Calorimetric study of intercalation of *n*-alkyldiamines into α-titanium hydrogenphosphate

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A series of *n*-alkyldiamines of general formula $H_2N(CH_2)_nNH_2$ ($n = 2$–9) has been intercalated into the crystalline lamellar compound α-Ti$(HPO_4)_2 \cdot H_2O$ (TiP) from aqueous solution. The amount intercalated was followed batchwise at 298 ± 1 K and the variation of the original interlayer distance for TiP (756 pm) was followed by X-ray powder diffraction. Linear correlations with good fits were obtained for the interlamellar distance (d) or for the number of moles intercalated (n_{int}) as a function of the number of carbon atoms in the aliphatic chain (n_c): $d = (883.14 \pm 12.76) + (108.51 \pm 2.20)n_c$ and $n_{int} = (5.79 \pm 0.12) - (0.28 \pm 0.02)n_c$. The exothermic enthalpies for the intercalation are related to the monomolecular layer arrangement with a longitudinal axis inclined by 58° to the inorganic sheets. The enthalpies for the overall reaction $2O_3P\!-\!OH(c) + H_2N(CH_2)_nNH_2(c,l) = O_3P\!-\!O^- \ ^+H_3N(CH_2)_nNH_3^+ \ ^-O\!-\!PO_3(c)$; $\Delta_{int}H$, determined by reaction-solution calorimetry at 298.15 ± 0.02 K are correlated with the number of carbons in the aliphatic chain or the interlamellar distance, by the equations $\Delta_{int}H = -(56.16 \pm 0.67) - (2.06 \pm 0.12)n_c$ and $\Delta_{int}H = -(39.41 \pm 1.41) - (1.80 \times 10^{-2} \pm 0.10 \times 10^{-2})d$. The enthalpic value for $n_c = 0$ gave -56.17 ± 0.67 kJ mol^{-1} which corresponds to the intercalation of two moles of ammonium cation.

Layered hydrogenphosphates of metals in oxidation state +4 normally exhibit α-crystalline compounds of the general form α-M$(HPO_4)_2 \cdot H_2O$ (M = Zr, Ti, Hf, Sn, Ge, *etc.*). In the zirconium compound, whose layered structure was first determined, the metal atoms lie in a plane and are bridged by phosphate groups which are located above and below the metal atom plane. Three oxygens of each tetrahedral phosphate are linked to three zirconium atoms and each metal is octahedrally coordinated by six oxygens of six different phosphate groups. The fourth oxygen of each phosphate group is bonded to a proton which is located in the interlayer space.[1,2] This arrangement of the phosphates groups forms zeolitic type cavities each containing a water molecule hydrogen bonded to three of the acid phosphate groups on the same layer. This arrangement permits the diffusion of spherical species with a theoretical size limit of 264 pm.[3] The layers are only weakly held together by dispersion forces. For the corresponding titanium compound, which is isomorphous with the zirconium compound, similar properties can be expected and the proton of the free phosphate group is available for acid–base reactions to intercalate bases into the interlamellar region.

During the intercalation of organic molecules into this kind of layered compound the inorganic host layers interact with the organic guest molecules by increasing the interlamellar separation. The fully intercalated material consists of regularly alternating organic and inorganic layers and both the physical nature and the chemical reactivity of the material can be significantly altered. For example, amine intercalation into zirconium hydrogenphosphate changes its properties when in contact with water. The thin lamellae formed may be reconstituted to form thin films which have potential applications in the field of ion exchange, chromatography, heterogeneous catalysis and as protonic conductors.[4] On the other hand, the same intercalated materials seem to be useful as precursors in pillaring reactions[5,6] because intercalation produces an increase in the interlayer space, favouring the exchange between the intercalated amine and the pillaring agent. Other applications involve the modifications of the host's optical properties, superconducting critical temperature, interlayer magnetic coupling and materials design.[7–9] Some recent and very interesting applications involve the use of these materials to modify electrode surfaces, in the preparation of low-dimensional con-

ducting polymers and to assemble molecular multilayers at solid/liquid interfaces.[10]

The proposed mechanism for amine intercalation is that the basic nitrogen group is first protonated by the free hydrogen of the phosphate group and therefore the maximum amount of intercalated amine should be two moles per unit of metal phosphate. The quantity of amine intercalated also depends on the free area of about 20.0×10^4 pm^2 surrounding each phosphate group, which permits the accommodation of one molecule of amine per phosphate group, for a cross-sectional area of a *trans–trans* alkyl chain evaluated as 18.6×10^4 pm^2.[11]

Among the α-metal(IV) phosphates, zirconium phosphate is the most explored in organic molecule intercalation processes and various features of intercalation of mono-,[12–14] di-[10,15] and aromatic[16,17] amines have been studied. For the analogous titanium phosphate, intercalation of only monoamines has been described.[18,19] The amount of alkylmonoamines intercalated into the titanium compound corresponds to two moles of amine per mole of the inorganic support with an inclination of the alkyl chain of 55°, which is very close to that presented by zirconium phosphate.

Although intercalation is a well established process, the great majority of the publications have focused on the structural aspects of these kinds of compounds. The main objective of this work is to report some calorimetric determinations involving the interaction of α-titanium hydrogenphosphate with *n*-alkyldiamines (C$_2$–C$_9$), in order to contribute to the understanding of the energetics of the intercalation. Thermochemical data related to the intercalation of organic molecules into the cavities of lamellar compounds are sparse in the literature.[18,20] These new intercalated compounds have been characterized through physical and thermal methods, showing that some data correlate with the energetics of intercalation.

Experimental

Materials

All chemicals used were of reagent grade. Demineralized water was used throughout the experiments. Titanium tetrachloride (Riedel), disodium hydrogenphosphate (Anidrol), hydrochloric acid (Merck) and phosphoric acid (Carlo Erba) were used for

preparations The diamines (Aldrich) of the general form $H_2N(CH_2)_nNH_2$ $(n=2-9)$, i e, 1,2-ethylenediamine (en), 1,3-propylenediamine (pda), 1,4-butylenediamine (buda), 1,5-pentamethylenediamine (pmda), 1,6-hexamethylenediamine (hmda), 1,8-octamethylenediamine (omda) and 1,9-nonamethylenediamine (nmda) were used without further purification

Preparations

The amorphous titanium phosphate was prepared by adding a hydrochloric acid solution of titanium tetrachloride to a phosphoric acid solution containing sodium hydrogenphosphate[18] The α-titanium hydrogenphosphate (TiP) was prepared by refluxing the amorphous material with 12 0 mol dm^{-3} H_3PO_4 for 160 h at 433 K[18] The crystalline solid was washed until pH 4 0 and dried to constant mass over P_2O_5, and was analysed as described previously[18]

Intercalation procedure

The intercalation process was followed batchwise in aqueous medium at 298 ± 1 K for diamines $H_2N(CH_2)_nNH_2$ $(n=2-9)$ Samples of TiP were suspended in variable concentrations of diamine in demineralized water in polyethylene flasks with a solid solution proportion of 1 0 g 0 10 dm^3 The system was mechanically stirred for 6 h The time required to reach equilibrium was first established through a series of intercalations involving a constant mass of the lamellar compound with the diamines as a function of time Although approximately 4 h were sufficient to attain equilibrium, 6 h was chosen to ensure maximum intercalation At the end of this time, the solid was separated by centrifuging the suspension, and was dried at 373 K From the titration of the supernatant with standard hydrochloric acid, the amount of the diamine intercalated (n_{int}) was determined by the expression $n_{int}=(n_i-n_s)/m$, where n_i is the initial number of moles of diamine in solution, n_s is the number of moles of diamine in solution in equilibrium with the solid phase and m is the mass of the lamellar compound For each experimental point, the reproducibility was checked by at least one duplicate run

Analytical procedures

The loss of mass determinations were performed on a DuPont model 1090B thermogravimetric instrument coupled with a model 951 thermobalance, with samples varying in mass from 15 0 to 30 0 mg, using a flux of dry nitrogen and a heating rate of $8 2 \times 10^{-2}$ Kα s^{-1} X-Ray powder patterns were obtained with nickel-filtered Cu-Kα radiation on a Shimadzu model XD3A diffractometer and the interlayer spacings of the compounds were calculated from the 002 plane IR spectra were obtained on a Perkin-Elmer FTIR 1600 spectrometer with solid samples ground to obtain a pulverized material The ^{31}P NMR spectra were obtained on an ac 300/P Bruker spectrometer with magic angle spinning, operating at 121 MHz at room temperature and using 85% H_3PO_4 as reference to calibrate the chemical shift scale

Calorimetry

An LKB 8700-1 isoperibolic precision calorimetric system was used for all reaction-solution measurements of the intercalation of diamines into lamellar titanium hydrogenphosphate in aqueous media The thermal effects caused by the entrance of the diamine into the lamellar space were determined by breaking thermostatted thin-glass ampoules containing TiP (ca 50 mg) in 0 10 dm^3 of diamine solutions of variable concentration and the heat produced was recorded During the breaking of the ampoules, the response obtained in the well stirred solution indicated a kinetically favourable system where the baseline was reached rapidly in a few minutes On the other hand, no heat was observed when only TiP samples

were broken into the calorimetric solvent The standard molar enthalpies of intercalation were obtained by breaking at least five ampoules at 298 15 ± 0 02 K The heat of of empty ampoule breaking was found to be negligible[21][22] Details of the operational procedure, calculations and accuracy of the apparatus have been previously described[23] After the thermochemical measurements, the resulting solution was filtered and aliquots of the supernatant were titrated with standard hydrochloric acid solution The isolated solid was dried and submitted to thermogravimetry, IR and X-ray measurements

Results and Discussion

The lamellar TiP compound can intercalate various kinds of polar organic molecules which are accommodated in the interlayer space Before intercalation, an interlamellar distance of 756 pm was obtained by X-ray measurements and are in accord with previous measurements An ion exchange capacity of 7 70 mmol g^{-1} was obtained from the exchange with an aqueous solution of n-butylamine[18] The thermogravimetric curve indicated a 14% total mass loss in two distinct steps The hydrated water was eliminated in the range 313–360 K, which was followed in the range of 490–600 K by the removal of water of condensation due to the interaction of phosphate groups to produce pyrophosphate[18] The IR spectrum showed the presence of characteristic peaks at 3555 and 3010 cm^{-1}, demonstrating the presence of water and the main P—O stretching vibration at 1033 cm^{-1}[18] The ^{31}P NMR CP MAS spectrum showed only a narrow and intense peak at $\delta - 18$ 4, which was attributed to protonated phosphate[24][26]

The number of moles of n-alkyldiamines intercalated is shown in Table 1 These values, which were obtained through a batchwise process, decreased with increasing alkyl chain length of the diamine From the analysis of the intercalated compound, the general formula can be written as $Ti(PO_4)H_{2-x}[H_3N(CH_2)_nNH_3]_xH_{2-x}(O_4P)Ti H_2O$, where x was determined by the titration of the supernatant after intercalation, and can be compared with thermogravimetric measurements Although the number of moles intercalated decreased with increasing chain length, the relationship between the number of moles of diamine and the number of moles of the lamellar compound was always close to unity For example, for pmda and hmda which differ by only one carbon atom, the number of moles intercalated were 4 31 and 4 08 mmol g^{-1} respectively, corresponding to a molar ratio of diamine/intercalated compound of 1 11 and 1 05, respectively

The decrease in the amount of the diamine intercalated with increasing chain length can be correlated with the size of the n-alkyl chain since larger diamines have less freedom to diffuse into the interlayer space to interact easily with the available pendant protons distributed on the inorganic support The smallest molecule, en, contrasts to the longest n-alkyldiamine, nmda, in its degree of intercalation, the values being 1 36 and 0 89 mmol g^{-1}, respectively Moreover, when a diamine is bonded to a phosphate group, this concomitantly renders an adjacent site unavailable for bonding due to the

Table 1 The number of moles of diamine intercalated (n_{int}), interlamellar distance (d), and x values in the formula $Ti(PO_4)_2H_{2\ 2x}[H_3N(CH_2)_nNH_3]_x \cdot H_2O$, where x_{tit} and x_{therm} were obtained by titration and thermogravimetry, respectively

diamine	n_{int}/mmol g^{-1}	d/pm	x_{tit}	x_{therm}
en	5 29	1090	1 36	1 38
pda	5 14	1210	1 32	1 30
buda	4 50	1318	1 16	1 13
pmda	4 31	1424	1 11	1 11
hmda	4 08	1549	1 05	1 04
omda	3 53	1766	0 91	0 89
nmda	3 41	1839	0 88	0 88

fact that it covers this site.[26] This behaviour is reflected directly in the number of moles intercalated, which is lower than the maximum capacity of the available protons as determined by intercalation of monoamines.

The quantity of intercalated organic molecules determined from titration data agreed closely with the thermogravimetric results, as shown in Table 1. The intercalated materials showed two mass losses: one, centred at 340 K, due to loss of water of hydration and the second, between 480 and 700 K, comprising the loss of diamine and water of condensation.

The intercalation process induces an increase in the inter-layer distance to accommodate the diamines in the free space of the cavity. This behaviour can be followed *via* the X-ray data shown in Table 1. The interlamellar distance increased with increasing length of the alkyl chain but also depended in the opposite manner on the degree of intercalation. For example, the end member diamines en $(n=2)$ and nmda $(n=9)$ with degrees of intercalation of 1.36 and 0.88 mmol g^{-1}, showed interlamellar distances of 1090 and 1839 pm, respectively.

Both the numbers of moles intercalated and interlamellar distance correlated linearly with the number of carbons in the aliphatic chain, as illustrated in Fig. 1 and 2 and according to eqn. (1) and (2).

$$n_f = (5.79 \pm 0.12) - (0.28 \pm 0.02)n_c \quad (r = 0.997) \quad (1)$$

$$d = (883.14 \pm 12.76) + (108.51 \pm 2.20)n_c \quad (r = 0.999) \quad (2)$$

From the interlamellar distance correlation shown in Fig. 2, the angular coefficient value enables an estimation of the inclination of the diamine molecule, as well its arrangement in either a mono- or a bi-layer manner. For a sequence of diamines the increment of one additional carbon atom in an all-*trans* alkyl chain length was, as expected, 127 pm. If the
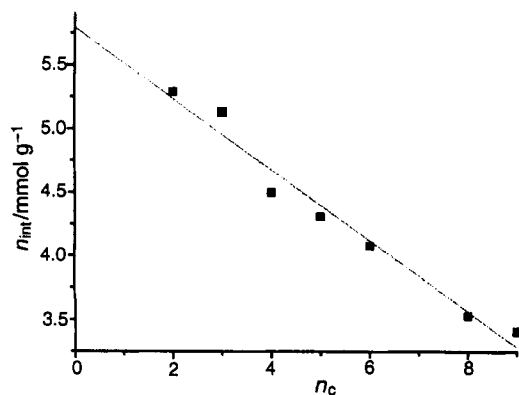
diamines are present as a monomolecular layer of extended molecules, their longitudinal axes are inclined at an angle of arcsin $(108/127) = 58°$ to the plane of the inorganic sheet. This same behaviour was found for zirconium phosphate, where the arrangement of the diamines was in monolayers with an angle of 58°, the same value found here.[11,15]

For an extrapolated diamine with no carbon atom $(n_c = 0)$, the above correlation gives an interlamellar distance of 883 pm, greater than that found for pure TiP, which can be attributed to the intercalation of two NH$_3^+$ species into the lamellar compound. A very similar behaviour was found for the inter-lamellar distance for hydrazine ions in zirconium phosphate, the value of which (850 pm) is comparable with our experimental value.[10]

The IR spectra of the intercalated materials showed a broad peak in the range 3200–2000 cm^{-1} attributed to N—H and NH$_3^+$ stretching, hydrogen bridging and C—H stretching. The characteristic peak at 1540 cm^{-1} can be attributed to NH$_3^+$ bending. A similar spectrum was also observed in the intercalation of amines into zirconium phosphate.[13]

The ^{31}P MAS NMR spectra of intercalated compounds showed peaks at $\delta - 18.4$ and $- 14.9$, which can be attributed to protonated and deprotonated phosphate, respectively.[25-27] The former peak can be assigned to unreactive phosphate groups, which are blocked by intercalated amines or are located in the bulk of the inorganic matrix and consequently are inaccessible to the reaction with the diamines.

In acquiring information about the thermodynamics of intercalation, the organic molecules were interacted with the inorganic matrix in aqueous solution and enthalpy changes were obtained by reaction-solution calorimetry. All data clearly showed that the process of intercalation of *n*-alkyldiamines in TiP can be interpreted as an acid–basic solid-state reaction between a layered acid host O$_3$P—OH and Brønsted-base guests according to eqn. (3).[15]

$$2O_3P-OH(c) + H_2N(CH_2)_nNH_2(c,l)$$
$$= O_3P-O^- {}^+H_3N(CH_2)_nNH_3^+ {}^-O-PO_3(c); \Delta_{int}H$$
$$(3)$$
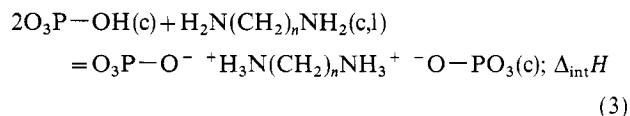
The standard enthalpy of intercalation of diamines in the condensed phase of the above process was calorimetrically determined and the values obtained are listed in Table 2, as well as the number of experiments conducted.

The results show that an increase in carbon number in the alkyl chain induces a corresponding enhancement in the exo-thermicity of the enthalpy of intercalation. For example, for en and nmda, the values of enthalpy of intercalation are -60.37 ± 1.99 and -74.22 ± 1.75 kJ mol^{-1}, respectively. These standard enthalpies are linearly correlated with the number of carbons of the diamine (n_c) and with the interlamellar distance (d), as illustrated in Fig. 3 and 4, and can be expressed in terms of eqn. (4) and (5).

$$\Delta_{int}H = -(56.16 \pm 0.67) - (2.06 \pm 0.12)n_c \quad (r = 0.992) \quad (4)$$

$$\Delta_{int}H = -(39.41 \pm 1.41)$$
$$- (1.80 \times 10^{-2} \pm 0.10 \times 10^{-2})d \quad (r = 0.994) \quad (5)$$

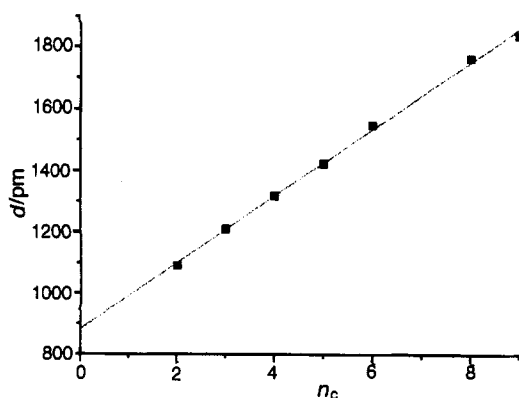**Fig. 1** Number of moles intercalated (n_{int}) as a function of the number of carbons (n_c) of *n*-alkyldiamine

Fig. 2 Interlamellar distance (d) after intercalation as a function of the number of carbons of *n*-alkyldiamine (n_c)

Table 2 Values of enthalpy of intercalation ($\Delta_{int}H$) and number of experiments (N) for all *n*-alkyldiamines

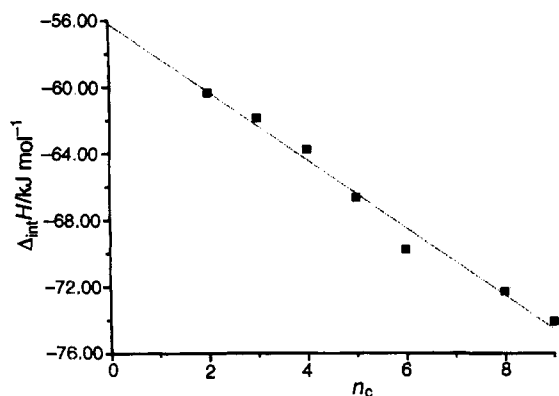| diamine	$-\Delta_{int}H/kJ\ mol^{-1}$	N
en	60.37 ± 1.99	7
pda	61.91 ± 4.99	5
buda	63.81 ± 2.07	6
pmda	66.70 ± 4.31	6
hmda	69.85 ± 3.16	9
omda	72.39 ± 1.70	8
nmda	74.22 ± 1.75	6

Fig. 3 Standard enthalpy of intercalation ($\Delta_{int}H$) of n-alkydiamines into α-titanium hydrogenphosphate as a function of the number of carbons (n_c)
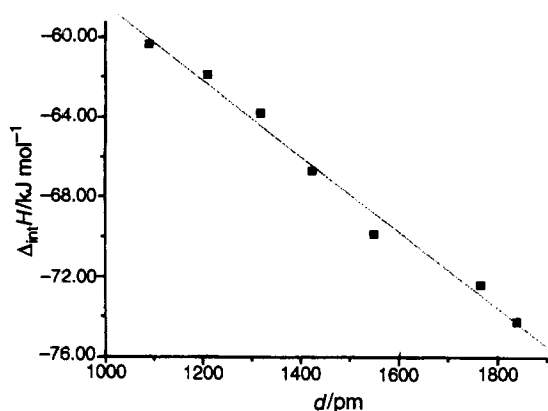

Fig. 4 Standard enthalpy of intercalation ($\Delta_{int}H$) of n-alkyldiamines into a α-titanium hydrogenphosphate as a function of the interlamellar distance (d)

The contribution to the enthalpy of each carbon added to the aliphatic chain of the diamine corresponds to -2.06 kJ mol^{-1} and, in terms of the variation in interlamellar spacing, this corresponds to 1.80×10^{-2} kJ mol^{-1} pm^{-1}. Extrapolating the linear behaviour of these correlations to $n_c = 0$, the enthalpy of intercalation of two moles of ammonium cations per mole of the inorganic matrix has a value of -56.16 ± 0.67 kJ mol^{-1}. When same procedure was used for the intercalation of alkylmonoamines into titanium hydrogenphosphate, a value of -28.04 ± 0.88 kJ mol^{-1} was obtained.[18] However, since monoalkylamines intercalate as double layers into the host, this value should be doubled, resulting in an enthalpic value of -56.08 ± 1.76 kJ mol^{-1}, very close to the value found here.

The sequence of the enthalpies determined here with a limited number of n-alkyldiamines contributes to the under-standing of these types of system. The linear correlations observed suggest that enthalpic values can be inferred for other intercalated species by using these linear correlations for n-alkyldiamines and can be readily estimated from the number of carbons in the alkyl chain or from the interlamellar distance.

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