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Intercalation of ferrocene and its alkyl derivatives into the vanadyl phosphate interlayer space

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Abstract

Ferrocene (Fc) and its alkyl-substituted derivatives (RFc; R = 1,1′-Me_2, Et, Bu^n, HOCH, and $HOCH_2CH_2$) intercalated into $VOPO_4 \cdot H_2O \cdot EtOH$ in ethanol and EtOH/acetone to afford $VOPO_4 \cdot H_2O \cdot (Fc^+)_{0.35}$, $VOPO_4 \cdot H_2O \cdot (Me_2Fc^+)_{0.21}$, $VOPO_4 \cdot H_2O \cdot (EtFc^+)_{0.19}$, $VOPO_4 \cdot H_2O \cdot (Bu^nFc^+)_{0.08}$, $VOPO_4 \cdot H_2O \cdot (HOCH_2Fc^+)_{0.23}$ and $VOPO_4 \cdot H_2O \cdot (HOCH_2CH_2Fc^+)_{0.31}$, respectively ($RFc^+$ = the ferrocenium cation and its alkyl derivatives). The cobaltocenium cation ($CoCp_2^+$) also intercalated into the VOPO, interlayer space in the presence of the iodide ion in ethanol to afford $VOPO_4 \cdot H_2O \cdot (CoCp_2^+)_{0.52}$. The intercalation compounds are constructed with layered $VOPO_4$ moieties in both V(IV) and V(V) states and the ferrocenium cation and its alkyl derivatives producing a single interlayer spacing. Based on the interlayer distances of the $VOPO_4$ moieties determined by the X-ray diffraction patterns, Fc^+ and Me_2Fc^+ cations are concluded to be stably located in the $VOPO_4$ interlayer space, the cyclopentadienyl rings being approximately parallel to the layers at the first stage, followed by the change to an orientation perpendicular to the layers after a long period of standing. In contrast to this finding, the $EtFc^+$ and Bu^nFc^+ cations are stably located between the VOPO, layers, the rings being perpendicular to the layers. Electronic states of the $VOPO_4$ moieties and the guest molecules are discussed on the basis of ESR, IR, X-ray photoelectron, electronic absorption and reflectance spectra.

Introduction

Lamellar inorganic solids have attracted considerable attention, since they can include various metal ions, organic and organometallic compounds in the interlayer spaces, exhibiting unique properties [1]. Vanadyl phosphate, $VOPO_4$ [2–4] and α-$VOPO_4 \cdot 2H_2O$ [5, 6], are known as lamellar compounds which undergo intercalation reactions with organic compounds having various functional groups; neutral polar molecules such as alcohols [7, 8], pyridine [9], and amides [10] can be included into the interlamellar space and with metal ions [11, 12] and alkylammonium iodides [13] the $VOPO_4$ moiety can be reduced to include the cationic species for charge compensation.

Intercalation of metallocenes having relatively low ionization potentials into lamellar inorganic compounds was reported for transition-metal dichalcogenides (MX_2), divalent-metal phosphorus trisulfides (MPS_3), and transition-metal oxyhalides [1], and tin disulfide [14]. However, ferrocene is difficult to intercalate into these compounds owing to its higher ionization potential [15]. Ferrocene and its alkyl derivatives may intercalate into $VOPO_4$ which easily undergoes a redox process. The intercalation of ferrocene into the $VOPO_4$ interlayer space has been reported briefly [16]. However, details on the geometry and electronic states of the ferrocene-$VOPO_4$ intercalation compound are not known.

This paper reports the intercalation reactions of ferrocene and 1,l'-dimethyl-, ethyl-, n-butyl-, hydroxymethyl- and hydroxyethylferrocenes into vanadyl phosphate ethanol hydrate, together with the intercalation of the cobaltocenium cation. The intercalation compounds were characterized by X-ray powder diffraction, ESR, IR, X-ray photoelectron and electronic reflectance spectroswpies and the electronic states of the included metallocene molecules and their orientations are discussed. An unusual rearrangement of the ferrocenium cation in the interlayer space is also described. A preliminary report of the present work has already appeared [17].

Experimental

Materials

$VOPO_4 \cdot 2H_2O$ [9] was prepared according to the literature. The compound was washed with ethanol

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several times to give $VOPO_4 \cdot H_2O \cdot EtOH$. *Anal.* Calc. for $C_2H_8O_7PV$: C, 10.62; H, 3.56. Found: C, 10.27; H, 3.67%. The presence of ethanol in the compound was confirmed from the ^1H NMR spectrum measured for a D_2O solution of the compound. Ferrocene and 1,1'-dimethyl-, ethyl- and n-butylferrocenes were commercially available. Hydroxymethyl- [18] and hydroxyethylferrocenes [19] were prepared according to the literature. Cobaltocenium hexafluorophosphate was kindly supplied by Professor M. Sorai, Osaka University.

Intercalation of ferrocene and its alkyl derivatives into $VOPO_4 \cdot H_2O \cdot EtOH$

Into an ethanol/acetone (1:1 vol./vol.; 20 cm') solution of ferrocene (820 mg, 4.4 mmol) was added finely powdered $VOPO_4 \cdot EtOH \cdot H_2O$ (200 mg, 880 μmol) and the suspended solution was stirred at room temperature for 7 days in darkness. The resulting precipitate was collected by centrifugation, washed with ethanol and dried *in vacuo*. The composition of the product was $VOPO_4 \cdot H_2O \cdot (Fc^+)_{0.35}$ (Fc^+ = the ferrocenium cation). *Anal.* Calc. for $C_{3.5}H_{5.5}Fe_{0.35}O_6PV$: C, 17.16; H 2.26; Fe, 7.9, V, 20.8. Found: C, 17.29; H, 2.22; Fe, 7.1; V, 21.4%.

An ethanol (10 cm") solution of 1,1'-dimethyl- (950 mg, 4.4 mmol), ethyl- (950 mg, 4.4 mmol), n-butyl- (1.07 g, 4.4 mmol), hydroxyrnethyl- (950 mg, 4.4 mmol), or hydroxyethylferrocene (1.01 g, 4.4 mmol) containing suspended powders of $VOPO_4 \cdot H_2O \cdot EtOH$ (200 mg, 880 μmol) was stirred at room temperature for 7 days. The resulting solids were collected, washed with ethanol, and dried as described above. $VOPO_4 \cdot H_2O \cdot (Me_2Fc^+)_{0.21}$: *Anal.* Calc. for $C_{2.52}H_{4.94}Fe_{0.21}O_6PV$: C, 13.46; H, 2.21; Fe, 5.2; V, 22.6. Found: C, 13.53; H, 2.35; Fe, 5.6; V, 21%. $VOPO_4 \cdot H_2O \cdot (EtFc^+)_{0.19}$: *Anal.* Calc. for $C_{2.28}H_{4.66}Fe_{0.19}O_6PV$: C, 12.41; H, 2.13; Fe, 4.8; V, 23.1. Found: C, 12.22; H, 2.46; Fe, 4.8; V, 21%. $VOPO_4 \cdot H_2O \cdot (Bu^nFc^+)_{0.08}$: *Anal.* Calc. for $C_{1.12}H_{3.44}Fe_{0.08}O_6PV$: C, 7.98; H, 2.05; Fe, 2.2; V, 24.9. Found: C, 7.21; H, 2.66; Fe, 2.8; V, 23.4%. $VOPO_4 \cdot H_2O \cdot (HOCH_2Fc^+)_{0.23}$: *Anal.* Calc. for $C_{2.53}H_{2.76}Fe_{0.23}O_{6.23}PV$: C, 13.23; H, 2.09. Found: C, 13.11; H, 2.32%. $VOPO_4 \cdot H_2O \cdot (HOCH_2CH_2Fc^+)_{0.31}$: *Anal.* Calc. for $C_{3.72}H_{6.34}Fe_{0.31}O_{6.31}PV$: C, 17.78; H, 2.54%. Found: C, 17.78; H, 2.61%. The presence of the ferrocenium and its derivative cations was confirmed from powder reflectance spectra.

A benzene (20 cm') solution containing suspended $VOPO_4 \cdot H_2O \cdot EtOH$ (200 mg, 880 μmol) and ferrocene (820 mg, 4.4 mmol) was stirred for 7 days, where the intercalation occurred partially to give $VOPO_4 \cdot H_2O \cdot (Fc^+)_{0.20}$ having both intercalated and unintercalated layers. On the other hand, a reaction of 1,1'-dimethylferrocene with suspended $VOPO_4 \cdot H_2O \cdot EtOH$ in benzene gave no compound intercalated with Me_2Fe or Me_2Fe^+ species.

Intercalation of the cobaltocenium cation ($CoCp_2^+$) into $VOPO_4 \cdot H_2O \cdot EtOH$

To an ethanol/acetone (1:1, 20 cm') solution containing $[CoCp_2][PF_6]$ (740 mg, 2.2 mmol) and $[NBu^n_4]I$ (810 mg, 2.2 mmol) was added finely powdered $VOPO_4 \cdot H_2O \cdot EtOH$ (100 mg, 440 μmol) and the suspended solution was stirred for 7 days. The resulting solids were collected by centrifugation, washed with ethanol and dried *in vacuo*. The composition of the product was $VOPO_4 \cdot H_2O \cdot (CoCp_2^+)_{0.52}$. *Anal.* Calc. for $C_{5.2}H_{7.2}Co_{0.52}O_6PV$: C, 22.42; H, 2.61; Co, 11.0, V, 18.3%. Found: C, 22.80; H, 2.27; Co, 10; V, 19%.

Analyses of the metals were performed by the inductively coupled plasma-emission spectroscopy (ICP-ES). The presence of water molecules in the $VOPO_4$ compounds was clear from the IR spectra. Contents of water were determined to be 0.97 and 0.96 for $VOPO_4 \cdot H_2O \cdot (HOCH_2Fc^+)_{0.23}$ and $VOPO_4 \cdot H_2O \cdot (HOCH_2CH_2Fc^+)_{0.31}$, respectively, by thermogravic analysis. Although determination of water contents was unsuccessful for the other intercalation compounds by the thermogravic analysis method, the presence of one molecule of water per $VOPO_4$ moiety is reasonable, based on the reported results of VOPO,-alkylammonium intercalation compounds [13].

Physical measurements

Electronic powder reflectance, absorption [20] and IR spectra [21] were measured as described previously. ESR measurements were carried out using a JEOL-2X spectrometer. *g* Values were calibrated based on signals of MnO_2. X-ray powder diffraction patterns were obtained with a Shimadzu XD-3A X-ray diffractometer using a graphite-monochromater. X-ray photoelectron spectra were measured by irradiating compounds with Mg Ka X-rays (240 W) at 298 K using a Shimadzu-ESCA 750 photoelectron spectrometer with the computer analyser ESCA PAC 760, and were calibrated with carbon $1s_{1/2}$ peak (285 eV) [22]. The error of the binding energy determination was estimated to be 0.1 eV. Thermogravic analysis was carried out on a Seiko I&E TG/DTA 30 instrument, using a heating rate of 5 °C/min under nitrogen atmosphere.

Results and discussion

Intercalation of ferrocene and its alkyl derivatives into the $VOPO_4$ interlayer space

Reaction of suspended $VOPO_4$ and $VOPO_4 \cdot 2H_2O$ powders in neat liquid of polar organic compounds, such as alcohols [7, 8], pyridine [9] and amides [10], afforded intercalation compounds. Various alkylammonium ions were also reported to intercalate into $VOPO_4\cdot 2H_2O$ by redox reactions with alkylammonium iodides [13]. Ferrocene and its alkyl derivatives can easily intercalate into the interlamellar space of $VOPO_4\cdot H_2O\cdot EtOH$ by their suspension-reactions in ethanol under a redox process described below. $VOPO_4$–ferrocene intercalation compounds obtained contain a single $VOPO_4$ interlayer spacing. On the other hand, an intercalation reaction of suspended $VOPO_4\cdot H_2O\cdot EtOH$ with ferrocene dissolved in benzene has afforded less intercalated compound having both intercalated and non-intercalated layers. The formation of less intercalated, inhomogeneous compounds is the same type of result as obtained in the intercalation reaction of $VOPO_4\cdot 2H_2O$ with ferrocene in acetone reported previously [16]. In benzene the intercalation of 1,1′-dimethylferrocene into the $VOPO_4$ moiety has been unsuccessful. These findings may suggest that the polar interlayer space of $VOPO_4$ surrounded by the V=O and PO_4 moieties easily attract ethanol molecules and ferrocene guest molecules exchangeable with ethanol molecules. In the present study alkyl-substituted feroccene derivatives also have effectively intercalated into the $VOPO_4$ interlamellar space in ethanol. A ferrocene derivative with a longer alkyl chain intercalates into the $VOPO_4$ moiety by a smaller amount, which is dominantly caused by a spatial limit due to the bulkiness of the intercalating molecule.

The cobaltocenium ion ($CoCp_2^+$) can also intercalate into the $VOPO_4$ layer by the reaction of suspended $VOPO_4\cdot H_2O\cdot EtOH$ with $[CoCp_2][PF_6]/[NBu^n_4]I$ dissolved in ethanol, where a redox reaction between the $VOPO_4$ moiety and the iodide ion results in the inclusion of the $CoCp_2^+$ ion for the compensation of the charge, as reported previously for $VOPO_4$ intercalation compounds with alkylammonium ions [13].

Electronic states of the $VOPO_4$ intercalation compounds

Figure 1 shows the electronic reflectance spectrum of $VOPO_4\cdot H_2O\cdot (Fc^+)_{0.35}$ as well as its absorption spectrum in an HCl(0.3 mol dm^{-3}) aqueous solution. The band at 620 nm observed in both the spectra is characteristic of the ferrocenium cation [23, 24]. The Me_2Fc–, EtFc–, Bu^nFc–, $HOCH_2Fc$– and $HOCH_2CH_2Fc$–$VOPO_4$ intercalation compounds have also shown reflection bands at 660, 630, 630, 620 and 615 nm, respectively. They are ascribed to 1,1′-dimethyl-, ethyl-, n-butyl-, hydroxymethyl- and hydroxyethylferrocenium cations. Since Fc, Me_2Fc, EtFc and Bu^nFc have rather low oxidation potentials (0.26-0.37 V versus SCE) [25], they may be readily oxidized in the $VOPO_4$ interlayer space.

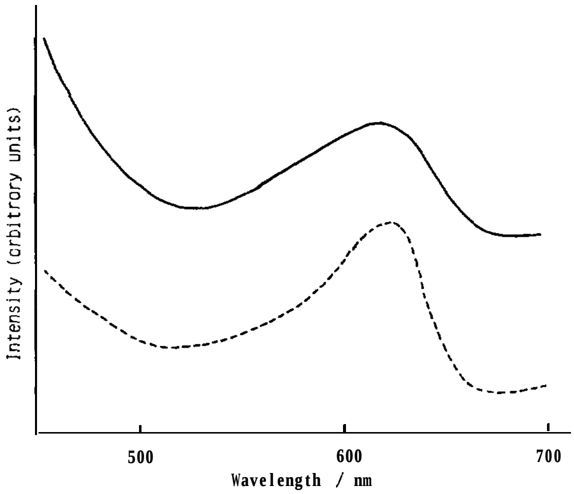


Fig. 1. The powder reflectance spectrum of $VOPO_4\cdot H_2O\cdot (Fc^+)_{0.35}$ (——) and the electronic absorption spectrum of it dissolved in an HCI (0.3 mol dm^{-3}) aqueous solution (– – –).

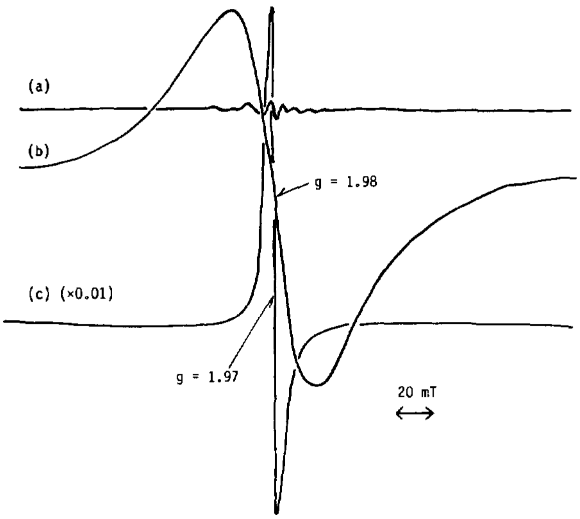


Fig. 2. Powder ESR spectra of (a) $VOPO_4\cdot H_2O\cdot EtOH$, (b) $VOPO_4\cdot H_2O\cdot (Fc^+)_{0.35}$ and (c) $VOPO_4\cdot H_2O\cdot (CoCp_2{}^+)_{0.52}$ at room temperature.

Figure 2 illustrates the powder ESR spectra of $VOPO_4\cdot H_2O\cdot EtOH$ and $VOPO_4\cdot H_2O\cdot (Fc^+)_{0.35}$ at room temperature as well as that of $VOPO_4\cdot H_2O\cdot (CoCp_2^+)_{0.52}$. The very weak signal observed for $VOPO_4\cdot H_2O\cdot EtOH$, which is an essentially diamagnetic V(V) species, is ascribed to a contaminated species in the V(IV) state; the content of the paramagnetic species in the present $VOPO_4\cdot H_2O\cdot EtOH$ has been estimated to be 1.5 mol% based on the intensity of the ESR signal.

The Fc^+ intercalation compound exhibits a broad, intense, approximately isotropic signal with the peak-to-peak linewidth of 45 mT (g = 1.98). This is almost the same as the other ferrocenium-intercalated $VOPO_4$ compounds (linewidths 31-47 mT, g = 1.98). These findings indicate the presence of the V(IV) state in the $VOPO_4$ moieties. Such a broad signal was observed for α-$VOPO_4$ (linewidth 15 mT, $g = 1.965$), which was suggested to be due to the consequence of magnetic exchange interactions through a somewhat short V-V distance (4.1 Å) perpendicular to the $VOPO_4$ layer [26]. These broad signals are a great contrast to the rather sharp signal of the $CoCp_2^+$ intercalation compound (linewidth, 5 mT; g = 1.97). Since the vanadium atom has nuclear spin (I= 7/2), the ESR signals generally split further owing to the spin-hyperfine coupling. In contrast to this, the $CoCp_2^+$–$VOPO_4$ compound exhibits a considerably sharp ESR signal without a distinct hyperfine structure. This is because of the dipolar and exchange interactions due to the increased V(IV) concentration, as were reported for reduced V_2O_5 species [27] and $Na_xVOPO_4(H_2O)_{2-x}$ [28]. The line broadening observed for $VOPO_4$ compounds intercalated with Fc^+ and its alkyl derivatives comes from a rapid electron-spin relaxation, which may be caused through an electronic interaction between the vanadium(IV) moieties and the paramagnetic Fc^+ and related cation species. This is not the case for the diamagnetic cobaltocenium species.

No ESR signals due to the ferrocenium cation and its derivatives have been observed even for the measurement at 77 K; the difficulty of detecting signals of these cations has already been reported [29, 30].

The presence of both the V(IV) and V(V) states in the present $VOPO_4$ intercalation compounds is confirmed from the X-ray photoelectron spectra. The band of V $2p_{3/2}$ electrons occurs at 518.6 eV for $VOPO_4 \cdot H_2O \cdot EtOH$ having the V(V) state, while the $VOPO_4$ intercalation compounds exhibit two bands at 517.0 and 518.6 eV which are ascribed to the V(IV) and V(V) states, respectively.

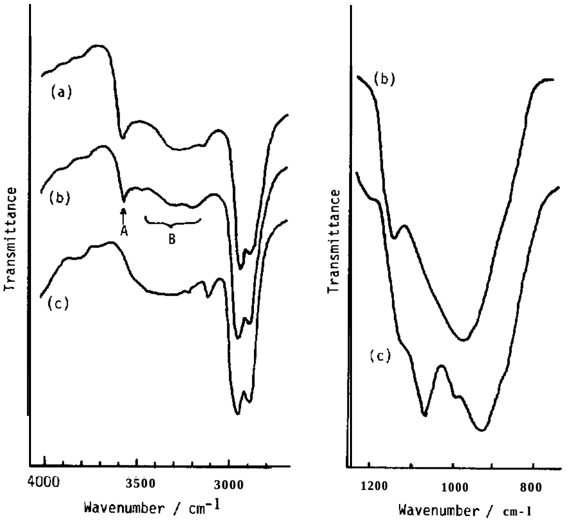
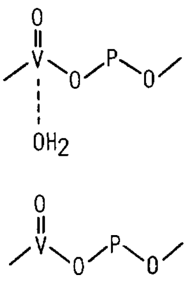


Fig. 3. IR spectra of (a) $VOPO_4 \cdot 2H_2O$, (b) $VOPO_4 \cdot H_2O \cdot EtOH$ and (c) $VOPO_4 \cdot H_2O$. $(Fc^+)_{0.35}$ in Nujol mulls.



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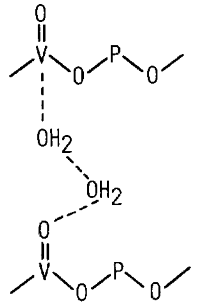


B

Arrangements of the ferrocenium cation and the alkyl derivatives in the $VOPO_4$ interlayer space

Figure 3 shows the IR spectra of $VOPO_4 \cdot 2H_2O$, $VOPO_4 \cdot H_2O \cdot EtOH$ and $VOPO_4 \cdot H_2O \cdot (Fc^+)_{0.35}$ (4000-2900 and 1200-800 cm^{-1} regions). As described in some reports [27, 31], $VOPO_4 \cdot 2H_2O$ has two types of water molecules in the interlayer space: the water molecule coordinated to the vanadyl group (A) and another hydrogen-bonded molecule (B). ν(O–H) bands of A occur near 3600 cm-’ and those of B are observed as broad bands around 3300 cm^{-1} in $VOPO_4 \cdot 2H_2O$. $VOPO_4 \cdot H_2O \cdot EtOH$ also exhibits a spectrum quite similar to that of $VOPO_4 \cdot 2H_2O$, indicating the presence of a water molecule coordinated to the vanadyl group and a hydrogen-bonded ethanol molecule. In the Fc^+–$VOPO_4$ intercalation compound a broad ν(O–H) band occurs at 3300 cm^{-1} and the band at 3600 cm^{-1} disappears, indicating that a water molecule is present in a hydrogen-bonded form in the $VOPO_4$ interlayer space.

The band at 980 cm-’ observed for $VOPO_4 \cdot H_2O \cdot EtOH$ is reasonably ascribed to the V=O stretching [27, 32]. This band is shifted to a lower frequency (935 cm-‘) for the Fc^+ intercalation compound. This is consistent with the valence reduction of the vanadyl ion (V to IV). The same IR frequency shift in this region has been observed for the other $VOPO_4$ compounds intercalated with ferrocenium derivatives.

Figure 4 displays X-ray powder patterns of $VOPO_4 \cdot H_2O \cdot EtOH$ and of $VOPO_4 \cdot H_2O \cdot (Fc^+)_{0.35}$. The intense peak at $2\theta = 11.8°$ for $VOPO_4 \cdot H_2O \cdot EtOH$ corresponds to the (001) reflection. The in-

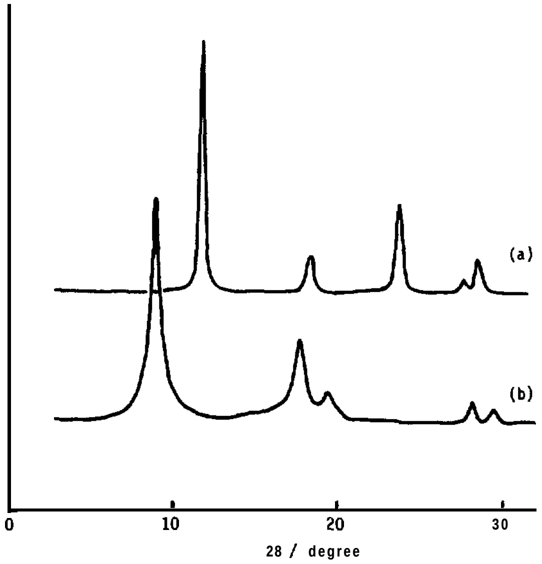


Fig. 4. Powder X-ray diffraction patterns of (a) $VOPO_4 \cdot H_2O \cdot EtOH$ and (b) $VOPO_4 \cdot H_2O \cdot (Fc^+)_{0.35}$ at room temperature.

TABLE 1. Interlayer distances of the $VOPO_4$ intercalation compounds (d, Å)

Compound	d	$(d-4.1^a)$
$VOPO_4 \cdot H_2O \cdot EtOH$	7.5	(3.4)
$VOPO_4 \cdot H_2O \cdot (Fc^+)_{0.35}$	9.9	(5.8)
$VOPO_4 \cdot H_2O \cdot (Me_2Fc^+)_{0.21}$	10.3	(6.2)
$VOPO_4 \cdot H_2O \cdot (EtFc^+)_{0.19}$	8.8	(4.7)
$VOPO_4 \cdot H_2O \cdot (Bu^nFc^+)_{0.08}$	8.8	(4.7)
$VOPO_4 \cdot H_2O \cdot (HOCH_2Fc^+)_{0.23}$	10.0	(5.9)
$VOPO_4 \cdot H_2O \cdot (HOCH_2CH_2Fc^+)_{0.31}$	10.0	(5.9)
$VOPO_4 \cdot H_2O \cdot (CoCp_2{}^+)_{0.52}$	10.1	(6.0)

^{a}Anhydrous $VOPO_4$ [4].

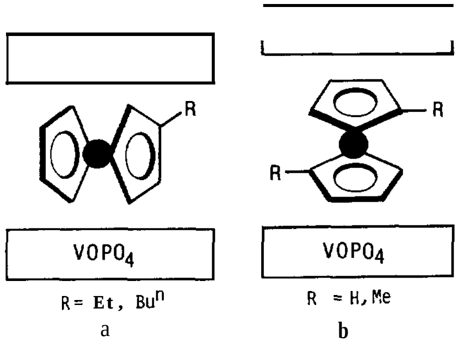
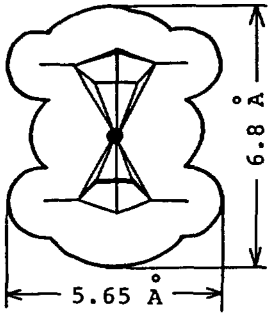


Fig. 5. Schematic arrangements of a metailocenium moiety in the $VOPO_4$ interlayer.



c

terlayer spacing determined from this reflection angle is 7.5 Å. The Fc^+–$VOPO_4$ compound exhibits one sharp peak for this reflection at a smaller angle ($2\theta = 8.4°$). This indicates that the homogeneous intercalation of the ferrocenium cation occurs between the $VOPO_4$ layers. The other RFc^+–$VOPO_4$ intercalation compounds have also shown a single interlayer spacing, although the Bu^nFc^+–$VOPO_4$ compound has given very broad reflection patterns.

Table 1 summarizes the interlayer distances of the $VOPO_4$ intercalation compounds determined by the X-ray powder patterns, together with expansions of the interlayer space with respect to that of anhydrous $VOPO_4$ (4.1 Å) [4]. The interlayer expansions of the Fc^+, Me_2Fc^+, $HOCH_2Fc^+$, $HOCH_2CH_2Fc^+$ and $CoCp_2{}^+$ intercalation compounds are c. 6.0 Å. On the other hand, the expansions of the $EtFc^+$ and Bu^nFc^+ compounds are 4.7 Å. Based on the estimated bulkiness of the metallocenium cation (C) [33], the orientation of these cations in the interlayer space for intercalation compounds is generally considered to assume form **a** in Fig. 5. The expansions of interlayer spacing were reported to be 5.4-5.6 Å for metallocene-metal dichalcogenide intercalation compounds ($MX_2(M'Cp_2)_y$; M = Ti, Zr, Hf, and Ta; X = S and Se; M' = Co and Cr; $y \approx 0.2$–0.4) [1] and 5.31 Å for $SnS_2(CoCp_2)_{0.31}$ [14]. In contrast to the intercalation of metallocenes to these smooth interlayer spaces, the intercalation into swelling interlayer spaces resulted in an appreciably shorter expansion; α-$Zr(HPO_4)_2 \cdot H_2O \cdot (CoCp_2)_{0.3}$, 4.4 Å [34] and $V_2O_5 \cdot (Fc)_{0.4} \cdot (H_2O)_x$ ($x < 0.5$), 4.4 Å [35]. The expansions in the $EtFc^+$– and Bu^nFc^+–$VOPO_4$ compounds correspond to this form. On the other hand, the expansions of the Fc^+– and Me_2Fc^+–$VOPO_4$ compounds seem to correspond to form **b**. The $HOCH_2Fc^+$– and $HOCH_2CH_2Fc^+$–$VOPO_4$ compounds also exhibit the space expansions around 6.0 Å, although they have bulky substituents similar to ethyl and butyl groups. The hydroxy groups may affect the arrangement of the guest molecules in the interlayer space. The $CoCp_2{}^+$–$VOPO_4$ compound also has almost the same expansion because the geometry of the $CoCp_2{}^+$ cation is almost the same as that of the Fc^+ cation.

Form a is more stable than form b, which can be confirmed by the fact that the interlayer expansion

(5.8 Å; form **b**) of $VOPO_4 \cdot H_2O \cdot (Fc^+)_{0.21}$ is changed after 30 days at room temperature to another expansion (4.6 Å) corresponding to form **a.** The interlayer spacing of the Me_2Fc^+–$VOPO_4$ compound has also been similarly changed after 30 days. However, $VOPO_4 \cdot H_2O \cdot (Fc^+)_{0.35}$ and $VOPO_4 \cdot H_2O \cdot (CoCp_2{}^+)_{0.52}$ did not change their interlayer spacings. These findings suggest that a large concentration of the intercalated cation species hinders molecular rearrangements of them in the interlayer space. $VOPO_4 \cdot H_2O \cdot (HOCH_2Fc^+)_{0.23}$ and –$(HOCH_2CH_2$-$Fc^+)_{0.31}$ also maintain the spacing of 5.9 Å, which may be due to some interaction of the hydroxy group. The $EtFc^+$– and Bu^nFc^+–$VOPO_4$ compounds in which the intercalated cations assume more stable orientations in the initial stage also did not changed their spacings.

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