Inorganica Chimica Acta, *177* (1990) 71–74

Intercalation of aliphatic amines into layered structure of vanadyl phosphate

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(Received April 10, 1990; revised June 13, 1990)

Abstract

Layered complexes $VOPO_4 \cdot 2RNH_2$ (R means aliphatic unbranched chain C_1–C_{10}) have been prepared and characterized by their basal spacings, DTA and IR spectra. The observed alternation of the basal spacing increments with the number of the carbon atoms of the chain indicates an oblique arrangement of these chains in the van der Waal's gap.

Introduction

The interaction of various compounds with a layered structure and aliphatic amines leads to the formation of intercalates. This process assumes the interaction of functional groups of guest molecules with a surface of the layers and the gradual opening of the interlayer van der Waal's space into which guest molecules can 'walk in'. Intercalation reactions of the aliphatic amines were first studied for layered materials of the silicate type [1]. The aliphatic chains have a bilayer arrangement in the van der Waal's gap, and the angle between the chain and the plane of the layers increases from 60° for the short chains to 90° for the chains with 16 carbon atoms at least. The arrangement of the aliphatic chains is similar for the intercalates of the amines into the lattice of FeOCl and the basal spacing increments alternation with odd or even numbers of the carbon atoms in the chain is marked [2]. The increase of the basal spacing goes as the drawing of the chain from the odd to the even carbon.

The intercalates, composition of which depends on the number of carbon atoms, were prepared by the reaction of TaS_2 with a complete series of aliphatic amines C_1–C_{18} [3]. For carbon atoms up to 4, *c*-axis expansion remains constant, indicating that the hydrocarbon chains lie parallel to the TaS_2 layers. As the chain length increases in this range, fewer amine molecules per TaS_2 are introduced. For the intercalates of C_5–C_{11} amines the lattice expansions were not precisely determined; for C_{11}–C_{18} amines the lattice parameters indicate a perpendicular orientation of the chains, their bilayer arrangement, and a stoichiometry $TaS_2 \cdot 2/3RNH_2$. The transition from the parallel orientation of the amine chains for C_4 to the perpendicular bilayer of the long chains has been found previously for NbS_2 and TiS_2 [4, 5].

Aliphatic amines from C_4 to C_{16} were intercalated into $NbOPO_4 \cdot 3H_2O$ and $VOPO_4 \cdot 2H_2O$ [6]. The dependence of the basal spacing increase on the number of the carbon atoms is nearly linear and the interlayer distance indicates the angle between the aliphatic chain and the plane of the layer about 60° for the chains up to C_{11}, longer chains having perpendicular orientation. The composition of these intercalates is $XOPO_4 \cdot H_2O \cdot 1.5RNH_2$ (X = V, Nb). The arrangement of the aliphatic chains of the alkylammonium ions into the interlayer space of the clay minerals, hydrated alkali silicates and titanates is also oblique for the chains up to 17 carbon atoms [7]. The dependence of the basal spacing increments on the number of carbon atoms has a pillared character. The basal spacing increases are bigger for the drawing of the chain from the even to the odd carbon atom. The angle between the chain and the layer increases from 56° to 90° with the chain length with chains greater than C_{18} arranged perpendicu-

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0020-1693/90/$3.50

larly. A similar dependence was found for $KNiAsO_4$ in which the 65% potassium interlayer cations are displaced by alkylammonium ions [8].

This paper deals with the intercalation of the unbranched aliphatic amines into the layered tetragonal lattice, $VOPO_4$. The layers of anhydrous $(VOPO_4)_\infty$ are formed from tetrahedrons of PO_4 and tetragonal pyramids of VO_5. The coordination of the vanadium atom is completed to the distorted octahedron by an oxygen atom from the adjacent layer [9]. During the intercalation, the sixth position is occupied by the donor atom of the guest molecule.

Experimental

Anhydrous $VOPO_4$ was prepared by heating $VOPO_4 \cdot 2H_2O$ [10, 11] at a temperature of about 300 °C in vacuum for 4 h. The amines were predried and distilled, their purity was checked by means of gas chromatography. The interaction of anhydrous $VOPO_4$ with an approximately fivefold molar excess of liquid amine was carried out in a closed system under the conditions given in Table 1. The minimum reaction time was checked by means of the disappearance of the diffractional lines of the original material. The solid phase was filtered after intercalation and with a minor surplus of amine was used for the powder diffractional analysis. The samples for IR spectra and DTA were washed with pentane and dried in a stream of air at room temperature for a very short time.

Diffractograms were obtained with an X-ray diffractometer HZG-4 (GDR); basal spacings of the layered lattices of the intercalates were calculated from the most intensive lines (00*l*) reflections [12].

For DTA of the intercalates a Derivatograph MOM (Hungary) was used, the measurements were carried out within 30–700 °C at heating rates of 5 °C min^{-1}. The weight of the samples was 100 mg.

The IR spectra of solid intercalates were measured in Nujol or Fluorolube suspension in the region of 4000–400 cm^{-1} using a Perkin-Elmer 684 spectrometer.

Results and discussion

The intercalates obtained by the direct reaction of anhydrous $VOPO_4$ and aliphatic amines with an unbranched chain C_1–C_{10} were yellow or yellow–green powders. The transition of the colour from yellow to light green is not connected with a basal spacing change. Table 1 indicates that reaction conditions which are necessary for the intercalation reaction, observable by the disappearance of reflection (00*l*) characteristic of the original material, increase with the length of the carbon chain. The isolation of the intercalates was difficult because the amine was liberated by washing and drying. The positions of the maximum of diffraction lines were shifted to higher angles (i.e. to smaller values of the basal spacings) during the intense drying. Therefore the diffractograms were measured on samples containing an excess of amine. In these diffractograms only lines of the type (00*l*) were found, and in agreement with all other papers it was expected that the other lattice parameters were not changed. Basal spacings and

TABLE 1. Preparation conditions, X-ray diffraction data and composition of $VOPO_4 \cdot xC_nH_{2n+1}NH_2$

$C_nH_{2n+1}NH_2$			Preparation conditions		Unit cell parameters			Composition	
n	Melting point (K)	Density ρ_n (g cm^{-3})	Time (min)	T (K)	c (nm)	Number of lines (00*l*)	V_{int} (nm^3)	x_1[a] (X-ray)	x (DTA)
1	179.5	0.792	5	240 max.	1.0903	3	0.422	2.02	
2	189	0.800	30	280	1.3523	3	0.523	1.95	
3	190	0.826	120	293	1.4593	4	0.564	1.70	
4	222.5	0.810	20	293	1.833	4	0.709	1.84	1.92
5	217.5	0.820	300	293	1.980	3	0.766	1.78	2.09
6	254	0.797	180	293	2.291	8	0.886	1.72	1.95
7	250	0.821	30	333	2.431	3	0.941	1.72	2.16
8	272	0.825	60	333	2.771	7	1.073	1.86	1.82
9	270	0.827	120	333	2.916	5	1.129	1.68	2.18
10	288	0.951	15	373	3.171	5	1.227	1.94	1.92

[a] $x_1 = \dfrac{V_{int} - V_{VOPO_4}}{2V_n}$; $V_{VOPO_4} = a^2c = 0.620^2 \times 0.411 = 0.158$ nm^3; $V_n = \dfrac{M_n}{\rho_n N_A}$ where M_n = mole weight of amine, ρ_n = density at m.p., N_A = Avogadro constant.

the number of the (00*l*) lines are also presented in Table 1.

The dependence between the basal spacings and the numbers of carbon atoms *n* in the aliphatic chain is given in Fig. 1. The basal spacings increase by about 0.14 nm drawing the chain from n = even to $n+1$ and by about 0.31 nm from n = odd to $n+1$. This alternation leading to the pillared curve agrees with similar dependences of the intercalates of aliphatic alcohols [10, 11] and acids [12]. It indicates an oblique arrangement for the chains. The dotted line in Fig. 1 was calculated for a perpendicular bilayer orientation of the chains with respect to the host layers from the known values of the bond lengths and van der Waal's radii of hydrogen atom. The dashed line was calculated for the location of two layers of the amine molecules forming an angle of 55°. The solid line corresponds to the experimental values and indicates an oblique arrangement of the aliphatic chains. It demonstrates that the angle between the chain and the plane of the host layers increases with the number of carbon atoms.

The unit cell volumes of the intercalates (Table 1) were calculated from the lattice parameters *c* of the intercalates prepared and from the parameter $a = 0.622$ nm [9] of $VOPO_4 \cdot 2H_2O$. The volume of the amine intercalated was calculated as the difference between the unit cell volume of the intercalate and anhydrous $VOPO_4$ ($V = 0.158$ nm^3, $a = 0.620$ nm, $c = 0.411$ nm [10]). The number of the amine molecules *x* belonging to the one formula unit $VOPO_4$ was determined as a ratio of this difference and the molar volume of the amine, which was calculated from its density at the melting points. These calculations take into account that one unit cell contains two formula units $VOPO_4$. Some densities at the melting point were obtained by graphic extrapolation from values tabelled at the higher temperatures. The composition calculated from the lattice parameters leads to the stoichiometric formulas from $VOPO_4 \cdot 1.68RNH_2$ to $VOPO_4 \cdot 2.02RNH_2$.

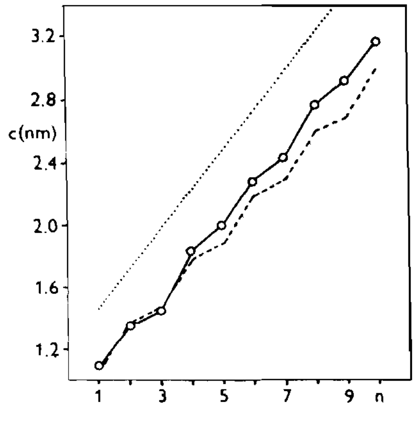

Fig. 1. Dependence of basal spacing *c* on the numbers *n* of carbon atoms in the aliphatic amine intercalated: dotted line = bilayer perpendicular orientation of the chains; dashed line = bilayer oblique orientation of the chains with an angle between the chain and the layers of 55°; solid line = experimental values.

The compositions of the intercalates were verified by means of DTA for the intercalates of the amines with the aliphatic chain containing more than four carbon atoms. These results are given in Table 1.

IR spectra of the intercalates do not permit unambiguous conclusions because the intensive bands of the PO_4 tetrahedron overlap the frequency region of the VO group. However, the characteristic bands of PO_4 ν_1 at 938 cm^{-1}, ν_3 at 1017 cm^{-1} and ν_4 at 567 cm^{-1} were found in the spectra of anhydrous $VOPO_4$. The band at 975 cm^{-1} was assigned to the V–O–V group forming a transversal connection of layers in anhydrous $(VOPO_4)_\infty$. This band disappeared or its intensity decrease was considerable in the spectra of all intercalates due to the increase of the interlayer distance. The new band in all spectra at about 1080 cm^{-1} was assigned to the valence vibration ν (C–N). The bands of the deformation vibrations NH_2 within the regions 840–810 and 740–725 cm^{-1} could be found in all spectra.

The wavenumbers of antisymmetric (3215–3180 cm^{-1}) and symmetric (3170–3142 cm^{-1}) valence vibrations of the NH_2 group are shifted downfield when compared to the regions of measured liquid amines (3395–3362 and 3327–3312 cm^{-1}) indicating stronger anchoring of the NH_2 group to the vanadium atom at the sixth position of the distorted octahedron than by hydrogen bridges in liquid amines. Since both the amine molecules in $VOPO_4 \cdot 2RNH_2$ cannot anchor at the vanadium atom of the VO_5 moiety assuming hexacoordinated vanadium, the bands in the regions of 3360–3340 and 3300–3280 cm^{-1} belong most probably to the interaction of the amine with the host lattice realized by the hydrogen bonding between oxygen atoms of the host lattice and hydrogen atoms from the NH_2 group of the amine molecules.

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