

portional to Dq because the latter parameter can influence not only the energies of the d electrons of the metal ion but also the centripetal force field and steric factors (through the ionic radius). This may account for the apparent success of ligand field theories in correlating ΔH^* data for several substitution reactions of the I_d type.¹

Acknowledgment. We thank the National Research Council of Canada for financial support.

Registry No. [Cr(DMF)₆](ClO₄)₃, 33594-59-1; [Cr(DMF)₆-(BPh₄)₃], 55156-33-7; DMF, 68-12-2; ClO₄⁻, 14797-73-0.

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Iron Complexes with Macrocyclic Ligands Containing the α -Diimine Functional Unit and Its Position-Specific Formation under the Influence of the Iron Atom

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Received October 3, 1974

AIC40690U

The low-spin iron(II) complex [Fe([14]aneN₄)(CH₃CN)₂](BF₄)₂, where [14]aneN₄ is the tetradentate macrocyclic ligand *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, is found to undergo oxidative dehydrogenation in acetonitrile solution. The product initially isolated is a cyclic triimine having an α -diimine functional unit. In basic acetone the coordinated triimine can be converted rapidly to a tetraimine ligand containing two α -diimine units. The isolated iron(II) complexes all have the general formula [Fe(MAC)(X)₂]ⁿ⁺, where MAC is the macrocycle and X is CH₃CN, imidazole, SCN⁻, NO₂⁻, CN⁻, CNH, CNCH₃, and Cl⁻ and $n = 0$ or 2. The complexes containing the triimine ligand are air sensitive and are further dehydrogenated by molecular oxygen to the corresponding complexes of the tetraimine macrocycle. The bound cyanide ligands of the dicyano complex with the tetraimine macrocycle are sensitive to electrophilic reagents and can be protonated in a stepwise manner or alkylated. All of the complexes isolated, with the exception of the two *trans*-dichloroiron(III) derivatives, display charge-transfer bands in the visible region of their electronic spectra. The positions of these bands have been discussed in terms of the π -bonding abilities of the axial ligands.

Introduction

We have recently reported a series of iron complexes incorporating the 14-membered cyclic structure *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane ([14]aneN₄)² Figure 1(a), and 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene ([14]4,11-dieneN₄)³ Figure 1(b). The six-coordinate low-spin divalent iron(II) complexes with both ligands are air sensitive, and in the presence of molecular oxygen they are oxidatively dehydrogenated to yield complexes of cyclic ligands that contain higher degrees of unsaturation.⁴ In the case of [Fe[14]4,11-dieneN₄](CH₃CN)₂²⁺, dehydrogenation produced complexes structurally identical with those obtained using Ni(II) as the central ion.⁵ However, the Fe(II) complex containing 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,4,8,11-tetraene ([14]1,4,8,11-tetraeneN₄), Figure 1(c), was found to undergo a tautomerization⁶ to give a coordinated macrocycle with two imines in the same five-membered chelate ring, i.e., an α -diimine group. Thus it was apparent early that the presence of iron as the central atom favored α -diimine formation in the ligands. To determine to what extent this tendency toward α -diimine formation affects the course of oxidative dehydrogenation reactions, [Fe^{II}([14]aneN₄)(CH₃CN)₂]²⁺ was

chosen as a reactant. Unlike [14]4,11-dieneN₄ no unsaturated linkages are present in the starting material so that dehydrogenation could occur at any of a number of positions in the macrocyclic ligand. Thus the formation of α -diimine groupings in this case demonstrates the strong directive influence of the iron atom in the oxidative dehydrogenation process. The products formed are among the most stable complexes of iron with synthetic macrocyclic ligands. A variety of interesting materials have been synthesized with these new ligands.

Experimental Section

Materials. All materials were reagent grade and used without further purification unless otherwise noted. Some of the syntheses were carried out in a Vacuum Atmospheres Corp. controlled-atmosphere drybox and the remainder on the "bench top" under a blanket of nitrogen gas.

Physical Measurements. Visible and near-infrared absorption spectra were obtained on a Cary Model 14-R recording spectrophotometer. All signals were recorded from 5 kK to the high-energy cutoff point resulting from the solvent absorption. For the air-sensitive complexes, spectra were recorded, using Teflon-stoppered cells, immediately after preparation under nitrogen and then again 30 min later. In order to determine extinction coefficients, weighings were carried out in contact with the atmosphere and the samples were quickly transferred to the drybox where solutions were prepared. The

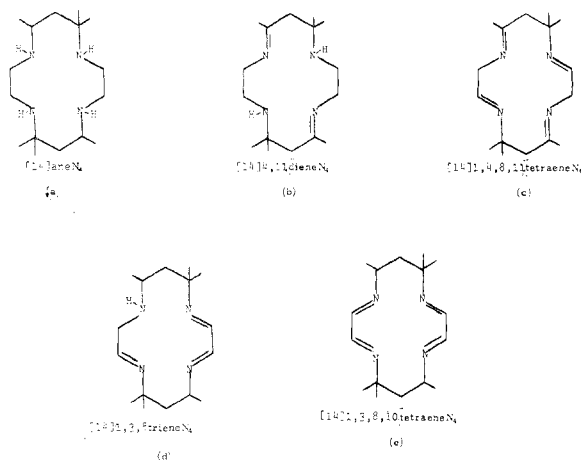


Figure 1. Structures of macrocyclic ligands. The abbreviations used for these macrocyclic ligands are described in ref 2 and 3.

mull spectrum of $\text{Fe}([\text{14}]1,3,8,10\text{-tetraeneN}_4)(\text{SCN})_2$ was determined using filter paper impregnated with Halocarbon 25-S5 grease (Halocarbon Products Corp.).

Infrared spectra were obtained on a Perkin-Elmer Model 337 recording spectrometer using Nujol mulls between KBr disks. The conductivities of the complexes were obtained using an Industrial Instruments Model RC-16B conductivity bridge. The measurements were determined at 25° at 1000 Hz on 10^{-3} M solutions. The nitromethane solvent was purified⁷ according to standard procedures.

Solid-state magnetic moments were determined at room temperature under 35 mm of helium gas using the Faraday method.⁸ The diamagnetic corrections for the new cyclic ligands were calculated using Pascal's constants⁹ and the known diamagnetic susceptibility of the saturated macrocycle $[\text{14}] \text{aneN}_4$ (-254×10^{-6} cgsu).¹⁰ The proton magnetic resonance spectra were obtained on a Varian HA-100 spectrometer using tetramethylsilane (TMS) as an internal standard. All elemental analyses were performed by Galbraith Laboratories.

Preparation of $[\text{Fe}([\text{14}]1,3,8\text{-trieneN}_4)(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$. Eight grams of $[\text{Fe}([\text{14}] \text{aneN}_4)(\text{CH}_3\text{CN})_2](\text{BF}_4)_2 \cdot 1.5\text{CH}_3\text{CN}^2$ (where $[\text{14}] \text{aneN}_4$ is *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) was slurried with 200 ml of CH_3CN and a few milliliters of 48% aqueous HBF_4 was added. Oxygen gas was bubbled through the stirred solution for 20 hr causing an intense red-violet color to develop. After oxygenation, the volume of the solution was reduced to about 50 ml in vacuo and diethyl ether was slowly added to induce precipitation of the crude red-violet $[\text{Fe}([\text{14}]1,3,8\text{-trieneN}_4)(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$. The resulting solid was redissolved in 50 ml of CH_3CN and filtered using "Celite" filter aid to remove a small amount of white insoluble material. Reduction of the filtrate volume at reduced pressure and addition of 200 ml of absolute ethanol saturated with NH_4PF_6 yielded 5.5 g of the crude $[\text{Fe}([\text{14}]1,3,8\text{-trieneN}_4)(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$. Infrared spectral data showed this material to be contaminated with a small amount of BF_4^- , which could be removed by repeating the above procedure. The yield of the red-violet solid was 50–60%. Anal. Calcd for $\text{C}_{20}\text{H}_{36}\text{N}_6\text{P}_2\text{F}_{12}\text{Fe}$: C, 34.01; H, 5.14; N, 11.90. Found: C, 34.22; H, 5.11; N, 12.05.

Preparation of $[\text{Fe}([\text{14}]1,3,8\text{-trieneN}_4)(\text{SCN})_2]$. The following synthesis was carried out under nitrogen gas. To 20 ml of acetone containing a suspension of 1.0 g of $[\text{Fe}([\text{14}]1,3,8\text{-trieneN}_4)(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ was slowly added 2 ml of acetone saturated with LiSCN . The solid dissolved producing a deep blue solution from which the blue *trans*-dithiocyanato derivative crystallized. The crude complex was removed by filtration and dried under nitrogen. Purification was accomplished by dissolving the complex in chloroform, filtering, and reducing the volume until crystallization occurred. The yield was about 0.3 g. Anal. Calcd for $\text{C}_{16}\text{H}_{30}\text{N}_6\text{S}_2\text{Fe}$: C, 48.00; H, 6.71; N, 18.66; S, 14.24. Found: C, 47.99; H, 6.25; N, 18.77; S, 14.20.

Preparation of $[\text{Fe}([\text{14}]1,3,8\text{-trieneN}_4)(\text{Im})_2](\text{BF}_4)_2$ (Where Im is Imidazole). The imidazole derivative was made by dissolving an excess of the base in acetone and adding 0.5 g of $[\text{Fe}([\text{14}]1,3,8\text{-trieneN}_4)(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ under N_2 gas. The acetone solution turned deep blue. Addition of a few milliliters of acetone saturated with LiBF_4 caused the immediate precipitation of $[\text{Fe}([\text{14}]1,3,8\text{-$

$\text{trieneN}_4)(\text{Im})_2](\text{BF}_4)_2$ which was removed by filtration and dried under a stream of N_2 gas. The complex was redissolved in a minimum amount of nitromethane, and diethyl ether was slowly added to induce crystallization. The yield of the blue solid was 0.2 g. Anal. Calcd for $\text{C}_{22}\text{H}_{38}\text{N}_8\text{B}_2\text{F}_8\text{Fe}$: C, 41.03; H, 5.95; N, 17.40; Fe, 8.67. Found: C, 40.82; H, 5.72; N, 17.22; Fe, 8.62.

Preparation of $[\text{Fe}([\text{14}]1,3,8\text{-trieneN}_4)(\text{Cl})_2]\text{PF}_6$ and $[\text{Fe}([\text{14}]1,3,8,10\text{-tetraeneN}_4)(\text{Cl})_2]\text{PF}_6$. Chlorine gas was bubbled through 15 ml of an acetonitrile solution containing 0.4 g of the appropriate *trans*- CH_3CN complex. After being purged for a few minutes the solution turned the deep red-brown color characteristic of the iron(III) derivative. Slow addition of ether until the cloud point caused the crystallization of the dichloro derivative which was removed by filtration and dried under N_2 . The yield was about 0.2 g. Anal. Calcd for $[\text{Fe}([\text{14}]1,3,8\text{-trieneN}_4)(\text{Cl})_2]\text{PF}_6$, $\text{C}_{16}\text{H}_{30}\text{N}_4\text{Cl}_2\text{PF}_6\text{Fe}$: C, 34.94; H, 5.50; N, 10.18. Found: C, 34.89; H, 5.38; N, 9.89. Anal. Calcd for $[\text{Fe}([\text{14}]1,3,8,10\text{-tetraeneN}_4)(\text{Cl})_2]\text{PF}_6$, $\text{C}_{16}\text{H}_{28}\text{N}_4\text{Cl}_2\text{PF}_6\text{Fe}$: C, 35.05; H, 5.15; N, 10.22. Found: C, 35.23; H, 5.13; N, 10.35.

Preparation of $[\text{Fe}([\text{14}]1,3,8,10\text{-tetraeneN}_4)(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$. Four grams of NaNO_2 was suspended in a solution of 2.0 g of $[\text{Fe}([\text{14}]1,3,8\text{-trieneN}_4)(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ dissolved in 150 ml of acetone. Oxygen gas was bubbled through the stirred suspension for 10 min causing the solution to turn deep blue. The remaining solid was removed by filtration and washed with four 50-ml portions of CHCl_3 . The chloroform washings which contained a small amount of $\text{Fe}([\text{14}]1,3,8,10\text{-tetraeneN}_4)(\text{NO}_2)_2$ were combined with the original filtrate and the solvent was removed in vacuo. After the residue was taken up with 15–20 ml of acetonitrile, the solution was acidified with HSO_3CF_3 until a deep red-violet color developed. This solution was filtered and about 100 ml of ethanol saturated with NH_4PF_6 was added. $[\text{Fe}([\text{14}]1,3,8,10\text{-tetraeneN}_4)(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ crystallized in 65–70% yield. Anal. Calcd for $\text{C}_{20}\text{H}_{34}\text{N}_6\text{P}_2\text{F}_{12}\text{Fe}$: C, 34.11; H, 4.87; N, 11.93. Found: C, 34.05; H, 4.59; N, 11.96.

The following compounds are not air sensitive and need not be prepared under N_2 gas.

Preparation of $[\text{Fe}([\text{14}]1,3,8,10\text{-tetraeneN}_4)(\text{NO}_2)_2]$. The chloroform washings obtained in the synthesis of the *trans*-acetonitrile adduct above were combined; the volume was reduced under vacuum and acetone was slowly added to induce crystallization. Anal. Calcd for $\text{C}_{16}\text{H}_{28}\text{N}_6\text{O}_4\text{Fe}$: C, 45.27; H, 6.65; N, 19.82. Found: C, 45.17; H, 6.67; N, 19.69.

Preparation of $[\text{Fe}([\text{14}]1,3,8,10\text{-tetraeneN}_4)(\text{SCN})_2]$. A nitromethane solution containing excess LiSCN was added to $[\text{Fe}([\text{14}]1,3,8,10\text{-tetraeneN}_4)(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ dissolved in nitromethane. The complex crystallized slowly and the yield was about 90%. Anal. Calcd for $\text{C}_{18}\text{H}_{28}\text{N}_6\text{S}_2\text{Fe}$: C, 48.21; H, 6.29; N, 18.74. Found: C, 47.91; H, 6.36; N, 18.75.

Preparation of $[\text{Fe}([\text{14}]1,3,8,10\text{-tetraeneN}_4)(\text{CN})_2]$. To 1 g of $[\text{Fe}([\text{14}]1,3,8,10\text{-tetraeneN}_4)(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ suspended in 50 ml of acetone under nitrogen gas was added 20 ml of an aqueous solution containing 0.14 g of NaCN . The deep blue solution was heated gently for a few minutes. After removal of the acetone and most of the water in vacuo, additional water (~ 10 ml) and a few drops of HSO_3CF_3 (*caution!* HCN) were added completely dissolving the cyanide complex. The solution was filtered and the crude dicyano complex was crystallized by addition of 150 ml of 10 N aqueous NaOH . The deep blue $[\text{Fe}([\text{14}]1,3,8,10\text{-tetraeneN}_4)(\text{CN})_2]$ which formed was removed by filtration and taken up in a slurry of CH_2Cl_2 and anhydrous Na_2SO_4 . After filtration, the filtrate volume was reduced and ether was slowly added to induce crystallization. The yield was about 25%. Anal. Calcd for $\text{C}_{18}\text{H}_{28}\text{N}_6\text{Fe}$: C, 56.26; H, 7.34; N, 21.81. Found: C, 55.96; H, 7.30; N, 21.61.

Preparation of $[\text{Fe}([\text{14}]1,3,8,10\text{-tetraeneN}_4)(\text{CNCH}_3)_2](\text{PF}_6)_2$. To 50 mg of $[\text{Fe}([\text{14}]1,3,8,10\text{-tetraeneN}_4)(\text{CN})_2]$ in CH_3CN was added 1 ml of $\text{CH}_3\text{SO}_3\text{F}$ and the solution was gently warmed. After 10 min, about 400 ml of ethanol saturated with NH_4PF_6 was added to the orange solution. The yield of the *trans*-dimethyl isocyanide-phosphorus hexafluoride complex was about 50 mg. Anal. Calcd for $\text{C}_{20}\text{H}_{34}\text{N}_6\text{P}_2\text{F}_{12}\text{Fe}$: C, 34.11; H, 4.87; N, 11.93. Found: C, 33.92; H, 4.91; N, 11.82.

Preparation of $[\text{Fe}([\text{14}]1,3,8,10\text{-tetraeneN}_4)(\text{CNH})_2](\text{SO}_3\text{CF}_3)_2$. Working under dry nitrogen gas, 50 mg of $[\text{Fe}([\text{14}]1,3,8,10\text{-tetraeneN}_4)(\text{CN})_2]$ was suspended in 5 ml of dry acetonitrile and a few drops of anhydrous HSO_3CF_3 was added. The deep blue dicyano complex dissolved to form a brown-orange solution. Slow addition of sodium-dried ether resulted in the crystallization of the diprotonated

Table I. Physical Properties of the Iron Complexes

Compd ^a	Color	μ , ^b BM	Λ , ^c cm ² ohm ⁻¹ mol	Ir bands, ^d cm ⁻¹
[Fe([14]1,3,8-trieneN ₄)(CH ₃ CN) ₂](PF ₆) ₂	Violet	Dia	310 (CH ₃ CN)	NH, 3290 m; C≡N, 2280 w; isolated C=N, 1640 m; α -C=N, 1600 w, 1510 m
[Fe([14]1,3,8-trieneN ₄)(Im) ₂](BF ₄) ₂	Blue	Dia	162 (CH ₃ NO ₂)	NH, 3330 s, 3140 m; N=C, 1620 m, 1560 w, 1530 m
Fe([14]1,3,8-trieneN ₄)(SCN) ₂	Blue	Dia	8 (CH ₃ NO ₂)	NH, 3260 w; C≡N, 2105 s; isolated C=N, 1640 m; α -C=N, 1570 w
[Fe([14]1,3,8-trieneN ₄)(Cl) ₂](PF ₆) ₂	Red-brown	2.13	146 (CH ₃ CN)	NH, 3215 m; isolated C=N, 1649 m
[Fe([14]1,3,8,10-tetraeneN ₄)(CH ₃ CN) ₂](PF ₆) ₂	Violet	Dia	322 (CH ₃ CN)	C≡N, 2280 w, 2240 w; α -C=N, 1630 w, 1550 m
Fe([14]1,3,8,10-tetraeneN ₄)(SCN) ₂	Blue-green	Dia		C≡N, 2120 s; α -C=N, 1540 w; S-C, 800 m
Fe([14]1,3,8,10-tetraeneN ₄)(CN) ₂	Blue	Dia	4 (CH ₃ CN)	Imine CH, 3075 s; C≡N, 2100 s; α -C=N, 1585 w
[Fe([14]1,3,8,10-tetraeneN ₄)(CNH) ₂](SO ₃ CF ₃) ₂	Brown	Dia	162 (CH ₃ NO ₂)	2600 s, b; 1620 w, b; α -C=N, 1530 w, b; SO ₃ -CF ₃ , 1390 s, 1200 vs, 1020 s, 630 s, 510 w, 515 w
[Fe([14]1,3,8,10-tetraeneN ₄)(CNCH ₃) ₂](PF ₆) ₂	Brown	Dia	289 (CH ₃ CN)	C≡N, 2210 s; N=C, 1620 w; 1535 m
Fe([14]1,3,8,10-tetraeneN ₄)(NO ₂) ₂	Green	Dia	2 (CH ₃ NO ₂)	Imine CH, 3010 m; C=N, 1600 w; 1505 m
[Fe([14]1,3,8,10-tetraeneN ₄)(Cl) ₂](PF ₆) ₂	Red-brown	2.06	158 (CH ₃ CN)	
[Co([14]1,3,8,10-tetraeneN ₄)(Cl) ₂](ClO ₄) ₂	Green	Dia		Imine CH, 3010 m

^a For the structures of the macrocyclic ligands see Figure 1. Abbreviation: Im = imidazole. ^b The diamagnetic (Dia) complexes have moments of 0.40–0.70 BM. ^c The conductance is given, in parentheses, followed by the solvent. ^d Infrared spectra were recorded using Nujol mulls between KBr disks except when otherwise noted. Isolated imine and α -diimine (α -C=N) are as defined in the text. ^e Halo oil infrared mull.

complex. The brown solid was removed by filtration, washed with ether, and dried under N₂ gas. The yield was about 50 mg. Anal. Calcd for C₂₀H₃₀N₄S₂O₆F₆Fe: C, 35.33; H, 4.52; N, 12.22; S, 9.59. Found: C, 35.09; H, 4.41; N, 12.27; S, 9.36.

Preparation of [Co([14]1,3,8,10-tetraeneN₄)(Cl)₂](ClO₄)₂. To 0.6 g (8.6 × 10⁻³ mol) of [Fe([14]1,3,8,10-tetraeneN₄)(CH₃CN)₂](PF₆)₂ in dry degassed CH₃CN was added 0.44 g (2.6 × 10⁻² mol) of *o*-phenanthroline (dried over P₄O₁₀). The solution was allowed to stand under N₂ for 1 day after which time the solvent was removed at reduced pressure (35°). The residue was washed with 30 ml of dry CH₂Cl₂. After filtration of the wash solution, the filtrate was added to 150 ml of dry acetonitrile containing 0.18 g of anhydrous CoCl₂. Heating for 30 min under N₂ caused a black solid to crystallize which was removed by filtration. The solid was dissolved in ethanol containing 1 ml of concentrated HCl and the solution heated in the atmosphere for 15 min. Addition of a few drops of HClO₄ caused the slow crystallization of the *trans*-dichloro derivative. The yield was about 50 mg. Anal. Calcd for C₁₆H₂₈N₄Cl₃O₄Co: C, 38.00; H, 5.58; N, 11.08. Found: C, 37.42; H, 5.71; N, 10.90.

Results and Discussion

Characterization of *trans*-[Fe([14]1,3,8-trieneN₄)(CH₃CN)₂](PF₆)₂. The iron(II) complex *trans*-[Fe([14]aneN₄)(CH₃CN)₂](BF₄)₂ reacts smoothly with molecular oxygen in acetonitrile solution to yield complexes containing dehydrogenated forms of the ligand. Upon exposure to O₂, acidified acetonitrile solutions of the complex turn a transient yellow-brown color which rapidly changes to deep red-violet. Although the oxidative dehydrogenation reaction produces some white organic material, which is probably the fragmented ligand, a significant amount (50–60%) of an Fe(II) complex containing the intact, but altered, coordinated ligand can be recovered. The isolated deep red-violet solid, [Fe([14]1,3,8-trieneN₄)(CH₃CN)₂](PF₆)₂ where [14]1,3,8-trieneN₄ is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8-triene (Figure 1(d)), is diamagnetic and is a 2:1 electrolyte in acetonitrile (Table I). Infrared evidence shows the presence of coordinated acetonitrile (C≡N, 2280 cm⁻¹) and absorptions in the imine region at 1640, 1600, and 1510 cm⁻¹. The starting complex containing the saturated ligand has no absorption in the region 1500–1700 cm⁻¹. The position and

moderate intensity of the highest energy imine absorption (1640 cm⁻¹) are very similar to those absorptions observed for coordinated isolated imine functions in [Fe([14]4,11-dieneN₄)(CH₃CN)₂](ClO₄)₂,³ [Fe([14]1,4,11-trieneN₄)(CH₃CN)₂](ClO₄)₂,⁴ and [Fe([14]1,4,8,11-tetraeneN₄)(CH₃CN)₂](ClO₄)₂⁴ (Figure 1). Accordingly, the infrared absorption at 1640 cm⁻¹ is assigned to the isolated imine located in one of the five-membered chelate rings (Figure 1(d)). Although the positioning of the imine function in the five-membered as opposed to the six-membered ring is not possible on the basis of the infrared data alone, the NMR evidence presented below fully supports this assignment.

The pattern and position of the lower energy absorptions in the double bond region of the infrared spectrum of [Fe([14]1,3,8-trieneN₄)(CH₃CN)₂]²⁺ are similar to those observed for [Fe([14]1,3,7,11-tetraeneN₄)(CH₃CN)₂](ClO₄)₂ which also contains two imine functions in the same five-membered chelate ring (α -diimine). The physical properties of this tetraene complex were reported earlier⁴ and it was inferred that the α -diimine bands were too weak to be observed. Our reexamination of the infrared spectrum disclosed that two absorptions of medium intensity at 1510 and 1530 cm⁻¹ are very likely associated with the α -diimine function. According to the normal-coordinate analysis performed by Nakamoto on α -diimine-iron(II) complexes,¹¹ absorptions associated with this functional unit should occur near 1500 cm⁻¹. The possibility that these bands are associated with other structural features of the cyclic ligands seems remote. They are not observed in the spectra of macrocycles having only saturated groupings or isolated imines complexed to iron(II).²⁻⁴ Based on the infrared absorptions of [14]1,3,8-trieneN₄ the remaining five-membered chelate ring must possess an α -diimine functional group. In addition to the imine absorptions, [Fe([14]1,3,8-trieneN₄)(CH₃CN)₂]²⁺ displays an N-H stretch at 3290 cm⁻¹ which is consistent with the structure shown in Figure 1(d).

The number and general positions of the unsaturated functions in the new macrocyclic ligand are supported by the uv-visible absorption spectrum of [Fe([14]1,3,8-trieneN₄)-

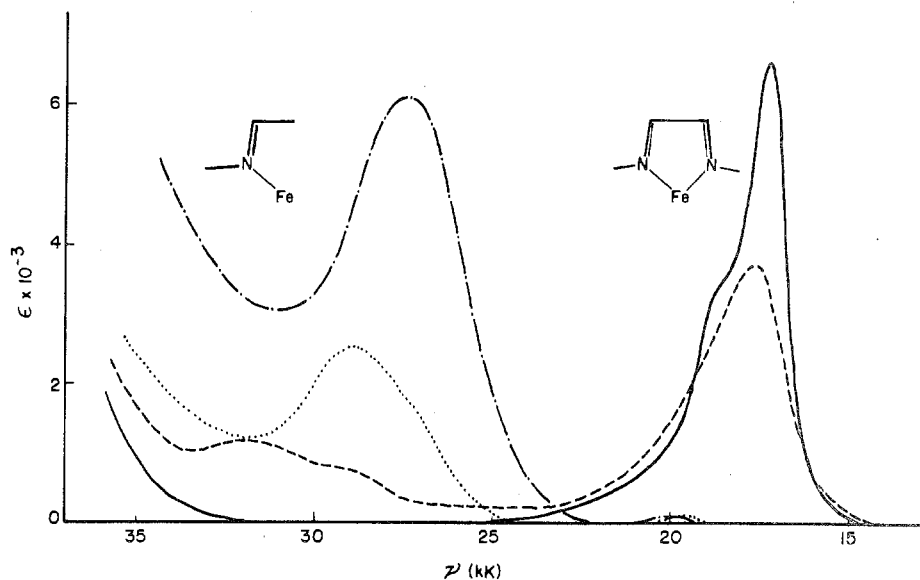


Figure 2. Charge-transfer spectra of the iron(II) complexes in acetonitrile solution: —, [Fe([14]1,3,8,10-tetraeneN₄)(CH₃CN)₂](PF₆)₂; ---, [Fe([14]1,3,8-trieneN₄)(CH₃CN)₂](PF₆)₂; ····, [Fe([14]4,11-dieneN₄)(CH₃CN)₂](PF₆)₂; - · - · - ·, [Fe([14]1,4,8,11-tetraeneN₄)(CH₃CN)₂](PF₆)₂.

Table II. Electronic Spectral Data for the Iron Complexes

Compd ^a	Solvent ^b	Absorption bands, kK ^c
[Fe([14]1,3,8-trieneN ₄)(CH ₃ CN) ₂](PF ₆) ₂	CH ₃ CN	17.9 (3670), 28.6 sh, 31.5 (1050)
[Fe([14]1,3,8-trieneN ₄)(Im) ₂](BF ₄) ₂	CH ₃ NO ₂	14.6 (1170), 17.1 (2950)
Fe([14]1,3,8-trieneN ₄)(SCN) ₂	CH ₃ NO ₂	15.7 (3400), 20.2 sh
[Fe([14]1,3,8-trieneN ₄)(Cl) ₂](PF ₆) ₂	CH ₃ CN	17.9 sh (580), 19.3 (880), 20.8 sh (605), 23.8 (1800), 29.4 sh (1220)
[Fe([14]1,3,8,10-tetraeneN ₄)(CH ₃ CN) ₂](PF ₆) ₂	CH ₃ CN	15.65 (470), 17.3 (6670), 18.5 sh (3580), 20.6 sh (850)
Fe([14]1,3,8,10-tetraeneN ₄)(SCN) ₂	SS	12.1, 13.6, 15.2, 16.8, 21.7
Fe([14]1,3,8,10-tetraeneN ₄)(CN) ₂	CH ₃ NO ₂	15.55 (9400), 16.7 sh
[Fe([14]1,3,8,10-tetraeneN ₄)(CNH) ₂](SO ₃ CF ₃) ₂	CH ₃ NO ₂	20.0 (3490)
[Fe([14]1,3,8,10-tetraeneN ₄)(CNCH ₃) ₂](PF ₆) ₂	CH ₃ CN	15.4 (93), 19.5 (7160), 21.3 sh, 26.3 (400), 32.0 (298)
Fe([14]1,3,8,10-tetraeneN ₄)(NO ₂) ₂	CH ₃ NO ₂	15.0 (5850), 16.2 (3700), 17.9 sh, 24.2 (1140)
Fe([14]1,3,8,10-tetraeneN ₄)(NO ₂) ₂	CHCl ₃	14.95 (6250), 16.3 sh (4000), 24.1 (1530), 32.1 (1920)
[Fe([14]1,3,8,10-tetraeneN ₄)(Cl) ₂](PF ₆) ₂	CH ₃ CN	18.2 sh, 19.4 (1180), 20.9 sh (650), 23.5 (2000), 29.5 (1270)
[Co([14]1,3,8,10-tetraeneN ₄)(Cl) ₂](ClO ₄) ₂	CH ₃ CN	17.7 (43), 22.0 sh, 24.2 (778), 29.4 (1130)

^a The structures of the cyclic ligands are shown in Figure 1. ^b SS = solid state. ^c The position of the band is given followed by the extinction coefficient in M⁻¹ cm⁻¹.

(CH₃CN)₂](PF₆)₂ (Table II, Figure 2). The deep red-violet complex exhibits a charge-transfer band (CT) at 17.9 kK that closely resembles those of the iron(II) complexes with *o*-phenanthroline, 2,2'-dipyridyl, and other α -diimine types of ligands.¹² The triene also exhibits a second weaker transition at 31.5 kK which also appears in the spectra of complexes whose C=N groups are unconjugated. Examples are [Fe([14]4,11-dieneN₄)(CH₃CN)₂]²⁺, [Fe([14]1,4,11-trieneN₄)(CH₃CN)₂]²⁺, and [Fe([14]1,4,8,11-tetraeneN₄)(CH₃CN)₂]²⁺.^{3,4} This characteristic absorption band probably involves the isolated imine group in a metal-to-ligand charge-transfer process. These charge-transfer bands will be more fully discussed below.

The 100-MHz NMR spectrum of the diamagnetic trans-acetonitrile complex strongly supports the structure proposed for the new cyclic ligand. The proton resonances of [Fe([14]1,3,8-trieneN₄)(CH₃CN)₂](PF₆)₂ in CD₃CN can conveniently be divided into three regions: 1–2, 2–8, and 8–9 ppm. The resonances at highest and lowest field are shown in Figure 3(a). In the methyl region, 1–2 ppm, five signals are found with relative intensities of 1.5:7.5:1.5:4.5:3.0 in order of increasing field strength (Table III). The structure shown in Figure 1(d) has C₁ symmetry and all of the methyl groups are nonequivalent by symmetry. The two methyl groups attached to the asymmetric carbon atoms appear as doublets at 1.43 and 1.66 ppm. Because of overlapping signals, the coupling constants cannot be determined accurately but

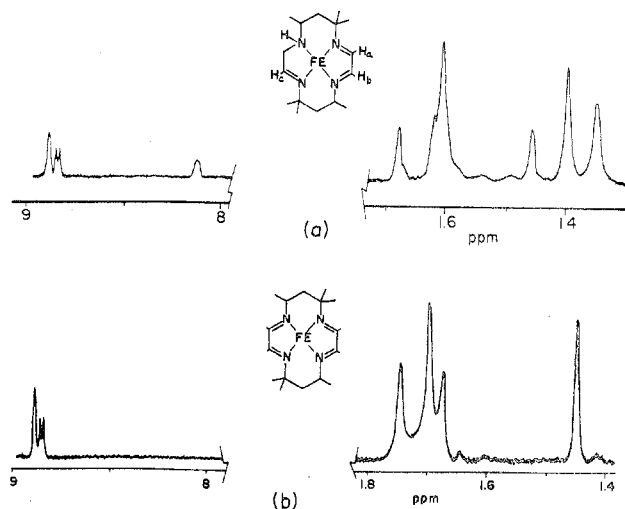


Figure 3. The 100-MHz NMR spectra of (a) [Fe([14]1,3,8-trieneN₄)(CH₃CN)₂](PF₆)₂ and (b) [Fe([14]1,3,8,10-tetraeneN₄)(CH₃CN)₂](PF₆)₂ in CD₃CN.

couplings of 6–7 Hz are found. Three singlets produced by the *gem*-dimethyl groups overlap the methyl doublet pattern. Two of the singlets are accidentally degenerate and resonate at the same field (~1.64 ppm) as one of the components of a

Table III. 100-MHz PMR Spectra of the Iron and Cobalt Complexes

Complex ^a	Assignments ^b				
	<i>gem</i> CH ₃ (s)	Asym CH ₃ (d)	Imine H ^c	Methine H (m)	Others
[Fe([14]1,3,8-trieneN ₄)(CH ₃ CN) ₂](PF ₆) ₂ ^d	1.35 (3)	1.66 (3)	8.90 (1) s, H _a		
	1.40 (3)	1.43 (3)	8.85 (1) d, H _b		
	1.62 (6)		8.17 (1) m, H _c		
[Fe([14]1,3,8,10-tetraeneN ₄)(CH ₃ CN) ₂](PF ₆) ₂ ^d	1.45 (6)	1.71 (6)	8.90 (2) s, H _a	4.40 (2)	2.06 (4) m, CH ₂
	1.70 (6)		8.85 (2) d, H _b		
[Fe([14]1,3,8,10-tetraeneN ₄)(CNH) ₂](SO ₃ CF ₃) ₂ ^e	1.62 (6)	1.68 (6)	8.63 (2) b, H _a	4.45 (2)	6.49 s, b, NH
	1.72 (6)		8.53 (2) b, H _b		
[Fe([14]1,3,8,10-tetraeneN ₄)(CNCH ₃) ₂](PF ₆) ₂ ^e	1.63 (6)	1.60 (6)	8.46 (2) s, H _a	4.23 (2)	3.36 (6), s, b, CNCH ₃
	1.50 (6)		8.36 (2) d, H _b		
[Co([14]1,3,8,10-tetraeneN ₄)(Cl) ₂](ClO ₄) ^e	1.77 (6)	1.85 (6)	8.51 (2) s, H _a	4.61 (2)	
	1.73 (6)		8.46 (2) d, H _b		

^a The structures of the ligands are given in Figure 1. ^b Assignments are given in ppm from TMS at 37°. The number of protons is given in parentheses; signal multiplicity is indicated in the heading or following the number of protons: s, singlet; d, doublet; m, multiplet; b, broad. The coupling constants for the imine doublets and methyl doublets are 3.0 and 7.0 Hz, respectively. ^c For assignments of imine protons refer to Figure 3. ^d Solvent CD₃CN. ^e Solvent is CD₃NO₂ with 1 drop of HSO₃CF₃.

methyl doublet. This gives rise to a signal accounting for 7.5 protons. The remaining two *gem*-methyl groups have different chemical shifts (Table III) but one overlaps a component of the second methyl doublet (~1.41 ppm). This gives a signal integrating for 4.5 protons.

Unsaturation in the cyclic ligand other than at the positions shown in Figure 1(d) can be discounted. If any of the methyl groups were involved in an imine linkage such as certain of the methyl groups of [Co([14]4,11-dieneN₄)Cl₂]⁺,¹³ [Ni([14]4,11-dieneN₄)]²⁺,¹⁴ and [Fe([14]4,11-dieneN₄)(CH₃CN)₂]²⁺,³ a singlet would be observed in the region 2–2.5 ppm. Such a resonance does not occur for [Fe([14]1,3,8-trieneN₄)(CH₃CN)₂]²⁺. The possibility of a carbon-carbon double bond in the five-membered chelate rings can be ruled out because of the absence of olefinic proton resonances (4.5–6.5 ppm).

The region between 2 and 8 ppm is very complex and accounts for the 6-methylene protons of the five- and six-membered rings, the two methine protons of the asymmetric carbons, and the single hydrogen attached to the nitrogen atom. Because of the low symmetry of the complex and the multiplicity of the patterns, no assignments were made.

The NMR spectrum of *trans*-[Fe([14]1,3,8-trieneN₄)(CH₃CN)₂](PF₆)₂ shows three resonances at low field (8–9 ppm) which integrate for one proton each. These absorptions are characteristic of azomethine protons¹⁵ and their chemical shifts and splitting patterns help determine the locations of the unsaturations. The lowest field singlet and the doublet are the proton resonances of the α -diimine functional group. Due to long-range coupling with the methine proton of the asymmetric carbon atom, H_b (Figure 3(a)) appears as a doublet with $J = 3.0$ Hz. The lowest field resonance at 8.90 ppm is assigned to H_a. The somewhat broadened (6-Hz width) signal at 8.17 ppm is the azomethine proton of the isolated imine function. The broadening of this resonance is the result of spin-spin coupling between it and the methylene protons of the five-membered ring. Attempts to simplify the signal for H_c by deuterium exchange of the methylene protons were not successful. Although this type of exchange has been demonstrated for similar structures,^{14,15} NMR and ir analyses of the deuterated iron complex showed that exchange occurred only for the amine hydrogen atom.

The precise location of the isolated imine function in the five-membered chelate ring cannot be determined with certainty on the basis of the data in hand. However, the chemical shifts of the two methyl doublets differ significantly (Table III), strongly suggesting that the imine function is adjacent to the *gem*-dimethyl group instead of the asymmetric carbon atom. If it were adjacent to the asymmetric carbon atom, the chemical shift of that CH₃ group should be similar to that

observed for the second methyl doublet which is adjacent to an imine of the α -diimine function.

Characterization of *trans*-[Fe([14]1,3,8,10-tetraeneN₄)(CH₃CN)₂](PF₆)₂. Exposure of neutral or acidic solutions of [Fe([14]1,3,8-trieneN₄)(CH₃CN)₂](PF₆)₂ to oxygen gas results in the introduction of additional unsaturation in the coordinated cyclic ligand to give 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene ([14]1,3,8,10-tetraeneN₄) (Figure 1(e)). The isolated diamagnetic solid is deep red-violet and a 2:1 electrolyte in acetonitrile (Table I). Infrared data show a weak α -diimine absorption at 1550 cm⁻¹ and the absence of the N-H stretch at 3290 cm⁻¹. The charge-transfer band in the visible absorption spectrum at 17.3 kK (Figure 2) is shifted slightly to lower energy and is about twice as intense as the corresponding absorption for [Fe([14]1,3,8-trieneN₄)(CH₃CN)₂]²⁺. Furthermore, the charge-transfer transition associated with isolated imine functional groups is not present in the spectrum of [Fe([14]1,3,8,10-tetraeneN₄)(CH₃CN)₂](PF₆)₂.

The NMR spectrum of the tetraimine displays a higher degree of symmetry than that of the triimine (Figure 3(b)). Since planar coordinated [14]1,3,8,10-tetraeneN₄ has a center of inversion, the methyl groups are pairwise equivalent so that the two methyl groups attached to the asymmetric carbon atoms are equivalent by symmetry and their NMR resonances occur at 1.71 ppm. A six-membered chelate ring probably exists in a distorted chair type conformation with two methyl groups equatorially disposed and the third (one of the *gem* pair) in an axial position. One of the *gem* methyls has a chemical shift nearly identical with that of the methyl doublet. Both are equatorially disposed.¹⁷ The remaining methyl singlet at high field is due to the axial methyl of the *gem*-dimethyl pair. The azomethine protons of the α -diimine functions exhibit splitting patterns and chemical shifts which are identical with those of the α -diimine function of the triene but, also, no signal appears near 8.17 ppm since there is no isolated imine. The region between 2 and 8 ppm is considerably simpler than in the case of the triene and additional assignments have been made (Table III).

Chemical Conditions for and Positional Selectivity of the Dehydrogenation. The conditions necessary to effect oxidative dehydrogenation are most readily examined by considering the triene-tetraene conversion. Spectral analysis of acetonitrile solutions which have been acidified with a few drops of HSO₃CH₃ and exposed to the air shows a slow conversion (2–4 days) of the triene to the tetraene. If the acidified solutions of the triene are kept under nitrogen, they are stable for months. The results of previous studies suggest that oxygen gas serves as an oxidant and oxidizes iron(II) to iron(III). The iron(III) complex thus formed is reduced in the course of

oxidizing the ligand. In the case of $[\text{Fe}(\text{[14]4,11-dieneN}_4)(\text{CH}_3\text{CN})_2](\text{ClO}_4)_3$, small amounts of water serve to promote the process and it appears that the presence of certain anionic ligands retards the reaction, while others promote it.

The oxidation of $[\text{Fe}(\text{[14]1,3,8-trieneN}_4)(\text{CH}_3\text{CN})_2]^{2+}$ can be carried out using chlorine gas to yield a relatively stable low-spin trans-dichloro derivative. However, attempts to isolate the corresponding trans-acetonitrile derivative by dissolving the iron(III) dichloride in CH_3CN under nitrogen and adding AgClO_4 to remove the chloride ligands failed. The trans-acetonitrile complex thus generated is unstable and quickly reverts to the characteristic deep red-violet iron(II) complex. A spectral examination of the reduced solution has shown that the following reaction occurs:¹⁸ $2[\text{Fe}^{\text{III}}(\text{[14]trieneN}_4)(\text{CH}_3\text{CN})_2]^{3+} \rightarrow [\text{Fe}^{\text{II}}(\text{[14]tetraeneN}_4)(\text{CH}_3\text{CN})_2]^{2+} + [\text{Fe}^{\text{II}}(\text{[14]trieneN}_4)(\text{CH}_3\text{CN})_2]^{2+} + 2\text{H}^+$. Thus 2 mol of iron(III) is reduced for every new C=N group formed.

Oxidative dehydrogenation of $[\text{Fe}(\text{[14]1,3,8-trieneN}_4)(\text{CH}_3\text{CN})_2]^{2+}$ appears to be accelerated by the presence of strong coordinating ligands such as CN^- , SCN^- , and NO_2^- . The addition of Li^+ or Na^+ salts of these ions to acetone solutions of $[\text{Fe}(\text{[14]1,3,8-trieneN}_4)(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ leads to a very rapid dehydrogenation. The precise function of these anions is not known but they could serve to control the iron(II)–iron(III) potential and/or accept protons produced in the oxidative dehydrogenation. An increase in the hydrogen ion concentration has been observed for this process.⁴ Under the same oxidative dehydrogenation conditions other potential iron(III)-stabilizing anions such as Cl^- , Br^- , and CH_3CO_2^- lead to rapid decomposition of the complex. Since these are relatively weak field ligands, it is possible that the spin states of the iron(II) and iron(III) complexes play an important part in the process. Work is currently under way to disclose more of the details of this interesting reaction.¹⁸

Oxidative dehydrogenations of cyclic complexes of Ni(II)^{5,18} and Fe(II) have been reported previously but the locations of the unsaturated linkages in the cyclic ligands were found to be different from those resulting from the dehydrogenation of $[\text{Fe}(\text{[14]aneN}_4)(\text{CH}_3\text{CN})_2]^{2+}$ as reported here. Curtis⁵ reported the dehydrogenation of $[\text{Ni}(\text{[14]4,11-dieneN}_4)]^{2+}$ in nitric acid to give complexes containing only isolated imine functions (Figure 1(c)). Nitric acid oxidation of $[\text{Ni}(\text{[14]aneN}_4)]^{2+}$ yields the same series of products.¹⁸ Oxidative dehydrogenation of $[\text{Fe}(\text{[14]4,11-dieneN}_4)(\text{CH}_3\text{CN})_2]^{2+}$ in acidified acetonitrile solutions was reported earlier and although the reaction is more facile than those of the Ni(II) system (molecular oxygen alone being required), the new ligands initially obtained are structurally identical with those obtained with the nickel complexes.⁴ Regardless of the central metal ion the dienes have only two secondary amines available for dehydrogenation (excluding formation of carbon–carbon unsaturation) and it is not surprising that the cyclic ligand produced by exhaustive dehydrogenation is $[\text{14]1,4,8,11-tetraeneN}_4$ (Figure 1(c)) in this case. However, the dehydrogenation of $[\text{Ni}(\text{[14]aneN}_4)]^{2+}$ could yield the same bis(α -diimine) ligand that the iron complex produces (Figure 1(e)) as its ultimate dehydrogenated product. In fact, only $[\text{14]1,4,8,11-tetraeneN}_4$ is found¹⁸ in the Ni(II) case. The corresponding dehydrogenation of the Fe(II) derivative behaves in a completely contrasting manner and only complexes having unsaturation in the five-membered rings are isolated. These results show that in the iron(II) system dehydrogenation is confined solely to the two five-membered chelate rings. The driving force for this strongly preferred formation of an iron(II)– α -diimine functional unit must be associated with the documented aromatic nature of this group.¹⁹ In this regard, a demonstration of the increase in stability which this functional

unit confers on iron(II) has recently been provided using electrochemical methods.⁶ Further evidence for the great stability of the iron(II)– α -diimine structural unit is provided by the tautomerization in acid solution of $[\text{Fe}(\text{[14]1,4,8,11-tetraeneN}_4)(\text{CH}_3\text{CN})_2]^{2+}$ (Figure 1(c)) to give the α -diimine derivative $[\text{Fe}(\text{[14]1,3,8,11-tetraeneN}_4)(\text{CH}_3\text{CN})_2]^{2+}$.^{6,7}

Reactivity of the Other Complexes. Since the tetraimine complexes contain four imine groups, they are not sensitive to further oxidative dehydrogenation. Although the formation of carbon–carbon unsaturations might seem feasible, no dehydrogenation process with these kinds of compounds has yet been observed to produce such a grouping. The complexes are insensitive to oxygen in the solid state and in acetonitrile or nitromethane solutions. However, dissolution in water causes a rapid discoloration, ultimately followed by the formation of rust and iron mirrors on the glassware.

As has been demonstrated for $[\text{Fe}(\text{[14]1,4,8,11-tetraeneN}_4)(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$,⁴ the free macrocyclic ligand $[\text{14]1,3,8,10-tetraeneN}_4$ can be removed from $[\text{Fe}(\text{[14]1,3,8,10-tetraeneN}_4)(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$. The addition of 3 equiv of *o*-phenanthroline (*o*-phen) to an acetonitrile solution of $[\text{Fe}(\text{[14]1,3,8,10-tetraeneN}_4)(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ yields $[\text{Fe}(\text{o-phen})_3](\text{PF}_6)_2$ and the free ligand. The ligand is isolated as an impure oil and is difficult to characterize. However, reaction of this oil with cobalt(II) chloride under anhydrous conditions ultimately gave the olive green diamagnetic *trans*- $[\text{Co}(\text{[14]1,3,8,10-tetraeneN}_4)(\text{Cl})_2]\text{ClO}_4$ complex. The NMR data given in Table III for this complex clearly show the characteristic absorptions of the azomethine protons of the α -diimine linkages and the methyl resonances of the intact cyclic ligand. The visible absorption spectral curve obtained for this dichloro complex closely resembles that reported for the macrocycle derivative $[\text{Co}^{\text{III}}(\text{TIM})\text{Cl}_2]\text{ClO}_4$.²⁰ TIM also has two α -diimine units in a 14-membered ring coordinated to cobalt(III). However, unlike that of $[\text{Co}^{\text{III}}(\text{TIM})\text{Cl}_2]\text{ClO}_4$, the infrared spectrum of $[\text{Co}^{\text{III}}(\text{[14]1,3,8,10-tetraeneN}_4)\text{Cl}_2]\text{ClO}_4$ gives no absorptions which can be attributed to the α -diimine group. The halo oil mull infrared spectra of $[\text{Fe}(\text{[14]1,3,8,10-tetraeneN}_4)(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ and $[\text{Co}(\text{[14]1,3,8,10-tetraeneN}_4)\text{Cl}_2]\text{ClO}_4$ were nearly superimposable in the region 4000–1400 cm^{-1} except for the missing α -diimine bands in the case of the cobalt complex. The reduction in intensity of these bands for certain Co(III) complexes has been noted previously but their complete disappearance has not been documented.²⁰ Attempts to remove $[\text{14]1,3,8-trieneN}_4$ from $[\text{Fe}(\text{[14]1,3,8-trieneN}_4)(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ in the manner described above were not successful. As before, an oil was isolated but no characterizable cobalt(III) complex could be generated from it. The successful removal of $[\text{14]1,3,8,10-tetraeneN}_4$ from iron(II) and preparation of the Co(III) complex demonstrate the further utility of the positionally directed metal ion controlled ligand synthesis.

The Fe([14]1,3,8,10-tetraeneN₄)(CN)₂ Complex. As is commonly true of iron–cyanide complexes,²¹ the bound cyanide groups of $[\text{Fe}(\text{[14]1,3,8,10-tetraeneN}_4)(\text{CN})_2]$ are sufficiently basic to be protonated in strongly acidic solutions. The addition of HSO_3CF_3 to the dicyano complex in acetonitrile permits the isolation of the brown hygroscopic compound, $[\text{Fe}(\text{[14]1,3,8,10-tetraeneN}_4)(\text{CNH})_2](\text{SO}_3\text{CF}_3)_2$. This complex is very sensitive to water in the solid state and rapidly changes color in moist air.

The NMR spectrum of the complex in CD_3NO_2 shows a broadened (¹⁴N quadrupolar effects) signal at 6.49 ppm which is very sensitive to the hydrogen ion concentration. The addition of 1 drop of HSO_3CF_3 to the solution used to measure the NMR spectrum results in a downfield shift of this signal by 4–5 ppm. Since this absorption occurs in the same region

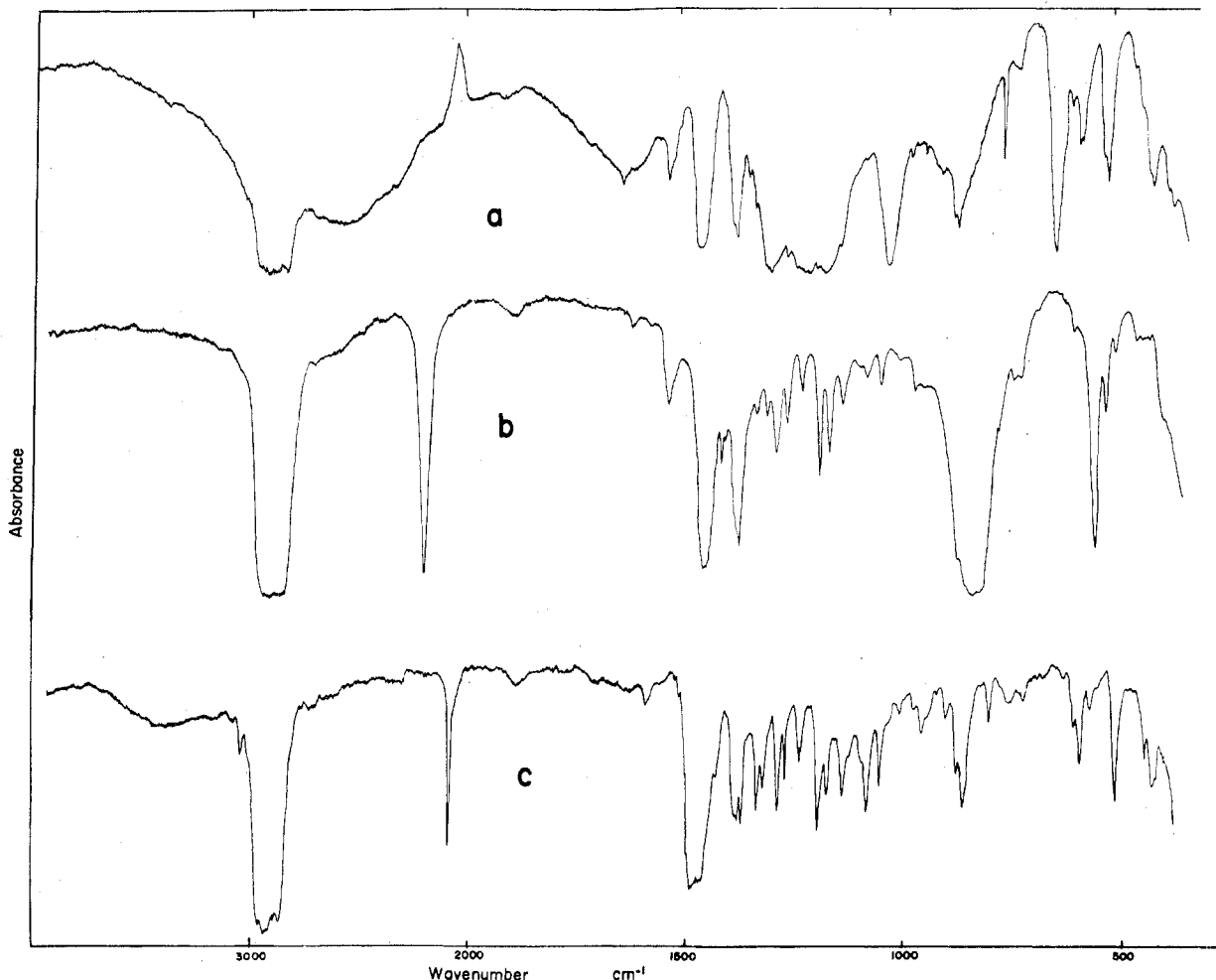


Figure 4. Infrared Nujol mull spectra of (a) $[\text{Fe}([\text{14}]1,3,8,10\text{-tetraeneN}_4)(\text{CNH})_2](\text{SO}_3\text{CF}_3)_2$, (b) $[\text{Fe}([\text{14}]1,3,8,10\text{-tetraeneN}_4)(\text{CNCH}_3)_2](\text{PF}_6)_2$, and (c) $\text{Fe}([\text{14}]1,3,8,10\text{-tetraeneN}_4)(\text{CN})_2$.

as the lone hydrogen resonance of $\text{HNCCr}(\text{CO})_5$ and $\text{HNCW}(\text{CO})_5$, 4.59 and 5.58 ppm, respectively,²² it is probably the NH of the coordinated isohydrocyanic acid. The patterns and the intensities of the remaining signals can be attributed to the protons of the macrocyclic ligand.

The infrared spectrum of the protonated complex is shown in Figure 4(a). The absorptions due to the $-\text{SO}_3\text{CF}_3$ anions are sharp and well defined (Table I), but the cation signals are broad and featureless. No distinct absorptions due to the bound isohydrocyanic acid group were observed. Based on the few previous reports of this ligand coordinated to metal ions, values of 2070–2130 cm^{-1} for the CN stretch have been documented.^{22,23} However, these absorptions are generally weak, and in at least one case, $\text{HNCMo}(\text{CO})_5$, no absorption could be found.

An analysis of the visible absorption spectrum of $[\text{Fe}([\text{14}]1,3,8,10\text{-tetraeneN}_4)(\text{CNH})_2](\text{SO}_3\text{CF}_3)_2$ shows that this complex can probably be stepwise deprotonated. The brown diprotonated complex can be dissolved in dry nitromethane with only a slight change in color. One drop of anhydrous HSO_3CF_3 serves to saturate the equilibrium. Water is sufficiently basic to titrate the strong acid $[\text{Fe}([\text{14}]1,3,8,10\text{-tetraeneN}_4)(\text{CNH})_2](\text{SO}_3\text{CF}_3)_2$ in nitromethane and this process can be conveniently followed using spectrophotometric means. The acidified nitromethane solution shows an absorption at 20.0 kK which is unsymmetrical with a shoulder on the high-energy side. The addition of small amounts of water to the spectrophotometer cell causes this absorption to decrease in intensity and a new band to appear at 17.9 kK. Continued addition of water produces an intensification of the

low-energy band until it is the only one present. Additional amounts of water cause only a broadening of this band on the low-energy side where $\text{Fe}([\text{14}]1,3,8,10\text{-tetraeneN}_4)(\text{CN})_2$ has an absorption. The introduction of bases such as pyridine and triethylamine into the spectrophotometer cell immediately restores the characteristic blue color of the dicyano complex. The absorption curve is identical with that of $\text{Fe}([\text{14}]1,3,8,10\text{-tetraeneN}_4)(\text{CN})_2$ dissolved in basic nitromethane. The above process is completely reversible suggesting that a stepwise deprotonation is taking place with the band at 17.9 kK corresponding to the monoprotonated complex. No attempt was made to isolate the intermediate complex.

The nitrogen atom of the bound cyanide ligand is reactive toward other electrophiles and it can readily be alkylated. The alkylating agent $\text{CH}_3\text{SO}_3\text{F}$ reacts rapidly with the dicyano complex to yield the brown isocyanide derivative $[\text{Fe}([\text{14}]1,3,8,10\text{-tetraeneN}_4)(\text{CNCH}_3)_2](\text{PF}_6)_2$. Unlike the protonated complex, the $\text{C}\equiv\text{N}$ stretching vibration is well defined (Figure 4(b)), but, compared to the cyano parent complex (Figure 4(c)), it is shifted 110 cm^{-1} toward higher energy. The NMR spectrum clearly shows a broadened methyl singlet (10 Hz in width) at 3.36 ppm integrating for six protons.

The Charge-Transfer Spectra. It is well established that the CT band observed for iron(II) complexes containing the α -diimine functional unit is associated with the transfer of charge from the metal t_{2g} orbitals to the antibonding orbitals of the α -diimine group.¹² This transition usually occurs in the visible region and for $\text{Fe}^{\text{II}}(o\text{-phen})_3$ ($o\text{-phen}$ = o -phenanthroline) is found at 19.6 kK.¹² The macrocyclic complexes with $[\text{14}]1,3,8\text{-trieneN}_4$ and $[\text{14}]1,3,8,10\text{-tetraeneN}_4$

have intense CT bands at 15–20 kK which are almost certainly associated with charge transfer to the α -diimine units (Figure 3). Although the assignments of these bands to CT transitions associated with the various axial groups CN^- , SCN^- , etc. cannot be ruled out, this possibility seems remote. For $[\text{Fe}(\text{CN})_6]^{4-}$, which contains only CN^- as a ligand the $t_{2g}^6 \rightarrow t_{2g}^5 \pi^*$ transition occurs at very high energy (45.9 kK).²⁴ The low-spin $[\text{Fe}(\text{NO}_2)_6]^{4-}$ ²⁵ and $[\text{Fe}(\text{CNCH}_3)_6]^{2+}$ ²⁶ complexes have been previously reported but electronic absorption data are lacking.

For a series of bis complexes of the general formula $\text{Fe}^{\text{II}}(o\text{-phen})_2(\text{CNBX}_3)_2$, where X = CH₃, H, F, Cl, and Br, Shriver and Posner²⁷ demonstrated the effects of the two monodentate ligands on the α -diimine CT absorptions. The CT bands for these complexes are shifted toward higher energies relative to the dicyano compound. It was suggested that the Lewis acid adducts of CN^- are very good π -bonding ligands and that they cause a lowering of the t_{2g} energy levels relative to the cyano derivative. This accounts for an increase in the energy of the CT transition. Similar arguments were given by Hamer and Orgel²⁸ for $[\text{Fe}^{\text{II}}(o\text{-phen})_2(\text{CNH})_2]^{2+}$ and $[\text{Fe}^{\text{II}}(o\text{-phen})_2(\text{CNCH}_3)_2]^{2+}$ which contain protonated and alkylated CN^- and are similar to the CNH and CNCH₃ derivatives of the macrocyclic complexes described here. The energies of the CT bands for both systems are in the order $\text{CNH} > \text{CNCH}_3 > \text{CN}^-$. For the entire series of [14]-tetraeneN₄ complexes the principal CT band varies with the axial ligand as follows: NO_2^- (15.0 kK), CN^- (15.6 kK), CH_3CN (17.3 kK), CH_3NC (19.5 kK), HNC (20.0 kK).

Acknowledgment. These studies were supported by Grant GM 10040 from the National Institute of General Medical Sciences of the U.S. Public Health Service.

Registry No. $[\text{Fe}(\text{[14]1,3,8\text{-trieneN}_4})(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$, 55177-55-4; $[\text{Fe}(\text{[14]1,3,8\text{-trieneN}_4})(\text{Im})_2](\text{BF}_4)_2$, 55177-57-6; $[\text{Fe}(\text{[14]1,3,8\text{-trieneN}_4})(\text{SCN})_2]$, 55177-58-7; $[\text{Fe}(\text{[14]1,3,8\text{-trieneN}_4})(\text{Cl})_2](\text{PF}_6)_2$, 55177-60-1; $[\text{Fe}(\text{[14]1,3,8,10\text{-tetraeneN}_4})(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$, 55221-62-0; $[\text{Fe}(\text{[14]1,3,8,10\text{-tetraeneN}_4})(\text{SCN})_2]$,

55221-63-1; $[\text{Fe}(\text{[14]1,3,8,10\text{-tetraeneN}_4})(\text{CN})_2]$, 55221-64-2; $[\text{Fe}(\text{[14]1,3,8,10\text{-tetraeneN}_4})(\text{CNH})_2](\text{SO}_3\text{CF}_3)_2$, 55221-65-3; $[\text{Fe}(\text{[14]1,3,8,10\text{-tetraeneN}_4})(\text{CNCH}_3)_2](\text{PF}_6)_2$, 55208-69-0; $[\text{Fe}(\text{[14]1,3,8,10\text{-tetraeneN}_4})(\text{NO}_2)_2]$, 55177-61-2; $[\text{Fe}(\text{[14]1,3,8,10\text{-tetraeneN}_4})(\text{Cl}_2)](\text{PF}_6)_2$, 55221-67-5; $[\text{Co}(\text{[14]1,3,8,10\text{-tetraeneN}_4})(\text{Cl})_2]\text{ClO}_4$, 55177-63-4; $[\text{Fe}(\text{[14]aneN}_4)(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$, 55221-69-7.

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Stereochemical Consequences of Ligand Rigidity in Nucleophilic Substitution. Reaction of Cyanide Ion with Tris(α -diimine)iron(II) Substrates¹

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Received December 4, 1974

AIC40816N

Specific stereochemical effects related to ligand rigidity appear to occur in the reactions between optically active tris(diimine)iron(II) ions and cyanide. Optical retention predominates in the reaction between cyanide and tris(2,2'-bipyridine)iron(II), which has a relatively flexible ligand, whereas earlier studies have shown a predominance of optical inversion for the correspondingly rigid 1,10-phenanthroline complex. The activation parameters (ΔH^\ddagger and ΔS^\ddagger) are higher for the retention path than for the inversion path as was also found for the 1,10-phenanthroline reaction in which inversion predominates. This trend is evident from the positive temperature dependence of the retained optical activity relative to the inverted temperature dependence of the net inversion in the 1,10-phenanthroline case.

Introduction

The reaction of optically active tris(2,2'-bipyridine)iron(II), $\Delta\text{-Fe}(\text{bipy})_3^{2+}$, with aqueous cyanide has been studied in detail in order to compare the stereochemistry and relevant activation parameters with the novel inversion reaction observed previously² for the analogous *o*-phenanthroline complex, $\Delta\text{-Fe}(\text{phen})_3^{2+}$. The bipyridine complex produces an excess of optically retained $\Delta\text{-Fe}(\text{bipy})_2(\text{CN})_2$ with activation parameters consistent with the *o*-phenanthroline complex studies, which under analogous conditions produce an excess of inverted $\Delta\text{-Fe}(\text{phen})_2(\text{CN})_2$. The stereochemical configurations are

based on the circular dichroism spectra of the $\pi\text{-}\pi^*$ transitions and assignments are based on the exciton theory.^{2,3} The absolute configuration of the $\text{Fe}(\text{phen})_3^{2+}$ ion⁴ is in agreement with the exciton assignment.

Previous kinetics investigations of aqueous cyanide with racemic tris(diimine)iron(II) complexes⁵ have shown the necessity of a composite rate law of the type

$$-\frac{d[\text{Fe}(\alpha\text{-diimine})_3^{2+}]}{dt} = (k_1 + k_2[\text{CN}^-])[\text{Fe}(\alpha\text{-diimine})_3^{2+}] \quad (1)$$