JOURNAL OF SOLID STATE CHEMISTRY **116**, 400–405 (1995)

Synthesis, Characterization, and Intercalation of Vanadyl Phosphate Modified with Manganese

Klára Richtrová, Jiří Votinský, and Jaroslava Kalousová

Department of General and Inorganic Chemistry, University of Pardubice, 532 10 Pardubice, Czech Republic

and

Ludvík Beneš and Vítězslav Zima

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

Received July 13, 1994; in revised form November 16, 1994; accepted November 21, 1994

A yellow-brown crystalline solid, stable in air and having a variable composition of $[Mn(H_2O)]_x(VO)_{1-x}PO_4 \cdot 2H_2O$ ($0 \leq x \leq 0.25$), has been prepared by the reaction of solid V_2O_5 with a boiling aqueous solution of H_3PO_4 and $KMnO_4$. The elementary cell of this compound is tetragonal (space symmetry group either *P4/n* or *P4/nmm*) with the following parameters for $x = 0.25$: $a = 0.62034$ nm, $c = 1.3814$ nm, $V = 0.51359$ nm^3, $Z = 4$, $M_r = 199.44$, $D_{calc} = 2.492$ g/cm^3, and $D_{exp} = 2.52$ g/cm^3. The magnetic behavior of this substance indicates the presence of manganese atoms at the oxidation level of III. The paramagnetic centers formed by the Mn^{III} atoms are not markedly magnetically coupled. The structure of the compound is probably derived from the original layered lattice of vanadyl phosphate hydrate $VOPO_4 \cdot 2H_2O$ by replacement of at most one quarter of the vanadyl groups $(V^VO)^{3+}$ by $[Mn^{III}(H_2O)]^{3+}$ groups. Upon being heated, the substance forms a monohydrate at first, then the anhydrous salt forms, and finally the water coordinated with manganese atoms escapes. The compound can be intercalated with foreign molecules and ions in the same way as vanadyl phosphate, and the results of intercalation experiments with methanol, ethanol, 1-propanol, 1-butanol, 1-butylamine, 1-octylamine, formic acid, acetic acid, and pyridine, as well as those of oxidation–reduction intercalation with a solution of sodium iodide in acetone, are presented. The experimental conditions of the intercalations are described. The layered complexes formed have been identified by powder X-ray structure analysis, thermogravimetry, differential thermal analysis, and infrared absorption spectroscopy.

INTRODUCTION

According to our findings, the microcrystalline $VOPO_4 \cdot 2H_2O$ prepared by boiling solid V_2O_5 with an aqueous solution of H_3PO_4 usually contains about 0.1 to 1.5% vanadium at the oxidation level of IV. The formation of V^{IV} is due to the presence of traces of reducing substances in the reaction mixture.

In order to prevent the partial reduction of vanadium during the preparation of vanadyl phosphate dihydrate, we carried out the syntheses with oxidizing agents present in the reaction mixture. Surprisingly, however, the application of $KMnO_4$ did not give vanadyl phosphate without traces of V^{IV} but gave a solid phase with the composition $[Mn(H_2O)]_x(VO)_{1-x}PO_4 \cdot 2H_2O$ ($x = 0$ to $\frac{1}{4}$) instead.

Some time ago we published the results of chemical analysis and diffractometric measurements of this compound (1) (with the limit composition of $[Mn(H_2O)]_{1/4}(VO)_{3/4}PO_4 \cdot 2H_2O$) and we suggested that the substance is formed by the gradual replacement of vanadyl VO^{3+} by $Mn(H_2O)^{3+}$ groups without decomposition or changes in the original structure of $VOPO_4 \cdot 2H_2O$.

The present communication deals with its further characterization and compares the dehydration course and some intercalations of $[Mn(H_2O)]_{1/4}(VO)_{3/4}PO_4 \cdot 2H_2O$ with analogous processes of $VOPO_4 \cdot 2H_2O$.

The compound $VOPO_4 \cdot 2H_2O$ itself is a layered substance with space symmetry group *P4/nmm* (2) or *P4/n* (3). Its structure is formed by layers of $(VOPO_4)_\infty$ built from PO_4 tetrahedra and tetragonal pyramids of VO_5.

Hydrate water molecules are located between these layers. One half of the water molecules are bound to V^V atoms in the $(VOPO_4)_\infty$ layers and complement their coordination to the octahedral coordination. The other half of the water molecules is anchored by H-bridges to $(VOPO_4)_\infty$ layers and to the water bound to vanadium atoms (2).

Heating of the dihydrate brings about its gradual dehydration. If this process is monitored by diffractometry, the presence of monohydrate is proved at about 63°C.

0022-4596/95 $6.00

TABLE 1

Lattice Parameters of Hydrates of Vanadyl Phosphate, Anhydrous Vanadyl Phosphate, and Analogous Manganese-Modified Compounds

	a (nm)	c (nm)	V_{eu} (nm^3)	Z	Ref
$VOPO_4 \cdot 2H_2O$	0.6202	0.7410[a]	0.2850	2	(2)
$VOPO_4 \cdot H_2O$	—[b]	0.63	—	—	(4)
$VOPO_4$	0.62	0.42	0.16	2	(4)
$[Mn(H_2O)]_{1/4}(VO)_{3/4}PO_4 \cdot 2H_2O$	0.6203_4	1.3814	0.5135_9	4	(1)
$[Mn(H_2O)]_{1/4}(VO)_{3/4}PO_4 \cdot H_2O$	0.6204_6	1.2561	0.4835_6	4	
$[Mn(H_2O)]_{1/4}(VO)_{3/4}PO_4$	0.6193	0.4314	0.1655	2	
$(Mn)_{1/4}(VO)_{3/4}PO_4$	—[c]	—	—	—	

[a] The parameter c shows an anomalous course in the temperature interval of 0–45 °C (5), which was elucidated recently using the idea of temperature changes in the arrangement of H-bridges in the layers of hydrate water (6).

[b] The parameter a cannot be determined since the X-ray diffractogram only contains lines of the (001) type.

[c] The diffractogram of the compound was not recorded because the substance changes extremely rapidly into $[Mn(H_2O)]_{1/4}(VO)_{3/4}PO_4$ by accepting water from air.

The anhydrous salt forms the only diffracting phase above 114°C. Differential thermal (DT) and thermogravimetric (TG) measurements do not indicate the moment of water escaping from the layers but only that of water escaping from the sample mass. Hence the DT and TG analyses provide somewhat higher temperatures of 88 and 126°C for the endothermic two-step dehydration (4).

Table 1 presents the lattice parameters of the hydrates and anhydrous substance, from which it follows that the dehydration is connected with the mutual approach of the $(VOPO_4)_\infty$ layers without any change in their structure.

The anhydrous vanadyl phosphate readily accepts the water molecules back to form the hydrates, but it can also intercalate other foreign molecules. An analogous reaction also proceeds with the dihydrate, which accepts the foreign molecules in exchange for water. These methods were adopted to prepare the intercalates of vanadyl phosphate with, e.g., aliphatic alcohols (7–9), amines (10), acids (11), metallocenes (12), pyridine (13), and a number of others.

A very interesting heterogeneous reaction of crystalline vanadyl phosphate is its intercalation upon contact with the acetone solution of an alkali metal iodide (14, 15). The reaction is of an oxidation–reduction nature. The iodide

TABLE 2

The Synthesis and Some Properties of Layered Complexes of Manganese-Modified Vanadyl Phosphate with Selected Molecular Guests and with Sodium Ions

	Condition of synthesis					Lattice parameters		
Guest	Preparation procedure	Temperature (°C)	Time	Denotation of phases	Number of diffraction lines	a (nm)	c (nm)	Temperatures of endothermic decompositions
CH_3OH	U	25	10 days	F1	11	0.6214	2.2690	—
				F2	5	0.622	0.763	100, 160
C_2H_4OH	U	25	10 days	F3	8	0.6211	1.3270	—
	H	25	14 days	F3	6	0.6212	1.3269	—
n-C_3H_7OH	H	25	8 days	F4	8	0.6216	1.4463	—
n-$C_4H_9NH_2$	UA	90	30 hr	F5	3	—	1.64	—
n-$C_8H_{17}NH_2$	UA	150	50 hr	F6	2	—	2.63	—
				F7	2	—	2.38	—
				F8	2	—	2.17	—
HCOOH	H	25	7 days	F9	5	0.6217	0.7209	130
CH_3COOH	H	25	10 days	F10	5	0.6199	0.9083	115, 290
Pyridine	UA	140	15 days	F11	5	0.6221	0.9630	120, 220, 400
Na^{+}[a]	see (16)	40	0.5 hr	F12	14	0.6269	1.3047	125, 150, 420
		40	1.0 hr	F13	12	0.6288	1.3044	130, 155, 420

[a] The intercalation of sodium ions is connected with the reduction of V^V to V^{IV} and oxidation of I^- to I_2.

ions present in the solution transfer electrons to the solid phase, reduce the V^V atoms to V^{IV}, and, at the same time, ions of the alkali metal penetrate between the phosphate layers. The final products are intercalates with the composition $Na_xV^{IV}_xV^V_{1-x}OPO_4 \cdot H_2O$ (16) or $Li_xV^{IV}_xV^V_{1-x}OPO_4 \cdot 2H_2O$ (17).

EXPERIMENTAL

1. Preparations

$[Mn(H_2O)]_{1/4}VO)_{3/4}PO_4 \cdot 2H_2O$ was prepared (with 65% yield) by reaction of 2.4 g solid V_2O_5 (c.p.) with a solution containing 0.82 g $KMnO_4$ (c.p.) (mole ratio V : Mn = 5 : 1), 16 cm^3 H_3PO_4 (p.a., 1.710 g/cm^3, 85 mass%), and 55 cm^3 redistilled water. The reaction mixture was refluxed for 16 hr. The suspension formed was hot filtered. The precipitate was washed with cold water (20 cm^3) and dried under vacuum over P_2O_5 for 3 days.

The anhydrous form of the compound expressed by the formula $Mn_{1/4}(VO)_{3/4}PO_4$ was obtained by complete dehydration under vacuum at 350°C for 3 hr. The product accepts moisture from the air extremely rapidly and changes into another anhydrous salt with coordinated water $[Mn(H_2O)]_{1/4}(VO)_{3/4}PO_4$.

The molecular intercalates were prepared by long-term contact of a crystalline powder of the dihydrate $[Mn(H_2O)]_{1/4}(VO)_{3/4}PO_4 \cdot 2H_2O$ (the preparation procedure is denoted H in Table 2), or its anhydrous form $[Mn(H_2O)]_{1/4}(VO)_{3/4}PO_4$ (denoted U) with the liquid guest at a suitable temperature. In some cases the suspension of dihydrate or anhydrous compound was refluxed in liquid guest (preparative procedure denoted as HB for hydrate or UB for unhydrated host, respectively), or the synthesis was carried in a sealed pressure ampoule (denoted as HA or UA, respectively). In all these preparations, we used the powdered host with a grain size from 0.01 to 0.05 mm.

The intercalates of sodium ions in the manganese-modified vanadyl phosphate were prepared by shaking a suspension of about 0.4 g dihydrate $[Mn(H_2O)]_{1/4}(VO)_{3/4}PO_4 \cdot 2H_2O$ in 20 cm^3 solution of sodium iodide in acetone (0.5 mole/dm^3) at 40°C in a sealed ampoule for either 30 or 60 min. These two oxidation–reduction reaction times gave $Na_{0.380}[Mn(H_2O)]_{1/4}(V^{IV,V}O)_{3/4}PO_4 \cdot 2H_2O$ and $Na_{0.473}[Mn(H_2O)]_{1/4}(V^{IV,V}O)_{3/4}PO_4 \cdot 2H_2O$, respectively.

The aliphatic alcohols (C_1 to C_4), 1-butylamine and 1-octylamine, formic and acetic acids, pyridine, acetone, and *n*-heptane were purified and dried before use by the usual procedures (18) (the water content was decreased below 0.1 mass%).

2. Characterization of Solid Substances

Gravimetric methods were used to determine the content of manganese (as Mn_3O_4), vanadium (as V_2O_5), and phosphorus (as $Mg_2P_2O_7$) in the magnanese-modified vanadyl phosphate. Thermogravimetry was adopted for determination of the water content.

The DT and TG analyses of powdered samples (100 mg) were performed using a Derivatograph C (MOM, Budapest, Hungary) in air between 20 and 900°C at a heating rate of 5 K · min^{-1}.

The density was measured with an automated helium pycnometer (AutoPycnometer 1320, Micromeritics) to ±0.01 g cm^{-3} accuracy.

The powder data were obtained with an HZG-4 X-ray diffractometer (Freiberger Präzisionsmechanik, Germany). The methods of measurement and checking were described in our previous work (1). The nonstable intercalates which release the guest molecules in air were measured as wet substances, i.e., in the presence of an overstoichiometric amount of liquid guest.

Temperature measurements (from 22 to 220°C) were carried out on the heated corundum plate with a thermocouple. The diffractogram was then measured at this temperature which was kept constant. Then the temperature was increased and the procedure was repeated. Each cycle of heating and measuring lasted about 12 min.

The temperature dependence of the magnetic susceptibility was measured with an accuracy of ±1% over the temperature interval 90–300 K using a variable temperature Gouy balance apparatus (Newport Instruments, UK). The values of magnetic molar susceptibility were corrected by means of the Pascal constants. The IR spectra of solid intercalates were measured in Nujol suspensions in the region of 4000–400 cm^{-1} using a Perkin–Elmer 684 spectrometer.

RESULTS AND DISCUSSION

1. Characterization of $[Mn(H_2O)]_{1/4}(VO)_{3/4}PO_4 \cdot 2H_2O$

The title compound was prepared by the procedure given under Experimental and was a fine crystalline yellow-brown powder stable in air. Elemental analysis (MW 199.44): calculated 6.89% Mn, 19.16% V, 15.58% P; found 6.76 ± 0.2% Mn, 19.04 ± 0.3% V, 15.82 ± 0.3% P.

The TG and DT analyses showed that the water is released from the substance in three endothermic steps at 90, 130, and 400°C. The overall mass decrease for the change of $[Mn(H_2O)]_{1/4}(VO)_{3/4}PO_4 \cdot 2H_2O$ into $[Mn(H_2O)]_{1/4}(VO)_{3/4}PO_4$ is 18.07 ± 0.2% (calculated 18.06%). From $[Mn(H_2O)]_{1/4}(VO)_{3/4}PO_4$, the water coordinated to Mn^{III} is released in air at the relatively high temperature of about 400°C and the found mass decrease is 2.10 ± 0.2% (calculated 2.26%).

The X-ray diffractogram of the dihydrate $[Mn(H_2O)]_{1/4}(VO)_{3/4}PO_4 \cdot 2H_2O$ (2θ = 5° to 120°) shows 35 lines (1). They can be assigned the indexes derived from the param-

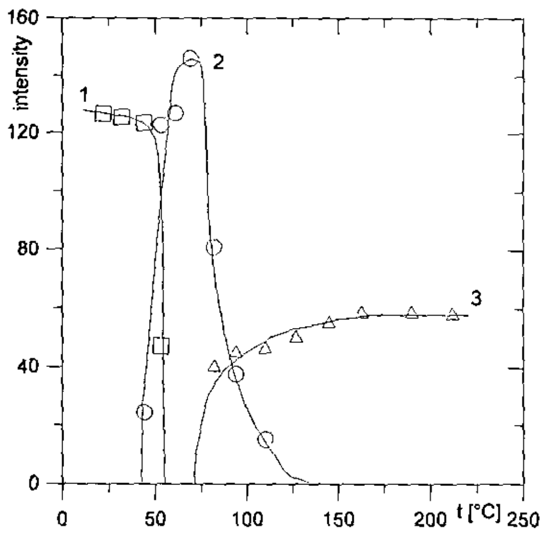

FIG. 1. The changes of integral intensities of basal diffraction lines of (1) dihydrate $[Mn(H_2O)]_{1/4}(VO)_{3/4}PO_4 \cdot 2H_2O$; (2) monohydrate $[Mn(H_2O)]_{1/4}(VO)_{3/4}PO_4 \cdot H_2O$; and (3) anhydrous $[Mn(H_2O)]_{1/4}(VO)_{3/4}PO_4$ during gradual heating to the temperatures from 22 to 212°C.

eters of a single elementary cell. Table 1 gives the cell parameters. Systematic extinction of lines (the absence of (*hk*0) lines fulfilling the condition $h + k = 2n + 1$ and of (*h*00) lines for which it is $h = 2n + 1$) indicates the space symmetry group *P*4/*nmm* or *P*4/*n*. Figure 1 shows changes in the integral intensities of the basal reflexes of all the three phases gradually formed. The line of the dihydrate vanishes at a temperature of 50 to 60°C. The line of the monohydrate $[Mn(H_2O)]_{1/4}(VO)_{3/4}PO_4 \cdot H_2O$ becomes dominant at about 70°C and it disappears at about 120°C. At the same time, beginning from about 100°C, the (001) line due to the compound $[Mn(H_2O)]_{1/4}(VO)_{3/4}PO_4$ can be observed. The above-mentioned temperatures of the transitions of dihydrate $[Mn(H_2O)]_{1/4}(VO)_{3/4}PO_4 \cdot 2H_2O$ into monohydrate $[Mn(H_2O)]_{1/4}(VO)_{3/4}PO_4 \cdot H_2O$ and into the anhydrous compound $[Mn(H_2O)]_{1/4}(VO)_{3/4}PO_4$ are very close to the corresponding temperatures of the dehydration steps of vanadyl phosphate. The apparatus we used to measure the temperature changes in diffractograms did not allow us to reach the temperature of the completely anhydrous phase of $Mn_{1/4}(VO)_{3/4}PO_4$ at about 400°C. The established parameters of cells of monohydrate and anhydrous salt are given in Table 1.

The temperature dependence (90 to 300 K) of reciprocal molar magnetic susceptibility is linear and corresponds to the Curie–Weiss equation. The values of the magnetic moment $\mu = 4.50$ B.M. and the Weiss constant $\theta = -2.7$ K for the compound $[Mn(H_2O)]_{1/4}(VO)_{3/4}PO_4 \cdot 2H_2O$ were obtained from this dependence. Obviously, the paramagnetic centers are the Mn atoms which have replaced the V atoms in the layered structure of $(VOPO_4)_\infty$. The magnetic moment corresponds to the pure spin contribution of four unpaired electrons. It seems likely that manganese is present in the lattice at the oxidation level of III (d^4). At the same time, the small value of the Weiss constant indicates that the paramagnetic centers are only slightly coupled with each other. It seems likely that the manganese-modified vanadyl phosphate retains the original layered structure of phosphate. However, one quarter of the VO^{3+} groups has been replaced by the $[Mn^{III}(H_2O)]^{3+}$ ions.

The introduction of $[Mn^{III}(H_2O)]^{3+}$ ions into vanadyl phosphate has no distinct effect on the temperatures of the two dehydration steps, but it introduces extraordinarily firmly bound water molecules into this structure.

2. *Intercalation of Molecules into the Structure of Manganese-Modified Vanadyl Phosphate*

The newly prepared host was submitted to reactions with selected liquid molecular guests. The preparation procedures used, temperatures, and time of contact of the compounds are listed in Table 2. The results of diffraction measurements of the intercalates prepared and, as the case may be with relatively stable compounds, the results of DT analyses are presented in the same table.

Anhydrous $[Mn(H_2O)]_{1/4}(VO)_{3/4}PO_4$ reacts with methanol to give a solid product of yellow-green color (denoted Fl) which is stable only in the presence of excess liquid CH_3OH. By passing air through the product or washing it with *n*-heptane, another relatively stable substance is formed, which is of yellow-green color (F2). The mass changes accompanying the heating of phase F2 indicate that it is $[Mn(CH_3OH)]_{1/4}(VO)_{3/4}PO_4 \cdot CH_3OH$, which releases one methanol molecule at 100°C and the remaining $\frac{1}{4}CH_3OH$ at 160°C. A comparison of basal spacings of the two phases Fl and F2, indicates that the unstable phase Fl probably has the composition $[Mn(CH_3OH)]_{1/4}(VO)_{3/4}PO_4 \cdot 2CH_3OH$. The basal spacings of both phases indicate that in Fl and F2 there are bimolecular and monomolecular layers of intercalated methanol, respectively.

The contact of anhydrous ethanol with $[Mn(H_2O)]_{1/4}(VO)_{3/4}PO_4$ or $[Mn(H_2O)]_{1/4}(VO)_{3/4}PO_4 \cdot 2H_2O$ leads to formation of a yellow-green substance (F3), which is very unstable unless wetted with excess C_2H_5OH. The increase in basal spacing due to the intercalation corresponds to a change in the volume of the elementary cell by the effective volume of 2 to 2.5 molecules of liquid alcohol; hence the composition of the intercalate F3 could correspond to the formulas $[Mn(C_2H_5OH)]_{1/4}(VO)_{3/4}PO_4 \cdot 2C_2H_5OH$ and $[Mn(H_2O)]_{1/4}(VO)_{3/4}PO_4 \cdot 2C_2H_5OH$.

The complex with 1-propanol (F4) has identical properties and is probably analogous in composition to those of the ethanol intercalate. Interestingly, this complex is formed only in the reaction of 1-propanol with the dihydrate and not in that with the anhydrous salt.

Attempts at intercalation of anhydrous 1-butanol into the new host entirely failed. The only effect of 1-butanol upon the dihydrate was to dehydrate it.

Both the aliphatic amines applied, 1-butylamine and 1-octylamine, intercalate into the new host only very unwillingly. The reaction needs heating to relatively high temperatures and the system must be closed in an ampoule, which is connected with a pressure increase.

1-Butylamine forms a green layered complex with the host (F5), which is unstable in air. The diffractogram of this substance contains only broadened lines of (001) type. The magnitude of the basal spacing of this compound indicates a bimolecular location of 1-butylamine in the van der Waals cavities of the host and the presence of two amine molecules in the formula of the product.

The contact of the host with 1-octylamine resulted in the formation of a three-phase system of solid reaction products (F6–F8). The diffractogram exhibits three pairs of lines of the (001) type corresponding to three values of basal spacing given in Table 2. This result can be interpreted by the presence of three layered complexes differing in amine content and, hence, also in the angle between the octylamine chains and the host layers.

The reaction of dihydrate host with anhydrous formic acid produces a stable pale yellow intercalate (F9) with composition (elemental analysis of C, H, Mn, V, P) corresponding to the formula $[Mn(H_2O)]_{1/4}(VO)_{3/4}PO_4 \cdot HCOOH$. The complex decomposes exothermally after reaching 130°C, giving unidentified gaseous products and a blue melt which is converted into an orange amorphous product upon further heating in air. The placement of acid molecules in the complex is probably monomolecular, judging from the estimated basal spacing.

The dihydrate of host exposed to the action of about a fivefold excess of acetic acid and acetic anhydride (3 : 1) gave the complex $[Mn(H_2O)]_{1/4}(VO)_{3/4}PO_4 \cdot CH_3COOH$ (F10), which endothermally releases acetic acid at 115°C and the coordinated water at 290°C. In this substance also, the acid is placed between the host layers in monomolecular form as indicated by the magnitude of basal spacing.

Both the long-term heating of an anhydrous host with liquid pyridine in a sealed ampoule and the refluxing of a dihydrate host with dry pyridine gave a relatively air-stable brown product (F11) which, however, slowly released pyridine. The thermal decomposition of this substance shows endothermal processes at 120, 220, and 400°C which, according to the mass changes, correspond to releases of $\frac{1}{2}$ C_5H_5N, C_5H_5N, and about $\frac{1}{4}$ H_2O, respectively, per one molecule of the complex. Hence the composition of F11 is most likely represented by the formula $[Mn(H_2O)]_{1/4}(VO)_{3/4}PO_4 \cdot 1.5C_5H_5N$. The basal spacing of the complex indicates that the planar pyridine molecules are located between the host layers perpendicularly to them.

An interesting result is encountered in the IR spectrum of compound F11, showing a band at 1446 cm^{-1} which corresponds to the valence vibration of C–C and C–N bonds of pyridine coordinated with a transition metal ion, as well as a band at 1540 cm^{-1}, which is characteristic of the same vibrations in the pyridinium cations (18, 19). This indicates that, in the complex, some pyridine molecules are bound by a donor–acceptor bond and the remaining ones are protonated and bound electrostatically or by a H-bridge. The reason may lie in the presence of the $Mn^{III}(H_2O)$ groups in the host structure. The respective water molecules can serve as a source of H^+ ions which can protonate a part of the intercalated pyridine molecules.

The valence vibration of vanadyl group τ(VO) was found at 980 cm^{-1} in the complex with pyridine. In the host dihydrate itself this vibration was observed at 1008 cm^{-1}. It is known that the position of this vibration is very sensitive to the basicity of the donor atom which coordinates with the vanadium atom at the *trans* position to the oxygen atom. If the *trans* position is not practically occupied, the valence vibration lies at 1030 cm^{-1}; if this position is occupied by a strong base, the band is shifted as far as the value 975 cm^{-1} (13). Hence, obviously, one water molecule is coordinated to vanadium atom in the host dihydrate, whereas in the intercalate this water molecule is replaced by a pyridine molecule.

The results of intercalations of organic molecules into the new host show that its layered structure accepts these molecules analogously to vanadyl phosphate; nonetheless, several differences are observed.

Methanol in $[Mn(CH_3OH)]_{1/4}(VO)_{3/4}PO_4 \cdot 2CH_3OH$ forms bimolecular layers and enforces an increase in the distance between host layers by 0.703 nm. On the other hand, methanol in $[Mn(CH_3OH)]_{1/4}(VO)_{3/4}PO_4 \cdot CH_3OH$ is placed in a monomolecular arrangement similarly to $VOPO_4 \cdot 1.33CH_3OH$ (8), and the distance between host layers increases by 0.374 nm only.

Methanol is probably the only guest which also replaces the water molecules coordinated with Mn^{III} ions in the new host.

The new host, in contrast to vanadyl phosphate, does not intercalate 1-butanol molecules when the same procedure of synthesis is used. The other two alcohols used, ethanol and 1-propanol, as well as butylamine and octylamine and formic and acetic acids, react with the new host to give structures practically identical with those of vanadyl phosphate.

The considerable stability of the complex of pyridine with the new host is interesting. Pyridine molecules in this complex seem to be bound in two ways: part of them electrostatically (as pyridinium cation, perhaps with additional H-bridge interaction) and the rest coordinatively. A similar phenomenon has already been observed with compounds of this type (13, 20).

3. *Intercalation of Na^+ Ions into the Structure of Manganese-Modified Vanadyl Phosphate*

The oxidation–reduction reaction of manganese-modified vanadyl phosphate with an acetone solution of sodium iodide produces a dark green substance with the formula $Na_{0.473}[Mn(H_2O)]_{0.25}(V^{IV}O)_{0.473}(V^{V}O)_{0.277}PO_4 \cdot 2H_2O$. An early interruption of the intercalation process in our experiments led to an only partial intercalation giving a product with the formula $Na_{0.380}[Mn(H_2O)]_{0.25}(V^{IV}O)_{0.38}(V^{V}O)_{0.37}PO_4 \cdot 2H_2O$. The lattice parameters of both these compounds (denoted as Phases F12 and F13) are given in Table 2. Their diffractograms contain relatively large numbers of very sharp lines which are all generated by a single tetragonal lattice with the given parameters (Table 2) and again with the space symmetry group *P4/nmm* or *P4/n*. The composition of the two phases has been proven by analyzing the content of Na, Mn, V^{IV}, $V^{IV,V}$, P, and H_2O and by estimating the amount of iodine formed in the reaction (which is equivalent to the amount of V^{IV} formed).

The course of this oxidation–reduction intercalation is analogous to that of vanadyl phosphate (14, 15) but with one significant difference. Whereas in the intercalation of vanadyl phosphate with ions of alkali metals the formation of the so-called states (16) was observed connected with more or less regular alternation layers filled with, or free of, sodium ions with molecules of hydrate water, undoubtedly no states are formed during the intercalation of the modified host. The diffractograms of both partially intercalated reaction products exhibit lines of only a single phase. This means that the distribution of guest ions over the host structure is most likely a random one. It is noteworthy that this principal change in the mechanism of intercalation process is brought about by replacing as little as a quarter of the vanadyl groups by manganese atoms.

A mild decrease in basal spacing accompanying the intercalation was observed in the quite similar reaction of $VOPO_4 \cdot 2H_2O$ (14–16). It is caused by the contraction of the thickness of layers of water molecules due to the incorporation of sodium ions into these layers and the therewith connected change in the structure of these layers. Another consequence of the incorporation of sodium ions is the fundamentally stronger linkage to the water molecules manifested by increased dehydration temperatures. The TG and DT analyses of the two partially intercalated samples show almost identical dehydration temperatures of 125 and 130°C (transition to the monohydrate) and 150 and 155°C (formation of anhydrous salt) and an identical temperature of 420°C for the release of water bound to Mn^{III}.

ACKNOWLEDGMENT

This work was financially supported by the Grant Agency of the Czech Republic under Grant 203/93/0157.

REFERENCES

1. L. Beneš, K. Richtrová, J. Votinský, J. Kalousová, and V. Zima, *Powder Diffr.* **8**(2), 130 (1993).
2. H. R. Tietze, *Aust. J. Chem.* **34,** 2035 (1981).
3. M. Tachez, F. Theobald, J. Bernard, and A. W. Hewat, *Rev. Chim. Min.* **19,** 291 (1982).
4. V. Zima, L. Beneš, J. Málek, M. Vlček, *Mater. Res. Bull.* **29,** 687 (1994).
5. M. Konno, T. Okamoto, and I. Shirotani, *Acta Crystallogr. Sect. B* **45,** 142 (1989).
6. P. Čapková, J. Vácha, and J. Votinský, *J. Phys. Chem. Solids* **53**(2), 215 (1992).
7. G. Ladwig, *Z. Anorg. Allg. Chem.* **338,** 266 (1965).
8. L. Beneš, J. Votinský, J. Kalousová, and J. Klikorka, *Inorg. Chim. Acta* **114,** 47 (1986).
9. J. Votinský, L. Beneš, J. Kalousová, and J. Klikorka, *Inorg. Chim. Acta* **126,** 19 (1987).
10. L. Beneš, R. Hyklová, J. Kalousová, and J. Votinský, *Inorg. Chim. Acta* **177,** 71 (1990).
11. L. Beneš, J. Votinský, J. Kalousová, and K. Handlíř, *Inorg. Chim. Acta* **176,** 255 (1990).
12. G. Matsubayashi and S. Ohta, *Chem. Lett.* 787 (1990).
13. J. W. Johnson, A. J. Jacobson, J. F. Brody, and S. M. Rich, *Inorg. Chem.* **21,** 3820 (1982).
14. J. W. Johnson and A. J. Jacobson, *Angew. Chem.* **95,** 422 (1983).
15. A. J. Jacobson, J. W. Johnson, J. F. Brody, J. C. Scanlon, and J. T. Lewandowski, *Inorg. Chem.* **24,** 1782 (1985).
16. R. Šišková, L. Beneš, V. Zima, M. Vlček, J. Votinský, and J. Kalousová, *Polyhedron* **12,** 181 (1993).
17. V. Zima, L. Beneš, R. Šišková, P. Fatěna, and J. Votinský, *Solid State Ionics* **67,** 277 (1994).
18. D. D. Perrin, and W. L. F. Armarego, "Purification of Laboratory Chemicals," 3rd ed. Pergamon Press, Oxford (1988).
19. E. P. Perry, *J. Catal.* **2,** 371 (1963).
20. R. Schöllhorn, H. Zagefka, T. Butz, and A. Lerf, *Mater. Res. Bull.* **14,** 369 (1979).