Characterization of the Interlayer Water in Niobyl Phosphate Hydrates by IR and NMR Spectroscopies

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Water in lamellar niobyl phosphate hydrates $NbOPO_4 \cdot nH_2O$ has been studied by IR and ^1H NMR spectroscopies. Water molecules with remarkable mobility and undefined orientation were present in the "trihydrate" phase ($n \sim 2.8$). In the dihydrate composition two kinds of water molecules with different orientations and interactions have been established: molecules coordinated to niobium atoms and water molecules in interaction with two adjacent sheets. In the monohydrate only the first type of water is present, having its binary axis perpendicular to the structural layers.

Introduction

The compounds with formula $MOXO_4$ (M = V, Nb, Ta; X = P, As) constitute an isomorphic series, and their structures have been established by X-ray diffraction.[1-3] The tetragonal form of $MOPO_4$ consists of chains of corner-shared MO_6 octahedra that run parallel to the *c* axis. In the *ab* plane, each MO_6 octahedron shares corners with four PO_4 tetrahedra, which link the octahedral chains to produce a three-dimensional lattice. The six oxygens surrounding the metal atom form an almost regular octahedron, but the fact that the metal atom is displaced from the center on the *c* axis gives rise to two types of M—O bonds, either long or short according to their orientation. In each case the lengths of the short bonds are typical of M=O bonds, while the long bond lengths are considerably greater than that of a single bond so that these M—O bonds are much weaker normal.

As one progresses along the V–Nb–Ta series, the differences between the long and short bonds become lower, and the overall length between corners, O—M=O, decreases. These characteristics determine whether or not it is possible to synthesize stable hydrates. When the two axial bond lengths are equalized, the intrusion of water is prevented: this explains why no hydrates of α-TaPO$_4$ have been found.[4] When the two bonds are not equalized, the water molecules can coordinate the M^{5+} cations and preclude the formation of octahedral chains. The hydrates of vanadyl and niobyl phosphates are formed in this way, and consequently their structure becomes lamellar. The presence of water molecules in the interlayer spaces further reduces the cohesion between the layers so that the hydrated solids can form intercalation compounds with neutral polar substances like amines, alcohols,[5] or amides.[6] In the case of vanadyl derivatives, if the vanadium is reduced, it is possible to introduce ionic species.[7,8]

In vanadyl phosphate hydrate, two types of water molecules have been established by neutron diffraction studies:[9] one is directly coordinated with the vanadium atom with its binary axis parallel to the crystal *c* axis; the other lies between the phosphate groups of continuous layers, but to date, its exact orientation and its hydrogen bond interactions are not precisely known.

The crystalline hydrates of niobium(V) orthophosphate were prepared by Chernorukov et al.,[10] who proposed a structure similar to that of vanadyl phosphate hydrate.

This paper reports IR and ^1H NMR spectroscopic studies to determine the orientation and interactions of the interlaminar water molecules of niobyl phosphate hydrates. These materials were selected because (i) they can be prepared as thin films of orientated aggregates and (ii) they do not exhibit the characteristic paramagnetism associated with V^{4+}, which always occurs in trace levels in all vanadyl derivatives and complicates the NMR analysis.

Experimental Section

To prepare $NbOPO_4 \cdot 3H_2O$, Nb_2O_5 (0.075 mol) was dissolved in 140 mL of hydrofluoric acid (40% w/w); then concentrated orthophosphoric acid (82 mL, 85% w/w) was added. The resulting solution was heated

Table I. Variation of the Basal Spacing (d_L) and Water Content in $NbOPO_4 \cdot nH_2O$ with Thermal Treatment

temp ranges, °C	d_L, Å	n^a
room temp	8.1–7.9	2.8–2.5
70–120	7.1–6.9	2–1
120–200	7.0–4.1	1–0.3
>240	4.1	<0.3

[a] Number of water molecules per formula determined from the mass loss by static heating.

in a steam bath until a crystalline precipitate formed. This suspension was treated with 560 mL of 5 M nitric acid solution. The solid was isolated by centrifugation, washed five times with distilled water, air-dried, and stored in a controlled-humidity environment. The chemical composition was determined by dissolving the solid in hydrofluoric acid, to precipitate the niobium as the cupferron complex, and then calcinating to Nb_2O_5 at 1000 °C. Phosphorus content was determined by colorimetric analysis as the molybdophosphate complex. Water content was measured by heating at 500 °C to anhydrous niobyl phosphate.

Thermal analysis (TGA and DTA) was carried out in air on a Rigaku Thermoflex apparatus at a heating rate of 5 K·min^{-1} with calcined Al_2O_3 as the internal standard reference.

Spectroscopic and X-ray diffraction studies were carried out on orientated aggregates prepared by evaporating aqueous suspensions on a Mylar film base; this was subsequently peeled away to leave a self-supported film, which permitted the more precise study of the 00*l* reflections in the X-ray diagrams. X-ray diffraction patterns were obtained with a Siemens D501 automated diffractometer using graphite-monochromated Cu Kα radiation.

The ^1H NMR spectra were obtained by using a pulse spectrometer SXP 4/100 (Bruker) with an Aspect 2000 Fourier transform unit. The NMR proton frequency was 70 MHz. All spectra were recorded at room temperature, and the number of accumulations was chosen in such a way that signal/noise ratio was higher than 50. The samples were formed by superimposing individual plaques from orientated aggregated films placed in the interior of a square-section Pyrex cell, designed to conserve the degree of hydration. The NMR spectra were recorded for the two most significant external magnetic field orientations, one perpendicular and one parallel to the plaque plane.

IR spectra of the self-supported films were recorded by using a Perkin-Elmer 580B double-beam spectrophotometer, coupled with a PE M-3500 data station. A classical IR vacuum cell, with CaF$_2$ windows, was used to control the dehydration–hydration conditions of the samples.

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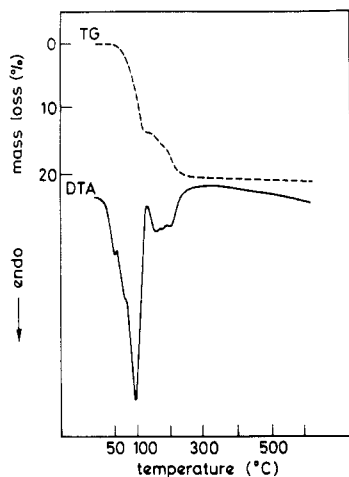
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Figure 1. Thermal analysis (TGA and DTA) of niobyl phosphate "tri-hydrate".
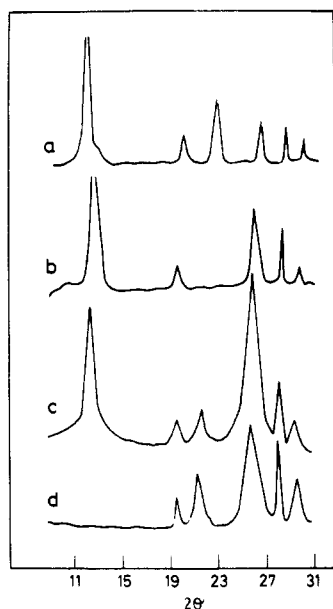

Figure 2. X-ray diffraction patterns of niobyl phosphate "trihydrate" (a), treated at 70 °C (b), 140 °C (c), and 280 °C (d) (anhydrous phase).

The arrangement also allowed the sample orientation to be changed relative to the incident IR beam.

Results

The TGA–DTA curves (Figure 1) of fully hydrated samples of niobyl phosphate show that dehydration occurred in two stages. In the first stage the mass lost was equivalent to between 1.6 and 1.7 water molecules per formula. In this temperature range the DTA curve shows three endothermic effects centered at 40, 70, and 95 °C. The remaining water (approximately 1 molecule per formula) was eliminated at temperatures greater than 120 °C. These results show that the niobyl phosphate compound, terms "trihydrate", only contains some 2.5–2.8 water molecules per formula at room temperature and in relative humidities between 50 and 80%. The existence of the monohydrated phase is confined to the range of temperature of 100–120 °C, while the dihydrated state is thermodynamically less stable.

The X-ray diffractograms for samples with different water contents is shown in Figure 2. Progressive dehydration by static heating produces a decrease in the interlayer distances (Table I). Only three differentiated phases were detected, their basal spacing being close to 8, 7, and 4.1 Å, respectively. Taking into account the TGA curves, these phases may be assigned (i) to the "trihydrate", (ii) to both the di- and monohydrated phases, and (iii) to the anhydrous phase. The range of temperature in which each hydrate phase was found and its corresponding water content are
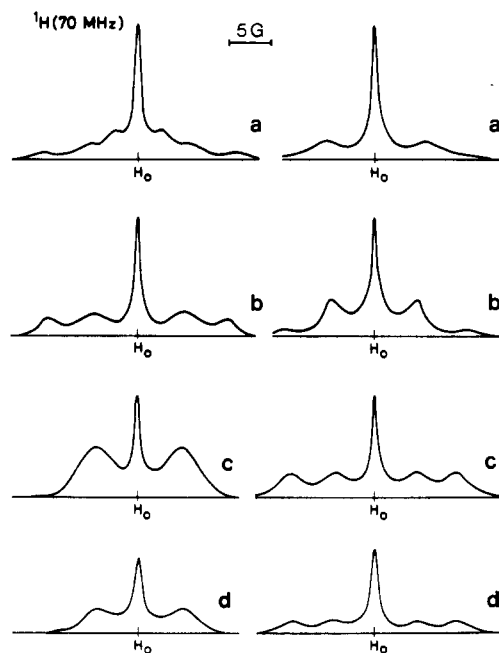

Figure 3. ¹H NMR spectra of niobyl phosphate "trihydrate" (a), treated at 70 °C (b), 120 °C (c), and 195 °C (d), recorded when the magnetic field was perpendicular (left side) and parallel (right side) to the layer plane. Intensities are given in arbitrary units.
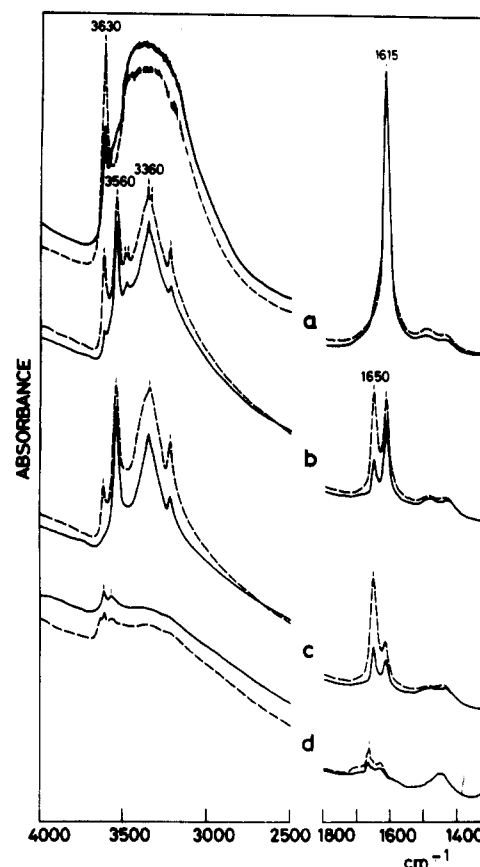

Figure 4. IR spectra of niobyl phosphate "trihydrate" (a), treated at 70 °C (b), 120 °C (c), and 195 °C (d), registered at two orientations with respect to the incident beam: perpendicular (—); tilted 45° (⋯).

shown in Table I. In the 120–200 °C interval, two phases, the anhydrous and monohydrate, coexist.

The NMR spectra (proton signal) and the IR spectra (region of OH group stretching 3800–3400 cm⁻¹ and water bending 1700–1600 cm⁻¹) of samples at different hydration stages are given in Figures 3 and 4.

The study of spectra obtained from the different sample orientations of the previously identified hydrates permit the determination of the water molecule arrangements relative to the layers. The IR spectra identify the OH group orientations, and those of NMR, the H–H vector orientations.

"Trihydrate" Phase (d_L = 8 Å). The NMR spectrum of the fully hydrated sample ($n \sim 2.8$), when the sample plaques are perpendicular to the H_0 field, consisted of a narrow line centered on the resonance frequency, a doublet whose component separation varied from 4 to 7 G (depending on the water content of the sample), and two low-intensity doublets whose component separations were 11 and 21 G, respectively (Figure 3a). As the sample was smoothly heated ($\sim$50 °C) and the more weakly retained water was partially eliminated, the intensities of the 4–7-G doublet and of the central line diminished relative to the other doublets. When the orientation of the sample was changed, the component separation of the individual doublets decreased (Figure 3a').

The IR spectrum of the "trihydrate" sample showed an intense absorption band between 3600 and 3200 cm^{-1} in the ν(OH) stretching region, together with another narrow band at 3630 cm^{-1}, when the film sample was perpendicular to the incident beam. In the water bending region there was only one component at 1615 cm^{-1} (Figure 4a). When the film was tilted 45° relative to the incident beam, a strong increase in the intensity of the band centered at 3630 cm^{-1} was observed, while the other two bands, in the ν(OH) and δ(HOH) regions, were not dichroic.

These results showed that in this hydration phase there is water with a high mobility so that it is difficult to establish the orientation adopted by the water molecule.

Dihydrate/Monohydrate Phases (d_L = 7.1–6.9 Å). Sample dehydration at 70 °C ($n \sim 2$) appreciably modified the NMR and IR spectra. When the magnetic field was perpendicular to the plaque plane, the NMR spectrum consisted of one line centered on the resonance value and two doublets with component separations of 10 and 21 G, respectively (Figure 3b). The previously observed doublet with component separation of 4–7 G completely disappeared from the spectrum. The intensity of the 21-G doublet diminished when the sample was heated at 120 °C ($n \sim 1$). The resulting spectrum consisted of only one doublet at 11 G (Figure 3c).

The NMR spectrum when the sample plaques were orientated parallel to the magnetic field H_0 contained principally (Figure 3b') a central line, plus one doublet with a component separation of 11 G and greater intensity than that of each one of two doublets observed in the perpendicular orientation. When the sample was heated at $T > 70$ °C, two doublets appeared at 11 and 21 G, which exhibited similar intensities when the sample was heated at 120 °C (Figure 3c').

The IR spectra of the samples heated at 70 °C consisted of a set of bands located in the 4000–3000-cm^{-1} region, centered at 3630, 3560, 3495, and 3360 cm^{-1}, and other bands in the O–H deformation region, at 1615 and 1650 cm^{-1} (Figure 4b). When the sample was tilted relative to the incident beam, an important increase in intensity of the bands at 3630 and 1650 cm^{-1} was observed, while the other bands showed minor changes in intensity. Heating the sample between 70 and 120 °C sharply decreased the nondichroic band centered at 1615 cm^{-1} and also the bands at 3630 and 3495 cm^{-1} in the ν(OH) region, which correspond to the weakly linked water (Figure 4c).

When the sample was heated at 120 °C (to attain monohydrate composition), the IR spectrum principally consisted of two components in the stretching region centered at 3560 and 3360 cm^{-1} and another band in the bending region centered at 1650 cm^{-1} (Figure 4c). When the sample was tilted to 45° relative to the incident beam, the intensities of the bands centered at 3360 and 1650 cm^{-1} increased.

The results of both techniques show the presence of two types of water with different orientations; they were eliminated at different temperatures. This will be dealt with in the Discussion.

Anhydrous Phase (d_L = 4.1 Å). Heating the sample above 120 °C ($0.3 < n < 1$) diminished the intensities of different bands associated with the water molecules in the IR (Figure 4d) and

NMR (Figure 3d,d') spectra. Further heating to 280 °C reduced the NMR spectra to just one line with reduced intensity and greater width compared to those of the lines previously observed. This component could be associated with the OH groups that might have formed in the solid during the synthesis and/or the heating process.

Discussion

From the above results, three types of water molecules can be identified in NbOPO$_4$·nH$_2$O. Spectroscopic analysis of the monohydrate phase shows the existence of one type of strongly bonded water (type I) assigned to water molecules coordinated to the niobium atoms, which are characterized by the 3560-, 3360-, and 1650-cm^{-1} bands in the IR spectrum (Figure 4c). The observed dichroic effect in the 1650-cm^{-1} band indicates that in the monohydrate phase the water molecules have their C_2 axes almost perpendicular to the plane of the (NbOPO$_4$)$_\infty$ sheets. This was clearly established from the NMR spectra: the doublet with 11-G component separation observed when the external magnetic field was perpendicular to the sample layers (Figure 3c) is assigned to water molecules with their H–H vectors oriented perpendicularly to the H_0 vector field and parallel to the structural layers.

Nevertheless, the H–H vector can assume any orientation between 0 and 360° relative to the H_0 vector when this is orientated parallel to the lattice layers. This means that the doublet components may have any value below 21 G, although the 11- and 21-G doublet intensities must be increased because they represent the maximum values in the expression

$$\Delta H = 2\mu(3 \cos^2 \theta - 1)/r^3$$

where ΔH represents the component separation of the doublet for a water molecule with a θ orientation of the H–H vector relative to the H_0 field, μ is the magnetic moment of the proton, and r is the H–H distance (1.6 Å). The great width of the components in each doublet reveals the heterogeneity of the H–H vector orientations in the molecule, relative to the external magnetic field H_0.

The described orientation of the water molecule and the available interlayer space in the monohydrate ($\sim$2.9 Å), as well as the high frequency found for the δ(HOH) vibration in the IR spectra, support the hypothesis of a strong interaction of the water molecules in the monohydrate and agree with the model proposed by Casañ[11] for the vanadyl phosphate hydrate, which is isostructural with niobyl phosphate. Nevertheless, in our case the low dichroic effect in the 3360-cm^{-1} band, which could be attributed to the ν_{sym}(OH) vibrations, makes it difficult to assert a C_{2v} symmetry in this type of water molecules.

The IR and NMR spectroscopic studies of more hydrated samples ($1 < n < 2$) show the existence of an additional type of water molecule (type II) that coexists with that observed in the monohydrate (type I). The IR absorption bands at 3630, 3495, and 1615 cm^{-1} are attributed to the new type of water molecules, involved in a weaker hydrogen-bond linkage (Figure 4b). The absence of dichroism in the 3495- and 1615-cm^{-1} bands (ν_{sym}(OH) and δ(HOH)) and the fact that the band at 3630 cm^{-1} (ν_{asym}(OH)) is dichroic indicate that these molecules have a different orientation, relative to the layers, than those present in the monohydrate.

The analysis of the NMR spectra of samples, which range from the mono- to dihydrate composition, permits us to precisely determine the orientations adopted by the new type of water molecules. These molecules are characterized by the appearance of a 21-G doublet, in addition to the 11-G doublet, when the sample plaques are orientated perpendicular to the magnetic field (Figure 3b). Its intensity increases as the water content increases, so the intensities of both doublets are almost equal when the sample is close to the dihydrate. Bear in mind that a doublet with component separation close to 21 G can only be observed when the water molecule H–H vector is oriented parallel to the external magnetic field, which implies in this case that the molecular binary

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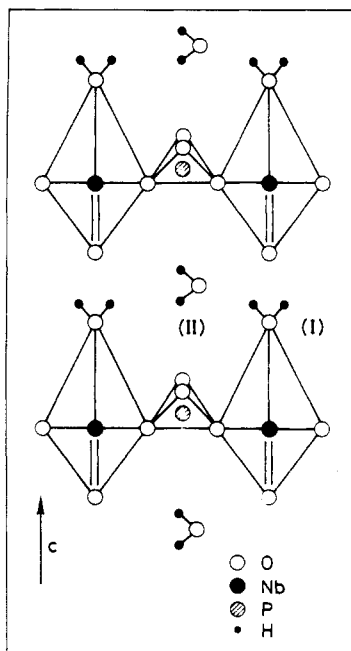
Figure 5. Schematic representation of the interlayer water molecules (types I and II) in the niobyl phosphate (dihydrate composition).

axis is parallel to the lattice layers. Thus, as might be expected, when the sample is orientated parallel to the external magnetic field, the intensity of the 11-G doublet is enhanced by the sum of the H–H vector contributions of the two types of water molecules. Furthermore, as a consequence of all the other orientations that may be adopted in the plane by the H–H vector of the type I water molecule, the relative intensities of the 21-G doublet will be less than that of the 11-G doublet.

The IR results may be similarly explained by using the orientation proposed for the type II water molecules. The dichroism seen in the antisymmetric vibration band at 3630 cm^{-1} of the type II water molecules could result from a C_{2v} symmetry when the H–H vector is perpendicular to the layers. The nondichroic character of the bands assigned to the ν_{sym}(OH) and δ(HOH) vibrations shows that the binary axis may have any orientation in a plane parallel to the layers so that the intensities of these IR absorption bands correspond to an average orientation that is insensitive to changes in the direction of the incident beam.

The orientation and symmetry (C_{2v}) of the type II water molecules are compatible with a hydrogen-bonding interaction with the oxygen atoms of the PO$_4$ tetrahedra of both sides of the interlayer space. On the other hand, the frequencies of the ν(OH) and δ(HOH) vibrations of the type I coordinated water are not affected by the presence of type II water; consequently, their

interactions must be weak, because the type I coordinated molecules establish hydrogen-bond interaction with the NbO$_6$ oxygen atoms in the immediately contiguous layer. On the other hand, the type II molecules might establish *bilaminar* interactions through oxygen atoms of two PO$_4$ groups, one in each adjacent layer (Figure 5).

In the 8-Å phase (2 < n < 3), the presence of a new type of water molecule, detected by the corresponding thermal analyses, provokes an additional separation of the contiguous layers, as is shown by the increase of basal spacing, which is lower than that expected for the intercalation of a new water layer (thickness ~2.8 Å). This could be explained by the existence of void spaces in the dihydrate phase, which accommodate additional water molecules so that the increase of the basal spacing is only ~1 Å. The absence of the δ(HOH) vibration at 1650 cm^{-1} assigned to the coordinated water molecules shows that the interaction between the H$_2$O (type I) and the layer is now broken. This situation favors the interaction of the new molecules with both type I and type II water molecules to change their original orientation. The interaction between molecules causes increased mobility, of either the rotational type (coordinated water) or the diffusional type (free water). This is shown in the NMR spectra in which the water doublets show smaller component separations (4.5–7 G) and much narrower central signals.

Conclusions

1. Three types of water molecules have been identified in NbOPO$_4$·nH$_2$O by IR and NMR analysis. Two of these types coexist in the dihydrate composition ($d_L \sim$ 7 Å): (i) water molecules coordinated to niobium atoms (type I) and (ii) water molecules in interaction with two adjacent sheets (type II). The third type of water, identified in the "trihydrate" composition ($d_L \sim$ 8 Å), exhibits a remarkable mobility.

2. In the mono-/dihydrate states, coordination of the type I molecules to niobium atoms determines a perpendicular disposition of the binary axis of the molecule to the layers, favoring cohesion between the contiguous layers.

3. In the dihydrate composition, water molecules of type II interact with the oxygens of the PO$_4$ tetrahedra of two contiguous layers. This implies that the orientations of the H–H vectors are perpendicular to the layers. In this case a C_{2v} symmetry is supported by the spectroscopic data.

4. In the more hydrated samples (2 < n < 3; $d_L \sim$ 8 Å), interactions between water molecules are favored with respect to the bilaminar interactions characteristic in the dihydrate state, showing a different orientation and arrangement of the interlamellar water.