# INTERCALATION OF ORGANOMETALLIC COMPOUNDS INTO LAYERED TRANSITION METAL OXYHALIDES

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The syntheses of the new intercalate compounds  $FeOCl[(EtMe_4Cp)_2Fe]_{0.16}$ ,  $VOCl(CoCp_2)_{0.16}$ , and  $TiOCl(CoCp_2)_{0.16}$  are reported. Their structures are found by X-ray powder diffraction to be qualitatively the same as those of the previously reported complexes  $FeOCl(CoCp_2)_{0.16}$  and  $FeOCl(FeCp_2)_{0.16}$ . Results of <sup>57</sup>Fe Mössbauer and magnetic susceptibility studies on the latter two compounds are reported, and shown to be consistent with electron transfer from the metallocene to the host upon intercalation.

#### 1. Introduction

The metal oxyhalides MOCI (M = Ti, V, Cr, Fe, In) are known to have a layered structure in which adjacent layers are held together primarily by Van der Waals forces. Some of these layered materials undergo intercalation reactions similar to those known for layered transition metal dichalcogenides. For example, the intercalation of nitrogen bases (e.g. pyridine) into FeOCl has been reported [1, 2] as has the intercalation of alkali metal ions [3, 4]. We recently reported [5] the synthesis and general structural characterization of FeOCl intercalated by the organometallic sandwich compounds (metallocenes) ferrocene (FeCp<sub>2</sub>) and cobaltocene ( $CoCp_2$ ). We have now extended this work to include intercalation compounds involving the hosts TiOCl and VOCl, as well as a highly substituted metallocene guest, bis(ethyltetramethylcyclopentadienyl)iron ((Et- $Me_4Cp)_2Fe$ ). In the cobaltocene and chromocene intercalation compounds of TaS<sub>2</sub>, magnetic susceptibility studies [6] indicated that charge transfer had taken place to give (metallocene<sup>+</sup>)<sub>x</sub>TaS $_{2}^{-x}$ . We have now carried out magnetic susceptibility and 57Fe Mössbauer studies on the cobaltocene and ferrocene intercalation compounds of FeOCl. The results, which clearly demonstrate charge transfer, are presented in this paper.

### 2. Synthesis and structure of materials

FeOCl was prepared by heating a mixture of FeCl<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> (molar ratio 4:3) at  $370 \pm 5^{\circ}$ C in an evacuated, sealed quartz tube. The product

was washed with anhydrous acetone under inert atmosphere (to remove excess FeCl<sub>3</sub>). VOCl and TiOCl were prepared in an analogous fashion. The metallocene intercalation compounds in table I were prepared by heating toluene solutions of the guest molecule with the appropriate host at 80–100°C in an evacuated, sealed Pyrex tube. Details have been reported elsewhere [5]. Attempts to intercalate ruthenocene into FeOCl, and ferrocene into TiOCl and VOCl, were unsuccessful.

Since FeOCl and its intercalation compounds are quite moisture sensitive [7], we have taken extensive precautions to avoid exposing our samples to moisture and air. In addition, a slow decomposition of the MOCl occurs in the presence of excess metallocene solution. Thus, it is difficult to prepare pure intercalate phases without some parallel decomposition. We have minimized this problem by using little or no excess metallocene; in consequence, unintercalated MOCl is sometimes present as a minor second phase. Even so, small amounts of decomposition products may be present in the samples.

The structure of FeOCl, VOCl and TiOCl is characterized by double layers of distorted, edge shared octahedra similar to those in  $\gamma$ -FeOOH. The van der Waals gap is bounded by Cl<sup>-</sup> layers. The X-ray powder diffraction data for all the metallocene intercalates can be fitted to an orthorhombic cell with *a* and *c* changed little from the starting host, and *b* (the stacking axis) expanded and doubled. Systematic absences suggest a body centered cell. Structural

Host	Guest	a (Å)	b (Å)	с (Å)	Layer expansion (Å)
FeOCl		3.770	7.907	3,302	
FeOCl	CoCp <sub>2</sub>	3.803	$2 \times 12.849$	3.335	4.94
FeOCl	FeCp <sub>2</sub>	3.792	$2 \times 13.032$	3.324	5.13
FeOCl	Fe(EtMe <sub>4</sub> Cp) <sub>2</sub>		2×15.46		7.55
VOCI	• • • • •	3.765	7.911	3.297	_
VOCI	CoCp <sub>2</sub>	3.846	$2 \times 12.77$	3.308	4.86
TiOC1	• -	3.79	8.03	3.36	
TiOC1	CoCp <sub>2</sub>	3.82	2×13.16	3.34	5.12

 Table I

 Structural parameters for intercalates and host compounds

parameters are presented in table I. The observed layer expansions are consistent with a structural model in which the cyclopentadiene rings of the guest are perpendicular to the host layers. In particular, the bulky alkyl groups of  $(EtMe_4Cp)_2Fe$  give rise to an increase in the layer expansion very close to what would be predicted on the basis of examination of CPK molecular models.

## 3. Mössbauer spectra

The <sup>57</sup>Fe Mössbauer spectra of FeOCl(MCp<sub>2</sub>)<sub>0.16</sub> (M = Fe, Co) at 300 K and 77 K and of FeOCl at 300 K, were measured. Spectra were fitted by a least squares procedure [8] to produce a series of peaks having Lorentzian shapes superposed on a constant background. Isomer shifts, quadrupole

Table II	
Mössbauer	data

splittings and observed line widths are summarized in table II. Fig. 1 shows the room temperature spectrum of sample four,  $FeOCl(FeCp_2)_{0.16}$ .

Several characteristics of the Mössbauer spectra of FeOCl(FeCp<sub>2</sub>)<sub>0.16</sub> can be understood based on the hypothesis that electron transfer from the FeCp<sub>2</sub> guest to the FeOCl host occurs upon intercalation. The first characteristic is the temperature dependence of the isomer shift (IS). Our data at 300 K and 77 K allow us to calculate a temperature coefficient (d(IS)/dT) of  $-9.9 \times$  $10^{-5}$  mm s<sup>-1</sup>/K, with a limiting IS of 0.50 mm s<sup>-1</sup> as  $T \rightarrow 0$ . In comparison, FeOCl itself exhibits d(IS)/dT of  $-6.1 \times 10^{-4}$  mm s<sup>-1</sup>/K and a limiting IS of 0.55 mm s<sup>-1</sup> [11]. Assuming the temperature dependence arises from a second-order Doppler

Sample	IS <sup>e</sup> (mm/s)	QS (mm/s)	<sup>г</sup> 1ª (mm/s)	<sup>Г</sup> 2ª (mm/s)	Т (К)	
(1) FeOCl <sup>c</sup>	0.392	0.92	0.24	0.25	300	
2) [FeOCI][Fe(Cp) <sub>2</sub> ] <sub>0.16</sub> <sup>b,c</sup>	$0.47_{3}$	0.66	0.35	0.29	300	
3) [FeOCI][Fe(Cp) <sub>2</sub> ] <sub>0.16</sub> <sup>b,c</sup>	0.495	0.66	0.37	0.29	77	
4) [FeOCl][Fe(Cp)_2]_{0.16}^{b.c}	0.47	0.70	0.40	0.26	300	
5) [FeOCl][Co(Cp) <sub>2</sub> ] <sub>0.16</sub> <sup>c,d</sup>	0.462	0.74	0.45	0.36	77	

a<sup>*T*</sup>1 and <sup>*T*</sup>2 are the observed line widths of the lower and higher velocity components of the quadrupole split doublets, respectively.

<sup>b</sup> X-ray powder diffraction shows FeOCI (0, 1, 0) line intensity  $\approx 2\%$  of FeOCI (FeCp<sub>2</sub>)<sub>0.16</sub> (0, 2, 0) line intensity in samples 2 and 3;  $\approx 7\%$  for sample 4.

<sup>c</sup> The small asymmetry is believed to be due to preferential orientation in the samples.

<sup>d</sup> These parameters should only be taken as approximate. The Mössbauer spectrum clearly showed a shoulder on one of the peaks indicating some impurity signal. The spectrum was fit by including a single additional peak (IS = 0.32). It accounted for 12% of the total peak area.

<sup>e</sup> Relative to zero velocity defined as the isomer shift of iron metal at room temperature.



Fig. 1. Mössbauer spectrum of FeOCl(FeCp<sub>2</sub>)<sub>0.16</sub>, sample four, at 300 K. The solid line represents the best fit of a simple doublet to the data; the small outer doublet (dotted line) was generated from the known Mössbauer parameters [9, 10] of FeCp<sub>2</sub> (IS = 0.45 mm s<sup>-1</sup>, QS = 2.36 mm s<sup>-1</sup>), while the small inner doublet (dashed line) was generated from the known parameters [10] of (FeCp<sub>2</sub>)<sup>+</sup>BF<sub>4</sub><sup>-</sup> (IS = 0.40 mm s<sup>-1</sup>), QS = 0.61 mm s<sup>-1</sup>). Both small doublets were scaled to be 0.16 times as intense as the experimentally observed doublet.

effect, the smaller temperature coefficient for FeOCl(FeCp<sub>2</sub>)<sub>0.16</sub> indicates a lower mean squared velocity of vibration for the iron atoms in the intercalation compound at a given temperature. This result is consistent with a general "stiffening" of the lattice of FeOCl(FeCp<sub>2</sub>)<sub>0.16</sub> in comparison to FeOCl, due to the replacement of van der Waals' forces by ionic forces as the principle interaction in the direction perpendicular to the FeOCl type layers.

The second characteristic is the quadrupole splitting (QS). QS values for both FeOCl [11] and FeOCl(FeCp<sub>2</sub>)<sub>0.16</sub> (table II) are virtually temperature independent between 77 and 300 K. We attribute the  $0.26 \text{ mm s}^{-1}$  difference in QS between samples one (FeOCl) and two (FeOCl(FeCp<sub>2</sub>)<sub>0.16</sub>), to electron transfer from guest to host. Evidently the transferred electrons contribute a component to the electric field gradient opposite in sign to that generated by the coordination shell of the iron atoms.

Finally, the characteristic which provides the strongest evidence for the applicability of the electron transfer model is graphically illustrated in fig. 1: there is no evidence of any Mössbauer resonance at the positions expected for un-oxidized ferrocene. In fact, no quadrupole split doublet associated specifically with the Fe of the guest molecules is observed; this is consistent with the electron transfer hypothesis in that the lines due to ferricinium (FeCp<sup>+</sup><sub>2</sub>) fall almost

directly on top of those from the Fe of the host lattice, and would not be resolved.

### 4. Magnetization measurements

Detailed magnetization data were obtained at 6.35 kOe with increasing temperature from 4 K to 300 K for both the metallocene intercalation compounds and for the FeOCl host. In order to extract the susceptibilities  $\chi$  of the compounds, these magnetization data were corrected for the ferromagnetic impurity contributions  $M_0(T)$ (which were equivalent to < 0.13 mole % iron metal); however, because  $M_0$  changes rapidly between 4 K and 77 K for FeOCl(FeCp<sub>2</sub>)<sub>0.16</sub>, and since a detailed study of  $M_0(T)$  was not carried out for this compound within this temperature range, the additional  $M_0$  increment below 77 K was not corrected for in determining  $\chi$  for this material below 77 K so as not to introduce a possibly spurious temperature dependence to the derived  $\chi(T)$ . The susceptibilities deduced as described above for FeOCl, FeOCl(CoCp<sub>2</sub>)<sub>0.16</sub> and  $FeOCl(FeCp_2)_{0.16}$  are plotted vs. temperature in fig. 2.



Fig. 2. Magnetic susceptibilities vs. temperature for FeOCl and for FeOCl(MCp<sub>2</sub>)<sub>0.16</sub> (M = Fe, Co). Ferromagnetic impurity contributions have been subtracted as explained in the text.

The susceptibility of the FeOCl host shows three peculiar features: (1)  $\chi$  is temperatureindependent to within  $\pm 10\%$  over the full temperature range between 4 K and 360 K; (2) within this small temperature dependence,  $\chi$  increases with temperature from 50 K to 300 K and is independent of temperature from 300 K to 354 K; (3) a small cusp occurs with a peak at  $\approx$ 15 K, and appears to ride on top of a small low-temperature paramagnetic impurity tail. The temperature dependence of  $\chi(T)$  above 50 K suggests that our FeOCl sample is antiferromagnetically ordered below 350 K. However, the above Mössbauer data show no evidence for magnetic ordering at 300 K for this sample. This discrepancy between the Mössbauer and susceptibility data suggests that the  $\chi(T)$  data below 350 K reflect short range antiferromagnetic ordering within the FeOCl layers [12] which fluctuates on a time scale faster than can be resolved by the Mössbauer measurements. The cusp we observe at about 15 K in our  $\chi(T)$  data for FeOCI may be due to long range magnetic ordering of the compound at this temperature, or to impurity effects; in a separate measurement of a different FeOCl sample, the cusp was absent in a field of 23.8 kOe, but the temperature dependence at higher temperatures was the same. The origin of the cusp and of the overall temperature independent susceptibility are currently under investigation. Our susceptibility data for FeOCl differ in most respects both qualitatively and quantitatively with the reported susceptibility of this compound [13]. The previously reported  $\chi(T)$  does exhibit a cusp at 21 K, but *decreases* monotonically with increasing temperature above 22 K, and coincidentally, is nearly identical above 30 K with our  $\chi(T)$  data for FeOCl(FeCp<sub>2</sub>)<sub>0.16</sub> shown in fig. 2.

The susceptibility data shown in fig. 2 for FeOCl(CoCp<sub>2</sub>)<sub>0.16</sub> and FeOCl(FeCp<sub>2</sub>)<sub>0.16</sub> exhibit strong temperature dependences, in contrast to the FeOCl host. As a first approximation to the interpretation of the data for these materials, we will assume that upon intercalation of the metallocenes into the host, the large  $\approx$  temperatureindependent term is preserved, and that the net effect of intercalation on the susceptibility is to introduce a Curie-term (C/T), i.e., that the susceptibilities of the intercalation compounds vary as  $\chi = \chi_0 + C/T$ . Thus, a plot of  $\chi T$  vs. T should to first approximation be a straight line. Shown in fig. 3 are plots of  $\chi T$  vs. T for both of the metallocene intercalation compounds. As seen from the figure, excellent straight-line fits are obtained over the temperature ranges 40-250 K and 80-300 K for the (CoCp<sub>2</sub>) and (FeCp<sub>2</sub>) intercalation compounds, respectively. The positive deviation of the data for the  $(FeCp_2)$  intercalation compound from the straight line below 70 K



Fig. 3. Plots of susceptibility times temperature vs. temperature, derived from the data in fig. 2.

probably arises from ferromagnetic ordering of an impurity phase as discussed above. The negative deviation of the data for both compounds at the lowest temperatures probably occurs via the existence of a small ( $\theta \approx -5$  K) antiferromagnetic interaction between the local moments which are responsible for the temperature dependence. The y-intercepts (C) and slopes ( $\chi_0$ ) of the lines fitting the data in fig. 3 are given in table II.

We will now show that the values of C and  $\chi_0$ in table III are physically reasonable. First, we note that the values of  $\chi_0$  are within 25% of the values  $(3.0 \pm 0.3 \times 10^{-3} \text{ cm}^3/\text{mole})$  found above for the FeOCl host. We next consider the origin of the Curie terms. The Mössbauer data above have shown that intercalation of  $(FeCp_2)$  into FeOCl is charge transfer accompanied by to form  $(FeCp_2)_{0.16}^{+1}(FeOCl)^{-0.16};$  similar ionization of cobaltocene is expected to hold for the cobaltocene intercalation compound. The effective moment  $\mu_{\text{eff}}$  of  $(\text{CoCp}_2)^+$  is zero, whereas that of  $(FeCp_2)^+$  has been found to be  $2.50 \pm 0.15 \mu_B$ , where the  $\pm 0.15 \mu_{\rm B}$  includes the reported variations of  $\mu_{\text{eff}}$  in different environments and vs. temperature [14, 15]. Since charge transfer to the FeOCl layers and presumably its effects on the magnetic properties are the same for the two intercalation compounds, the difference in the Curie terms ( $\Delta C$ ) for the ferrocenium and cobaltocenium intercalation compounds should just be the Curie constant predicted for 0.16 mole of (FeCp<sub>2</sub>)<sup>+</sup>. Utilizing the above-cited value for  $\mu_{\rm eff}$  for (FeCp<sub>2</sub>)<sup>+</sup>, we calculate  $\Delta C =$  $0.125 \pm 0.016$  cm<sup>3</sup>-K/mole. From table III, the experimentally determined value is  $\Delta C =$  $0.11 \pm 0.02$  cm<sup>3</sup>-K/mole, in agreement with the calculated value. Finally, we are left with the question of the origin of the Curie term in the (CoCp<sub>2</sub>)<sub>0.16</sub>FeOCl compound. This Curie term may be associated with the localization of electrons donated to the FeOCl by the metallocene; however, impurity effects cannot be ruled out and further experimental work will be necessary to establish the origin of the Curie term. Elec-

Table III Parameters describing  $\chi(T)$  in terms of the equation  $\chi(T) = \chi_0 + C/T$ 

Compound	$\chi_0$ (10 <sup>-3</sup> cm <sup>3</sup> /mole)	C (cm <sup>3</sup> -K/mole)
FeOCl(CoCp <sub>2</sub> )0.16	$4.0 \pm 0.1$	$0.12 \pm 0.02$
FeOCl(FeCp <sub>2</sub> ) <sub>0.16</sub>	$3.3 \pm 0.1$	$0.23 \pm 0.01$

trical conductivity studies on FeOCl and on the metallocene intercalation compounds show that the conductivity does not change upon intercalation. This observation supports the above hypothesis that the transferred electrons are localized.

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