Inorg. Chem. **2002**, *41*, 6211–6216

Inorganic Chemistry
Article

Analysis of Problematic Complexing Behavior of Ferric Chloride with *N*,*N*-Dimethylformamide Using Combined Techniques of FT-IR, XPS, and TGA/DTG

Young Jeon Kim and Chong Rae Park*

Enviro-Polymers Design Laboratory, Hyperstructured Organic Materials Research Center (HOMRC) and School of Materials Science and Engineering, Seoul National University E445-F, Seoul 151-744, Korea

Received December 26, 2001

A problematic coordination behavior of highly hygroscopic $FeCl_3$ in DMF solution was studied. From the compositional and structural analyses for the adduct of $FeCl_3$/DMF using various techniques such as FTIR, elemental analysis, UV/vis, XPS, and TGA/DTG, it was found that the iron cation exists in the form of an Fe^{3+} cation and coordinates via the carbonyl oxygen atom of amide bond in DMF. The analyses of both FT-IR and XPS C 1s spectra for the adduct revealed that 2.1 molecules of DMF coordinate with a more electron-deficient Fe^{3+}; otherwise 1.2 molecules of DMF coordinated with a relatively electron-rich Fe^{3+}. The Cl 2p spectrum indicated that the electron-deficient Fe^{3+} coordinated with two chlorine ions and the electron-rich Fe^{3+} with four chlorines so that the chemical formula of the adduct is of $[FeCl_2(DMF)_{1.2}(H_2O)_{2.7}]^+[FeCl_4(DMF)_{2.1}]^-$. The water molecules in the adduct were found chemisorbed rather than physisorbed, with a singular binding energy.

Introduction

Of common solvents which have been used in organic and/or inorganic reactions, MeCN, pyridine, Me_2SO (DMSO), and DMF may be the ones most likely to act as ligands and therefore perhaps to divert the reactions using a catalyst from their intended goal.[1] For DMF, the simplest disubstituted carboxylic acid amide, many researchers have reported the adducts between DMF and various metallic catalysts, such as 3d transition metals, e.g. $Mn(DMF)_6(ClO_4)_3$,[2] the 2B family,[3] Cd_2Cl_4·3DMF, Zn_2Cl_4·2DMF, and Hg_3Cl_6·2DMF, and the 4B family,[4] $TiCl_4$·2DMF and $ZrCl_4$·2DMF.

However, for 8B transition metals, such as iron, cobalt, and nickel, that are very hygroscopic, the chemical composition and the coordination complex structure have been somewhat in dispute. For example, when ferric chloride ($FeCl_3$) was dissolved in DMF and then recrystallized by solvent evaporation at room temperature under reduced pressure of 0.6 Torr, the obtained yellowish crystalline complex was reported to have the composition of $FeCl_3$·3DMF, being insoluble in nonpolar solvents, such as ether or ethyl acetate.[5] However, when Yilmaz et al.[3] prepared the same system by dissolving anhydrous $FeCl_3$ in an excess amount of DMF and crystallizing the adduct after 2 h of stirring, the composition was Fe_2Cl_6·3DMF·$2H_2O$, characterized by UV/vis and IR spectral and thermal analyses. Despite the difference in the reported composition of the $FeCl_3$/DMF coordination complex system, there has not been any further study on this issue. Moreover, even in the previous studies, the coordination behavior of $FeCl_3$ with DMF and/or water molecules was not fully understood.

It is thus the aim of this work to clarify the above-mentioned problematic situation, using various techniques such as elemental and thermal analyses, FT-IR, UV−vis, and X-ray photoelectron spectroscopy (XPS). Although XPS has been conventionally used to investigate the electronic status and distribution around a specific probe atom,[6−10] it was tried

---

* To whom correspondence should be addressed. E-mail: crpark@snu.ac.kr. Tel: +82-2-880-8030. Fax: +82-2-885-1748.

(1) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; John Wiley & Sons: New York, 1994.
(2) Prabhakaran, J. P.; Patel, C. C. *J. Inorg. Nucl. Chem.* **1968**, *30*, 867−869.
(3) Yilmaz, Y. T.; Topcu, Y. *Thermochim. Acta* **1997**, *307*, 143−147.
(4) Randall, E. W.; Yoder, C. M. S.; Zuckerman, J. J. *Inorg. Chem.* **1966**, *5*, 2240−2242.
(5) U.K. Patent No. GB774956 to BASF AG, 1957.
(6) Briggs, D.; Seah, M. P. *Practical Surface Analysis*; John Wiley & Sons: New York, 1990; Vol. 1.
(7) Miao, Q.; Yie, X.; Xin, X.; Adachi, H.; Tanaka, I. *Appl. Surf. Sci.* **2001**, *171*, 49−56.
(8) Malengreau, F.; Hautier, V.; Vermeersch, M.; Sporken, R.; Caudano, R. *Surf. Sci.* **1995**, *330*, 75−85.

10.1021/ic011306p CCC: $22.00

Table 1. Atomic Compositions of cc-$FeCl_3$ Obtained from the Elemental Analysis and the Relative Peak Area in XPS High-Resolution Spectra

composn	method	param	C^a	N^a	H^a	O	Fe	Cl
$(FeCl_3)_2(DMF)_{3.3}(H_2O)_{2.7}$	EA	wt %	19.33 (19.50)	7.61 (7.58)	3.33 (4.66)		69.733	
	XPS	area	6914	2938		9715	14 883	10 967
		mol	4.9	1.3		2.9	0.9	3

[a] Calculated value in parentheses.

in this study to apply the XPS technique to the elucidation of the coordination complex structure both quantitatively and qualitatively, which had never been done in earlier studies.

Experimental Section

Materials and Formation of the $FeCl_3$/DMF Coordination Complex (cc-$FeCl_3$). Considering that a compositional difference was reported even though experimental procedures were almost the same in the previous two studies, basically the same experimental procedures as in the previous studies[3,5] were followed to avoid the complexity in the coordination structure that may be caused by adopting different experimental procedures.

Anhydrous iron(III) chloride (97%, Fluka, USA) (0.283 g) was completely dissolved in excess DMF (99%, Daejong, Korea) that was distilled before use to get a clear yellow solution under dried N_2 atmosphere. After thorough dissolution, the excess DMF was vacuum-evaporated at 55 °C for 5 days to get a pale yellow crystalline powder (recrystallization). The yellowish crystalline compound was finally obtained after washing with anhydrous dimethyl ether (98%, Daejong, Korea) and drying in a vacuum at 55 °C.

Structural Characterization of cc-$FeCl_3$. Interaction between the metal and DMF molecules was monitored with a KBr-pelleted sample on an FT-IR spectrometer (Perkin-Elmer Spectrum 2000 spectrometer, USA) with a scan number of 32 and a resolution of 4 cm^{-1}.

C, H, and N elemental analyses were carried out with a CHNS-932 (LECO, USA), and thermogravimetric analysis (TGA) was carried out on a TGA/DTA220 (Seiko, Japan) with heating rate of 2 °C/min under dry nitrogen atmosphere from 20 to 500 °C.

XPS spectra were recorded on a Surface Science Instruments spectrometer (SSI, 2803-S) equipped with a monochromatic Al Kα X-ray source of 200 W (base pressure $< 1 \times 10^{-9}$ Torr). The pass energy was 44.75 eV (0.5 eV steps) and 17.90 eV (0.05 eV steps) for the survey and high-resolution spectra, respectively. A takeoff angle of 75° relative to the surface plane was used to obtain all spectra. All the XPS spectra were corrected for charging effect by referencing the C 1s peak of hydrocarbons to 285.0 eV. High-resolution spectra were analyzed to identify various chemical species present. Each spectrum was curve-deconvoluted using the XPSPEAK2 software.[11,12] Quantification of XPS spectra was achieved by curve integration after baseline correction using a Shirley baseline equation and correcting the integrated area using each elemental sensitivity factor.

To examine the status of the iron cation, the UV−visible spectrum was recorded on a 8452A diode-array UV−visible spectrophotometer (Hewlett-Packard, USA).[13−15]

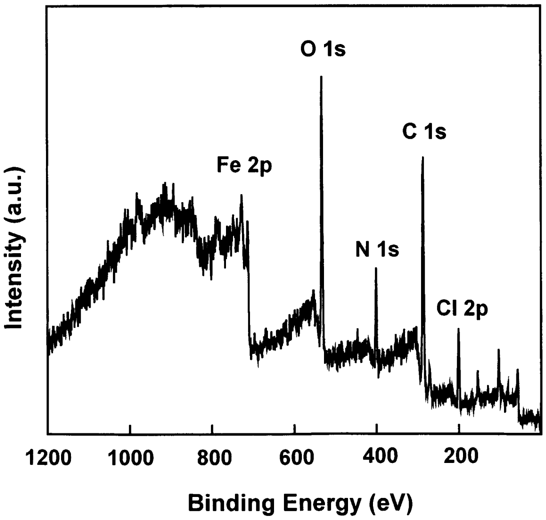


Figure 1. XPS survey spectrum of cc-$FeCl_3$.

Results and Discussion

Composition of cc-$FeCl_3$. To determine the chemical composition of cc-$FeCl_3$, the XPS survey spectra and elemental analyses were obtained and the results were shown in Figure 1 and Table 1. Figure 1, exhibiting five characteristic peaks corresponding to C 1s, O 1s, N 1s, Fe 2p, and Cl 2p, apparently shows that the intensity of the O ls peak is considerably higher than the expected one from DMF, while the peak intensities of the other atoms, such as C 1s and N 1s, remain the same compared with the theoretically expected one from DMF. This observation implies that another chemical species containing an oxygen atom may exist in cc-$FeCl_3$. Indeed, the FT-IR spectrum of cc-$FeCl_3$, shown in Figure 2, suggests the existence of a water molecule in the cc-$FeCl_3$, evidenced by the appearance of the peak at 3300 cm^{-1} arising from an −OH group. The involvement of moisture in the adduct may be likely due to the hygroscopicity of $FeCl_3$.

From the quantitative analyses by XPS and elemental analysis as shown in Table 1, the composition of cc-$FeCl_3$ could be determined as $(FeCl_3)_2(DMF)_{3.3}(H_2O)_{2.7}$. Compared with the two earlier studies, the present result is in very good agreement with the result of Yilmaz et al., i.e., $(FeCl_3)_2(DMF)_3(H_2O)_2$, despite the bit higher amounts of DMF and H_2O. The involvement of H_2O in the adduct formation and the subtle discrepancy in the chemical composition may indeed be caused by the hygroscopicity of

---

(9) Graat, P. C. J.; Somers, M. A. J. *Appl. Surf. Sci.* **1996**, *100/101*, 36−40.
(10) Ardizzone, S.; Bianchi, C. L.; Fadoni, M.; Vercelli, B. *Appl. Surf. Sci.* **1997**, *119*, 253−259.
(11) Kim, D. H.; Jo, W. H. *Macromolecules* **2000**, *33*, 3050−3058.
(12) Losito, I.; De Giglio, E.; Cioffi, N.; Malitesta, C. *J. Mater. Chem.* **2001**, *11*, 1812−1817.
(13) Caemelbecke, E. V.; Will, S.; Autret, M.; Adamian, V. A.; Lex, J.; Gisselbrecht, J.-P.; Gross, M.; Vogel, E.; Kadish, K. M. *Inorg. Chem.* **1996**, *35*, 184−192.
(14) Arulsamy, N.; Bohle, D. S.; Hansert, B.; Powell, A. K.; Thomson, A. J.; Wocaldo, S. *Inorg. Chem.* **1998**, *37*, 746−750.
(15) Durfey, D. A.; Kirss, R. U.; Frommen, C.; Feighery, W. *Inorg. Chem.* **2000**, *39*, 3506−3514.

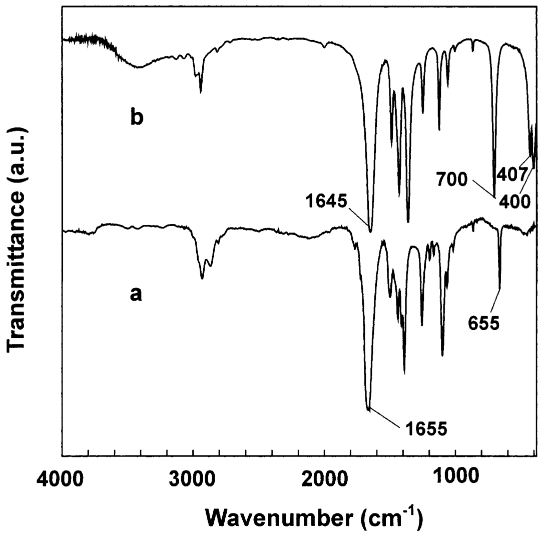


Figure 2. FT-IR spectra of (a) DMF and (b) cc-$FeCl_3$.

Table 2. Donor Number (DN), Acceptor Number (AN), and Relative Permittivity (Dielectric Constant, ϵ/ϵ_0) of Selected Solvents[a,16]

solvent	DN	AN	ϵ/ϵ_0
acetic acid		52.9	6.2
acetone	17.0	12.5	20.7
benzene	0.1	8.2	2.3
carbon tetrachloride		8.6	2.2
dimethylformamide (DMF)	24.0	16.0	36.7
ethanol	19.0	37.1	24.3
methanol	20.0	41.3	32.6
propionitrile	16.1		
pyridine (py)	33.1	14.2	12.3
tetrahydrofuran	20.0	8.0	7.3

[a] The ratio ϵ/ϵ_0 is more convenient to use than the value of the permittivity in absolute units.

$FeCl_3$ with which the measure of hydration varies inevitably with the experimental conditions.

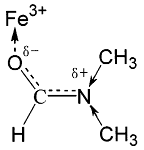
Coordination Sites. To find out the coordination site, the nature of interaction between $FeCl_3$ and DMF was investigated using transmission FT-IR spectroscopy for DMF and cc-$FeCl_3$, respectively.

From the viewpoint of coordination site, DMF has two possible ligands, i.e., oxygen in the C═O and nitrogen in the C−N bond. Gutmann[16] has introduced the donor number (DN) and acceptor number (AN) as a measure of the basicity and acidity of a solvent, respectively, to describe the measure of interactions between metal and nonaqueous solvent molecules. Donor number is defined as the negative reaction enthalpy of a base with the Lewis acid antimony pentachloride, $SbCl_5$:

$$B + SbCl_5 \rightarrow B \rightarrow SbCl_5 \quad DN_{SbCl_5} \equiv -\Delta H_r$$

These donor numbers provide an interesting comparison of the relative donor abilities of the various solvents (see Table 2). Since DMF has DN and AN values (DN = 24.0, AN = 16.0[16]) similar to those of pyridine (DN = 33.1, AN = 14.2) that has been generally known as one of the best donors, DMF is likely to behave a strong donor.

Chart 1. Resonance Structure of DMF in cc-$FeCl_3$



As shown in Figure 2, DMF shows characteristic absorption bands[17] at 1655 and 655 cm^{-1}. When DMF binds to $FeCl_3$, the band at 1655 cm^{-1} shifts to 1645 cm^{-1} due to the weakening of the double-bond nature of the carbonyl bond, the one at 655 cm^{-1} shifts to 700 cm^{-1}, possibly due to the increase in the order of the amide C−N bond[3,4] (see Chart 1), and new peaks appear at 400 and 407 cm^{-1}, which can be attributed to Fe−O bond formation,[18] as shown in Figure 2b.

The appearance of a lower shifted peak at 1645 cm^{-1}, a higher shifted peak at 700 cm^{-1}, and the F−O bond formation indicate that $FeCl_3$ coordinates to an oxygen atom in the C═O bond but not to the nitrogen atom of DMF. And double peaks at 400 and 407 cm^{-1} attributed to the Fe−O bond may imply the existence of two different kinds of coordination conditions between $FeCl_3$ and DMF. The details of this issue are discussed in the following sections.

Coordination Complex Structure of cc-$FeCl_3$. To examine the nature of the Fe−O bond in cc-$FeCl_3$, the high-resolution XPS spectrum of each component atom was obtained. First of all, with the inspection of the Fe 2p spectrum shown in Figure 3, two characteristic peaks of Fe 2p3/2 and Fe 2p1/2 with broad satellites were observed at 711.6 and 724.8 eV, respectively. Graat and Somers[9] reported from the study of iron oxide films that Fe^{3+} cation exhibits the two characteristic peaks of Fe 2p3/2 and Fe 2p1/2 at 711.2 and 724.3 eV, with two satellite peaks at 719.5 and 733.6 eV, respectively. For the Fe^{2+}cation, the two characteristic peaks appear at 709.8 and 722.8 eV, with two satellites at 716.4 and 730.0 eV, respectively. Although there is some overlap, due to the broadness in satellite peaks, between the literature reported and the experimentally observed, Figure 3 clearly shows that the two characteristic peaks coincide with those of literally reported for Fe^{3+} cation. This observation is also supported by the UV−vis spectrum of cc-$FeCl_3$ shown in Figure 4 that exhibits two separate peaks: one is a strong and sharp peak at $\lambda_{max} = 275$ nm, and the other is a relatively low-intensity peak at $\lambda_{max} = 475$ nm. The peak at $\lambda_{max} = 275$ nm can be attributed to a $\pi \rightarrow \pi^*$ transition of the resonance structure of DMF in cc-$FeCl_3$ as shown in Chart 1.[19,20] The peak at $\lambda_{max} = 475$ nm can be due to the O → Fe^{3+} charge-transfer complex as indicated by earlier studies.[21−23] It may thus be possible to

---

(16) Gutmann, V. *The Donor−Acceptor Approach to Molecular Interactions*; Plenum: New York, 1978.

(17) Pavia, D. L.; Lampman, G. M.; Kriz, G. S., Jr *Introduction to Spectroscopy: A Guide for Students of Organic Chemistry*; W. B. Saunders Co.: Philadelphia, PA, 1979.

(18) Nakamato, N. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1978.

(19) Stranger, R.; Mcgrady, J. E.; Arnold, D. P.; Lane, I.; Heath, G. A. *Inorg. Chem.* **1996**, *35*, 7791−7797.

(20) Graf, D. D.; Mann, K. R. *Inorg. Chem.* **1997**, *36*, 141−149.

(21) Nozaki, C.; Kiyoto, I.; Minai, Y.; Misono, M.; Mizuno, N. *Inorg. Chem.* **1999**, *38*, 5724−5729.

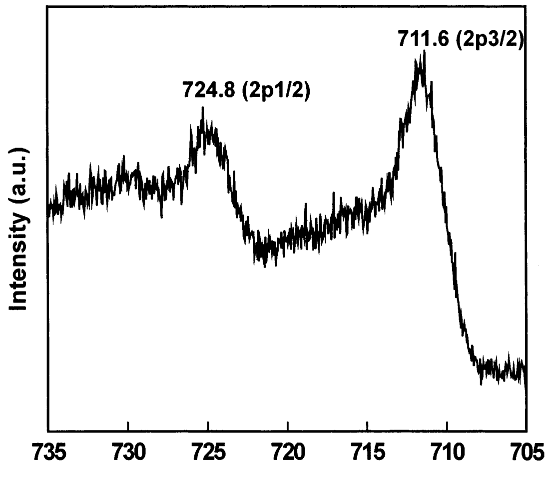


Figure 3. XPS high-resolution spectrum of Fe 2p in cc-$FeCl_3$.

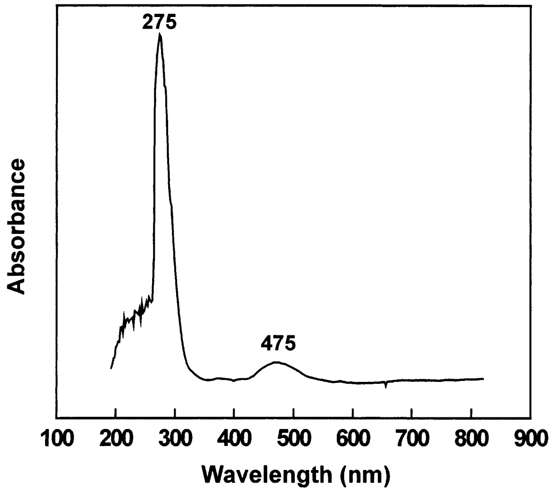


Figure 4. UV−visible spectrum of cc-$FeCl_3$ in DMF.

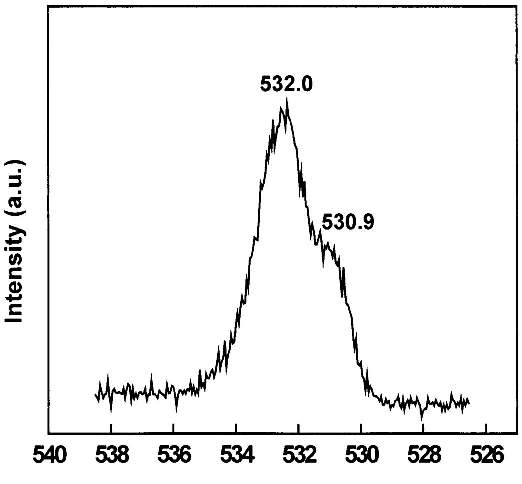


Figure 5. XPS high-resolution O 1s spectrum of cc-$FeCl_3$.

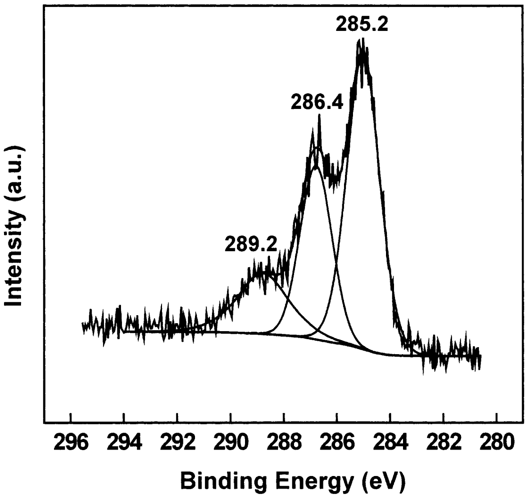


Figure 6. Curve-fitted XPS high-resolution C 1s spectrum of cc-$FeCl_3$.

draw a tentative conclusion at this juncture that the bond of Fe−O is of the Fe^{3+}−O type rather than anything else.

However, from the two peaks of Fe−O at 400 and 407 cm^{-1} in the FT-IR spectrum and the above discussion for the peaks in the Fe 2p spectrum, we may possibly expect two different binding energy states of Fe^{3+}−O bond. It is thus necessary to examine closely the O 1s spectra of the DMF molecule and cc-$FeCl_3$ as shown in Figure 5. There are apparently two peaks that may be identified as one from an absorbed H_2O molecule at 532.0 eV[24−27] and another from DMF at 530.9 eV. But it should be noted here that the area of the peak at 532.0 eV is higher than the expected value, i.e., 2.7:3.3, from the composition of the $(FeCl_3)_2(DMF)_{3.3}(H_2O)_{2.7}$ complex. So, it would be reasonable to postulate that this peak consists of more than one component peak. By recollection that the two characteristic absorption bands due to the formation of the Fe−O bond were observed in the FTIR spectrum (see Figure 2), it can be reasoned that an additional component peak contributing to the intensity of the peak at 532.0 eV would come from the one type of O 1s of DMF molecules of two different coordination states in $(FeCl_3)_2(DMF)_{3.3}(H_2O)_{2.7}$.

To manifest the above argument, further analyses on the detailed structures of $(FeCl_3)_2(DMF)_{3.3}(H_2O)_{2.7}$ were carefully made with C 1s and Cl 2p spectra.

As shown in Figure 6, the high-resolution spectrum of C 1s shows three definite peaks due to the carbon atoms with different binding environments. Since the carbon atoms are included only in DMF, three peaks may be attributed to the two carbon atoms of the methyl groups and the one in the amide carbonyl group. However, since the two methyl carbons have identical electron densities at the core level and the electron density can only be changed within at most two neighboring bonds from the coordination site, it is likely that the electron densities of those two methyl carbon atoms remain almost intact even though the environments around

---

(22) Zonnevijlle, F.; Tourne, C. M.; Tourne, G. F. *Inorg. Chem.* **1982**, *21*, 2751−2757.
(23) Mohamed, N. A. *Eur. Polym. J.* **1998**, *34*, 387−398.
(24) McIntyre, N. S.; Zetaruk, D. G. *Anal. Chem.* **1977**, *49*, 1521−1529.
(25) Pratt, A. R,; Muir, I. J.; Nesbitt, H. W. *Geochim. Cosmochim. Acta* **1994**, *58*, 827−841.
(26) Banerjee, D.; Nesbitt, H. W. *Geochim. Cosmochim. Acta* **2001**, *65*, 1703−1714.
(27) Herman, G. S.; McDaniel, E. P.; Joyce, S. A. *J. Electron Spectrosc.* **1999**, *101*−*103*, 433−438.

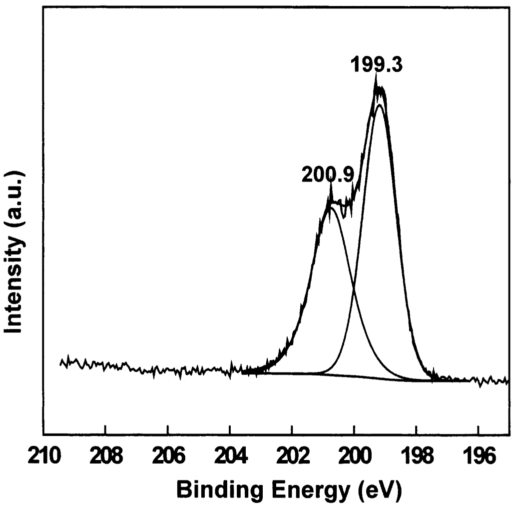


Figure 7. Curve-fitted XPS high-resolution Cl 2p spectrum of cc-$FeCl_3$.

the coordination site varies. It is thus reasonable for three peaks to expect that, in addition to a single peak by the two methyl carbons, there exist two different coordination states of carbonyl oxygen so that the binding energy at the core level of carbonyl carbon becomes higher to a different extent due to the difference in the induction of electrons surrounding the carbon atom toward the coordinated oxygen atom. Indeed, this speculation can be evidenced with the FT-IR spectrum (Figure 2b) that shows the doublet peak at 400 and 407 cm^{-1}, due to Fe−O bonds with different interaction energies caused by different electronic environments around the Fe atom. So three carbon peaks can be assigned as the two methyl carbons at 285.2 eV and the other states of carbonyl carbons of DMF molecules at 286.4 and 289.2 eV, respectively. In addition, since the area ratio of the carbonyl carbons with two different binding energies is 1.75, it is now clear that the total number of DMF molecules in cc-$FeCl_3$ is shared by Fe^{3+} ions so that 2.1 DMFs out of 3.3 DMFs in the complex composition coordinate with one type of Fe^{3+} ion to give the peak at 286.4 eV and 1.2 DMFs with another type of Fe^{3+} ion result in the peak at 289.2 eV.

A close examination of the Cl 2p spectrum can provide further information on the chemical structure of cc-$FeCl_3$. As seen in Figure 7, the Cl ions are in two different energy states in cc-$FeCl_3$, evidenced by the two peaks at 199.3 and 200.9 eV. Since the area ratio of two peaks is 2:1, it can be deduced that, in $(FeCl_3)_2(DMF)_{3.3}(H_2O)_{2.7}$, two of six chlorine atoms bind to Fe^{3+} so as to give the net charge of +1, while the other four chlorine atoms bind to Fe^{3+} to result in the net charge of −1. The former Fe^{3+} ion being more positive than the latter Fe^{3+} ion is expected to give rise to a peak at the higher binding energy of 200.9 eV. As more electrons are required by the Fe^{3+} bound with two chlorine ions than by the one with four chlorine ions to neutralize the charge, the former may attract more electrons from the carbonyl oxygen atom of DMF than may do the latter. So it is now possible to draw a conclusion that 2.1 DMFs bind to Fe^{3+} with four chlorine atoms and 1.2 DMFs bind to Fe^{3+} with two chlorine atoms so as to give the structure of $[FeCl_2(DMF)_{1.2}]^+[FeCl_4(DMF)_{2.1}]^-(H_2O)_{2.7}$.

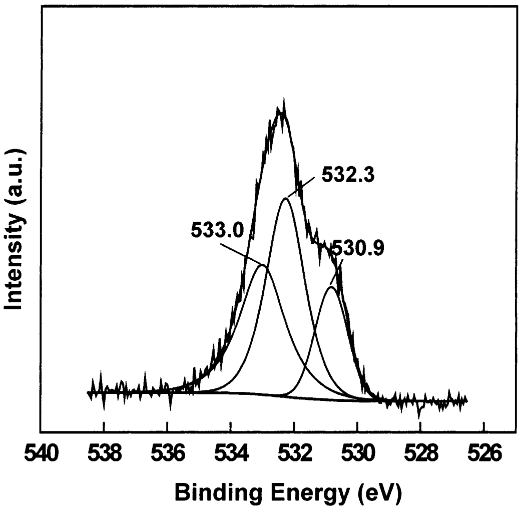


Figure 8. Curve-fitted XPS high-resolution O 1s spectrum of cc-$FeCl_3$.

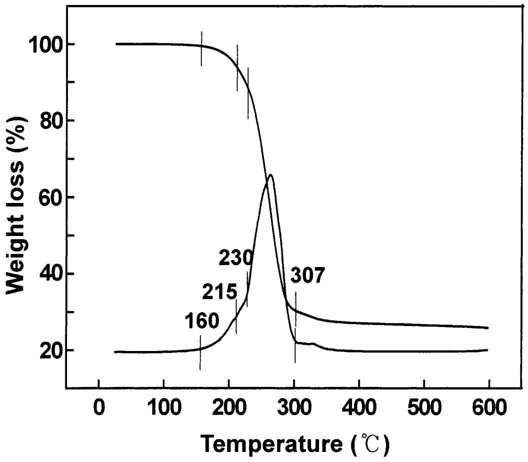


Figure 9. TG/DTG thermograms of cc-$FeCl_3$.

To determine the binding state of water molecule in the complex, the high-resolution O 1s spectrum was curve-deconvoluted on the basis of the chemical composition of $[FeCl_2(DMF)_{1.2}]^+[FeCl_4(DMF)_{2.1}]^-(H_2O)_{2.7}$. As shown in Figure 8, three component peaks are resolved with the area ratio of 2.1 (533.0 eV):2.6 (532.3 eV):1.2 (530.9 eV), and thus the peak at 533.0 eV can be attributed to the more electron-deficient carbonyl oxygen of DMF, the peak at 532.3 eV to the water molecules, and the peak at 530.9 eV to the lesser electron-deficient carbonyl oxygen of DMF. Although water molecule can be in either a chemisorbed or a physisorbed state, it has indeed been known that either case has almost the same binding energy at around 533−532 eV.[24−27] Moreover, as the peak at 530.9 eV is generally known to arise from O 1s of metal oxide[27] and the peak at 532.3 eV is singlet, it is reasonable enough to conclude that there exists only one type of water molecule, i.e., chemisorbed H_2O, in the complex structure to form of $[FeCl_2(DMF)_{1.2}(H_2O)_{2.7}]^+[FeCl_4(DMF)_{2.1}]^-$. Indeed, TGA/DTG thermograms shown in Figure 9 indicate that there exists little physisorbed water molecules, evidenced by no weight loss due to the loss of H_2O in the temperature range from 50 to 120 °C.[26]

A closer examination of the TG/DTG thermogram of the cc-$FeCl_3$ complex indicates that the complex is thermally decomposed in a successive three decomposition stages (Figure 9). The first weight loss of ca. 7.3% within the temperature range of 160−215 °C may be attributed to the loss of chemisorbed or “lattice” water[23,28,29] and is in good agreement with the theoretical value of 7.50%. The second stage in the short temperature range of 215−230 °C is presumably due to the decomposition of $1/2Cl_2$ with weight loss of 3.98% as compared with the theoretical value of 3.79%. The third stage in the 230−307 °C range may be attributed to the decomposition of DMF and loss of chloride molecules leaving behind ferric oxide as the product of decomposition.

Conclusions

From the compositional and structural analyses for the adduct of $FeCl_3$/DMF using various techniques such as FTIR, elemental analysis, UV/vis, XPS, and TGA/DTG, it was found that iron cation exists in the form of the Fe^{3+} cation and coordinates via the carbonyl oxygen atom of the amide bond in DMF so that the chemical formula of the adduct is $[FeCl_2(DMF)_{1.2}(H_2O)_{2.7}]^+[FeCl_4(DMF)_{2.1}]^-$. The water molecules in the adduct were found chemisorbed rather than physisorbed.

It is believed that the results obtained from this work may give us some clues to the coordination complex structures of other hygroscopic metals, such as the 8B transition metals including Ni and Co, etc.

Acknowledgment. This work was financially supported by the Korea Science and Engineering Foundation (KOSEF) through the Hyperstructured Organic Materials Research Center (HOMRC) at Seoul National University (SNU).

IC011306P

---

(28) Mohamed, G. G. *Spectrochim. Acta A* **2001**, *57*, 1643−1648.
(29) Becht, M.; Dahmen, K. H.; Gramlich, V.; Marteletti, A. *Inorg. Chim. Acta* **1996**, *248*, 27−33.