Intercalation of Ferrocenylalkylammonium Cations into the Layered Lattice of $VOPO_4$†

Shoji Okuno and Gen-etsu Matsubayashi *

Institute of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka 560, Japan

Some ferrocenylalkylammonium iodides, $[\mathrm{Fe^{II}}(C_5H_5)\{C_5H_4(CH_2)_nNR_2R'\}]^+I^-$ ($n = 1$ or 2; R,R′ = H or Me), benzyldimethyl- and benzyltrimethyl-ammonium iodides reacted with $\mathrm{V^{V}}OPO_4{\cdot}H_2O{\cdot}EtOH$ suspended in ethanol to afford intercalation compounds of $VOPO_4{\cdot}H_2O$ with $0.45[\mathrm{Fe^{II}}(C_5H_5)(C_5H_4CH_2NHMe_2)]^+$, $0.20[\mathrm{Fe^{II}}(C_5H_5)(C_5H_4CH_2NMe_3)]^+$, $0.43[\mathrm{Fe^{II}}(C_5H_5)(C_5H_4CH_2CH_2NH_3)]^+$, $0.17[\mathrm{Fe^{III}}(C_5H_5)(C_5H_4CH_2CH_2NMe_3)]^{2+}$, $0.54PhCH_2NHMe_2{}^+$ and $0.45PhCH_2NMe_3{}^+$. Ferrocenylalkylammonium chlorides, $[\mathrm{Fe^{II}}(C_5H_5)(C_5H_4CH_2NHMe_2)]^+Cl^-$ and $[\mathrm{Fe^{II}}(C_5H_5)(C_5H_4CH_2CH_2NH_3)]^+Cl^-$, were also intercalated to give compounds of $VOPO_4{\cdot}H_2O$ with $0.29[\mathrm{Fe^{III}}(C_5H_5)(C_5H_4CH_2NHMe_2{}^+Cl^-)]^+$ and $0.18[\mathrm{Fe^{III}}(C_5H_5)(C_5H_4CH_2CH_2NH_3{}^+Cl^-)]^+$. The intercalation compounds comprise layered $VOPO_4$ moieties having both the vanadium-(IV) and -(V) states and the ferrocenylalkyl-, benzyldimethyl-, and benzyltrimethyl-ammonium cations as well as ferrocenium-substituted alkylammonium chlorides, $[\mathrm{Fe^{III}}(C_5H_5)(C_5H_4CH_2NHMe_2{}^+Cl^-)]^+$ and $[\mathrm{Fe^{III}}(C_5H_5)(C_5H_4CH_2CH_2NH_3{}^+Cl^-)]^+$, in the interlayer space, producing $VOPO_4$–interlayer spacings of 9.8–21.0 Å. The molecular arrangements of these alkylammonium-substituted ferrocene and ferrocenium species in the interlayer space and the electronic states of the guest and host moieties are discussed on the basis of powder X-ray diffraction patterns, and IR, ESR and X-ray photoelectron spectra.

Lamellar inorganic crystals intercalated with organic and organometallic compounds are expected to show unique properties.[1] Vanadyl phosphates, $VOPO_4$[2–4] and α-$VOPO_4{\cdot}2H_2O$,[3,5–7] known as lamellar compounds can be intercalated with various organic compounds, including alkylamines[8,9] and alkylammonium iodides.[10] Ferrocene and its alkyl-substituted derivatives were reported to intercalate into the $\mathrm{V^{V}}OPO_4$ interlayer space as the ferrocenium and alkylferrocenium cations.[11–13] As reported previously,[13] $VOPO_4{\cdot}2H_2O$ treated with ethanol gives $VOPO_4{\cdot}H_2O{\cdot}EtOH$, which can easily include various organic and organometallic compounds into the interlayer in ethanol, forming a single interlayer spacing. Intercalation of ferrocenyl compounds substituted with alkylammonium groups may afford significant information on the molecular arrangements and electronic states of the guest molecules in the single interlayer space, because the intercalation can be caused by some kinds of redox reactions of the vanadyl moiety with the ferrocenyl centre, the amine groups, and the iodide ion.

This paper reports intercalation of several ferrocenylalkylammonium compounds into the $VOPO_4$ interlayer space accompanied with reduction of the vanadium(V) site.

Experimental

Materials.—The compound $VOPO_4{\cdot}2H_2O$ was prepared according to the literature.[14] It was treated with ethanol to give $VOPO_4{\cdot}H_2O{\cdot}EtOH$, as described previously.[12,13] 2-Amino-1-ferrocenylethane,[15] (ferrocenylmethyl)trimethylammonium iodide,[16] and (2-ferrocenylethyl)trimethylammonium iodide[16] were prepared according to the literature. (Dimethylaminomethyl)ferrocene (commercially available) was treated with HCl and HI aqueous solutions to afford (ferrocenylmethyl)dimethylammonium chloride and iodide. Similarly, (2-ferrocenylethyl)ammonium chloride and iodide were prepared from 2-amino-1-ferrocenylethane. Benzyldimethylamine was treated with an HI aqueous solution and methyl iodide to afford benzyldimethylammonium and benzyltrimethylammonium iodides, respectively.

Intercalation of Ferrocenylalkylammonium Derivatives into $VOPO_4{\cdot}H_2O{\cdot}EtOH$.—Into an ethanol (150 cm^3) solution of (ferrocenylmethyl)dimethylammonium iodide (1.48 g, 3.9 mmol) was added finely powdered $\mathrm{V^{V}}OPO_4{\cdot}H_2O{\cdot}EtOH$ (300 mg, 1.3 mmol) and the suspension was stirred at room temperature for 3 d in the dark. The resulting precipitate was collected by centrifugation, washed with ethanol and dried *in vacuo*. The composition of the product was $\mathrm{V^{IV}}_{0.45}\mathrm{V^{V}}_{0.55}OPO_4{}^{0.45-}{\cdot}H_2O{\cdot}0.45[\mathrm{Fe^{II}}(C_5H_5)(C_5H_4CH_2NHMe_2)]^+$ **1** (Found: C, 24.25; H, 3.5; N, 2.15. Calc. for $C_{5.9}H_{10.1}Fe_{0.45}N_{0.45}O_6PV$: C, 24.5; H, 3.8; N, 2.05%). Similarly, an ethanol (150 cm^3) solution of (ferrocenylmethyl)trimethylammonium iodide, (1.52 g, 3.9 mmol), (2-ferrocenylethyl)ammonium iodide (1.39 g, 3.9 mmol), or (2-ferrocenylethyl)trimethylammonium iodide (1.56 g, 3.9 mmol) suspended with $VOPO_4{\cdot}H_2O{\cdot}EtOH$ (300 mg, 1.3 mmol) was stirred at room temperature for 3 d to afford the intercalation compounds $\mathrm{V^{IV}}_{0.20}\mathrm{V^{V}}_{0.80}OPO_4{}^{0.20-}{\cdot}H_2O{\cdot}0.20[\mathrm{Fe^{II}}(C_5H_5)(C_5H_4CH_2NMe_3)]^+$ **2** (Found: C, 14.4; H, 2.7; N, 1.8. Calc. for $C_{2.6}H_{5.6}Fe_{0.2}N_{0.2}O_6VP$: C, 14.5; H, 2.6; N, 1.2%), $\mathrm{V^{IV}}_{0.43}\mathrm{V^{V}}_{0.57}OPO_4{}^{0.43-}{\cdot}H_2O{\cdot}0.43[\mathrm{Fe^{II}}(C_5H_5)(C_5H_4CH_2CH_2NH_3)]^+$ **3** (Found: C, 22.3; H, 3.0; N, 2.1. Calc. for $C_{5.2}H_{8.9}Fe_{0.43}N_{0.43}O_6PV$: C, 22.2; H, 3.2; N, 2.2%) and $\mathrm{V^{IV}}_{0.34}\mathrm{V^{V}}_{0.66}OPO_4{\cdot}H_2O^{0.34-}{\cdot}0.17[\mathrm{Fe^{III}}(C_5H_5)(C_5H_4CH_2CH_2NMe_3)]^{2+}$ **4** (Found: C, 13.45; H, 2.55; N, 0.85. Calc. for $C_{2.6}H_{5.7}Fe_{0.17}N_{0.17}O_6PV$: C, 13.5; H, 2.6; N, 1.05%).

Finely powdered $VOPO_4{\cdot}H_2O{\cdot}EtOH$ (300 mg, 1.3 mmol) was suspended in an ethanol (100 cm^3) solution containing an excess amount of $[Fe(C_5H_5)(C_5H_4CH_2NHMe_2)]^+Cl^-$ (1.09 g, 3.9 mmol) or $[Fe(C_5H_5)(C_5H_4CH_2CH_2NH_3)]^+Cl^-$ (1.04 g, 3.9 mmol) and the suspension was stirred for 2 d at room temperature to afford a precipitate of $\mathrm{V^{IV}}_{0.29}\mathrm{V^{V}}_{0.71}OPO_4{}^{0.29-}{\cdot}H_2O{\cdot}0.29[\mathrm{Fe^{III}}(C_5H_5)(C_5H_4CH_2NHMe_2{}^+Cl^-)]^+$ **5** (Found: C, 17.4; H, 2.25; N, 1.4. Calc. for $C_{3.8}H_{7.2}Cl_{0.29}$-

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† *Non SI unit employed:* eV ≈ 1.60 × 10^{-19} J.

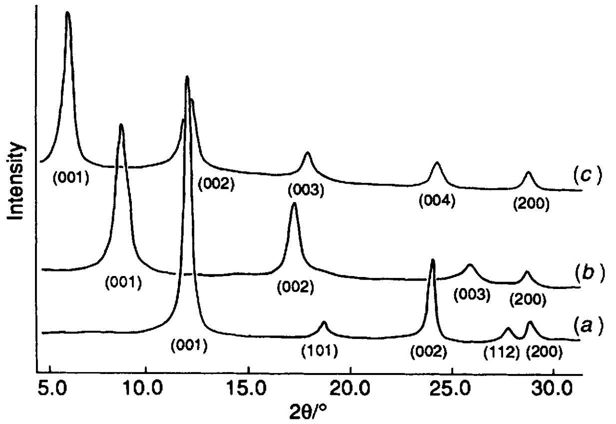


Fig. 1 X-Ray diffraction spectra of (*a*) $V^{V}OPO_4{\cdot}H_2O{\cdot}EtOH$, (*b*) $V^{IV}{}_{0.28}V^{V}{}_{0.72}OPO_4{}^{0.28-}{\cdot}H_2O{\cdot}0.28[Fe^{III}(C_5H_5)(C_5H_4CH_2CH_2NH_3{}^{+}\text{-}Cl^{-})]^{+}$ **6** and (*c*) $V^{II}{}_{0.54}V^{V}{}_{0.46}OPO_4{}^{0.54-}{\cdot}H_2O{\cdot}0.54PhCH_2NHMe_2{}^{+}$ **7**

$Fe_{0.29}N_{0.29}O_6PV$: C, 17.35; H, 2.8; N, 1.55%) or $V^{IV}{}_{0.18}V^{V}{}_{0.82}\text{-}OPO_4{}^{0.18-}{\cdot}H_2O{\cdot}0.18[Fe^{III}(C_5H_5)(C_5H_4CH_2CH_2NH_3{}^{+}\text{-}Cl^{-})]^{+}$ **6** (Found: C, 11.15; H, 2.35; N, 1.05. Calc. for $C_{2.2}H_{4.9}\text{-}Cl_{0.18}Fe_{0.18}N_{0.18}O_6PV$: C, 11.4; H, 2.15; N, 1.1%).

The compounds intercalated with the benzylammonium analogues were also prepared by reactions of powdered $VOPO_4{\cdot}H_2O{\cdot}EtOH$ suspended in ethanol with excess amounts of $PhCH_2NHMe_2{}^{+}I^{-}$ and $PhCH_2NMe_3{}^{+}I^{-}$, as described above: $V^{IV}{}_{0.54}V^{V}{}_{0.46}OPO_4{}^{0.54-}{\cdot}H_2O{\cdot}0.54PhCH_2NHMe_2{}^{+}$ **7** (Found: C, 23.05; H, 3.55; N, 3.1. Calc. for $C_{4.9}H_{9.6}N_{0.54}O_6PV$: C, 23.0; H, 3.8; N, 3.0%) and $V^{IV}{}_{0.45}V^{V}{}_{0.55}OPO_4{}^{0.45-}{\cdot}H_2O{\cdot}0.45PhCH_2NMe_3{}^{+}$ **8** (Found: C, 21.45; H, 3.2; N, 3.0. Calc. for $C_{4.5}H_{9.2}N_{0.45}O_6PV$: C, 21.8; H, 2.95; N, 2.55%).

Reactions of powdered $VOPO_4{\cdot}H_2O{\cdot}EtOH$ suspended in ethanol with excess amounts of $[Fe(C_5H_5)(C_5H_4CH_2NMe_2)]$ and $[Fe(C_5H_5)(C_5H_4CH_2CH_2NH_2)]$ afforded also $VOPO_4$ intercalation compounds. During the reactions the $VOPO_4$ compound was dissolved and addition of diethyl ether gave $V^{IV}{}_{0.9}V^{V}{}_{0.1}OPO_4{}^{0.9-}{\cdot}H_2O{\cdot}0.9[Fe^{II}(C_5H_5)(C_5H_4CH_2NH\text{-}Me_2)]^{+}$ (Found: C, 34.6; H, 4.3; N, 3.3. Calc. for $C_{11.7}H_{18.2}\text{-}Fe_{0.9}N_{0.9}O_6PV$: C, 34.6; H, 4.55; N, 3.1%) and $V^{IV}OPO_4{}^{-}{\cdot}H_2O{\cdot}[Fe^{II}(C_5H_5)(C_5H_4CH_2CH_2NH_3)]^{+}$ (Found: C, 35.4; H, 4.55; N, 3.5. Calc. for $C_{12}H_{18}FeNO_6PV$: C, 35.15; H, 4.4; N, 3.4%). However, they exhibit no appreciable powder X-ray reflection patterns characteristic of layered compounds.

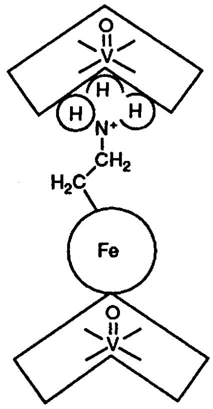
The presence of one molecule of water per $VOPO_4$ moiety was confirmed for several intercalation compounds by the thermogravimetric method. Experimental (calc.) % (w/w) water per $VOPO_4$: **1**, 6.1 (6.2); **2**, 7.7 (7.8); **3**, 6.2 (6.5); **4**, 8.0 (8.0).

Physical Measurements.—Infrared.,[17] ESR,[18] and X-ray powder diffraction patterns[13] were measured as described previously. X-Ray photoelectron spectra were obtained by irradiating the complexes with Mg-Kα X-rays (240 W) at 298 K using a Shimadzu-ESCA 750 photoelectron spectrometer equipped with an ESCA PAC 760 computer analyser and were calibrated with the carbon $1s_{\frac{1}{2}}$ photoelectron peak (285 eV). The peak shift caused by the charge-up effect was corrected with the silicon $2s_{\frac{1}{2}}$ peak. Thermogravimetric analysis was also carried out as described previously.[13]

Results and Discussion

Intercalation of Ferrocenylalkylammonium Derivatives into the $VOPO_4$ *Interlayer.*—The $VOPO_4$ intercalation compounds obtained here contain almost 1 mol of water (0.95–1.0) per $VOPO_4$ moiety according to thermogravimetric analysis. This is consistent with findings reported for $VOPO_4$–alkylammonium intercalation compounds.[10]

The ferrocenylalkylammonium iodides can reduce the vanadium(v) ion in the $VOPO_4$ sheet by the iodide ion and the ferrocenylalkylammonium cation is intercalated to give charge compensation (**1**–**4**); the ferrocenyl centre remains non-oxidized because it is well separated from the vanadium(v) site (**1**–**3**), as described below. By contrast, ferrocenyl compounds with alkylammonium chloride moieties are intercalated into the $VOPO_4$ interlayer through oxidation of the ferrocenyl centres (**5** and **6**).



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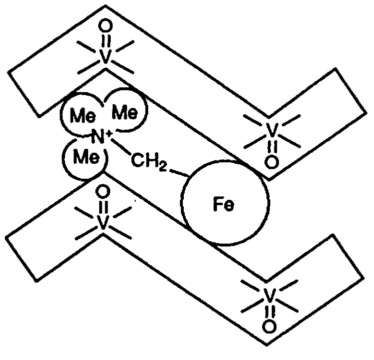

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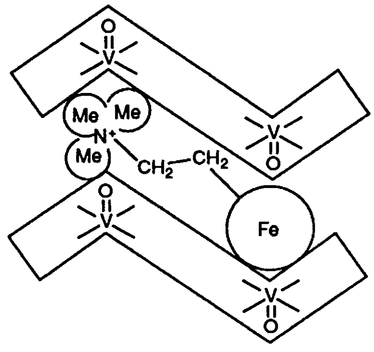

C

The interlayer distances of the $VOPO_4$ intercalation compounds have been determined from the powder X-ray diffraction patterns as illustrated in Fig. 1. Interlayer distances are summarized in Table 1, together with peak-to-peak linewidths of the ESR signals described below. The long interlayer distances of compounds **1**, **3** and **7** suggest large expansions of the interlayer spaces caused by a close proximity of the ammonium groups to the vanadium(iv) site, the long axis direction of the guest molecules being arranged approximately perpendicular to the two-dimensional sheet of the $VOPO_4$ interlayer (arrangement **A**). This arrangement is close to the molecular arrangements of some alkylammonium–$VOPO_4$ intercalation compounds.[8] Another arrangement with molecular bilayers is also possible, as seen in the ferrocene

Table 1 Interlayer distances (d) and ESR peak-to-peak linewidths[a] (b) of the $VOPO_4$ intercalation compounds

Compound	d/Å	(d – 4.1[b])/Å	b/mT
$V^{V}OPO_4 \cdot H_2O \cdot EtOH$	7.5	3.4	—
$V^{IV}_{0.35}V^{V}_{0.65}OPO_4^{0.35-} \cdot H_2O \cdot 0.35[Fe^{III}(C_5H_5)_2]^{+\,c}$	9.9	5.8	45.0
1 $V^{IV}_{0.45}V^{V}_{0.55}OPO_4^{0.45-} \cdot H_2O \cdot 0.45[Fe^{II}(C_5H_5)(C_5H_4CH_2NHMe_2)]^+$	17.1	13.0	16.5
2 $V^{IV}_{0.20}V^{V}_{0.80}OPO_4^{0.20-} \cdot H_2O \cdot 0.20[Fe^{II}(C_5H_5)(C_5H_4CH_2NMe_3]^+$	9.8	5.7	16.0
3 $V^{IV}_{0.43}V^{V}_{0.57}OPO_4^{0.43-} \cdot H_2O \cdot 0.43[Fe^{II}(C_5H_5)(C_5H_4CH_2CH_2NH_3]^+$	21.0	13.0	16.5
4 $V^{IV}_{0.34}V^{V}_{0.66}OPO_4^{0.34-} \cdot H_2O \cdot 0.17[Fe^{III}(C_5H_5)(C_5H_4CH_2CH_2NMe_3]^{2+}$	10.3	6.2	20.0
5 $V^{IX}_{0.29}V^{V}_{0.71}OPO_4^{0.29-} \cdot H_2O \cdot 0.29[Fe^{III}(C_5H_5)(C_5H_4CH_2NHMe_2{}^+Cl^-)]^+$	9.9	5.8	28.0
6 $V^{IV}_{0.18}V^{V}_{0.82}OPO_4^{0.18-} \cdot H_2O \cdot 0.18[Fe^{III}(C_5H_5)(C_5H_4CH_2CH_2NH_3{}^+Cl^-)]^+$	10.3	6.2	31.0
7 $V^{IV}_{0.54}V^{V}_{0.46}OPO_4^{0.54-} \cdot H_2O \cdot 0.54PhCH_2NHMe_2{}^+$	15.0	10.9	13.5
8 $V^{IV}_{0.45}V^{V}_{0.55}OPO_4^{0.45-} \cdot H_2O \cdot 0.45PhCH_2NMe_3{}^+$	10.0	5.9	13.5

[a] g = 1.98 at room temperature. [b] For anhydrous $VOPO_4$.[4] [c] Ref. 13.

Table 2 Binding energies (E_b) and linewidths (b) of iron $2p_{\frac{3}{2}}$ electrons determined from X-ray photoelectron spectroscopy

Compound	E_b/eV	b/eV
$V^{IV}_{0.35}V^{V}_{0.65}OPO_4^{0.35-} \cdot H_2O \cdot 0.35[Fe^{III}(C_5H_5)_2]^+$	711.2	4.0
1	708.6	1.8
2	708.5	1.8
3	708.5	1.7
4	709.7	3.7
5	712.0	4.1
6	712.9	5.2
$[Fe^{II}(C_5H_5)_2]$*	707.6	1.7
$[Fe^{II}(C_5H_5)(C_5H_4CH_2NHMe_2)]^+I^-$	708.6	1.6
$[Fe^{II}(C_5H_5)(C_5H_4CH_2NMe_3)]^+I^-$	708.4	1.8
$[Fe^{II}(C_5H_5)(C_5H_4CH_2CH_2NMe_3)]^+I^-$	708.5	1.8
$[Fe^{II}(C_5H_5)(C_5H_4CH_2CH_2NH_3)]^+Cl^-$	708.6	1.6

* ref. 23.

intercalates of MoS_2.[19] The proximity of the $NHMe_2{}^+$ group to the vanadium(IV) site has been revealed by the N–H stretching IR band at 2630 cm^{-1} for compound **1** which is 40 cm^{-1} lower than that of $[Fe^{II}(C_5H_5)(C_5H_4CH_2NHMe_2)]^+I^-$.

However, the other compounds have interlayer distances of 9.8–10.3 Å which correspond to an increased interlayer spacing of 5.7–6.2 Å compared with that of anhydrous $VOPO_4$ (4.1 Å).[4] As previously described,[13] this is consistent with the bulkiness (5.65–6.8 Å)[20] of the ferrocenyl and ferrocenium moieties (in interlayer spacings). The $NMe_3{}^+$ group is estimated to have a bulkiness (≈6.0 Å) close to those of the ferrocenyl and ferrocenium centres. Thus, the long-axis direction of the guest moieties (in the interlayer space) may be arranged approximately parallel to the swelling $VOPO_4$ sheet, as shown in **B** and **C**. In compound **2** the $NMe_3{}^+$ group approaches the vanadium(IV) site, the ferrocenyl centre being located somewhat apart from another vanadium(V) site (**B**) and remaining non-oxidized. On the other hand, both the $NMe_3{}^+$ group and the ferrocenyl centre of **4** can be located in close proximity to the vanadium sites (**C**) as estimated from the crystal structure of the $VOPO_4$ sheet[5] and the shape of the guest molecule. This may cause oxidation of the ferrocenyl centre.

Electronic States of the Ferrocenylalkylammonium Derivatives in the Interlayer Space.—The vanadium(V) moiety of $VOPO_4$ can be reduced by iodide and/or the ferrocenyl centres to give the $VOPO_4$ intercalation compounds containing some vanadium(IV) species. The X-ray photoelectron spectra of $VOPO_4 \cdot 2H_2O$ and $VOPO_4 \cdot H_2O \cdot EtOH$ which contain the vanadium(V) state show a vanadium $2p_{\frac{3}{2}}$ electron peak at 518.6 eV, while somewhat broad peaks are observed around 517.0 eV for all the $VOPO_4$ intercalation compounds. In accordance with this, they exhibit approximately isotropic, intense ESR signals due to the vanadium(IV) moieties, as described below. Broad X-ray photoelectron peaks of iron $2p_{\frac{3}{2}}$ electrons of compounds **4**–**6**, as well as of $V^{IV}_{0.35}V^{V}_{0.65}OPO_4^{0.35-} \cdot H_2O \cdot 0.35[Fe^{II}(C_5H_5)_2]^+$, are observed at 709.7–712.9 eV, which are characteristic of paramagnetic iron(III) species.[21,22] The values for the corresponding parent ferrocenyl compounds are 708.4–708.6 eV. Table 2 lists binding energies of iron $2p_{\frac{3}{2}}$ electrons for the ferrocenyl compounds and their $VOPO_4$ intercalation compounds. These findings for compounds **4**–**6** indicate the presence of ferrocenium(Fe^{III}) centres. The energy separations between the iron(III) $2p_{\frac{3}{2}}$ and iron(II) $2p_{\frac{3}{2}}$ states are 1.2–4.3 eV, which are close to those reported for $KFe^{III}[Fe^{II}(CN)_6]$ (4.4 eV),[21] biferrocene-$Fe^{II}Fe^{III}$ (3.4 eV),[22] and the polymerized compounds of dichloro(1,1′-ferrocenediyl)silane electrolysed on the electrode (3.0 eV).[24] On the other hand, **1**–**3** exhibit peaks at 708.5–708.6 eV due to ferrocenyl moieties containing the iron(II) ion, resulting from the distant location of the ferrocenyl and the vanadium(V) centres in the interlayer space.

Broad ESR signals due to the vanadium(IV) state have been observed for the $VOPO_4$ compounds intercalated with the ferrocenium centre. However, the signals due to the ferrocenium centres were not observed even at 77 K; it was previously reported to be difficult to detect any signal from these cations.[25,26] The line broadening of the ESR signals (see Table 1) arises from rapid electron-spin relaxation, which may be caused by an electronic interaction between the vanadium(IV) moieties and the paramagnetic ferrocenium centre. Compounds **5** and **6** having the latter centre in close proximity to the vanadium(IV) species show broad signals as does $V^{IV}_{0.35}V^{V}_{0.65}OPO_4^{0.35-} \cdot H_2O \cdot 0.35[Fe^{III}(C_5H_5)_2]^+$. On the other hand, **1** and **3** contain essentially non-oxidized ferrocenyl centres, because the ammonium groups approach the vanadium(IV) species and the ferrocenyl centres are distant from another vanadium species. Compound **2** also contains a ferrocenyl centre owing to some separation between it and the vanadium(V) species, as in arrangement **B**. Thus, appreciably less broad signals are observed for these compounds, their linewidths being rather close to those (13.5 mT) of **7** and **8** where the diamagnetic guest moieties are in the interlayer space.

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