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Magnetism and X-Ray Photoelectron Spectroscopic Study on FeMoO_4Cl and $\text{LiFeMoO}_4\text{Cl}$

Jin-Ho Choy*, Dong-Youn Noh, Kyoung-A Son, and Do-Young Seung†

Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul 151-742. Received November 25, 1988

The general mechanism of intercalation reaction is still not experimentally clarified. All of the compounds that exhibit intercalation reaction have in common two-dimensional structure. FeMoO_4Cl is one of the good host candidates to investigate intercalation mechanism for more insight into the unique role of interlayer bonding character.

FeMoO_4Cl is a layer type compound whose synthesis, structure and some physical properties have been reported¹. It has tetragonal symmetry with unit cell parameters $a = 6.672$ and $c = 5.223\text{\AA}$ in the space group $P4/nmm$ ($Z = 2$). Individual layers consist of MoO_4 tetrahedra and FeO_4Cl square pyramids by sharing the corner-oxygen. The octahedral coordination of ferric ion of $\text{FeO}_4\text{ClCl}'$ is achieved by stacking layers on top of one another in such a way that each chlorine in the adjacent layer is in contact with ferric ion in the layer below or above it (Cl and Cl' denote the chlorine coordinated around Fe in intralayer and interlayer, respectively).

Recently intercalation reaction of FeMoO_4Cl with *n*-alkylamines has been systematically studied², and with alkali metals (*e.g.*, lithium and sodium) has also been investigated by electrochemical as well as chemical methods^{2,3}. As reported in the previous paper³, we could see that the crystal was changed from tetragonal (FeMoO_4Cl) to monoclinic ($\text{LiFeMoO}_4\text{Cl}$) symmetry with cell parameters $a = 6.994$, $b = 6.871$, $c = 5.015\text{\AA}$ and $\beta = 91.27^\circ$ by electrochemical and chemical lithiations.

In this report, an attempt was made to analyze the elements participating in the redox reaction and also to understand the bonding nature of intra and interlayer before and

after lithium intercalation into FeMoO_4Cl -host lattice. To achieve these purposes, we have performed magnetic susceptibility measurements and X-ray photoelectron spectroscopic analysis.

The host material, FeMoO_4Cl , has been synthesized with Fe_2O_3 , MoO_3 and FeCl_3 by chemical vapor transport (CVT) technique as described elsewhere². Lithiation has been carried out with excess LiI in purified acetonitrile at ambient temperature for a week under an inert atmosphere. Considering the coincidence of EMF *vs.* Li/Li⁺ for LiI (2.8V) with the open circuit voltage (OCV) of $\text{LiFeMoO}_4\text{Cl}$ (2.2V)⁴, it is thought that LiI is more suitable reducing reagent than *n*-BuLi (-1V). In practice, the crystals of FeMoO_4Cl was turned out to be X-ray amorphous after reaction with *n*-BuLi.

Magnetic susceptibility measurements were performed in an inert atmosphere with Faraday-type magnetobalance from 77K to 350K.

X-ray photoelectron spectra using an unmonochromatized Mg-K α radiation (1253.6 eV) were recorded on an PHI 5100 Perkin-Elmer X-ray photoelectron spectrometer equipped with PE 7700 computer system. The base pressure was maintained in the $\sim 10^{-9}$ torr throughout all operations. Instrumental work function was calibrated by the Au(4f_{7/2}) binding energy at 83.8 eV. Samples were mixed with graphite ($C_{1s} = 284.4$ eV) as an internal standard, which were mounted on the specially designed sample holder covered with gold sheet and put into the chamber without exposure to air.

Molar susceptibility (χ'_m), reciprocal susceptibility ($\chi'_m{}^{-1}$) and effective magnetic moment (μ_{eff}) for FeMoO_4Cl and $\text{LiFeMoO}_4\text{Cl}$ have been measured over the temperature range from 77K to 350K as shown in Figures 1 and 2. The reciprocal susceptibility *vs.* temperature for FeMoO_4Cl exhibits a typical two dimensional antiferromagnetic behavior in

*Material Devices Research Center, Samsung Advanced Institute of Technology, C.P.O. Box 111 (Suwon)

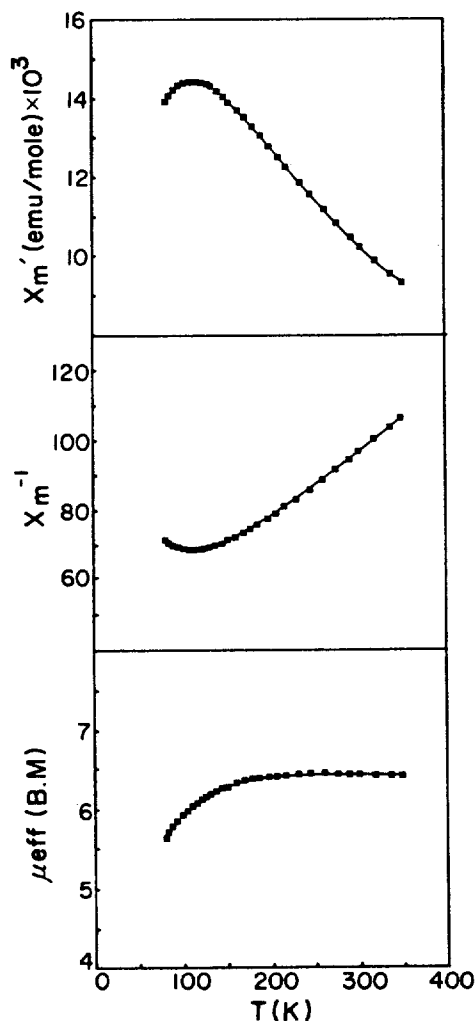


Figure 1. Temperature dependence of corrected molar susceptibility (top), reciprocal susceptibility (middle) and effective magnetic moment (bottom) for FeMoO_4Cl . ($\mu_{eff} = 6.46\text{B.M.}$, $C_m = 5.21\text{ emu/mole}$, $\mu_{eff}^{s.o.} = 5.92\text{B.M.}$ and $\theta = -207\text{K}$).

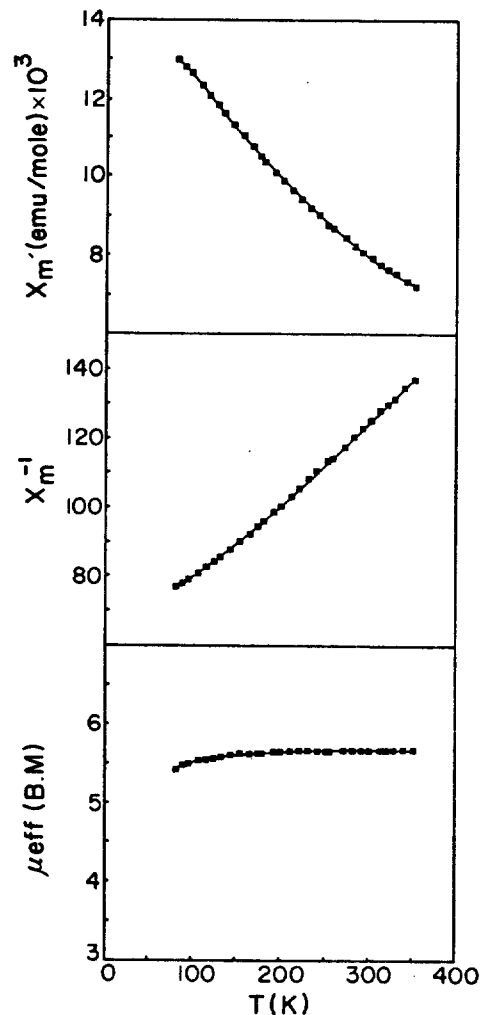


Figure 2. Temperature dependence of corrected molar susceptibility (top), reciprocal susceptibility (middle) and effective magnetic moment (bottom) for $\text{LiFeMoO}_4\text{Cl}$. ($\mu_{eff} = 5.67\text{B.M.}$, $C_m = 4.02\text{ emu/mole}$, $\mu_{eff}^{s.o.} = 4.90\text{B.M.}$ and $\theta = -204\text{K}$).

the low temperature region with broad minimum at about 110K ($T_{N\acute{e}el}$). But in the temperature range $200\text{K} < T < 350\text{K}$, it appears to follow the Curie-Weiss law with an effective magnetic moment of 6.46B.M., which is slightly higher than spin-only value for high-spin Fe^{3+} which might be due to the antiferromagnetic coupling remained in this temperature region. The large negative value of paramagnetic Curie temperature ($\theta = -207\text{K}$) also supports the existence of an antiferromagnetic coupling. As in case of FeMoO_4Cl , the same tendency could be observed in reciprocal magnetic susceptibility ($\theta = -204\text{K}$) of $\text{LiFeMoO}_4\text{Cl}$. Moreover, the effective magnetic moment ($\mu_{eff} = 5.67\text{B.M.}$) of $\text{LiFeMoO}_4\text{Cl}$ is approximately 0.8B.M. smaller than that of FeMoO_4Cl , and is more close to that of high-spin $\text{Fe}^{2+}(t_{2g}^4 e_g^2) < \mu^{s.o.} = 4.90\text{B.M.} >$ than to that of low-spin $\text{Fe}^{2+}(t_{2g}^6 e_g^0) < \mu^{s.o.} = 0\text{B.M.} >$.

X-ray photoelectron (XPE) spectroscopy measurements were carried out for all elements in FeMoO_4Cl and $\text{LiFeMoO}_4\text{Cl}$. Figure 3 clearly shows the difference in B.E.'s of Fe 2p core electrons for two compounds. Fe 2p XPE spectrum of FeMoO_4Cl (Figure 3a) gives Fe 2p_{1/2} and Fe 2p_{3/2} core electron B.E.'s of 724.3 and 711.0 eV which are the same values as those of other compounds such as $\alpha\text{-Fe}_2\text{O}_3$

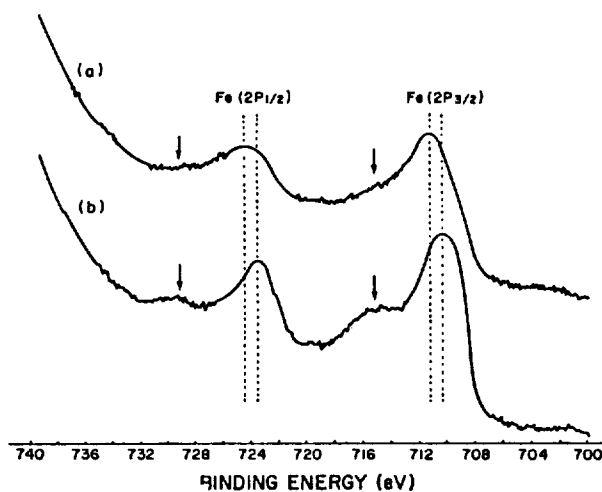


Figure 3. $\text{Fe}(2P_{1/2}\text{-}2P_{3/2})$ photoelectron spectra of (a) FeMoO_4Cl and (b) $\text{LiFeMoO}_4\text{Cl}$ after Ar ion sputtering for several min. Major satellite lines are indicated by arrows.

(724.6-711.4 eV), α -FeOOH (724.5-711.0 eV) and KFeO_2 (724.6-711.3 eV)⁵ having Fe^{3+} ions in the lattice. After the lithiation, Fe 2*p* core lines become sharper considerably and shift to lower B.E. region by ~1 eV (723.3-710.2 eV). The lowering of B.E. means the decreasing in valence state, from Fe^{3+} to Fe^{2+} in this case. The B.E.'s of Fe 2*p* electrons in $\text{LiFeMoO}_4\text{Cl}$ also coincide with other Fe^{2+} -containing compound such as FeO (723.8-710.3 eV)⁵. The B.E.'s of core level electrons of other elements in FeMoO_4Cl (e.g., molybdenum, oxygen and chlorine) are not changed after lithiation. That is, intercalated lithium ions selectively reduce Fe^{3+} to Fe^{2+} rather than Mo^{6+} . Generally the XPE spectra of paramagnetic Fe 2*p* levels are highly complex and have many satellite peaks with main XPE lines (FWHM = 3.3 eV for Fe 2*p*_{3/2}), which are the characteristic feature of the compounds with 3*d*-group transition metals⁶. The existence of complex satellites in the Fe 2*p* spectra confirms that Fe^{3+} and Fe^{2+} are in high-spin state with 5 and 4 unpaired electrons, since no shake-up satellite peaks could be expected for the diamagnetic ions like $\text{Fe}^{2+}(t_{2g}^6e_g^0)$ with low spin state.

B.E.'s of Mo 3*d*_{3/2} and 3*d*_{5/2} electrons for FeMoO_4Cl and $\text{LiFeMoO}_4\text{Cl}$ are measured as $(235.4 \pm 0.1)\text{eV}$ and $(232.2 \pm 0.1)\text{eV}$, respectively, which are almost the same as those of other Mo^{6+} species such as $\text{MoO}_3 < 235.6-232.5 \text{ eV} >$, $\text{CoMoO}_4 < 235.0-231.8 \text{ eV} >$, $\text{Al}_2(\text{MoO}_4)_3 < 235.8-232.7 \text{ eV} >$ and $\text{Fe}_2(\text{MoO}_4)_3 < 235.3-232.2 \text{ eV} >$ ^{7,8}. XPE lines for O 1*s* (530.3 \pm 0.1 eV) and Cl 2*p* (198.2 \pm 0.1 eV) in FeMoO_4Cl and $\text{LiFeMoO}_4\text{Cl}$ are not changed as expected. Due to the broadening of Li 1*s* line with long tail toward high B.E. region by overlapping with other lines such as Fe 3*p* and Au 5*p*, and moreover with complicated satellites, the exact B.E. of Li 1*s* line could not be measured.

In summary, it has been confirmed that ferric ions in FeMoO_4Cl are selectively reduced to ferrous ions upon lithium intercalation with a decrease of crystal symmetry from tetragonal to monoclinic ($\text{LiFeMoO}_4\text{Cl}$). From the magnetic and XPS data along with X-ray structural analysis, it has been concluded that high spin configuration of $\text{Fe}^{2+}(e_g^3t_{2g}^3)$, corresponding to 5E_g ground term in D_{4h} symmetry, can be stabilized by the elongation of $\text{FeO}_4\text{ClCl}'$ -distorted octahedra in a weak ligand field. And both compounds show an extensive short range intralayer antiferromagnetic correlation.

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Syntheses and Biological Activities of Copolymers Composed of Dihydropyran, Acrylic Acid and Their Derivatives

Man Jung Han^{*}, Dae Hee Lee, Won-Young Lee[†], and Bo Sup Hahn[‡]

Departments of Applied Chemistry and [†]Chemistry, Ajou University, Suwon 440-749

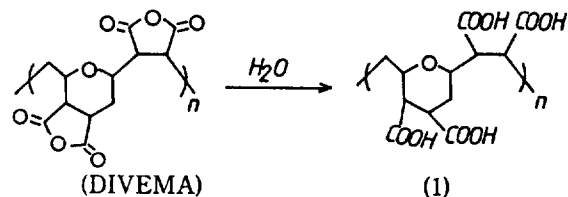
^{*}Department of Microbiology, College of Medicine, Yonsei University, Seoul 120-749

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Various polyanions of both natural and synthetic origin are known to exhibit a broad spectrum of interesting biological activities.¹⁻⁵ Among those synthetic polyanions, divinyl ether-maleic anhydride (1:2) alternating copolymer (DIVEMA) has been extensively studied due to its antiviral, antitumor and interferon-inducing properties.⁶⁻¹¹

The structural feature of hydrolyzed product (I), an intrinsic active form in the biological system of DIVEMA, (I) contains tetrahydropyran rings and carboxylate groups attached on the polymer backbone as functionalities.

Hypothesizing that the polymers having similar structure to that of DIVEMA would manifest relevant biological activities, we synthesized several copolymers which contained



both tetrahydropyran rings and carbonyl groups. It was surprising to find that most of the polyanions synthesized and tested up to date for their biological activities were designed to contain only carboxylates as polar and/or functional groups even though sugar moieties-pyran or furan ring-may, in general, play rather important role in biological systems.