Intercalation of Ferrocene and Dimethylaminomethylferrocene into α-Sn(HPO$_4$)$_2$ · H$_2$O and α-VOPO$_4$ · 2 H$_2$O

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Abstract. The intercalation of ferrocene and dimethylaminomethylferrocene into α-tin(IV) hydrogen phosphate (SnP) and α-vanadyl phosphate has been investigated. Successful intercalation of 0.81 mol of dimethylaminomethylferrocene into α-SnP by an acid–base reaction in aqueous medium to form a bilayer of protonated amines was achieved. However, ferrocene was not intercalated under the same conditions. Intercalation of α-vanadyl phosphate by 0.11 mol of ferrocene in acetonic medium at room temperature was effected by a redox topotactic reaction. The voluminous dimethylaminomethylferrocene was not intercalated into α-vanadyl phosphate.

Key words: Intercalation, α-tin(IV) hydrogen phosphate, α-vanadyl phosphate, ferrocene, dimethylaminomethylferrocene.

1. Introduction

Intercalation compounds of cobaltocene in phosphates with a layered structure, such as α-zirconium hydrogen phosphate (α-ZrP) and hydrogen uranyl phosphate (HUP), have been readily prepared by redox reactions in which the oxidation of the neutral cobaltocene takes place [1]. However, redox intercalation of stable metallocenes such as ferrocene or its derivatives in layered phosphates is difficult because of the redox potential of these organometallics.

α-Tin(IV) hydrogen phosphate, α-Sn(HPO$_4$)$_2$ · H$_2$O (α-SnP), is isostructural with α-ZrP and it exhibits intercalation properties with polar organic substances [2,3] and can ion exchange transition metal complexes between the layers [4]. Generally, the intercalation mechanism in α-SnP is of the acid–base type in which the phosphate acts as an acid.

α-Vanadyl phosphate, α-VOPO$_4$ · 2 H$_2$O (α-VP) is a well-characterized compound that crystallizes in the tetragonal system [5], and it intercalates organic and inorganic cations by means of electron transfer between the host lattice and a reducing guest [6,7].

Both of these phosphates may be used as a catalyst or as a catalyst support and as the intercalated species containing organometallics often have two functional components they can be used as bifunctional catalysts.

This work studied the intercalation of ferrocene, and one basic derivative, dimethylaminomethylferrocene (DMAMferrocene), in α-SnP and also the redox intercalation of ferrocene into α-VP. The intercalates were characterized by means of chemical analysis, X-ray powder diffractometry, IR spectroscopy, diffuse reflectance UV-vis. spectroscopy, magnetic susceptibility, and thermal analysis.

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2. Experimental

2.1. MATERIALS

All chemicals were of reagent grade and were used without further purification. Ferrocene and dimethylaminomethylferrocene were purchased from EGA Chemie, α-SnP and α-VP were prepared as described elsewhere [3,6].

Intercalation of ferrocene into α-SnP did not take place at room temperature in aqueous, acetonic or ethanolic media. Intercalation of DMAMferrocene was achieved by adding 1.00 g of α-SnP to a mixture of 2.97 g of DMAMferrocene and 50 ml of water. The suspension was stirred and then washed with acetone. The composition of the product was: $Sn(C_{13}H_{17}N)_{0.81}(HPO_4)_2 \cdot 2.55 H_2O$; found: P, 11.27; Sn, 21.78; Fe, 81.7; N, 2.07; H_2O, 8.27. Calculated: P, 11.18; Sn, 21.42; Fe, 8.16; N, 2.05; H_2O, 8.29. In the absence of water, intercalation did not occur.

Ferrocene was intercalated into α-VP by adding 1.00 g of α-VP to 50 ml of acetone solution that contained 1.86 g of ferrocene. Four similar suspensions were continuously stirred by a magnetic stirrer for 4, 20, 90 and 168 hours respectively.

2.2. ANALYTICAL PROCEDURE AND INSTRUMENTS

The iron content was determined using a Varian Techtron 475 ABD atomic absorption spectrophotometer. The nitrogen content of the DMAMferrocene-α-SnP intercalate was determined by a micro-Kjeldahl method. The phosphate was determined colorimetrically [8]. Tin(IV) was determined by precipitation with cupferron and calcination to SnO_2 [9]. Vanadium(V) was determined by a redox titration with Mohr salt.

Thermal analysis was carried out on a Rigaku Thermoflex instrument, using a heating rate of $10°C/min$. X-Ray powder diffraction patterns were obtained with a Siemens D-500 diffractometer using a graphite monochromator. Diffuse reflectance spectra were recorded on a Kontron Uvikon 810 spectrophotometer with an integrating sphere attachment, using $BaSO_4$ as the reference. Infrared spectra were obtained with a Beckman 4260 spectrophotometer. Magnetic susceptibility data were obtained with a Cahn 2000 electrobalance coupled to an Oxford N 100 electromagnet with Faraday pole tips, and calibrated with $HgCo(NCS)_4$.

3. Results and Discussion

3.1. INTERCALATION INTO α-SnP

Although cobaltocene can be intercalated into α-ZrP by a redox reaction in which cobaltocinium ion was inserted between the layers, ferrocene was not taken up by α-SnP. This is not surprising, because ferrocene is the most stable metallocene yet discovered [10], but even though ferrocene is basic according to the Lewis theory, the metal hydride $(\eta^5C_5H_5)_2FeH^+$) was not formed in this acid medium. However, if a basic ferrocene derivative such as DMAMferrocene is used, an acid–base reaction takes place accompanied by a swelling of the interlamellar space. This reaction did not take place in ethanol, acetone, or ether solutions, or even with the pure amine. However, when water was added, the protonation of the organometallic and its intercalation occurred. This might indicate that the proton transfer occurs by a Grotthus mechanism through the water molecules.

Table I. X-ray powder diffraction data for (DMAM-ferrocene)$_{0.81}$Sn(HPO$_4$)$_2 \cdot$ 2.55 H$_2$O

hkl	$d_{obsd.}$ (Å)	$d_{cacd.}$ (Å)	I/I_0
002	20.73	20.73	100
004	10.38	10.36	41
006	6.91	6.91	23
	5.87		17
	5.40		19
110	4.27	4.28	28
0010	4.12	4.14	39
114	3.814	3.817	33
0012	3.460	3.454	33
	3.120		24
020	2.509	2.501	24
	2.179		12
$\bar{1}$30	1.643	1.638	13
330	1.452	1.450	12

Lattice constants: $a = 8.59$ (7) Å, $b = 5.01$ (5) Å,
$c = 41.87$ (15) Å, $\beta = 98.1°$, $\lambda = 1.5418$ Å

The powder X-ray diffraction patterns of the intercalate can be indexed on a monoclinic unit cell (see Table I). The a and b lattice constants are very similar to those of α-SnP. The data indicate that the layered structure has been preserved and that the interlamellar space has expanded. The X-ray powder diagram showed reflection lines corresponding to the 002, and the higher harmonics (004, 006, 008, 0010) while the original reflections due to the $hk0$ planes persisted. The basal spacing increase was 12.9 Å (20.7–7.8 Å) and suggest that DMAMferrocene forms a bilayer. The Van der Waals thickness of the metallocene is 6.65 Å (12). This implies an increment of 13.3 Å in the interlayer distance assuming a near parallel orientation of the C$_5$H$_5$ rings to the sheets. The difference between the expected interlayer distance (13.3 Å) and that experimentally obtained (12.9 Å), is only 0.4 Å. This difference is, perhaps, to be expected as the moelcular ion may pucker the phosphate layer. This phenomenon is the explanation for the even more pronounced shortening in V$_2$O$_5$ and metallocene [13].

The intercalate I.R. spectrum (Figure 1) was a composite of that of α-SnP and DMAMferrocene, except for an absorption band due to R$_3$NH$^+$ (2660 cm^{-1}). In effect, in Figure 1, the following bands can be seen at: 3425 cm^{-1}, νO—H (H$_2$O); 1640 cm^{-1}, δ H$_2$O; 1240 cm^{-1}, δ P—O—H; 1070 cm^{-1}, νP—SnO; 3100, 3080 cm^{-1}, νC—H; 1480 cm^{-1}, δ CH$_2$—N; 1420 cm^{-1}, ν_s C—C, or ring deformation; 1385, 1300, 1250 cm^{-1}, νC—N; 1115 cm^{-1}, ν_{as} C—C; 835 cm^{-1}, π C—H; 810 cm^{-1}, π(C—H); 490 cm^{-1}, ring tilt. These I.R. data indicate that the sheet—DMAMferrocene interaction is by the protonated nitrogen.

The composition of the resulting phase does not correspond to a complete solid-host neutralization since the product composition arises from the covering effect of the guest molecule, in this case, DMAMferrocene bonded to a O$_3$POH group, so that the adjacent site is now covered and consequently unavailable for bonding. Assuming a near parallel orientation of the cyclopentadienyl rings to the layer, the projected Van der Waals area of the organometallic molecule on the sheet is 50 Å^2. The free area around an active site in α-SnP is 21.4 Å^2 [14], which implies that (21.4 Å^2/50 Å^2) × 2 = 0.86 mol of DMAMferrocene/mol of α-SnP is the theoretical composition. This value is similar to that of the experimentally
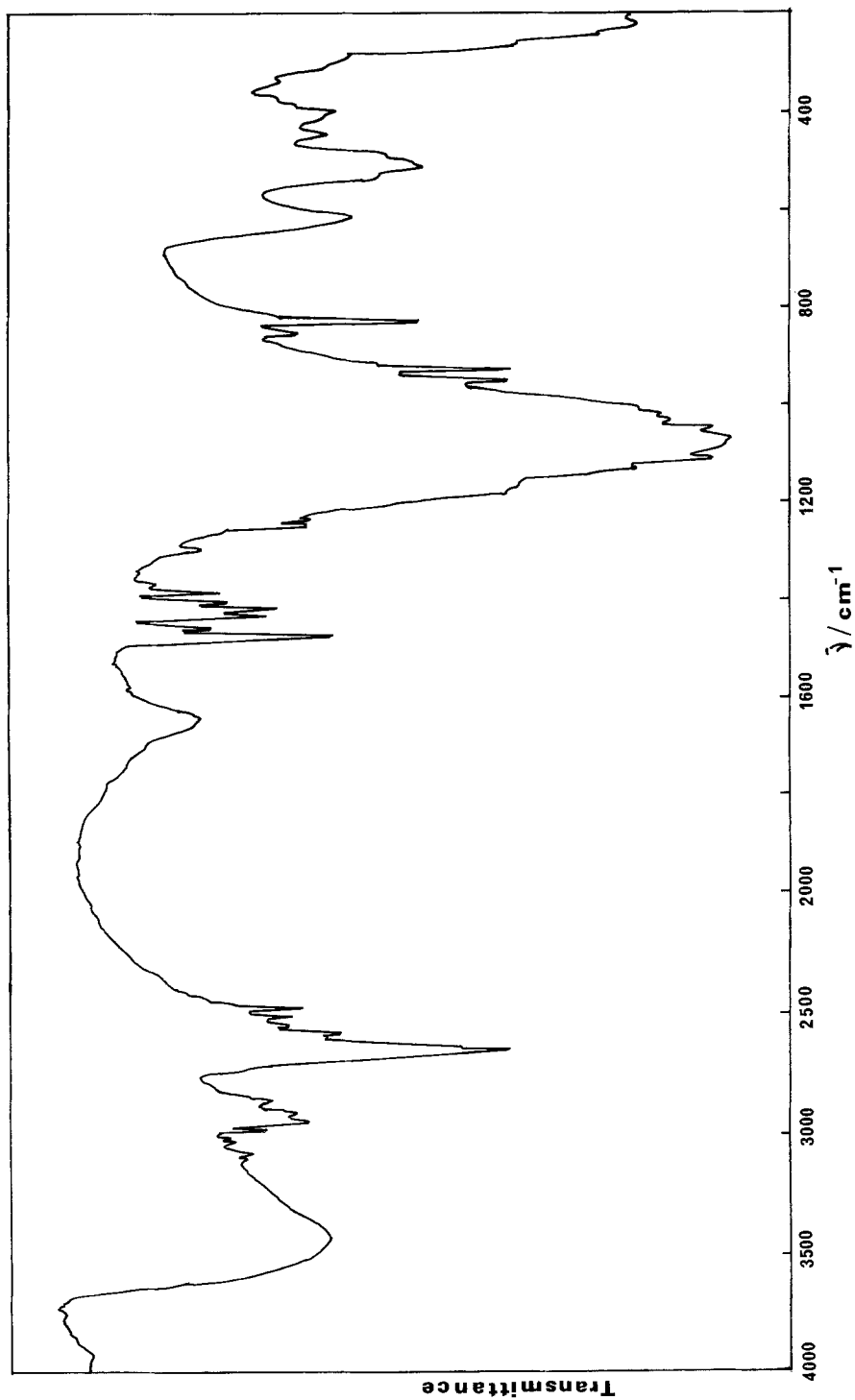
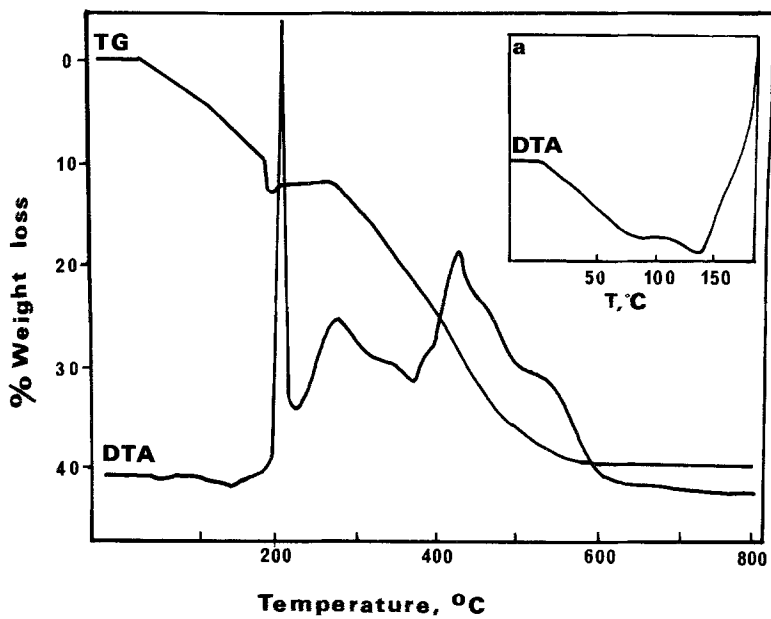Fig. 1.   I.R. Spectrum of $(DMAMferrocene)_{0.81}Sn(HPO_4)_2 \cdot 2.55\ H_2O$.

Fig. 2.   DTA–TG curves of (DMAMferrocene)$_{0.81}$Sn(HPO$_4$)$_2$ · 2.55 H$_2$O. (a) DTA at low temperature, magnified.
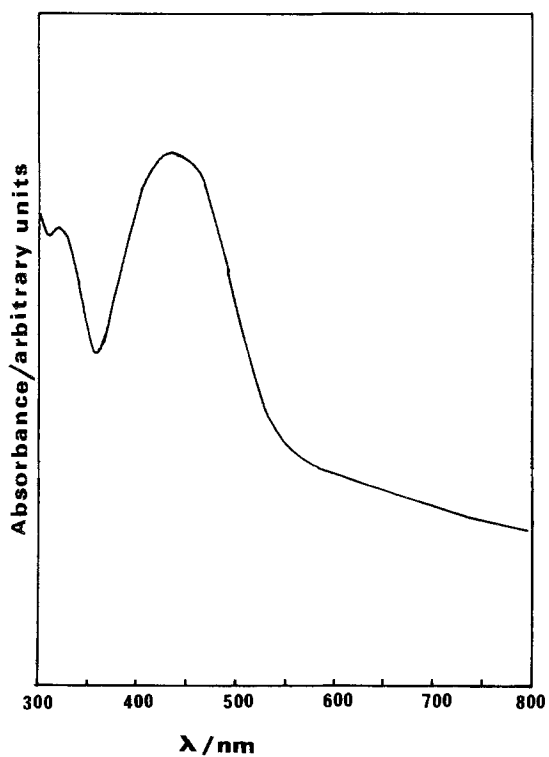
Fig. 3.   Diffuse reflectance spectrum of (DMAMferrocene)$_{0.81}$(HPO$_4$)$_2$ · 2.55 H$_2$O.

obtained value, 0.81 mol of DMAMferrocene/mol α-SnP. The existence of non-neutralized P—O—H groups is confirmed by a band at 1240 cm^{-1} (δ POH) in the IR spectrum.

The DTA curve (Figure 2), shows an endothermic peak at 140°C which corresponds to water loss. The exothermal effects correspond to the pyrolysis and oxidation of the inter-calated organic matter. The exothermic peak at 200°C is higher than the boiling point of the organic substance and implies that DMAMferrocene is strongly bonded to the sheet. The weight loss agrees with the calculated formula of the intercalate.

The diffuse reflectance spectrum (Figure 3) shows two maxima at 320 and 430 nm, derived from the spectrum of the metallocene, because α-SnP is inactive in the 300–900 nm region [15]. Magnetic measurements indicate that the DMAMferrocene intercalate is diamagnetic.

These data confirm the presence of DMAMferrocene between the sheets forming a bilayer and that the metallic atom conserves its oxidation state.

3.2. INTERCALATION INTO α—VP

In acetone solution, when ferrocene comes in contact with α-VP, a rapid change of colour from yellow to green is observed, which indicates the presence of vanadium(IV) and therefore, that reduction of the substrate has occurred by oxidation of ferrocene.

The reaction was studied after different contact times: 4, 20, 90 and 168 hours. Table II shows the X-ray diffraction data for the products at the different intervals of time, together with the data of α-VP. The data show that the products are mixtures of several phases. It can be seen that the 4 and 20 h. samples contained the initial phase, together with another partially

Table II. X-ray diffraction data of the products from the reaction α-VP + Ferrocene at different times.

0 h		4 h		20 h		90 h		168 h	
d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0
7.41	100	9.90	10	9.94	11	9.89	15	9.85	39
4.76	4	8.64	10	8.46	7	8.32	18	8.44	30
3.700	16	7.39	72	7.39	23	7.04	100	8.02	29
3.179	2	7.19	100	7.18	100	6.67	27	6.61	100
3.104	7	5.76	8	4.97	8	5.83	12	6.42	39
2.861	2	4.98	7	4.55	4	4.94	13	5.63	34
2.467	1	4.75	4	3.883	5	4.52	9	4.93	48
2.378	2	4.54	4	3.702	6	3.503	25	4.53	34
2.293	4	3.697	15	3.582	20	3.431	12	3.291	35
2.194	1	3.581	19	3.115	5	3.327	11	3.124	37
1.970	2	3.400	4	3.037	7	3.113	9	3.033	35
		3.321	3	2.974	3	3.043	12	2.971	27
		3.181	3	2.759	3	2.977	8	1.983	18
		3.104	4	2.606	3	2.441	4		
		3.033	4	2.578	3	2.399	6		
		2.967	2	2.383	4	2.208	5		
		2.857	2	2.299	2	1.972	4		
		2.582	2	1.988	3				
		2.468	3						
		2.384	4						
		2.204	4						
		1.996	4						

dehydrated phase (7.19 Å). In both cases, two basal spacings, of 9.9 and 8.5 Å, may be seen. However, when these samples are treated at $100°C$, the reflection band at 9.9 Å disappears, but the 8.5 Å line persists. The observed increase in basal spacing (8.5–4.1 = 4.4 Å) agrees well with that reported for the intercalation of the same ion in V_2O_5 gels [14]. So that one is led to suppose that in the present case too the cyclopentadienyl rings are perpendicular to the layer planes which they considerably overlap.

When the contact time increased to 90 h, the same phenomena were observed, but with the appearance of an additional reflection line at 6.6 Å which was previously observed in the studies of the reduction of α-VP by alkylammonium iodides [6], and which appears to correspond to a partial alteration of the starting compound. Nevertheless, in each case, one can see the reflection line corresponding to the 200 plane; this is a clear indication that the initial structure persists.

Chemical analysis of the samples revealed that the ferrocene content is always low (0.11–0.12 mol of ferrocene per mol of α-VP), and that the water content decreases with contact time.

The presence of ferrocinium ion may be suggested by IR spectroscopy. The metal–ring stretching band of ferrocene at 478 cm^{-1} shifts to 418 cm^{-1} in the spectrum of the ferrocinium ion [15]. In the IR spectrum of the intercalate (Figure 4), it is not possible to
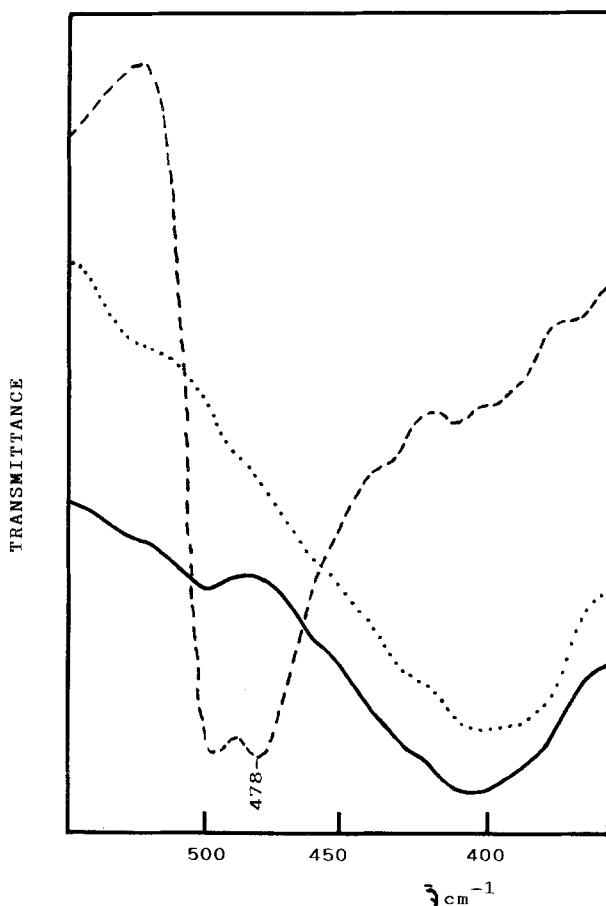

Fig. 4.   I.R. Spectra of ferrocene (–––), α-VP ($\cdots$), and α-VP + Ferrocene (——).

observe this shift, because of the presence of broad bands corresponding to phosphate group bending. However, the band at 478 cm^{-1} disappears.

The diffuse reflectance spectra show a band centered at 620 nm. This band may be related to the $^2B_1 \leftarrow \, ^2B_2$ transition of the V(IV) [16], or with the ferrocinium ion which gives a band at 619 nm [17].

The study of the ferrocinium arrangement in the interlayer space must be deferred until we have more information of the intercalate structure from EXAFS spectroscopy.

The voluminous DMAMferrocene was not intercalated into α-VP.

Acknowledgements

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