

## Macrocyclic Ligands and their Metal Ion Complexes. Part VIII\*. Preparation and structure of Isomeric Tetramethyl-1,4,8,11-tetra- azacyclotetradeca-4,11-diene-iron(II) Diperchlorates and their Dehydrogenation by Elemental Oxygen for Elucidation of the Ligands' Constitutional Isomerism

R. A. KOLIŃSKI, B. KORYBUT-DASZKIEWICZ, Z. KUBAJ and R. STACHURA

*Institute of Organic Chemistry, Polish Academy of Sciences, 01224 Warsaw, Poland*

Received April 8, 1981

Low spin  $Fe^{2+}L \cdot 2CH_3CN(ClO_4)_2$  complexes were obtained from individual diene ligands *L* (see Part VII) and iron(II) perchlorate in acetonitrile. The dehydrogenation by elemental oxygen to triene-iron(II) and tetraene-iron(II) complexes allowed us to assign the 2,5,9,12; 2,5,10,12; and 3,5,10,12 locations of methyl groups to ligands II and IV, to ligand III and to ligand I respectively. The structures of the complexes were established by spectroscopic methods IR, UV-VIS, and PMR.

### Introduction

Condensation of methyl vinyl ketone with *R,S*-1,2-propylenediamine monohydrogen perchlorate, followed by the reaction with nickel(II) acetate, leads to four isomeric tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienenickel(II) perchlorates I–IVNi(ClO<sub>4</sub>)<sub>2</sub>. When optically active 1,2-propylenediamine was used in the reaction, optically active complexes IIINi(ClO<sub>4</sub>)<sub>2</sub>, IVNi(ClO<sub>4</sub>)<sub>2</sub> and a fifth additional isomeric complex VNi(ClO<sub>4</sub>)<sub>2</sub> were isolated [1].

Combination of two molecules of methyl vinyl ketone and two molecules of 1,2-propylenediamine

may lead to the synthesis of six cyclic amines differing in the location of their methyl substituents (3,5,10,12-tetramethyl-, 2,5,9,12-tetramethyl- or 2,5,9,12-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) and in the relative configuration of the asymmetric carbon atoms (*C-meso* and *C-racemic*). Transition metal complexes of 1,4,8,11-tetraazacyclotetradeca-4,11-dienes, due to the presence of chiral centers on nitrogen atoms, may exist in interconvertible forms possessing *N-meso* or *N-racemic* configurations [1]. This leads to the possibility of ten isomers for each symmetrically substituted ligand (2,9- and 3,10-substituted) and twelve isomers for the 2,10-substituted ligand.

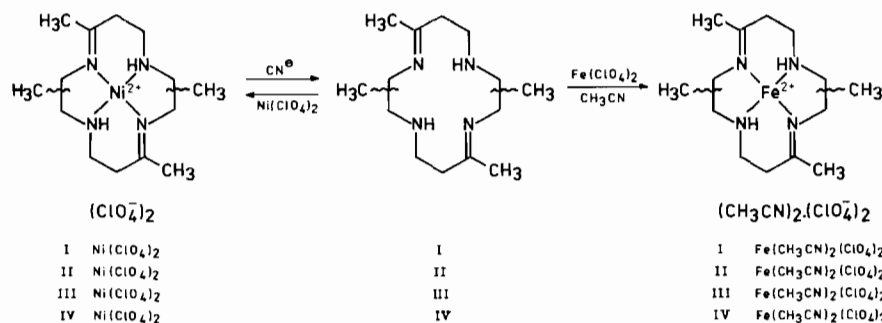
The aim of the present work is to elucidate the substitution pattern of ligands I–IV using the oxidative dehydrogenation of the ligands in iron(II) complexes by molecular oxygen, and to establish their stereochemistry.

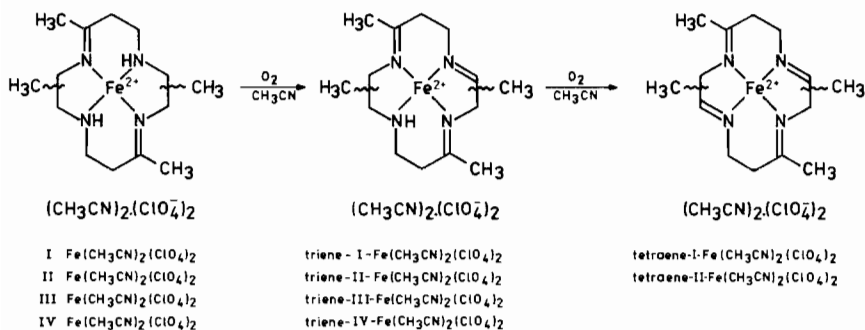
### Results and Discussion

#### Synthesis

The free macrocyclic Schiff's bases I–IV were liberated from their nickel(II) complexes in the reaction with potassium cyanide [1]. Iron(II) complexes of the isomeric tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienes were obtained by the known

\*For Part VII see the preceding paper, Ref. 1.





method [2, 3] from the free macrocyclic amines I–IV and iron(II) perchlorate in acetonitrile solution. The complexes were isolated by column chromatography on alumina with acetonitrile as eluent. Only one isomer at nitrogen was isolated for each isomeric ligand.

#### Location of Substituents

In order to establish the location of the methyl substituents in the propylenediamine part of the macrocyclic ring, we undertook a study of the ligand dehydrogenation reaction. Dehydrogenation of the nickel(II) complexes with nitric acid was only successful in the case of ligand I, and 3,10-methyl substitution was established for this ligand [1]. We were however unable to isolate any dehydrogenation products in the reaction of nickel(II) complexes of ligands II, III, and IV with nitric acid.

Busch [2, 3] has reported the oxidative dehydrogenation of fourteen-membered macrocyclic iron(II) complexes with molecular oxygen, and has shown that this dehydrogenation occurs in the five-membered chelate rings. Therefore, we employed this ligand dehydrogenation method to establish location of the substituents in the macrocyclic ring.

Tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-dieneiron(II) perchlorates I–IV  $\text{Fe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$  were submitted to oxidation with molecular oxygen in acetonitrile solution. After bubbling air through the solution for three or twenty-four hours, the reaction products were isolated by column chromatography on alumina using acetonitrile as eluent.

We first tried the reaction with complex I  $\text{Fe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$ , in which the 3,10-location of the methyl groups was already known, to check the applicability of the method. The I  $\text{Fe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$  complex gave a typical PMR spectrum (Fig. 1), very similar to that of the I  $\text{Ni}(\text{ClO}_4)_2$  [1], with the imine methyl singlet at 2.36 ppm and the 3,10-methyl's doublet at 1.16 ppm. The methyl doublet is coupled with the multiplet of 3,10-protons at 4.3 ppm. After oxidation for three hours we isolated a compound with a much more complicated PMR spectrum than that of the substrate, presented schematically in Fig. 1; interpreted as the spectrum

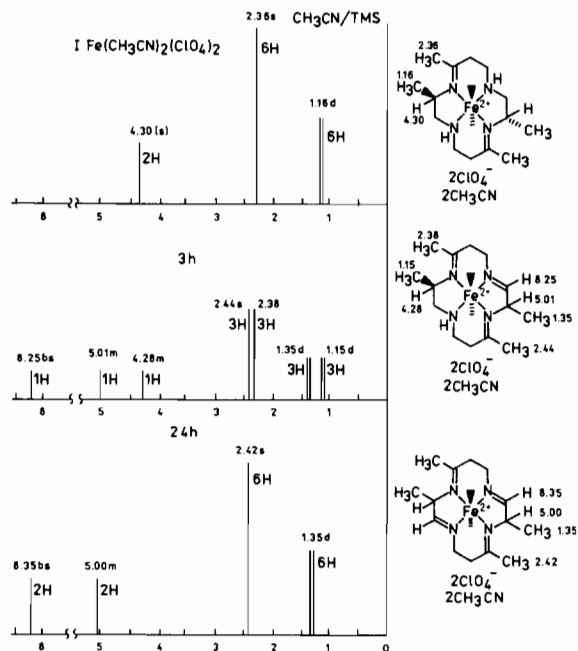


Fig. 1. PMR spectrum of I  $\text{Fe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$  and its dehydrogenation products.

of 3,5,10,12-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,4,11-trieneiron(II) perchlorate [triene-I  $\text{Fe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$ ]. After oxidation for 24 hours we obtained the 1,4,8,11-tetraene complex [tetraene-I  $\text{Fe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$ ] whose PMR spectrum is also interpreted in Fig. 1.

The PMR spectra of the complex II  $\text{Fe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$  and its dehydrogenation products are shown in Fig. 2. A short dehydrogenation gave a triene [triene-II  $\text{Fe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$ ] with no signal at ca. 8 ppm. Three singlet signals were observed in the imine methyl region at 2.44 ppm, 2.36 ppm and 2.31 ppm with relative intensities 3:3:3, and one methyl doublet at 1.39 ppm with relative intensity 3. For the tetraene [tetraene II  $\text{Fe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$ ] only two singlet signals of relative intensity 6:6 were observed in the imine methyl region at 2.44 ppm and 2.31 ppm. This means that, since the new double

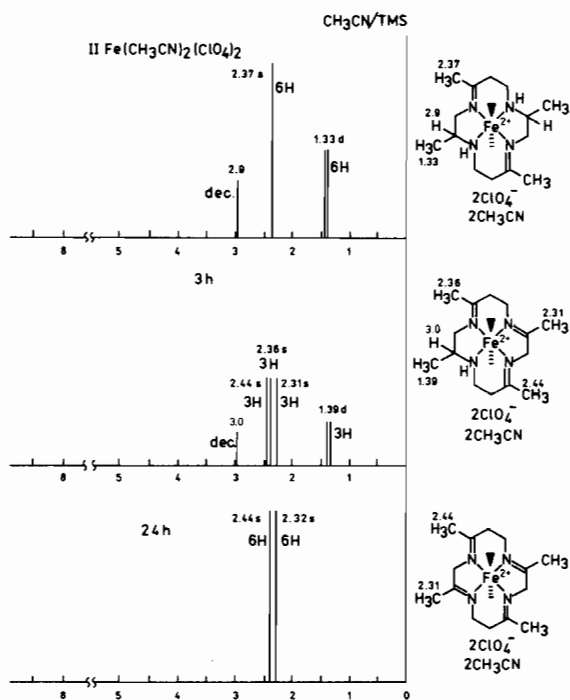


Fig. 2. PMR spectra of  $\text{IFe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$  and its dehydrogenation products.

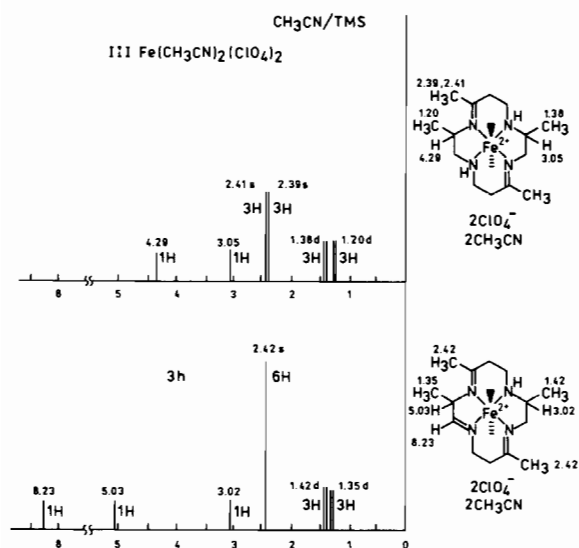


Fig. 3. PMR spectrum of  $\text{IIIFe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$  and its dehydrogenation products.

bonds are formed between ring atoms 1–2 and 8–9, the methyl groups in ligand II must occupy positions 2 and 9.

The iron(II) complex of diene III [ $\text{IIIFe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$ ] has a more complicated PMR spectrum which is a superimposition of the spectra of complexes  $\text{IFe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$  and  $\text{IIFe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$ .

$\text{CN})_2(\text{ClO}_4)_2$ . A short dehydrogenation led to triene [ $\text{triene-III}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$ ] with a vinyl proton signal in the PMR spectrum at 8.23 ppm (Fig. 3). This indicated that the unsubstituted carbon atom 9, as in ligand I, was more susceptible to dehydrogenation than methyl substituted carbon atom 2, as in ligand II. The tetraene iron(II) complex from ligand III was not isolated, because the compound decomposed after a long dehydrogenation. These results show the nonsymmetrical 2,10-location of methyl substituents in the ligand III.

Dehydrogenation of diene  $\text{IVFe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$  was only done to the triene step. Since one chiral center was destroyed by oxidation we isolated a triene identical with one obtained from the  $\text{IIFe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$  complex. This is unequivocal evidence that ligand IV contains methyl groups in the 2,9-positions, as in ligand II.

### Infrared Spectra

The characteristic infrared absorption bands for the iron(II) complexes are collected in Table I. In the spectra of all of the diene complexes we observed an N–H stretching absorption band at *ca.* 3260  $\text{cm}^{-1}$  and an intensive imine C=N stretching absorption band in the 1645–1665  $\text{cm}^{-1}$  region. The N–H absorption band became weaker in the spectra of the triene complexes and disappeared for the tetraenes. A second imine C=N stretching absorption band appeared in the spectra of the dehydrogenated complexes.

TABLE I. Characteristic Infrared Absorption Bands of Iron(II) Complexes (Nujol mulls,  $\text{cm}^{-1}$ ).

Compound	$\nu_{\text{N-H}}$	$\nu_{\text{C=N}}$	$\nu_{\text{ClO}_4^-}$
$\text{IFe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$	3270	1645	1090
$\text{IIFe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$	3260	1665	1100
$\text{IIIFe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$	3260	1650	1100
$\text{IVFe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$	3260	1665	1100
triene- $\text{IFe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$	3280	1670	1100
triene- $\text{IIFe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$	3260	1680	1100
triene- $\text{IIIFe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$	3250	1650	1100
tetraene- $\text{IFe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$	—	1670	1100
tetraene- $\text{IIFe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$	—	1660	1100
tetraene- $\text{IIIFe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$	—	1675	1090
tetraene- $\text{IVFe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$	—	1650	1090

### Ultraviolet and Visible Spectra

The electronic spectra of all of the iron(II) complexes (Table II) are very similar to those described

TABLE II. Electronic Spectra of Iron(II) Complexes (Acetonitrile,  $\lambda_{\max}$  in nm).

Compound	Charge Transfer		d-d
	$\lambda_{\max}$ (e)	$\lambda_{\max}$ (e)	$\lambda_{\max}$ (e)
I $\text{Fe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$	257(11350)	339(4550)	529(105)
II $\text{Fe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$	254(13050)	338(5350)	520(84)
III $\text{Fe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$	256(13200)	338(5300)	526(81)
IV $\text{Fe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$	252(10400)	331(4200)	521(140)
triene-I $\text{Fe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$	250(10200)	342(5150)	507(82)
triene-II $\text{Fe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$	250(11400)	342(6350)	521(107)
triene-III $\text{Fe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$	251(11550)	343(6400)	513(109)
tetraene-I $\text{Fe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$	245(10400)	352(7150)	485(79)
tetraene-II $\text{Fe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$	248(11000)	349(7600)	510(111)

TABLE III. Proton Magnetic Resonance Data of Iron(II) Complexes in  $\text{CD}_3\text{CN}$  Solution ( $\delta$  in ppm downfield from internal TMS, 100 MHz).

Compound	Imine- $\text{CH}_3^a$	$\begin{array}{c} \text{CH}_3^a \\ \diagup \\ \text{C} \\ \diagdown \\ \text{H} \end{array}$	$\begin{array}{c} \text{CH}_3^{a,b} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{H} \end{array}$	$\text{N}=\text{C}-\text{H}^a$
I $\text{Fe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$	2.36s (6)	1.16d J = 7.0 (6)	4.30 (2)	—
II $\text{Fe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$	2.37s (6)	1.33d J = 4.5 (6)	2.9	—
III $\text{Fe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$	2.41s (3)	1.38d J = 4.5 (3)	3.05 (1)	—
	2.39s (3)	1.20d J = 7.0 (3)	4.29 (1)	—
IV $\text{Fe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$	2.35s (6)	1.35d J = 4.5 (6)	2.8	—
triene-I $\text{Fe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$	2.44s (3)	1.35d J = 7.0 (3)	5.01 (1)	8.25 (1)
	2.38s (3)	1.15d J = 7.0 (3)	4.28 (1)	—
triene-II $\text{Fe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$	2.44s (3)	1.39d J = 5.7 (3)	3.0	—
	2.36s (3)	—	—	—
	2.31s (3)	—	—	—
triene-III $\text{Fe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$	2.42s (6)	1.42d J = 5.5 (3)	3.02 (1)	—
tetraene-I $\text{Fe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$	2.42s (6)	1.35d J = 7.0 (3)	5.03 (1)	8.23 (1)
	—	1.35d J = 5.5 (6)	5.00 (2)	8.35 (2)
tetraene-II $\text{Fe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$	2.44s (6)	—	—	—
	2.31s (6)	—	—	—

<sup>a</sup>Relative intensities in parentheses, J in Hz, s-singlet, d-doublet. The metal to ligand  $d-\pi$  charge-transfer transitions were observed at about 340 nm and the molar extinction coefficient for these bands increased with the number of C=N double bonds in the molecule. Another charge-transfer absorption band was observed in the region 245–257 nm.

<sup>b</sup>Coupling of these protons with methyl groups was confirmed by double resonance experiments.

by Busch [2, 4] for the six-coordinate low-spin  $[\text{Fe}(\text{[14]dieneN}_4)(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$  complexes and their triene and tetraene dehydrogenation products.

The single observable  $d-d$  absorption band occurs in the 485–529 nm region with  $\epsilon_{\max}$  of about 100. The metal to ligand  $d-\pi$  charge-transfer transitions were observed at about 340 nm and the molar extinction coefficient for these bands increased with the number of C=N double bonds in the molecule. Another charge-transfer absorption band was observed in the region 245–257 nm.

### Proton Magnetic Resonance Spectra

The results of PMR measurements are given in Table III. The signals of the ring protons are very complicated and difficult to interpret. The spectra simplify progressively as the degree of unsaturation increases. The introduction of each double bond removes an asymmetric center on nitrogen and consequently reduces the number of possible chelate ring conformations. This feature was discussed and used to establish the substituent locations in the macrocyclic ring.

The most prominent PMR signals were those of the methyl substituents. The chemical shifts of the ring protons coupled to the methyl groups were determined by double resonance experiments.

Buckingham and Stevens [5, 6] have predicted large shielding effects for the axial protons situated above the plane of  $d^6$  low-spin complexes and deshielding effects for the protons located above the plane in low-spin  $d^8$  metal ion systems. This deshielding effect was observed for the axially oriented methyl groups and protons on various nickel(II) macrocyclic complexes [1, 7, 8]. We used this shielding effect together with symmetry properties to determine the ligand conformation in the iron(II) complexes.

The imine methyl groups were observed in the PMR spectra of every iron(II) complex as a singlet at 2.35–2.44 ppm. The methyl doublet resonances in the spectra of the diene iron(II) complexes occur at two distinct positions, 1.16–1.20 ppm for 3 and 10-methyl groups, and 1.33–1.38 ppm for 2 and 9-methyl groups. The coupled protons also absorb in narrow ranges of chemical shifts at 4.3 and 2.8–3.0 ppm respectively. The very large chemical shift (4.3 ppm) of the protons in positions 3 and 10 indicates that these protons occupy equatorial positions, where they are strongly deshielded by the C=N double bond. Similar chemical shifts were observed for equatorial protons in these positions in the spectra of nickel(II) complexes [1]. An axial proton in these positions should be shifted upfield by the joint action of the C=N double bond and the iron(II) ion shielding effects. This is observed for 3 and 10-methyl groups in the spectrum of the  $\text{IFe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$  complex (1.16 ppm) and for the 10-methyl group of  $\text{IIIFe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$  complex (1.20 ppm). Therefore, we assign the conformation of these methyl groups as an axial.

The small chemical shifts of the 2,9-protons in the spectra of complexes  $\text{IIFe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$  (2.9 ppm) and  $\text{IVFe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$  (2.8 ppm), and that of the 2-proton in the complex  $\text{IIIFe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$  (3.0 ppm) are explained by their axial positions where they are shielded by the iron(II) ion. All these protons are shielded in comparison to axial protons in the nickel(II) complexes (3.3–3.6 ppm) [1]. Thus, the 2 and 9-methyl groups occupy an equatorial position in the iron(II) complexes of ligands II, III and IV.

The knowledge of the relative configurations of the asymmetric carbon atoms in macrocyclic ligands [1] and the location of substituents enables the assignment of the structures of isolated iron(II) complexes as follows (Fig. 4):

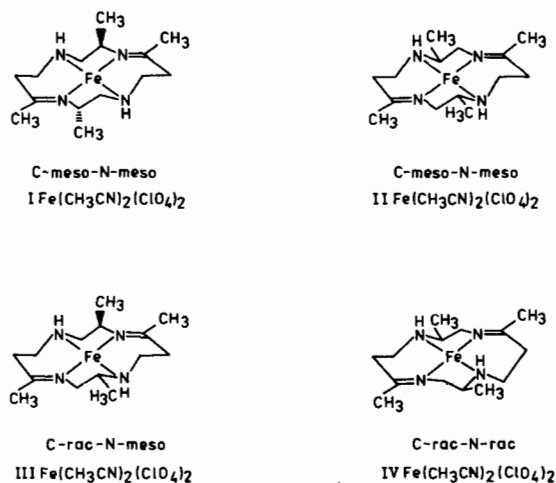
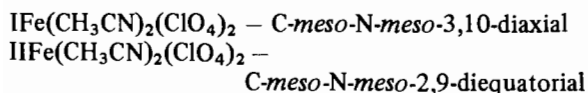
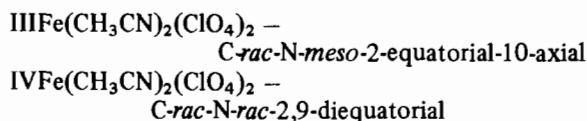


Fig. 4. Assignment of the structures of Fe(II) complexes.



Axially coordinated acetonitrile molecules destabilize those conformations of the isomers which contain axial methyl groups by nonbonding repulsions, which explains why such isomers of 2,9-substituted ligands II, IV and the 2-axial isomer of complex  $\text{IIIFe}(\text{CH}_3\text{CN})_2(\text{ClO}_4)_2$  were not isolated. For 3- and 10-methyl substituted ligands the interaction of an equatorial methyl with the imine methyl group seems to be substantial, since such isomers were not observed.

### Experimental\*

#### Materials

Triethyl orthoformate was commercial grade material and was used without further purification. Acetonitrile was distilled under nitrogen after being dried over  $\text{P}_4\text{O}_{10}$ . Iron(II) perchlorate hexahydrate was prepared from elemental iron (powder, 'reduced by hydrogen' grade) and 5% perchloric acid, crystallised from water and dried *in vacuo* over  $\text{H}_2\text{SO}_4$ . Neutral alumina (Woelm) activity grade I was used for column chromatography.

#### Ligands

Tetramethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-dienes I–IV were prepared from their nickel(II) complexes by the previously described procedure [1].

\*CAUTION! Complex perchlorates described in this paper are very sensitive explosive materials.

TABLE IV. Elemental Analysis of Iron(II) Complexes.

Compound	Colour	Required, %			Found, %		
		C	H	N	C	H	N
IFe(CH <sub>3</sub> CN) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	pale violet	36.7	5.8	14.3	36.2	5.9	14.2
IIFe(CH <sub>3</sub> CN) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	pink				36.4	5.9	14.0
IIIFe(CH <sub>3</sub> CN) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	pink				36.2	5.6	14.0
IVFe(CH <sub>3</sub> CN) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	pink				36.7	5.8	14.9
triene-IFe(CH <sub>3</sub> CN) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	red	36.8	5.5	14.3	37.6	6.1	14.6
triene-IIFe(CH <sub>3</sub> CN) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	pink				36.8	5.5	14.4
triene-IIIFe(CH <sub>3</sub> CN) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	pink				36.5	5.4	14.1
tetraene-IFe(CH <sub>3</sub> CN) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	pink orange	36.9	5.2	14.4	36.4	5.3	14.1
tetraene-IIFe(CH <sub>3</sub> CN) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	pink				36.9	5.0	14.4

*Tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dieneiron(II) diperchlorates* [I–IVFe(CH<sub>3</sub>CN)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>]. CAUTION! Explosive substances.

A solution of iron(II) perchlorate hexahydrate (4.8 g, 0.013 mol) in a 1:1 mixture of acetonitrile and triethyl orthoformate (30 ml) was heated at 50 °C under nitrogen for 10 hours. An appropriate ligand (I–VI, 2.5 g, 0.01 mol) solution in acetonitrile (5 ml) was then added dropwise to the reaction mixture. The solution turned a deep red colour and a pink precipitate was formed. After 1 hour the precipitate was filtered off under nitrogen, washed with acetonitrile and dried *in vacuo*. Yield ca. 60%.

*Tetramethyl-1,4,8,11-tetra-azacyclotetradeca-1,4,11-trieneiron(II) diperchlorates* [triene-I–IIIFe(CH<sub>3</sub>CN)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>]

A reaction mixture prepared by the method described above was diluted with acetonitrile (50 ml) and dry air was bubbled through the stirred solution. Oxygenation was prolonged for three hours and the volume of the solution was then reduced under vacuum to about 30 ml, loaded onto a column packed with alumina (1.5 cm X 40 cm) and eluted with acetonitrile. The volume of eluate was reduced under vacuum and the precipitated product was filtered off, recrystallised from acetonitrile and dried *in vacuo*. For the oxidation of complexes IFe(CH<sub>3</sub>CN)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> and IIFe(CH<sub>3</sub>CN)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>, small amounts of tetraenes were separated as the first fraction from the chromatography. Yields were not reproducible 10–50%.

*Tetramethyl-1,4,8,11-tetra-azacyclotetradeca-1,4,8,11-tetraeneiron(II) diperchlorates* [I and IIFe(CH<sub>3</sub>CN)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>]

The reaction mixture, prepared as in the preceding procedure, was dehydrogenated by dry air for 24 hours. The products were isolated by chromatography on alumina with acetonitrile as eluent, recryst-

allised from acetonitrile and dried *in vacuo*. Yields varied from 10 to 50%.

Results of elemental analyses of all iron(II) complexes are given in Table IV.

#### Measurements

Infrared spectra were recorded as nujol mulls on a Unicam SP-200 spectrometer. Electronic spectra were measured on Unicam SP-500 spectrometer. PMR spectra were obtained on a JEOL INM 4H-100 spectrometer with TMS as internal standard.

#### Acknowledgements

The authors thank Mrs. Z. Celler, M.Sc., and the staff of the Analytical Department of the Institute for the elemental analysis of the unstable iron(II) complexes, A. Jankowski, Eng., M. Chada, A. Ilciewicz, and A. Sokół, of the Spectroscopic Department of the Institute for the assistance in the measurements of spectra of unstable iron(II) complexes, and K. Tomaszewska for technical assistance.

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