

Intercalation of N-Alkylamines into Mixed Niobyl-Vanadyl Phosphate

A. L. GARCÍA-PONCE, L. MORENO-REAL, AND A. JIMÉNEZ LÓPEZ¹

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Málaga, Apartado 59, 29071, Málaga, Spain

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Niobyl-vanadyl phosphate ($V_{0.14}Nb_{0.86}OPO_4 \cdot 2.7 H_2O$ (NbVP) intercalates *n*-alkylamine molecules to yield stable layered compounds with high basal spacings and compositions close to 1.7 mole of amine and 2 mole of water per mole of phosphate. The X-ray diffraction, differential thermal analysis, thermogravimetry, and IR and diffuse reflectance spectroscopy (UV-vis-nIR) techniques allow us to establish that the amine molecules are protonated in the interlayer space, where the $R-NH_3^+$ groups interact with the layers via hydrogen bonds. These amines form a molecular bilayer inclined at 58° with respect to the phosphate layers. © 1990 Academic Press, Inc.

Introduction

Mixed niobyl-vanadyl phosphates (NbVP) are solid-solutions of vanadyl phosphate in niobyl phosphate in which up to 21% of the niobyl ions are replaced with vanadyl ions (1). These solid-solutions are isostructural with their precursors and are thus laminar substances in which the metal atoms are coordinated in plane *ab* to four phosphate groups with which they share oxygen atoms. The octahedral coordination of the metal atoms is completed by an oxygen atom linked via a double bond and a water molecule, both located at the octahedron vertices along axis *c* (2). The interlayer space is occupied by water molecules up to an overall composition of about 2.7 mole per mole of phosphate. These water molecules bind the layers together.

The aim behind the synthesis of these

mixed phosphates is to stabilize vanadyl phosphate against topotactic redox reactions because of the greater solubility of its reduced phase (3, 4). However, we also considered the interest of conducting intercalation reactions involving simple molecules such as those of *n*-alkylamines in order to clarify the behavior of these solids toward them and establish their intercalation mechanism. Notwithstanding the fact that, as stated before, the mixed phosphates can be up to 21% substituted, the phase studied in this work was only 14% substituted as the preparation of more extensively substituted phases is rather expensive because of the low yields obtained.

Experimental

The synthesis and characterization of the NbVP (14% V) used was described elsewhere (1). The mixed arsenate (NbVAs, 6% V) was obtained by a similar procedure.

¹ To whom correspondence should be addressed.

All the amines were of reagent grade and were used as supplied, without further purification. The solid amines, viz. *n*-tetradecylamine and *n*-octadecylamine, were dissolved in *n*-heptane at 70°C or 1:2.5 ethanol/ether at 25°C (4 g of amine in 20 ml of the solvent concerned). After a present contact time (72 hr), the solids were filtered and washed with the same solvent and subsequently air-dried.

The liquid amines were brought into contact with the host compounds (0.25–0.4 g in 5–10 ml of pure amine) at 25°C for 24–72 hr. Then, the suspensions were filtered and the solids were washed with ether until all excess amine was removed, after which the products were vacuum-dried.

The more volatile amines, *n*-propylamine and *n*-butylamine, were adsorbed from the vapor phase. Thus, the amine and a beaker containing 0.4 g of NbVP were placed in a desiccator. The reaction was monitored by means of the X-ray diffractograms until the complete disappearance of the initial phase. Then the intercalate was placed under vacuum (10^{-2} mm Hg) and allowed to stand in a desiccator over 50% H₂SO₄ for 2 days in order to remove all the amine adsorbed on its surface.

Amounts of the intercalated amine were determined by CNH analysis and/or Kjeldahl microanalysis, while the water contents were calculated from TG-DTA curves. All intercalates were studied by X-ray diffraction, UV-vis-nIR and IR spectroscopy, and differential thermal and thermogravimetric analyses.

Powder X-ray diffraction patterns were recorded on an automatic Siemens D-501 diffractometer using graphite-monochromated CuK α radiation. Infrared spectra were obtained on a Perkin-Elmer 883 double-beam spectrophotometer using KBr pellets containing 2% of the products. The diffuse reflectance (UV-vis) spectra were recorded on a Kontron Uvikon 810 instrument, while their UV-vis-nIR counterparts

were obtained on a Shimadzu UV 3100 double-beam spectrophotometer, using BaSO₄ pressed tablets as reference. The thermogravimetric and differential thermal analyses were carried out in the air on a Rigaku Thermoflex instrument using calcined alumina as internal reference and heating from room temperature to 1273°K at a rate of 10 or 3°K/min. Platinum crucibles were used and the thermocouple employed consisted of Pt/Pt-Rh.

Results and Discussion

Although the intercalation of *n*-alkylamines into NbVP reaches completion within a few hours, we allowed the reaction to proceed for 48 or 72 hr. Bringing the solid into contact with the amine resulted in its color changing rapidly from yellow to whitish and in a substantial increase in its volume.

Compositions and X-Ray Diffraction Analyses

Table I lists the compositions of the synthesized intercalates and their basal spacings. As can be seen, PA, BA, and PtA have similar compositions which in turn are consistent with those found by Beneke and Lagaly (5) for the intercalation of *n*-alkylamines with $n \leq 10$ in α -NbP. However, the compositions of the intercalates involving amines with $5 < n \leq 12$ are divergent (1.7–1.8 mole of amine per mole of phosphate). This increased content of amine might arise from the increased van der Waals forces resulting from increasing molecular volumes—some authors believe that this effect may even dominate the host-guest interaction (6). However, the amine contents of intercalates involving amines with $n = 14$ and $n = 18$ are again lower, which may be a result of the increased steric hindrance posed by the longer chains or from the influence of the solvent on the intercalation process as both amines are solid and are

TABLE I
COMPOSITION AND BASAL SPACINGS OF INTERCALATION COMPOUNDS $(V_{0.14}Nb_{0.86})OPO_4 \cdot x(n\text{-ALKYLAMINE}) \cdot yH_2O$

Amine	Symbol	x	y	$d_1(\text{Å})$	Medium
<i>n</i> -Propylamine	<i>n</i> -PA	1.5	2.5	15.05	Liquid
<i>n</i> -Butylamine	<i>n</i> -BA	1.5	2.2	17.10	Liquid
<i>n</i> -Pentylamine	<i>n</i> -PtA	1.5	1.9	18.96	Liquid
<i>n</i> -Hexylamine	<i>n</i> -HA	1.7	2.2	21.22	Liquid
<i>n</i> -Heptylamine	<i>n</i> -HpA	1.7	2.2	23.43	Liquid
<i>n</i> -Octylamine	<i>n</i> -OA	1.8	2.4	25.58	Liquid
<i>n</i> -Decylamine	<i>n</i> -DA	1.7	2.0	29.84	Liquid
<i>n</i> -Dodecylamine	<i>n</i> -DdA	1.8	2.2	34.56	Liquid
<i>n</i> -Tetradecylamine	<i>n</i> -TdA	1.3	2.2	37.82	<i>n</i> -heptane
<i>n</i> -Octadecylamine	<i>n</i> -OdA	1.2	2.0	53.29	<i>n</i> -heptane
<i>n</i> -Tetradecylamine	<i>n</i> -TdA	1.1	2.0	34.68	Ether/ethanol
<i>n</i> -Octadecylamine	<i>n</i> -OdA	1.0	2.0	43.66	Ether/ethanol
<i>n</i> -Propylamine	(<i>n</i> -PA) _v	1.6	2.3	15.07	Vapor
<i>n</i> -Butylamine	(<i>n</i> -BA) _v	1.6	2.1	17.05	Vapor
<i>n</i> -Butylamine (NbVAs)	<i>n</i> -BA.NbVAs	1.7	2.5	16.92	Liquid

thus intercalated in solution. This point was checked by using two different solvents in the process; the extent of intercalation was greater with *n*-heptane than with the more polar ethanol/ether mixed medium—the latter may even extract the amine in washing the intercalate as found by Beneke and Lagaly (5) for niobyl phosphate.

The water content of all the intercalates ranged between 2.0 and 2.3 mole of water per mole of phosphate and varied only slightly with the relative humidity of the room atmosphere. These high water contents are in clear contrast with the compositions found for the intercalates of niobyl phosphate with *n*-alkylamines (5).

The small variation in the degree of hydration resulted in no significant changes in the degree of swelling of the intercalates, so that the X-ray diffractograms show a single, fixed value for the 00 l reflections (Table I). These diffractograms feature fewer reflections than that of the original host matrix and show only a few harmonics of the 00 l

reflections and the 200 reflection at 3.22 Å, which indicates that the *ab* planes of the original structure are preserved.

Figure 1 shows the variation of the intercalate spacings with the number of atoms of the carbon chain of the amine. The straight line defined by such a variation has a slope $\Delta d/\Delta n = 2.16$ and a regression coefficient

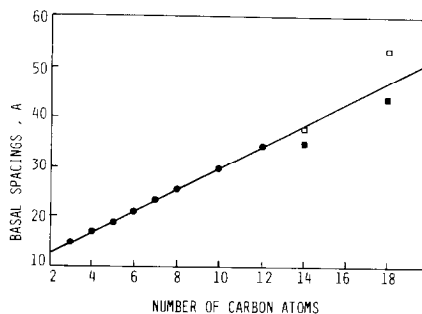


FIG. 1. Interlayer distances of the *n*-alkylamine. —Intercalates as a function of the number of carbon atoms in the alkyl chain. (□, *n*-heptane solution; ■, ether/ethanol solution).

$r = 0.999$. As the chain length increases by 1.27 \AA per carbon atom, the values found indicate that the amines form a molecular bilayer at an angle of 58° with respect to plane ab . This orientation implies that the C–N bond of the amine is perpendicular to the layers, thereby ensuring the greatest possible interaction (7). Using the tilting angles (58°) and the cross-sectional area of an alkyl chain ($4.6 \times 4.2 \text{ \AA}^2$) (8), the number of guest molecules per mole of phosphate is 1.9. This value is close to the experimental composition found, 1.8. This agrees with a compact packing of molecules into the interlayer space. On the other hand, the bilayer arrangement is the most favorable for molecules in which the end facing the amine group is hydrophobic whenever high-density solids at active sites are involved (9).

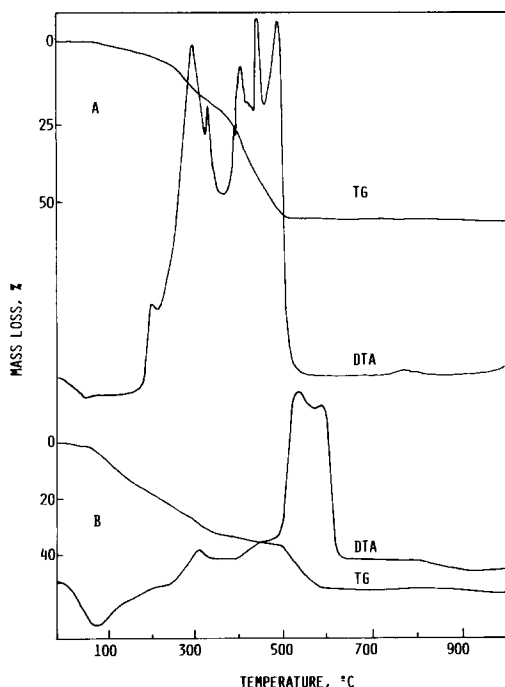


FIG. 2. Thermal analyses (DTA and TG) of (A) tetradecylamine-VNbP and (B) butylamine-VNbAs intercalates.

TABLE II
THERMAL DATA OF *n*-ALKYLAMINE INTERCALATES

Intercalate	Endo (°C)		Exo (°C)			
	Start	End	Start	End	Start	
<i>n</i> -PA	83	300	—	336	—	448
<i>n</i> -BA	75	293	—	—	—	446
<i>n</i> -PtA	94	286	—	409	—	545
<i>n</i> -HA	95	286	—	409	—	543
<i>n</i> -HpA	95	287	—	403	—	528
<i>n</i> -OA	98	290	—	406	—	524
<i>n</i> -DA	97	307	—	404	—	500
<i>n</i> -DdA	96	320	—	406	446	500
<i>n</i> -TdA	89	312	—	400	458	504
<i>n</i> -OdA	60	306	340	397	450	492
<i>n</i> -BA.NbVAs	80	300	—	458	535	585

Figure 2 shows the DTA-TG curves of the intercalate of TdA in the mixed phosphate, while Table II gathers their most outstanding effects. In all cases, the heating process can be considered to consist of three stages. The first, an endothermic stage, takes place between 60 and 100°C and corresponds to a first loss of water. This effect is overlapped with another centered at about 200°C and corresponding to the loss of the water molecules coordinated to the metal. Finally, there are several exothermic effects resulting from the pyrolysis and combustion of the alkylamines. The high temperatures at which the amines are removed from the host matrix compared with their boiling points (10) reveal that these organic bases interact strongly with the mixed phosphates. The solids resulting from the thermal heating at 1000°C are orange in color and give X-ray diffractograms identical with that of the anhydrous mixed phosphate obtained upon heating the host matrix at the same temperature.

Infrared Spectroscopy

Infrared spectroscopy is normally of great use in elucidating interactions between host molecules and their guests. Fig-

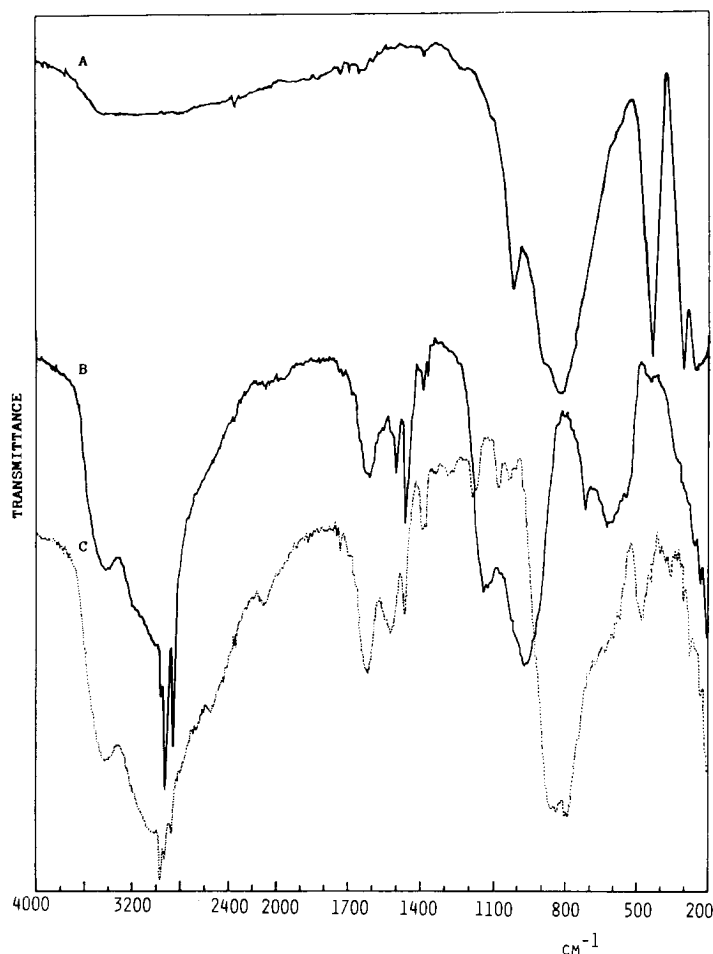


FIG. 3. Infrared spectra of (A) VNbAs, (B) tetradecylamine-VNbP, and (C) butylamine-VNbAs intercalates.

ure 3 shows the IR spectra of the intercalates of TdA in NbVP, as well as that of BA in NbVAs, which is included for comparison in order to study the modifications involved in the $M=O$ absorptions because the phosphate group of NbVP absorbs in the same IR region.

Table III lists the most salient absorptions of the aforesaid intercalates. As can be seen, all show a band centered between 3423 and 3340 cm^{-1} which corresponds to the γOH of the 2 mole of water per mole of phosphate. The typical stretching bands of

the amine groups, $\gamma_a\text{NH}$ and $\gamma_s\text{NH}$, which usually appear at about 3410 and 3325 cm^{-1} , respectively, cannot be detected in the spectra of the intercalates; in fact, the former is overlapped with the absorptions of water and the latter is shifted to 3020–3040 cm^{-1} as a result of the protonation of the amine groups to form ammonium ions (10).

The spectral region close to 1600 cm^{-1} is rather complex for elucidation purposes as it contains the absorptions of water, the amine groups, and the ammonium ion. On

the other hand, the region providing the best information about the location of the *n*-alkylamines in the interlayer space is that close to 1490 cm⁻¹ (12), where $\delta_s \text{NH}_3^+$ is clearly seen as it is not overlapped with the bending vibrations of water. The band appears clearly in the spectra of all the intercalates, which indicates that the amines are protonated in the interlayer space as a result of their strong basic character and of the presence of water. Nevertheless, the band appears split or with a shoulder at 1495–1510 and 1515–1530 cm⁻¹ and always at frequencies above 1490 cm⁻¹, which suggests that the NH_3^+ groups interact via hydrogen bonds (13) and in two different ways—split band. This may be related with the presence of two types of water molecules: one, more acidic, coordinated to the octahedra, which would form the stronger hydrogen bonds, and another which would occupy the vacancies in the structure of the layered compounds. The higher acidity of the coordinated water molecules could be expected from the high oxidation state of the metal as has already been demonstrated by other authors (14). As the metal octahedra bear $\text{H}_2\text{O}-\text{M}=\text{O}$ at their apices, the protonation of the amines will increase the negative charge on the OH-formed, which this can transfer to the metal; hence the $\text{M}=\text{O}$ bond can relax and the $\gamma\text{M}=\text{O}$ is shifted to lower frequencies. This is clearly observed in the spectrum of BA intercalated in NbVAs (Fig. 3), in which the $\gamma\text{M}=\text{O}$, which appears at 998 cm⁻¹ in the original compound, is shifted to the region where the AsO_4^{3-} groups absorb.

Finally, all the intercalates show stretching CH bands near 2960, 2930, and 2870 cm⁻¹, the intensity of which increase with the length of the carbon chain of the amine.

Diffuse Reflectance Spectroscopy

The information provided by the IR spectra was complemented by that obtained

TABLE III
SELECTED VIBRATION BANDS OF THE IR SPECTRA OF PURE *n*-BA, *n*-BA HYDROCHLORIDE, AND AMINE INTERCALATES

Compounds	$\gamma(\text{OH})$	$\gamma(\text{NH}_2)_a$	$\gamma(\text{NH}_2)_b$	$\gamma(\text{NH}^+)$	$\gamma(\text{CH}_2)_a$	$\gamma(\text{CH}_2)_{a+s}$	$\gamma(\text{CH}_2)_s$	$\delta(\text{NH}_3^+)_{a+s} + \delta(\text{H}_2\text{O})$	$\delta(\text{NH}_2)$	$\delta(\text{NH}_3^+)_s$	$\delta(\text{CH}_2)$	$\gamma\delta(\text{CH}_3)$	$\delta(\text{CH}_2)$	$\gamma\delta(\text{CH}_3)$
<i>n</i> -BA (CCl ₄)	—	3410	3325	—	2975	2948	2900	—	1618	—	1477	—	1381	—
<i>n</i> -BA (HCl)	—	—	—	—	2976	2930	—	1594	—	1505	1470	1456	1385	—
<i>n</i> -PA.VNbP	3423	—	—	3040	2972	2940	2893	1570/1619	—	1530/1502	1472	1460	1394	1323
<i>n</i> -BA.VNbP	3430	—	—	3020	2960	2930	2870	1620	—	1520/1495	1465	1455	1390	1325
<i>n</i> -PA.VNbP	3420	—	—	3020	2950	2920	2866	1620	—	1520/1495	1460	1453	1382	—
<i>n</i> -HA.VNbP	3430	—	—	3020	2953	2926	2853	1625	—	1525/1500	1465	1457	1387	1330
<i>n</i> -HpA.VNbP	3430	—	—	3020	2953	2926	2853	1625	—	1520/1505	1463	1455	1383	1330
<i>n</i> -OA.VNbP	3440	—	—	3000	2950	2920	2850	1625	—	1530/1505	1463	1455	1383	1310
<i>n</i> -DA.VNbP	3440	—	—	3000	2950	2917	2846	1620	—	1525/1500	1460	1450	1386	—
<i>n</i> -DdA.VNbP	3430	—	—	3000	2960	2920	2850	1620	—	1525/1510	1463	1455	1390	1335
<i>n</i> -TGA.VNbP	3441	—	—	3020	2964	2924	2856	1617	—	1520/1504	1465	—	1395	1330
<i>n</i> -Oda.VNbP	3440	—	—	3160/3010	2963	2925	2856	1617	—	1520/1506	1465	1455	1410	—
<i>n</i> -BA.VNbAs	3443	—	—	3020	2968	2939	2879	1615	—	1521	1465	—	1390	—

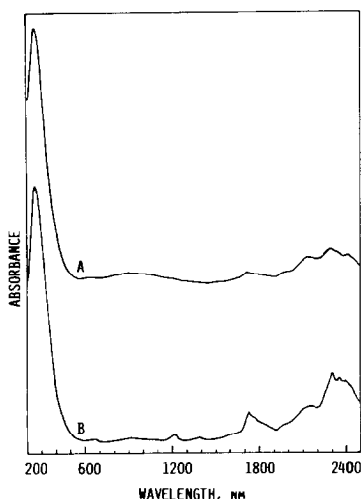


FIG. 4. Diffuse-reflectance spectrum in the 200- to 2500-nm region of *n*-butylamine (A) and dodecylamine intercalates (B).

from the diffuse reflectance spectra run between 200 and 2500 nm (Fig. 4). As can be seen, the charge transfer bands responsible for the yellow color of the original NbVP are modified in the intercalates, so that these become white and show a single band centered at about 250 nm. This indicates that the interaction between coordinated water and amine molecules, which involves the transfer of a proton as stated above, modified the $M \leftarrow L$ donation of the two oxygens coordinated at the apices, $R-NH_3^+ \dots ^-HO-M=O$, shifting the bands to higher-energy regions.

On the other hand, the nIR region shows several bands of lower intensity than the charge transfer bands. Such bands (Fig. 5) are yielded by two intercalates of *n*-alkylamine, *n*-propylammonium iodide, and *n*-tetradecylamine. The bands appearing in this spectral region are known to correspond basically to combinations of stretching and bending vibrations of the N-H, C-H, and O-H bonds and their first harmonics (15). Table IV gathers together the most outstanding vibrations in this re-

spect. The C-H stretching and bending vibration bands appear between 2250 and 2455 nm, while their first and second harmonics appear at 1700–1800 and 1100–1200 nm, respectively.

A pure alkylamine shows a $\gamma_{NH}-\delta_{NH}$ combination band at 2032 nm, with the $\gamma_s NH$ and $\gamma_a NH$ harmonics appearing at 1550 and 1425 nm, respectively. These bands are substantially modified by the protonation of the amine group; thus, the bands of *n*-propylammonium iodide appear associated to those of the carbon groups and only the maxima at 2150 and 1635 nm are clearly observed. The spectra of the intercalates coincide with that of the *n*-propylammonium ion, which confirms the occurrence of the protonation of the intercalated amine molecules.

Intercalation Mechanism and Molecular Arrangement

The above data allow us to conclude that the intercalation of *n*-alkylamines takes place via an acid–base reaction in which

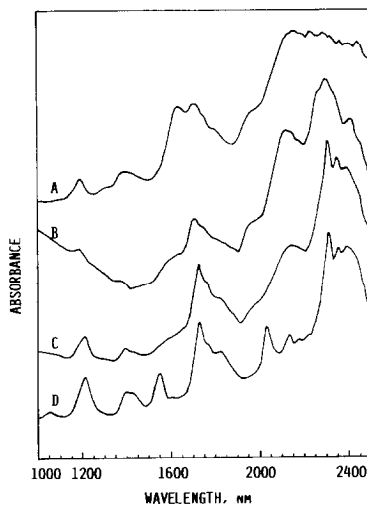
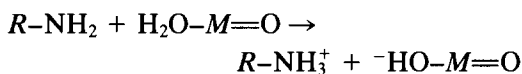


FIG. 5. Infrared spectra, in the 1000- to 2500-nm region, of (A) propylammonium iodide, (B) *n*-butylamine-VNbP intercalate, (C) *n*-dodecylamine-VNbP intercalate, and (D) *n*-tetradecylamine.

TABLE IV
WAVELENGTHS (nm) AND VIBRATIONAL MODES IN THE *n* IR REGION

Pure <i>n</i> -TdA	Propylammonium iodide	<i>n</i> -BA intercalate	<i>n</i> -DdA intercalate	Assignations
2395	2445	2412	2392	
2355	2365		2351	
2313	2326	2305	2310	$\gamma(\text{CH}) + \delta(\text{CH})_2$
	2287			
	2230			
2133	2150	2126	2141	$\gamma(\text{NH}^+) + \delta(\text{NH}_3^+)$
2032				$\gamma(\text{NH}) + \delta(\text{NH}_2)$
		1990 sh	1990 sh	$\gamma(\text{OH}) + \delta(\text{H}_2\text{O})$
1816			1825	First harmonics $\gamma(\text{CH})$
1732	1713	1713	1728	
	1635	1635 sh	1635 sh	First harmonics $\gamma(\text{NH}^+)$
1550				First harmonics $\gamma(\text{NH})$
1425				
1400	1391	1375	1392	(CH), first harmonics $\gamma(\text{OH})$
1214	1192	1200	1212	Second harmonics $\gamma(\text{CH})$
1054				Second harmonics $\gamma(\text{NH})$

the protons involved are supplied by the water molecules in the interlayer space. One such molecule, namely that coordinated to the metal atom, is the more acidic and hence causes the formation of an ammonium ion according to



although the two charged species interact subsequently via a hydrogen bond as was inferred from the IR spectra.

The X-ray data prompt that the chain is inclined 58° with respect to the layer, which allows the C-N bond to lie perpendicular to it and the plane containing the three hydrogens of the $-\text{NH}_3^+$ group to be parallel to it, which in turn allows for a linear hydrogen bond interaction, $\text{N}-\text{H}^+ \dots ^-\text{OH}-\text{M}=\text{O}$, i.e., the most favorable situation (16). As the hydrophobic group of the alkylamine cannot interact with the upper layer, the compound takes in another amine molecule which interacts with the second water molecule, although the interaction is weaker on

account of the lower acidity of the water molecule. The best geometric alternative entails the $R-\text{NH}_3^+ \dots ^-\text{OH}$ groups formed occupying the structural vacancies of the upper layer, where they will interact with the PO_4^{3-} groups.

All these data allow us to propose the scheme depicted in Fig. 6, which was established from the bond lengths of these compounds (17) and the corresponding van der

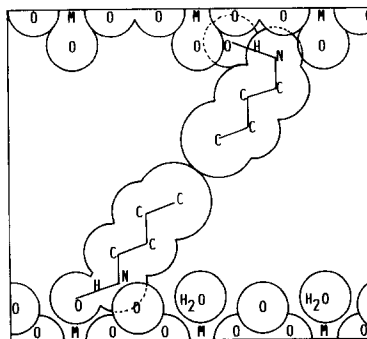


FIG. 6. Schematic arrangement of *n*-alkylamine molecules in the interlayer space of mixed phosphate.

Waals and covalent Pauling radii (18), so that the basal spacings found for all the alkylamines intercalated are reproduced with the experimental angle found for the molecules (58°). This strong interaction of the amines with the neighboring layers endows the intercalates formed with high stability as stated above in discussing their thermal behavior.

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