(PIO/P No. 730/00239) for T.-T. The use of the UNIVAC 1108 computer at the University of Wisconsin Computing Center was made available by partial financial support from the National Science Foundation and the Wisconsin Alumni Research Foundation administered through the University Research Committee.

# Complexes of Iron(II) and Iron(III) with the Tetradentate Macrocycle 5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene

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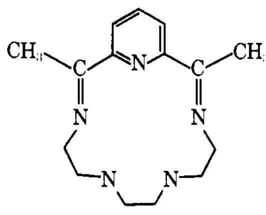
**Abstract:** A series of iron complexes of the cyclic ligand 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, [14]dieneN$_4$, have been isolated. The coordination number and spin state of the metal atom are dependent on the axial ligands. High-spin, five-coordinate iron(II) complexes were isolated when weak axial ligands were present and low-spin, six-coordinate complexes were isolated with strong axial ligands. One complex has a moment intermediate between the high-spin and low-spin values and has been shown to exist in spin-state equilibrium by the study of the temperature dependence of the magnetic susceptibility. The iron(II) complexes can be oxidized, yielding low-spin, six-coordinate iron(III) complexes.

The uncommon stability of the metal complexes of the new synthetic macrocyclic ligands makes them ideal candidates for studying a great variety of chemical phenomena. For example, they are especially suited to the study of ligand reactions[1,2] and unusual redox behavior.[3,4] It has been shown that oxidation states of copper, nickel, and cobalt which are not normally accessible can be stabilized with macrocyclic ligands. The facile redox behavior of iron, especially in naturally occurring systems, in conjunction with the many favorable characteristics of macrocyclic ligands, makes the study of these systems especially appealing.

Only a few iron complexes of the new nonporphyrin type macrocyclic ligands have been reported. Those iron complexes of 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene (I) form a unique series of seven-coordinate pentagonal-bipyramidal iron(III) complexes.[5] These structures have been confirmed by X-ray analyses.[6] The formation and subsequent stability of this pentadentate 15-membered ring with iron(III) may, in part, be due to special properties related to the $d^5$ metal ion. The containment of the iron(III) atom in the plane of the pentadentate macrocycle stands in contrast to the behavior of porphyrins. The 16-membered inner ring of porphyrin yields high-spin iron(III) species, in which it appears that the iron atom is too large to fit in the plane of the four nitrogen atoms so that it is significantly (0.5 Å) removed from that plane.[7]

We report here the synthesis and characterization of a variety of iron complexes containing the macrocycle 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (II, abbreviated 5,7,7,12,14,14-Me$_6$-[14]-diene-1,4,8,11-N$_4$ or, more simply, [14]dieneN$_4$).[8]



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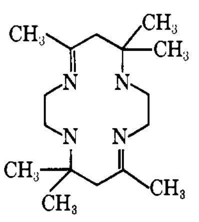

II

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(1) V. Katović, L. Taylor, and D. H. Busch, *J. Amer. Chem. Soc.*, **91**, 2122 (1969).

(2) N. F. Curtis, *Chem. Commun.*, 881 (1966).

(3) D. C. Olson and J. Vasilevskis, *Inorg. Chem.*, **8**, 1611 (1969).

(4) N. E. Tokel, V. Katović, K. Farmery, L. B. Anderson, and D. H. Busch, *J. Amer. Chem. Soc.*, **92**, 400 (1970).

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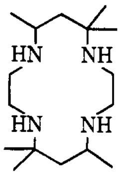
(8) The complexity of the ligands discussed here, and their congeners, requires that the disparate nomenclatures that have been in use be reconciled [compare ref 9 with D. H. Busch, *Helv. Chim. Acta, Fasciculus extraordinarius, Alfred Werner*, 174 (1967)]. Curtis has used a systematic set of abbreviations, while Busch has used a trivial system. Further, the unsaturated ligands can be named according to two possible numbering systems (K. L. Loening, private communication). Since precedence is given to the heteroatoms, the locants for the four nitrogens in structure II are 1, 4, 8, 11 by either sequence. The simplest numbering technique would assign the locants 4, 11 to the two C=N groups. The alternate system, which we have previously used, minimizes the locants for the C=N groups as well as those for the heteroatoms, but it has the disadvantage that one, in effect, counts backward to assign a locant to the first (sequentially) C=N group. These locants become 1, 7 in this system, and to avoid confusion, the locant at the other end of the N=C group should be cited parenthetically 1(14), 7. To avoid the misunderstandings that follow from the use of the more subtle system, we are changing our practice and adopting the convention that always requires numbering in a single direction.

In order to represent these and related ligands by meaningful abbreviations, we are adopting, modifying, and extending Curtis' system. The principle modification involves the use of locants to indicate the positions of unsaturated linkages, rather than the less general cis and trans prefixes. Macrocyclic ring size is still to be indicated by a number in brackets. The complete abbreviation for structure II is 5,7,7,12,-14,14-Me$_6$-[14]-4,11-diene. More often than not, the locants for substituents will not be included when formulas for complexes are written, Ni(Me$_6$-[14]-4,11-diene)$^{2+}$, and upon repetition the substituents will

The complexes of this well-known macrocycle of Curtis with the metal ions of cobalt, nickel, and copper have been studied in great detail.[9] Some preliminary results on the iron complexes described herein have been reported,[10] and the redox behavior of a few related complexes has been described.[11] The compounds described in this paper represent part of an extensive investigation to determine the effects of chelate ring size, degree of unsaturation, and charge on the coordination numbers, spin state, redox behavior, and other chemical properties of iron derivatives of macrocyclic ligands. In the present case, it is shown that this ring, probably because of the metal site size, manifests constrictive effects on the metal atom, leading to an abnormally high ligand field, or to lower coordination numbers, where the metal ion may lie out of the plane of the four nitrogen donor atoms.

## Discussion

The primary difficulty in preparing iron(II) complexes of aliphatic amine ligands is related to the very great tendency of iron to form hydroxo species and their pronounced tendency to oxidize to various iron(III) oxo species in the presence of traces of water. This behavior is observed with simple amines such as ammonia, linear polydentate amines such as triethylenetetraamine, and even macrocyclic ligands such as the hydrogenated Curtis ligand, 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (III).[12] To circumvent these difficulties, the synthetic procedure in this work utilized the dehydrating properties of triethyl orthoformate, and all reactions were carried out under a nitrogen atmosphere. Hydrated iron(II) perchlorate solutions in acetonitrile were dehydrated by refluxing with an excess of triethyl orthoformate for several hours. The perchloric acid salt of the ligand, [14]dieneN$_4$·2HClO$_4$, was then added and neutralized with triethylamine. The resultant pink product, [Fe([14]dieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$, is a convenient starting material for the preparation of other iron compounds, as described in this work. The axially coordinated acetonitrile molecules are very labile and may be replaced readily by a variety of other axial ligands. *CAUTION:* The conditions under which this product is obtained are hazardous! Related experiments under similar conditions have produced violent explosions.[13] Utmost safety precautions should be observed in the preparation and in the handling of [Fe([14]dieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$. This compound as well as all other derivatives containing ClO$_4^-$ are both thermally and shock sensitive and detonate with sharp reports. These properties are in marked contrast to those of the perchlorate salts of the [14]dieneN$_4$ complexes of copper, nickel, and cobalt, which generally decompose nonviolently when heated.



III

To avoid use of the treacherous perchlorate salts, a number of iron complexes were isolated using tetraphenylborate as the counteranion. These complexes generally had similar properties to the perchlorate salts in the solid state; however, much more limited solubilities presented difficulties when solution studies were required. Furthermore, the tetraphenylborate derivatives had the undesirable feature of spontaneously decomposing over a period of days or weeks, yielding darkened residues and producing a white crystalline sublimate on the tops of the containers. The infrared spectrum, melting point, and mass spectrum (parent peak at 154) identify the sublimate as biphenyl. Consequently, the work in this investigation was carried out using minimum quantities of the perchlorate complexes.[14]

It was also possible to prepare the [Fe([14]dieneN$_4$)(CH$_3$CN)$_2$]$^{2+}$ species by the reaction of anhydrous iron(II) acetate with [14]dieneN$_4$·2HClO$_4$, [14]dieneN$_4$·2HBF$_4$, or [14]dieneN$_4$·2HI in acetonitrile. However, both reactants are insoluble in the solvent and the reaction proceeds very slowly; 24 hr is required to obtain a significant yield. The yields by this method were never very good, and considerable effort was required to rid the desired material of impurities. The difficulty probably is related to the formation of acetic acid as a by-product of the reaction, for it was found that these iron–[14]dieneN$_4$ complexes are destroyed by acid orders of magnitudes more rapidly than are the corresponding Co(II), Ni(II), and Cu(II) complexes.

The iron complexes of the [14]dieneN$_4$ ligand generally fall into three categories: five-coordinate, high-spin iron(II); six-coordinate, low-spin iron(II); and six-coordinate, low-spin iron(III). One complex, a phenanthroline adduct, [Fe([14]dieneN$_4$)phen](ClO$_4$)$_2$,

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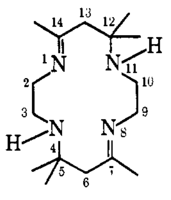
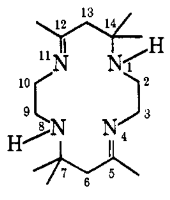
often be neglected if they are not varied in the particular work at hand, Ni([14]-4,11-diene)$^{2+}$. While still more cumbersome than we might like, these abbreviations are short enough to use in tabular entries and one can readily learn to quickly perceive from them much pertinent structural information. We extend the nomenclature to explicitly include hetero-



old system and basis for names we have previously used



preferred system and basis for names used here and in publications to follow

atoms by indicating their nature and number at the end of the abbreviation—locants may be used or omitted, depending on the information required. Thus the most complex abbreviation for structure II would be 5,7,7,12,14,14-Me$_6$-[14]-4,11-diene-1,4,8,11-N$_4$. Despite its many digits, it is far short of the name, and the abbreviation will usually be applied without locants; *i.e.*, Me$_6$-[14]-diene-N$_4$. In this extended form, the convention is applicable to all macrocyclic ligands not involving fused rings. We continue to treat the latter with trivial abbreviations.

(9) N. F. Curtis, *Coord. Chem. Rev.*, 3, 3 (1968).

(10) D. H. Busch, K. Farmery, V. Goedken, V. Katović, A. C. Melnyk, C. R. Sperati, and N. Tokel, *Advan. Chem. Ser.*, No. 100, 44 (1971).

(11) D. P. Rillema, J. F. Endicott, and E. Papaconstantinou, *Inorg. Chem.*, 10, 1739 (1971).

(12) J. C. Dabrowiak, P. H. Merrell, and D. H. Busch, in press.

(13) R. C. Dickinson and G. R. Long, *Chem. Eng. News*, 48, 6 (July 6, 1970).

(14) Recently, the hexafluorophosphate derivatives have been found to have suitable solution and storage properties. The BF$_4^-$ salt can also be prepared. No attempt should be made to store the perchlorate salts for extended periods (longer than 1 week). Samples of [Fe([14]dieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$ gradually turn brown during storage, if exposed to air, and detonate when disturbed.

Table I. Some Properties of the New Macrocyclic Iron Complexes

| Complex | Color | $\mu_{eff}$[a] | $\Lambda_M$[b] (Solvent) |
|---|---|---|---|
| $[Fe([14]dieneN_4)(CH_3CN)_2](ClO_4)_2$ | Pink | 0.40 | 199 ($CH_3NO_2$)<br>300 ($CH_3CN$) |
| $[Fe([14]dieneN_4)(NCS)_2]$ | Brown | 0.50 | 8 ($CH_3NO_2$) |
| $[Fe([14]dieneN_4)(CH_3CN)_2]I_2$ | Dark red | 0.62 | 244 ($CH_3CN$) |
| $[Fe([14]dieneN_4)(CH_3CN)(C_3H_4N_2)](BPh_4)_2$ | Red-brown | 0.42 | 170 ($CH_3NO_2$) |
| $[Fe([14]dieneN_4)(C_{12}H_8N_2)](ClO_4)_2$ | Deep purple | 3.70[c] | 189 ($CH_3NO_2$) |
| $[Fe([14]dieneN_4)Cl_2]ClO_4$ | Green | 2.30 | 101 ($CH_3NO_2$) |
| $[Fe([14]dieneN_4)(CH_3CN)_2](ClO_4)_3$ | Yellow | 2.19 | 491 ($CH_3CN$) |
| $[Fe([14]dieneN_4)(NCS)_2](BPh_4)$ | Blue-black | 2.14 | 79 ($CH_3NO_2$) |
| $[\{Fe([14]]dieneN_4)H_2O\}_2O](ClO_4)_4$ | Beige | 2.11 | |
| $[Fe([14]dieneN_4)Cl]ClO_4$ | Off-white | 5.05 | 95 ($CH_3NO_2$) |
| $[Fe([14]dieneN_4)Br]ClO_4$ | Off-white | 5.11 | 106 ($CH_3NO_2$) |
| $[Fe([14]dieneN_4)I]ClO_4$ | Pale yellow-green | 5.15 | 93 ($CH_3NO_2$) |
| $[\{Fe([14]dieneN_4)\}_2OH](ClO_4)_3 \cdot H_2O$ | White | 4.85[d] | |
| $Fe([14](dieneN_4)I_2$ | Brown | 5.25 | 90 ($CH_3NO_2$) |

[a] Solid state, room temperature, corrected for ligand diamagnetism. [b] Approximately $10^{-3}$ *M* solutions, in cm²/(ohm mol). [c] Measured at 20°C. [d] The extreme reactivity of this substance and the tendency for it to occur with contaminants combine to make characterization very difficult. This value of $\mu_{eff}$ is somewhat in doubt.

Table II. Electronic Spectra of the Complexes

| Complex | | |
|---|---|---|
| $[Fe([14]dieneN_4)(CH_3CN)_2](ClO_4)_2$[a] | $CH_3CN$ | 19.6 (85), 29.1 (2440) |
| | Solid state | 20.0, 29.4 |
| $[Fe([14]dieneN_4)(CH_3CN)_2](ClO_4)_2$[b] | $CH_3CN$ | 19.6 (75), 29.1 (2500) |
| $[Fe([14]dieneN_4)(CH_3CN)_2]_2I_2$ | $CH_3CN$ | 19.6 (81), 29.4 (5200) |
| $Fe([14]dieneN_4)(NCS)_2$ | Solid state | 19.0 (w),[c] 23.25, 25.0 (s) |
| $[Fe([14]dieneN_4)(CH_3CN)(C_3H_4N_2)](BPh_4)_2$ | $CH_3CN$ | 20.0 (70), 24.9 (sh), 31.7 (sh) |
| | Solid state | 19.8, 24.9 (sh), 31.7 (sh) |
| $[Fe([14]dieneN_4)Cl_2]ClO_4$ | $CH_3OH$[d] | 14.3 (6), 17.3 (22), 20.8 (sh, 32) |
| | Solid state | 14.3, 17.4, 20.8, 25.0 |
| $[Fe([14]dieneN_4)(CH_3CN)_2](ClO_4)_3$ | Solid state | 19.0 (sh), 27.4, 33.3 |
| $[Fe([14]dieneN_4)(NCS)_2]BPh_4$ | $CH_2Cl_2$ | 17.24 (6290) |
| $[\{Fe([14]dieneN_4)H_2O\}_2O](ClO_4)_4$ | Solid state | 19.23 (w), 20.83 (w,) 32.26 (s) |
| $[\{Fe([14]diene)\}_2OH](ClO_4)_3$ | Solid state | 5.12 (w), 12.2 (w) |
| $[Fe([14]dieneN_4)Cl]ClO_4$[e,f] | $CH_3NO_2$ | 4.7 (7), 12.2 (5) |
| $[Fe([14]dieneN_4)Br]ClO_4$[e,f] | $CH_3NO_2$ | ~5 (~5), 12.2 (4.9) |
| $[Fe([14]dieneN_4)I]ClO_4$[e,f] | $CH_3NO_2$ | ~4.5 (~4), 12.2 (4) |
| $Fe([14]dieneN_4)I_2$ | MeOH | 12.2 (13) |

[a] Most soluble isomer. [b] Least soluble isomer. [c] Abbreviations: w = weak, s = strong. [d] Solution contained 0.05 *M* tetraethylammonium chloride to suppress dissociation. [e] Equimolar portions of $[Ni([14]dieneN_4)](ClO_4)_2$ were used in reference cell to balance vibrational ligand overtones which interfere in the low-energy regions. [f] Excess halide ion was added to suppress dissociation effects.

is an unusual example of a compound existing in a state of spin equilibrium between singlet and quintet forms at room temperature. Some of the physical properties of these complexes are listed in Table I, and their electronic spectra are summarized in Table II.

**Infrared Spectra.** The infrared spectra of all the iron–[14]diene$N_4$ complexes have many prominent features in common with [14]diene$N_4$ complexes of nickel(II) and copper(II). They all have very intense N-H stretching absorptions near 3220 cm$^{-1}$ and an intense imine C=N stretching absorption in the 1670–1640-cm$^{-1}$ region. The acetonitrile-containing iron(II) complexes, $[Fe([14]dieneN_4)(CH_3CN)_2](ClO_4)_2$ and $[Fe([14]dieneN_4)(CH_3CN)_2](BPh_4)_2 \cdot 4CH_3CN$, have a weak absorption at 2275 cm$^{-1}$ attributable to the C≡N stretching mode of acetonitrile. In addition, the latter complex has a very sharp strong band at 2240 cm$^{-1}$ due to the uncoordinated acetonitrile. The yellow iron(III) complex containing acetonitrile has five very sharp, closely spaced absorptions of moderate intensity in these same regions, a doublet at 2330 cm$^{-1}$, another doublet at 2300 cm$^{-1}$, and a sharp absorption at 2250 cm$^{-1}$.

The two isomeric forms of $[Fe([14]dieneN_4)(CH_3CN)_2](ClO_4)_2$ have infrared spectra which differ primarily in the C-H stretching region (Figure 1) and in the imine C=N stretching region. The least soluble isomer has, as its distinctive feature, a sharp intense spike in the C—H region, and its C=N absorption is a sharp singlet; whereas the C=N stretching absorption of the other isomer consists of a closely spaced doublet with pronounced shoulders. Both forms are sensitive to oxygen in the solid state, and each displays a gradual weakening of the N-H stretching absorption and the appearance of a second imine C=N stretch at 1660 cm$^{-1}$ when the complexes are allowed to stand in the air.

The iron(II) and iron(III) complexes, $[Fe([14]dieneN_4)(NCS)_2]$ and $[Fe([14]dieneN_4)(NCS)_2]BPh_4$, have a strong C≡N stretching absorption at 2090 cm$^{-1}$, and each has a band of moderate intensity near 790 cm$^{-1}$. These thiocyanate absorptions are typical of those observed for N-bonded thiocyanate.[15]

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(15) J. L. Burmeister, *Coord. Chem. Rev.*, 1, 205 (1966), and references contained therein.

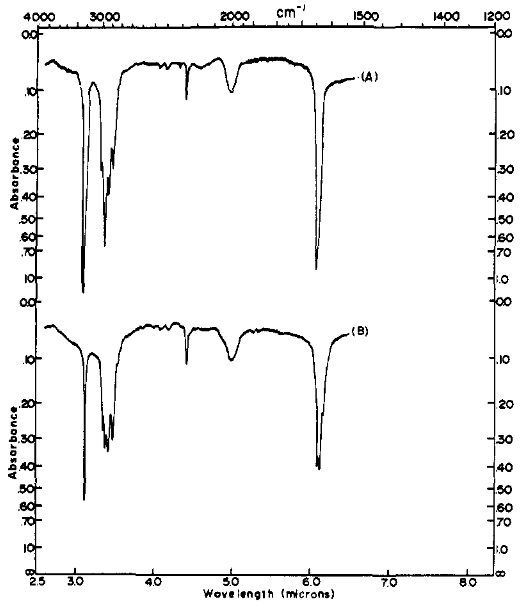

Figure 1. Infrared spectra of the stereoisomers of [Fe([14]dieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$: (A) least soluble isomer, (B) most soluble isomer.

All of the complexes containing perchlorate anions have very strong unsplit absorptions at 1100 cm$^{-1}$ and a sharp intense absorption at 630 cm$^{-1}$ characteristic of uncoordinated perchlorate anions.[16] The oxo-bridged dimer, [Fe([14]dieneN$_4$)(H$_2$O)$_2$O](ClO$_4$)$_4$, has a broad O-H stretch at 3500 cm$^{-1}$, typical of H$_2$O, and a strong, medium-broad absorption at 890 cm$^{-1}$ which is absent in all of the other iron-[14]dieneN$_4$ complexes. This band is characteristic of all Fe(III) complexes which are known to have oxo bridges.[5, 17]

**Low-Spin Six-Coordinate Complexes.** When ligands of moderate to strong ligand-field strength are available for coordination in the axial sites, low-spin six-coordinate complexes of the stoichiometry [Fe([14]dieneN$_4$)Y$_2$]ClO$_4$, Y = neutral ligand, or [Fe([14]dieneN$_4$)X$_2$], X = uninegative ligand, are obtained. Nitrogen donor ligands, such as thiocyanate, acetonitrile, and imidazole, all yield low-spin complexes. The application of diamagnetic corrections for the ligands to the molar magnetic susceptibilities gave values of about $100 \times 10^{-6}$ cgs unit, corresponding to residual magnetic moments of 0.4–0.6 BM. This is in the range usually found for TIP in d$^6$ systems.[18] Molar conductivities generally agree with these formulations (Table I). The values for those complexes containing the Fe([14]dieneN$_4$)(CH$_3$CN)$_2$$^{2+}$ cation and the imidazole derivative are typical for 2:1 electrolytes, while the result for Fe([14]dieneN$_4$)(NCS)$_2$ shows it to be a nonelectrolyte.

The electronic spectra of these complexes have been interpreted in terms of their low-spin d$^6$ electronic configurations. The acetonitrile complex [Fe([14]dieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$ has a single observable d-d absorption at 19.7 kK with $\epsilon_{\max}$ of about 80 (Figure 2). Very concentrated solutions (about 0.1 *M*) were examined throughout the range of 5 kK and upward in energy, and no absorptions lower in energy than the 19.6-kK bands were observed. In the absence of any lower energy bands characteristic of d–d transitions, the band at 19.6 kK is assumed to be associated with either, or both, the $^1E_g$ or $^1A_{2g}$ tetragonal components of the $^1T_{1g}$ excited state of low-spin Fe(II). All such assignments of the 19.6-kK band result in an extraordinarily high value (around 20 kK for 10*Dq*) for the in-plane field generated by the macrocycle. This band occurs at a comparable, though slightly higher, energy, with the cobalt(III) complexes of the same macrocyclic ligand having acetonitrile in the axial positions.[19] The value for the "in-plane" 10*Dq* of Co(III) complexes of the [14]dieneN$_4$ ligand are around 25.0 kK.[9, 20] Values of 10*Dq* for divalent transition metal ions are generally only about 50% of the values typically observed for trivalent metal ions in similar ligand environments. However, in the case of macrocyclic complexes, the donor atom–metal distance is fairly constant, in contrast to the variable metal–ligand distances possible with simple linear polydentate or monodentate ligands. These observations, together with the fact that the ligand field varies as a high power of the metal–ligand distance, probably account for the unexpected high-field strength toward Fe(II) of the macrocycle.

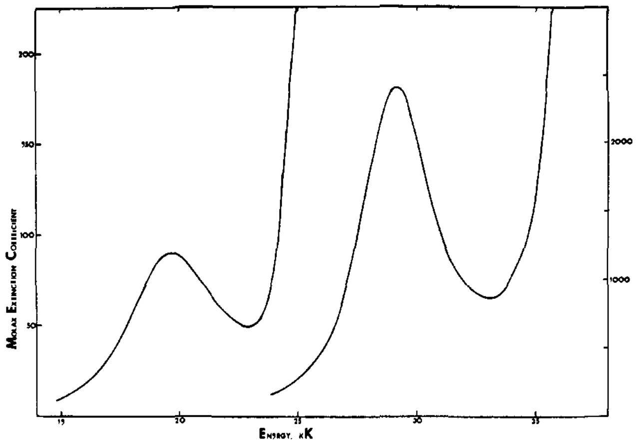

Figure 2. Electronic spectrum of [Fe([14]dieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$ in acetonitrile solution.

The remaining high-energy absorptions are also intense. The one at 27.7 kK ($\epsilon_{\max}$ 2440) is probably associated with the metal → $\pi^*$ transition to the imine. This assignment is based on the trends observed for a similar band which appears in the Cu(II), Ni(II), and Co(II) complexes of the [14]dieneN$_4$ ligand. The energy for this band decreases for these divalent complexes from right to left across the periodic table; the values are 38.5, 35.7, and 32.0 kK for the Cu(II)-, Ni(II)-, and Co(II)-[14]dieneN$_4$ complexes, respectively, and parallels the ease with which each species is oxidized to the trivalent state.[21] The spectra for the thiocyanate and imidazole iron(II)-[14]dieneN$_4$ complexes are not as well resolved because of other charge-transfer bands, but each displays a shoulder near 20.0 kK which is assumed to arise from the $^1T_{1g}$ term.

The room-temperature magnetic moment for the phenanthroline complex [Fe([14]dieneN$_4$)phen](ClO$_4$)$_2$

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[16] A. F. Wickenden and R. A. Krause, *Inorg. Chem.*, 4, 404 (1965); S. Buffagni, L. M. Vallarino, and J. V. Quagliano, *ibid.*, 3, 671 (1964); S. F. Pavkovic and D. W. Meek, *ibid.*, 4, 1091 (1965).

[17] D. J. Hawkins and W. P. Griffith, *J. Chem. Soc.*, 472 (1966).

[18] J. S. Griffith and L. E. Orgel, *Trans. Faraday Soc.*, 53, 601 (1957); S. S. Dharmotti and C. R. Kanekur, *J. Chem. Phys.*, 31, 1436 (1959).

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[20] N. Sadasivan, J. A. Kernohan, and J. F. Endicott, *Inorg. Chem.*, 6, 770 (1967).

[21] J. Vasilevskis and D. C. Olson, *ibid.*, 10, 1228 (1971).

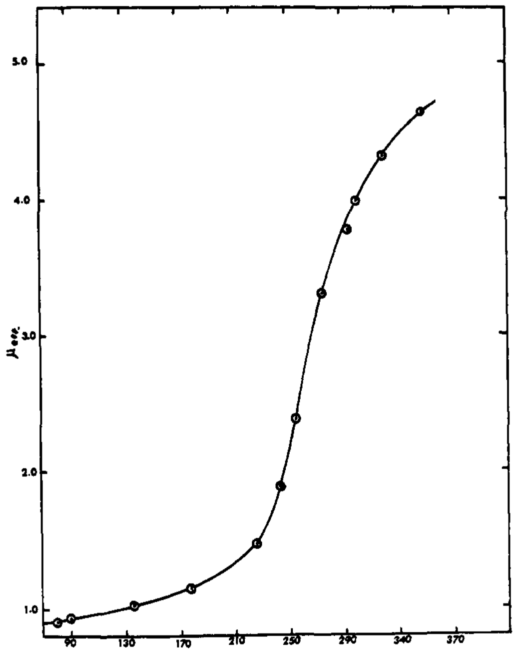

Figure 3. Variation of magnetic moment with temperature for [Fe([14]dieneN$_4$)phen](ClO$_4$)$_2$.

is around 3.7 BM, and variable-temperature magnetic studies show that the magnetic moment is extremely temperature dependent (Figure 3; Table III). The susceptibility at each temperature is independent of field strength and there is no time dependence, such as that observed for [Fe(phen)$_2$(NCS)$_2$][22] and bis[2-(2-pyridylamino)-4-(2-pyridyl)thiazole]iron(II) nitrate.[23] These results indicate the presence of a spin equilibrium between a $^1A_{1g}$ ground state and a thermally accessible $^5T_{2g}$ (ignoring lower symmetry components) level in this compound.

**Table III.** Susceptibility of [Fe([14]dieneN$_4$)(phen)](ClO$_4$)$_2$ at Various Temperatures

| Temp, °C | $\chi_M \times 10^{-6}$, cgs units |
|---|---|
| −190 | 1255 |
| −182 | 1201 |
| −135 | 968 |
| −92 | 914 |
| −44 | 1075 |
| −27 | 1628 |
| 4.5 | 2741 |
| 25 | 6012 |
| 29.5 | 6253 |
| 47 | 6794 |
| 51 | 6995 |
| 79 | 7567 |

The temperature dependence of the magnetic moment of this substance has been interpreted quantitatively in a manner similar to that described by Busch, *et al.*,[24] for some Co(II) complexes having thermal equilibrium between doublet and quartet states, and Melson and Busch[25] for singlet and triplet states.

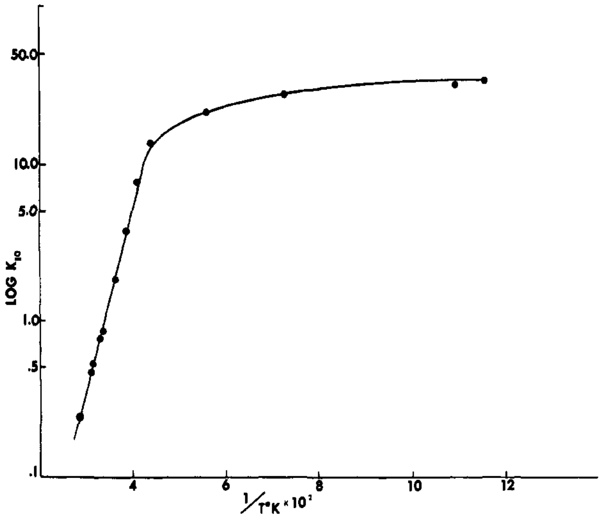

Figure 4. Temperature dependence for log $K_{eq}$ for the spin-state equilibrium involving [Fe([14]dieneN$_4$)phen](ClO$_4$)$_2$.

The equilibrium constant is calculated in terms of the relative concentrations of the high- and low-spin forms. The temperature dependence of the log $K_{eq}$ calculated from the experimental susceptibilities of [Fe([14]dieneN$_4$)phen](ClO$_4$)$_2$ is shown in Figure 4. These calculations have assumed that the high-spin form obeys the Curie–Weiss law, with $\chi_m$ value of 11,000 × 10$^{-6}$ cgs unit/mol at 300°K and that the second-order Zeeman contribution to the susceptibility of the $S = 0$ species would be 100 × 10$^{-6}$ cgs unit/mol.

The curvature of the log $K$ *vs.* $1/T$ plot reveals that the treatment given is inadequate over the full temperature range studied. However, $\Delta H$ is essentially constant at 6.58 kcal/mol over the range 350–180°K and yields a $\Delta S$ value of 22 eu. These values are considerably larger than those expected on the basis of a change in spin state alone, and it is assumed that there may be changes in bond lengths and angles accompanying the changes in spin state. These thermodynamic parameters are close to those found for bis[tris(1-pyrazolyl)borate]iron(II)[26] and tris[2-(2′-pyridyl)imidazole]iron(II) perchlorate.[27]

Similarly, the visible and ultraviolet spectrum of [Fe([14]dieneN$_4$)phen](ClO$_4$)$_2$ is almost exclusively characterized by strong, presumable charge-transfer bands. Because of the very strong temperature dependence of the magnetic moment, the visible and uv spectral characteristics should also be markedly dependent on the temperature. Even the solid, which is purple-black, reversibly lightens in color when heated to 150°, taking on a pink-red color.

**Five-Coordinate Complexes.** High-spin, five-coordinate complexes are obtained when only ligands of weak field strength are available for coordination in the axial positions. Thus, the reaction of [Fe([14]dieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$ with halide ions in methanol yields complexes of the stoichiometry [Fe([14]dieneN$_4$)X]ClO$_4$, X = Cl, Br, I. The assignment of the coordination number five to these complexes rests on their stoichiometry, their 1:1 electrolyte type in nitromethane (Table

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[22] A. T. Casey and F. Isaac, *Aust. J. Chem.*, 20, 2765 (1967).

[23] R. N. Sylva and H. A. Goodwin, *ibid.*, 20, 479 (1967).

[24] R. C. Stoufer, D. H. Busch, and W. B. Hadley, *J. Amer. Chem. Soc.*, 83, 3732 (1961).

[25] G. A. Melson and D. H. Busch, *ibid.*, 86, 4830 (1964).

[26] J. P. Jesson, S. Trofimenko, and D. R. Eaton, *ibid.*, 89, 3158 (1967).

[27] D. M. L. Goodgame and A. Machado, *Inorg. Chem.*, 8, 2031 (1969).

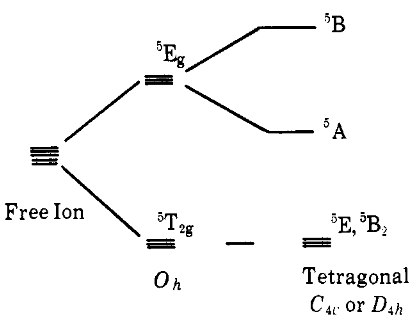

Figure 5. Energy level diagram for the five-coordinate complexes; d$^6$ metal ion in $C_{4v}$ symmetry.

I), and their vibrational and electronic spectra. The Mössbauer spectra of these five-coordinate species yield some of the largest quadrupole splittings ever observed for iron complexes.[28] The complexes have magnetic moments of about 5.1 BM (Table I). This is slightly less than those found for high-spin, six-coordinate complexes which are normally around 5.4 BM.[29] The compounds are almost colorless.

The d–d electronic spectra of the high-spin iron(II) complexes of the type $[Fe([14]dieneN_4)X]ClO_4$, X = Cl, Br, I, indicate an extremely high degree of tetragonal distortion and support the assignment of the coordination number five to this series of compounds. Careful spectroscopic measurements on these complexes in nitromethane solution and in the solid state reveal for each compound two broad weak d–d transitions near 5 and 12.5 kK, having molar extinction coefficients of about 5 (Table II). These two absorptions are assigned to transitions to the $^5B_1$ and $^5A_1$ states derived from the splitting of the $^5E$ spectroscopic term in a tetragonal ligand field (Figure 5). The higher energy absorption occurs at the same energy for each complex and is assigned to the transition to $^5B_1$ $(d_{x^2-y^2})$. It is primarily dependent upon the constant "in-plane" field of the macrocyclic ligand. The value of the maximum for the energy of this transition, 12.5 kK, is slightly higher than the value of 10*Dq* observed for octahedral iron(II) complexes containing six nitrogen donor atoms (11 kK).[30] The position of the lower energy absorption (transition to $^5A_1(d_{z^2})$) is dependent upon the field strength of the axial ligand, varying from about 4 kK for iodide to 5.12 for water. The separation between the $^5B_1$ and $^5A_1$ states, ~7.4 kK, although large, is not unreasonable. The separation of the $^5B_1$ and $^5A_1$ states in known tetragonal iron complexes, *e.g.*, $Fe(py)_4Cl_2$, is about 3.0 kK.[31] The absence of one axial ligand, plus the unusually high field strengths observed when donor atoms are part of a macrocycle[32] lead to an expected high separation.[33]

The possibility of the lowest observed transition being due to a transition within the $^5T_1$ manifold (split into $^5B_2$ and $^5E$ states) is excluded. The separation between these for some hemoglobin complexes has been determined to be less than 500 cm$^{-1}$.[34]

**Low-Spin Iron(III) Complexes.** Low-spin iron(III) complexes of the $[14]dieneN_4$ ligand can be prepared from $[Fe([14]dieneN_4)(CH_3CN)_2](ClO_4)_2$ using oxidants such as halogens or molecular oxygen.[35] For example, bubbling chlorine gas through a methanol dispersion of $[Fe([14]dieneN_4)(CH_3CN)_2](ClO_4)_2$ immediately produces pale green crystalline $[Fe([14]dieneN_4)Cl_2](ClO_4)$. In the absence of air, acetonitrile solutions of the pink starting material are stable for days with no discernible change in their visible or ultraviolet spectra. However, exposing the solutions to air, followed by acidification with $HClO_4$, produces the yellow low-spin ($\mu_{\text{eff}}$ = 2.19) iron(III) complex, $[Fe([14]dieneN_4)(CH_3CN)_2](ClO_4)_3$. The addition of thiocyanate to solutions of this yellow iron(III) complex immediately produces the intense blue $[Fe([14]dieneN_4)(NCS)_2]^+$ species.

The iron(III) complexes are all low spin and have moments in the range of 2.15–2.30 BM. These are slightly less than those found for typical low-spin iron(III) complexes, such as hexacyanoferrate(III) (2.40 BM).[29] $[Fe([14]dieneN_4)Cl_2]ClO_4$ and $[Fe([14]dieneN_4)(NCS)_2]BPh_4$ behave as 1:1 electrolytes in nitromethane. These complexes have conductances in the range of 80–110, which is typical of 1:1 electrolytes in nitromethane.[36] The conductance values of some of these complexes are in the higher ranges of those found for 1:1 electrolytes and may indicate a small amount of halide dissociation.

Of the iron(III) complexes, only the $[Fe([14]dieneN_4)Cl_2]ClO_4$ has clearly defined d–d absorption bands. Very few low-spin six-coordinate iron(III) complexes are known, and their d–d spectra are generally not well characterized.

The blue thiocyanate complex, $[Fe([14]dieneN_4)(NCS)_2](BPh_4)$, has a very intense absorption at 17.27 kK ($\epsilon$ 6290), which is similar in nature to the charge-transfer bands observed in the spectra of the simpler iron(III) thiocyanate species.

Oxo-bridged iron(III) species can be obtained in the absence of acid in oxygen donor solvents, such as alcohols and acetone. For example, pink $[Fe([14]dieneN_4)(CH_3CN)_2](ClO_4)_2$ dissolved in acetone to yield very pale green solutions. When oxygen is admitted to the system, a beige-colored precipitate slowly forms. The stoichiometry of the solid corresponds to $[\{Fe([14]dieneN_4)H_2O\}_2O](ClO_4)_4$, and the magnetic moment, $\mu_{\text{eff}}$ = 2.17, indicates it to be an oxo-bridged species. This formulation is also supported by the presence of an Fe–O–Fe stretching mode in the infrared spectrum of the substance at 890 cm$^{-1}$.[5,17]

**Isomers of $[Fe([14]dieneN_4)(CH_3CN)_2](ClO_4)_2$.** The synthesis of $[Fe([14]dieneN_4)(CH_3CN)_2](ClO_4)_2$, as described in the Experimental Section, generally yields two distinct forms of the complex. These two interconvertible isomers, although having identical analyses, differ in their solubilities, infrared and visible spectra, and nmr spectrum. All the evidence indicates that these isomers are the meso and racemic forms which are related by the absolute configurations about the

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(28) P. H. Merrell, V. L. Goedken, J. A. Stone, and D. H. Busch, *J. Amer. Chem. Soc.*, **92**, 7590 (1970).

(29) J. Lewis and R. Wilkins, "Modern Coordination Chemistry," Interscience, New York, N. Y., 1960, p 407.

(30) B. J. Hathaway and D. G. Holah, *J. Chem. Soc.*, 2408 (1964); D. Foster and D. M. L. Goodgame, *Inorg. Chem.*, **4**, 1712 (1965).

(31) D. M. L. Goodgame, M. Goodgame, M. A. Hitchman, and M. J. Weeks, *ibid.*, **5**, 635 (1966).

(32) D. H. Busch, *Helv. Chim. Acta, Fasciculus Extraordinarius Alfred Werner*, 174 (1967).

(33) An X-ray structural investigation has confirmed the five-coordinate geometry of the $[Fe([14]dieneN_4)Cl]ClO_4$ complex: V. Goedken and C. Christoph, unpublished results.

(34) U. Gonser and R. W. Grant, *Biophys. J.*, **5**, 823 (1965).

(35) They can also be obtained electrochemically: F. Lovecchio and D. H. Busch, unpublished work.

(36) R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964).

asymmetric nitrogen atoms. Similar meso and *d,l* isomers have been isolated with Ni([14]dieneN$_4$)(ClO$_4$)$_2$.[37] The percentages of the two diastereomeric forms are dependent upon the reaction conditions. The addition of excess of the neutralizing base, triethylamine, followed by prolonged heating, generates the least soluble form in yields varying from 30 to 60%. The most soluble form can then be precipitated with ethyl ether.

The least soluble isomer is tentatively assigned the meso configuration, and the most soluble form is thought to be the *d,l* isomer. This is based on the changes which occur in the extinction coefficient of the 19.6-kK bands for each isomer. Acetonitrile solutions of the least soluble isomer initially have an $\epsilon_{\max}$ of 75, which gradually increases to 80 over a period of 10 hr, whereas the most soluble isomer initially has an $\epsilon_{\max}$ of around 85, which gradually decreases to 80. The meso diastereomer has a center of inversion with *Ci* symmetry and is expected to have a lower extinction coefficient for d–d transitions than the *d,l* isomer which has $C_2$ symmetry.[38]

Although neither perchlorate is soluble enough for pmr studies, the hexafluorophosphate salts are easily prepared by metathetical reactions and are well suited for such studies. The pmr of each isomer indicated a small amount of the other to be present as a result of isomerization (inversion of a secondary nitrogen). Acid cannot be added to prevent this isomerization, as was done in the case of the extremely stable [Ni([14]dieneN$_4$)](ClO$_4$)$_2$ complexes, because the iron complexes slowly react with protons to yield solutions containing paramagnetic species. The pmr spectrum of each isomer is characterized by three widely spaced singlets of equal intensity near 2.4, 1.4, and 1.0 ppm and two broad regions of absorption in the vicinity of 2.8 and 3.6 ppm. In addition, there is a peak at 1.95 ppm attributable to the acetonitrile which has exchanged for deuterioacetonitrile. The most soluble form has its three singlets at 2.57, 1.58, and 1.13 ppm, and these are assigned to the imine methyl and geminal dimethyl resonances. The peak at 2.57 ppm is assigned to the imine methyl group because of its close proximity to the position (2.5 ppm) reported for that group in the spectrum of [Ni([14]dieneN$_4$)](ClO$_4$)$_2$.[37]

The two geminal dimethyl groups of [14]dieneN$_4$ metal ion complexes are not equivalent because of their axial and equatorial orientations. Their environments are dependent upon nonbonding effects related to the electronic configuration of the metal atom,[39,40] and the axial methyl substituents will also be influenced by the presence of ligands occupying the extraplanar sites of the complex. Buckingham and Stevens predict large shielding effects for protons situated above the plane of a low-spin d$^6$ metal system[39] and deshielding effects for protons located above the plane in low-spin d$^8$ metal ion systems.[40] The deshielding effects have been observed for the axially oriented methyl groups on various nickel(II)–Curtis macrocyclic complexes.[37]

On this basis, the methyl resonance at 1.39 ppm is assigned to the equatorial geminal methyl protons, and this position is also in close proximity to the location of the equatorial geminal proton resonance in the spectra of the Ni(II) complexes. The methyl resonance at 1.13 ppm is then assigned to the axial methyl protons which experience a very marked shielding effect, as predicted by Buckingham and Stevens.

The methyl resonances of the least soluble isomer occur at 2.42, 1.39, and 1.00 ppm. Each resonance is shifted by a constant factor, 0.12 ppm, to higher fields as compared to the most soluble isomer. Because of the constancy of these shifts compared with the other isomer, they cannot be used in substantiating the assignment of the meso and *d,l* diastereomers.

When solutions are allowed to reach equilibrium (about 10 hr), the pmr spectra show that the two isomers are present in approximately equal amounts, with the methyl portion of the spectrum consisting of six singlets. The effect of the axially coordinated acetonitrile groups must be to destabilize the *d,l* form, which has both of its axial methyl groups on the same side of the plane, through nonbonding repulsions. For the [Ni([14]dieneN$_4$)](ClO$_4$)$_2$ system it was found that the *d,l* isomer is the most stable and accounted for about 85% of the species in solution at equilibrium.[37]

**Chemical Reactivity.** All of the iron complexes of the [14]dieneN$_4$ ligand reported in this paper are quite reactive species, especially in comparison to the very stable [14]dieneN$_4$ complexes of cobalt, nickel, and copper. The types of reactions that each iron complex undergoes are markedly dependent upon the coordination number, the spin state, and the oxidation state of the iron atom.

First we will consider the behavior of [Fe([14]dieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$ in the solid state. This complex is sensitive to oxygen even in the solid state and the changes which occur in the infrared spectrum are especially significant. There is a gradual diminution of the intensity of the N—H stretching absorption and a second imine C=N stretching band appears. These solid-state reactions with oxygen, which also occur in solution, have been found to consist of a complicated series of oxidative dehydrogenations of the ligand.[41]

Although oxygen-free acetonitrile solutions of this complex are stable indefinitely, the solutions are only moderately stable to acids. For example, 0.01 *M* acetonitrile solutions of [Fe([14]dieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$ containing 0.05 *M* HClO$_4$ undergo ligand displacement with a half-life of about 40 min. This is much more stable than are iron(II) complexes of linear polydentate amines, which dissociate within the time of mixing under the conditions used here. The reactivity is also in considerable contrast with that of [14]dieneN$_4$ complexes of nickel, cobalt, and copper, which exist for weeks in acidic media with virtually no ligand displacement.[9,42]

Aqueous solutions of [Fe([14]dieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$ appear to contain the high-spin, five coordinate species, [Fe([14]dieneN$_4$)H$_2$O]$^+$. These solutions yield a white crystalline solid whose analyses are consistent with the formulation [Fe([14]dieneN$_4$)H$_2$O](ClO$_4$)$_2$·[Fe([14]dieneN$_4$)OH]ClO$_4$. The Mössbauer parameters indicate that only one kind of iron is present in the complex and, further, that the iron is five-coordinate.[28]

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(37) L. G. Warner, N. J. Rose, and D. H. Busch, *J. Amer. Chem. Soc.*, 90, 6938 (1968).

(38) L. E. Orgel, "An Introduction to Transition Metal Chemistry—Ligand Field Theory," Butler and Tanner, Ltd., London, 1960, p 92.

(39) A. D. Buckingham and P. J. Stevens, *J. Chem. Soc.*, 2747 (1964).

(40) P. J. Stevens and A. D. Buckingham, *ibid.*, 4583 (1964).

(41) V. L. Goedken and D. H. Busch, to be published.

(42) D. K. Cabbiness and D. W. Margerum, *J. Amer. Chem. Soc.*, **92**, 2151 (1970); C. R. Sperati and D. H. Busch, unpublished results.

The visible solution spectra and solid-state spectra of this substance are virtually identical, indicating a similar environment about the iron(II) ion in each phase. Consequently, it is assumed that the complex is [Fe([14]dieneN$_4$)–O(H)–Fe([14]dieneN$_4$)](ClO$_4$)$_3$·H$_2$O. The formulation of the product as a hydroxo species is consistent with the observation that the crude compound is often contaminated with some [14]dieneN$_4$·2HClO$_4$ which is readily identifiable from its characteristic infrared spectrum. The addition of perchloric acid to aqueous solutions of the complex yields white crystalline [14]dieneN$_4$·2HClO$_4$ within minutes. Neutral aqueous solutions containing the [Fe([14]dieneN$_4$)H$_2$O]$^{2+}$ species are very sensitive to oxygen, with the nearly colorless solutions turning purple when exposed to oxygen. This color fades rapidly as the ligand is stripped from the metal (yielding some [14]dieneN$_4$·2HClO$_4$ and ferric hydroxide). This undesirable reaction is greatly accelerated by warming the solution.

Although the coordinated acetonitrile in Fe([14]dieneN$_4$)(CH$_3$CN)$_2{}^{2+}$ is easily replaced by a variety of ligands, the Fe([14]dieneN$_4$)$^{2+}$ moiety appears to have a special affinity for this ligand. Aqueous 0.01 *M* solutions are colorless at room temperature, but on chilling the solutions to near 0°, the pink color of [Fe([14]dieneN$_4$)(CH$_3$CN)$_2$]$^{2+}$ is regained even though water is present in about 5000 *M* excess.

The five-coordinate species, [Fe([14]dieneN$_4$)X]ClO$_4$, are more sensitive to oxygen than are the low-spin, six-coordinate iron(II) species. Solutions of [Fe([14]dieneN$_4$)X]ClO$_4$ in methanol or ethanol react with oxygen within seconds undergoing a complicated series of reactions. They yield yellow, brown, and blue species, depending on conditions, for example, the amount of oxygen admitted. Even in acetonitrile solutions, the addition of halide ions to [Fe([14]dieneN$_4$)(CH$_3$CN)$_2$]$^{2+}$ leads to extremely rapid reactions with oxygen, or to destruction of the macrocyclic complex, when acid is present.

The tendency of the iron(II)–[14]dieneN$_4$ complexes to attain the unusual coordination number of five and the abnormally high ligand-field strengths observed for the low-spin six-coordinate species can be rationalized in the following way. The ionic radii of transition metals are dependent on the spin state of the metal atom and may be anisotropic, depending on the electronic configuration of the metal atom being considered. For a low-spin d$^6$ system, with the d$_{z^2}$ and d$_{x^2-y^2}$ orbitals vacant, significantly shorter radii and metal–ligand bond distances are to be expected.[43,44] A perusal of the X-ray structures of various high- and low-spin d$^6$ and d$^8$ metal ion systems reveals that metal–ligand distances are generally shorter for the low-spin than the high-spin configuration. Generally for a tetragonal system, the primary requirement for six-coordination is that the metal atom lie nominally in the plane of the equatorial donor atoms. For the low-spin forms of both the iron(II) and iron(III) complexes of [14]dieneN$_4$, the axial ligands must have sufficient ligand-field strength to cause pairing of the electrons, leaving the d$_{x^2-y^2}$ and d$_{z^2}$ orbitals vacant. This causes a radial contraction of the metal ion, allowing it to fit into the in-plane "hole" within the macrocycle. For iron(II), ligands such as acetonitrile and imidazole are required, whereas in the case of iron(III), even weak ligands such as halide suffice. For the case of iron(II), however, weak donors such as halides are too weak to promote spin pairing and consequent radial contraction. High-spin iron(II) ions may be too large to fit into the plane of the macrocycle donor atoms, and they are presumed to be displaced either above or below the plane to the extent that only one axial ligand can coordinate.

This view is supported by the ease with which the Fe([14]dieneN$_4$)$^{2+}$ moiety forms adducts with the strong, chelating agent 1,10-phenanthroline. This tendency is not observed with Co(II), Ni(II), or Cu(II) complexes of the [14]dieneN$_4$ ligand. The action of this chelate serves to remove the iron from the plane and force the [14]dieneN$_4$ ligand into a folded conformation, resulting in the iron(II) complex being susceptible to further substitution by phenanthroline. The addition of excess 1,10-phenanthroline to methanol solutions of [Fe([14]dieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$[45] immediately produces a very intensely colored purple solution from which black (deep purple) crystalline [Fe([14]dieneN$_4$)(C$_{18}$H$_8$N$_2$)](ClO$_4$)$_2$ can be isolated. In solution this compound reacts with excess phenanthroline to yield [Fe(C$_{12}$H$_8$N$_2$)$_3$](ClO$_4$)$_2$ and the free ligand, [14]dieneN$_4$.

The low-spin iron(III) species formed by aerial oxidation in acetonitrile, [Fe([14]dieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_3$, and by chlorine oxidation, [Fe([14]dieneN$_4$)Cl$_2$]ClO$_4$, are unstable and have a strong tendency to decompose or revert back to iron(II) species, especially when in contact with moisture. For example, the yellow [Fe([14]dieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_3$ is stable indefinitely in dry acetonitrile, but the solid decomposes to a tan material under N$_2$ or vacuum. When a drop or two of water is added to an acetonitrile solution (or suspension, since the complex is only sparingly soluble in acetonitrile), a slow redox process occurs to give back a low-spin pink iron(II)–[14]dieneN$_4$ complex. Similar behavior is observed for the [Fe([14]dieneN$_4$)Cl$_2$]ClO$_4$ complex.

## Experimental Section

**Materials.** All solvents and chemicals except nitromethane were reagent grade and used without further purification. All solvents were dried with size 4A molecular sieves for several weeks and deaerated with nitrogen before using. Practical grade nitromethane was purified by the method of Olah, *et al.*[46]

**Physical Measurements.** Visible, near-infrared, and ultraviolet spectra were obtained with a Cary Model 14 recording spectrophotometer modified with a special high-intensity lamp in the visible and infrared portions. Spectra were obtained with solid samples of Nujol mulls impregnated on filter paper as well as with solution.

A Perkin-Elmer Model 337 recording spectrophotometer was used to obtain all infrared spectra. Infrared spectra were obtained using Nujol and hexachlorobutadiene mulls.

Elemental analyses for carbon, hydrogen, nitrogen, and iron were all determined by commercial analytical laboratories.

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(43) J. H. Van Santen and J. S. Van Wieringer, *Recl. Trav. Chim. Pays-Bas*, 71, 420 (1952).

(44) Single-crystal X-ray structural determinations of high-spin (high-temperature form) and low-spin (low-temperature form) Fe(bipy)$_2$(NCS)$_2$ indicate that the low-spin configuration has metal–ligand distances approximately 0.1 Å shorter than those of the high-spin configuration: E. König and K. Watson, *Chem. Phys. Lett.*, 6, 457 (1970).

(45) The d–d spectrum of methanol solutions of [Fe([14]dieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_2$ indicates that the dissolved species is actually [Fe([14]dieneN$_4$)CH$_3$OH].$^{2+}$

(46) G. A. Olah, S. J. Kuhn, S. H. Flood, and B. A. Hardin, *J. Am. Chem. Soc.*, **86**, 1043 (1964).

Electrical resistances of solutions of compounds were measured using an Industrial Instruments RC 16B conductivity bridge and a conductance cell with a constant of 2.12 $cm^{-1}$. Conductances were determined at room temperature at 1000 cps on solutions approximately $10^{-3}$ *M* in concentration.

The magnetic susceptibilities of solid samples were determined by the Faraday method using a system equipped with a Cahn Electrobalance and accurate temperature control.[47] All susceptibilities were corrected for diamagnetism.

**[14]diene$N_4\cdot 2HClO_4$ and [14]diene$N_4\cdot 2HI$.** The acid salts of the ligand [14]diene$N_4\cdot 2HClO_4$ and [14]diene$N_4\cdot 2HI$ were prepared by the method of Curtis.[48] All syntheses of complexes were carried out under nitrogen unless otherwise indicated.

**[Fe([14]diene$N_4$)$(CH_3CN)_2$]$(ClO_4)_2$, Isomer A.** *CAUTION! Explosive Substance.* A solution of 4 g of $Fe(ClO_4)_2\cdot 6H_2O$ in 25 ml of a 1:1 mixture of acetonitrile and triethyl orthoformate was heated at 50° under nitrogen for several hours. These solutions are potentially hazardous and should be kept behind shields. The addition of triethyl orthoformate to acetonitrile solutions of hydrated iron perchlorate causes a darkening of the solution. After heating for several hours the color of the solution lightens to yellow. [14]diene$N_4\cdot 2HClO_4$ (4 g) was then added and neutralized by the dropwise addition of triethylamine until all the solid [14]diene$N_4\cdot 2HClO_4$ had gone into solution. The solution turns a deep red color as neutralization proceeds, and a pink precipitate forms on continued heating. The precipitate was filtered, washed with a 3:1 mixture of acetonitrile and ether, and dried *in vacuo*. *Anal.* Calcd for $FeC_{20}H_{36}N_6Cl_2O_8$: C, 38.9; H, 6.16; N, 13.6; Cl, 11.5. Found: C, 38.8; H, 6.24; N, 13.9; Cl, 11.3.

**[Fe([14]diene$N_4$)$(CH_3CN)_2$]$(ClO_4)_2$, Isomer B.** *CAUTION! Explosive Substance.* Ether (25 ml) was added to the filtrate from the above preparation. The second crop of pink crystals was filtered, washed with a 1:1 acetonitrile solution and dried *in vacuo*. *Anal.* Calcd for $FeC_{20}H_{36}N_6Cl_2O_8$: C, 38.9; H, 6.16; N, 13.6; Cl, 11.5. Found: C, 38.5; H, 6.09; N, 13.0; Cl, 11.3.

**[Fe([14]diene$N_4$)$(CH_3CN)_2$]$I_2$.** A slurry of 1.0 g of anhydrous iron(II) acetate and 3.0 g of [14]diene$N_4\cdot 2HI$ in 100 ml of warm acetonitrile (45°) was stirred for 1 day. The color of the solution gradually became a deep maroon after 24 hr. The solution was filtered, concentrated, and chilled. Maroon crystals of the produdt were filtered and dried *in vacuo*. *Anal.* Calcd for $FeC_{20}H_{36}N_6I_2$: C, 35.8; H, 5.66; N, 12.55; I, 37.5. Found: C, 35.61; H, 5.73; N, 12.35; I, 37.06.

**Fe([14]diene$N_4$)$I_2$.** A sample of [Fe([14]diene$N_4$)$(CH_3CN)_2$]$I_2$ was placed in a drying pestle for 24 hr at 100° under vacuum. The maroon starting material slowly turned brown as acetonitrile dissociated. *Anal.* Calcd for $FeC_{16}H_{32}N_4I_2$: C, 33.2; H, 5.45; N, 9.50. Found: C, 32.65; H, 5.67; N, 9.42.

**[Fe([14]diene$N_4$)$(CH_3CN)_2$][$B(C_6H_5)_4$]$_2\cdot 4CH_3CN$.** [Fe([14]diene$N_4$)$(CH_3CN)_2$]$(ClO_4)_2$ (2 g) was dissolved in hot actonitrile and 2.5 g of sodium tetraphenyl borate, dissolved in methanol, added. The red crystalline product which forms on chilling over a period of hours was filtered, washed with acetonitrile, and dried *in vacuo*. *Anal.* Calcd for $FeC_{76}H_{90}N_{10}B_2$: C, 74.8; H, 7.38; N, 11.48; Fe, 4.58. Found: C, 75.4; H, 7.39; N, 11.53; Fe, 4.42.

**[Fe([14]diene$N_4$)$(CH_3CN)_2$]$(PF_6)_2$.** [Fe([14]diene$N_4$)$(CH_3CN)_2$]$(ClO_4)_2$ (2 g) was dissolved in a minimum amount of hot acetonitrile, and 2 g of ammonium hexafluorophosphate added. After chilling, the $NH_4ClO_4$ which formed was filtered from the solution and water was added until the solution was slightly turbid. The pink product, which precipitates over a period of hours, was filtered, washed with water, and dried *in vacuo*. *Anal.* Calcd for $FeC_{20}H_{36}N_6P_2F_{12}$: C, 33.81; H, 5.53; N, 11.83. Found: C, 33.60; H, 5.44; N, 11.6.

**[Fe([14]diene$N_4$)Cl]$(ClO_4)$.** *CAUTION! Explosive substance.* [Fe([14]diene$N_4$)$(CH_3CN)_2$]$(ClO_4)_2$ (1 g) was dissolved in 25 ml of hot, deaereated methanol and 1 g of LiCl, dissolved in methanol, was added. The flask was stoppered and allowed to cool. Lustrous, nearly white, fibrous crystals form on standing. These were filtered, washed with cold methanol, and dried and stored *in vacuo*. *Anal.* Calcd for $FeC_{16}H_{32}N_4Cl_2O_4$: C, 40.7; H, 6.79; N, 11.8; Cl, 15.1. Found: C, 39.7; H, 6.79; N, 11.7; Cl, 15.4.

**[Fe([14]diene$N_4$)Br]$ClO_4$ and [Fe([14]diene$N_4$)I]$ClO_4$.** *CAUTION! Explosive substances.* These were prepared metathetically in the same manner as the chloro compound except that LiBr or NaI was used as the source of halide ion. Both compounds were off-white in color. *Anal.* Calcd for $FeC_{16}H_{32}N_4BrClO_4$: C, 37.3; H, 6.21; N, 10.9; Br, 15.5. Found: C, 36.7; H, 6.16; N, 10.9; Br, 15.4. Calcd for $FeC_{16}H_{32}N_4IClO_4$: C, 34.1; H, 5.69; N, 9.95. Found: C, 33.6; H, 5.92; N, 9.63.

**[Fe([14]diene$N_4$)$(NCS)_2$].** [Fe([14]diene$N_4$)$(CH_3CN)_2$]$(ClO_4)_2$ (1 g) was dissolved in 25 ml of ethanol. NaSCN (0.5 g), dissolved in deaerated methanol, was added. An olive-brown precipitate formed immediately. The solution was filtered, washed with deaerated methanol, and dried *in vacuo*. *Anal.* Calcd for $FeC_{18}H_{32}N_6S_2$: C, 47.8; H, 7.08; N, 18.6. Fe, 12.4. Found: C, 47.5; H, 7.00; N, 18.2; Fe, 12.2.

**[Fe([14]diene$N_4$)$Cl_2$]$ClO_4$.** *CAUTION! Explosive substance.* For 2 min chlorine gas was gently bubbled through a dispersion of 1 g of [Fe([14]diene$N_4$)$(CH_3CN)_2$]$ClO_4$ in 15 ml of methanol with continuous mechanical stirring. The pink starting material dissolved and the green product precipitated on formation. The solution was filtered and the product was washed with several portions of anhydrous methanol and dried *in vacuo*. *Anal.* Calcd for $FeC_{16}H_{32}N_4Cl_3O_4$: C, 38.2; H, 5.58; N, 11.1; Cl, 21.0; Fe, 11.1. Found: C, 37.9; H, 5.76; N, 10.8; Cl, 20.7; Fe, 10.8.

**[Fe([14]diene$N_4$)$(NCS)_2$]$BPh_4$.** The pale green [Fe([14]diene$N_4$)$Cl_2$]$ClO_4$ (0.5 g) was dissolved in methanol. The addition of 0.5 g of sodium tetraphenylborate yielded a deep blue finely divided precipitate. The product was collected by filtration, washed with several portions of methanol, and dried *in vacuo*. *Anal.* Calcd for $FeC_{42}H_{52}N_6S_2B$: C, 65.4; H, 6.74; N, 10.9; Fe, 7.24. Found: C, 65.7; H, 6.80; N, 10.7; Fe, 7.10.

**[Fe([14]diene$N_4$)$(CH_3CN)_2$]$(ClO_4)_2$.** *CAUTION! Explosive substance.* Oxygen was slowly bubbled through a solution of 1 g of [Fe([14]diene$N_4$)$(CH_3CN)_2$]$(ClO_4)_2$ in 25 ml of acetonitrile. 70% aqueous perchloric acid (0.5 ml), dissolved in acetonitrile, was slowly added. *CAUTION! The presence of $HClO_4$ in organic solvents constitutes an explosion hazard.* The color of the solution changes from purple to bright yellow as the acid is added, and the bright yellow product slowly crystallizes from solution. The product was filtered from solution, washed with acetonitrile, and dried *in vacuo*. *Anal.* Calcd for $FeC_{20}H_{38}N_6Cl_3O_{12}$: C, 33.7; H, 5.33; N, 11.8; Cl, 14.9; Fe, 7.84. Found: C, 33.4; H, 5.62; N, 11.8; Cl, 14.6; Fe, 7.48.

**[Fe([14]diene$N_4$)$C_{12}H_8N_2$]$(ClO_4)_2$.** *CAUTION! Explosive substance.* [Fe([14]diene$N_4$)$(CH_3CN)_2$]$(ClO_4)_2$ (1 g) was dissolved in a minimum amount of methanol and 0.5 g of 1,10-phenanthroline, dissolved in methanol, was added. The solution was filtered and the filtrate concentrated under reduced pressure. The purple-black product, which slowly crystallized, was filtered, washed with methanol, and dried *in vacuo*. *Anal.* Calcd for $FeC_{28}H_{40}N_6Cl_2O_8$: C, 47.00; H, 5.59; N, 11.75; Cl, 9.93. Found: C, 46.9; H, 5.63; H, 11.7; Cl, 10.2.

**[Fe([14]diene$N_4$)$(CH_3CN)(C_3H_4N_2)$]$(ClO_4)_2$.** *CAUTION! Explosive substance.* [Fe([14]diene$N_4$)$(CH_3CN)_2$]$(ClO_4)_2$ (1 g) was dissolved in a minimum amount of acetonitrile and 0.5 g of imidazole was added. Sodium perchlorate (0.5 g) dissolved in methanol was added, and water was added dropwise until the solution became turbid. A red-brown product slowly crystallized on standing. This was filtered, washed with methanol, and dried *in vacuo*. *Anal.* Calcd for $FeC_{21}H_{39}N_6Cl_2O_8$: C, 76.7; H, 7.29; N, 9.05. Found: C, 76.9; H, 7.30; N, 8.98.

**[{Fe([14]diene$N_4$)$H_2O$}$_2$O]$(ClO_4)_4$.** *CAUTION! Explosive substance.* [Fe([14]diene$N_4$)$(CH_3CN)_2$]$(ClO_4)_2$ (1 g) was dissolved in acetone and air was bubbled through the solution. The tan product that slowly precipitated was filtered, washed with acetone, and dried *in vacuo*. *Anal.* Calcd for $Fe_2C_{32}H_{68}N_8Cl_4O_{19}$: C, 34.2; N, 5.71; N, 9.98; Cl, 12.6. Found: C, 33.9; H, 5.87; N, 9.76; Cl, 12.4.

**[{Fe[14]diene$N_4$)}$_2$OH]$(ClO_4)_3\cdot H_2O$.** *CAUTION! Explosive substance.* The most soluble isomer of [Fe([14]diene$N_4$)$(CH_3CN)_2$]$(ClO_4)_2$ (1 g) was dissolved in a minimum amount of water. The solution takes on a very pale green color as the pink starting material dissolves. White crystals form after standing for several hours. The crystals were scraped from the sides of the vessel, washed with water, and dried *in vacuo*. The first small fraction of the precipitate was used for all experimental purposes because later fractions contain impurities of [14]diene$N_4\cdot 2HClO_4$ which are difficult to remove. *Anal.* Calcd for $Fe_2C_{32}H_{67}N_8Cl_3O_{14}$: C, 38.2; H, 6.65; N, 11.1; Cl, 10.6. Found: C, 38.2; H, 6.80; N, 10.8; Cl, 10.6.

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