

Intercalation of Aldehydes into Vanadyl Phosphate

Klára Melánová, Ludvík Beneš,¹ and Vítězslav Zima

Joint Laboratory of Solid State Chemistry, Academy of Sciences of the Czech Republic and University of Pardubice, Studentská 84,
532 10 Pardubice, Czech Republic

and

Jiří Votinský

Department of General and Inorganic Chemistry, University of Pardubice, Nám. Legií 565, 532 10 Pardubice, Czech Republic

Received July 7, 2000; in revised form November 1, 2000; accepted December 1, 2000

Intercalates of VOPO₄ with several aliphatic aldehydes, benzaldehyde, and 4-methylbenzaldehyde were prepared and characterized by thermogravimetric analysis, X-ray diffractometry, and IR and UV–vis spectroscopies. Aliphatic aldehyde intercalates are unstable and the guests undergo aldol condensation and oxidation. The arrangement of the guest molecules in the interlayer space of the host is discussed. A part of aliphatic aldehydes is anchored to the host layers by coordination of their carbonyl oxygen to the vanadium atom; the rest is probably bonded by weak van der Waals forces. In the benzaldehyde and 4-methylbenzaldehyde intercalates, all guest molecules are coordinated to the vanadium atoms with their benzene rings perpendicular to the sheets of the host. © 2001 Academic Press

Key Words: vanadyl phosphate; aldehydes; intercalation.

INTRODUCTION

Vanadyl phosphate and other isostructural layered compounds are able to accommodate some types of organic molecules in the interlayer space by their coordination to the metal center of the host (1, 2). Nitrogen- and oxygen-containing organic molecules form two main groups of such guests. Amines (3, 4), carboxamides (5), amino acids (6), and heterocycles (7, 8) can be anchored to the layers by a V–N donor–acceptor bond. Aliphatic alcohols (9, 10), diols (9, 11, 12), and polyols (13), carboxylic acids (14), and ketones (15, 16) represent the guests which are coordinated to the vanadium atom of the host layers by oxygen. Among them ketone intercalates form surprisingly stable intercalates. Nevertheless, to the best of our knowledge, intercalation of organic molecules containing a similar aldehyde functional group has not yet been described.

EXPERIMENTAL SECTION

Vanadyl phosphate dihydrate was synthesized as previously described (17). All aldehydes were dried with a Dusimo S3 molecular sieve before use. Intercalates with all aldehydes were prepared by a reintercalation reaction. The solid 2-propanol-intercalated host was prepared in advance (18) and used as a starting material for the reactions with aldehydes. About 0.25 g of dry VOPO₄ intercalated with 2-propanol in 10 ml of dried aliphatic aldehyde was shaken at laboratory temperature for 30 minutes. After that the excess of aldehyde was removed by decantation, the solid product was washed with dry ether, and the product was freeze-dried in vacuum. Similarly, about 0.25 g of dry VOPO₄ intercalated with 2-propanol in 20 ml of 4-methylbenzaldehyde or a mixture of benzaldehyde and toluene 1:1 was shaken at laboratory temperature for 2 hours. The solid product was filtered off, washed with toluene, and dried at ambient temperature in air.

The powder diffraction data of the intercalates with a minor excess of the liquid guest were obtained with an X-ray diffractometer (HZG-4, Germany) using CuK α 1 radiation ($\lambda = 1.54051 \text{ \AA}$) with discrimination of the CuK β by a Ni filter. The CuK α 2 intensities were removed from the original data. Silicon ($a = 5.43055 \text{ \AA}$) was used as an internal standard. Diffraction angles were measured from 3° to 37° (2 θ). The samples were kept under protective foil during the measurements and the signal of this foil was compensated. Temperature measurements (from 22 to 240°C) were carried out on a heated corundum plate equipped with a thermocouple (19).

The TGAs of the intercalates were performed with a Derivatograph C (MOM, Hungary) at 30–600°C in air at a heating rate of 5°C/min. The weight of the samples was 20 mg.

¹To whom correspondence should be addressed.

Identification of the products of the side reactions of VOPO_4 with propionaldehyde was carried out on a CHROM 4 chromatograph (Czech Republic) equipped with a flame ionization detector.

Infrared spectra of the solid intercalates were recorded in a Nujol suspension in the region of $4000\text{--}500\text{ cm}^{-1}$ using a Bio-Rad FTS spectrometer.

UV-vis diffuse reflectance spectra were measured on a dual-beam UV-vis-NIR spectrometer JASCO V570 equipped with an integrating sphere attachment ISN-470.

RESULTS AND DISCUSSION

Aldehydes cannot be intercalated in anhydrous vanadyl phosphate and replacement of water molecules in $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ does not lead to intercalation. Intercalates of aldehydes can be prepared by replacing 1-propanol or 2-propanol in the corresponding VOPO_4 intercalates. Aliphatic aldehydes must be carefully dried, to avoid preferential intercalation of water and formation of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$. All freshly prepared intercalates are yellow. The valence of vanadium in the product was confirmed by UV-vis reflectance spectra measurements. The spectrum of freshly prepared propionaldehyde-intercalated VOPO_4 is given in Fig. 1 together with the spectra of $\text{V}^{\text{V}}\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{HV}^{\text{IV}}\text{VOPO}_4 \cdot 3.6\text{H}_2\text{O}$ (20). As can be seen from the figure, the spectrum of the intercalate is similar to that of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$, which indicates that vanadium(V) is not significantly reduced in freshly prepared intercalate. Nevertheless, side reactions can occur during the preparation especially when aldehydes with longer carbon chains are

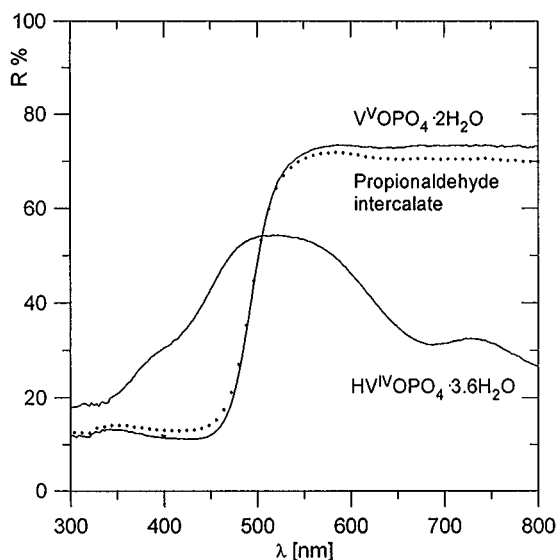


FIG. 1. UV-vis reflectance spectrum of propionaldehyde-intercalated VOPO_4 together with the spectra of $\text{V}^{\text{V}}\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{HV}^{\text{IV}}\text{VOPO}_4 \cdot 3.6\text{H}_2\text{O}$.

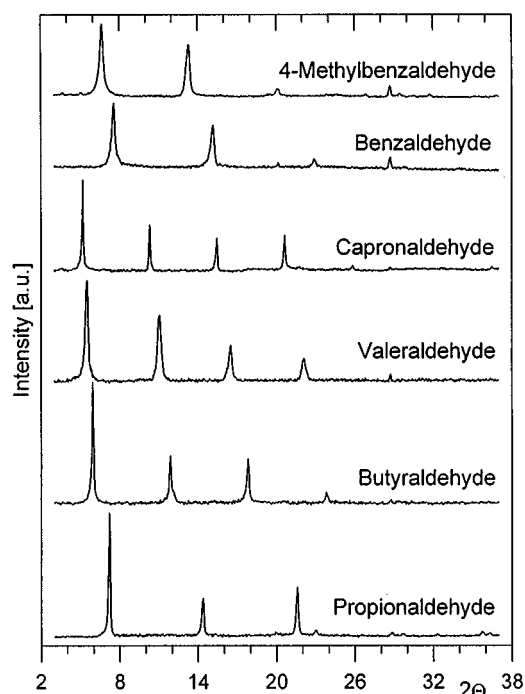


FIG. 2. Diffractograms ($\text{CuK}\alpha$) of VOPO_4 intercalated with aldehydes.

intercalated. Aldehydes tend to be oxidized by $\text{V}(\text{V})$. This is observed during prolonged intercalation reactions and is indicated by a green color of the products. Moreover, in the acid environment in the interlayer space of VOPO_4 , water is released due to aldol condensation of the aldehydes used and the product is therefore a mixture of an intercalate with an organic guest and vanadyl phosphate hydrate. For instance, by long contact of 2-propanol-intercalated VOPO_4 with propionaldehyde, a mixture of proton (hydronium) redox intercalates with basal spacing of 6.67 and 6.5 \AA was formed as a solid product. In the liquid phase, propionic acid and the product of aldol condensation were found by gas chromatography. No such redox and aldol reactions were observed for benzaldehyde and 4-methylbenzaldehyde intercalates.

The intercalates prepared were well crystallized and their diffractograms showed a series of relatively sharp ($00l$) reflections (see Fig. 2). The diffractogram of propionaldehyde intercalate contains a number of (hkl) diffraction lines giving evidence for a regular stacking of host layers. These lines can be indexed using the c parameter of double the basal spacing (see Table 1). This is most likely caused by a mutual shift of the host layers by $a/2$. For other intercalates, the a parameter of the tetragonal lattice was determined from the position of the (200) line. The lattice parameters are given in Table 2.

The compositions of the intercalates were determined by thermogravimetric analysis. Dry samples of the intercalates were checked by XRD before TG measurements. It was

TABLE 1
Powder Data for Vanadyl Phosphate Intercalated with Propionaldehyde

| d_{exp} (Å) | Intensity | h | k | l | d_{calc} (Å) |
|----------------------|-----------|-----|-----|-----|-----------------------|
| 12.390 | 100 | 0 | 0 | 2 | 12.390 |
| 6.198 | 35 | 0 | 0 | 4 | 6.195 |
| 4.398 | 2 | 1 | 1 | 0 | 4.394 |
| 4.130 | 46 | 0 | 0 | 6 | 4.130 |
| 3.877 | 6 | 1 | 0 | 5 | 3.874 |
| | | 1 | 1 | 3 | 3.879 |
| 3.104 | 3 | 2 | 0 | 0 | 3.107 |
| 3.017 | 2 | 2 | 0 | 2 | 3.013 |
| 2.776 | 2 | 2 | 0 | 4 | 2.777 |
| 2.517 | 5 | 1 | 0 | 9 | 2.517 |
| 2.477 | 2 | 0 | 0 | 10 | 2.478 |

found that valeraldehyde and capronaldehyde intercalates decompose partially during drying and their composition cannot be determined. The total weight losses correspond to the stoichiometric ratio x_{exp} given in Table 2. Values of x_{calc} were calculated as a ratio of the volume of aldehyde intercalated and the molar volume of aldehyde, which was calculated from its density. The volume of aldehyde intercalated was calculated as a difference between the unit cell volume of the intercalate and anhydrous VOPO_4 . As follows from the results obtained, the intercalates of aliphatic aldehydes contain more than one molecule of aldehyde per formula unit. A formation of mixed intercalates aldehyde-2-propanol was excluded by gas chromatography. The benzaldehyde and 4-methylbenzaldehyde intercalates contain one guest molecule per formula unit.

As an example, the thermal decomposition of propionaldehyde intercalate is given in Fig. 3. The guest is released from the sample in two steps. A gradual formation of a new phase with basal spacing 9.45 \AA was also observed by thermal XRD measurements (see Fig. 4). This phase exists in the temperature range from 60 to 95°C , and further decomposition is accompanied by a color change and the product becoming amorphous.

TABLE 2
Lattice Parameters and the Contents of the Guest x in the Intercalates Prepared

| Guest | n_c^a | a (Å) | c (Å) | x_{exp} | x_{calc} |
|----------------------|---------|---------|---------|------------------|-------------------|
| Propionaldehyde | 3 | 6.21 | 24.78 | 1.44 | 1.32 |
| Butyraldehyde | 4 | 6.21 | 14.36 | 1.47 | 1.33 |
| Valeraldehyde | 5 | 6.21 | 16.10 | — | 1.30 |
| Capronaldehyde | 6 | 6.21 | 17.32 | — | 1.24 |
| Benzaldehyde | | 6.22 | 11.68 | 0.99 | 0.87 |
| 4-Methylbenzaldehyde | | 6.22 | 13.28 | 0.95 | 0.94 |

^aNumber of carbon atoms in the aliphatic chain of the guests.

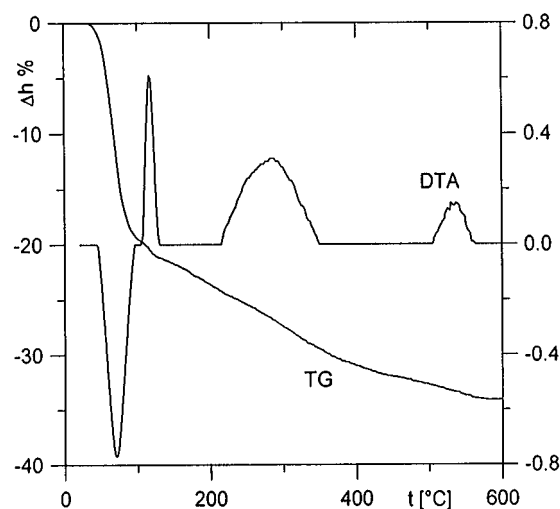


FIG. 3. TG-DTA curves of propionaldehyde-intercalated VOPO_4 .

The intercalates of aliphatic aldehydes are less stable in air than ketone intercalates (15). In the case of the VOPO_4 intercalate with propionaldehyde, the lines of the dihydrate appear in the diffractogram after 15 minutes when exposed to air at ambient humidity. In the VOPO_4 intercalate with acetone, these lines are observed after more than 1 hour. The course of hydration of propionaldehyde-intercalated VOPO_4 is given in Fig. 5. Although $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ is formed very quickly, the intensities of the lines of the intercalate decrease slowly and these lines are still present in the diffractogram after 4 hours. Simultaneously, the sample turns green and the intensity of the basal reflections of the dihydrate decreases. This is probably caused by concomitant reduction of vanadium(V) to vanadium(IV) and formation of hydronium intercalate. After 22 hours, the lines of intercalate disappear and the basal spacing of the

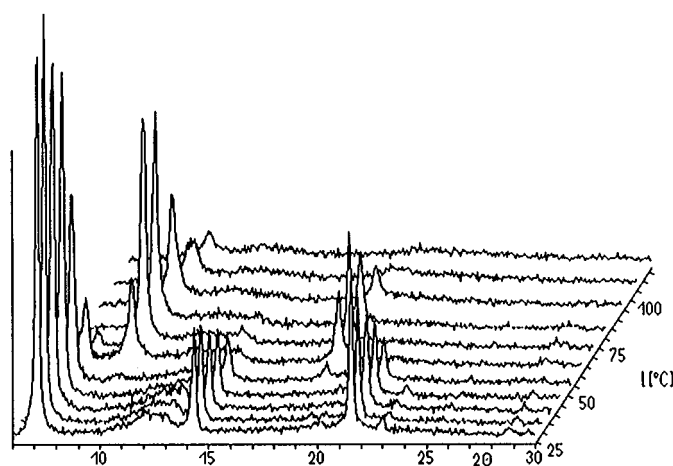


FIG. 4. The changes in diffractograms of propionaldehyde-intercalated VOPO_4 during heating.

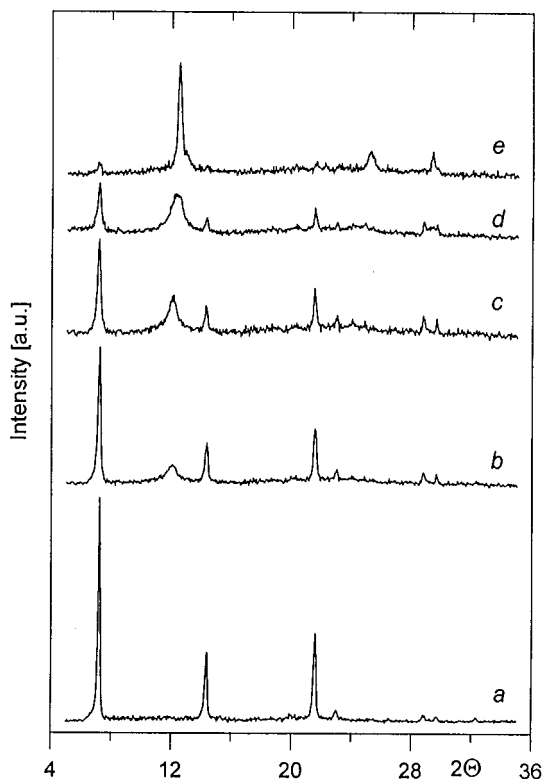


FIG. 5. The changes in diffractograms of propionaldehyde-intercalated VOPO_4 exposed to air (r.h. = 35%): a, freshly prepared sample; b, after 15 minutes; c, after 1 hour; d, after 4 hours; e, after 22 hours.

significantly reduced “dihydrate” is 7.09 Å. The stability of the intercalates decreases with increasing length of the aliphatic chain of aldehyde. On the other hand, the benzaldehyde intercalate is stable in air for more than 2 weeks. The 4-methylbenzaldehyde intercalate slowly decomposes in air and $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ is formed (about 50% of the intercalate is decomposed in 6 hours standing in air).

Dry intercalates of VOPO_4 with aliphatic aldehydes are very unstable even when the sample is stored in an evacuated sealed ampoule. Most probably acid character of VOPO_4 layers causes partial aldolization of the intercalated aldehyde and subsequent condensation of the aldol formed. In addition, aldehyde is oxidized to carboxylic acid by vanadium(V). The reduction of VOPO_4 was confirmed by the changes in the UV-vis spectra, as can be seen in Fig. 6. The reaction is so fast that the major part of V(V) is reduced in 1 day and the reaction is completed within 10 days. During this process, the sample becomes amorphous. The formation of aldol and propionic acid was proved by gas chromatography of the hydrolyzed sample. On the other hand, the benzaldehyde and 4-methylbenzaldehyde intercalates do not undergo this decomposition.

To elucidate interactions between the guest molecules and the host lattice, infrared spectra were measured. In the

spectra of the intercalates the peaks in the region from 500 to 1100 cm^{-1} corresponding to vibrations of the PO_4 tetrahedron (557 , 926 , and 1084 cm^{-1}) and a vanadyl group (shoulder 997 cm^{-1}), and to a lattice vibration (685 cm^{-1}), remain in the same position as those in the pristine host (21,22). From the point of view of the host-guest interactions, the position of the C=O group vibrations is the most important. A very intense peak of the carbonyl group in the benzaldehyde intercalate is shifted to lower wavenumber (1682 cm^{-1}) in comparison with its position in pure benzaldehyde (1708 cm^{-1}). This indicates a strong interaction of carbonyl oxygen with vanadium atom of the host layer. A similar shift of the C=O stretching vibration to lower wavenumber was observed during formation of charge-transfer complexes of benzaldehyde with ICl (1678 cm^{-1}) (23), IBr (1680 cm^{-1}) (24), I_2 (1689 cm^{-1}) (25), and BF_3 (1632 cm^{-1}) (26).

The IR spectrum of the propionaldehyde intercalate changes with time, as can be seen from Fig. 7. In the freshly prepared intercalate, the band corresponding to the carbonyl group is split (1722 and 1692 cm^{-1}). The lower value corresponds most probably to propionaldehyde coordinated to a vanadium atom through its carbonyl group; the higher value corresponds to noncoordinated aldehyde (about 0.3 aldehyde molecule per formula unit). Both values are lower than that in pure propionaldehyde (1738 cm^{-1}). In the region around 3350 cm^{-1} a weak broad band is present, which can be ascribed to a product formed by aldolization or oxidation. Besides the carbonyl band, a new band at about 1630 cm^{-1} appears, which corresponds most probably to a deformation vibration of water molecules

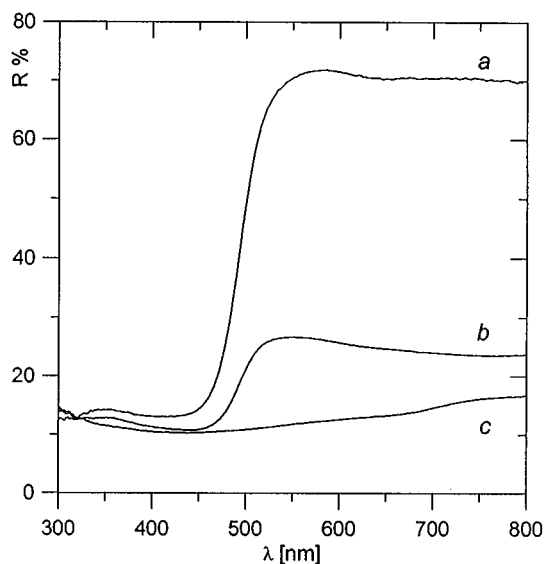


FIG. 6. UV-vis reflectance spectrum of propionaldehyde-intercalated VOPO_4 stored in an evacuated ampoule: a, freshly prepared; b, after 1 day; c, after 10 days.

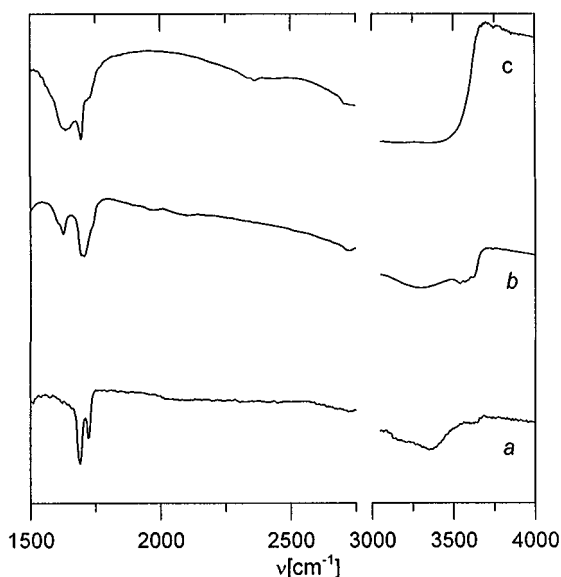


FIG. 7. Changes in IR spectra of propionaldehyde intercalate: a, freshly prepared; b, after 6 hours; and c, after 10 days.

formed by aldol condensation. The changes described are in agreement with the decomposition of the propionaldehyde intercalate described above.

As inferred from the increment of the basal spacing of aldehyde-intercalated VOPO_4 and from the x_{exp} values (Table 2), the guest molecules must be arranged in a bimolecular way (i.e., two layers of the guest molecules exists in the interlayer space of the host) and their carbon chains are tilted relative to the host layers. Only a part of the aldehyde molecules can be anchored to the vanadium atoms, and the rest is bonded by weak van der Waals forces.

In contrast, the benzaldehyde and 4-methylbenzaldehyde molecules are all anchored to the vanadium atoms by their oxygen atoms as follows from the results of the thermogravimetric analysis (Table 2). There are two possible arrangements of these aromatic aldehydes in the interlayer space of the host: with the plane of the benzene rings (i) parallel or (ii) perpendicular to the host layer. In case (i), the guest molecules are arranged in two layers. In the perpendicular arrangement, the guest molecules form one layer with functional groups directed alternately to the two host layers. For the benzaldehyde intercalate, both possibilities are plausible regarding the height of the interlayer space. For the 4-methylbenzaldehyde molecules, the parallel arrangement is impossible as the cross section of the guest molecule is too large and the molecule cannot be bonded to every vanadium atom. Therefore, the perpendicular arrangement is more probable. The idea of the perpendicular arrangement is also supported by the fact that the basal spacing of the 4-methylbenzaldehyde intercalate is 1.6 \AA higher compared with that of the benzaldehyde intercalate.

In conclusion, we can presume that the two aromatic aldehydes are arranged in the way shown in Fig. 8 for the benzaldehyde intercalate. Every benzaldehyde molecule with the functional CHO group directed toward the lower host layer (G_l) is surrounded by four benzaldehyde molecules with CHO groups directed to the upper host layer (G_u) and vice versa. Moreover, the plane of the benzene ring of the surrounding G_u molecules is perpendicular to the plane of the benzene ring of G_l placed among them (Fig. 9). Due to the arrangement of the CHO groups in G_u and G_l , the upper VOPO_4 layers are shifted in the a direction compared to the lower layer of the host. Whether the shift is in the x or y direction depends on the orientation of the benzene ring plane of the benzaldehyde molecules. As this orientation can be different in every interlayer space, the directions of the shifts are random, which causes an absence of the (hkl) reflections in the diffractograms and formation of a turbostratic structure.

As mentioned in the Introduction, aldehydes belong to the group of organic oxygen compounds anchored to the host layer by their oxygen of the functional group. These compounds—alcohols, ethers, aldehydes, and ketones—can be generally divided into two groups. The bonding in the alcohol and ether intercalates is analogous to that in $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$; that is, there is an $R_2\text{O} \cdots \text{V}$ ($R = \text{alkyl or H}$) coordination bond. Bonding in the ketone and aldehyde intercalates with a $\text{C}=\text{O} \cdots \text{V}$ coordination between vanadium and the oxygen atom of the $\text{C}=\text{O}$ group is analogous to the bonding in anhydrous VOPO_4 , where the layers are held together by the $\text{V}=\text{O} \cdots \text{V}$ bond. Compared to the ketone intercalates, the intercalates with aliphatic aldehydes are less stable due to the redox properties of the guests. In contrast to amines (4) and alcohols with short carbon chains (27), aldehydes do not intercalate directly with anhydrous VOPO_4 . The behavior of aldehydes is similar to that of ketones and ethers in this aspect. Generally said, only guests containing “active” hydrogen (i.e., hydrogen bonded to oxygen or nitrogen) are able to break the

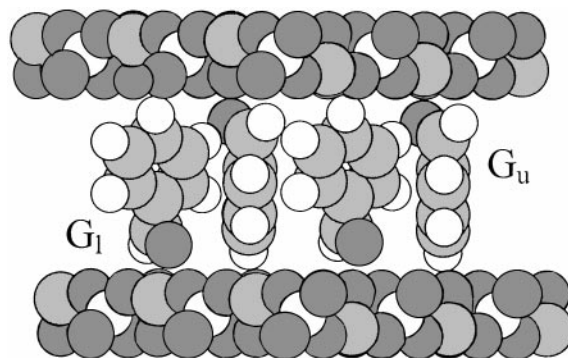


FIG. 8. Proposed arrangement of benzaldehyde molecules in $\text{VOPO}_4 \cdot \text{C}_6\text{H}_5\text{CHO}$ intercalate viewed in the direction of the xy diagonal.

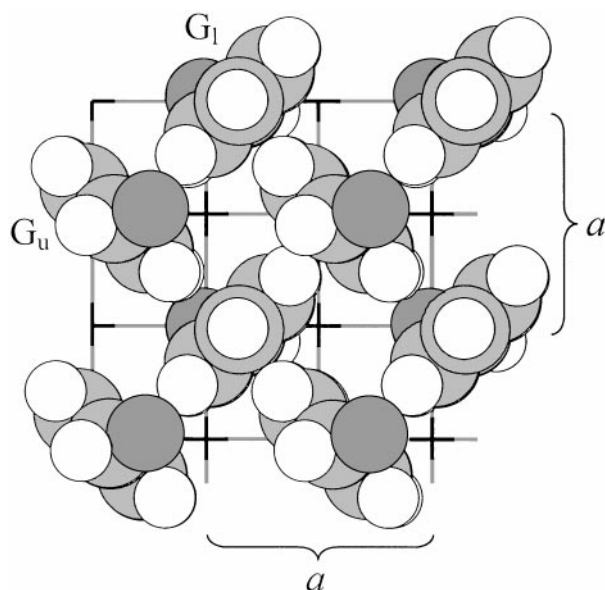


FIG. 9. Arrangement of benzaldehyde molecules on the VOPO_4 layer viewed along the z axis. Open circles, hydrogen; gray circles, carbon; and black circles, oxygen.

$\text{V}=\text{O} \cdots \text{V}$ coordination bonds in anhydrous VOPO_4 . Other compounds from this group can only be intercalated into complexes with a broken $\text{V}=\text{O} \cdots \text{V}$ bond, for instance by replacing alcohol in $\text{VOPO}_4 \cdot 2\text{C}_3\text{H}_7\text{OH}$.

ACKNOWLEDGMENT

The authors thank the Academy of Sciences of the Czech Republic for the financial support (Key Project No. 12).

REFERENCES

1. A. J. Jacobson, in "Encyclopaedia of Inorganic Chemistry" (R. B. King, Ed.), Vol. 3, p. 1576. Wiley, New York, 1994.
2. J. Kalousová, J. Votinský, L. Beneš, K. Melánová, and V. Zima, *Collect. Czech. Chem. Commun.* **63**, 1 (1998).
3. K. Beneke and G. Lagaly, *Inorg. Chem.* **22**, 1503 (1983).
4. L. Beneš, R. Hyklová, J. Kalousová, and J. Votinský, *Inorg. Chim. Acta* **177**, 71 (1990).
5. M. Martinez-Lara, L. Moreno-Real, A. Jimenez-Lopez, S. Bruque-Gamez, and A. Rodriguez-Garcia, *Mater. Res. Bull.* **21**, 13 (1986).
6. V. Zima, L. Beneš, and K. Melánová, *Solid State Ionics* **106**, 285 (1998).
7. J. W. Johnson, A. J. Jacobson, J. F. Brody, and S. M. Rich, *Inorg. Chem.* **21**, 3820 (1982).
8. A. De Stefanis, S. Foglia, and A. A. G. Tomlinson, *J. Mater. Chem.* **5**, 475 (1995).
9. L. Beneš, K. Melánová, V. Zima, J. Kalousová, and J. Votinský, *Inorg. Chem.* **36**, 2850 (1997).
10. K. Melánová, L. Beneš, V. Zima, J. Kalousová, and J. Votinský, *J. Inclusion Phenom.* **33**, 391 (1999).
11. L. Beneš, K. Melánová, and V. Zima, *J. Solid State Chem.* **151**, 225 (2000).
12. K. Melánová, L. Beneš, and V. Zima, *J. Inclusion Phenom.* **36**, 301 (2000).
13. K. Melánová, L. Beneš, V. Zima, R. Vahalová, and M. Kilián, *Chem. Mater.* **11**, 2173 (1999).
14. L. Beneš, J. Votinský, J. Kalousová, and K. Handlíř, *Inorg. Chim. Acta* **176**, 255 (1990).
15. K. Melánová, L. Beneš, V. Zima, P. Čapková, and M. Trchová, *Collect. Czech. Chem. Commun.* **64**, 1975 (1999).
16. P. Čapková, M. Trchová, V. Zima, and H. Schenk, *J. Solid State Chem.* **150**, 356 (2000).
17. G. Ladwig, *Z. Anorg. Allg. Chem.* **338**, 266 (1965).
18. L. Beneš, V. Zima, and K. Melánová, *J. Inclusion Phenom.*, submitted.
19. L. Beneš, *Sci. Pap. Univ. Pardubice Ser. A* **2**, 151 (1996).
20. V. Zima, L. Beneš, J. Votinský, and J. Kalousová, *Solid State Ionics* **82**, 33 (1995).
21. M. Trchová, P. Čapková, P. Matějka, K. Melánová, L. Beneš, and E. Uhlířová, *J. Solid State Chem.* **148**, 197 (1999).
22. L. Beneš, K. Melánová, M. Trchová, P. Čapková, and P. Matějka, *Eur. J. Inorg. Chem.* **1999**, 2289.
23. E. Augdahl and P. Klæboe, *Acta Chem. Scand.* **16**, 1647 (1962).
24. E. Augdahl and P. Klæboe, *Acta Chem. Scand.* **16**, 1655 (1962).
25. E. Augdahl and P. Klæboe, *Acta Chem. Scand.* **16**, 1637 (1962).
26. E. Taillandier, Y. Liquier, and K. Taillandier, *J. Mol. Struct.* **10**, 463 (1971).
27. L. Beneš, J. Votinský, J. Kalousová, and J. Klikorka, *Inorg. Chim. Acta* **114**, 47 (1990).