Synthesis and Ground State Electronic Properties of Tetraaza Macrocyclic Iron(II, III) Complexes Containing [14]-, [15]-, and [16]-Membered Rings

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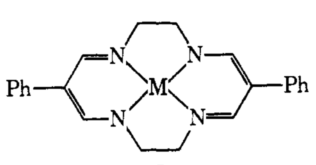
Abstract: Reaction of ferrous acetate and basic ferric acetate with [14]-, [15]-, and [16]-membered bis(β-iminoamine) macrocycles affords complexes of the general types $Fe^{II}N_4$ and $Fe^{III}N_4(OAc)$ having the ring structures I-III. By a combination of oxidative addition and ligand substitution reactions an extensive series of five-coordinate complexes $Fe^{III}N_4X$, X = Cl, Br, I, O_2CR, SPh, and SCH_2Ph, was obtained. Ground spin states were established by magnetic susceptibility, Mossbauer, and EPR measurements, and were found to be dependent upon both macrocycle ring size and axial ligand X. All [14]- and [15]-ring complexes with X = halide and carboxylate were found to have the uncommon intermediate ($S = \frac{3}{2}$) spin state whereas similar compounds in the [16]-ring series are high spin ($S = \frac{5}{2}$). A unique magnetic series was established using the three ring systems and axial thiolate ligands, encompassing the three possible spin states for noncubic Fe(III): [14]-SPh, low spin ($S = \frac{1}{2}$); [15,16]-SPh ($S = \frac{3}{2}$); [16]-SCH_2Ph ($S = \frac{5}{2}$). Factors affecting stabilization of the different spin states are considered, and similarities and differences in synthetic methods, stabilities, and electronic properties between the macrocyclic complexes obtained in this work and Fe(III) porphyrins are noted.

Substantial interest continues in the employment of synthetic tetraaza macrocyclic complexes[2-5] and their ligands[6] as models for natural corrin and porphyrin ring systems, and as otherwise useful vehicles for probing the structural, electronic, and reactivity features of metal ions in various tetragonal N_4 environments. In the area of tetraaza macrocyclic chemistry recent research in this laboratory has included the following: (i) development of nontemplate syntheses of 12π bis(β-iminoamine) macrocycles containing [14]-, [15]-, and [16]-membered rings[7-10] and formation of metal(II) complexes of these ring systems, illustrated by $M(Ph_2[14]tetraenatoN_4)$ (I), $M(Ph_2[15]tetraenatoN_4)$ (II), and $M(Ph_2[16]tetraenatoN_4)$ (III);[11] (ii) oxidative dehydrogenation of the complexes in (i) affording in particular Co(III), Ni(II), and Cu(II) complexes containing the 14π [15]-membered corrin inner ring[8,12] and 14-16π Ni(II), Pd(II), and Cu(II) complexes which exhibit ligand-based redox reactions involving a tetraaza[14]annulene ligand system;[7,14] (iii) synthesis of the $[Fe^{III}N_4SR]$ coordination unit based on the ligands in I-III.[15]



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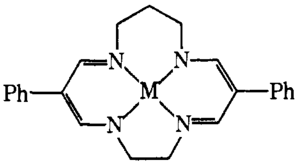

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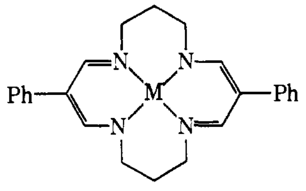

III

Despite the extensive research on synthetic macrocyclic complexes,[2-5] it is only relatively recently that attention has been directed toward development of the chemistry of Fe(II, III) complexes. Exclusive of research aimed at synthetic oxygen carriers, the majority of results now available for macrocyclic systems have been afforded by the work of Busch, Goedken, and their collaborators,[2,13,16-24] which has dealt primarily with Fe(II) complexes, usually cationic and derived from [14]-membered macrocycles. The present research has been undertaken with two related purposes in mind. First, we wished to generate an extensive series of complexes containing the tetragonal coordination unit $[Fe^{III}N_4X]$ in order to investigate the effect of variations in ring size (I-III) and axial ligands X on reactivity and electronic properties. Of the latter the principal interest concerns ground spin states, which without exception are high spin ($S = \frac{5}{2}$) in five-coordinate Fe(III) porphyrins.[25] Second, a means of introducing axial thiolate ligands was desired in order to obtain complexes containing the $[Fe^{III}N_4SR]$ coordination unit, which is of considerable current interest in view of possible Fe(III)-cysteinyl binding in one or both oxidized reaction states of cytochrome P-450 enzymes.[26,27] It was felt that methods affording axial thiolate ligation might also be applicable to porphyrins, and, if so, that a companion study of synthetic macrocyclic and porphyrin complexes could be highly useful in establishing the properties of the $[Fe^{III}N_4SR]$ unit, previously unknown in stable, isolable complexes. As shown by our recent reports,[15,28] as well as those by others,[29] this unit can be stabilized in both types of complexes. Here we present a detailed account of the synthesis and certain electronic properties of $[Fe^{III}N_4X]$ complexes, derived from the macrocycles in I-III, with X = halide, carboxylate, and thiolate.

Experimental Section

Preparation of Compounds. Synthetic methods for new compounds are summarized and structural formulas are set out in Figure 1. The macrocycles $H_2(Ph_2[14]tetraeneN_4)$ (**1**), $H_2(Ph_2[15]tetraeneN_4)$ (**2**), and $H_2(Ph_2[16]tetraeneN_4)$ (**3**) were synthesized by previous methods.[9] Anhydrous ferrous acetate was obtained as a white solid by a procedure similar to that of Hardt and Möller.[30] Exposure of a slurry of this compound in hot glacial acetic acid to air afforded anhydrous basic ferric acetate is a brick red solid. Based on the structure of the ClO_4^- salt of $[Fe_3O(OAc)_6]^+$,[31] this material is assigned the composition $Fe_3O(OAc)_7$. In the synthesis of Fe(II, III) complexes described below, all operations were performed under a pure dinitrogen atmosphere. Melting points were determined in sealed tubes and are uncorrected.

Iron(II) Complexes. (a) $Fe(Ph_2[14]tetraenatoN_4)$ (4). Ferrous acetate (2.5 g, 15 mmol) and **1** (5.0 g, 13 mmol) were heated in 20 ml of DMF at 80° for 1 hr, during which time red crystals formed in a green solution. The product was collected by filtration and washed with ethanol affording 4.7 g (80%) of product, mp 312–314°. The compound was not recrystallized due to low solubility. Anal. Calcd for $C_{22}H_{22}N_4Fe$: C, 66.35; H, 5.57; N, 14.07. Found: C, 66.29; H, 5.51; N, 14.12.

(b) Fe(Ph$_2$[15]tetraenatoN$_4$) (5). Method I. Ferrous acetate (0.65 g, 3.7 mmol) and **2** (1.3 g, 3.6 mmol) were allowed to react in 15 ml of DMF at 80° for 1 hr. The red crystalline product was isolated and washed as in the preceding preparation. Recrystallization from 40 ml of hot DMF gave red plates (1.3 g, 84%), mp 246–248°. Anal. Calcd for $C_{23}H_{24}N_4Fe$: C, 67.00; H, 5.87; N, 13.59. Found: C, 66.96; H, 5.91; N, 13.61.

Method II. This procedure takes advantage of the more readily obtained macrocycle **3** compared to **2**.[9] Ferrous acetate (0.93 g, 5.4 mmol) and **3** (2.0 g, 5.4 mmol) were heated in 20 ml of DMF at 80° for 20 min, whereupon 0.4 g of ethylenediamine was added. Heating was continued for 30 min during which time the reaction mixture changed from green-brown to red-brown. Addition of ethanol and cooling afforded the red crystalline product (0.40 g, 18%), identical by mixture melting point to that obtained by method I.

(c) Fe(Ph$_2$[16]tetraenatoN$_4$) (6). Ferrous acetate (1.4 g, 8.1 mmol), **3** (3.0 g, 8.0 mmol), and pyridine (1.3 g, 16 mmol) were stirred in 20 ml of DMF at 60° for 3 hr. Crystalline product was removed by filtration, washed with ethanol, and recrystallized from ~180 ml of hot DMF (90°), affording the red crystalline product (1.9 g, 55%) containing no pyridine. This material was dried in vacuo for 24 hr, mp 204–205°. Anal. Calcd for $C_{24}H_{26}N_4Fe$: C, 67.61; H, 6.15; N, 13.14. Found: C, 67.60; H, 6.37; N, 13.32.

Iron(III) Carboxylate and Halide Complexes. Analytical data for these and other Fe(III) complexes whose preparations are given in a following section are collected in Table I.

(a) Fe(Ph$_2$[14]tetraenatoN$_4$)(OAc) (7). Ferric acetate (3.5 g, 18 mmol) and **1** (5.0 g, 15 mmol) were heated in 35 ml of ethanol at 70° for 2 hr during which time a brown-green-purple color change ensued. After cooling, filtration, and washing with isopropyl alcohol 4.7 g of black crystals was obtained. Two recrystallizations from hot ethanol were necessary to obtain an analytically pure sample as black crystals in reduced yield: ν_{OAc} 1600 cm^{-1} (mull); mp 305–307°.

(b) Fe(Ph$_2$[14]tetraenatoN$_4$)Cl (8). To a suspension of **7** (1.8 g, 3.9 mmol) in 50 ml of ethanol was added 4 ml (16 mmol) of 4 *N* HCl. After overnight stirring and product collection, the complex was twice recrystallized from DMF–isopropyl alcohol to yield black crystals (1.3 g, 76%), mp 283–286°. Alternatively the complex may be prepared by the reaction of **4** and chloroform for a period of ca. 12 hr with stirring at room temperature.

(c) Fe(Ph$_2$[14]tetraenatoN$_4$)Br (9). To a suspension of **4** (2.6 g, 6.5 mmol) in 30 ml of DMF, bromine (0.53 g, 3.3 mmol) in 5 ml of DMF was added. The reaction mixture immediately turned red-violet and a crystalline solid gradually separated over 1 hr. Slow addition of 200 ml of ethanol afforded further product separation. The solid was collected and dissolved in 200 ml of warm DMF to which after filtration was added slowly 200 ml of ethanol, affording purple-black crystals (2.0 g, 64%), mp 256–258°.

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(d) Fe(Ph$_2$[14]tetraenatoN$_4$)I (10). To a suspension of **7** (1.5 g, 3.2 mmol) in 50 ml of ethanol was added 0.82 ml (6.2 mmol) of 57% HI. After stirring overnight the collected solid was twice recrystallized from DMF–ethanol to afford purple-black crystals (0.70 g, 41%), mp 273–275°.

(e) Fe(Ph$_2$[15]tetraenatoN$_4$)Cl, (11). Fe(Ph$_2$[15]tetraenatoN$_4$)(OAc) was prepared in isopropyl alcohol by a method analogous to that for **7**; a satisfactory combustion analysis for the purple-black crystalline material was not obtained. This material was used in a preparation (HCl, isopropyl alcohol solvent) similar to that for **8**. After two recrystallizations from DMF ethanol (60°) a blue-green microcrystalline product was obtained (26%), mp 223–225°.

(f) Fe(Ph$_2$[15]tetraenatoN$_4$)Br (12). The procedure for **9** was employed. Reaction of bromine with an ethanol suspension of **5** followed by the dissolution of the crude product in the minimum volume of warm DMF and slow addition of ethanol gave a green-black microcrystalline solid (50%), mp 236–238°.

(g) Fe(Ph$_2$[16]tetraenatoN$_4$)(OAc) (13). **3** (2.0 g, 5.4 mmol) and ferric acetate (1.3 g, 6.5 mmol) were heated in 30 ml of DMF at 80° for 1 hr. (Prolonged heating causes product decomposition.) After filtration of the deep green solution and solvent removal in vacuo the residue was recrystallized from 40 ml of isopropyl alcohol (80°) to give dark green crystals (0.8 g, 31%), mp 178–180°.

(h) Fe(Ph$_2$[16]tetraenatoN$_4$)(O$_2$CPh) (14). Dibenzoyl peroxide (0.71 g, 3.0 mmol) in 15 ml of DMF was added slowly to a stirred suspension of 2.4 g (5.9 mmol) of **6** in 15 ml of DMF. The reaction is exothermic and a blue-green color appeared immediately. Stirring for 1 hr resulted in crystallization of the product; addition of 40 ml of ethanol completed product separation. The product was collected and dissolved in 50 ml of DMF (~70°). Slow addition of 200 ml of ethanol to the filtered solution followed by cooling afforded green-black crystals (1.4 g, 44%), mp 208–210°.

(i) Fe(Ph$_2$[16]tetraenatoN$_4$)Br (15). The procedure for **9** was employed. The crude product was dissolved in the minimum volume of warm DMF (50°) and slow addition of isopropyl alcohol to the filtered solution followed by cooling produced dark green crystals (2.0 g, 90%), mp 221–222°.

(j) [Fe(Ph$_2$[16]tetraenatoN$_4$)]$_2$O (16). **14** (1.0 g, 1.8 mmol) was partially dissolved in 20 ml of DMF. Addition of 0.10 g (2.5 mmol) of sodium hydroxide in 10 ml of DMF resulted in immediate reaction and the precipitation of a brown powder. This material was collected, washed with water and isopropyl alcohol, and dissolved in hot DMF. Slow addition of isopropyl alcohol to the filtered solution caused separation of black crystals (0.37 g, 23%): mp 225–227°, ν_{FeOFe} 855 cm^{-1}.

Iron(III) Thiolate Complexes. (a) Fe(Ph$_2$[14]tetraenatoN$_4$)(SPh) (17). Method I. Benzenethiol (0.48 g, 4.4 mmol) was added to a suspension of 2.0 g (4.4 mmol) of **7** in 35 ml of ethanol. The reaction mixture turned immediately from red-purple to red-brown and red-brown crystals of the product appeared. These were collected by filtration, washed with ethanol, and dissolved in 25 ml of DMF. Slow addition of methanol (150 ml) to the filtered DMF solution caused separation of product as brown fibrous crystals (1.9 g, 86%), mp 178–180°.

Method II. **4** (0.6 g, 1.5 mmol) and diphenyl disulfide (0.20 g, 0.92 mmol) were suspended in 40 ml of 1/1 (v/v) DMF–ethanol. Benzenethiol (0.05 ml) was added and the mixture was warmed to 35°. The solid which crystallized was collected by filtration (0.55 g, 72%) and was shown to be identical with that obtained by method I.

(b) Fe(Ph$_2$[15]tetraenatoN$_4$)(SPh) (18). **5** (0.90 g, 2.2 mmol), diphenyl disulfide (0.30 g, 1.4 mmol), and benzenethiol (0.05 ml) were stirred in 10 ml of DMF for 1 hr. Slow addition of ethanol caused separation of crystalline product, which was recrystallized from DMF–isopropyl alcohol at room temperature giving the black crystalline complex (0.55 g, 50%), mp 148–152°.

(c) Fe(Ph$_2$[16]tetraenatoN$_4$)(SPh) (19). **6** (1.8 g, 4.1 mmol), diphenyl disulfide (0.50 g, 2.3 mmol), and benzenethiol (0.05 ml) were stirred in 50 ml of 1/1 (v/v) DMF–ethanol at room temperature. The mixture gradually formed a deep blue solution and product crystallization occurred on stirring overnight. After collection by filtration the product was dissolved in 80 ml of DMF (35°), 150 ml of ethanol was added very slowly, and the product was caused to crystallize by cooling the solution. After collection and washing with ethanol purple-black crystals were obtained (1.3 g, 59%), mp 172–174°.

(d) Fe(Ph$_2$[16]tetraenatoN$_4$)(SCH$_2$Ph) (20). Benzylthiol (0.4 ml) was added to a suspension of 1.7 g (3.1 mmol) of **14** in 20 ml of DMF. The reaction mixture immediately formed an intense blue solution. Very slow addition of 150 ml of ethanol and cooling caused crystallization of the product, which was recrystallized from DMF–isopropyl alcohol affording black crystals (1.5 g, 88%), mp 149–152°.

(e) Fe(Ph$_2$[14]tetraenatoN$_4$)(SPh)(py) (21). From the reaction of pyridine (1.5 ml) and **17** (0.50 g, 0.99 mmol) in 30 ml of DMF the black crystalline adduct precipitated. After washing with ethanol and drying in vacuo for 24 hr, 0.40 g (69%) of product was obtained, mp 160° dec.

(f) Fe(Ph$_2$[15]tetraenatoN$_4$)(SPh)(py) (22). This compound was obtained as a black-brown crystalline material by a method analogous to that in the preceding preparation, mp 167–170°.

(g) Fe(salen)(SPh). Benzenethiol (0.60 g, 5.5 mmol) was added to

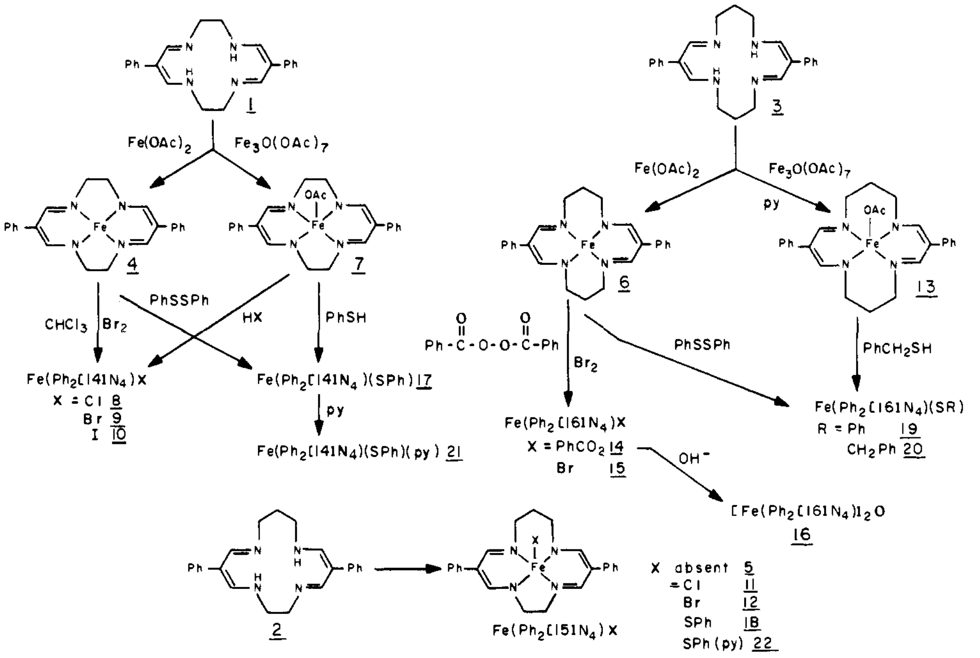


Figure 1. Summary of synthetic schemes for Fe(II, III) complexes based on macrocycles 1 and 3. Similar reactions apply to the complexes based on macrocycle 2.

a suspension of Fe(salen)OAc[32] (2.0 g, 5.3 mmol). The reaction mixture immediately was converted to a fibrous mass which gradually changed to black-purple crystals (1.7 g) on stirring. After recrystallization from DMF-methanol at room temperature black-purple crystals were obtained in small yield, mp 169° dec.

Physical Measurements. All measurements were performed with exclusion of oxygen. Electronic spectra were obtained using a Cary Model 14 or 17 spectrophotometer. EPR measurements were made with a Varian E-9 spectrometer operating at X-band frequencies; the magnetic field was monitored with a Harvey-Wells Precision NMR gaussmeter (Model G-502) and the microwave frequency was measured with a Sperry microline frequency meter (Model 1241). Infrared spectra were recorded on a Perkin-Elmer 337 spectrophotometer. Magnetic susceptibilities of solids were determined in the range of ca. 17-295 K using a Bruker Faraday apparatus interfaced with a Leybold-Hereaus helium flow-type cryostat whose temperature was monitored with a germanium-arsenic diode (12-40 K) and a platinum resistance thermometer (40-300 K); temperature control was ±0.25°. Calibrants were Ni(en)$_3$(S$_2$O$_3$) and CoHg(SCN)$_4$; independent measurements of the latter were in good agreement with the most recent reported values.[33] Solution susceptibilities were measured by the Evans method[34] using concentric tubes and 2% v/v TMS-dichloromethane solutions to which density corrections were applied. Polarographic measurements were performed with a PAR Model 170 electrochemistry system using a rotating platinum working electrode. Solutions were $\sim 10^{-3}$ M in complex and 0.05 M in supporting electrolyte ((n-Bu$_4$N)(ClO$_4$) or (n-Pr$_4$N)(ClO$_4$)). Potentials were determined at 25.0 ± 0.1° vs. a saturated calomel electrode. Mössbauer measurements were made from 4.2 K to room temperature with a constant acceleration spectrometer. The source was located in the cryostat and was maintained at the same temperature as the absorber. Additional measurements with the absorber in applied magnetic fields up to 80 kOe were carried out with a superconducting magnet operating in a longitudinal configuration.

Results and Discussion

Synthesis. The synthetic methods described in the Experimental Section which afford Fe(II) and Fe(III) complexes of the [14]-, [15]-, and [16]-membered macrocycles **1, 2,** and **3**, respectively, are shown in Figure 1. Related reactions not so described are mentioned below; new compounds are also listed in Table I.

(a) Incorporation of Fe(II, III) into Macrocycles. Anhydrous ferrous acetate is a convenient reagent for insertion of Fe(II) into the diprotic macrocycles **1-3**. Reaction of this compound with **1** and **2** in hot DMF gives Fe(Ph$_2$[14]N$_4$) (**4**) and Fe(Ph$_2$[15]N$_4$) (**5**) in good yield. The preparation of Fe(Ph$_2$[16]N$_4$) (**6**) by a similar means requires the presence of 2 equiv of pyridine, whose function is unknown.[35] The red crystalline complexes **4-6** are very reactive to oxygen in the solid and solution phases but are quite stable when stored under a pure dinitrogen atmosphere.

Under similar conditions basic ferric acetate with **1** and **3** gives Fe(Ph$_2$[14]N$_4$)(OAc) (**7**) and Fe(Ph$_2$[16]N$_4$)(OAc) (**13**); a somewhat impure sample of Fe(Ph$_2$[15]N$_4$)(OAc) was also obtained. These reactions appear to be solvent dependent. Thus, while the acetate and **1** in hot ethanol produces **7**, the same reactants in DMF afford **4** in high yield. The reaction of **3** and basic ferric acetate in hot DMF gives **13** in moderate yield whereas in ethanol no product is formed.

(b) Fe(III) Macrocyclic Complexes. The preceding ferrous macrocycles and macrocyclic ferric acetates have been found to be effective precursors of [Fe$^{\rm III}$N$_4$X] complexes of the three ring systems which are formed by two types of reactions. The first, eq 1,

$$[\mathrm{Fe^{II}N_4}] + \tfrac{1}{2}\mathrm{X_2} \rightarrow [\mathrm{Fe^{III}N_4X}] \qquad (1)$$

is one of oxidative addition and affords the bromide (**9, 12, 15**) and benzoate (**14**) complexes in good yield. The second reaction, eq 2,

$$[\mathrm{Fe^{III}N_4(OAc)}] + \mathrm{HX} \rightarrow [\mathrm{Fe^{III}N_4X}] + \mathrm{HOAc} \qquad (2)$$

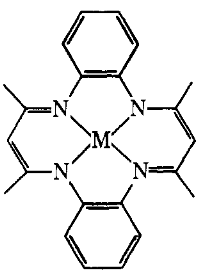
is an axial ligand substitution process and offers a convenient route to the X = Cl (**8, 11**) and I (**10**) complexes. Complex **8** may also be obtained directly by treatment of **4** with chloroform. Surprisingly, all Fe(III) compounds were found to be quite sensitive to oxygen; reaction products were not characterized but appear to result from ligand degradation. However, treatment of the Fe(II) complex **6** with limited oxygen yields the μ-oxo dimer [Fe(Ph$_2$[16]N$_4$)]$_2$O (**16**), which is more conveniently prepared by the reaction of the benzoate complex **14** with aqueous sodium hydroxide. Neither of these methods led to isolable μ-oxo dimers in the [14]- and [15]-membered ring series.

Table I. Characterization Data for Iron(III) Macrocyclic Complexes

	Calcd, %				Found, %			
Compound	C	H	N	S	C	H	N	S
$Fe(Ph_2[14]N_4)(OAc)$	63.03	5.51	12.25	—	63.12	5.44	12.24	—
$Fe(Ph_2[14]N_4)Cl$	60.92	5.10	12.92	—	60.98	5.03	12.95	—
$Fe(Ph_2[14]N_4)Br$	55.26	4.64	11.72	—	55.43	4.78	11.95	—
$Fe(Ph_2[14]N_4)I$	50.31	4.22	10.67	—	50.27	4.18	10.66	—
$Fe(Ph_2[14]N_4)(SPh)$	66.27	5.36	11.04	6.32	66.12	5.41	11.08	6.18
$Fe(Ph_2[14]N_4)(SPh)(py)$	67.57	5.50	11.94	5.47	67.59	5.63	12.02	5.59
$Fe(Ph_2[15]N_4)Cl$	61.70	5.40	12.51	—	61.88	5.49	12.51	—
$Fe(Ph_2[15]N_4)Br$	56.12	4.92	11.38	—	56.04	5.14	11.28	—
$Fe(Ph_2[15]N_4)(SPh)$	66.79	5.61	10.74	6.15	66.88	5.50	10.69	6.06
$Fe(Ph_2[15]N_4)(SPh)(py)$	68.00	5.71	11.66	5.34	67.93	5.74	11.53	5.27
$Fe(Ph_2[16]N_4)(OAc)$	64.34	6.02	11.54	—	64.09	6.11	11.40	—
$Fe(Ph_2[16]N_4)(O_2CPh)$	68.01	5.71	10.23	—	67.83	5.55	10.19	—
$Fe(Ph_2[16]N_4)Br$	56.94	5.18	11.06	—	56.78	5.24	11.06	—
$Fe(Ph_2[16]N_4)(SPh)$	67.29	5.84	10.46	5.99	66.89	5.77	10.61	6.04
$Fe(Ph_2[16]N_4)(SCH_2Ph)$	67.76	6.05	10.20	5.84	67.59	5.82	10.04	5.85
$[Fe(Ph_2[16]N_4)]_2O$	66.37	6.03	12.90	—	66.28	5.94	12.92	—
Fe(salen)SPh[a]	61.26	4.44	6.50	7.43	61.54	4.23	6.63	7.44

[a] Nonmacrocylic.

Among other synthetic tetraaza macrocycles the reactivity properties of the Fe(II) complexes described here are most closely paralleled by the Fe(II) complex derived from the ring system IV,[21b] a dibenzo analog of I. $Fe(Me_4[14]dibenzoN_4)$ reacts with chloroform and carbon tetrachloride to give $Fe(Me_4[14]dibenzoN_4)Cl$. In contrast to $Fe(Ph_2[14]N_4)$ this complex yields a μ-oxo dimer upon treatment with oxygen. Other reactivity features of $Fe(Me_4[14]dibenzoN_4)$, viz., binding of carbon monoxide and formation of stable Fe(III)-C σ bonds, reported by Goedken et al.,[21] have not been investigated with **4–6**.



IV

Both the ferric complexes considered thus far and the methods affording them have distinct analogies in the chemistry of iron with porphyrins which, as **1–3**, are diprotic macrocycles (H_2P). Numerous compounds of the Fe(P)X type with X = halide and carboxylate are known.[25] Fe(II) has been inserted into a porphyrin using ferrous carboxylates,[36a,b] Fe(P) oxidized to Fe(P)Cl in chlorinated solvents,[36c] $Fe(P)(O_2CR)$ metathesized to Fe(P)X,[36d] and the latter compounds converted to $[Fe(P)]_2O$ with aqueous base.[36e] The principal difference in the syntheses reported here is the use of basic ferric acetate in a one-step macrocyclic incorporation of Fe(III). This reagent does not appear to have been used with porphyrins where the usual method involves aerial oxidation of the $Fe(OAc)_2$-H_2P-X^- or HX reaction mixture, yielding Fe(P)X.[36f] Reduction of the latter rather than direct synthesis is the conventional route to Fe(II) porphyrins.[36f-h]

(c) **Fe(III) Macrocyclic Thiolates.** In contrast to Fe(III) porphyrin halides and carboxylates, prior to the inception of this work there had been no clear evidence that the corresponding thiolate complexes were of sufficient stability to be isolated. Earlier reports had included a spectral observation of one Fe(P)(SPh) complex[25] and in situ generations of related species, usually in the presence of excess nitrogen bases at low temperature.[26,37] Recently described results[28,29] together with ongoing research[38] fully support formulation of the EPR detectable[37] complexes as low spin Fe(P)(SR)(N-base), which are, however, unstable with respect to $Fe(P)(N\text{-base})_2$ and RSSR. The first syntheses of stable $[Fe^{III}N_4(SR)]$ complexes were achieved by simple extensions (eq 3 and 4)

$$[Fe^{II}N_4] + \tfrac{1}{2}RSSR \rightarrow [Fe^{III}N_4(SR)] \quad (3)$$

$$[Fe^{III}N_4(OAc)] + RSH \rightarrow [Fe^{III}N_4(SR)] + HOAc \quad (4)$$

of reactions 1 and 2. Reaction of the Fe(II) complexes **4**, **5**, and **6** with diphenyl disulfide (and a catalytic amount of benzenethiol) gives the benzenethiolate species **17**, **18**, and **19**, respectively, in good yield. These same complexes can also be prepared by the reactions of the corresponding Fe(III) carboxylates with benzenethiol. Substitution reactions with benzylthiol exhibit a dependence on macrocycle structure. Whereas the reaction of **13** with the thiol gives $Fe(Ph_2[16]N_4)(SCH_2Ph)$ (**20**) in 88% yield, similar treatment of the two smaller ring acetate complexes gives only the Fe(II) macrocycles **4** and **5**. Among nonmacrocyclic complexes both Fe(salen)(OAc) and $[Fe(salen)]_2O$ react with benzenethiol to yield Fe(salen)(SPh).[39] This compound cleanly reverts to the μ-oxo dimer upon reaction with oxygen. All $[Fe^{III}N_4(SR)]$ complexes are even more sensitive to oxygen than are their halide and carboxylate analogs; oxidation products were not characterized. These complexes react rapidly with chloroform (but very slowly with dichloromethane) at ambient temperature to give $[Fe^{III}N_4Cl]$ species.

The successful preparation of the macrocyclic Fe(III) thiolates **17–20** preceded attempts to secure the related five-coordinate porphyrin complexes Fe(P)(SR) and suggested that the latter might be stable and accessible by similar routes. Such has proven to be the case,[28,29] but that preparative method which in our hands furnishes materials with the highest magnetic purity is bridge cleavage of $[Fe(P)]_2O$ with thiols rather than reactions 3 and 4.[28,38] One important stability limitation of the ferric thiolate complexes is evident. With the exception of **20** all complexes sufficiently stable for isolation contain R = aryl. This situation also obtains with many porphyrin[28,38] and salen complexes, which are reduced to the Fe(II) state when reactions 3, 4, and μ-oxo bridge cleavage are attempted with alkyl thiols. At least for solution reactions the more electronegative thiolates are required in order to prevent in-

Table II. Polarographic Data for Metal Redox Processes of Fe(II, III) Macrocyclic Complexes in DMF Solution at 25°

Complex		Couple[a]	$E_{1/2}$, V	Slope,[b] mV
$Fe(Ph_2[14]N_4)$[c,d]	(4)	0/+	−0.37	61
$Fe(Ph_2[15]N_4)$	(5)	0/+	−0.32	73
$Fe(Ph_2[16]N_4)$	(6)	0/+	−0.36	75
$Fe(Ph_2[14]N_4)(SPh)$[d]	(17)	−/0	−0.79	74
$Fe(Ph_2[15]N_4)(SPh)$	(18)	−/0	−0.69	72
$Fe(Ph_2[16]N_4)(SPh)$	(19)	−/0	−0.69	69
$Fe(Ph_2[16]N_4)(SCH_2Ph)$	(**20**)	−/0	−0.82	60
$[Fe(Ph_2[16]N_4)]_2O$	(16)	−/0	−1.19	65

[a] Notation indicates one-electron processes but does not imply strict electrochemical reversibility; number of electrons transferred determined by comparison of diffusion currents with that for $[Ni(tdt)_2]^{2-/-}$. [b] From plots of E vs. log $[i/(i_d - i)]$; theoretical value for reversible one-electron process is 59 mV. [c] DMSO solution. [d] Additional waves corresponding to irreversible oxidation by one or more electrons are observed for thiolate complexes at ca. +0.1 to +0.2 V and for the ferrous complexes at ca. +0.4 to +0.5 V; these are considered to be ligand oxidations and may be related to the reactivity of the complexes with oxygen.

tramolecular redox, a process presumably facilitated by the formation of disulfide, i.e., the reverse of reaction 3.

Polarographic Results. The redox behavior of Fe(II) macrocycles and Fe(III) macrocyclic thiolates was investigated polarographically. Potentials assigned to metal-centered redox processes are collected in Table II. As judged from current-voltage slope criteria most of these processes depart from strict reversibility, possibly because of changes in axial ligation upon oxidation or reduction. Potentials for oxidation of the Fe(II) complexes are moderately negative, in keeping with the oxidative instability of these species, and are similar in magnitude to reduction potentials of Fe(III) porphyrins.[40] Exposure of a polarographic solution of $Fe(Ph_2[16]N_4)$ to oxygen results ultimately in elimination of the −0.36 V wave and appearance of a new reduction wave at −1.19 V. The latter was found in the polarogram of an isolated sample of the μ-oxo dimer **16** and is assigned to the $[Fe^{III}]_2O \rightarrow Fe^{III}\text{-}O\text{-}Fe^{II}$ reduction. This process has been observed for $[Fe(TPP)]_2O$ at −0.9 V.[40b] No further reductions of **16** were found. The thiolate complexes **17–20** exhibited Fe(III)/Fe(II) reductions at ca. −0.7 to −0.8 V. The potentials in Table II reveal no systematic dependence on ring size, nor on spin-states (vide infra) in the thiolate series. The Fe(II)/Fe(III) potentials obtained here are substantially more negative than those reported for cationic $Fe^{II}[14]N_4$ complexes,[16] whose mode of reaction with oxygen involves ligand oxidative dehydrogenation[13,16] rather than metal oxidation.

Ground State Electronic Properties. Magnetic susceptibility data and Mossbauer and EPR spectral results relevant to the establishment of magnetic ground states of complexes **4–22** are given in Tables III and IV and Figures 2–5.

(a) **Fe(II) Complexes.** Complexes **4–6** were synthesized primarily for the purpose of investigating their reactivity properties. They are among a quite small number of ostensibly four-coordinate complexes which have been adequately characterized. Measurements of electronic properties were confined to solid state magnetic susceptibilities of $Fe(Ph_2[14]N_4)$ (**4**) and $Fe(Ph_2[16]N_4)$ (**6**) in the 17–295 K range. As shown by the data in Table III, ambient temperature magnetic moments are above the $S = 1$ spin-only value (2.83 μ_B) with quite different orbital contributions. Both compounds follow the Curie–Weiss law, with **6** showing a negligible variation from Curie behavior. These results rule out the spin mixture $S = 0/2$ and indicate that these complexes possess the intermediate spin ($S = 1$) ground state. Measurements at lower temperatures are required for fits to theoretical susceptibility expressions for a triplet state,[41] which has been established by magnetic anisotropy measurements for the related complex Fe(II) phthalocyanine (FePc, 3.89 μ_B, 23°).[41] This ground state may be of frequent occurrence in approximately or exactly planar $[Fe^{II}N_4]$ complexes. Room temperature moments of $Fe(Me_4[14]tetraenatoN_4)$,[7] $Fe(Me_4[14]dibenzoN_4)$,[21b] and similar compounds[24a] are 3.6–4.0 μ_B. For the porphyrin complex Fe(TPP)[36a,b,h] and one derivative[42] μ = 4.4–5.0 μ_B (~25°). Although the $S = 2$ ground state assignment has been made,[36a,b] the established planar coordination in Fe(TPP) strongly argues for an intermediate spin ground state.[43] Fe(II) octamethyltetrabenzoporphyrin, whose detailed structure is unknown, is high spin.[44]

(b) **Fe(III) Halides and Carboxylates.** Ground state spin assignments rest primarily on the magnetic data in Table III and the following results (solid state, 298°K): $Fe(Ph_2[14]N_4)X$, X = Cl (3.98 μ_B), I (3.88), OAc (3.92); $Fe(Ph_2[15]N_4)Cl$ (4.10); $Fe(Ph_2[16]N_4)X$, X = Br (5.80), O_2CPh (5.88). As may be seen from Figure 2 the bromides **9** and **12** and the acetate **13** accurately follow the Curie–Weiss law from 17 to 295 K, thus establishing their ground state as intermediate ($S = 3/2$) and high spin ($S = 5/2$), respectively. The preceding complexes with room temperature magnetic moments close to those of **9**, **12**, and **13** are assigned corresponding spin states. The moments of **9** and **12** in dichloromethane solution are slightly higher than those in the solid, but serve to show that solid state effects are not responsible for the intermediate spin states. $Fe(Ph_2[16]N_4)(O_2CPh)$ exhibits a low temperature EPR spectrum (Table IV) fully consistent with a high-spin state and substantial rhombic distortion.[45,46] From the symmetric g value splitting around $g = 6$ the ratio of spin Hamiltonian parameters $E/D \simeq 0.067$, or 20% "rhombicity",[46] above the 0–0.05 range normally encountered in heme complexes and proteins[46,47] and doubtless due mainly to the lack of fourfold ligand symmetry in III. These results show that at parity of axial ligand macrocycle structure exerts a definite influence on spin state: [14]- and [15]-membered rings uniformly stabilize the $S = 3/2$ spin state whereas complexes of the [16]-ring system are high spin. Complexes **7–12** are presently the only definite examples of $[Fe^{III}N_4X]$ species (X = halide, RCO_2) having the uncommon intermediate spin state.[48]

The effect of additional axial ligation on the spin states of halide and carboxylate complexes was investigated by EPR employing the glass-forming solvent mixture 1:1 v/v $DMF\text{-}CH_2Cl_2$, containing a base sufficiently weak to minimize replacement of the original axial ligands. Relevant data are contained in Table IV. The spectrum of $Fe(Ph_2[14]N_4)(OAc)$ consisted of a broad resonance centered at $g \sim 4.5$ and three sharp signals near $g \sim 2$. In the series $Fe(Ph_2[14]N_4)X$ (**7–10**) and $Fe(Ph_2[15]N_4)X$ (**11**, **12**), the intensities of the latter signals increased and that of the former signal decreased, indicating that the tendency of DMF adduct formation is OAc, Cl < Br < I. The set of rhombic signals near $g \sim 2$ arises from low-spin six-coordinate species[45,49] while that of $g \sim 4.5$ is assigned to the unligated quartet-state species.[50] In the case of the iodide complex **10** only the resonances at g = 2.09, 2.06, and 1.99 were observed, indicating that formation of the adduct $Fe(Ph_2[14]N_4I)(DMF)$ was complete. Adduct formation was further evidenced in this case by the reversible color change upon cooling the purple solution of **10** to give a brown glass at 77 K. Complexes of the [16]-ring type remained high spin under these conditions.

(c) **μ-Oxo Dimer.** Formation of $[Fe(Ph_2[16]N_4)]_2O$ by aerial oxidation of **6** or base hydrolysis of **14** has been described. The magnetic moment of 1.88 μ_B/Fe (298 K), ob-

Table III. Magnetic and Mossbauer Properties of Fe(II, III) Macrocycles

Complex		Spin state	μ_{obsd}, $(\mu_B)^a$ 295 K	C^b	θ,^{b} deg	δ,^{c} mm/sec	ΔE_Q,^{c} mm/sec	H_{hf},^{h} kOe
$Fe(Ph_2[14]N_4)$	(4)	$S = 1$	3.26	1.35	6.8	*d*	*d*	—
$Fe(Ph_2[16]N_4)$	(6)	$S = 1$	4.54	2.56	0.2	*d*	*d*	—
$Fe(Ph_2[14]N_4)Br^f$	(9)	$S = {}^3/_2$	3.91	1.96	7.9	*d*	*d*	—
$Fe(Ph_2[14]N_4)(SPh)$	(17)	$S = {}^1/_2$	1.95	*d*	*d*	0.04	3.60	~−70
$Fe(Ph_2[14]N_4)(SPh)(py)$	(21)	$S = {}^1/_2$	1.82	*d*	*d*	-0.02^e	3.22^e	*d*
$Fe(Ph_2[15]N_4)Br^g$	(12)	$S = {}^3/_2$	4.08	2.11	4.6	*d*	*d*	*d*
$Fe(Ph_2[15]N_4(SPh)$	(18)	$S = {}^3/_2$	3.97	1.97	3.0	0.13^e	2.55^e	*d*
$Fe(Ph_2[15]N_4)(SPh)(py)$	(22)	$S = {}^1/_2$	1.87	*d*	*d*	*d*	*d*	*d*
$Fe(Ph_2[16]N_4)(OAc)$	(13)	$S = {}^5/_2$	5.82	4.23	0.1	*d*	*d*	*d*
$Fe(Ph_2[16]N_4)(SPh)$	(19)	$S = {}^3/_2$	4.17	1.94^i	5.9^i	0.26	1.93, 2.28^e	~−270
$Fe(Ph_2[16]N_4)(SCH_2Ph)$	(20)	$S = {}^5/_2$	5.91	4.39	2.0	0.35	0.71	~−450

[a] Solid state; calculated from Curie law. [b] Evaluated from least-squares fit of data to $\chi^{M}{}_{\mathrm{corr}} = C/(T + \theta)$, T = 17–295 K unless otherwise noted. [c] At 300 K, δ relative to Fe metal. [d] Not measured. [e] At 77 K. [f] 4.08 (300), 4.05 (248), 4.06 μ_B (224 K), dichloromethane solution. [g] 4.18 μ_B (298 K), dichloromethane solution. [h] At 4.2 K, H_0 = 80 kOe. [i] At 17–200 K (cf. Figure 2).

Table IV. EPR Data for Fe(III) Macrocyclic Complexes at ~95 K

Complex		Spin state	*g* values		
$Fe(Ph_2[14]N_4)Br(DMF)^a$		$S = {}^1/_2$	2.09	2.06	1.99
$Fe(Ph_2[14]N_4)I(DMF)^a$		$S = {}^1/_2$	2.09	2.06	1.99
$Fe(Ph_2[14]N_4)(SPh)^b$	(17)	$S = {}^1/_2$	2.11	2.04	2.01
$Fe(Ph_2[14]N_4)(SPh)(py)^b$	(21)	$S = {}^1/_2$	2.13	2.03	2.00
$Fe(Ph_2[14]N_4)(SPh)(DMF)^a$		$S = {}^1/_2$	2.12	2.04	1.99
$Fe(Ph_2[14]N_4)(py)_2{}^{+a}$		$S = {}^1/_2$	2.08	2.02	2.00
$Fe(Ph_2[14]N_4)(N\text{-}Me\text{-}Im)_2{}^{+a}$		$S = {}^1/_2$	2.10	2.04	1.99
$Fe(Ph_2[15]N_4)(SPh)^{b,c}$	(18)	$S = {}^1/_2$	2.15	2.06	2.01
$Fe(Ph_2[15]N_4)(SPh)(py)^b$	(22)	$S = {}^1/_2$	2.19, 2.16	2.06	1.99
$Fe(Ph_2[15]N_4)(py)_2{}^{+a}$		$S = {}^1/_2$	2.09	2.05	1.99
$Fe(Ph_2[15]N_4)(N\text{-}Me\text{-}Im)_2{}^{+a}$		$S = {}^1/_2$	2.12	2.07	1.99
$Fe(Ph_2[16]N_4)(SPh)^b$	(19)	$S = {}^5/_2$	7.4	4.6	1.9
$Fe(Ph_2[16]N_4)(O_2CPh)^a$	(14)	$S = {}^5/_2$	7.6	4.4	1.9
$Fe(Ph_2[16]N_4)(SCH_2Ph)^b$	(20)	$S = {}^5/_2$	7.5	4.5	1.9
$Fe(Ph_2[16]N_4)(SPh)(py)^b$		$S = {}^1/_2$	2.41	2.10	1.96
$Fe(Ph_2[16]N_4)(SCH_2Ph)(py)^b$		$S = {}^1/_2$	2.32	2.10	1.97

[a] 1/1 (v/v) $DMF-CH_2Cl_2$ glass. [b] Toluene glass. [c] Low spin component; see text.

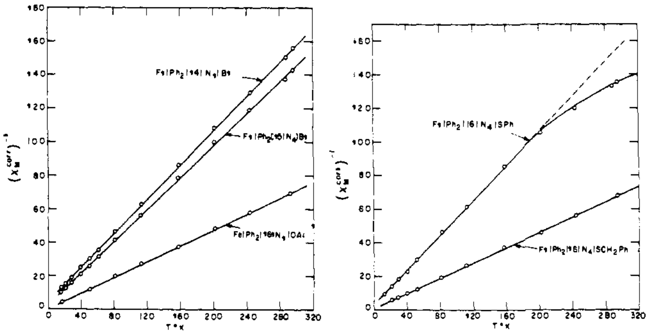


Figure 2. Temperature dependencies of magnetic susceptibilities in the solid state: (left) $Fe(Ph_2[14]N_4)Br$ and $Fe(Ph_2[15]N_4)Br$ ($S = {}^3/_2$), $Fe(Ph_2[16]N_4)(OAc)$ ($S = {}^5/_2$); (right) $Fe(Ph_2[16]N_4)(SPh)$ ($S = {}^3/_2$), $Fe(Ph_2[16]N_4)(SCH_2Ph)$ ($S = {}^5/_2$).

tained for a sample prepared by the latter method, and the observation of an infrared band at 855 cm^{-1} are adequate to establish the μ-oxo structure which has been demonstrated for numerous other Fe(III) complexes using the same criteria.[52]

(d) Fe(III) Thiolates. Ground spin states for the five-coordinate thiolate complexes **17–20** in the solid state were established by a combination of magnetic susceptibility and Mossbauer spectral measurements, which reveal that these complexes form a unique series encompassing the three possible spin states ($S = {}^1/_2, {}^3/_2, {}^5/_2$) for Fe(III) in a noncubic ligand field. Magnetic data in Table III are consistent with the assigned spin states. Fe(salen)(SPh) was found to be high spin (5.90 μ_B, 295 K). The only complicated behavior was observed with $Fe(Ph_2[16]N_4)(SPh)$ (**19**, Figure 2). Whereas $Fe(Ph_2[15]N_4)(SPh)$ (**18**, $S = {}^3/_2$) and $Fe(Ph_2[16]N_4)(SCH_2Ph)$ (**20**, $S = {}^5/_2$) follow the Curie-Weiss law over the 17-295 K range, **19** deviates above 200 K giving 4.17 μ_B at 295 K compared to the value of 3.91 μ_B calculated from the $S = {}^3/_2$ Curie-Weiss relation apparent at lower temperatures. This deviation may reflect small population of a sextet state at the higher temperatures.

The Mossbauer spectra of **17–20** in zero external magnetic field are characterized by single quadrupole doublets. Isomer shifts and quadrupole splittings are listed in Table III and velocity spectra obtained at 77 K for **17**, **19**, and **20** are plotted in Figure 3. Spectra of these compounds were also taken at 4.2 K in longitudinal magnetic fields up to 80 kOe, and the spectra obtained at 80 kOe are given in Figure 4.

The isomer shift and quadrupole splitting of $Fe(Ph_2[16]N_4)(SCH_2Ph)$ (**20**) are temperature invariant and are similar to those obtained for high-spin tetragonal $Fe^{III}N_4$ complexes[20b,53] including hemin chloride. The high-spin assignment is also supported by the large magnetic hyperfine interaction induced at low temperature by the applied magnetic field (Table III). The reduction in the hyperfine field H_{hf} from the usual value of ca. −500 kOe for high-spin ferric ion[54] is due to a large zero field splitting of the spin sextet ground state into three Kramer's doublets. The EPR spectrum of **20** (Figure 5, Table IV) is of the high-spin type,[45,46] and shows that the zero-field splitting is nonaxial ($E/D \simeq 0.063$) and that the spin states which are mostly $m_s = \pm{}^1/_2$ lie lowest in energy. The value $H_{\mathrm{hf}} \sim -450$ kOe observed at H_0 = 80 kOe and 4.2 K is slightly greater than that obtained under the same conditions in hemin chloride,[38,55] implying that if the hyperfine interaction constants are the same, the zero field splitting in the present case is slightly less than that in hemin chloride,[55] viz., $D \sim$ 5-7 cm^{-1}. As in the latter H_{hf} induced by the applied field lies in the plane defined by the four nitrogens of the macrocycle.[55,56] The positions of the residual $\Delta M = 0$ lines in the H_0 = 80 kOe spectrum define an electric quadrupole splitting of negative sign and approximately one-half the magnitude observed at $H_0 = 0$. This implies that the principal component of the electric field gradient tensor lies perpendicular to the $Fe-N_4$ mean plane and has a positive sign, as in hemin chloride.

The Mossbauer spectral parameters for $Fe(Ph_2[14]N_4)(SPh)$ (**17**) are considerably different from those of the high-spin complex **20** with an isomer shift typical of tetragonal low-spin $Fe^{III}N_4$ complexes.[20a,57] The

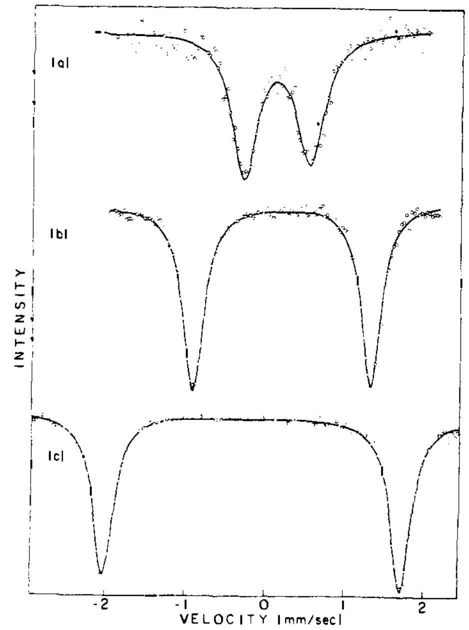


Figure 3. Mossbauer spectra at room temperature: (a) $Fe(Ph_2[16]N_4)(SCH_2Ph)$ ($S = \frac{5}{2}$); (b) $Fe(Ph_2[16]N_4)(SPh)$ ($S = \frac{3}{2}$); (c) $Fe(Ph_2[14]N_4)(SPh)$ ($S = \frac{1}{2}$). The solid lines are theoretical least-squares fits to the data assuming Lorentzian line shapes.

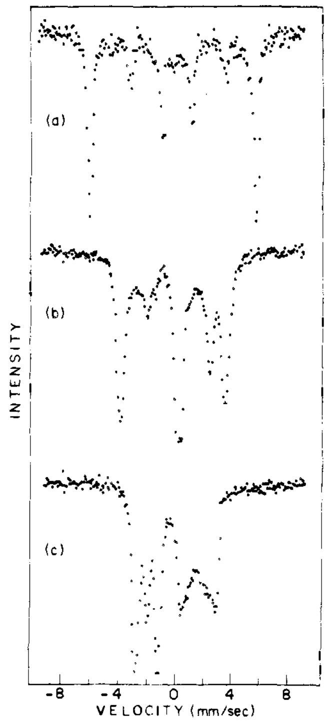


Figure 4. Mossbauer spectra at 4.2 K in a longitudinal magnetic field of 80 kOe: (a) $Fe(Ph_2[16]N_4)(SCH_2Ph)$ ($S = \frac{5}{2}$); (b) $Fe(Ph_2[16]N_4)(SPh)$ ($S = \frac{3}{2}$); (c) $Fe(Ph_2[14]N_4)(SPh)$ ($S = \frac{1}{2}$).

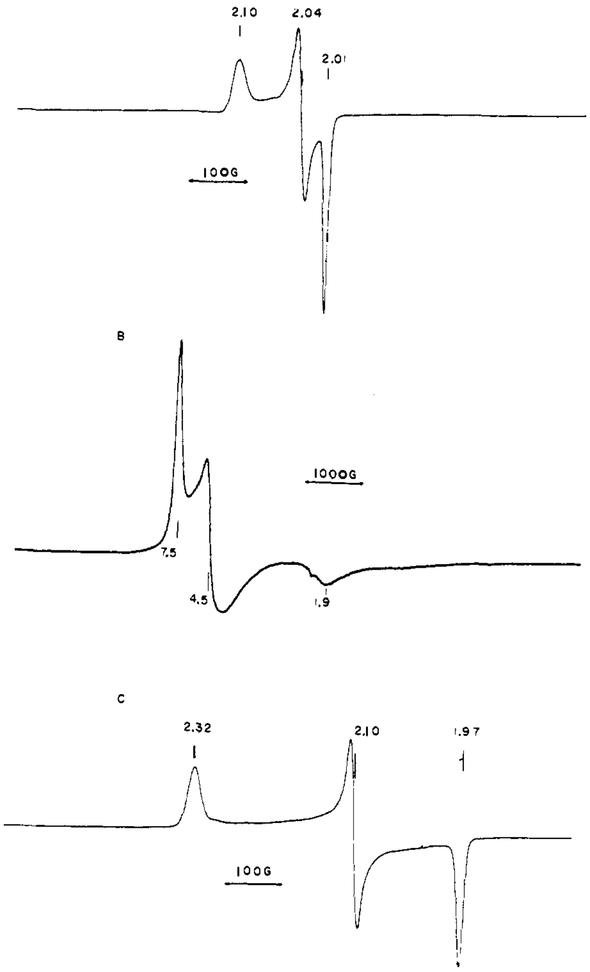


Figure 5. EPR spectra in toluene glass at ~95 K: A, $Fe(Ph_2[14]N_4)(SPh)$ ($S = \frac{1}{2}$); B, $Fe(Ph_2[16]N_4)(SCH_2Ph)$ ($S = \frac{5}{2}$); C, $Fe(Ph_2[16]N_4)(SCH_2Ph)(py)$ ($S = \frac{1}{2}$) generated by the addition of pyridine to B.

EPR spectrum of **17** (Figure 5, Table IV) is like those of the DMF adducts discussed above and can be reconciled only with a doublet ground state.[45,49] Application of an external magnetic field at 4.2 K results in a typical apparent doublet-triplet Mossbauer spectrum (Figure 4), with the sign of V_{zz} positive and the magnetic hyperfine interaction induced by the applied field small and anisotropic, consistent with $H_{hf} \sim -70$ kOe. This value is close to the "spin-only" hyperfine field of −100 kOe for $S = \frac{1}{2}$ expected with the usual core polarization hyperfine interaction of ca. −200 kOe/unit of spin ($S = 1$).[54] The large positive quadrupole splitting of 3.60 mm/sec, which is essentially temperature independent, and the hyperfine interaction can be qualitatively interpreted in terms of a tetragonal splitting of a $^2T_{2g}$ octahedral ground state with partial quenching of the orbital angular momentum. This would result in a reduced orbital contribution to the magnetic hyperfine interaction, a temperature invariance of the quadrupole splitting, and the maximum valence contribution to the electric quadrupole interaction which can be as large as 2.6 mm/sec. The difference between the latter value and the observed value of ΔE_Q can reasonably be ascribed to a ligand contribution. In a simple crystal field model, the level ordering for a square pyramidal complex is $e(d_{xz}, d_{yz}) < b_2(d_{xy}) < a_1(d_{z^2}) < b_1(d_{x^2-y^2})$. In a low-spin configuration the hole in the b_2 orbital would result in a negative electric field gradient. However, the lack of fourfold symmetry of the [14]-ring in I together with some extent of out-of-plane π bonding should split the low-lying e orbitals and could account for a positive valence contribution to the field gradient.

The magnitudes of the quadrupole splitting and isomer shift of $Fe(Ph_2[16]N_4)(SPh)$ (**19**) are intermediate between the high-spin and low-spin cases cited above. The quadrupole splitting is comparable to those observed in $Fe(S_2CNR_2)_2X$ complexes[51] for which spin quartet ground states have been established,[51,58] whereas the isomer shifts of the latter complexes are ca. 0.15 mm/sec higher than those reported here. However, the latter complexes have fourfold sulfur coordination, and, moreover, it has been observed that sextet and quartet Fe(III) cannot in general be distinguished by isomer shifts alone.[59] The strongest Mossbauer evidence for the spin quartet ground state in the present case comes from the magnetic hyperfine interaction induced by an applied field (Figure 4). The spectrum consists of the typical doublet-triplet type and is consistent with an anisotropic hyperfine interaction of ca. −270 kOe and V_{zz} positive. For the ferric core polarization of ca. −200 kOe/spin a hyperfine field of −300 kOe is expected for an $S = 3/2$ ground state. The difference between the latter and the observed value could arise from covalency effects and zero-field splitting of the quartet state.[60] The isomer shift and quadrupole splitting of $Fe(Ph_2[15]N_4)(SPh)$ (**18**) are quite similar to those of **19** and, together with magnetic data, establish a quartet ground state.

(e) **Fe(III) Thiolate Base Adducts.** The thiolate complexes **17–20**, as the halide and carboxylate complexes considered above, were found to be susceptible to adduct formation. Because of our current interest in $Fe^{III}N_4$ complexes containing RS-Fe-N axial ligation,[28,38] the majority of the studies employed pyridine. Mossbauer and EPR data for adducts are contained in Tables III and IV. Because of their lability in solution, established by spectral measurements, the adducts were most conveniently examined by EPR at ~95 K in glasses containing excess base. In toluene $Fe(Ph_2[14]N_4)(SPh)$ (**17**) exhibits a simple low-spin rhombic spectrum (Figure 5) whereas in $DMF-CH_2Cl_2$ two overlapping rhombic spectra are observed, indicating partial adduct formation. Addition of pyridine produces a new spectrum, slightly but discernibly different from that of $[Fe(Ph_2[14]N_4)(py)_2]^+$ generated from **8** and excess pyridine, and identical with that of the isolated adduct $Fe(Ph_2[14]N_4)(SPh)(py)$ (**21**) in toluene. Excess *N*-methylimidazole with **17** also gave a low-spin spectrum assigned to the base diadduct resulting from Fe-S bond cleavage. $Fe(Ph_2[15]N_4)(SPh)$ (**18**) in toluene displayed an intense low-spin spectrum and a very broad signal at $g \sim 4.5$ indicating that upon passage from the solid to a glass medium a significant proportion of the molecules are converted from the intermediate to the low-spin state. The behavior of **18** with various bases parallels that of **17**; low-spin adducts are found in each case. A difference was observed in the spectrum of the isolated adduct $Fe(Ph_2[15]N_4)(SPh)(py)$ (**22**), which gave a doubled low field resonance ($g = 2.16, 2.19$) in the rhombic set. These might arise from two frozen-out ring conformations of II or two different orientations of the pyridine ring with respect to the $Fe-N_4$ plane.

In toluene $Fe(Ph_2[16]N_4)(SCH_2Ph)$ (**20**) gives a high-spin EPR spectrum consistent with its solid state behavior. However, $Fe(Ph_2[16]N_4)(SPh)$ (**19**), which is mainly intermediate spin in the solid, exhibits a strong high-spin spectrum in toluene. Pyridine adducts of neither complex could be isolated but were readily generated in a toluene glass and were found to be low spin. Spectra of **20** and its pyridine adduct are shown in Figure 5.

The behavior of **17–20** with pyridine is similar to that of ferric porphyrin thiolates, which with this and other nitrogen bases form low-spin Fe(P)(SR)(N-base) at reduced temperatures.[28,29,38] The g values and g tensor anisotropies of the adducts of **19** and **20** are quite close to those of the porphyrin adducts.[28,29,37,38] In contrast to the latter, N-base adduct formation by **17–20** does not result in reduction to Fe(II) complexes; **21** and **22** are the first cases of isolable complexes containing $RS-Fe^{III}-N$ axial coordination.

Summary

From the results and conclusions described above the following significant features of the chemistry of tetragonal iron complexes of macrocycles I, II, and III emerge from this investigation.

(a) **Intermediate Spin States.** The Fe(II) complexes **4–6** appear to be well-defined examples of intermediate spin ($S = 1$) d^6 cases with probable planar stereochemistry. Other apparent examples of this spin state in four-coordinate complexes are not numerous and, with the exception of FePc,[41] are not as yet magnetically well characterized. Previous instances of intermediate spin ($S = 3/2$) d^5 cases are rare and, for a general class of complexes, have been found only for $Fe(S_2CNR_2)_2X$[51,59] (X = halide, pseudohalide) of tetragonal pyramidal stereochemistry.[51,61] In the present group of $[Fe^{III}N_4X]$ complexes the intermediate spin state is in fact the most common. Abbreviating the latter in terms of ring size and axial ligand, all [14]-X (except X = SPh), all [15]-X, and the [16]-SPh complex have quartet ground states, at least in the solid state. No synthetic Fe(III) porphyrin with this ground state has yet been found. In the biological realm the magnetic properties of ferricytochrome c' have been interpreted in terms of quantum mechanical admixtures of intermediate and high-spin states.[62]

(b) **Low-spin Tetragonal Fe(III).** Without exception five-coordinate Fe(III) porphyrin complexes, including $Fe(PPIXDME)(SC_6H_4NO_2)$,[28] are high-spin with a tetragonal pyramidal structure and Fe(III) displaced ca. 0.4–0.5 Å toward the axial ligand.[63] The situation is clearly different with $Fe(Ph_2[14]N_4)(SPh)$ (**17**) where the ligand field is strong enough to give a low-spin ground state. The anticipated structure corresponds to that for the complex $[Fe(Me_4[14]N_4)Ph]$,[21] derived from a closely related macrocycle. This complex has a 0.23 Å axial displacement of the metal, and it and analogous organoiron(III) macrocycles[21] are the only other examples of doublet-state pyramidal Fe(III) molecules.

(c) **Axial Ligand Effects.** Using spin-state changes as an indication of relative ligand field strengths of axial ligands in Fe(III) complexes of the same ring structure,[64] series 5 and 6 are evident from the experimental results.

$$[14]\text{-ring: } X = SPh^- \; (S = 1/2) > \text{halide, } OAc^- \; (S = 3/2) \quad (5)$$

$$[16]\text{-ring: } X = SPh^- \; (S = 3/2) > Br^-, RCO_2^- \; (S = 5/2) \quad (6)$$

At constant in-plane ligand field strength an increasing axial field component will destabilize d_{z^2} relative to d_{xz}, d_{yz}, d_{xy} (neglecting π-interactions), leading ultimately to a reduction in spin multiplicity. Evidently, thiolate is more effective than halide or carboxylate in this regard. The two series are consistent with the order $RS^- > Br^-, Cl^-$ deduced from spectra of the tetrahedral Fe(II) and Co(II) complexes $M(SR)_4{}^{2-}$ [65] and $MX_4{}^{2-}$.[66]

(d) **Ring-Size Effect.** At parity of axial ligand the following effects of macrocycle ring size on spin states are recognized (series 7–9).

$$[14]\text{-OAc } (S = 3/2) > [16]\text{-}O_2CR \; (S = 5/2) \quad (7)$$

$$[14,15]\text{-Br } (S = 3/2) > [16]\text{-Br } (S = 5/2) \quad (8)$$

$$[14]\text{-SPh } (S = 1/2) > [15,16]\text{-SPh } (S = 3/2) \quad (9)$$

The higher spin states are stabilized as the ring size increases, implying progressively weakened in-plane ligand fields. This behavior has been nicely illustrated by the ligand field spectra of Ni(II) and Co(III) complexes of saturated tetraaza macrocycles upon incremental increase of ring size in one [13]- to [16]-ring series,[67] and presumably results from increasing size of the N_4 "hole". A detailed rationalization of the ring size effect in the present group of complexes requires experimental establishment of d-orbital energy orders, which currently are lacking.

It has been assumed throughout, in the absence of X-ray structural information, that the five-coordinate Fe(III) complexes have overall tetragonal pyramidal stereochemistry. If true, the spin state variations summarized in series 5-9 reflect the consequences of the inherent ligand field components generated by the axial ligands and the three ring systems in the solid state. This assumption appears adequate for complexes of the rather rigid macrocycle I. However, combinations of the less rigid rings II and, particularly, III with certain axial ligands may allow structural changes concomitant with changes in spin state and indeed may induce the latter. The departure of solid $Fe(Ph_2[16]N_4)(SPh)$ from $S = \frac{3}{2}$ Curie-Weiss behavior at higher temperatures and the formation of some proportion of high-spin form by this complex and by $Fe(Ph_2[15]N_4)(SPh)$ in toluene glasses may be examples of this effect. The spin state difference between the former complex and $Fe(Ph_2[16]N_4)(SCH_2Ph)$ in the solid state is difficult to interpret on the basis of axial ligand field effects, and the two complexes may have different structures. In any case it is clear that with thiolate ligands the energy differences between [15]- and [16]-ring quartet and sextet species is not large. Further research will be directed toward the factors which stabilize these spin states and will include X-ray structural determinations.

Throughout the preceding discussions similarities and differences in synthesis, stability, and electronic properties of Fe(II, III) macrocycles derived from I-III and related iron porphyrin complexes have been pointed out. The former are not represented as models or close analogs of the latter. However, the properties of these and other synthetic macrocyclic iron complexes,[2,13,16-24] which contain a broad array of ring structures and axial ligation, are, expectedly, no less diverse than those of the porphyrins. In one respect, viz., stabilization of all possible ground spin states of noncubic Fe(III), the complexes reported here (**17-20**) constitute a unique group.

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Cobalt(III) Carboxypeptidase A

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Abstract: Cobalt(III) carboxypeptidase A has been prepared by the oxidation of cobalt(II) carboxypeptidase A with hydrogen peroxide at pH 7.5. The oxidized enzyme shows negligible peptidase activity after dialysis against metal-free buffer or 1,10-phenanthroline while its esterase activity toward hippuryl-L-β-phenyllactate and *trans-p*-nitrocinnamoyl-L-β-phenyllactate is comparable to that of cobalt(II) carboxypeptidase A. Carbobenzyloxyglycyl-L-phenylalanine, toward which the cobalt(II) enzyme is active, competitively inhibits the activity of the cobalt(III) protein toward hippuryl-D,L-β-phenyllactate. The metal in the oxidized enzyme is no longer removable by dialysis against metal-free buffer, but may be reduced back to cobalt(II) and exchanged by dialysis against excess cobalt(II). Cobalt(III) carboxypeptidase A has a visible absorption maximum at 503 nm (ϵ 500). The pH dependence of ester hydrolysis by cobalt(III) carboxypeptidase A shows that catalysis requires the basic form of a group on the enzyme with pK_a 6.3–6.5 and the acidic form of a group with pK_a 9.1–9.5. These results have a bearing on the mechanism of action of carboxypeptidase A. In particular, they imply that the group of higher pK_a is not a water molecule bound to the metal and that ligation of substrates within the first coordination sphere of the metal does not occur during ester hydrolysis catalyzed by cobalt(III) carboxypeptidase A.

Carboxypeptidase A is a metalloenzyme with a molecular weight of about 34,500.[2,3] It catalyzes the hydrolysis of the C-terminal peptide bond of peptides as well as the corresponding ester bond of L-α-acyloxycarboxylic acids. Bovine pancreatic preparations have been obtained in several forms displaying some heterogeneity in their amino-terminal sequences.[4] It has been shown to require one atom of Zn(II) per molecule of protein for its normal peptidase activity.[5] Since the discovery of this metal ion involvement, there has been a great deal of effort put forth in attempting to elucidate both the manner in which Zn(II) is bound to the protein and the role the metal plays in the hydrolysis of substrate peptide or ester bonds. These results have been reviewed extensively in recent articles.[6-11] A large number of derivatives of carboxypeptidase A have been made in the course of these studies. Many of these have involved replacement of the Zn(II) with metals such as Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Cd(II), and Hg(II).[4,6] Although these metals differ in such physical properties as coordination geometry and ionic radius, they all belong to the exchange labile class of metal ions.[12] This exchange lability of the ligands in the first coordination sphere of the metal ion is necessary in order to introduce the ion into the protein. On the other hand, it would be quite useful, for both protein structure determination and mechanistic investigations, to have an exchange inert metal ion incorporated into a metalloenzyme. This property of exchange lability vs. exchange inertness is controlled largely by the d electron configuration of the metal ion. Some metals can be taken from one class to the other simply be changing their oxidation states. Such a situation exists with Co(II) (d^7), exchange labile, and Co(III) (d^6), exchange inert.

We report here the preparation of a metalloprotein containing an exchange inert metal ion, Co(III)-CPA.[13] A preliminary account of this work has appeared.[14] A similar oxidation of cobalt(II) carbonic anhydrase to the Co(III) enzyme has been reported.[15]

Experimental Section

Materials, Carboxypeptidase A (EC 3.4.12.2) prepared by the method of Anson[16] was obtained as an aqueous suspension of crystals, grade COA, from Worthington Biochemical Corporation. The substrates used in this study were obtained from the following sources: Gly-Gly-L-Phe, Nutritional Biochemical Co.; Z-Gly-L-Phe, Mann Research Laboratories; D,L-HPLA, Calbiochem Co.; L-HPLA, Cyclo Chemical Co.; and NCPLA, Eastman Organic Chemicals. Cobalt(II) solutions were prepared by dissolving cobalt sponge (99.999% pure), obtained from K and K Laboratories, in metal free hydrochloric acid. Radioactive cobalt solutions were prepared by adding $^{57}CoCl_2$, obtained from New England Nuclear, to nonradioactive solutions of $CoCl_2$. Special precautions against metal ion contamination included the use of polypropylene apparatus where possible, leaching glassware with 1:1 nitric acid: sulfuric acid, and extraction of buffers and other solutions with carbon tetrachloride containing 0.1 g/l. of diphenylthiocarbazone.[17]

Methods, Enzyme Preparations, All enzyme treatments except for concentration determinations and kinetic measurements were