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Intercalation of substituted pyridine derivatives and bipyridine compounds into gel-V_2O_5 and $VOPO_4$ interlayer spaces and protonation of the guest molecules

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Substituted pyridine derivatives (X-py: X = H, 2,4-Me_2, 2-Me, 3-Cl, 3-Br and 4-CN) and bipyridine compounds (2,2′- and 4,4′-pyYpy: —Y— = none, —C_2H_2—, —SS— and —C_2H_4—) reacted with powdered gel-$V_2O_5 \cdot 1.6H_2O$ or $VOPO_4 \cdot 2H_2O$ suspended in ethanol to afford intercalation compounds. They contained 0.1–0.4 mol of guest molecules per vanadium ion. In the V_2O_5-intercalation compounds, intercalation essentially occurs through the diffusion of the guest molecules accompanied by the protonation on the nitrogen atoms to some extent in the interlayer space, resulting in a net expansion of the spacings of 4.0–5.0 Å. The long-axis direction of the guest molecules is arranged approximately parallel to the V_2O_5-sheet, and hydrogen bonds are formed between the N-components of the protonated guest molecules and the V=O sites. The interlayer distances are lengthened with an increase of the amount of the N-protonated pyridyl moieties in the interlayer space. In the $VOPO_4$-intercalation compounds, the net expansions of the interlayer spaces were 7.0–12.0 Å, the guest molecules being arranged approximately perpendicular to the host layer. There is no appreciable relationship between the interlayer distances and the amounts of N-protonated pyridyl moieties.

Vanadium pentoxide xerogel (gel-V_2O_5) has a lamellar structure[1] and can be intercalated with various metal ions,[2,3] organic[4–9] and organometallic compounds[10–13] by diffusion and redox reactions. $VOPO_4 \cdot 2H_2O$ is also known as a layered compound[14–17] which upon intercalation undergoes reactions with organic and organometallic compounds.[12,18–23] In these host compounds, distances between the nearest neighboring vanadium atoms are appreciably different, which cause different orientations of the inserted guest molecules and various electronic states of the host and guest lattices.

Previously we found that 2- and 4-sulfanylpyridines can be intercalated into the gel-V_2O_5 lattice through the oxidative sulfur–sulfur coupling of the guest molecules, accompanied with the reduction of vanadium(V) to vanadium(IV).[8] During intercalation, N-protonation occurred for the guest molecules as charge compensation for the reduced vanadium(IV) ion, with varying relative abundances of protonated and unprotonated nitrogen atoms of the guest moieties in the interlayer space. Protonation of the guest molecules in the interlayer spaces is expected to be affected by the sizes and basicities of the guest pyridyl molecules.

In this work, we have tried to intercalate several substituted pyridine derivatives (py-X; X = H, 2,4-Me_2, 2-Me, 3-Cl, 3-Br and 4-CN) and bipyridine compounds (2,2′- and 4,4′-pyYpy; Y = none, —C_2H_2—, —SS— and —C_2H_4—) into the gel-V_2O_5 and $VOPO_4$ interlayer spaces. Arrangements and protonation of the guest molecules in the interlayer spaces are discussed on the basis of thermal analyses, spectroscopic data and magnetic susceptibilities.

Experimental

Materials

The layered host compounds, gel-$V_2O_5 \cdot 1.6H_2O$[24] and $VOPO_4 \cdot 2H_2O$,[19] were prepared according to the literature procedures. Substituted pyridine derivatives and bipyridine compounds used as guest molecules were commercially available.

Preparations of V_2O_5-intercalation compounds

Finely powdered gel-$V_2O_5 \cdot 1.6H_2O$ (300 mg, 1.4 mmol) was added into an ethanol solution (20 cm^3) containing pyridine (4.2 mmol) as a guest molecule and the suspended solution was stirred at room temperature for 5 days in the dark. The resulting precipitates were collected by centrifugation, washed with acetone several times and then dried *in vacuo* to afford $V_2O_5(H_2O)_{0.89}(py)_{0.38}$ **1**. Found: C, 9.90; H, 1.62; N, 2.32. Calc. for $C_{1.9}H_{3.68}N_{0.38}O_{5.89}V_2$: C, 10.01; H, 1.63; N, 2.33%.

Similarly, pyridine or bipyridine derivatives were reacted with gel-$V_2O_5 \cdot 1.6H_2O$ to give intercalation compounds. $V_2O_5(H_2O)_{0.48}(2,4\text{-}Me_2py)_{0.33}$ **2**. Found: C, 12.62; H, 1.76; N, 2.02. Calc. for $C_{2.31}H_{3.93}N_{0.33}O_{5.48}V_2$: C, 12.28; H, 1.75; N, 2.05%. $V_2O_5(H_2O)_{0.73}(2\text{-}Mepy)_{0.39}$ **3**. Found: C, 11.97; H, 1.83; N, 2.38. Calc. for $C_{2.34}H_{4.19}N_{0.39}O_{5.73}V_2$: C, 12.15; H, 1.83; N, 2.36%. $V_2O_5(H_2O)_{0.51}(3\text{-}Clpy)_{0.37}$ **4**. Found: C, 9.92; H, 1.08; N, 2.17. Calc. for $C_{1.85}H_{2.5}Cl_{0.37}N_{0.37}O_{5.51}V_2$: C, 9.53; H, 1.08; N, 2.22%. $V_2O_5(H_2O)_{0.57}(3\text{-}Brpy)_{0.35}$ **5**. Found: C, 8.68; H, 1.03; N, 1.94. Calc. for $C_{1.75}H_{2.54}Br_{0.35}N_{0.35}O_{5.57}V_2$: C, 8.49; H, 1.03; N, 1.98%. $V_2O_5(H_2O)_{0.72}(4\text{-}CNpy)_{0.35}$ **6**. Found: C, 10.98; H, 1.23; N, 4.11. Calc. for $C_{2.1}H_{2.87}N_{0.7}O_{5.72}V_2$: C, 10.91; H, 1.24; N, 4.24%. $V_2O_5(H_2O)_{0.8}(2,2'\text{-}bpy)_{0.21}$ **7**. Found: C, 11.05; H, 1.23; N, 2.50. Calc. for $C_{2.1}H_{3.28}N_{0.42}O_{5.8}V_2$: C, 11.01; H, 1.24; N, 2.57%. $V_2O_5(H_2O)_{0.57}(4,4'\text{-}bpy)_{0.31}$ **8**. Found: C, 15.68; H, 1.57; N, 3.76. Calc. for $C_{3.1}H_{3.62}N_{0.62}O_{5.57}V_2$: C, 15.48; H, 1.52; N, 3.61%. $V_2O_5(H_2O)_{0.55}(2,2'\text{-}pyC_2H_2py)_{0.24}$ **9**. Found: C, 14.73; H, 1.55; N, 2.81. Calc. for $C_{2.88}H_{3.5}N_{0.48}O_{5.55}V_2$: C, 14.68; H, 1.40; N, 2.85%. $V_2O_5(H_2O)_{0.82}(4,4'\text{-}pyC_2H_2py)_{0.25}$ **10**. Found: C, 15.06; H, 1.74; N, 2.89. Calc. for $C_3H_{4.14}N_{0.5}O_{5.82}V_2$: C, 15.35; H, 1.75; N, 2.89%. $V_2O_5(H_2O)_{0.26}(2,2'\text{-}pySSpy)_{0.18}$ **11**. Found: C, 9.98; H, 1.11; N, 2.38. Calc. for $C_{1.8}H_{1.96}N_{0.36}O_{5.26}S_{0.36}V_2$: C, 9.56; H, 0.87; N, 2.23%. $V_2O_5(H_2O)_{0.68}(4,4'\text{-}pySSpy)_{0.18}$ **12**. Found: C, 9.65; H, 1.34; N, 2.11. Calc. for $C_{1.8}H_{2.8}N_{0.36}O_{5.68}S_{0.36}V_2$: C, 9.25; H, 1.21; N, 2.16%. $V_2O_5(H_2O)_{0.6}(4,4'\text{-}pyC_2H_4py)_{0.25}$ **13**. Found: C, 15.40; H, 1.78; N, 2.89. Calc. for $C_3H_{4.2}N_{0.5}O_{5.6}V_2$: C, 15.09; H, 1.77; N, 2.93%. Water contents were determined by thermogravimetry.

Preparation of $VOPO_4$-intercalation compounds

Finely powdered solids of $VOPO_4 \cdot 2H_2O$ (300 mg, 1.5 mmol) were added to an ethanol solution (20 cm^3) containing 2,2′-bpy (4.5 mmol) and the suspended solution was stirred at room temperature for 5 days in the dark. The resulting solids were collected by centrifugation, washed with acetone several times and then dried *in vacuo* to afford $VOPO_4(H_2O)_{0.22}(EtOH)_{0.73}$(2,2′-bpy)$_{0.69}$ **14**. Found: C, 32.70, H, 3.40; N, 6.29. Calc. for $C_{8.36}H_{10.34}N_{1.38}O_{5.95}PV$: C, 32.68; H, 3.39; N, 6.29%.

Similarly, bipyridine derivatives were reacted with $VOPO_4 \cdot 2H_2O$ to give intercalation compounds. $VOPO_4(H_2O)_{0.33}(EtOH)_{0.31}$(4,4′-bpy)$_{0.46}$ **15**. Found: C, 24.79, H, 2.47; N, 5.07. Calc. for $C_{5.22}H_{6.2}N_{0.92}O_{5.64}PV$: C, 24.69; H, 2.46; N, 5.07%. $VOPO_4(H_2O)_{0.1}(EtOH)_{0.57}$(2,2′-py$C_2H_2$py)$_{0.4}$ **16**. Found: C, 27.09, H, 3.03; N, 4.44. Calc. for $C_{5.94}H_{7.62}N_{0.8}O_{5.67}PV$: C, 27.14; H, 2.92; N, 4.26%. $VOPO_4(H_2O)_{0.67}(EtOH)_{0.72}$(4,4′-py$C_2H_2$py)$_{0.45}$ **17**. Found: C, 28.43, H, 3.54; N, 4.73. Calc. for $C_{6.84}H_{10.16}N_{0.9}O_{6.39}PV$: C, 28.39; H, 3.55; N, 4.36%. $VOPO_4(H_2O)_{0.3}(EtOH)_{0.9}$(2,2′-pySSpy)$_{0.15}$ **18**. Found: C, 16.93, H, 2.68; N, 1.79. Calc. for $C_{3.3}H_{7.2}N_{0.3}O_{6.2}PS_{0.3}V$: C, 16.39; H, 3.00; N, 1.74%.

Physical measurements

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Geigerfled RAD-IA diffractometer of the Faculty of Science, Osaka University. Finely powdered samples were mounted on a glass plate and irradiated by the Cu-Kα line (30 kV, 20 mA). The scan rate was 2° min^{-1} with the sampling step of 0.5°. X-Ray photoelectron spectra (XPS) for the intercalation compounds were measured by irradiating the compounds with the Mg-Kα line (240 W) using a Shimadzu ESCA-750 spectrometer with the ESCA PAC 760 computer analyzer of Osaka Municipal Technical Research Institute and a Shimadzu HIPS-70 spectrometer of the Faculty of Science, Osaka University. Electron binding energies were calibrated with a carbon $1s_{1/2}$ peak (285.0 eV). Thermogravimetry (TG) was carried out on a Seiko TG/DTA 200 instrument with a heating rate of 2 K min^{-1} from room temperature to 450 °C. Samples were mounted on an aluminium pan and the measured mass changes were calibrated with α-alumina. Magnetic susceptibilities were obtained by the Gouy method at room temperature using the instrument of the Faculty of Science, Osaka University.

Results and Discussion

Arrangement of the guest molecules in the V_2O_5 interlayer space

Intercalation compounds **1**–**13** were obtained by reactions of substituted pyridines or bipyridine compounds with powdered gel-$V_2O_5 \cdot 1.6\ H_2O$ solids suspended in ethanol. These compounds include 0.2–0.4 organic guest molecules per V_2O_5 unit. Fig. 1 shows powder X-ray diffraction (XRD) patterns of compound **11** and gel-$V_2O_5 \cdot 1.6H_2O$. Clear 001–003 reflections appear, indicating a homogenous intercalation of the guest molecule into the V_2O_5 interlayer space for **11**. Table 1 lists interlayer distances for the intercalation compounds determined by the low order diffraction peaks of the XRD patterns, together with expansions of the interlayer space with respect to that (8.8 Å) of $V_2O_5 \cdot 0.6H_2O$.[25,26] The net expansions of the interlayer spaces for these compounds are 4.0–5.0 Å, which are scarcely affected by sizes of the guest molecules. This finding implies that the long-axis direction of the guest molecules is arranged approximately parallel to the two-dimensional sheet of the V_2O_5 host layer, as reported for the V_2O_5-intercalation compounds containing ferrocenyl compounds.[12,13]

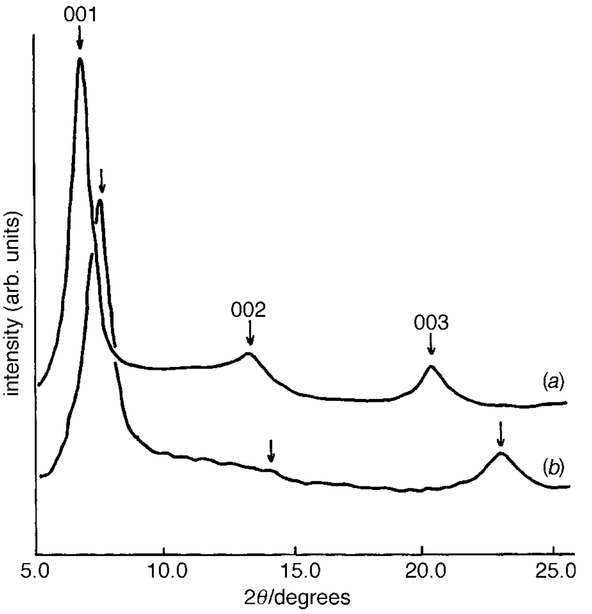

Fig. 1 Powder X-ray diffraction patterns of (*a*) $V_2O_5(H_2O)_{0.26}$(2,2′-pySSpy)$_{0.18}$ **11** and (*b*) gel-$V_2O_5 \cdot 1.6H_2O$

Table 1 Interlayer distances (*d*) of the V_2O_5-intercalation compounds

compound	d/Å	$\Delta d\ (=d-8.8^a)$/Å
1	13.0	4.2
2	13.8	5.0
3	13.4	4.6
4	12.9	4.1
5	12.9	4.1
6	13.4	4.6
7	13.0	4.2
8	13.8	5.0
9	12.8	4.0
10	13.6	4.8
11	13.1	4.3
12	13.3	4.5
13	13.0	4.2

[a] $d = 8.8$ Å for $V_2O_5 \cdot 0.6H_2O$.[25,26]

IR spectra of the V_2O_5-intercalation compounds show bands at 1000–1600 cm^{-1} ascribed to the pyridyl and pyridinium rings, which indicate the presence of guest molecules in the V_2O_5 interlayer space. Broad bands observed at 3000–3600 cm^{-1} have been assigned to the N—H stretching vibration,[7] suggesting the presence of N-protonated pyridyl rings in the interlayer space.

Thermogravimetry for the intercalation compounds shows mass loss due to the release of water molecules upon heating to *ca.* 200 °C. In the temperature range 200–450 °C, the TG curves exhibit two mass loss steps owing to the release of the guest molecules at *ca.* 280 and 360 °C. These findings indicate two different environments of the guest molecules in the interlayer space; that is, some of the guest molecules have a stronger interaction with the V_2O_5 host layer than others. This stronger interaction may be due to hydrogen bonding between V=O sites and the N—H components of protonated guest molecules, which is consistent with the results of IR spectra as well as the results of XRD described below.

Mechanism of intercalation into the V_2O_5 interlayer space

The V_2O_5-intercalation compounds exhibit XPS bands due to vanadium $2p_{3/2}$ electrons at 517.0–517.5 eV. The binding energies are essentially the same as that (517.5 eV) of gel-$V_2O_5 \cdot 1.6H_2O$. Gel-$V_2O_5 \cdot 1.6H_2O$ was reported to contain a small amount of the paramagnetic vanadium(IV) ion,[27] estimated as 5.2% based on magnetic susceptibility measurements. The amounts of vanadium(IV) ion present in the intercalation compounds have been calculated by their magnetic susceptibilities, and are summarized in Table 2, together with the amounts of the N-protonated pyridyl moieties determined by XPS as described below. Intercalation of the pyridyl compounds has resulted in a slight increase of the amount of vanadium(IV) ions in the host layer, although compounds **11** and **12** contain somewhat increased amounts of vanadium(IV) ion.

The vanadium(IV) ion content leads to negative charges in the host layer, which have to be compensated with positive charges in the interlayer space. However, they are less than the amounts of the N-protonated pyridyl moieties ([NH$^+$]) per vanadium ion sites as calculated by the deconvolution of nitrogen $1s_{1/2}$ XPS bands (Table 2). These findings imply the presence of anions other than formally negatively charged vanadium(IV) moieties in the interlayer space. Thus, the intercalation can be explained based on the charge separation of water molecules in the interlayer space, as schematically illustrated in Fig. 2. Gel-$V_2O_5 \cdot 1.6H_2O$ contains protons in the interlayer as a counter cation for the formally negatively charged host layer due to vanadium(IV) ions. Guest molecules intercalated into the V_2O_5 interlayer are protonated. However, the host layer cannot supply sufficient amounts of protons for these, the charge separation of water molecules compensating this lack of protons. The N-protonated pyridyl cation moieties are electrically compensated with both the formally negatively charged host layer and hydroxide ions in the interlayer space.

Table 2 Magnetic susceptibilities (χ_p), contents of the vanadium(IV) ion ([V^{IV}]) and of the N-protonated pyridyl moiety per vanadium ion ([NH$^+$]) for the V_2O_5-intercalation compounds

compound	10 χ_p/cm^3 mol^{-1}	10^2[V^{IV}]	10^2[NH$^+$]
$V_2O_5 \cdot 1.6H_2O$	6.32	5.2	—
1	6.89	5.6	15.0
2	9.12	6.3	15.0
3	7.76	7.4	15.5
4	7.77	7.5	12.0
5	9.30	6.3	12.0
6	8.09	6.7	14.0
7	7.91	6.8	10.5
8	8.15	6.7	16.0
9	8.67	7.0	12.0
10	8.97	7.2	15.0
11	14.3	11.6	13.0
12	11.3	9.2	15.0
13	7.74	6.3	14.5

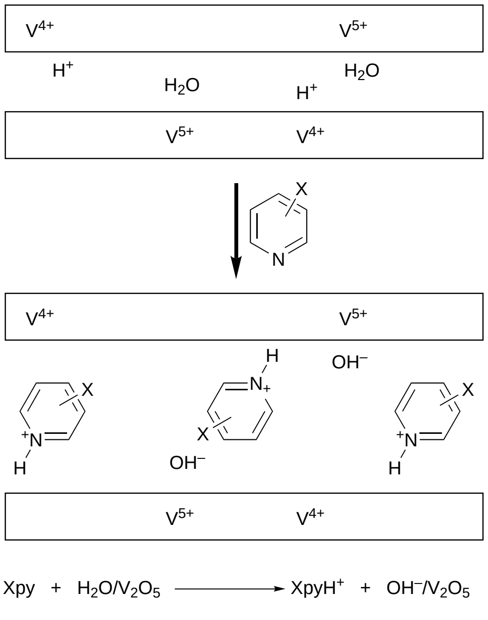

Fig. 2 Schematic representation of the intercalation of pyridine derivatives into the gel-V_2O_5 interlayer space

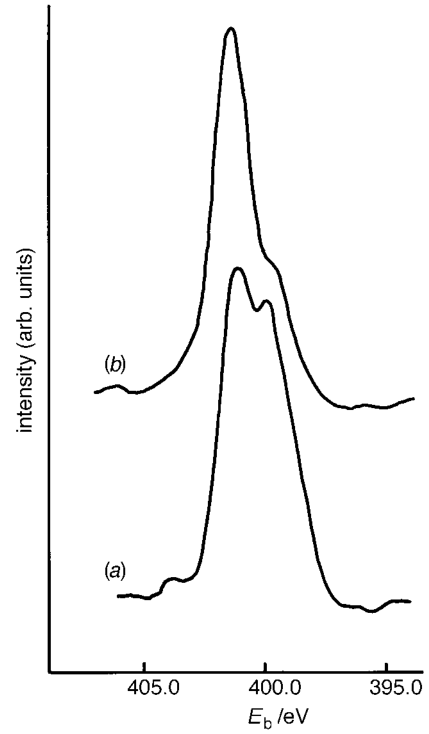

Fig. 3 X-Ray photoelectron spectra of N $1s_{1/2}$ electrons of (*a*) $V_2O_5(H_2O)_{0.55}(2,2'\text{-}pyC_2H_2py)_{0.24}$ **9** and (*b*) $V_2O_5(H_2O)_{0.68}(4,4'\text{-}pySSpy)_{0.18}$ **12**

N-Protonation of the guest molecules in the V_2O_5 interlayer space

Fig. 3 shows nitrogen $1s_{1/2}$ XPS bands of compounds **9** and **12**. The bands around 399 and 401 eV observed in both the spectra are assigned to unprotonated and protonated nitrogen atoms, respectively. They indicate that protonation of the guest molecules occurs during the intercalation process, which is consistent with the results of the IR and TG measurements. The other intercalation compounds also show two XPS bands due to the unprotonated and protonated nitrogen atoms.

The relative abundances of the protonated pyridyl moieties to the unprotonated pyridyl ones ([NH$^+$]/[N]) have been calculated by the deconvolution of the nitrogen $1s_{1/2}$ XPS bands into two Gaussian peaks. They vary with the guest molecules. However, they exhibit no appreciable relationship with sizes and basicities[28–30] of the guest molecules.

In the intercalation compounds, the locations and orientations of the guest molecules are restricted by the host layer, and the host–guest interaction should be considered to elucidate the protonation behavior of the guest molecules. There is an appreciable relationship in the plots of the interlayer distances of the intercalation compounds *vs.* amount of N-protonated pyridyl moieties per vanadium ion site ([NH$^+$] in Table 2), as displayed in Fig. 4. For compound **7** containing 2,2′-bpy as a guest molecule, the [NH$^+$] content is exceptionally low. This is likely to arise from the extreme stabilization of the 2,2′-bpyH$^+$ species due to chelation through the two pyridyl nitrogen atoms.

The above approximate linear correlation can be rationalized based on the distribution of positive charges in the limited interlayer space as follows. In the V_2O_5-intercalation compounds, negative charges are bound on the surface of the host layer, and positive charges are distributed on the NH$^+$ sites of the guest molecules to form layers in proximity with the negative charge layers. Dominant energetic factors affecting

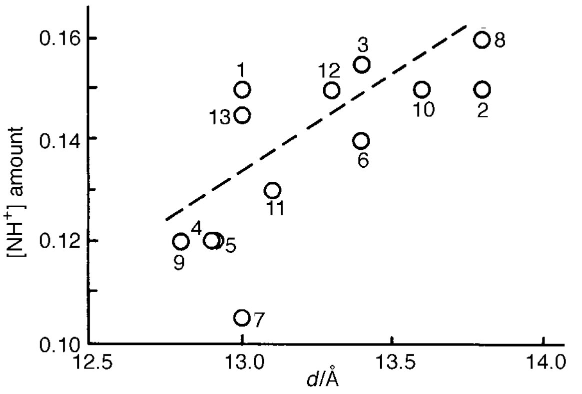

Fig. 4 Plots of the amounts of the N-protonated pyridyl moiety per vanadium ion ([NH$^+$]) *vs.* the interlayer distances (*d*) of the V_2O_5 intercalation compounds

the host interlayer distances are coulombic repulsion and van der Waals attraction between the negative host layers.[31] The coulombic repulsion is shielded by the NH$^+$ cation moieties in the interlayer space. Thus, the equilibrium interlayer distances are expected to be longer as the screening effect due to the positive charges in the interlayer space is weakened. However, the experimental observation shows that interlayer distances are enlarged with increase of the [NH$^+$] content (Fig. 4).

If the positive cloud of the cations is freely deformable like the case of the charged surface in contact with a bulk solution, an electrolytic double layer inversely proportional to the concentration of an electrolyte is formed, where the coulombic repulsion is shielded efficiently within the double layer. In this case, the reduction of the positive density due to the cations results in an expansion of the interlayer space. On the other hand, in the V_2O_5-intercalation compounds the increased amounts of the NH$^+$ cation in the interlayer space appear to weaken the shielding of the host–host coulombic repulsion, leading to an increase of interlayer distances. This effect weakening the shielding arises from the characteristic distribution of negative and positive charges in the interlayer space.

The interlayer space is constructed with three layers; two hydrophilic regions consisting of water molecules and the hydroxide ions near the V=O groups of the host layer surface and the hydrophobic middle region consisting of guest molecules which carry positive charges. In this construction, the NH$^+$ cation moieties stay apart from the anionic host surface and the positive regions of the cations. The NH$^+$ cation moieties formed by the charge separation of water molecules are confined in the narrow hydrophobic layer of the guest molecules. Increasing amounts of cation moieties increase the repulsion between the cation layers of the guest array, which causes the expansion of the thickness of the middle hydrophobic layer leading to enlargement of the interlayer distance.

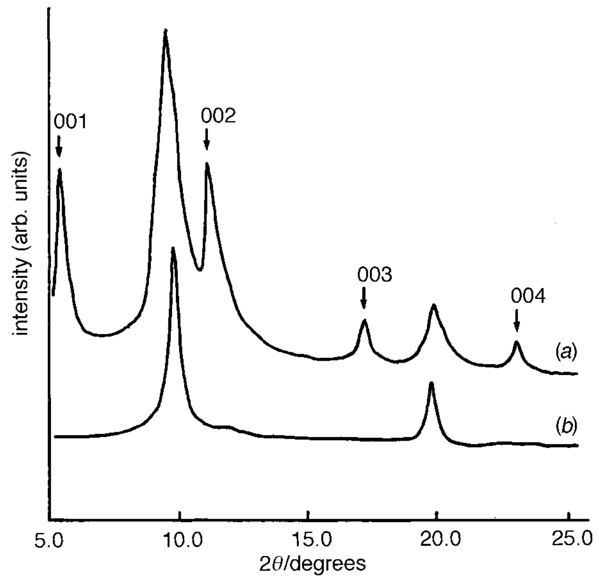

Fig. 5 Powder X-ray diffraction patterns of (*a*) $VOPO_4(H_2O)_{0.30}(EtOH)_{0.90}(2,2'\text{-pySSpy})_{0.15}$ **18** and (*b*) the solids obtained by stirring of an ethanol solution suspended with powdered $VOPO_4 \cdot 2H_2O$ for 5 days

Table 3 Interlayer distances (*d*) of the $VOPO_4$-intercalation compounds

compound	*d*/Å	Δ*d* (=*d*−4.4[a])/Å
14	11.6	7.2
15	13.0	8.6
16	14.5	10.1
17	15.2	10.8
18	16.1	11.7

[a] *d*=4.4 Å for anhydrous $VOPO_4$.[32]

$VOPO_4$-intercalation compounds

Intercalation compounds **14**–**18** were obtained by reactions of the bipyridine compounds with powdered $VOPO_4 \cdot 2H_2O$ suspended in ethanol. These compounds contain 0.2–0.7 guest moieties per $VOPO_4$ unit. Fig. 5 displays the XRD pattern of compound **18**, together with that of the $VOPO_4$ solids containing water and ethanol molecules. The XRD pattern of compound **18** indicates that it has layers containing both 2,2′-pySSpy moieties and ethanol/water molecules. The other $VOPO_4$-intercalation compounds also show two types of interlayer spacings. Table 3 lists the interlayer distances as a result of intercalation of the guest molecules determined by the lowest order diffraction peaks of the XRD patterns, together with expansions of the interlayer space with respect to that (4.4 Å) of anhydrous $VOPO_4$.[32] The net expansions of the interlayer spaces for these compounds are 7.0–12.0 Å. In the $VOPO_4$-intercalation compounds, the interlayer distances depend on the sizes of the guest molecules arranged approximately perpendicular to the $VOPO_4$-sheets, as reported for amine and ferrocenyl compounds.[12,23] Varying interlayer distances which depend on the sizes of the guest molecules are ascribed to a rather weak interaction between the $VOPO_4$-host layers compared with that between the V_2O_5-host layers.

There is no appreciable relationship between the amounts of N-protonated pyridyl moieties per vanadium ion and the interlayer distances of the $VOPO_4$-intercalation compounds, which is in contrast to the correlation observed for the above-described V_2O_5-intercalation compounds. This is due to the fact that the $VOPO_4$-host layer has a more distorted layered structure with weaker interactions between the neighboring host layers compared with the V_2O_5-host layer.

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