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.

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Registry No. $FeO(O_2C_2H_4)_{1/2}$, 71411-55-7; FeOCl, 13870-10-5; $FeOCl(4\text{-}AP)_{1/4}$, 59532-68-2.

Notes

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Immediate Formation of a Layered Compound, $FeOOCH_3$, by a Topochemical Reaction

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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_3O, was prepared by soaking an intercalated compound, $FeOCl(4\text{-}AP)_{1/4}$, where 4-AP indicates 4-aminopyridine, in methanol at 110 °C for 6 days.[1] In this case the reaction was expressed by

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

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_3ONa, 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_3ONa and FeOCl is

$$FeOCl + CH_3ONa \rightarrow FeOOCH_3 + NaCl$$

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_3O 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_2O_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_3O and the inorganic layers.

We also attempted to prepare $VOOCH_3$ from VOCl and CH_3ONa 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_3O in the interlayer region.

Registry No. $FeOOCH_3$, 59473-94-8; FeOCl, 13870-10-5; CH_3ONa, 124-41-4.

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

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

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

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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]

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