

incorporated 4-AP. Their oxygen atoms replace chloride ions in the interlayer surface of FeOCl as in the case of FeOOCH₃, 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(O₂C₂H₄)_{1/2}, 71411-55-7; FeOCl, 13870-10-5; FeOCl(4-AP)_{1/4}, 59532-68-2.

Notes

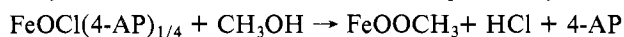
Contribution from The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka 565, Japan

Immediate Formation of a Layered Compound, FeOOCH₃, by a Topochemical Reaction

S. Son, S. Kikkawa, F. Kanamaru, and M. Koizumi*

Received June 11, 1979

We have recently reported that FeOOCH₃, a new layered compound, whose structure can be derived from γ -FeOOH or FeOCl by replacing OH or Cl with CH₃O, 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



This new compound, FeOOCH₃, 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 FeOOCH₃ by the direct reaction of FeOCl with sodium methoxide. In this paper, the preparation and some properties of FeOOCH₃ are presented.

Experimental Section

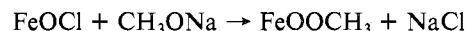
Preparation of FeOCl was carried out by the same method published previously.¹ The thin, blade-like FeOCl crystals were crushed to powder form before use as a host material. Sodium methoxide (28% in methanol) used here was purchased from Nakarai Chemicals Ltd. About 3 mmol of FeOCl and 1 mL of sodium 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 K α 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 CH₃ONa, 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 FeOOCH₃

by chemical, IR, X-ray diffraction, and differential thermogravimetric analyses as described below. Anal. Calcd for FeOOCH₃: C, 11.7; H, 2.94; Cl, 0.00. Found: C, 9.26; H, 2.33; Cl, 0.00. The reaction to give FeOOCH₃ from CH₃ONa and FeOCl is



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, FeOOCH₃ was produced by the interlayer substitution of CH₃O 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 FeOOCH₃, a strong band at 1050 cm⁻¹ assigned to the stretching vibration of the C–O bond was found. Thermal analysis data of FeOOCH₃ showed that the compound decomposed at 300 °C associated with 19% weight loss. The sample cooled from 350 °C was identified to be γ -Fe₂O₃ by X-ray diffractometry. These results indicate that FeOOCH₃ prepared by the present method is not a sorption-type complex but a layered-type compound with a strong bonding between the CH₃O and the inorganic layers.

We also attempted to prepare VOOCH₃ from VOCl and CH₃ONa by the present method, but the desired compound could not be prepared. VOCl₂ 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 VOOCH₃ was not obtained and the mechanism of substitutional reaction between Cl and CH₃O in the interlayer region.

Registry No. FeOOCH₃, 59473-94-8; FeOCl, 13870-10-5; CH₃ONa, 124-41-4.

(2) M. C. Levayer and M. J. Rouxel, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **268**, 167 (1969).

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843

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

P. S. Eugene Dai and Jack H. Lunsford*

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^{II}(py)₄]²⁺.¹⁻⁴

(1) S. Kikkawa, F. Kanamaru, and M. Koizumi, *Inorg. Chem.*, **15**, 2195 (1976).