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Intercalation Compounds FeOCl(Pyridine derivatives)$_{1/n}$ and FeOCl(n-Propylamine)$_{1/4}$

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Some pyridine derivatives were intercalated into the van der Waals gap of layered compound FeOCl. Pyridine, 2,6-dimethylpyridine, 4-aminopyridine, 2,4,6-trimethylpyridine, and n-propylamine were used as intercalates having different Lewis basicities. X-Ray diffraction, Mössbauer effect, electrical resistivity, ESR and electronic spectra were studied, some correlations being found between the measured parameters of these complexes and the basicities of organic intercalates. It is assumed that organic intercalates transfer their lone pair electrons on the nitrogen atom to FeOCl layers.

Iron oxychloride is a layered compound belonging to an orthorhombic space group Pmnm with $a=3.780$, $b=7.917$, $c=3.302$ Å, and $Z=2$.[1] The crystal structure consists of a stack of double layer sheet of *cis*-$FeCl_2O_4$ octahedra linked together with shared edges. The outermost atoms at each side of the layers are Cl ions. The interlayer bonding between adjacent layers is van der Waals interaction. Hagenmüller *et al.* found that FeOCl reacts with ammonia and some amine molecules.[2] Kanamaru *et al.* reported the intercalation of pyridine into FeOCl, and observed remarkable changes in electrical and magnetic properties.[3–5] The changes can be attributed to charge transfer from the nitrogen atom of the intercalated pyridine molecule to the FeOCl layer.

Transition metal dichalcogenides (MX_2) intercalate some organic bases. Their superconducting transition temperatures (T_c) change with organic intercalation. Bray and Sauer measured the lone pair electron densities on nitrogen atoms of organic bases by means of nuclear quadrupole resonance.[6] The electron densities were correlated with T_c of the intercalated MX_2. Lewis basicity of organic base is a measure of the ability to donate electrons to acids. pK_a value would be qualitatively related to the change of the property of host caused by intercalation if charge-transfer interaction is significant in the bonding between host layer and guest molecule.

Effect of pK_a on the properties of FeOCl-organic complexes can be checked by use of some pyridine derivatives having different basicities. Pyridine derivatives can act as either n- or π-donor.[7] Study on aliphatic amine is useful to distinguish the effects of these two kinds of electrons in comparison with pyridine intercalated complexes.

The present report deals with intercalation of some pyridine derivatives and n-propylamine into FeOCl. Electrical resistivity, Mössbauer effect, ESR and electronic spectrum were studied for these intercalated compounds. Some correlations were found between basicities of the intercalate and properties of the products. The possibility of charge transfer is discussed on FeOCl (organic compound)$_{1/n}$.

Experimental

Preparation. Iron oxychloride was prepared by heating a mixture of α-Fe_2O_3 and $FeCl_3$ with mole ratio 1 : 4/3 in a sealed Pyrex glass tube at 370 °C for two days. The product was washed with water and dried. Reddish violet and thin blade-like FeOCl crystals were obtained.

The reactions with pyridine (Py) and its derivatives, 2,6-dimethylpyridine (DMP), 4-aminopyridine (AP), and 2,4,6-trimethylpyridine (TMP), were conducted at 100 and 40 °C, respectively, in a closed system for about a week. Intercalation of n-propylamine (PA) was completed within 1 h at room temperature. Since Py, DMP, TMP, and PA are liquid at room temperature, FeOCl was directly soaked into these liquids. The acetone solution of AP was used for solid AP. The intercalated compounds obtained were black crystals. X-Ray diffractometry showed no unreacted FeOCl. Chemical analyses of C, H, and N showed that each intercalated compound has a stoichiometric composition. If the complex is represented by FeOCl(organic compound)$_{1/n}$, n-values are four for Py, DMP, AP, and PA, and six for TMP, respectively

Measurement. X-Ray analysis was carried out with a Rigaku-Denki diffractomer using Fe-filtered Co $K\alpha$ radiations. The electrical resistivities of FeOCl and its complexes were measured in the temperature range 373—200 K using carbon electrodes. The Mössbauer spectra were measured at room temperature and at liquid nitrogen temperature using radiation from ^{57}Co in Pd metal with a 200 channel multichannel analyzer. Samples were dispersed with silicon grease, the thickness being *ca.* 30 mg/cm^2. Calibration was based on the Mössbauer spectrum of Fe metal. The ESR measurements of FeOCl and its complexes were carried out on a JES-ME-2X spectrometer at 77 K and at room temperature. Ultraviolet spectra of FeOCl and the intercalated complexes were obtained by the diffuse reflectance method. Samples were dispersed in MgO. Transmission method was used for the intercalates themselves, which were diluted with cyclo hexane.

Results

The b-values corresponding to the interlayer distances are summarized in Table 1. Each b-value for the complexes is much larger than 7.92 Å for FeOCl. The expansion is explained by the insertion of organic intercalates into the van der Waals gap of FeOCl.

FeOCl is a semiconductor with resistivity of 10^6 Ω cm at room temperature. The intercalated complexes are still semiconductive, but exhibit improved electrical conductivities along their c-axis. Their electrical resistivities are 10—10^3 Ω cm at room temperature. The values are smaller than that of FeOCl by a factor of

10^{3-5}. The electrical activation energy also changes from 0.6 eV to 0.2—0.3 eV for the complexes.

Mössbauer spectra were obtained as shown in Fig. 1. The pertinent parameters at room temperature obtained with a least-squares fit computer program are summarized in Table 1. Isomer shifts of the intercalated pyridine derivative complexes are 0.40—0.44 mm/s. The values seem to increase with pK_a of organic intercalates, and are larger than 0.40 mm/s for FeOCl. Isomer shifts of Py– and PA–FeOCl complexes are also larger than that of FeOCl. Quadrupole splittings are 0.67—0.92 mm/s for the intercalated complexes, being smaller than 0.93 mm/s for pure FeOCl. Q.S. tends to decrease with increase in I.S.

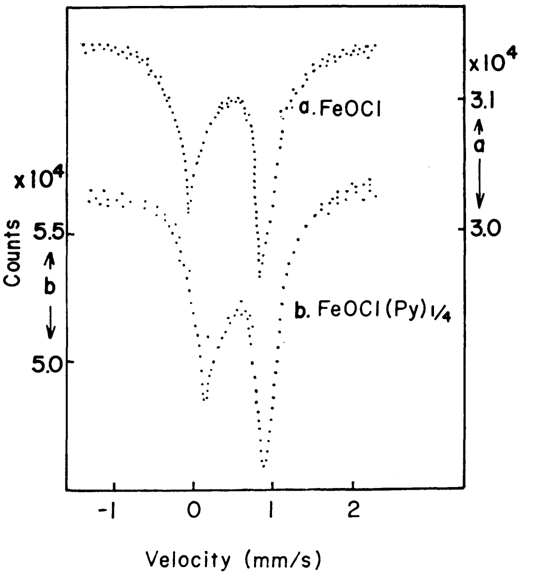

Fig. 1. Mössbauer spectra of FeOCl and FeOCl$(Py)_{1/4}$.

TABLE 1. PARAMETERS FOR FeOCl AND FeOCl(ORGANIC COMPOUND)$_{1/n}$

	pK_a	b(Å)	ρ (Ω cm)	E_a (eV)	I.S. (mm/s)	Q.S. (mm/s)	$\Delta H_{1/2}$ (G)
FeOCl		7.92	10^6	0.6	0.40	0.93	
FeOCl-$(Py)_{1/4}$	5.2	13.27	10	0.2	0.45	0.67	200
FeOCl-$(DMP)_{1/4}$	6.8	14.98	10^2	0.3	0.40	0.92	600
FeOCl-$(AP)_{1/4}$	9.2	13.57	10^3	0.2	0.42	0.84	1000
FeOCl-$(TMP)_{1/6}$	9.6	11.79	10^3	0.2	0.44	0.81	—
FeOCl-$(PA)_{1/4}$	10.5	11.89	10^2	0.2	0.44	0.68	900

The ESR spectra of FeOCl(pyridine derivative)$_{1/n}$ were recorded at room temperature and at 77 K. Except for TMP, broad singlet spectra were observed at g=2.003, their line shapes being almost Lorentzian. Neither FeOCl nor pyridine derivatives show any signals by themselves. The linewidth $\Delta H_{1/2}$ shows no change with temperature but changes with the kind of intercalate (Table 1). No signal was detected for TMP complex. In order to avoid the skin effect, some samples were dispersed in γ-alumina. Neither linewidths nor g-values were affected by dilution. Anisotropic effects were checked on highly preferred oriented samples. Signals did not change with directions of the samples to magnetic field.

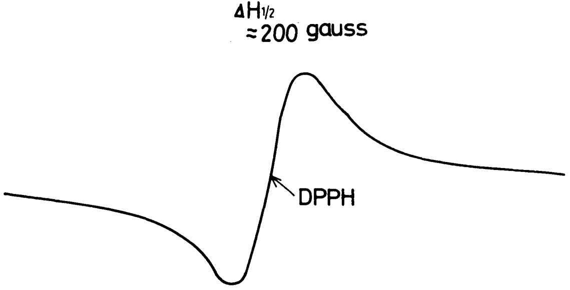

Fig. 2. ESR signal obtained for FeOCl$(Py)_{1/4}$.

Iron oxychloride shows no absorption in its ultraviolet spectrum. Pyridine has an intense $\pi \rightarrow \pi^*$ absorption at 250 nm, and a weak $n \rightarrow \pi^*$ one at 285 nm.[8] FeOCl-$(Py)_{1/4}$ complex has a broad and asymmetric absorption at about 270 nm, and FeOCl(pyridine derivative)$_{1/n}$ have absorptions around 265 nm. The latter absorptions are in almost the same regions as those of pyridine derivatives. n-Propylamine without π-electrons has an absorption at 261 nm with a shoulder at around 252 nm, but complex FeOCl$(PA)_{1/4}$ has a weak absorption at 248 nm. Furthermore, very broad absorptions around 310 nm were observed for both FeOCl$(Py)_{1/4}$ and FeOCl$(PA)_{1/4}$. Neither FeOCl nor the intercalates show any absorptions in this region; DMP, TMP, and AP complexes have no prominent absorptions.

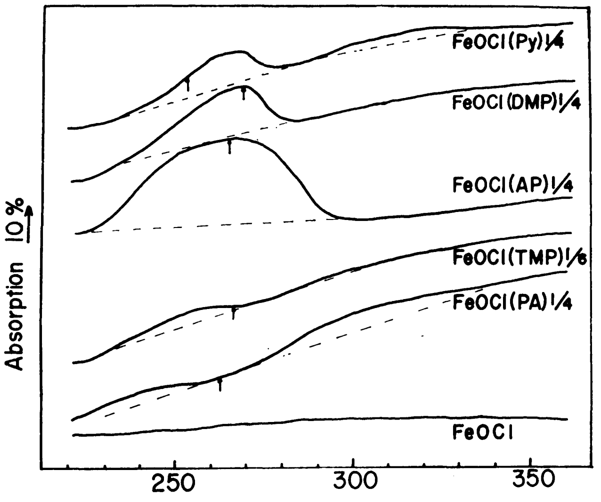

Fig. 3. Ultraviolet spectra of FeOCl and FeOCl(organic compound)$_{1/n}$. (Solid line).
Arrows show the positions of absorption maxima of organic compounds.

Discussion

Layered inorganic compound FeOCl intercalates some organic molecules. Each intercalated compound has an expanded spacing between 11.79 and 14.98 Å (Table 1). The expanded spacings are explained by the insertion of organic intercalates into the van der Waals gap of FeOCl. Kanamaru *et al.* showed that planes of pyridine rings are perpendicular to the host layers so that nitrogen atoms face the layers in the pyridine complex.4) However, FeOCl(PA)$_{1/4}$ seems to be in a different situation from pyridine complex since no more than approximately 4.0 Å is available between the layers. One of the sp^3 hybridized orbitals of terminal nitrogen atom, which contains lone pair electrons, faces the FeOCl layer, but the alkyl chain is nearly parallel to the host layer. For FeOCl(DMP)$_{1/4}$, FeOCl(AP)$_{1/4}$, and FeOCl(TMP)$_{1/6}$, molecular orientations of pyridine derivatives in the interlayer space of FeOCl have been estimated using the results of one-dimensional electron density projections based on X-ray diffractions.9) The pyridine ring of DMP is perpendicular to the host layer, but rotates a little around the center of the ring due to the steric effect of methyl groups. For FeOCl(AP)$_{1/4}$, the pyridine ring tilts slightly from a plane perpendicular to the layer. The inclination arises from a steric effect and the hydrogen bond between the amino group and the host layer. The pyridine ring of TMP is more tilted than that of DMP because of the larger steric effect of methyl groups of the former. However, in all cases, organic molecules are in the van der Waals gap so that their nitrogen atoms are as close to FeOCl layer as possible.

Parameters for FeOCl and FeOCl(organic compound)$_{1/n}$ are summarized in Table 1 with pK_a values of organic intercalates, which are values for pure organic compounds and not for the intercalated ones.10) Formation of the complexes caused much reduction in electrical resistivity in the direction parallel to the host layer. The improved electrical conductivity can be explained by increased number of charge carriers. Mössbauer parameters change with intercalation. Isomer shifts of the complexes are slightly larger than that of FeOCl, but they are still those for ferric ions. The observed increase in I.S. values suggests the increased d-electron density around Fe atom in the intercalated FeOCl layer. However Fe^{2+} is not detected above liquid nitrogen temperature. A correlation between pK_a and I.S. is observed for pyridine derivative complexes. But FeOCl(Py)$_{1/4}$ has the largest I.S., pyridine having the smallest pK_a. This suggests the importance of the effect of interaction between the side groups and Cl ions on the surface of FeOCl layer as well as that of pK_a. With increase of interaction between host and guest, charge carriers in the complexes tend to localize, electrical conductivity decreasing with increase in pK_a. The reduction of electrical resistivity and the increase of the isomer shift are explained by assuming the charge transfer from the nitrogen atoms of the intercalated organics to the FeOCl layer. The assumption seems to be supported by the molecular arrangements of intercalated organics in the interlayer region of FeOCl. ESR and UV spectroscopy were used in order to obtain direct evidences of the charge transfer.

Charge transfer interactions which involve formation of unpaired electrons were observed on ESR spectroscopy.11,12) Very broad signals are detected on the intercalated FeOCl except for TMP complex. These signals are Lorentzian. They show no hyperfine, fine structures and anisotropic effects to magnetic field. g-Values are 2.003. Conduction electrons in metals and semiconductors sometimes show resonance of Lorentzian shape at around $g=2.003$, the linewidth becoming broader with increase of electrons.13) ESR signal of charge transfer complex in solid state often loses its fine structure because of delocalization of the transferred electrons. In the case of FeOCl(organic compound)$_{1/n}$, the very broad ESR signal may be attributed to the conduction electrons formed in the host layer due to intercalation.

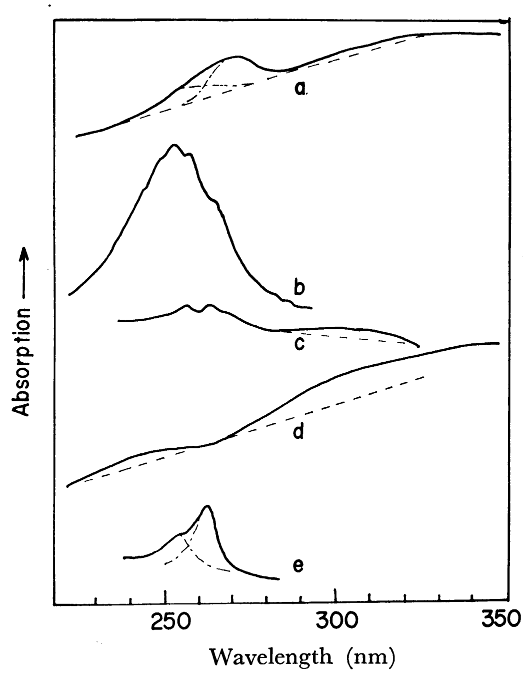

Fig. 4. Ultraviolet spectra of FeOCl(organic compound)$_{1/n}$.
a: FeOCl(Py)$_{1/4}$, b: pyridine c: $[IrOH(py)_2(NH_3)_3]^{2+}$
d: FeOCl(PA)$_{1/4}$, e: PA.

Figure 4 (a) and (d) show ultraviolet spectra of FeOCl(Py)$_{1/4}$ and FeOCl(PA)$_{1/4}$, respectively. They have very broad absorptions around 310 nm observed in neither FeOCl nor the intercalates. These absorptions may be assigned to charge transfer bands as compared with that of $[IrOH(py)_2(NH_3)_3]^{2+}$ in which a similarly broad charge transfer band is observed at around 300 nm (Fig. 4 (c)).14) For DMP-, AP-, and TMP-complexes, however, no clear C.T. absorptions are found in ultraviolet and visible regions. On the other hand, absorptions of the intercalates are perturbed by the intercalation into FeOCl. The pyridine $\pi \rightarrow \pi^*$ absorption in FeOCl(Py)$_{1/4}$ shifts to longer wavelength by 20 nm, turning asymmetric. Red shift of pyridine absorption is also observed on Ir–Py complexes.14) Absorptions of the pyridine derivatives do not clearly shift by intercalation, the peaks being broad and asymmetric in the respective FeOCl complexes. The asymmetric absorption can be divided into two or more components (Fig. 4(a)). Further analysis is difficult, since pyridine and pyridine derivatives have both lone pair and π-electrons. These two kinds of electrons can contribute to charge transfer. In order to observe the absorption of lone pair electron which is in non-bonding orbital, aliphatic amine is more suitable than pyridine derivatives. *n*-Propylamine shows an absorption from non-bonding orbital to σ^* one at 261 nm. A broad blue shifted absorption is observed at around 248 nm on the spectrum of $FeOCl(PA)_{1/4}$. Since chlorine is the outermost ion in each FeOCl layer and the nitrogen atoms of the intercalates are very close to FeOCl layer, it is reasonable to assume a certain interaction between the non-bonding orbital of the intercalated donor and the σ orbital of chlorine. The amount of blue shift of $n \rightarrow \sigma^*$ absorption is 13 nm on PA. The present value for the Cl···N pair is in the range of blue shifts of other n-donor and iodine pairs. Thiourea and thioacetoamide show blue shifts of 10 and 21 nm, respectively.[15] This suggests that the bonding between FeOCl and PA is similar to that of other n-donor and I_2 molecular complexes. A similar blue-shift of lone pair electron absorption might also contribute to the asymmetric absorption observed on FeOCl(pyridine derivative)$_{1/n}$.

$FeOCl(PA)_{1/4}$ is similar to FeOCl(pyridine derivative)$_{1/n}$ as regards electrical resistivity, Mössbauer effect and ESR. This suggests that FeOCl(pyridine derivative)$_{1/n}$ having lone pair electrons has almost the same bonding character between host and guest as $FeOCl(PA)_{1/4}$.

The charge-transfer interaction has been confirmed in the intercalated FeOCl complexes. In Mulliken's charge-transfer formulation of donor-acceptor systems, pyridine can work as either a π-donor or an n-donor.[7] Correlations are found between pK_a and properties of the obtained complexes. Thus, we assume that lone pair electrons of the nitrogen atom are involved in the donor-acceptor interactions, and pK_a values of the respective compounds can be used as a measure of n-ionization potential. A similar speculation was made by Chaudhuri and Basu for the system of iodine and many aza-aromatics.[16] They found the proportionality between the logarithm of equilibrium constants for charge transfer type interaction and pK_a values.

In conclusion, pyridine, pyridine derivatives, and propylamine molecules having nitrogen atoms are intercalated into the van der Waals gap of FeOCl. The properties of the products are explained by means of a charge-transfer model. It is assumed that lone pair electrons on the nitrogen atoms of the organic molecules transfer to FeOCl layer in the intercalated complexes.

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