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Synthesis and Physical Properties of High-Spin Five-Coordinate Iron(II) Complexes of 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane

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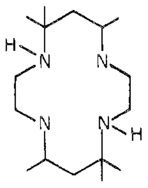
The synthesis and characterization of $[Fe(TMC)(NCCH_3)](BF_4)_2$, [Fe(TMC)Br]Br, and $[Fe(TMC)X]BF_4$ ($X = Cl^-$, NCS^-, N_3^-) are reported, where TMC is 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane. Five-coordinate, high-spin iron(II) complexes are found for each compound. Magnetic susceptibilities (4.2–267 K) are reported for all of the compounds as well as for samples of $[Fe(Me_6[14]4,11\text{-diene})Cl](PF_6)$, which has a diene macrocyclic ligand, and $[Fe(Me_6[14]\text{-}1,4,8,11\text{-tetraene } N_4)Cl](PF_6)$, which has a tetraene macrocyclic ligand. The susceptibility data for the seven iron(II) complexes are least-squares fit to the spin Hamiltonian parameters $g_{\parallel}$, $g_{\perp}$, and D (the axial zero-field splitting parameter). For the [Fe(TMC)X]Y series, the D value varies in the order N_3^- (2.1) < $NCCH_3$ (3.4) < NCS^- (5.4) < Br^- (5.7) < Cl^- (6.2 cm^{-1}). Zero-field splitting in these complexes results from spin–orbital admixture of the ^5E excited state into the $^5B_2$ ground state and the above series approximately parallels the ordering of the ligands in the spectrochemical series. The diene complex has $D = 8.8\ cm^{-1}$ while the D value for the tetraene complex is 3.1 cm^{-1}. Iron-57 Mössbauer data are given for the [Fe(TMC)X]Y compounds. The quadrupole splittings at 77 K are $NCCH_3$ (3.027), Br^- (3.610), Cl^- (3.923), NCS^- (2.881), and N_3^- (3.535 mm/s), whereas the isomer shifts are in the range of 0.85 to 0.91 mm/s relative to iron foil. The compounds $[Fe(TMC)(N_3)](BF_4)$ and $[Fe(TMC)(NCS)](BF_4)$ react as solids with humid air at room temperature to give dark red-brown solids, which, based on magnetism and Mössbauer results, are tentatively assigned as six-coordinate $S = 1$ iron(II) compounds with a water molecule in the sixth coordination site.

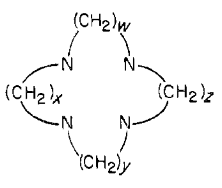
Introduction

Examples of high-spin, five-coordinate iron(II) complexes were until recently rather rare, although some biologically important iron complexes were thought to exist in this form under certain conditions. Busch et al.[3] reported several examples of high-spin, five-coordinate iron(II) complexes in 1970. These were complexes of *unsaturated* macrocyclic tetraamine ligands. Since then, a number of papers dealing with iron complexes of unsaturated macrocyclic ligands have appeared.[4-16] The coordination number and spin state of iron(II) in these complexes are dependent upon the availability and type of axial ligand. High-spin, five-coordinate complexes can be obtained with weak axial ligands and low-spin, six-coordinate complexes with strong axial ligands. In addition, four-coordinate, $S = 1$, complexes have been prepared with charged unsaturated macrocyclic ligands.[8,15]

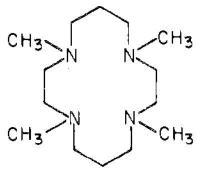
Less work has been done with iron complexes of *saturated* macrocyclic tetraamine ligands, which, in general, have lower ligand field strengths than the unsaturated type. High-spin and low-spin tetragonal complexes were prepared with I in early studies.[17] More recently, complexes of 13-, 14-, 15-, and 16-membered saturated, unsubstituted tetraamine ligands (II–V) were studied.[18] Cis and trans six-coordinate complexes, which included low-spin ($S = 0$), intermediate ($S = 1$), and high-spin ($S = 2$) spin states, were prepared. No pentacoordinate complexes of these ligands were reported.



I

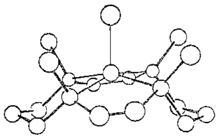


II, $w, x, y = 2; z = 3$
III, $x, z = 2; w, y = 3$
IV, $x = 2; w, y, z = 3$
V, $w, x, y, z = 3$



VI

Recent reports from these laboratories have dealt with the synthesis and stereochemistry of Ni, Cu, and Zn complexes of tetraamine VI, commonly called tetramethylcyclam, TMC.[19-21] Complexes of these metal ions prepared with preformed VI displayed a strong propensity for five coordination.[19] A crystal structure on $[Ni(TMC)N_3]ClO_4$ showed that five coordination is forced on the metal ion by the stereochemistry of the nitrogen donor set.[21] In complexed form, all four of the *N*-methyl groups are on the same side of the molecule. Thus, the two axial sites of the complexed metal ion are strongly differentiated and a single anion is bound on the same side as the *N*-methyl groups as shown schematically below.



The unique stereochemical features inherent in the complexed form of this ligand could be utilized to force pentacoordination on iron and thus provide an opportunity for a study of five-coordinate iron(II) in a relatively weak ligand field. This paper reports the synthesis and characterization of a number of five-coordinate, iron(II) complexes of VI with the primary goal being a determination of the magnitude of zero-field splitting of the $^5B_2$ ground state by variable-temperature magnetic-susceptibility studies. Mössbauer spectral parameters are also reported. A paper to be published later will deal with the structure and properties of nitrosyl complexes obtained by reaction of NO and NO^+ with certain of the iron(II) complexes reported here.

Experimental Section

Materials. 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane (TMC) was prepared by the published procedure.[19] $[Fe(NCCH_3)_6](BF_4)_2$ was prepared by the method of Hathaway.[22] Ferrous bromide was obtained from Alfa. All solvents were dried by standard methods and purged with dry nitrogen before use. All syntheses and manipulations of iron(II) complexes, unless otherwise noted, were carried out under a nitrogen atmosphere in a drybox or with suitable glassware on the bench.

Analyses were performed by J. Nemeth and his assistants of the School of Chemical Sciences Microanalytical Laboratory. Analytical results are given in Table I.

$[Fe(TMC)(NCCH_3)](BF_4)_2$. In a typical preparation, 4.75 g (0.01 mol) of $[Fe(NCCH_3)_6](BF_4)_2$ was dissolved in 75 mL of CH_3CN. Tetramethylcyclam, TMC (2.56 g, 0.01 mol), was added and the solution was stirred for 2 h. Filtration and concentration of the solution afforded pale blue-green crystals which were collected, washed with ether, and dried in vacuo. Recrystallization, when necessary, was from CH_3CN. Yield: 3.7 g, 71%.

Table I. Analytical and Conductivity Data

	Anal. data								
	Calcd				Found				
Compd	C	H	N	Fe	C	H	N	Fe	Λ_M,[a] ohm^{-1} cm^{-2} M^{-1}
$[Fe(TMC)NCCH_3](BF_4)_2$	36.42	6.73	13.34	10.58	36.31	6.56	13.19	10.54	338
$[Fe(TMC)Cl]BF_4$	38.69	7.42	12.89	12.85	38.52	7.34	12.89	12.71	174
$[Fe(TMC)NCS]BF_4$	39.40	7.06	15.32	12.21	39.36	7.12	15.34	12.18	180
$[Fe(TMC)N_3]BF_4$	38.11	7.31	22.23	12.66	38.41	7.34	22.50	12.53	172
$[Fe(TMC)Br]Br$	35.61	6.83	11.87	11.82	35.81	6.84	11.88	11.62	146

[a] Acetonitrile solution, ~10^{-3} M.

[Fe(TMC)Br]Br. $FeBr_2$ (1.30 g, 6 mmol) was suspended in ca. 70 mL of CH_3CN and TMC (1.54 g, 6 mmol) was added as a solid to the well-stirred suspension. After stirring for 3 h, the solution was filtered and the solvent was evaporated to ca. 20 mL to induce crystallization. The pale pink crystals were collected, washed with ether, and dried in vacuo. Yield: 2.05 g, 72%. Recrystallization, when necessary, was from hot CH_3CN.

[Fe(TMC)X]BF$_4$ (X = Cl$^-$, SCN$^-$, N$_3^-$). These compounds were prepared by one of two general methods. **Method A:** $[Fe(TMC)(NCCH_3)](BF_4)_2$ (0.52 g, 1 mmol) was suspended in ca. 10 mL of acetone by vigorous stirring. One equivalent of the appropriate Li, Na, or K salt was added and the mixture was stirred overnight. The pale blue solid dissolved slowly to yield pink solutions with suspended white solids. The solids were filtered off and the volume was reduced to give pale pink crystals. The products were recrystallized by dissolution in the minimum amount of boiling acetone and cooling in a tightly stoppered flask in a freezer overnight. The NCS$^-$ complex crystallized as the acetone solvate, but heating to 80 °C in vacuo overnight afforded the nonsolvated complex. Yields were ca. 60%. **Method B:** $[Fe(TMC)(NCCH_3)](BF_4)_2$ (0.52 g, 1 mmol) was dissolved in 20 mL of hot, degassed methanol to give a pale pink solution. Addition of 5 mL of methanol containing an excess of the appropriate alkali metal salt, cooling to room temperature, filtration, and cooling overnight in a freezer gave pale pink crystals. The products were collected, washed with ether, and dried in vacuo. The complexes could be recrystallized from hot methanol by cooling, if necessary. The thiocyanato complex crystallized as the methanol solvate, but heating to 80 °C in vacuo afforded the solvent-free material. Yields were ca. 65%.

Theoretical Section

The free-ion ground state of a ferrous ion is ^5D, which gives rise to either a $^5B_2$ or a ^5E ground state in a tetragonal ligand field. The $^5B_2$ state has been established as the ground state for one square-pyramidal, macrocyclic iron(II) complex through a magnetically perturbed ^{57}Fe Mössbauer study.[23] In the analysis of our variable-temperature magnetic-susceptibility data, we have assumed a $^5B_2$ ground state which is split, in zero field, by spin–orbit interactions with excited states. The complexes that we are dealing with are largely axial and, if we neglect quartic zero-field terms, the spin Hamiltonian for the orbitally nondegenerate $^5B_2$ state is

$$\hat{H} = D\hat{S}_z^{\,2} + g_{\parallel}\beta H_z\hat{S}_z + {}^1\!/_2 g_{\perp}\beta[H_x(\hat{S}_+ + \hat{S}_-) - iH_y(\hat{S}_+ - \hat{S}_-)]$$

In this equation, $\hat{S}_+$ and $\hat{S}_-$ are the raising and lowering spin operators, respectively. The above Hamiltonian operator is used with the basis set of spin functions $|S,M_s\rangle$, $S = 2$ (M_s = 2, 1, 0, −1, −2), to set out the Hamiltonian matrices for the cases of the magnetic field parallel to the molecular z axis or perpendicular to the z axis.

With the magnetic field in a parallel orentation, the Hamiltonian matrix is diagonal and the energies, $E(S,M_s)$, are very easily found.

$$E(2,\pm2) = 4D \pm 2g_{\parallel}\beta H_z$$

$$E(2,\pm1) = D \pm g_{\parallel}\beta H_z$$

$$E(2,0) = 0$$

When the magnetic field lies along the x axis, the following secular determinant is obtained.

$$\begin{vmatrix} 4D-E & g_{\perp}\beta H_x & 0 & 0 & 0 \\ g_{\perp}\beta H_x & D-E & (6^{1/2}/2)\cdot g_{\perp}\beta H_x & 0 & 0 \\ 0 & (6^{1/2}/2)\cdot g_{\perp}\beta H_x & -E & (6^{1/2}/2)\cdot g_{\perp}\beta H_x & 0 \\ 0 & 0 & (6^{1/2}/2)\cdot g_{\perp}\beta H_x & D-E & g_{\perp}\beta H_x \\ 0 & 0 & 0 & g_{\perp}\beta H_x & 4D-E \end{vmatrix} = 0$$

The energy eigenvalues are obtained by numerical computer diagonalization of the Hamiltonian matrix corresponding to the above determinant. The matrix for the magnetic field along the y axis will obviously give identical eigenvalues.

The parallel and perpendicular magnetic susceptibilities were calculated by using the Van Vleck equation:

$$\chi_k = \frac{N}{H}\,\frac{\sum_i(-\partial E_i/\partial H_k)\exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)}$$

where $k = x, y$, or z. Since $\chi_x = \chi_y \equiv \chi_{\perp}$ and $\chi_z \equiv \chi_{\parallel}$, the total molar paramagnetic susceptibility was taken as:

$$\chi = {}^1\!/_3\chi_{\parallel} + {}^2\!/_3\chi_{\perp}$$

The function minimization computer program STEPT[24] was used to fit the magnetic susceptibility data. The fitting parameters are D, $g_{\parallel}$, and $g_{\perp}$. The function minimized was the sum of the squares of the weighted residuals (SSWR) defined by:

$$\mathrm{SSWR} = \sum_i^{\mathrm{NP}} [(\chi_i(\mathrm{calcd}) - \chi_i(\mathrm{exptl}))/\chi_i(\mathrm{exptl})]^2$$

In this equation, NP is the number of experimental data points. The goodness of fit was gauged by the standard error of estimate[25] and by the SSWR. It was found that the SSWR was a more sensitive gauge of the goodness of fit for the susceptibility data than the standard error estimate. Error correlation coefficients between parameters were calculated. For all cases except one, the correlation coefficients between $g_{\parallel}$ and $g_{\perp}$ were less than 0.07, which is indicative of little correlation. In the case of $[Fe(TMC)(N_3)](BF_4)$, the $g_{\parallel} - g_{\perp}$ correlation coefficient was found to be 0.24. Correlation coefficients between D and $g_{\parallel}$ and between D and $g_{\perp}$ ranged from 0.001 to 0.35.

Mössbauer data were least-squares fit to Lorentzian lines with a previously described computer program.[26] In all cases, the two lines of a quadrupole-split doublet were constrained to have equal areas.

Results and Discussion

Preparations. $[Fe(TMC)(NCCH_3)](BF_4)_2$, which served as starting material for synthesis of the acido complexes, $[Fe(TMC)X]BF_4$ (X$^-$ = Cl$^-$, NCS$^-$, N$_3^-$), was readily prepared from $[Fe(NCCH_3)_6](BF_4)_2$ and the tetraamine in acetonitrile. Substitution of the coordinated acetonitrile with the appropriate anion yielded the pale colored acido complexes. The compound [Fe(TMC)Br]Br was prepared from anhydrous $FeBr_2$ and the tetraamine in acetonitrile. No evidence was obtained for the formation of neutral, diacido species. As expected, the acetonitrile complex was a 2:1 electrolyte in acetonitrile; the other complexes were 1:1 electrolytes (see Table I). The thiocyanato complex is assumed to contain a nitrogen-bonded NCS^- group. The C≡N stretching frequency of 2040 cm^{-1} is consistent with this but the C–S stretching absorption region was obscured by BF_4^- absorption. That the structure of these complexes is related to that of the nickel(II) complexes, as described in the Introduction, can be inferred on the basis of structure determinations[27] on two nitrosyl derivatives which were obtained by reaction of $[Fe(TMC)(NCCH_3)](BF_4)_2$ with NO or $NOBF_4$ and which should have the same set of nitrogen configurations as the parent compound.

All complexes were moderately air sensitive in solution but dry solids were reasonably resistant to oxygen when they were exposed for a few hours. They did undergo reaction upon longer exposure, vide infra. Electrochemical measurements on the acetonitrile complex showed it to undergo an irreversible oxidation in acetonitrile at a platinum electrode with a potential of +1.18 V (vs. Ag|0.10 M Ag^+ in CH_3CN).

Magnetic Susceptibility. A variable-temperature magnetic susceptibility study was initiated to gauge the magnitude and range of axial zero-field interactions (i.e., $D\hat{S}_z{}^2$) present in the ground state of [Fe(TMC)X]Y. As indicated in the Theoretical Section, the ground state of these five-coordinate iron(II) complexes is probably a $^5B_2$ state[23] which is split into three levels as a result of axial zero-field interactions. The relative energies of the three zero-field levels are 0, D, and $4D$. When the zero-field splitting parameter is nonzero and positive and the sample temperature is decreased, the $M_S = 2$ and $M_S = 1$ levels are depopulated according to Boltzmann statistics at low temperatures and this is manifested as a decrease in the effective magnetic moment, μ_{eff}. Since D was expected to be less than 10 cm^{-1}, we measured to 4.2 K the magnetic susceptibilities of five tetramethylcyclam iron(II) complexes: $[Fe(TMC)X]BF_4$ (X = Cl, N_3, NCS), $[Fe(TMC)(NCCH_3)](BF_4)_2$, and [Fe(TMC)Br]Br. In addition, two complexes with unsaturated macrocyclic ligands were studied: $[Fe(Me_6[14]\text{-}4,11\text{-diene }N_4)Cl]PF_6$, which contains the tetraamine ligand derived by oxidation of I, and $[Fe(Me_6[14]\text{-}1,4,8,11\text{-tetraene }N_4)Cl]PF_6$, which contains the tetraamine ligand derived by even further oxidation of I. The latter two complexes were studied to investigate the effects of ligand unsaturation, which approaches that found in porphyrin iron(II) complexes, on the zero-field splitting.

Five-coordinate iron(II) sites are found in deoxymyoglobin and deoxyhemoglobin and several attempts have been made to assess the magnitude of the zero-field interactions that are present. Variable-temperature magnetic susceptibility data have been fit by using an orientational averaging procedure in conjunction with perturbation theory to third order.[28,29] Cylindrical symmetry was assumed in this orientational averaging procedure and Nakano et al.[29] found $D = 5.3$ cm^{-1} for deoxymyoglobin (nonaxial zero-field interaction $E = 0.9$ cm^{-1}). With such a large D value, it is very understandable that no EPR signal has been observed for these high-spin iron(II) species.

The [Fe(TMC)X]Y compounds all show similar magnetic susceptibility and μ_{eff} temperature curves. Table II summarizes a typical data set as obtained for the chloro complex and Figure 1 illustrates the data. At 267 K, μ_{eff} for this compound is 5.02 μ_B and the value gradually decreases to 4.80 μ_B at ~17 K, whereupon there is a more pronounced decrease in μ_{eff} to a value of 3.91 μ_B at 4.2 K. Susceptibility data for the other high-spin ferrous complexes are available in the supplementary material.

Table II. Magnetic Susceptibility Data for $[Fe(TMC)Cl](BF_4)$[a]

	$10^3\chi_M$, cgsu		μ_{eff}, μ_B	
T, K	Obsd	Calcd	Obsd	Calcd
267	11.81	11.41	5.02	4.93
94.9	30.79	31.75	4.83	4.91
72.5	39.56	41.44	4.79	4.90
62.4	47.48	48.06	4.87	4.90
56.9	52.32	52.63	4.88	4.89
50.0	59.03	59.76	4.86	4.89
42.7	69.16	69.73	4.86	4.88
33.0	88.34	89.54	4.83	4.86
27.5	107.3	106.6	4.86	4.84
20.6	143.0	139.9	4.85	4.80
19.5	152.7	147.1	4.88	4.79
18.6	157.9	153.7	4.84	4.78
17.7	164.4	160.7	4.82	4.77
16.9	170.5	167.6	4.80	4.76
16.1	177.6	175.1	4.78	4.75
15.2	185.1	184.3	4.74	4.73
14.3	195.1	194.5	4.72	4.72
13.3	206.4	207.1	4.68	4.69
12.3	219.3	221.5	4.64	4.67
11.4	234.8	236.2	4.63	4.64
10.5	251.5	252.8	4.60	4.61
9.9	266.0	264.1	4.60	4.58
9.4	280.1	276.4	4.59	4.52
8.6	298.0	295.0	4.54	4.52
7.9	316.1	316.0	4.47	4.47
7.1	340.6	339.7	4.41	4.41
6.4	365.4	366.6	4.32	4.33
4.2	455.8	462.9	3.91	3.94

[a] The diamagnetic correction used is -264×10^{-6} cgsu/mol. Least-squares fitting parameters from theoretically calculated curve are given in Table III.

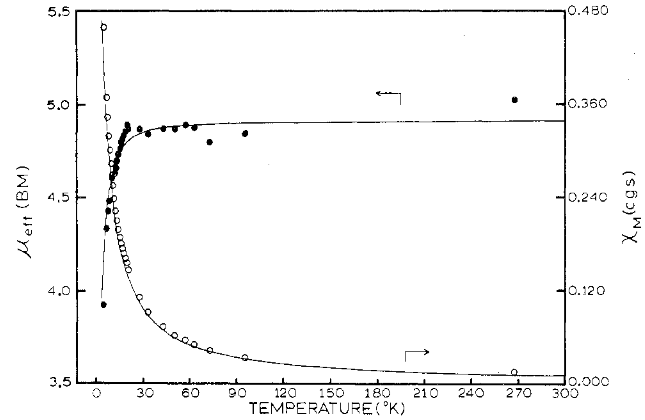


Figure 1. Corrected molar paramagnetic susceptibility (χ_M) and effective magnetic moment (μ_{eff}) as a function of temperature for $[Fe(TMC)Cl](BF_4)$. The solid lines are least-squares-fit theoretical lines; see Table III for parameters.

Initially, we attempted to fit our data with a theoretical analysis analogous to the orientational averaging perturbation calculation that was successful for deoxymyoglobin and deoxyhemoglobin.[28,29] We found that our computerization of this approach was not nearly as successful at least-squares fitting our data as the direct matrix diagonalization approach outlined in the Theoretical Section. The susceptibility data for the seven ferrous complexes were least-squares fit to the spin Hamiltonian parameters $g_\parallel$, $g_\perp$, and D. Typical theoretical fitting results for $[Fe(TMC)Cl](BF_4)$ are given in Table II. In Figure 1, the theoretical fit to χ_M (and μ_{eff}) is shown as a solid line. Figure 2 illustrates the fit for [Fe(TMC)Br]Br. In Table III, we summarize the spin Hamiltonian parameters derived from the various least-squares fits. It should be pointed

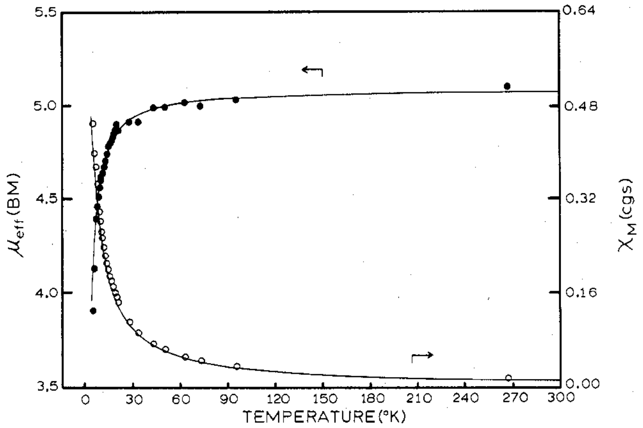


Figure 2. Corrected molar paramagnetic susceptibility (χ_M) and effective magnetic moment (μ_{eff}) as a function of temperature for [Fe(TMC)Br]Br. The solid lines are least-squares-fit theoretical lines; see Table III for parameters.

Table III. Parameters from Least-Squares Fittings of the Magnetic Susceptibility Data[a]

Compd	D, cm^{-1}	$g_{\parallel}$	$g_{\perp}$	$\langle g \rangle$[b]	SS-WR[c]
[Fe(TMC)(N_3)](BF_4)	2.1 (7)	2.39 (75)	2.01 (6)	2.14	0.018
[Fe(TMC)($NCCH_3$)]-(BF_4)$_2$	3.4 (1)	2.63 (5)	2.00 (8)	2.23	0.120
[Fe(TMC)(NCS)](BF_4)	5.4 (1)	2.58 (10)	1.96 (3)	2.19	0.006
[Fe(TMC)(Br)](Br)	5.7 (14)	2.32 (32)	1.95 (7)	2.08	0.005
[Fe(TMC)(Cl)](BF_4)	6.2 (0)	2.03 (6)	2.00 (3)	2.01	0.009
[Fe(1,7-CT)(Cl)](PF_6)	8.8 (2)	2.28 (13)	1.94 (2)	2.06	0.006
[Fe(1,3,7,10-CT)(Cl)]-(PF_6)	3.1 (4)	2.22 (30)	2.01 (2)	2.08	0.006

[a] Errors in the last significant figures, as indicated by the fitting program, are shown in parentheses. [b] $\langle g \rangle = [{}^1/_3(g_{\parallel}{}^2 + 2g_{\perp}{}^2)]^{1/2}$. [c] SSWR is the sum of the squares of the weighted residuals as defined in the Theoretical Section.

out that we assumed that nonaxial zero-field splitting, E, is negligible. This seems reasonable in light of the recent results[10] of EPR measurements on unsaturated iron(III) macrocyclic complexes. A value of 0.065 was found for E/D from the EPR spectra of these iron(III) complexes.

The values of $g_{\parallel}$ and $g_{\perp}$ obtained from our fittings are in the neighborhood of the g values reported for ferrous fluorosilicate.[30] Ideally, experimental g values should be used in the fitting equations. However, high-spin ferrous complexes are notorious for large zero-field splittings and short spin–lattice relaxation times which render EPR detection next to impossible. We could not detect an EPR signal for the [Fe(TMC)X]Y complexes maintained at either liquid-helium or liquid-nitrogen temperatures, either at X-band or Q-band frequencies. The absence of EPR signals agrees with the assessment of D values as summarized in Table III. Even the larger frequency (1.1 cm^{-1}) of the Q-band spectrometer is not sufficient to permit an observation of a $\Delta M_S = 1$ transition.

The zero-field splitting of the $^5B_2$ ground state is due to spin–orbit interactions with excited states. It has been shown[28] that spin–orbit interaction of the $^5B_2$ ground state with the nearby ^5E excited state gives a contribution to the zero-field splitting that is given by:

$$D = \frac{\xi^2}{16}\left\{\frac{1}{E(^5E) - E(^5B_2)}\right\}$$

Thus, the magnitude of the zero-field splitting parameter is inversely proportional to the energy separation between the ^5E and $^5B_2$ states and proportional to the square of the single-electron spin–orbit coupling parameter ξ. It has been estimated[6,7] that $E(^5E) - E(^5B_2)$ is in the range of 300–900 cm^{-1}. The parameter ξ is related to the corresponding free-ion value ξ_0 by the relation $\xi = k\xi_0$ and ξ_0 is taken as 400 cm^{-1}.[31] If the orbital reduction parameter, k, is taken as 0.7 and $E(^5E) - E(^5B_2) = 600$ cm^{-1}, a D value of 8.2 cm^{-1} is calculated. This D value is in the range of those obtained for our high-spin ferrous macrocyclic compounds. Since we are dealing with a series of similar complexes, it would be expected that the variation in low-symmetry crystal-field contributions to the zero-field splitting would be small. It is certainly the case that the dipolar zero-field interaction is negligible.

The inspection of Table III shows that in the [Fe(TMC)X]Y series the zero-field splitting varies in the order $N_3^- < NCCH_3 < NCS^- < Br^- < Cl^-$. It could be of some importance to note that the bromo compound has a counterion other than BF_4^- and that the acetonitrile complex necessarily has two BF_4^- ions per cation. It is interesting that the ordering of D values approximately follows the ordering of these ligands in the spectrochemical series. Thus, the azide ion gives the greatest energy difference between the ^5E and $^5B_2$ states and this leads to the smallest zero-field splitting. The reversal of Br^- and Cl^- D values relative to the spectrochemical series could be the result of having different counterions.

It was of interest to see how the zero-field splitting in high-spin Fe(II) complexes of macrocyclic ligands varied as unsaturation was incorporated into the macrocyclic ligand. As can be seen in Table III, an increase in double-bond content of the macrocyclic ligand results in a decrease in the axial zero-field splitting. Thus, the diene complex has $D = 8.8$ cm^{-1}, whereas the tetraene complex has a D value of 3.1 cm^{-1}. Apparently, the system with a greater degree of unsaturation has a greater ^5E–$^5B_2$ energy separation as a result of increased σ- and π-electron interactions. Along these same lines of argument, it might be naively expected that the zero-field splitting for [Fe(TMC)Cl](BF_4) would be *greater* than that for [Fe[Me_6[14]4,11-diene N_4)Cl](PF_6). This is not the case because the methyl groups in the TMC case are electron donating and this effectively increases the basicity of the nitrogen centers. It is unfortunate that, because of solubility and low extinction coefficient problems, we were not able to determine good electronic absorption spectra for the [Fe(TMC)X]Y species.

Very recently[32] the technique of far-infrared magnetic resonance was used to investigate the zero-field splittings of two high-spin ferrous compounds. Ferrous fluorosilicate gave $D = 11.78$ cm^{-1} and $E = 0.67$ cm^{-1}, while a salt of $Fe(SPh)_4{}^{2-}$ gave $D = 5.98$ cm^{-1} and $E = 1.42$ cm^{-1}. It is also relevant to note that zero-field splittings have been determined for a series of high-spin ferric porphyrins.[33] In this case, the zero-field splitting in the $^6A_1$ ground state is due to spin–orbit interaction with a low-lying $^4T_1$ excited state. Previous investigators have argued that the important interactions that govern the size of D for the ferric porphyrins are the axially coordinated ligand. As with the present complexes, the ligands that are higher in the spectrochemical series lead to the smaller D values.

^{57}Fe Mössbauer. Early in this work, it was thought that the [Fe(TMC)X]Y compounds were relatively stable in air for several days at room temperature. It was through the use of ^{57}Fe Mössbauer spectroscopy that we realized the fallacy of this assumption. It was fortunate that samples for magnetic susceptibility studies were kept in sealed ampules right up to the time of data collection.

Perhaps the most definitive comment on the air stability of the [Fe(TMC)X]Y compounds came in work on [Fe(TMC)Br]Br. Figure 3 illustrates the ^{57}Fe Mössbauer spectra that were obtained in two separate experiments on [Fe(TMC)Br]Br. The bottom part of Figure 3 shows the 100 K spectrum of a sample of [Fe(TMC)Br]Br which was loaded

Table IV. Isomer Shifts and Quadrupole Splittings from ^{57}Fe Mössbauer Data

Compd	T, K	$\delta^{a,b}$	$\Delta E_Q{}^a$	$\Gamma^{a,c}$
[Fe(TMC)(N_3)](BF_4)	100	0.877 (1)	3.535 (1)	0.140 (1), 0.139 (1)
	4.2	0.899 (1)	3.617 (1)	0.159 (1), 0.163 (1)
[Fe(TMC)($NCCH_3$)](BF_4)$_2$	90	0.912 (4)	3.027 (4)	0.379 (4), 0.374 (4)
	90	0.847 (2)^d	2.903 (2)^d	0.179 (2), 0.183 (2)
[Fe(TMC)(NCS)](BF_4)	90	0.884 (4)	2.881 (4)	0.258 (4), 0.263 (4)
[Fe(TMC)(Br)](Br)	100	0.884 (2)	3.610 (2)	0.175 (2), 0.168 (2)
	100	0.877 (8)^d	3.705 (8)^d	0.185 (6), 0.187 (6)
		0.881 (6)^d	3.016 (6)^d	0.196 (5), 0.195 (5)
[Fe(TMC)(Cl)](BF_4)	80	0.867 (1)	3.923 (1)	0.136 (1), 0.143 (1)
[Fe(1,7-CT)(Cl)](PF_6)	100	0.853 (3)	3.819 (3)	0.177 (2), 0.224 (2)
[Fe(TMC)(N_3)](BF_4) "red"	100	0.350 (3)	0.802 (6)	0.263 (3), 0.261 (3)
[Fe(TMC)(NCS)](BF_4) "red"	100	0.339 (5)	0.791 (5)	0.273 (5), 0.275 (5)

[a] The units are mm/s; fitting error of last significant figure is given in parentheses. [b] Relative to Fe metal. [c] Half-width at half-maximum. [d] A second sample which had been exposed to a certain amount of oxygen.

into a Mössbauer cell (pressed-fit nylon container) in a glove box but was then kept in a screw-cap vial under N_2 gas for several days. This spectrum clearly shows two quadrupole-split doublets and least-squares fitting gives ΔE_Q values of 3.705 (8) and 3.016 (6) mm/s. The sample used in this experiment initially had an excellent chemical analysis, so it was concluded that the compound was probably reacting with water to displace the coordinated Br^- ligand to give [Fe(TMC)-(H_2O)](Br_2). In a second experiment, another analytically pure sample of the bromo compound was prepared and this time the sample was kept in a sealed ampule under N_2 up to the time the spectrum was run. In this case, the top spectrum of Figure 3 was obtained for a sample at 100 K. Only a single doublet can be seen with ΔE_Q = 3.610 (2) mm/s. This single doublet corresponds to the other doublet in the lower spectrum in Figure 3. Thus, [Fe(TMC)Br]Br is converted in air to a compound that also has a Mössbauer spectrum consisting of a doublet with a large ΔE_Q value. The line widths of the doublet in the top spectrum of Figure 3 and the line widths for the two doublets in the lower spectrum are close to the natural line width expected for ^{57}Fe.

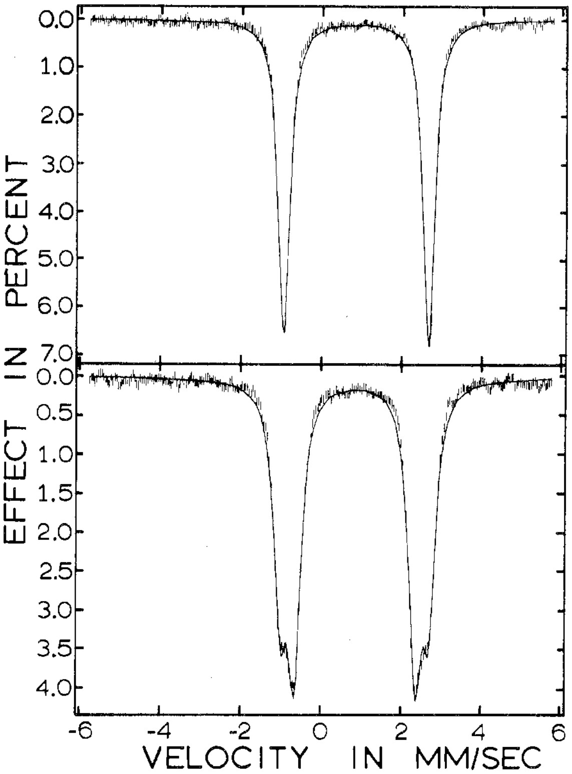


Figure 3. ^{57}Fe Mössbauer spectra at 100 K for two samples of [Fe(TMC)Br]Br. Bottom: sample after a limited contact with air. Top: sample after a minimal contact with air. Isomer shift relative to iron foil.

As a consequence of our observations on [Fe(TMC)Br]Br, the other compounds were also treated in such a way so as to minimize their contact with air. Three samples of [Fe-(TMC)(N_3)](BF_4) were run at 80–100 K and in each case a single doublet with the same isomer shift (δ), quadrupole splitting (ΔE_Q), and line width (Γ) values were found. Two samples of the NCS^- compound gave the same results, one doublet with a ΔE_Q value 0.7 mm/s smaller than that for the N_3^- compound. The largest quadrupole splitting was found for [Fe(TMC)Cl](BF_4) where ΔE_Q = 3.923 (1) mm/s. In the case of [Fe(TMC)($NCCH_3$)](BF_4)$_2$, there is some evidence for two high-spin ferrous species. A sample that had been exposed to air for a short time gave a spectrum consisting of a single, relatively sharp doublet. A second sample which was handled with *minimal air contact* gave a spectrum consisting of one doublet with line widths about twice as large. It is possible that the acetonitrile compound reacts rapidly with water and that in the latter case there are two different species which have nearly overlapping doublets.

A sample of [Fe(Me_6[14]4,11-diene N_4)Cl](PF_6) was also investigated with ^{57}Fe Mössbauer spectroscopy and with the sample maintained at 100 K we found one doublet with ΔE_Q = 3.819 (3) mm/s. Busch et al.[34] reported that [Fe(Me_6-[14]4,11-diene N_4)Cl](ClO_4)$_2$ shows a doublet with ΔE_Q = 3.78 (5) mm/s at room temperature, which is in agreement. The effects of temperature can be gauged by results on [Fe(TMC)(N_3)](BF_4) where the ΔE_Q value changed from 3.535 (1) to 3.617 (1) mm/s as the sample temperature was changed from 100 to 4.2 K (see Table IV).

Busch et al.[34] have reported Mössbauer data for several high-spin five-coordinate iron(II) complexes. ΔE_Q values for these compounds ranged from 3.6 to 3.84 mm/s and it has been suggested that such large values are characteristic of these compounds. The N_3^-, Cl^-, and Br^- derivatives of Fe(TMC)$^{2+}$ fall into this range; however, the $NCCH_3$ and NCS^- derivatives also appear to be five coordinate but have significantly lower ΔE_Q ($\sim$3 mm/s) values. It appears likely that the range of ΔE_Q values corresponding to five-coordinate iron(II) complexes may be greater than that established by the earlier investigations.

In the course of carrying out the Mössbauer experiments, it was noted that for two compounds, [Fe(TMC)(N_3)](BF_4) and [Fe(TMC)(NCS)](BF_4), exposure to humid air at room temperature causes the pink-colored solids to change to a dark red-brown color. Chemical analyses for the two red compounds gave results that are close to those for the corresponding unexposed compounds. The variable-temperature (4.2–270 K) magnetic susceptibility data for the "red" forms of [Fe(TMC)(N_3)](BF_4) and (Fe(TMC)(NCS)](BF_4) are tabulated in the supplementary material. Both red compounds exhibit μ_{eff} values of 3.8 μ_B at 270 K. The magnetic moments decrease gradually down to ~60–100 K, whereupon the rate of decrease increases down to 4.2 K where the μ_{eff} values are 1.6 and 2.0 μ_B for "red" [Fe(TMC)(N$_3$)](BF$_4$) and [Fe(TMC)(NCS)](BF$_4$), respectively. Iron-57 Mössbauer spectra were also obtained for samples of both of these red compounds at 100 K. As can be seen in Table IV, the two spectra are essentially identical, each showing one quadrupole-split doublet with $\delta = 0.35$ mm/s (vs. Fe metal) and $\Delta E_Q \simeq 0.8$ mm/s.

In a very recent paper Riley et al.[8] reported magnetic susceptibility and ^{57}Fe Mössbauer data for several square-planar Fe(II)-unsaturated macrocyclic complexes that exhibit the $S = 1$ spin state. The data for the two "red" compounds are very similar and, in view of the relatively high oxidation potential for Fe(II)–TMC complexes, we tentatively suggest that the two "red" complexes are also $S = 1$ iron(II) complexes. Thus, in the case of the relatively strong-field ligands NCS$^-$ and N$_3^-$, the Fe(TMC)X$^+$ complex may react with H$_2$O to form a six-coordinate complex which has the $S = 1$ ground state.

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Registry No. [Fe(TMC)NCCH$_3$](BF$_4$)$_2$, 63976-95-4; [Fe(TMC)Cl]BF$_4$, 63976-93-2; [Fe(TMC)NCS]BF$_4$, 63976-91-0; [Fe(TMC)N$_3$]BF$_4$, 63976-89-6; [Fe(TMC)Br]Br, 63976-87-4; [Fe(Me$_6$[14]4,11-diene N$_4$)Cl]PF$_6$, 64024-01-7; [Fe(Me$_6$[14]-1,4,8,11-tetraene N$_4$)Cl]PF$_6$, 63976-86-3; [Fe(TMC)(N$_3$)](BF$_4$) "red", 63976-85-2; [Fe(TMC)(NCS)](BF$_4$) "red", 63976-83-0; [Fe(NCCH$_3$)$_6$](BF$_4$)$_2$, 63976-81-8.

Supplementary Material Available: Magnetic susceptibility data for [Fe(1,7-CT)(Cl)](PF$_6$), [Fe(1,4,8,11-CT)(Cl)](PF$_6$), [Fe(TMC)(N$_3$)](BF$_4$), [Fe(TMC)(NCCH$_3$)](BF$_4$)$_2$, [Fe(TMC)(NCS)](BF$_4$), [Fe(TMC)(Br)](Br), "red" [Fe(TMC)(N$_3$)](BF$_4$), and "red" [Fe(TMC)(NCS)](BF$_4$), Tables V–XII (8 pages). Ordering information is given on any current masthead page.

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