Intercalates of Vanadyl Phosphate with Branched Alcohols

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Intercalates of $VOPO_4$ with several branched alcohols (2-propanol, 2-methyl-1-propanol, 3-methyl-1-butanol, 4-methyl-1-pentanol, 2-methyl-2-propanol, 2,2-dimethyl-1-propanol, 3,3-dimethylbutanol, 3-methyl-1-pentanol, 2-methyl-1-pentanol, 2-hexanol, 2-ethyl-1-butanol, 2-propyl-1-pentanol) were prepared and characterized by powder X-ray diffractometry and thermogravimetry. Only 2-propanol, 2-methyl-1-propanol and 3-methyl-1-butanol were directly intercalated into vanadyl phosphate dihydrate. The other intercalates were prepared by the displacement of 2-propanol. Gas chromatography of the solid intercalates showed that no mixed intercalates still containing the starting alcohol are formed, except the 4-methyl-1-pentanol intercalate. The arrangement of the guest molecules in the interlayer space of the host is discussed. The alcohols are anchored to the host layers by donor-acceptor bonds between their oxygen atoms and the vanadium atoms of the host structure, and by hydrogen bonding.

Introduction

A number of papers have reported attempts to find the principles governing the structure arrangements of unbranched aliphatic molecules with terminal functional groups during their intercalation into various host structures.[1,2] With this aim the intercalations of, for example, aliphatic alcohols, diols and amines into some natural silicates,[3,4] vanadyl phosphate and sulfate,[5−8] α- and γ-$Zr(HPO_4)_2{\cdot}H_2O$,[9,10] and other similar hosts were investigated.

The reaction of solid $VOPO_4{\cdot}2H_2O$ with liquid or molten 1-alkanols in a microwave field leads to intercalation compounds with the general formula $VOPO_4{\cdot}2C_nH_{2n+1}OH$ ($n = 2-18$).[8] The structure of these polycrystalline layered complexes retains the original layers of $(VOPO_4)_\infty$. The molecules of the alcohols are placed between the host layers in a bimolecular arrangement, and are anchored by donor-acceptor bonds between the oxygen atom of the OH group and the vanadium atom, as well as by hydrogen bonds. The aliphatic chains of the intercalated alcohol molecules possess an *all-trans* configuration and their axes are perpendicular to the host layers.

Little attention has been paid to the intercalation of molecules with branched alkyl chains. The intercalation of 2-butylamine, isobutylamine and neopentylamine into mixed niobyl-vanadyl phosphate was studied.[11] Smaller amounts of 2-butylamine than isobutylamine are intercalated, because of the larger cross-section area. An increase in the molecular volume (neopentylamine) also decreases the amine content. The basal spacing of these amine intercalates is close to that of 1-propylamine and their molecules are arranged in a bimolecular way with their main axis tilted at an angle of 58° with respect to the layer. 2-Propanol, 2-methyl-1-propanol and 3-methyl-1-butanol were intercalated into anhydrous vanadyl sulfate.[6] The basal spacing of these intercalates is very similar to that of the unbranched alcohol with the same length of the main alkyl chain. The content of isoalcohols in the intercalates is lower than that for 1-alkanols.

In this paper the structure of the $VOPO_4$ intercalates with several branched alcohols is discussed.

Results and Discussion

Preparation and Characterization of Intercalates

Only 2-propanol, 2-methyl-1-propanol and 3-methyl-1-butanol were directly intercalated into vanadyl phosphate dihydrate. The intercalates of vanadyl phosphate with other branched alcohols were prepared by displacement of 2-propanol. To exclude the possible formation of a mixed intercalate of 2-propanol with the branched alcohol, an analogous reaction was carried out starting from the 1-propanol intercalate as a precursor. All intercalates are yellow, indicating that vanadium(V) is not significantly reduced. The intercalates of the branched alcohols are distinctly less stable than the intercalates of 1-alkanols,[8] and rapidly decompose in air (relative humidity of 50%) and hydrate to $VOPO_4{\cdot}2H_2O$.

The intercalates prepared are crystalline solids. The diffractograms show a series of sharp (00*l*) reflections (typical diffractograms are shown in Figure 1). The *a* parameter of the tetragonal lattice was determined from the (200) and (201) diffraction lines (Table 1). The same lattice parameter *c* was obtained for the intercalates prepared by displacement of 1-propanol. Gas chromatography of the solid intercalates showed that no mixed intercalates containing starting alcohol were formed, with just one exception (see below). The stoichiometric quotient x_{exp} obtained by the thermogravimetric analysis and several checking analyses of

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carbon and hydrogen contents are given in Table 1, together with the values of x_{calc} calculated as a ratio of the volume of alcohol intercalated and the molar volume of alcohol calculated from its density. The volume of the alcohol intercalated was calculated as a difference between the unit cell volume of the intercalate and anhydrous $VOPO_4$.

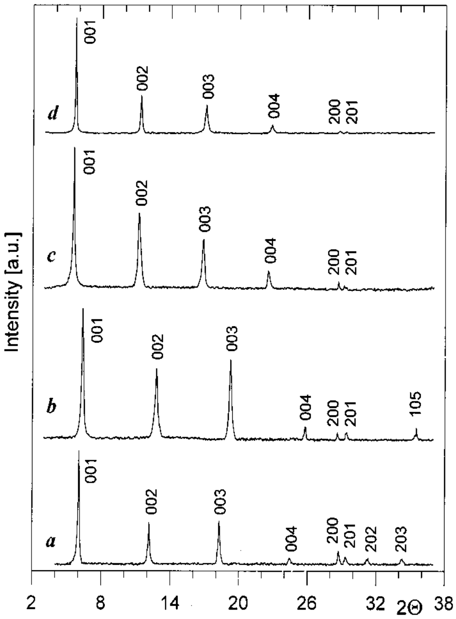

Figure 1. Diffractograms of the $VOPO_4$ intercalates with: (a) 2-methyl-1-propanol, B; (b) 2,2-dimethyl-1-propanol, K; (c) 3,3-dimethyl-1-butanol, J; (d) 2-ethyl-1-butanol, I

Table 1. Lattice parameters and composition of intercalates (mol alcohol/mol $VOPO_4$)

Alcohol	Denotation	a [Å]	c [Å]	x_{exp}	x_{calc}
2-Propanol	A	6.21	13.26	1.45	1.39
2-Methyl-1-propanol	B	6.22	14.58	1.20	1.32
3-Methyl-1-butanol	C	6.21	16.27	1.40	1.29
4-Methyl-1-pentanol	D	6.21	19.67	-	-
3-Methyl-1-pentanol	E	6.21	16.94	1.05	1.20
2-Methyl-1-pentanol	F	6.21	16.80	0.90	1.18
2-Hexanol	G	6.20	16.83	0.95	1.17
2-Propyl-1-pentanol	H	6.21	16.60	1.03	0.93
2-Ethyl-1-butanol	I	6.22	15.64	0.90	1.09
3,3-Dimethyl -1-butanol	J	6.22	15.80	1.05	1.08
2,2-Dimethyl-1-propanol	K	6.20	14.20	0.98	1.06
2-Methyl-2-propanol	L	6.21	12.80	1.00	1.07

The IR spectra of the $VOPO_4$ intercalates shows a ν(V=O) band in the region 1000−1007 cm^{-1}, overlapping the intense bands of the PO_4 tetrahedron. This indicates the presence of a donor-acceptor bond between the oxygen atom of the alcohol and the vanadium atom similar to the bond between the water or 1-alkanol molecules and the host layers.[12,13] Several broad bands in the region from 3600 to 3100 cm^{-1} were found, which could be assigned to a valence vibration of the OH group affected by the interaction of the alcohol with the host lattice.

Suggested Arrangements of Guest Molecules

A set of 12 alcohols with branched aliphatic chains was chosen so as to provide maximum information about the influence of the chain branching on the composition, basal spacing, and stability of the intercalates formed. The structures of the chains are shown in Figure 2. In the following text, the properties of these intercalates are compared with the intercalates of $VOPO_4$ with the 1-alkanols and 2-alkanols studied earlier.[8,15] The influence of the number of the carbon atoms in the main chain on properties of the intercalates is examined. A chain with increasing number of the carbon atoms in a series is considered as the main chain.

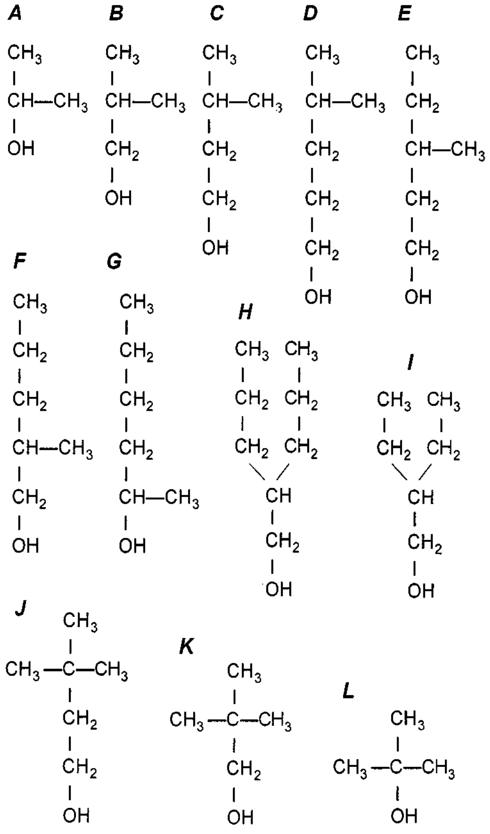

Figure 2. Structure of the guest molecules; see also Table 1

Intercalates with Isoalcohols

With increasing length of the main chain the basal spacing of the intercalates of the first three isoalcohols (A−C) changes linearly, increasing by one carbon atom (1.51 Å) at a time. This increase is equal to 1.28 Å for an unbranched alkyl *all-trans* chain placed perpendicularly to the host layers.[14] It is obvious that the molecules of these three isoalcohols form a bilayer system between the $(VOPO_4)_\infty$ sheets, and their main chains are tilted at an angle $\alpha = 36°$ to the host layers.

The experimental stoichiometric coefficient (TGA) and that calculated from the changes of the volume is ≈1.3 for these intercalates (Table 1). For 3-methyl-1-butanol, $x_{exp} =$

1.4 and $x_{calc} = 1.3$. The free interlayer volume available to 3-methyl-1-butanol in the intercalate is given by

$$V_i = (d - d_H) \times a^2 = 466.24\ \text{Å}^3$$

where d is the basal spacing of the intercalate, d_H is the thickness of the host layer (which is equal to the basal spacing of anhydrous $VOPO_4$), and a is the parameter of the tetragonal layer. The molecular volume of 3-methyl-1-butanol is $V_g = 180.8$ Å^3 (calculated by the ChemSketch program). The theoretical number of the guest molecules which can be placed at one vanadium site is therefore

$$x_{theor} = V_i/(V_g \times Z) = 1.29$$

where $Z = 2$ (number of formula units per cell as found for $VOPO_4{\cdot}2H_2O$).[16] To complement the coordination sphere of every vanadium atom in the host layer to an octahedron, one alcohol molecule should be bonded by a donor-acceptor bond to every vanadium atom. The rest of the alcohol molecules should be bonded by hydrogen bonds only and placed in the cavities among the donor-acceptor-bonded molecules. A similar principle of the guest arrangement was proposed for the intercalate of vanadyl phosphate with propargyl alcohol.[17]

The intercalate with 4-methyl-1-pentanol has a distinctly higher basal spacing than the other three alcohols from this group (see Table 1). Only this intercalate decomposes to a multiphase during drying carried out either by vacuum distillation at 25 °C in an evacuated ampoule or by washing with ether and subsequent blowing with dry nitrogen. The basal spacing is practically the same as that for the 1-pentanol intercalate (19.71 Å),[8] indicating that the guest molecules are roughly perpendicular to the host layers. We can assume that the intercalate prepared is in fact a cointercalate containing 2-propanol or 1-propanol (according to the precursor used) in the cavities among the methyl groups of the 4-methyl-1-pentanol molecules. The presence of 2-propanol or 1-propanol was confirmed by gas chromatography of the hydrolyzate of the wet samples after washing with 4-methyl-1-pentanol; propanol was not found in the hydrolyzate of the dry multiphase product. The decomposition of the sample during drying is connected to the release of the propanol molecules from the intercalate structure.

Intercalates with Alcohols Having Three Methyl Groups at the Terminal Carbon Atom of the Main Chain

Three alcohols were intercalated into $VOPO_4$: 2-methyl-2-propanol (*tert*-butyl alcohol, see structure L in Figure 2), 2,2-dimethyl-1-propanol (K), and 3,3-dimethylbutanol (J). As for the isoalcohols, alcohols with three terminal methyl groups change the basal spacing linearly with increasing chain length in increments of 1.50 Å per carbon atom. This implies that these alcohols are also present in the space in two layers and their main chain is tilted to the host layer at an angle of 36°. The amount of alcohol intercalated was distinctly lower than that for the isoalcohol intercalates and the stoichiometric coefficient is ≈1. This value and the value of the basal spacing allow us to propose a relatively simple arrangement of the alcohol molecules in the interlayer space as depicted in Figure 3.

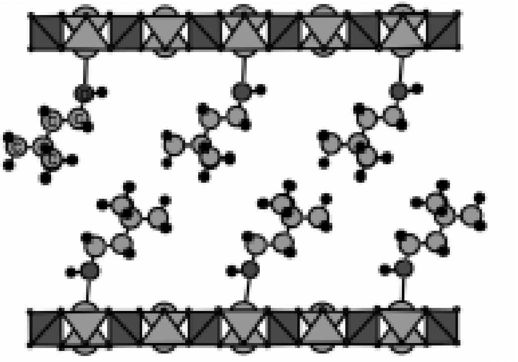

Figure 3. Proposed arrangement of 3,3-dimethyl-1-butanol between the $VOPO_4$ layers viewed in the direction of the *xy* diagonal

From a comparison of the isoalcohol intercalates with this group of intercalates we deduced that the amount of intercalated alcohol was lower for more-branched alcohols; nevertheless the basal spacing and, consequently, the orientation of the main chain with respect to the host layers remained the same.

The Effect of the Position of the Methyl Group in the Main Chain

This effect on the composition and structure was followed in the series 4-methyl-1-pentanol (see structure D in Figure 2), 3-methyl-1-pentanol (E), 2-methyl-1-pentanol (F), and 2-hexanol (which can be considered as "1-methyl-1-pentanol" in the given series, G). As mentioned above, 4-methyl-1-pentanol forms a very unstable cointercalate containing propanol and having a distinctly higher basal spacing. The other three alcohols form intercalates with roughly the same basal spacing and their stoichiometric coefficient x is equal to 1 (see Table 1). A two-layer arrangement of the guest molecules was proposed for the 2-alkanol intercalates, with the guest chain tilted with respect to the host layers at α = 25.6°; this also applies to the 2-hexanol intercalate (see Figure 4).[15] With regard to the similar

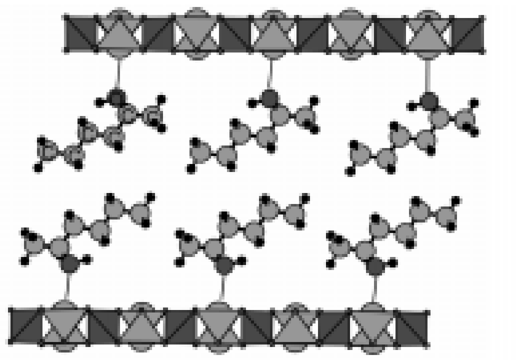

Figure 4. Proposed arrangement of the 2-hexanol molecules between the $VOPO_4$ layers viewed in the direction of the *xy* diagonal

basal spacing, it is very probable that the 2-methyl-1-pentanol and 3-methyl-1-pentanol molecules are found in the interlayer space in a similar arrangement. This means that the position of the methyl group probably does not influence the arrangement of these alcohols in the intercalates. In contrast to 1-pentanol ($x = 2$), which forms a bilayer arrangement with the chains perpendicular to the host layers, there is a significant decrease of the amount of intercalated alcohol ($x = 1$), which is connected to a distinct inclination of the carbon chain. Only a methyl group placed at the end of the long chain allows a perpendicular arrangement as inferred from the higher value of the basal spacing for the 4-methyl-1-pentanol intercalate.

Influence of the Size of Two Identical Alkyl Groups in 2,2-Dialkyl-1-ethanol

Intercalates with 2-methyl-1-propanol (B), 2-ethyl-1-butanol (H), and 2-propyl-1-pentanol (I) were prepared in this series. In contrast to the ethanol intercalate there is a distinct decrease of the stoichiometric coefficient, which is equal to one for the longer alcohols. An arrangement of the 2-propyl-1-pentanol molecules in the interlayer space is proposed in Figure 5. For this alcohol we can consider the heptane chain as a main alkyl chain in the *all-trans* configuration with a -CH_2CH_2OH group (a hydroxyethyl group) bonded to its fourth carbon atom. The hydroxyethyl group is anchored to the host layers by a donor-acceptor bond between the guest oxygen atom and the vanadium atom of $VOPO_4$. The heptane chain is oriented in the direction of the diagonal of the host sheet and is inclined to this sheet at an angle of less than 90°.

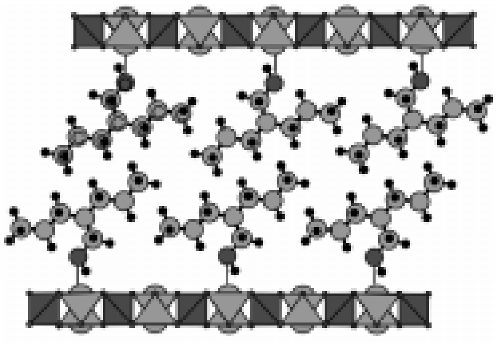

Figure 5. Proposed arrangement of the 2-propyl-1-pentanol molecules between the $VOPO_4$ layers viewed in the direction of the *xy* diagonal

Comparison of Ethanol, 2-Propanol, and *tert*-Butyl Alcohol Intercalates

Whereas the basal spacing of the intercalates of all three alcohols discussed is roughly the same, the stoichiometric coefficient decreases in the series $VOPO_4$·ethanol > $VOPO_4$·(2-propanol) > $VOPO_4$·(*tert*-butyl alcohol), with a value of $x = 1$ for the *tert*-butyl alcohol intercalate. It can be presumed that the molecules of all three alcohols are arranged in two layers in the interlayer space. The decrease of the stoichiometric coefficient with increasing branching is due to steric effects. The molecules of 2-propanol and *tert*-butyl alcohol, anchored by their oxygen atoms to the vanadium atoms of the layers, do not allow other molecules bonded only by the H bonds to fill the space between coordinated molecules as they have larger cross-sections than ethanol.

Experimental Section

Preparation: Intercalates of the isoalcohols were prepared by suspending $VOPO_4 \cdot 2H_2O$ (0.3 g) in dry alcohol (7 mL) and subsequent short exposure (0.5−2 min.) to a microwave field. Intercalates of other branched alcohols were obtained by a displacement reaction. The solid 2-propanol intercalated host was prepared in advance and used as a starting material for the reactions with other alcohols. After cooling, the solid product formed was filtered off. All samples used for X-ray diffraction analyses contained small amounts of the free alcohol. The samples for TG-DTA and elemental analyses were washed with dry ether and dried in nitrogen at room temperature.

Analyses: The TGAs of the intercalates were performed with a Derivatograph MOM (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 the composition was determined by elemental analysis (C, H).

Gas chromatography was used to check whether the intercalates contained starting alcohol (2-propanol or 1-propanol) or not. The sample was washed with an excess of the alcohol intercalated to remove 2-propanol or 1-propanol released by the intercalation. The intercalate was then hydrolyzed in a small amount of water and the hydrolysate was analyzed by GC with a Chrom4 chromatograph (Czech Republic).

X-ray Diffraction Measurements: The powder data of the intercalates with a small excess of the guest alcohol were obtained with an X-ray diffractometer (HZG-4, Germany) using Cu-$K_{\alpha 1}$ radiation ($\lambda = 1.54051$ Å) with removal of the Cu-K_β radiation by a nickel filter. The Cu-$K_{\alpha 2}$ intensities were removed from the original data. Silicon ($a = 5.43055$ Å) was used as the internal standard. Diffraction angles were measured from 1.5° to 37° (2Θ).

IR Spectroscopy: Infrared spectra of the solid intercalates were measured in Nujol suspensions in the region of 4000−400 cm^{-1} using a Perkin−Elmer 684 spectrometer.

Acknowledgments

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