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Intercalation of Ferrocene and (Ferrocenylalkyl)ammonium Halides into the Gel-V_2O_5 Interlayer Space

Shoji OKUNO and Gen-etsu MATSUBAYASHI*
Institute of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka 560

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Ferrocene, FcH, 1, 1′-dimethylferrocene, $FcMe_2$, some (ferrocenylalkyl)ammonium iodides, $Fc(CH_2)_nNR_2R'^+I^-$, chlorides, $Fc(CH_2)_nNR_2R'^+Cl^-$ [$Fc=(C_5H_5)Fe(C_5H_4)$; $n=1$ and 2; R, R′ = H and Me], benzyldimethyl-, benzyltrimethylammonium and octylammonium iodides reacted with powdered gel-V_2O_5 suspended in ethanol to afford intercalation compounds; $V_2O_5{\cdot}(H_2O)_{0.6}{\cdot}[Fc^+H]_{0.27}$, $V_2O_5{\cdot}(H_2O)_{0.6}{\cdot}[Fc^+Me_2]_{0.22}$, $V_2O_5{\cdot}(H_2O)_{0.6}{\cdot}[Fc^+CH_2NHMe_2{}^+]_{0.16}$, $V_2O_5{\cdot}(H_2O)_{0.6}{\cdot}[Fc^+CH_2NMe_3{}^+]_{0.15}$, $V_2O_5{\cdot}(H_2O)_{0.8}{\cdot}[Fc^+CH_2CH_2NH_3{}^+]_{0.21}$, $V_2O_5{\cdot}(H_2O)_{0.8}{\cdot}[Fc^+CH_2CH_2NMe_3{}^+]_{0.14}$, $V_2O_5{\cdot}(H_2O)_{0.6}{\cdot}[Fc^+CH_2NHMe_2{}^+]_{0.18}$, $V_2O_5{\cdot}(H_2O)_{0.6}{\cdot}[Fc^+CH_2CH_2NH_3{}^+]_{0.22}$, $V_2O_5{\cdot}(H_2O)_{0.6}{\cdot}[PhCH_2NHMe_2{}^+]_{0.29}$, $V_2O_5{\cdot}(H_2O)_{0.6}{\cdot}[PhCH_2NMe_3{}^+]_{0.24}$, and $V_2O_5{\cdot}(H_2O)_{0.6}{\cdot}[n\text{-}C_8H_{17}NH_3{}^+]_{0.33}$. The intercalation compounds are constructed with layered V_2O_5 moieties in both V(IV) and V(V) states and the ferrocenium, the ferrocenium derivatives, the benzyldimethyl-, the benzyltrimethylammonium or the octylammonium cation in the interlayer space, producing the single V_2O_5-interlayer spacings. Molecular arrangements of these (ferrocenylalkyl)ammonium species in the interlayer space and electronic states of the guest and the host moieties are discussed on the basis of powder X-ray diffraction patterns as well as powder reflectance, ESR and X-ray photoelectron spectra.

Lamellar inorganic solids have been investigated with much interest, because they can include various metal ions, organic and organometallic compounds in the interlayer spaces, and these guest molecules have characteristic structures and electronic states.[1] As reported previously,[2—5] ferrocene and (ferrocenylalkyl)ammonium derivatives can be intercalated into the vanadium oxide phosphate ($VOPO_4$) interlayer space through the redox reaction. Molecular arrangements and the oxidation states of the guest molecules in the interlayer space are greatly affected by the extent of proximity of the ammonio groups and the ferrocenyl center to the vanadium site of the host skeleton.[5]

Vanadium(V) oxide xerogel (gel-V_2O_5) has also a lamellar structure,[6] and can be intercalated with various metal ions,[7,8] organic compounds[9—11] and organometallic compounds[12] by the cation exchange or the redox reaction. Its structure has been investigated with electron, X-ray,[13] and neutron diffraction analyses.[14] The distance between the nearest neighboring vanadium ions as a redox site of gel-V_2O_5 is estimated to be shorter than that of $VOPO_4$.[15—18] Thus, the molecular arrangements and electronic states of the (ferrocenylalkyl)ammonium compounds intercalated into the gel-V_2O_5 interlayer space can be interestingly compared with those of the $VOPO_4$ intercalation compounds, and important factors for their intercalation into the $VOPO_4$- and V_2O_5-interlayer spaces may be clarified.

This paper reports the intercalation of ferrocene, 1,1′-dimethylferrocene and several (ferrocenylalkyl)ammonium compounds into the V_2O_5 interlayer space accompanied with the reduction of the V(V)- to V(IV) site. On the basis of powder X-ray diffraction patterns, electronic reflectance, ESR and X-ray photoelectron spectra, electronic states and molecular arrangements of the V_2O_5-intercalation compounds are discussed in comparison with those of the $VOPO_4$-intercalation ones.

Experimental

Materials. Gel-V_2O_5 [$V_2O_5{\cdot}(H_2O)_{1.6}$] was prepared according to the literature.[19] Ferrocene, FcH, and 1,1′-dimethylferrocene, $FcMe_2$, were commercially available. (Ferrocenylalkyl)ammonium iodide and chloride were prepared as reported previously.[5] 2-Ferrocenylethanamine, $FcCH_2CH_2NH_2$,[20] (ferrocenylmethyl)trimethylammonium iodide, $FcCH_2NMe_3{}^+I^-$, and (2-ferrocenylethyl)trimethylammonium iodide, $FcCH_2CH_2NMe_3{}^+I^-$,[21] were prepared according to the literatures. Commercially available [(dimethylamino)methyl]ferrocene, $FcCH_2NMe_2$, reacted with HCl and HI aqueous solutions to afford (ferrocenylmethyl)dimethylammonium chloride, $FcCH_2NHMe_2{}^+Cl^-$, and iodide, $FcCH_2NHMe_2{}^+I^-$. Similarly, (2-ferrocenylethyl)ammonium chloride, $FcCH_2CH_2NH_3{}^+Cl^-$, and iodide, $FcCH_2CH_2NH_3{}^+I^-$, were prepared from 2-ferrocenylethanamine. N,N-Dimethylbenzylamine reacted with an HI aqueous solution or methyl iodide to afford benzyldimethylammonium iodide or benzyltrimethylammonium iodide. Octylamine reacted with an HI aqueous solution to give octylammonium iodide.

Intercalation of the Ferrocene Derivatives into Gel-V_2O_5. Into an ethanol (100 cm^3) solution of FcH (0.78 g, 4.2 mmol) or $FcMe_2$ (0.90 g, 4.2 mmol) was added finely powdered gel-V_2O_5 (300 mg, 1.4 mmol) and the suspended solution was stirred at room temperature for 30 d in darkness. The resulting precipitate was collected by centrifugation, washed with ethanol and dried in vacuo. The compositions of the products were $V_2O_5{\cdot}(H_2O)_{0.6}{\cdot}[Fc^+H]_{0.27}$ (**1**) (Found: C, 13.22; H, 1.61%. Calcd for $C_{2.7}H_{3.9}Fe_{0.27}O_{5.6}V_2$: C, 13.35; H, 1.62%) and $V_2O_5{\cdot}(H_2O)_{0.6}{\cdot}[Fc^+Me_2]_{0.22}$ (**2**) (Found: C, 13.33; H, 1.82%. Calcd for $C_{2.65}H_{4.3}Fe_{0.22}O_{5.6}V_2$: C, 13.27; H, 1.81%). Similarly, an ethanol (200 cm^3) solution of $FcCH_2NHMe_2{}^+I^-$ (1.56 g, 4.2 mmol), $FcCH_2NMe_3{}^+I^-$ (1.62 g, 4.2 mmol), $FcCH_2CH_2NH_3{}^+I^-$

(1.50 g, 4.2 mmol), or $FcCH_2CH_2NMe_3{}^+I^-$ (1.68 g, 4.2 mmol) suspended with gel-V_2O_5(300 mg, 1.4 mmol) was stirred at room temperature for 21 d to afford intercalation compounds: $V_2O_5 \cdot (H_2O)_{0.6} \cdot [Fc^+CH_2NHMe_2{}^+]_{0.16}$ (**3**) (Found: C, 10.59; H, 1.30; N, 1.22%. Calcd for $C_{2.1}H_{4.1}Fe_{0.16}N_{0.16}O_{5.6}V_2$: C, 10.87; H, 1.78; N, 0.97%), $V_2O_5 \cdot (H_2O)_{0.6} \cdot [Fc^+CH_2NMe_3{}^+]_{0.15}$ (**4**) (Found: C, 10.52; H, 1.87; N, 1.30%. Calcd for $C_{2.1}H_{4.2}Fe_{0.15}N_{0.15}O_{5.6}V_2$: C, 10.90; H, 1.83; N, 0.91%), $V_2O_5 \cdot (H_2O)_{0.8} \cdot [Fc^+CH_2CH_2NH_3{}^+]_{0.21}$ (**5**) (Found: C, 12.36; H, 1.75; N, 1.06%. Calcd for $C_{2.5}H_{4.95}Fe_{0.21}N_{0.21}O_{5.8}V_2$: C, 12.29; H, 2.04; N, 1.20%) or $V_2O_5 \cdot (H_2O)_{0.8} \cdot [Fc^+CH_2CH_2NMe_3{}^+]_{0.14}$ (**6**) (Found: C, 10.91; H, 1.60; N, 0.86%. Calcd for $C_{2.1}H_{4.7}Fe_{0.14}N_{0.14}O_{5.8}V_2$: C, 10.76; H, 2.02; N, 0.84%).

Finely powdered gel-V_2O_5 (300 mg, 1.4 mmol) was suspended in an ethanol (100 cm^3) solution containing an excess amount of $FcCH_2NHMe_2{}^+Cl^-$ (1.71 g, 4.2 mmol) or $FcCH_2CH_2NH_3{}^+Cl^-$ (1.12 g, 4.2 mmol) and the suspended solution was stirred for 30 d at room temperature to afford a precipitate of $V_2O_5 \cdot (H_2O)_{0.6} \cdot [Fc^+CH_2NHMe_2{}^+]_{0.18}$ (**7**) (Found: C, 11.76; H, 1.99; N, 1.51%. Calcd for $C_{2.4}H_{4.4}Fe_{0.18}N_{0.18}O_{5.6}V_2$: C, 11.92; H, 1.89; N, 1.06%) or $V_2O_5 \cdot (H_2O)_{0.6} \cdot [Fc^+CH_2CH_2NH_3{}^+]_{0.22}$ (**8**) (Found: C, 13.00; H, 2.24; N, 1.14%. Calcd for $C_{2.7}H_{4.7}Fe_{0.22}N_{0.22}O_{5.6}V_2$: C, 13.08; H, 1.95; N, 1.27%). The compound intercalated with the benzyldimethylammonium, the benzyltrimethylammonium or the octylammonium cation was also prepared by the reaction of finely powdered gel-V_2O_5 suspended in ethanol with an excess amount of $PhCH_2NHMe_2{}^+I^-$, $PhCH_2NMe_3{}^+I^-$ or $n\text{-}C_8H_{17}NH_3{}^+I^-$, as described above: $V_2O_5 \cdot (H_2O)_{0.6} \cdot [PhCH_2NHMe_2{}^+]_{0.29}$ (**9**) (Found: C, 13.31; H, 1.95; N, 1.82%. Calcd for $C_{2.6}H_{5.25}N_{0.29}O_{5.6}V_2$: C, 13.46; H, 2.28; N, 1.75%), $V_2O_5 \cdot (H_2O)_{0.6} \cdot [PhCH_2NMe_3{}^+]_{0.24}$ (**10**) (Found: C, 12.68; H, 1.95; N, 1.39%. Calcd for $C_{2.4}H_{5.05}N_{0.24}O_{5.6}V_2$: C, 12.60; H, 2.23; N, 1.47%), or $V_2O_5 \cdot (H_2O)_{0.6} \cdot [n\text{-}C_8H_{17}NH_3{}^+]_{0.33}$ (**11**) (Found: C, 13.51; H, 3.19; N, 2.05%. Calcd for $C_{2.65}H_{7.8}N_{0.33}O_{5.6}V_2$: C, 13.50; H, 3.33; N, 1.96%). Weight percents of included water per the V_2O_5 unit were determined for all the intercalation compounds by the thermogravic method; weight percent of water (calcd for H_2O molecules per V_2O_5): **1**, 4.1 (4.4); **2**, 4.3 (4.5); **3**, 4.0 (4.7); **4**, 4.3(4.7); **5**, 6.2 (5.9); **6**, 5.9 (6.1); **7**, 4.9 (4.6); **8**, 5.0 (4.4); **9**, 4.0 (4.7); **10**, 4.7 (4.7); **11**, 4.8 (4.6%).

Physical Measurements. Powder reflectance spectra were recorded on a Shimadzu UV-2200 spectrophotometer equipped with a 60ϕ integrating sphere unit at room temperature. X-ray photoelectron spectra (XPS) were measured by irradiating the compounds with Mg $K\alpha$ X-rays (240 W) at 298 K using a Shimadzu-ESCA 750 photoelectron spectrometer equipped with an ESCA PAC 760 computer analyzer. All the spectra were referenced to the carbon $1s_{1/2}$ photoelectron peak (285.0 eV) for correction of the charge effect. ESR and X-ray powder diffraction patterns were measured at room temperature, as described previously.[4] Thermogravic analysis was also carried out as described previously.[4]

Results and Discussion

Intercalation of the Ferrocene Derivatives into the V_2O_5 Interlayer. The vanadium(V) site of the gel-V_2O_5 can be reduced by the iodide ion and the ferrocenyl (Fc) center to form the intercalation compounds containing the cations having ammonium and ferrocenium (Fc^+) centers to compensate the charge. $FcCH_2NHMe_2{}^+I^-$ and $FcCH_2CH_2NH_3{}^+I^-$ can reduce V_2O_5 with both the Fc center and the iodide ion to afford intercalation compounds **3** and **5**, which are similar to the $VOPO_4$-intercalation compounds.[5] On the other hand, in the reactions of $FcCH_2NHMe_2{}^+Cl^-$ and $FcCH_2CH_2NH_3{}^+Cl^-$, only the Fc centers can reduce the vanadium (V) site to yield compounds **5** and **6**. In the intercalation reaction of $VOPO_4$ with these salts, $Fc^+CH_2NHMe_2{}^+Cl^-$ and $Fc^+CH_2CH_2NH_3{}^+Cl^-$ are included in the $VOPO_4$ interlayer space.[5] However, compounds **5** and **6** do not contain the chloride ion. This finding indicates that these ferrocenyl compounds are intercalated into the V_2O_5 interlayer through the redox reaction of the Fc center together with the ion exchange as reported for V_2O_5-intercalation compounds with several cations included in the interlayer space.[7—10,12]

Figure 1 shows the X-ray diffraction pattern of compound **1**, together with that of gel-V_2O_5. The interlayer distances of the V_2O_5-intercalation compounds have been determined by these spectra. They are summarized in Table 1. Compound **1** has almost the same interlayer distance as the V_2O_5–Fc^+H intercalation compound in which the Fc^+H cation was intercalated by an ion-exchange reaction (13.22—13.27 Å).[12] All the ferrocenyl derivative compounds **1**—**8** as well as the benzylammonium compounds **9** and **10** have similar interlayer distances (13.2—14.2 Å). Dehydration of $V_2O_5 \cdot (H_2O)_{1.6}$ to $V_2O_5 \cdot (H_2O)_{0.6}$ was reported to result in the decrease of the interlayer spacing to 8.8 Å.[22] The space-expansion between the neighboring V_2O_5 layers for the present compounds are estimated to be 4.4—5.4 Å. Thus, the (ferrocenylalkyl)ammonium and the benzylammonium cations seem to be intercalated into the V_2O_5 interlayer space with the

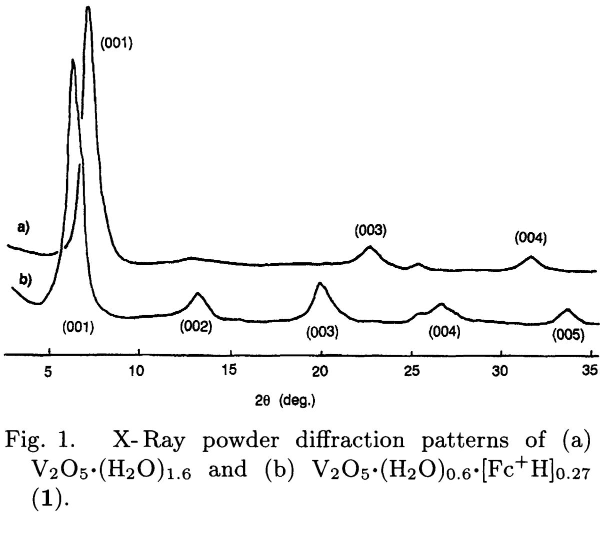

Fig. 1. X-Ray powder diffraction patterns of (a) $V_2O_5 \cdot (H_2O)_{1.6}$ and (b) $V_2O_5 \cdot (H_2O)_{0.6} \cdot [Fc^+H]_{0.27}$ (**1**).

Table 1. Interlayer Distances (*d*) of the V_2O_5 Intercalation Compounds

Compound	d/Å
$V_2O_5 \cdot (H_2O)_{1.6}$	11.6[a]
$V_2O_5 \cdot (H_2O)_{0.6} \cdot [Fc^+H]_{0.27}$ (**1**)	13.4
$V_2O_5 \cdot (H_2O)_{0.6} \cdot [Fc^+Me_2]_{0.22}$ (**2**)	13.4
$V_2O_5 \cdot (H_2O)_{0.6} \cdot [Fc^+CH_2NHMe_2{}^+]_{0.16}$ (**3**)	13.5
$V_2O_5 \cdot (H_2O)_{0.6} \cdot [Fc^+CH_2NMe_3{}^+]_{0.15}$ (**4**)	13.2
$V_2O_5 \cdot (H_2O)_{0.8} \cdot [Fc^+CH_2CH_2NH_3{}^+]_{0.21}$ (**5**)	13.4
$V_2O_5 \cdot (H_2O)_{0.8} \cdot [Fc^+CH_2CH_2NMe_3{}^+]_{0.14}$ (**6**)	13.5
$V_2O_5 \cdot (H_2O)_{0.6} \cdot [Fc^+CH_2NHMe_2{}^+]_{0.18}$ (**7**)	13.0
$V_2O_5 \cdot (H_2O)_{0.6} \cdot [Fc^+CH_2CH_2NH_3{}^+]_{0.22}$ (**8**)	13.4
$V_2O_5 \cdot (H_2O)_{0.6} \cdot [PhCH_2NHMe_2{}^+]_{0.29}$ (**9**)	14.2
$V_2O_5 \cdot (H_2O)_{0.6} \cdot [PhCH_2NMe_3{}^+]_{0.24}$ (**10**)	14.1
$V_2O_5 \cdot (H_2O)_{0.6} \cdot [n\text{-}C_8H_{17}NH_3{}^+]_{0.33}$ (**11**)	26.0

a) Ref. 22.

long directions of these cations arranged approximately parallel to the swelling V_2O_5 sheet (Fig. 2). This arrangement of the (ferrocenylalkyl)ammonium cations is close to those of (ferrocenylalkyl)trimethylammonium and benzyltrimethylammonium–$VOPO_4$ intercalation compounds.[5] On the other hand, compound **11** exhibits a long interlayer distance, indicating an orientation of the octylammonium cation declined to the perpendicular direction of the V_2O_5 sheet. Such an arrangement of the guest molecule was reported for V_2O_5 intercalation compounds having alkylammonium cations with long alkyl chains.[9] (Ferrocenylalkyl)ammonium cations with the $-NHR_2{}^+$groups (R=H and Me) can be intercalated into the $VOPO_4$ interlayer with the arrangement approximately perpendicular to the $VOPO_4$ sheet,[5] which is in contrast to the orientation of these cations parallel to the V_2O_5 sheet observed for the present intercalation compounds.

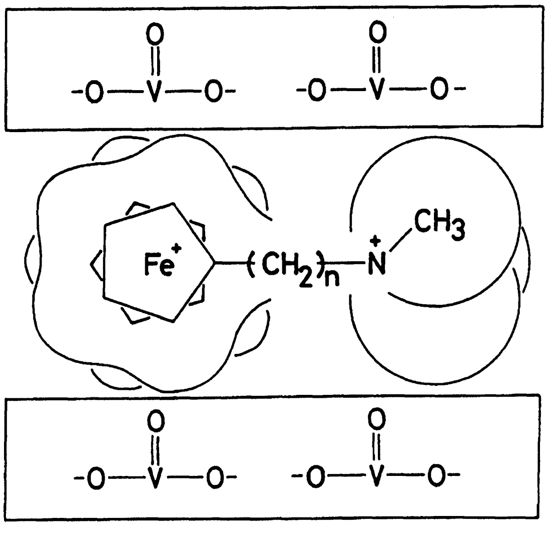

Fig. 2. Schematic arrangement of (ferrocenylalkyl)ammonium compounds in the V_2O_5 interlayer space.

Electronic States of the (Ferrocenylalkyl)ammonium Derivatives in the Interlayer Space. The reflectance spectra of compounds **3** and **9**, together with that of $V_2O_5 \cdot (H_2O)_{1.6}$, are illustrated in Fig. 3. All the compounds show an intense band at 440 nm accompanied with a reflectance edge tailed to around 600 nm, which is due to the charge-transfer transition between the oxygen and vanadium atoms.[23] Compound **3** shows a band at 639 nm which is characteristic of the Fc^+ center.[24] All the intercalation compounds **1**—**8** show the bands around 640 nm. In accordance with these findings, XPS of compounds **1**—**8** have exhibited broad peaks at 710.1—711.6 eV which are due to Fe^{III} $2p_{3/2}$ electrons.[25—27] They are in contrast to the peaks observed at 708.4—708.6 eV for the corresponding Fc compounds having the Fe(II) state. The observed reflectance bands due to the Fc^+ centers and the binding energies of Fe $2p_{3/2}$ electrons of the compounds determined from XPS are summarized in Table 2. The presence of the Fc^+ centers in the intercalation compounds indicates that the redox reaction occurs between the Fc centers and the vanadium(V) sites. On the other hand, in the $VOPO_4$ interlayer[5] the Fc centers of (ferrocenylalkyl)ammonium cations with the $-NHR_2{}^+$ groups (R=H and Me) are not oxidized because they are arranged approximately perpendicular to the $VOPO_4$ sheet, the Fc centers not being close to another vanadium(V) site. In the $VOPO_4$ intercala-

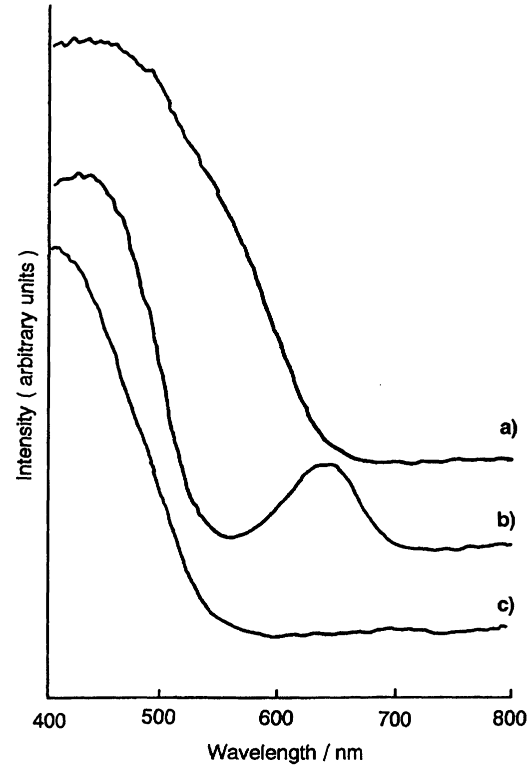

Fig. 3. Powder reflectance spectra of (a) $V_2O_5 \cdot (H_2O)_{1.6}$, (b) $V_2O_5 \cdot (H_2O)_{0.6} \cdot [Fc^+CH_2NHMe_2{}^+]_{0.16}$ (**3**), and (c) $V_2O_5 \cdot (H_2O)_{0.6} \cdot [PhCH_2NHMe_2{}^+]_{0.29}$ (**9**) at room temperature.

Table 2. Band Maxima (λ_{max}) in the Reflectance Spectra, Binding Energies (E_b) of Fe $2p_{3/2}$ Electrons Determined by XPS and ESR Peak-to-peak Linewidths (b)[a] of the V_2O_5 Intercalation Compounds

Compound	λ_{max} / nm	E_b / eV	b / mT
1	622	711.3	44.0
2	636	711.3	43.0
3	639	710.6	26.0
4	645	710.5	20.0
5	639	710.6	24.0
6	640	710.1	24.0
7	640	711.2	35.0
8	640	711.2	36.0
9			10.0
10			13.0
$FcCH_2NHMe_2^+I^-$		708.6[b]	
$FcCH_2NHMe_2^+Cl^-$		708.6	
$FcCH_2NMe_3^+I^-$		708.4[b]	
$FcCH_2CH_2NH_3^+Cl^-$		708.6[b]	
$FcCH_2CH_2NMe_3^+I^-$		708.5[b]	

a) $g=1.97$. b) Ref. 5.

tion compounds containing (ferrocenylalkyl)ammonium cations with the $-NMe_3^+$ group the cations are arranged parallel to the $VOPO_4$ sheet, where the Fc center of the $FcCH_2NMe_3^+$ cation is not oxidized because it cannot be close to another neighboring vanadium(V) site, while the Fc center of the $FcCH_2CH_2NMe_3^+$ cation can be oxidized owing to the proximity of the Fc center to another vanadium(V) site.[5] On the contrary, all the present (ferrocenylalkyl)ammonium cation moieties are intercalated into the V_2O_5 interlayer accompanied with the oxidation of all the Fc centers. This suggests that the Fc centers of the (ferrocenylalkyl)ammonium cations can be located close to another vanadium site in the V_2O_5 interlayer in which the distance between the nearest neighboring vanadium atoms can be estimated shorter than that in the $VOPO_4$ interlayer.

The vanadium(V) moiety of gel-V_2O_5 is reduced both by the iodide ion and by the Fc center to form the vanadium(IV) site which gives an approximately isotropic, intense ESR signal. The ESR signals of compounds **1**, **3**, and **9** are illustrated in Fig. 4, together with that of gel-V_2O_5. Since gel-V_2O_5 contains the vanadium(IV) moiety in ca. 20%,[28] it exhibits an ESR signal having the hyperfine structure due to the coupling of the unpaired electron with the ^{51}V nuclear spin ($I=7/2$, 100%). The intercalation compounds show a signal at $g=1.97$ without a distinct hyperfine structure, as observed for compounds **9** and **10** having a diamagnetic guest cations in the interlayer space. This is because of the dipolar and exchange interactions due to the increased V(IV) sites.[4] On the other hand, the V_2O_5 compounds intercalated with the Fc^+ centers exhibit much broad signals. These broadening seems to be due to the rapid electron-spin relaxation process which is caused by strong spin–spin interactions furnished by the nearby paramagnetic Fc^+ centers, as was suggested for the Mo_2^{5+}-intercalated $VOPO_4$ compound.[29] The peak-to-peak linewidths of the compounds are listed in Table 2. The similar broadening of the signals due to the V(IV) state was observed for the $VOPO_4$-(ferrocenylalkyl)ammonium intercalation compounds in which the Fc^+ centers are located close to the vanadium(IV) site.[5] All the present V_2O_5 compounds intercalated with the (ferrocenylalkyl)ammonium cations exhibit broad signals, which confirm the proximity of the Fc^+ center to the vanadium(IV) site. This is consistent with the arrangement of the guest molecules parallel to the V_2O_5 sheet, as displayed in Fig. 2. ESR signals due to the Fc^+ centers have not been observed even at 77 K, as was pointed out the difficulty of detecting the signal of the ferrocenium cation and its derivatives.[30,31]

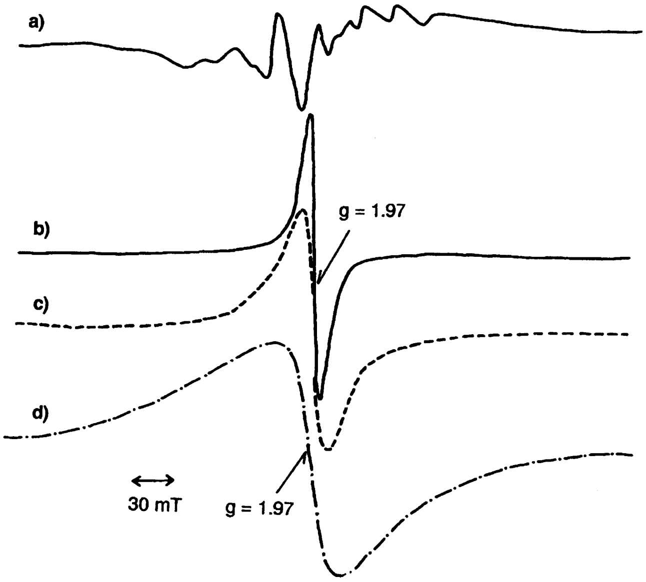

Fig. 4. ESR spectra of (a) $V_2O_5\cdot(H_2O)_{1.6}$, (b) $V_2O_5\cdot(H_2O)_{0.6}\cdot[PhCH_2NHMe_2^+]_{0.29}$ (**9**), (c) $V_2O_5\cdot(H_2O)_{0.6}\cdot[Fc^+CH_2NHMe_2^+]_{0.16}$ (**3**), and (d) $V_2O_5\cdot(H_2O)_{0.6}\cdot[Fc^+H]_{0.27}$ (**1**) at room temperature.

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