

predominating effect of the crown ether, therefore, is the conformational factor to produce more exposed carbon centers.

References and Notes

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- (2) The two geometric isomers were not separately estimated in the

present study.

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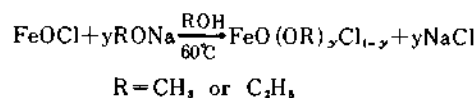
Formation of Layered Compounds of $\text{FeO}(\text{OCH}_3)_{0.7}\text{Cl}_{0.3}$ and $\text{FeO}(\text{OC}_2\text{H}_5)_{0.3}\text{Cl}_{0.7}$ by Topochemical Reaction

Jin-Ho Choy, Jun-Kun Kang, and Young-Uk Kwon

Department of Chemistry, College of Natural Science, Seoul National University, Seoul 151, Korea

Organic molecules can be included in the interlayer space of layered transition metal chalcogenohalides which are maintained together only by van der Waals forces.¹ In the case of FeOCl which belongs to the orthorhombic space group P_{mnn} with $a = 378.0$ pm, $b = 330.2$ pm, $c = 791.7$ pm and $Z = 2$,² it was shown that the chemical behavior towards polar neutral guests like ammonia, amines,^{3,4} aromatic heterocycles^{5,6} and alkali metals⁷ or organometallic cations⁸⁻¹¹ can be attributed to two kinds of reactions; namely, intercalation by the partial reduction of Fe^{3+} centers and/or substitution of Cl^- layers by NH_2^- , RNH^- or RO^- , etc. Such compounds are of interest because of their unusual chemical and physical properties such as large enhancement of chemical reactivity in partially reduced FeOCl to neutral guests¹⁶ and increase of electrical conductivity from semiconducting FeOCl to conductor on intercalation reaction by $10^7 \Omega \cdot \text{cm}^{12}$. Substitution of chloride layers in FeOCl lattice with methoxide has been reported by Kikkawa, *et al.*^{13,14} Surprisingly the chloride ions were totally substituted by methoxide ions and b-axis of unit cell was expanded from 330 pm to 399 pm for methoxy derivative assigned as FeOCH_3 . But this total substitution is scarcely expected because the methoxy groups on the Fe atom are sufficiently bulky, and presumable tend to sweep out large volumes as they rotate randomly. As an evidence, *n*-alkanols or *n*-alkylamines can be intercalated into FeOCl lattice as much as ca. 0.54 mole per 1 mole of FeOCl.^{4,15} From this reason, there has been a great expectation that the value of y in $\text{FeO}(\text{OR})_y\text{Cl}_{1-y}$ should be less than

0.54, or slightly greater in the case of methoxy substituent and approaches to any constant values as the chain length of alkoxide increases. To certify our presupposition to be true or not we have prepared the methoxy and ethoxy derivatives of FeOCl as follows:



The host lattice, FeOCl, was prepared by heating the mixture of $\alpha\text{-Fe}_2\text{O}_3$ and FeCl₃ with the mole ratio of 3:4 in a sealed pyrex tube at 370~300°C for 5 days according to chemical vapor transport technique.^{3,4} For intercalation and successive substitution reaction in the alkoxide/alcohol solution, the concentration of alkoxides were chosen as 1 mole per 1 mole of FeOCl which was controlled by adding sodium into the excess alcohol and all the batches were incubated at 60°C for about 4 days. The color of reaction products was changed from lustrous dark brown to gold tint, but somewhat different depending upon the number of carbon atoms in alkoxide. The resulting intercalates were washed with the corresponding water free alcohol and dried in vacuo.

The elemental analyses are not only consistent with those of theoretically calculated for iron oxyalkoxide $\text{FeOOC}_x\text{H}_{2x+1}$, but also with the values reported by Kikkawa, *et al.*¹³ as shown in Table 1. If the methoxide ions are fully substituted, the bond angle of $\text{Cl}(1)\text{-Fe-Cl}(1)$ in distorted octahedron of *cis*- FeCl_2O_4 ($= 88.42^\circ$)² must be changed to ca. 143° of $\text{CH}_3\text{O-Fe-OCH}_3$

TABLE 1: Elemental Analyses Data for *n*-alkoxy Substituents of Iron(III) Oxychloride; $\text{FeO}(\text{OCH}_3)_y\text{Cl}_{1-y}$ and $\text{FeO}(\text{OC}_2\text{H}_5)_y\text{Cl}_{1-y}$ (weight percent)

Compound	C	H	Cl	Remarks
$\text{FeO}(\text{OCH}_3)_y\text{Cl}_{1-y}$	8.24 (0.71)	2.05 (0.71)	9.20 (0.73)	this work
	9.29 (0.80)	2.43 (0.84) ^b	4.20 (0.88)	Kikkawa, <i>et al.</i> ¹³
	11.70 (1.00)	2.94 (1.00)	0.00 (0.00)	theoretical values for FeOCH_3 ($y = 1$)
$\text{FeO}(\text{OC}_2\text{H}_5)_y\text{Cl}_{1-y}$	6.85 (0.31)	1.45 (0.32)	21.01 (0.35)	this work
	20.50 (1.00)	4.31 (1.00)	0.00 (0.00)	theoretical values for FeOOC_2H_5 ($Y = 1$)

^aThe approximate chemical compositions derived from these data were chosen as $\text{FeO}(\text{OCH}_3)_{0.7}\text{Cl}_{0.3}$ and $\text{FeO}(\text{OC}_2\text{H}_5)_{0.3}\text{Cl}_{0.7}$. Values in parentheses denote the extent of substitution (y).

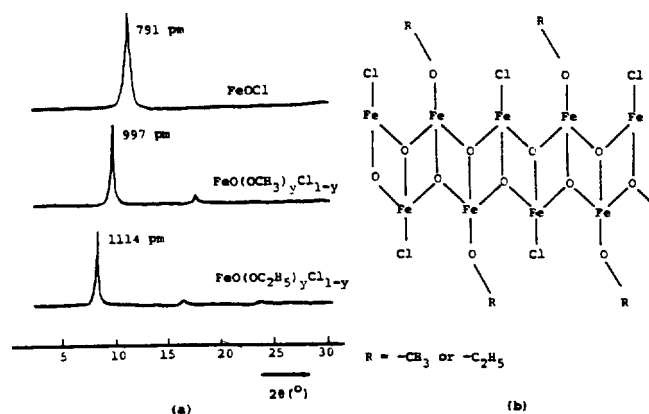


Figure 1. (a) The X-ray diffraction patterns of FeOCl, FeO(OCH₃)_{0.7}Cl_{0.3}, and FeO(OC₂H₅)_{0.3}Cl_{0.7}. (b) The structure model of the *n*-alkoxy derivatives.

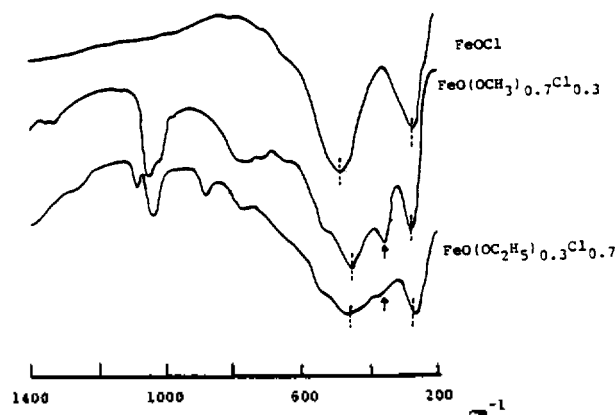


Figure 2. Infrared spectra of FeOCl and alkoxy-derivatives: peaks near 270 cm⁻¹ and near 480 cm⁻¹ are due to Fe-Cl and Fe-O stretching vibrations, respectively. Peaks with arrows (f) are referred to Fe-OR bond.

in *cis*-Fe(OCH₃)₂O₄ assuming that the bond distance of Fe-OCH₃ does not markedly differ from that of Fe-O(1). Such a large distortion, therefore, can be hardly expected with retaining the structural stability of layer lattice. X-ray powder diffraction pattern exhibited new reflections of 998(1) pm basal spacing for methoxy substituted phase which is surprisingly identical with the value of 997(3) pm from Kikkawa within the limit of experimental error and of 1,114(2) pm basal spacing for ethoxy one, respectively. And characteristic 791 pm of (001) reflection of original FeOCl is absent. The interlamellar distance thus increases by ca. 207 pm for methoxy- and 323 pm for ethoxy- derivative and suggests the alkoxy orientation tilted because of the bond angle of Fe-O-R and the increase of volume demand in interlayer space (Figure 1). Infrared spectra of the substituents indicate that the outer most ions of FeOCl layer, chloride ions, are not fully but partially substituted by alkoxy ion. In the case of pure FeOCl, only two bands appear around 480 cm⁻¹ corresponding $\nu_{(\text{Fe-O})}$ and 270 cm⁻¹ for $\nu_{(\text{Fe-Cl})}$, respectively.⁷ In alkoxy substituents, new bands appear near 350 cm⁻¹ which refers to Fe-OR bond and 1050 cm⁻¹ due to the stretching vibration of the C-O bond, but none to the O-H stretching vibration. And $\nu_{(\text{Fe-Cl})}$ and $\nu_{(\text{Fe-O})}$ still remain and are almost not shifted after substitution, except for the remarkable decrease in intensity of $\nu_{(\text{Fe-Cl})}$ (Figure 2).

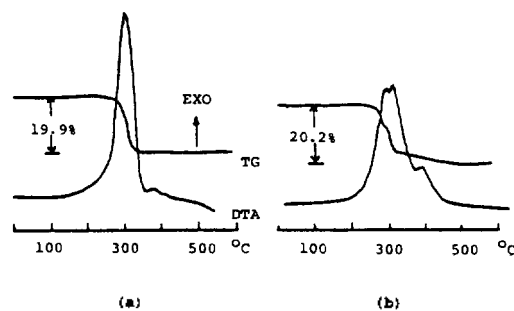
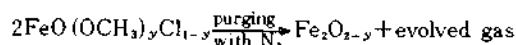


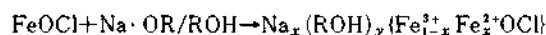
Figure 3. Thermograms of TG and DTA for FeO(OCH₃)_{0.7}Cl_{0.3}, (a) and FeO(OC₂H₅)_{0.3}Cl_{0.7}, (b), respectively.

Along with these facts, elemental analysis and X-ray diffraction patterns, the literature data for methoxy derivative are strongly suspicious, but our products can be always reproducibly prepared under the given experimental conditions and assigned as FeO(OCH₃)_{0.7}Cl_{0.3} and FeO(OC₂H₅)_{0.3}Cl_{0.7}, which are well commensurate with the bulkiness of alkoxy ions. According to the thermal analysis (TG and DTA) for methoxy derivative, important changes are not observed below 290°C, indicating that no void space does exist in the interlayer space of FeO(OCH₃)_{0.7}Cl_{0.3} to include the guest molecules like methanol. But a sharp exothermic peak at 328°C with 19.9% weight loss nearly by single step which is exactly the same result as Kikkawa reported.¹³ If his FeOOCH₃ was correctly characterized, the weight loss in TG must be 22.4% theoretically. But the observed weight loss of 19.9% does agree exactly with the theoretical value of FeO(OCH₃)_{0.7}Cl_{0.3} as we experimentally assigned.



The ethoxy derivatives shows also similar thermal decomposition pattern, but the inflection point on the TG curve spans from 300°C to 326°C (Figure 3).

So as to confirm the partial reduction of FeOCl influenced by sodium ion in alcohol solution,^{7,16}



XPS analysis was performed before and after the substitution reaction, but any meaningful difference in binding energies of Fe2p_{1/2} (724.07 eV), Fe2p_{3/2} (710.82 eV), O1s (530.80 eV) and Cl2p (199.10 eV) in FeOCl and its alkoxy derivatives were not observed.

Acknowledgement. We are grateful to the Ministry of Education (Grant No. ED83-314) for support of this work.

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