CHEMISTRY LETTERS, pp. 799-802, 1993.

Intercalation of Alkyl-bridged Biferrocene Compounds into $VOPO_4$ and Gel-V_2O_5 Interlayer Spaces

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Alkyl-bridged biferrocene compounds, $Fc(CH_2)_nFc$ [Fc = $(C_5H_5)Fe(C_5H_4)$; n = 1 and 2] were intercalated into the $VOPO_4$ and V_2O_5 interlayer spaces by the redox reaction between the ferrocenyl (Fc) group and the V(V) ion site. Further oxidation of the Fc center in the interlayer space depends on its proximity to another V(V) ion site.

Layered inorganic solids intercalated with organic and organometallic compounds have been extensively studied because of their characteristic properties of molecular geometries and electronic states.1) In our studies on several $VOPO_4$- and gel-V_2O_5-(ferrocenylalkyl)ammonium intercalation compounds, arrangements and electronic states of the guest molecules in the interlayer spaces have been suggested to be affected by the extent of proximity of both the ammonium group and the ferrocenyl (Fc) center to the vanadium ion site.2,3) The Fc center can be oxidized by the V(V) ion and intercalated into the $VOPO_4$ and V_2O_5 interlayer spaces.4-6) Thus, the intercalation of the alkyl-bridged biferrocene compounds, Fc-$(CH_2)_nFc$ (n = 1 and 2), into $VOPO_4$ and gel-V_2O_5 is of much interest to clarify the electronic states of these two Fc centers in connection with the distance between the neighboring V(V) ion sites as well as molecular arrangements in the interlayer spaces. This paper reports electronic states and arrangements of the guest molecules of the above $VOPO_4$- and gel-V_2O_5-$Fc(CH_2)_nFc$ intercalation compounds.

Into a mixture of ethanol and chloroform(2:1 v/v, 300 cm^3) containing $FcCH_2CH_2Fc$(890 mg, 2.6 mmol) was added finely powdered $VOPO_4{\cdot}H_2O{\cdot}EtOH$4,5) (300 mg, 1.3 mmol). The suspended solution was stirred at 60 °C for 1 d in darkness. The resulting precipitate was collected by centrifugation and washed with chloroform until the visible spectrum of a supernatant solution showed no band of $FcCH_2CH_2Fc$. The composition of the product was $VOPO_4{\cdot}H_2O{\cdot}(Fc^+CH_2CH_2Fc^+)_{0.15}$ (**1**). A similar reaction of $VOPO_4{\cdot}H_2O{\cdot}EtOH$

Table 1. Interlayer distances (d) of the $VOPO_4$ and V_2O_5 intercalation compounds

Compound	d/Å	(d - 4.1[a])/Å	(d - 8.8[b])/Å
$VOPO_4 \cdot H_2O \cdot EtOH$[c]	7.5	(3.4)	
$VOPO_4 \cdot H_2O \cdot (Fc^+H)_{0.35}$[c]	9.9	(5.8)	
$VOPO_4 \cdot H_2O \cdot (Fc^+CH_2CH_2Fc^+)_{0.15}$ (**1**)	10.9	(6.8)	
$VOPO_4 \cdot H_2O \cdot (Fc^+CH_2Fc)_{0.12}$ (**2**)	10.6	(6.5)	
$V_2O_5 \cdot (H_2O)_{1.6}$[b]	11.6		(2.8)
$V_2O_5 \cdot (H_2O)_{0.6} \cdot (FcH^+)_{0.27}$[d]	13.4		(4.4)
$V_2O_5 \cdot (H_2O)_{0.8} \cdot (Fc^+CH_2CH_2Fc^+)_{0.23}$ (**3**)	13.5		(4.5)
$V_2O_5 \cdot (H_2O)_{0.7} \cdot (Fc^+CH_2Fc^+)_{0.24}$ (**4**)	13.6		(4.6)

a) For anhydrous $VOPO_4$.[9] b) For dehydrated gel-V_2O_5 [$V_2O_5 \cdot (H_2O)_{0.6}$].[11] c) Ref. 5. d) Ref. 3.

with $FcCH_2Fc$[7] afforded $VOPO_4 \cdot H_2O \cdot (Fc^+CH_2Fc)_{0.12}$ (**2**). At reaction times longer than 2 d, the microcrystalline structures of the compounds were appreciably destroyed. No intercalation compounds were obtained by reactions at room temperature for 7 d. Finely powdered gel-V_2O_5 [$V_2O_5 \cdot (H_2O)_{1.6}$][8] was also suspended in a mixture of ethanol and chloroform(2:1 v/v) containing twice molar amounts of $FcCH_2CH_2Fc$ or $FcCH_2Fc$. The suspended solutions were stirred for 10 d at 60 °C to afford precipitates of $V_2O_5 \cdot (H_2O)_{0.8} \cdot (Fc^+CH_2CH_2Fc^+)_{0.23}$ (**3**) or $V_2O_5 \cdot (H_2O)_{0.7} \cdot (Fc^+CH_2Fc^+)_{0.24}$ (**4**).[10]

The alkyl-bridged biferrocene compounds can be intercalated into the interlayer spaces of the $VOPO_4$ and gel-V_2O_5 layered compounds through the redox reaction between the Fc center and the V(V) ion site, as observed for the ferrocene and its alkylammonium derivatives.[2-5] The interlayer distances of the $VOPO_4$ and V_2O_5 intercalation compounds have been determined by the X-ray powder method. They are summarized in Table 1, together with those of the original $VOPO_4$ and V_2O_5 compounds and their ferrocene-intercalated compounds. The distances of the present $VOPO_4$ and V_2O_5 compounds are very close to those of ferrocene- and (ferrocenylalkyl)ammonium-intercalated compounds. Thus, these findings suggest that the long-axis direction of these guest molecules is arranged approximately parallel to the sheets of the host lattices (Fig. 1), as illustrated for the $VOPO_4$-$Fc(CH_2)_nNMe_3^+$ (n = 1 and 2) intercalation compounds.[2] This is consistent with the fact that the bulkiness of the Fc group is close to that of the $-NMe_3^+$ group.

In compound **1** both the Fc centers are oxidized to form the Fc^+ moieties. This has been confirmed by the observation of the X-ray photo-

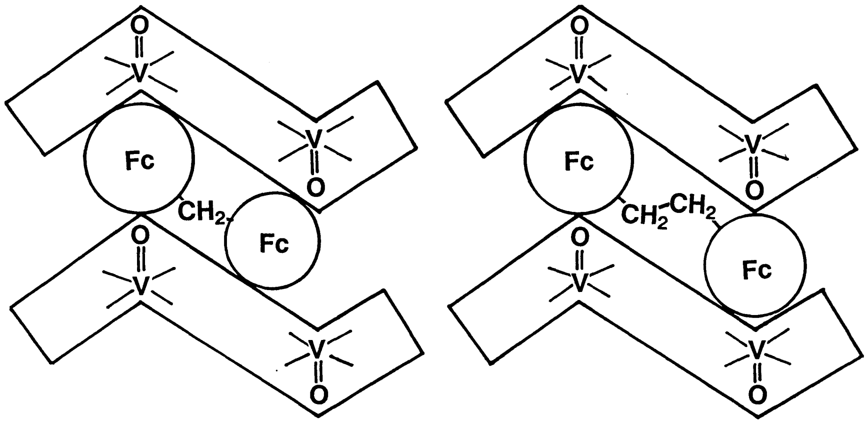

Fig. 1. Schematic arrangement of the biferrocene moieties in the $VOPO_4$ interlayer space.

electron (XPS) bands of Fe $2p_{3/2}$ electrons at 712.4 eV corresponding to the Fc^+ center (Fig. 2-a). In accordance with this, the band for the Fc^+ center has been observed at 640 nm in the powder diffuse reflectance spectrum. On the other hand, compound **2** shows two XPS bands at 708.7 and 711.6 eV which are ascribed to the Fc and Fc^+ centers, respectively (Fig. 2-b). This is close to the spectrum for biferrocene(Fe^{II}-Fe^{III}) picrate.[12] One of the Fc centers of $FcCH_2Fc$ is not oxidized in the $VOPO_4$ interlayer space. This comes from the arrangement of the $FcCH_2Fc$ molecule where one Fc center accesses to one V site and the other Fc center cannot be located in proximity of another V site. The similar molecular arrangement and the oxidation state of the Fc group were observed for the $VOPO_4$-$FcCH_2NMe_3{}^+$ intercalation compound.[2] The $VOPO_4$-$FcCH_2CH_2Fc$ intercalation compound results in the oxidation of both the Fc moieties owing to the adequate proximity of two Fc centers to V sites, which is also similar to the case of the $VOPO_4$-$FcCH_2CH_2NMe_3{}^+$ intercalation compound.[2] Thus, the relationship between the oxidation of the Fc centers and the proximity of them to the V site suggested for $VOPO_4$-$Fc(CH_2)_nNMe_3{}^+$ (n = 1 and 2) intercalation compounds can be confirmed for the $VOPO_4$-$Fc(CH_2)_nFc$ (n = 1 and 2) compounds. Intercalation of these biferrocene derivatives into the gel-V_2O_5 interlayer leads to the oxidation of both the Fc centers independent of the lengths of methylene chains: XPS

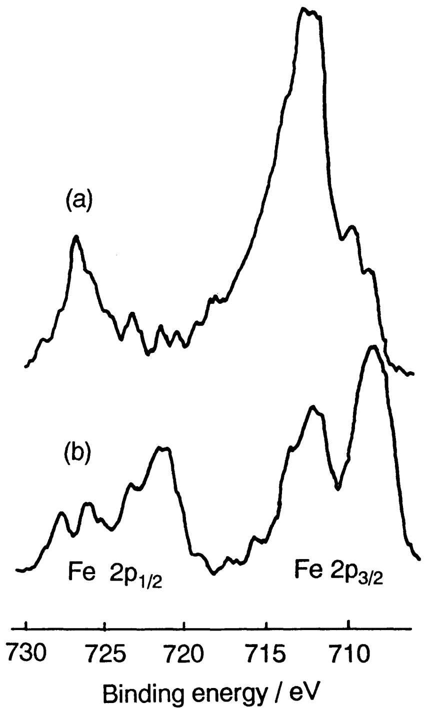

Fig. 2. The X-ray photoelectron spectra[13] of (a) $VOPO_4 \cdot (H_2O) \cdot (Fc^+CH_2CH_2Fc^+)_{0.15}$ (**1**) and (b) $VOPO_4 \cdot (H_2O) \cdot (Fc^+CH_2Fc)_{0.12}$ (**2**).

bands of Fe $2p_{3/2}$ electrons have been observed at 711.7 and 711.8 eV for **3** and **4**, respectively. A short distance between the neighboring V(V) ion sites causes the oxidation of both the Fc centers.

The $VOPO_4$ and V_2O_5 intercalation compounds show intense powder ESR signals due to the presence of the V(IV) ions. Compounds **1** and **2** exhibit approximately isotropic, much broad signals (the peak-to-peak linewidths, 45 and 40 mT, respectively) at g = 1.97, which are in contrast to that of the benzylammonium-$VOPO_4$ intercalation compound (the linewidth, 13 mT). These findings are close to those of the $VOPO_4$-$Fc(CH_2)_nNMe_3^+$ intercalation compounds. The signal broadening comes from an accelerated spin-spin interaction between the paramagnetic Fc^+ group and the V(IV) site.2) Compounds **3** and **4** have also exhibited broad ESR signals (the linewidths, >50 mT), although they are not isotropic.

It is concluded that the redox reaction between the V(V) ion site and the Fc center of $Fc(CH_2)_nFc$ or the iodide ion of $Fc(CH_2)_nNMe_3^+I^-$ (n = 1 and 2) leads to the intercalation of these molecules into the $VOPO_4$ and V_2O_5 interlayer spaces, followed by the oxidation of the other Fc center depending on its proximity to another V(V) ion site.

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10) Anal. **1**, Found: C, 16.51; H, 2.48%. Calcd for $C_{3.3}H_{5.3}Fe_{0.30}O_6PV$: C, 16.54; H, 2.23%. **2**, Found: C, 13.01; H, 2.08%. Calcd for $C_{2.5}H_{4.4}Fe_{0.24}O_6PV$: C, 13.39; H, 1.96%. **3**, Found: C, 21.21; H, 2.36%. Calcd for $C_{5.1}H_{6.7}Fe_{0.46}O_{5.8}V_2$: C, 21.25; H, 2.34%. **4**, Found: C, 20.85; H, 2.32%. Calcd for $C_{5.0}H_{6.2}Fe_{0.48}O_{5.7}V_2$: C, 20.97; H, 2.25%. The presence of water molecules were confirmed by the IR spectra. Their weight percents were determined by the thermogravic analysis.2)
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(Received February 1, 1993)