Layer-type Complexes Consisting of $VOSO_4$ or $VOPO_4$ and Aliphatic Alcohols

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Abstract

The intercalates of unhydrated $VOSO_4$ and $VOPO_4$ with alcohols (C_1 to C_8) have been prepared and characterized by their compositions, basal spacings and thermal stabilities. X-ray powder studies show that the layered structures of $VOSO_4$ and $VOPO_4$ lattices are maintained in these complexes. The alcohol molecules are penetrated into van der Waal's gaps of the host lattices and form bimolecular layers. The observed alternation of the basal spacing increments with the number of carbon atoms of the linear aliphatic chain is explained from the arrangement of these chains.

Introduction

Intercalation of various molecules into inorganic layered structures leads to new materials with interesting properties. The structure of $VOSO_4$ [1] and the isostructural α_1-$VOPO_4$ [2, 3] is shown in Fig. 1; the layer structure is maintained in the hydrates. This was demonstrated by determining the structure of $VOPO_4 \cdot 2D_2O$ [4] and $VOPO_4 \cdot 2H_2O$ [5].

Ladwig [6] showed that water molecules could be substituted by ethyl alcohol or butylamine in the hydrates $VOPO_4 \cdot nH_2O$. Beneke and Lagaly [7] prepared intercalates by exchanging water molecules with aliphatic amine; their structure was determined from powder diffractograms. The hydrates $VOSO_4 \cdot nH_2O$ and the anhydrous $VOSO_4$ react with aliphatic alcohols, pyridine, 4,4′-bipyridine and 4-phenylpyridine [8, 9] in similar way.

The intercalation of alcohols or amine molecules into $VOPO_4$ or $VOSO_4$ can be explained by structural considerations (Fig. 1). Sulphur or phosphorus atoms have a tetrahedral coordination of oxygen. Vanadium atoms are surrounded by five oxygen atoms in square pyramidal coordination. In anhydrous compounds, the coordination number six is reached by an approaching of the adjacent layers. Each axial oxygen atom in the square pyramid around the vanadium atom completes the coordination polyhedron of the layer adjacent to the distorted octahedron. The approaching of the oxygen atoms of the adjacent layers is shown in Fig. 1 (marked with dotted darts). During intercalation, the distance between the layers of the primary lattice is increased and the sixth position in the octahedron is occupied by the donor atom. It is in this way that half of the D_2O molecules in $VOPO_4 \cdot 2D_2O$ [4] are arranged. The remaining molecules are freely movable in the van der Waal's gap. The structure of the layered phosphates intercalated by various molecules may be arranged in an analogous manner.

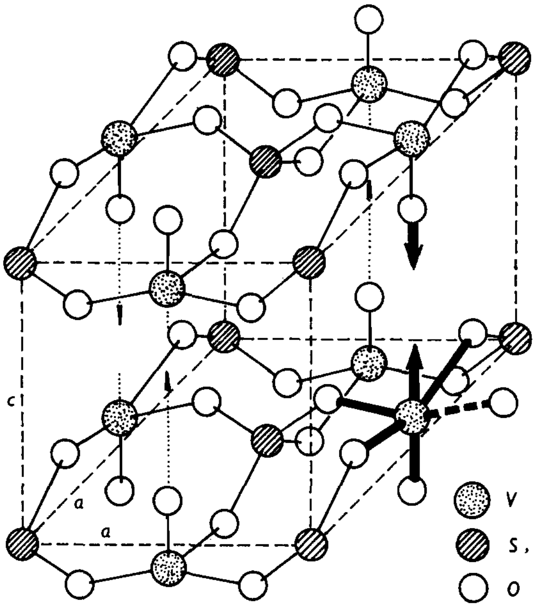

Fig. 1. Schematic view of the structure of $(VOSO_4)_\infty$ or $(VOPO_4)_\infty$ layers.

Experimental

$VOSO_4 \cdot 2H_2O$ was prepared by reaction of V_2O_5 with H_2SO_4 in aqueous solution and with SO_2 as reduction agent [10]. $VOPO_4 \cdot 2H_2O$ was prepared by reaction of V_2O_5 with H_3PO_4 [6]. Dried alcohols were distilled immediately prior to use.

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TABLE I. Preparation Conditions, Composition and X-ray Diffraction Data of $VOSO_4 \cdot nC_qH_{2q+1}OH$ Complexes

Alcohol	Preparation conditions		Composition n	Decomposition temperature T_{decomp} (K)	Unit cell parameters			Number of lines hkl and $(00l)$
	T (K)	time (h)			a (nm)	$c = c_q$ (nm)	V (nm^3)	
–	–	–	0	–	0.626	0.410	0.161	[a]
CH_3OH	298	10 (l)	1.33	–	0.635	0.804	0.324	3(2)
	303	24 (g)						
CH_3CH_2OH	298	10 (l)	2	–	0.634	1.284	0.516	4(3)
	303	24 (g)						
$CH_3(CH_2)_2OH$	303	24 (l)	2	–	0.635	1.442	0.582	5(4)
$(CH_3)_2CHOH$	323	24 (l)	1.75	–	0.634	1.333	0.536	5(4)
	313	48 (g)						
$CH_2{=}CHCH_2OH$	298	24 (l)	2	389	0.635	1.473	0.594	6(4)
$CH_3(CH_2)_3OH$	313	24 (l)	2	–	0.635	1.777	0.712	5(4)
$(CH_3)_2CHCH_2OH$	298	48 (l)	1.75	–	0.635	1.483	0.597	8(4)
$CH_3CH{=}CHCH_2OH$	298	36 (l)	2	–	0.634	1.831	0.736	7(5)
$CH_3(CH_2)_4OH$	323	12 (l)	2	–	0.634	1.965	0.790	6(5)
$(CH_3)_2CH(CH_2)_2OH$	323	16 (l)	1.75	440	0.634	1.715	0.689	6(5)
$CH_3(CH_2)_5OH$	393	4 (l)	2	494	0.633	2.248	0.901	7(5)
$CH_3(CH_2)_6OH$	403	4 (l)	2	503	0.634	2.457	0.988	11(7)
$CH_3(CH_2)_7OH$	413	12 (l)	2	491	0.634	2.763	1.111	8(7)

[a] See refs. 1, 4. (l) = liquid alcohol, (g) = vapour of alcohol.

TABLE II. Preparation Conditions, Composition and X-ray Diffraction Data of $VOPO_4 \cdot nC_qH_{2q+1}OH$ Complexes

Alcohol	Preparation conditions		Composition n	Unit cell parameters			Number of lines hkl and $(00l)$
	T (K)	time (h)		a (nm)	$c = c_q$ (nm)	V (nm^3)	
–	–	–	0	0.620	0.411	0.158	[a]
CH_3OH	298	24 (l)	1.33	–	0.785	–	4(4)
	303	120 (g)					
CH_3CH_2OH	298	24 (l)	2	0.622	1.317	0.510	16(9)
	303	48 (g)					
$CH_3(CH_2)_2OH$	323	16 (l)	2	–	1.440	–	4(4)
$CH_3(CH_2)_3OH$	333	16 (l)	2	–	1.796	–	5(5)

[a] See ref. 4. (l) = liquid alcohol, (g) = vapour of alcohol.

Anhydrous $VOSO_4$ and $VOPO_4$ were prepared from $VOSO_4 \cdot 2H_2O$ and $VOPO_4 \cdot 2H_2O$ by heating at 573 K in vacuum for 4h. The reactions of the anhydrous compounds with an excess of liquid alcohol were carried out in glass ampullae. For the reactions with sufficiently volatile alcohols, another method was used. The anhydrous host compound was exposed to vapours of alcohols in a sealed evacuated glass double-ampullae. The temperature gradient of 5 K between the reaction vessel and the alcohol reservoir prevented the product from being moistened by alcohol vapour. The experimental conditions of both methods are given in Tables I and II.

The composition of the complexes was determined from the weight changes connected with the intercalation reaction and the elementary analysis of the dry products (determination of V, C, H). All operations were carried out in dry inert gas because of the sensitivity of the complexes and the anhydrous host compounds to moisture.

The powder data of the intercalates with a minor surplus of the guest alcohol were obtained with an X-ray diffractometer (HZG-4, GDR) using Cu Kα radiation (λ = 0.15418 nm for the angles $2\theta < 35°$) and Cu Kα_1 (λ = 0.15405 nm, for $2\theta > 35°$) with discrimination of the Cu K_β radiation by a Ni-filter. Silicium (a = 0.543055 nm) was used as internal standard. Diffraction angles were measured from 4° to 90° (2θ). The obtained data were refined by the least squares programme minimizing $(2\theta_{exp} - 2\theta_{cal})^2$.

TABLE III. Basal Spacing Increments of $VOSO_4$ and $VOPO_4$ after Intercalation of Unbranched Alkanols.

Formula	Number of carbon atoms in the chain q	Basal spacing increments Δc_q (nm)	
		q = even to q + 1	q = odd to q + 1
$VOSO_4 \cdot 2C_qH_{2q+1}OH$	1[a]	(0.480)	
	2		0.158
	3	0.335	
	4		0.188
	5	0.283	
	6		0.209
	7	0.306	
	8		
$VOPO_4 \cdot 2C_qH_{2q+1}OH$	1[a]	(0.532)	
	2		0.123
	3	0.356	
	4		

[a] Number of methanol molecules in the formula is n = 1.33.

Thermal decompositions of complexes were measured with Derivatograph MOM (Budapest) within 300–700 K and with heating rates of 5 K min^{-1}. The weight of the sample was 100 mg.

Results and Discussion

The composition of the complexes $VOSO_4 \cdot n$ROH and $VOPO_4 \cdot n$ROH is shown in Tables I and II. All $VOSO_4 \cdot n$ROH complexes are light blue in colour and are very fine crystalline compounds. The alcohols are readily liberated in air and are replaced with water. Thermal decomposition liberates the alcohol at one distinct temperature, and the original host structure is produced. The decomposition temperatures of some intercalates are given in Table I. The complexes $VOPO_4 \cdot n$ROH are yellow–green, microcrystalline compounds with extreme sensitivity to humidity. No alcohols longer than C_4 can be intercalated. The lattice parameters *a* and *c* for hexagonal unit cells of the alkanol complexes are given in Tables I and II. These tables also give the number of (*hkl*) and (00*l*) reflections.

The distance between the adjacent layers $c_q - c_o$ (c_q, basal spacing of the alkanol complexes, c_o, basal spacing of the anhydrous $VOPO_4$ or $VOSO_4$) varies with the number of carbon atoms q in the alkyl chain ($CH_3(CH_2)_{q-1}OH$, q = 1 to 8), as shown in Fig. 2. The increase of the basal spacing alternates regularly according the relationship

$$c_q - c_{q-1} < c_{q+1} - c_q \text{ with } q = 2r + 1, r = 0, 1, 2, \ldots n.$$

The basal spacings increase by about 0.32 nm from q = even to q + 1 (except methanol) and by about 0.17 nm from q = odd to q + 1 (Table III).

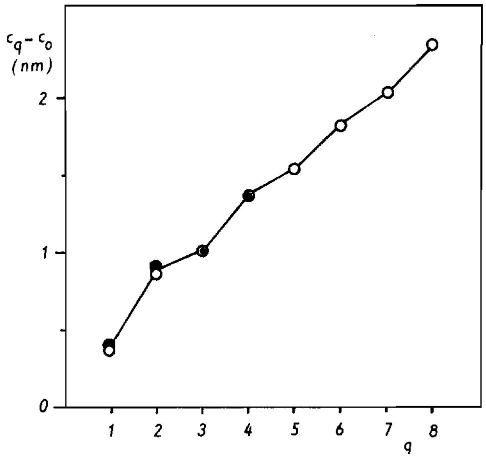

Fig. 2. Basal spacing increments ($c_q - c_o$) of $VOSO_4 \cdot nC_qH_{2q+1}OH$ (○) and $VOPO_4 \cdot nC_qH_{2q+1}OH$ (●) with number of carbon atoms in the alkyl chain.

The increase of the lattice parameter *c* after intercalation of the alcohols into $VOSO_4$ and $VOPO_4$ is so large that it can only be accounted for by a bilayer arrangement of the alcohol molecules. Our results are in agreement with the suggestion [9, 11–13] that the aliphatic chains are arranged perpendicularly, or nearly perpendicularly, to the layers of the host compounds.

Most of the intercalated samples have the composition $VOSO_4 \cdot 2ROH$ and $VOPO_4 \cdot 2ROH$. Four alcohol molecules are therefore bonded both sides of the layer, with area a_o^2 = 0.402 nm^2. The unit cell contains four molecules of ROH and two $VOSO_4$ or $VOPO_4$ formula units.

When alcohols with a branched aliphatic chain are intercalated, the molar ratio of the alcohol to the most material is reduced ($n = 1.75$). This is obviously caused by sterical reasons. The complexes of $VOSO_4$ and $VOPO_4$ with methanol show the lowest content of alcohol ($n = 1.33$). The basal spacing indicates a monolayer of methanol molecules. Their alternate orientation to the vanadium atoms in the adjacent layers is conceivable.

The found alternation of the basal spacing increments with the number carbon atoms of the aliphatic chain results from the arrangement of these chains in the van der Waal's gap. Similar alternations were found for layered complexes of the aliphatic amines [11] and were also explained by the chain arrangement [9]. In accordance with ref. 9, we suppose the arrangement of the alcohol molecules in our systems to be as in Fig. 3a. The angle of the bonds $C_2–C_3$, $C_4–C_5$ ... with a plane parallel to the layer is about 20°; the bonds $C_1–C_2$, $C_3–C_4$ ... are perpendicular to the layers. The arrangement of the aliphatic amine molecules in intercalates [9] is shown in Fig. 3b. The different arrangement of the carbon chains in Fig. 3a and 3b results in the different dependence of the basal spacing increments with the carbon number for these two systems.

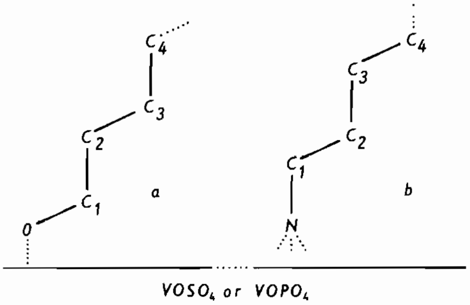

Fig. 3. Orientation of C–C bonds in layer-type complexes of alcohols (a) and amines (b).

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