$$CO(g) + H_2O = CO_2(g) + 2H^+ \qquad \Delta G^\circ = -5.8 \text{ kcal/mol}$$

$$CO(g) + H_2O + 2Ce(IV) = CO_2(g) + 2Ce(III) + 2H^+ \qquad \Delta G^\circ = -40.3 \text{ kcal/mol}$$

to the oxidation of other pentaammineruthenium(II) adducts in which the metal becomes oxidized and the adduct ligands are either released or remain attached to the oxidized metal. The activation of CO toward oxidation must certainly be a result of its being bound to $[Ru(NH_3)_5]^{2+}$, although excess Ce(IV) might also play an important role since a dark brown, stable intermediate was formed when the $Ce(IV)/Ru(NH_3)_5CO]^{2+}$ ratio was less than about 3. The details of this reaction are certainly of interest because understanding this reaction may lead to methods for activating related molecules, *e.g.*, N_2, toward oxidation.

Acknowledgments. Thanks are expressed to Drs. W. E. Newton, W. A. Bulen, J. Corbin, J. McDonald, and K. L. Hadfield of the Nitrogen Fixation Branch at this laboratory for helpful comments and discussions.

Facile Promotion of Oxidative Dehydrogenation by Iron Ions and the Synthesis of New Complexes of Iron with Highly Unsaturated Tetraaza Macrocycles

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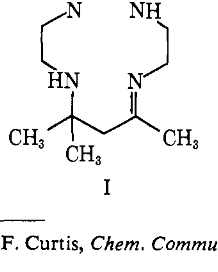
Abstract: We have discovered an extreme facility on the part of the ions of iron to promote the oxidative dehydrogenation of secondary amine groups bound to the iron as part of a macrocyclic ligand. The product complexes contain newly formed, coordinated azomethine functions. Atmospheric oxygen readily performs the oxidation under the influence of Fe(III), while stronger oxidizing agents are generally required in the case of nickel or copper complexes, and cobalt has failed to give the reaction. As a result of these and related studies, it is becoming possible to synthesize macrocyclic complexes having any desired degree of unsaturation. The reaction has been applied to synthesize important new macrocyclic complexes of iron, wherein the degree of unsaturation exceeds that previously built into such synthetic iron derivatives. Beginning with $Fe(Me_6[14]4,11\text{-dieneN}_4)(CH_3CN)_2^{2+}$ oxidative dehydrogenation produces a triimine complex $Fe(Me_6[14]1,4,11\text{-trieneN}_4)(CH_3CN)_2^{2+}$ and, under appropriate conditions, a tetraimine complex $Fe(Me_6[14]1,4,8,11\text{-tetraeneN}_4)(CH_3CN)_2^{2+}$. The presence of more double bonds in the ligand structure enhances the stability of iron(II). Several derivatives of the new complexes have been synthesized and all have been characterized by physical methods. In the presence of weak axial ligands, such as halide ions, only one of the axial sites is occupied and the resultant complexes are high spin, five coordinate with a square-pyramidal geometry. The ligand field strength is surprisingly low suggesting that the Fe^{2+} ion has been extruded from the plane of the four nitrogen donors. These complexes are stereochemical and electronic analogs of deoxyhemoglobin and deoxymyoglobin. Relatively strong axial ligands bind in pairs, producing low-spin, six-coordinate structures. The ligand field strength of the macrocycle in these complexes exceeds that of less highly unsaturated macrocyclic ligands of the same ring size, as expected. $Fe(Me_6[14]4,14\text{-dieneN}_4)(CH_3CN)_2^{2+}$ has also been oxidatively dehydrogenated to produce the complex of a tetraimine which contains a conjugated α-diimine linkage, $Fe(Me_4[14]1,3,7,11\text{-tetraeneN}_4)(CH_3CN)_2^{2+}$. The tetraimine, $Me_6[14]1,4,8,11\text{-tetraeneN}_4$, has been removed from the iron(II) complex, characterized in the free state (where it exists as a tautomer), and coordinated to cobalt(III). This shows how the facile promotion of oxidative dehydrogenation exhibited by iron can be used to obtain materials not available *via* other synthetic routes.

Under the proper conditions and in the presence of suitable reagents, complexes in which the metal has an unusual oxidation number, particularly the higher unstable states such as Ni(III),[1-3] can undergo intramolecular redox reactions which generate complexes with oxidized forms of the ligands.

The first example of this type of reaction involving a macrocyclic ligand was reported by Curtis who observed that the nickel(II) complex of 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (abbreviated $[14]4,11\text{-dieneN}_4$ or more simply $[14]\text{dieneN}_4$) (I) reacts with concentrated nitric acid to yield a complex containing the new macrocyclic ligand, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,4,8,11-tetraene (abbreviated $[14]1,4,8,11\text{-tetraeneN}_4$ or $[14]\text{tetraeneN}_4$) (II).[4]



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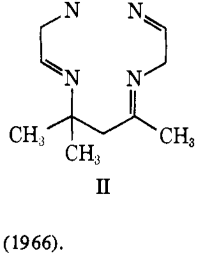

II

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[1] N. E. Tokel, V. Katović, K. Farmery, L. B. Anderson, and D. H. Busch, *J. Amer. Chem. Soc.*, **92**, 400 (1970).

[2] D. C. Olson and J. Vasilevskis, *Inorg. Chem.*, **8**, 1611 (1969).

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[4] N. F. Curtis, *Chem. Commun.*, 881 (1966).

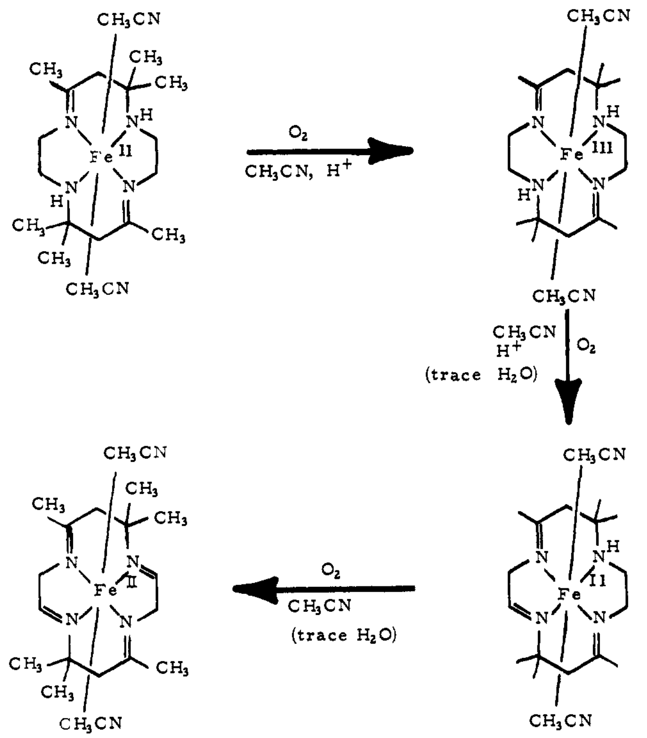

Figure 1. Oxidation processes involving the iron complex [Fe(Me$_6$[14]4,11-dieneN$_4$)(CH$_3$CN)$_2$]$^{2+}$. The names and abbreviations of the new ligands are 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,4,11-triene, Me$_6$[14]1,4,11-trieneN$_4$, or [14]trieneN$_4$; and 5,7,7,12,14,14-hexamethyl-1,4,8,11-*tetraazacyclotetra*deca-1,4,8,11-tetraene, Me$_6$[14]1,4,8,11-tetraeneN$_4$, or [14]tetraeneN$_4$.

Nickel(III) appears to be an intermediate in these oxidations.[4,5] Although the trivalent state of copper does not appear to be achieved with nitric acid, it can be obtained electrochemically with copper complexes of macrocyclic ligands. These Cu(III) complexes are quite unstable and spontaneously undergo an internal redox process in which an aldimine linkage is introduced into the macrocyclic ligand.[3] Such ligand oxidation has not been achieved with cobalt complexes.[6,7]

With labile transition metal complexes of noncyclic amine ligands, higher unstable oxidation states can be obtained. These lead to ligand oxidation but the activated ligand species generally dissociate and react with the solvent, thereby preventing the isolation of imine derivatives.[8] The uncommon stability of the new synthetic macrocyclic complexes toward dissociation facilitates the study of this type of reaction, even with metal ions whose complexes are normally considered to be labile.

In view of the apparent requirements for the metal-assisted oxidative dehydrogenation of ligands, iron complexes appeared to be ideal candidates for similar studies. Iron is particularly attractive because of the facile Fe$^{\rm II}$–Fe$^{\rm III}$ redox couple, as well as the conjecture that higher oxidation states, such as IV and V, may be involved in biologically important iron systems.[9]

The macrocyclic ligand selected for this study, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (abbreviated [14]dieneN$_4$, structure I), was chosen because of its ease of preparation[10] and the wealth of information accumulated in extensive studies of its cobalt, nickel, and copper complexes.[11] The previously investigated iron(II) complexes[10] of the [14]dieneN$_4$ ligand fell into two general categories: five-coordinate, high-spin complexes and six-coordinate, low-spin complexes.[10] The five-coordinate complexes are very reactive toward molecular oxygen and yield intractable oxo species which have not been further characterized. The reaction of the low-spin, six-coordinate species, Fe[14]dieneN$_4$(CH$_3$CN)$_2$(ClO$_4$)$_2$, with molecular oxygen has led to interesting new products.

Results and Discussion

The complex [Fe([14]dieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$, although not as sensitive to molecular oxygen as the five-coordinate species, reacts with oxygen to yield new iron(II) complexes which contain additional sites of unsaturation in the macrocyclic ligand. Similar reactions occur for those low-spin, six-coordinate derivatives of Fe which contain other strong field, nitrogen donor atoms, such as cyanide, thiocyanate, and imidazole. However, with these strong field axial ligands, there were problems associated with the purification and characterization of the products.[12] In contrast, the complex containing acetonitrile in the axial positions reacts quite smoothly with oxygen under slightly acidic conditions to yield, successively, an iron(III) complex, [Fe([14]dieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_3$, an iron(II) complex with three imine linkages in its ligand, [Fe([14]trieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$, and, finally, an iron(II)–tetraimine complex, [Fe([14]tetraeneN$_4$)(CH$_3$CN)$_2$](ClO$_4$) (Figure 1).

Other intermediate species, such as molecular oxygen adducts or oxo-bridged species, probably exist, at least as transients during the complicated processes. The occurrence of otherwise unexplained absorption bands in the spectra of solutions undergoing oxidation suggests this possibility.

The intermediate iron(III) complex, [Fe([14]4,11-dieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_3$, is readily isolated as a precipitate that separates prior to ligand oxidation. This intermediate is quite unstable when isolated from acetonitrile solutions but it is stable indefinitely when kept under dry acetonitrile. However, the addition of a small amount of water to the acetonitrile solution induces a rapid internal metal–ligand redox process. In this reaction the iron(III) is reduced to iron(II) and an additional imine linkage is introduced into the coordinated ligand as indicated by the infrared, nmr, and electronic spectra of the products. The role of the water in this reaction is not clear at this time. A simple model can be tentatively proposed to account for the action of the metal ion and its ability to act as sole

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(11) N. F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968).

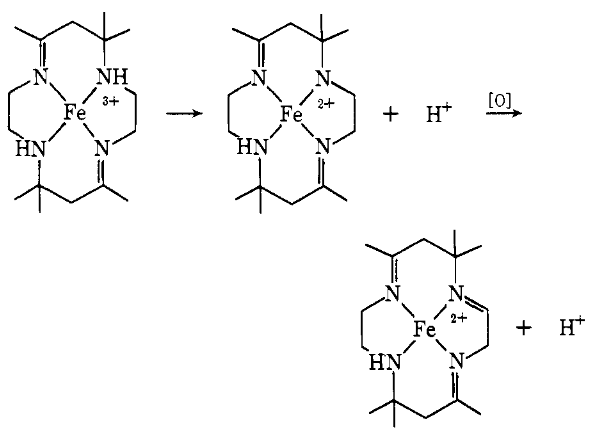
(12) These problems were associated with tautomerization of the β-diimine grouping to an α-diimine in the oxidized form of the ligands. Although the complexes isolated yielded good analytical data, they were always contaminated with impurities involving ligands containing the iron(II) α-diimine chromophore. The tautomerization reaction will be reported separately (Abstracts of the 162nd National Meeting of the American Chemical Society, Washington, D. C., 1971).

Table I. Physical Properties of the New Complexes

Compound	Color	μ_{eff}, BM	Λ_M	Solvent
	Six-Coordinate Complexes			
$[Fe([14]1,4,11\text{-}trienN_4)(CH_3CN)_2](ClO_4)_2$	Pink	*a*	320	CH_3CN
$[Fe([14]1,4,8,11\text{-}tetraeneN_4)(CH_3CN)_2](ClO_4)_2$	Pink	*a*	316	CH_3CN
$[Fe([14]1,4,8,11\text{-}tetraeneN_4)(Im)_2](BPh_4)_2$	Yellow-brown	*a*	300	CH_3CN^b
$[Fe([14]1,4,8,11\text{-}tetraeneN_4)(NCS)_2]$	Brown	*a*	12	CH_3NO_2
$[Fe([14]1,4,8,11\text{-}tetraeneN_4)(phen)](ClO_4)_2$	Pink	5.0	310	CH_3OH^b
$[Fe([14]1,4,8,11\text{-}tetraeneN_4)Cl_2](ClO_4)$	Yellow	2.29	97	CH_3NO_2
$[Fe([14]1,3,7,11\text{-}tetraenN_4)(CH_3CN)_2](PF_6)_2$	Deep purple	*a*	315	CH_3CN
	Five-Coordinate Complexes			
$[Fe([14]1,4,8,11\text{-}tetraeneN_4)Cl](ClO_4)$	Pale green	5.00	97	CH_3NO_2
$[Fe([14]1,4,8,11\text{-}tetraeneN_4)Br](ClO_4)$	Pale green	5.14	99	CH_3NO_2
$[Fe([14]1,4,8,11\text{-}tetraeneN_4)I](ClO_4)$	Pale green	5.10	102	CH_3NO_2
	Cobalt(III) Complexes			
$[Co([14]1,4,8,11\text{-}tetraeneN_4)Br_2](ClO_4)$	Green	*a*	94	CH_3NO_2
$[Co([14]1,4,8,11\text{-}tetraeneN_4)Cl_2](ClO_4)$	Green	*a*	90	CH_3NO_2

[a] These complexes displayed magnetic moments in the range 0.4–0.60 BM resulting from the temperature-independent paramagnetism associated with low spin d^6 systems. [b] Spectrophotometric evidence suggests that partial dissociation of the imidazole and phenanthroline occurs under the conditions of the measurement.

oxidizing agent. We suggest that the central ferric ion abstracts an electron from one of its coordinated secondary amine groups. This would generate a radical and a proton. Whatever *external oxidizing agent* is available then oxidizes the radical; whereupon, the ionization of a second proton consummates the process. The observation that the [H+] increases during the reaction is consistent with this scheme (eq 1). The two



(1)

oxidation steps might be concerted, depending on the availability of an external oxidizing agent. In fact, the stability of $Fe^{III}([14]dieneN_4)^{2+}$ in dry acetonitrile and its dehydrogenation reaction in the presence of small amounts of water suggests the possibility that oxidation products of water, probably O_2, may enter into the process under these carefully controlled conditions. In addition to atmospheric oxygen, hydrogen peroxide is also effective as an oxidant, yielding the same products.

The triimine iron(II) compound, $[Fe([14]1,4,11\text{-}trieneN_4)(CH_3CN)_2](ClO_4)_2$, is similar in most of its properties to the diene derivative (Table I). The ir spectrum of this compound contains a second imine absorption at 1660 cm^{-1} in addition to that found at 1652 cm^{-1} in both the starting material and the product. The intensity of the N–H stretching mode at 3230 cm^{-1} is reduced considerably from that of the parent diene complex. The nmr spectrum (Figure 2) clearly indicates the presence of a single proton on an imine carbon at 8.3 ppm in addition to the complicated pattern expected for the various axial and equatorial methyl substituents present in the very low symmetry complex. The electronic spectrum contains a single d–d absorption at 20,250 cm^{-1}. The charge-transfer band associated with the iron(II) → ligand π system at 27,540 is increased in intensity over that found for the iron(II) diene complex.

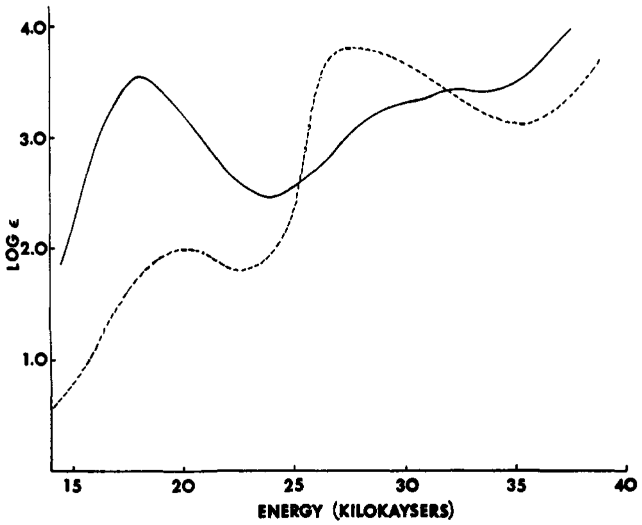


Figure 2. Electronic spectra of (a) (– – –) $[Fe(Me_6[14]1,4,8,11\text{-}tetraeneN_4)(CH_3CN)_2](ClO_4)_2$ and (b) $[Fe(Me_6[14]1,3,7,11\text{-}tetraeneN_4)(CH_3CN)_2](ClO_4)_2$ (——).

The triimine iron(II) complex is less sensitive to oxygen than is the diimine complex, but on exposure to air for about 24 hr, a pink complex forms. It was isolated and identified as the tetraamine complex, $[Fe([14]1,4,8,11\text{-}tetraeneN_4)(CH_3CN)_2](ClO_4)_2$. Its infrared spectrum contains no absorptions attributable to N–H or O–H stretching modes, and the nmr spectrum of the compound contains the same simple five-line spectrum as was obtained for the tetraimine complex of nickel(II), $[Ni([14]1,4,8,11\text{-}tetraeneN_4)](ClO_4)_2$.[13]

The iron(II) complex derived from the related *cis*-diene undergoes similar ligand oxidation reactions with molecular oxygen as shown in eq 2 below. The addi-

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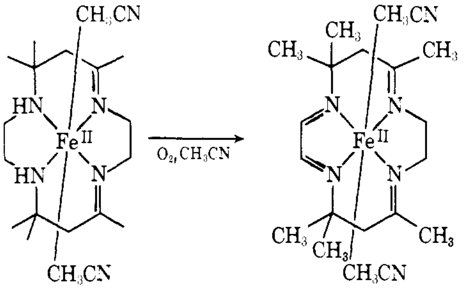
(13) V. L. Goedken and D. H. Busch, *Inorg. Chem.*, 10, 2697 (1971).

Table II. Electronic Spectra of the Complexes[a]

Complex	Solvent	Electronic spectra, kK[b]
$[Fe([14]4,11\text{-diene}N_4)(CH_3CN)_2](ClO_4)_2$	CH_3CN	19.6 (82), 29.1 (2440)
$[Fe([14]1,4,11\text{-triene}N_4)(CH_3CN)_2](ClO_4)_2$	CH_3CN	19.5 (111), 27.77 (3703) sh
$[Fe([14]1,4,8,11\text{-tetraene}N_4)(CH_3CN)_2](ClO_4)_2$	CH_3CN	20.0 (100), 27.54 (6023)
$[Fe([14]1,3,7,11\text{-tetraene}N_4)(CH_3CN)_2](PF_6)_2$	CH_3CN	17.85 (3565), 29.8 (2032) sh, 32.26 (2389)
$[Fe([14]1,4,8,11\text{-tetraene}N_4)(Im)_2](BPh_4)_2$	CH_3CN	19.6 (186.8)
	SS	19.23, 23.52, 25.0
$[Fe([14]1,4,8,11\text{-tetraene}N_4)(NCS)_2]$	SS	19.23, 22.73, 25.0 (sh)
$[Fe([14]1,4,8,11\text{-tetraene}N_4)Cl_2]ClO_4$	CH_3OH	14.7 (36), 17.8 (67), 20.8 (108), 24.1 (13,400), 27.0 (11,300) sh
	SS	14.28, 17.5, 19.6, 20.83, 24.4
$[Fe([14]1,4,8,11\text{-tetraene}N_4)(phen)](ClO_4)_2$	SS	11.1, 19.6
$[Fe([14]1,4,8,11\text{-tetraene}N_4)Cl]ClO_4$	CH_3NO_2	4.65 (3), 11.62 (3)
$Fe([14]1,4,8,11\text{-tetraene}N_4)Br]ClO_4$	CH_3NO_2	4.76 (3), 11.66 (3)
$[Fe([14]1,4,8,11\text{-tetraene}N_4)I]ClO_4$	CH_3NO_2	~5, 11.65 (5)
$[Co([14]1,4,8,11\text{-tetraene}N_4)Cl_2]ClO_4$	CH_3NO_2	16.66 (50)[c]
	CH_3OH	33.89 (10,000)[d]
$[Co([14]1,4,8,11\text{-tetraene}N_4)Br_2]ClO_4$	CH_3NO_2	15.75 (117), 19.23 sh[c]
	CH_3OH	15.75, 19.23 sh, 25.3 (3280), 30.3 (18.000)

[a] Abbreviations: Im = imidazole, phen = phenanthroline, BPh_4 = tetraphenylborate, sh = shoulder, SS = solid state spectra. [b] Numbers in parentheses are molar extinction coefficients. [c] Absorption due to solvent precludes observation of higher energy absorption bands. [d] Very low solubilities in methanol did not permit observations of weaker d–d absorptions.



(2)

tional imine linkages in the derived tetraimine must be located α to one another and the iron(II) α-diimine chromophore is responsible for the very intense red color of this low-spin iron(II) complex, $[Fe([14]1,3,7,11\text{-tetraene}N_4)(CH_3CN)_2](PF_6)_2$. This metal–ligand charge-transfer absorption is typical of that observed in all low-spin iron(II) complexes containing ligands with α-diimine linkages.[14,15] The infrared spectrum of this oxidized ligand complex shows no N–H absorptions. A single strong sharp C=N stretching band is observed at 1652 cm^{-1} and is barely altered from its appearance in the parent $[14]4,14\text{-diene}N_4$ complex. This is not surprising since two C=N groups of an α-diimine chromophore are strongly coupled and the intensity of the stretching vibration is frequently very small.[16] The same phenomenon is observed for the analogous nickel(II) complex, $[Ni([14]1,3,7,11\text{-tetraene}N_4)](ClO_4)_2$.

Other low-spin, six-coordinate complexes can be derived from $[Fe([14]1,4,8,11\text{-tetraene}N_4)(CH_3CN)_2](ClO_4)_2$ by metathesis in methanol using other nitrogen donor ligands, such as thiocyanate, imidazole, or pyridine. With pyridine, only one acetonitrile molecule is displaced, yielding a complex of the formula $[Fe([14]1,4,8,11\text{-tetraene}N_4)(CH_3CN)(py)](ClO_4)_2$. The behaviors of these iron(II) complexes are similar to those of the six-coordinate low-spin $Fe([14]4,11\text{-diene}N_4)$ complexes reported earlier.[10] A tabulation of the complexes prepared in this study appears along with some of their physical properties in Table I.

Electronic Spectra of the Six-Coordinate Species. The electronic spectra of $[Fe([14]1,4,11\text{-triene}N_4)(CH_3CN)_2](ClO_4)_2$ and $[Fe([14]1,4,8,11\text{-tetraene}N_4)(CH_3CN)_2](ClO_4)_2$ are similar to those of the diene complexes with the major change being an enhancement of the intensity of the metal–ligand charge-transfer absorptions (Table II). The d–d absorption band occurs at slightly higher energy (~500 cm^{-1}) than in the diene spectrum and appears at 20.0 kK for the tetraene complex. The charge-transfer absorption band appears at 27.54 kK with a molar extinction coefficient of 6023, which is approximately double that for the diene complex. The electronic absorption spectrum of the triene is intermediate between those of the diene and tetraimine complexes.

The electronic spectrum of the tetraimine produced by the oxidation of $[Fe([14]4,14\text{-diene}N_4)(CH_3CN)_2]^{2+}$ (eq 2) contains an intense absorption at 17.85 kK (ϵ_{max} 3560) which is characteristic of metal–ligand charge-transfer bands observed for other iron(II) complexes of α-diimines (see Figure 2). There is also an absorption at 32.27 kK (ϵ_{max} 2388) which is most probably associated with metal–ligand charge transfer (isolated imines). The d–d absorption bands in this compound are obscured by these charge-transfer absorptions.

The spectra of those complexes containing imidazole, pyridine, or thiocyanate in the axial positions are more complicated as a result of the charge-transfer absorptions associated with the axial ligands. However, each complex has a shoulder near 19.5 kK which may be d–d in nature.

Five-Coordinate Complexes. A series of five-coordinate complexes can be prepared from $[Fe([14]1,4,8,11\text{-tetraene}N_4)(CH_3CN)_2](ClO_4)_2$ by metathetical displacement of the coordinated axial acetonitrile molecules by a single halide ion. The addition of

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(14) P. Krumholz, *J. Amer. Chem. Soc.*, **75**, 2163 (1953).

(15) D. H. Busch and J. C. Bailar, *ibid.*, **78**, 1137 (1956).

(16) P. E. Figgins and D. H. Busch, *J. Phys. Chem.*, **65**, 2336 (1961); K. Nakamoto, "Advances in the Chemistry of Coordination Compounds," Macmillan, New York, N. Y., 1961.

lithium halides to methanol solutions of [Fe([14]1,4,8,11-tetraeneN_4)(CH_3CN)$_2$](ClO_4)$_2$ yields complexes of the composition [Fe([14]tetraeneN_4)X](ClO_4), X = Cl, Br, I. These five-coordinate, high-spin complexes have conductances around 95 ohm^{-1} cm^2 mol^{-1} which are characteristic of uni-univalent electrolytes in nitromethane solution.[17,18] The magnetic moments are near 5.10 BM which is compatible with four unpaired electrons.[19] Solutions of these five-coordinate complexes are extremely reactive toward molecular oxygen and decompose to rust if left exposed to the atmosphere for extended periods of time. Exposure to limited amounts of oxygen results in the initial formation of yellow to brown flocculent precipitates which slowly turn to a very intense blue color. The color change appears to be related to the formation of tautomeric form of the ligand containing an α-diimine chromophore.[12] The complexes are readily decomposed in acidic media with hydrolytic cleavage of the azomethine linkages and solvation of the iron(II).

Electronic Spectra of the Five-Coordinate Complexes. The d–d electronic spectra of the five-coordinate complexes, [Fe([14]1,4,8,11-tetraeneN_4)X](ClO_4), are similar to those of the diimine complexes, [Fe([14]4,11-dieneN_4)X](ClO_4).[11] The d–d spectra consist of two broad and very weak absorptions in the infrared occurring near 5.0 and 11.75 kK (Table II). The positions of these absorption bands are compatible with that expected from a strong tetragonal perturbation arising from a five-coordinate square-pyramidal ligand environment. This is also in agreement with the Mossbauer spectra which have very large quadrupole splitting values and range from 3.3 to 3.8 mm/sec.[20] Quadrupole splitting values in this range appear to be characteristic of five-coordinate iron in a square-pyramidal ligand geometry. A qualitative splitting diagram depicting the relative energies of the term states for d–d transitions in a square-pyramidal ligand environment is shown in Figure 3. The energy maxima for the lower energy transitions occur at the same energy within experimental error for a given halide in the spectra of the pair of compounds [Fe([14]4,11-dieneN_4)X](ClO_4) and [Fe([14]1,4,8,11-tetraeneN_4)X](ClO_4). This is to be expected since the lower energy transition, which is either ^5E or $^5B \rightarrow {}^5A$ (d_{z^2}), is primarily influenced by the field strength of the axial ligands. For each ligand, the energy of the transition decreases slightly as the field strength of the axial ligand decreases and varies from 4.7 for chloro ligands to about 5 kK for iodide. The maximum for the higher energy transition to the B state ($x^2 - y^2$) occurs at 11.6 kK and is invariant with the nature of the axial substituents, as expected since the excited state energy level is primarily dependent upon the "in-plane" ligand field. It is noteworthy that the energy of this transition for the Fe([14]1,4,8,11-tetraeneN_4)X]ClO_4 complexes occurs at lower frequency than for the corresponding diimine complexes, [Fe([14]4,11-dieneN_4)X]ClO_4.[12] This is somewhat surprising because imines generally generate higher ligand field strengths than do amines[21] and the energy of the d–d transition in low-spin [Fe([14]1,4,8,11-tetraeneN_4)(CH_3CN)$_2$]$^{2+}$ occurs about 400 cm^{-1} higher in energy than does the band for the corresponding [14]4,11-dieneN_4 complex. An appealing rationalization for this observation can be based on the assumption that the metal ion lies above the plane of the four nitrogen donors of the macrocycle. In such a structure the bond shortening accompanying imine formation may decrease the radius of the macrocycle and have the effect of lifting the metal atom further out of the plane of the macrocycle, thereby weakening the metal–nitrogen interaction and producing a concomitant reduction in apparent ligand field strength. We have discussed this situation in conjunction with the Fe(II) complexes of the corresponding saturated ligand Me_6[14]aneN_4.[22]

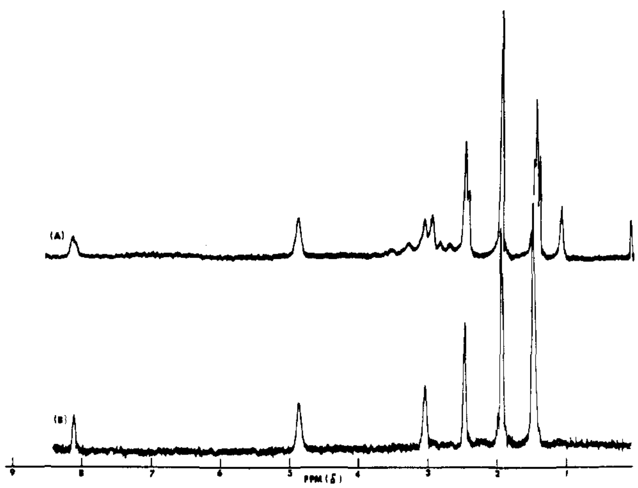

Figure 3. Proton nmr spectra of (A) [Fe(Me_6[14]1,4,11-trieneN_4)(CH_3CN)$_2$]$^{2+}$ and (B) [Fe(Me_6[14]1,4,8,11-tetraeneN_4)(CH_3CN)$_2$]$^{2+}$.

Reactions of the Complexes. The six-coordinate, low-spin complexes are moderately inert toward dissociation of the ligand in acids with the degree of stability increasing with the number of imine linkages in the macrocyclic ligand. Free ligand salts, *e.g.*, [14]-diene·2$HClO_4$, can be isolated from the reactions. For example, 0.01 *M* acetonitrile solutions of [Fe([14]4,11-dieneN_4)(CH_3CN)$_2$](ClO_4)$_2$ have a half-life of about 30 min in 0.05 *M* $HClO_4$. For the fully oxidized tetraimine, the half-life under the same conditions is about 24 hr. The α-diimine complex, [Fe([14]1,3,7,11-tetraeneN_4)(CH_3CN)$_2$](ClO_4)$_2$, is the most stable of all. A 2.7 × 10^{-4} *M* solution of this complex in acetonitrile containing 0.05 *M* $HClO_4$ has a half-life on the order of weeks. In oxygen donor solvents, the solvent displaces the acetonitrile axial ligands, and the complexes become high spin. The high-spin complexes are very rapidly attacked by acids liberating Fe(II) ions and the protonated form of the ligands. Similarly, the five-coordinate halo species are also readily decomposed by acids. Solutions of the five-coordinate species are very reactive toward molecular oxygen and, if left exposed to the atmosphere for considerable periods of time (hours), the complexes are completely destroyed

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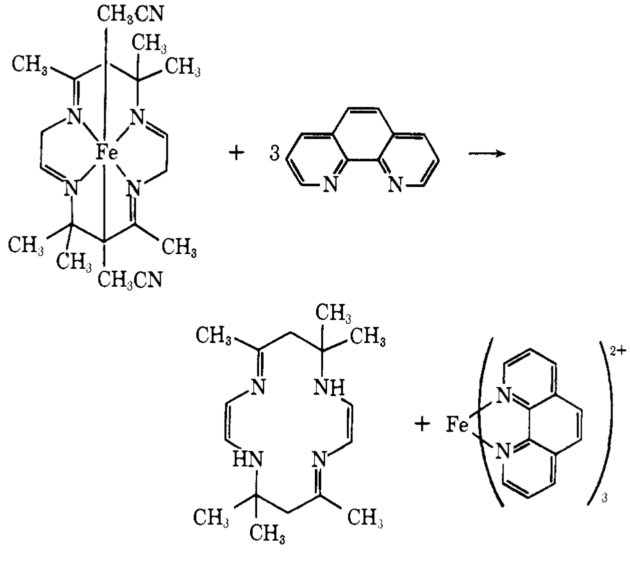
with rust mirrors forming on the sides of the containers.

Low-spin iron(III) complexes can be obtained by the oxidation of the tetraimine [Fe([14]1,4,8,11-tetraeneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$ with chlorine to yield the yellow-brown [Fe([14]1,4,8,11-tetraeneN$_4$)Cl$_2$]ClO$_4$. This iron(III) species is moderately stable in the solid state and in solution. However, if the chloride ions are removed with AgClO$_4$, there is a considerable tendency for the iron(III) to revert to an iron(II) complex. Although [Fe([14]4,11-dieneN$_4$)(CH$_3$CN)$_2$]$^{2+}$ can be oxidized to the Fe(III) complex, [Fe([14]4,11-dieneN$_4$)Cl$_2$]ClO$_4$, with chlorine gas, no ligand oxidation was observed under these conditions. Also, this dichloro iron(III) species was considerably more stable toward reduction to iron(II) than the iron(III) acetonitrile complex, [Fe([14]4,11-dieneN$_4$)(CH$_3$CN)$_2$]$^{3+}$. The negatively charged chloride ions undoubtedly stabilize the iron(III) state. It has been shown that the redox potentials of low-spin iron(II) and iron(III) systems are markedly dependent upon the electrostatic environment about the coordinated iron ions.[23] Also, our unpublished electrochemical studies on these and related synthetic compounds will clarify these relationships.[24]

Concentrated solutions of the tetraimine complex, [Fe([14]1,4,8,11-tetraeneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$, react with phenanthroline to form a high-spin, six-coordinate complex, [Fe([14]1,4,8,11-tetraeneN$_4$)(phen)](ClO$_4$)$_2$. The high-spin configuration is most likely a consequence of the strongly coordinating bidentate ligand which forces the planar array of nitrogen donor atoms of the macrocycle into less favorable bonding orientations. Whereas the low spin d^6 electronic configuration yielded stable inert complex systems, the change to the high-spin system leads to bonding lengthening[25] and more labile metal–ligand bonds. The result is that high-spin [Fe([14]1,4,8,11-tetraeneN$_4$)(phen)](ClO$_4$)$_2$ disproportionates to two stable low-spin iron(II) species, [Fe([14]1,4,8,11-tetraeneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$ and [Fe(phen)$_3$](ClO$_4$)$_2$, with some free ligand also being produced. The addition of 3 molar equiv of phenanthroline per mole of iron complex eventually yields free macrocyclic ligand and [Fe(phen)$_3$](ClO$_4$)$_2$, and provides a convenient method for the isolation and characterization of the free ligand.

Isolation and Characterization of the Free Ligand, [14]1,4,8,11-tetraeneN$_4$. The addition of 3 mol of 1,10-phenanthroline to 1 mol of [Fe([14]1,4,8,11-tetraeneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$ in dry acetonitrile generates the characteristic deep red color of [Fe(phen)$_3$]$^{2+}$ within minutes and the reaction nears completion after approximately 24 hr at room temperature. A white crystalline organic material having the composition C$_{16}$H$_{28}$N$_4$ was isolated and identified as a tautomeric form of the free ligand. The molecular weight, 276, was obtained from the parent peak in the mass spectrum of the material. The infrared spectrum and the nmr spectrum of the compound indicate that the free ligand and the complexed ligand exist in tautomeric forms which are related by the migration of a double bond from the positions 1 and 8 to positions 2 and 9 as shown below.



This enamine–imine arrangement of double bonds and concomitant conjugation produced a stabilizing effect on the imine linkages. Normal imine linkages in nonaromatic systems are subject to facile hydrolysis and are difficult to isolate. For example, the [14]4,11-dieneN$_4$ ligand can be isolated in a number of ways,[26] but the product, even when crystallized, tends to oil and decompose readily. The isolated tetraimine ligand is quite stable in the solid state and in a number of neutral and basic organic solvents.

The evidence for the enamine–imine structure of the free ligand rests primarily on the ir and nmr spectra. The ir indicates the absence of water but shows a strong sharp N–H stretching mode at 3245 cm^{-1}. The imine absorptions which occur in the range 1670–1640 cm^{-1} in the complexes of [14]4,11-dieneN$_4$, and [14]1,4,8,11-tetraeneN$_4$, as well as in the acid salts of the ligand, have decreased in energy and broadened and occur at 1612 cm^{-1} as might be expected for imine and enamine functions located α to one another. There is also a sharp absorption of weak to moderate intensity at 3030 cm^{-1}, characteristic of that observed for vinylic or olefinic type C–H's. The nmr spectrum is discussed below.

Cobalt(III) Complexes of the [14]1,4,8,11-tetraeneN$_4$ Ligand. To prove that a form of the free ligand had indeed been isolated, and to demonstrate that other transition metal complexes of the tetraimine ligand could be prepared from this free ligand, diacido complexes of cobalt(III) were prepared from the free ligand *via* the cobalt(II) intermediates. The cobalt(II) species were prepared as outlined in the Experimental Section and then oxidized to cobalt(III) complexes in order to utilize the nmr spectra to characterize the ligand. The addition of equimolar portions of the free ligand to anhydrous acetonitrile solutions of cobalt(II) perchlorate yielded yellow cobalt(II) complexes which were similar in their properties to the low-spin cobalt(II) complexes of the [14]4,11-dieneN$_4$ and [14]4,14-dieneN$_4$ Curtis ligands;[27] these were not characterized further. Addi-

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Table III. Nuclear Magnetic Resonance Spectra of the Complexes

Complex	Solvent	Chemical shift[a]
[Fe([14]1,4,8,11-tetraeneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$	CD$_3$CN	8.12 (2), 4.90 (4), 3.08 (4), 2.48 (6), 1.45 (12)
[Fe([14]1,4,11-trieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$	CD$_3$CN	8.15 (1); 4.90 (2); 3.50, 3.25, 3.04, 2.93, 2.80, 2.65 (7); 2.45, 2.41 (6); 1.48, 1.45, 1.39 (9); 1.07 (3)
[Fe([14]1,3,7,11-tetraeneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$	CD$_3$CN	9.02 (2), 4.15 (4), 2.95 (4), 2.46 (6), 1.50 (12)
[Co([14]1,4,8,11-tetraeneN$_4$)Cl$_2$]ClO$_4$	CD$_3$SOCD$_3$	8.20 (2), 5.32 (4), 3.49 (4), 2.68 (6), 1.60 (12)
[Ni([14]1,4,8,11-tetraeneN$_4$)](ClO$_4$)$_2$[b]	CD$_3$SOCD$_3$	7.95 (2), 4.70 (4), 2.85 (4), 2.19 (6), 1.28 (12)
[Ni([14]1,4,8,11-tetraeneN$_4$)](PF$_6$)$_2$[b]	CD$_3$CN	7.70 (2), 4.55 (4), 2.84 (4), 2.22 (6), 1.37 (12)
[Ni([14]1,3,7,11-tetraeneN$_4$)](ClO$_4$)$_2$[b]	CD$_3$SOCD$_3$	9.05 (2), 4.10 (4), 2.78 (4), 2.21 (6), 1.38 (12)
[Ni([14]1,3,7,11-tetraeneN$_4$)](ClO$_4$)$_2$[b]	CD$_3$CN	8.42 (2), 3.70 (4), 2.99 (4), 2.30 (6), 1.43 (12)
C$_{16}$H$_{28}$N$_4$ (free ligand)	CCl$_4$	7.85, 7.62 (2); 5.97, 5.90, 5.70, 5.62 (4); 2.29 (4); 1.82 (6); 1.18 (12)
C$_{16}$H$_{28}$N$_4$ (free ligand)	C$_6$D$_5$NO$_2$	8.27, 8.08 (2); 6.23, 6.15, 5.95, 5.87 (4); 2.33 (6), 1.82 (6); 1.20 (12)
C$_{16}$H$_{28}$N$_4$ (free ligand)	C$_6$D$_5$N	8.25, 88.05 (2); 6.17, 6.10, 5.88, 5.80 (4); 2.09 (4); 1.56 (6); 0.99 (12)

[a] Chemical shifts in parts per million relative to TMS internal standard. Number of protons indicated in parentheses. [b] Data taken from ref 13. [c] Absorptions due to CH$_3$CN at 1.95 ppm have been omitted. All acetonitrile complexes have a peak at 1.95, but its relative intensity could not be determined due to impurities of CD$_2$HCN in the solvent.

tion of either hydrochloric or hydrobromic acid to the solutions followed by exposure to the atmosphere for several days resulted in the formation of green crystalline [Co([14]1,4,8,11-tetraeneN$_4$)X$_2$]ClO$_4$. The physical and spectral properties of these complexes were quite similar to those of the related tetragonal [Co([14]4,11-dieneN$_4$)X$_2$]$^+$ species.[28] The infrared spectra of these cobalt complexes contain two bands above 3050 cm^{-1} that could be attributed to N–H stretching absorptions. The two imine C=N stretching frequencies (of the groups in the five- and six-membered rings) appear at 1655 and 1645 cm^{-1}. These are virtually the same positions as were found in the spectra of the [14]1,4,8,11-tetraeneN$_4$ complexes of iron(II) and nickel(II). Similarly, the pmr spectrum (see below) consists of a simple five-line pattern very similar in detail to that of [Ni([14]1,4,8,11-tetraeneN$_4$)](ClO$_4$)$_2$.[13] Although the free ligand exists in the enamine–imine form, complexation to certain metal ions appears to stabilize the β-diimine form of the ligand. It is quite possible that certain transition metal ions could stabilize the α-enamine–imine form or the α-diimine form of the ligand.

Nmr Spectra. The proton magnetic resonance spectra of the three complexes, [Fe([14]4,11-dieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$, [Fe([14]1,4,11-trieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$, and [Fe([14]1,4,8,11-tetraeneN$_4$)(CN$_3$CN)$_2$](ClO$_4$)$_2$, simplify progressively as the degree of unsaturation increases (Table III). The addition of each double bond removes an asymmetric center and, consequently, reduces the possible number of chelate ring conformations. The *dl* and meso forms of [Fe([14]4,11-dieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$ have been isolated.[10] This isomerism is related to the absolute configurations about the two asymmetric nitrogen atoms.[29] For a given isomer of [Fe([14]4,11-dieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$, the most prominent nmr absorptions are those of the methyl substituents, which occur as three peaks at 2.4, 1.4, and 1.0 ppm for one of the isomers. The low-field singlet is due to the deshielded methyl substituent of the six-membered ring imine group and the two higher field absorptions have been attributed to the axially (1.0 ppm) and equatorially (1.4 ppm) positioned geminal methyl groups. These assignments rest heavily on the results of extensive nmr studies of the [Ni([14]4,11-dieneN$_4$)]$^{2+}$ cations[29] and the theoretical predictions made for the nmr shifts of nuclei in various spatial arrangements in the environment of low-spin d^6 and d^8 systems.[30] The absorptions of the ethylenediamine residues and the bridgehead amines produce a broad overlapping multiplet structure, making assignments difficult.[29] The introduction of a third imine linkage removes one of the asymmetric nitrogen centers and only one diastereoisomer is possible. The spectrum contains seven major absorptions (Figure 3). The single imine C–H of the five-membered ring appears at 8.15 ppm and displays a small amount of triplet character. The methylene protons of this ring appear as a slightly broadened singlet at 4.90 ppm. The bridgehead methylene protons of the two six-membered rings are not equivalent (due to the increased puckering of the ring containing the tetrahedral nitrogen) and occur at 3.04 and 2.93 ppm. The methyl groups attached to the imine linkages absorb near 2.45 ppm and the absorption envelope contains some structure resulting from the inequivalences associated with the uneven puckering of the two rings. The axially oriented methyl group in the six-membered ring containing the tetrahedral nitrogen is found furthest upfield, at 1.07 ppm. This is in agreement with the predictions of Buckingham and Stephens[30] for octahedral d^6 metal ions systems, in which nuclei situated above the strong "in-plane" field should experience some shielding effects and appear at higher field strengths.[29] There are three absorptions between 1.48 and 1.39 ppm which are assigned to the *gem*-dimethyl protons of the flattened six-membered ring and the equatorial methyl of the more puckered ring. Apparently none of the methyl groups are equivalent; those of the flattened six-membered ring apparently possess a small amount of axial and equatorial character and the barrier to ring inversion is too high to produce equivalence on the nmr time scale at room temperature. The dimethylene protons of the ethylenediamine ring should present an ABCD pattern

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(29) L. G. Warner, N. J. Rose, and D. H. Busch, *J. Amer. Chem. Soc.*, **90**, 6938 (1968); L. G. Warner and D. H. Busch, *ibid.*, **91**, 4092 (1969); E. Gore and D. H. Busch, *ibid.*, in press (this provides an analysis of several related Co$^{\mathrm{III}}$ d^6 systems).

(30) A. D. Buckingham and P. J. Stephens, *J. Chem. Soc.*, 4583 (1964).

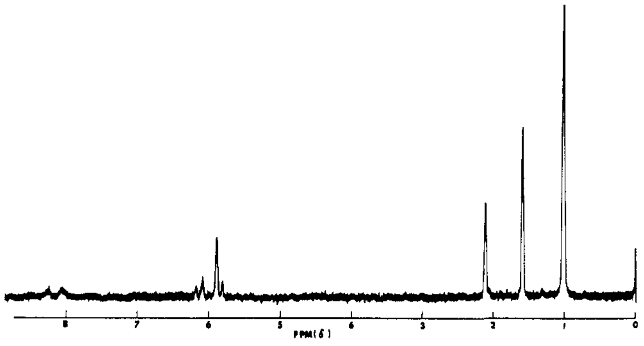

Figure 4. Proton nmr spectrum of the free ligand $Me_6[14]2,4,9,11$-tetraeneN$_4$.

resulting from the axial–equatorial nature of the protons in this five-membered ring and chemical shift differences arising from variations in distance from the imine linkage. They appear as a broad multiplet structure between 2.3 and 3.3 ppm.

The pmr spectra of the tetraimine complexes $[Fe([1,4]$-$1,4,8,11$-tetraeneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$ and [Co([14]1,4,-8,11-tetraeneN$_4$)Br$_2$](ClO$_4$) appear as simple five-line patterns very similar to that reported for [Ni([14]1,4,-8,11-tetraeneN$_4$)](ClO$_4$)$_2$[13] (with the exception of the acetonitrile absorption in the iron complex) (Figure 3). Although stereochemical models indicate that the *gem*-dimethyl groups have axial and equatorial orientations, the energy barrier for the interconversion of the axial and equatorial substituents is expected to be small and interconversion is probably rapid in solution. Thus, the *gem*-dimethyl protons appear as a singlet at 1.45 ppm. The imine methyl protons absorb at 2.48 ppm. The bridgehead methylene protons of the six-membered ring appear at 3.08 ppm and the methylene protons of the five-membered ring, which are sandwiched between an electronegative nitrogen and an imine function, appear at lower field, 4.90 ppm. These assignments have been verified by deuteration studies on [Ni([14]-1,4,8,11-tetraeneN$_4$)](ClO$_4$)$_2$.[13] The C–H protons of the imine linkages in the five-membered rings are the most deshielded in the system, 8.18 ppm, and occur at much lower fields than normal olefin C–H's.

The [Fe([14]1,3,7,11-tetraeneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$ isomer, which contains an α-diimine linkage, has a similar six-line spectrum. The α-diimine protons occur at even lower fields, 9.02 ppm, as a consequence of the delocalization afforded by the α-diimines iron chelate ring.

The nmr spectrum of the free ligand differs substantially from that obtained when the substance is coordinated to transition metals (Figure 4). Some of the departure (small changes in chemical shifts) can be attributed to the elimination of the electronic field gradients (and concomitant magnetic effects) associated with the metal ions. The changes in multiplet structure can only be interpreted in terms of a tautomer produced by a proton shift and double bond migration. The spectrum consists of five regions of absorption and the assignments of these absorptions follow.

The high-field portion of the spectrum contains three sharp absorptions at 1.18, 1.82, and 2.29 ppm of relative intensities in the ratio 12:6:4. On the basis of the intensities and the assignments for the nickel complex of the tetraimine ligand, these are assigned to the *gem*-dimethyl protons, imine methyl protons, and bridgehead methylene protons, respectively. The remaining two absorptions are considerably more complex. A four-lined absorption pattern appears in the 5.6–6.0-ppm region and a broad doublet occurs at 8.05 and 8.25 ppm. The broad doublet (relative intensity 2) is readily assigned to the N–H protons of the tautomeric structure on the basis of its breadth and the rapid disappearance of the absorption when a few drops of deuterated ethanol are added to a deuteriopyridine solution of the ligand. The 6.17- and 6.10-ppm absorption must be attributed to the protons of the carbon atoms 2 and 7, since these absorptions partially collapse when the N–H hydrogens are replaced by deuterons. The most intense peak at 5.88 ppm is associated with protons attached to carbon atoms 3 and 10. The tautomeric equilibrium of the free ligand lies completely in the direction of the enamine–imine structure since the relative intensity of the pmr absorptions is independent of the basicity of the solvent (Table II).

Experimental Section

Materials. All metal salts, solvents, and organic starting materials were of reagent grade. Metal perchlorates were purchased from G. Frederick Smith and Co. and the organic materials were purchased from Aldrich Chemical Co.

Physical Measurements. Visible, near-infrared, and ultraviolet spectra were obtained with a Cary Model 14 recording spectrophotometer. Spectra of solid samples were run on Nujol mulls on filter paper using Nujol impregnated filter paper in the reference beam to compensate for energy losses due to light scattering. Infrared spectra were obtained from Nujol and hexachlorobutadiene mulls on a Perkin-Elmer Model 337 recording spectrophotometer.

The electrical resistances of solutions of the compounds were measured using an Industrial Instruments RC 16B conductivity bridge and a conductance cell with platinum electrodes with a cell constant of 2.13 cm^{-1}. Conductances were determined at 25° at 1000 cps with approximately 10^{-3} *M* solutions.

The magnetic susceptibilities of solid samples were determined by the Faraday technique using Hg[Co(NCS)$_4$] as a standard. All of the measured susceptibilities were corrected for ligand diamagnetism.

Elemental analyses were performed by Galbraith Laboratories, Inc., and by Alfred Bernhardt Microanalytical Laboratories.

Preparation of Complexes. [Fe(Me$_6$[14]4,11-dieneN$_1$)(CH$_3$CN)$_2$]-(ClO$_4$)$_2$ was prepared as previously described.[10]

[Fe([Me$_6$[14]1,4,11-trieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$. [Fe(Me$_6$[14]4,11-dieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$ (2 g) was dissolved in 25 ml of acetonitrile, acidified with a few drops (−0.5 ml) of concentrated perchloric acid, and aerated for 1 hr. The solution was filtered and concentrated under vacuum, and crystallization was induced with a small amount of diethyl ether. The product was filtered, recrystallized from a minimum amount of anhydrous acetonitrile, and dried *in vacuo*. *Anal.* Calcd for FeC$_{20}$H$_{36}$N$_4$Cl$_2$O$_8$: C, 39.03; H, 5.87; N, 13.66; Cl, 11.55. Found: C, 39.22; H, 5.77; N, 13.68; Cl, 11.37.

[Fe(Me$_6$[14]1,4,8,11-tetraeneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$. [Fe(Me$_6$[14]4,-11-(dieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$ (2 g) was dissolved in 25 ml of acetonitrile, acidified with 0.5 ml of concentrated perchloric acid, and aereated for 24 hr. The solution was filtered, concentrated under reduced pressure, and chilled in an ice box for several hours. The product was filtered, then recrystallized several times from a minimum amount of acetonitrile, and dried under reduced pressure. These recrystallizations are needed to purify the desired product from the acid degradation products of the hydrolyzed ligand. Purity was checked by monitoring the ir spectra to check for unwanted OH$^-$ or N–H absorptions. *Anal.* Calcd for FeC$_{20}$H$_{34}$N$_4$Cl$_2$O$_8$: C, 39.22; H, 5.55; N, 13.72; Cl, 11.60. Found: C, 39.01; H, 5.50; N, 13.61; Cl, 11.72.

[Fe(Me$_6$[14]1,4,8,11-tetraeneN$_4$)(CH$_3$CN)$_2$](BPh$_4$)$_2$. [Fe(Me$_6$-[14]1,4,8,11-tetraeneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$ (0.5 g) was dissolved in 15 ml of acetonitrile and 1 g of sodium tetraphenylborate dissolved in 5 ml of acetonitrile was added. The product was recrystallized within 5 min, filtered, washed with acetonitrile, and dried under reduced pressure. *Anal.* Calcd for FeC$_{68}$H$_{74}$N$_6$B$_2$: C, 77.57;

H, 7.04; N, 7.99; Fe, 5.31. Found: C, 77.53; H, 7.21; N, 7.79; Fe, 5.30.

[Fe(Me$_6$[14]1,3,7,11-tetraeneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$. The Me$_6$[14]4,14-dieneN$_4$ ligand was removed from [Ni(Me$_6$[14]4,14-dieneN$_4$)](ClO$_4$)$_2$ with cyanide in methanol solution by the method described by Love and Powell.[26] The methanol solution was taken to near dryness under reduced pressure and the residue dissolved in anhydrous acetonitrile. This solution of Me$_6$[14]4,14-dieneN$_4$ was added to an anhydrous acetonitrile solution of Fe(ClO$_4$)$_2$ prepared by refluxing Fe(ClO$_4$)·6H$_2$O in acetonitrile with an excess of triethyl orthoformate. Upon aerial oxidation for 1 hr, the pink solution turned an intense purple. The product precipitated upon addition of an aqueous solution of ammonium hexafluorophosphate. The dark purple product was filtered, washed with a 1:1 water–acetonitrile solution, and dried under reduced pressure. *Anal.* Calcd for $FeC_{20}H_{34}N_2P_2F_{12}$: C, 34.09; H, 4.83; N, 11.93. Found: C, 34.03; H, 4.64; N, 11.79.

[Fe(Me$_6$[14]1,4,8,11-tetraeneN$_4$)Cl]ClO$_4$. [Fe(Me$_6$[14]1,4,8,11-tetraeneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$ (1 g) was dissolved in the minimum amount of hot methanol (about 25 ml) in a nitrogen atmosphere. LiCl (0.5 g) in 5 ml of deaerated methanol was added. The flask was stoppered and chilled for several hours. The product was filtered under a nitrogen blanket, washed several times with a 2:1 methanol–ether solution, and dried under reduced pressure. *Anal.* Calcd for $FeC_{16}H_{28}N_4Cl_2O_4$: C, 41.11; H, 6.00; N, 12.00; Cl, 15.20. Found: C, 41.00; H, 5.98; N, 11.79; Cl, 15.34.

[Fe(Me$_6$[14]1,4,8,11-tetraeneN$_4$)Br]ClO$_4$. This compound was prepared by the same method as the chloro compound by substituting the LiBr for LiCl. *Anal.* Calcd for $FeC_{16}H_{28}BrClO_4$: C, 37.55; H, 5.47; N, 10.95; Br, 15.63. Found: C, 37.32; H, 5.52; N, 10.99; Br, 15.48.

[Fe(Me$_6$[14]1,4,8,11-tetraeneN$_4$)I]ClO$_4$. This compound was also prepared in the same manner as the chloro complex by substituting NaI for LiCl. *Anal.* Calcd for $FeC_{16}H_{28}N_4IClO_4$: C, 34.38; H, 5.01; N, 10.03. Found: C, 33.06; H, 5.15; N, 9.63.

[Fe(Me$_6$[14]1,4,8,11-tetraeneN$_4$)(NCS)$_2$]. [Fe(Me$_6$[14]1,4,8,11-tetraeneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$ (1 g) was dissolved in 25 ml of methanol and 0.5 g of NaNCS dissolved in 5 ml of methanol was added under a nitrogen atmosphere. The precipitate was filtered under a nitrogen blanket, washed with several generous portions of methanol, and dried under reduced pressure. *Anal.* Calcd for $FeC_{18}H_{28}N_6S_2$: C, 48.31; H, 6.16; N, 18.75; Fe, 12.39. Found: C, 48.23; H, 6.25; N, 18.75; Fe, 12.47.

[Fe(Me$_6$[14]1,4,8,11-tetraeneN$_4$)Cl$_2$]ClO$_4$. [Fe(Me$_6$[14]1,4,8,11-tetraeneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$ (1 g) was dissolved in the minimum amount of acetonitrile (about 20 ml) and chlorine gas was bubbled gently through the solution for 1 min. The color of the solution changed from red to yellow brown as the oxidation proceeded. Diethyl ether was added dropwise to the solution until the solution was slightly turbid. The solution was chilled and crystallization was induced by scratching the walls of the vessel with a glass stirring rod. The product was filtered, washed with several portions of a 1:1 acetonitrile–diethyl ether solution, and dried under reduced pressure. *Anal.* Calcd for $FeC_{16}H_{28}N_4Cl_3O_4$: C, 38.22; H, 5.57; N, 11.15; Cl, 21.19. Found: C, 38.23; H, 5.48; N, 11.30; Cl, 21.08.

[Fe(Me$_6$[14]1,4,8,11-tetraeneN$_4$)(C$_{12}$H$_8$N$_2$)](ClO$_4$)$_2$. [Fe(Me$_6$[14]-1,4,8,11-tetraeneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$ (1 g) was dissolved in the minimum amount of methanol at 40–50°, under a nitrogen atmosphere, and 0.5 g of phenanthroline was added. The flask was immediately stoppered and chilled in an ice–salt slush. The precipitate which formed was filtered, washed with a methanol–ether solvent mixture, and dried under reduced pressure. This preparation is delicate because, if too much MeOH is used, little or no precipitate will form and, if the solution is heated or allowed to stand for a few hours, free ligand and $Fe(phen)_3^{2+}$ form. Alternatively, if phen is added to a MeOH slurry of the starting compound, the product contains some of the tetraimine starting material as an impurity. *Anal.* Calcd for $FeC_{28}H_{36}N_6Cl_2O_8$: C, 47.00; H, 5.59; N, 11.75; Cl, 9.93. Found: C, 46.96; H, 5.20; N, 11.70; Cl, 9.92.

Me$_6$[14]2,4,9,11-tetraeneN$_4$(C$_{16}$H$_{28}$N$_4$). [Fe(Me$_6$[14]1,4,8,11-tetraeneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$ (4 g, 6.52 mmol) was dissolved in the minimum amount of dry acetonitrile (approximately 20 ml) and 3.52 g (19.56 mmol) of phenanthroline was added. The solution was tightly stoppered and allowed to stand at room temperature for approximately 36 hr. The color gradually changed from red to the characteristic deep red brown of [Fe(phen)$_3$](ClO$_4$)$_2$. The solution was concentrated on a rotary evaporator at room temperature. When approximately one-half of the solvent had evaporated, the solution contained a white crystalline precipitate. The white crystals were filtered from the solution and stored while the filtrate was taken to dryness. The residue consisted of [Fe(phen)$_3$](ClO$_4$)$_2$ and more free ligand, which was recovered by extraction with diethyl ether. *Anal.* Calcd for $C_{16}H_{28}N_4$: C, 69.56; H, 10.14; N, 20.28. Found: C, 69.43; H, 9.90; N, 20.03.

[Co(Me$_6$[14]1,4,8,11-tetraeneN$_4$)Cl$_2$]ClO$_4$. A solution of anhydrous cobalt perchlorate was prepared by dissolving 0.25 g of Co(ClO$_4$)$_2$·6H$_2$O in 5 ml of ethanol and 2 ml of triethyl orthoformate. An ethanol solution containing 0.25 g of the free ligand, $C_{16}H_{28}N_4$, was added to the cobalt(II) solution dropwise. The color of the solution turned from pink to yellow as the macrocyclic cobalt(II) complex formed. Crystallization was induced by the addition of 2 ml of diethyl ether and chilling the solution in a refrigerator for several hours. The yellow crystals were filtered from the solution and washed several times with an ethanol–ether mixture. The cobalt(III) complex was prepared by dissolving 100 mg of the Co(II) complex in ethanol, adding several drops of concentrated HCl to the solution, and exposing the solution to the atmosphere for several days. The product was filtered, washed with several generous portions of ethanol, and dried under reduced pressure. *Anal.* Calcd for $CoC_{16}H_{28}N_4Cl_3O_4$: C, 38.00; H, 5.54; N, 11.08; Cl, 21.05. Found: C, 38.08; H, 5.50; H, 5.50; N, 10.94; Cl, 21.38.

[Co(Me$_6$[14]1,4,8,11-tetraeneN$_4$)Br$_2$]ClO$_4$. This compound was prepared by the same method as the chloro complex with HBr substituted for HCl. *Anal.* Calcd for $CoC_{16}H_{28}N_4Br_2ClO_4$: C, 32.31; H, 4.71; N, 9.42. Found: C, 32.07, H, 4.81; N, 9.34.

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