The two schemes differ in the behavior of TPPFeN. In step 2, TPPFeN attacks $\mathrm{TPPFeN_3}$ at the open coordination site of the metal and could be considered a nucleophilic pathway. In step 4, TPPFeN attacks $\mathrm{TPPFeN_3}$ at the azide and is thus an electrophilic pathway. Step 5 produces $\mathrm{TPPFe^{II}N_2}$, which is still unknown and thus proposed to lose $\mathrm{N_2}$. The $\mathrm{TPPFe^{II}}$ formed is attacked at the metal by TPPFeN to produce the product in step 7.

The evaluation of the reaction scheme after step 1 will thus provide insight into the nucleophilicity of the intermediate TPPFeN. This will then allow the assignment of TPPFeN as either a nitrene or a nitride species. Further experiments are in progress regarding this question.

Finally, the difference in the degree of magnetic coupling between the two iron atoms in $\mathrm{(TPPFe)_2N}$ and $\mathrm{(TPPFe)_2O}$ is striking. It is not obvious to us why the N bridge should be so effective in this regard although there are no other N-bridged first transition series dinuclear metal complexes with which a comparison can be drawn.

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References and Notes

(1) (a) Portions of this work were presented at the 169th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1975, Abstracts, paper INOR 7. (b) Taken from the dissertation of D. A. Summerville, submitted to the Faculty of the Polytechnic Institute of New York in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry, 1975.

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The Synthesis, Structures, and Properties of New Macrocyclic Ligands and Novel Sexadentate Iron Complexes Produced by Electrophilic Reactions of the Iron Derivatives

Dennis P. Riley,[1a] John A. Stone,[1b] and Daryle H. Busch*[1a]

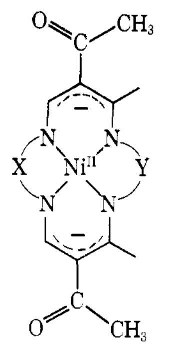
Contribution from The Evans Chemical Laboratory, The Ohio State University, Columbus, Ohio 43210, and the Savannah River Laboratory, E. I. duPont de Nemours and Co., Aiken, South Carolina 29801. *Received July 28, 1975*

Abstract: A template synthesis of ionizable 14-, 15-, and 16-membered tetraaza, tetraene macrocyclic ligands, devoid of functional substituents, has been devised. Also, the synthesis of six-coordinate dicationic iron(II) complexes of the new ligands are described. For the 14-membered ligand a trans diacetonitrile complex was obtained, but for both the 15- and 16-membered ligands, acetonitrile molecules add electrophilically to the γ-carbons of the macrocycle, producing the complex of novel sexadentate ligands. The latter represent examples in which coordinate saturation is achieved by the appending of two donor groups to a tetradentate macrocyclic ligand. These structures are formally analogous to such natural heme proteins as cytochrome *c*.

In recent years many advances have been made in the design and synthesis of tetraaza macrocyclic ligands and their transition metal complexes.[2-5] Systematic variations in ring size, unsaturation, and substituents have provided a basis for elucidating and understanding the effects these structural features have on both physical and chemical properties.[5-7] The subject of this study has been the preparation of new 14-, 15-, and 16-membered tetraaza, tetraene macrocyclic ligands, devoid of functional substituents, and the synthesis and characterization of their novel complexes with the biologically significant metal iron.

The ligands II have been prepared via a template route based on the work of Jager[8,9] and the observation of Hipp and Busch[10] that the 15-membered Jager complex (Ib) can be deacylated by strong acid in a nucleophilic solvent. In addition, a 16-membered ligand, structurally analogous to the ligands II, was synthesized by a modification of the procedure used by Holm and co-workers[4] for preparation of ligand IIIa.

The synthesis of the iron(II) complexes of these new ligands has led to the isolation and characterization of a series of low-spin six-coordinate dicationic complexes. For the 14-membered ligand a *trans*-diacetonitrile, "bis-β-diimine" complex (structure IV) was obtained, but for the 15- and 16-membered ligands, complexes were obtained which displayed physical and chemical properties totally unlike those exhibited by the 14-membered complex. In order to determine the correct structure of these latter complexes, a de-



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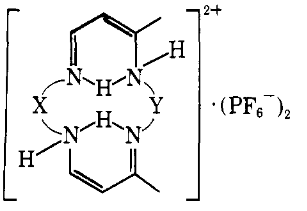


II

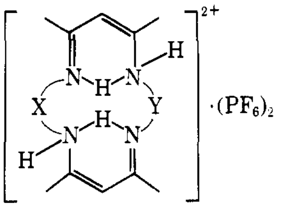
a, $X = Y = C_2H_4$

b, $X = C_2H_4$; $Y = C_3H_6$

c, $X = (CH_3)_2CCH_2$;
$Y = C_3H_6$

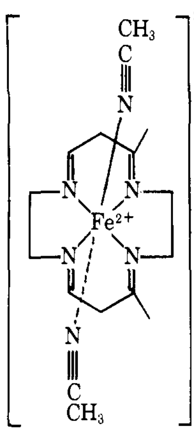
d, $X = (CH_3)_2CC(CH_3)_2$;
$Y = C_3H_6$

e, $X = Y = C_3H_6$

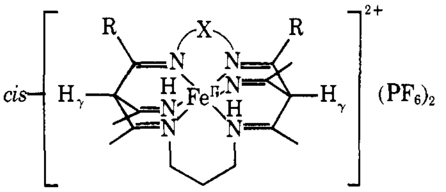


III, $X = Y = C_3H_6$

IIIa, $X = Y = C_2H_4$



IV



Va, $X = -CH_2CH_2-$; $R = H_\delta$

Vb, $X = CH_2C(CH_3)_2$; $R = H_\delta$

Vc, $X = -C(CH_3)_2C(CH_3)_2-$; $R = H_\delta$

Vd, $X = -CH_2CH_2CH_2-$; $R = H_\delta$

Ve, $X = -CH_2CH_2CH_2-$; $R = CH_3$

finitive structure determination by x-ray diffraction methods was carried out on a single crystal of the 16-membered complex Vd, *cis*-[Fe(Me_2IE_2[16]tetraeneN_4)].[11] From the crystallographic results the 16-membered ligand derivative, Vd, has been found to possess the structure in which acetonitrile molecules have added electrophilically to the apical (γ) carbons of the unsaturated six-membered ring of the macrocycle, producing the cis complex of a novel sexadentate ligand (structures Va–e). The resulting cis hexaene ligand structure has also been assigned to the 15- and 16-membered ligand derivatives, Va–c and Ve. These assignments have been based largely on spectroscopic evidence, ^1H NMR, and ir, although other physical and chemical properties of these complexes are virtually identical with those found for the 16-membered derivative Vd, *cis*-[Fe(Me_2IE_2[16]tetraeneN_4)].

These complexes are also remarkable not only because of their ease of formation and unusual ligand geometry but also because they (Va–e) represent the first examples of low-spin iron(II) coordinated exclusively to six nonconjugated imine donor groups. Thus, it has been possible to examine the spectroscopic, Mossbauer, and electrochemical properties associated with this unusual donor set. Also the structure of the sexadentate hexaene complex, Vd, is very nearly octahedral with a slight twist about the pseudo-C_3 rotation axis. This geometry is very similar to that found with some other sexadentate hexaene ligands, for example, tris(glyoximato) clathro chelate[12,13] complexes having the tris-α-diimine donor set. Thus, both electronic spectral and Mossbauer spectral parameters for these new sexadentate iron(II) derivatives have been compared to the values found for some of the previously reported clathro chelate complexes.[13]

Experimental Section

Materials. All metal salts, solvents, and organic starting materials were reagent grade. Acetonitrile, ethanol, and diethyl ether were dried and degassed by refluxing over calcium hydride for 12 h and distilling them under nitrogen; nitromethane was purified by literature methods.[14] All manipulations on iron complexes were carried out in a Vacuum Atmospheres Corp. controlled atmosphere chamber.

Physical Measurements. Visible and ultraviolet spectra were obtained with a Cary Model 14R recording spectrophotometer. Infrared spectra were obtained from Nujol mulls applied between KBr disks on a Perkin-Elmer Model 337 recording spectrophotometer. ^{57}Fe Mossbauer spectra were obtained with a conventional constant-acceleration spectrometer operated in time mode, with a $^{57}Co(Cu)$ source. Experiments were performed with both source and absorber at room temperature. The spectrometer was calibrated with sodium nitroprusside, Fe_2O_3, and iron metal.

Isomer shifts and quadrupole splittings were determined by inspection with an accuracy of ±0.01 mm/s. The absorber thickness was normally less than 75 mg/cm^2 of the compound.

The electrical resistances of solutions of the new compounds were measured using an Industrial Instruments RC16B conductivity bridge and a conductance cell with a cell constant of 0.1 cm^{-1}. Conductances were measured at 25° at 1000 Hz with approximately 10^{-3} M solutions.

The magnetic susceptibilities of solid samples were determined by the Faraday method,[15] using Hg[Co(NCS)$_4$] as the standard. All measured susceptibilities were corrected for ligand diamagnetism using Pascal's constants.[16]

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Syntheses. 6,13-Diacetyl-5,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenatonickel(II) (Ia). This complex was prepared according to literature methods.[9]

6,14-Diacetyl-7,13-dimethyl-1,4,8,12-tetraazacyclopentadeca-4,-6,12,14-tetraenatonickel(II) (Ib). This complex was prepared according to literature methods.[8]

6,14-Diacetyl-2,2,7,13-tetramethyl-1,4,8,12-tetraazacyclopentadeca-4,6,12,14-tetraenatonickel(II) (Ic). This complex was prepared by the method used for Ib, substituting 1,2-diamino-2-methylpropane for ethylenediamine.[17]

6,14-Diacetyl-2,2,3,3,7,13-hexamethyl-1,4,8,12-tetraazacyclopentadeca-4,6,12,14-tetraenatonickel(II) (Id). This complex was prepared by the method used for Ib substituting 2,3-diamino-2,3-dimethylbutane[18] for ethylenediamine.

3,11-Diacetyl-2,12-dimethyl-1,5,9,13-tetraazacyclohexadeca-

Table I. Analytical Data for the New Macrocyclic Ligands and Iron Complexes

Compound	% calcd C	% calcd H	% calcd N	% found C	% found H	% found N
$H_2[Me_2[14]tetraene N_4](PF_6)_2$ (IIa)	28.13	4.30	10.94	28.19	3.97	10.87
$H_2[Me_2[15]tetraene N_4](PF_6)_2$ (IIb)	29.66	4.56	10.65	29.57	4.37	10.46
$H_2[Me_4[15]tetraene N_4](PF_6)_2$ (IIc)	32.65	4.72	10.14	32.47	4.63	10.01
$H_2[Me_6[15]tetraene N_4](PF_6)_2$ (IId)	35.05	5.50	9.62	34.93	5.46	9.53
$H_2[Me_2[16]tetraene N_4](PF_6)_2$ (IIe)	31.12	4.85	10.37	31.18	4.77	10.27
$H_2[Me_4[16]tetraene N_4](PF_6)_2$ (III)	33.81	5.28	9.86	34.06	5.36	9.92
trans-$[Fe(Me_2[14]tetraene N_4)(NCCH_3)_2](PF_6)_2$ (IV)	29.64	4.01	12.97	29.79	4.10	12.83
cis-$[Fe(Me_2IE_2[15]tetraene N_4)](PF_6)_2$ (Va)	30.83	4.23	12.69	31.07	4.29	12.54
cis-$[Fe(Me_4IE_2[15]tetraene N_4)](PF_6)_2$ (Vb)	33.05	4.35	12.18	33.08	4.62	12.05
cis-$[Fe(Me_6IE_2[15]tetraene N_4)](PF_6)_2$ (Vc)	35.50	5.02	11.70	35.33	4.76	11.74
cis-$[Fe(Me_2IE_2[16]tetraene N_4)](PF_6)_2$ (Vd)	31.96	4.42	12.43	32.06	4.47	12.47
cis-$[Fe(Me_4IE_2[16]tetraene N_4)](PF_6)_2$ (Ve)	34.20	4.56	11.97	34.54	4.84	12.01
trans-$[Fe(Me_2[14]tetraene N_4)(NCS)_2]$ (VI)	42.88	5.10	21.44	43.17	5.26	21.30
trans-$[Fe(Me_2[14]tetraene N_4)(NO_2)_2]$ (VII)	39.15	5.44	22.84	38.79	5.10	23.40
trans-$[Fe(Me_2[14]tetraene N_4)(py)_2](PF_6)_2$ (VIII)	36.45	4.15	11.60	36.55	4.12	11.55
$[Me_2[14]tetraene N_4]$ (XIV)	65.40	9.09	25.42	65.14	8.97	25.21

1,3,9,11-tetraenatonickel(II) (Ie). This complex was prepared according to literature methods.[8]

5,14-Dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene Dihydrohexafluorophosphate, $H_2[Me_2[14]$-4,6,11,13-tetraene$N_4](PF_6)_2$ (IIa). To a slurry of 18.0 g (0.05 mol) of Ia in hot water is added dropwise with stirring 37% hydrochloric acid until all solid dissolves (30-40 ml) giving an orange solution. The solution is filtered hot, and to the filtrate is added an aqueous solution containing 21.0 g (0.10 mol) of ammonium hexafluorophosphate. Yellow crystals precipitate upon cooling, and they are collected by filtration, washed with absolute ethanol and diethyl ether, and dried in vacuo at 80 °C for 24 h. The yellow crystals are then added to 400 ml of absolute ethanol. The resulting slurry is stirred vigorously while hydrogen chloride gas is bubbled through the ethanol. The yellow salt gradually dissolves and after 30 min the solution turns deep blue-green. The ethanol is then removed by rotary evaporation, and to the solid is added 100 ml of water containing an additional 21.0 g of ammonium hexafluorophosphate. The white ligand salt precipitates as the solution cools. It is collected by filtration, washed with absolute ethanol and diethyl ether, and dried in vacuo. In a typical preparation 24 g of ligand salt was obtained for a 48% yield based on complex Ia.

The free ligand was prepared by slurrying 24.0 g (0.0469 mol) of the ligand salt in warm absolute ethanol, followed by the addition of an ethanolic sodium ethoxide solution (0.0938 mol). After stirring for 1 h, the ethanol was removed by rotary evaporation and the solid mass was extracted with chloroform. The chloroform washings were filtered to remove salt contaminants. The chloroform was then removed under vacuum, the solid was dissolved in a minimum volume of boiling absolute ethanol, and the resultant solution was filtered. This solution was allowed to cool in a freezer overnight. Large cream-colored platelets were obtained and collected via filtration. The yield was 8.8 g for an 84% yield based on the ligand salt. After recrystallization from $CHCl_3$-absolute ethanol, a 72% yield of the pale yellow platelets, compound XIV, was obtained: mp 141-142 °C; mass spectrum, *m/e* calcd = 220, *m/e* found = 220.

7,13-Dimethyl-1,4,8,12-tetraazacyclopentadeca-4,6,12,14-tetraene Dihydrohexafluorophosphate ($H_2[Me_2[15]$-4,6,12,14-tetraene$N_4](PF_6)_2$) (IIb). This ligand was prepared by the method described for IIa, substituting Ib for Ia. Yields of 40-50% based on complex Ib are obtained.

2,2,7,13-Tetramethyl-1,4,8,12-tetraazacyclopentadeca-4,6,12,14-tetraene Dihydrohexafluorophosphate ($H_2[Me_4[15]$-4,6,12,14-tetraene$N_4](PF_6)_2$) (IIc). This ligand was prepared by the method used for IIa, substituting Ic for Ia. Yield, 40% based on complex Ic.

2,2,3,3,7,13-Hexamethyl-1,4,8,12-tetraazacyclopentadeca-4,6,12,14-tetraene Dihydrohexafluorophosphate ($H_2[Me_6[15]$-4,6,12,14-tetraene$N_4](PF_6)_2$) (IId). This ligand was prepared by the method used for IIa, substituting Id for Ia. Yield, 40% based on complex Id.

2,12-Dimethyl-1,5,9,13-tetraazacyclohexadeca-1,3,9,11-tetraene Dihydrohexafluorophosphate ($H_2[Me_2[16]$-1,3,9,11-tetraene$N_4](PF_6)_2$) (IIe). This ligand was prepared by the method outlined for IIa, substituting Ie for Ia. Yield, 65% based on complex Ie.

2,4,10,12-Tetramethyl-1,5,9,13-tetraazacyclohexadeca-1,3,9,11-tetraene Dihydrohexafluorophosphate ($H_2[Me_4[16]$-1,3,9,11-tetraene$N_4](PF_6)_2$) (III). Methyl fluorosulfonate (28.5 g, 10.25 mol) was added dropwise under nitrogen to a 150-ml dichloromethane solution containing 29.8 g (0.125 mol) of bis(acetylacetone)trimethylenediamine.[19] After stirring for 0.5 h, white crystals formed and at this point an additional 1000 ml of dichloromethane was added. nopropane (9.25 g, 0.125 mol) was added dropwise over a period of 1 h to give a white precipitate. The solvent was removed by vacuum and the yellow oil remaining was dissolved in 400 ml of hot water. To this solution was added a filtered aqueous solution containing 52.0 g (0.25 mol) of ammonium hexafluorophosphate. Upon cooling, white solid formed and was collected by filtration, washed with absolute ethanol and diethyl ether, and dried in vacuo; 10-15% yields of III were obtained, based on bis(acetylacetone)propylenediamine.

$[Fe(Me_2[14]$-1,4,8,11-tetraene$N_4)(NCCH_3)_2](PF_6)_2$ (IV). To 200 ml of acetonitrile solution containing $[Fe(CH_3CN)_6](SO_3CF_3)_2$ (0.0195 mol)[20] was added 10.0 g (0.0195 mol) of the ligand salt, IIa. The solution was heated with stirring until all of the salt dissolved. At this point 3.95 g (0.039 mol) of triethylamine was added dropwise and the solution turned to a deep red color. The volume was reduced to 30 ml and the solution was filtered while hot. Then 75 ml of absolute ethanol was added and the volume was slowly reduced under vacuum. After the volume had been reduced to 70 ml, the complex IV crystallized as orange-brown crystals which were collected by filtration and washed with ethanol and ether. The product was recrystallized from acetonitrile and ethanol and the final yield based on ligand salt was 80%.

***cis*-[(6,14-Bis(1-iminoethyl)-7,13-dimethyl-1,4,8,12-tetraazacyclopentadeca-4,6,12,14-tetraene)iron(II)] Hexafluorophosphate (*cis*-$[Fe(Me_2IE_2[15]tetraeneN_4](PF_6)_2$) (Va)**

***cis*-[(6,14-Bis(1-iminoethyl)-2,2,7,13-tetramethyl-1,4,8,12-tetraazacyclopentadeca-4,6,12,14-tetraene)iron(II)] Hexafluorophosphate (*cis*-$[Fe(Me_4IE_2[15]tetraeneN_4)](PF_6)_2$) (Vb)**

***cis*[(6,14-Bis(1-iminoethyl)-2,2,3,3,7,13-hexamethyl-1,4,8,12-tetraazacyclopentadeca-4,6,12,14-tetraene)iron(II)] Hexafluorophosphate (cis-$[Fe(Me_6IE_2[15]tetraeneN_4)](PF_6)_2$) (Vc)**

***cis*-[(3,11-Bis(1-iminoethyl)-2,12-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,3,9,11-tetraene)iron(II)] Hexafluorophosphate (*cis*-$[Fe(Me_2IE_2[16]tetraeneN_4)](PF_6)_2$) (Vd)**

***cis*-[(3,11-Bis(1-iminoethyl)-2,4,10,12-tetramethyl-1,5,9,13-tetraazacyclohexadeca-1,3,9,11-tetraene)iron(II)] Hexafluorophosphate (*cis*-$[Fe(Me_4IE_2[16]tetraeneN_4)](PF_6)_2$) (Ve).**

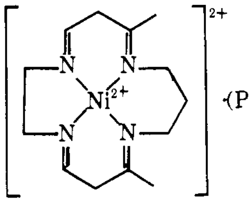
The general procedure used for the preparation of the iron complexes Va-e was identical in each case with that outlined for complex IV $[FeMe_2[14]tetraeneN_4)(NCCH_3)_2](PF_6)_2$. In addition, the yields based on the corresponding ligand salt were in all cases 70-80%.

$[Fe(Me_2[14]$-1,4,8,11-tetraene$N_4)X_2]$, Where $X^- = NO_2^-$ and SCN^-. To 30 ml of hot acetone solution containing 2.0 g of complex $[Fe(Me_2[14]\text{-}1,4,8,11\text{-}tetraeneN_4)(CH_3CN)_2](PF_6)_2$, IV, a hot methanolic solution containing 2 equiv of either $NaNO_2$ or NaSCN was added dropwise. Allowing the solutions to cool gave highly crystalline complexes VI (X = SCN) and VII (X = NO_2). Yields after washing with methanol and diethyl ether were 70–80% based on the starting complex, IV. $[Fe(Me_4[14]tetraeneN_4)(NO_2)_2]$ (VII) could not be recrystallized because it is insoluble in all common solvents; e.g., $CHCl_3$, THF, EtOH, MeOH, CH_3CN, DMF, C_6H_6, acetone, $MeNO_2$, etc.

$[Fe(ME_2[14]\text{-}1,4,8,11\text{-}tetraeneN_4)(pyridine)_2](PF_6)_2$, VIII. Complex IV (2 g) was dissolved in 30 ml of boiling pyridine. After refluxing for 10 min, the volume was reduced to 5 ml; at this point 50 ml of hot ethanol was added. Upon cooling, orange crystals of the bis(pyridine) complex formed. They were collected by filtration, washed with ethanol and ether, and dried in vacuo. Yield, 80% based on IV.

Results and Discussion

Preparation and Characterization of the Ligand Salts II and III, $H_2(Me_n[Z]tetraeneN_4)(PF_6)_2$. In a recent communication[10] it was reported that the 15-membered ring derivative $[Ni(Ac_2Me_2[15]tetraenatoN_4)]$, Ib, could be deacylated in water by treatment with nitric acid to yield the nickel complex $[Ni(Me_2[15]tetraeneN_4)]^{2+}$, IX. It was proposed that the mechanism involves protonation at the apical (γ)-carbon atoms with the acetyl groups subsequently being removed by nucleophilic displacement by solvent. This behavior was found to be in contrast to that of the 14-membered complex $[Ni(Ac_2Me_2[14]tetraenatoN_4)]$, Ia, which, under the same conditions, undergoes reversible protonation without loss of the acyl groups.[9]



IX

The effect which ring size has on the ease of deacylation prompted us to seek conditions under which deacylation would take place regardless of ring size. Treatment of the complexes $[Ni(Ac_2Me_2[Z]tetraenatoN_4)]$, I, in water with an excess of hydrochloric acid followed by the addition of 2 equiv of ammonium hexafluorophosphate gave the yellow crystalline products $[Ni(Ac_2Me_2[Z]tetraeneN_4)]^{2+}$ (X); which could be deprotonated to give the starting complexes (Scheme I). The complexes X when dried in vacuo at 70 °C for 48 h show no bands in their infrared spectra attributable to either N-H or O-H absorptions. This and the fact that their NMR spectra show a single kind of vinyl proton agree with the assumption that the starting materials (I) reversibly protonate on the apical (γ)-carbon atom as shown in Scheme I. Treatment of the protonated complexes (X) in the nucleophilic solvent ethanol with a continuous stream of hydrogen chloride gas results in the deacylation. Deacylation is followed by demetalation as indicated by the formation of an intense deep blue color due to the presence of the tetrahedral tetrachloronickelate(2−) anion (XI). Removal of the ethanol followed by the addition of water destroys the tetrahedral nickel anion, and, with cooling, the ligands can be precipitated as their white hexafluorophosphate salts.

The nontemplate synthesis of $H_2(Me_4[16]tetraeneN_4)(PF_6)_2$ (III, Scheme II) was carried out by a procedure in which the intermediate (XIII) was not isolated. Synthesis is based on the procedure outlined by Holm et al.[4] O-Methylation of the bis(acetylacetone)propanediamine (XII)[19] increases the reactivity of the -COMe carbon toward nucleophilic attack by one end of an additional 1,3-propanediamine molecule. The yields from this synthetic procedure average 10–15%, and are accompanied by large amounts of tarry material that is produced in the closure step. The pure ligand salt can be isolated by removing the dichloromethane, dissolving the crude closure products in a minimum amount of hot water, and addition of ammonium hexafluorophosphate followed by cooling.

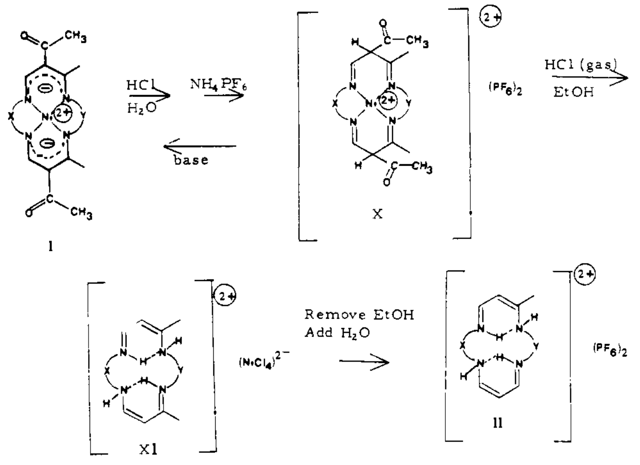
The salts of the various ligands (II and III) have in common a characteristic set of infrared absorptions. They have

Table II. Selected Ir Bands (cm^{-1})

Compounds	NH	Double bond region
IIa[c]	3430 (vs)[a]	1620 (vs),[b] 1521 (s)
IIb[c]	3450 (vs), 3500 (vs)	1620 (vs),[b] 1530 (s)
IIc[c]	3395 (vs)[a]	1620 (vs),[b] 1540 (s)
IId[c]	3370 (vs)[a]	1620 (vs),[b] 1550 (s)
IIe[c]	3440 (vs), 3410 (vs)	1610 (vs),[b] 1520 (s)
III[c]	3440 (vs), 3410 (vs)	1575 (vs)[b]
IV[c]	None	1675 (m), 1635 (m)
Va[c]	3340 (vs)[a]	1630 (s), 1610 (s)
Vb[c]	3300 (vs)	1630 (s), 1610 (s)
Vc[c]	3310 (vs)	1630 (s), 1615 (s), 1605 (s)
Vd[c]	3310 (vs)	1635 (s), 1620 (s)
Ve[c]	3310 (vs)	1640 (s)
VI[d]	None	1665 (m), 1640 (m)
VII[d]	None	1625 (s), 1600 (s)
VIII[e,f]	None	1645 (s),[a] 1600 (m)[e]
XIV	[g]	1620 (vs), 1590 (vs)

[a] Doublet. [b] Broad. [c] PF_6 at 860 (vs) and 560 (s). [d] SCN absorptions appear at 2100 (vs) and 795 (vs). [e] Pyridine. [f] Pyridine C–H stretch at 3065 (w). [g] NH absorption is obscured by Nujol, but in KBr pellet appears near 3000 cm^{-1}.

Scheme I



Scheme II

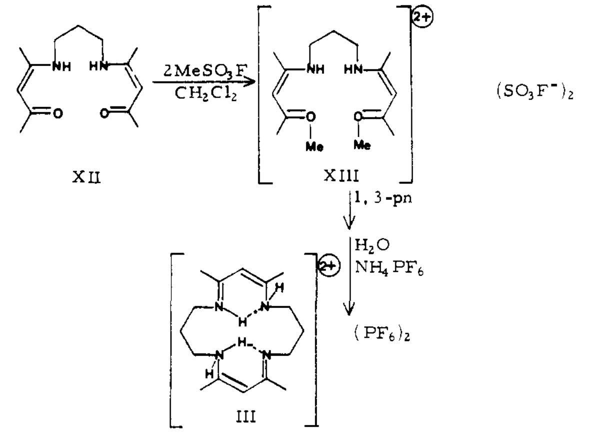


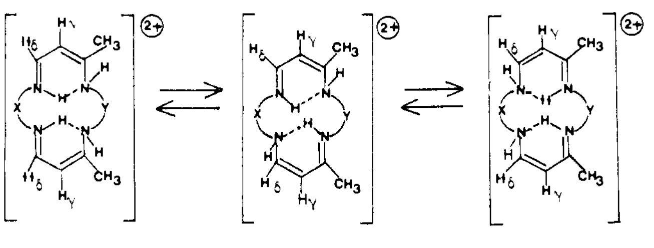
Table III. Proton Magnetic Resonance Spectra for Ligands and Complexes[a]

Compound	Methyl	Methylene[b]	Vinyl[c]	NH	Bridgehead
IIa	2.41	3.83[d]	6.46 (γ),[e] 8.00 (δ), 8.10 (δ)[e]	7.6[d]	
IIb	2.43	2.0 (β), 3.64,[d] 3.53 (α)	5.73 (γ), 5.86 (γ), 5.96 (γ), 6.08 (γ), 6.21 (γ), 6.34 (γ), 8.0 (γ)[f]	7.5[d]	
IIc	2.34, 1.38[g]	1.98 (β), 3.60,[d] 3.51 (α)	5.3 (γ), 7.6 (δ)[f]	7.7[d]	
IId	2.34, 1.38[g]	1.97 (β), 3.52 (α)	5.18 (γ),[e] 7.49 (δ), 7.72 (δ)	7.7[d]	
IIe	2.48	2.1 (β),[f] 3.6 (α)[f]	5.78 (γ),[e] 7.99 (δ),[e] 8.12 (δ)[e]	7.5[d]	
III	2.48	2.1 (β),[f] 3.6 (α)[f]	5.41	7.4[d]	
IV	2.45, 2.08[h]	4.20, 4.42	8.29	None	None
Va	2.76	3.74, 3.80, 2.07 (α), 4.25 (α), 2.95 (β)	8.73, 8.78[i]	10.68, 11.02	5.82[j]
Vb	2.77, 0.80,[g] 0.87,[g] 1.53[g]	3.72, 3.87, 1.91 (α), 4.17 (α), 2.94 (β)	8.32, 8.37,[i] 8.68, 8.73[i]	10.66, 11.23	5.83[j]
Vc	2.64, 0.64,[g] 0.75,[g] 1.52[g]	1.96 (α), 4.20 (α), 2.94 (β)	8.61, 8.66[i]	10.65, 11.25	5.79[j]
Vd	2.62	2.00 (α), 4.22 (α), 2.99 (β)	8.69, 8.74[i]	10.79	5.82[j]
Ve	2.62	1.93 (α), 4.22 (α), 2.91 (β)	None	10.89	5.69, 5.70
XIV[l]	1.90	3.45[f]	4.54 (γ),[k] 7.59 (δ)[k]	11.4[d]	

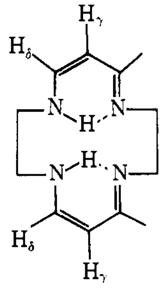
[a] Chemical shifts, in ppm relative to Me_4Si internal standard. Solvent used for all samples, CD_3NO_2. [b] Notation for trimethylene bridges: $N-CH_2(\alpha)-CH_2(\beta)-CH_2(\alpha)-N$. [c] Notation for vinyl region: $N{=}CH(\delta)-CH(\gamma)-CCH_3{=}N$. [d] Broad. [e] Center of a doublet, split 20 Hz. [f] Complex multiplet. [g] Methyls on five-membered rings. [h] Coordinated acetonitrile. [i] Doublet, $J = 5$ Hz, splitting due to coupling with bridgehead proton. [j] Doublet of doublets, splitting 5 and 1 Hz. [k] Vinyls are split, $J = 2.5$ Hz. [l] Solvent, $CDCl_3$.

a sharp N-H stretch near 3400 cm^{-1}, a broad band in the double bond region centered at 1620 cm^{-1}, and hexafluorophosphate bands at 860 and 560 cm^{-1} (Table II). The NMR spectra of the salts $H_2(Me_2[Z]tetraeneN_4)(PF_6)_2$ (II) exhibit characteristic vinyl resonances (Table III). For each compound the complex pattern of vinyl resonances indicates that more than one tautomeric form of the ligand salt exists in solution (Scheme III). For example, the NMR of the salt of the 14-membered ligand, IIa, is shown in Figure 1a. The hydrogen H_γ is a doublet with a splitting of 20 Hz, whereas the hydrogen H_δ is a set of two doublets each split by 20 Hz. By field dependent NMR and homonuclear spin-decoupling it has been shown that the two vinyl protons H_γ and H_δ are coupled with $J_{H_\delta H_\gamma}$ = 20 Hz. The NMR spectrum of the salt of the 16-membered ligand IIe is identical with that of IIa in the vinyl region, while the salts of the 15-membered ligands IIb-d have more complex NMR spectra due to their increased dissymetry, which is associated with the fact that the saturated rings X and Y are no longer identical. In contrast, the vinyl region of the NMR spectrum for $H_2(Me_4[16]tetraeneN_4)(PF_6)_2$ (III, Figure 1b) has only one sharp singlet. Due to the higher symmetry of the ligand (III), this vinyl pattern is as expected. Since one vinyl hydrogen (H_δ) has been replaced by a methyl group in ligand III, the only vinyl resonance observed is the singlet at δ 5.41. Further, the assignment of the downfield vinyl resonances to H_δ in the NMR of the ligand salt having structures IIa-e is supported by the fact that in the NMR of ligand salt III this vinyl pattern is absent.

Scheme III



An attempt was also made to produce the neutral ligands by deprotonation of their respective salts with 2 equiv of base. Only one neutral ligand was obtained in a pure state, and this was the 14-membered ring derivative, $Me_4[14]tetraeneN_4$ (XIV). Attempts to obtain the neutral 16-membered ring ligands by the same procedure yielded only dark red oils. The 15-membered neutral ligand $Me_2[15]tetraeneN_4$ could be obtained as an impure yellow-brown solid by this route but this product was extremely hydroscopic. In Figure 1c ^1H NMR the ^1H NMR spectrum of $Me_4[14]tetraeneN_4$ (XIV) is shown. Prominent features are broad NH resonances at δ 11.4, doublet vinyl resonances at δ 7.59 and 4.54, and the sharp singlet methyl resonances at δ 1.90. Integration of all peaks gave the NH:vinyl:vinyl:methylene:methyl intensity ratios as 1:1:1:4:3. This ^1H NMR spectrum agrees with the structure assigned to the ligand salt in Scheme III, in which the double bonds are conjugated. Also the highly deshielded NH proton resonance (δ 11.4) is indicative of hydrogen bonding as is shown for XIV.



XIV

Preparation of the Iron(II) Complexes. The general approach to the synthesis of the iron(II) complexes of the new ligands utilized (hexaacetonitrile)iron(II), $[Fe(CH_3CN)_6]^{2+}$, as the anhydrous source of iron(II).[20] To an acetonitrile solution containing the desired PF_6 salt of the li-

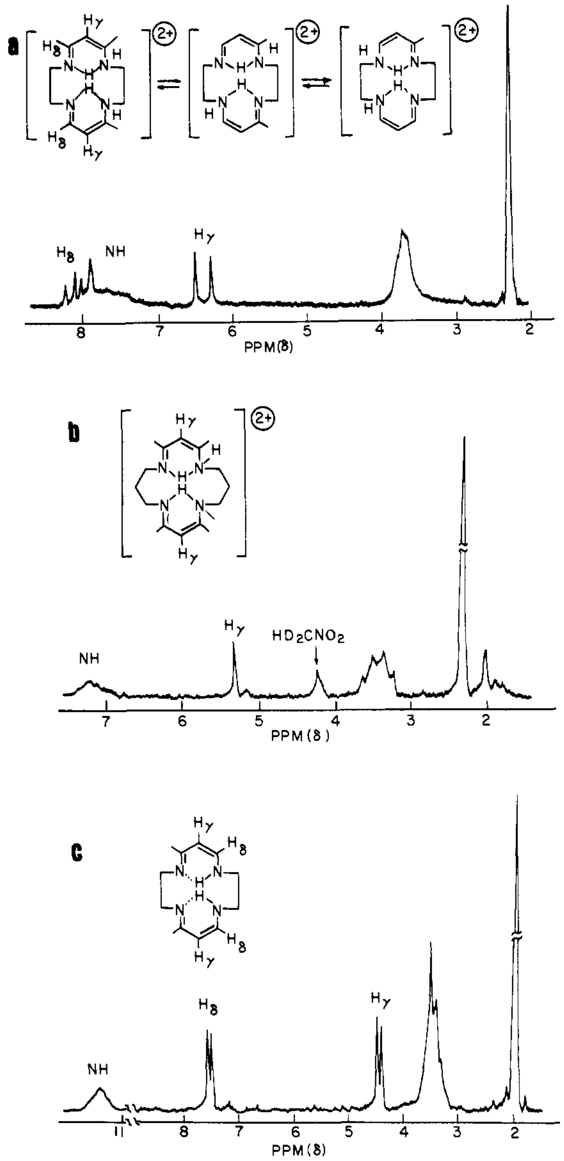


Figure 1. (a) ^1H NMR spectrum of ligand salt Ia, $H_2[Me_2[14]$-4,6,11,13-tetraene$N_4](PF_6)_2$. (b) ^1H NMR spectrum of ligand salt III, $H_2[Me_4[16]$-1,3,9,11-tetraene$N_4](PF_6)_2$. (c) ^1H NMR spectrum of the free ligand XIV, $Me_2[14]$tetraeneN_4.

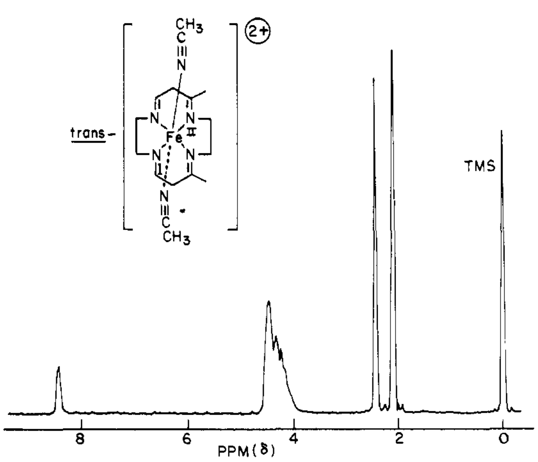


Figure 2. ^1H NMR spectrum of complex IV, $[Fe(Me_2[14]$-1,4,8,11-tetraene$N_4)(NCCH_3)_2](PF_6)_2$.

Table IV. Physical Properties of the New Compounds

Compound	Color	μ_{eff} $(\mu_B)^a$	Λ, cm² ohm⁻¹ M⁻¹ ^{b,c}
IIa	Cream		$MeNO_2$, 189.7
IIb	White		$MeNO_2$, 188.9
IIc	White		$MeNO_2$, 188.3
IId	White		$MeNO_2$, 186.1
IIe	White		$MeNO_2$, 187.6
III	White		$MeNO_2$, 188.4
IV	Pale orange	0.49	MeCN, 315; $MeNO_2$, 189.0
Va	Red	0.50	MeCN, 320
Vb	Red	0.58	MeCN, 306
Vc	Red	0.61	MeCN, 295
Vd	Orange	0.68	MeCN, 305
Ve	Orange	0.60	MeCN, 308
VI	Brown	0.51	Nonelectrolyte
VII	Black	0.70	Insoluble
VIII	Yellow-orange	0.49	$MeNO_2$, 185.2

[a] The magnetic moments at 25 °C. [b] The solvent is given followed by the value of the molar conductance at 25 °C. [c] For typical conductance values see R. L. Dutta, D. W. Meek, and D. H. Busch, *Inorg. Chem.*, **9**, 1215 (1970), and references therein.

gand and the (hexaacetonitrile)iron(II) complex, dropwise addition of 2 equiv of triethylamine gives an immediate color change to deep red. After addition of the base was complete, the solutions were allowed to reflux for 0.5 h. Crystals of the orange-red dicationic complexes could be obtained as their hexafluorophosphate salts by removing acetonitrile until 25 ml remained and then adding 100 ml of hot absolute ethanol and allowing the solution to cool. All preparations of the iron complexes must be carried out under an inert atmosphere and under anhydrous conditions. The complexes are all air sensitive and the yields drop markedly whenever "wet" solvents are used in their preparations. After recrystallization from acetonitrile–ethanol, satisfactory elemental analyses (Table I) were obtained for all the new complexes.

Characterization of the Iron(II) Complexes. All of the iron(II) complexes reported here are low-spin derivatives, having residual moments in the range 0.5–0.7 μ_B (Table IV), values that are consistent with the temperature independent paramagnetism associated with low-spin d^6 derivatives.[21] This feature has been very important to the study of the compounds for it has permitted proton magnetic resonance techniques to be used in the determination of the structures of the complexes. For example, the iron(II) complex, $[Fe(Me_2[14]tetraeneN_4)(NCCH_3)_2](PF_6)_2$ (IV), has the ^1H NMR spectrum shown in Figure 2 (also see Table III). There are two different methyl resonances at δ 2.45 and 2.08 corresponding to the methyl on the macrocyclic ligand and on the coordinated acetonitrile, respectively. A broad unresolved methylene region and a single vinyl proton are the only other features. From the ^1H NMR results and the infrared spectrum (Table II), which shows no N–H stretching bands, this complex has been assigned structure IV having the "bis-β-diimine" macrocyclic ligand and two coordinated acetonitrile molecules. This formulation is consistent with the results of elemental analyses, and the results of molar conductivity measurements which in both nitromethane and acetonitrile give molar conductivities consistent with diunivalent electrolytes (Table IV). The coordination sphere of this complex IV is assumed to have a planar array of the four imine donor groups of the macrocyclic ligand and a trans arrangement of the two coordinated acetonitrile molecules. This is supported by earlier work[22-24] with the low-spin iron(II) of tetraaza 14-membered macrocyclic ligands, where the iron atom is in the plane defined by the donor atoms of the macrocyclic ligand. In addition, this trans formulation is supported by the Mossbauer spectra of complex IV and its derivatives having other axial donor groups (vide infra).

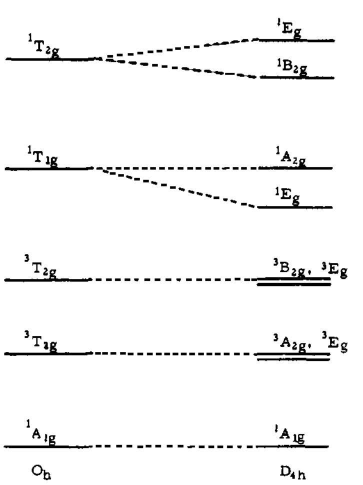


Figure 3. Energy level diagram for low-spin d^6 configuration, showing tetragonal splitting of excited states.

Table V. Electronic Spectra of Iron(II) Complexes

Compound	Solvent	"d–d" bands[a]	Charge transfer[a]
IV	$MeNO_2$	13.7 (46), 21.3 (sh),	Obscured by solvent
	MeCN[b]	13.7 (46), 21.3 (105)	29.7 (9750)
Va	MeCN	None	24.1 (7130), 34.1 (3750)
Vb	MeCN	None	23.7 (8400), 34.1 (3470)
Vc	MeCN	None	23.6 (9140), 34.1 (3470)
Vd	MeCN	None	24.0 (7650), 34.2 (5150)
Ve	MeCN	None	23.8 (10 650), 33.4 (3490)
VI	THF	15.9 (235), 20.2 (sh)	22.8 (2710), 30.9 (3910), 35.7 (4320)
VIII	$MeNO_2$	12.42 (580), 20.0 (493)	Obscured by solvent

[a] Peak maxima given in kK, followed by the extinction coefficient in parentheses. [b] 1% HSO_3CF_3 added to prevent ionization.

Table VI. Ligand Field Parameters[a] Calculated from Observed Electronic Spectra

Complex	Axial ligand	Dq^{xy}	Dq^z	D_t
IV	CH_3CN	2460	939	869
VI	NCS^-	2350	1490	491
VIII	Pyridine	2330	814	866

[a] Energies in wave numbers, cm^{-1}.

To provide chemical evidence for intact coordinated acetonitrile molecules in complex IV, a series of low-spin iron(II) derivatives having SCN^-, NO_2^-, and pyridine as axial donors was prepared by metathesis of the acetonitrile. These derivatives are also low-spin iron(II) complexes and, from their infrared spectra, the ligand has remained in the bis-β-diimine form. The bispyridine complex VIII was found to be a biunivalent electrolyte in nitromethane, as expected, and the bisthiocyanato complex is a nonelectrolyte. The black, crystalline bisnitro complex (VII) is too insoluble in all common solvents to permit solution measurements. In addition, solid-state mull spectra of $[Fe(Me_2[14]tetraeneN_4)(NO_2)_2]$ (VII) show no bands assignable to "d–d" transitions since intense charge transfer bands obscure the visible region. The electronic spectra of these complexes (IV, VI, and VIII, Table V) are of interest, for they each have two bands with intensities consistent with Laport-forbidden spin-allowed electronic transitions. Assuming that the iron(II) chromophore is in a tetragonal ligand field which is approximated by D_{4h} symmetry, three different interpretations can be made for assigning the two observed bands of each complex. The transitions (see Figure 3) can be assigned to (1) $^1A_{1g} \rightarrow {}^3B_{2g}, {}^3E_g({}^3T_{2g})$, and $^1A_{1g} \rightarrow {}^1E_g, {}^1A_{2g}({}^1T_{1g})$, (2) $^1A_{1g} \rightarrow {}^1E_g, {}^1A_{2g}({}^1T_{1g})$, and $^1A_{1g} \rightarrow {}^1B_{2g}, {}^1E_g({}^1T_{2g})$, or (3) $^1A_{1g} \rightarrow {}^1E_g({}^1T_{1g})$ and $^1A_{1g} \rightarrow {}^1A_{2g}({}^1T_{1g})$. The first assignment requires the lower energy band to be spin-forbidden, but, since the observed extinction coefficients are much too large to be of spin-forbidden origin, this assignment will not be considered further. The second assignment requires that the site symmetry about the iron(II) chromophore be pseudo-octahedral, since the observed bands show no splitting. Application of the equations given by Wentworth and Piper[26] for the energies of the two absorption bands in O_h symmetry

$$^1A_{1g} \rightarrow {}^1T_{1g} = 10Dq - C \tag{1}$$

$$^1A_{1g} \rightarrow {}^1T_{2g} = 10Dq + 16B - C \tag{2}$$

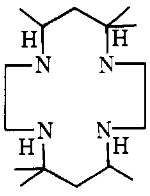
and an assumption for the value of the Racah parameter C equal to 3300 ± 300 cm^{-1},[27] allows the calculation of an approximate value for Dq^{xy} of the macrocyclic ligand. The value obtained for the acetonitrile complex is approximately 1700 cm^{-1}. This value is nearly 400 cm^{-1} less than that found for the fully reduced 14-membered tetraaza macrocycle shown in structure XV.[22] This result is contrary to expectations, since the presence of imine groups in the macrocyclic ligand has been observed to increase the Dq^{xy}.[22] The third assignment requires that the two observed bands arise from transitions from the ground state to the two states arising from the tetragonally split $^1T_{1g}$ excited state. The energies of the two absorptions bands to a first-order approximation as given by Wentworth and Piper[26] are

$$^1A_{1g} \rightarrow {}^1A_{2g} = 10Dq - C \tag{3}$$

$$^1A_{1g} \rightarrow {}^1E_g = 10Dq - \tfrac{35}{4}D_t - C \tag{4}$$

$$D_t(D_{4h}) = \tfrac{4}{7}(Dq^{xy} - Dq^z) \tag{5}$$

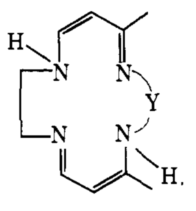
Assuming $C \sim 3300 \pm 300\ cm^{-1}$ [27] and noting that Dq^{xy} depends only on the inplane ligand field, we obtain Dq^{xy} for the bis-β-diimine 14-membered ligand using eq 3 above. The results for Dq^{xy}, Dq^z, and D_t are shown in Table VI. The value for $Dq^{xy} \simeq 2400\ cm^{-1}$ is in the range expected for the tetraimine macrocyclic ligand.[23] On this basis, the two observed bands in these complexes are assigned to the transitions: $^1A_{1g} \rightarrow {}^1E_g$ and $^1A_{1g} \rightarrow {}^1A_{2g}$.



XV

The remaining dicationic iron(II) complexes Va–e, prepared from salts of the 15-membered and 16-membered ligands, revealed unusual chemical and physical properties when characterized by the standard physical and chemical methods. Most striking among the physical properties were the appearance of a sharp absorption in the infrared spectra, that appeared to be an N–H stretching vibration at 3310 cm^{-1}, and their proton magnetic resonance spectra which were much more complex than that observed for $[Fe(Me_2[14]tetraeneN_4)(NCCH_3)_2]^{2+}$ (Figure 4). Elemental analyses show that the complexes uniformly have the composition of bis(acetonitrile) solvates, i.e., $Fe(MAC)(PF_6)_2 \cdot 2CH_3CN$ in analogy to the 14-membered derivative IV. Molar conductivities, based on a molecular weight calculated from the above formulation, were in the range normally found for biunivalent electrolytes. (Table

III). While the spectral difficulties could be partially explained away by assuming the tautomeric structure XVI,



XVI

for the macrocycle, several chemical observations still lacked explanation. The 14-membered ring derivative [Fe(Me$_2$[14]tetraeneN$_4$)]$^{2+}$ can be deprotonated with relatively mild bases, i.e., NEt$_3$, to give the complex of the planar dianionic ligand (subject of a later report). In contrast, Va–e are much more stable toward base and can be deprotonated only with such strong bases as alkoxide. In addition, attempts to replace the "coordinated acetonitriles" in these complexes by metatheses resulted in no reaction, a behavior that again contrasted strongly with that observed for [Fe(Me$_2$[14]tetraeneN$_4$)(NCCH$_3$)$_2$]$^{2+}$ (IV). To determine the correct structures of these complexes, an x-ray crystallographic study was performed on the 16-membered derivative (Vd),[11] revealing an unusual structure and an interesting ligand reaction as well. The crystallographic results, which are discussed in greater detail in a separate paper,[11] show that acetonitrile molecules add electrophilically to the apical (γ)-carbons of the unsaturated six-membered ring of the ligand producing the complex of a unique cis sexadentate, hexaene ligand (structure Va–e).

The ^{1}H NMR spectra of all five of the hexaene complexes V have several striking features in common (Table III, Figure 4). The methyl protons of the parent macrocycle and those of the iminoethyl substituents are accidentally degenerate; a sharp multiplet occurs near δ 5.8; a vinyl pattern is observed near δ 8.7 for most of these substances but is absent from the spectrum of *cis*-[Fe(Me$_4$IE$_2$[16]tetraeneN$_4$)] (Ve) due to methyl substitution, and the broad NH pattern near δ 11.0 occurs in all cases. Due to the similarities in both the ir and ^{1}H NMR spectra of these complexes (Va–e), it is assumed that all have the same basic structure as that found for Vd, namely, the complex of the cis sexadentate hexaene ligand. Although the gross features of these ^{1}H NMR in the downfield region are all identical, a few anomalies are apparent (see Figure 4). The NH resonance for the 16-membered ring derivatives consists of one broad absorption; whereas, for the 15-membered ring derivatives two different NH absorptions occur. The most likely explanation for the magnetic nonequivalence of the two hydrogens on the nitrogens of the 15-membered ring derivatives is that each individual NH proton is either much closer to a five-membered or a six-membered saturated chelate ring. Thus, the chemical and magnetic environment of each hydrogen would be different, but in the 16-membered derivatives no difference would be expected since the saturated rings are identical. In the ^{1}H NMR spectra of the [Fe(Me$_2$IE$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$ (Vd), fine structure appears in the region of the vinyl proton H$_\delta$ (see Figure 4a). The source of this fine structure is not understood, especially since the 15-membered ring derivatives show no unexpected fine structure (Figure 4c). It could be possible that coupling with an equatorial methylene proton on the α-carbon of the adjacent saturated ring gives rise to additional splitting, but the integrated intensities of the three peaks do not support this.

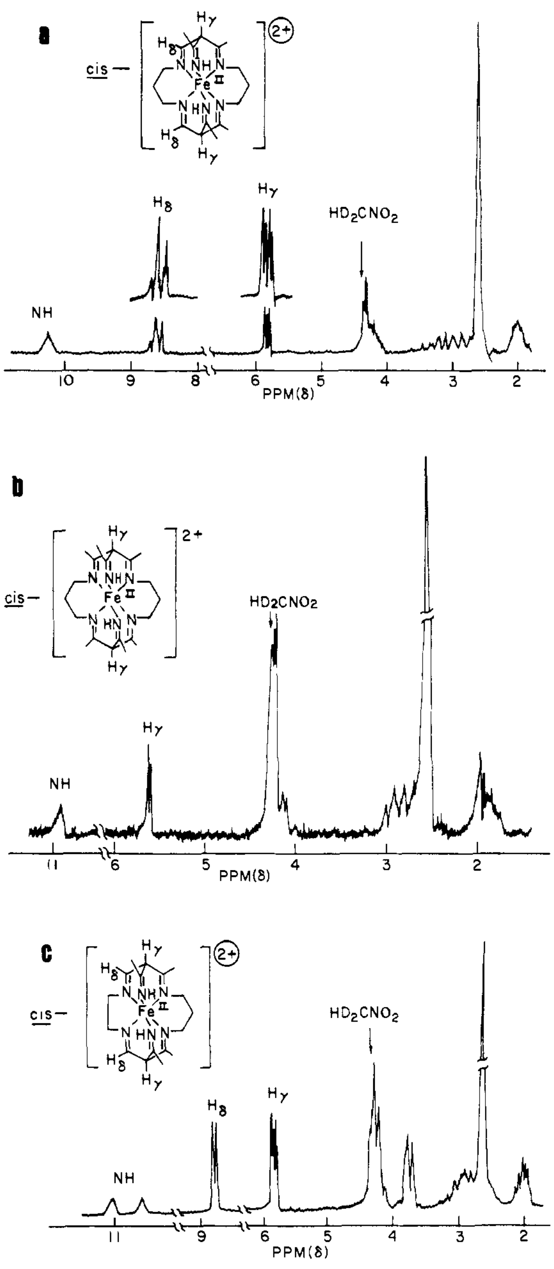


Figure 4. (a) ^{1}H NMR spectrum of complex Vd, *cis*-[Fe(Me$_2$IE$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$. (b) ^{1}H NMR spectrum of complex Ve, *cis*-[Fe(Me$_4$IE$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$. (c) ^{1}H NMR spectrum of complex Va, *cis*-[Fe(Me$_2$IE$_2$[15]tetraeneN$_4$)](PF$_6$)$_2$.

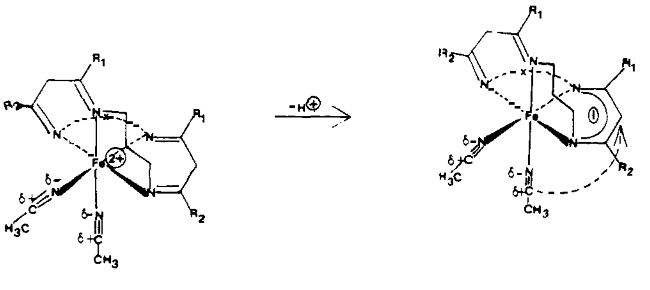
To correctly assign the resonances in the ^{1}H NMR spectra of the hexaene complexes (Va–e) homonuclear spin-decoupling techniques were used. In the following discussion of the spin-decoupling results only the ^{1}H NMR spectra of the two 16-membered ring derivatives (Vd and Ve) will be considered. The spin-decoupling results for the three 15-membered ring complexes (Va–c) are identical with those observed for [Fe(Me$_2$IE$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$ (Vd).

When the spectrum of [Fe(Me$_2$IE$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$ (Vd, Figure 4a) was run while simultaneously irradiating at the frequency of the vinyl proton H$_\delta$, the only change in the spectrum was that the signal for H$_\gamma$ collapsed to a doublet with a splitting of 1 Hz. The H$_\gamma$ resonance then appeared identical with that of H$_\gamma$ in the ^{1}H NMR spectrum of [Fe(Me$_4$IE$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$ (Ve, Figure 4b). When the spectrum of Vd was run while simultaneously irradiating at the frequency of H$_\gamma$, the two larger peaks of the H$_\delta$ signal collapsed to a sharp singlet but fine structure still remained. When the spectrum was run while irradiating at the frequency of the NH, the only change was that the H$_\gamma$ signal collapsed to a doublet of 5 Hz splitting.

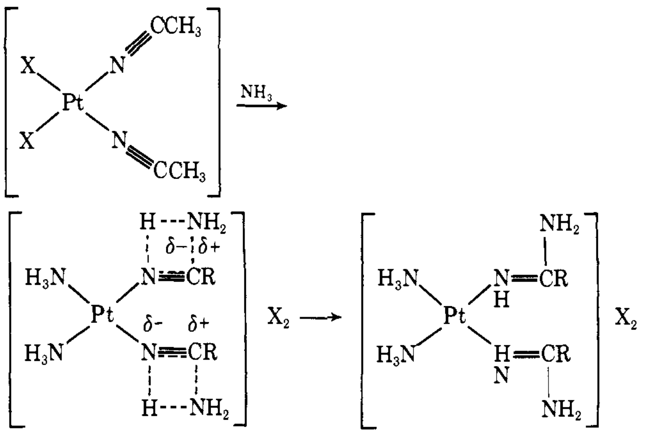
From these results and from a comparison of the ^{1}H NMR of complexes Vd and Ve, the following assignments have been made for complexes Va–d: (1) the resonances near δ 5.7 are assigned to the bridgehead proton H_γ, which is coupled to the vinyl proton H_δ, $J_{H_\gamma H_\delta}$ = 5 Hz, and further coupled with the NH proton four bonds away, J_{NHH_γ} = 1 Hz. (2) The resonance near δ 8.7 is assigned to the vinyl proton H_δ, which is coupled to the bridgehead proton H_γ. In the spectrum of Ve no corresponding vinyl signal is observed; this is consistent with expectations since the vinyl proton has been replaced by a methyl group, but the resonance due to the bridgehead proton H_γ at δ 5.70 is split into a doublet. Homonuclear spin decoupling showed that this splitting is again due to coupling between H_γ and the NH protons, where J_{NHH_γ} = 1 Hz.

The electronic spectra of the hexaene complexes (Va–e) also support the conclusion that the structures of all five complexes correspond to cis sexadentate hexaene derivatives. The electronic spectrum, taken in acetonitrile solution, of each complex has two bands (see Table V). The similarity between the band positions and extinction coefficients among the five complexes is striking and suggests that the iron(II) chromophore is virtually identical for all the complexes. It is also of interest to compare these electronic spectra to those observed for other hexaene complexes, including the tris-α-diimine clathrochelate complexes. The electronic spectra of the $[Fe(DMG)_3(BX)_2]$[13] complexes consist of two bands, ~22.6 kK (18 000) and 27–30 kK (2000), assigned to M → π* transitions. Also iron(II) tris(diimine) complexes are characterized by an intense band in the visible region assigned to M → π* transitions; for example, $[Fe(bpy)_3]^{2+}$, ν_{max} = 19.1 kK and $[Fe(o\text{-phen})_3]^{2+}$, ν_{max} = 19.6 kK.[28] The two bands observed for the hexaene ligands reported here are also assigned to M → π* transitions by analogy to the clathrochelate complexes.[13] These cis hexaene ligands consist of a tris-β-diimine donor set and, as a result, their iron(II) complexes would be expected to show M → π* transitions at higher energy than those observed for tris-α-diimine complexes. This is expected since the ligand π* imine orbitals will be at higher energy for the isolated imines than the π* orbitals in the conjugated α-diimine donor set. This is indeed the trend observed. The hexaene ligand iron(II) complexes reported here also have two charge transfer bands, 22.8–24.1 kK (7000–10 000) and 33.4–34.2 kK (~3500); these bands occur at higher energies compared with those observed for the clathrochelate and tris-α-diimine complexes.

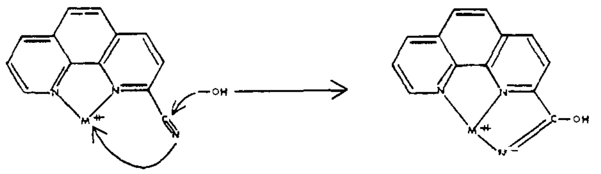
Scheme IV



The formation of the cis sexadentate, hexaene complexes (V) is remarkable in view of the mild conditions employed and the general inertness of nitrile functions toward nucleophilic addition, although a few metal ion promoted nucleophilic additions have been reported in the literature.[29–33] A relevant example of such metal ion promoted nucleophilic addition is the formation of the "anomalous" amine-nitrile complexes of bivalent platinum.[32,33] The reaction of nitrile platinum(II) compounds with ammonia and other amines has been found to result in the formation of amidines; for example:



Another interesting example is provided by the results of Breslow, Fairweather, and Keana,[31] who studied the kinetics of the hydrolysis of 2-cyano-1,10-phenanthroline. They found that the hydrolysis reaction rate is accelerated by as much as 10^9 by metal ions, i.e., Cu^{2+}, Ni^{2+}, and Zn^{2+}. These results were interpreted in terms of the following mechanism:



In view of these previously reported examples of metal ion promotion of the electrophilicity of nitriles, we propose certain general aspects of the mechanism for the formation of the cis hexaene ligands. The process is assumed to require prior coordination of both the macrocycle and the acetonitrile molecule to a single iron(II) center. The ionization of a proton from the apical (γ)-carbon of one of the β-diimine linkages produces a nucleophile adjacent to the coordinated and electrophilically activated acetonitrile (Scheme IV). Intramolecular condensation then yields one of the new linkages found in this unusual class of compounds.

Mossbauer Spectra of the Iron(II) Derivatives. In Table VII are listed the isomer shift values (δ) and the quadrupolar splitting values (ΔE_q) for the new complexes. The isomer shifts for all the new iron(II) complexes are in the range normally found for a low-spin iron(II) derivative. This agrees with the results of magnetic susceptibility measurements for these compounds. In a recent report from these laboratories,[34] the center shift (δ) and quadrupolar splitting (ΔE_q) for the ligating groups involved in six-coordinate low-spin macrocyclic complexes were separated into additive quantities, the partial center shift (pcs) and partial quadrupole splitting (pqs).[34] From these additive quantities (pcs and pqs), assigned to each ligating group, the total isomer shift or quadrupolar splitting for any combination of ligands bonded to iron(II) may be calculated. In Table VIII are listed a few selected ligand values from ref 34 for partial center shifts and partial quadrupole splittings. The calculated isomer shift value is obtained by summing the individual pcs values for the contributing ligands. The form of the expression used for calculating quadrupolar splitting from pqs values[35] is shown below for two cases:

$$trans\text{-}FeA_2B_4,\ \Delta E_q = 4[pqs_A] - 4[pqs_B]$$

$$cis\text{-}FeA_2B_4,\ \Delta E_q = -2[pqs_A] + 2[pqs_B]$$

The magnitude and sign of the quadrupole splitting in the two cases differ by the ratio trans:cis = 2:−1.

Table VII. Mossbauer Parameters for the Iron Complexes

Compound	$\delta^{a,b}$ (mm/s)	ΔE_q (mm/s)	% effect	Calcd δ (mm/s)^e	Calcd ΔE_q (mm/s)
IV	0.59 (0.43)	1.58	1.01	0.426	1.48,^{c} -0.74^d
Va	0.54 (0.38)	0.85	1.03	0.36	$0.00^{c,d}$
Vb	0.52 (0.36)	0.71	1.60	0.36	$0.00^{c,d}$
Vc	0.52 (0.36)	0.67	3.16	0.36	$0.00^{c,d}$
Vd	0.52 (0.36)	0.26	2.30	0.36	$0.00^{c,d}$
Ve	0.50 (0.34)	0.30	2.90	0.36	$0.00^{c,d}$
VI	0.58 (0.42)	1.41	4.05	0.44	1.20,^{c} -0.60^d
VII	0.45 (0.29)	1.66	1.73	0.37	1.08,^{c} -0.54^d
VIII	0.56 (0.40)	1.75	3.14	0.38	1.28,^{c} -0.64^d

^{a} Values with respect to sodium nitroprusside. ^{b} Values in parentheses with respect to stainless steel. ^{c} Calculated for *trans*-$\mathrm{FeA_2B_4}$. ^{d} Calculated for *cis*-$\mathrm{FeA_2B_4}$. ^{e} With respect to stainless steel.

Table VIII. Partial Center Shifts and Partial Quadrupole Shifts for Some Ligands Bound to Low-Spin Fe(II)

Ligand	pcs (mm/s)$^{a-c}$	pqs (mm/s)^{b,c}
$\mathrm{SCN^-}$	0.100	-0.49
$\mathrm{CH_3CN}$	0.093	-0.42
$\mathrm{NO_2^-}$	0.065	-0.52
Isolated, N=C^b	0.060	-0.79
Pyridine	0.07^c	-0.47^d

^{a} pcs values are relative to stainless steel. ^{b} pcs and pqs values are per isolated imine of the cyclic ligand. ^{c} Values from G. M. Bancroft and R. H. Platt, *Adv. Inorg. Chem. Radiochem.*, **15**, 173 ff (1972).

Table VII also lists the calculated isomer shifts and quadrupolar splittings. For the 14-membered ring derivatives $[\mathrm{Fe(Me_2[14]tetraeneN_4)X_2}]^{n+}$, X = $\mathrm{NCCH_3}$, NCS, and $\mathrm{NC_5H_5}$, respectively (IV, VI, and VIII), the calculated isomer shift values agree very well with those found; whereas, for the bisnitro derivative (VII), the agreement is not as good. For all four complexes the calculated quadrupole splittings for both the *trans*- and *cis*-$\mathrm{FeA_2B_4}$ cases are listed in Table VII. Comparison of the magnitude of the observed splitting for the complexes IV, VI, VII, and VIII with the calculated values shows that much better agreement between absolute value of calculated ΔE_q and observed ΔE_q is obtained if the complexes are assumed to be trans. This supports the earlier assumption that these complexes have the trans configuration.

A comparison of the observed Mossbauer parameters for the cis hexaene complexes V with their calculated values reveals some interesting correlations. The calculated isomer shift values, based on the sum of the contributions from six isolated imine donor groups,[34] are virtually identical with those observed for the cis hexaene complexes regardless of ring size. This observation is a bit surprising since the partial center shift value obtained from ref 34 is based on trans complexes with 14-membered macrocyclic rings. This excellent agreement lends support to the assumption that the pcs values are additive for the individual ligands on low-spin iron(II). For complex IV, $[\mathrm{Fe(Me_2[14]tetraeneN_4)(NCCH_3)_2](PF_6)_2}$, the observed and calculated isomer shift values are identical. This result and the results observed for the cis hexaene complexes further indicate that the isomer shift can be divided into individual contributions from each imine donor (or other ligand) regardless of geometrical considerations. The observed quadrupolar splittings do not agree with the predicted value of zero for the cis hexaene complexes. This is easily rationalized since each complex is distorted from cubic symmetry by its extensive chelate framework and a nonzero electric field gradient is expected. The magnitude of the splitting for the cis hexaene complexes is observed to be smaller for the 16-membered ring derivatives than for the 15-membered ring derivatives. This observation is consistent with the expectation that the larger rings may be less strained by the imposed cis coordination, resulting in less distortion of the coordination polyhedron from cubic symmetry.

It also is of interest to compare the Mossbauer parameters of these cis hexaene complexes to those reported[13] for a series of trisglyoximato, clathrochelate iron(II) complexes. The clathrochelate complexes have isomer shift values (0.32–0.42 relative to SNP) somewhat lower than those observed for the cis hexaene complexes. This difference is expected since these tris-α-diimine ligands should exert stronger ligand fields; i.e., they are both better σ donors and π acceptors. The quadrupole splitting values reported for the clathrochelates were in the range 0.64–1.05 mm/s. The values are higher than that observed for $[\mathrm{Fe(Me_nIE_2[16]tetraeneN_4)}]^{2+}$ but those for $[\mathrm{Fe(Me_nIE_2[15]tetraeneN_4)}]^{2+}$ lie in this range. The large quadrupole splittings observed for the clathrochelates were attributed[13] to a significant distortion from O_h symmetry (these complexes have a significant twist angle of approximately 17°). Thus, since the cis hexaene complexes derived from 15-membered rings have quadrupolar splittings significantly larger than those observed for the 16-membered ring derivatives and since they are in the range observed for the clathrochelates, it is likely that the structures of the 15-membered ring derivatives are also distorted by a significantly large twist angle.

The synthesis of the new tetraaza, tetraene macrocyclic ligands, devoid of functional substituents can be accomplished routinely in large quantity and good yield. The reactions of these ligands with hexaacetonitrileiron(II) have led to the isolation and characterization of a novel series of iron(II) complexes. One aspect of this reaction that has not yet been discussed is the dramatic effect of the macrocyclic ligand ring size on the course of the reaction. As has been noted, the 14-membered macrocycle does not undergo attack from acetonitrile. Our rationale for this behavior is based on the study of models of the complexes. These models indicate that for the 14-membered ligand case the cis hexaene ligand could not form due to strain; i.e., no acetonitrile attack would be expected since the resultant structure would be very strained. Models of the complexes of both the 15- and 16-membered macrocycles showed no strain, indicating that the cis-hexaene ligands could indeed form.

The sexadentate hexaeneiron(II) complexes are very stable in oxygen-free media, including aqueous and acidic media; although as mentioned earlier, the presence of water during their synthesis does decrease the yield of the cis hexaene complex. These complexes are stable in air in the solid state for periods of up to several hours, but they do react in the air when in solution. When solutions of these complexes are exposed to the air, highly colored solutions are observed to form within minutes. An electrochemical study of these complexes was performed,[36] and it was found that only one oxidation was present, and that was reversible. This oxidation process was assigned to the $\mathrm{Fe^{II}/Fe^{III}}$ couple and its potential was found to be essentially constant for these cis hexaene complexes regardless of ring size and also quite small (0.63–0.66 V vs. SCE) when compared to iron complexes with other highly unsaturated and uncharged macrocycles.[37] These observations support the contention that these sexadentate ligands do not accept dπ electron density into their ligand imine π^* orbitals as extensively as do other imine donor arrangements, noteably the α-diimines. This is reflected in their ease of oxidation and in their electronic spectra which show the M $\rightarrow$ π^* transitions at higher energy than is observed for tris-α-diimine derivatives.

As mentioned earlier, all of the iron(II) derivatives reported here are base sensitive, although the hexaene derivatives can be deprotonated only under severe conditions, i.e., alkoxides. The electrophilic reactions of anionic chelate rings produced by deprotonation of these iron(II) complexes are the subject of on-going studies.

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