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## Synthesis and Some Properties of FeOOCH<sub>3</sub>. A New Layered Compound

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A new layered compound was synthesized by soaking an intercalated compound FeOCl(4-AP)<sub>1/4</sub> in methanol at 110 °C for 6 days. This new compound had a chemical composition of FeOOCH<sub>3</sub> and its interlayer spacing was 9.97 Å. The infrared spectrum showed two kinds of absorption bands of C-O stretching vibration around 1050 cm<sup>-1</sup>, but no O-H stretching vibration. A study of the Mossbauer effect of FeOOCH<sub>3</sub> at room temperature indicated that the isomer shift and the quadrupole splitting were 0.37 and 0.60 mm/s, respectively. The crystal structure is characterized by a layer structure derived from FeOCl or γ-FeOOH.

### Introduction

Many organic intercalation complexes of layered compounds have been prepared and characterized. Among them, clay-organic complexes have been extensively investigated in the field of earth science, agriculture, and crystal chemistry.<sup>1,2</sup> In recent years, many investigations have been done on the complexes of layered inorganic compounds and organic molecules, for example, TaS<sub>2</sub>(py)<sub>1/n</sub>, from the viewpoint of material science.<sup>3</sup> In these complexes the intercalated organic molecules are loosely bonded to the layer surface of the host inorganic material. Kanamaru et al. have reported the synthesis and properties of this type of complex of FeOCl and pyridine.<sup>4</sup> On the other hand, few compounds of the directly bonded type have been reported, that is to say organic derivatives in which the layered structure is retained.<sup>5</sup> We succeeded in the preparation of the latter type compound FeOOCH<sub>3</sub> by replacing Cl of FeOCl with OCH<sub>3</sub>. This paper describes the preparation and some properties of the FeOOCH<sub>3</sub>.

### Experimental Section

**Preparation.** FeOCl was prepared by heating the mixture of α-Fe<sub>2</sub>O<sub>3</sub> and FeCl<sub>3</sub> with the mole ratio of 1 to 4/3 in a sealed Pyrex glass tube at 370 °C for 2 days. Reddish violet and thin blade-like FeOCl crystals with dimensions 10 × 2 × 0.5 mm were obtained. To remove excess FeCl<sub>3</sub>, the product was washed with water and dried. Then FeOCl was reacted with acetone solution of 4-aminopyridine (4-AP) at 110 °C for 6 days in a sealed glass tube. Black crystals of the intercalation compound of 4-AP and FeOCl were obtained. This compound was soaked in methanol in a sealed Pyrex glass tube. The duration of the reaction which produced brown crystals of FeOOCH<sub>3</sub> was about 10 days at 80 °C but 6 days at 110 °C.

**Analysis.** X-ray analysis was conducted with a Rigaku-Denki diffractometer using Cu Kα and Co Kα radiation. A C, H, N, and Cl analysis of this complex was made using standard techniques. Infrared absorption spectra were obtained using a Japan Spectroscopic Co. Ltd. DS-402G spectrometer by the usual KBr pellet technique and Nujol method. Mossbauer spectra using radiation from <sup>57</sup>Co in Cu metal were measured at room temperature with a 200 channel multichannel analyzer. Calibration was based on the Mossbauer spectrum of Fe metal. For differential thermal analysis a Rigaku-Denki apparatus fitted with a platinum-platinum-rhodium thermocouple was used and Al<sub>2</sub>O<sub>3</sub> was used as reference. The rate of temperature increase was 10 °C/min.

Table I. X-Ray Powder Diffraction Data for FeOOCH<sub>3</sub><sup>a, b</sup>

<i>hkl</i>	I	<i>d</i> <sub>obsd</sub>	<i>d</i> <sub>calcd</sub>
010	vs	9.91	9.97
020	m	4.99	4.98
001	w	3.99	3.99
110	mm	3.58	3.58
030	mm	3.33	3.32
120	w	3.03	3.04
040	w	2.491	2.492
002	vw	2.003	1.995
050	mm	1.992	1.994
200	w	1.921	1.915
060	mm	1.662	1.662
070	vw	1.426	1.425

<sup>a</sup> Debye-Scherrer data; Co Kα radiation. <sup>b</sup> *a* = 3.83 (1) Å, *b* = 9.97 (1) Å, *c* = 3.99 (1) Å.

### Results and Discussion

Due to a strong preferred orientation effect, each x-ray diffraction pattern presented in Figure 1 consists of only basal reflection lines of each product obtained in the above-mentioned reaction process. FeOCl belongs to the orthorhombic space group *Pmnm* with *a* = 3.780, *b* = 7.917, *c* = 3.302 Å, and *Z* = 2.<sup>6</sup> The crystal structure is characterized by the layer structure similar to that of γ-FeOOH. The layer consists of a double sheet of *cis*-FeCl<sub>2</sub>O<sub>4</sub> octahedra linked together by shared edges through oxygens. The outermost atoms on each side of the layers are Cl<sup>-</sup> ions. The interlayer force between adjacent layers is weak van der Waals'. When FeOCl was heated with acetone solution of 4-AP, 4-AP molecules could penetrate into the van der Waals gap, and then the sorption complex FeOCl(4-AP)<sub>1/4</sub> was obtained.<sup>7</sup> This reaction was accompanied by the expansion of FeOCl lattice along the *b* axis to give the basal spacing of 13.57 Å as shown in Figure 1b. One-dimensional electron-density projection on the *b* axis of FeOCl(4-AP)<sub>1/4</sub> was synthesized using the eight (0*k*0) reflections. The schematic structure based on the projection is illustrated in Figure 2b. During the reaction of the sorption complex FeOCl(4-AP)<sub>1/4</sub> and methanol, methanol molecules were easily intercalated in the expanded interlayer spaces of FeOCl, and the third phase appeared. The last phase gave the basal spacing of 9.97 Å as depicted in Figure 1c and Table

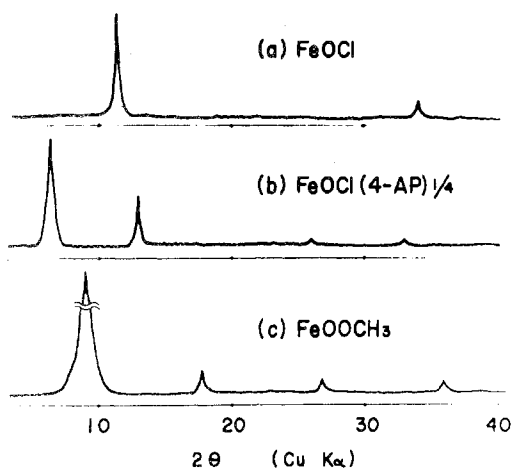


Figure 1. X-ray diffraction patterns of FeOCl, FeOCl(4-AP)<sub>1/4</sub>, and FeOOCH<sub>3</sub>.

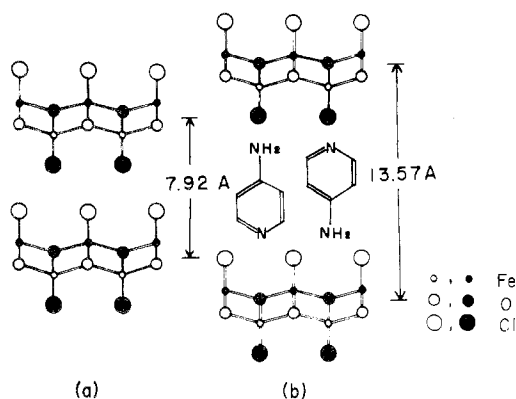


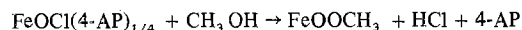
Figure 2. Schematic representations of the structures of FeOCl and FeOCl(4-AP)<sub>1/4</sub>.

Table II. FeOOCH<sub>3</sub> Chemical Analysis Data (Weight Percent)

Element	C	H	N	Cl
Obsd value	9.29	2.43	0.33	4.20
Calcd value	11.7	2.94	0.00	0.00

I. After the reaction, Cl ion and 4-AP were qualitatively detected in the solution.

In order to determine the chemical composition of the last product, a chemical analysis of C, H, N, and Cl was conducted, and the results are given in Table II. For carbon and hydrogen the experimental values were smaller than the theoretical ones and small amounts of nitrogen and chlorine were observed. The traces of nitrogen and chlorine were still detected after prolonged reaction of more than 1 month. From the C, H, N, and Cl values, the chemical formula of the compound is evaluated to be FeOOCH<sub>3</sub>. Then the above-mentioned reaction is described as follows



where HCl and 4-AP go into solution leaving solid FeOOCH<sub>3</sub>. On the other hand, any direct reaction between FeOCl and methanol was not observed in a temperature range from room temperature to 110 °C. These results represent the fact that the expansion of interlayer distance of FeOCl makes it easy for methanol molecules to penetrate into the interlayer spaces resulting in desorption of 4-AP molecules and chlorine ions from the interlayer.

Infrared spectra and the Mössbauer effect study of FeOOCH<sub>3</sub> also showed this displacement. The solid line in Figure 3 indicated the infrared spectrum of FeOOCH<sub>3</sub> ob-

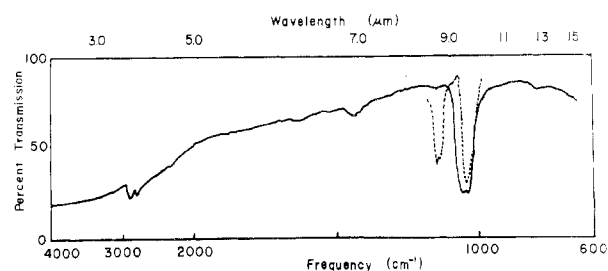


Figure 3. Infrared spectrum of FeOOCH<sub>3</sub> using the KBr pellet technique (solid line) and orientation infrared spectrum obtained by the Nujol method (dotted line).

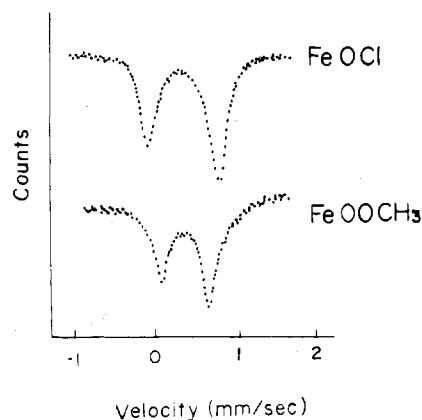


Figure 4. Mössbauer spectra of FeOCl and FeOOCH<sub>3</sub> at room temperature. Velocity scale is relative to Fe metal.

Table III. Mössbauer Parameters (mm/s) of FeOCl and FeOOCH<sub>3</sub><sup>a,b</sup>

	Isomer shift	Quadrupole splitting
FeOCl	0.36	0.92
FeOOCH <sub>3</sub>	0.37	0.60

<sup>a</sup> Measurement was conducted at room temperature. <sup>b</sup> Velocity scale is relative to Fe metal.

tained using the KBr pellet technique. This spectrum gave the absorption band at 1050 cm<sup>-1</sup> assigned to the stretching vibration of the C–O bond, but none for the O–H stretching vibration. This result indicates that the methanol molecule absorbed in the interlayer region changed to methoxide ion, CH<sub>3</sub>O<sup>-</sup>, which substituted for the chlorine ion, the outermost ion of the FeOCl layer. Moreover, the absorption band of the C–O stretching vibration split into two bands. Since these bands had almost the same intensities, this compound was considered to have two kinds of C–O bond. And further to find the cause of this splitting, the orientation effect of the FeOOCH<sub>3</sub> crystal was investigated. Large and very thin FeOOCH<sub>3</sub> crystals were held between NaCl disks dipped with Nujol mull and exposed vertically to infrared rays. The dotted line in Figure 3 shows this experimental result. In this case, the absorption band of higher wavenumber disappeared and only the lower one remained. This fact indicates that the former is the absorption of the C–O bond which is perpendicular to the inorganic layer and the latter is slightly inclined. Furthermore, the intensity of the absorption band at 1150 cm<sup>-1</sup> increased and was assigned to the rocking mode of the methyl group.<sup>8</sup> The increase of this absorption intensity is quite reasonable from the viewpoint of bond orientation.

The Mössbauer spectra of FeOCl and of FeOOCH<sub>3</sub> are illustrated in Figure 4 and the pertinent parameters are summarized in Table III. The measured value of quadrupole splitting for FeOOCH<sub>3</sub> is much smaller than that for FeOCl. This result is explained as follows. The chlorine atoms of

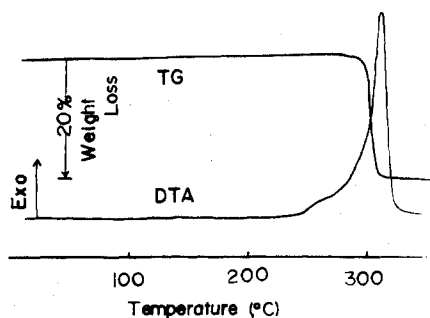


Figure 5. Differential thermal analysis and thermogravimetry of  $\text{FeOOCH}_3$ .

distorted  $\text{FeCl}_2\text{O}_4$  octahedra in  $\text{FeOCl}$  layers have been replaced by oxygen atoms of methoxide ions. Consequently the crystal field symmetry around the Fe atom has been raised. On the other hand, isomer shift of  $\text{FeOOCH}_3$  showed almost the equal value to that of  $\text{FeOCl}$ . So, even with the methoxide ions coordinated to Fe atoms, the valence state of Fe atom remains the 3+ state.

Figure 5 presents the result of differential thermal analysis and thermogravimetry of  $\text{FeOOCH}_3$ . As seen in the figure, no change was observed below 290 °C, indicating that  $\text{FeOOCH}_3$  is not a sorption type complex, but a new layered type compound with strong bonding between the intercalated  $\text{CH}_3\text{O}^-$  and the inorganic layer. A sharp exothermic peak and a 20% weight loss were observed in the temperature region from 290 to 300 °C. The sample cooled from 350 °C exhibited strong magnetism and was identified to be  $\gamma\text{-Fe}_2\text{O}_3$  by x-ray diffractometry. If  $\text{FeOOCH}_3$  thermally decomposes at 290 °C and gives rise to  $\gamma\text{-Fe}_2\text{O}_3$ , this observed weight loss agrees with the theoretical one.

A one-dimensional electron-density projection on the  $b$  axis was synthesized using seven ( $0k0$ ) x-ray reflections of  $\text{FeOOCH}_3$ . The sign of each reflection was determined by considering the contribution of Fe and O in the skeleton of the inorganic layers, FeO double layer. As shown in Figure 6, there are five peaks in the interlayer region. On the basis of this projection together with the above-mentioned Mossbauer effect, the infrared absorption and orientation infrared absorption results, and so on the crystal structure of  $\text{FeOOCH}_3$  is deduced as indicated in Figure 6. In this structure, it is apparent that the oxygens of methoxide groups are directly bonded to ferric ions, and that there are two kinds of methoxide groups. Moreover, a small central peak in the electron-density projection may arise from a small amount of 4-AP molecules remaining in the last product.

The crystal structure of  $\text{FeOOCH}_3$  is closely related to that of  $\gamma\text{-FeOOH}$  as described below, even though hydrogen ions of the latter are substituted for  $\text{CH}_3^+$  in the former.  $\gamma\text{-FeOOH}$  can toptaxially convert to  $\gamma\text{-Fe}_2\text{O}_3$  with the cubic closest packing of oxygens, which is a metastable phase of iron oxides, by dehydration. As mentioned above,  $\text{FeOOCH}_3$  also converted to  $\gamma\text{-Fe}_2\text{O}_3$  in the temperature region between 290 and 300 °C in air. Furthermore, it is confirmed by thermomagnetic measurements that  $\text{FeOOCH}_3$  converted to a ferromagnetic compound at 290 °C and then to a nonmagnetic compound,  $\alpha\text{-Fe}_2\text{O}_3$ , above 450 °C in vacuum. If the magnetic substance was magnetite,  $\text{Fe}_3\text{O}_4$ , the substance did not convert to  $\alpha\text{-Fe}_2\text{O}_3$  at 450 °C in vacuum. So this fact indicates that  $\text{FeOOCH}_3$  did not convert to magnetite at 290 °C, but did

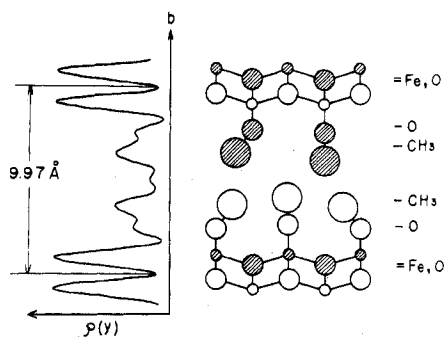


Figure 6. One-dimensional electron-density map, obtained using diffractometry, projected on the  $b$  axis and schematic representation of the structure of  $\text{FeOOCH}_3$ . A small central peak and a larger peak intensity for carbon than for oxygen in the electron-density projection may arise from a small amount of 4-AP molecules remaining in the last product.

convert directly to  $\gamma\text{-Fe}_2\text{O}_3$ . The ease of conversion from  $\text{FeOOCH}_3$  to  $\gamma\text{-Fe}_2\text{O}_3$  is considered to be due to the similarity of the atomic arrangements of oxygen and iron ions between  $\text{FeOOCH}_3$  and  $\gamma\text{-FeOOH}$ . The dense packing of the methyl group,  $\text{CH}_3$ , in the interlayer region caused slight expansions of  $a$  and  $c$  axes from 3.78 and 3.30 Å of  $\text{FeOCl}$  to 3.83 and 3.99 Å of  $\text{FeOOCH}_3$ , respectively.

$\text{FeOCl}$  did not directly react with methanol as mentioned above, and the  $\text{FeOCl}(\text{py})_{1/n}$  ( $n = 3$  or 4) complex,<sup>4</sup> a sorption complex such as  $\text{FeOCl}(4\text{-AP})_{1/4}$ , did not react very rapidly with methanol to produce  $\text{FeOOCH}_3$ . These facts indicate that the intercalated 4-AP not only makes it easy for methanol to penetrate the interlayer region of  $\text{FeOCl}$ , but also enhances the replacement of Cl with  $\text{CH}_3\text{O}$  by forming a hydrogen bond between  $\text{NH}_2$  of 4-AP and Cl on the surface of the  $\text{FeOCl}$  layer, resulting in reduction of the binding force of Fe-Cl. The structure of  $\text{FeOOCH}_3$  can be derived from  $\gamma\text{-FeOOH}$  or  $\text{FeOCl}$  by replacing OH or Cl with  $\text{CH}_3\text{O}$ . These kinds of compounds have been prepared as the precipitate of the reaction in solution.<sup>9</sup> However,  $\text{FeOOCH}_3$  was produced by the interlayer substitution of methoxide groups for chlorine atoms of  $\text{FeOCl}$  with the iron and oxygen double layers of  $\text{FeOCl}$  remaining without destruction.

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**Registry No.**  $\text{FeOOCH}_3$ , 59473-94-8;  $\text{FeOCl}(4\text{-AP})_{1/4}$ , 59532-68-2;  $\text{FeOCl}$ , 13870-10-5; methanol, 67-56-1.

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