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Studies of porphyrin zinc compounds intercalated into V_2O_5 xerogel

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The intercalation of *meso*-tetrakis(4-pyridyl)porphyrin zinc, the cationic salts of *meso*-tetrakis(*N*-methylpyridinium-4-yl)porphyrin zinc, and zwitterionic *meso*-tetrakis-[*N*-(3-sulfonatopropyl)pyridinium-4-yl]porphyrin zinc from aqueous solutions as well as of *meso*-tetrakis(*N*-methylpyridinium-4-yl)porphyrin zinc from pyridine solutions into V_2O_5 xerogel was studied. The intercalation complexes obtained were characterized by X-ray diffraction analysis, TG analysis, IR, and UV reflectance spectroscopy.

Key words: intercalation, intercalation compounds, vanadium pentoxide xerogel, pyridine, porphyrin.

Intercalation of organic and organometallic compounds into lamellar xerogel $V_2O_5 \cdot nH_2O$ is a convenient method for the synthesis of novel organo-inorganic materials.[1] The interest in xerogel arose 25 years ago in the connection with the discovery of its semiconducting properties and the use of xerogels as antistatic coatings in photographic industry.[2] Different methods of synthesis of vanadium(V) pentoxide xerogel both from inorganic[3] and organic starting materials are known.[4] The first of them was described in 1885.[5] The intercalation compounds based on vanadium(V) pentoxide xerogel can possess predominantly ionic or electronic as well as mixed-type conductivity. The ionic conductivity is specified by the mobility of the introduced cations, while the electronic one depends on the vanadium(IV) content. The use of compounds intercalated into $V_2O_5 \cdot nH_2O$ xerogel as chemical sources of electric energy, as cathode materials, is based on these phenomena.[6] The specific feature of novel organo-inorganic materials obtained by intercalation into $V_2O_5 \cdot nH_2O$ xerogel is the retention of catalytic, photochemical, and magnetic properties of intercalation compounds as well as electrochemical properties of the initial xerogel matrix. Thus, one can predict properties of novel materials in different fields of application such as optics, biology, electronics, and catalysis.[7] Currently the intercalation of porphyrins and phthalocyanines into the layered inorganic materials such as layered double hydroxides,[8—11] clays,[12,13] niobates,[14—17] silicates,[18—20] and titanates[21] are especially promising. The intercalation complexes obtained possess better catalytic activity compared to the starting phthalocyanines and porphyrins. The increase in catalytic activity of the macrocycles intercalated into the layered materials is caused by the fact that the intercalation of porphyrins and phthalocyanines prevents its inactivating dimerization and crystallization, enhances the selectivity of oxidation and decreases the possibility of formation of μ-peroxocomplexes, low-active in the oxidation process, between the neighboring molecules due to the better molecular distribution of porphyrins and phthanlocyanines between the layers compared to solutions.[9,11,12]

The materials based on the porphyrins intercalated into $V_2O_5 \cdot nH_2O$ xerogel possess the high application potential as catalysts, sensors, and modified electrodes. *Meso*-tetrakis(*N*-methylpyridinium-4-yl)porphyrin salts intercalated in $V_2O_5 \cdot nH_2O$ xerogel were described.[7,22,23] It was found that materials based on the porphyrins intercalated into vanadium(V) pentoxide xerogel possess good volt-ampere characteristics.[23]

The aim of the present work was the study of intercalation of *meso*-tetrakis(4-pyridyl)porphyrin zinc, the cationic salts of *meso*-tetrakis(*N*-methylpyridinium-4-yl)porphyrin zinc, and zwitterionic *meso*-tetrakis-[*N*-(3-sulfonatopropyl)pyridinium-4-yl]porphyrin zinc from aqueous solutions into the lamellar $V_2O_5 \cdot nH_2O$ xerogel and the determination of the composition and the structure of the obtained intercalation compounds.

Results and Discussion

The $V_2O_5 \cdot nH_2O$ xerogel was obtained by dissolving crystalline V_2O_5 in concentrated (30% w/w) hydrogen peroxide.[3] The structure of xerogel $V_2O_5 \cdot nH_2O$ is similar to the lattice of vanadium pentoxide (orthorhombic cell, space group of symmetry *Pmmn*, $a = 11.51$ Å, $b = 3.56$ Å, $c = 4.37$ Å) expanded along the *c* axis.[6] The interlayer distance (*d*) depends on the water content in the layers of the lattice of vanadium(V) oxide and equal to 11.15 Å

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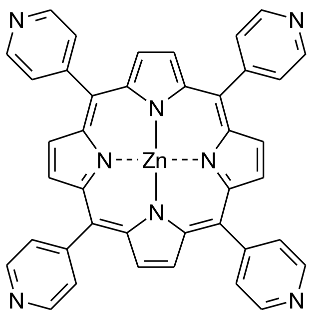
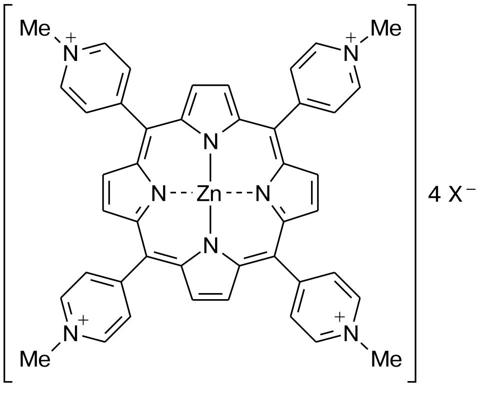
for $V_2O_5 \cdot 1.7H_2O$. The main adsorption bands at 1611 (δ(H—O—H)); 1015, 975 (ν(V=O)); 927 (δ(V—O...H); 754 (δ(V—O—V)); and 504 cm^{-1} (δ(V—O)) are observed in the IR spectrum of vanadium(v) pentoxide xerogel. According to thermogravimetric analysis (TGA), the composition of xerogel corresponds to the formula $V_2O_5 \cdot 1.7H_2O$. On heating, the xerogel undergoes dehydration in two steps (Table 1): first, weakly bound interlayer water is eliminated, then chemically bound water is removed and crystallization of V_2O_5 begins, which is finished at 700 °C.

The vanadium pentoxide xerogel is polyvanadium acid consisting of V_2O_5 layers with partly negative charge and H_3O^+ cations in the interlayer space.[2,4,6] The introduction of porphyrins into $V_2O_5 \cdot nH_2O$ xerogel occurs due to cation exchange of the hydroxonium ions.

The synthesis and properties of intercalation compounds obtained by introduction of cationic forms of substituted porphyrins from aqueous solutions into $V_2O_5 \cdot nH_2O$ xerogel have previously been described.[7,22,23] These intercalation complexes are insoluble in water (unlike the starting reagents), stable, and exhibit good electrochemical properties. The following porphyrins were used in the present study: $ZnPor(py)_4$ (Por is porphyrin), $ZnPor(py^+Me)_4 \cdot (X^-)_4$ (X = I, Cl), $ZnPor[py^+(CH_2)_3SO_3^-]_4$ (see below).


$ZnPor(py)_4$


$ZnPor(py^+Me)_4 \cdot (X^-)_4$
(X = I, Cl)

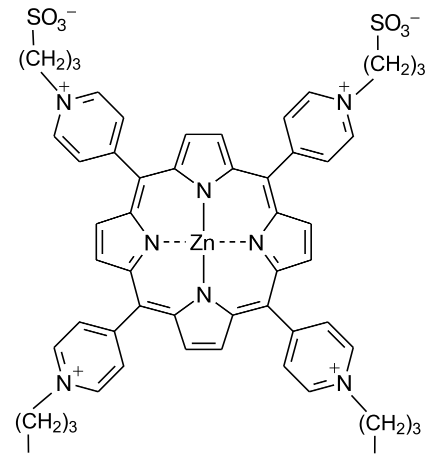

$ZnPor[py^+(CH_2)_3SO_3^-]_4$

Table 1. The thermogravimetric analysis data of samples of xerogel and the intercalation compounds

Sample	T/°C	Weight loss (%)	Object
$V_2O_5 \cdot 1.7H_2O$	40—130	10.71	H_2O
	130—420	3.85	H_2O
	420—700	0.04	H_2O
$V_2O_5 \cdot 1.4H_2O \cdot 0.45py$	40—109	4.15	H_2O
	109—256	6.36	H_2O
	256—389	10.32	Pyridine
	389—499	4.37	Pyridine
$[PorZn(py^+Me)_4]_{0.02}V_2O_5 \cdot 1H_2O \cdot 0.4py$ (**1**)	40—222	7.27	H_2O
	222—313	6.07	Pyridine
	313—489	13.30	4 Me, 4 py
	489—585	4.84	Porphyrin ring
$[PorZn(py^+Me)_4]_{0.09}V_2O_5 \cdot 1H_2O$ (**2**)	40—285	11.70	H_2O
	285—419	7.04	4 Me
	419—478	3.55	4 py,
	478—561	5.50	Porphyrin ring
$[PorZn(py^+Me)_4]_{0.03}V_2O_5 \cdot 1H_2O \cdot 0.2py$ (**5**)	40—227	9.11	H_2O
	227—390	12.02	Pyridine, 4 Me
	390—497	6.03	4 py,
	497—592	2.03	Porphyrin ring
$[PorZn(py^+(CH_2)_3SO_3^-)]_{0.05}V_2O_5 \cdot 2.5H_2O$ (**6**)	40—287	10.27	H_2O
	287—344	4.11	4 SO_3
	344—387	8.81	4 ($CH_2CH_2CH_2py$)
	387—641	10.78	Porphyrin ring

The choice of pyridine as a solvent for porphyrins was based on the ability of pyridine to coordinate a metal atom due to the electron pair on the N atom, and its ability to easily penetrate into $V_2O_5 \cdot nH_2O$ xerogel (see Refs 24, 25). We assumed that the use of pyridine as a solvent would allow incorporation of porphyrin into $V_2O_5 \cdot nH_2O$ lattice due to the increase in the interlayer distance as a result of pyridine intercalation. According to X-ray phase analysis data, the structure of xerogel intercalated with pyridine is a set of planes with the interlayer distance d = 13.09 Å, and the composition of xerogel according to the data from elemental analysis and thermogravimetry (see Table 1) is described by the formula $V_2O_5 \cdot 1.4H_2O \cdot 0.45py$.

The complex $[PorZn(py^+Me)_4]_{0.02}V_2O_5 \cdot 1H_2O \cdot 0.4py$ (sample **1**) was obtained by intercalation of *meso*-tetrakis(*N*-methylpyridinium-4-yl)porphyrin zinc tetraiodide from a solution in pyridine into $V_2O_5 \cdot nH_2O$ xerogel. According to diffractogram of the sample **1**, the interlayer distance is 13.15 Å. In the starting xerogel with d = 11.15 Å the distance between the planes passing through the oxygen atoms in the tetrahedron apices of the adjacent V_2O_5 layers facing each other in the unit cell is equal to ~5 Å (see Ref. 26). This is the width of the interlayer region occupied with water molecules and H_3O^+ cations in $V_2O_5 \cdot nH_2O$. If porphyrin substitutes the hydroxonium cations during intercalation, the interlayer distance d in the intercalation compound should increase in comparison with that in xerogel. In the intercalation complex $[PorZn(py^+Me)_4]_{0.02}V_2O_5 \cdot 1H_2O \cdot 0.4py$ (**1**) with d = 13.15 Å, the width of the interlayer region achieves 7 Å. Such an increase assumes the parallel orientation of the macrocycles in the layers of xerogel. The presence of absorption bands of the initial porphyrin in the IR spectrum of intercalation complex **1** proves that no changes in the porphyrin macrocycle occurs upon intercalation. The hypsochromic shift of the band, which characterizes the δ(V—O) vibration, and bathochromic shift of the bands corresponding to ν(V=O) and δ(V—O...H) vibrations prove that porphyrin interacts with the xerogel lattice (Table 2). In the electronic reflectance spectra of sample **1**, two bands are observed at 563 and 613 nm that characterize the presence of porphyrin in the intercalation compound **1**. In the region of $\lambda < 400$ nm, the Soret band of the porphyrin complex is overlapped with xerogel bands.

The behavior of sample **1** under conditions of TG analysis differs from that observed for the starting xerogel and porphyrin. Thus the weight loss of this sample proceeds in four steps (see Table 1). The first process is the loss of the weakly bound interlayer water on heating. After subsequent temperature increase, pyridine present in the xerogel layers is removed. In the next step, the weight loss is caused by the elimination of methylpyridinium substituents from the porphyrin core and subsequent decomposition of the porphyrin macrocycle at the temperatures above 550 °C. Finally, the crystallization of V_2O_5 takes place.

We performed intercalation of *meso*-tetrakis(*N*-methylpyridinium-4-yl)porphyrin zinc tetraiodide (sample **2**) and tetrachloride (sample **3**) from aqueous solutions, and *meso*-tetrakis(4-pyridyl)porphyrin zinc (sample **4**) from the acidified aqueous solution into $V_2O_5 \cdot nH_2O$ xerogel. The data from X-ray phase analysis of $[PorZn(py^+Me)_4]_{0.09}V_2O_5 \cdot 1H_2O$ (sample **2**, d = 17.4 Å), $[PorZn(py^+Me)_4]_{0.03}V_2O_5 \cdot 1H_2O$ (sample **3**, d = 17.1 Å), $[PorZn(py^+H)_4]_{0.12}V_2O_5 \cdot 1H_2O$ (sample **4**, d = 19.7 Å) suggest the presence of the porphyrins intercalated into $V_2O_5 \cdot nH_2O$ xerogel. The reflexes of two phases are present on the diffractograms of the samples obtained by intercalation from aqueous solutions of porphyrins, which we have identified as $V_2O_5 \cdot nH_2O$ xerogel with the interlayer distances d = 17.0—19.7 Å and 12.5 Å intercalated by porphyrins. During the experiment, the aqueous porphyrin solution was applied onto films of xerogel over a long period of time. Under these conditions, the saturation of the $V_2O_5 \cdot nH_2O$ surface proceeds faster. The registration

Table 2. The frequencies (ν/cm^{-1}) in the IR spectra (KBr) of samples of the intercalation compounds

$V_2O_5 \cdot nH_2O$	Sample **1**	Sample **2**	Sample **3**	Sample **4**	Sample **5**	Attribution
			Porphyrin bands			
—	3466	3454	3376	3454	3462	NH
—	1634, 1527	1634, 1526	1634, 1524	1630, 1515	1634, 1526	CC_{py}
—	1483,1452	1483, 1452	1453	1492, 1452	1483, 1452	CH
—	1278	1278	1276	1292	1278	CN_{py}
—	1195	1180	1192	1184	1195	CH
			Xerogel bands			
1611	1611	1613	1611	1611	1611	δ(H—O—H)
1015, 975	1004, 968	1015, 995, 964	1017, 993, 971	1013, 970	1007, 968	ν(V=O)
927	911	895	894	914	915	ν(V—O...H)
754	756	757	760	758	757	δ(V—O—V)
504	522	515	520	522	518	δ(V—O)

of the diffractogram of sample **2** (Fig. 1) in a sliding beam showed that the content of the phase with the interlayer distance $d = 12.5$ Å on the surface of intercalated film is lower than inside the film. In the surface layer of the film, the phase with $d = 18.0$ Å predominates. The existence of a two-phase system suggests that, first, the introduction of one layer of porphyrin into xerogel proceeds (the intercalation compound with $d = 12.5$ Å forms), and after subsequent application of the porphyrin solution onto $V_2O_5 \cdot nH_2O$ films the introduction of the second layer of porphyrin takes place (the interlayer distances are 17.0—19.7 Å), *i.e.*, compared to initial xerogel, in the intercalation compounds the value of d increases by 6—8 Å. This increase in the width of interlayer cavity is evidence of realization of two-layer packing of porphyrin macrocycles in the layes of $V_2O_5 \cdot nH_2O$ xerogel. We also obtained the diffractogram profile of sample **2** deconvoluted into peaks (Fig. 2). Stacked packing of porphyrins in the layers of xerogel for the intercalation compounds is due to the association of porphyrin complexes in aqueous solutions. The sample diffractograms have broadened peaks due to the small crystallite sizes.

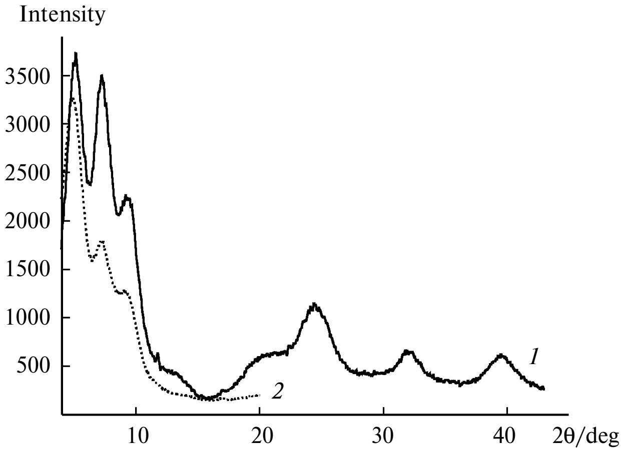


Fig. 1. The diffractogram of sample **2** in a standard mode of registration (*1*) and with registration in a sliding beam (*2*).

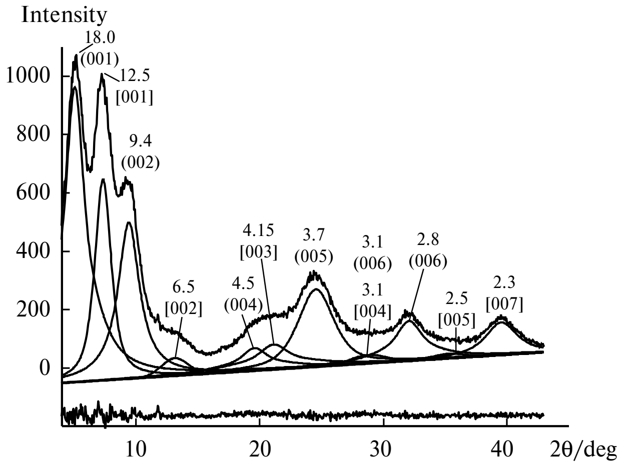


Fig. 2. The profile of the diffractogram of sample **2**. The digits are interlayer distances characteristic of each intercalate. The sets of planes (001) for the intercalates with interlayer distances 18 and 12.5 Å, respectively, are in the parentheses and square brackets.

The frequencies in the IR spectra of the obtained intercalation compounds are listed in Table 2. The adsorption bands of porphyrin are present in the IR spectra of samples **2**—**4**, which confirm the integrity of the porphyrin complexes following their incorporation into the xerogel. The hypsochromic shift of the band characterizing the δ(V—O) vibration and the bathochromic shift of the bands corresponding to the δ(V—O...H) vibrations are connected with the electrostatic interaction of the porphyrin cations with the xerogel layers. Besides, the adsorption band at ~970 cm^{-1} corresponding to the $\nu(V^{4+}{=}O)$ vibrations is present in the spectra of intercalation compounds.

In the electronic reflectance spectra of samples **2**—**4** (Fig. 3), the bands in the region of $\lambda < 400$ nm corresponding to $V_2O_5 \cdot nH_2O$ xerogel overlap the Soret band of the porphyrin complexes. The existence of Q-bands in the region 570 and 620 nm in the reflectance spectra suggests the presence of porphyrins in the obtained intercalation complexes.

We compared characteristics of three intercalation complexes of *meso*-tetrakis(*N*-methylpyridinium-4-yl)-porphyrin zinc in $V_2O_5 \cdot nH_2O$ xerogel prepared from the solution of $[PorZn(py^+Me)_4]_{0.02}V_2O_5 \cdot 1H_2O \cdot 0.4py$ in pyridine (sample **1**), from aqueous solution of $[PorZn(py^+Me)_4]_{0.09}V_2O_5 \cdot 1H_2O$ (sample **2**), and from aqueous solution of $[PorZn(py^+Me)_4]_{0.03}V_2O_5 \cdot 1H_2O \cdot 0.2py$ with the addition of pyridine (sample **5**).

The diffraction patterns of samples **1** and **5** are identical, the interlayer distance $d = 13$ Å corresponds to the parallel orientation of porphyrin to the layers of vanadium pentoxide xerogel. Reflexes from two phases are present on the diffractogram of sample **2**. We identified them as

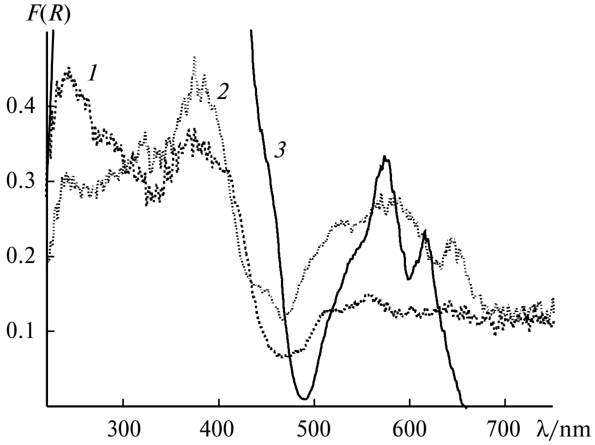
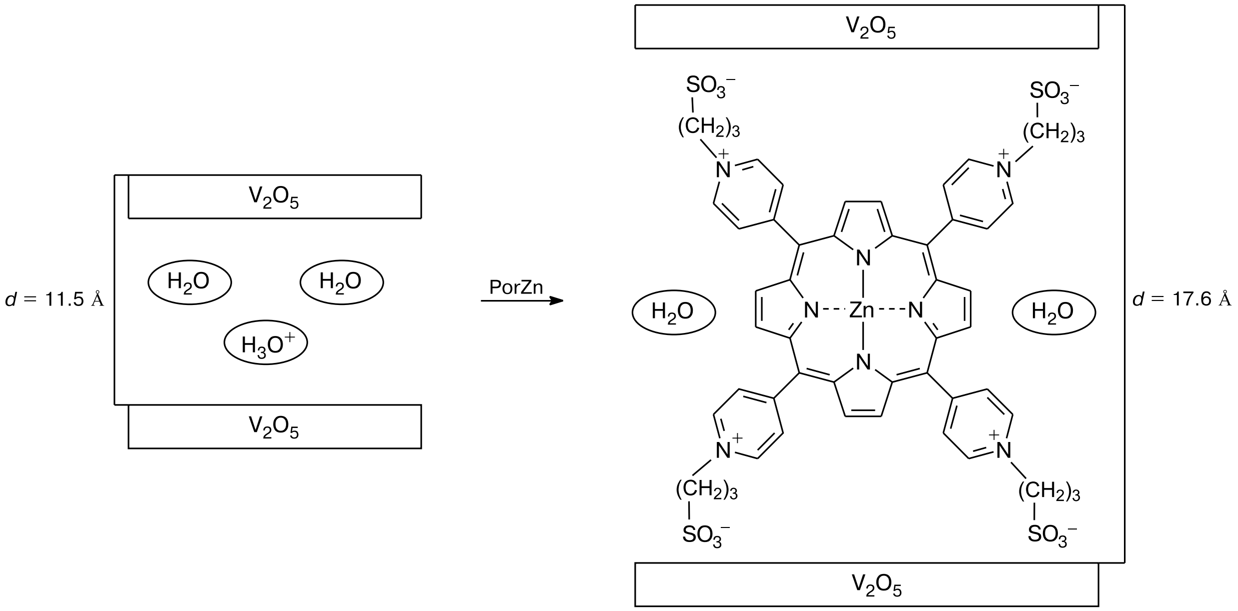


Fig. 3. The reflectance spectra of samples **2** (*1*), **3** (*2*), and **4** (*3*) (*F*(*R*) is the intensity).

Scheme 1



the phases intercalated with porphyrin with the interlayer distances d = 17.4 and 12.5 Å (see Figs 2, 3). The use of pyridine as a solvent of porphyrins prevents their association in the solution. Therefore, monophase intercalation complexes were observed for samples **1** and **5**, where the porphyrin molecules were oriented parallel to the xerogel layers.

The weight loss on heating complexes **2** and **5** proceeds in several steps, as in the case of sample **1** (see Table 1). In the first step, weakly bound water is removed, the next step is the loss of pyridine intercalated into xerogel layers (samples **1** and **5**), then the elimination of methylpyridinium substituents takes place at 300—480 °C, then the decomposition of the porphyrin ring and the crystallization of V_2O_5 occur.

Besides, we intercalated zwitterionic *meso*-tetrakis-[*N*-(3-sulfonatopropyl)pyridinium-4-yl]porphyrin zinc into $V_2O_5 \cdot nH_2O$ xerogel (sample **6**). According to X-ray phase analysis (Fig. 4, Table 3), the intercalation compound **6** obtained is the monophase system (homogeneous powder) with the interlayer distance d = 17.6 Å (Scheme 1) without any other phases with different values of d. The width of the interlayer region for sample **6** achieves 11 Å. This fact gives us the reason to consider inclined orientation of the zwitterionic porphyrin inside the xerogel layers.

The composition of sample **6** was determined by elemental analysis: $[PorZn(py^+(CH_2)_3SO_3^-)]_{0.05}V_2O_5 \cdot 2.5H_2O$. In the IR spectra of sample **6**, the absorption bands of the starting *meso*-tetrakis[*N*-(3-sulfonatopropyl)pyridinium-4-yl]porphyrin zinc are present. The band at 515 cm^{-1}

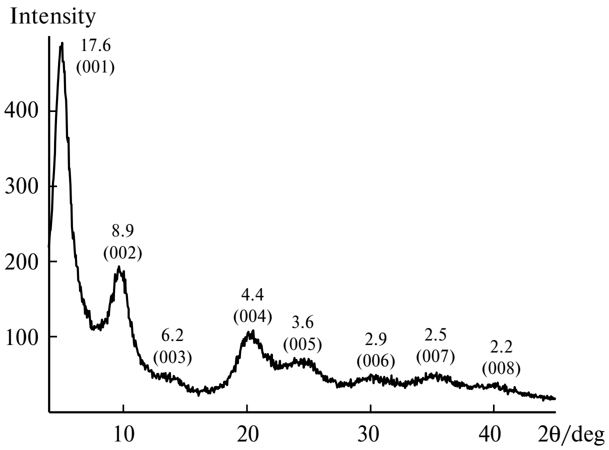


Fig. 4. The diffractogram of sample **6**. The digits are interlayer distances characteristic of each intercalate. The sets of planes (001) are in parentheses.

Table 3. The data of X-ray phase analysis of the xerogel and samples **1** and **6**

Sample	d/Å	K^a	D^b /nm
$V_2O_5 \cdot nH_2O$	11.15	0.045	32.5
$[PorZn(py^+Me)_4]_{0.02}V_2O_5 \cdot 1H_2O \cdot 0.4py$ (**1**)	13.15	0.063	17.0
$[PorZn(py^+(CH_2)_3SO_3^-)]_{0.05}V_2O_5 \cdot$ $\cdot 2.5H_2O$ (**6**)	17.60	0.150	10.0

[a] Coefficient of disorder.

[b] The size of crystallites.

Table 4. The conditions of the reactions and the data from X-ray phase analysis for the porphyrin intercalation products into $V_2O_5 \cdot nH_2O$ xerogel

Substance	Conditions of intercalation	d/Å	Width of the interlayer region,[a] Å
$V_2O_5 \cdot nH_2O$	—	11.15	5.1
$V_2O_5 \cdot 1.4H_2O \cdot 0.45py$	Powder	13.09	7.0
1	Pyridine/ powder	13.15	7.1
2, **3**	H_2O/film	~17	~11
4	$H_2O + H^+$/film	19.7	13.6
5	H_2O + pyridine /film	~13	~7
6	H_2O/powder	17.6	11.6

[a] Calculated taking into account the width of the vanadium oxide layer ~6.1 Å (according to the authors' data).

characterizing the δ(V—O) vibrations of xerogel is shifted to the high-frequency region as the result of interaction of porphyrin with the V_2O_5 layers. The TG analysis data for the intercalation complex **6** are also listed in Table 1. The weight loss on heating of $[PorZn(py^+(CH_2)_3SO_3^-)]_{0.05}V_2O_5 \cdot 2.5H_2O$ proceeds in several steps. In the first step, weakly bound interlayer water is lost followed by elimination of sulfonatopropyl pyridinium substituents, decomposition of the porphyrin macrocycle, and crystallization of V_2O_5 at the temperature above 640 °C.

Thus, we obtained intercalation complexes with different orientation of the porphyrin macrocycles in the xerogel layers. The conditions of their syntheses as well as X-ray phase analysis data are summarized in Table 4. The intercalation of cationic *meso*-tetrakis(*N*-methylpyridinium-4-yl)porphyrin zinc into $V_2O_5 \cdot nH_2O$ from the pyridine solution resulted in samples **1** and **5** with the parallel orientation of the porphyrin macrocycle to xerogel layers. The intercalation of *meso*-tetrakis(*N*-methylpyridinium-4-yl)porphyrin zinc tetraiodide and tetrachloride into $V_2O_5 \cdot nH_2O$ xerogel from aqueous solutions and *meso*-tetrakis(4-pyridyl)porphyrin zinc from acidified aqueous solution resulted in samples **2**—**4**, respectively, with double layer packing of porphyrin complexes in the xerogel layers. Intercalation of zwitterionic *meso*-tetrakis-[*N*-(3-sulfonatopropyl)pyridinium-4-yl]porphyrin zinc into $V_2O_5 \cdot nH_2O$ xerogel led to sample **6** with the inclined orientaion of porphyrin macrocycles in the interlayer space of xerogel. Note that the use of $V_2O_5 \cdot nH_2O$ powder instead of the film allows preparation of homogeneous intercalation products.

Experimental

The thermogravimetric analysis was performed on a Pyris 6 TGA instrument in a nitrogen atmosphere. The X-ray phase analysis was performed on a DRON-3M diffractometer connected to a PC (Cu-Kα-radiation, the graphite monochromator on the diffracted beam), in the point measurement mode. Samples were the films with the width of several tenth of a millimeter (both immobilized on the cover-glass—support flakes, and exfoliated ones). The films that were not detached were fixed in the cuvettes together with the support, while the flakes were either poured into cuvette, or ground to eliminate the texture effects. IR spectra were registered on a Perkin—Elmer SP 1000 spectrometer in KBr pellets. The electronic reflectance spectra were recorded on a Perkin—Elmer Lambda 9 instrument. For the registration of electronic reflectance spectra small amount of sample (10—30 mg) was thoroughly ground in a mortar with barium sulphate (0.6 g), then the cuvette (2 mm) was filled with the obtained mixture and placed into the spectrometer. The reference cuvette was filled with pure $BaSO_4$.

Vanadium pentoxide $V_2O_5 \cdot nH_2O$ xerogel. The $V_2O_5 \cdot nH_2O$ xerogel was obtained by dissolving crystalline V_2O_5 (5 g) in 250 mL of concentrated (30% w/w) hydrogen peroxide at ~20 °C (see Ref. 3). The dark-red solution formed as a result of highly exothermic reaction, which spontaneously transforms into the dark-red gel. The gel was supplied onto glass plates with a brush in a regular layer and dried in air. The structure of xerogel was determined on the base of X-ray diffraction and IR spectra, the composition of $V_2O_5 \cdot 1.7H_2O$ was determined by the data from elemental and thermogravimetric analysis.

The synthesis of the starting porphyrins were performed in accordance with the known procedures.[27]

5,10,15,20-Tetrakis(4-pyridyl)porphyrin zinc(II). 5,10,15,20-Tetrakis(4-pyridyl)-21*H*,23*H*-porphine (210 mg, 0.339 mmol) was dissolved in DMF (20 mL). An excess of $Zn(AcO)_2 \cdot 2H_2O$ (440 mg, 2 mmol) was added, the solution was stirred for 48 h at 100 °C. The reaction product was precipitated with water, filtered off, washed with water and acetone and dried at 80 °C. The yield was 226 mg (98%). IR (KBr), ν/cm^{-1}: 3042, 1635, 1561, 1528, 1460, 1276, 996, 799. UV (DMF), λ_{max}/nm: 423, 557, 597.

5,10,15,20-Tetrakis(*N*-methylpyridinium-4-yl)porphyrin zinc(II) tetraiodide. 5,10,15,20-Tetrakis(4-pyridyl)porphyrin zinc(II) (90 mg, 0.13 mmol) was dissolved in DMF (20 mL). An excess of methyl iodide (5 mL, 80 mmol) was added, the solution was stirred for 18 h at 50 °C under argon. The product was precipitated with CH_2Cl_2, dissolved in hot water, the solvent was removed *in vacuo*. The yield was 159 mg (98%). IR (KBr), ν/cm^{-1}: 3120, 3042, 1639, 1560, 1527, 1510, 1460, 1278, 1191, 1118, 995, 864, 800, 618. UV (pyridine), λ_{max}/nm: 438, 563, 609.

5,10,15,20-Tetrakis[*N*-(3-sulfonatopropyl)pyridinium-4-yl]porphyrin zinc(II). 5,10,15,20-Tetrakis(4-pyridyl)porphyrin zinc(II) (90 mg, 0.13 mmol) and 1,3-propane sultone (0.5 g, 4.09 mmol) were dissolved in DMF (15 mL) and heated for 16 h at 80 °C with stirring in a nitrogen atmosphere. The product was precipitated with CH_2Cl_2, filtered off, and washed with CH_2Cl_2, the excess of 1,3-propane sultone being removed. The resulting compound was dissolved in hot water, the solvent was removed *in vacuo*. The yield was 146 mg (96%). IR (KBr), ν/cm^{-1}: 3115, 3047, 1634, 1529, 1496, 1459, 1420, 1202, 1184 (SO_2); 1041 (SO_2); 994, 866, 799, 721, 599, 571, 528. UV (H_2O, pH 13), λ_{max}/nm: 451, 569, 615.

Intercalation of *meso*-tetrakis(*N*-methylpyridinium-4-yl)porphyrin zinc tetraiodide from a pyridine solution into $V_2O_5 \cdot nH_2O$ xerogel. A powder of $V_2O_5 \cdot nH_2O$ xerogel was added to a solution of porphyrin in pyridine (3 mL) and the resulting mixture was magnetically stirred for 3 days in an argon atmosphere. The molar ratio porphyrin : xerogel was 0.03 : 1.00. Xerogel was filtered off, washed with pyridine, and dried in air. Found (%): C, 13.82; H, 1.79; N, 3.41; C/N, 4.0. $[\mathrm{PorZn(py^{+}Me)_4}]_{0.02}\mathrm{V_2O_5 \cdot 1H_2O \cdot 0.4py}$ (sample **1**). Calculated (%): C, 14.02; H, 1.91; N, 3.18; C/N, 4.4. IR spectrum of sample **1** is presented in Table 2. The similar procedure was performed with xerogel in the absence of porphyrin. The xerogel intercalated with pyridine $\mathrm{V_2O_5 \cdot 1.4H_2O \cdot 0.45py}$ was obtained. IR (KBr), ν/cm^{-1}: 1634 cm^{-1} (C=C$_{\mathrm{py}}$); 1526 cm^{-1} (C=C$_{\mathrm{py}}$).

Intercalation of *meso*-tetrakis(4-pyridyl) porphyrin zinc, *meso*-tetrakis(*N*-methylpyridinium-4-yl)porphyrin zinc tetraiodide and tetrachloride from aqueous solutions into films of vanadium pentoxide xerogel. Aqueous solutions of porphyrins (3 mg mL^{-1}) were supplied onto the $\mathrm{V_2O_5 \cdot}n\mathrm{H_2O}$ xerogel films during several days and then they were left in air until complete removal of the solvent. A few drops of concentrated HCl were added to dissolve *meso*-tetrakis(4-pyridyl)porphyrin zinc. The molar ratio porphyrin : xerogel was 0.1 : 1.0. The films obtained were washed with water and acetone and dried in air. The films intercalated with porphyrin colored blue with the metallic glare.

The composition of compounds was determined by elemental analysis. Sample **2**. Found (%): C, 18.06; H, 1.99; N, 3.99; C/N, 4.5. $[\mathrm{PorZn(py^{+}Me)_4}]_{0.09}\mathrm{V_2O_5 \cdot 1H_2O}$. Calculated (%): C, 17.81; H, 1.96; N, 3.78; C/N, 4.7.

Sample **3**. Found (%): C, 7.36; H, 1.49; N, 1.78; C/N, 4.1. $[\mathrm{PorZn(py^{+}Me)_4}]_{0.03}\mathrm{V_2O_5 \cdot 1H_2O}$. Calculated (%): C, 7.13; H, 1.38; N, 1.51; C/N, 4.7.

Sample **4**. Found (%): C, 20.39; H, 1.81; N, 5.13; C/N, 3.9. $[\mathrm{PorZn(py^{+}H)_4}]_{0.12}\mathrm{V_2O_5 \cdot 1H_2O}$. Calculated (%): C, 20.4; H, 1.89; N, 4.76; C/N, 4.3.

Intercalation of *meso*-tetrakis(*N*-methylpyridinium-4-yl)-porphyrin zinc tetraiodide into $\mathrm{V_2O_5 \cdot}n\mathrm{H_2O}$ xerogel was also performed from aqueous solution with the addition of 3—5 drops of pyridine. Sample **5** was obtained. Found (%): C, 11.86; H, 1.59; N, 2.63; C/N, 4.5. $[\mathrm{PorZn(py^{+}Me)_4}]_{0.03}\mathrm{V_2O_5 \cdot 1H_2O \cdot 0.2py}$. Calculated (%): C, 11.69; H, 1.71; N, 2.58; C/N, 4.5.

The IR spectra of samples **2**—**5** are presented in Table 2.

Intercalation of *meso*-tetrakis[*N*-(3-sulfonatopropyl)-pyridinium-4-yl]porphyrin zinc from aqueous solution into $\mathbf{V_2O_5 \cdot}n\mathbf{H_2O}$ xerogel. A powder of $\mathrm{V_2O_5 \cdot}n\mathrm{H_2O}$ xerogel was added to an aqueous solution of porphyrin. The resulting mixture was magnetically stirred for 7 days in an argon atmosphere. The molar ratio porphyrin : xerogel was 0.1 : 1.0. Xerogel was filtered off, washed with water and acetone, and dried in air. Sample **6** was obtained. Found (%): C, 11.60; H, 2.62; N, 2.1; C/N, 5.5. $[\mathrm{PorZn(py^{+}(CH_2)_3SO_3^{-})}]_{0.05}\mathrm{V_2O_5 \cdot 2.5H_2O}$. Calculated (%): C, 10.93; H, 2.59; N, 1.96; C/N, 5.5. IR (KBr), ν/cm^{-1}: 3424 (NH); 1630 (CC$_{\mathrm{py}}$); 1498 (CN$_{\mathrm{py}}$); 1452 (CC$_{\mathrm{py}}$); 1180 (SO$_2$); 1043 (SO$_2$); 1611 (δ(H—O—H)); 1012, 978 (ν(V=O)); 914 (δ(V—O...H)); 758 (δ(V—O—V)); 515 (δ(V—O)).

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References

1. V. R. L. Constantino, C. A. S. Barbosa, M. A. Bizeto, P. M. Dias, *An. Acad. Bras. Ci.*, 2000, **72**, No. 1, 45.
2. J. Livage, *Chem. Mater.*, 1991, **3**, 578.
3. W. Ostermann, *Wiss. Ind. Hamburg*, 1922, **1**, 17.
4. J. Livage, *Coord. Chem. Rev.*, 1999, 190; 391.
5. A. Ditte, *C. R. Acad. Sci. Paris*, 1885, **101**, 698.
6. G. S. Zakharova, V. L. Volkov, *Usp. Khim.*, 2003, **72**, 346 [*Russ. Chem. Rev.* (*Engl. Transl.*), 2003, **72**, 311].
7. H. P. Oliveira, G. F. O. Graeff, J. M. Rosolen, *Mater. Res. Bull.*, 1999, **34**, 1891.
8. D. L. A. Faria, V. R. L. Constantino, K. J. Baldwin, D. N. Batchelder, T. J. Pinnavaia, M. Chibwe, *J. Raman Spectroscopy*, 1998, **29**, 103.
9. Z. Tong, T. Shichi, K. Takagi, *Mater. Lett.*, 2003, **57**, 2258.
10. C. A. S. Barbosa, A. D. C. Ferreira, V. R. L. Constantino, *Eur. J. Inorg. Chem.*, 2005, 1577.
11. V. I. Iliev, A. I. Ileva, L. D. Dimitrov, *Appl. Catal. A: General*, 1995, **126**, 333.
12. M. Chibwe, L. Ukrainczyk, S. A. Boyd, T. J. Pinnavaia, *J. Mol. Catal. A: Chem.*, 1996, **113**, 249.
13. K. A. Carrado, J. E. Forman, R. E. Botto, R. E. Winans, *Chem. Mater.*, 1993, **5**, 472.
14. M. A. Bizeto, D. L. A. Faria, V. R. L. Constantino, *J. Mater. Sci. Lett.*, 1999, **18**, 643.
15. Z. Tong, T. Shichi, K. Takagi, *J. Phys. Chem. B*, 2002, **106**, 13306.
16. M. A. Bizeto, D. L. A. Faria, V. R. L. Constantino, *J. Mater. Sci.*, 2002, **37**, 265.
17. M. A. Bizeto, V. R. L. Constantino, *Microporous Mesoporous Materials*, 2005, **83**, 212.
18. S. S. Cady, T. J. Pinnavaia, *Inorg. Chem.*, 1978, **17**, 1501.
19. D. Delmarre, C. Bied-Charreton, *Sensors Actuators B*, 2000, **62**, 136.
20. S. Nakagaki, G. S. Machado, M. Halma, A. A. S. Marangon, K. A. D. Freitas Castro, N. Mattoso, F. Wypych, *J. Catal.*, 2006, **242**, 110.
21. T. Nakato, Y. Iwata, K. Kuroda, M. Kaneko, C. Kato, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 1405.
22. H. E. Toma, H. P. Oliveira, H. R. Rechenberg, *J. Inclus. Phenom. Mol. Recog. Chem.*, 1994, **17**, 351.
23. F. J. Anaissi, F. M. Engelmann, K. Araki, H. E. Toma, *Solid State Sci.*, 2003, **5**, 621.
24. E. Ruiz-Hitzky, B. Casal, *J. Chem. Soc.*, *Faraday Trans. 1*, 1986, **82**, 1597.
25. B. Casal, E. Ruiz-Hitzky, M. Crespin, D. Tinet, J. C. Galvan, *J. Chem. Soc.*, *Faraday Trans. 1*, 1989, **85**, 4167.
26. P. N. Trikalitis, V. Petkov, M. G. Kanatzidis, *Chem. Mater.*, 2003, **15**, 3337.
27. L. Lapok, Dissertation Dr. rer. Nat., Universität Bremen, Bremen, 2006, 219 S.

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