Intercalation Compounds of FeOCl. Systematics of Amine Containing Lewis Base Intercalants

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New intercalated compounds of FeOCl and aniline derivatives were synthesized by soaking FeOCl in ethanol solution containing Lewis base intercalants. Only those Lewis base intercalants whose acid-dissociation constant is greater than 5 intercalate into the lattice of FeOCl. The acid-strength of the solvent is important for the formation of an intercalation compound. The intercalates of iron(III) chloride oxide $FeOCl(G)_{1/n}$ have been characterized by elemental analysis, powder pattern of X-ray diffraction, Fe-57 Mössbauer and infrared spectroscopies. The research on expansion of the b-axis of the unit cell and IR data confirm the location of the "guest" molecule within the van der Waals layer or the FeOCl lattice. Effective vibrating mass and lattice temperature derived from the Mössbauer spectra are affected by chemical bonding in the first coordination sphere of the iron atom.

Iron(III) chloride oxide (host matrix) is a layered compound whose crystal structure consists of a stack of double sheets of *cis*-$FeCl_2O_4$ octahedra, linked together with shared edges.[1] The length of the crystallographic b axis ($c<a<b$) perpendicular to the van der Waals plane (chlorine atom planes) increases along with the progress of intercalation. It has been shown recently that layered FeOCl reacts chemically with ammonia,[2] pyridine,[3,4] pyridine derivatives,[5] and phosphine[6] to give intercalated products.

It is not possible at present to predict whether a particular guest molecule will be able to intercalate or not into the FeOCl lattice. This is due to deficient knowledge of the intercalation of host lattice/guest species and of the influence of kinetics on solid state reactions. Lewis base (guest molecule) aniline does not intercalate into the layered plane of the van der Waals bonding. However, some derivatives of aniline have been found to intercalate into this plane in the present study. Our investigation indicates that a large number of layered compounds form intercalates when treated with Lewis bases of $pK_a>5$ and that the rate of the intercalation depends upon acid-strength of the solvent used.

The present study was also undertaken to examine the interlayer spacing and hence the molecular packing, the hyperfine interactions, lattice dynamics and vibrational spectra of the intercalate system.

Experimental

Sample Preparation. Iron(III) chloride oxide was prepared from Fe_2O_3 and $FeCl_3$ by the usual sealed tube technique discussed in the literature,[7] and was characterized by colorimetric iron determination and X-ray powder patterns. The intercalates listed in Table 1 were obtained by soaking FeOCl in the Lewis base or in the base dissolved in a dehydrated solvent. The experimental conditions for preparation of the compounds and analytical data are summarized in Tables 1 and 2. The stoichiometry was obtained by calculating iron and carbon contents. The progress of the intercalation was followed by X-ray observation of decay in the strongest (010) plane of FeOCl. At the end of the reaction period, the reaction mixture was filtered through sintered glass, the solid product was washed with absolute alcohol, dried *in vacuo*, and stored under nitrogen. The solvents used were dehydrated to avoid the influence of water. The reflection lines due to the (010) and (020) planes of the intercalates were used to calculate the length of the b-axis of the unit cell. The b-axis parameters are listed in Table 1.

Spectroscopy. Mössbauer measurements were carried out with an Austin Science Associates(ASA) spectrometer. The Iron-57 Mössbauer spectra of a powdered thin sample of the compound were recorded between 80 and 300 K using an ASA cryostat. A cobalt-57 source diffused into palladium foil was used. The isomer shift, δ_{Fe} was measured relative to the center of the spectrum of an iron foil enriched with iron-57 at 296 K, which was also used as a standard material for the velocity calibration. Calculation of Mössbauer spectroscopic

TABLE 1. PREPARATIVE CONDITIONS AND pK_a FOR $FeOCl(G)_{1/n}$ INTERCALATES

Intercalates	n[a]	Reaction time / d	Reaction temp / °C	Solvent	b[b] / Å	pK_a
8-Aminoquinoline	5	7	60	Et[c]	15.54	—
N,N-Dimethylaniline	9	1	29	—	13.91	5.10
p-Methoxyaniline	6	2	60	Et	14.39	5.30
p-Phenylenediamine	9	3	20	Et	13.61	6.16
					11.42	
p-Aminophenol	4	18	20	Et	13.78	5.50
p-Aminodiphenylamine	15	14	20	Et	13.35	—
p-Methylaniline	12	7	23	Et	13.68	5.10

a) $FeOCl(G)_{1/n}$. b) A b is the unit cell dimension of b-axis. The easy cleavage plane is perpendicular to the b direction.
c) Et: Ethanol.

Table 2. Analytical data for $FeOCl(G)_{1/n}$ intercalates

Intercalates	Calcd (%)				Found (%)			
	C	H	N	Fe	C	H	N	Fe
8-Aminoquinoline	17.07	1.58	3.98	39.67	17.14	1.74	3.90	39.90
N,N-Dimethylaniline	8.84	1.02	1.29	46.24	8.90	1.94	1.21	45.11
p-Methoxyaniline	10.96	1.18	1.83	43.68	11.59	1.73	1.77	44.89
p-Phenylenediamine	7.71	0.75	2.61	46.80	7.11	1.63	2.54	43.62
p-Aminophenol	13.44	1.32	2.61	41.65	12.05	1.89	2.30	41.01
p-Aminodiphenylamine	8.04	0.67	1.56	46.70	8.41	1.91	1.53	46.88
p-Methylaniline	6.03	0.65	1.00	48.05	5.62	2.25	0.95	47.63

data was effected using the least squares method at the Computer Center, Kyushu University. The infrared spectra of the samples in the potassium bromide region (650—4000 cm^{-1}) were obtained using a Hitachi Grating Infrared Spectrophotometer, type 215. X-Ray powder diffraction patterns of the samples were observed using a Rigakudenki Geigerflex Diffractrometer model DF.

Results and Discussion

Lattice Parameter of Intercalated FeOCl. The b-axis parameters of intercalated FeOCl are listed in Table 1 for compounds which attained a reproducible limiting composition. The X-ray powder pattern can be understood on the basis of an expansion of every layer ("stage 1" compound) in the direction of the b-axis of the unit cell. The powder X-ray diffraction patterns of the FeOCl intercalation compounds are usually dominated by (010) and (020) lines. The diffraction lines in a- and c-axis of the unit cell cannot be observed. However, they are assumed not to be significantly different from those in FeOCl pyridine intercalated compounds except that the b-axis parameter has variable values.[3,4] There are several possible orientations which a non-cubic symmetry guest molecule can adopt with respect to the van der Waals planes. In particular, it is interesting to ascertain the orientation of the nitrogen lone pair electrons with respect to the van der Waals plane. The b-axis parameter of 7.91 Å for FeOCl becomes about 13—14 Å for aniline derivatives and for *p*-aminodiphenylamine intercalates whose values are nearly equivalent to 13.27 Å for $FeOCl(pyridine)_{1/3}$. On the other hand, the b-axis parameter for 8-aminoquinoline intercalation is 15.54 Å. The value of 15.54 Å is the maximum in FeOCl intercalated compounds and the interlayer spacing of this compound is calculated to be 7.63 Å. Several structural models are proposed in Fig. 1 to account for the orientation of the Lewis bases, guest molecules in the FeOCl lattice. Substituting the hydrogen in the 4-position of a phenyl ring with a bulky group brings about lower content of the guest molecule with no increase in the b-axis parameter. This phenomena can be understood with model (a) of Fig. 1, which shows the orientation of Lewis bases in the FeOCl lattice.

The powder X-ray diffraction pattern for $FeOCl(p\text{-phenylenediamine})_{1/9}$ suggests that there are two orientations for the guest molecule in this sample, as shown in Fig. 1(b). The superhyperfine pattern could not be observed in the X-ray and electron diffraction patterns. However, it seems reasonable to infer that the presence of the two b-axis parameters is due to the superlattice structure as shown in Fig. 1(b), rather than due to a mixture of the 13.61 Å b-axis parameter sample with the 11.42 Å b-axis parameter sample, although we do not have any evidence for this. The larger b-axis parameter (13.61 Å) is in the same range as that for the FeOCl intercalation compound of aniline derivatives. The interlayer spacing parameter of 3.51 Å is calculated for the part with b-axis parameter of 11.42 Å. In the case of $FeOCl(NH_3)_{3/4}$ an increase of 3.42 Å in the direction of the b-axis of a unit cell has been observed.[2,4] The thickness of the plane of a phenyl ring is assumed to be about 2.0 Å. Accordingly the b-axis expansion of 3.51 Å in this compound would account for an orientation such that the phenyl plane of *p*-phenylenediamine is parallel to the van der Waals plane.

Acid-dissociation Constant and the Rate of Intercalation. All the values of the acid-dissociation constants, pK_a, of the guest molecule listed in Table 1 are larger than 5. The substituted aniline derivatives which could not

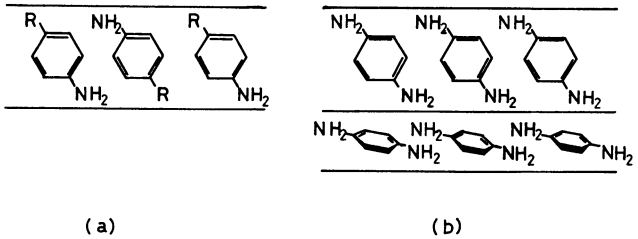

Fig. 1. The orientations assumed for aniline derivatives (a) and for phenylenediamine (b) within the FeOCl layer lattice. The chlorine atom layers of the matrix are shown by straight lines.

Table 3. Chemical and physical properties of the solvents

Solvents	pK_a[a]	ε[b]	D[c]	η[d] (at 20 °C)	$\frac{t}{d}$[e]
Ethylene glycol	—	38	—	17.33	30
Methanol	16—18	33.2	11.7	0.61	3
Ethanol	18	24.3	1.69	1.19	7
2-Propanol	18	18.3	1.6	2.39	1/4

a) Acid dissociation constant. b) Dielectric constant. c) Dipole moment ($D=10^{-18}$ cgs). d) Viscocity (cP= 10^{-3} N s m^{-2}). e) Reaction time required to complete the intercalation.

intercalate into the FeOCl lattice are *p*-nitroaniline ($pK_a=1.0$), *p*-chloroaniline ($pK_a=4.0$), aniline-4-sulphonic acid ($pK_a=3.2$), and aniline ($pK_a=4.6$). It can be inferred that a neccesary (but not sufficient) condition for forming the FeOCl intercalation of these molecules under the conditions discussed above is that pK_a of guest molecule must be larger than 5. The analogous phenomena have been observed in pyridine intercalation of FeOCl[4] and TaS_2.[8] Table 3 shows the physical properties of various solvents and the relative rate of the intercalation when FeOCl(*p*-methylaniline)$_{1/12}$ is prepared in these solvents. The rate of the intercalation examined in this study depends upon the acid-strength of the solvents, as have been reported by Gerrard and Macklen.[9] The order of acid-strength is ethylene glycol≫methanol>water>ethanol >1-butanol>2-propanol. However, we must take into consideration the dielectric constant of the solvents because there are not such great differences in the pK_a values of the solvents examined; it is reasonable to consider that van der Waals bonding in liquid-solid systems may depend upon the dielectric constant of the solvent. Thus the Lewis base *p*-methylaniline could not intercalate into FeOCl lattice in a solvent of acetone, benzene, chloroform, dichloromethane, isopentyl alcohol, hexane, nitrobenzene, nitromethane, pentane, tetrahydrofuran, toluene, or trichloroethylene.

Mössbauer Spectra and Lattice Dynamics. The X-ray powder pattern can be understood as showing the formation of a "stage 1" compound in which every van der Waals layer includes an array of "guest" molecules. All the Mössbauer spectra were doublets, although the stoichiometry of the intercalation compounds examined in this study shows that not all of the iron atoms in FeOCl(G)$_{1/n}$ are structurally identical. The Mössbauer parameters for the FeOCl intercalates are summarized in Table 4. Full width at half-maximum (0.32—0.40 mm s^{-1}) is somewhat larger than natural line width. The full width at half-maximum of FeOCl(*p*-phenylenediamine)$_{1/9}$ is in the same range as that for other intercalates, which supports the view that all iron atoms of FeOCl(*p*-phenylenediamine)$_{1/9}$ are situated in the same coordination sphere, that is, in the structure of a mixed phase as shown in Fig. 1(b).

Mössbauer spectra for selected samples were measured at various temperatures to calculate the effective vibration mass and "lattice temperature" for the intercalation compounds. Using a Debye model for the solid, and assuming that the appropriate mass of the probe atom corresponds to the free-atom value, leads to a temperature dependence of the recoil-free fraction f, given by[10]

$$\mathrm{d}\ln f/\mathrm{d}T = -6E_R/k_B\theta_M^2 \quad (1)$$

in which E_R is the recoil energy after gamma ray emission and k_B is Boltzmann's constant. At temperatures well above the magnetic ordering temperature, the temperature dependence of the area under the resonance curve can be used to estimate a "lattice temperature," θ_M' based on the thermal motion of the Mössbauer active atom. In the case of ^{57}Fe Mössbauer data, two "lattice temperatures" can be calculated from the temperature dependence of the area under the resonance curve. In Eq. 1 $\mathrm{d}\ln f/\mathrm{d}T$ can be replaced for a thin absorber by the $\mathrm{d}\ln A/\mathrm{d}T$ (the temperature dependence of the area under the resonance curve) to yield the following relationship

$$\theta_M = \frac{E_\gamma}{C}\left[\frac{-3}{M_{eff}k_B\mathrm{d}\ln[A(T)/A(80)]/\mathrm{d}T}\right]^{1/2} = 11.659\left[\frac{-\mathrm{d}\ln(A(T)/A(80))}{\mathrm{d}T}\right]^{-1/2}. \quad (2)$$

A limitation of this approach is that when the Mössbauer active atom is incorporated in the solid by largely covalent bonding forces, the appropriate mass needed to describe its motion may be significantly larger than the atomic mass. The effective vibrating mass can frequently be estimated from the second order Doppler

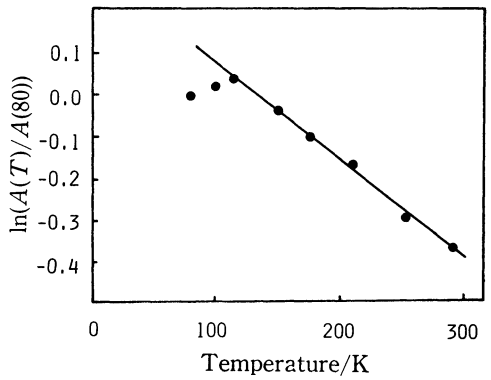

Fig. 2. Temperature dependence of the normalized ln (Area) parameter for FeOCl(8-aminoquinoline)$_{1/5}$.

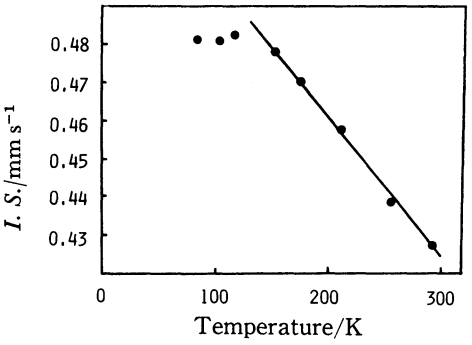

Fig. 3. Temperature dependence of the *I.S.* parameter for FeOCl(8-aminoquinoline)$_{1/5}$.

TABLE 4. MÖSSBAUER PARAMETERS OF FeOCl(G)$_{1/n}$ INTERCALATES

Intercalates	*I.S.*[a]		*Q.S.*[b]	
	80 K	297 K	80 K	297 K
8-Aminoquinoline	0.48	0.43	1.14	0.74
N,N-Dimethylaniline	0.47	0.39	1.11	0.69
p-Methoxyaniline	0.49	0.44	0.84	0.77
p-Phenylenediamine	0.51	0.41	1.01	0.72
p-Aminophenol	0.49	0.47	0.93	0.68
p-Aminodiphenylamine	0.37	0.38	0.93	0.74
p-Methylaniline	0.44	0.40	0.82	0.73

a) Isomer shift/mm s^{-1}. b) Quadrupole splitting/mm s^{-1}.

Table 5. Effective vibrating mass and lattice temperatures of $FeOCl(G)_{1/n}$ intercalates

Intercalates	M_{eff}/mass unit[a)]	θ_M/K[b)]	θ'_M/K[c)]	T_{range}/K
8-Aminoquinoline	115±1	240±5	169±7	150—297
N,N-Dimethylaniline	72±1	d)	d)	170—297
p-Aminodiphenylamine	85±1	270±6	222±8	225—297

a) Effective vibrating mass. b) Lattice temperature. c) Modified lattice temperature. d) This value is not calculated because plots of ln $(A(T)/A(80))$ show a linear curve only above 250 K.

shift, as follows:

$$M_{eff} = -4.168 \times 10^{-2}[d(IS)/dT]^{-1}. \quad (3)$$

Using this value for M_{eff} in Eq. 2, a modified "lattice temperature" θ'_M is calculated as follows:

$$\theta'_M = 4.3202 \times 10^2 \left[\frac{d(IS)/dT}{d\ln(A(T)/A(80))/dT}\right]^{1/2}. \quad (4)$$

Figures 2 and 3 show the temperature dependence of the ln $(A(T)/A(80))$ and isomer shift for FeOCl(8-aminoquinoline)$_{1/5}$, respectively. Linear regressions for both parameters were obtained above 150 K. The temperature ranges (T_{range}) for each sample in which a linear regression is maintained are listed in Table 5. The Mössbauer spectra become highly complex below 120 K because the magnetic ordering temperature of the intercalation compounds is about 120 K but is not sharply defined.

FeOCl (*N,N*-dimethylaniline)$_{1/9}$ does not give a linear curve for the temperature dependence of ln A because of the interference of the magnetic hyperfine structure at low temperature (<250 K). It is well known that a solution of *N,N*-dimethylaniline products triphenylmethane dye in the presence of an iron ion. A deep blue color appears in the process of preparing FeOCl(*N,N*-dimethylaniline)$_{1/9}$ and letting the solution stand overnight brings about decomposition of the intercalation compound. This observation suggests that FeOCl(*N,N*-dimethylaniline)$_{1/9}$ may not be pure material although no other peaks except those due to the intercalates are observed in X-ray powder pattern.

The fact that $\theta_M/\theta'_M > 1$, as understood from Table 5, leads to the conclusion that M_{eff} is substantially larger than the free-atom value in consonance with covalency of the iron atom bonding in the matrix. However, the concomitant b-axis expansion of the unit cell does not significantly affect the effective mass and "lattice temperature." Therefore, the significance of these data lies in the conclusion that M_{eff} and θ_M are significantly affected by the chemical bonding in the first coordination sphere of iron atoms.

The temperature dependence of the quadrupole splitting parameter for FeOCl (1.0×10^{-4} mm s^{-1} deg^{-1})[4)] is very small as shown in Fig. 4. However, most of the FeOCl intercalates examined in the present study show sigmoidal temperature dependence in the quadrupole hyperfine interaction. The value of the quadrupole hyperfine interaction in the intercalates is larger than that observed for FeOCl at low temperature and decreases at high temperatures, as listed in

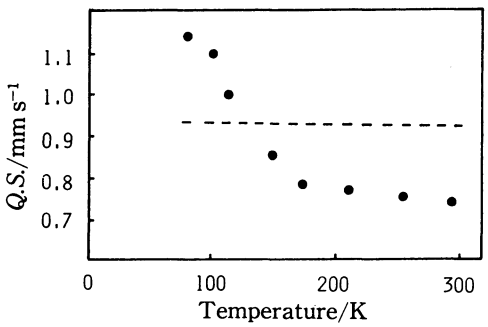

Fig. 4. Temperature dependence of the *Q.S.* parameter for FeOCl(8-aminoquinoline)$_{1/5}$. The dashed line represents the comparison data for unintercalated FeOCl over the same temperature range.

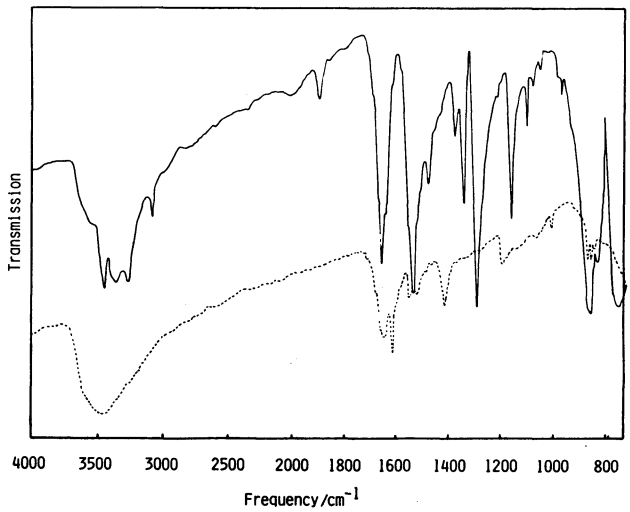

Fig. 5. Infrared spectra of FeOCl(*p*-phenylenediamine)$_{1/9}$ (dotted curve) and *p*-phenylenediamine (full curve).

Table 4.

Infrared Spectra. Some of the IR spectra of the FeOCl intercalates are shown in Figs. 5—8. The FeOCl matrix has absorptions at the bands 1640 (s) and 1400—1500(w) cm^{-1}. Most notable in a comparison between the FeOCl and the intercalation compounds are the facts that the out-of-plane bending modes of phenyl (700—800 cm^{-1}) are clearly noted in the intercalation compounds and that the ring expansion modes between 960—1200 cm^{-1} are strongly suppressed in the intercalate spectra. These observations indicate that the orientation of the aniline derivatives molecule is such that the plane of the aniline ring is perpendicular to the van der Waals layer, except in the case of FeOCl (*p*-phenylenediamine)$_{1/9}$.

In the IR spectrum of FeOCl (*p*-phenylenediamine)$_{1/9}$ the strong C–N stretching band at 1275 cm^{-1} (unintercalate base) is strongly suppressed as shown in Fig. 5. The bands at 1320 and 1352 cm^{-1} of phenyl origin are shifted to 1398 cm^{-1} or suppressed in the intercalation. The band at 1140 cm^{-1} is shifted to 1178 cm^{-1} in the intercalate. The ring expansion bands in plane (960—1200 cm^{-1}) are observed and a new sharp band appears at 1600 cm^{-1} in the intercalate. The IR

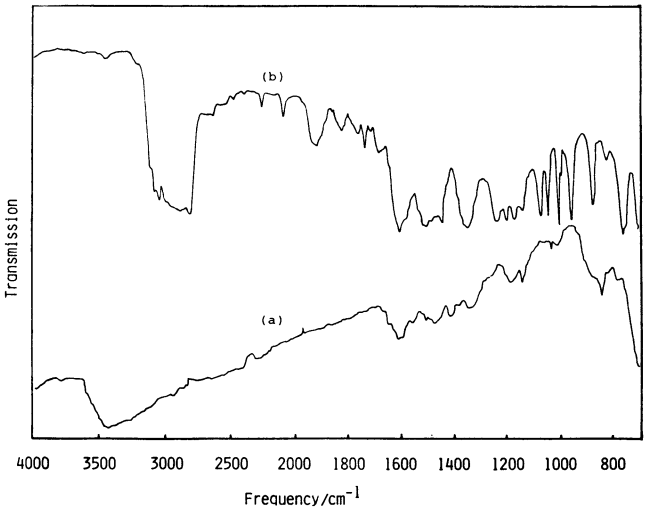

Fig. 6. Infrared spectra of FeOCl(N,N-dimethylaniline)$_{1/9}$ (a) N,N-dimethylaniline (b).

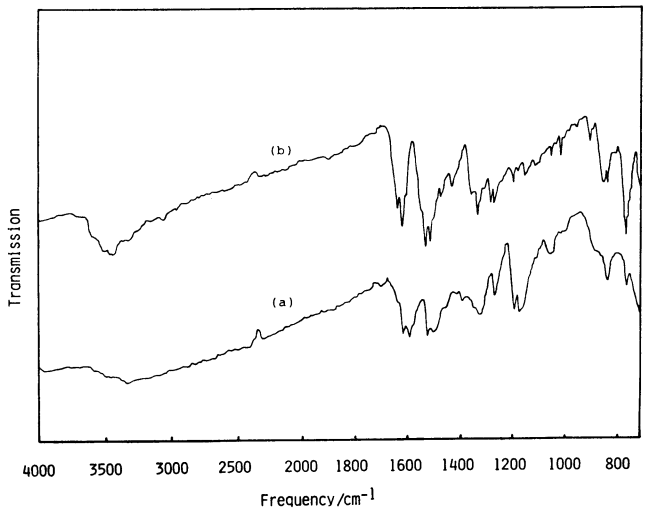

Fig. 7. Infrared spectra of FeOCl(p-aminodiphenylamine)$_{1/15}$ (a) and p-aminodiphenylamine (b).

spectrum of FeOCl (N,N-dimethylaniline)$_{1/9}$ in a KBr matrix is shown in Fig. 6. The symmetric stretching band of C–H in the methyl group at about 2814 cm^{-1} in the unintercalated base, the methyl group asymmetric deformation observed at 1459 cm^{-1} (liquid) and the ring expansion band in the plane between 1200 and 960 cm^{-1} (unintercalate) are not observed in the intercalate. Figure 7 shows the IR spectrum of FeOCl-(p-aminodiphenylamine)$_{1/15}$ in which new bands appear at 1580(s), 1180(s), 1160(s), and 1040(m) cm^{-1} The absorption due to tertiary amine at 1515 cm^{-1} (unintercalate base) is observed at the same position. Most of the bands of the base are observed in the intercalate, although the band at 750 cm^{-1} becomes weak in the intercalate. In the IR spectrum of FeOCl(p-aminophenol)$_{1/4}$ (Fig. 8) the ring expansion bands at 1100, and 983 cm^{-1} and the band at about 900 cm^{-1} (observed in unintercalate base) are not observed, and the phenyl band at 1490 cm^{-1} becomes weak in the intercalate.

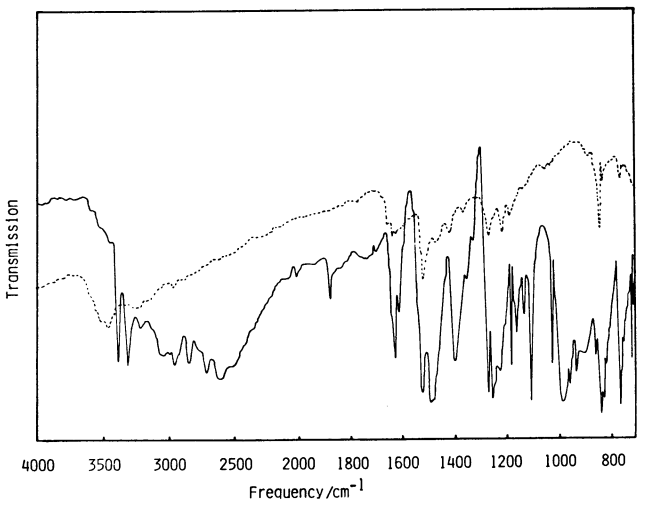

Fig. 8. Infrared spectra of FeOCl(p-aminophenol)$_{1/4}$ (dotted curve) and p-aminophenol (full curve).

It is notable that most of the absorptions observed in unintercalated base are observed in the IR spectrum of FeOCl(p-methoxyaniline)$_{1/6}$, except for the N–H stretching band at about 2900—3000 cm^{-1}. These data reflect a significant non-bonding (Coulomb) interaction between the base and van der Waals chlorine planes. The datum of FeOCl(p-methylaniline)$_{1/12}$ shows that the C–N stretching band of the methyl group is suppressed.

The molecular diameter of an aniline molecule is estimated to be about 4—5.3 Å on the ring plane and the ring thickness to be about 2.0 Å. The observed b-axis expansion of FeOCl intercalation is 5.4—6.5 Å and indicates that the orientation of aniline-derivatives molecule is perpendicular to the van der Waals layer. Within that restriction, two extreme orientations of the intercalant are still possible; an imaginary C_{2v} axis of aniline ring plane is either parallel to or perpendicular to the a direction of the FeOCl lattice. However, no clear-cut distinction between the two orientations can be drawn from the present data alone. The suppression of C–N stretching band supports the view that a lone-pair electron on the nitrogen atom coordinates to the iron atom, *viz.* the coordination structure drawn in Fig. 1.

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