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DIRECT INTERCALATION OF ALKALI METAL IONS IN FeOCl

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ABSTRACT

The direct intercalation of Li^+, Na^+, K^+ and their crown ether complexes has been observed when FeOCl reacts with the respective methoxide salts of these ions. The lattice parameters of the compounds formed are reported. The intercalation process is interpreted in terms of oxidation of the methoxide ion accompanied by a partial reduction of the Fe(III) in the FeOCl, with the intercalation of the alkali metal ion in the lattice for charge compensaion.

Introduction

Iron(III) oxychloride, FeOCl, is a layered solid that has been used as a host lattice for a number of intercalation reactions. Pure FeOCl consists of sheets of edge shared cis-$FeCl_2O_4$ octahedra with the chlorine atoms lining the van der Waals gap between the layers. The unit cell parameters are a=0.3780 nm, b=0.7917 nm, and c=0.3302 nm with the b axis perpendicular to the layers (1). Upon intercalation, the b axis increases to accommodate the guest species.

Neutral guest molecules that have been found to intercalate directly into FeOCl include aliphatic (2,3) and aromatic (4-6) amines, metallocenes (7-10), trimethyl phosphite and triethylphosphene (11), and tetrathiafulvalene (12). Other species have been intercalated indirectly by exchange with a previously intercalated guest (13). The intercalation of a number of alkali metal and tetraalkyl ammonium cations has been accomplished by partial electrolytic (14) or chemical reduction (15) of the FeOCl in solutions containing these cations. One of the few examples of direct cation intercalation into FeOCl is the reaction of FeOCl with butyllithium which yielded $FeOCl{\cdot}Li_x$ $(0<x<0.5)$ (5).

We report herein the direct intercalation of a number of alkali metal ions and their crown ether complexes by reaction of FeOCl with the respective metal methoxide salts.

Experimental

Since FeOCl is known to react slowly with water (2) and the intercalates formed in this study are extremely moisture sensitive, care was taken to insure anhydrous conditions. All glassware used was either flame or oven dried and allowed to cool in a dry atmosphere. Unless otherwise stated, all measurements and manipulations were carried out under dry nitrogen or dry argon atmospheres.

Anhydrous $FeCl_3$ was refluxed with freshly distilled $SOCl_2$ and pumped *in vacuo* to remove excess $SOCl_2$ before use. Iron(III) oxychloride was prepared by reacting 4:3 molar ratios of $FeCl_3$ and Fe_2O_3 in an evacuated Pyrex tube at 350°C for one week. Excess $FeCl_3$ was removed from the reaction mixture by extraction with anhydrous methanol under dry nitrogen. The purity of the FeOCl was checked by x-ray diffraction and chemical analysis.

The intercalates were formed by immersing FeOCl in approximately 1M methanol solutions of the alkali metal methoxides in sealed Pyrex ampoules for varying lengths of time. The methoxide salts used were $KOCH_3$, $NaOCH_3$, $LiOCH_3$, $Li(C_{12}H_{24}O_6)OCH_3$, $K(C_{12}H_{24}O_6)OCH_3$, and $Na(C_{12}H_{24}O_6)OCH_3$ (where $C_{12}H_{24}O_6$ = 1,4,7,10,13,16-hexaoxacyclooctadecane, 18-crown-6 ether). The methoxide solutions were prepared by reaction of the particular alkali metal with excess methanol and diluting to the desired volume with methanol. The 18-crown-6 complexes were made by dissolving the crown ether in about a 10% excess in a solution of the alkali metal methoxide. In all cases, the methoxide salt and the FeOCl were in a 2:1 molar ratio, respectively. Progress of the reaction was followed by monitoring the disappearance of the (010) reflection of the FeOCl and the appearance of lower angle reflections, due to the intercalates, in the x-ray diffraction pattern of the solid. The time required for complete intercalation varied with the particle size of the FeOCl, temperature, and the nature of the methoxide salt. For a given FeOCl particle size, the speed of intercalation decreased in the order $KOCH_3 > NaOCH_3 > LiOCH_3$. The crown ether complexes all reacted at the same rate, which was approximately that of $NaOCH_3$.

The kinetic behavior of the intercalation of all salts followed the same general pattern. An initial rapid decrease in the (010) FeOCl x-ray reflection was observed, followed by a much slower decrease in this reflection. For completeness of intercalation, diffusion into the interior body of the crystal is required and this is apparently a slow process. At room temperature, complete intercalation was achieved after three weeks reaction.

Son, Kikkawa, Kanamaru and Koizumi (15) have described the preparation of $FeOOCH_3$ by the reaction of a methanol solution of $NaOCH_3$ with FeOCl at 100°C. All the methoxide salts used in our investigation will ultimately yield $FeOOCH_3$ if left too long at a particular temperature. This is especially true for $KOCH_3$ and $NaOCH_3$ where the insolubility of the corresponding chloride salts promotes topochemical substitution. Since LiCl is much more soluble in methanol than either KCl or NaCl, substitution was not as fast. Because topochemical substitution was found to be more rapid at higher temperatures, all reactions were run at room temperature. In addition, when the reaction ampoules were opened and the solid tested for completeness of intercalation, the supernatant liquid was analyzed for chloride. When chloride was detected, the run was discarded.

The solid intercalates were analyzed for Fe(II) spectrophotometrically using the 1,10-phenanthroline complex. For this analysis a known mass of the intercalate was dissolved in 2M HCl, the solution was then buffered to a pH of 3.5 using an acetate/acetic acid buffer, an excess of 0.3% aqueous 1,10·phenanthroline was added, and the solution was made up to a known volume. The concentration of Fe(II) was calculated from the absorbance of this solution at 511 nm. Although 1,10-phenanthroline slowly reduces Fe(III) to Fe(II), runs with synthetic mixtures of Fe(III) and Fe(II) in approximately the same concentration ranges and molar ratios expected from the intercalates showed that the correct Fe(II) content could be determined by following the change in absorbance at 511 nm with time and extrapolating back to zero time. All solutions and solvents used in this analysis were deoxygenated by saturating with nitrogen before use.

Samples were routinely analyzed for total iron and alkali metal content using a Perkin-Elmer Model 4000 atomic absorption spectrophotometer and the appropriate hollow cathode tube. Chloride content was determined by the Volhard method (16). Carbon and hydrogen analyses were performed by Galbraith Lab., Knoxville, TN. Powder x-ray diffraction patterns were obtained using a Philips Diffractometer equipped with a scintillation counter and graphite monochromator using CuKα radiation. The samples were mounted on glass slides using double backed cellophane tape. The sample stage of the diffractometer was enclosed in a glove bag that could be inflated with dry nitrogen. Thermograms were measured on a duPont model 1090 Thermal Analyzer and a model 951 Thermogravimetric Analyzer module. The module was housed in a dry box filled with dry argon. All thermograms were obtained under a dynamic flow of dry argon.

Results and Discussion

Table 1 lists the analytical data and formulas for the intercalation compounds formed from the reaction of the alkali metal methoxides and FeOCl. For the intercalates formed by $LiOCH_3$ and $NaOCH_3$, it is not possible from chemical analysis data to distinguish between $MOCH_3$ intercalation in which the cation is solvated and the intercalation of just the solvated cation. Formulation of the guest species as solvated Li^+ and Na^+ can be justified from the data in Table 2, which shows an approximately 1:1 molar ratio for the intercalated cations and Fe(II) found in the solid compound. The larger Li^+ to Fe(II) ratio shown in Table 2 could indicate some $LiOCH_3$ intercalation, but is most likely due to physically adsorbed $LiOCH_3$ rather than intercalation of the salt. The less than 1:1 molar ratio of CH_3OH to K^+ and the absence of CH_3OH in the 18-crown-6 complexes of Li^+, Na^+, and K^+ clearly demonstrate that the metal ion is the only species retained in the intercalation compound formed when the methoxide salts react with FeOCl. These results are consistent with an electron transfer mechanism for intercalation where the CH_3O^- transfers an electron to the FeOCl lattice, reducing some of the Fe(III) to Fe(II). The oxidized product can then leave the lattice, with the cation, in varying degrees of solvation, remaining in the van der Waals gap of the FeOCl lattice to maintain electrical neutrality on the solid. Such an electron transfer mechanism has been proposed by Schäfer-Stahl and Abele (7) for metallocene intercalation into FeOCl. On the basis of temperature dependent Mössbauer studies, Eckert and Herber (6) have proposed an electron transfer mechanism for the intercalation of various amine and pyridine bases.

Attempts to identify the oxidized product resulting from the CH_3O^- electron transfer have proved unsuccessful. The infrared spectra of the supernatant liquids after intercalation show no evidence of a C=O stretch. The normally expected product in the oxidation of CH_3OH is formaldehyde. However, this involves a two-electron transfer process which, in our case, seems unlikely. A one-electron transfer would result in the formation of a peroxide. Methoxide is not unique in its ability to form intercalation compounds with FeOCl. The alkali metal salts of a number of alkoxides also form intercalation compounds, including $KOC(CH_3)_3$ (17). This is of interest since $HOC(CH_3)_3$ does not tend to undergo two-electron transfer oxidations. Attempts to isolate the oxidized products using chromatographic techniques are currently under way.

The unit cell parameters of the intercalates are shown in Table 3. As expected for intercalation reactions, the unit cell distances parallel to the planes are essentially the same as in pristine FeOCl. For the alkali metal intercalates, the increase in the b spacing, which is perpendicular to the van der Waals gap, is in accord with the degree of solvation of the alkali metal. The $(FeOCl)_6\,Li(CH_3OH)_x$ ($x>4$) shows an increase in b of 0.713 nm. This is somewhat less than the diameter of 0.756 nm estimated by Hartley and Parkes (18) for the solvated Li^+ ion from conductivity studies of Li^+ salts in methanol. This difference could be due to some interpenetration of the solvated Li^+ between the chlorides lining the sides of the van der Waals gap. Interpenetration of guest species into the van der Waals gap has been suggested as a possible explanation of the smaller than expected increase in the b parameter in the intercalation of substituted pyridines and ferrocene in FeOCl (19). However, in our case, in view of the uncertainty in assigning a "radius" to the solvated Li^+ ion, the difference between these two values may not be significant.

Upon removal of solvating methanol molecules about the Li^+, the b spacings decrease. The thermograms of the $(FeOCl)_6Li(CH_3OH)_4$ show several poorly resolved low temperature plateaus which indicate a progressive loss of solvating methanols. At a heating rate of 1°C/min under a dynamic stream of Ar, the thermogram shows an immediate loss of mass at room temperature with an inflection temperature of 57°C followed by another loss with an inflection temperature of 104°C. The largest mass loss, due to the destruction of the intercalate itself, has an onset temperature of 184 °C with an inflection temperature of 208.6 °C. Powder x-ray diffraction patterns of the intercalate after being heated to 80 °C, a temperature in the plateau region between the first and second decompositions, show an intercalate with a b spacing of 1.030 nm in addition to the reappearance of reflections corresponding to the original FeOCl. On exposure to methanol vapor, the reflections due to the 1.030 nm b spacings and the FeOCl disappear with the restoration of the original intercalate's reflections (b spacing of 1.183 nm). It has been shown that the intercalation of unsolvated Li^+, from the reaction of butyllithium and FeOCl, does not cause a change in the b spacing (11). Therefore, the reappearance of the original FeOCl reflections in the thermally treated $(FeOCl)_6Li(CH_3OH)_4$ intercalate reflects removal of all solvating methanols, with the 1.030 nm b value corresponding to an intercalate containing intermediately solvated Li^+. Although the details of the thermogravimetric study of these alkali metal intercalates will be discussed in a later report, the above results demonstrate that the species being intercalated is $Li(CH_3OH)_4^+$ and that the increase in b spacing is a sensitive measure of the degree of solvation of the lithium ion.

The $(FeOCl)_{3.8}Na(CH_3OH)$ intercalate, containing only one solvating methanol, shows an increase in b spacing of 0.310 nm, which is smaller than that shown by the more highly solvated lithium intercalate. The $(FeOCl)_{4.5}K(CH_3OH)_{0.25}$, in which the potassium is present as essentially the unsolvated cation, shows the smallest increase in b spacing, about 0.126 nm. This is very much smaller than the crystallographic diameter of K^+ of 0.276 nm (20). In addition, reflections appear in the diffraction pattern of this complex that cannot be indexed in the orthorhombic space group P_{mnm} (D_{2h}^{13}) which would exist if FeOCl simply expanded its b spacing to accommodate the K^+ guest. The pattern can be indexed assuming a shift in the interlayer stacking of the planes of the FeOCl yielding a centro-symmetric system which leads to a doubling of the already expanded b parameters. This shift in the planes of FeOCl has been observed for the ferrocene intercalate (9) as well as in a number of substituted pyridine intercaltes of FeOCl (19,6). The size of the K^+ ion is evidently such that such a shift would lead to a greater stability by having eight chlorines around the K^+ rather than the five that would be present in an unshifted lattice. The unsolvated Li^+ is small enough to reside in a distorted octahedral cavity defined by four chlorines and an oxygen in one layer and a chlorine in an adjacent layer in the unexpanded and unshifted FeOCl lattice. It is surprising that the larger solvated Li^+ and Na^+ ions and the 18-crown-6 complexes of the alkali metals do not promote a similar shift in the layers of FeOCl as does K^+. In these cases it may be that, when chloride ions do not constitute the primary coordination sphere of the alkali metal, no extra stability is gained by such a shift in the stacking sequence of the planes of FeOCl. On the other hand, it may be that K^+ is unique in that it is a spherically symmetric ion whose size is such that a shift leads to singular stability. It should be pointed out that ferrocene (9) and substituted pyridines (20), whose intercalations also lead to a shift in the layer-stacking, are not spherically symmetric molecules but are ones having definite spatial patterns of various functional groups that have different specific interactions with the chloride ions lining the van der Waals gap in FeOCl. It could be that shift in the stacking sequence on intercalation of these molecules is promoted by specific guest-host interactions rather than general size accommodation.

The 18-crown-6 complexes of the alkali metal methoxides all give intercalates of similar stoichiometries and b expansions. The rather large increases in the b axis, 0.726 to 0.792 nm, indicate that either the plane of the cyclic ether is not coplanar with the FeOCl layers or that the alkali metals are displaced out of the plane of the crown ether cavity. The crystal structure of the crown ether complexes of several K^+ salts shows that the nature of the anion influences the position of the K^+ relative to the crown ether plane. In $K(C_{12}H_{24}O_6)SCN$, the K^+ is situated exactly in the mean plane of the crown ether (21) while in the 18-crown-6-potassium ethyl acetoacetate enolate salt, the K^+ is displaced out of the plane of the crown towards the enolate anion (22). Considering the rather uniform environment within the van der Waals gallery of the FeOCl, it does not seem likely that the K^+, or the other two alkali metals, would be displaced out of the plane of the crown ether.

The x-ray powder diffraction pattern of the K^+ 18-crown-6 ether intercalate contained 12 (0,k,0) reflections which were sufficient to yield a reasonable electron density projection along the b axis. This is shown in Figure 1. The magnitudes of the structure factors were obtained from the measured intensities of the reflections and the signs of the structure factors were assigned by assuming that the Fe-Cl and Fe-O bond distances in the intercalate were the same as in FeOCl and optimizing the relative positions and intensities of the Fe, O, and Cl electron density maxima. As can be seen from Fig. 1, the electron density projection is more consistent with an intercalate where the plane of the crown ether is aligned perpendicular to the FeOCl layers rather than with a horizontal alignment for the crown ether. The reason for such an alignment is not apparent. However, the b spacings for a number of substituted pyridine molecules suggest that the planes of the pyridines are not parallel to the layers of the FeOCl host (6,19).

The specific resistances of pressed powder samples of the intercalates, using gold electrodes, were measured and the room temperature values are listed in Table 4. The increase in electrical conductivity observed is what would be expected if electron transfer to the FeOCl occurred during the process of intercalation. A similar increase has been noted during the intercalation of pyridine derivatives in FeOCl (23).

The 18-crown-6 untercalates all have comparable specific resistances that are only slightly lower than that of pristine FeOCl. This is not surprising in view of their stoichiometries and b spacing. There seems to be a general trend downward in specific resistance with increasing b spacing. However, in view of the differences in stoichiometries and nonuniformity in particle size, this trend could be coincidental.

There seems to be little doubt that chemical reduction is the mechanism operative in the intercalation of the methoxide salts. Other studies, which will be reported later, indicate that this is not an isolated instance.

TABLE 1

Analytical Data for Intercalates Found From Reactions of FeOCl

Intercalate	Weight Percent[a] Fe	Cl	M	C	H
$(FeOCl)_6Li(CH_3OH)_4$	44.51	25.49	0.89	5.50	1.97
	(43.02)	(27.31)	(0.89)	(6.17)	(2.07)
$(FeOCl)_{3.8}Na(CH_3OH)$	44.43	27.81	4.18	2.67	1.17
	(45.86)	(29.11)	(4.97)	(2.60)	(0.87)
$(FeOCl)_{4.5}K(CH_3OH)_{0.25}$	47.18	29.63	7.32	0.56	0.27
	(47.76)	(30.32)	(7.43)	(0.57)	(0.19)
$(FeOCl)_{10}$ Li(18-C-6)[b]	38.47	24.60	0.47	9.28	2.48
	(41.55)	(26.37)	(0.52)	(10.72)	(1.80)
$(FeOCl)_{11}$ Na(18-C-6)	41.63	25.43	1.50	9.71	1.89
	(41.86)	(26.57)	(1.57)	(9.82)	(1.65)
$(FeOCl)_{11}$ K(18-C-6)	40.20	25.43	2.60	10.41	2.12
	(41.40)	(26.28)	(2.64)	(9.71)	(1.63)

a. Calculated weight percent values are in parentheses.
b. 18-C-6 = 18-crown-6-ether = $C_{12}H_{24}O_6$

TABLE 2

Alkali Metal/Iron(II) Molar Ratios

Intercalate	M^+/Fe	Intercalate	M^+/Fe
$(FeOCl)_6Li(CH_3OH)_4$	1.46	$(FeOCl)_{10}Li(C_{12}H_{24}O_6)$	0.84
$(FeOCl)_{3.8}Na(CH_3OH)$	1.01	$(FeOCl)_{11}Na(C_{12}H_{24}O_6)$	1.11
$(FeOCl)_{4.5}K(CH_3OH)_{0.25}$	1.11	$(FeOCl)_{11}K(C_{12}H_{24}O_6)$	0.86

TABLE 3

Cell Parameters for $(FeOCl)_xG_y$ Intercalates from n Reflections

Intercalate	a/nm	b/nm	c/nm	n
FeOCl[a]	0.3780	0.7917	0.3302	
$(FeOCl)_6Li(CH_3OH)_4$[c]	0.3800±.0001[b]	1.1823±.0011	0.3300±.0001	25
$(FeOCl)_6Li(CH_3OH)_x$	0.3797±.0001	1.5048±.0082	0.3318±.0001	16
$(FeOCl)_{3.8}Na(CH_3OH)$	0.3796±.0009	1.5048±.0082	0.3318±.0001	16
$(FeOCl)_{4.5}K(CH_3OH)_{0.25}$	0.3783±.0001	0.9174±.0031[d]	0.3313±.0001	26
$(FeOCl)_{10}Li(C_{12}H_{24}O_6)$	0.3778±.0001	1.5611±.0069	0.3297±.0001	22
$(FeOCl)_{11}Na(C_{12}H_{24}O_6)$	0.3760±.0007	1.5177±.0462	0.3241±.0005	17
$(FeOCl)_{11}K(C_{12}H_{24}O_6)$	0.3800±.0001	1.5869±.0078	0.3317±.0001	28

a. From Reference (1) b. Uncertainties are Standard Deviations.
c. In presence of CH_3OH (g), x>4. d. Value listed is b/2.

TABLE 4

Specific Resistances at 20°C on Pressed Powder Samples of FeOCl and Intercalates

Compound	Specific Resistance/Ω cm
FeOCl	8×10^6
$(FeOCl)_6Li(CH_3OH)_4$	3×10^4
$(FeOCl)_{3.8}Na(CH_3OH)$	4×10^4
$(FeOCl)_{4.5}K(CH_3OH)_{0.25}$	9×10^4
$(FeOCl)_{10}Li(C_{12}H_{24}O_6)$	3×10^5
$(FeOCl)_{11}Na(C_{12}H_{24}O_6)$	1×10^5
$(FeOCl)_{11}K(C_{12}H_{24}O_6)$	1×10^5

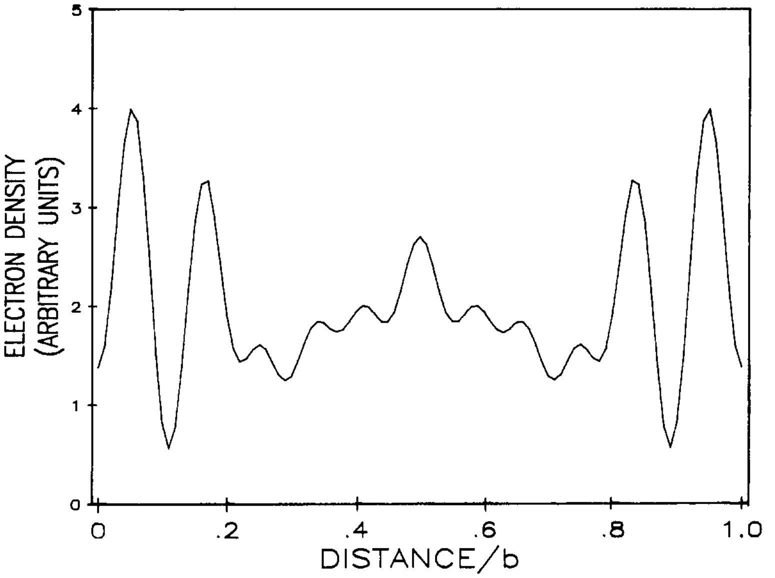

FIG. 1. Electron density projection along the b axis of $(FeOCl)_{11}\ K(C_{12}H_{24}O_6)$.

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