Table VII. Comparison between the Ratio of the Reaction Rate via k_0 Path to the Overall Reaction Rate and the Product Ratio of $[[Cr(ida)(H_2O)_3]^+]$ to $\{[[Cr(ida)(H_2O)_3]^+] + [[Cr(H_n ida)(H_2O)_5]^{(n+1)+}]\}$ in the Reaction of $[Co(H_n ida)(NH_3)_5]^{(n+1)+}$ with Cr^{2+} at 25.5 °C and $I = 1.0$ M ($LiClO_4$)

$[H^+]$, M	rate ratio[a]	product ratio[b]
0.090	0.810	0.797
0.121	0.718	0.692
0.150	0.635	0.608
0.196	0.516	0.484
0.276	0.361	0.320
0.523	0.143	0.131
0.938	0.051	0.055

[a] $k_0K_1K_2/(k_0K_1K_2 + k_1K_1[H^+] + k_2[H^+]^2)$. [b] $[[Cr(ida)(H_2O)_3]^+]/\{[[Cr(ida)(H_2O)_3]^+] + [[Cr(ida)(H_2O)_5]^{(n+1)+}]\}$.

rate of the k_0 path to the overall reaction rate ($k_0K_1K_2/k\alpha(H) = k_0K_1K_2/(k_0K_1K_2 + k_1H_1[H^+] + [H^+]^2)$) was found to agree well with the ratio of the yield of $[Cr(ida)(H_2O)_3]^+$ to that of the total chromium(III) products containing IDA ($[[Cr(ida)(H_2O)_3]^+]/([[Cr(ida)(H_2O)_3]^+] + [[Cr(H_n ida)(H_2O)_5]^{(n+1)+}])$) as shown in Table VII. Therefore, it is concluded that $[Cr(ida)(H_2O)_3]^+$ is formed exclusively by the k_0 path. The proposed paths for the reaction of $[Co(H_n ida)(NH_3)_5]^{(n+1)+}$ with Cr^{2+} are summarized in Scheme I.

Acknowledgment. The authors wish to thank the Ministry of Education for Scientific Research Grant-in-Aid No. 147043.

Registry No. $[Co(Hida)(NH_3)_5](ClO_4)_2$, 72016-80-9; $[Co(H_2edda)(NH_3)_5](ClO_4)_3$, 72016-83-2; $Cr(H_2O)_6^{2+}$, 20574-26-9; $[Cr(H_2ida)(H_2O)_5]^{3+}$, 72016-84-3; $[Cr(H_2edda)(H_2O)_5]^{3+}$, 72016-85-4; $[Co(ida)(NH_3)_5]^+$, 72016-78-5; $[Co(H_2ida)(NH_3)_5]^{3+}$, 72016-86-5; $[Cr(ida)(H_2O)_3]^+$, 72059-09-7; $[Cr(edda)(H_2O)_2]^+$, 32151-23-8; $[(NH_3)_5Co(Hida)Co(NH_3)_5](ClO_4)_5$, 72016-89-8; $[(NH_3)_5Co(H_2edda)Co(NH_3)_5](ClO_4)_6$, 72016-92-3.

Supplementary Material Available: Table I listing analytical data, Table II listing numerical data for the electronic spectra, and Table V listing product analyses of the reaction of $[Co(H_n edda)(NH_3)_5]^{(n+1)+}$ with Cr^{2+} (3 pages). Ordering information is given on any current masthead page.

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Preparation and Properties of $FeO(O_2C_2H_4)_{1/2}$

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An organic derivative of the layer compound FeOCl was obtained by the reaction of an intercalated compound $FeOCl(4\text{-}NH_2py)_{1/4}$ and ethylene glycol $C_2H_4(OH)_2$ at 110 °C for 6 days. The reaction product was a brown crystal of flake shape. Its basal spacing was 14.5 Å when the product was still in ethylene glycol, but it shrank to 10.98 Å by washing with acetone. The chemical composition of the final product was $FeO(O_2C_2H_4)_{1/2}$. Mössbauer isomer shift and quadrupole splitting were respectively 0.38 mm/s and 0.59 mm/s at room temperature. Thermal analysis and the infrared spectrum suggested a substitution of ethylene glycolate anions $O_2C_2H_4^{2-}$ for chloride ions in the FeOCl layer. A possible layer structure derived from FeOCl is proposed.

Introduction

Some layer compounds intercalate many kinds of organic molecules and metal ions. Intercalation compounds are divided into three classes according to their bonding characteristics between host layer and guest molecules. One is the sorption-type complex in which organic molecules are loosely bonded to host layers by hydrogen bonds, ion–dipole interactions, charge-transfer bonds, and so on.[1-3] Transition-metal dichalcogenides are typical of charge-transfer type complexes. Some clay–organic complexes are representative of the other class of intercalation compounds.[4,5] In these complexes organic cations are bonded to host aluminosilicate layers by electrostatic interaction. The last type of complex is organic derivatives of layered inorganic compounds. Organic molecules in the derivatives are directly bonded to the host layers by covalent bonds or by replacing the outermost atoms of the layers with organics. Few examples of this kind of complex have been reported.[6,7] We have reported the synthesis of $FeOOCH_3$ with a layer structure derived from the substitution of OCH_3^- ions for chloride ions in FeOCl.[8]

The oxychloride FeOCl has layers formed by the sharing of O–O and O–Cl edges of *cis*-$FeCl_2O_4$ octahedra. Its layers pack together so that the Cl^- ions on the outsides of adjacent layers are closely packed. In FeOCl, there are layers similar to those in γ-FeOOH with Cl^- ions instead of OH^- ions. The chloride ions can really be substituted by NH_2^-, OCH_3^-, and so on without the reconstruction of the other part of the layers. This unaltered part of the layer is hereafter called the FeO double layer since it can be assumed to be a double sheet formed with Fe and O.

One of the interesting approaches is the preparation of another type of organic derivative of FeOCl, in which organic molecules such as diols bridge two adjacent FeO double layers. This paper deals with the reaction of $FeOCl(4\text{-}NH_2py)_{1/4}$ with ethylene glycol, hereafter denoted as EG, and the structural characterization of the product.

Experimental Section

Preparation. Reddish violet and thin, bladelike FeOCl crystals were prepared by heating the mixture of α-Fe_2O_3 and $FeCl_3$ in a sealed Pyrex tube at 370 °C for 2 days. FeOCl was reacted with 4-aminopyridine, hereafter called 4-AP, in acetone solution at 110 °C

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Table I. Chemical Analysis Data (Weight Percent) for $FeO(O_2C_2H_4)_{1/2}$

	Fe	C	H	N	O
obsd	54.2	11.61	2.21	...	32.00
calcd	54.82	11.78	1.98	0.00	31.43

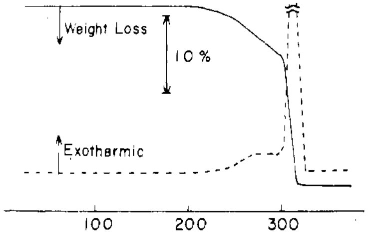

Figure 1. Differential thermal analysis (dotted line) and thermogravimetric analysis (solid line) of $FeO(O_2C_2H_4)_{1/2}$.

for 6 days. Black crystals of the intercalation compound $FeOCl(4\text{-}AP)_{1/4}$ were obtained. This compound was then well ground and soaked in EG with a small amount of 4-AP in a sealed glass tube. The addition of 4-AP was important in order to complete the reaction of $FeOCl(4\text{-}AP)_{1/4}$ with EG. The duration of the last reaction was about 1 week at 110 °C. The products were brown flake crystals. They were washed with acetone until the silver chloride test was negative.

Analysis. X-ray analysis was conducted with a Rigaku-Denki diffractometer using Fe-filtered Co Kα radiation. C, H, and N were quantitatively determined by using standard techniques. Iron content was determined by atomic absorption. Chlorine was not observed in the product. For TGA–DTA, a Rigaku-Denki apparatus fitted with a platinum/platinum–rhodium thermocouple was used and the reference was Al_2O_3; the rate of temperature increase was 10 °C/min. The infrared absorption spectra were obtained by using a Japan Spectroscopic Co. Ltd. DS-402G spectrometer with the usual KBr-pellet technique. The Mössbauer spectra, with radiation from ^{57}Co in Pd metal, were measured at room temperature with a 200-channel analyzer. Calibration was based on the spectrum of Fe metal.

Results and Discussion

$FeOCl(4\text{-}AP)_{1/4}$ is a sorption-type complex with the basal spacing of 13.57 Å. The structure and some properties of this compound have been given elsewhere.[9] The reaction product of $FeOCl(4\text{-}AP)_{1/4}$ with EG was examined by X-ray diffractometry. The interlayer distance was 14.5 Å for the product wet with EG. The basal spacing decreased to 10.89 Å, and the line widths of the basal reflections were broadened when the product was washed with acetone to remove free EG. The sharpness of the lines was recovered by heating the product at 110 °C for 3 h, but the spacing did not change. The interlayer distance did not reexpand to 14.5 Å even if the contracted complex was dipped again in EG. Measurements described below were done for the finally contracted product.

C, H, and N were determined by the usual methods. Fe content was determined by atomic absorption. The results of the chemical analysis are given in Table I. Only a trace amount of nitrogen was detected. Beilstein's test was negative, showing that chloride was absent in the product. These results suggest that the $FeOCl(4\text{-}AP)_{1/4}$ complex lost its chloride ions and the intercalated 4-AP molecules during the reaction with EG. With the assumption that EG molecules do not decompose during the reaction, the analytical data for carbon content give a glycol/Fe ratio of 0.50. Thus the chemical formula of the product is evaluated to be $FeO(O_2C_2H_4)_{1/2}$. Observed values of chemical analysis are in agreement with the calculated value for $FeO(O_2C_2H_4)_{1/2}$. The released chloride ion from FeOCl into excess EG was qualitatively detected by the silver chloride test in the reaction system $FeOCl(4\text{-}AP)_{1/4} + {}^1/_2C_2H_4(OH)_2 \rightarrow FeO(O_2C_2H_4)_{1/2} + HCl + {}^1/_4(4\text{-}AP)$.

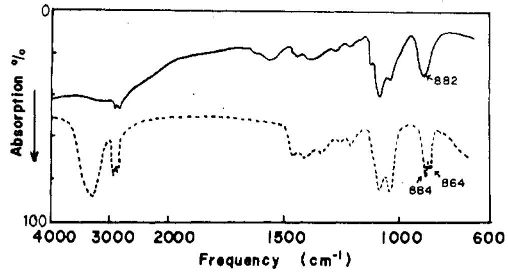

Figure 2. Infrared spectra of $FeO(O_2C_2H_4)_{1/2}$ (solid line) and free ethylene glycol (dotted line).

Table II. Mössbauer Parameters (mm/s)

	isomer shift	quadrupole splitting
FeOCl	0.36	0.92
$FeOCl(O_2C_2H_4)_{1/2}$	0.38	0.59
$FeOOCH_3$	0.37	0.60

Figure 1 shows a differential thermogram. A large exothermic peak and 23% weight loss are observed at about 300 °C, but there is no drastic change below this temperature for either TGA or DTA. This observation shows that the intercalated organic compound is strongly bonded to the inorganic layer. The sample calcined at about 350 °C showed ferrimagnetism. This magnetism probably is due to the $\gamma\text{-}Fe_2O_3$ detected by X-ray diffractometry of the heated sample. These thermal behaviors are very similar to those of the organic derivative $FeOOCH_3$. The observed weight loss at 300 °C agrees well with the calculated ignition loss of 22% under the supposition that $FeO(O_2C_2H_4)_{1/2}$ changes to Fe_2O_3.

The infrared spectrum of this compound had characteristic absorptions for ethylene glycol in the region below 1500 cm^{-1} but none for O–H above 3000 cm^{-1} as shown in Figure 2. These features of the spectrum show that this compound certainly contains EG but that the EG molecules are in the host lattice as ethylene glycolate ions just as methoxide ions in $FeOOCH_3$. There are split absorptions of C–O stretching vibrations at about 1050 cm^{-1}. Miyake also observed the splitting of C–O bands between 1000 and 1100 cm^{-1} into several components in nickel and cobalt complexes of ethylene glycol or diethylene glycol.[10] There have been reports of the splitting of C–O vibration absorptions in alkoxides, but the origin is not well-known.[11,12] The spectrum of $FeO(O_2C_2H_4)_{1/2}$ has an extra absorption at about 1600 cm^{-1}, which is not observed for EG. The origin of this absorption is not known, but spectra of γ-FeOOH and FeOCl have this absorption in the same region.[13] It may be related to the vibration of the host FeO double layer.

The Mössbauer spectrum of $FeO(O_2C_2H_4)_{1/2}$ consisted of a quadrupole doublet at room temperature. The pertinent parameters are summarized in Table II with those of FeOCl and $FeOOCH_3$. Isomer shift values are almost the same for these compounds. All Fe ions in the product are ferric. Quadrupole splitting (QS) of $FeO(O_2C_2H_4)_{1/2}$ is 0.59 mm/s, being almost the same as 0.60 mm/s for $FeOOCH_3$ but much smaller than 0.92 mm/s for FeOCl. Ferric ions in FeOCl are in octahedral sites of *cis*-$FeCl_2O_4$. Reduction of the QS value with the reaction corresponds to an increase in crystal field

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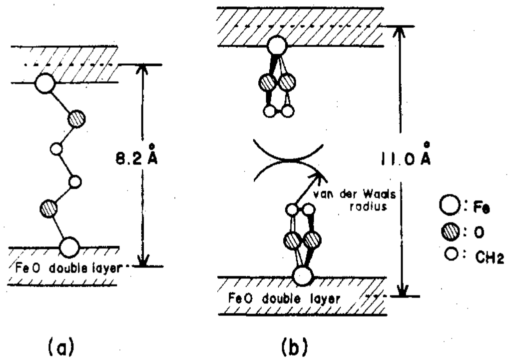

Figure 3. Model structures of $FeO(O_2C_2H_4)_{1/2}$. (a) and (b) represent the interlayer bridging and the intralayer bonding, respectively.

symmetry around the Fe atom. This higher symmetry would be expected if the chloride ions of FeOCl are replaced by oxygen of EG as in the case of $FeOOCH_3$. The Mössbauer results also show that ferric ions in the starting material are not reduced to ferrous during the reaction of $FeOCl(4\text{-}AP)_{1/4}$ with EG at 110 °C. By comparison, Fuls et al. obtained an iron alkoxide from the reaction of iron oxide with glycerol at 245 °C,[11] but their product contained ferrous and ferric ions together.

From these observations, we conclude that a new organic derivative $FeO(O_2C_2H_4)_{1/2}$ is obtained, having a crystal structure derived from that of FeOCl. Ferric ions are octahedrally coordinated by oxygens. EG is directly bonded to iron in the FeO double layers by its own oxygen atoms. Two model structures shown in Figure 3 are proposed for the product. One is an interlayer bridging model illustrated in Figure 3a, and the other is an intralayer bonding scheme indicated in Figure 3b. Lengths are estimated to be about 1.2 Å for the C–O bond, 1.3 Å for the C–C bond, and 1.5 Å for Fe–O when they are projected in the direction perpendicular to the layer. The interlayer distance for the interlayer bridge model is estimated to be below 8.2 Å even if the molecules have the trans configurations in order to have the longest possible molecular lengths. In contrast, the interlayer distance is about 11.0 Å if EG molecules coordinate to Fe ions within the same layer as shown in Figure 3b. Methylene groups belonging to upper and lower layers contact each other at a distance of twice their van der Waals radii. The observed interlayer distance was 10.89 Å after excess EG was removed by washing with acetone. Thus, the intralayer bonding model given in Figure 3b is more probable. The basal spacing of the product collapsed from 14.5 to 10.89 Å when the sample was washed with acetone. The difference of 3.6 Å almost corresponds to twice the van der Waals radius of the methylene group. Before being washed with acetone, the interlayer region of $FeO(O_2C_2H_4)_{1/2}$ probably contains an excess amount of EG molecules as a monolayer in which the EG molecules lie parallel to the host layer.

The intralayer bonding structure is also supported by infrared data. An absorption at 864 cm^{-1} appears only for free EG as indicated in Figure 2. The assignment of this absorption has been confused for a long time. Kanbayashi and Nukada described the details of solvent and temperature dependence of the vibrational band of EG. They concluded that only the gauche configuration is present in all states of the compound.[14] They assigned this absorption to the A-type rocking mode of the CH_2 group. On the other hand, Sawodny et al. attributed this absorption to the C–C valence vibration shown in Figure 4 on the basis of comparison of IR and Raman spectra of $DO(CH_2)_2OD$ and $HO(CH_2)_2OH$.[15] In the intralayer bonding model, the EG molecules having a gauche configuration are fixed to FeO double layers by their own oxygen ions. Both A-type rocking and C–C valence vibrations would be more restricted in this case than in the state of free EG itself. Thus the absorption at about 864 cm^{-1} is absent or observed just as a tail of the absorption at 882 cm^{-1} in the IR spectrum of $FeO(O_2C_2H_4)_{1/2}$.

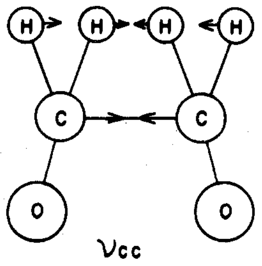

Figure 4. C–C valence vibration of ethylene glycol described by Sawodny et al.[15]

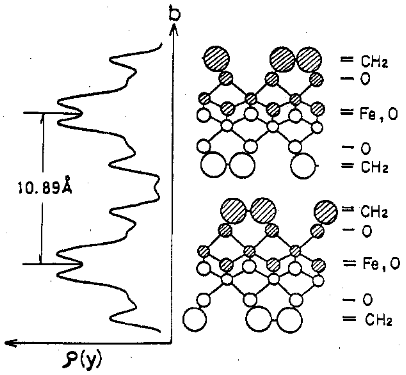

Figure 5. One-dimensional electron-density map projected on *b* axis obtained by X-ray diffractometry and schematic representation of structure of $FeO(O_2C_2H_4)_{1/2}$. Open and shaded circles are for $x = 0$ and $^1/_2$, respectively. A small central peak in the map arises from the remaining trace amounts of EG and 4-AP in the product. Small, medium, and large circles respectively represent Fe, O, and CH_2.

For better insight into this structure, a one-dimensional electron density projection on the *b* axis illustrated in Figure 5 was synthesized by using seven (0*k*0) X-ray reflections of $FeO(O_2C_2H_4)_{1/2}$. The sign of each reflection was determined by considering the contribution of Fe and O in the skelton of the inorganic layer. There are five peaks in the interlayer region except for those of the FeO layer. The partial crystal structure of $FeO(O_2C_2H_4)_{1/2}$ is deduced as shown in Figure 5. The ionized glycol molecules, $O_2C_2H_4^{2-}$, coordinate to ferric ions by their own two oxygen atoms in the product. The ferric ions are octahedrally surrounded by six oxygens. This improved symmetry around ferric ions results in a smaller QS value than that for FeOCl in which ferric ions are surrounded by four oxygens and two chlorines. In $FeO(O_2C_2H_4)_{1/2}$, each oxygen ligand supplied by EG is shared by two ferric ions and every ferric ion is coordinated to EG through two of these oxygen bridges. However half of the ferric ions are chelated by two oxygen atoms in the same $(O_2C_2H_4)^{2-}$ ion, and the other half are just coordinated by oxygens belonging to two different EG ions. Thus two kinds of ferric ions should be observed in the Mössbauer spectrum. However the spectrum could not be clearly divided into two sets of doublets, probably because the methylene group has little effect on ferric ions.

In summary, a new type of organic derivative of FeOCl has been prepared. Ethylene glycolates are intercalated into the expanded interlayer space of FeOCl with the aid of previously

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[14] Kanbayashi, U.; Nukada, K. *Nippon Kagaku Zasshi.* **1963**, *84*, 297.

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incorporated 4-AP. Their oxygen atoms replace chloride ions in the interlayer surface of FeOCl as in the case of FeOOCH$_3$, but half of the grafted EG molecules are chelated to ferric ions within the same layer plane.

Acknowledgment. We wish to express our appreciation to Professor R. Kikuchi and Mr. T. Sawai for their aid in the measurement of Mössbauer effect and to Dr. T. Fujino for his help on the C, H, N, and Cl determinations. We also express our thanks to Dr. M. Shimada for his interesting and valuable discussion. A part of the cost of this research was defrayed by a Grant-in-Aid of Special Research Projects from the Ministry of Education.

Registry No. FeO(O$_2$C$_2$H$_4$)$_{1/2}$, 71411-55-7; FeOCl, 13870-10-5; FeOCl(4-AP)$_{1/4}$, 59532-68-2.

Notes

Contribution from The Institute of Scientific and
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Immediate Formation of a Layered Compound, FeOOCH$_3$, by a Topochemical Reaction

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Received June 11, 1979

We have recently reported that FeOOCH$_3$, a new layered compound, whose structure can be derived from γ-FeOOH or FeOCl by replacing OH or Cl with CH$_3$O, was prepared by soaking an intercalated compound, FeOCl(4-AP)$_{1/4}$, where 4-AP indicates 4-aminopyridine, in methanol at 110 °C for 6 days.[1] In this case the reaction was expressed by

$$\mathrm{FeOCl(4\text{-}AP)_{1/4} + CH_3OH \rightarrow FeOOCH_3 + HCl + 4\text{-}AP}$$

This new compound, FeOOCH$_3$, could not be obtained by direct reaction between FeOCl and methanol in a temperature range from room temperature to 110 °C. However, we have found quite a simple method to prepare FeOOCH$_3$ by the direct reaction of FeOCl with sodium methoxide. In this paper, the preparation and some properties of FeOOCH$_3$ are presented.

Experimental Section

Preparation of FeOCl was carried out by the same method published previously.[1] The thin, bladelike FeOCl crystals were crushed to powder form before use as a host material. Sodium methoxide (28% in methanol) used here was purchased from Nakarai Chemicals Ltd. About 3 mmol of FeOCl and 1 mL of sodium methoxide were put into a 20-mL heavy-walled Pyrex tube equipped with a screw cap, and the mixture was allowed to warm at 60 °C. Upon being warmed, the vessel was placed in a water bath with occasional shaking at 60 °C for 10 h to ensure complete reaction. The product was separated from the solution by filtration, washed with methanol and then with water to remove NaCl which was produced by subreaction, and finally dried under vacuum.

X-ray analysis was carried out with a Rigaku-Denki diffractometer using Cu Kα radiation. Chemical analysis of the complex was made by using standard techniques. Differential thermogravimetric analysis was made by using a Rigaku-Denki unit programmed for a heating rate of 10 °C/min. The infrared spectra in the region 4000–700 cm^{-1} were obtained on a Hitachi Perkin-Elmer spectrophotometer fitted with a sodium chloride prism. Samples were dispersed in potassium bromide disks. Calibration of the spectrophotometer was made by using polystyrene bands.

Results and Discussion

After the complete reaction of FeOCl and CH$_3$ONa, FeOCl changed from reddish violet to brown. The quite same phenomenon was observed for the compound prepared by the previous method.[1] The product was stable in air for a long period of time. The compound was identified to be FeOOCH$_3$ by chemical, IR, X-ray diffraction, and differential thermogravimetric analyses as described below. Anal. Calcd for FeOOCH$_3$: C, 11.7; H, 2.94; Cl, 0.00. Found: C, 9.26; H, 2.33; Cl, 0.00. The reaction to give FeOOCH$_3$ from CH$_3$ONa and FeOCl is

$$\mathrm{FeOCl + CH_3ONa \rightarrow FeOOCH_3 + NaCl}$$

The presence of NaCl was recognized by X-ray diffraction of the product before washing. During the reaction, no coloring in solution and no changing in shape were recognized. These facts suggest that the reaction might have proceeded topotaxially; that is, FeOOCH$_3$ was produced by the interlayer substitution of CH$_3$O for Cl of FeOCl, remaining the iron and oxygen double layers of FeOCl. From X-ray diffraction, it was found that the compound had the basal spacing of 10 Å which is about 2 Å larger than that of FeOCl, and the X-ray powder diffraction data were superposed on previous data.[1] In the infrared spectrum of FeOOCH$_3$, a strong band at 1050 cm^{-1} assigned to the stretching virbration of the C–O bond was found. Thermal analysis data of FeOOCH$_3$ showed that the compound decomposed at 300 °C associated with 19% weight loss. The sample cooled from 350 °C was identified to be γ-Fe$_2$O$_3$ by X-ray diffractometry. These results indicate that FeOOCH$_3$ prepared by the present method is not a sorption-type complex but a layered-type compound with a strong bonding between the CH$_3$O and the inorganic layers.

We also attempted to prepare VOOCH$_3$ from VOCl and CH$_3$ONa by the present method, but the desired compound could not be prepared. VOCl[2] has a crystal structure similar to that of FeOCl, and both compounds intercalate pyridine molecules. This phenomenon is very difficult to explain, but it is interesting for us to investigate why VOOCH$_3$ was not obtained and the mechanism of substitutional reaction between Cl and CH$_3$O in the interlayer region.

Registry No. FeOOCH$_3$, 59473-94-8; FeOCl, 13870-10-5; CH$_3$ONa, 124-41-4.

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Spectroscopic Characterization of Tetrakis(pyridine)copper(II) Complexes in Zeolite Y

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Received October 25, 1978

Adsorbed pyridine (py) reacts with copper ions in both X- and Y-type zeolites, forming a complex which has been identified on the basis of its EPR spectrum as [Cu$^{\mathrm{II}}$(py)$_4$]$^{2+}$.[1-4]