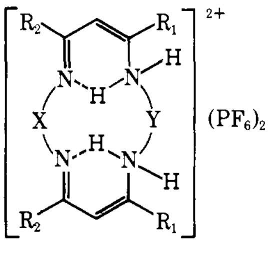
Synthesis and Characterization of Square-Planar Iron(II) Complexes with Dianionic Tetraaza Macrocyclic Ligands and Their Novel Derivatives

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

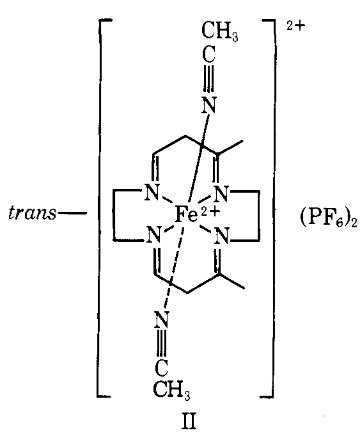
Contribution from the Evans Chemical Laboratory, The Ohio State University, Columbus, Ohio 43210, and the Savannah River Laboratory, E. I. duPont de Nemours and Company, Aiken, South Carolina 29801. *Received June 11, 1976*

Abstract: A series of square-planar iron(II) complexes has been prepared with synthetic dianionic unsaturated tetraaza macrocyclic ligands that are devoid of functional substituents and vary in ring size from 14 to 16 members. The temperature dependence of the magnetic susceptibility confirms the unusual intermediate spin ($S = 1$) ground state for these square-planar derivatives. In addition, dicationic iron(II) complexes of these ligands have been prepared by protonation of the neutral square-planar complexes. Two types of protonation products have been obtained, including the complexes of tetradentate bis-β-diimine macrocyclic ligands and two novel derivatives in which acetonitrile molecules have added to the apical γ-carbon of the charged six-membered chelate rings. Ring size effects appear most dramatically in the reactions of the planar complexes with acetonitrile, in which case ring size determines the nature of the product. However, it is also evident both in electronic and Mössbauer spectral data that ring size exerts a great influence on ligand field strengths. The six-coordinate complexes Fe(macrocycle)(pyridine)$_2{}^{2+}$ containing 14- and 15-membered ring macrocyclic ligands have low-spin ground states, while a 16-membered ring derivative exhibits a spin-state equilibrium.

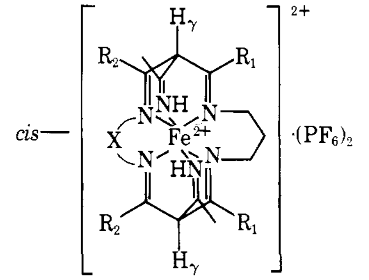
We have recently reported[2] the synthesis and characterization of a series of 14-, 15-, and 16-membered tetraaza, tetraene macrocyclic ligands (Ia–e) that are devoid of functional substituents. The synthesis of dicationic iron(II) complexes with these ligands was also reported and it was shown that, for the 14-membered ligand (Ia), the bis-β-diimine complex (II) (structure II) is obtained when the neutral ligand is allowed to react with hexaacetonitrile iron(II) in acetonitrile solution. Application of the same synthetic procedure with the larger ligands (Ib–e) produces six-coordinate dipositive complexes that have the novel structure III. This assignment was made possible by a definitive x-ray crystallographic study on one compound, accompanied by the use of nuclear magnetic resonance and infrared spectra techniques to show the generality of the structure. The novel *cis*-hexaene ligands were presumed to form by the electrophilic attack of a coordinated acetonitrile at the γ-carbon of a coordinated and partially ionized macrocyclic ligand (Scheme I). Although examples of electrophilically activated nitriles are rare, this type of reaction scheme does have precedent in the metal-catalyzed hydrolysis of phenanthroline nitrile[3] and the formation of platinum(II) amidine complexes by nucleophilic attack of ammonia[4] on the corresponding platinum(II) nitrile complex.



Ia, $X = Y = -(CH_2)_2-$; $R_1 = CH_3$; $R_2 = H$
b, $X = -(CH_2)_2-$; $Y = -(CH_2)_3-$; $R_1 = CH_3$; $R_2 = H$
c, $X = -(C(CH_3)_2)_2-$; $Y = -(CH_2)_3-$; $R_1 = CH_3$; $R_2 = H$
d, $X = Y = -(CH_2)_3-$; $R_1 = CH_3$; $R_2 = H$
e, $X = Y = -(CH_2)_3-$; $R_1 = R_2 = CH_3$
f, $X = Y = -(CH_2)_2-$; $R_1 = R_2 = CH_3$



II

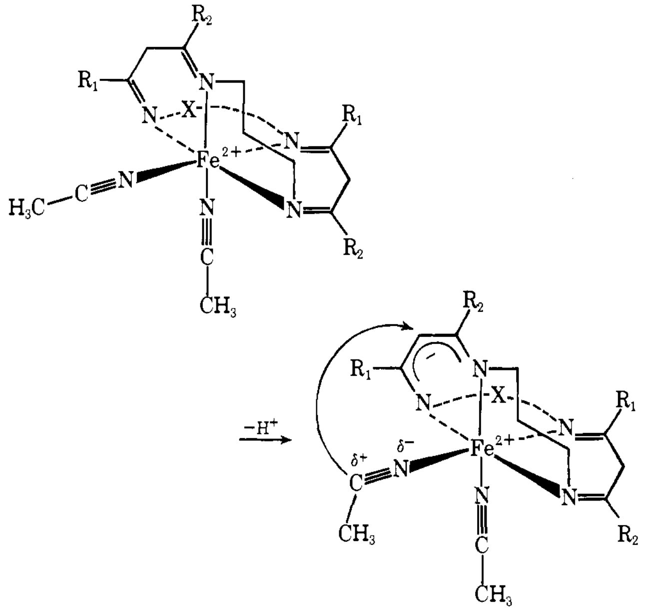


IIIa, $X = -(CH_2)_2-$; $R_1 = CH_3$; $R_2 = H_\delta$
b, $X = -(C(CH_3)_2)_2-$; $R_1 = CH_3$; $R_2 = H_\delta$
c, $X = -(CH_2)_3-$; $R_1 = CH_3$; $R_2 = H_\delta$
d, $X = -(CH_2)_3-$; $R_1 = R_2 = CH_3$

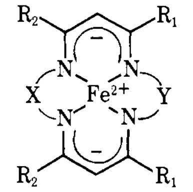
This report is primarily concerned with the deprotonation products of the iron(II) complexes having structures II and III, and the complexes that form when the products of that reaction are again protonated. Two protons can be removed from the complexes of structures II and III to form the neutral iron(II) complexes [Fe(Me$_n$[Z]tetraenatoN$_4$)], IV, which have been characterized as neutral, four-coordinate square-planar iron(II) species, a rare coordination geometry for iron(II).[5] This square-planar geometry has been confirmed by the preliminary results of an x-ray crystallographic investigation on complex [Fe(Me$_6$[15]tetraenatoN$_4$)] (IVc).[2c] In addition, the square-planar derivatives exhibit a magnetic behavior which indicates that they exist in an intermediate spin ($S = 1$) ground state. Magnetic studies and Mössbauer parameters are presented and discussed for this unusual class of compounds.

The square-planar derivatives have also been reprotonated

Scheme I

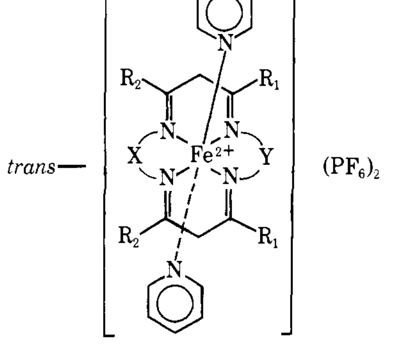


in the presence of the neutral monodentate donor molecules, acetonitrile and pyridine, to yield dipositive six-coordinate



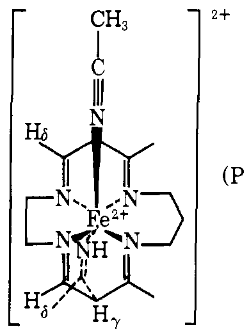
IVa, X = Y = $-(CH_2)_2-$; $R_1 = CH_3$; $R_2 = H$
b, X = $-(CH_2)_2$, Y = $-(CH_2)_3-$; $R_1 = CH_3$; $R_2 = H$
c, X = $-(C(CH_3)_2)_2$, Y = $-(CH_2)_3-$; $R_1 = CH_3$; $R_2 = H$
d, X = Y = $-(CH_2)_3-$; $R_1 = CH_3$; $R_2 = H$
e, X = Y = $-(CH_2)_3-$; $R_1 = R_2 = CH_3$
f, X = Y = $-(CH_2)_2-$; $R_1 = R_2 = CH_3$

iron(II) complexes. In the case of pyridine the *trans*-bis(pyridine)bis(β-diimine) complexes V were obtained. In the case

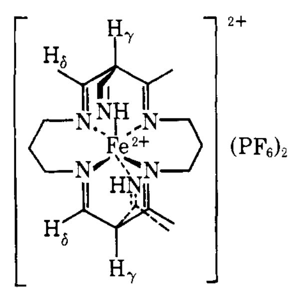


Va, X = Y = $-(CH_2)_2-$; $R_1 = CH_3$; $R_2 = H$
b, X = $-(CH_2)_2-$; Y = $-(CH_2)_3-$; $R_1 = CH_3$; $R_2 = H$
c, X = Y = $-(CH_2)_3-$; $R_1 = CH_3$; $R_2 = H$
d, X = Y = $-(CH_2)_3-$; $R_1 = R_2 = CH_3$
e, X = Y = $-(CH_2)_2-$; $R_1 = R_2 = CH_3$

of the acetonitrile solution, it was found that protonation of the complex with the 14-membered ring (IVa) regenerated the simple adduct of structure II. However, for the 15- and 16-membered ring derivatives (IVb and IVd), the products of the protonation reaction exhibited unusual properties. The protonation of the complex of the 15-membered ring (IVb) in the presence of acetonitrile gives the *trans*-acetonitrilepentaene derivative (VI), and protonation of the complex IVd gives the complex of the *trans*-hexaene ligand (VII). Thus, acetonitrile has again been observed to electrophilically attack the γ-carbon of a charge-delocalized six-membered chelate ring. However, the structures of the product are determined by the fact that the macrocycle is previously coordinated in a planar fashion. The structural assignments for the complexes given in structures VI and VII have been made on the basis of spectroscopic results. Particular attention has also been given to ring size effects, to the Mössbauer parameters, and to electronic spectral parameters.



VI



VII

Experimental Section

Physical Measurements. ^{57}Fe Mössbauer spectra were obtained with a conventional constant acceleration spectrometer operated in the 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 quadrupolar splittings were determined by inspection with an accuracy of ±0.01 mm/s. Samples of air-sensitive compounds were suitably encapsulated in an argon atmosphere by packing the compound into an aluminum die between two sheets of polyester tape.

The NMR spectra were obtained on Varian A-60 and HA-100 spectrometers. The solvents used for ionic compounds were CD_3NO_2 and CD_3CN. In all cases chemical shifts were calculated relative to tetramethylsilane (Me_4Si). The samples of air-sensitive compounds were prepared in a glove box and were run immediately after their removal from the inert atmosphere.

Visible and near-infrared spectra were obtained on a Cary Model 14-R recording spectrophotometer. Air-sensitive samples were prepared in an inert atmosphere and placed in quartz cells tightly sealed with Teflon stoppers. The spectra were run immediately after removal from the inert atmosphere and were repeated after exposing the sample to the air. For determination of extinction coefficients, stoppered volumetric flasks were weighed, then transferred to the glove box where an approximate weight of the compound was placed in the flask. The stoppered flask and contents were removed from the glove box, reweighed, and returned to the glove box for solution preparation. Solid state spectra were obtained by use of mulls prepared in the glove box using filter paper impregnated with Halocarbon 25-85 grease (Halocarbon Products Corp.). The filter paper was pressed between glass slides before mounting in the spectrophotometer. The liquid N_2 mull spectra were obtained by means of a Dewar flask having quartz windows and filled with liquid nitrogen; the sealed mull was lowered into the liquid, and the spectrum was recorded by passing the light beam through the Dewar, liquid, and mull.

Infrared spectra were obtained with a Perkin-Elmer Model 337 recording spectrometer using Nujol mulls. Mulls of air-sensitive compounds were prepared in the glove box, and their spectra were recorded immediately after removal from the glove box.

Solid-state magnetic susceptibilities were measured by the Faraday method.[6] Diamagnetic corrections for ligands and counterions were made using Pascal's constants.[7] Measurements were made at room temperature under a pressure of 35 mm of helium gas. Variable-temperature (2–100 K) measurements of susceptibilities were made by the use of a vibrating sample magnetometer[8] operating at a field strength of 10 kG and calibrated vs. nickel metal. This method permits the facile measurement of the low-temperature susceptibility of very air-sensitive compounds. The samples are packed into a preweighed plastic holder in an inert atmosphere drybox, then removed and reweighed. In addition, variable-temperature susceptibilities were measured by the Faraday method in the temperature range 90–350 K. Solution susceptibilities were measured by the Evans method with a Varian A-60 NMR spectrometer.

Conductance measurements were made with an Industrial Instruments Model RC 16B conductivity bridge. The conductance measurements were made at 25 °C at 1000 Hz on 10^{-3} M solutions in the drybox. Analyses were performed by Galbraith Laboratories. Mass spectra were obtained using an MS-9 spectrometer at an ionizing potential of 70 eV.

Materials. Acetonitrile, diethyl ether, and ethanol were distilled from calcium hydride, and pyridine was stored over KOH and then distilled before use. Spectral grade nitromethane was purified by literature methods.[9] All distillations were carried out under nitrogen and all syntheses of the iron complexes were carried out under nitrogen in a Vacuum Atmospheres controlled atmosphere chamber.

5,14-Dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenatoiron(II), [Fe(Me$_2$[14]tetraenato(2−)N$_4$)] (IVa). Method A. Ligand salt Ia[2c] (10.3 g, 0.02 mol) and 3.48 g (0.02 mol) of anhydrous ferrous acetate are stirred vigorously in 100 ml of refluxing absolute ethanol. To this slurry is added 4 equiv of sodium ethoxide in ethanol, and the solution is heated and stirred for an additional 5 min. The solvent is then removed under a vacuum, and to the resultant solid red mass 100 ml of boiling benzene is added with stirring. The resultant benzene solution is filtered to remove salts and then the solvent again removed under a vacuum. The solid mass is again extracted with hot benzene and the resulting solution filtered. The volume of the red solution is reduced to 20 ml and 50 ml of absolute ethanol is added. After cooling, red crystalline platelets form. They are collected by filtration and dried in vacuo. Yield was 3.2 g, 80% based on ligand salt Ia.

Method B. [Fe(Me$_2$[14]tetraeneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$[2a] (10.0 g, 0.016 mol) is dissolved in 20 ml of acetonitrile. To the solution is added 0.0325 g (0.032 mol) of triethylamine. Deep red crystals immediately precipitate and are collected via filtration and dried in vacuo. Yield was 3.95 g, 80% based on the starting complex II.

7,13-Dimethyl-1,4,8,12-tetraazacyclopentadeca-4,6,12,14-tetraenatoiron(II), [Fe(Me$_2$[15]tetraenato(2−)N$_4$)] (IVb). Method A. This synthesis corresponds to method A cited above for the preparation of [Fe(Me$_2$[14]tetraenato(2-)N$_4$)] (IVa), but the product is crystallized from diethyl ether, not benzene. The yield of deep red crystals was 70% based on ligand salt.

Method B. [Fe(Me$_2$(IE)$_2$[15]tetraeneN$_4$)](PF$_6$)$_2$ (10.0 g, 0.0157 mol) is slurried in 100 ml of warm diethyl ether, and to this slurry is added 3.52 g (0.0328 mol) of potassium *tert*-butoxide. The mixture is allowed to reflux with stirring for 1 h. The ether solution becomes an intense red-orange color. The solution is filtered to remove the salts and the solid is washed with ether, leaving only a white residue. The volume of the resulting ether solution is reduced under a vacuum. When the volume nears 25–30 ml deep red crystals begin to form and upon reducing the volume further under vacuum a large amount of crystalline product forms. The solid is collected by filtration, recrystallized from diethyl ether, re-collected, and dried in vacuo. Yield of deep red crystalline product was 70–80% based on starting complex IIIa.

2,2,3,3,7,13-Hexamethyl-1,4,8,12-tetraazacyclopentadeca-4,6,-12,14-tetraenatoiron(II), [Fe(Me$_6$[15]tetraenato(2−)N$_4$)] (IVc). This complex can also be prepared by both methods A and B outlined above beginning with [Fe(Me$_6$IE$_2$[15]tetraeneN$_4$)](PF$_6$)$_2$ (IIIb). The yields by both methods were comparable to those obtained for IVb.

2,12-Dimethyl-1,5,9,13-tetraazacyclohexadeca-1,3,9,11-tetraenatoiron(II), [Fe(Me$_2$[16]tetraenato(2−)N$_4$)] (IVd). This complex was prepared by the method B outlined above beginning with [Fe(Me$_2$IE$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$ (IIIc). Yield based on complex IIIc was 70%.

2,4,10,12-Tetramethyl-1,5,9,13-tetraazacyclohexadeca-1,3,9,-11-tetraenatoiron(II), [Fe(Me$_4$[16]tetraenato(2−)N$_4$)] (IVe). This complex was prepared by method B outlined above beginning with [Fe(Me$_4$IE$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$ (IIId). Yield based on complex IIId was 80%.

[Fe(Me$_2$[14]tetraeneN$_4$)(py)$_2$](PF$_6$)$_2$ (Va). This complex was prepared by slurrying 1.0 g (3.65 mmol) of the corresponding square-planar complex (IVa) in 50 ml of absolute ethanol and adding 2–3 ml of pyridine followed by dropwise addition of 2 equiv of HSO$_3$CF$_3$ (0.55 g). An immediate reaction occurs as is evidenced by the change in color of the solution from a deep red to a light brown-yellow. To the resulting solution is added an ethanolic solution containing 2.0 g of ammonium hexafluorophosphate. The solution turns cloudy instantly and after allowing the flask to sit undisturbed for 0.5 h, yellow-orange crystals form. The product is collected by filtration, washed with absolute ethanol and diethyl ether, and dried in vacuo for several hours. Yield based on starting complex was consistently in the range 70–85%.

[Fe(Me$_2$[15]tetraeneN$_4$)(py)$_2$](PF$_6$)$_2$ (Vb). Prepared by the same scheme as that outlined for Va. Yield based on IVb was 80%.

[Fe(Me$_2$[16]tetraeneN$_4$)(py)$_2$](PF$_6$)$_2$ (Vc). Prepared by the method outlined for complex Va. Yield based on IVd was 75%.

[Fe(Me$_4$[16]tetraeneN$_4$)(py)$_2$](PF$_6$)$_2$ (Vd). Prepared by the same method outlined for complex Va. Yield based on complex IVe was 75%.

[Fe(Me$_4$[14]tetraeneN$_4$)(py)$_2$](PF$_6$)$_2$ (Ve). Prepared by the method outlined for complex Va. Yield based on complex IVf was 85%.

***trans*-[(6-(1-Iminoethyl)-7,13-dimethyl-1,4,8,12-tetraazacyclopentadeca-4,6,12,14-tetraene)(acetonitrile)iron(II)] Hexafluorophosphate, *trans*-[Fe(Me$_2$IE[15]tetraeneN$_4$)(CH$_3$CN)](PF$_6$)$_2$ (VI).** [Fe(Me$_2$[15]tetraenato(2-)N$_4$)] (IVb) (1.0 g, 0.035 mol) was dissolved in 30 ml of acetonitrile. To this solution was added 1.04 g (70.0 mmol) of trifluoromethanesulfonic acid, followed by 1.14 g (70.0 mmol) of NH$_4$PF$_6$ in 100 ml of hot absolute ethanol. As the solution cooled orange crystals of complex VI formed. Yield was 60% based on complex IVb.

***trans*-[(3,11-Bis(1-iminoethyl)-2,12-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,3,9,11-tetraene)iron(II)] Hexafluorophosphate, *trans*-[Fe(Me$_2$(IE)$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$ (VII).** This complex was prepared via the method outlined above for complex VI. Yield based on complex IVd was 70%.

Results and Discussion

Syntheses and Reactions. The general approach to the synthesis of the deprotonated, neutral complexes [Fe(Me$_n$-[Z]tetraenato(2−)N$_4$)] (IV) involves treatment of a solution or slurry of the precursor complex [Fe(Me$_2$[14]tetraeneN$_4$)-(CH$_3$CN)$_2$](PF$_6$)$_2$ (II) or [Fe(Me$_n$(IE)$_2$[Z]tetraeneN$_4$)]-(PF$_6$)$_2$ (III) with 2 equiv of base under an inert atmosphere. All reactions of these iron(II) complexes were carried out in the strict absence of oxygen, since all of the complexes reported here are air sensitive. This is especially true of the square-planar derivatives. The complex [Fe(Me$_2$[14]tetraeneN$_4$)-(NCCH$_3$)$_2$](PF$_6$)$_2$ (II) can be deprotonated under relatively mild conditions, for example, with triethylamine. In fact, as was indicated previously,[2c] this cationic complex II partially ionizes when dissolved in dry acetonitrile. The *cis*-hexaene derivatives [Fe(Me$_n$(IE)$_2$[Z]tetraeneN$_4$)](PF$_6$)$_2$ (III) are more inert toward base attack; i.e., no reaction occurs with triethylamine. They can be deprotonated by treatment with the very strong bases such as *tert*-butoxide, ethoxide, etc. The square-planar product obtained by deprotonation of the complexes II and III is a rare structure for iron(II) with only a few known examples: the mineral gillespite[10] contains high-spin iron(II) coordinated to oxygen in a square-planar environment; the quadridentate ligand salen[11,12] has been shown to form square-planar iron(II) complexes that are high-spin and very air sensitive; phthalocyaninatoiron(II),[13] a recent tetraphenylporphinatoiron(II),[14] and the previously reported square-planar complexes [Fe(II)(Me$_4$[14]tetraenato(2−)N$_4$)] (IVf)[15] and [Fe(Ph$_2$[Z]tetraenato(2−)N$_4$)] (Ph = phenyl and Z = 14, 15, or 16)[5] complete the list of known examples. The latter study, while principally concerned with Fe(III) complexes, provides three clear examples of complexes of the classes discussed here. The formation of the square-planar derivatives from III is also interesting because it shows that the integrity of the *cis*-hexaene ligand structure is lost; that is, that deprotonation is followed by elimination of a neutral acetonitrile molecule. This certainly indicates that, even though the spin state changes from $S = 0$ to $S = 1$ (Table II) upon deprotonation, the square-planar environment is the stable one for these complexes in basic media.

The square-planar complexes can also be prepared by direct

Table I. Analytical Data for the New Complexes

	Compd	%C		%H		%N	
		Calcd	Found	Calcd	Found	Calcd	Found
IVa	[Fe(Me$_2$[14]tetraenato(2−)N$_4$)]	52.59	52.44	6.57	6.60	20.45	20.33
IVb	[Fe(Me$_2$[15]tetraenato(2−)N$_4$)]	54.18	54.54	6.95	6.87	19.46	19.72
IVc	[Fe(Me$_6$[15]tetraenato(2−)N$_4$)]	59.34	59.18	8.14	8.04	16.29	16.18
IVd	[Fe(Me$_2$[16]tetraenato(2−)N$_4$)]	55.67	55.52	7.29	7.40	18.56	18.40
IVe	[Fe(Me$_4$[16]tetraenato(2−)N$_4$)]	58.22	58.19	7.88	7.96	16.98	16.77
Va	[Fe(Me$_2$[14]tetraeneN$_4$)(py)$_2$](PF$_6$)$_2$	36.45	36.55	4.15	4.12	11.60	11.55
Vb	[Fe(Me$_2$[15]tetraeneN$_4$)(py)$_2$](PF$_6$)$_2$	37.41	37.71	4.34	4.27	11.38	11.10
Vc	[Fe(Me$_2$[16]tetraeneN$_4$)(py)$_2$](PF$_6$)$_2$	38.31	38.23	4.53	4.61	11.18	10.86
Vd	[Fe(Me$_4$[16]tetraeneN$_4$)(py)$_2$](PF$_6$)$_2$	40.01	39.91	4.87	4.76	10.77	10.69
Ve	[Fe(Me$_4$[14]tetraeneN$_4$)(py)$_2$](PF$_6$)$_2$	38.31	38.23	4.53	4.47	11.18	11.25
VI	[Fe(Me$_2$IE[15]tetraeneN$_4$)(CH$_3$CN)](PF$_6$)$_2$	30.83	31.07	4.23	4.18	12.69	12.74
VII	[Fe(Me$_2$(IE)$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$	31.75	32.06	4.36	4.47	12.31	12.47

Table II. Physical Properties of the New Complexes

Compd	Color	*M/e*	μ_{eff}, μ_B[a]	Λ,[b] ohm^{-1} cm^2 mol^{-1}
IVa	Red	274	3.23[c] 3.45,[d] 4.5[e]	
IVb	Red	288	3.57[c] 3.60,[d] 4.98[e]	
IVc	Red	344	3.67[c] 3.70,[d] 5.05[e]	
IVd	Red	302	3.83[c] 3.90,[d] 5.15[e]	
IVe	Red	330	4.60[c] 4.30,[d] 5.35[e]	
Va	Orange		0.50	CH$_3$NO$_2$,[f] 185.2[f]
Vb	Orange		0.55	CH$_3$NO$_2$, 191.9
Vc	Yellow		0.50	CH$_3$NO$_2$, 185.6
Vd	Yellow		3.22	CH$_3$NO$_2$, 183.4
Ve	Orange		0.60	CH$_3$NO$_2$, 178.1
VI	Orange		0.55	CH$_3$NO$_2$, 181.1
VII	Orange		0.50	CH$_3$NO$_2$, 189.4

[a] Magnetic moment at 25 °C. [b] The solvent is given followed by molar conductance at 25 °C for 10^{-3} M solutions. [c] Faraday method. [d] Solution moment in toluene by Evans method. [e] 5% pyridine solution also determined by Evans method. [f] For typical conductance values see R. L. Dutta, D. W. Meek, and D. H. Busch, *Inorg. Chem.*, **9**, 1215 (1970).

reaction of the desired ligand salt with anhydrous ferrous acetate in absolute ethanol, upon addition of 4 equiv of sodium ethoxide. This route fails for the two 16-membered ring ligand salts Id and Ie. Repeated attempts to prepare the corresponding square-planar iron(II) complexes IVd and IVe by this method were unsuccessful. A similar result was noted in attempts to prepare nickel(II) complexes of varying ring sizes.[15b]

Square-planar four coordination has been assigned to the new iron(II) derivatives on the basis of elemental analyses (Table I) and mass spectra (Table II), as well as the preliminary results of an x-ray crystallographic study of [Fe(Me$_6$[15]tetraenato(2−)N$_4$)] (IVc).[5] The formation of the four-coordinate, square-planar complexes in the reactions described above was surprising, since they are prepared in the good donor solvent acetonitrile. However, these complexes show no tendency to coordinate acetonitrile. This is indicated by the fact that their electronic spectra in acetonitrile are identical with those obtained in toluene and diethyl ether solutions. These derivatives (IV) do coordinate other neutral molecules, but only weakly. For example, piperidine and pyridine react in solution with all six square-planar complexes IV, forming intense red (14-membered ring derivatives) or purple-red (15- and 16-membered ring derivatives) solutions. Although crystals could be obtained from ethyl ether–pyridine solvent mixtures by adding heptane, pure materials could not be isolated. Simply allowing the materials to remain exposed to the atmosphere in a drybox resulted in loss of the axial ligand and formation of the parent square-planar complex IV. Consequently, an attempt was made to determine the structures of these substances in solution. The electronic spectra of all the new complexes are listed in Table V. The spectra of the square-planar derivatives are markedly changed when pyridine is present. In order to determine the spin state produced by pyridine coordination, the solution susceptibilities were measured. In all cases (Table II) the presence of pyridine increases the magnetic susceptibility of the square-planar derivatives to values acceptable for high-spin iron(II). It is interesting to note that the square-planar complexes do not react with imidazole, *N*-methylimidazole, or triphenylphosphine at room temperature, but they do react with carbon monoxide in a highly reversible manner. These reactions are presently under more intensive investigation.

The protonation reactions of the square-planar complexes IV in the presence of excess pyridine have made possible the isolation of a series of bis(pyridine)bis(β-diimine)iron(II) complexes. The complexes are assumed to have a trans configuration since the macrocycle preexists in a planar arrangement about the metal before the additional ligands are coordinated in the fifth and sixth sites. The structures of these complexes (V) are supported by their IR spectra (Table III), which show no bands assignable to NH but do exhibit a pyridine band at 1600 cm^{-1}. Further, the assignment is supported by the results of elemental analyses (Table I) and molar conductivity measurements in nitromethane (Table II); the latter support their formulation as diunivalent electrolytes. These complexes are not highly colored and have no charge transfer bands in the visible region of the spectrum. This has permitted the observation of d-d bands in their electronic spectra (Table V) and facilitated correlation of the spectral parameters with ring size and Mössbauer parameters (vide infra).

The protonation of the complexes [Fe(Me$_n$[*Z*]tetraenato(2−)N$_4$)] (IVa, IVb, and IVd) with HSO$_3$CF$_3$ in the presence of acetonitrile has led to the isolation of the dicationic complexes II, VI, and VII, respectively. In all three cases analyses and molar conductivity measurements agree with the formulation, [Fe(macrocycle)](PF$_6$)$_2$·2CH$_3$CN. To determine the structures of the pure products both ^{1}H NMR and IR spectra were used. Protonation of the square-planar iron(II) complex of the 14-membered ring (IVa) gives the *trans*-bisacetonitrile complex II, the starting complex for the preparation of IVa. Thus, the deprotonation of [Fe(Me$_2$[14]tetraeneN$_4$)(CH$_3$CN)$_2$]$^{2+}$ to give [Fe(Me$_2$[14]tetraenato(2−)N$_4$)] (IVa) is completely reversible in acetonitrile. This has been further

Table III. Selected Infrared Assignments (cm^{-1})

	Assignments			
Compd	NH stretch	C=C or C=N	Pyridine	PF_6^-
IVa		1582, 1548, 1508		
IVb		1571, 1515		
IVc		1568, 1500		
IVd		1565, 1513		
IVe		1546, 1517		
Va		1642	1593	860, 560
Vb		1672, 1664, 1613	1598	860, 560
Vc		1653,[b] 1610	1597	860, 560
Vd		1645[a]	1585[b]	860, 560
Ve		1645	1600	860, 560
VI	3425, 3344	2257,[c] 1629, 1600		860, 560
VII	3333[b]	1634, 1615		860, 560

[a] Broad. [b] Doublet. [c] Nitrile stretch.

Table IV. ^1H NMR Spectral Data for Complexes VI and VII

Compd[a,b]	Methyl	Methylene	Vinyl	Bridgehead	NH
VI	2.47	2.00, 2.90, 4.10	8.66	5.76	10.6
VII	2.58, 2.50	2.26, 4.20	8.09, 8.77	5.74	10.17

[a] All spectra were run in $MeNO_2$-d_3 and are reported relative to Me_4Si, internal standard. [b] Values given in δ (ppm).

established by the fact that the electronic spectra, IR, and ^1H NMR spectra of the complex II[2a] are identical with those of the product obtained by protonating complex IVa.

In contrast, protonation of the 15- and 16-membered ring derivatives (IVb and IVd) in acetonitrile does not yield their corresponding precursor complexes, the *cis*-hexaene derivatives (IIIa and IIIc). This is easily rationalized because the ligands to be protonated in complexes IVb and IVd are in a square-planar array about the iron(II), whereas the ring is folded in the *cis*-hexaene complexes. Thus, it is unlikely that the parent macrocyclic ligand would rearrange about the metal to give the cis geometry of the starting hexaene complexes (III). The complexes VI and VII that were isolated were found to have IR (Table III) and ^1H NMR spectra (Table IV, Figure 1) strikingly different from $[Fe(Me_2[14]tetraeneN_4)(CH_3CN)_2](PF_6)_2$, but not unlike those observed[2a] for hexaene complexes IIIa and IIIc. For example, the infrared spectrum of the complex prepared by protonation of $[Fe(Me_4[16]tetraenato(2-)N_4)]$ (IVe) was virtually identical with that obtained with the corresponding cis complex $[Fe(Me_4(IE)_2[16]tetraeneN_4)]^{2+}$ (IIId). Also the ^1H NMR spectra of the two complexes are very nearly identical, the only differences being very slight changes in chemical shift values and in the NH resonance. The latter is centered at δ 10.6 in the spectrum of VII and shows some splitting, but in the *cis*-hexaene complex (IIId) this resonance shows no splittings. The assignment of a structure to the product obtained from the protonation of the square-planar complex derived from the 16-membered ring is made possible by the earlier characterization of the cis complex IIIc by a crystal structure determination.[2b] From the similarities in their properties, chemical and spectral, the trans structure VII is assigned to the 16-membered derivative. It is also interesting to note that the pattern at δ 5.76, assigned to the bridgehead proton H_γ, is identical with that observed for the *cis*-hexaene complexes, namely, a doublet of doublets. By homonuclear spin decoupling it has been found that H_γ is coupled to the H_δ with $J_{H_\gamma H_\delta} = 5$ Hz, and in addition that H_γ is coupled with the NH protons four bonds away, $J_{H_\gamma NH} = 1$ Hz.

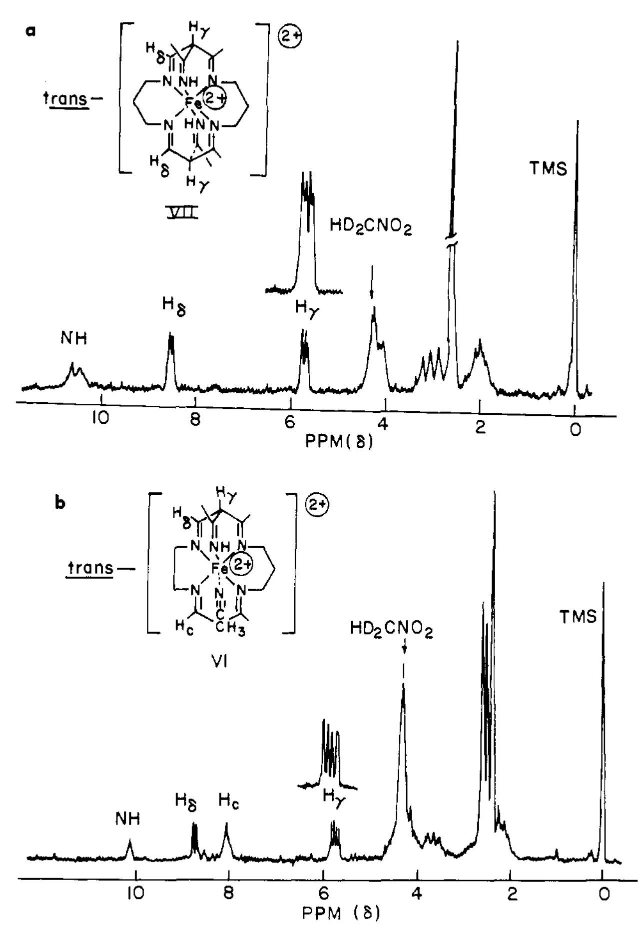
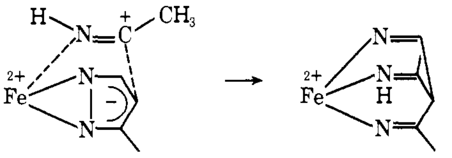


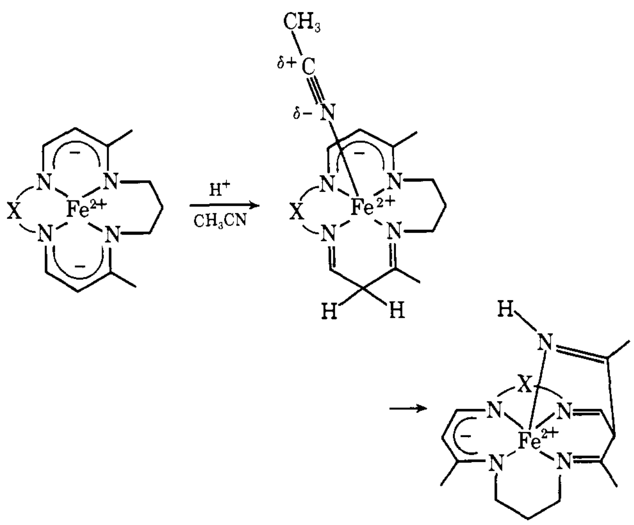
Figure 1. (a) ^1H NMR spectrum of *trans*-$[Fe(Me_2(IE)_2[16]tetraeneN_4)](PF_6)_2$ (VII). (b) ^1H NMR spectrum of *trans*-$[Fe(Me_2IE[15]tetraeneN_4)(NCCH_3)](PF_6)_2$ (VI).

The product obtained by protonating in acetonitrile the square-planar complex $[Fe(Me_2[15]tetraenato(2-)N_4)]$ (IVb) has a ^1H NMR and an IR spectrum which suggest that the product has a structure in which acetonitrile adds electrophilically to the γ-carbon of a charged six-membered chelate ring, in analogy to the 16-membered ring derivative. This is supported by the IR spectrum, which exhibits an NH stretching mode, and by the ^1H NMR spectrum, which shows the complex bridgehead pattern at δ 5.75, the NH resonance at δ 10.2, and the doublet vinyl resonance centered at δ 8.77. However, several features are apparent in both the IR and ^1H NMR spectra of this product that are not present in the spectra of the *cis*-hexaene complexes or the *trans*-hexaene complex VII: (1) the IR spectrum of this product has a sharp band at 2257 cm^{-1}; (2) the IR spectrum has a larger number of bands in the double bond region; (3) the ^1H NMR spectrum of this product has a resonance in the vinyl region at δ 8.09, which is not present in any of the other hexaene complexes; (4) the integrated intensity ratios in the ^1H NMR spectrum for the NH/vinyl/vinyl/bridgehead protons are 1:1:1:1; and (5) the methyl resonances in the ^1H NMR show not one band, as is found for all the hexaene complexes, but three bands with integrated intensity ratios of 3:3:6. These data can be explained very well by the structure VI, which we have assigned to this protonation product. The vinyl proton resonance at δ 8.09 can be assigned to the vinyl H_a. Indeed, this assignment is supported by the ^1H NMR spectrum of structure II where the lone vinyl resonance occurs at δ 8.3.[2a] The observed intensity ratios of 1:1:1:1 in the downfield portion of the ^1H NMR spectrum are also consistent with structure VI. Further, the observed methyl resonance pattern corresponds well with that predicted for structure VI. The methyls are all equivalent in the *cis*-hexaene complexes[2a] and in the *trans*-hexaene complex VII. Thus, one might expect that the methyl of the iminoethyl and the adjacent methyl on the macrocycle would be equivalent. The observation of three types of methyl resonances with the intensity ratios of 3:3:6 is consistent with the structure VI. The resonance at δ 8.77 is similar to those observed for the *cis*-hexaene complexes in this region; i.e., a doublet of doublets, and is therefore assigned to the bridgehead proton H_γ. By homonuclear spin decoupling it was found that H_γ is coupled with H_δ, $J_{H_\gamma H_\delta} = 5$ Hz, and that H_γ is also coupled to the NH, $J_{H_\gamma NH} = 1$ Hz. These assignments are identical with those observed with the *cis*- and *trans*-hexaene complexes. Finally, the sharp band at 2257 cm^{-1} in the IR spectrum of product VI is assigned to the C≡N stretching vibration of the lone coordinated acetonitrile molecule. Thus, by comparing the ^1H NMR and IR spectra of these products with those of the known *cis*-hexaene complexes III and with those of the acetonitrile complex II, we have been able to assign the unique structures VI and VII to the products of the protonation in acetonitrile of the square-planar complexes IVb and IVd, respectively.

We conclude that a most dramatic effect of ring size occurs when the square-planar complexes are protonated in acetonitrile to give trans low-spin, six-coordinate iron(II) complexes. The products were obtained in high yields, and it was shown that the $[Fe(Me_2[14]tetraenato(2-)N_4)]$ (IVa) gives the *trans*-bisacetonitrile complex II when protonated. In contrast $[Fe(Me_2[15]\text{-}tetraenato(2-)N_4)]$ gives $[Fe(Me_2IE[15]\text{-}tetraeneN_4)(CH_3CN)]^{2+}$ (VI), in which one CH_3CN has condensed with the macrocycle, and $[FeMe_2[16]tetraenato(2-)N_4)]$ gives $[Fe(Me_2(IE)_2[16]tetraeneN_4)]^{2+}$ (VII), in which two molecules of CH_3CN have added electrophilically to the γ-carbons of the macrocycle. An explanation for this example of product determination by the size of the macrocycle can be suggested from the study of molecular models. The models indicate that the presence of two five-membered chelate rings produces a great deal of strain when a 1-iminoethyl substituent bonded to the γ-carbon of the ring is coordinated to the iron(II). If there is one five-membered and one six-membered saturated chelate ring present, as in the 15-membered ring derivative, models predict that only one acetonitrile could both react at the γ-carbon and bond to the iron(II) in a trans structure. Finally, if there are two six-membered saturated chelate rings there is no strain involved in structure VII.

Two obvious possible mechanisms for the formation of these novel complexes (VI and VII) merit brief consideration. The first involves the nucleophilic attack of the γ-carbon of the macrocyclic ligand on a protonated and electrophilically activated acetonitrile molecule. The other mechanism involves the initial protonation of the macrocycle followed by coordination and electrophilic activation of an acetonitrile molecule. The major difference between the two mechanisms is the order of protonation; is the macrocycle or the acetonitrile protonated first? Both mechanisms require the metal to activate and orient the attacking acetonitrile and are consistent with previously proposed mechanisms for metal ion activation of nitriles.[2a,3,4] The results of a deuteration reaction tend to support the second mechanism. When $[Fe(Me_2[16]tetraenato(2-)N_4)]$ reacts with $CF_3C(=O)OD$ in CH_3CN, the product contains 50% ND and 50% NH. The first mechanism predicts 100% ND in this case.





Magnetic Susceptibilities. The square-planar derivatives IV that are reported here all displayed magnetic moments at room temperature that are too low for high-spin iron(II) (Table II). In all cases the agreement between the observed moments in solution and in the solid state was good, thus eliminating the possibility of solid state effects. The magnetic susceptibility data obtained at room temperature would be consistent with either the presence of a mixture of the spin states $S = 0$ and $S = 2$ or the presence of a discrete intermediate $S = 1$ ground state for these derivatives. There are but a few examples of compounds that exhibit the $S = 1$ ground state among d^6 ions. The following examples are known: bis(benzene-1,2-dithiolato(2−))cobalt(III) complexes,[16] μ_{eff} in the range 3.1-3.9 μ_B; bis(biuretato(2−))cobalt(III) complexes,[17] μ_{eff} in the range 3.1-3.5 μ_B; phthalocyaninatoiron(II), $\mu_{eff} = 3.83$ μ_B;[13c] tetraphenylporphinatoiron(II), $\mu_{eff} = 4.4$ μ_B;[14a] certain six-coordinate iron(II) complexes, $\mu_{eff} = 3.7\text{-}3.9$ μ_B;[18] $[Fe(Me_4[14]tetraenato(2-)N_4)]$ (IVf), $\mu_{eff} = 3.8$ μ_B;[15a] $[Fe(Ph[14]tetraenato(2-)N_4)]$,[5] and $[Fe(Ph[16]tetraenato(2-)N_4)]$.[5] The temperature dependence of the magnetic moments has been studied for the last two examples and the phthalocyanine derivative. In order to decide between the alternate possibilities stated for these complexes (IV) the temperature dependences of the magnetic susceptibilities were studied. These complexes are all extremely air sensitive even in the solid state. This frustrated all attempts to study the temperature dependence of the magnetic susceptibility by the Faraday method because exposure to the air occurred during the loading stage. In order to circumvent this problem the susceptibilities were determined by use of a vibrating sample magnetometer of the Foner type. The available temperature range with this instrument was 2-100 K.

Figures 2a and 2b show graphs of $1/\chi_M$ vs. temperature for the complexes IVa-IVf. The data for the two complexes containing 14-membered rings (IVa and IVf) obey the Curie-Weiss law ($1/\chi_M = C/(T + \theta)$) over the available temperature range; whereas, that for the 15- and 16-membered ring derivatives shows deviations from the Curie-Weiss law at lower temperatures. From the slope of the straight line graph of $1/\chi_M$ vs. temperature the magnetic moment over that temperature range can be calculated. Thus, a least-squares calculation for the 14-membered ring derivatives, over the entire temperature range studied, gave $\mu_{eff} = 3.14$ μ_B for IVa and $\mu_{eff} = 3.17$ μ_B for IVf, with Weiss constants of approximately 0 and 2.0 K, respectively. Thus, these two complexes are confirmed examples of iron(II) with an $S = 1$, intermediate spin, ground state. For the four remaining complexes, which display substantial departures from Curie-Weiss law behavior, it can be

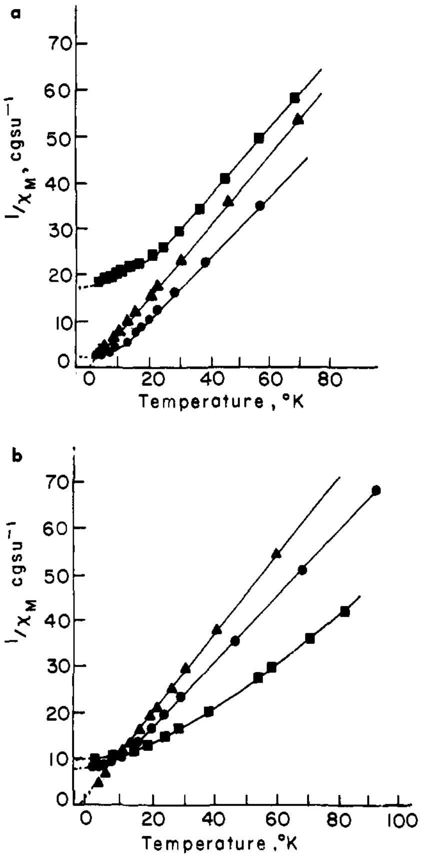


Figure 2. (a) Graph of $1/\chi_M$ vs. temperature for ▲, [Fe(Me$_2$[14]tetraenatoN$_4$)](IVa); ●, [Fe(Me$_2$[15]tetraenatoN$_4$)](IVb); ■, [Fe(Me$_2$[16]tetraenatoN$_4$)] (IVd). (b) Graph of $1/\chi_M$ vs. temperature for ▲, [Fe(Me$_4$[14]tetraenatoN$_4$)] (IVf); ●, [Fe(Me$_6$[15]tetraenatoN$_4$)] (IVc); ■ [Fe(Me$_4$[16]tetraenatoN$_4$)] (IVe).

seen that at temperatures greater than the region of curvature the magnetic moments are in the range previously found for $S = 1$ ground d^6 complexes (3.00–3.90 μ_B, Figure 3). It is concluded that the square-planar complexes IVb–IVe also have the $S = 1$ ground state at temperatures exceeding the regions of curvature in the graphs.

Deviations from Curie–Weiss behavior of the sort observed here for complexes IVb–IVe have been reported in the low-temperature magnetic studies on phthalocyaninatoiron(II),[13a,b] on the six-coordinate iron(II) complexes having $S = 1$ ground states,[18] and on the square-planar cobalt(III) complexes having this ground state.[16a,17] Departures from the Curie–Weiss law of this type have been attributed to a large zero-field splitting of the ground term state (Figure 4) arising from second-order spin-orbit coupling.[13] At higher temperatures with $kT \gg D$, the $M_s = +1$ and the $M_s = 0$ levels are populated, but at lower temperatures such that $kT < D$, the $M_s = 0$ begins to be filled exclusively, following Boltzmann statistics, with the result that the magnetic moment lowers dramatically in a narrow temperature range.

In eq 1 is given the expression for the molar susceptibility of a spin-triplet state in a tetragonal (D_{4h}) ligand field:[19]

$$\chi_M = \frac{2N\beta^2}{3}\left\{\frac{g_\parallel^{\,2} e^{(-D/kT)}}{kT[1 + 2e^{(-D/kT)}]} + \frac{g_\perp^{\,2}[1 - e^{(-D/kT)}]}{D[1 + 2e^{(-D/kT)}]}\right\} \tag{1}$$

In the limit of very low temperature this equation reduces to

$$\chi_M = 4N\beta^2 g_\perp^{\,2}/3D,\ kT \ll D \tag{2}$$

Thus, by extrapolating the value of $1/\chi_M$ to $T = 0$ K from the graph of $1/\chi_M$ vs. temperature, the value of χ_M can be estimated at $T = 0$ K. Although ESR spectra could not be observed for these complexes, an approximate value of D can be estimated from eq 2 using g values determined from a previous study[13a] of phthalocyaninatoiron(II) ($g_\perp = 2.74$). The results are as follows: [Fe(Me$_2$[15]tetraenato(2−)N$_4$)] (IVb), D = 6 cm^{-1}; [Fe(Me$_6$[15]tetraenato(2−)N$_4$)] (IVc), D = 20 cm^{-1}; [Fe(Me$_2$[16]tetraenato(2−)N$_4$)] (IVd), D = 46 cm^{-1}; and [Fe(Me$_4$[16]tetraenato(2−)N$_4$)] (IVe), D = 26 cm^{-1}. These splittings are reasonable and agree well with the values obtained by similar methods for the previously mentioned square-planar cobalt(III) complexes ($D \sim 40$ cm^{-1}),[16a] phthalocyaninatoiron(II) (D = 70 cm^{-1}),[13a] and six-coordinate ($S = 1$) iron(II) complexes ($D \sim 2$–3 cm^{-1}).[18a]

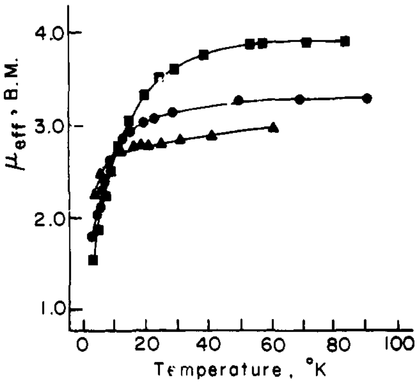


Figure 3. Variation in μ_{eff} with temperature for ▲, [Fe(Me$_4$[14]tetraenatoN$_4$)](IVf); ●, [Fe(Me$_6$[15]tetraenatoN$_4$)](IVc); ■, [Fe(Me$_4$[16]tetraenatoN$_4$)] (IVe).

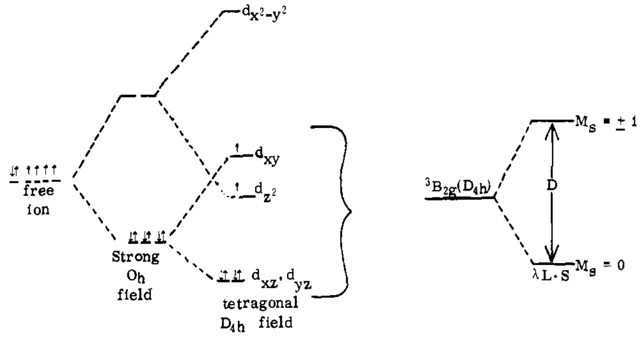


Figure 4. A representation of the electronic configuration of iron(II) showing zero-field splitting.

Of the remaining seven complexes only [Fe(Me$_4$[16]tetraeneN$_4$)(py)$_2$](PF$_6$)$_2$ (Vd) displayed a magnetic moment which is not consistent with low-spin iron(II). The observed magnetic moment at room temperature was 3.22 μ_B for this complex. This value can also be rationalized by assuming either an $S = 1$ ground state or a mixture of low- and high-spin iron(II). To confirm the nature of the spin ground state, the temperature dependence of the magnetic susceptibility was determined over the range 90–350 K. The results are graphed in Figure 5, showing that μ_{eff} varies with temperature over part of this range. This behavior is typical of iron(II) complexes involving a thermal equilibrium[20] between the low-spin $^1A_1$ state and the high-spin $^5T_2$ state. The data were used to calculate[21] an empirical equilibrium constant, K = [low spin]/[high spin], at each temperature. For the calculations it is assumed that the high-spin state has a molar susceptibility of 12 000 × 10^{-6} cgs, that the high-spin form would, in the absence of a spin equilibrium, obey the Curie–Weiss law, and further that χ_M for the low-spin form is 100 × 10^{-6} cgs and temperature independent. Figure 6 shows the graph of ln K_{eq} against $1/T$. The scattering of points at the low-temperature

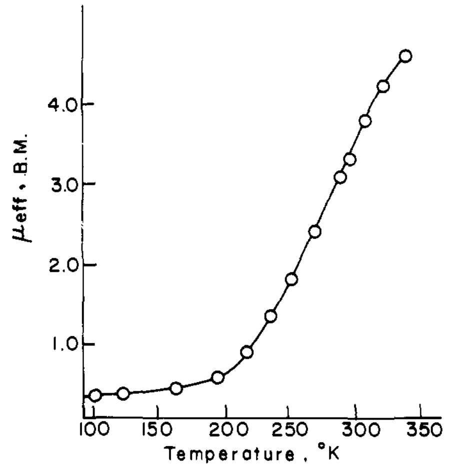


Figure 5. Variation in μ_{eff} with temperature for [Fe(Me$_4$[16]tetraeneN$_4$)(py)$_2$](PF$_6$)$_2$ (Vd).

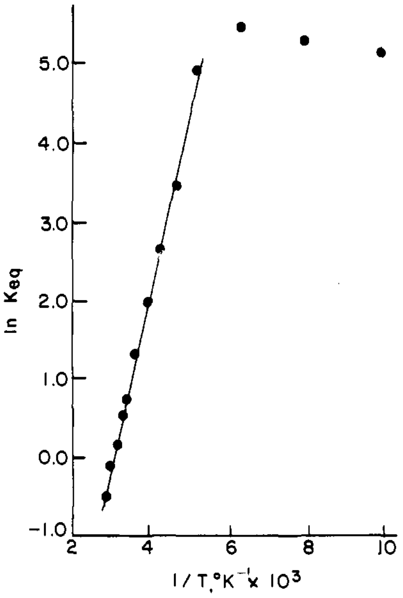


Figure 6. Temperature dependence of ln K_{eq} for spin equilibrium involving [Fe(Me$_4$[16]tetraeneN$_4$)(py)$_2$](PF$_6$)$_2$ (Vd).

extreme reflects the uncertainty of the determination when the concentrations of the reactants and products become very different. However, the straight line corresponding to the higher temperature data indicates a value of ΔH for the process of -4.70 kcal/mol and a ΔS of -14.8 eu. these thermodynamic parameters are within the range found for other iron(II) spin-equilibrium systems.[20] Although ΔH favors the low-spin form and is of the magnitude that is expected, the ΔS term is negative and much larger in absolute magnitude than expected for the electronic process alone. Since for a simple spin equilibrium between quintet and singlet levels ΔS would be -3.2 eu, it appears that other factors, such as bond length and bond angle changes, are operative during the spin state change.

Electronic Spectra. Table V lists the electronic spectra for all of the new iron(II) complexes. The square-planar complexes IV all show transitions in the low-energy portion of the spectrum. From their low extinction coefficients, it is assumed that these bands are primarily d-d in nature. All six square-planar complexes also show several relatively low-energy charge transfer bands. The spectra of these materials change dramatically in pyridine as compared to a noncoordinating medium such as toluene. The origin of this change may be a spin state difference, as discussed above. The solid state mull spectra of the planar complexes at liquid nitrogen temperature show that the low-energy transitions are virtually unchanged from those observed at room temperature in toluene solutions. This fact is interpreted as further evidence for the presence of an $S = 1$ ground state for the complexes. If these lower energy bands involve d-d transitions, spin state change at lower temperature would certainly be expected to change the low-energy portion of the spectra of these complexes.

The electronic spectrum of *trans*-[Fe(Me$_2$(IE)$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$, VII, shows no bands assignable to d-d transitions, but only higher energy bands with high extinction coefficients. This spectrum is very similar to the spectra observed for the *cis*-hexaene complexes (III). Similarity is anticipated since the iron(II) center is bonded to six isolated imines in both cases. As a result we assign these bands to M → π^* (imine π^*) charge transfer transitions.[2a] The spectrum of the *trans*-[Fe(Me$_2$IE[15]tetraeneN$_4$)(CH$_3$CN)](PF$_6$)$_2$ (VI) shows, in addition to three charge transfer (M → π^*) bands at higher energy, one lower energy transition at 1.28 μm^{-1} with an approximate extinction coefficient of 41. This band is assumed to arise from a d-d transition, but no definite assignment can be made. It is interesting to note that the cis 15-membered ring hexaene ligands show no low-energy bands, but that [Fe(Me$_2$[14]tetraeneN$_4$)(CH$_3$CN)$_2$]$^{2+}$, II, having the bis-β-diimine macrocycle, does show a d-d band[2c] at almost the same energy and with a similar extinction coefficient. This lends support to the assignment of the band at 1.28 μm^{-1} as a d-d transition and to the assignment of structure VI to this compound.

The electronic spectra of the bis-β-diimine, bispyridine complexes V have no low-lying charge transfer bands (except for complex Vd). This fact has permitted higher energy d-d transitions to be observed for these complexes; thus, in most cases (except Vd) we have been able to observe two d-d bands for these low-spin d^6 complexes. In an earlier paper[2a] corresponding bands were assigned to the transitions $^1A_{1g} \rightarrow {}^1E_{1g}$ and $^1A_{1g} \rightarrow {}^1A_{2g}$ for [Fe(Me$_2$[14]tetraeneN$_4$)(py)$_2$]$^{2+}$. These two excited states arise from the tetragonally split $^1T_{1g}$ (O_h) excited state. Treatment of the observed data by the method of Wentworth and Piper[22] yielded approximate values of Dq^{xy}, Dq^z, and Dt for the 14-membered ring derivatives. The new complexes have been subjected to a similar treatment, and as a result, we have been able to calculate Dq^{xy}, Dq^z (pyridine), and Dt values for complexes of varying ring sizes. These results (Table VI) demonstrate the dramatic effect of ring size, as well as the effects of methyl group substitution. The Dq^{xy} values calculated show that increasing the ring size decreases the ligand field strength of the inplane donors. This same trend was also observed[23] for a series of low-spin trans-dicyano [13]-, [14]-, and [15]aneN$_4$ complexes of iron(II) (Dq^{xy} = 2208, 2029, and 1842 cm^{-1} respectively). For the complexes with the tetraimine macrocycles studied here, the Dq^{xy} values are 2330, 2290, and 2230 cm^{-1} for the Me$_2$ complexes Va, Vb, and Vc, respectively. Another trend which is evident is that as the in-plane macrocycle increases in size (decreasing Dq^{xy}) the axial ligand field increases. This is opposite to what was observed for the complexes with saturated ligands,[23] but it is consistent with more extensive studies with nickel(II) complexes.[24] Thus, as the ring size increases and Dq^{xy} decreases, the difference between Dq^{xy} and Dq^z would be expected to decrease (given that $Dq^{xy} > Dq^z$). This trend is also manifested in the decreasing value of Dt as the ring size increases. For the complex [Fe(Me$_4$[14]tetraeneN$_4$)(py)$_2$](PF$_6$)$_2$ (Ve) Dq^{xy} is lower than the corresponding value observed for [Fe(Me$_2$[14]tetraeneN$_4$)(py)$_2$](PF$_6$) (Va). The effect of increased methyl substitution is even more dramatically evidenced by the differences in the behaviors of the two 16-membered ring derivatives Vc and Vd. [Fe(Me$_2$[16]tetra-

Table V. Electronic Spectra of the Complexes

Compds	Solvent	d-d bands[a]	Charge transfer[a]
IVa	Toluene	6.21 (10.5), 14.0 (21)	20.45 (5220), 22.6 (5370), 25.0 (4755)
	Mull, 77 K	6.45, 13.6	
	Pyridine	7.93 (32), 12.3 (33.6)	18.35 (6050), 27.0 (10760)
IVb	Toluene	4.8 (14), 11.8 (26)	20.83 (2952), 23.0 (3675), 24.4 (4640)
	Mull, 77 K	~5.0, 11.0	
	Pyridine	6.76 (13), 12.0 (46)	18.9 (4065), 21.3 (sh), 25.6 (10570)
IVc	Toluene	4.8 (11), 11.8 (28)	20.8 (2910), 23.4 (4640), 24.3 (4580)
	Mull, 77 K	~5.0, 11.0	
	Pyridine	6.4 (14), 11.8 (19.3)	18.7 (3600), 21.7 (2600)
IVd	Toluene	5.92 (14.7), 15.4 (119)	22.7 (3777)
	Mull, 77 K	5.86	
	Pyridine	6.10 (11)	18.87 (3600), 20.0 (sh), 26.6 (9060)
IVe	Toluene	5.85 (8), 14.5 (88)	23.25 (3231)
	Mull, 77 K	6.0	
	Pyridine	5.9 (9)	18.05 (2617), 19.8 (2114), 26.4 (9060)
IVf	DMF[b,c]	7.69 (87), 10.1 (140)	
	Mull, 77 K	6.6, 12.9	
	Pyridine	8.0 (38), 12.3 (193)	18.45 (5345), 25.3 (3867)
Va	$MeNO_2$[d]	12.42 (579), 20.0 (493)	
Vb	$MeNO_2$[d]	13.2 (23.2), 19.6 (320)	
Vc	$MeNO_2$[d]	13.5 (20.0), 19.0 (133)	
Vd	$MeNO_2$[d]	12.9 (267)	24.1 (4545)
Ve	$MeNO_2$[d]	12.1 (528), 19.25 (560)	
VI	CH_3CN	12.8 (41)	25.6 (5597), 27.8 (4860), 34.6 (7640)
	Mull	12.10	
VII	CH_3CN		22.8 (2713), 30.7 (3910), 35.7 (4320)

[a] Peak maximum is given in kK ($1\,\text{kK} = 1 \times 10^{-1}\ \mu\text{m}^{-1}$) followed by approximate extinction coefficient in parentheses. [b] Data from ref 15a. [c] This complex has very low solubility in most solvents. [d] Solvent window does not extend into ultraviolet region (380-nm cutoff).

Table VI. Ligand Field Parameters Calculated from Spectrophotometric Data[a,b]

Compd	Dq^{xy}	Dq^z	Dt
Va	2330	814	866
Ve	2255	825	817
Vb	2290	1011	731
Vc	2230	1129	629

[a] For details of calculations, see ref 2c and references cited therein. [b] Energies given in cm^{-1}.

Table VII. Mössbauer Parameters for the Complexes at 298 K

Compd	δ,[a] mm/s	ΔE_q, mm/s	% effect	Spin state (s)
IVa	0.33	3.06	4.18	1
IVb	0.46	2.00	3.88	1
IVc	0.45	1.99	6.61	1
IVd	0.48	1.21	3.75	1
IVe	0.56	0.61	3.75	1
IVf	0.36	2.85	2.10	1
Va	0.40	1.75	3.11	0
Vb	0.48	0.90	1.2	0
Vc	0.52	0.33	2.10	0
Vd[b]	0.54	0	2.94	0
	~1.1	1.5-2.0	1.73	2
Ve	0.44	1.57	1.70	0
VI	0.39	0.86	2.20	0
VII	0.38	0.11	4.30	0
[Fe(II)(phthalocyanine)]	0.52[c]	2.67[c]		1
	0.56[d]	2.60[d]		

[a] Shift is relative to stainless steel; to convert to sodium nitroprusside add 0.16 mm/s. [b] Complex spectrum, indicative of more than one type of iron; one sharp singlet and two broader peaks, one partially obscured under the singlet. [c] Data from ref 25a. [d] Data from ref 25b.

$eneN_4)(py)_2](PF_6)_2$ (Vc) is in the low-spin state at room temperature, but the complex $[Fe(Me_4[16]tetraeneN_4)(py)_2](PF_6)_2$ (Vd) exists as a mixture of high- and low-spin states at room temperature. Apparently, methyl substituents on the α-carbons of the six-membered chelate rings can cause a reduction in the ligand field strength of the macrocycle. Such an effect has been observed for two series of iron(II) complexes with the saturated ligands $[14]aneN_4$ and $Me_6[14]aneN_4$.[23] This may arise, in the present case, from conformational strain due to steric interactions between the methyl groups and the methylene hydrogens of the adjacent saturated chelate rings.

Mössbauer Spectra. The Mössbauer parameters for the iron(II) complexes are listed in Table VII. Except for the complex Vd, which exhibits a spin equilibrium at room temperature, each spectrum consists of a single quadrupole-split doublet with no evidence of iron contaminants. Previous Mössbauer studies on iron(II) complexes having the $S = 1$ ground state have shown that the isomer shift value, δ, for this configuration is typically small. For example, six-coordinate complexes with $S = 1$ have been found to have δ values in the range 0.30–0.50 with respect to stainless steel,[18] while phthalocyaninatoiron(II)[25] has been reported to have a δ value of about 0.52 mm/s relative to stainless steel. Thus, further confirmation for the assignment of the $S = 1$ ground state to these complexes is provided by their isomer shift values, which fall in the range 0.33–0.56 mm/s with respect to stainless steel. The remaining complexes (except for Vd) have isomer shift values in the range normally observed for low-spin iron(II) and thus agree with the spin state assignments that were made on the basis of the magnetic data. The Mössbauer spectrum of $[Fe(Me_4[16]tetraeneN_4)(py)_2](PF_6)_2$, Vd, is unusual. The spectrum of this material supports the contention that two different types of iron are present. One type has a single narrow resonance, showing no splitting, with a δ value of 0.54 mm/s relative to stainless steel. The other type of iron shows two peaks of equal intensity, with one peak partially obscured by the single sharp resonance. The quadrupole splitting for this species is in the range 1.5–2.0 mm/s and has an approximate center shift, δ, of 1.1 mm/s with respect to stainless steel. The two different patterns observed agree well with values expected for a mixture of low-spin and high-spin iron(II). Consequently, the Mössbauer spectrum of this complex confirms the assignment of a spin state equilibrium for this complex.

In a recent report from our laboratories,[23] we discussed the effect of ring size on the Mössbauer parameters for a series of low-spin iron(II) complexes with unsubstituted saturated tetraaza macrocyclic ligands. It was found that as the total ligand field exerted by the macrocycle and the axial ligands increases, the isomer shift, δ, decreases. The isomer shift value, δ is dependent upon the s-electron density at the iron nucleus, with increasing s-electron density causing a decrease in the isomer shift. For low-spin iron(II), increasing the σ-donor strength and/or increasing the δ-acceptor ability of the coordinated ligands will result in lower isomer shift values. Therefore, a decrease in ring size should produce a decrease in the isomer shift, since the smaller ring exerts a greater ligand field strength. This trend is observed for both the square-planar complexes IV and for the six-coordinate dipyridine complexes V. For the square-planar ($S = 1$) complexes the smallest δ values are observed for the two 14-membered derivatives (IVa and IVf, 0.33 and 0.36 mm/s, respectively); whereas, the largest δ values are observed for the two 16-membered ring derivatives (IVd and IVe, 0.48 and 0.56 mm/s, respectively). Comparison with the δ value reported for phthalocyaninatoiron(II) suggests that the 16-membered ring ligand phthalocyaninato(2−) exerts a total ligand field (summation of σ and π effects) somewhat greater than that of Me_4-[16]tetraenato(2−) and somewhat less than that of Me_2[16]-tetraenato(2−). The isomer shift values observed for the series of bis(pyridine)bis(β-diimine) complexes (V) also show a marked decrease as the ring size decreases. For the series of rings with two methyl substituents (Va, Vb, and Vc), δ decreases 0.08 mm/s on going from a 14- to 15-membered ring and 0.4 mm/s on going from a 15- to 16-membered ring. Another important aspect of this isomer shift data is the fact that in both series of complexes (IV and V), increasing the number of methyl groups from two to four on the α-carbon of the unsaturated six-membered chelate rings results in large isomer shifts for both the 14- and 16-membered ring derivatives. Thus, the isomer shift parameters add further support to the conclusion that these methyl groups cause the ligands to exert weaker ligand fields.

In our earlier reports on low-spin iron(II) complexes, we have suggested that ΔE_q may reflect the tetragonality ($Dq^{xy} - Dq^z$) of a tetradentate macrocyclic complex. The complexes V presented here also support this contention. In the series $[Fe(Me_2[Z]tetraeneN_4)(py)_2]^{2+}$ (Va, Vb, and Vc) the splittings decrease in the order 1.75, 0.90, to 0.33 mm/s for the complexes of the 14-, 15-, and 16-membered rings, respectively. This parallels the trend in $Dq^{xy} - Dq^z$ differences, 1515, 1279, and 1101 cm^{-1}, calculated for Va, Vb, and Vc, respectively (Table VI). The square-planar ($S = 1$) complexes reported here show a similar trend. ΔE_q varies from 3.06 mm/s for $[Fe(Me_2[14]tetraenato(2-)N_4)]$ (IVa) to 0.61 mm/s for $[Fe(Me_4[16]tetraenato(2-)N_4)]$ (IVe). Since the electronic population of an $S = 1$ ground state will make a fixed contribution to the electric field gradient about an iron nucleus, deviations from this fixed value must result from ligand dissymmetry. This interpretation also requires that the ligand and valence electron contributions be of the same sign, since the greatest distortion would occur with the smallest rings. For both $[Fe(Me_n[Z]tetraenatoN_4(2-))]$ and $[Fe(Me_n[Z]tetraeneN_4)(py)_2](PF_6)_2$ the ΔE_q values are smaller for the tetramethyl derivatives than for the corresponding dimethyl congeners. This again can be interpreted in terms of the weaker in-plane ligand field exerted by the Me_4 ligands as compared to the Me_2 ligands.

The Mössbauer parameters observed for the remaining two complexes $[Fe(Me_2IE[15]tetraeneN_4)(CH_3CN)](PF_6)_2$ (VI) and $[Fe(Me_2(IE)_2[16]tetraeneN_4)](PF_6)_2$ (VII) are very similar to those observed for the corresponding 15- and 16-membered ring *cis*-hexaene complexes. The only major distinction is that the *trans*-hexaene derivative VII has a very small ΔE_q value (0.11 mm/s) which is 0.15 mm/s less than that observed for the corresponding *cis*-hexaene derivative IIIc.[2a] This indicates that the distortion of the ligand framework from O_h symmetry is much less extensive for the trans complex than that for the cis complex.

Acknowledgment. These studies were supported by Grant No. GM-10040 of the National Institute of General Medical Sciences of the U.S. Public Health Service. Part of the information contained in this article was developed during the course of work under Contract AT(07-2)-1 with the U.S. Energy Research and Development Administration. We thank Dr. David G. Karraker for assistance with the temperature-dependent magnetic susceptibilities studies.

References and Notes

(1) (a) Evans Chemical Laboratory, The Ohio State University; (b) Savannah River Laboratory, E. I. duPont de Nemours and Co.

(2) (a) D. P. Riley, J. A. Stone, and D. H. Busch, *J. Am. Chem. Soc.*, **98**, 1752 (1976); (b) K. S. Bowman, D. P. Riley, D. H. Busch, and P. W. R. Corfield, *ibid.*, **97**, 5036 (1975); (c) K. S. Bowman and D. H. Busch, unpublished results.

(3) R. Breslow, R. Fairweather, and J. Keana, *J. Am. Chem. Soc.*, **89**, 2135 (1967).

(4) (a) A. A. Grinberg and Kh. I. Gil'dengershel', *Neorg. Khim. Akad. Nauk SSSR*, **26**, 115 (1951); (b) V. A. Golovnya and Chia-Chien Ni, *Zh. Neorg. Khim.*, **6**, 131 (1961); (c) Y. Y. Kharitonov, Chia-Chien NI, and A. V. Babaeva, *Dokl. Akad. Nauk SSSR*, **141**, 645 (1961); (d) Y. Y. Kharitonov, Chia-Chien Ni, and A. V. Babaeva, *Zh. Neorg. Khim.*, **7**, 997 (1962); (e) Y. Y. Kharitonov, Chia-Chien Ni. and A. V. Babaeva, *ibid.*, **8**, 34 (1963).

(5) S. Koch, R. H. Holm, and R. B. Frankel, *J. Am. Chem. Soc.*, 97, 6714 (1975).

(6) L. F. Lindoy, V. Katović, and D. H. Busch, *J. Chem. Educ.*, **49**, 117 (1972).

(7) J. Lewis and R. G. Wilkins, "Modern Coordination Chemistry", Interscience, New York, N.Y., 1960, p 403.

(8) D. G. Karraker, J. A. Stone, E. R. Jones, Jr., and N. Edelstein, *J. Am. Chem. Soc.*, **92**, 4841 (1970).

(9) G. S. Olah, S. J. Kuhn, S. H. Flood, and B. A. Hardie, *J. Am. Chem. Soc.*, **86**, 1039 (1964).

(10) R. G. Burns, M. G. Clark, and A. J. Stone, *Inorg. Chem.*, **5**, 1268 (1966).

(11) D. Hall and F. H. Moore, *J. Chem. Soc. A*, 1822 (1966).

(12) A. Earnshaw, E. A. King, and L. F. Larkworthy, *J. Chem. Soc. A*, 1048 (1968).

(13) (a) C. G. Barraclough, R. L. Martin, S. Mitra, and R. C. Sherwood, *J. Chem. Phys.*, **53**, 1643 (1970); (b) B. W. Dale, R. J. P. Williams, C. E. Johnson, and T. L. Thorp, *ibid.*, **49**, 3441 (1968); (c) A. B. P. Lever, *J. Chem. Soc.*, 1821 (1965).

(14) (a) J. P. Collman and C. A. Reed, *J. Am. Chem. Soc.*, **95**, 2048 (1973); (b) J. P. Collman, N. Kim, J. L. Hoard, G. Lang, L. J. Radonovich, and C. A. Reed, Abstracts, 167th National Meeting of the American Chemical Society, Los Angeles, Calif., Spring, 1974, No. INOR-29.

(15) (a) T. J. Truex and R. H. Holm, *J. Am. Chem. Soc.*, **94**, 4529 (1972); (b) S. C. Tang, S. Koch, G. N. Weinstein, R. W. Lane, and R. H. Holm, *Inorg. Chem.*, **12**, 2589 (1973).

(16) (a) P. J. van der Put and A. A. Schilperoord, *Inorg. Chem.*, **13**, 2476 (1974); (b) M. J. Baker-Hawkes, E. Billig, and H. B. Gray, *J. Am Chem. Soc.*, **88**, 4870 (1966); (c) R. Williams, E. Billig, J. H. Waters, and H. B. Gray, *ibid.*, **88**, 43 (1966).

(17) P. J. M. W. L. Birker, J. J. Bour, and J. J. Steggerda, *Inorg. Chem.*, **12**, 1254 (1973), and references cited therein.

(18) (a) E. König, G. Ritter, and B. Kanellakopulos, *J. Chem. Phys.*, **58**, 3001 (1973); (b) E. König and K. Madeja, *Inorg. Chem.*, **7**, 1848 (1968).

(19) R. L. Carlin, *J. Chem. Educ.*, **43**, 521 (1966).

(20) (a) J. P. Jesson, S. Trofimenko, and D. R. Eaton, *J. Am. Chem. Soc.*, **89**, 3158 (1967); (b) D. M. L. Goodgame and A. A. S. C. Machado, *Inorg. Chem.*, **8**, 2031 (1969); (c) J. C. Dabrowiak, P. H. Merrell, and D. H. Busch, *ibid.*, **11**, 1979 (1972); (d) V. L. Goedken, P. H. Merrell, and D. H. Busch, *J. Am. Chem. Soc.*, **94**, 3397 (1972).

(21) R. C. Stoufer, D. H. Busch, and W. B. Hadley, *J. Am. Chem. Soc.*, **83**, 3732 (1961).

(22) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).

(23) D. D. Watkins, Jr., D. P. Riley, J. A. Stone, and D. H. Busch, *Inorg. Chem.*, **15**, 387 (1976).

(24) D. H. Busch, *Helv. Chim Acta, Alfred Werner Commemoration Volume*, 174 (1967); R. Sperati, Ph.D. Thesis, The Ohio State University, 1971.

(25) (a) A. Hudson and H. J. Whitfield, *Inorg. Chem.*, **6**, 1120 (1967); (b) T. H. Moss and A. B. Robinson, *ibid.*, 7, 1692 (1968); (c) I. Dezsi, A. Balazs, B. Molnar, V. D. Gorobchenko, and I. I. Lukashevich, *J. Inorg. Nucl. Chem.*, **31**, 1661 (1969).

Hydroxo-Bridged Platinum(II) Complexes. 1. Di-μ-hydroxo-bis[diammineplatinum(II)] Nitrate, $[(NH_3)_2Pt(OH)_2Pt(NH_3)_2](NO_3)_2$. Crystalline Structure and Vibrational Spectra

R. Faggiani,[1a] **B. Lippert,**[1b] **C. J. L. Lock,***[1a] **and B. Rosenberg***[1b]

Contribution from the Department of Biophysics, Michigan State University, East Lansing, Michigan 48823, and from the Institute for Materials Research, McMaster University, Hamilton, Ontario L8S 4M1, Canada. *Received June 4, 1976*

Abstract: The crystal structure of the complex di-μ-hydroxo-bis[diammineplatinum(II)] nitrate, $[(NH_3)_2Pt(OH)_2Pt(NH_3)_2](NO_3)_2$ has been determined by x-ray diffraction. The triclinic crystal, space group $P\bar{1}$, has cell dimensions $a = 6.763$ (12) Å, $b = 7.890$ (18) Å, $c = 7.256$ (13) Å, $\alpha = 92.3$ (1)°, $\beta = 133.1$ (1)°, and $\gamma = 91.0$ (2)° and has one formula unit in the unit cell. Data were collected using Mo Kα radiation and a Syntex P$\bar{1}$ diffractometer. The crystal structure was determined by standard methods and refined to $R_2 = 0.0575$. The cation is a centrosymmetric hydroxo-bridged dimer with each platinum atom having roughly square planar coordination. Infrared and Raman spectra are discussed.

Coordination complexes of platinum have received much attention in recent years because they represent a new class of potent antitumor agents.[2] *cis*-Dichlorodiammineplatinum(II), the first active platinum complex discovered, is meanwhile in phase II clinical trials in man and results show that it is a drug of high activity in a series of malignant diseases.[3] Of the "second generation" platinum drugs with antitumor activity the so called "platinum-pyrimidine blues" are particularly interesting.[4] They are water soluble, deep blue or purple compounds formed when the diaquo species of *cis*-dichlorodiammineplatinum(II), $[cis\text{-}Pt(NH_3)_2(H_2O)_2]^{2+}$, is reacted with 2,4-dihydroxopyrimidines or substituted derivatives. Although the nature and structure of these completely amorphous compounds are still unclear there are indications from their EPR spectra as well as from the platinum concentration dependency of their formation that they might contain species which exhibit strong metal-metal interactions.[5] It was in this respect interesting that from a solution of the platinum starting material, *cis*-diaquodiammineplatinum(II) dinitrate, an air-stable dimeric hydroxo-bridged platinum compound, di-μ-hydroxo-bis[diammineplatinum(II)] nitrate, could be isolated and characterized. Moreover, this compound is formed in a pH range where, with the 2,4-dihydroxopyrimidine, the blues are formed. It is one of the very rare examples of isolated hydroxo complexes of platinum(II). To our knowledge only one other platinum(II)-hydroxo complex, a dimer with two phosphinato bridges and tertiary phosphines and hydroxo groups as terminal ligands is sufficiently well characterized.[6] Other isolated platinum(II) complexes claimed to contain hydroxo groups are generally doubted today.[6,7] It is known, however, that platinum(II) hydroxo complexes exist in aqueous solution and that their formation from the corresponding aquo complexes is responsible for the acidity of many dissolved platinum(II) complexes.[7] Di-μ-hydroxo-bis[diammineplatinum(II)] nitrate has been prepared previously but its dimeric structure was not recognized and the obtained product had been formulated as a monomer, *cis*-monohydroxomononitratoplatinum(II), $cis\text{-}Pt(NH_3)_2(OH)(NO_3)$.[8]

Experimental Section

Preparation of Compounds. Di-μ-hydroxo-bis[diammineplatinum(II)] nitrate was prepared in the following way: 3 g of *cis*-dichlorodiammineplatinum(II) (Engelhard Industries) was stirred with 3.35 g of $AgNO_3$ (99% of theory) in 50 ml of water in a stoppered flask at room temperature for 20 h. The flask was wrapped in Al-foil because of the photosensitivity of the formed diaquo species.[9] The precipitated silver chloride was filtered and washed with 5 ml of water. The pale yellow solution (pH $\simeq$ 2) was then titrated with 1 N NaOH to pH 6.44, slightly warmed to prevent early precipitation, quickly filtered, and kept in a stoppered flask for 1 day at 0 °C in the refrigerator. The precipitate was then filtered, washed with 20 ml of water, then with ether, and dried under rotary pump vacuum for several hours; 1.56 g of the white microcrystalline compound was thus obtained. It was recrystallized once from water.

Concentration of the filtrate (rotary evaporator, 30 °C water bath) to 30 ml volume and cooling to 0 °C for 24 h gave a second crop of crystals, yield 0.2 g.

Further concentration of the filtrate to 15 ml volume produced a yellow solution and after a day at 0 °C, 0.1 g of the colorless platinum dimer was obtained and also 0.25 g of a crystalline species which was deep yellow and transparent. Single-crystal x-ray analysis showed that it is a cyclic hydroxo-bridged platinum trimer. We shall report on this in detail later.[10]

The yield of the second and third crop of di-μ-hydroxo-bis[diammineplatinum(II)] nitrate could be increased if the pH of the filtrate of the previous fraction was readjusted to about 6.4 by means of NaOH. The yield of the compound was decreased if the solution of the *cis*-diaquodiammineplatinum(II) dinitrate was titrated to a pH to below 6.44, for example, only to 4.5–6.

Crystals of the compound of suitable size for x-ray analysis were obtained if the preparation was slightly modified such that the titrated and filtered solution of pH 6.44 was kept in an open beaker in a water bath at 37 °C which was covered with Al-foil. After 18 h very pale yellow transparent crystals up to 3 mm long were filtered, washed with 10 ml of water, and dried as mentioned above. The yield of the first fraction was 0.56 g. The pH of the filtrate was readjusted from 5.0 to 6.44 and after two more days 0.76 g of the compound was collected. A further crop was obtained after two more days (pH readjusted to 6.44). The crystals were no longer pale yellow, however, but light