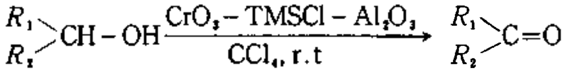
129–131 °C). This oxidation can be carried out on a 1 - 30g scale without any problems or major modification of the procedure. The yields and reaction conditions for the oxidation of other alcohols are summarized in Table 1.


$$R_1R_2CH-OH \xrightarrow[CCl_4,\ r.t]{CrO_3-TMSCl-Al_2O_3} R_1R_2C=O$$

This new reagent system is superior or comparable in yields to any other popular chromium(VI) oxidizing agents such as PDC[4], PCC[5] and chromyl chloride adsorbed on silica-alumina.[6] The reagent can be prepared from the cheap and easily accessible chemicals in less than an hour. The procedure is simple and straightforward.

The true oxidizing species generated from chromic anhydride and chlorotrimethylsilane is believed to be chromyl chloride or polyoxochromium(VI) dichloride rather than trimethylsilyl chlorochromate as Aizpurua and Palomo[3] have postulated. The proton nmr spectrum of this reagent system shows only two kind of protons characteristic of chlorotrimethylsilane and hexamethyldisiloxane. It showed close resemblance to chromyl chloride in its reactions with olefins[7] and arylmethanes[8].

Chromyl chloride is known to be too vigorous to be used for the oxidation of alcohols, but silica-alumina chemi-adsorbed chromyl chloride was proved efficient for the oxidation of all kinds of primary and secondary alcohols to aldehydes and ketones[6]. Both acidic and basic alumina were proved to be effective for moderating the reactivity of chromic anhydride chlorotrimethylsilane pair, but the oxidation is very sluggish in the presence of neutral alumina. The oxidation of primary alcohols to aldehydes was successful only with basic alumina. By keeping the reaction mixture basic, further oxidation to the acid or chlorotrimethylsilane-catalyzed acetal formation from unreacted alcohol and the product aldehyde seems to be greatly retarded. Addition of pyridine or sodium carbonate to keep the reaction media basic, however, did not improved the yield of carbonyl compounds.

Acknowledgement. This work was supported by non-directed research fund, Korea Research Foundation.

References

1. K. B. Wiberg, *Oxidation in Organic Chemistry*, Part A, Academic Press, New York, pp. 142–170 (1965).
2. G. Gainelli and G. Cardillo, *Chromium Oxidations in Organic Chemistry*, Springer-Verlag, New York, pp. 118–211, (1984).
3. J. M. Aizpurua and G. Palomo, *Tetrahedron Lett.* 4367 (1983).
4. E. J. Corey and G. Schmidt, *Tetrahedron Lett.* 399 (1979).
5. G. Piancatelli, A. Scettri, and M. D. D'Auria, *Synthesis*, 245 (1985). E. J. Corey and J. W. Suggs, *Tetrahedron Lett.* 2647, (1975).
6. J. SanFillippo Jr. and C. I. Chern, *J. Org. Chem.* **42**, 2182 (1977).
7. J. G. Lee and D. S. Ha, *Tetrahedron Lett.* **30**, 193 (1989).
8. J. G. Lee and D. S. Ha, *Bull. Korean Chem. Soc.* **8**, 435 (1987).
9. Chlorotrimethylsilane is known to be very effective for acetal formation from an alcohol and a carbonyl compound.
10. *Dictionary of Organic Compounds*, 4th Ed. New York, Oxford University Press, 1965 and references cited therein.

Medium-spin ($S=3/2$) Ferric Complex of $Fe^{3+}Mo^{6+}O_4Cl\cdot(C_{14}H_{29}NH_2)_{1.7}$ as a Two-Dimensional Heisenberg Antiferromagnet

Jin-Ho Choy* and Dong-Youn Noh

Department of Chemistry, College of Natural Science, Seoul National University,
Seoul 151-742. *Received June 5, 1989*

The magnetic behavior of ferric ion is simple in general. They exhibit either high-spin ($t_{2g}{}^3e_g{}^2$) or low-spin ($t_{2g}{}^5e_g{}^0$) states with $S=5/2$ and $1/2$, respectively. Only a few cases of molecular compound containing Fe^{3+} are known as a medium-spin ($t_{2g}{}^4e_g{}^1$) state with $S=3/2$. The spin state of the complex is determined by the balance between the ligand field strength and the magnitude of exchange energy. Deviations from the normal spin states (high- and low-spin) can take place for ferric ions when the ligand field strength is of the same order as the mean pairing energy for the d^5 configuration. Recently we have, for the first time, prepared this kind of polymeric ferric complexes, $FeMoO_4Cl\cdot(C_nH_{2n+1}NH_2)_{1.7}$, in which the medium-spin state with ($t_{2g}{}^4e_g{}^1$) electronic configuration is stabilized.

$FeMoO_4Cl$ is a layer type compound of which the synthesis, structure and some physical properties have been already reported in the previous papers.[1-4] Intercalation complexes of $FeMoO_4Cl$ with *n*-alkylamines also have been reported for the first time with its EPR, IR and XRD results.[1] From XRD investigation, it has been verified that the intercalated *n*-alkylamines are arranged as paraffin-like bimolecular layers between the basal planes of the $FeMoO_4Cl$ matrix. And as already shown in the idealized model of *n*-alkylamine complex, the pseudooctahedral FeO_4Cl_2 unit with D_{4h} symmetry in $FeMoO_4Cl$ is degraded into the square pyramidral FeO_4Cl one with C_{4v} symmetry by the intercalation of *n*-alkylamines.[1]

$FeMoO_4Cl\cdot(C_{14}H_{29}NH_2)_{1.7}$ is prepared by direct thermal

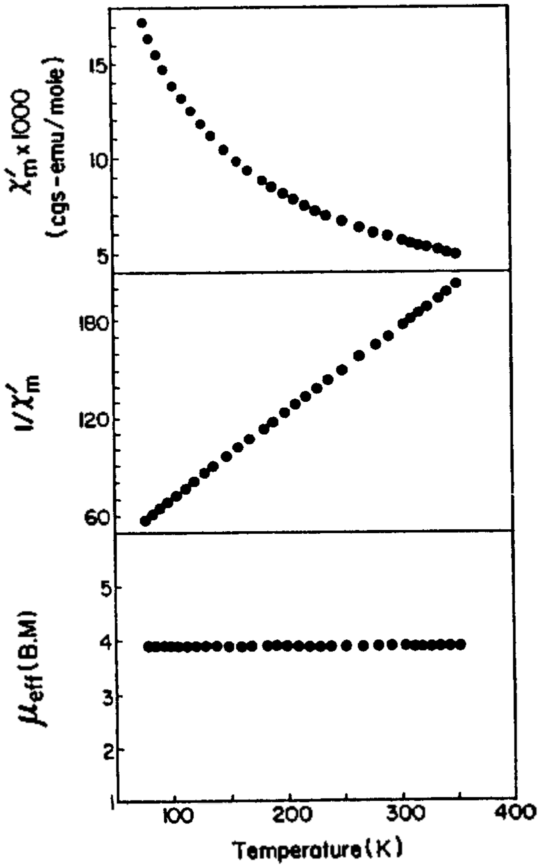


Figure 1. Temperature dependence of molar susceptibility(Xm'), reciprocal susceptibility($1/Xm'$) and effective magnetic moment (μ_{eff}) for $FeMoO_4Cl{\cdot}(C_{14}H_{29}NH_2)_{1.7}$ (C = 1.90 emu/mole, θ = -32.7K, μ_{eff} = 3.90 B.M and $\mu^{s.o}$ = 3.87 B.M).

reaction of $FeMoO_4Cl$ with excess *n*-tetradecylamine in sealed pyrex tube at about 120°C. The swelling of $FeMoO_4Cl$ due to intercalation of *n*-tetradecylamine could be perceived easily on the way of the reaction and the achievement of the reaction was monitored by X-ray diffraction.

Magnetic susceptibility measurement was performed on the powdered sample of 80 mg in an inert atmosphere with a Faraday type magnetobalance from 77 K to 380 K. The field dependency of the susceptibility was checked at several temperatures. The applied magnetic field was in the range 0.4-0.7 Tesla. Gd_2O_3(99.999%) was used as a susceptibility standard. The diamagnetic corrections were estimated according to the Pascal constants and constitutive corrections as follows (in 10^{-6} emu/g): Mo^{6+}(-7.5), O^{2-}(-12), Cl^-(-26), C (-6.00), H(-2.93) and N in open chain(-5.57).[4]

After the diamagnetic corrections, the molar susceptibility(Xm'), reciprocal susceptibility($1/Xm'$) and effective magnetic moment(μ_{eff}) for $FeMoO_4Cl{\cdot}(C_{14}H_{29}NH_2)_{1.7}$ complex are plotted in Figure 1. Least-square computer fit of $1/Xm'$ *vs* T shows that this complex obeys Curie-Weiss law, $1/Xm' = (T-\theta)/C$, over the temperature range measured and leads to the following parameters: effective magnetic moment μ_{eff} = 3.90 B.M, paramagnetic Curie temperature θ = -32.7K and Curie constant C = 1.90 emu/mole. The effective magnetic moment of this complex is far from the spin-only magnetic moments of high-spin (5.92 B.M : S = 5/2) and low-spin (1.73 B.M: S = 1/2) states.[5] But it is rather same as the spin-only magnetic moment of the state with S = 3/2(3.87 B.M). This means that ferric ion(d^5) in the complex has three unpaired electrons, and the rest of the two electrons might be paired so that they cannot contribute to the paramagnetism, of which the electronic configuration could be denoted as ($t_{2g}^4e_g^1$) with S = 3/2. The stabilization of medium-spin state with S = 3/2 could be explained as the consequence of the lowering in the degree of point symmetry[6] around ferric ion ($C_{4v} \leftarrow D_{4h}$) due to the intercalation reaction. Other complexes with medium-spin ferric ions (S = 3/2) were also found only in some molecular compounds such as $[FeX(S_2CNR_2)]$ where X is halides and R = CH_3, C_2H_5, sec-C_4H_9,[7] and $Fe(TPP)[C{=}C(p\text{-}ClAr)_2](Cl)$ where TPP is tetraphenylporphyrin,[8] which have lower degree of symmetry below C_{2v}.

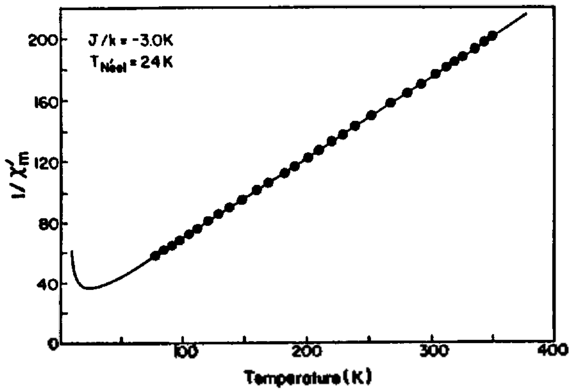


Figure 2. Reciprocal susceptibility($1/Xm'$) of $FeMoO_4Cl{\cdot}(C_{14}H_{29}NH_2)_{1.7}$. The solid line represents a fit to the calculated series expansion for a two dimensional Heisenberg system with g = 2.0, S = 3/2 and J/k = -3.0K (T_{Neel} = 24.0K).

Calculation of reciprocal susceptibility on the *2D* Heisenberg antiferromagnet with S = 3/2 has been carried out and shows good agreement with observed one as shown in Figure 2. The magnetic susceptibility for the quadratic layer Heisenberg antiferromagnet could be expressed as the series expansion:[9]

$$\frac{Ng^2\mu_B^2}{X\cdot J} = 3\theta + \sum_{n=1}^{\infty}\frac{C_n}{\theta^{n-1}}$$

where $\theta = kT/JS(S+1)$, g = Landé g-factor, μ_B = Bohr magneton, N = number of spins in the lattice and the coefficients are C_1 = 4, C_2 = 1.600, C_3 = 0.304, C_4 = 0.249, C_5 = 0.132 and C_6 = 0.013 for S = 3/2. The observed and calculated susceptibilities show excellent coincidence (Figure 2) with an exchange constant (J/k = -3.0K) and the Neel temperature (T_{Neel} = 24.0K). The Neel temperature of this complex is comparable with that of $Fe_2(MoO_4)_3$(13K)[10] which has O-Mo-O superexchange pathway only as the *n*-alkylamine complex, but much smaller than that of $FeMoO_4Cl$(109K)[2] which has additional 180° pathway of $[-Fe\cdots Cl-Fe\cdots Cl-]_n$ along the *c*-axis. From this calculation and comparison, we could easily know that the complex, $FeMoO_4Cl{\cdot}(C_{14}H_{29}NH_2)_{1.7}$, is a complete two-dimensional Heisenberg antiferromagnet with medium-spin state (S = 3/2).

Acknowledgement. This research was supported by Korean Science and Engineering Foundation (KOSEF).

References

1. J. H. Choy, D. Y. Noh, J. C. Park, S. H. Chang, C. Delmas and P. Hagenmuller, *Mat. Res. Bull.*, **23**, 73 (1988).
2. J. H. Choy, S. H. Chang, D. Y. Noh and K. A. Son, *Bull. Korean Chem. Soc.*, **10**, 27 (1989).
3. J. H. Choy, D. Y. Noh, K. A. Son and D. Y. Seung, *Bull. Korean Chem. Soc.*, **10**, 210 (1989).
4. C. C. Torardi, J. C. Calabrese, K. Lázár and W. M. Reiff, *J. Solid State Chem.*, **51**, 376 (1984).
5. Landolt-Bornstein II/2, Springer Verlag, Berlin, 1966.
6. J. S. Griffith, *J. Inorg. Nucl. Chem.*, **2**, 1 (1956).
7. R. L. Martin and A. H. White, *Inorg. Chem.*, **6**, 712 (1967).
8. D. Mansuy, I. Morgenstern-Badarau, M. Lange and P. Gans, *Inorg. Chem.*, **21**, 1427 (1982).
9. M. E. Lines, *J. Phys. Chem. Solids*, **31**, 101 (1970).
10. Z. Jirak, R. Salmon, L. Fournes, F. Menil and P. Hagenmuller, *Inorg. Chem.*, **21**, 4218 (1982).

Cyclization of β-Amino Acids to β-Lactams by Using 1-Methanesulfonyloxy-6-trifluoromethylbenzotriazole

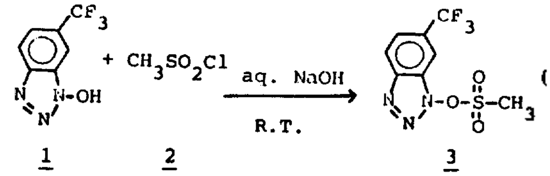
Young Haeng Lee[*], Won Sik Choi[†], and Dong-Seok Loh[‡]

Department of Chemistry, Won Kwang University, Iri 570-749
[†]Department of Genetic Science, Soon Chun Hyang University, Asan 330-62
[‡]Korea Advanced Institute of Science and Technology, Doping Control Center, Seoul 135-090

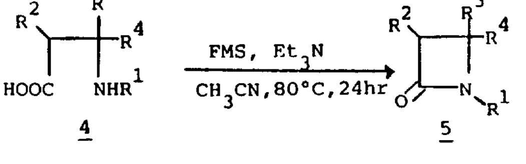
Received June 8, 1989

One of the popular synthetic methods for the β-lactam formation is based on the intramolecular cyclization of β-amino acids using coupling reagents[1]. Among various coupling reagents currently available, benzenesulfonyl chloride[2], triphenylphosphine/2,2'-dipyridyl disulfide[3], 2-chloro-1-methylpyridinium iodide[4], and benzotriazol-1-yloxytris(dimethylamino)phosphonium hexafluorophosphate[5] are the most effective and reliable.

In connection with our research program directed toward the development of new synthetic methodologies for the formation of β-lactam derivatives from β-amino acids, we have examined the β-lactam formation from β-amino acids using 1-methanesulfonyloxy-6-trifluoromethylbenzotriazole(FMS reagent, **3**). It has been reported that FMS reagent is the effective coupling reagent for the acylation of cephalosporins[6] and the esterification of dihydropyridine-3-carboxylic acid[7]. On the other hand, there are no reports on the application of FMS reagent for β-lactam formation from β-amino acids. In this paper, we wish to report a new method for the preparation of β-lactam derivatives (**4**) from β-amino acids (**5**) by using FMS reagent.



(eq.1)



(eq.2)

Table 1. Synthesis of β-Lactams from β-Amino Acids

Description	Isolated yield(%)
$R^1 = CH_2Ph$, $R^2 = H$, $R^3 = R^4 = CH_3$	94
$R^1 = CH_2Ph$, $R^2 = R^4 = H$, $R^3 = CH_3$	71
$R^1 = CH_2Ph$, $R^2 = CH_3$, $R^3 = R^4 = H$	50
$R^1 = CH_2Ph$, $R^2 = R^4 = H$, $R^3 = CO_2Ph$	58
$R^1 = CH_2Ph$, $R^2 = R^4 = H$, $R^3 = Et$	65
$R^1 = CH_2Ph$, $R^2 = R^4 = H$, $R^3 = Pr$	60
$R^1 = c\text{-}C_6H_{11}$, $R^2 = CH_3$, $R^3 = R^4 = H$	76
$R^1 = c\text{-}C_6H_{11}$, $R^2 = R^4 = H$, $R^3 = CH_3$	65
$R^1 = R^2 = H$, $R^3 = R^4 = CH_3$	22

FMS reagent was conveniently prepared by the reaction of 1-hydroxy-6-(trifluoromethyl)benzotriazole with methanesulfonyl chloride in aqueous sodium hydroxide solution at room temperature (eq. 1). The reagent **3** is a white crystalline solid melting at 98-100 °C and can be stored in a refrigerator for several weeks without any decomposition, and is generally used without further purification.

The representative experimental procedure is a follows (eq. 2); To a mixture of 3-benzylamino-3-methylbutanoic acid (310mg, 1.5mmol) and FMS reagent (510mg, 1.8mmol) in acetonitrile (150m*l*) was added triethylamine (360mg, 3.6mmol) at room temperature. After being stirred for 24 hr at 80 °C, the reaction mixture was concentrated under reduced pressure and the residue was passed through silica gel column using ether-chloroform (2:1) as an eluent to yield 1-benzyl-4,4-dimethyl-2-azetidinone (267mg, 94% yield) as an