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PREPARATION AND PROPERTIES OF INTERCALATION COMPOUNDS FeOCl (ORGANIC COMPOUNDS)$_{1/n}$

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The preparation of the intercalation compounds FeOCl (pyridine)$_{1/4}$, FeOCl (2,6-dimethylpyridine)$_{1/4}$, FeOCl (4-aminopyridine)$_{1/4}$, and FeOCl (2, 4, 6-trimethylpyridine)$_{1/6}$ are reported. Their properties are measured by X-ray diffraction, electrical resistivity, and Mössbauer effect. The results are correlated with the electron transfer from the organic intercalants to the host FeOCl layer.

1. Introduction

The transition metal oxychlorides MOCl (M = Ti, V, Cr, Fe) are known to have a layered structure in which adjacent layers are held together only by van der Waals contact. Some of these layered materials undergo intercalations similar to those known for layered transition metal dichalcogenides [1]. The intercalations into FeOCl have been reported on organic bases (e.g. pyridine) [2, 3], alkali metal ions [4], and organometallic sandwich compounds [5]. We have studied the effect of intercalants' basicities on the properties of FeOCl-organic complexes by using some pyridine derivatives having different basicities [6]. We have now carried out Mössbauer studies on the pyridine derivative intercalation compounds of FeOCl. The results, which clearly demonstrate charge transfer, are presented in this paper.

2. Preparation

FeOCl was prepared by heating a mixture of $FeCl_3$ and Fe_2O_3 with molar ratio 4:3 at 370°C in a sealed glass tube for two days. The product was washed with water and dried in vacuo. Reddish-violet and thin blade-like FeOCl crystals were obtained. Its X-ray diffraction was indexed as an orthorhombic space group with $a = 3.78$, $b = 7.92$, and $c = 3.30$ Å [7].

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°C for about a week. Since Py, DMP, and TMP are liquid at room temperature, FeOCl was directly soaked into these liquids. Acetone solution of AP was used for the solid AP. The intercalated compounds obtained were black crystals. Chemical analyses of C, H, and N showed that each intercalation compound has a stoichiometric composition. If the complex is represented as FeOCl (organic compound)$_{1/n}$, n-values are four for Py, DMP, AP and six for TMP. X-ray diffractometry showed no unreacted FeOCl. The diffraction data for all the pyridine derivative intercalates can be fitted to an orthorhombic cell with a and c changed little from the starting host. The b-values corresponding to the interlayer distances are 7.92 Å for FeOCl, 13.27 Å for FeOCl (Py)$_{1/4}$, 14.98 Å for FeOCl (DMP)$_{1/4}$, 13.57 Å for FeOCl (AP)$_{1/4}$, and 11.79 Å for FeOCl (TMP)$_{1/6}$. The expansions of the interlayer distance are explained by the insertion of organic bases into the van der Waals gap of FeOCl.

3. Mössbauer spectra

The Mössbauer spectra were measured at 300 and 77 K using radiation from ^{57}Co in Pd metal with a 200 channel multichannel analyzer. Samples were dispersed with silicon grease. Calibration was based on the spectrum of Fe metal. Spectra were fitted by a least-squares procedure

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to produce a series of peaks having Lorentzian shapes. Isomer shifts, quadrupole splittings, and observed half line widths are summarized in table I. Fig. 1 shows the room temperature spectra of FeOCl and FeOCl $(Py)_{1/4}$.

Two characteristics of the Mössbauer spectra of FeOCl (organic compound)$_{1/n}$ can be understood based on the hypothesis that electron transfer from the intercalated organic compound to the FeOCl host occurs upon intercalation. The first characteristic is the temperature dependence of the isomer shift (*IS*). The temperature coefficients ($d(IS)/dT$) are calculated as -2.36×10^{-4} mm s^{-1}/K for FeOCl $(Py)_{1/4}$, -2.83×10^{-4} mm s^{-1}/K for FeOCl $(DMP)_{1/4}$, -2.87×10^{-4} mm s^{-1}/K for FeOCl $(AP)_{1/4}$, and -2.31×10^{-4} mm s^{-1}/K for FeOCl $(TMP)_{1/6}$ using the data at 300 and 105 K. In comparison, FeOCl itself exhibits $d(IS)/dT$ of -4.82×10^{-4} mm s^{-1}/K. Assuming that the temperature dependence arises from a second-order Doppler effect, the smaller temperature coefficients for FeOCl (organic compound)$_{1/n}$ indicate lower mean squared velocities of vibration for iron atoms in the intercalation compounds at a given temperature. This result is consistent with a general "stiffening" of the lattice of FeOCl (organic compound)$_{1/n}$ in comparison to FeOCl, due to the replacement of van der Waals forces by ionic forces resulting from the charge transfer interaction between the host and the guests. Similar discussion was made on the intercalation compound FeOCl (ferrocene)$_{1/6}$ [8].

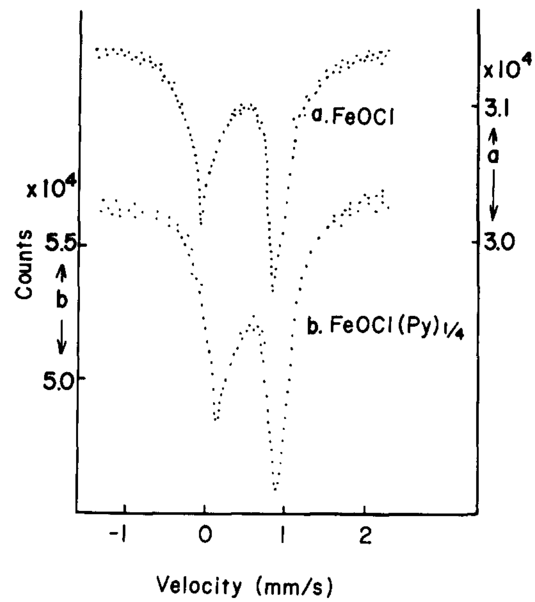

Fig. 1. Mössbauer spectra of FeOCl and FeOCl $(Py)_{1/4}$ at room temperature.

The second characteristic is the quadrupole splitting (QS). QS values for FeOCl are virtually temperature independent at the range between 105 and 300 K. This result suggests that thermal expansion of the FeOCl lattice results principally

TableI
Mössbauer data

Sample	*IS* (mm/s)	*QS* (mm/s)	Γ_1^a (mm/s)	Γ_2^a (mm/s)	T^b (K)
FeOCl	0.399	0.926	0.13	0.09	300
	0.493	0.934	0.19	0.18	105
FeOCl $(Py)_{1/4}$	0.446	0.666	0.18	0.18	300
	0.492	1.250	0.19	0.17	105
FeOCl $(DMP)_{1/4}$	0.403	0.918	0.18	0.18	300
	0.458	1.138	0.15	0.17	105
FeOCl $(AP)_{1/4}$	0.416	0.843	0.23	0.23	300
	0.472	1.154	0.25	0.26	105
FeOCl $(TMP)_{1/6}$	0.435	0.809	0.18	0.13	300
	0.480	1.047	0.23	0.22	105

[a] Γ_1 and Γ_2 are respectively the observed half line widths of the lower and higher velocity components of the quadrupole split doublet.

[b] The samples were not cooled enough to the liquid nitrogen temperature.

in an increase in the interlayer spacing, leaving the local environment around the Fe^{3+} atom unaffected. In contrast, the values for FeOCl (organic compound)$_{1/n}$ drastically change with temperature. Ionic forces result from the charge transfer interaction between the host layer and the guest molecules replacing the van der Waals force between FeOCl layer in the original host. Owing to the ionic bonding, thermal expansion of the FeOCl lattice in the intercalation compound results not only in an increase of the interlayer spacing but also in the relative displacement between the host and the guests. If the transferred electrons localized on iron atoms in the intercalated compounds, Fe^{2+} might be partly detected on Mössbauer spectra. However, the irons in the compounds are still ferric in high spin state. The transferred charges are hopping faster in the host layer than the speed with which Mössbauer spectroscopy can resolve.

4. Electrical resistivity

The electrical resistivities of FeOCl and its complexes were measured in the temperature range 373–200 K using carbon electrodes. Table II summarizes the results on electrical resistivities at room temperature and on electrical activation energies with the values of the interlayer distances. FeOCl is a semiconductor with resistivity of 10^6 Ωcm at room temperature. The intercalated complexes were still semiconducting, but exhibited improved electrical conductivities along their c-axes. Their electrical resistivities were 10–10^3 Ωm at room temperature. The values are much smaller than that of FeOCl by a factor of 10^{3-5}. The electrical activation energy also changed from 0.6 to 0.2–0.3 eV for the complexes. Formation of the intercalation compounds caused much reduction in electrical resistivity in the direction parallel to the host layer. The improved electrical conductivity may be explained by an increased number of charge carriers due to the charge transfer from the guest to the host FeOCl layer.

Table II
Interlayer distance and electrical resistivity

Sample	pk_a[a]	b (Å)	ρ[b] (Ωcm)	E_a (eV)
FeOCl		7.92	10^6	0.6
FeOCl $(Py)_{1/4}$	5.2	13.27	10	0.2
FeOCl $(DMP)_{1/4}$	6.8	14.98	10^2	0.3
FeOCl $(AP)_{1/4}$	9.2	13.57	10^3	0.2
FeOCl $(TMP)_{1/6}$	9.6	11.79	10^3	0.2

[a] The values are the measure of basicity for organic intercalants themselves.
[b] Data obtained at room temperature.

The expanded interlayer spacings are explained by the insertion of organic intercalants into the van der Waals gap of FeOCl. Molecular orientations of pyridine derivatives in the interlayer space of FeOCl have been estimated using the results of one-dimensional electron density projections [9]. The pyridine ring is perpendicular to the host layers so that nitrogen atoms face to the layers in the pyridine complex. The pyridine ring of DMP is also 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 due to 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 or lies almost parallel to the host layer. There is no particular reason to exclude the structural model proposed by Schöllhorn for TaS_2 $(Py)_{1/2}$ [10]. However, the present results can be explained by the model in which organic intercalants are in the van der Waals gap so that their nitrogen atoms are as close to the FeOCl layer as possible.

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