CHEMISTRY LETTERS, pp. 787-790, 1990.

Intercalation of Ferrocene and Related Compounds into Interlayer Spaces of Vanadyl Phosphate

Gen-etsu MATSUBAYASHI* and Seiji OHTA
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Yamadaoka, Suita, Osaka 565

Ferrocene and its alkyl-substituted derivatives intercalate into the lamellar $VOPO_4$ compound, where the ferrocenium and related cation species are located in the interlayer space of the V(IV)/V(V) moieties. Based on powder X-ray diffraction patterns and ESR spectra, arrangements of the cations and electronic interactions between the cations and $VOPO_4$ moieties are discussed.

α-$VOPO_4$ $2H_2O$ is known as a lamellar compound[1,2] which undergoes intercalation reactions with organic polar compounds; neutral molecules such as alcohols,[3,4] pyridines,[5] and amides[6] can be included in the interlayer space, and with metal ions[7,8] and alkylammonium iodides[9] the $VOPO_4$ moiety can be reduced to include the cation species in the interlayer space for the compensation of the charge. Intercalation of metallocenes into the $VOPO_4$ moiety which are active for a redox reaction is of interest in their electronic states and geometries. However, only an intercalation reaction of ferrocene into $VOPO_4 \cdot 2H_2O$ was reported briefly, where the intercalation occurred partly.[10]

This paper reports intercalation reactions of ferrocene (Fc), 1,1'-dimethyl- (Me_2Fc), ethyl- (EtFc), and n-butylferrocenes (Bu^nFc) as well as the cobaltocenium cation ($CoCp_2^+$) into $VOPO_4 \cdot H_2O \cdot EtOH$ in ethanol, affording compounds with a uniform interlayer spacing. Unusual molecular rearrangements of the ferrocenium moieties have been observed in the interlayer space.

$VOPO_4 \cdot 2H_2O$[5] was treated with ethanol to afford $VOPO_4 \cdot H_2O \cdot EtOH$. This compound was suspended in an ethanol or ethanol/acetone solution containing an excess amount of Fc, Me_2Fc, EtFc, or Bu^nFc and the solution was stirred for a week at room temperature to afford intercalation compounds. They were collected with centrifugation and dried in vacuo. Similarly, a suspension of $VOPO_4 \cdot H_2O \cdot EtOH$ in ethanol/acetonitrile (1:1

v/v) containing excess amounts of equimolar $[CoCp_2][PF_6]$ and $[NBu^n{}_4]I$ was stirred for a week at room temperature to yield $VOPO_4 \cdot H_2O \cdot (CoCp_2{}^+)_{0.52}$. In this reaction the $VOPO_4$ moiety was reduced by the iodide ion to include the $CoCp_2{}^+$ cation. C,H,N-elemental analysis and ICP emission analysis for Fe and V atoms determined the composition of the compounds in Table 1.

Table 1. Interlayer distances (d) of the $VOPO_4$ Intercalation compounds

$VOPO_4 \cdot H_2O \cdot L$	d/Å	(d-4.1[a])/Å
L = EtOH	7.5	(3.4)
$(Fc^+)_{0.35}$	9.9	(5.8)
$(Me_2Fc^+)_{0.21}$	10.3	(6.2)
$(EtFc^+)_{0.19}$	8.8	(4.7)
$(Bu^nFc^+)_{0.08}$	8.9	(4.8)
$(CoCp_2{}^+)_{0.52}$	10.1	(6.0)

a) $VOPO_4$; d = 4.1 Å.[14)]

IR spectra of these intercalation compounds show a broad band around 3300 cm^{-1}, suggesting the presence of a hydrogen-bonded water molecule[11)] in the interlayer space.

The electronic absorption spectra of the $VOPO_4$ compounds dissolved in HCl (0.3 mol dm^{-3}) aqueous solution as well as their powder reflectance spectra have exhibited a band in the region of 620-660 nm which is ascribed to the ferrocenium (Fc^+) and related cations (Me_2Fc^+, $EtFc^+$ and Bu^nFc^+). The X-ray photoelectron spectrum[12)] of $VOPO_4 \cdot H_2O \cdot EtOH$ in the V(V) state shows a V $2p_{3/2}$ electron peak at 516.8 eV, while all the other $VOPO_4$ intercalation compounds obtained here give two peaks at 518.6 and 517.0 eV corresponding to the V(V) and V(IV) states.

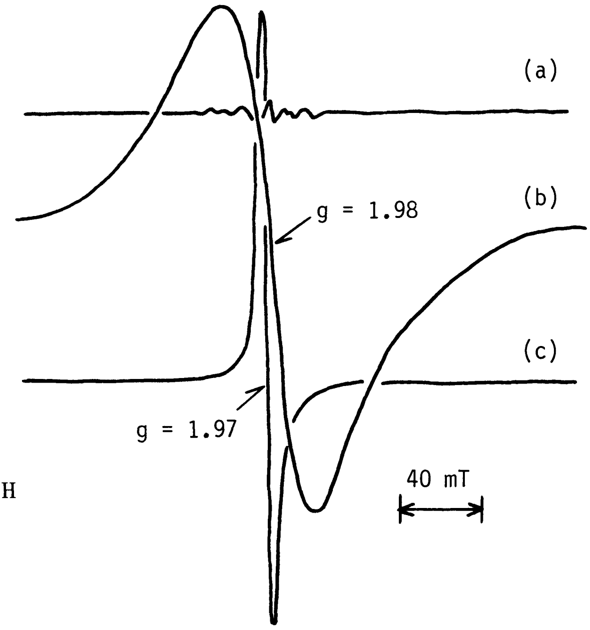


Fig. 1. Powder ESR spectra of $VOPO_4 \cdot H_2O \cdot EtOH$ (a), $VOPO_4 \cdot H_2O \cdot (Fc^+)_{0.35}$ (b), and $VOPO_4 \cdot H_2O \cdot (CoCp_2{}^+)_{0.52}$ (c) at room temperature.

Figure 1 shows the ESR spectra of the $VOPO_4$ compounds. The very weak signal observed for $VOPO_4 \cdot H_2O \cdot EtOH$ is due to the contaminated paramagnetic V(IV) species (the content 1.5 mol%). The Fc^+-intercalated compound (g = 1.98, the peak-to-peak linewidth 46 mT) as well as the RFc^+-ones (R = Me_2, Et and Bu^n) exhibits an approximately isotropic, broad, intense signal (g = 1.98, the linewidth 30-49 mT). The signal broadening may come from a rapid spin relaxation which is due to magnetic exchange interactions through the paramagnetic V(IV) moieties and Fc^+ or related cation species, as observed for the V(IV) species in the α-$VOPO_4$ lattice.[13)] This is in contrast to the rather sharp signal (g = 1.97, the linewidth 5.0 mT) observed for the $CoCp_2^+$-intercalated compound having the diamagnetic cation species in the space.

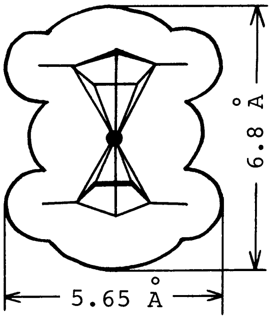
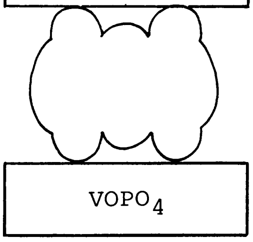
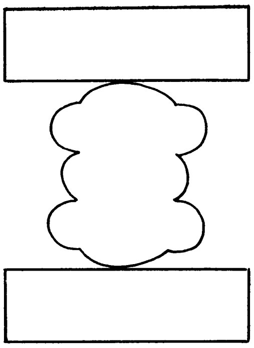


Fig. 2. Space-filling structure of metallocenes of the first transition series.[15)]



A



B

Interlayer spacings of the intercalation compounds are listed in Table, together with expansions of spacings in comparison with that of anhydrous $VOPO_4$ (4.1 Å).[14)] The expansions of the Fc^+- and Me_2Fc^+-$VOPO_4$ compounds as well as the $CoCp_2^+$-$VOPO_4$ one are ca. 6.0 Å, while those of the $EtFc^+$- and Bu^nFc^+-$VOPO_4$ compounds are 4.7 Å. Based on the estimated bulkiness of the metallocenium cation (Fig. 2), the orientation of the metallocenium cations in the interlayer space of lamellar inorganic solids is generally considered to assume the form (**A**),[15,16)] with the Cp rings perpendicular to the inorganic layers. Metallocene molecules were reported to intercalate into the compounds with smooth interlayer spaces, such as transition-metal dichalcogenides and divalent-metal phosphorus trisulfides, having the layer expansions of 5.4-5.6 Å.[16)] However, the intercalation into swelling interlayer spaces resulted in an appreciably shorter expansion with the orientation of form **A**; $Zr(HPO_4)_2\cdot H_2O\cdot(CoCp_2^+)_{0.3}$, 4.4 Å[17)] and $V_2O_5\cdot(Fc^+)_{0.4}\cdot(H_2O)_x$ ($x < 0.5$), 4.4 Å.[18)] The space expansions of the $EtFc^+$- and Bu^nFc^+-$VOPO_4$ compounds correspond to this form. On the other hand, the space expansions of the Fc^+-, Me_2Fc^+- and $CoCp_2^+$-$VOPO_4$ compounds correspond to form **B**. Form **A** is more stable than form **B** with the Cp rings parallel to the $VOPO_4$ layers. This can be confirmed with the fact that the interlayer spacing of $VOPO_4\cdot H_2O\cdot(Fc^+)_{0.21}$[19)] (9.9 Å; form **B**) changes after 30 d at room temperature to another spacing (8.8 Å) corresponding to form **A**. This can be determined by the change of powder X-ray diffraction patterns. The Me_2Fc^+-$VOPO_4$ compound also changes its interlayer spacing (from 10.3 to 8.9 Å; from **B** to **A**). However, $VOPO_4\cdot H_2O\cdot(Fc^+)_{0.35}$ and $VOPO_4\cdot H_2O\cdot(CoCp_2^+)_{0.52}$ do not change their interlayer spacings because larger concentrations of the intercalated cation species hinder their rearrangements in the interlayer space.

References

1) R. Gopal and C. Calvo, J. Solid State Chem., 5, 432 (1972).
2) B. Jordan and C. Calvo, Can. J. Chem., 51, 2621 (1973).
3) L. Benes, J. Votinsky, J. Kalousova, and J. Klikorka, Inorg. Chim. Acta, 114, 47 (1986).
4) K. Beneke and G. Lagaly, Inorg. Chem., 22, 1503 (1983).
5) J. W. Johnson, A. J. Jacobson, J. F. Brody, and S. M. Rich, Inorg. Chem., 21, 3820 (1982).
6) M. Martinez-Lara, L. Moreno-Real, A. Jimenez-Lopez, S. Bruque-Gamez, and A. Rodriguez-Garcia, Mat. Res. Bull., 21, 13 (1986).
7) J. W. Johnson and A. J. Jacobson, Angew. Chem., 95, 422 (1983).
8) M. R. Antonio, R. L. Barbour, and P. R. Blum, Inorg. Chem., 26, 1235 (1987).
9) M. Martinez-Lara, A. Jimez-Lopez, L. Moreno-Real, S. Bruque, B. Casal, and E. Ruiz-Hitzky, Mat. Res. Bull., 20, 549 (1985).
10) E. Rodriguez-Castellon, A. Jimenz-Lopez, M. Martinez-Lara, and L. Moreno-Real, J. Incl. Phenom., 5, 335 (1987).
11) C. R'Kha, M. T. Vandenborre, J. Livage, R. Prost, and E. Huard, J. Solid State Chem., 63, 202 (1986).
12) The XPS spectra were calibrated with the carbon $1s_{1/2}$ photoelectron peak (285 eV).
13) D. Ballutaud, E. Bordes, and P. Courtine, Mat. Res. Bull., 17, 519 (1982).
14) E. Bordes, P. Courtine, and G. Pannetier, Ann. Chim. (Paris), 8, 105 (1973).
15) M. B. Dines, Science, 188, 1210 (1975).
16) "Intercalation Chemistry," ed by M. S. Whittingham and A. J. Jacobson, Academic Press, New York (1982).
17) J. W. Johnson, J. Chem. Soc., Chem. Commun., 1980, 263.
18) P. Aldebert and V. Paul-Boncour, Mat. Res. Bull., 18, 1263 (1983).
19) The compound was prepared by the reaction of suspended $VOPO_4\cdot H_2O\cdot EtOH$ with ferrocene in ethanol for 3 h.

(Received March 8, 1990)