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SYNTHESIS AND SOME PROPERTIES OF A LAYER-TYPE INORGANIC-ORGANIC COMPLEX OF FeOCl AND PYRIDINE

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New intercalated compounds of FeOCl and pyridine were synthesized by soaking FeOCl in pyridine vapor at a temperature range from 30° to 120°C. Number of pyridine molecules per FeOCl in the product was, within the experimental error, a rational number, 1/n where n=3 and 4 depending on the temperature of preparation. The complexes have an orthorhombic unit-cell with a=3.78(1), b=13.45(3), c=3.30(1) Å. Mössbauer effect study on FeOCl $(\text{pyridine})_{1/3}$ at room temperature showed that the isomershift relative to Fe metal and the quadrupole splitting were 0.36(1)mm/sec and 0.92(1)mm/sec respectively. The E.S.R. spectrum of FeOCl $(\text{pyridine})_{1/3}$ represented a broad singlet absorption line at g=2.003 with Hmsl=200 gauss, suggesting the existence of conduction electrons resulted from partial transfer of the lone pair electrons of the nitrogen atom into FeOCl layer.

Reaction mechanisms between layer-type silicates and organic molecules have been extensively studied on clay-organic complexes from the viewpoints of crystal chemistry and earth science. In recent years, it was found that the superconducting transition temperatures of some transition metal dichalcogenides(MX_2) were strongly influenced by absorbing pyridine molecules between the successive MX_2 layers.1-4) Since these discoveries, the synthesis and characterization of intercalated inorganic compounds are attaining a position of consequence in the field of material science. In all intercalated MX_2 synthesized so far, the lone pair electrons on the nitrogen of the intercalated organic molecules and the partially filled conduction band of the MX_2 layer are involved in a chemical bond between them. Therefore, it has been said that metallic compounds with layer structure such as TaS_2 can form the charge transfer-type complexes, but semiconductors such as MoS_2 are inert. Recently, it was found in our laboratory that FeOCl, a semiconductor, react with pyridine molecules to form intercalated compounds. The FeOCl-pyridine complexes exhibit a good electrical conductivity along the c-axis which is larger by a factor of 10^7 than that of FeOCl. The details will be published elsewhere. It suggests that the complexes are a charge transfer-type one. In this paper, the preparation of FeOCl-pyridine complex and the partial characterizations concerning the charge transfer in the complex will be described.

FeOCl was prepared by heating equimolar mixture of $FeCl_3$ and Fe_2O_3 in an evacuated and sealed pyrex glass tube at 350°C for two weeks followed by slow cooling to room temperature. Thin blade-like crystals with dimensions as large as 5x2x0.02mm and with a well developed b-plane and the longest platelet dimension parallel to the c-axis were obtained. The X-ray powder diffraction pattern of the product agrees with that recorded on ASTM Data Card 1-81. FeOCl belongs to the orthorhombic space group Pmnm with a=3.780, b=7.917, c=3.302Å, and Z=2.5) The crystal structure consists of stack of double layer sheet of oxygen octahedra linked together with shared edges. The outermost atoms on each of the layers are the Cl^- ions. The interlayer $Cl^- - Cl^-$ distance, 3.680Å, is approximately twice the van der Waals radius of chlorine. It is expected, therefore, that FeOCl absorbs some kind of organic molecules in the interlayer region to form intercalated compounds. The reaction with pyridine was conducted in the closed system, in which FeOCl was placed at one end and distilled pyridine at opposite end. Only FeOCl was heated at the desired temperatures(30∼120°C) and then soaked in pyridine vapor which was equilibrated with pyridine remained at room temperature. The duration of the reaction was 4 days. This procedure was followed by degassing for two hours to remove pyridine molecule absorbed on the surface of the intercalated compound. The complexes produced were black and had two selected composition, i.e. $FeOCl(pyridine)_{1/3}$ above 60°C and $FeOCl(pyridine)_{1/4}$ below 60°C. These stoichiometries were confirmed by both the weight gain and the chemical analysis of the materials as represented in Table 1.

Table 1 C.H.N. analysis of $FeOCl(pyridine)_{1/n}$ produced at 40° and 80°C.

Reaction temperature	H(%)	C(%)	N(%)	n
40°C	1.16	12.86	2.99	4
80°C	1.34	15.88	3.73	3

The X-ray diffraction data of both complexes were obtained using filtered Co-Kα and Mo-Kα radiations. Both of $FeOCl(pyridine)_{1/4}$ and $FeOCl(pyridine)_{1/3}$ had the same orthorhombic unit cell with a=3.78(1), b=13.45(2), c=3.30(1)Å, and Z=2.

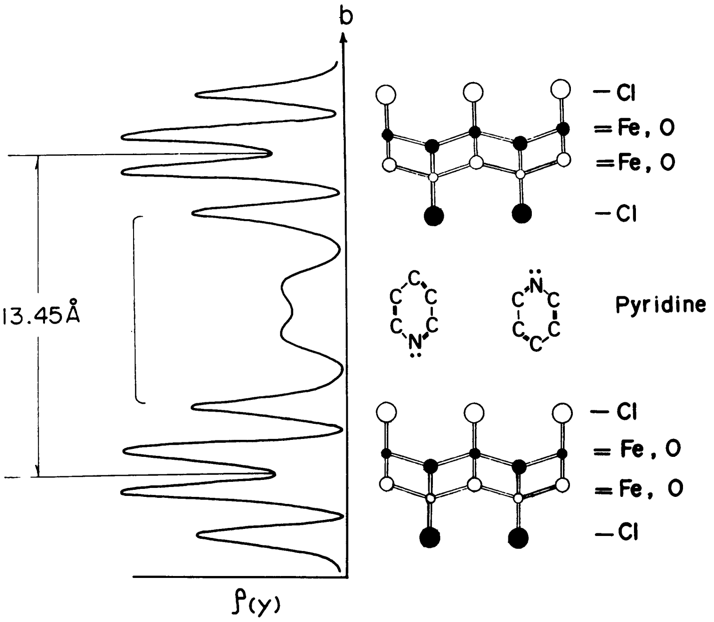

Fig. 1 One dimensional electron density map projected on the b-axis and schematic representation of the structure of FeOCl(pyridine)$_{1/3}$.

From the comparison of the lattice constants between FeOCl and its pyridine complexes, it is seen that absorption of pyridine molecules does not induce any effect on atomic arrangements in the double layered sheet of FeOCl, but only on the interlayer separation.

One dimensional electron density projection on the b-axis was synthesized using nine (00ℓ) reflections of FeOCl(pyridine)$_{1/3}$. As shown in Fig. 1, there are two peaks in the interlayer region between adjacent FeOCl layers indicating that pyridine molecules are placed between the layers so that the plane of the molecule is perpendicular to the layer and the nitrogen atom faces to the layer.

The ESR spectrum of FeOCl(pyridine)$_{1/3}$ was recorded on a JES-ME-X spectrometer with 100 KHz field modulation at 77 K and room temperature. To void the skin effect, the powdered sample was dispersed with γ-alumina powder. A broad singlet spectrum was observed at g=2.003. The linewidth H_{msl} was ca. 200 gauss at the both temperatures and not affected by the extent of dilution. The signal did not disappear after the evacuation at room temperature. Moreover, no spectrum was detected

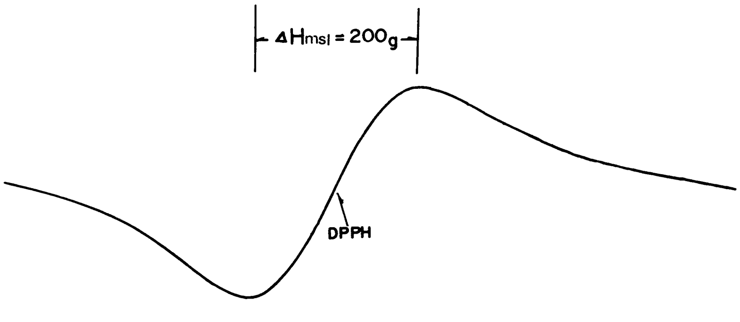

Fig. 2 ESR spectrum of FeOCl(pyridine)$_{1/3}$ dispersed on γ-alumina powder at 77K.

from FeOCl. The spectrum of the complex, therefore, may be due to conduction electrons resulting from partial transfer of the lone pair electrons of the nitrogen atom to FeOCl layer.

Table 2 Mössbauer parameters of FeOCl and $FeOCl(pyridine)_{1/3}$ at room temperature

	IS(mm/sec)	QS(mm/sec)
FeOCl	0.36	0.92
$FeOCl(pyridine)_{1/3}$	0.36±0.01	0.92±0.01

The Mössbauer spectrum was measured at room temperature using radiation from ^{57}Co in Cu metal with a 400 channel multichannel analyzer. Calibration was based on the Mössbauer spectrum of Fe metal. The pertinent data are summerized in Table 2. The Mössbauer parameters of the complex are the same as those of FeOCl; i.e. the isomer shift was 0.36(1) mm/sec with respect to Fe, the value of which is typical of a high spin Fe^{3+} ion, and the quadrupole splitting was 0.92(1) mm/sec. It is seen from this result that the transferred electrons from the nitrogen are not localized at the iron ions, but behave as collective electrons.

Though the detailed analysis of the structure and the ESR spectrum would be required, the present results are consistent with the above mentioned electrical property of the complex with $\rho_{RT} \simeq 1$ ohm cm.

The complexes were stable up to 150°C in air, but on heating it above 150°C, pyridine molecules were desorbed gradually with increasing temperature, and the material reverted to FeOCl after being deintercalated at 250°C.

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