) | | |

octahedra stacked along the [001] direction. The bond distances between the metal atoms and oxygen (mean 2.05 \AA) are similar to the corresponding distances in $\alpha\text{-HfP}$. The water molecules are hydrogen bonded to each other forming a zigzag chain between layers along the *b* axis. On the other hand, water molecules are connected with the terminal hydroxyl groups. Atom O(9) only has a possible hydrogen contact to O(7); atom O(10) is close to three hydroxyl groups, O(7) [3.07(3) \AA] and O(8) [3.20(3) \AA] in the same layer and symmetry-related O(8') [2.67(3) \AA] in the other layer. By comparison with $\gamma\text{-ZrP}$, in this case O(10) seems to link adjacent layers through hydrogen bonding to the oxygen atoms O(7) and O(8') instead of O(8) and O(8'). However a complete description of the hydrogen-bond network will only be possible when a neutron diffraction study becomes available for these compounds.

The intercalation of *n*-alkylamines (*n* = 1–6) and cyclic amines (aniline, benzylamine, cyclohexylamine, piperidine and pyridine) in $\gamma\text{-HfP}$ was studied in order to confirm its lamellar structure and verify its behaviour as intercalation host. X-Ray patterns of the intercalates show the formation of new phases with interlayer distances higher than that of the starting compound (Table 5) and the total disappearance of the reflections corresponding to $\gamma\text{-HfP}$.

The formula of the intercalates was determined from elemental and thermal analysis. The phosphorus content in the equilibrium solutions showed that hydrolysis is negligible. From the total weight loss deduced from TG curves, the number of water molecules of each intercalate was deduced. The phases obtained have a composition $\text{Hf}(\text{PO}_4)(\text{H}_2\text{PO}_4)\cdot x\text{amine}\cdot \text{H}_2\text{O}$ where *x* varies from 1.4 to 2 for *n*-alkylamines and 0.8 to 1.5 for cyclic amines (Table 5).

Thermal decomposition of the intercalates takes place at least in four steps. At $\approx 100^\circ\text{C}$ the crystallization water is lost. The amine is desorbed in several consecutive steps between 150 and 350°C and condensation of the hydrogenphosphate groups into pyrophosphate occurs at $>400^\circ\text{C}$.

The compound $\gamma\text{-HfP}$ reacts easily with some pure amines giving rise to new pure phases with expanded interlayer distances which, for *n*-alkylamines, increase with the number of C

Table 5 The *d* spacings of γ -hafnium phosphate amine intercalates and their tentative formulae

| Amine | <i>d</i> /Å | Analysis (%) | | Formula |
|------------------|-------------|--------------|------|---|
| | | C | N | |
| Methylamine | 14.2 | 5.06 | 6.03 | Hf(PO ₄)(H ₂ PO ₄)·2CH ₃ N·2H ₂ O |
| Ethylamine | 16.2 | 7.46 | 4.47 | Hf(PO ₄)(H ₂ PO ₄)·1.5C ₂ H ₇ N·2H ₂ O |
| Propylamine | 19.4 | 11.55 | 4.40 | Hf(PO ₄)(H ₂ PO ₄)·1.6C ₃ H ₉ N·2H ₂ O |
| Butylamine | 20.8 | 14.01 | 4.03 | Hf(PO ₄)(H ₂ PO ₄)·1.5C ₄ H ₁₁ N·2H ₂ O |
| Pentylamine | 21.7 | 16.72 | 3.90 | Hf(PO ₄)(H ₂ PO ₄)·1.5C ₅ H ₁₃ N·2H ₂ O |
| Hexylamine | 23.9 | 18.41 | 3.55 | Hf(PO ₄)(H ₂ PO ₄)·1.4C ₆ H ₁₅ N·2H ₂ O |
| Aniline | 19.8 | 14.37 | 2.82 | Hf(PO ₄)(H ₂ PO ₄)·C ₆ H ₇ N·2H ₂ O |
| Benzylamine | 23.2 | 22.20 | 3.71 | Hf(PO ₄)(H ₂ PO ₄)·1.5C ₇ H ₉ N·2H ₂ O |
| Cyclohexyl-amine | 20.8 | 14.21 | 3.76 | Hf(PO ₄)(H ₂ PO ₄)·C ₆ H ₁₃ N·2H ₂ O |
| Piperidine | 18.0 | 12.20 | 2.85 | Hf(PO ₄)(H ₂ PO ₄)·C ₅ H ₁₁ N·2H ₂ O |
| Pyridine | 20.3 | 12.34 | 2.89 | Hf(PO ₄)(H ₂ PO ₄)·C ₅ H ₅ N·2H ₂ O |

atoms of the alkyl chain. The most striking feature of these data is that in none of the cases the amines are able to saturate all the acidic groups of the exchanger, except for methylamine which intercalates 2 mol of amine per mol of γ -HfP. The intercalation levels reached with γ -HfP/amines show up to two molecules amine, unlike in the cases of γ -ZrP and -TiP⁸ where the intercalation of aliphatic amines is usually limited to half of the substitution. This behaviour is attributed to the different intercalation procedure used in our case. The behaviour of γ -HfP as intercalation host makes it an adequate precursor for the insertion of large species into the interlayer space.

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