On the Structure and Properties of Iron Halide–Graphite Intercalates: A Comparison of the Reactivity of Free and Graphite-intercalated Iron(III) Chloride *

Robert Schlögl and William Jones
Department of Physical Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EP

Using different preparation procedures, distinctly different types of first-stage graphite intercalates of $FeCl_3$ have been synthesized in a routine manner. Amongst these is identified, for the first time, a charge-transfer complex containing $[FeCl_4]^-$, with the graphite host acting as the counter ion. Using results obtained from Mössbauer spectroscopy and *X*-ray powder diffractometry, a direct comparison is made between the sequence of events which accompany exposure to air of crystalline bulk $FeCl_3$ and intercalated $FeCl_3$. Whereas intercalated $FeCl_3$ slowly hydrolyses to yield both tetrahedrally and octahedrally co-ordinated complexes between the graphite layers, free $FeCl_3$ converts either, following slow exposure, into partially hydrated species, or when the reaction is rapid to a mixture of FeO(OH) and $HFeCl_4$. The overall expulsion of the metal halide from between the host sheets is considered to proceed *via* both ' electronic ' and ' physical ' de-intercalation steps.

There is renewed interest at present in graphite intercalation compounds (g.i.c.s), principally because of their novel catalytic [1] and electronic properties.[2] Previous work on such materials has primarily focused on donor-type compounds,[3] although more recently attention has turned to the family of acceptor intercalates, suitably exemplified by the intercalates of $SbCl_5$, AsF_5, and $FeCl_3$.[4]

We have previously demonstrated that the nature and properties of iron chloride g.i.c.s depend critically upon both the sample history and the conditions under which it is prepared.[5] In this paper we describe our results on the characterization of four different intercalates of $FeCl_3$, each prepared using distinctly different procedures, and we have also monitored, using principally Mössbauer spectroscopy and *X*-ray powder diffractometry, the processes which result from exposure of the intercalates to air. In addition, we have followed the sequence of events which accompany the exposure of crystalline $FeCl_3$ to air, and demonstrate a direct similarity to the chemistry of concentrated iron(III) chloride (aqueous) solutions. It transpires that air exposure of crystalline $FeCl_3$ results (*via* hydrolysis) in the formation of hydrated iron oxyhydroxides. The results obtained under known sample environments provide useful information about the reaction of both free and intercalated $FeCl_3$ with water and with air, and when taken together lead to a more detailed understanding of the nature of the sub-lattice of intercalated iron(III) chloride: in particular, they permit a critical examination to be made of the vacancy structure [6] which has recently been proposed for this sub-lattice.

Experimental

Materials.—Natural graphites from Kropfmühl (Bavaria) of particle size 1—10 μm or 1—2 mm (designated AF and S40 respectively) with a purity of 99% were used as the host material.[7] Iron(III) chloride (Merck) was purified by sublimation in a chlorine gas stream. Elemental analyses were performed twice using the procedure previously described.[5]

Analytical Techniques.—*X*-Ray diffraction data were obtained using a Philips APD10 diffractometer, with computer control facilities and monochromated Cu-K_α radiation. Mössbauer spectra were obtained using a standard constant-acceleration spectrometer, with either a *ca.* 10 or 50 mCi ^{57}Co/Rh source, calibrated using a standard iron foil. All isomer shifts are given relative to α-iron at 25 °C.

Table 1. Conditions of synthesis and elemental analyses

Sample	A	C	B	D
Starting graphite	AF	AF	S40	AF
Molar ratio C : $FeCl_3$	6 : 1	6 : 1	3 : 1	6 : 1 [a]
Chlorine pressure/bar	1	10	10	—
Temperature/°C [b]	305	305	325	250
Reaction time/h	24	24	24	24
%Fe	21.9	17.8	16.2	7.4
%Cl	43.9	34.8	30.8	28.7
Cl : Fe ratio	3.08	3.07	2.99	6.10

[a] In a 1 : 1 molar mixture of $AlCl_3$ and $FeCl_3$. [b] Of the graphite, the metal chloride side being *ca.* 20 °C lower (see ref. 5).

Sample Preparation.—Four sample preparation procedures were followed, each using the conventional two-bulb vapour-phase method.[5] Specific conditions are in Table 1 and as follows.

Method A. Stoicheiometric amounts of graphite and $FeCl_3$ to form the first-stage compound C_6FeCl_3, using a surrounding chlorine gas pressure of 1 atm.

Method B. A two-fold excess of $FeCl_3$ above that required to form C_6FeCl_3; a chlorine overpressure of 10 atm was used.

Method C. Stoicheiometric amounts of $FeCl_3$ and graphite to form C_6FeCl_3, with a chlorine overpressure of 10 atm. This yielded an undersaturated g.i.c., presumably as a consequence of the considerable disintegration of the graphite flakes which accompanies intercalation.[8]

Method D. Using $AlCl_3$ as a catalyst [9] for the intercalation reaction. The addition of $AlCl_3$ is a general method for facilitating the intercalation of metal halides, and relies upon the formation of a highly volatile gas-phase complex between the metal halide to be inserted and $AlCl_3$. The purpose of employing this method here was in an attempt to intercalate not the pure halide but the gas-phase complex itself. Attempts at co-intercalation of $FeCl_3$ and $AlCl_3$ have been reported earlier,[10] and although the accompanying analytical data were similar to those reported here, it appears that the higher intercalation temperatures previously used may have led to

---

* *Non-S.I. units employed:* atm = 101 325 Pa; bar = 10^5 Pa.

Table 2. Mössbauer parameters [a]

Sample	Treatment	T/K	Isomer shift	Quadrupole splitting	Linewidth	Rel. area	Goodness of fit
				mm s^{-1}			χ^2
A	None	300	0.01(1)	—	0.28(3)	4	728 (502)
			0.45(1)	—	0.34(1)	82	
			0.63(1)	—	0.24(1)	14	
	60 h in air	300	0.41(1)	0.86(2) [b]	0.45(3)	46	662 (497)
			0.45(1)	—	0.23(1)	35	
			0.61(1)	—	0.23(1)	19	
B	None (blue)	78	0.29(1)	—	0.51(1)	64	539 (505)
			0.48(1)	—	0.39(1)	36	
	None (blue)	300	0.37(1)	—	0.51(1)	61	501 (500)
			0.70(1)	—	0.44(1)	39	
	40 min in air (black)	78	0.23(1)	—	0.49(2)	38	499 (503)
			0.56(1)	—	0.61(2)	62	
	4 weeks in air (black)	300	0.52(1)	—	0.54(1)	—	612 (506)
D	None	300	0.34(1)	—	0.32(3)	—	248 (250)
	4 weeks in air	78 [c]	0.08(2)	—	0.38(5)	16	514 (500)
			0.45(5)	—	0.36(5)	39	
			0.61(3)	—	0.34(5)	45	
	12 weeks in air	300 [d]	0.02(1)	—	0.35 [e]	29	301 (249)
			0.42(2)	—	0.35 [e]	32	
			0.65(2)	—	0.35 [e]	39	
$FeCl_3$	Anhydrous	300	0.42(1)	—	0.39(1)	—	492 (506)
	19 h in air	300	0.44(2)	0.91(4) [b]	0.34(5)	8	492 (506)
			0.42(1)	—	0.38(1)	92	
	100 h in air	300	0.42(1)	0.96(2) [b]	0.33(2)	36	499 (500)
			0.41(1)	—	0.45(1)	64	
	Rapid air exposure [f]	300	0.48(1)	0.46(2)	0.37(5)	—	786 (503)
			0.25(1) [g]	—	0.42(1)	68	
			0.71(1)	—	0.31(1)	32	
	Pure $FeCl_3 \cdot 6H_2O$	300	0.55(2)	0.92(2)	—	—	568 (503)
			0.07(1) [g]	—	1.25(2)	54	
			1.03(1)	—	0.44(1)	46	

[a] Relative to natural iron foil at 300 K; standard deviations are given in parentheses for shifts, splittings, and linewidths. [b] The individual lines are at *ca.* 0.02 and *ca.* 0.84 mm s^{-1}. [c] At 300 K only slight changes in intensities. [d] At 78 K only slight changes in intensities. [e] Fixed value. [f] After 24-h slow exposure to air (see text). [g] Fit as individual lines.

the formation of a normal $FeCl_3$ g.i.c. without significant co-intercalation of $AlCl_3$. The analytical data (chlorine : iron ratio of *ca.* 6 : 1) obtained for our samples (see Table 1) suggests that insertion of the gas-phase complex has indeed occurred. This was confirmed by energy-dispersive *X*-ray microanalysis which indicated that comparable amounts of aluminium and iron were present inside the individual graphite flakes.

Results

(*A*) *Intercalates*.—(1) *Obtained using methods A and C*. The intercalates obtained following methods A and C were black in colour. Their Mössbauer spectra are identical and in good agreement with those previously reported for iron(III) chloride intercalates.[5] They consisted of a single absorption which could be satisfactorily fitted to two iron(III) singlets, the parameters of which are given in Table 2. *X*-Ray diffraction patterns indicated that these materials were essentially first stage with an interplanar distance (I_c) of *ca.* 948 pm. As previously reported,[5] exposure of these materials to air results in changes in both the Mössbauer spectrum and the diffraction pattern. The present study, however, concentrates on the initial stages of reaction, and thereby covers a time period between the onset of air exposure and the first data points presented in ref. 5.

Figure 1(*a*) illustrates the Mössbauer spectrum of a sample, prepared using method A, after 24-h exposure to air and indicates the presence of an additional absorption at *ca.* 0 mm s^{-1}. Further exposure results in the spectrum shown in Figure 1(*b*) which may be reasonably fitted to four peaks, the parameters of which are given in Table 2. Two peaks are associated with the initial iron(III) species,[5] and the two remaining peaks may be assigned to a complex hydrated iron(III) chloride species, the exact identity of which is discussed later. The associated diffraction trace [Figure 1(*c*)] indicates that the sample remains (with only minor contributions of second and higher stages) predominantly first stage and, as may be concluded from Figure 1(*c*) and (*d*), there is no evidence for crystalline hydrated $FeCl_3$ as a possible product of de-intercalation. Furthermore, examination of this sample by

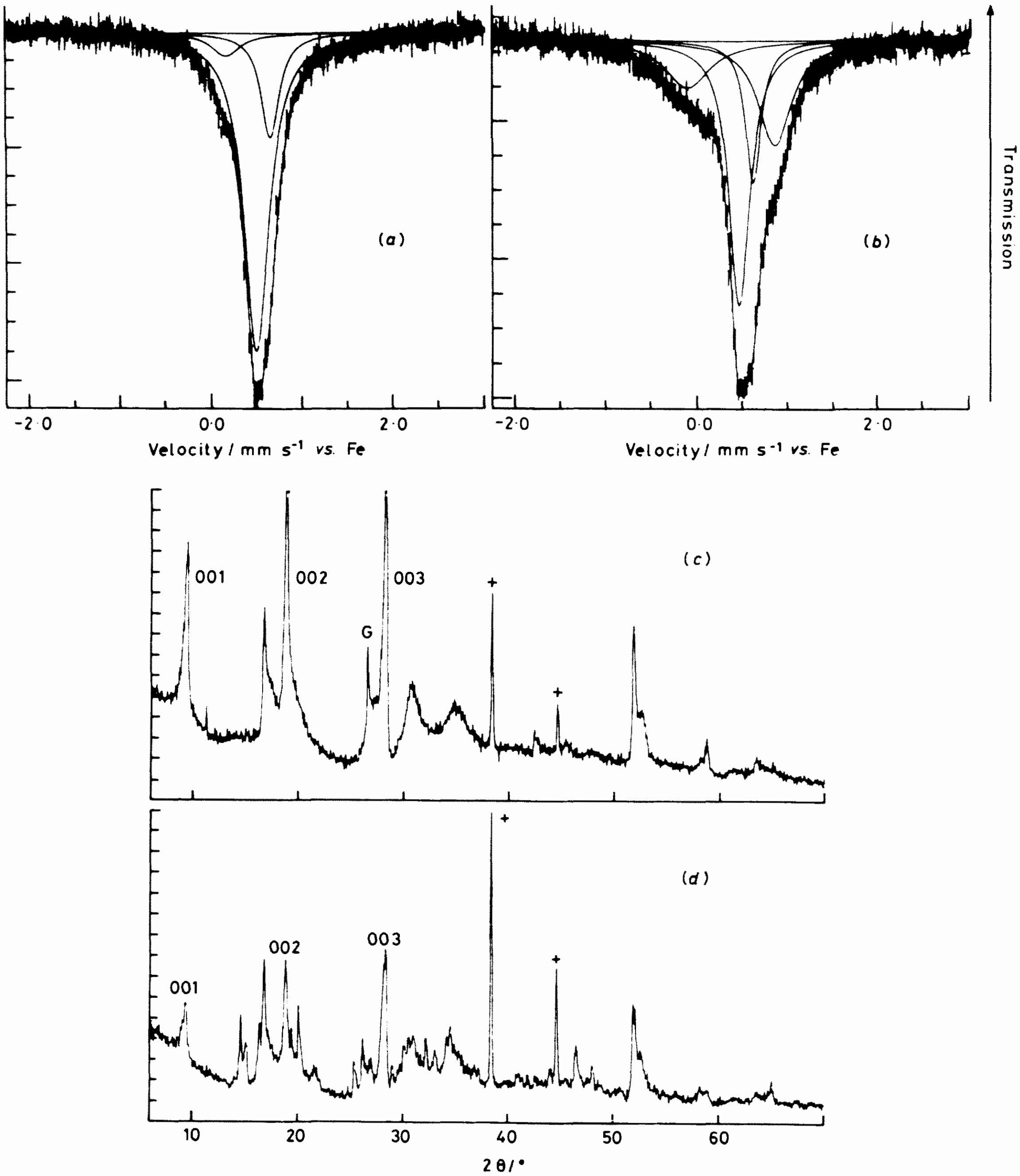


Figure 1. Sample A: Mössbauer spectra recorded at room temperature and in air of (*a*) fresh material and (*b*) after 60-h exposure; diffraction traces after (*c*) 18 h in air and (*d*) after addition of 25 wt. % $FeCl_3{\cdot}6H_2O$. G denotes the position of the (002) reflection of free graphite; +, reflections of the sample holder

transmission electron microscopy gave no indication of any separate (and possibly *X*-ray amorphous) phase. We conclude, therefore, that the formation of the hydration product occurs within the graphite sheets.

(2) *Obtained using method B.* When preparation B is used (*i.e.* in the presence of a two-fold excess of $FeCl_3$) a first-stage material is again produced, with $I_C = 946$ pm. This intercalate is, however, blue with the graphite host as revealed by optical and electron microscopy having undergone considerable exfoliation. The *X*-ray diffraction pattern obtained for this material suggests a fairly well ordered intercalate [Figure 2(*a*)], although the unusual shape of the (001) reflection coupled with the broad background near the (002) position suggests that there may also be an additional disordered component associated with this sample. Significantly, despite the excess of $FeCl_3$ used in this preparation, chemical analysis demonstrates (see Table 1) that for this compound less $FeCl_3$ is intercalated than in, for example, preparations A and C. Figure 3 illustrates the Mössbauer spectra observed at room temperature (*a*) and at 77 K (*b*). In both spectra two iron(III) species are resolved, with isomer shifts which, at room temperature, are distinctly different to the values expected for pure $FeCl_3$. The component with $\delta = 0.37$ mm s^{-1} may well arise[11] from $[FeCl_4]^-$, with the graphite matrix as the

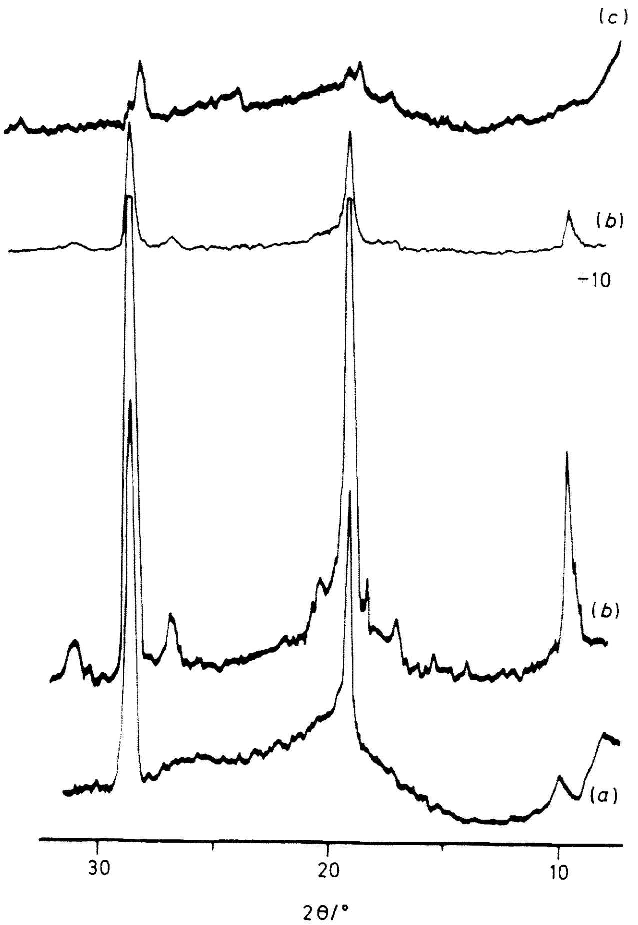


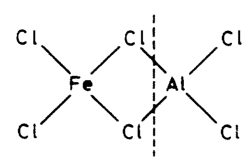
Figure 2. *X*-Ray diffraction traces of sample B: (*a*) fresh (blue) state; (*b*) after 40-min exposure to air (black); and (*c*) after 4 weeks in air

counter ion. This blue g.i.c. may then be appropriately described as a graphite salt of composition $C_x^+[FeCl_4]^-$. Such a salt-like formula has been earlier proposed to describe those $FeCl_3$ graphite intercalates prepared following the generally employed method A.[12] In addition, examples are known of mineral acid intercalates, which contain considerable amounts of neutral molecules between the charged units and which act as space fillers, *e.g.* H_2SO_4 in $C_8^+[HSO_4]^-\cdot 2.2H_2SO_4$.[13] The other iron(III) component in the spectrum is, therefore, thought to arise from some type of disordered $FeCl_3$, composed of regular $[FeCl_6]^{3-}$ octahedra, playing overall a similar role as H_2SO_4. It is clear from Table 2 that the isomer shifts and linewidths decrease with temperature: a pronounced temperature dependence for other $[FeCl_4]^-$ compounds has been previously reported,[14] although the actual value of the isomer shift does not readily distinguish between $[FeCl_4]^-$ and $[FeCl_6]^{3-}$, primarily because there is a pronounced dependence upon the identity of the counter ion.[11,14]

Exposure of this type of intercalate to air for 40 min results in the loss of the blue colour, in agreement with observations on other graphite salts, and a reversal in the intensity ratio of the two iron(III) components [Figure 3(*c*)], possibly indicating the gradual disappearance of the charged species and the loss of the (blue) charge-transfer complex. The process appears optically to occur initially at near-surface regions, suggesting that diffusion of water into the material is important.

The diffraction trace at this stage [Figure 2(*b*)] indicates that the material is still a well ordered first-stage compound with traces of highly disordered second- and third-stage components which are probably associated with the near-surface regions of the crystallites.[5] No identifiable crystalline products resulting from de-intercalation [*e.g.* $FeCl_3$ hydrates, FeO(OH), or FeOCl] occur. Following 4-weeks exposure of the sample to air the Mössbauer spectrum [Figure 3(*d*)] consists of a broad single absorption (of halfwidth 0.54 mm s^{-1}) which proved impossible to fit to more than one component. At this stage the diffraction trace is essentially structureless [Figure 2(*c*)] and gives no evidence of graphite or de-intercalated halide. The exact nature of the material is not clear.

(3) *Obtained using method D.* The Mössbauer spectrum obtained from a sample intercalated in the presence of $AlCl_3$ is shown in Figure 4(*a*). The particularly narrow singlet observed (of halfwidth 0.32 mm s^{-1}, see Table 2) may be assigned to a single $[FeCl_4]^-$ species which is close to that of the ' iron(III) salt ' described above; the absence of a second absorption in the spectrum, taken alongside the presence of a stoicheiometric amount of aluminium and the absence of the blue colour, suggests that in this case the nature of $[FeCl_4]^-$ is somewhat different. It is possible that the intercalant is the well established [15] dimeric complex shown below.



These results, when compared with those described previously,[10] clearly demonstrate the importance of the temperature at which intercalation occurs; the relatively low temperature of 250 °C used here apparently allows the intercalation of the complex. Energy-dispersive *X*-ray microanalysis confirms that extensive chlorination of the graphite has occurred during intercalation with the graphite matrix forming highly turbostratic, *ca.* 100-Å thick, particles.

The Mössbauer parameters obtained for a sample which was exposed to air for 4 weeks [see Figure 4(*b*)] are very similar to those of sample A after 60 h in air, consisting of the two singlets for intercalated $FeCl_3$ and the absorption corresponding to the hydrolysis product (at 0 mm s^{-1}).

Transmission electron microscopy at this stage clearly shows some de-intercalated material which from energy-dispersive *X*-ray microanalysis is known to be very rich in Al, and is presumably AlO(OH). The corresponding diffraction trace is essentially structureless. It should be noted that the Mössbauer spectrum, and in particular the component at *ca.* 0 mm s^{-1}, showed little change on cooling to 78 K. The dissociation of the iron–aluminium complex may be achieved by hydrolysis of the g.i.c. during exposure to air, the time-scale for this reaction being greatly reduced compared to normal AF-$FeCl_3$ g.i.c.s.[5]

Prolonged exposure to air results in a decrease in the recoil-free fraction [the accumulation time for the Mössbauer spectrum in Figure 4(*c*) increasing three-fold] with an increase in area for the absorption (at *ca.* 0 mm s^{-1}) associated with the hydrolysis product. Note that exposure to air of materials from preparation A results in a distinct high-velocity component around 0.8 mm s^{-1}; this component is still absent in samples from preparation D after exposure to air for 1 year.

(*B* *Crystalline* $FeCl_3$.—In order to rationalize the different chemical processes which accompany exposure of the

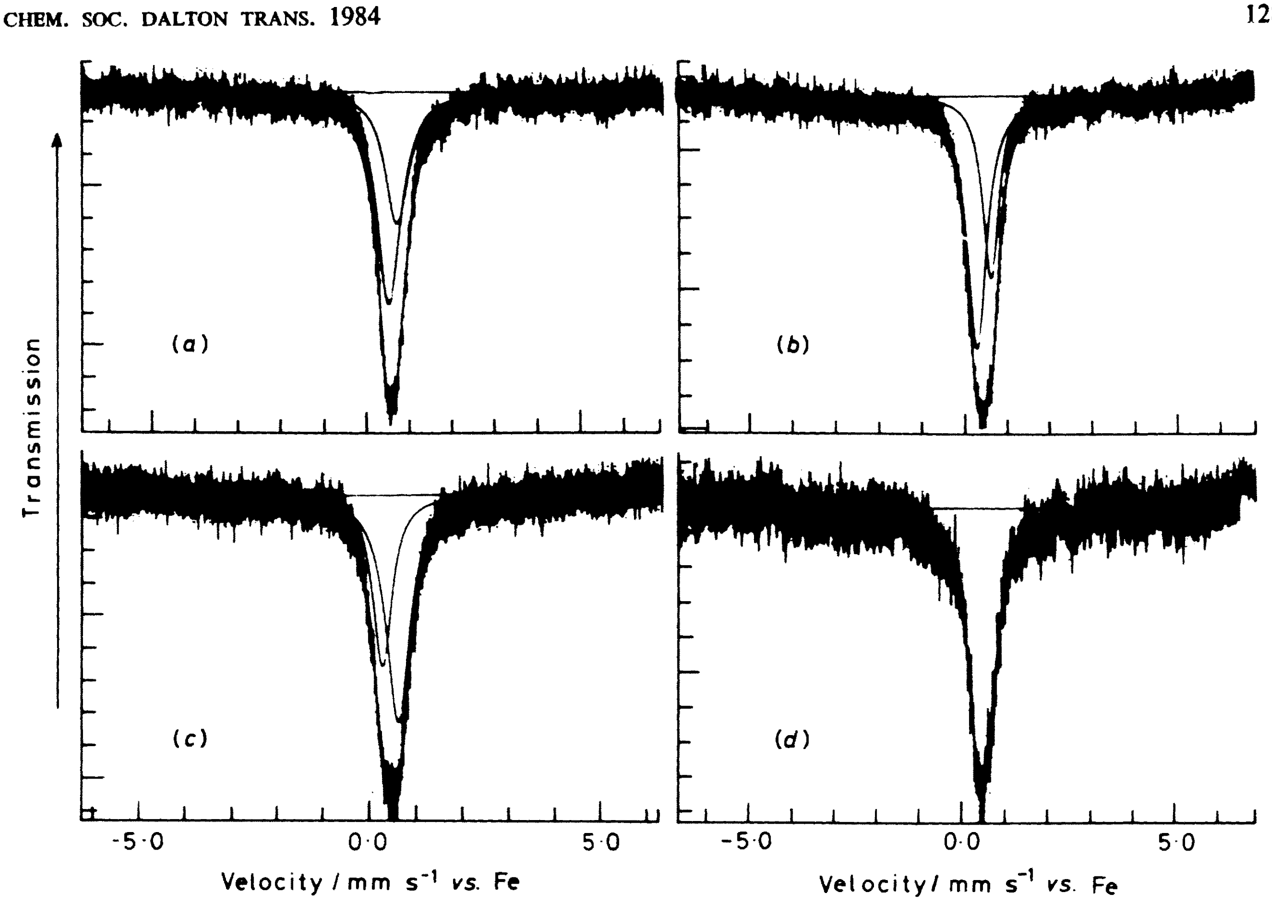


Figure 3. Mössbauer spectra of sample B. See text and Table 2

iron(III) chloride graphite intercalates, the hydration of crystalline $FeCl_3$ itself upon exposure to air was investigated. The Mössbauer spectrum obtained for anhydrous $FeCl_3$, accumulated with the sample under vacuum, is shown in Figure 5(*a*) and may be fitted to a single absorption with an isomer shift in good agreement with literature values [16] (see Table 2). The associated linewidths, however, are strongly influenced by the purification procedure adopted. The particular value of $\Gamma = 0.39$ mm s^{-1} quoted in Table 2 is for a sample purified by sublimation under a chlorine atmosphere and with subsequent storage under dry argon. Crystallization from non-aqueous solvents, such as $C_2H_4Cl_2$ or CCl_4, and u.v. irradiation of dispersions of $FeCl_3$ in CCl_4 increase the linewidth of the peak to 0.58 mm s^{-1}. Diffraction traces taken from these samples are, nevertheless, very similar.

The effect of exposure for these samples depends on the general accessibility of the material to air. In general two different reaction pathways are followed: direct exposure of $FeCl_3$ to air results in the rapid formation of a yellow corrosive liquid which contains HCl and from which a brown, partially crystalline precipitate is formed within *ca.* 24 h. The formation of a liquid, well documented in the literature,[17] was followed in detail for single crystals using an optical (transmission) microscope: the dark red crystals become, within seconds, yellow and polycrystalline; they then form a yellow liquid from which the brown precipitate forms. The diffraction pattern of this final product consists of a large number of very weak lines, which may be attributed to FeO(OH) and FeOCl. (Since the actual crystal parameters for these non-stoicheiometric compounds are highly preparation-dependent, comparison of literature data with the observed pattern is not unambiguous.)

The Mössbauer spectrum of the brown precipitate is shown in Figure 5(*b*). Although fitted to two iron(III) lines it is believed to represent $[FeCl_4]^-$ (low-velocity singlet) and a doublet ($\delta = 0.48$ mm s^{-1} and $\Delta = 0.96$ mm s^{-1}) which might be attributed to a chloride-containing iron oxyhydroxide. Since these compounds usually exhibit asymmetric doublets at room temperature and 78 K no attempt was made to separate the two sub-spectra. The parameters vary between those of γ-FeO(OH) ($\delta = 0.30$, $\Delta = 0.55$ mm s^{-1}), FeOCl ($\delta = 0.62$, $\Delta = 0.91$ mm s^{-1}), and the basic FeO(OH,Cl) ($\delta = 0.38$, $\Delta = 0.70$ mm s^{-1}).[16,18,19] It is known, furthermore, that dilute solutions of $FeCl_3$ in water contain, after ageing, precipitates of β-FeO(OH).[20] It is noteworthy that anhydrous $FeCl_3$ is not converted into $FeCl_3 \cdot 6H_2O$ following direct exposure to air.

The Mössbauer spectrum of $FeCl_3 \cdot 6H_2O$ (recrystallized from 6 mol dm^{-3} HCl) is shown in Figure 5(*c*). The distinct anisotropy is well understood in terms of both relaxation broadening of the low-velocity transition and a preferential orientation of the highly anisotropic crystals.[21] The structure of $FeCl_3 \cdot 6H_2O$ consists of chains of *trans*-$[FeCl_2(OH_2)_4]^+$ octahedra with additional chlorine and water molecules placed between.[22] The anisotropy in the Mössbauer spectrum results from the different bonding properties of the two *trans*-Cl ligands compared with the four equatorial water ligands. This is probably caused by a substantial π character of the Fe–Cl bond as reflected in the ligand-field parameters of hexa-aquairon(III).[23]

In order more closely to mimic the relatively slow access of water molecules which necessarily exists for the intercalated samples, a series of slow air-exposure experiments with pure anhydrous $FeCl_3$ were performed. Under these conditions no

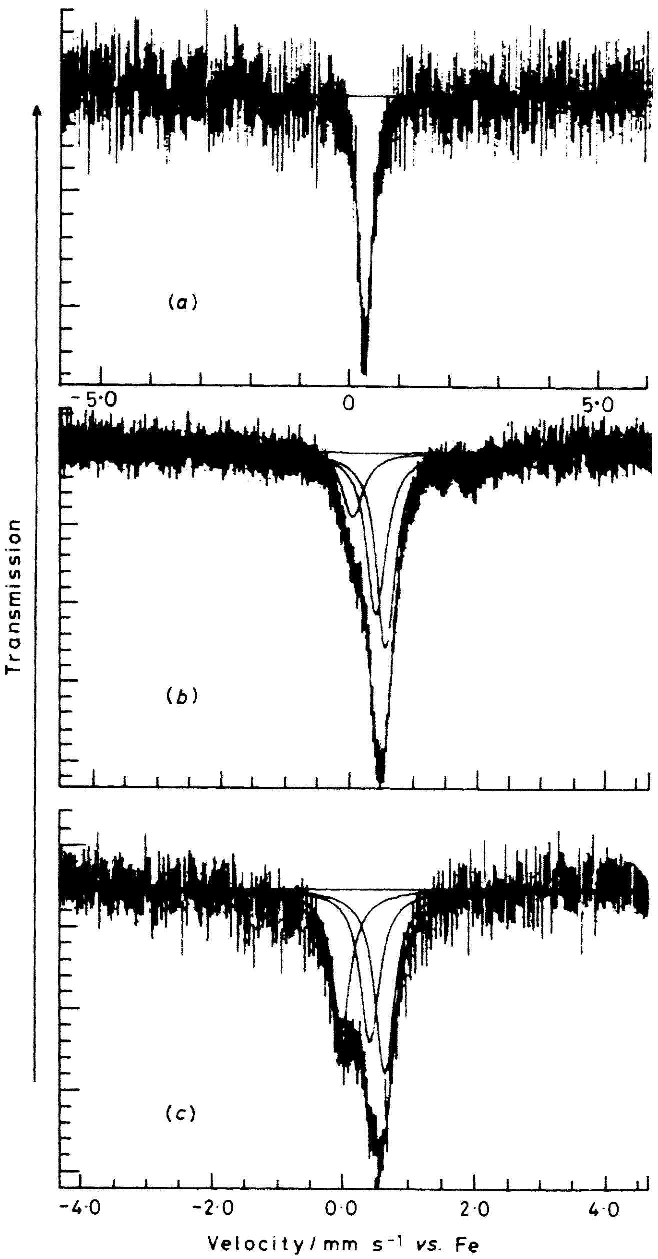


Figure 4. Mössbauer spectra of the intercalated $[AlCl_2]^+[FeCl_4]^-$ complex; (*a*) fresh; (*b*) after 4 weeks in air; and (*c*) after 12 weeks in air

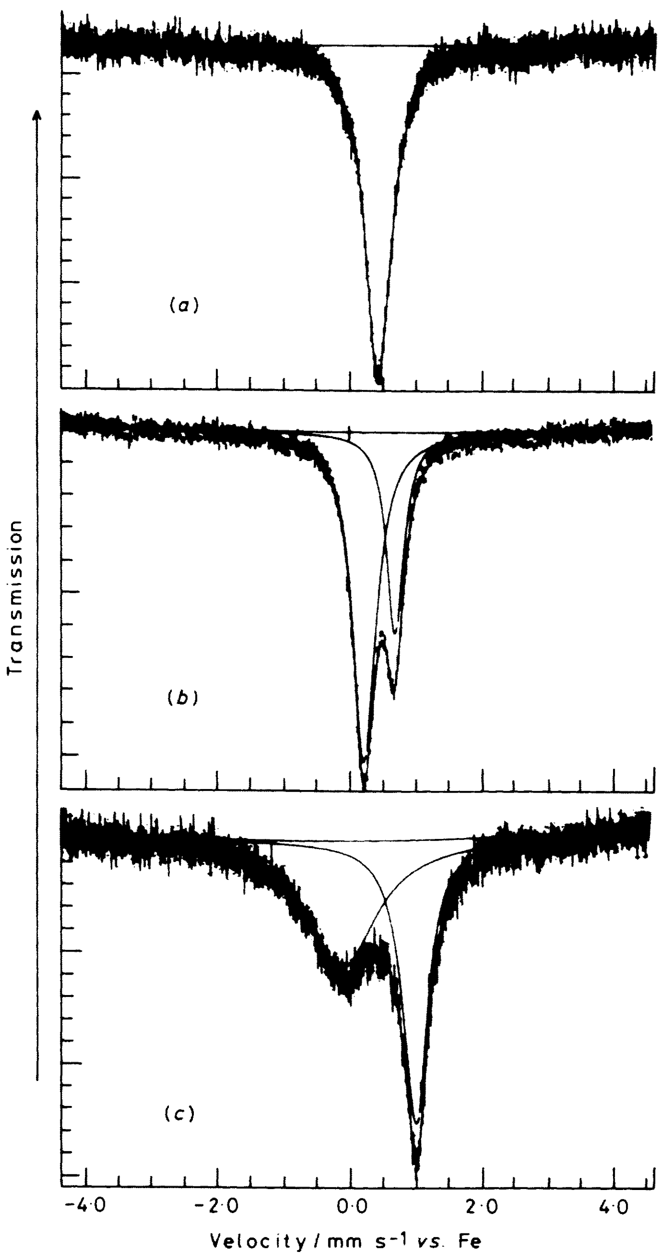


Figure 5. Room-temperature Mössbauer spectra of (*a*) anhydrous $FeCl_3$, accumulated under vacuum, (*b*) after 24-h rapid air exposure, and (*c*) of $FeCl_3{\cdot}6H_2O$

liquid intermediate product was formed. The brown product obtained from this reaction, however, immediately took up more water and yielded a liquid product on subsequent unhindered exposure to air. A series of Mössbauer spectra taken during slow exposure are shown in Figure 6. As may be seen two additional lines result which although invariant in position (see Table 2) grow to different intensities. The asymmetry increases steadily from about 1.2 to 2.6 and we conclude that this slow exposure to air proceeds *via* a gradual interconversion of previously identified, partially hydrated $FeCl_3$ phases.[24]

A recent study [25] of the iron(III) chloride–water phase diagram indicates that under equilibrium conditions $FeCl_3{\cdot}2H_2O$ is initially formed, followed by $2FeCl_3{\cdot}5H_2O$ and $2FeCl_3{\cdot}7H_2O$. The structures of these partially hydrated species are known from i.r.,[26] Mössbauer,[24] and *X*-ray diffraction studies,[27] and they all consist of octahedra of *trans*- or *cis*-$[FeCl_2(OH_2)_4]^+$ and tetrahedra of $[FeCl_4]^-$ with different amounts of lattice water. The Mössbauer spectrum of each hydrate is expected, therefore, to consist of two doublets, one for the cation and one for the anion. With this assumption two doublets have been previously fitted.[24] The parameters reported for the cation of the *trans* isomer range between $\delta = 0.58$ and 0.51 mm s^{-1} and $\Delta = 0.87$ and 0.79 mm s^{-1}, with, as expected, for the *cis* isomer a similar isomer shift but much smaller quadrupole splitting of $\Delta = 0.30$ mm s^{-1}. For the anionic component, literature for $[FeCl_4]^-$ clearly shows that the presence of a singlet or a doublet depends strongly on the associated cation.[11-14] Consequently, although possible, the previous fit [24] to a doublet with isomer shifts in the range

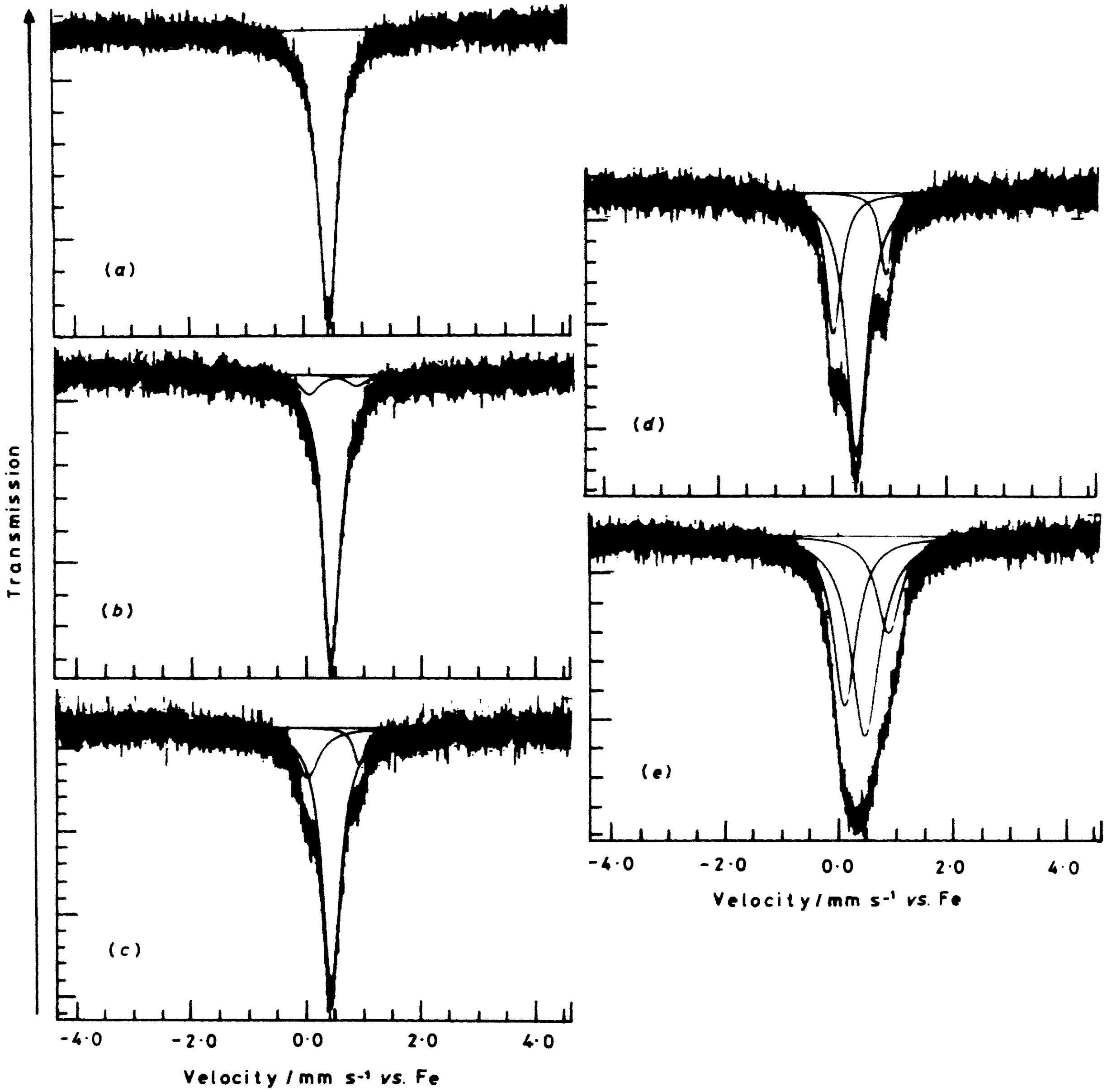


Figure 6. Mössbauer spectra following the slow exposure to air of anhydrous $FeCl_3$, see Table 2. Exposure times: (*a*) 0, (*b*) 24 h, (*c*) 48 h, (*d*) 72 h, and (*e*) 100 h

0.35—0.40 mm s^{-1} is not necessarily justified, especially when the unusually narrow linewidths [for an iron(III) species] of 0.26 and 0.28 mm s^{-1} are taken into account.[24]

Therefore we believe that the two asymmetric lines in Figure 6 may be attributed to a combination of *trans*-iron(III) chlorohydrate and $[FeCl_4]^-$, the latter either contributing to the low-velocity component or being hidden under the absorption of the residual anhydrous $FeCl_3$. The increasing anisotropy with exposure time may well suggest that the absorption around *ca.* 0 mm s^{-1} consists of two lines, although all attempts to fit two lines in that region were only partially successful.

The isomer shift of the doublet (*viz.* 0.44 mm s^{-1}, see Table 2) is smaller than that of *trans*-$[FeCl_2(OH_2)_4]^+$ ($\delta = 0.51$ and $\Delta = 0.58$ mm s^{-1})[24] suggesting that under the non-equilibrium conditions existing here a partially hydrated chloro-complex is formed. The presence of additional chlorine ligands accounts for the lower isomer shift as a result of an increased delocalization of valence electrons in the iron–chlorine bond, resulting from the accompanying π donation of the chlorine ligands (see later).

In order to confirm the presence of partially hydrated phases the slow exposure to air was simulated in a variable-temperature diffraction camera using the following procedure. Under dry nitrogen a sample of anhydrous $FeCl_3$ was mounted and warmed to 50 °C. The dry nitrogen flow was then stopped for 10 s and air was admitted to the camera. Afterwards a series of rapid diffraction patterns were recorded under nitrogen ($2\theta = 18$—$40°$). Figure 7 illustrates two patterns which clearly indicate the formation of crystalline $2FeCl_3{\cdot}7H_2O$.[28]

Discussion

(*A*) *Hydrolysis of Crystalline Iron*(III) *Chloride*.—We have demonstrated that two different reaction pathways exist upon exposure of $FeCl_3$ to air. Which particular pathway is followed

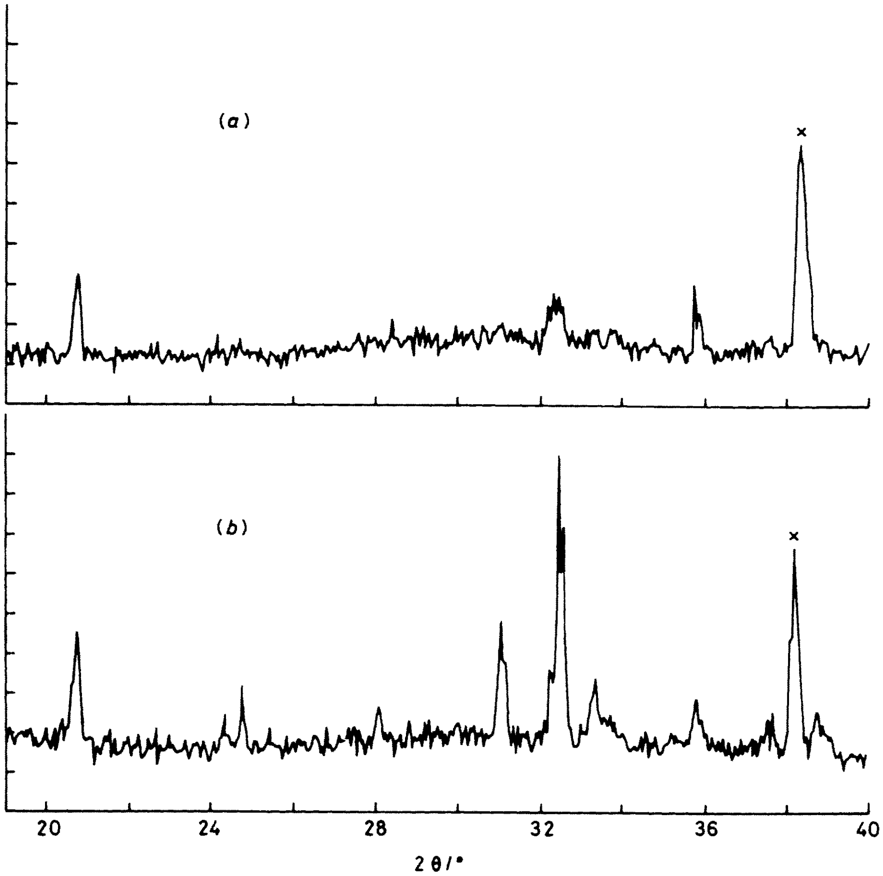
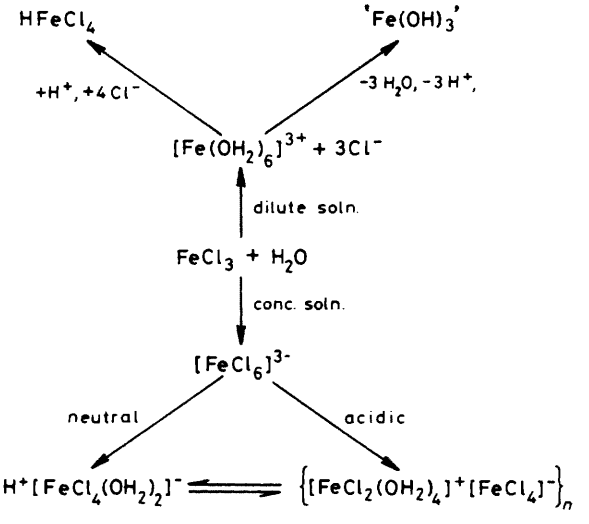
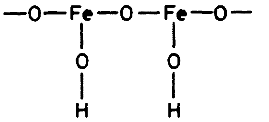


Figure 7. *X*-Ray powder diffraction traces of (*a*) anhydrous $FeCl_3$ and (*b*) after 10-s exposure to air. The additional reflections belong to $2FeCl_3{\cdot}7H_2O$; ×, reflections from the sample holder



Scheme.



$$-O-\underset{\substack{|\\ O\\ |\\ H}}{Fe}-O-\underset{\substack{|\\ O\\ |\\ H}}{Fe}-O-$$

appears to depend upon the rate of exposure, and the latter also determines whether or not a liquid intermediate product is formed. In order to interpret our results we draw upon data previously reported for the hydrolysis of $FeCl_3$ in liquid water[29] (see Scheme). In fairly dilute solutions[30,31] the predominant reactions are the formation of $HFeCl_4$, and hydrolysis followed by polycondensation to FeO(OH).[32] In highly concentrated solutions, however, the hydrolysis reaction is replaced by a partial ligand-exchange reaction, leading in moderately acidic solutions (of pH 3—4) to solution-stabilized $[FeCl_4]^-$ and some known species with co-ordination number less than four. These transform in more acidic media to polymer chains of *trans*-chloro-octahedra linked by $[FeCl_4]^-$ tetrahedra.[30]

In the rapid-air-exposure reactions reported here and which are, at least on the time-scale followed, non-equilibrium reactions, the situation corresponds more closely to the case of a dilute solution, with precipitates of FeO(OH) and residual $[FeCl_4]^-$. The possible counter ion $[FeCl_2]^+$ would not be resolved in our Mössbauer spectrum; $HFeCl_4$, adsorbed on the polycondensation product, is another possible description in agreement with the Mössbauer data.

The case where the exposure to air is slow may be considered relative to the concentrated solution case with excess of acid where, as mentioned above, ligand exchange takes place. This particular reaction will necessarily break up the close-packed chloride sub-lattice of the $FeCl_3$ structure.

Furthermore, the arrangement of the iron ions within the polymer is already preset for the subsequent exchange reaction leading to FeO(OH) (outside the present time-scale) *via* partially chlorinated intermediates of the type $FeOCl_{1-y}(OH)_y$.

Consequently, the solid-state reaction proceeds significantly faster than the formation of crystalline FeO(OH) from aqueous $FeCl_3$.[5,31]

(*B*) *Hydrolysis of Iron*(III) *Chloride Intercalates*.—Our present observations highlight how very different properties may be ascribed to $FeCl_3$ intercalates despite the apparent similarity of the material as evidenced by *X*-ray diffraction alone. The differences in the observed Mössbauer spectra,[6] which will also be manifested in other properties such as conductivity measurements, are related to the preparation conditions; the iron(III) chloride to graphite ratio determines (at sufficiently high temperatures) whether a graphite salt or the conventional g.i.c. is formed, and the chlorine overpressure controls the structural integrity of the resulting intercalate.[33] In the presence of $AlCl_3$ the temperature determines whether or not the ' catalyst ' is co-intercalated.

The identification of a blue $FeCl_3$ g.i.c. is a clear example of the fact that, as a result of a chemical reaction outside the graphite matrix, the actual material inserted may be significantly different to the starting compound and will lead, therefore, to different charge-transfer effects between the guest and the host. In this particular case the charge transfer resulting from intercalation is clearly not responsible for the resulting chemical nature of the guest species. Interestingly, this chemical transformation may, following air exposure, be reversed, inside the graphite sheets, leading to a well ordered normal $FeCl_3$ g.i.c. The subsequent reactions in air are then like those of other $FeCl_3$ g.i.c.s, the time-scale for reaction only being influenced by the large number of defects introduced during synthesis (partial exfoliation).

The observations made on the reaction of pure crystalline $FeCl_3$ in air enable us to give a fairly detailed picture of the chemistry involved in the de-intercalation of $FeCl_3$ g.i.c. This process, previously described for vapour-phase grown g.i.c.,[5] involves initially the partial hydration of the $FeCl_3$ layers inside the graphite sheets. During this ligand-exchange reaction a new type of ternary g.i.c. is formed, the existence of which has been previously proposed.[34] The charge transfer from the graphite modifies [35] the π interaction within the iron–chlorine bond of the intercalated $FeCl_3$ and prevents the occurrence of a stoicheiometric reaction. This leaves the major amount of $FeCl_3$ unreacted, along with a fraction of intercalated $[FeCl_{2+x}(OH_2)_{4-x}]^{(1-x)+}$, with either graphite or $[FeCl_4]^-$ as the counter ion. It is, however, difficult to assess to what extent the course of this reaction is stereochemically controlled by the surrounding graphite sheets. The graphite layers may well limit the diffusion of water and lead to reaction only at the edges of a crystallite or a particular $FeCl_3$ domain. After this ' electronic ' de-intercalation the ' physical ' de-intercalation with phase separation may well be induced by ligand exchange of the chlorohydrate polymers to FeO(OH) which does not interact with the graphite and is therefore de-intercalated.

In a recent series of publications [6,36] the Mössbauer spectra of first- and second-stage $FeCl_3$ highly oriented pyrolytic graphite intercalates were analysed predominantly in terms of the low-temperature magnetic behaviour of such materials. The room-temperature spectra were fitted with a single line. We have obtained similar spectra, but find an improved fit with two iron(III) species, the average of which closely corresponds to the previous single value. In addition, reduction of such materials leads to two distinct iron(II) species. It should be noted that the Mössbauer spectra reported for in-plane undersaturated intercalates [6,37] resemble very closely those obtained during exposure of bulk $FeCl_3$ to air. The previous interpretation of these spectra [6,36] in terms of ' vacancies ' in the $FeCl_3$ structure has been supported by photoemission studies.[38] However, because it is now clear that iron(III) chloride graphites are air sensitive, we would attribute the formation of vacancies to the hydration reaction described above. Because of this, it is not surprising that such samples do not show, at low temperatures, either magnetic ordering or the localization of electron density from the graphite to the iron(III) sites,[6] effects which might otherwise have been expected.[36]

Conclusions

This paper demonstrates how different the properties of a material known as $FeCl_3$ g.i.c. may be, and how the preparation details control some of these properties. Furthermore, it shows clearly that neither *X*-ray diffraction nor Mössbauer spectroscopy alone is able to characterize adequately the intercalate. Taken together, however, these techniques yield a somewhat more realistic picture.

The chemistry of the guest material itself plays a much more important role in the determination of the composition and properties of a given g.i.c. than is generally assumed.[2] It is believed to be of greater significance than any effect of charge transfer accompanying intercalation.

In much the same way that water may replace the original chlorine ligands of the intercalated metal halide, it ought to be possible systematically to prepare new graphite intercalates with guest molecules which may not otherwise be inserted.

Acknowledgements

We appreciate the financial support of the S.E.R.C. and the National Coal Board.

References

1 M. S. Whittingham and L. B. Ebert, in ' Intercalated Materials,' ed. F. Levy, D. Reidel, Holland, 1979, p. 533.
2 J. E. Fisher, in ' Intercalated Materials,' ed. F. Levy, D. Reidel, Holland, 1979, p. 481.
3 A. Herold, ' Physics of Intercalation Compounds,' eds. L. Pietronero and E. Tosatti, Springer, Berlin, 1981, p. 7.
4 W. C. Forsman, T. Dziemianowicz, K. Leong, and D. Carl, *Synth. Met.*, 1983, **5**, 77.
5 R. Schlögl, P. Bowen, G. R. Millward, W. Jones, and H. P. Boehm, *J. Chem. Soc., Faraday Trans. 1*, 1983, 1793.
6 S. E. Millman, M. R. Corson, and G. R. Hoy, *Phys. Rev. B*, 1982, **25**, 6595.
7 R. Schlögl and H. P. Boehm, *Carbon*, 1983, **21**, 345.
8 R. Wacknik, R. Vangelisti, E. McRae, A. Herold, and F. Vogel, Extended Abstracts, Carbon '80, Int. Carbon Conf., Baden-Baden, 1980, p. 120.
9 E. Stumpp and G. Nietfeld, *Z. Anorg. Allg. Chem.*, 1979, **456**, 261.
10 T. Tominaga, T. Sakai, and T. Kimura, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 2755.
11 P. R. Edwards and C. E. Johnson, *J. Chem. Phys.*, 1968, **49**, 211.
12 M. L. Dzurus and G. R. Hennig, *J. Am. Chem. Soc.*, 1957, **79**, 1051.
13 W. Rudorff and U. Hoffmann, *Z. Anorg. Allg. Chem.*, 1938, **283**, 1.
14 P. R. Edwards, C. E. Johnson, and R. J. P. Williams, *J. Chem. Phys.*, 1967, **47**, 2074.
15 H. Schafer, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 713.
16 N. N. Greenwood and T. C. Gibbs, ' Mössbauer Spectroscopy,' Chapman and Hall, London, 1971.
17 D. Nicholls, in ' Comprehensive Inorganic Chemistry,' Pergamon Press, Oxford, 1973, vol. 3, p. 1039.
18 E. Kostener and J. Steger, *J. Solid State Chem.*, 1971, **3**, 273.
19 C. E. Johnson, *J. Phys. C, Ser. 2*, 1969, **2**, 1996.
20 S. Music, J. Nagy-Czako, and A. Vertes, *Colloid Polym. Sci.*, 1980, **258**, 469.

21 N. Thrane and G. Trumpy, *Phys. Rev. B*, 1970, **1**, 153.
22 M. D. Lind, *J. Chem. Phys.*, 1967, **47**, 990.
23 S. Balt and A. M. A. Verwey, *Spectrochim. Acta, Part A*, 1967, **23**, 2069.
24 C. Bordeleau and D. R. Wiles, *Inorg. Chim. Acta*, 1980, **41**, 194.
25 L. A. Akerman and E. D. Kuznets, *Khim. Promst. Ser. Kholornaya Promst.*, 1981, p. 13 (*Chem. Abstr.*, 1981, **95**, 95-231141).
26 L. T. Kossar-Nechan and J. Roziere, *C.R. Acad. Sci., Ser. C*, 1974, **279**, 461.
27 J. T. Szymanski, *Acta Crystallogr., Sect. B*, 1979, **35**, 1958.
28 JCPDS card no. 1-0132.
29 H. L. Friedman, *J. Am. Chem. Soc.*, 1952, **74**, 5.
30 G. W. Brady, M. B. Robin, and J. Varimbi, *Inorg. Chem.*, 1964, **3**, 1168.
31 W. Feitknecht, R. Giovanoli, W. Michaelis, and M. Muller, *Z. Anorg. Allg. Chem.*, 1975, **417**, 114.
32 T. Misawa, K. Hashimoto, W. Suetaka, and S. Shimodaira, *J. Inorg. Nucl. Chem.*, 1973, **35**, 4159.
33 W. Metz and D. Holwein, *Carbon*, 1975, **13**, 84.
34 D. Berger and J. Maire, *Mater. Sci. Eng.*, 1977, **31**, 331.
35 R. Schlögl, W. Jones, and H. P. Boehm, *Synth. Metals.*, 1983, **7**, 133.
36 S. E. Millman and G. Kirczenow, *Solid State Commun.*, 1982, **44**, 1217.
37 S. E. Millman, *Synth. Metals*, 1983, **5**, 147.
38 G. K. Wertheim, P. M. Th. M. van Attekum, H. J. Guggenheim, and K. E. Clements, *Solid State Commun.*, 1980, **32**, 809.

Received 23rd *May* 1983; *Paper* 3/830