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High- and Low-Spin Six-Coordinate Complexes of Iron(II) with a Saturated Tetradentate Macrocyclic Ligand

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Received November 15, 1971

Six-coordinate tetragonal complexes of iron(II) have been synthesized with a 14-membered, fully saturated, macrocyclic, tetradentate ligand having nitrogen donors. The ligand is *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (abbreviated [14]aneN₄) and the complexes are of the general formula Fe^{II}([14]aneN₄)X₂, where X⁻ = CN⁻, NO₂⁻, NCS⁻, Cl⁻, Br⁻, I⁻, CH₃CO₂⁻, and BF₄⁻. Salts of the cation Fe^{II}([14]aneN₄)(CH₃CN)₂²⁺ have also been studied. The iron(II) atom exists predominantly in the low-spin form when the axial ligands are relatively strong. In spectrochemical order the examples are CN⁻, NO₂⁻, NCS⁻, or CH₃CN. These compounds are the first examples of stabilization of the low-spin state of Fe²⁺ with saturated nitrogen as the most abundant donors, an accomplishment attributable to the enhanced ligand field strength due to the constrictive effect of the mechanically confining in-plane macrocyclic ligand. The absence of low-energy charge-transfer bands permits the study of the d-d spectra of these complexes, from which we estimate $Dq^{low\ spin} = 2100\text{ cm}^{-1}$ and $B = 540\text{ cm}^{-1}$ (for the acetonitrile complex of Fe([14]aneN₄)²⁺). The remaining derivatives constitute a series of high-spin six-coordinate iron(II) complexes showing the spectrochemical series CH₃CO₂⁻ > Cl⁻ > Br⁻ > I⁻ > BF₄⁻. From the spectra $Dq^{high\ spin} = 1400\text{ cm}^{-1}$, so that these systems have made it possible to compare the high- and low-spin Dq values for a single metal ion-ligand combination in fixed geometry (tetragonal). The NCS⁻ (and possibly the NO₂⁻ and CH₃CN) derivative exists as a mixture of spin states. It is inferred that other 14-membered macrocycles having unsaturated donors produce five-coordinated high-spin structures because the high-spin metal ion is too large to remain symmetrically encompassed by the ring. This view is supported by the fact that $Dq^{high\ spin}$ is greater toward Fe²⁺ for the saturated ligand [14]aneN₄ than for the corresponding diimine or tetraimine macrocycles, although the ligand fields of the latter two have both been proven to be greater than that of [14]aneN₄.

Introduction

During the last decade a variety of new tetradentate macrocyclic ligands containing nitrogen donors have been prepared and their metal complexes with Ni(II), Co(I), -(II), -(III), Cu(I), -(II), and Zn(II) have been studied extensively and thoroughly characterized.¹⁻⁴ One of the striking features about the previous work is the relatively small number of complexes reported with the biologically interesting element, iron. Unlike the native iron-porphyrin complexes, their synthetic relatives are well suited for providing additional information on various structural parameters such as ring size and degree of unsaturation and the ways in which they affect the chemistry of the coordinated metal ion. We are engaged in an extensive study of the iron complexes of synthetic macrocycles and have disclosed a few of their properties in preliminary communications.^{5,6}

Recently, the characterization and isolation of a

variety of iron complexes containing the macrocycle 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene ([14]4,11-dieneN₄) have been reported.⁷ This cyclic ligand which was discovered by Curtis^{8,9} contains two isolated imine functions that can be reduced to yield a saturated cyclic secondary amine. We report here the synthesis and characterization of several iron(II) and iron(III) complexes of *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane which is abbreviated *ms*-5,5,7,12,12,14-Me₆[14]aneN₄ or more simply [14]aneN₄¹⁰ (Figure 1). The properties of the iron complexes are similar in some respects but simultaneously quite different from those ascribed to the structures containing the diimine ligand [14]4,11-dieneN₄.

Experimental Section

Materials.—All materials were reagent grade and used without further purification unless otherwise noted. Some of the syntheses were carried out in a Vacuum Atmospheres Corp. controlled-atmosphere drybox and the remainder on the "benchtop" under a blanket of nitrogen gas. Solvents referred to as "dry and degassed" were dried over molecular sieves for 2 days before being refluxed under nitrogen gas for 30 min.

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(2) D. H. Busch, *Helv. Chim. Acta, Fasciculus extraordinarius Alfred Werner*, 174 (1967).
(3) N. F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968).
(4) L. F. Lindoy and D. H. Busch, "Preparative Inorganic Reactions," Vol. VI, W. L. Jolly, Ed., Interscience, New York, N. Y., in press.
(5) P. H. Merrell, V. L. Goedken, D. H. Busch, and J. A. Stone, *J. Amer. Chem. Soc.*, **92**, 7590 (1970).
(6) D. H. Busch, K. Farmery, V. Katovic, A. C. Melnyk, C. R. Sperati, and N. E. Tokel, *Advan. Chem. Ser.*, **No. 100**, 44 (1971).

(7) V. L. Goedken, P. H. Merrell, and D. H. Busch, *J. Amer. Chem. Soc.*, **94**, 3397 (1972).
(8) N. F. Curtis, *J. Chem. Soc.*, 4409 (1960).
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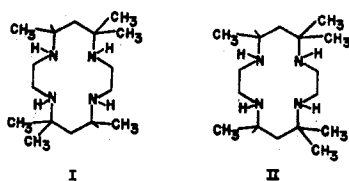


Figure 1.—The saturated 14-membered macrocycles first reported by Curtis: I, *ms*-[14]aneN₄ and *rac*-[14]aneN₄; II, *ms*-12-Me₄[14]aneN₄ and *rac*-12-Me₄[14]aneN₄. *ms* (*meso*) and *rac* (*racemic*) refer to the arrangement of groups about the two asymmetric carbon atoms.

Physical Measurements.—Visible and near-infrared absorption spectra were obtained on a Cary Model 14-R recording spectrophotometer. The solvents used were dry and degassed acetonitrile and chloroform. In the case of chloroform, the ethanol used as a stabilizer was removed using standard procedures¹¹ and the solvent was stored in a dark brown bottle until needed. Spectra were recorded using Teflon-stoppered cells and run immediately after preparation under nitrogen and then again 30 min later. For determination of extinction coefficients, weighings were made on the solids in the atmosphere and the samples were quickly transferred to the drybox where 10⁻³–10⁻¹ M solutions were prepared. The absorption spectra between 4.5 and 30 kK were recorded. Mulls were prepared in an inert atmosphere using filter paper impregnated with Halocarbon 25-S5 grease (Halocarbon Products Corp). The thermostated mull spectra were obtained by means of a dewar flask with quartz windows which contained liquid nitrogen. In the case of the thiocyanate complex the dewar was filled with dibutyl phthalate at 70°. The sealed mull was lowered into the liquid, 10 min was allowed for temperature equilibration and the spectrum was recorded by passing the spectrometer beam through the dewar thermostating liquid and mull.

Infrared spectra were obtained on a Perkin-Elmer Model 337 recording spectrometer using Nujol mulls between KBr disks. In the case of Fe([14]aneN₄)(BF₄)₂ Nujol mulls between Irtran-2 plates (Barnes Engineering Co.) and polyethylene plates were used to record the spectrum from 2.5 to 24 μ. The conductivities of the complexes were obtained using an Industrial Instruments Model RC 16B conductivity bridge. The measurements were determined at 25° at 1000 Hz on 10⁻³ M solutions. The nitromethane solvent was purified¹² according to standard procedures.

Solid-state magnetic moments were determined at room tem-

(10) The complexity of the ligands discussed here requires that nomenclatures now in use be changed [compare N. F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968), with D. H. Busch, *Helv. Chim. Acta, Fasciculus extraordinarius Alfred Werner*, 174 (1967). Both authors adopted trivial names (*tet a* and *m-1,7CTH*) for the ligand under discussion.] In order to represent these and more complicated related ligands by meaningful abbreviations we are recommending a new system based in part on the one suggested by Curtis for cyclic unsaturated structures. In this system the macrocyclic ring size is still indicated by a number in brackets. In the names for the compounds, the locants for the heteroatoms are minimized. Thus the locants of the nitrogen atoms of I and II of Figure 1 (numbering first through the dimethylene bridge) become 1,4,8,11. In the absence of any unsaturation the ending "ane" is adopted. Substituents may be indicated with or without locants depending on the information that needs to be conveyed. The full abbreviation for structure I then becomes *ms*- or *rac*-5,5,7,12,12,14-Me₄[14]ane-1,4,8,11-N₄ whereas II is *ms*- or *rac*-5,5,7,12,14,14-Me₄[14]ane-1,4,8,11-N₄. These represent the most complex abbreviations possible and often would be shortened further, for example, Me₄[14]aneN₄. Now if we require that the information carried in the abbreviation should be sufficient to distinguish between the two structures (I and II), we preserve the first locants in the abbreviations that are different: 12-Me₄[14]aneN₄ and 14-Me₄[14]aneN₄. Since the subject of this report deals almost exclusively with metal complexes of the *meso* form of I, the short abbreviation [14]aneN₄ will be used. Our system is designed to use the simplest abbreviation that contains the necessary structural information in the context of the discussion that is at hand. While these abbreviations are still more cumbersome than we might like, they are short enough to use in tabulation entries and one can readily learn to derive from them much pertinent structural information. In this extended form the convention is applicable to all macrocyclic ligands not involving fused rings. We continue to treat the latter with trivial abbreviations.

(11) A. I. Vogel, "Textbook of Practical Organic Chemistry," 3rd ed, Longmans, Green and Co., London, 1956, p 176.

(12) G. A. Olah, S. J. Kuhn, S. H. Flood, and B. A. Herdin, *J. Amer. Chem. Soc.*, **86**, 1043 (1964).

perature unless otherwise noted under 35 mm of helium gas using the Faraday method.¹³ The diamagnetic correction for [14]aneN₄ was measured and found to be -254×10^{-6} cgsu.¹⁴ Diamagnetic corrections for the other ligands and counterions were made using Pascal's constants.¹⁵

Proton magnetic resonance spectra (pmr) were obtained on Varian A-60A and HA-100 spectrometers fitted with variable-temperature probes. Sample temperatures were determined by chemical shifts for methanol. The solvent used for the iron complexes was 3:1 CDCl₃-CHCl₃ and shifts were calculated relative to tetramethylsilane (TMS) using 7.24 ppm for the hydrogen resonance of chloroform relative to TMS. Samples were run immediately following their preparation under dry nitrogen.

The esr spectrum was obtained using a Varian V4500-10A spectrometer on the solid thiocyanate complex by Dr. Ernest Gore of this department. Mass spectra were run using an MS-9 spectrometer at an ionizing potential of 70 eV. Elemental analyses were performed by Chemalytics, Inc., Alfred Bernhardt, Galbraith Laboratories, and Crotian Laboratories.

Preparation of the Ligand.—The acid salt of the ligand, [14],4,11-dieneN₄·2HClO₄ or [14],4,11-dieneN₄·2HBF₄, was prepared by the method of Curtis¹⁶ and the corresponding nickel(II) complex was synthesized by the reaction of nickel acetate with the acid salt in methanol.¹⁷ Reduction of the imine functions was accomplished using Raney nickel alloy and NaOH according to the method of Warner and Busch.¹⁸ Separation of the *meso* and *racemic* nickel complexes, as well as the recovery of the ligand, was as previously described.¹⁴ The isolated ligand was once recrystallized from ethanol-water and the resulting dihydrate was dried under vacuum (0.02 mm) for 2 days using P₄O₁₀. Mass spectrum *m/e* of parent ion: calcd, 284; obsd, 284.

[Fe([14]aneN₄)(CH₃CN)₂](BF₄)₂·1.5CH₃CN.—(This and the following syntheses were carried out in an inert atmosphere.) To 800 ml of dry and degassed acetonitrile, which was heated to 50–60°, was added 3.68 g (21 mmol) of anhydrous ferrous acetate. The resulting suspension was stirred for 10 min prior to the addition of 6.0 g (21 mmol) of [14]aneN₄. The ligand and the iron salt dissolved slowly to form first a light blue solution, which after 30 min turned a blue color with a small amount of green suspended solid. A portion of the solid Fe([14]aneN₄)(CH₃CO₂)₂ was removed by filtration, washed with a few milliliters of CH₃CN, and dried under a stream of nitrogen. To the bulk of the remaining suspension was added slowly 7.64 g (42 mmol) of 48% aqueous HBF₄. Addition of the acid to the warm solution resulted in the dissolution of the diacetato salt and the formation of the deep purple bis(acetonitrile) adduct. The solution was filtered hot and the volume was reduced *in vacuo*, using mild heat, to 150 ml. The [Fe([14]aneN₄)(CH₃CN)₂](BF₄)₂·1.5CH₃CN which crystallized was removed by filtration and washed with a small amount of CH₃CN. Additional material was recovered from the filtrate by addition of about 200 ml of dry, degassed tetrahydrofuran (THF) followed by about 50 ml of diethyl ether. The acetonitrile adduct was recrystallized from hot acetonitrile to give a 70–90% yield.

Fe([14]aneN₄)(BF₄)₂.—One gram of Fe([14]aneN₄)(CH₃CN)₂(BF₄)₂·1.5CH₃CN was placed *in vacuo* (about 4 days) (0.02 mm) until the color changed from violet to pale blue. The product is sensitive to air and water and must be handled as a solid under dry nitrogen.

Fe([14]aneN₄)X₂ (X⁻ = NO₂⁻, SCN⁻, Cl⁻, Br⁻, and I⁻).—Synthesis of the nitrite and thiocyanate derivatives was accomplished by slowly adding a saturated solution (at 50–60°) of the bis(acetonitrile) adduct in 15 ml of acetonitrile to 20–30 ml of a solution containing an excess of NaNO₂ or LiSCN in a 1:1 ethanol-water mixture. The precipitates which formed upon cooling were removed by filtration, washed with ethanol and ether, and dried under nitrogen. The halides were prepared in a similar manner using the sodium or lithium salts in absolute ethanol. Synthesis of the cyanide compound was accomplished

(13) V. Katovic, L. Lindoy, and D. H. Busch, *J. Chem. Educ.*, **49**, 117 (1972).

(14) L. G. Warner, Ph.D. Thesis, The Ohio State University, 1969.

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

(16) N. F. Curtis and R. W. Hay, *Chem. Commun.*, 524 (1966).

(17) P. H. Merrell, Ph.D. Thesis, The Ohio State University, 1971.

(18) L. G. Warner and D. H. Busch, *J. Amer. Chem. Soc.*, **91**, 4092 (1969).

TABLE I
 ELEMENTAL ANALYSES FOR SOME [14]aneN₄-Fe Complexes

No.	Compd	% C		% H		% N		% Fe	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
III	Fe([14]aneN ₄)(CH ₃ CN) ₂ (BF ₄) ₂ ^a	41.96	41.93	7.11	6.89	16.00	16.06		
IV	Fe([14]aneN ₄)(CN) ₂	55.10	54.41	9.25	9.08	21.42	20.83		
V	Fe([14]aneN ₄)(NO ₂) ₂	44.45	43.83	8.39	8.23	19.44	19.76	12.92	13.12
VI	Fe([14]aneN ₄)(NCS) ₂	47.36	47.03	7.95	7.93	18.41	18.13	12.23	12.03
VII	Fe([14]aneN ₄)Cl ₂	46.71	47.01	8.76	9.03	13.62	13.77		
VIII	Fe([14]aneN ₄)Br ₂	38.40	38.21	7.20	7.44	11.20	11.10	32.00 ^b	32.30 ^b
IX	Fe([14]aneN ₄)I ₂	32.34	32.32	6.06	6.26	9.43	9.48		
X	Fe([14]aneN ₄)(CH ₃ CO ₂) ₂	52.38	52.41	9.24	8.67	12.23	12.06	12.19	12.33
XI	Fe([14]aneN ₄)(BF ₄) ₂	37.37	36.88	7.06	7.34	10.90	10.70	10.87	10.57
XII	[Fe([14]aneN ₄)Cl ₂]ClO ₄	37.62	37.58	7.05	7.48	10.97	10.99		

^a Contains 1.5 CH₃CN of crystallization. ^b Bromide analysis.

by rapid stirring of a suspension of 75 mg (1.5 mmol) of NaCN and 500 mg (0.75 mmol) of [Fe([14]aneN₄)(CH₃CN)₂](BF₄)₂·1.5CH₃CN in 25 ml of absolute ethanol. After 10 min the solids dissolved to form a yellow solution and slow addition of 25 ml of H₂O caused the crystallization of the light brown dihydrate of the cyanide complex. This material was removed by filtration, washed with THF and ether, and dried under nitrogen. Drying the solid *in vacuo* (0.02 mm) for 2 days over P₂O₅ removed the waters of hydration leaving a light brown powder. All of these complexes could be recrystallized by redissolving in a minimum amount of chloroform, filtering, and reducing the filtrate volume until crystallization occurred. The yields were 50–90%.

[Fe([14]aneN₄)Cl₂]ClO₄.—A 1-mmol (0.4-g) sample of Fe([14]aneN₄)Cl₂ was dissolved in 50 ml of CH₃CN and 5 drops of 70% HClO₄ was added. *Caution!* This compound was prepared in early stages of the investigation before realization of the hazardous nature of perchlorate salts of these complexes. Detonations have occurred with some of the Fe([14]aneN₄)-ClO₄ derivatives previously described⁷ suggesting the preparation and handling of the structurally similar [14]aneN₄ complexes are inadvisable. After the addition of the acid, air was bubbled through the solutions for a few minutes and ether was added to the cloud point. The solution was cooled and the yellow crystalline compound was removed by filtration.

Discussion

The reduced Curtis ligand exists in four isomeric forms (Figure 1). An extensive stereochemical investigation of the nickel complexes of these ligands revealed that the meso form of [14]aneN₄ isomer (I) and the racemate of the 14-Me₆[14]aneN₄ macrocycle (II) are most likely to form planar metal complexes.^{14,18} Molecular models indicated that nonbonding interactions developed between the substituents on the chelate rings in the folded cis structures and that these are alleviated in the planar arrangement of the ligand. These earlier observations greatly facilitated the stereochemical characterization of the newly synthesized iron complexes (Table I). For all of the iron complexes of this report it is assumed that the monodentate ligands occupy trans axial sites with the iron atom in the plane defined by the four donor atoms of the macrocycle (Figure 2). The meso form of [14]aneN₄ was chosen over 14-Me₆[14]aneN₄ (II) for the study because synthesis of the latter required the slow reaction of Ni(en)₃(ClO₄)₂ with acetone (4–8 days) followed by a tedious separation of the 14-Me₆[14]aneN₄ and [14]aneN₄-Ni complexes.¹⁹ The pure diacid salt of [14]aneN₄ on the other hand could be made with rapidity and in large quantities by reaction of ethylenediamine and acetone in the presence of a strong acid.¹⁶ Formation of the nickel complex for use in the hydrogenation step was easily accomplished and the final

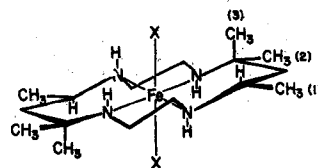


Figure 2.—The idealized stereochemistry of the isolated iron complexes Fe([14]aneN₄)X₂ where X is a monodentate ligand.

product was not contaminated with 14-Me₆[14]aneN₄.

The infrared spectrum of the pure, dry [14]aneN₄ ligand, which was obtained by treating [Ni([14]aneN₄)](ClO₄)₂ with excess CN⁻ ion, shows a characteristic peak in the N–H stretching region at 3279 cm⁻¹ (Table II). However the dihydrate [14]aneN₄·

TABLE II
INFRARED ASSIGNMENTS^a (CM⁻¹)

Compd ^b	Axial ligand	Assignments
[14]aneN ₄		(NH) 3279 (vs), 1300 (m), 1280 (m), 1270 (m), 1242 (m), 1220 (vs), 807 (vs), 790 (vs), 740 (vs)
III	CH ₃ CN	(NH) 3240 (vs); (CN) 2280, (vw), 2250 (vs), 2230 (s); (BF ₄) ₂ 1065 (s, br); ν ₄ 522
IV	CN ⁻	(NH) 3240 (w), 3180 (vs); (CN) 2040 (vs)
V	NO ₂ ⁻	(NH) 3160 (vs); ν _{as} (NO ₂) 1350 (m), 1315 (s, br); ν _s 1240 (s, br), 1210 (s); δ(NO ₂) 820 (s), 830 (s); ρ _w (NO ₂) 610 (w), 645 (w)
VI	NCS ⁻	(NH) 3240 (w), 3220 (s); ν ₁ (CN) 2090 (s), 2080 (s); ν ₂ 485 (w), 490 (w); ν ₃ 790 (s)
VII	Cl ⁻	(NH) 3210 (s)
VIII	Br ⁻	(NH) 3160 (s)
IX	I ⁻	(NH) 3188 (s), 3130 (s)
X ^c	CH ₃ CO ₂ ⁻	(NH) 3240 (s), 3140 (s); ν _{as} (CO ₂ ⁻) 1590 (s, br); ν _{ss} 1400 (s); ν ₅ 650 (s)
XI	BF ₄ ⁻	(NH) 3265 (s); ν ₃ (T _d)(BF ₄) 1080 (s, br), 960 (s, br); ν ₄ (T _d) 522 (s), 512 (s)
XII	Cl ^{-d}	(NH) 3215 (s); ν ₃ (ClO ₄) 1080 (s, br); ν ₄ 625 (s)

^a K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1970. ^b Structure of compounds shown in Table I and Figure 2. ^c Assignments from J. D. Donaldson, J. F. Knifton, and S. D. Ross, *Spectrochim. Acta*, **21**, 275 (1965). ^d This is an Fe³⁺ complex.

2H₂O which crystallizes from aqueous-ethanol solutions shows a second band at 3247 cm⁻¹ which is probably due to hydrogen-bonded N–H. The ligand has no absorptions in the region characteristic of imine bonds (1500–1600 cm⁻¹) indicating that it is free of the starting material. It has many sharp bands in the so-

(19) N. F. Curtis, Y. M. Curtis, and H. K. J. Powell, *J. Chem. Soc.*, 1015 (1966).

TABLE III
 SOME PHYSICAL PROPERTIES OF [14]aneN₄-Fe Complexes

Compd ^a	Axial ligands	Color	μ_{eff}^b BM	$\Lambda, ^\circ \text{ohm}^{-1} M^{-1}$	Mass spectrum (<i>m/e</i> of parent ion)	
					Calcd	Obsd
III	CH ₃ CN	Purple	1.03	CH ₃ CN, 312		
IV	CN ⁻	Tan	0.53			
V	NO ₂ ⁻	Red-brown	0.67			
VI	NCS ⁻	Turquoise	1.53		456	456
VII	Cl ⁻	Pale green	5.58	CH ₃ NO ₂ , 14 ^d	411	411
VIII	Br ⁻	Pale green	5.47		500	500
IX	I ⁻	Pale green	5.37		594	594
X	CH ₃ CO ₂ ⁻	Pale green	5.70	CH ₃ NO ₂ , 7 ^d	458	458
XI	BF ₄ ⁻	Pale blue	5.70			
XII	Cl ⁻ ^e	Yellow	5.95	CH ₃ OH, 133		

^a The structures of the complexes are given in Table I and Figure 2. ^b Magnetic moment at 25°. ^c The solvent is given followed by the value of the molar conductance at 25°. ^d These values were determined immediately following complete dissolution of the compound. ^e Fe³⁺ complex.

called skeletal region between 1000 and 1400 cm⁻¹, which are useful in detecting the macrocycle in the iron complexes.

Low-Spin Iron(II) Complexes.—The spin state of the iron(II) ion with the [14]aneN₄ macrocycle depends on the ligand field strength of the axial ligand, and both low- and high-spin examples, as well as one exhibiting spin-state equilibrium, were isolated. Most important of the low-spin examples is the bis(acetonitrile) derivative whose general physical and chemical properties are representative of the group; from this compound all the remaining complexes can be derived.

This complex was synthesized from anhydrous iron(II) acetate and the ligand in dry acetonitrile after the addition of a strong acid, such as HBF₄ or HClO₄. However, only very limited use of the latter acid was employed since the resulting perchlorate salts are structurally similar to [Fe([14]aneN₄)(CH₃CN)₂](ClO₄)₂ which is known to be explosive.⁷ In the synthesis, the strong acid functions as a source of hydrogen ions which destroys the intermediate acetate complex by protonation of the acetate anion thus allowing the solvent to enter the primary coordination sphere. The water present in the aqueous strong acids appears to have little effect on the purity of the product. It is, however, necessary to eliminate moisture during the initial stages of the reaction since its presence causes the formation of large amounts of hydrous oxides of iron. This significantly lowers the yield and gives rise to impure materials with very high susceptibilities (~20,000 × 10⁻⁶ cgsu).

The compound [Fe([14]aneN₄)(CH₃CN)₂](BF₄)₂ is only moderately sensitive to oxygen in the solid state and can be handled for short periods of time in the atmosphere. However, upon standing in the atmosphere, its acetonitrile solutions quickly turn a yellow-brown color which changes over a period of hours to an intense red-violet color. Yellow solids can be isolated in early stages of the oxidation but analyses were poor for the expected iron(III) derivative. In addition the infrared spectra of these materials indicated the presence of various amounts of an amine salt which is probably due to the destruction of the complex and possibly also the fragmentation of the ligand itself. On the other hand the products isolated from the red-violet solution show that the macrocycle is intact and iron(II) complexes containing dehydrogenated forms of the ligand can be isolated. The properties and structures of the products from the reaction with

molecular oxygen constitute the subject of a future communication.²⁰

The infrared spectral data for [Fe([14]aneN₄)(CH₃CN)₂](BF₄)₂·1.5CH₃CN (III) show a strong, very sharp N-H stretch at 3240 cm⁻¹ which is shifted to lower energy than that of the free amine. Coordinated acetonitrile gives two very weak absorptions at 2280 and 2250 cm⁻¹ which occur at higher energy than the uncoordinated CH₃CN signal (2230 cm⁻¹). Typical absorptions for the uncoordinated BF₄⁻ anion are also found at 1065 and 522 cm⁻¹. The molar conductance of the compound in acetonitrile (Table III) suggests that the material is a 2:1 electrolyte²¹ which is consistent with the structural assignment.

Magnetic studies on the solid acetonitrile complex gave a value of 1.03 BM for the μ_{eff} (Table III) which is high for spin-paired iron(II). Low-spin iron(II) has an A_{1g} ground state and gives a temperature-independent susceptibility of about 50 × 10⁻⁶ cgsu (about 0.6 BM) due to second-order Zeeman interactions with higher ligand field terms.²² In the present case the high anomalous moment is due in part to the fact that the compound very readily loses the coordinated nitrile ligands to generate a high-spin species. In fact, considerable effort was expended in measuring the moments of freshly prepared samples exhibiting various degrees of crystallinity until the value recorded in Table III was achieved. It is not unlikely that this compound also involves a spin-state equilibrium as does the thiocyanate derivative (see below) of which it is a structural relative. However, the visible spectrum is that of spin-paired iron(II); it is discussed fully below.

The infrared spectra of the remaining low-spin compounds show the presence of coordinated CN⁻, NO₂⁻, and N-bonded NCS⁻. Correct elemental analyses and the absence of evidence for uncoordinated anions (infrared spectra) prove that these materials contain six-coordinated iron(II). This structure is further substantiated by the mass spectrum of the thiocyanate derivative (Table III) which shows the correct parent ion at *m/e* 456 and a second intense peak corresponding to the loss of one of the axial ligands. The CN⁻ and

(20) J. C. Dabrowiak, F. V. Lovecchio, and D. H. Busch, Abstracts, 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, No. INOR 140; J. C. Dabrowiak and D. H. Busch, to be submitted for publication.

(21) For typical conductance values see R. L. Dutta, D. W. Meek, and D. H. Busch, *Inorg. Chem.*, **9**, 1215 (1970), and references therein.

(22) B. N. Figgis, "Introduction to Ligand Fields," Interscience, New York, N. Y., 1966, p 280.

NO_2^- complexes decompose at the probe temperature of the mass spectrometer and produce spectra having only low m/e values. These complexes are all soluble in chloroform and the NO_2^- and SCN^- derivatives are soluble in benzene without noticeable changes in color. However, attempts to determine conductance values or to run solution spectra under nitrogen in nitromethane, acetonitrile, or alcohols proved impossible because of either limited solubility or drastic color changes accompanying dissolution.

The proton magnetic resonance (pmr) data for the methyl resonances of these complexes are presented in Table IV. Unlike the bis(acetonitrile) adduct these

TABLE IV
PMR SPECTRA OF SOME Fe-[14]aneN₄ COMPLEXES^a

Compd	Axial ligands	CH ₃ (1) ^b	CH ₃ (2)	CH ₃ (3)
IV ^c	CN ⁻	0.99	1.02 s	1.42 s
V ^c	NO_2^-	1.17	1.21 s	0.61 s
VI ^d	NCS ⁻	1.40	1.44 s	1.03 s

^a Spectra were recorded in CDCl_3 and shifts are reported in ppm relative to TMS. For the signal assignments refer to Figure 2. ^b A doublet with $J = 7.0$ Hz. ^c Recorded at $37 \pm 2^\circ$. ^d Recorded at $-61 \pm 2^\circ$.

complexes have sufficient solubilities in suitable solvents to permit a more detailed stereochemical analysis through the use of pmr. The spectrum of the corresponding nickel(II) complex in $\text{DMSO}-d_6$ ¹⁸ shows sharp singlets at 1.15 and 1.72 ppm with the methyl doublet of the asymmetric carbon atom occurring at 1.12 ppm. The remainder of the spectrum gave a complicated series of resonances which are associated with the other protons of the macrocycle. This same pattern occurs with the *trans*-diacidoiron(II) derivatives, strongly suggesting that the macrocyclic ligand has the same configuration about the four asymmetric nitrogen atoms as that proposed for the nickel(II) complex. Molecular models show that the most stable ring conformations are two chair-formed six-membered rings with two equatorial and one axial methyl each and one δ and one λ conformation for the five-membered rings. This produces C_2 symmetry and the structure is shown in Figure 2. Deprotonation of the nitrogen is known to lead to rapid interconversion between isomeric forms but this is not likely to occur in chloroform so that only one form is present during the pmr measurement. The methyl resonances of the iron compounds are all displaced to higher fields relative to those of the nickel complex but the shifts for the cyanide derivatives are particularly interesting. Buckingham and Stevens^{23,24} have shown that large shielding effects should occur for protons situated above the plane of a low-spin d^6 metal system; this is consistent with the relative shifts for the NO_2^- and SCN^- derivatives. The same effect was observed for the $[\text{Fe}([\text{14}]\text{4,11-dieneN}_4)(\text{CH}_3\text{CN})_2]^{2+}$ isomers⁷ reported earlier. However, for $[\text{Fe}([\text{14}]\text{aneN}_4)(\text{CN})_2]$ the opposite effect is observed, wherein the axial methyl resonances lie at low field relative to the equatorial methyl resonances. This reversal in the ordering of the shifts also occurs for the corresponding cobalt(III) complexes and the phenomenon will be discussed more

fully in a future report.²⁵ Of course, an alternate explanation is to assume that the cyanide complex actually has four axial and two equatorial methyl groups but this seems unlikely since the conformations of the chelate rings must almost certainly be identical with those in the NO_2^- and SCN^- derivatives, whose spectra give the expected shifts. Furthermore, this structure would also be unusually strained and intense study of the nickel system has given no evidence for such structures.

The High-Spin Complexes.—The magnetic moments for five of the complexes listed in Table III show that the iron ion has four unpaired electrons. These complexes are six-coordinate and contain axial ligands having weak field strengths, Cl^- , Br^- , I^- , CH_3CO_2^- , and BF_4^- . Following the notion of an average ligand field we conclude that the splitting of the d orbitals is not sufficient to cause spin pairing. These complexes, with the exception of the BF_4^- derivative, are sparingly soluble in acetonitrile at room temperature and only the acetate and chloride have sufficient solubility (10^{-3} M) in nitromethane to obtain conductance values. The acetate readily dissolves giving a pale green solution of low conductance which slowly turns yellow, a change accompanied by increasing conductivity. The same phenomenon is observed for the chloro derivative. This strongly suggests that these materials are originally six-coordinate neutral structures and that nitromethane slowly displaces the axial ligand. In addition, the solubilities of these complexes (except of the BF_4^- species) in chloroform and benzene and the mass spectral parent molecular ions (Table III) are consistent with six-coordination. All of the high-spin complexes are sensitive to oxygen in the solid state and continued exposure produces yellow-brown solids which are difficult to characterize. Chloroform solutions of these materials are very sensitive to oxygen and only small amounts of the gas cause intensely colored solutions to develop. An authentic iron(III) dichloro derivative was isolated from the air oxidation of the iron(II) salt in acetonitrile but obtaining products of acceptable purity is difficult. Problems similar to those described for the attempted oxidation of the acetonitrile adduct were encountered.

The $[\text{Fe}([\text{14}]\text{aneN}_4)(\text{CH}_3\text{CN})_2](\text{BF}_4)_2 \cdot 1.5\text{CH}_3\text{CN}$ (III) complex can be converted into a compound containing the coordinated BF_4^- ion by removal of the acetonitrile under vacuum. Infrared data on $\text{Fe}([\text{14}]\text{aneN}_4)(\text{BF}_4)_2$ show the absence of both the coordinated and the uncoordinated acetonitrile stretching modes. In addition the $\nu_3(T_d)$ band of the BF_4^- ion is split (1080 and 960 cm^{-1}) as is the $\nu_4(T_d)$ band (522 and 512 cm^{-1}) indicating the presence of monodentate BF_4^- . Complexes with this ligand are rare but at least one example has been reported, $\text{Ni}(\text{py})_4(\text{BF}_4)_2$,²⁶ which also has a split $\nu_3(T_d)$ band but only a single $\nu_4(T_d)$ absorption. However, monodentate coordination of a tetrahedral anion lowers the symmetry to C_{3v} causing splitting of both of these bands as has been observed for some sulfato and perchlorato complexes.²⁷ This complex is quite sensitive to moisture

(25) E. Gore, J. C. Dabrowiak, and D. H. Busch, *J. Chem. Soc., Chem. Commun.* in press.

(26) M. R. Rosenthal and R. S. Drago, *Inorg. Chem.*, **4**, 840 (1965).

(27) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1970.

(23) D. A. Buckingham and P. J. Stephens, *J. Chem. Soc.*, 2747 (1964).

(24) P. J. Stephens and D. A. Buckingham, *ibid.*, 4583 (1964).

TABLE V
 ELECTRONIC SPECTRA OF SOME [14]aneN₄-Fe COMPLEXES

Compd ^a	Axial ligand	Medium	Absorption ^b	
			λ (nm)	ε (l/mol·cm)
III	CH ₃ CN	CH ₃ CN	17.9 (44)	26.6 (47)
		Mull, 77°K	18.5, 27.6	
IV	CN ⁻	CHCl ₃	16.1 (5), 20.2 (38)	26.4 sh (~65)
		Mull	16.6, 19.6, 21.4, 23.4, 26.6	
		Mull, 77°K	16.8, 20.4, 22.0, 23.8	
V	NO ₂ ⁻	CHCl ₃	21.0 (4060)	27.2 (550)
VI	NCS ⁻	CHCl ₃	16.4 (97)	24.4 (111)
		Mull	16.7, 24.4	
		Mull, 77°K	17.3, 25.0	
VII	Cl ⁻	Mull, 343°K	16.9, 24.4	
		CHCl ₃	5.5 (~1), 14.0 (1.9)	
VIII	Br ⁻	Mull	6.1, 14.4	
		CHCl ₃	~5.0, 14.1 (4.8), 19.2, 20.4, 24.4, 27.0	
		Mull	~5.0, 14.7, 19.5, 21.0, 25.0	
IX	I ⁻	CHCl ₃	14.2 (7), 19.2, 20.5, 22.0, 23.3, 23.8, 25.4	
		Mull	14.7, 19.1, 20.8, 22.0, 23.8, 26.4	
		CHCl ₃	10.7 (1), 14.0 (1.9)	
X	CH ₃ CO ₂ ⁻	Mull	13.7, 10.9	
		Mull, 77°K	14.1, 11.4	
		Mull	15.6	
XI	BF ₄ ⁻	Mull	15.6	
XII	Cl ^{-c}	Methanol	No peaks observed	

^a Structures for the compounds are found in Table I and Figure 2. ^b Peak maximum is given in kK followed by the extinction coefficient at 298°K unless otherwise noted. ^c Fe³⁺ complex.

and handling it for brief periods of time in the atmosphere gives a pale green solid which, according to the infrared spectrum, contains water. Longer exposure yields brown rustlike materials which are probably hydrous oxides of iron. The compound is soluble in acetonitrile and gives a uv-visible absorption curve which is indistinguishable from the starting acetonitrile adduct. Dissolution in nitromethane yields a pale brown-pink solution which is very oxygen sensitive and rapidly changes in the atmosphere.

Electronic Spectra of the Low-Spin Complexes.—The low-spin iron(II) electronic spectrum has not been the subject of extended study in the past because it is often obscured by intense charge-transfer bands of the metal-to-ligand type. Ligand fields necessary to pair the six d electrons of iron(II) are usually provided by highly conjugated nitrogen donor ligands of the α-diimine type,²⁸ such as 1,10-phenanthroline or dipyridyl, which invariably produce charge-transfer absorptions in the visible region. Recently, however, complexes of low-spin iron(II) with [14]4,11-dieneN₄,⁷ some poly[(1-pyrazolyl)borates],²⁹ and the *o*-phenylenebis(dimethylarsine) (dars)³⁰ have been reported to exhibit essentially unobscured d-d spectra. This is also the case for three of the low-spin iron(II) complexes with [14]aneN₄ (Table V). Unfortunately the NO₂⁻ derivative gives intense charge-transfer bands which obscure part of the d-d spectrum. The NCS⁻, CN⁻, and CH₃CN derivatives give only two bands with intensities consistent with Laport-forbidden, spin-allowed electronic transitions.³¹ Efforts to locate

(28) P. Krumholz, *Struct. Bonding (Berlin)*, **9**, 139 (1971), and references quoted therein.

(29) J. P. Jesson, S. Trofimenko, and D. R. Eaton, *J. Amer. Chem. Soc.*, **89**, 3158 (1967).

(30) R. D. Feltham and W. Silverthorn, *Inorg. Chem.*, **7**, 1154 (1968).

(31) Reference 15, pp 279-280.

weaker bands which might be present were unsuccessful partly because of the limited solubility of the compounds in the solvents and partly as the result of their sensitivity to oxygen which produced intensely colored species.

From Figure 2 it is evident that while site symmetry at the iron atom is rigorously *C_i* it may appear higher in spectra, since the field strengths of the four secondary amine functions of the macrocycle are nearly equivalent and they occupy the same plane as the central metal ion. Structures of this class have been substantiated by X-ray analyses of γ-[Ni(*ms*-14-Me₆[14]aneN₄)Br₂] and [Ni(*rac*-14-Me₆[14]aneN₄)Br₂].³² Those results also indicate that the nitrogen-metal-nitrogen angles are close to 90° with the six-membered chelate rings sustaining a slightly larger angle than the five-membered ones. A similar small distortion was found for [Ni(cyclam)Cl₂]³³ but for the purpose of analyzing the electronic spectra of this and related macrocyclic complexes it can probably be neglected.³⁴ On this basis, then, the site symmetry at the iron(II) chromophore in the *trans*-diacido complexes is *D_{4h}* and may even be as high as *O_h* depending on the field strength of the axial ligands relative to the macrocycle. For low-spin d⁶ systems in octahedral symmetry the A_{1g} → T_{1g} and A_{1g} → T_{2g} transitions are easily accessible. The acetonitrile and the thiocyanate derivatives both give two d-d absorption bands which have a gaussian appearance when absorptivity is plotted against energy. Furthermore, low-temperature mull spectra of both of the complexes do not result in the appearance of additional shoulders or absorptions, showing that the splitting of the T_{1g} state (lowest energy band) is small. The assignment of the lowest energy band to T_{1g} and the higher absorption to T_{2g} is substantiated by the low-temperature mull spectra. For both of these transitions dE/d(Dq) is positive and thus a shift to higher energy upon lowering the temperature is expected as is observed for both absorptions. An alternate but unsatisfying approach is to assume that the two observed bands actually represent the splitting of the T_{1g}(*O_h*) state upon reduction in symmetry to *D_{4h}*. However, this explanation is rejected because of the very large ligand field requirements of the macrocycle (Dq^{zv} about 3000 cm⁻¹) needed to produce this splitting. Dq for the macrocycle was estimated from the *trans* acetonitrile derivative on the assumption that this configuration of ligands produces a nearly octahedral field about the iron atom.

The energies of the two absorption bands in octahedral symmetry as given by Wentworth and Piper³⁵ are

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

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

It can be shown that the calculation of the Racah parameter *C* and hence *Dq* from the A_{1g} → T_{2g} transition requires the assignment of a spin-forbidden transition which was not observed for these complexes.

(32) G. Gainsford, V. L. Goedken, P. Corfield, and D. H. Busch, to be submitted for publication.

(33) B. Bosnich, R. Mason, P. J. Pauling, G. B. Robertson, and M. L. Tobe, *Chem. Commun.*, 97 (1965).

(34) D. H. Busch and J. L. Karn, *Nature (London)*, **211**, 160 (1966).

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

Examining the reported values of C for $\text{Fe}(\text{diars})_6^{2+}$,³⁰ $\text{Fe}(\text{CN})_6^{4-}$,³⁶ and $\text{Fe}(\text{CNO})_6^{4-}$ ³⁷ shows that (similar to low-spin $\text{Co}(\text{III})$ complexes) the number is relatively constant and about $3300 \pm 300 \text{ cm}^{-1}$. On this basis $Dq(\text{CH}_3\text{CN}) \cong Dq([\text{14}] \text{aneN}_4) \cong 2100 \text{ cm}^{-1}$.

The position of the T_{1g} absorption band (16.4 kK) for the thiocyanate is shifted to lower energy relative to the acetonitrile adduct. Using the equations of Wentworth and Piper³⁵ for D_{4h} cobalt(III) systems the Dq of NCS^- is calculated to be about 1800 cm^{-1} which is 90% the value for the corresponding cobalt(III) complex. The spectrum of the cyanide derivative shows d-d transitions at 16.1 and 20.2 kK and a shoulder on a charge-transfer band at 26.4 kK. Since Dq of CN^- is much greater than the Dq of the macrocycle, the $A_2(D_{4h})$ band is the lowest energy transition, and the $E_g(D_{4h})$, the higher energy absorption at 20.2 kK. Using this splitting to determine Dq' the calculated value of Dq for the cyanide ion is 2700 cm^{-1} which is lower than the value 3460 cm^{-1} obtained from the $\text{Fe}(\text{CN})_6^{4-}$ ion. The room-temperature and liquid nitrogen mull spectra of this complex exhibit additional weak bands which may be due to spin-forbidden transitions. It should be pointed out that the preceding analyses require that the ligand field strength of the macrocycle be constant and transferable from complex to complex, which is probably not strictly true. However, variations in Dq^{2v} are expected to be small³⁸ so that the preceding values may be considered to be acceptable.

The spectrochemical order for the four axial ligands is worth noting. The NO_2^- falls between CN^- and CH_3CN ; this series can also be generated by considering the room-temperature magnetic moments of the complexes. The thiocyanate complex which is an authentic mixture of compounds related by spin equilibrium (see below) has a room-temperature moment of about 1.5 BM. For this compound the susceptibility is a measure of the population of the high-spin state which is determined by the "total Dq " experienced by the iron ion. If the macrocycle remains unchanged in the series CN^- , NO_2^- , NCS^- , then the population of the high-spin state should decrease with increasing axial Dq as the values of the μ_{eff} suggest (Table III). This implies that, to a limited extent at least, two of the complexes are spin-equilibrium systems. This is supported by the lowering of the moment of the NO_2^- complex at 77°K. The study of the temperature dependence of μ_{eff} for the solid CH_3CN derivative was impossible due to the propensity of the compound to lose acetonitrile and form a high-spin complex.

The Electronic Spectra of the High-Spin Complexes.—High-spin, six-coordinate iron(II) in octahedral symmetry gives one weak spin-allowed transition corresponding to ${}^5T_{2g} \rightarrow {}^5E_g$. This transition has $h\nu$ equal to $10Dq$ and for the $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ ion it occurs at 10.4 kK.³⁹ Lowering the symmetry to D_{4h} causes a splitting of both the ground- and excited-state terms⁴⁰ (Figure 3). Such a splitting was observed for a series of tetragonally distorted, six-co-

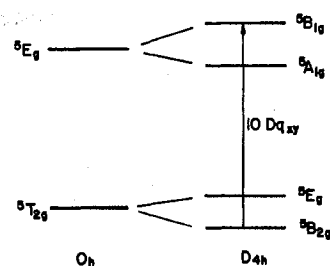


Figure 3.—Energy-level diagram for high-spin $\text{Fe}([\text{14}] \text{aneN}_4)(\text{X})_2$, where X is monodentate and $Dq(\text{X}) < Dq([\text{14}] \text{aneN}_4)$.

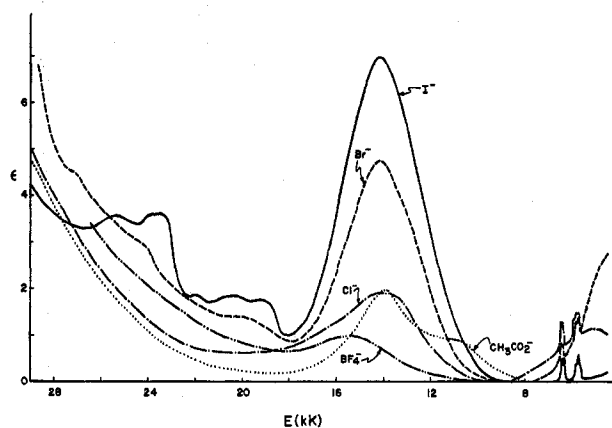


Figure 4.—The electronic spectra of high-spin $\text{Fe}([\text{14}] \text{aneN}_4)(\text{X})_2$ in CHCl_3 , where $\text{X}^- = \text{I}^-$ (—), Br^- (---), Cl^- (···), CH_3CO_2^- (-·-·-), and BF_4^- (-·-·-·) (mull spectrum).

ordinate iron(II) complexes of the type $\text{Fe}(\text{py})_4\text{X}_2$,⁴¹ where $\text{X}^- = \text{Cl}^-$, Br^- , or I^- . Extensive Mössbauer studies on some of these pyridine compounds⁴² indicate that the splitting of the ${}^5T_{2g}$ level upon reduction in symmetry to D_{4h} is about 500 cm^{-1} and that the B_{2g} level is probably the ground state. The spectra of the high-spin $\text{Fe}-[\text{14}] \text{aneN}_4$ complexes are illustrated in Figure 4. All but the I^- and BF_4^- derivatives show two weak absorptions with intensities and bandwidths consistent with the quintet–quintet transitions of high-spin $\text{Fe}(\text{II})$. The bromide and, especially, the iodide derivatives also show a series of complicated weak transitions which are probably associated with the spin-forbidden transitions ${}^5T_{2g} \rightarrow {}^3T_{1g}$, ${}^5T_{2g} \rightarrow {}^3T_{2g}$, etc. The higher than expected intensities for these absorptions are most likely due to "intensity stealing" from nearby charge-transfer transitions. In view of the lowered symmetry of the ligand field (D_{4h}) and close proximity of these bands to one another no assignment was attempted. If it is assumed that the ground state is ${}^5B_{2g}$ for these complexes, then ${}^5B_{2g} \rightarrow {}^5B_{1g}$ is $10Dq^{2v}$ which is assigned to the band at 14 kK. The remaining low-energy band is either the ${}^5A_{1g}$ transition or a transition between the components of the split ground term. Since the band position for the lowest observed transition of $\text{Fe}([\text{14}] \text{aneN}_4)\text{Br}_2$ is about 5 kK, which is a factor of 10 greater than the ground-state splitting for similar systems, the lower energy band is assigned to the transition to the ${}^5A_{1g}$ component. This assignment results in a splitting of the 5E_g excited state which is quite large (about 9 kK

(36) H. B. Gray and N. A. Beach, *J. Amer. Chem. Soc.*, **85**, 2922 (1963).

(37) W. Beck and K. Feldt, *Z. Anorg. Allg. Chem.*, **341**, 113 (1965).

(38) D. A. Rowley and R. S. Drago, *Inorg. Chem.*, **7**, 795 (1968).

(39) F. A. Cotton and N. D. Meyers, *J. Amer. Chem. Soc.*, **82**, 5023 (1960).

(40) A. B. P. Lever, *Coord. Chem. Rev.*, **3**, 119 (1968).

(41) D. M. L. Goodgame, M. Goodgame, M. A. Hetchman, and M. J. Weeks, *Inorg. Chem.*, **5**, 635 (1966).

(42) P. B. Merrithew, P. G. Rasmussen, and D. H. Vincent, *ibid.*, **10**, 1401 (1971).

for the Br^- ; theoretical value = $4D_s + 5D_t$). In order of decreasing Dq^2 the axial ligand spectrochemical series is $\text{CH}_3\text{CO}_2^- > \text{Cl}^- > \text{Br}^- > \text{I}^- > \text{BF}_4^-$. The acetato complex shows a splitting of 3300 cm^{-1} while the Cl^- and Br^- complexes give values of 9000 cm^{-1} and greater than 9000 cm^{-1} , respectively. For the iodide complex the beginning of a band is detected but due to the limit of the spectrometer the position of the maximum could not be determined. The complex which suffers from the greatest amount of tetragonal distortion $[\text{Fe}([\text{14}] \text{aneN}_4)(\text{BF}_4)_2]$ gives only one band which is shifted by about 1500 cm^{-1} toward higher energy relative to the other complexes. This kind of shift of the Dq^{xy} band to higher energy with a decrease in Dq^2 has been observed with some six-coordinate nickel complexes of $[\text{14}] \text{aneN}_4$, as well as with other saturated³¹ and unsaturated³⁸ amine ligands. For the iron complexes this effect is relatively small for the halides and the acetate but is most pronounced, as expected, for the poorly coordinating BF_4^- anion.

It is of interest to compare the results of these spectral assignments with the work of Goodgame, *et al.*⁴¹ They reported splittings of $2000\text{--}5000\text{ cm}^{-1}$ for tetragonally distorted iron(II) halide complexes with pyridine and isoquinoline. They observed a $10Dq^{xy}$ band at about 11 kK which also increased in energy with decreasing Dq of the axial ligand (Dq^2). Since the in-plane Dq band for the complexes reported here is shifted 3000 cm^{-1} to higher energy and the same axial ligands are involved in both cases, it is not unreasonable to conclude that the splitting of the 5E_g state for the $[\text{14}] \text{aneN}_4$ complexes is much greater than in any case previously observed.

The large splittings are also in agreement with the behavior of the recently reported five-coordinate $[\text{Fe}([\text{14}]4,11\text{-dieneN}_4)\text{X}]\text{ClO}_4$ complexes,⁷ where $\text{X}^- = \text{Cl}^-$, Br^- , or I^- . In these systems the splitting between the ${}^5A_{1g}$ and ${}^5B_{1g}$ states was about 7000 cm^{-1} with the $10Dq^{xy}$ transition occurring at 12.5 kK. Since this diimine ligand is known to have a greater Dq^{xy} value⁴³ than $[\text{14}] \text{aneN}_4$, the low in-plane Dq transitions probably reflect the fact the iron atom is not in the plane of the four nitrogens of the macrocycle but remains above it, thereby decreasing the effective Dq^{xy} value. This possibility was previously alluded to⁷ and now gains further support since no such distortion is expected for the rather symmetric, six-coordinated complexes of $[\text{14}] \text{aneN}_4$. For the saturated ligand the high-spin iron(II) atom should be nominally in the plane defined by the four donor atoms of the macrocycle. Molecular models indicate $[\text{14}] \text{aneN}_4$ is able to accommodate larger metal ions than is the $[\text{14}]4,11\text{-dieneN}_4$ ligand. This is due mainly to the constraining features of sp^2 hybridization on the nitrogen and carbon atoms of the imine linkages in the latter. In fact, ligands of the $[\text{14}] \text{aneN}_4$ class with more than two imine functions in the molecule also produce five-coordinate structures⁴⁴ and they give a Dq^{xy} band at lower energy than do the five-coordinate $[\text{14}]4,11\text{-dieneN}_4$ complexes. This must also be due to the iron atom being out of the plane of the ring so that it does not experience the full ligating power of the macrocycle.

(43) The ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition of $[\text{Fe}([\text{14}]4,11\text{-dieneN}_4)(\text{CH}_3\text{CN})_3]^{2+}$ occurs at higher energy than that for the corresponding $[\text{14}] \text{aneN}_4$ complex. The same is true for the Co(III) complex also.

(44) V. L. Goedken and D. H. Busch, *J. Amer. Chem. Soc.*, in press.

The Spin Equilibrium of the Thiocyanate Derivative.—The room-temperature moment for the trans thiocyanato derivative is about 1.5 BM, a value so high for low-spin iron(II) that it is suspect. Furthermore, an esr spectrum of the complex in the solid state gave a weak signal with $g = 2.285$, which is consistent with the presence of high-spin iron(II).⁴⁵ A temperature-dependence study (Table VI) on the solid using the

TABLE VI
SUSCEPTIBILITY OF $\text{Fe}([\text{14}] \text{aneN}_4)(\text{SCN})_2$ AT
VARIOUS TEMPERATURES

Temp, °C	$10^{-3}\chi_M$, cgsu	Temp, °C	$10^{-3}\chi_M$, cgsu	Temp, °C	$10^{-3}\chi_M$, cgsu
-184	164	-16	299	52	2108
-152	136	1	475	70	3598
-103	130	16	733	83	4743
-79	136	28	977	102	6417
-48	157	37	1329		

Faraday method revealed that the measured magnetic susceptibility is independent of the field strength and does not follow the simple Curie-Weiss equation. For most of the temperature range studied ($77\text{--}343^\circ\text{K}$) reproducible susceptibilities were obtained by approaching equilibrium from above or below a given temperature, indicating that no hysteresis effects were present. Subjecting the compound to temperatures in excess of about 343°K and subsequent cooling to room temperature gave moments which were higher than 1.5 BM showing that some decomposition occurs at elevated temperatures. This kind of solid-state magnetic behavior for iron(II) complexes is characteristic of spin-state equilibrium between the low-spin ${}^1A_{1g}$ ground state and the high-lying ${}^5T_{2g}$ high-spin ground state. It follows for this complex that the total ligand field arising from the two thiocyanates and the macrocycle is such that the difference in energy between the two spin states of the iron ion is of the order of kT and that the population of the states in question can be altered by changes in temperature. If it is assumed that the high-spin state has a susceptibility of about $11,000 \times 10^{-6}$ cgsu, the magnetic data can be treated in the manner described for $[\text{Fe}([\text{14}]4,11\text{-dieneN}_4)(\text{phen})]\text{ClO}_4$.⁷ For all but a few of the low-temperature susceptibility values a plot of $\log K$ vs. $1/T$, where K is the equilibrium constant, $[\text{low spin}]/[\text{high spin}]$, was linear and gave values of -6.95 kcal/mol for ΔH and -19 eu for ΔS . These thermodynamic properties are similar to those found for other spin equilibria of iron(II).^{7,28,46}

Efforts to detect the presence of the high-spin species by observing its optical spectrum gave only marginal results. Visually the compound appears deep blue at liquid nitrogen temperature and green at the higher temperature. Spectroscopically, a slight shift to higher energy, as well as the disappearance of the long-wavelength tail, of the band at 16.4 kK, was found with lowering the temperature. This behavior is reasonable since lowering the temperature depopulates the higher vibrational levels of the ground state which give rise to the low-energy electronic transitions under the band envelope.⁴⁷ However, the high-spin species is also expected to have an absorption in this region, about 14

(45) B. R. McGarvey, *Transition Metal Chem.*, **3**, 39 (1966).

(46) D. M. L. Goodgame and A. A. S. C. Machado, *Inorg. Chem.*, **8**, 2031 (1969).

(47) Reference 15, pp 282-285.

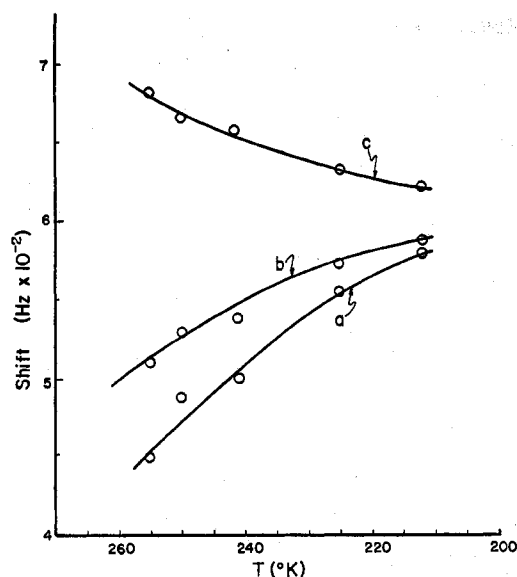


Figure 5.—Variation of pmr band positions (100 MHz) with temperatures for Fe([14]aneN₄)(SCN)₂ (solvent CHCl₃-CDCl₃). Shifts to lower field with increasing temperature are defined as negative: (a) CH₃(2), (b) CH₃(1), and (c) CH₃(3). See Figure 2 for assignment.

kK, which may, in part, account for the loss of the low-energy absorption. The absence of any distinct band in the high-temperature spectrum (343°K) which could be attributed to the high-spin complex is due to the expected population of the two spin states as well as the relative intensities of their transitions and the proximity of the singlet-singlet and quintet-quintet transitions.

The pmr spectrum of the complex at 37° in chloroform shows extremely broad, barely discernible proton resonances. Lowering the temperature to -18° produced three sharp resonances which were recognized from their relative intensities and splitting patterns as the two *gem*-dimethyl signals and the methyl doublet of the asymmetric carbon atom. This behavior with temperature can be explained by the presence of both the diamagnetic ¹A_{1g} and paramagnetic ⁵T_{2g} ground states in solution and offers further evidence that this type of equilibrium is operating. The equilibrium between the two forms must be rapid (>10⁵ sec⁻¹) since on the pmr time scale only the "average" resonances are observed.⁴⁸ From Figure 5 and Table VII it is evident

TABLE VII
100-MHz PMR DATA FOR Fe([14]aneN₄)(SCN)₂ in CHCl₃-CDCl₃ AT VARIOUS TEMPERATURES^a

Temp, °C	CH ₃ (1) ^b	CH ₃ (2) ^b	CH ₃ (3) ^b
-18	510	450	681
-24	529	484	665
-32	538	497	658
-48	574	556	633
-61	584	580	621

^a All shifts are given in Hz and occur on the high-field side of CH₃Cl₃ where C(H)Cl₃ is 0.0 Hz. ^b As indicated in Figure 2.

that lowering the temperature causes the signals for CH₃(1) and CH₃(2) (Figure 2) to shift to higher field relative to their counterparts in the diamagnetic complex (negative shift). The exact shifts of these signals in the fully diamagnetic complex are unknown but the

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direction of the shifts is clear. The third signal, CH₃(3), of Figure 2 shows a shift to low field with decreasing temperature relative to the diamagnetic complex.

The effect of the paramagnetic metal center on the methyl nuclei can be transmitted by two mechanisms. Electronic density from the iron atom can reach the affected nuclei through the σ -bonding system of the macrocycle, or it can be transmitted *via* a "through-space" effect. The former gives rise to Fermi contact shifts while the latter is the pseudocontact interaction.⁴⁹ Generally speaking the observed shift for paramagnetic molecules is the sum of the two contributions. That is

$$\left(\frac{\Delta H}{H}\right)_{\text{obsd}} = \left(\frac{\Delta H}{H}\right)_{\text{Fermi}} + \left(\frac{\Delta H}{H}\right)_{\text{pseudo}} \quad (1)$$

In principle, the separation and estimation of the relative magnitudes that each contribution makes to the observed shift are difficult. For saturated ligand systems such as [14]aneN₄ the Fermi-contact contribution should be negative. Work on a variety of octahedral nickel(II)-amine complexes has shown only an attenuation of magnitude with distance from the paramagnetic center but no change in sign for $\Delta H/H$.⁵⁰ Since the pseudocontact contribution can be either negative or positive depending on the geometric relationship of the protons to the paramagnetic center, its contribution to the axial proton must be greater in magnitude than and opposite in sign to that of the Fermi contribution. It is doubtless true that the Fermi interaction makes some contribution to all the shifts but the unique stereochemistry of the ligand shows the importance of the pseudocontact interaction for this molecule. A quantitative treatment of the two effects must await determination of the values of the *g* tensors and the detailed stereochemistry of the complex in solution.⁴⁹

The Pairing Energy of Iron(II).—Information on the pairing energy of iron(II) is difficult to obtain because the relevant d-d electronic transitions are rarely observed. The *trans*-diacido compounds of iron(II) and [14]aneN₄ yield both high- and low-spin complexes having well-defined electronic spectra which makes them ideally suited for evaluating the pairing energy. The value of the total pairing energy (π) for covalently bonded d⁶ metal ions as given by Griffith⁵¹ is

$$\pi = 2.5B + 4C \quad (2)$$

Calculation⁵⁵ of the Racah parameter *B* for the nearly octahedral CH₃CN derivative from the data in Table V gives the value 540 cm⁻¹. If *C* is 3300 ± 300 cm⁻¹, the calculated pairing energy for the two d electrons of this complex is 14,500 ± 1200 cm⁻¹. If the *trans* acetato high-spin complex is considered to be an octahedral system, the "total *Dq*" is less than 14,000 cm⁻¹. Since the *Dq* of the singlet ground state is about 2100 cm⁻¹, the following equality is satisfied

$$10Dq(^1A_{1g}) > \pi > 10Dq(^5T_{2g}) \quad (3)$$

Earlier work on several substituted iron(II) poly[(1-pyrazolyl)borate] complexes²⁹ gave values of *Dq*(low spin) = 21,000 cm⁻¹ and *Dq*(high spin) = 12,500 cm⁻¹

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with $\pi \approx 16,400 \text{ cm}^{-1}$. Estimates⁵² for the spin-equilibrium complex $\text{Fe}(o\text{-phen})_2(\text{NCS})_2$ resulted in values of $Dq(\text{low spin}) \approx 16,300 \text{ cm}^{-1}$ and $Dq(\text{high spin}) \approx 11,900 \text{ cm}^{-1}$. The results of the earlier studies are in good agreement with those obtained from

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the spectral data of the $[\text{14}] \text{aneN}_4\text{-Fe}$ complexes.

Acknowledgment.—This research was supported by Grant No. GM 10040 from the National Institute of General Medical Science of the U. S. Public Health Service. We wish to acknowledge Dr. E. Gore of this department for helpful discussion concerning the pmr results.

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Synthesis of Metal Complexes with Macrocyclic Ligands Having Prescribed Patterns of Unsaturation. Oxidative Dehydrogenation of Fused-Ring Systems Involving Charged, Delocalized Six-Membered Chelate Rings

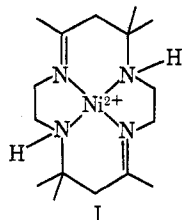
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Received January 4, 1972

Metal ion promoted oxidative dehydrogenation shares with coordination template effects the distinction of being a new synthetic technique uniquely suited to the preparation of ligands that are difficult to produce by other means. Oxidation of the chelate rings that are formed by deprotonation of β -diimines produces a pattern of unsaturation that has not previously been achieved by this general class of reaction. This pattern both places a localized $\text{C}=\text{C}$ group in the six-membered ring and extends the unsaturation into the adjacent chelate ring. This reaction has been effected by bromine oxidation of the macrocyclic nickel(II) complexes 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-dienatonickel(II) perchlorate and 12,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-11,13-dienatonickel(II) perchlorate (or hexafluorophosphate). The structures of the products were established through conductivity and magnetic susceptibility measurements and visible, infrared, and nmr spectroscopy.

Introduction

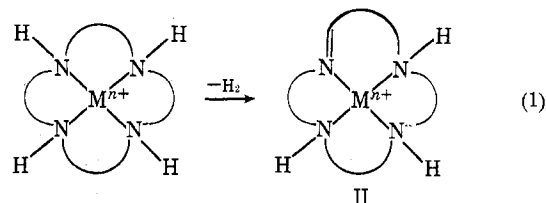
The discovery that the complex having structure I



is formed by the reaction between ethylenediamine and acetone in the presence of nickel(II) salts^{1,2} represented the initial example of the new synthetic macrocyclic ligands containing four nitrogen donors. Many such substances are known now³ and they form an important new class of coordination compounds that have aroused much interest because of the fundamental structural relationship they bear to such critical natural products as heme proteins, chlorophyll, and vitamin B₁₂.⁴

Two novel chemical reactions have figured in the synthesis of many of these new complexes—coordination template reactions³⁻⁵ and oxidative dehydrogenation reactions.^{3,6,7} The latter reactions have uniformly involved the conversion of secondary amine

groups into azomethine linkages through the abstraction of 1 mol of hydrogen (eq 1). Such linkages have



been introduced into five-⁸ and six-membered chelate rings.⁷ Goedken⁸ has shown that simple bidentate ligands, e.g., ethylenediamine and *o*-phenylenediamine, in $\text{Fe}^{\text{II}}(\text{diamine})(\text{CN})_4^{2-}$ can be oxidatively dehydrogenated to α -diimines while remaining coordinated. Also, the early work of Vassian and Murmann⁹ showed that, when two α -diimine linkages are produced in one chelate ring, ionization of a proton may occur producing a β -diketonate-like chelate structure.

The converse process, hydrogenation of coordinated imine groups, is well documented among complexes containing macrocyclic ligands.^{6,10,11} Such processes have been observed both chemically^{6,10,12} and electrochemically.^{11,13}

The mechanism of the oxidative dehydrogenation

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