

Intercalation of 1-Alkanols and 1, ω -Alkanediols into NbOPO₄ and NbOAsO₄

Ludvík Beneš,¹ Klára Melánová, and Vítězslav Zima

Joint Laboratory of Solid State Chemistry of the Academy of Sciences of the Czech Republic and University of Pardubice, Studentská 84, 530 09 Pardubice, Czech Republic

and

Jiří Votinský

Department of General and Inorganic Chemistry of the University of Pardubice, Nám. Legií 565, 532 10 Pardubice, Czech Republic

Received January 13, 1998; in revised form June 3, 1998; accepted June 4, 1998

Intercalation compounds NbOXO₄ · 2C_nH_{2n+1}OH (X = P, As; and n = 2–18) and NbOXO₄ · C_nH_{2n}(OH)₂ (n = 2–10) have been prepared. The molecules of alcohols are placed between the host layers in a bimolecular way, being anchored to them by donor–acceptor bonds between the oxygen atom of an OH group and a niobium atom as well as by hydrogen bonds. The molecules of diols are arranged in a monomolecular way and form bridges linking the adjacent layers of the host. The aliphatic chains of the guest molecules possess the *all-trans* configuration and are inclined with respect to the host layers. The stability of the intercalates of NbOPO₄ with 1-tetradecanol and 1,10-decanediol has been studied by XRD as a function of temperature and by thermogravimetry. © 1998 Academic Press

INTRODUCTION

Intercalation of various molecules into inorganic layered structures leads to new materials with interesting properties and structures. A number of recently published papers have reported attempts to find the structural principles governing the deposition of aliphatic molecules with terminal functional groups between the layers of hosts. With this aim, the intercalations of, for example, aliphatic alcohols, diols, amines, and carboxylic acids with unbranched carbon chains into some natural silicates (1–4), α -zirconium phosphate (5, 6), calcium niobates (7), vanadyl or niobyl phosphates, arsenates, and sulfates (8–13), and vanadyl alkylphosphonates (14, 15) have been investigated.

As follows from the results obtained, the intercalated molecules are always anchored to the host layers by their functional groups (16, 17). At room temperature and with

sufficient amounts of the guest molecules, the chains in the intercalate possess the *all-trans* configuration (1,18) and their axes form either an acute angle (usually 55–60°) (11, 16) or a right angle (1, 13, 14, 17) with the host layers. The arrangement of the guest molecules in the interlayer space of the host is most often bimolecular (10, 14, 17). Monomolecular arrangement is usually found for guest molecules with two functional groups (12, 14).

Recently, we have prepared the VOPO₄ intercalates with 1-alkanols (up to 1-octadecanol) and 1, ω -alkanediols (up to 1,10-decanediol) using microwave heating (13). Having determined the lattice parameters of all of these complexes, we suggest the alcohol molecules are placed between the host layers in a bimolecular way. Molecules are anchored by donor–acceptor bonds between the oxygen atom of an OH group and a vanadium atom of the layer as well as by hydrogen bonds. The molecules of diols are in monomolecular arrangement and form bridges linking the adjacent layers of the host using similar bonds. The aliphatic chains of both intercalated alcohol and diol molecules possess *all-trans* configurations, and their axes are perpendicular to the host layers.

This paper presents the results of intercalation of 1-alkanols (up to 1-octadecanol) and 1, ω -alkanediols (up to 1,10-decanediol) into isostructural tetragonal niobyl phosphate and niobyl arsenate.

EXPERIMENTAL

1. Preparations

Niobyl phosphate trihydrate was obtained by the method of Chernorukov (19) as modified by Bruque (20). Nb₂O₅ (10 g) was added to 70 ml of HF (40% w/w) and refluxed under a Teflon-coated condenser for 2 days. Concentrated

¹To whom correspondence should be addressed.

H₃PO₄ (41 ml, 85% w/w) was then added and the mixture was heated to evaporate HF. A constant volume of the mixture was maintained by addition of distilled water. The resultant precipitate was filtered, and washed with 5 M HNO₃ and with distilled water several times to remove free acid. The solid was dried at room temperature. Niobyl arsenate tetrahydrate was prepared in a similar way.

The layered complexes with alcohols with short aliphatic chains (up to butanol) were prepared by suspending microcrystalline NbOXO₄·yH₂O (ca. 0.25 g) in dry liquid alcohol (ca. 7–10 g). This reaction mixture was placed in a 15-cm³ glass flask equipped with a reflux condenser and put into the waveguide of a microwave generator where the mixture was heated under stirring (about 10 min). Intercalates with diols and alcohols with longer carbon chains were prepared by reintercalation reaction. The solid propanol-intercalated hosts were prepared in advance and used as a starting material for the reactions with other alcohols. After cooling, the solid product formed was filtered off. When starting from a solid alcohol, the suspension was separated from the melt by hot filtration. All samples for X-ray diffraction analyses were left with a small residue of the respective alcohol. The samples for TG-DTA and elemental analyses were washed with dry acetone or toluene and dried at room temperature.

The microwave apparatus used for preparing the complexes was specially constructed by Radan Ltd. Pardubice, the Czech Republic. It operates at a frequency of 2450 ± 30 MHz with a total generator output of 800 W of which 30–50 W is absorbed by the reaction mixture. The metal waveguide consists of a square cavity (5.2 × 5.2 cm) with an opening of 2-cm diameter, which serves for locating the reaction vessel in the waveguide axis.

2. Characterization of Intercalates

The powder data of the intercalates with a minor surplus of the guest alcohol were obtained with an X-ray diffractometer (HZG-4, Germany) using CuKα₁ radiation (λ = 1.54051 Å) with discrimination of the CuKβ by an Ni-filter. The CuKα₂ intensities were removed from the original data. Silicium (a = 5.43055 Å) was used as internal standard. Diffraction angles were measured from 1.5° to 50° (2θ). The obtained data were refined by a least-squares program minimizing (2θ_{exp} - 2θ_{calc})². Temperature measurements (from 22 to 310°C) were carried out on a heated corundum plate with a thermocouple. The diffractogram was then measured at this temperature, which was kept constant. The temperature was then increased and the procedure was repeated. Each cycle of heating and measuring lasted about 20 min.

The TGA's of the intercalates were performed with an MOM Derivatograph (Hungary), the measurements being carried out in the temperature interval of 30–600°C in air at

a heating rate of 5°C/min. The weight of the samples was 100 mg. In some cases, particularly for complexes of solid alcohols and diols, the composition was determined by elemental analysis (C, H).

The content of water in the intercalate of both hosts with propanol was determined in the following way: About 1 g of the intercalate was sealed in an evacuated double ampoule. The part of the ampoule containing the intercalate was heated to 200°C while the other part was cooled to -80°C. After distillation of the liquid from the intercalate, the parts of the ampoule were separated and the amount of water in the condensed liquid was determined by titration according to the Fischer method (Karl Fischer AF8 Autotitrator, Orion, U.S.A.).

Infrared spectra were recorded on a Bio-Rad FTS spectrometer with a spectral range 4000–500 cm⁻¹ using a dry KBr powder containing 10% of the intercalate. The resultant reflectance spectra were converted into Kubelka–Munk format.

RESULTS AND DISCUSSION

Only ethanol and propanol can be intercalated directly into niobyl phosphate and only ethanol, propanol, and butanol into niobyl arsenate. In contrast to vanadyl phosphate dihydrate (13), direct intercalation of longer alcohols and diols into NbOXO₄ was not successful. The intercalates with these longer alcohols and all diols had to be prepared by reintercalation of propanol intercalate with both hosts. To avoid formation of cointercalates containing propanol and longer alcohol, propanol intercalate with an excess of the given alcohol was exposed to microwave radiation for 10 min and then filtered off. The solid obtained was mixed with a new dose of given alcohol and then exposed to a microwave field for another 10 min.

The intercalates prepared were crystalline solids and their diffractograms showed a series of relatively sharp (00*l*) reflections (some examples of the diffractograms are given in Figs. 1 and 2). The *a* parameter of the tetragonal lattice was determined from the diffraction lines (110) and (200). The values found for the lattice parameters *a* and *c* are presented in Tables 1 and 2 for all the intercalates prepared. The results of thermogravimetry of NbOPO₄ intercalates together with several results of elemental analyses showed that 1-alkanols form complexes with 1.93 ± 0.09 mole of alkanol per mol of NbOPO₄; hence their composition roughly corresponds to the formula NbOPO₄·2C_{*n*}H_{2*n*+1}OH. The intercalates with 1,ω-alkanediols have stoichiometric coefficient *x* = 0.96 ± 0.06, corresponding to the formula NbOPO₄·C_{*n*}H_{2*n*}(OH)₂. The composition of intercalates of NbOAsO₄ with alkanols and alkanediols determined by elemental analyses is almost the same as in the case of niobyl phosphate intercalates. Thermogravimetry could not be used for determination of the composition because the host

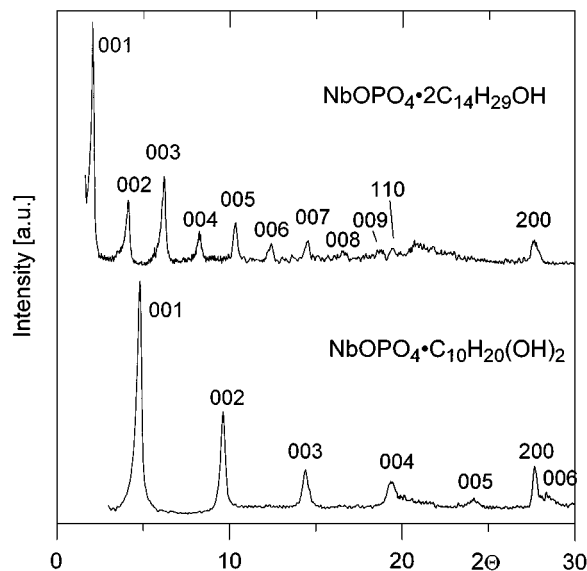


FIG. 1. Diffractograms of the intercalates of NbOPO_4 with 1-tetra-decanol and 1,10-decanediol.

is decomposed at about 500°C . Probably, As^{V} is reduced to As^{III} by the rest of the organic guest during heating and As_2O_3 formed escapes.

By thermal decomposition of the intercalates of both hosts with propanol, it was found that these intercalates contain less than 1 mol% of water. This amount is small in comparison with that found for amine intercalates (8, 9) and does not imply regular participation of water molecules in the interlayer arrangement of the guest molecules. As all other alcohol intercalates were prepared by reintercalation from the propanol intercalates, one can assume that the role of water in these intercalates is also negligible.

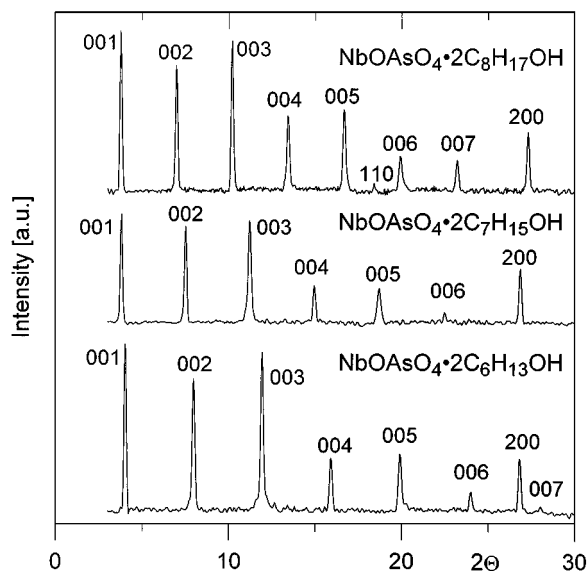


FIG. 2. Diffractograms of the intercalates of NbOAsO_4 with 1-octanol, 1-heptanol, and 1-hexanol.

TABLE 1
Lattice Parameters of 1-Alkanol-Intercalated Niobyl Phosphate and Arsenate

n	$\text{NbOPO}_4 \cdot 2\text{C}_n\text{H}_{2n+1}\text{OH}$		$\text{NbOAsO}_4 \cdot 2\text{C}_n\text{H}_{2n+1}\text{OH}$			
	a [Å]	c [Å]	a [Å]	c [Å]		
2		12.94	6.65	12.85		
3	6.43	14.75	6.66	14.36		
4	6.43	17.83	6.66	17.49		
5	6.42	19.23	6.66	19.44		
6	6.42	21.84	6.65	22.32		
7	6.44	23.54	6.66	23.78		
8	6.44	27.16	6.66	27.43		
9	6.42	29.79	6.65	29.73		
10	6.44	32.67	6.65	32.59		
11	6.42	34.30	6.65	34.88		
12	6.43	37.75	6.66	37.53		
13	6.44	39.70	6.66	40.10		
14	6.45	42.70	41.73 ^a	6.66	42.86	
15	6.44	45.06	43.50 ^a	6.65	45.40	42.01 ^a
16	6.44	46.65	45.83 ^a	6.66	47.44	44.68 ^a
17	6.43	49.50	47.56 ^a	6.65	—	47.20 ^a
18	6.44	51.40	49.52 ^a	6.67	—	49.50 ^a

^a Basal spacings of freshly prepared intercalates.

Infrared spectra were measured to elucidate interactions between the guest molecules and the host lattice. The valence vibration band of the $M=\text{O}$ group ($M = \text{V}, \text{Nb}$) in this type of compound is sensitive to the donor ability of the ligand which coordinates the metal atom at the position opposite to the oxygen atom (21). In anhydrous niobyl arsenate, the $\nu(\text{Nb}=\text{O})$ vibration is found at 1020 cm^{-1} (22). In $\text{NbOAsO}_4 \cdot 4\text{H}_2\text{O}$, the wavenumber of this band is 998 cm^{-1} but intercalation of basic molecules leads to the shift of this band to lower wavenumbers (990 cm^{-1} for amides, $950\text{--}970\text{ cm}^{-1}$ for n -alkylamines) (9, 23). In the case of NbOPO_4 , this region is overlapped by the intense bands of the PO_4 tetrahedron. The IR spectra of all of the intercalates of NbOAsO_4 with alcohols and diols contain the

TABLE 2
Lattice Parameters of 1, ω -Alkanediol-Intercalated Niobyl Phosphate and Arsenate

n	$\text{NbOPO}_4 \cdot \text{C}_n\text{H}_{2n}(\text{OH})_2$		$\text{NbOAsO}_4 \cdot \text{C}_n\text{H}_{2n}(\text{OH})_2$	
	a [Å]	c [Å]	a [Å]	c [Å]
2	6.45	8.14	6.64	8.07
3	6.44	9.89	6.65	9.67
4	6.42	10.83	6.65	10.57
5	6.44	12.26	6.65	12.12
6	6.43	13.56	6.65	12.9
7	6.44	14.48	6.64	14.59
8	6.43	15.77	6.65	15.54
9	6.42	16.87	6.66	16.45
10	6.42	18.36	6.65	17.56

$\nu(\text{Nb}=\text{O})$ band in the 995 to 1000 cm^{-1} region. This indicates the presence of a donor–acceptor bond between an oxygen atom of the alcohol or diol and the niobium atom analogous to the bond of water molecules. A medium-intense band was found at about 3500 cm^{-1} , which probably corresponds to the valence vibration of the OH group of the guest molecule coordinated to the host. A very broad band with a maximum at about 3100 cm^{-1} belongs most probably to the interaction of the guest with the host lattice resulting in the hydrogen bond between oxygen atoms of the host lattice and the OH group of the guest. All the intercalates show C–H stretching bands in the 2850 to 2960 cm^{-1} region.

Figures 3 and 4 show the dependencies of the basal spacing of the intercalates prepared on the number of carbon atoms in the aliphatic chain of the guest molecule. The layered complexes of 1-alkanols and 1, ω -alkanediols with both niobyl phosphate and niobyl arsenate show a linear dependence of their c parameters on the number of carbon atoms n . Parameters of individual straight lines together with their correlation coefficients are given in Table 3.

Assuming that the alkyl chains of 1-alkanols are in the *all-trans* configuration, the slope of 2.49 Å for niobyl phosphate and 2.54 Å for niobyl arsenate indicates a bilayer arrangement of the alkyl chains. The alcohol bilayers are tilted at an angle 77° in niobyl phosphate intercalates and 83° in niobyl arsenate intercalates. Both values are close to those for the perpendicular arrangement which was observed for vanadyl phosphate intercalated with 1-alkanols (13). In the case of alkanediols, the slopes are less than half

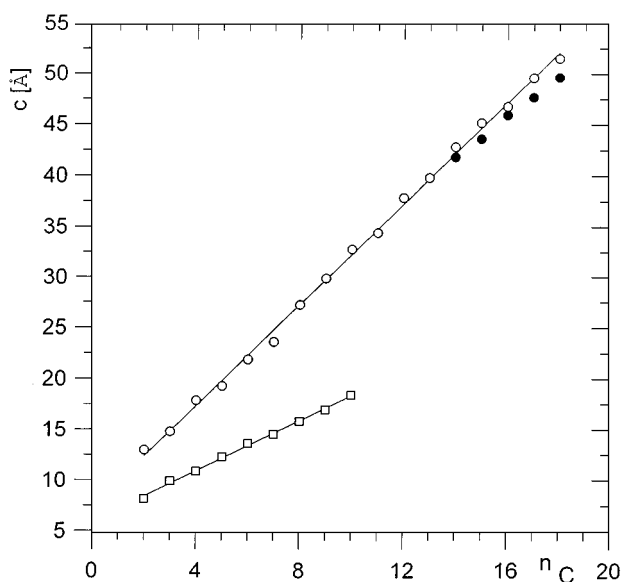


FIG. 3. Dependence of basal spacing of NbOPO₄ intercalates with alcohols (circles) and diols (squares) on the number of carbon atoms in the aliphatic chain.

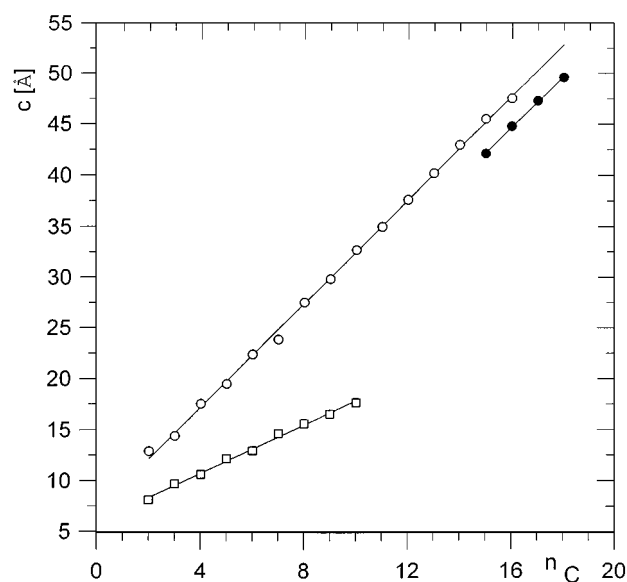


FIG. 4. Dependence of basal spacing of NbOAsO₄ intercalates with alcohols (circles) and diols (squares) on the number of carbon atoms in the aliphatic chain.

of those for alcohol intercalates. This indicates a monomolecular arrangement of diol molecules, where the alkyl chains are oriented at 74° to the NbOPO₄ layers and 67° to the niobyl arsenate layers. The bilayer arrangement of alcohol molecules and monolayer arrangement of diol molecules in the interlayer space of both hosts agrees with the difference found between the stoichiometries of these intercalates.

The values of basal spacing of freshly prepared intercalates of both hosts with longer alcohols are distinctly lower than those corresponding to the straight lines found (see Figs. 3 and 4, dark circles). When the intercalate is left at room temperature for a longer time (1 month), the values of basal spacing increase and reach the values corresponding to the linear dependence. This deviation is probably caused by a disorder of the *all-trans* configuration accompanied by a kink-block or a gauche-block formation. The presence of these disorders was observed during heating of bimolecular films of silicate layers and discussed in detail by Lagaly (18).

TABLE 3
Parameters of Straight Lines Calculated from the Dependencies of Basal Spacings on the Number of Carbon Atoms in the Guest Chain

Intercalate	Slope [Å]	y intercept [Å]	R ² -squared
NbOPO ₄ · 2C _n H _{2n+1} OH	2.49 ± 0.03	7.2 ± 0.3	0.998
NbOAsO ₄ · 2C _n H _{2n+1} OH	2.54 ± 0.02	7.0 ± 0.2	0.999
NbOPO ₄ · C _n H _{2n} (OH) ₂	1.23 ± 0.02	6.0 ± 0.2	0.997
NbOAsO ₄ · C _n H _{2n} (OH) ₂	1.18 ± 0.03	6.0 ± 0.2	0.995

As the synthesis of the intercalates in the microwave field proceeds at relatively high temperature, in molten alcohols, these disorders are retained during cooling of the melt and are removed by long standing at room temperature.

An isolated kink defect in an otherwise *all-trans* aliphatic chain causes it to shorten by $\Delta l = l_{CC} \sin \beta$, where $l_{CC} = 1.537 \text{ \AA}$ is the C–C bond distance and $\beta = 56.3^\circ$ is half of the CCC angle. In the case of the chain in the perpendicular position, this shortening is equal to 1.28 \AA and decreases with increasing angle of tilting of the chain. In the case of a kink-block, this shortening is $1.0\text{--}1.2 \text{ \AA}$ (18). In the case of freshly prepared NbOPO_4 intercalates, a deviation of $0.8\text{--}1.9 \text{ \AA}$ was found for alcohols from C_{14} to C_{18} . This indicates the presence of either one kink per pair of chains (i.e., two chains one above the other in the bimolecular film) or two kinks per pair of chains (either each chain of the pair contains one kink or one of the chains contains both kinks). The decrease of basal spacing for NbOAsO_4 intercalates is 2.8 and 3.4 \AA for pentadecanol and hexadecanol, respectively, which indicates the formation of a block containing probably three kinks per pair of chains or a gauche block. The formation of kink or gauche defects is more sterically demanding; therefore it occurs in the intercalates of NbOXO_4 , which have higher lattice parameter a , and the area in which one chain is anchored to the host is larger. In the case of VOPO_4 , which has the smallest parameter a of its tetragonal lattice, the formation of the intercalate with any basal spacing deviation has not been observed (13).

The results of thermogravimetric analysis and the thermal dependence of the basal spacing of $\text{NbOPO}_4 \cdot 2\text{C}_{14}\text{H}_{29}\text{OH}$ intercalate are given in Fig. 5. As can be seen from the TG analysis, tetradecanol is released in two steps at 240 and 280°C . The total weight loss corresponds to the presumed stoichiometric composition. The decrease of the basal spacing is observed at considerably lower temperature. The first small decrease at $80\text{--}85^\circ\text{C}$ corresponds to the disturbing of the *all-trans* configuration. At 90°C , alcohol is released from the interlayer space as evidenced by a steep decrease of the basal spacing. This phenomenon is accompanied by broadening of the (001) diffraction lines, which is caused by disorder of the regular stacking of the layers along the c -axis. In the temperature region between 145 and 175°C , basal spacing is almost constant, with a value around 23 \AA . The most probable composition of the intercalate is $\text{NbOPO}_4 \cdot \text{C}_{14}\text{H}_{29}\text{OH}$ in this temperature region. If the basal spacing of anhydrous niobyl phosphate is 4.12 \AA and that of the intercalate with bimolecular alcohol layers is 42.70 \AA , then one molecule of tetradecanol in the intercalate possesses 19.29 \AA of the interlayer distance. The basal spacing of the intercalate with alcohol in monomolecular arrangement should be, under the same inclination of the carbon chain, equal to $4.12 + 19.29 = 23.41 \text{ \AA}$. This value is in good agreement with that found experimentally ($24.0\text{--}22.6 \text{ \AA}$). The consequent steep decrease of the

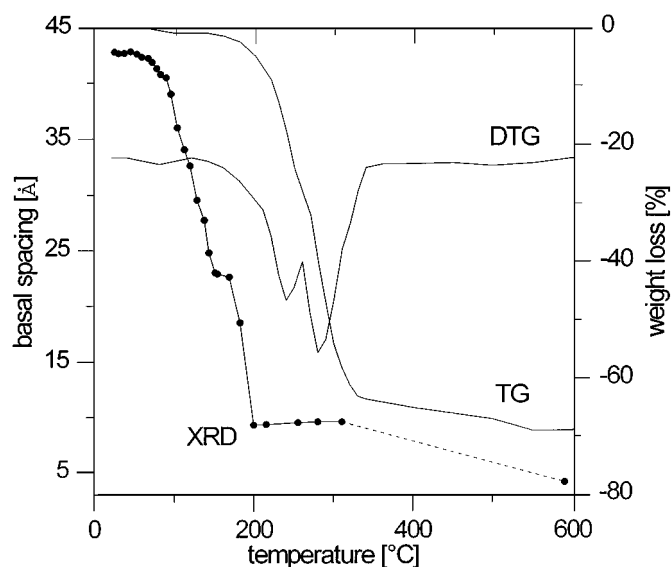


FIG. 5. Thermal decomposition of $\text{NbOPO}_4 \cdot 2\text{C}_{14}\text{H}_{29}\text{OH}$ followed by XRD and thermogravimetry.

basal spacing, connected with the deintercalation of the second molecule of alcohol, reaches a value of 9.5 \AA at 200°C and remains constant up to the end of the measurement (310°C). The sample turns gray to black in this temperature region due to the pyrolysis of alcohol. White anhydrous niobyl phosphate ($c = 4.12 \text{ \AA}$) is formed by calcination at 600°C in air. The slow decrease of weight in the region $300\text{--}600^\circ\text{C}$ corresponds to this process. The $\text{NbOPO}_4 \cdot \text{C}_{14}\text{H}_{29}\text{OH}$ intercalate was prepared by heating $\text{NbOPO}_4 \cdot 2\text{C}_{14}\text{H}_{29}\text{OH}$ *in vacuo* to 170°C for 4 h. The alcohol content was checked by thermogravimetry (weight loss: calculated for $\text{NbOPO}_4 \cdot \text{C}_{14}\text{H}_{29}\text{OH}$ 51.25%, found 50.9%). Lattice parameters of this intercalate are $a = 6.40 \text{ \AA}$ and $c = 23.94 \text{ \AA}$.

The results of the thermogravimetric analysis and the thermal dependence of the basal spacing of $\text{NbOPO}_4 \cdot \text{C}_{10}\text{H}_{20}(\text{OH})_2$ intercalate are given in Fig. 6. This diol intercalate is more stable than the previous alcohol intercalate studied as follows from the XRD results and its basal spacing is almost constant up to 120°C . Higher stability of the diol intercalates is probably due to the fact that the diol molecules are anchored to the layers by two functional groups. A small decrease of basal spacing (about 0.6 \AA) is observed in the region $120\text{--}158^\circ\text{C}$. A steep decrease of basal spacing accompanied by a considerable broadening of the (001) diffraction lines between 158 and 185°C is given by deintercalation of a part of the diol molecules. A stable phase with a basal spacing of 14.1 \AA and with sharp (001) diffraction lines is present in the region $185\text{--}230^\circ\text{C}$. It can be presumed from the first weight loss of the sample that this phase contains about 0.6 mol of diol per mol of niobyl phosphate. In this phase, the angle at which the chain is

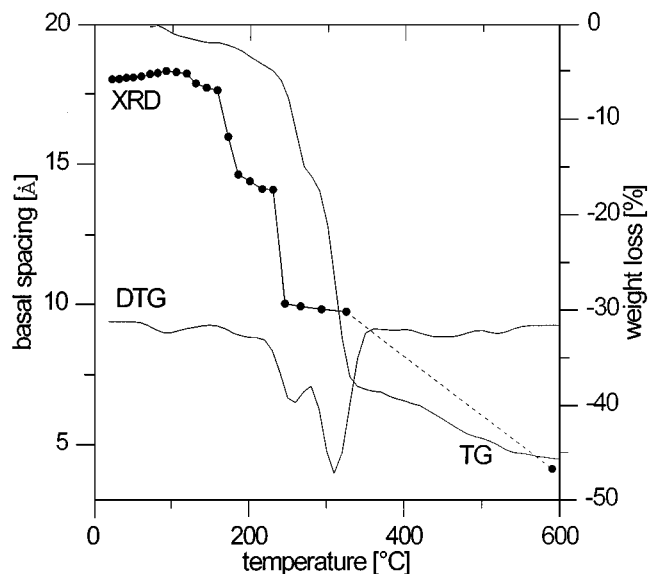


FIG. 6. Thermal decomposition of NbOPO₄·C₁₀H₂₀(OH)₂ followed by XRD and thermogravimetry.

tilted decreases to a value of 43°. This region is followed by a considerable decrease of basal spacing to 9.7 Å at 245°C. The thermal behavior of the sample at higher temperature is similar to that of the tetradecanol intercalate. The NbOPO₄·yC₁₀H₂₀(OH)₂ intercalate was prepared by heating NbOPO₄·C₁₀H₂₀(OH)₂ to 210°C *in vacuo* for 16 h. The stoichiometric coefficient $y = 0.55$ was determined by thermogravimetry. Lattice parameters of this intercalate are $a = 6.42$ Å and $c = 14.51$ Å.

As follows from the comparison of TG and powder XRD measurements, the temperatures of deintercalation found by these methods can be very different in the case of the guests with high boiling point. This difference is caused by the insensitivity of TG to crystal structure changes which occur during releasing of guest molecules from the interlayer space before their evaporation from the sample.

ACKNOWLEDGMENTS

This work was supported by the Grant Agency of the Czech Republic (Grants 203/97/1321 and 203/97/1010) and by the Academy of Sciences of the Czech Republic, Key Project No. 12.

REFERENCES

1. G. Lagaly, S. Fritz, and A. Weiss, *Clays Clay Miner.* **23**, 45 (1975).
2. G. Lagaly, *Angew. Chem.* **88**, 628 (1976).
3. D. Behrend, K. Beneke, and G. Lagaly, *Angew. Chem.* **88**, 608 (1976).
4. G. Lagaly, *Clay Miner.* **16**, 1 (1981).
5. U. Costantino, *J. Chem. Soc., Dalton Trans.* 1979, 402.
6. A. Clearfield and R. M. Tindwa, *J. Inorg. Nucl. Chem.* **41**, 871 (1979).
7. A. J. Jacobson, J. W. Johnson, and J. T. Lewandowski, *Mater. Res. Bull.* **22**, 45 (1987).
8. K. Beneke and G. Lagaly, *Inorg. Chem.* **22**, 1503 (1983).
9. A. L. Garcia-Ponce, L. Moreno-Real, and A. Jimenez-Lopez, *J. Solid State Chem.* **87**, 20 (1990).
10. L. Beneš, J. Votinský, J. Kalousová, and J. Klikorka, *Inorg. Chim. Acta* **114**, 47 (1986).
11. L. Beneš, R. Hyklová, J. Kalousová, and J. Votinský, *Inorg. Chim. Acta* **177**, 71 (1990).
12. L. Beneš, J. Votinský, J. Kalousová, and K. Handlíř, *Inorg. Chim. Acta* **176**, 255 (1990).
13. L. Beneš, K. Melánová, V. Zima, J. Kalousová, and J. Votinský, *Inorg. Chem.* **36**, 2850 (1997).
14. J. W. Johnson, A. J. Jacobson, W. M. Butler, S. H. Rosenthal, J. F. Brody, and J. T. Lewandowski, *J. Am. Chem. Soc.* **111**, 381 (1989).
15. P. Gendraud, M. E. de Roy, and J. P. Besse, *Inorg. Chem.* **35**, 6108 (1996).
16. "Intercalation Chemistry", M. S. Whittingham and A. J. Jacobson, (Eds.), Academic Press, New York, 1982.
17. G. Lagaly, and K. Beneke, *Colloid Polym. Sci.* **269**, 1198 (1991).
18. G. Lagaly, *Angew. Chem., Int. Ed. Engl.* **15**, 575 (1976).
19. N. G. Chernorukov, N. P. Egorov, and I. R. Mochalova, *Zh. Neorg. Khim.* **23**, 2931 (1978).
20. S. Bruque, M. Martinez-Lara, L. Moreno-Real, A. Jimenez-Lopez, B. Casal, and E. Ruiz-Hitzky, *Inorg. Chem.* **26**, 847 (1987).
21. J. W. Johnson, A. J. Jacobson, J. F. Brody, and S. M. Rich, *Inorg. Chem.* **21**, 3820 (1982).
22. N. G. Chernorukov, N. P. Egorov, and I. A. Korshunov, *Neorg. Mater.* **15**, 335 (1979).
23. A. L. Garcia-Ponce, L. Moreno-Real, and A. Jimenez-Lopez, *J. Incl. Phenom.* **9**, 355 (1990).