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# Iron(II) Complexes with Unsubstituted Saturated Tetraaza Macrocyclic Ligands of Varying Ring Size

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Iron(II) complexes have been synthesized with 13-, 14-, 15-, and 16-membered, unsubstituted, fully saturated, tetradentate, macrocyclic ligands having nitrogen donor atoms. The complexes exhibit cis, trans, and dimeric six-coordinate geometries while displaying spin states which include low spin ($S = 0$), intermediate spin ($S = 1$), and high spin ($S = 2$). Mössbauer spectra and d–d electronic spectra have been obtained and correlated with structural features. Limited but significant series of compounds in both the high-spin and low-spin configurations show that ligand field strength increases dramatically as ring size decreases. Comparisons with earlier results on $Me_6[14]aneN_4$ indicate that the interactions of axial methyl groups weaken the metal–ligand interaction for both the axial ligands and the macrocycles. The effect of ring size on partial center shifts has been evaluated.

## Introduction

A number of iron complexes with synthetic tetradentate macrocyclic ligands containing nitrogen donor atoms (Figure 1) have now been prepared and characterized.[2-8] The Mössbauer spectra of many of these complexes, including $Me_2[14]aneN_4$ (I), $Me_6[14]aneN_4$ (II), and derivatives of the latter having various degrees of unsaturation (e.g., III, IV, and V) have been measured and subjected to detailed interpretation.[6,7] All of these earlier studies have used ligands that contain methyl substituents. While these ligands are convenient to synthesize, the methyl substituents tend to confuse the effects of steric and electronic factors. The unsubstituted ligand $[14]aneN_4$ (VII, also called cyclam) has long been known and its complexes with nickel(II)[9] and cobalt(III)[10,11] have been prepared and characterized. The corresponding unsubstituted ligands having 13, 15, and 16 ring members ($[13]aneN_4$, $[15]aneN_4$, and $[16]aneN_4$) have recently been prepared in these laboratories[12,13] and used in the study of complexes with nickel(II) and cobalt(III) in order to establish the relationships that exist between ring size and ligand field strength. We have synthesized the iron(II) complexes with these ligands ($[13]aneN_4$, $[14]aneN_4$, $[15]aneN_4$, and $[16]aneN_4$) in an attempt to elucidate the effects of ring size and steric factors on the electronic and Mössbauer spectral parameters for this important element.

## Experimental Section

**Materials.** Acetonitrile, diethyl ether, methanol, and ethanol were distilled from calcium hydride. Acetone was distilled from magnesium. Nitromethane and chloroform were distilled after being dried over molecular sieves. All distillations were carried out under nitrogen. All syntheses and recrystallizations of the iron complexes were carried out under nitrogen in a controlled-atmosphere enclosure.

**Physical Measurements.** Infrared spectra were obtained on a Perkin-Elmer 337 or 457 grating spectrometer using KBr pellets, Nujol mulls, and NaCl solution cells with Teflon stoppers.

Visible and near-infrared absorption spectra were obtained on a Cary Model 14-R recording spectrophotometer. Solution spectra were obtained as previously described.[2] All of the mulls and solutions for spectral work were prepared in the drybox. The spectra were subjected to Gaussian analyses where appropriate.

The conductivities of the complexes were obtained using an Industrial Instruments Model RC 16B conductivity bridge. The measurements were determined at 25°C at 1000 Hz on $\sim 10^{-3}$ M solutions in the drybox.

Solid-state magnetic moments were determined under 35 Torr of helium gas using the Faraday method.[14] Diamagnetic corrections for the ligands and counteranions were made using Pascal's constants.[15]

$^{57}Fe$ Mössbauer spectra were obtained with a conventional constant-acceleration spectrometer operated in the time mode, with a $^{57}Co(Cu)$ source. Experiments were performed with both source and absorber at room temperature. The spectrometer was calibrated with a sodium nitroprusside standard; $Fe_2O_3$ and iron metal were employed as secondary standards. Isomer shifts and quadrupole splittings were determined by inspection with an accuracy of ±0.01 mm/s. Isomer shifts are quoted relative to stainless steel (to convert to sodium nitroprusside, add 0.16 mm/s). The absorber thickness was normally less than 75 mg/cm² of the compound. The samples were suitably encapsulated in an argon atmosphere to prevent reaction during the experiment.

Elemental analyses were performed by Galbraith Laboratories, Schwarzkopf Microanalytical Laboratory, and Mr. Wayne Schammel of this laboratory.

**$[Fe(CH_3CN)_6](CF_3SO_3)_2$.**[16] This material was prepared by refluxing a mixture of $CF_3SO_3H$, acetonitrile, and excess iron filings for 15 h. The excess iron was removed by filtration and the $[Fe(CH_3CN)_6](CF_3SO_3)_2$ was used in situ.

**Ligands.** The ligands $[13]aneN_4$, $[14]aneN_4$, $[15]aneN_4$, and $[16]aneN_4$ were prepared by published procedures[12] with some modifications as suggested by Richman and Atkins.[17] The parent linear tetraamine was treated with 4 equiv of *p*-toluenesulfonyl chloride (TsCl) to form $TsNH(CH_2)_nN(Ts)(CH_2)_mN(Ts)(CH_2)_nNHTs$[12] ($n$ = 2 or 3; $m$ = 2 or 3). Two equivalents of sodium ethoxide was added to ~50 g of the tosylated linear tetraamine in 200 ml of boiling ethanol. After boiling of the mixture for 20 min, the ethanol was removed by rotary evaporation to yield $Na_2(TsN(CH_2)_nN(Ts)(CH_2)_mN(Ts)(CH_2)_nNTs)$. A 0.1 M solution of the sodium salt in DMF was heated

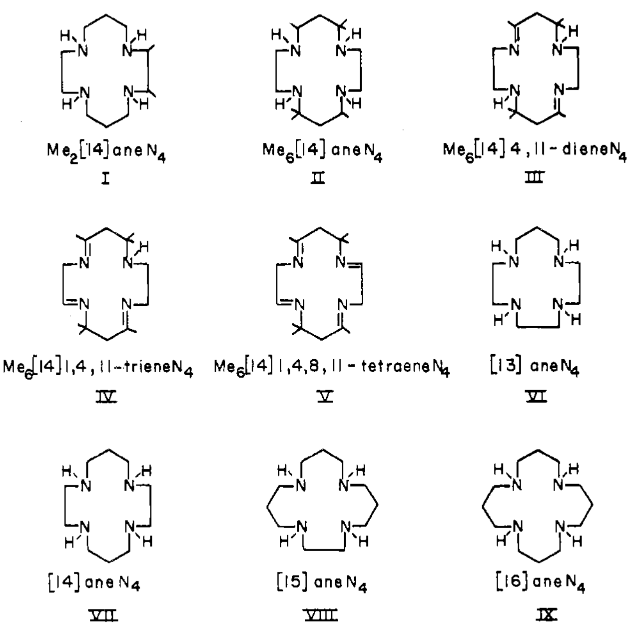

Figure 1. Arrangements and abbreviated names of some common macrocycles.

to 110°C, and 1 equiv of 1,3-dibromopropane (0.2 M in DMF) was added dropwise over a period of 1 h while the solution was stirred vigorously. The tosylated cyclic amine was then isolated and treated as reported previously.[12]

**Fe([13]aneN$_4$)(NCS)$_2$.** To a solution containing 4.83 g (8.05 mmol) of [Fe(CH$_3$CN)$_6$](CF$_3$SO$_3$)$_2$ (calculated from amount of CF$_3$SO$_3$H used) in 75 ml of acetonitrile was added 1.50 g (8.05 mmol) of [13]aneN$_4$. The mixture was refluxed for 30 min and then the volume of the solution was reduced to 25 ml. Two equivalents of KSCN in 50 ml of methanol was added to the iron solution which was then refluxed for 15 min. The volume of the solution was reduced to 25 ml, and 50 ml of ethanol was added. The volume of the solution was again reduced to 25 ml, and the product was collected by filtration. The crude product was recrystallized from acetonitrile and ethanol.

**Fe([13]aneN$_4$)(CN)$_2$.** To 75 ml of hot acetonitrile containing 1.46 g (4.07 mmol) of Fe([13]aneN$_4$)(NCS)$_2$ was added 0.53 g (8.15 mmol) of KCN in 25 ml of hot methanol. The solution was taken to dryness and the residue dissolved in 50 ml of methanol. The solution was filtered and the volume reduced to 20 ml. Acetonitrile (80 ml) was added and the volume of the solution reduced to 20 ml. A subsequent addition of acetonitrile followed by reduction of the volume to 20 ml caused precipitation of the crude product which was recrystallized from acetonitrile and methanol.

**[Fe([14]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$, [Fe([15]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$, and [Fe([16]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$.** To a boiling acetonitrile solution of [Fe(CH$_3$CN)$_6$](CF$_3$SO$_3$)$_2$ (~1 g, 50 ml) was added 1 equiv of the appropriate ligand. The mixture was refluxed for 30 min and then a hot ethanolic solution containing 2 equivalents of NH$_4$PF$_6$ (~1 g, 25 ml) was added. Precipitation of the crude product was brought about by azeotropic distillation of the acetonitrile with ethanol. The product was collected by filtration and recrystallized from acetonitrile and ethanol.

**Fe([14]aneN$_4$)(NCS)$_2$, Fe([15]aneN$_4$)(NCS)$_2$, and Fe([16]aneN$_4$)(NCS)$_2$.** One gram of [Fe([$x$]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$ ($x$ = 14, 15, or 16) in 30 ml of boiling acetone was treated with 2 equiv of KSCN in 25 ml of hot methanol. The solution was taken to dryness and the residue extracted with 50 ml of boiling chloroform. The volume of the chloroform was reduced to 20 ml and diethyl ether was added until precipitation of the product was complete. Fe([14]aneN$_4$)(NCS)$_2$ was recrystallized from acetone. Fe([15]aneN$_4$)(NCS)$_2$ and Fe([16]aneN$_4$)(NCS)$_2$ were washed with diethyl ether.

**Fe([14]aneN$_4$)(NO$_2$)$_2$.** In 50 ml of boiling acetonitrile, 1.00 g (1.59 mmol) of [Fe([14]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$ was treated with 0.30 g (3.5 mmol) of KNO$_2$ in 50 ml of hot methanol. The resulting solution was refluxed for 15 min and then taken to dryness. The residue was extracted with 75 ml of boiling chloroform. The solution was filtered and then reduced in volume to 15 ml. The addition of 60 ml of hot ethanol followed by reduction of the solution volume to 25 ml gave the desired crystals which were collected by filtration.

**[Fe([15]aneN$_4$)(NO$_2$)](PF$_6$).** A twofold excess of NaNO$_2$ in 50 ml of ethanol was added to 2.00 g (3.12 mmol) of [Fe([15]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$ in 30 ml of boiling acetonitrile. The volume of the solution was reduced to 15 ml and 50 ml of ethanol was added. This process was repeated several times until the crude product precipitated. The crude product was collected by filtration and recrystallized from acetonitrile and ethanol.

**[{Fe([16]aneN$_4$)(NO$_2$)}$_2$(NO$_2$)](PF$_6$).** To 2.00 g (3.05 mmol) of [Fe([16]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$ in 20 ml of hot acetonitrile was added 0.57 g (6.7 mmol) of KNO$_2$ in 25 ml of ethanol. After the solution was refluxed for 30 min, the acetonitrile was azeotropically distilled with ethanol. The crude product precipitated from 25 ml of cold ethanol. The compound was recrystallized twice from methanol.

**Fe([14]aneN$_4$)(CN)$_2$ and Fe([15]aneN$_4$)(CN)$_2$.** To 1.00 g of [Fe([$x$]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$ ($x$ = 14 or 15) in 50 ml of boiling acetonitrile was added 2 equiv of KCN in 25 ml of hot methanol. The solution was refluxed 10 min and then taken to dryness. The residue was extracted with two 50-ml portions of boiling chloroform. The volume of the chloroform was reduced to 15 ml and the solution was filtered. Fe([14]aneN$_4$)(CN)$_2$ was precipitated by the addition of 40 ml of diethyl ether and then was recrystallized from chloroform and diethyl ether. Fe([15]aneN$_4$)(CN)$_2$ was recovered upon removal of the chloroform.

**Reaction of [Fe([16]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$ with KCN.** To 2.00 g (3.05 mmol) of [Fe([16]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$ in 50 ml of refluxing acetonitrile was added 0.40 g (6.15 mmol) of KCN in 50 ml of hot methanol. The yellow precipitate that formed immediately was found to be insoluble in all common organic solvents. The material is extremely air and moisture sensitive, turning green upon very brief contact with air and forming intensely blue solutions with water in the presence of air. The infrared spectrum (Nujol) gave $\nu$(NH) at 3255 (w) and 3235 (w) cm$^{-1}$, $\nu$(CN) at 2040 (s) cm$^{-1}$, and other absorptions due to the ligand. No PF$_6^-$ absorptions were detected in the spectrum. The electronic spectrum (halocarbon mull) gave a weak broad band at 9.53 kK and a shoulder at 25.2 kK. $\mu_{\text{eff}}$ was found to be 4.66 BM assuming a molecular weight of 336. The Mössbauer spectrum showed a broad peak (~0.80-mm/s base width) with an isomer shift of 0.01 mm/s with respect to stainless steel. Anal. Found: C, 40.35; H, 6.74; N, 18.46; Fe, 17.74.

## Results and Discussion

Many iron(II) complexes of saturated cyclic amines react with oxygen to form iron(III) species which, in the presence of a suitable base, react further resulting in the oxidative dehydrogenation of the ligand.[2,3] To prevent contamination by iron(III) or unsaturated species, extreme care was exercised in the present study to avoid exposure of such complexes to oxygen or water.

**[14]aneN$_4$ Complexes.** The addition of [14]aneN$_4$ to an acetonitrile solution of Fe(CH$_3$CN)$_6^{2+}$ resulted in the formation of a dark purple solution from which [Fe([14]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$ was isolated. Fe([14]aneN$_4$)(NCS)$_2$, Fe([14]aneN$_4$)(NO$_2$)$_2$, and Fe([14]aneN$_4$)(CN)$_2$ were prepared by treating the acetonitrile complex with the appropriate potassium salt. The analytical data (Table I) and the conductivities and magnetic moments (Table II) are consistent with the formulation of these complexes as low-spin six-coordinate iron(II) derivatives. The infrared spectra of the acetonitrile, thiocyanato, and cyano complexes all show single C≡N ($\nu$(CN), Table III) stretching frequencies. This indicates that the monodentate ligands are mutually trans in all of these complexes. For the cis structure, both the symmetric and antisymmetric stretching modes of the CN bonds should be infrared active, but for trans complexes the symmetric mode should cause relatively little dipole moment change. This simple rationale assumes the two sides of the plane of coordination of the ring to be equivalent. It is assumed that the nitro complex also has the trans configuration. In addition, the colors and electronic spectra of these complexes are very similar to those found for the analogous complexes formed with *ms*-Me$_6$[14]aneN$_4$ which is somewhat constrained

**Table I.** Analytical Data and Yields for the Complexes

| Compd | %C | | %H | | %N | | % yield |
|---|---|---|---|---|---|---|---|
| | Calcd | Found | Calcd | Found | Calcd | Found | |
| Fe([13]aneN$_4$)(NCS)$_2$ | 36.87 | 37.63 | 6.19 | 6.66 | 23.45 | 23.79 | 51 |
| Fe([13]aneN$_4$)(CN)$_2$ | 44.91 | 44.84 | 7.54 | 7.43 | 28.52 | 28.07 | 77 |
| [Fe([14]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$ | 26.77 | 26.90 | 4.81 | 4.95 | 13.38 | 13.74 | 87 |
| Fe([14]aneN$_4$)(NCS)$_2$ | 38.71 | 38.62 | 6.50 | 6.58 | 22.57 | 22.56 | 91 |
| Fe([14]aneN$_4$)(NO$_2$)$_2$ | 34.50 | 34.71 | 6.95 | 6.94 | 24.14 | 23.92 | 74 |
| Fe([14]aneN$_4$)(CN)$_2$ | 46.76 | 46.78 | 7.85 | 7.71 | 27.27 | 26.97 | 80 |
| [Fe([15]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$ | 28.05 | 28.35 | 5.02 | 5.14 | 13.09 | 13.19 | 73 |
| Fe([15]aneN$_4$)(NCS)$_2$ | 40.41 | 40.56 | 6.78 | 7.00 | 21.75 | 22.09 | 85 |
| [Fe([15]aneN$_4$)(NO$_2$)](PF$_6$) | 28.65 | 28.83 | 5.68 | 5.71 | 15.19 | 15.36 | 75 |
| Fe([15]aneN$_4$)(CN)$_2$ | 48.46 | 48.49 | 8.13 | 8.45 | 26.08 | 25.99 | 64 |
| [Fe([16]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$ | 29.28 | 29.40 | 5.22 | 5.40 | 12.81 | 12.70 | 79 |
| Fe([16]aneN$_4$)(NCS)$_2$ | 42.00 | 41.64 | 7.05 | 6.98 | 20.99 | 21.02 | 87 |
| [{Fe([16]aneN$_4$)(NO$_2$)}$_2$(NO$_2$)](PF$_6$) | 33.86 | 33.78 | 6.63 | 6.69 | 18.10 | 18.02 | 71 |

**Table II.** Some Physical Properties of the Complexes

| Compd | Color | $\mu_{eff}$,[a] BM | Solvent; $\lambda$,[b] ohm$^{-1}$ M |
|---|---|---|---|
| Fe([13]aneN$_4$)(NCS)$_2$ | White | 5.42 | CH$_3$NO$_2$; 31 |
| Fe([13]aneN$_4$)(CN)$_2$ | Orange | 0.76 | CH$_3$OH; 8 |
| [Fe([14]aneN$_4$)-(CH$_3$CN)$_2$](PF$_6$)$_2$ | Purple | 0.43 | CH$_3$CN; 307 |
| Fe([14]aneN$_4$)(NCS)$_2$ | Blue | 0.72 | (CH$_3$)$_2$CO; 32 |
| Fe([14]aneN$_4$)(NO$_2$)$_2$ | Red | 0.57 | CH$_3$NO$_2$; 7 |
| Fe([14]aneN$_4$)(CN)$_2$ | Orange | 0.77 | CH$_3$OH; 1 |
| [Fe([15]aneN$_4$)-(CH$_3$CN)$_2$](PF$_6$)$_2$ | White | 5.52 | CH$_3$CN; 284 |
| Fe([15]aneN$_4$)(NCS)$_2$ | White | 5.32 | CH$_3$OH; 37 |
| [Fe([15]aneN$_4$)(NO$_2$)]-(PF$_6$) | Magenta | 3.36 | CH$_3$NO$_2$; 80 |
| Fe([15]aneN$_4$)(CN)$_2$ | Lavendar | 0.69 | CH$_3$OH; 1 |
| [Fe([16]aneN$_4$)-(CH$_3$CN)$_2$](PF$_6$)$_2$ | White | 5.55 | CH$_3$CN; 268 |
| Fe([16]aneN$_4$)(NCS)$_2$ | White | 5.52 | CH$_3$OH; 20 |
| [{Fe([16]aneN$_4$)(NO$_2$)}$_2$-(NO$_2$)](PF$_6$) | Orange | 5.53 | CH$_3$CN; 148 |

[a] Magnetic moment at 25°C. [b] At 25°C for $10^{-3}$ M solutions.

to yield trans configurations.[2]

It is of interest to note that Fe([14]aneN$_4$)(NCS)$_2$ does not show a $^1A_{1g} \rightleftarrows {^5T_{2g}}$ spin equilibrium as was found for Fe(Me$_6$[14]aneN$_4$)(NCS)$_2$ nor does [Fe([14]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$ demonstrate a tendency to lose axially coordinated acetonitrile to form a high-spin five-coordinate complex as does the analogous compound prepared from Me$_6$[14]aneN$_4$.[2] As the two macrocycles are the same size and contain identical donor atoms, these differences are attributed to steric interactions of the Me$_6$[14]aneN$_4$ axial methyl groups. This interaction is of course absent in the complexes formed with [14]aneN$_4$. Additional evidence to support this suggestion is found in the electronic and Mossbauer spectra to be discussed later.

**[13]aneN$_4$ Complexes.** The addition of [13]aneN$_4$ to an acetonitrile solution of Fe(CH$_3$CN)$_6{}^{2+}$ resulted in the formation of a dark purple solution similar to that produced by [14]aneN$_4$. However, all attempts to isolate this presumably low-spin (bis(acetonitrile)) complex were unsuccessful.

The addition of KSCN to an acetonitrile solution containing the presumed [Fe([13]aneN$_4$)(CH$_3$CN)$_2$]$^{2+}$ ion resulted in an immediate loss of color with the formation of Fe([13]aneN$_4$)(NCS)$_2$. The fact that Fe([13]aneN$_4$)(NCS)$_2$ is high spin (Table III) indicates that the thiocyanates are cis rather than trans to each other. If the 13-membered ring encircled the metal, it should exert a stronger ligand field[12,13] than does the 14-membered ring, which gives a low-spin iron complex with thiocyanate. The solution infrared spectrum (Table III) supports this contention as two bands (2060 and 2075 cm$^{-1}$, CH$_3$OH) assignable to $\nu$(CN) are found. The replacement of thiocyanate with cyanide led to the isolation of a low-spin compound with a single $\nu$(CN) (2048 cm$^{-1}$, CH$_3$OH) in its infrared spectrum. It is formulated as *trans*-Fe([13]aneN$_4$)(CN)$_2$.

**[15]aneN$_4$ Complexes.** The treatment of Fe(CH$_3$CN)$_6{}^{2+}$ in acetonitrile with [15]aneN$_4$ led to the formation of a light-colored solution from which [Fe([15]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$ was isolated. In sharp contrast to [Fe([14]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$ which is low spin, [Fe([15]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$ is high spin (Table II). The solution infrared spectrum (Table III) of the compound gave one absorption at 2255 cm$^{-1}$ (acetone) that could be assigned to $\nu$(CN), indicating a trans configuration. Fe([15]aneN$_4$)(NCS)$_2$ was also found to be high spin (Table II) and to have the trans configuration as shown by the single $\nu$(CN) at 2060 cm$^{-1}$ in chloroform solution. The cyanide complex Fe([15]aneN$_4$)(CN)$_2$ shares this trans structure ($\nu$(CN) 2050 cm$^{-1}$, CH$_3$OH) but it is low spin in electronic configuration. Thus, for the axial ligands acetonitrile and thiocyanate, the 15-membered macrocycle does not exert sufficient ligand field strength to cause spin pairing (as occurs with the 14-membered ring). With cyanide, however, the total ligand field is so

**Table III.** Selected Infrared Bands[a] (cm$^{-1}$)

| Compd | Assignments |
|---|---|
| Fe([13]aneN$_4$)(NCS)$_2$ | $\nu$(NH) 3316 w, 3260 m, 3230 m; $\nu$(CN) 2075 s, 2060 s in CH$_3$OH; $\nu$(SC) 790 m |
| Fe([13]aneN$_4$)(CN)$_2$ | $\nu$(NH) 3306 m, 3247 s; $\nu$(CN) 2048 vs in CH$_3$OH |
| [Fe([14]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$ | $\nu$(NH) 3290 m; $\nu$(CN) 2260 vw; $\nu$(PF$_6$) 835 vs; $\delta$(PF$_6$) 557 s |
| Fe([14]aneN$_4$)(NCS)$_2$ | $\nu$(NH) 3300 w, 3210 m; $\nu$(CN) 2095 s; $\nu$(SC) 790 m |
| Fe([14]aneN$_4$)(NO$_2$)$_2$ | $\nu$(NH) 3185 s; $\nu_{as}$(NO$_2$) 1309 s, 1287 vs; $\nu_s$(NO$_2$) 1241 vs, 1224 vs; $\delta$(NO$_2$) 813 |
| Fe([14]aneN$_4$)(CN)$_2$ | $\nu$(NH) 3255 m, 3275 s; $\nu$(CN) 2033 vs |
| [Fe([15]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$ | $\nu$(NH) 3305 m; $\nu$(CN) 2255 vs in acetone; $\nu$(PF$_6$) 837 vs; $\delta$(PF$_6$) 555 vs |
| Fe([15] aneN$_4$)(NCS)$_2$ | $\nu$(NH) 3200 s; $\nu$(CN) 2060 vs in CHCl$_3$; $\nu$(SC) 783 m |
| [Fe([15]aneN$_4$)(NO$_2$)](PF$_6$) | $\nu$(NH) 3225 m, 3180 sh; $\nu$(NO$_2$) 1270 m, 1180 m; $\nu$(PF$_6$) 835 vs; $\delta$(PF$_6$) 558 s |
| Fe([15]aneN$_4$)(CN)$_2$ | $\nu$(NH) 3260 sh, 3215 m; $\nu$(CN) 2050 vs in CH$_3$OH |
| [Fe([16]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$ | $\nu$(NH) 3280 m; $\nu$(CN) 2252 vs in acetone; $\nu$(PF$_6$) 837 vs; $\delta$(PF$_6$) 558 s |
| Fe([16]aneN$_4$)(NCS)$_2$ | $\nu$(NH) 3262 sh, 3235 w; $\nu$(CN) 2058 vs in CHCl$_3$ |
| [{(Fe([16]aneN$_4$)(NO$_2$)}$_2$(NO$_2$)](PF$_6$) | $\nu$(NH) 3268 s; $\nu_{as}$(NO$_2$) 1395 s; $\nu_s$(NO$_2$) 1259 s; $\delta$(NO$_2$) 811 s; $\nu$(PF$_6$) 851 vs; $\delta$(PF$_6$) 557 s |

[a] Measured in KBr pellet unless otherwise noted.

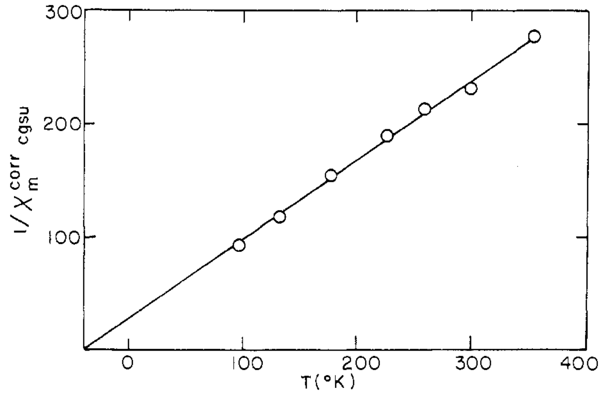

**Figure 2.** $1/\chi_m^{cor}$ vs. temperature for $[Fe([15]aneN_4)(NO_2)](PF_6)$.

enhanced that spin pairing does occur.

Treatment of an acetonitrile solution of $[Fe([15]aneN_4)(CH_3CN)_2](PF_6)_2$ with $KNO_2$ in methanol led to the isolation of a product which analyzes as $[Fe([15]aneN_4)(NO_2)](PF_6)$ (Table I). The conductivity (Table II) agrees with the formulation of the compound as a 1:1 electrolyte. Its infrared spectrum (Table III) confirms the presence of the $PF_6^-$ ion. The infrared spectrum also contains two medium-intensity bands at 1270 and 1180 $cm^{-1}$ that can be assigned to the $NO_2^-$ ligand. These frequencies fall in the range predicted for nitrito complexes where the nitro group coordinates through both oxygens.[18] The anomalous magnetic moment of 3.36 BM (Table II) could possibly arise from a spin-state equilibrium, from a singlet state contaminated with ferromagnetic impurities (iron or iron oxides), or from a triplet ground state ($S = 1$). A variable-temperature study of the magnetic susceptibility was undertaken and it was found that within the temperature range from 96 to 352 K, the susceptibility may be approximated by the Curie–Weiss law (Figure 2), $\chi_m^{cor} = C^{cor}/(T + \theta)$ where $\theta = 39.88°$. The occurrence of spin-state equilibria involving singlet and quartet states is accompanied by a large temperature dependence[2,19] and thus can be eliminated from consideration. Further study showed the magnetic susceptibility of the compound to decrease slightly with an increase in field strength, thus discounting the possibility of ferromagnetic impurities. The triplet state cannot be the ground state for iron(II) in an octahedral environment but it has been observed in complexes of lower symmetry, e.g., where there is severe distortion from octahedral coordination.[19-21] The presence of a bidentate *O,O*-nitrito group with the macrocycle serving as the only other ligand in the complex would certainly cause a large distortion from $O_h$ symmetry. Presumably this causes the triplet state to become the ground state.

**[16]aneN$_6$ Complexes.** The complexes $[Fe([16]aneN_4)(CH_3CN)_2](PF_6)_2$ and $Fe([16]aneN_4)(NCS)_2$ were prepared in the same manner as the analogous 15-membered ring complexes and were found to have the trans stereochemistry and the high-spin electronic configuration. The treatment of $[Fe([16]aneN_4)(CH_3CN)_2](PF_6)_2$ with excess $KNO_2$ led to the isolation of a product that has been formulated as $[\{Fe([16]aneN_4)(NO_2)\}_2(NO_2)](PF_6)$, principally on the basis of the analytical data (Table I) and the molar conductivity (Table II). The complex contains high-spin iron(II) (Table II) but is of undetermined stereochemistry. The infrared spectrum (Table III) contains strong bands at 1395, 1259, and 811 $cm^{-1}$ which are assigned to $\nu_{as}(NO_2)$, $\nu_s(NO_2)$, and $\delta(NO_2)$, respectively, and are in agreement with the presence of N-bonded nitro groups.[18] It is assumed that the complex has two N-bonded nitro ligands with a bridging nitrito group. Although an *N,O*-nitrito bridging group should give rise to an absorption in the region 1480–1520 $cm^{-1}$,[18] we observe no such peak. An *O,O*-nitrito bridging group would give rise to absorptions in the regions of 1250–1315 and 1175–1205 $cm^{-1}$.[18] These bands could be obscured by overlapping with the strong nitro absorptions and the weaker ligand peaks. Alternatively, models indicate that bridging could occur via the macrocyclic ligands and that this might give rise to steric interactions that would prevent the coordination of a fourth nitro group. To elucidate the mode of bridging, a crystal structure determination has been initiated.

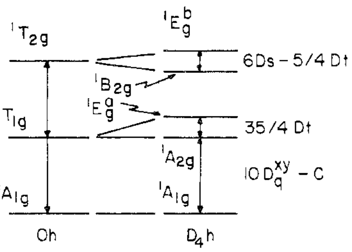

**Figure 3.** Energy level diagram for low-spin $Fe([x]aneN_4)(CN)_2$ (where $x$ = 13, 14, or 15), $Dt = {}^4/_7(Dq^{xy} - Dq^z)$.

The variation in chemistry with ring size again manifests itself in the failure of extensive efforts to synthesize $Fe([16]aneN_4)(CN)_2$ from $[Fe([16]aneN_4)(CH_3CN)_2](PF_6)_2$ by metathesis with KCN (see Experimental Section).

**Electronic Spectra.** The electronic spectral data are analyzed as previously described[2] where the low-spin complexes are treated by the method of Wentworth and Piper[22] and the high-spin complexes by the method of Lever.[23] A direct comparison of the ligand field strengths for the [13]-, [14]-, and $[15]aneN_4$ complexes of low-spin iron is possible for the cases where the axial ligands are cyanide. As cyanide exerts a larger ligand field that does the macrocycle, the energy levels are as represented in Figure 3 for the low-spin case. The separation of the $^1B_{2g}$ and $^1E_g{}^b$ levels is relatively small compared to the $^1A_{2g}$–$^1E_g{}^a$ interval and generally is not observed.[9] Calculation of the Racah parameter $C$ requires the detection and assignment of a spin-forbidden transition which was not observed in the spectra of these complexes. It has been shown that the value of $C$ is relatively constant for the complexes of a given $d^6$ metal ion and a value[2] of 3300 $cm^{-1}$ has been used in these studies. The $^1A_{1g} \rightarrow {}^1A_{2g}$ band was observed as a shoulder on the $^1A_{2g} \rightarrow {}^1E_g$ band in the 77 K mull spectrum of $Fe([14]aneN_4)(CN)_2$ but was not observed in the room-temperature solution spectrum. The position of the $^1A_{1g} \rightarrow {}^1A_{2g}$ band used here was determined by Gaussian analyses of the room-temperature solution spectrum. With these assumptions, the values of $Dq^{xy}$ for the [13]-, [14]-, and $[15]aneN_4$ ligands and the values of $Dq^z$ for cyanide have been calculated. The values of $Dq^{xy}$ found for $Fe([x]aneN_4)(CN)_2$ ($x$ = 13, 14, or 15) are 2208, 2029, and 1842 $cm^{-1}$ for the 13-, 14-, and 15-membered rings, respectively. This trend coincides with that found for these rings on nickel(II) and cobalt(III) where it has been shown that the mechanical constriction due to the ring may increase its ligand field strength.[13] The $Dq^z$ values for cyanide were found not to be constant but decreased as $Dq^{xy}$ decreased. $Dq^z$ decreased from 3057 to 2847 to 2732 $cm^{-1}$ for the [13]-, [14]-, and $[15]aneN_4$ complexes, respectively.

The remaining low-spin complexes are $[Fe([14]aneN_4)(CH_3CN)_2](PF_6)_2$, $Fe([14]aneN_4)(NCS)_2$, and $Fe([14]aneN_4)(NO_2)_2$. Unfortunately, the d–d transitions in the spectrum of the nitro compound are obscured by intense charge-transfer bands. The thiocyanato and acetonitrile complexes both exhibit two bands spaced as would be expected for an octahedral structure (Table IV), with no observable splitting of the $^1T_{1g}$ ($O_h$) band in either case. This indicates that $Dq^{xy}$ decreased with $Dq^z$. Since the thiocyanato complex exhibits a value of 2010 $cm^{-1}$ for $Dq$ and the acetonitrile

**Table IV.** Electronic Spectra of the Complexes

| Compd | Solvent | Absorption bands[a] |
|---|---|---|
| $Fe([13]aneN_4)(NCS)_2$ | Mull | 8.78, 11.46 |
| | Mull, 77 K | 9.1, 12.0 |
| $Fe([13]aneN_4)(CN)_2$ | $CH_3OH$ | 18.78 (18), 23.03 (78), 27.90 (71) |
| $[Fe([14]aneN_4\text{-}(CH_3CN)_2](PF_6)_2$ | $CH_3CN$ | 18.51 (65), 27.2 (140) |
| $Fe([14]aneN_4)(NCS)_2$ | $CHCl_3$ | 16.75 (105), 25.2 (110) |
| $Fe([14]aneN_4)(NO_2)_2$ | $CHCl_3$ | 21.5 (3700), 28.3 (1200) |
| $Fe([14]aneN_4)(CN)_2$ | $CH_3OH$ | 16.99 (5.1), 21.08 (49), 27.28 (110) |
| | Mull, 77 K | 17.7 sh, 21.9, 27.9, 27.6 |
| $[Fe([15]aneN_4)\text{-}(CH_3CN)_2](PF_6)_2$ | $CH_3CN$ | 9.63 (3.6), 14.06 (3.9) |
| $Fe([15]aneN_4)(NCS)_2$ | $CHCl_3$ | 10.42 (6.1), 12.59 (5.2) |
| $[Fe([15]aneN_4)(NO_2)]\text{-}(PF_6)$ | $CH_3NO_2$ | 11.1 (10), 20.7 (1600), 27.5 (230) |
| $Fe([15]aneN_4)(CN)_2$ | $CH_3OH$ | 15.12 (6.2), 19.57 (27), 25.69 (64) |
| $[Fe([16]aneN_4)\text{-}(CH_3CN)_2](PF_6)_2$ | $CH_3CN$ | 9.30 (3.1), 12.34 (4.4) |
| $Fe([16]aneN_4)(NCS)_2$ | $CHCl_3$ | 9.12 (1.3), 11.08 (4.6) |
| $[\{Fe([16]aneN_4)(NO_2)\}_2\text{-}(NO_2)](PF_6)$ | $CHCl_3$ | 9.73 (2.8), 11.84 (12), 22.9 (290), 27.6 (320) |

[a] Peak maximum is given in kK followed by the extinction coefficient in parentheses at 298 K unless otherwise noted. Band maxima located by Gaussian analyses are given to two decimal places; others, to one.

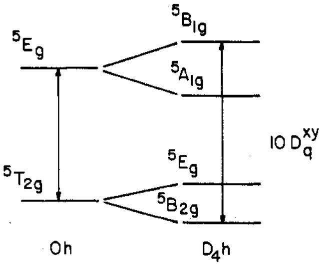

**Figure 4.** Energy level diagram for high-spin *trans*-$Fe([x]aneN_4)L_2$ (where $x = 15$ or 16 and L is monodentate).

complex has a value of 2180 $cm^{-1}$, it is apparent that *Dq* (average) responds to changes in $Dq^z$, as would be expected.

The $Dq^{xy}$ values presented for the 14-membered rings represent increases in the in-plane ligand field strength of 90 $cm^{-1}$ for $Fe([14]aneN_4)(CN)_2$, 60 $cm^{-1}$ for $[Fe([14]aneN_4)(CH_3CN)_2](PF_6)_2$, and 40 $cm^{-1}$ for $Fe([14]aneN_4)(NCS)_2$ over those values found for the analogous complexes formed with $Me_6[14]aneN_4$.[2] In addition, $Fe([14]aneN_4)(CN)_2$ gave a value of $Dq^z$ (2847 $cm^{-1}$) which is 147 $cm^{-1}$ greater than that found for $Fe(Me_6[14]aneN_4)(CN)_2$.[2] This supports the contention that the axial methyl groups on $Me_6[14]aneN_4$ exert a strong repulsive interaction on the axial ligands and that this weakens both binding in the axial sites and the overall ligand field strength.

For the high-spin trans complexes the energy levels are as shown in Figure 4 where the separation between the $^5B_{2g}$ and $^5E_g$ states is generally assumed to be on the order of 500 $cm^{-1}$.[2] Among these complexes there is a decrease in the in-plane ligand field strength when the axial ligand is changed from acetonitrile to thiocyanate. For $Fe([15]aneN_4)L_2$, $Dq^{xy}$ decreases from 1400 to 1259 $cm^{-1}$ when L is changed from acetonitrile to thiocyanate; $Dq^{xy}$ changes from 1234 to 1108 $cm^{-1}$ for $Fe([16]aneN_4)L_2$. It is also noted that $Dq^{xy}$ decreases by 172 and 151 $cm^{-1}$ for the acetonitrile and thiocyanato complexes, respectively, as the ring size is increased from 15 to 16 atoms.

**Table V.** Mössbauer Parameters for the Complexes at 298 K

| Compd | $\delta$,[a,b] mm/s | $\Delta E_q$, mm/s | % effect | Spin state |
|---|---|---|---|---|
| $Fe([13]aneN_4)(NCS)_2$ | 1.12 | 1.92 | 11.4 | $S = 2$ |
| $Fe([13]aneN_4)(CN)_2$ | 0.40 | 0.79 | 3.16 | $S = 0$ |
| $[Fe([14]aneN_4)(CH_3\text{-}CN)_2](PF_6)_2$ | 0.57 | 0.66 | 2.75 | $S = 0$ |
| $[Fe(Me_6[14]aneN_4)\text{-}(CH_3CN)_2](PF_6)_2$[c] | 0.60 | 0.55 | | $S = 0$ |
| $Fe([14]aneN_4)(NCS)_2$ | 0.62 | 0.35 | 4.17 | $S = 0$ |
| $Fe(Me_6[14]aneN_4)\text{-}(NCS)_2$[c] | 0.63 | 0.29 | | $S = 0$ |
| $Fe([14]aneN_4)(NO_2)_2$ | 0.49 | 0.67 | 5.33 | $S = 0$ |
| $Fe(Me_6[14]aneN_4)\text{-}(NO_2)_2$[c] | 0.54 | 0.75 | | $S = 0$ |
| $Fe([14]aneN_4)(CN)_2$ | 0.44 | 0.94 | 4.02 | $S = 0$ |
| $Fe(Me_6[14]aneN_4)\text{-}(CN)_2$[c] | 0.43 | 1.10 | | $S = 0$ |
| $[Fe([15]aneN_4)(CH_3\text{-}CN)_2](PF_6)_2$ | 1.14 | 1.29 | 1.00 | $S = 2$ |
| $Fe([15]aneN_4)(NCS)_2$[c] | 1.20 | 1.22 | 1.66 | $S = 2$ |
| $[Fe([15]aneN_4)(NO_2)]\text{-}(PF_6)$ | 0.33[d] | Broad, ≤0.40 | 0.37 | $S = 1$ |
| $Fe([15]aneN_4)(CN)_2$ | 0.48 | 1.44 | 2.54 | $S = 0$ |
| $[Fe([16]aneN_4)(CH_3\text{-}CN)_2](PF_6)_2$ | 1.17 | 1.38 | 2.60 | $S = 2$ |
| $Fe([16]aneN_4)(NCS)_2$ | 1.25 | 1.97 | 1.34 | $S = 2$ |
| $[\{Fe([16]aneN_4)(NO_2)\}_2\text{-}(NO_2)](PF_6)$[d] | 1.05 | 1.91 | 3.10 | $S = 2$ |

[a] Shift is relative to stainless steel; to convert to sodium nitroprusside add 0.16 mm/s. [b] Typical values are as follows: for high-spin iron(II) 0.80–1.70 mm/s relative to stainless steel[6,24,25] and for low-spin iron(II) 0.00–0.70 mm/s relative to stainless steel.[6,24,25] [c] Taken from ref 6. [d] Broad peak, with an uncertainty of about ±0.05 mm/s in $\delta$.

$Fe([13]aneN_4)(NCS)_2$ and $[Fe([15]aneN_4)(NO_2)](PF_6)$ have cis configurations while $\{Fe([16]aneN_4)(NO_2)\}_2(NO_2)](PF_6)$ is of unknown stereochemistry. The electronic spectra of these complexes are presented in Table IV and will not be discussed here other than to point out that a single d–d transition was observed at 11.1 kK for $[Fe([15]aneN_4)(NO_2)](PF_6)$ and it is comparable to the band at 11.6 kK found for a series of compounds (including $Fe(phen)_2Ox\cdot 5H_2O$) which also have triplet ground states and a similar geometry.[21]

**Mössbauer Spectra.** In Table V are listed the room-temperature Mössbauer parameters for these new complexes. Except for $[Fe([15]aneN_4)NO_2]PF_6$ and the unidentified $[16]aneN_4$ cyanide derivative, each spectrum consists of one quadrupole-split doublet, with no evidence of iron contaminants. In addition, the observed isomer shifts ($\delta$) and quadrupole splittings ($\Delta E_Q$) for these complexes support each assignment of spin state made on the basis of the magnetic susceptibility data.

In a recent report[6] from these laboratories the Mössbauer spectra of an extensive series of 14-membered macrocyclic low-spin iron(II) complexes were discussed. In that series of trans low-spin iron(II) derivatives, both the isomer shifts and quadrupole splittings could be correlated quantitatively with various structural and electronic effects, including variations in axial ligands and the positions and extent of unsaturation in the macrocycles. The complexes reported here provide an important extension of the data to include ring size and a few other effects. Since the new iron(II) derivatives reported here display such a diverse chemistry, a variety of additional classes of systems is also considered.

Of these new complexes six were found to be low-spin *trans*-diacido derivatives. Three of the low-spin complexes are the [13]-, [14]-, and $[15]aneN_4$ dicyano complexes. For this series of dicyano derivatives a linear decrease in the isomer shift is observed as the ring size decreases. This result is readily understood in terms of the spectral studies reported above and earlier studies with other metal ions.[12,13] Since the isomer shift is directly related to the s-electron density at the iron nucleus,[24] with increasing s-electron density manifested by a decrease in the isomer shift, factors that increase s-electron density at the iron(II) nucleus in low-spin complexes (increasing $\sigma$-donor strength and increasing $\pi$-acceptor ability of the coordinated ligands) will result in lower isomer shift values. The smaller ring exerts a greater ligand field strength on the metal[13] and thus is a stronger $\sigma$ donor than is a larger macrocyclic ligand. As a result, the s-electron density on the iron atom increases and the isomer shift decreases with decreasing ring size.

In earlier studies restricted to 14-membered rings[6] we defined a set of partial center shifts[26] appropriate to pseudotetragonal complexes of tetraaza macrocycles with low-spin iron(II). These values imply that the center shift is simply an additive property (eq 1). Implicit in eq 1 is the assumption

$$\mathrm{cs} = \sum_{i=1}^{6} (\mathrm{pcs})_i \tag{1}$$

that a given donor group bound to the iron atom will always exhibit the same pcs. This assumption reflects the prevalent presumption that the strength and nature of interactions of a given donor group with a given metal atom are essentially always the same. As has been indicated here, and more emphatically in our earlier work,[13] the latter is not true. In fact the strain energy effects associated with poor fits of metal atoms into macrocyclic ligands can greatly alter this interaction. It follows that strain energy effects should also alter the Mössbauer parameters as has been shown above. A reasonable technique for incorporating these and other effects involves the time honored practice of adding a second summation to the more elementary equation. This second summation is a set of constituative pcs(c) values (eq 2).

$$\mathrm{cs} = \sum_{i=1}^{6} (\mathrm{pcs(e)})_i + \sum_j (\mathrm{pcs(c)})_j \tag{2}$$

The detailed study[13] of the complexes of Co(III) with the macrocycles described here showed that low-spin $d^6$ metal ion fits best into a 14-membered tetraaza macrocycle. In fact, Co(III) is probably slightly small for that ring. Now low-spin Fe(II) is very nearly the same size as low-spin Co(III), at least in its complexes with nitrogen donors.[27] Perhaps it is even a bit larger; it might therefore fit the 14-membered ring even better. The point of this discussion is that most of our previously reported Mössbauer data utilized 14-membered macrocyclic ligand derivatives and that they should show essentially no strain energy effects associated with metal atom–ring misfit. We can therefore suggest that the value of pcs(c) for changing to a 13-membered ring from a 14-membered ring is −0.04 mm/s while pcs(c) for changing to a 15-membered ring is +0.04 mm/s. This treatment is totally consistent with the electronic spectral data and further illustrates the utility of the Mössbauer data.

The quadrupole splittings of these three complexes also display a significant trend: the larger the ring size the larger the observed $\Delta E_q$ value. For low-spin iron(II) in a rigorously octahedral environment $\Delta E_q$ would be zero, whereas, in $D_{4h}$ symmetry $\Delta E_q$ is expected to vary in the same way as $Dq^{xy} - Dq^z$.[6] Thus, for these complexes the least distortion from $O_h$ symmetry is expected for the complex with the largest in-plane ligand field, namely, the complexes of the smallest ring, the 13-membered ring. This trend was not observed with the spectral parameters calculated for these complexes. In fact from the spectra of these three dicyano derivatives the calculated values $Dq^z - Dq^{xy}$ were found to be 849, 818, and 890 cm$^{-1}$ for the [13]-, [14]-, and [15]ane$N_4$ complexes, respectively. This disagreement between the observed quadrupole splitting values and the calculated spectral parameters is no doubt best attributed to the fact that the uncertainties in the four spectrochemical parameters that go into the calculation are large and cumulative and also to the failure of the model[22] to consider $\pi$-bonding effects. From this and other results discussed below, we suggest that $\Delta E_q$ values should provide a better estimate of the relative tetragonalities of complexes of this kind than the spectral parameters.

The remaining low-spin derivatives are all complexes of the 14-membered ligand and therefore provide a convenient comparison with the complexes of $Me_6$[14]ane$N_4$.[6] It was suggested earlier that the axial methyl groups of the $Me_6$[14]ane$N_4$ ligand sterically interact with the axial ligands, with the net effect being a decrease in the total ligand field exerted by the macrocycle and axial ligands. If this is the case, a lowering of the isomer shift (greater s-electron density at the nucleus) might be observed for the unsubstituted [14]ane$N_4$ complexes as compared to those complexes with $Me_6$[14]ane$N_4$. This trend is observed for the acetonitrile and nitro derivatives. $\delta$ for the acetonitrile is lowered 0.03 mm/s and $\delta$ for the nitro derivative is lowered 0.05 mm/s. In contrast, the cyano and thiocyanato derivatives for the two ligands have $\delta$ values whose lowering is very small or zero within experimental error. However, overall, the isomer shift data do add very weak support to the conclusion that the unsubstituted macrocyclic tetraamine exerts a greater in-plane ligand field.

The variation in quadrupole splittings between pairs of these species provide some interesting possibilities. The cyanide derivatives Fe($Me_6$[14]ane$N_4$)$(CN)_2$ and Fe([14]ane$N_4$)$(CN)_2$ are considered first because it is possible to make some crude estimates of $Dq^{xy}$ and $Dq^z$ for both species and $\Delta E_q$ may be related to the interval $|Dq^{xy} - Dq^z|$.[6] $\Delta E_q$ is negative[6] ($Dq^z > Dq^{xy}$) for both cyano complexes and it decreases in absolute magnitude by 0.16 mm/s on going from $Me_6$[14]ane$N_4$ to [14]ane$N_4$. The respective $Dq$ values and $Dq$ differences are as follows: $Me_6$[14]ane$N_4$, $Dq^{xy}$ = 1940 cm$^{-1}$, $Dq^z$ = 2700 cm$^{-1}$, $|Dq^{xy} - Dq^z|$ = 760 cm$^{-1}$; [14]ane$N_4$, $Dq^{xy}$ = 2029 cm$^{-1}$, $Dq^z$ = 2847 cm$^{-1}$, $|Dq^{xy} - Dq^z|$ = 818 cm$^{-1}$. Thus, since $\Delta E_q$ is negative for these complexes[6] and because there is a large difference in $\Delta E_q$ between these two complexes, it is obvious that the tetragonality of Fe($Me_6$[14]ane$N_4$)$(CN)_2$ exceeds that of Fe([14]ane$N_4$)$(CN)_2$. However, the spectroscopically calculated difference $Dq^z - Dq^{xy}$ for the Fe($Me_6$[14]ane$N_4$) is less than that calculated for [14]ane$N_4$, indicating that the tetragonality of the Fe([14]ane$N_4$)$(CN)_2$ complex is greater. It is obvious that the difference in the calculated interval $Dq^z - Dq^{xy}$ for the two complexes is rather small, especially in view of the uncertainties involved in the calculation. With this result we again suggest that the $\Delta E_q$ provides a much better estimate of the relative tetragonalities of these types of complexes. And since the tetragonality of the Fe([14]ane$N_4$)$(CN)_2$ complex is less than that of Fe($Me_6$[14]ane$N_4$)$(CN)_2$, the [14]ane$N_4$ ligand is then assumed to be a stronger ligand than $Me_6$[14]ane$N_4$.

The thiocyanato and acetonitrile derivatives are all associated with positive[6] values of $\Delta E_q$ ($Dq^{xy} > Dq^z$) and those observed for the unsubstituted ligand [14]ane$N_4$ are larger. This is consistent with the conclusion made immediately above that $Dq^{xy}$ is larger for the unsubstituted ligand.

The quadrupole splitting values for the dinitro derivatives demonstrate the usefulness of discussing complexes of this kind in terms of their relative tetragonalities. The quadrupole splitting value observed for the Fe([14]ane$N_4$)$(NO_2)_2$ complex is 0.08 mm/s less than that observed for the methyl-substituted complex; thus, the Fe($Me_6$[14]ane$N_4$)$(NO_2)_2$ complex displays the greater tetragonal distortion ($|Dq^{xy} - Dq^z|$ for this complex is greater than that for Fe([14]ane$N_4$)$(NO_2)_2$). This result can be interpreted based on the assumption that $Dq^z > Dq^{xy}$ for the two complexes and hence the sign of $\Delta E_q$ is negative. Thus, we again conclude that the unsubstituted ligand possesses the greater ligand field strength and that the nitro ligand, like cyanide, causes the reversal of the iron(II) energy levels in the tetragonally split $^1T_{1g}$ state. This reversal of energy levels is common for both nitro and cyanide ligands in the case of cobalt(III),[22] but it has not been possible to demonstrate this relationship spectroscopically for macrocyclic iron(II) derivatives because charge-transfer bands obscure the visible region of the spectrum.

Of the remaining complexes whose Mössbauer spectra are reported, six were characterized as high-spin iron(II) derivatives and one as an intermediate-spin ($S = 1$) iron(II) derivative. The latter compound [Fe([15]aneN$_4$)NO$_2$]PF$_6$ gave broad, unresolved Mössbauer spectra. It gave an isomer shift of 0.33 mm/s, which is in the range of $\delta$ values (0.33–0.46 mm/s with respect to stainless steel) that König et al.[20,21] reported for a series of six-coordinate complexes with $S = 1$ containing two cis oxygen and four nitrogen donors.

The remaining high-spin complexes all gave Mössbauer spectral isomer shifts in the range 1.05–1.25 mm/s, indicating the insensitivity of this Mössbauer parameter to such significant effects as variations in the ligands and stereochemical changes in the arrangement of the macrocyclic ligand. Surprisingly, the quadrupole splitting of the cis thiocyanato complex with [13]aneN$_4$ is very similar to that of the trans thiocyanato derivative of [16]aneN$_4$. Both the thiocyanato and acetonitrile derivatives of [15]aneN$_4$ have lower $\Delta E_q$ values than those found for the corresponding [16]aneN$_4$ derivatives. Since $Dq^{xy} > Dq^z$ for these complexes, this result is interpreted as showing that $Dq^{xy}$ is larger for the 15-membered derivative than for the 16-membered complex, which gives a larger tetragonal distortion in the 15-membered complex. This results in an increase in the contribution of ligand dissymmetry to the net electric field gradient but a decrease in $\Delta E_q$ because the sign of this contribution is opposite to that of the valence contribution. This is supported by the electronic spectra which indicate that $Dq^{xy}$ is larger for the 15-membered ring complexes. The Mössbauer pattern observed for the nitro derivative of the 16-membered ring complex made no useful contribution toward a structural assignment. The pattern consists of a quadrupole-split doublet with slightly broadened peaks, thus leaving unanswered the question of whether or not two different types of iron are present in the dimeric molecule cation.

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**Registry No.** Fe([13]aneN$_4$)(NCS)$_2$, 57550-27-3; Fe([13]aneN$_4$)(CN)$_2$, 57559-88-3; [Fe([14]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$, 57550-29-5; Fe([14]aneN$_4$)(NCS)$_2$, 57550-30-8; Fe([14]aneN$_4$)(NO$_2$)$_2$, 57550-31-9; Fe([14]aneN$_4$)(CN)$_2$, 57550-32-0; [Fe([15]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$, 57550-34-2; Fe([15]aneN$_4$)(NCS)$_2$, 57550-35-3; [Fe([15]aneN$_4$)(NO$_2$)](PF$_6$), 57550-37-5; Fe([15]aneN$_4$)(CN)$_2$, 57535-29-2; [Fe([16]aneN$_4$)(CH$_3$CN)$_2$](PF$_6$)$_2$, 57535-31-6; Fe([16]aneN$_4$)(NCS)$_2$, 57535-32-7; [{Fe([16]aneN$_4$)(NO$_2$)}$_2$(NO$_2$)](PF$_6$), 57559-87-2; [Fe(CH$_3$CN)$_6$](CF$_3$SO$_3$)$_2$, 57535-33-8; KCN, 151-50-8.

## References and Notes

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