1, 4, 8, 11-테트라아자사이클로테트라데칸의 높은 스핀 다섯배위철(II) 착화합물과 1, 5, 8, 12-테트라아자도데칸의 높은 스핀 여섯배위철(II) 착화합물의 합성

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Preparation of High Spin Five-Coordinate Iron(II) Complexes of 1, 4, 8, 11-Tetraazacyclotetradecane and High Spin Six-Coordinate Iron(II) Complexes of 1, 5, 8, 12-Tetraazadodecane

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요 약. 마크로사이클리간드인 1, 4, 8, 11-테트라아자사이클로테트라데칸 (cyclam)과 비환형 리간드인 1, 5, 8, 12-테트라아자도데칸 (3, 2, 3-tet)의 높은 스핀철(II) 착화합물이 합성되었다. 낮은 스핀인 $[Fe(cyclam)(CH_3CN)_2](ClO_4)_2$ 는 메탄올속에서 염소이온과 반응하여 높은 스핀인 $[Fe(cyclam)Cl]-ClO_4$ 를 생성한다. $[Fe(cyclam)(CH_3CN)_2](ClO_4)_2$ 는 낮은 스핀이지만 $[Fe(3, 2, 3-tet)(CH_3CN)_2]-(ClO_4)_2$ 는 높은 스핀을 가지며 이 차이는 비환형 리간드가 환형 리간드보다 압축효과가 작은 것으로 설명된다. $[Fe(cyclam)Cl]ClO_4$ 의 합성은 마크로사이클리간드가 불포화되어 있거나 치환체가 있어야 높은 스핀 다섯배위철(II) 착화합물의 합성이 가능하다는 지금까지의 견해에 반대되는 증거가 된다. $[Fe(cyclam)Cl]ClO_4$ 와 $[Fe(3, 2, 3-tet)(CH_3CN)_2](ClO_4)_2$ 는 일산화탄소와 반응해서 각기 낮은 스핀 여섯배위인 $[Fe(cyclam)Cl(CO)]ClO_4$ 와 $[Fe(3, 2, 3-tet)(CH_3CN)(CO)](ClO_4)_2$ 를 만든다.

ABSTRACT. High spin iron(II) complexes of 1,4,8,11-tetraazacyclotetradecane (cyclam), a macrocyclic ligand, and 1,5,8,12-tetraazadodecane (3,2,3-tet), a noncyclic ligand, have been prepared. The reaction of low spin $[Fe(cyclam)(CH_3CN)_2](ClO_4)_2$ with chloride ion in methanol produces high-spin $[Fe(cyclam)Cl]ClO_4$. Although $[Fe(cyclam)(CH_3CN)_2](ClO_4)_2$ is low spin, $[Fe(3,2,3-tet)(CH_3CN)_2](ClO_4)_2$ isolated in the present study is high spin. This difference is explained in terms of the smaller constrictive effect exerted by the noncyclic ligand than the cyclic ligand. The isolation of $[Fe(cyclam)Cl]ClO_4$ provides evidences against the current view that the presence of either unsaturation or substituents on the macrocyclic ligands is necessary for the successful preparation of high spin five-coordinate iron(II) complexes. Reactions of $[Fe(cyclam)Cl]ClO_4$ and $[Fe(3,2,3-tet)(CH_3CN)_2]$ $(ClO_4)_2$ with carbon monoxide yield low spin six-coordinate $[Fe(cyclam)Cl(CO)]ClO_4$ and $[Fe(3,2,3-tet)(CH_3CN)(CO)](ClO_4)_2$, respectively.

INTRODUCTION

In view of the fundamental similarities in structure with the active sites of naturally occurring heme proteins, importance of the high spin five–coordinate iron(II) complexes of tetra-azacyclic ligands cannot be overemphasized. However, examples of high spin five–coordinate iron (II) complexes have been rather rarely reported until recently.

A number of iron(II) complexes of tetraaza-macrocyclic ligands have been synthesized and characterized.[1~14] The coordination number and spin state of iron(II) in these complexes depend not only on the degree of unsaturation, charges, and ring size of the planar ligand but also on the nature of the axial ligand. In general, high spin five- or six-coordinate iron(II) macrocyclic complexes are obtained with weak axial ligands, and low spin six-coordinate complexes with relatively strong axial ligands. Isolation of four –coordinate complexes (S=1) has been also reported with a charged macrocyclic ligand.[14]

In this article, isolation of a high spin five-coordinate iron(II) complex of cyclam is described. This is the first report of a high spin five-coordinate iron(II) complex ever prepared containing a fully saturated and unsubstituted tetraazamacrocyclic ligand. Also reported are the synthesis and properties of iron(II) complexes containing 3, 2, 3-tet which is structurally similar to cyclam but noncyclic.
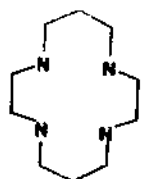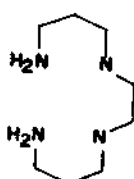
cyclam   3, 2, 3-tet

EXPERIMENTAL

Materials

All solvents and chemicals were of reagent grade and carbon monoxide gas was of CP grade. Solvents were dried over 4 Å molecular sieves and degassed with dry nitrogen before use. Synthesis and manipulation of the complexes were carried out under nitrogen atmosphere.

Cyclam. This was prepared according to the published methods[15] and recrystallized several times from chlorobenzene.

[Fe(cyclam)(CH₃CN)₂](ClO₄)₂. Although the synthetic procedure of this compound is reported in the literature,[1] we developed a new method. To a hot solution of o-phenylenediamine (o-pda) (16 g) in 60 ml methanol, Fe(ClO₄)₂·6H₂O (18 g) dissolved in 30 ml methanol was added under nitrogen. The white crystals of [Fe(o-pda)₃](ClO₄)₂ formed upon chilling. The crystals were filtered, washed with cold methanol, and dried *in vacuo*. To a solution of [Fe(o-pda)₃](ClO₄)₂ (5.8 g) in 30 ml acetonitrile, cyclam (2 g) dissolved in a few ml of methanol was added dropwise under nitrogen atmosphere. The solution turned deep blue and the violet-crystalline product formed within 30 min. The crystals were filtered under nitrogen, washed with acetonitrile, and dried *in vacuo*.

Anal. Calcd. for $FeC_{14}H_{30}N_6Cl_2O_8$: C, 31.30; H, 5.63; N, 15.65. Found: C, 31.69; H, 5.96; N, 15.22.

[Fe(cyclam)Cl]ClO₄. To a hot suspension of [Fe(cyclam)(CH₃CN)₂](ClO₄)₂ (0.4 g) in 20 ml methanol, an excess of LiCl, dissolved in 3 ml methanol, was added under nitrogen. When the insoluble diacetonitrile complex went into solution, the resulting solution turned pale green. The white product which precipitated on standing was filtered, washed with methanol, and dried *in vacuo*.

Anal. Calcd. for $FeC_{10}H_{24}N_4Cl_2O_4$: C, 30.71; H, 6.19; N, 14.33; Cl, 18.13. Found: C, 30.48; H, 6.70; N, 14.47; Cl, 18.31.

[Fe(cyclam)Cl(CO)]ClO₄. Carbon monoxide was bubbled through a solution obtained by dissolving [Fe(cyclam)Cl]ClO₄ (0.3 g) in 10 ml hot methanol until the solution became yellow. Diethyl ether was added, and the resulting mixture was left at room temperature for several days under carbon monoxide pressure. Yellow plate-like crystals formed, which were filtered, washed with methanol-diethyl ether mixture, and dried.

Anal. Calcd. for $FeC_{11}H_{24}N_4Cl_2O_5$: C, 31.52; H, 5.77; N, 13.37; Cl, 16.92. Found: C, 32.60; H, 5.51; N, 12.92; Cl, 16.38.

3, 2, 3-tet. This was prepared according to the reported methods[16] and distilled *in vacuo*, 138~140° at 2 mmHg.

[Fe(3, 2, 3-tet) (CH₃CN)₂](ClO₄)₂. A solution of $Fe(ClO_4)_2 \cdot 6H_2O$ in 25 ml 1:1 acetonitrile-triethylorthoformate was heated at 50 °C under nitrogen for 12 hrs. To the resulting solution whose color lightened to yellow during heating, 3, 2, 3-tet (1.8 g) was added dropwise with stirring. After the mixture was left at room temperature for several days, pale purple crystals formed, which were filtered, washed with 1:2 acetonitrile-diethyl ether, and dried *in vacuo*.

Anal. Calcd. for $FeC_{12}H_{28}N_6Cl_2O_8$: C, 28.20; H, 5.52; N, 16.44. Found: C, 28.27; H, 5.64; N, 16.66.

[Fe(3, 2, 3-tet) (CH₃CN) (CO)] (ClO₄)₂. Carbon monoxide gas was bubbled through a solution of [Fe(3, 2, 3-tet) (CH₃CN)₂] (ClO₄)₂ in acetonitrile contained in a serum capped bottle vented with a syringe needle. The addition of diethyl ether to the resulting yellow solution induced crystallization of the compound. The yellow precipitates were filtered under nitrogen and dried with a carbon monoxide stream.

Anal. Calcd. for Fe $C_{11}H_{25}N_5Cl_2O_9$: C, 26.52; H, 5.06; N, 14.06. Found: C, 26.59; H, 5.11; N, 13.92.

[Fe(3, 2, 3-tet) (CH₃COO)₂]. Anhydrous ferrous acetate (1 g) was suspended in acetonitrile, and 3, 2, 3-tet (1 g) was added to the stirred suspension under nitrogen. A pale yellow solution was obtained after dissolution of the ferrous acetate. The solvent was evaporated under a nitrogen stream in an ice bath. The white crystals which formed were filtered and dried *in vacuo*.

Anal. Calcd. for $FeC_{12}H_{28}N_4O_4$: C, 41.39; H, 8.10; N, 16.09. Found: C, 41.01; H, 7.98; N, 15.96.

Physical measurements

Infrared spectra were recorded on a Beckman IR-10 infrared spectrophotometer. Samples were prepared as nujol mulls and the spectra were calibrated with a polystyrene film. Ultraviolet and visible electronic absorption spectra were measured with a Cary Model 14 recording spectrophotometer. The conductivities of the complexes were obtained using an Industrial Instruments Model RC 16B conductivity bridge. Magnetic susceptibilities were measured under vacuum by the Faraday method using HgCo-(NCS)₄ as a calibrant. Molar susceptibilities were corrected for diamagnetism of the ligands with Pascal's contants. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee, U.S.A.

RESULTS AND DISCUSSION

[Fe(cyclam)Cl]ClO₄. The reaction of [Fe-(cyclam) (CH₃CN)₂] (ClO₄)₂ with excess chloride ion in methanol solution yields crystals of [Fe-(cyclam)Cl]ClO₄. It is soluble in nitromethane but insoluble in alcohol, ether, or other nonpolar solvents. It is relatively sensitive to oxygen in crystalline state, and extremely sensitive in solution leading to an unidentified product. Assignment of coordination number five to the complex was made on the basis of the results
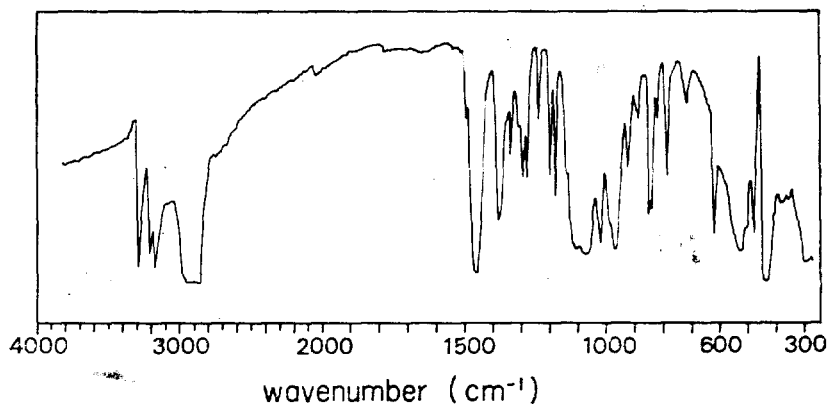
Fig. 1. The ir spectrum of [Fe(cyclam)Cl]ClO₄.

of elemental analysis, infrared spectrum, and conductivity measurements. The elemental analysis of the product corresponds to Fe(cyclam)-Cl·ClO₄ instead of Fe(cyclam)Cl₂, regardless of the amount of chloride ion used in the synthesis. Infrared spectrum (*Fig.* 1) of the isolated crystal shows a strong and broad peak around 1100 cm⁻¹ which is assigned to the uncoordinated perchlorate. The spectrum also shows three N-H stretching frequencies in the range of 3100∼3300 cm⁻¹ while that of [Fe(cyclam) (CH₃CN)₂](ClO₄)₂ gives only one N-H stretching band.[1] One would expect all of the four N-H's of the cyclam complex to be chemically equivalent in solution, but different extent of hydrogen bonding by the N-H's can lead to distinctly different N-H frequencies in solid state. The value of molar conductance of the complex in nitromethane (78cm²/ohm·mole)[17] implicates that the complex is a 1:1 type electrolyte. Magnetic moment of the complex is 5.62 BM at room temperature, which implies the presence of four unpaired electrons in the complex. The electronic spectra of the complex in nitromethane shows two broad *d-d* transitions in 4.5KK($\epsilon = \sim 5$) and 12.0 KK ($\epsilon = 4.8$).[18] These absorption peaks are due to transition to the $^5B_1$ and $^5A_1$ states derived
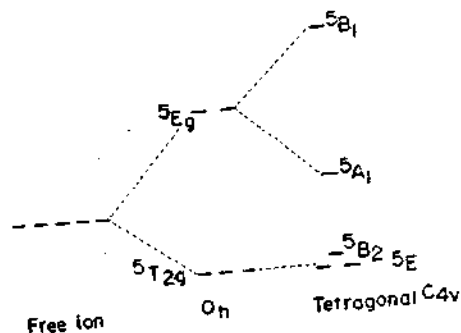

Scheme 1.

from the splitting of the ^5E_g term in a tetragonal ligand field (*Scheme* 1). The spectra indicate a high degree of tetragonal distortion and support the assignment of coordination number five to the complex.

High spin five coordinate iron(II) complex is highly interesting because the active site of biologically important deoxymyoglobin also contains a five-coordinate high spin iron(II).[19]

Busch and coworkers have reported a few high spin five coordinate iron(II) complexes of tetraaza macrocyclic ligands I and II by coordinating a weak ligand in the axial site.[7,8] However, with saturated tetraazamacrocyclic ligand III they obtained only six-coordinate iron(II) complexes.[4] The spin state of these complexes was either high or low depending
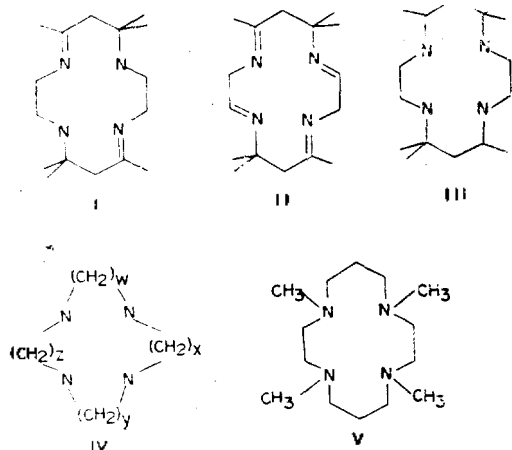
upon the ligand field strength of the axial ligand. They also prepared a number of iron (II) complexes of 13-, 14-, 15-, and 16-membered saturated macrocyclic ligand **IV**, but failed to obtain high spin complexes.[1] Quite recently, Barefield prepared iron(II) complexes of N-substituted macrocyclic ligand **V** and isolated five-coordinate high spin species $[Fe^{II}(V)X]$ where X was CH_3CN, Br^-, Cl^-, or NCS^-.[13] Therefore, it has been generally accepted[13] that either unsaturation or substitution on the nitrogen donor atom in the macrocycle is necessary for the preparation of high spin five-coordinate iron(II) complexes of macrocyclic ligands. This was supported by the failure to isolate high spin iron(II) complexes of **IV**.[1] This view, however, is questionable since attempts to isolate such high spin iron(II) complexes were made in acetonitrile solvent by substitution of the axial ligands of the corresponding diacetonitrile iron-(II) complexes with weak ligands. In general, substitution reactions of low spin six-coordinate iron(II) complexes proceed through dissociative mechanism,[20~25] and, consequently, there exist competitive equilibria between acetonitrile and weak axial ligands as described by eq. 1. Therefore, a high spin five- or six- coordinate
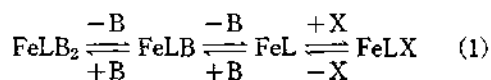
complex containing weak axial ligands would hardly be prepared when the competitive ligands are used as solvent. High spin five-coordinate complexes of **V** prepared by Barefield are unique because the stereochemistry of the nitrogen donor set forces five-coordinate on metal ion, and leads to high spin five-coordinate iron(II) complexes even with the moderately strong axial ligands such as CH_3CN and NCS^-.

The isolation of high spin five-coordinate iron(II) complex in the present investigation indicates that unsaturation or substitution of planar ligand is not always required for the preparation of high spin five-coordinate iron (II) complexes.

3, 2, 3-tet Complexes. Syntheses of $[Fe(3,2,-3-tet)(CH_3CN)_2](ClO_4)_2$ and $[Fe(3,2,3-tet)(CH_3-COO)_2]$ were performed with the free ligand 3, 2, 3-tet and appropriate anhydrous sources of iron(II) as described in the experimental section. They are extremely sensitive to air and moisture, and decompose immediately upon exposure to air producing oily materials. They are very soluble in acetonitrile and alcohol.

The infrared spectrum (*Fig.* 2) of $[Fe(3,2,3-tet)(CH_3CN)_2](ClO_4)_2$ shows a strong and broad band around $1100 \, cm^{-1}$ due to the perchlorate anion, three peaks between $3300 \sim 3150$ cm^{-1} due to N-H stretching modes, and a peak at $1600 \, cm^{-1}$ due to N-H bending. The coordinated acetonitriles show intense peaks at 2260 cm^{-1} and $2290 \, cm^{-1}$. These are higher than those of free acetonitrile ($\nu_2:2251 \, cm^{-1}$, $\bar{\nu}_3+\bar{\nu}_4$: $2289 \, cm^{-1}$)[26]. Usually CN stretching frequencies of simple nitriles increase upon complexation on metal acceptors,[27,28] and the origin of the change is well documented.[26]

Magnetic moments of $[Fe(3, 2, 3-tet)(CH_3-CN)_2](ClO_4)_2$ and $[Fe(3,2,3-tet)(CH_3COO)_2]$ are 5.44 BM and 5.37 BM, respectively. Thus, the iron(II) in these compexes is in high spin
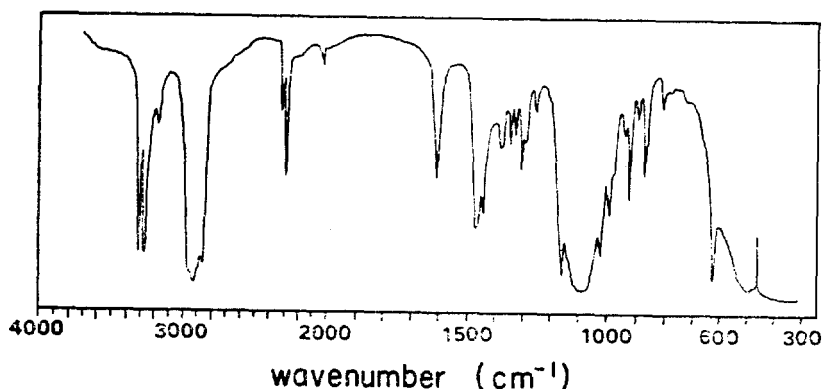
$$FeLB_2 \underset{+B}{\overset{-B}{\rightleftharpoons}} FeLB \underset{+B}{\overset{-B}{\rightleftharpoons}} FeL \underset{-X}{\overset{+X}{\rightleftharpoons}} FeLX \quad (1)$$

Fig. 2. The ir spectrum of [Fe(3,2,3-tet) (CH₃CN)₂] (ClO₄)₂.

state. This stands in marked contrast with [Fe-(cyclam)(CH₃CN)₂](ClO₄)₂[1] and most of the acetonitrile derivatives of iron(II) macrocyclic ligands,[4~9] which are low spin. This difference in spin state between six-coordinate iron(II) complexes of 3,2,3-tet and those of macrocyclic ligands may be attributed to the difference in the corresponding ligand field strength. Macrocyclic planar ligands can produce stronger ligand field than the flexible noncyclic planar ligands because of the greater constrictive effect exerted by the macrocyclic ligands. Thus, whether the planar ligand is cyclic or not is important in the chemistry of metal complexes.

Carbon Monoxide Complexes. Both high spin five-coordinate [Fe(cyclam)Cl](ClO₄) and high spin six-coordinate [Fe(3,2,3-tet)(CH₃-CN)₂](ClO₄)₂ bind carbon monoxide readily in solution. The resulting monocarbon monoxide adducts are [Fe(cyclam)Cl(CO)](ClO₄) and [Fe(3,2,3-tet)(CH₃CN)(CO)](ClO₄)₂, respectively. The isolated carbon monoxide adducts are moderately stable in the absence of oxygen and moisture.

The CO stretching frequency of [Fe(cyclam)(Cl)(CO)](ClO₄) is 1930 cm⁻¹, and that of [Fe(3,2,3-tet)(CH₃CN)(CO)](ClO₄)₂ is 1975cm⁻¹. The ν_{CO} value of [Fe(cyclam)(Cl)(CO)](ClO₄)₂

is much lower than those of the carbonyl derivatives of hemoglobin (1951 cm⁻¹) and myoglobin (1944 cm⁻¹).[19,29] This indicates that the Fe-CO bond in [Fe(cyclam)(Cl)(CO)]ClO₄ is much stronger than those in the carbonyl derivatives of heme proteins. The negatively charged chloride ligand *trans* to CO in [Fe(cyclam)(Cl)(CO)]ClO₄ causes the radial expansion of the $d\pi$ orbitals of iron(II), facilitating $\pi(Fe)-\pi^*(CO)$ back bonding leading to a stronger Fe-CO bond.

Both [Fe(cyclam)(Cl)(CO)]ClO₄ and [Fe-(3,2,3-tet)(CH₃CN)(CO)](ClO₄)₂ are diamagnetic. Overlap of empty π^* orbital of carbon monoxide with filled π orbital of iron ion lowers t_{2g} molecular orbital and causes spin-pairing.

Electronic spectrum of [Fe(cyclam)Cl(CO)]-ClO₄ shows a maximum at 22.5KK(ϵ=373) in nitromethane solution.[30]

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