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Intercalation of aliphatic carboxylic acids into layered structures of vanadyl sulfate, phosphate and arsenate

L. Beneš, J. Votinský, J. Kalousová and K. Handlíř

Joint Laboratory of Solid State Chemistry of Czechoslovak Academy of Sciences and Institute of Chemical Technology, 532 10 Pardubice (Czechoslovakia)

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Abstract

Layered complexes $VOSO_4 \cdot RCOOH$, $VOPO_4 \cdot RCOOH$ and $VOAsO_4 \cdot RCOOH$ (RCOOH means formic, acetic, propionic and butyric acids) have been prepared. The complexes are formed either by the intercalation reaction of the anhydrous host lattice of $VOXO_4$ (X = S, P, As) with liquid carboxylic acids or by exchange reactions of the hydrates $VOXO_4 \cdot nH_2O$ ($n = 2$ or 3) or of the intercalates $VOXO_4 \cdot 2C_2H_5OH$ with the acids in the presence of a dehydrating agent. For all the complexes prepared the heat stability, products of temperature decomposition, the lattice parameters (determined by means of X-ray diffraction) and IR spectra are presented. A probable structure of the complexes and the way of location and anchoring of the intercalated acid molecules between the host layers are suggested.

Introduction

Hydrates of vanadyl sulfate, phosphate and arsenate form a group of isomorphous substances of general formula $VOXO_4 \cdot nH_2O$ (X = S, P, As; $n = 2$ or 3). The substances have a tetragonal layered structure. It is reasonable to presume that their layers $(VOXO_4)_\infty$ are formed by condensation of tetragonal pyramids, VO_5 with the tetrahedrons of XO_4 [1]. Between the layers, in the van der Waals zones, water molecules are bound. Each tetragonal pyramid of VO_5 is completed by a water molecule bound to the vanadium atom in a deformed octahedron. Further water molecules assume crystallographically nonspecified positions between the $(VOXO_4)_\infty$ layers [2]. The mentioned hydrates have a character of layered complexes–intercalates.

The guests (not very firmly bound) of these substances can also be compounds other than water. Such a role can be played, for example, by molecules of organic compounds if they penetrate between the layers of an anhydrous host or if they displace water from its hydrate. So far in this way complexes of $VOXO_4$ with aliphatic alcohols [3, 4], amines [5, 6], pyridine [7] and ferrocene [8] have been prepared and characterized.

Interesting results are obtained from an investigation into the way the aliphatic chains of the organic molecules are located between the host layers. Since the layered complexes can only be prepared in powder form, it is impossible to determine their complete structure by X-ray diffraction. Therefore the position of the chains with respect to the host layers in the intercalates with aliphatic molecules are inferred from the value of their basal spacing or, as the case may be, more conclusively from the dependence of basal spacing of a series of homologous complexes of the same host on the number of carbon atoms in the guest chains [3, 6, 9].

An oblique arrangement of chains was found in this way for complexes of $VOSO_4$ and $VOPO_4$ with aliphatic alcohols and amines, respectively [3, 6], the chain axis forming an angle of about 55° with the host layers. Oblique location of chains in intercalates was also found with other hosts and it is even found in monomolecular layers of aliphatic compounds formed by adsorption on a phase interface [10].

This present report gives results of studies of intercalation of aliphatic carboxylic acids into the above-mentioned three hosts.

Experimental

$VOSO_4 \cdot 2H_2O$ was prepared by reaction of solid V_2O_5 suspended in aqueous sulfuric acid with gaseous SO_2 [11].

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$VOPO_4 \cdot 2H_2O$ and $VOAsO_4 \cdot 3H_2O$ were obtained by long-term boiling of V_2O_5 suspensions in aqueous phosphoric and arsenic acids, respectively [12].

The anhydrous compounds $VOSO_4$, $VOPO_4$ and $VOAsO_4$ were prepared by dehydration of the corresponding hydrates at a temperature of about 300 °C in vacuum for 4 h.

Commercial samples of the carboxylic acids were distilled with a small amount of phosphorus pentoxide before use. Formic acid and the acid anhydrides used were only distilled without P_2O_5.

Five variants were examined for the preparation of intercalates in all the systems studied:

A. Reaction of anhydrous $VOXO_4$ with an about threefold molar excess of liquid (100%) carboxylic acid at room temperature or at enhanced temperatures (up to the boiling point of the acid).

B. Reaction of the hydrate $VOXO_4 \cdot nH_2O$ with liquid carboxylic acid under conditions similar to A.

C. Reaction of the hydrate $VOXO_4 \cdot nH_2O$ (h) with a mixture of carboxylic acid (a) and its anhydride (aa) in the molar ratio h:a:aa = 1:3:2 at room temperature or higher temperatures, the anhydride acting as a dehydrating agent.

D. Extraction of the hydrate $VOXO_4 \cdot nH_2O$ in Soxhlet apparatus in the presence of a dehydrating agent (phosphorus pentoxide) added into the distillation flask. The molar ratio of the components placed into the apparatus was h:a:P_2O_5 = 1:10:2.

E. Reintercalation reaction of $VOXO_4 \cdot 2C_2H_5OH$ with liquid carboxylic acid at room temperature (molar ratio of the components 1:3). The starting intercalate was obtained by several hours contact of anhydrous $VOXO_4$ with excess liquid ethanol [3].

The powder data of the intercalates were obtained with an X-ray diffractometer (HZG-4, G.D.R.) using Cu $K\alpha$ ($\lambda = 0.15418$ nm for the angles $2\theta < 35°$) and Cu $K\alpha_1$ ($\lambda_1 = 0.15405$ nm, for $2\theta > 35°$) radiation. Silicon ($a = 0.543055$ nm) was used as internal standard. The obtained data were refined by the least-squares programme minimizing $(2\theta_{exp} - 2\theta_{cal})^2$. Basal spacings of the layered lattices of the intercalates were calculated from the most intensive 001 reflections and the parameter *a* from weak *hkl* reflections.

The samples containing – according to the X-ray analysis mentioned – a single diffracting phase were washed with acetone, dried, and submitted to differential thermal and thermogravimetric analyses. For the DTA and TGA of the complexes we used a Derivatograph MOM (Hungary). The measurements were carried out within 20–600 °C at heating rates of 5 °C min^{-1}. The weight of the samples was 100 mg; atmosphere N_2 or air.

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

The attempts at preparation of the complexes by the procedures A–E showed that the intercalates of all the three hosts are formed the most easily (and are the purest ones) with formic acid. For these syntheses the best suited procedures were A or B which consist in direct reaction of the anhydrous host or its hydrate with excess liquid carboxylic acid.

The complexes with formic acid have the composition corresponding to the formula $VOXO_4 \cdot HCOOH$ (X = S, P, As). Their thermal decomposition produces the corresponding anhydrous salt $VOXO_4$. The decomposition of $VOSO_4 \cdot HCOOH$ represents an exception, giving VO_2 and V_2O_5 under nitrogen and in air, respectively.

The complexes with acetic acid are prepared less easily. Procedure A cannot be applied, since the components do not react, and procedure B cannot be used either, since the equilibrium of the exchange reaction of hydrate with carboxylic acid is shifted towards the side of the hydrate. Other suitable procedures are those adopting a dehydration agent or the reintercalation reaction of $VOXO_4 \cdot 2C_2H_5OH$ with excess carboxylic acid. The analysis proved the composition of the products expressed by the formula $VOXO_4 \cdot CH_3COOH$, and this composition was also verified thermogravimetrically. Thermal decomposition of all three complexes gives the corresponding anhydrous salts and releases acetic acid.

Higher carboxylic acids enter the layers of the hosts very unwillingly. Only in the system $VOPO_4 \cdot 2H_2O$–propionic acid did we succeed in preparing the pure intercalate $VOPO_4 \cdot C_2H_5COOH$ by procedure D. In the other systems (i.e. vanadyl sulfate or arsenate with propionic acid) the intercalates are formed but contain admixtures of other phases (hydrates or anhydrous salts). In these systems the content of intercalates was below 50 mass % of the solid phase. Due to their lability the complexes cannot be recrystallized and thus prepared in pure form, and their existence is only inferred from diffractographic measurement. Butyric acid could only be intercalated into the layered lattice of $VOPO_4$, and the attempts at preparation of the complexes with still higher carboxylic acids failed.

Table 1 presents a survey of results of preparation of the intercalates and characterization of the complexes. The first column gives the procedures leading to formation of the complex in very pure form or (in brackets) the procedure giving the re-

TABLE 1. Some properties of the $VOXO_4 \cdot RCOOH$ complexes

Host	Guest	Preparation procedure	Decomposition temperature (°C)	Lattice parameter		Increment Δc (nm)
				a (nm)	*c* (nm)	
$VOSO_4$				0.626	0.410 (c_0)	
	HCOOH	A	140, 235	0.635	0.709	0.299
	CH_3COOH	E	170	0.635	0.888	0.478
	n-C_2H_5COOH	(E)		0.635	0.914	0.504
$VOPO_4$				0.620	0.411 (c_0)	
	HCOOH	B	170	0.621	0.719	0.308
	CH_3COOH	C	190	0.622	0.896	0.485
	n-C_2H_5COOH	D	250	0.623	0.937	0.526
	n-C_3H_7COOH	(D)		0.622	1.142	0.731
$VOAsO_4$				0.633	0.418 (c_0)	
	HCOOH	B	150	0.635	0.724	0.306
	CH_3COOH	C	215	0.636	0.901	0.483
	n-C_2H_5COOH	(D)		0.635	0.922	0.505

latively purest product. The second column of Table 1 gives the temperatures of endothermic decompositions of the complexes to give the anhydrous host and carboxylic acid. The already mentioned anomalous decomposition of the $VOSO_4 \cdot HCOOH$ complex under inert atmosphere is characterized by two endothermic processes.

The diffractograms of all the intercalates prepared are characterized by the presence of sharp and intensive 00*l* lines and weak to very weak *hkl* lines. The third and fourth columns of the Table present the *a* and *c* parameters determined from the diffractograms for the tetragonal elementary cells of the complexes. The slight changes in parameter *a* and, on the other hand, the distinct increase in basal spacing *c* which accompanies the entering of carboxylic acid into the structure of the anhydrous host give evidence in support of the layered nature of the complexes formed. The fifth column of Table 1 presents the increments Δc in the basal spacing calculated as the difference between the lattice parameter *c* of the intercalate and c_0 of the anhydrous host.

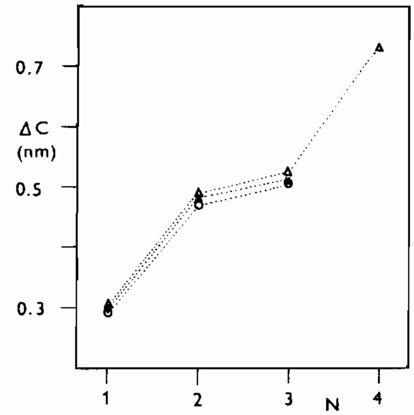

Fig. 1. Dependence of Δc increment of basal spacing of the complexes on the number *N* of carbon atoms in the carboxylic acid intercalated: ○, $VOSO_4 \cdot RCOOH$; △, $VOPO_4 \cdot RCOOH$; ★, $VOAsO_4 \cdot RCOOH$.

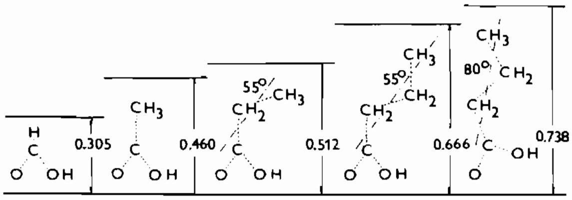

Fig. 2. Steric demands of molecules of aliphatic carboxylic acids deposited between host layers. The calculated layer distance value is given in nanometers.

Significant regularity was found between the increments *c* and the number of carbon atoms *N* in the carboxylic acid molecule. This dependence is represented in Fig. 1 for all the systems studied. It is obvious that the dependence is identical for all three hosts. The basal spacing is changed by about 0.18 nm when going from the complexes with formic acid to those with acetic acid, and the change is the same (0.20 nm) when going from propionic to butyric acid. On the other hand, when replacing acetic acid by propionic acid we find an increase of only 0.02–0.04 nm in the basal spacing. This phenomenon can be explained by an oblique arrangement of the chains, which is schematically represented in Fig. 2. The Figure gives the distances Δc calculated for location of one layer of carboxylic acid molecules forming an angle of 55°. For butyric acid we also determined the Δc value in the case of an almost perpendicular orientation of its chain with respect to the host layers. For this simple calculation we adopted the known values of C–H and C–C bond lengths and van der Waals radii of the hydrogen atom and carboxylic group.

The distances calculated correspond very well to the results obtained from diffractograms. The experimentally found basal spacing of the $VOPO_4 \cdot C_3H_7COOH$ complex is higher than the value calculated for the placement of chains at an angle of 55° and, instead, it corresponds to an angle of about 80°. The decrease in the slope of the chains accompanying the increase in the chain length (till the perpendicular location) represents a phenomenon already observed in other systems [13, 14].

The experimental values of basal spacing of all the complexes prepared indicate a monomolecular layer arrangement of the deposited molecules of carboxylic acids. From the stoichiometry of the complexes (V:COOH = 1:1) and from the fact that the vanadium atoms are not coordination saturated in the original structure of the anhydrous host it follows that the probable way of anchoring of the carboxylic acid molecules in the host layers consists in their coordination by their carboxylic group to the vanadium atoms with simultanous formation of a hydrogen bond to the oxygen atoms of the host layer. This method for the deposition of the carboxylic acid molecules is represented schematically in Fig. 3.

The above idea about the structure of the intercalates is supported by analysis of their IR spectra.

The valence vibration band of the vanadyl group $\nu(V=O)$ in vanadyl salts is found within the frequency region 1050–980 cm^{-1} [15], and it is sensitive to the donor ability of the ligand which coordinates the vanadium atom at the position opposite to the oxygen atom. In anhydrous vanadyl phosphate and arsenate $\nu(V=O)$ is found at 1027 and 1033 cm^{-1}, respectively. In both these compounds the above-mentioned position at the vanadium atom is occupied by an oxygen atom from the neighbouring layer, but, with respect to the large bonding distance between both these atoms (0.25 nm [16]), it can rather be considered unoccupied. In the hydrates of both these compounds, where water molecules are bound to vanadium atoms [2], the wavenumbers of the mentioned band are 1015 and 1020 cm^{-1}, respectively. If the position is occupied by strong electron donors such as, for example, pyridine, the vibration is shifted down to about 990 cm^{-1} [6]. Reduction of vanadium to the oxidation state IV has similar consequences [17]. With the intercalates prepared from $VOPO_4$ and formic or acetic acid we found this band approximately in the region of 1010 cm^{-1} superposed with the intensive bands of PO_4 tetrahedron. In a more conclusive way the band position was determined for the intercalates of vanadyl arsenate with the same carboxylic acids (here the bands of the AsO_4 formation do not interfere), viz. at 1018 and 1019 cm^{-1}, respectively. These findings support the statement that the sixth position of the vanadium atoms really is occupied in the intercalates, and that the donor ability of the ligands is approximately identical with that of the water molecules.

Similar conclusions are arrived at when evaluating the changes of position of ν (V=O) in $VOSO_4$ after intercalation with carboxylic acids. Anhydrous $VOSO_4$, which has vanadium at the oxidation level of IV, exhibits this band at 993 cm^{-1}, whereas the complexes prepared with carboxylic acids exhibit the band within the region 1002–1005 cm^{-1} and the same is true of $VOSO_4 \cdot 2H_2O$ (1005 cm^{-1}).

Consistent with the results mentioned and with the intercalate structure suggested is the conclusion following from the found position of the valence vibration ν (C=O) of the molecules of intercalated carboxylic acids. All these intercalates exhibit a pair of very close intensive bands at about 1700 cm^{-1}, which indicates that the carboxylic acid molecules are anchored by their functional group and that obviously also a strong hydrogen bond is present. It is absolutely clear that the spectra do not contain any bands due to the carboxylate ion, hence no proton transfer occurs from the carboxylic acids to the host lattice.

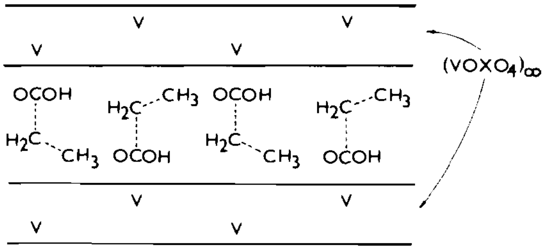

Fig. 3. Schematic representation of a probable arrangement of propionic acid molecules between the host layers.

References

1 H. R. Tietze, *Aust. J. Chem.*, *34* (1981) 2035.
2 M. Tachez, F. Theobald, J. Bernard and A. W. Hewat, *Rev. Chim. Miner.*, *19* (1982) 29.
3 L. Beneš, J. Votinský, J. Kalousová and J. Klikorka, *Inorg. Chim. Acta*, *114* (1986) 47.
4 J. Votinský, L. Beneš, J. Kalousová and J. Klikorka, *Inorg. Chim. Acta*, *126* (1987) 19.

5 M. M. Lara, L. M. Real, A. J. Lopez, S. B. Gamez and A. R. Garcia, *Mater. Res. Bull.*, *21* (1986) 13.

6 K. Beneke and G. Lagaly, *Inorg. Chem.*, *22* (1983) 1503.

7 J. W. Johnson, A. J. Jacobson, J. F. Brody and S. M. Rich, *Inorg. Chem.*, *21* (1982) 3820.

8 E. R. Castellón, A. J. Lopez, M. M. Lara and L. M. Real, *J. Inclus. Phenom.*, *5* (1987) 335.

9 M. S. Whittingham and A. J. Jacobson (eds.) *Intercalation Chemistry,* Academic Press, New York, 1982, p. 229.

10 G. Lagaly, *Naturwissenschaften, 68* (1981) 82.

11 G. Brauer, *Handbuch der Präparativen Anorganischen Chemie,* F. Enke, Stuttgart, 1962, p. 1124.

12 G. Ladwig, *Z. Anorg. Allg. Chem.*, *338* (1965) 266.

13 G. Lagaly, *Solid State Ionics, 22* (1986) 43.

14 K. Beneke and G. Lagaly, *Inorg. Chem.*, *26* (1987) 2537.

15 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds,* Wiley, New York, 1964.

16 B. Jordan and C. Calvo, *Can. J. Chem.*, *51* (1973) 2621.

17 M. M. Lara, A. J. Lopez, L. M. Real, S. Bruque, B. Casal and E. Ruiz-Hitzky, *Mater. Res. Bull.*, *20* (1985) 549.