A New Family of Clathrochelate Complexes Produced by a Ligand Rearrangement Reaction

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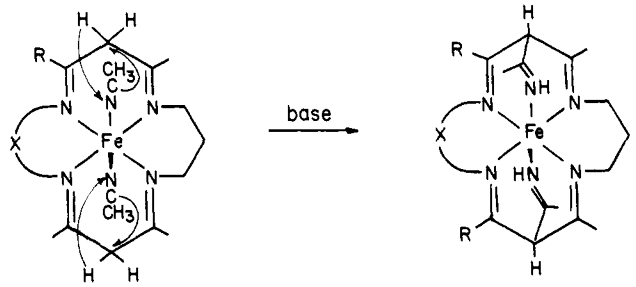
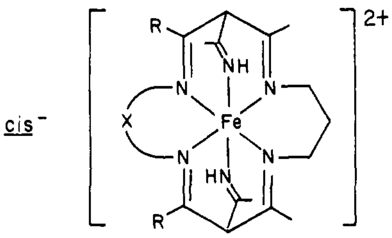
Abstract: Iron(II) complexes of a quadridentate 16-membered macrocycle having four imine donors have been shown to rearrange so that peripherally located secondary amine groups that were initially *not* coordinated become coordinated as imine groups. The novel hexa- or pentadentate ligands generated in this rearrangement enclose the low-spin iron(II) cation in a shell of imine donors. The internal rearrangement of the ligand involves the transfer of an amine proton to the γ-carbon of the parent macrocycle and is base promoted. The cis hexaene complexes are air-stable whereas the proposed trans pentadentate ligand complexes remain oxygen sensitive, like the parent compounds. A three-dimensional X-ray crystallographic structure determination has confirmed the nature of one of the hexaene complexes, *cis*-[(2,10,12,18-tetramethyl-3,9,13,17,20,24-hexaazabicyclo[9.7.7]-pentacosa-2,9,12,17,19,24-hexaene-N_6)iron(II)] hexafluorophosphate–0.5-methanol, which crystallizes in the monoclinic space group $P2_1/c$, $a = 11.058$ (2) Å, $b = 18.693$ (3) Å, $c = 15.044$ (3) Å, $\beta = 90.56$ (2)°, and the structure was solved by the heavy atom method to $R = 8.5\%$, $R_w = 2.9\%$ for 5471 reflections. The six imine groups form a slightly distorted octahedron with a trigonal twist of 5° and Fe–N distances in the range 1.93–1.99 Å. The original macrocycle has become folded into a cis configuration, and the rearranged ligand encapsulates the metal atom inside a novel clathrochelate structure.

The synthesis of coordination complexes containing a metal ion totally encapsulated by an organic ligand has given rise to the class of compounds known as the clathrochelates;[1] to date, these complexes have been produced by one of two routes. By adding alkali metal ions to the ether donor cryptands and cryptates of Lehn et al.,[2] a nonrigid clathrated metal can be produced directly.[1] These complexes are exceptional, however, in that the extreme flexibility of the ligands and high lability of the metal ions permit such a direct synthesis. Transition-metal clathrochelate complexes, on the other hand, have been synthesized exclusively by variations of a procedure which involves initial coordination of constituent ligands to the metal ion followed by an organic reaction of the still-coordinated ligands in a template synthesis of the encapsulating clathrochelate ligand. Once formed, such clathrochelates cannot be easily displaced from the metal ion and cannot be used in direct syntheses of other metal ion complexes. Such is the case with the complexes of Rose,[3] Holm,[4] Sargeson,[5] and Goedken.[6] In the present study we wish to report a third alternative (and possibly reversible) synthesis of a clathrochelate complex via the internal rearrangement of a quadridentate macrocycle with appropriate superstructure. The quadridentate ligand may be synthesized and transferred from metal to metal intact. In the case of Fe^{II} and under appropriate pH conditions, this ligand can be induced to rearrange such that the potential donor groups of the superstructure of the starting complex become coordinated, thereby completing the clathro structure, as the ligand becomes hexadentate. Preliminary studies indicate that this rearrangement may be reversed under certain conditions, e.g., addition of CO. Such a system has attractive possibilities that are reminiscent of proenzyme behavior. It may be useful to take advantage of the relative inertness of the clathrochelate structure in order to preserve an otherwise unstable or highly reactive state. The reverse rearrangement can then provide the reactive species when desired. In the present case, the coordinate saturation of the iron(II) complex and the highly positive value of its Fe^{2+}/Fe^{3+} electrode potential preserve the iron(II) in an essentially unreactive state. Reverse rearrangement, back to the quadridentate complex, produces a coordinatively unsaturated species having a corresponding electrode potential some 0.8 V more negative. This complex readily reacts with such biologically important small molecules as carbon monoxide, dioxygen, and hydrogen peroxide.

Scheme I



We have previously reported the synthesis and structural characterization of several novel low-spin iron(II) complexes of hexa- and pentaene ligands[7-9] (structure I) which were the result



Ia, X = $(CH_2)_2$, R = H
Ib, X = $(CH_2C(CH_3)_2)$, R = H
Ic, X = $(C(CH_3)_2)_2$, R = H
Id, X = $(CH_2)_3$, R = H
Ie, X = $(CH_2)_3$, R = CH_3

of an adventitious reaction between a certain coordinated unsaturated quadridentate macrocycle and coordinated acetonitrile

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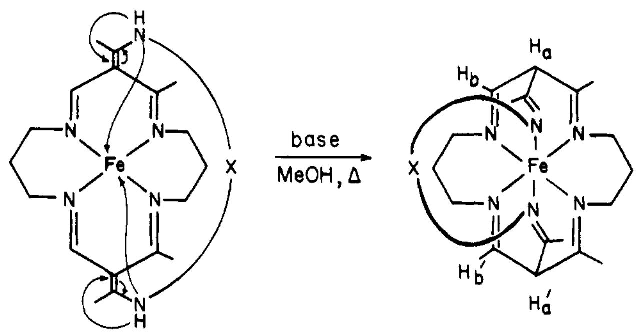
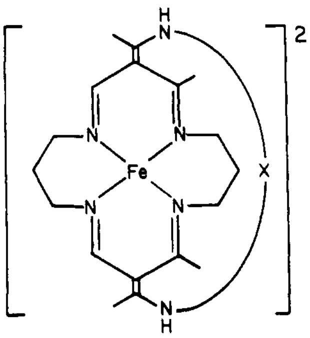
Scheme II



moieties within the same iron(II) complex (Scheme I). This reaction was found to proceed only in the cases of the 15- and 16-membered macrocycles, the 14-membered ring yielding instead a simple trans diacetonitrile complex.[7,9] A crystal structure[8] of the 16-membered ring complex showed that the acetonitrile molecules had added to the apical (γ) carbons of the unsaturated six-membered chelate ring of the parent macrocycle, producing the cis complex of a novel hexadentate ligand (Ic). Several other analogous cis structures were also reported[9] (I). In one instance the 16-membered ring complex could be manipulated to yield the trans isomer of structure Ic, while under identical conditions the 15-membered ring complex gave rise to a trans acetonitrile–pentaene derivative.[9] In the latter case only one of the two coordinated acetonitrile molecules had become attached to the macrocycle, giving an unusual pentadentate ligand.

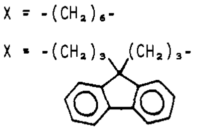
In all cases the novel ligands were presumed to arise from the electrophilic attack of a coordinated acetonitrile at the γ-carbon of the coordinated and partially ionized macrocyclic ligand. Deuteration experiments tend to support such a mechanism, and this type of scheme has precedent[10,11] in a few metal ion promoted nucleophilic additions. The complexes themselves are remarkable, not only because of their ease of formation and unusual ligand geometry but also because they represent the first examples of low-spin iron(II) coordinated exclusively to six nonconjugated imine donor groups. This new area of iron chemistry stimulated further research and led us to investigate other possible routes to such hexaene and pentaene complexes.

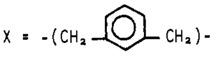


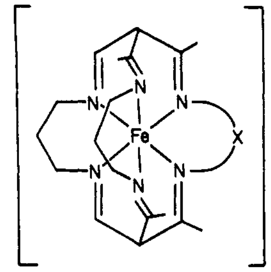
IIa, X = $-(CH_3)_2$

IIb, X = $-(CH_2)_5-$

IIc, X = $-(CH_2)_6-$

IId, X =

$-(CH_2)_3-C_{13}H_8-(CH_2)_3-$

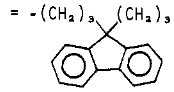
IIe, X =

$-(CH_2-C_6H_4-CH_2)-$



IIIa, X = $-(CH_3)_2$

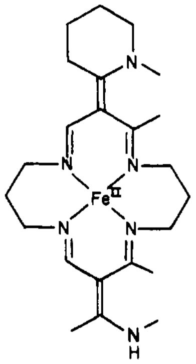
IIIb, X = $-(CH_2)_5-$

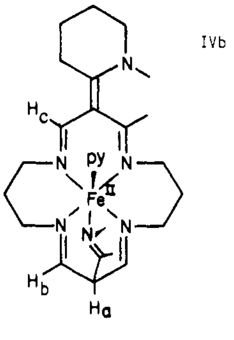
IIIc, X = $-(CH_2)_6-$

IIId, X =

$-(CH_2)_3-C_{13}H_8-(CH_2)_3-$

This report is concerned with the internal rearrangement of iron(II) complexes of an unsaturated macrocycle having a series of peripherally appended secondary amine groups (II). All of these complexes are derived from the basic Jäger type macrocycle[12] which may be synthesized and, if desired, bridged to form a bicyclo complex while coordinated to a nickel(II) template ion, as previously described.[13] The ligands themselves may then be removed from nickel(II)[13] and coordinated to iron(II), yielding complexes of the type shown in structure II.[14] Treatment of these complexes with strong base in hot methanol under an inert atmosphere leads to a tautomeric rearrangement of the conjugated π systems of the macrocycle involving transfer of the amine proton to the γ-carbon and coordination of either one or two of the resultant imine groups (Scheme II). Complexes IIa–d will all rearrange to give low-spin hexadentate ligand complexes (structure III), and the generality of the cis structure of the resultant complexes is shown by X-ray analysis of IIIb and the similarity of their spectral properties to those of the previously known members of the series (I). In addition, steric considerations indicate that structures IIc–e can only rearrange to give cis coordination of the new donor groups in the clathrochelated product (III), in which the parent macrocycle is folded.

Under controlled conditions, complexes IIa and IIe will rearrange to give diamagnetic pentadentate ligand complexes, in which the parent ligand remains planar. Another example of this type of structure is provided by the rearrangement of the unsymmetrical complex IVa. This complex is postulated to have the structure IVb with a trans pentadentate ligand, while pyridine completes the coordination sphere.


IVa



IVb

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Table I. Analytical Data for the New Complexes

complex	% calcd				% found			
	C	H	N	M	C	H	N	M
IIIa	34.10	4.87	11.93		33.78	4.91	11.72	
IIIb	37.11	5.14	11.29		37.02	5.25	11.18	
IIIc	38.01	5.32	11.08		38.06	5.30	11.14	
IIId	48.17	5.24	9.11		48.21	5.64	9.60	
IVb	40.84	5.26	11.91	6.78	40.70	5.33	11.87	6.67 (Fe)
Va	34.33	4.68	11.48		33.78	4.48	11.35	
Vb	46.69	5.43	12.56		46.39	5.90	12.48	

Spectral parameters for all these complexes have been correlated and compared with those of the previously reported acetonitrile adducts[7-9] and clathrochelate complexes.[3-6]

Experimental Section

Materials. All metal salts, solvents, and organic reagents were reagent grade. Acetonitrile and diethyl ether were dried and distilled over calcium hydride under nitrogen. Ethanol and methanol were distilled from magnesium turnings under nitrogen. Pyridine was stored over KOH and distilled before use. All syntheses of iron complexes were carried out under nitrogen in a Vacuum Atmospheres controlled atmosphere chamber.

Physical Measurements. NMR spectra were recorded on Varian EM360L and Bruker WP80 spectrometers for ^{1}H (60 MHz) and ^{13}C (20.115 MHz), respectively. The solvent used was CD_3CN, and in all cases, shift measurements were made relative to tetramethylsilane, δ 0. Air-sensitive samples were prepared in a glovebox and run immediately upon their removal from the inert atmosphere. The diamagnetism of complexes was checked by magnetic susceptibility measurements using the Evans method in CD_3CN with an acetone reference.

Visible and ultraviolet spectra were obtained with a Cary Model 17D recording spectrophotometer while infrared spectra were recorded as Nujol mulls between KBr disks with a Perkin-Elmer Model 283B recording spectrophotometer. Air-sensitive samples were prepared in an inert atmosphere and run immediately upon removal from the glovebox. Electrochemistry was performed by use of a Princeton Applied Research Corp. Potentiostat/Galvanostat Model 173 equipped with a Model 175 linear programmer and a Model 179 digital Coulometer. Current vs. potential curves were measured on a Houston Instruments Model 2000 XY recorder. All measurements were performed in a Vacuum Atmospheres glovebox under an atmosphere of dry nitrogen. The working electrode for voltametric curves was a platinum disk, with potentials measured vs. a Ag^0/Ag^+ (0.1 M) reference. The working electrode was spun at 600 rpm by a synchronous motor for the rotating platinum electrode (RPE) voltamograms, and peak potentials were measured from cyclic voltamograms at a 50 mV/s scan rate. Half-wave potentials ($E_{1/2}$) were taken as the potential at one-half the height of the RPE voltamogram. The value $E_{3/4-1/4}$ also obtained from the RPE voltamogram was used as a measure of the reversibility of the couple ($E_{3/4-1/4}$ for a reversible one electron couple is 60 mV). Elemental analyses were performed by Galbraith, Inc., Knoxville, TN.

Syntheses. The syntheses of the bridged ligands in II as their nickel complexes have been described previously,[13] as has their removal from nickel(II) and transferal to iron(II).[14] Elemental analyses for new compounds are given in Table I.

***cis*-[(3,11-bis(1-(methylimino)ethyl)-2,12-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,3,9,11-tetraene-N_6)iron(II)] Hexafluorophosphate, [Fe[(Me-iminoethyl)$_2$[16]tetraene-N_6]](PF$_6$)$_2$, (IIIa).** Bis(acetonitrile)iron(II) chloride (0.33 g, 0.0016 mol) and triethylamine (0.94 g, 0.0093 mol) were added to a slurry of 1.2 g (0.0015 mol) of the ligand salt H_4[(HMeNEthi)$_2$[16]tetraene-N_4]$(ZnCl_4)_2$[13] in 20 mL of methanol. The solution was refluxed for 45 min during which a red precipitate formed. Methanol was added to a total volume of 50 mL and the solution filtered until clear. Ammonium hexafluorophosphate (2.0 g, 0.0123 mol) in methanol was added dropwise to the warm solution, which on standing overnight precipitated a red-orange crystalline material. This was collected, washed (methanol, diethyl ether), and dried in vacuo; yield, 0.75 g (69%).

***cis*-[(2,10,12,18-Tetramethyl-3,9,13,17,20,24-hexaazabicyclo[9.7.7]pentacosa-2,9,12,17,19,24-hexaene-N_6)iron(II)] Hexafluorophosphate, [Fe[(CH$_2$)$_5$(iminoethyl)$_2$[16]tetraene-N_6]](PF$_6$)$_2$ (IIIb).** A solution containing 0.35 g (0.00055 mol) of IIb·ClPF$_6$[14] and 0.35 g (0.0044 mol) of pyridine in 50 mL of methanol was heated to reflux for 1 h. After cooling and standing for 3 days the solution had changed color from orange to red, and addition of excess tetra-*n*-butylammonium hexafluorophosphate in methanol precipitated the red crystalline product. The material was filtered, washed (methanol, diethyl ether), and dried in vacuo; yield, 0.29 g (71%).

***cis*-[(2,11,13,19-Tetramethyl-3,10,14,18,21,25-hexaazabicyclo[10.7.7]hexacosa-2,10,13,18,20,25-hexaene-N_6)iron(II)] Hexafluorophosphate, [Fe[(CH$_2$)$_6$(iminoethyl)$_2$[16]tetraene-N_6]](PF$_6$)$_2$ (IIIc). *cis*-[(2,12,21,27-Tetramethyl-3,11,15,19,22,26-hexaazapentacyclo[11.7.7.4^{7,7}.4^{28,29}.4^{30,31}]nonatriaconta-2,11,14,19,21,26,28,30,32,34,36,38-dodecaene-N_6)iron(II)] Hexafluorophosphate, [Fe[(C$_7$Fl)(iminoethyl)$_2$[16]tetraene-N_6]](PF$_6$)$_2$ (IIId).** Complexes IIIc and IIId were synthesized by using conditions similar to those described for IIIb except 1-methylimidazole was substituted for pyridine as the base catalyst. Yields based on IIc·Cl,PF$_6$[14] and IId·Cl,PF$_6$[14] were 54% and 68%, respectively.

***trans*-[Pyridine(3-(1-(methylimino)ethyl)-11-(1-methylpiperidin-2-ylidene)-2,12-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene-N_5)iron(II)] Hexafluorophosphate, [Fe[(MeNiminoethyl)(MeNPip)[16]tetraene-N$_5$]py](PF$_6$)$_2$ (IVb).** The ligand salt H_4[HMeNEthi)(MeNPip)[16]tetraene-N_4]$(ZnCl_4)_2$ (0.82 g, 0.001 mol) and bis(pyridine)iron(II) chloride (0.28 g, 0.0008 mol) were slurried in 20 mL of methanol while triethylamine (0.5 g, 0.0045 mol) was slowly dripped in. The resultant deep red-orange solution was heated to reflux for ~10 min after which methanol, saturated with ammonium hexafluorophosphate, was dripped into the solution. Red-violet microcrystals were precipitated, collected, and recrystallized from acetone/ethanol containing 1% pyridine to yield 0.66 g (80%).

***trans*-[(Carbonyl)(1-(methylamino)-3-ethylidene)-11-(1-(methylimino)ethyl)-2,12-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,3,9,11-tetraene-N_5)iron(II)] Hexafluorophosphate, [Fe[(HMeNEthi)(MeNiminoethyl)[16]tetraene-N_5]CO](PF$_6$)$_2$ (Va).** IIa[14] (0.3 g, 0.0004 mol) was dissolved in 3 mL of acetonitrile and to this was added 0.3 g of either pyridine or 1-methylimidazole, and 50 mL of ethanol. After exposure to 1 atm of CO gas, a very slow color change from red to orange was noted, and on standing overnight, addition of excess ammonium hexafluorophosphate gave a red-orange precipitate. This material was collected and dried in vacuo; yield, 0.14 g (47%).

***trans*-[Chloro-(2,12,14,20-tetramethyl-3,11,15,19,22,26-hexaazatricyclo[11.7.7.1^{5,9}]octacosa-2,5,7,9(28),12,14,19,21,26-nonaene-N_5)iron(II)] Hexafluorophosphate, [Fe[(*m*-xylyl)(HNEthi)(iminoethyl)[16]tetraene-N_5]Cl](PF$_6$) (Vb).** The ligand salt H_4[(*m*-xylyl)(HNEthi)$_2$[16]tetraene-N_4]$(PF_6)_3Cl$[13] (1.0 g, 0.0011 mol) was dissolved in 20 mL of acetonitrile, and 0.67 g (0.0011 mol) of hexakis(acetonitrileiron(II)) hexafluorophosphate and 0.35 g (0.0034 mol) of triethylamine were added. The solution was refluxed for 10 min and filtered. The volume was reduced to 10 mL and 20 mL of methanol was added to produce an orange-red crystalline precipitate on standing overnight; yield, 0.4 g (47%).

Crystal Data. Red rhombic crystals of the complex [Fe[(CH$_2$)$_5$(iminoethyl)$_2$[16]tetraene-N_6]](PF$_6$)$_2$·0.5CH$_3$OH, IIIb, suitable for X-ray diffraction were prepared by slow precipitation from a methanol solution. A crystal was ground to a sphere of diameter 0.64 mm and examined with a Syntex $P\bar{1}$ four-circle automated diffractometer. The unit cell dimensions and their esds were obtained from a least-squares fit to 15 high-angle reflections ($2\theta > 20°$) by use of Mo Kα graphite monochromatized radiation (λ = 0.71069 Å) at −70 °C. Systematic absences, $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, indicate the space group $P2_1/c$. The crystal data obtained were as follows: $FeP_2F_{12}N_6C_{23}H_{38}$ M_r 760.3, monoclinic space group $P2_1/c$, a = 11.058 (2) Å, b = 18.693 (3) Å, c = 15.044 (3) Å, β = 90.56 (2)°, V = 3109.8 Å^3, T = 203K, d_M(benzene/bromoform) = 1.60 g cm^{-3}, d_X = 1.63 g cm^{-3}, Z = 4, μ(Mo Kα) = 7.14 cm^{-1}. $F(000)$ = 1564. Intensity data were collected by the ω–2θ scan technique with variable scan rate between 2.0 and 16.0°/min; three check reflections were monitored every 80 reflections throughout the set and displayed no decay of intensity. A total of 5471 independent reflections with $2\theta < 50°$ were collected and used in structure determination. Lorentz and polarization corrections were applied, but no correction for absorption or extinction was used because of the crystal size and low absorption coefficient (μ_r = 0.22).

Solution and Refinement of the Crystal Structure. The structure was solved by the heavy atom method and refined by the full-matrix least-squares method. In the least-squares procedure, the function minimized was $\sum w|F_0^2 - F_c^2|^2$, where $w = 1/\alpha^2(F_0^2)$. The atomic scattering factors were taken from "International Tables for X-ray Crystallography", Vol. IV, for H, C_{cov}, N, O, F, P, and Fe.[15] Anomalous dispersion correction was applied to Fe. All the calculations were carried out on a IBM 3170/165 computer in the Computer Center of The Ohio State University with CRYM crystallographic computing system.[16]

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(15) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

The coordinates of the iron atom were obtained from a three-dimensional Patterson synthesis. Successive Fourier and difference Fourier syntheses revealed all the nonhydrogen atoms except for the methanol of crystallization. Refinement with isotropic thermal parameters was carried out and the discrepancy indices $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = \sum w^2(|F_o|^2 - |F_c|^2)^2/\sum w^2|F_c|^4$ were 17.5 and 11.2%, respectively. A full-matrix least-squares refinement with anisotropic thermal parameters yielded $R_1 = 12.1$ and $R_w = 7.4\%$, respectively. At this stage, a difference Fourier synthesis was calculated and revealed the missing disordered methanol and all the hydrogen atoms. An occupancy factor of 0.5 was adopted for the methanol, considering the peak height and the adjustment of the elemental analysis.

Further refinement including these atoms yielded the final values of 8.5 and 2.9% for R_1 and R_w, respectively. A final difference Fourier synthesis showed no significant features, peaks being $I < 0.45$ e A^{-3} except for several diffuse peaks around the methanol.

Final positional parameters with their estimated standard deviations are given in Table II, a and b. A list of observed and calculated structure factors is listed as supplementary data. Bond lengths and angles are included in Table III, a and b, respectively.

Discussion

The bridged bicyclo-macrocyclic ligand systems used to produce the clathrochelated iron(II) complexes were originally reported and their syntheses detailed as the nickel(II) complexes.[13] Removal of the ligands from nickel(II)[13] and subsequent coordination to iron(II) generally resulted in the production of complexes II as their chlorohexafluorophosphate or bis(hexafluorophosphate) salts.[14] The rearrangement of these latter complexes to the hexadentate and pentadentate complexes is now discussed below.

Syntheses and Characterization of Hexadentate Iron(II) Complexes III. The low-spin hexadentate iron(II) complexes III have been prepared by two related routes, either (a) directly from ligand salt and iron(II) ions or (b) by isolation and then further reaction of the complexes with the quadridentate ligands which are the probable intermediates of reaction a. The simple unrearranged quadridentate iron(II) complexes II have been reported previously,[14] and their rearrangement as indicated in Scheme II is seen to involve proton transfer from the amine functions to the γ-carbons of the unsaturated chelate rings. This transfer, not unexpectedly, appears to proceed most readily in the presence of a base such as triethylamine, 1-methylimidazole, or pyridine and in a hot hydroxylic solvent such as methanol. In reaction a, the presence of excess base in the reaction medium is sufficient to drive the product all the way through the quadridentate complex II to the hexadentate structure III.

The rearrangement process (Scheme II) clearly destroys the conjugation in the unsaturated chelate rings producing six nonconjugated coordinated imine groups. Iron(II) is the only metal ion so far investigated which is capable of promoting such a rearrangement, and it seems that the preference of the metal ion for imine donors provides a considerable driving force for overcoming the stability energy of conjugation. This bias toward imine donors is quite common in iron chemistry and has been the driving force for a number of unusual rearrangement[7-9] and ligand oxidation reactions.[17]

The stereochemistry of all the rearranged octahedral complexes appears to place the two newly formed imine donors exclusively in cis positions (vide infra). Such a geometry requires that the original planar quadridentate macrocycle rearrange between octahedral sites, and naively, this would seem less likely than formation of a trans complex where no reorientation of the macrocycle is required. However, consideration of the "saddle" shape of the parent molecule[13] (imposed by the chair or boat conformations of the saturated chelate rings) and the physical restrictions imposed by the length of the bridges (which are too short to allow spanning of axial sites) indicates that a trans geometry for the new imine groups is impossible.

Infrared spectra of these hexadentate clathrochelate complexes differ dramatically from those of the parent bridged complexes,[14] most notably in the absence of the secondary amine NH stretch (3200–3400 cm^{-1}) and in the marked change in the azomethine (1500–1650 cm^{-1}) region (Table IV). These data compare favorably with those observed for the closely related compounds I,[7] where the azomethine stretches occur exclusively in the narrow range 1605–1640 cm^{-1}.

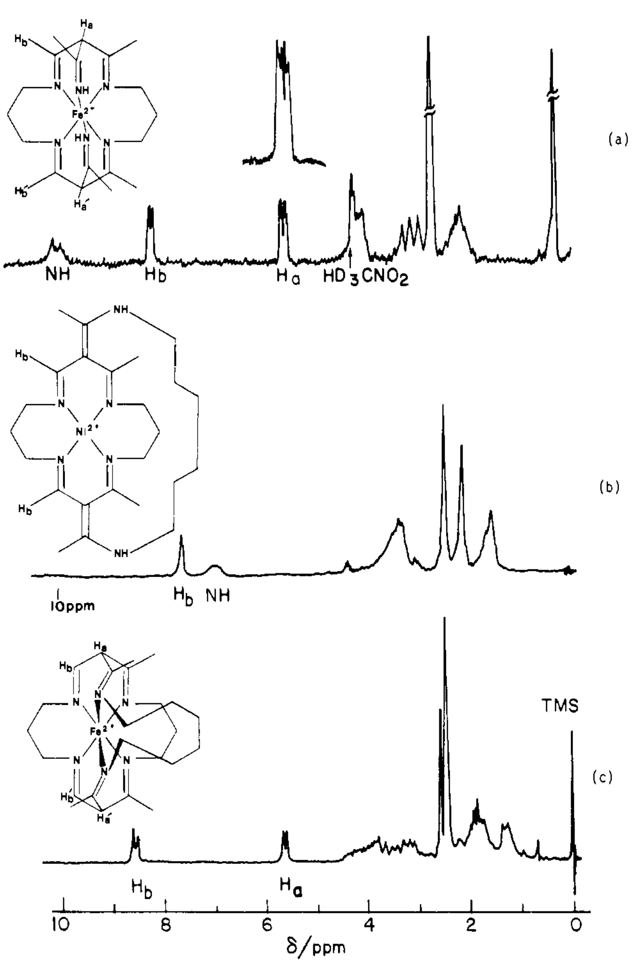

Figure 1. ^{1}H NMR spectra of rearranged (a, c) and parent (b) ligand systems in acetonitrile-d_3 solution, referenced to internal Me_4Si. (a) Complex Id, (b) nickel complex of ligand IIc, and (c) complex IIIc.

^{1}H NMR spectra of compounds III all show similar features characteristic of the rearranged ligand. The spectra of compounds Id, the nickel complex of ligand IIc, and IIIc are illustrated in Figure 1 where it is clear that the clathro complex IIIc has a markedly different spectrum from that of the unrearranged parent nickel complex IIc (the Fe^{II} complex of ligand IIc is 5-coordinate and paramagnetic), especially in the δ 5–7 region. The spectrum of IIIc is very similar, however, to compound Id previously shown to have the closely related structure I.[7,8] In both Id and IIIc (and all compounds III) the bridgehead proton H_a and the vinyl proton H_b (Scheme II) couple together such that both appear as doublets ($^3J_{^1H-^1H} \sim 5.0$ Hz). Identical coupling between the related yet magnetically distinct pair H_a' and H_b' produces the possibility of a complex doublet of doublets at their two resonance positions (Figure 1a). The lack of symmetry elements within the cis complex indicated by this complexity is further illustrated by the methyl proton resonances which show more peaks than expected for a higher symmetry molecule. This lack of symmetry is a direct consequence of the methyl substituents of the parent macrocycle. The ^{1}H NMR data (Table V) are again in excellent agreement with those reported for compounds I, where protons H_a and H_b gave complex resonances at δ 5.8 and 8.7, respectively,[7] and where a cis structure has been established crystallographically.[8]

Limited availability and solubility meant that ^{13}C NMR spectra were obtained only for compounds IIIa and IIIc (Figure 2) and in both instances showed the uniqueness of every carbon atom

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(16) DuChamp, D. J. "Program and Abstracts", American Crystallographic Association Meeting, Bozeman, MT, 1964, Paper B14, as modified by Christoph, G. G. at the Ohio State University.

(17) Goedken, G. L.; Busch, D. H. J. Am. Chem. Soc. 1972, 94, 7355.

Table II. Final Atomic Parameters for Clathrochelate Complex IIIb

A. Nonhydrogen Atoms[a]

atom	x/a	y/b	z/c	U_{11} or B, Å^2	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	2400.1 (0.7)	765.6 (0.4)	1991.3 (0.4)	16.5 (0.4)	15.3 (0.3)	19.1 (0.3)	−0.9 (0.3)	0.8 (0.3)	0.0 (0.3)
P(1)	1297 (1)	7537 (1)	4776 (1)	42 (1)	49 (1)	60 (1)	−5.3 (0.9)	−9 (1)	−12.0 (0.9)
P(2)	3187 (1)	4130.4 (0.7)	2040.3 (0.9)	35 (1)	27.9 (0.8)	30.1 (0.8)	−5.1 (0.7)	5.3 (0.7)	−2.9 (0.6)
F(1)	585 (5)	6841 (2)	4510 (3)	110 (4)	90 (3)	95 (3)	−50 (3)	9 (3)	−26 (2)
F(2)	8 (5)	7912 (3)	4823 (4)	103 (4)	158 (5)	138 (5)	74 (4)	−25 (4)	−17 (4)
F(3)	1986 (8)	8219 (3)	5003 (5)	252 (10)	92 (4)	227 (8)	−109 (5)	−111 (7)	20 (4)
F(4)	2486 (5)	7089 (3)	4822 (4)	68 (3)	112 (4)	188 (6)	25 (3)	48 (4)	23 (4)
F(5)	1141 (5)	7353 (3)	5793 (3)	94 (4)	173 (5)	59 (3)	32 (4)	−8 (3)	−10 (3)
F(6)	1385 (6)	7738 (3)	3766 (3)	193 (6)	128 (4)	79 (3)	−70 (4)	16 (4)	25 (3)
F(7)	3550 (3)	3343 (1)	2377 (2)	50 (2)	41 (2)	55 (2)	5 (2)	1 (2)	9 (1)
F(8)	1835 (3)	3971 (2)	2342 (2)	35 (2)	61 (2)	84 (2)	5 (2)	16 (2)	12 (2)
F(9)	2810 (4)	4905 (1)	1705 (2)	95 (3)	29 (1)	66 (2)	5 (2)	11 (2)	7 (1)
F(10)	4545 (3)	4280 (2)	1749 (3)	40 (2)	95 (3)	92 (3)	−18 (2)	22 (2)	20 (2)
F(11)	3500 (4)	4438 (2)	2997 (2)	131 (4)	64 (2)	39 (2)	−45 (3)	2 (2)	−13 (1)
F(12)	2897 (4)	3812 (1)	1087 (2)	98 (3)	43 (2)	34 (1)	−7 (2)	−5 (8)	−5 (1)
N(1)	923 (4)	258 (2)	2269 (2)	20 (2)	30 (2)	27 (2)	−4 (2)	−1 (2)	0 (2)
N(2)	3130 (4)	−162 (2)	1662 (2)	24 (2)	20 (2)	26 (2)	0 (2)	−1 (2)	−1 (1)
N(3)	1985 (3)	837 (2)	722 (2)	20 (2)	24 (2)	22 (2)	2 (2)	2 (1)	−2 (1)
N(4)	1537 (3)	1644 (2)	2223 (2)	13 (2)	24 (2)	24 (2)	1 (2)	1 (2)	−5 (1)
N(5)	2881 (4)	606 (2)	3235 (2)	25 (2)	21 (2)	21 (2)	−1 (2)	0 (2)	0 (1)
N(6)	3902 (3)	1319 (2)	1751 (2)	18 (2)	18 (2)	27 (2)	2 (2)	2 (2)	−1 (1)
C(1)	994 (5)	−329 (2)	2705 (3)	30 (3)	32 (3)	35 (3)	−12 (2)	0 (2)	5 (2)
C(2)	2229 (5)	−592 (2)	2975 (3)	39 (3)	21 (2)	33 (2)	−7 (2)	−6 (2)	8 (2)
C(3)	2971 (5)	−714 (2)	2143 (3)	26 (3)	21 (2)	33 (2)	−1 (2)	−9 (2)	−1 (2)
C(4)	3338 (6)	−1465 (3)	1960 (4)	50 (4)	22 (3)	59 (4)	4 (3)	−10 (3)	−3 (2)
C(5)	3718 (5)	−211 (2)	777 (3)	36 (3)	24 (2)	38 (3)	4 (2)	7 (2)	−5 (2)
C(6)	2767 (5)	−220 (3)	28 (3)	46 (4)	32 (3)	33 (3)	3 (3)	4 (2)	−11 (2)
C(7)	1647 (5)	233 (3)	219 (3)	34 (3)	37 (3)	29 (3)	−2 (3)	−4 (2)	−5 (2)
C(8)	2106 (4)	1492 (2)	344 (3)	20 (3)	34 (3)	25 (2)	6 (2)	4 (2)	1 (2)
C(9)	1951 (6)	1669 (3)	−620 (3)	57 (5)	48 (3)	26 (3)	12 (3)	3 (3)	7 (2)
C(10)	2545 (5)	2099 (2)	954 (3)	25 (3)	19 (2)	31 (2)	4 (2)	4 (2)	3 (2)
C(11)	1696 (4)	2175 (2)	1708 (3)	18 (3)	20 (2)	34 (3)	3 (2)	−3 (2)	−2 (2)
C(12)	594 (5)	1676 (3)	2909 (3)	27 (3)	41 (3)	30 (3)	4 (2)	10 (2)	−2 (2)
C(13)	−518 (5)	1226 (3)	2641 (3)	23 (3)	45 (3)	42 (3)	2 (3)	10 (2)	7 (2)
C(14)	−267 (5)	579 (3)	2048 (3)	20 (3)	39 (3)	45 (3)	−1 (2)	1 (2)	8 (2)
C(15)	3178 (6)	−254 (3)	4485 (3)	50 (4)	36 (3)	32 (3)	0 (3)	−9 (3)	6 (2)
C(16)	2807 (5)	−21 (2)	3573 (3)	28 (3)	29 (2)	26 (2)	−3 (2)	1 (2)	1 (2)
C(17)	3303 (5)	1202 (2)	3820 (3)	39 (3)	27 (2)	26 (2)	−3 (2)	−5 (2)	−4 (2)
C(18)	4674 (5)	1241 (2)	4014 (3)	43 (4)	30 (3)	35 (3)	−2 (3)	−19 (2)	−3 (2)
C(19)	5344 (6)	1802 (3)	3448 (4)	35 (4)	31 (3)	57 (4)	−9 (3)	−20 (3)	−2 (3)
C(20)	5901 (5)	1513 (3)	2618 (4)	19 (3)	33 (3)	62 (4)	−4 (2)	−9 (3)	8 (3)
C(21)	5111 (4)	1042 (2)	2010 (3)	16 (2)	26 (2)	48 (3)	2 (2)	4 (2)	3 (2)
C(22)	3829 (5)	1882 (2)	1247 (3)	26 (3)	21 (2)	31 (2)	1 (2)	6 (2)	−1 (2)
C(23)	4835 (5)	2287 (3)	850 (4)	31 (3)	32 (3)	55 (3)	−3 (2)	18 (3)	8 (2)
O	0	0	5000	9.8 (4)					
C	406 (15)	430 (8)	4640 (10)	8.3 (4)					

B. Hydrogen Atoms[b]

atom	x/a	y/b	z/c	B, Å^2	Å	atom	x/a	y/b	z/c	B, Å^2	Å
H(1)	43 (5)	−55 (2)	287 (3)	3.4	0.79	H(18B)	467 (5)	131 (2)	465 (3)	2.8	0.97
H(2)	216 (5)	−97 (2)	331 (3)	1.9	0.88	H(19A)	585 (5)	198 (2)	376 (3)	2.4	0.80
H(10)	266 (5)	249 (2)	60 (3)	2.7	0.91	H(19B)	471 (5)	218 (2)	329 (3)	4.0	1.02
H(11)	119 (5)	256 (2)	173 (3)	1.7	0.91	H(20A)	638 (5)	124 (2)	271 (3)	2.1	0.74
H(5A)	414 (5)	−56 (2)	74 (3)	1.4	0.80	H(20B)	623 (5)	188 (2)	230 (3)	3.3	0.91
H(5B)	421 (5)	−13 (2)	68 (3)	2.6	0.86	H(21A)	498 (5)	64 (2)	232 (3)	1.1	0.90
H(6A)	249 (5)	−73 (2)	−5 (3)	4.0	1.01	H(21B)	550 (5)	92 (2)	149 (3)	2.5	0.90
H(6B)	308 (5)	−5 (2)	−45 (3)	3.4	0.87	H(4A)	319 (5)	−171 (2)	243 (3)	6.8	0.87
H(7A)	115 (5)	−4 (2)	51 (3)	1.9	0.88	H(4B)	417 (5)	−147 (2)	193 (3)	8.1	0.91
H(7B)	124 (5)	37 (2)	−33 (3)	4.0	0.97	H(4C)	305 (5)	−159 (2)	148 (3)	5.8	0.81
H(12A)	45 (5)	214 (2)	305 (3)	2.2	0.90	H(15A)	304 (5)	−70 (2)	461 (3)	7.1	0.87
H(12B)	98 (5)	150 (2)	343 (3)	3.7	0.94	H(15B)	273 (5)	−4 (3)	483 (3)	10.1	0.82
H(13A)	−106 (5)	148 (2)	235 (3)	3.8	0.88	H(15C)	387 (5)	−22 (2)	454 (3)	6.4	0.77
H(13B)	−90 (5)	109 (2)	313 (3)	2.3	0.89	H(23A)	454 (5)	259 (2)	44 (3)	9.8	0.89
H(14A)	−19 (5)	73 (2)	141 (3)	2.2	0.99	H(23B)	541 (5)	199 (2)	55 (3)	10.2	0.95
H(14B)	−101 (5)	20 (2)	202 (3)	3.1	1.08	H(23C)	521 (5)	247 (2)	125 (3)	9.2	0.80
H(17A)	286 (5)	114 (2)	426 (3)	2.6	0.83	H(9A)	208 (5)	212 (2)	−78 (3)	9.1	0.89
H(17B)	293 (5)	168 (2)	355 (3)	1.6	1.07	H(9B)	114 (5)	151 (2)	−85 (3)	8.4	0.99
H(18A)	500 (5)	81 (2)	391 (3)	1.3	0.89	H(9C)	249 (5)	147 (2)	−96 (3)	9.6	0.87

[a] Atomic coordinates and thermal parameters have been multiplied by 10^4 and 10^3, respectively. The anisotropic thermal factors are expressed in the form of $\exp[-2\pi^2(h^2U_{11}a^{*2} + k^2U_{22}b^{*2} + l^2U_{33}c^{*2} + 2hkU_{12}a^*b^* + 2hlU_{13}a^*c^* + 2klU_{23}b^*c^*)]$. [b] The hydrogen atoms are labeled in terms of the atoms to which they are attached. The coordinate values have been multiplied by 10^3. The average standard deviations of isotropic thermal parameter and bond distance are 1.2 Å^2 and 0.04 Å, respectively.

Table III. Bond Distances (Å) and Angles (Deg) with Their Estimated Standard Deviations for Clathrochelate Complex IIIb

A. Bond Distances			
(a) Coordination Sphere			
Fe-N(1)	1.933 (4)	Fe-N(4)	1.930 (3)
Fe-N(2)	1.974 (3)	Fe-N(5)	1.961 (3)
Fe-N(3)	1.969 (3)	Fe-N(6)	1.989 (3)
(b) Imine N=C Double Bond			
N(1)-C(1)	1.279 (5)	N(4)-C(11)	1.271 (5)
N(2)-C(3)	1.271 (5)	N(5)-C(16)	1.279 (5)
N(3)-C(8)	1.271 (5)	N(6)-C(22)	1.296 (5)
(c) Ligand			
C(1)-C(2)	1.500 (7)	N(4)-C(12)	1.474 (5)
C(2)-C(16)	1.529 (6)	C(12)-C(13)	1.537 (7)
C(2)-C(3)	1.518 (6)	C(13)-C(14)	1.526 (7)
C(3)-C(4)	1.486 (6)	N(1)-C(14)	1.479 (6)
N(2)-C(5)	1.490 (5)	C(15)-C(16)	1.490 (6)
C(5)-C(6)	1.529 (7)	N(5)-C(17)	1.490 (5)
C(6)-C(7)	1.528 (7)	C(17)-C(18)	1.539 (7)
N(3)-C(7)	1.481 (6)	C(18)-C(19)	1.543 (7)
C(8)-C(9)	1.495 (6)	C(19)-C(20)	1.497 (8)
C(8)-C(10)	1.532 (5)	C(20)-C(21)	1.532 (7)
C(10)-C(11)	1.485 (6)	N(6)-C(21)	1.478 (5)
C(10)-C(22)	1.534 (7)	C(22)-C(23)	1.475 (7)
(d) PF_6^- Ions			
P(1)-F(1)	1.566 (4)	P(2)-F(7)	1.602 (2)
P(1)-F(2)	1.586 (5)	P(2)-F(8)	1.591 (4)
P(1)-F(3)	1.519 (6)	P(2)-F(9)	1.584 (2)
P(1)-F(4)	1.556 (5)	P(2)-F(10)	1.590 (3)
P(1)-F(5)	1.577 (3)	P(2)-F(11)	1.584 (3)
P(1)-F(6)	1.568 (4)	P(2)-F(12)	1.579 (3)
B. Bond Angles			
(a) Metal Coordination Sphere			
N(2)-Fe-N(1)	88.4 (1)	N(6)-Fe-N(2)	93.8 (1)
N(3)-Fe-N(1)	94.5 (1)	N(4)-Fe-N(3)	88.1 (1)
N(4)-Fe-N(1)	87.6 (1)	N(5)-Fe-N(3)	176.8 (1)
N(5)-Fe-N(1)	86.5 (1)	N(6)-Fe-N(3)	87.0 (1)
N(6)-Fe-N(1)	177.2 (1)	N(5)-Fe-N(4)	94.8 (1)
N(3)-Fe-N(2)	87.1 (1)	N(6)-Fe-N(4)	90.2 (1)
N(4)-Fe-N(2)	173.5 (1)	N(6)-Fe-N(5)	91.9 (1)
N(5)-Fe-N(2)	89.9 (1)	N(6)-Fe-N(5)	91.9 (1)
(b) Ligand			
C(1)-N(1)-Fe	118.8 (3)	C(11)-N(4)-Fe	118.7 (2)
C(14)-N(1)-Fe	120.1 (3)	C(12)-N(4)-Fe	120.9 (3)
C(14)-N(1)-C(1)	120.8 (4)	C(12)-N(4)-C(11)	119.8 (3)
C(3)-N(2)-Fe	120.5 (3)	C(16)-N(5)-Fe	120.0 (3)
C(5)-N(2)-Fe	117.4 (4)	C(17)-N(5)-Fe	121.9 (2)
C(5)-N(2)-C(3)	121.4 (3)	C(17)-N(5)-C(16)	118.0 (3)
C(7)-N(3)-Fe	117.0 (2)	C(21)-N(6)-Fe	121.4 (2)
C(8)-N(3)-Fe	120.7 (3)	C(22)-N(6)-Fe	118.6 (3)
C(8)-N(3)-C(7)	122.0 (3)	C(22)-N(6)-C(21)	119.1 (3)
C(2)-C(1)-N(1)	118.0 (4)	C(10)-C(11)-N(4)	118.9 (3)
C(3)-C(2)-C(1)	108.8 (3)	C(13)-C(12)-N(4)	111.2 (3)
C(16)-C(2)-C(1)	107.5 (3)	C(14)-C(13)-C(12)	115.8 (4)
C(16)-C(2)-C(3)	111.3 (4)	C(13)-C(14)-N(1)	110.7 (3)
C(2)-C(3)-N(2)	115.1 (3)	C(2)-C(16)-N(5)	115.5 (3)
C(4)-C(3)-N(2)	128.2 (4)	C(15)-C(16)-N(5)	127.9 (4)
C(4)-C(3)-C(2)	116.3 (3)	C(15)-C(16)-C(2)	116.4 (3)
C(6)-C(5)-N(2)	110.8 (4)	C(18)-C(17)-C(5)	116.5 (3)
C(7)-C(6)-C(5)	113.9 (3)	C(19)-C(18)-C(17)	113.8 (4)
C(6)-C(7)-N(3)	110.6 (4)	C(20)-C(19)-C(18)	114.6 (4)
C(9)-C(8)-N(3)	128.2 (4)	C(21)-C(20)-C(19)	117.9 (4)
C(10)-C(8)-N(3)	115.0 (3)	C(20)-C(21)-N(6)	117.5 (3)
C(10)-C(8)-C(9)	116.6 (3)	C(10)-C(22)-N(6)	115.6 (4)
C(11)-C(10)-C(8)	109.2 (3)	C(23)-C(22)-N(6)	127.5 (4)
C(22)-C(10)-C(8)	105.1 (3)	C(23)-C(22)-C(10)	116.4 (3)
C(22)-C(10)-C(11)	113.2 (3)		
(c) PF_6^- Ions			
F(2)-P(1)-F(1)	85.9 (2)	F(8)-P(2)-F(7)	88.3 (2)
F(3)-P(1)-F(1)	178.0 (3)	F(9)-P(2)-F(7)	179.2 (2)
F(4)-P(1)-F(1)	89.2 (2)	F(10)-P(2)-F(7)	90.8 (1)
F(5)-P(1)-F(1)	90.4 (2)	F(11)-P(2)-F(7)	89.6 (1)
F(6)-P(1)-F(1)	89.2 (2)	F(12)-P(2)-F(7)	89.4 (1)
F(3)-P(1)-F(2)	93.8 (3)	F(9)-P(2)-F(8)	91.0 (2)
F(4)-P(1)-F(2)	171.9 (3)	F(10)-P(2)-F(8)	179.1 (3)
F(5)-P(1)-F(2)	86.9 (3)	F(11)-P(2)-F(8)	90.2 (4)
F(6)-P(1)-F(2)	90.1 (3)	F(12)-P(2)-F(8)	90.4 (4)
F(4)-P(1)-F(3)	91.1 (3)	F(10)-P(2)-F(9)	89.8 (2)
F(5)-P(1)-F(3)	91.4 (3)	F(11)-P(2)-F(9)	90.6 (1)
F(6)-P(1)-F(3)	88.8 (3)	F(12)-P(2)-F(9)	90.3 (1)
F(5)-P(1)-F(4)	86.6 (3)	F(11)-P(2)-F(10)	89.3 (2)
F(6)-P(1)-F(4)	96.3 (3)	F(12)-P(2)-F(10)	89.9 (2)
F(6)-P(1)-F(5)	177.0 (3)	F(12)-P(2)-F(11)	178.8 (2)

Table IV. Selected IR Data for Rearranged Ligands and Their Parent Compounds

compound	NH, cm^{-1}	C=N, C=C, cm^{-1}
IIIa		1637
IIa	3430 sh	1625, 1580
IIIb		1647, 1632, 1611
IIb	3200 sh	1610, 1575
IIIc		1639, 1631, 1621
IIc	3300 sh	1610, 1550
IIId		1648, 1629, 1610
IId	3220 br	1611, 1580

Table V. Selected ^1H NMR Data (δ) for Rearranged Complexes III[a]

compound	H_a[b]	H_b[b]	CH_3
IIIa	5.63	8.70	2.46, 2.58, 2.76, 2.99, 3.06
IIIb	5.69	8.61	2.48, 2.52, 2.55
IIIc	5.70	8.64	2.47, 2.58
IIId	5.79	8.76	2.47, 2.52, 2.56, 2.66

[a] In CD_3CN, Me_4Si reference. Assignments based on decoupling and integration data. [b] Complex multiplet centered at δ given.

in the structure. This is consistent with the expected absence of symmetry elements, on the basis of the ^1H NMR data: Compound IIIa contains 20 carbon atoms and displays 18 resonances while IIIc resolves 22 of 24 possible resonances (Table VI). The most striking feature of the spectra is the absence of resonances between 105 and 115 ppm (typical of the γ-carbon of unrearranged ligands[13]) and the appearance of resonances near 65 ppm which split to doublets in the coupled spectrum. This conversion of nonprotonated (δ 110) to singly protonated (δ 65) nature for the

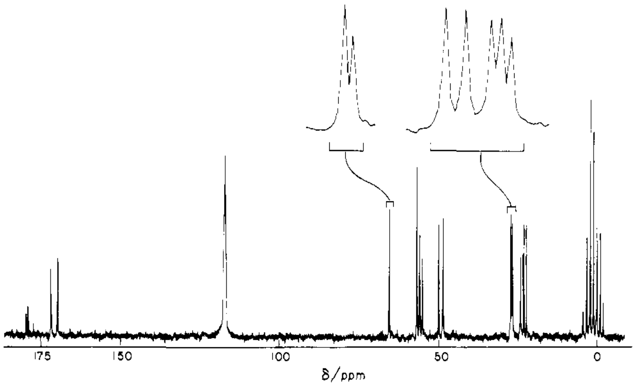

Figure 2. ^{13}C NMR spectrum of the clathrochelate iron complex IIIc at 20.11 MHz in acetonitrile-d_3.

Table VI. ^{13}C NMR Shift Data (δ) for Complexes IIIa and IIIc[a]

compound	C
IIIa	171.8, 170.6, 170.1, 65.6, 65.2, 56.3, 55.4, 49.9, 49.3, 44.9, 44.6, 43.2, 27.3, 27.1, 25.0, 24.5, 24.3, 23.2
IIIc	180.7, 180.2, 180.1, 178.5, 173.0, 170.7, 65.9, 65.8, 57.2, 56.3, 55.3, 50.25, 48.9, 27.6, 27.4, 27.2, 27.1, 27.0, 24.3, 23.5, 23.3, 22.3

[a] In CD_3CN, Me_4Si reference.

Table VII. Electronic Spectra of Hexadentate Iron(II) Complexes in CH_3CN Solution

compound	λ_{max}/nm (ϵ/(dm^3 mol^{-1} cm^{-1}))
IIIa	423 (8030), 407 sh, 301 (5160)
IIIb	447 (8400), 405 sh, 303 (4300)
IIIc	447 (7100), 405 sh, 302 (3700)
IIId	451 (6100), 400 sh, 296 (9700), 287 (7000), 265 (14 600)

Table VIII. Electrochemical Data (V) for Fe^{II}/Fe^{III} Couple of the Iron Species

compound	$E_{1/2}$[a]	$E_{3/4} - E_{1/4}$
IIa	−0.045	0.070
IIIa	0.390	0.065
IIb	−0.400	0.070
IIIb	0.370	0.070
IIc	−0.400	0.075
IIIc	0.385	0.070
IId	−0.445	0.110
IIId	0.380	0.075

[a] vs. Ag^0/Ag^+ (0.1 M in CH_3CN) at rotating platinum disk electrode.

γ-carbon is consistent with the proposed Scheme II.

The electronic spectra of the complexes are dominated by intense charge-transfer bands ($\epsilon > 6000$ dm^3 mol^{-1} cm^{-1}) with λ_{max} at ~450 nm (22.2 × 10^3 cm^{-1}) and a shoulder at 405 nm (24.6 × 10^3 cm^{-1}) Table VII. A second charge-transfer band occurs at higher energy 303 nm (32.6 × 10^3 cm^{-1}) $\epsilon \sim 4000$ dm^3 mol^{-1} cm^{-2}. Both bands are at slightly lower energies than those observed for the related complexes I[7] but are in general very similar ($\nu = 23.9 \times 10^3$ cm^{-1}; ϵ 7000–10 500; 33.7 × 10^3 cm^{-1}; ϵ 3500–5000 dm^3 mol^{-1} cm^{-1}). Comparison of these data with those of other hexaene complexes shows that the tris(α-diimine) clathrochelate complexes of Rose et al.[3] $[Fe(DMG)_3(BX)_2]$ display two bands at ~22.6 × 10^3 cm^{-1} (18 000 dm^3 mol^{-1} cm^{-1}) and (27–30) × 10^3 cm^{-1} (2000) dm^3 mol^{-1} cm^{-1}) assigned as M → π^* transitions. Also, iron(II) tris(diimine) complexes are characterized by an intense M → π^* transition in the visible region; e.g., $[Fe(bpy)_3]^{2+}$, $\nu_{max} = 19.1 \times 10^3$ cm^{-1} and $[Fe(o\text{-phen})_3]^{2+}$ $\nu_{max} = 19.6 \times 10^3$ cm^{-1}.[18] The two bands observed in the present study are, by analogy, assigned to the M → π^* transition, and since these complexes consist of an isolated tris(β-diimine) donor set, they would be expected to show M → π^* transitions at higher energy relative to the conjugated tris(α-diimine) complexes. This is indeed the trend observed.

The electrochemical behavior of these complexes is extremely simple. In 0.1 M tetra-*n*-butylammonium fluoroborate in acetonitrile at a Pt disk electrode (reference Ag^0/Ag^+ (0.1 M in CH_3CN)), the only observed process is the Fe^{II}/Fe^{III} redox couple. The $E_{1/2}$ values (Table VIII) reflect a dramatic change from those of the parent bridged complexes II. Compounds II oxidize at potentials up to 80 mV more cathodic than the hexaene complexes III.[14] The complexes of the rearranged ligands are stable indefinitely in air whereas the parent complexes are highly oxygen sensitive. The $E_{1/2}$ values here are approximately 90 mV more positive than the values for the related hexaene compounds of iron(II).[19]

The spectroscopic and electrochemical data listed above strongly indicate that all four complexes III have very similar structures. The close similarity of much of this data to that of complexes I indicates that complexes III also possess the geometry derived by folding the parent macrocycle. In order to absolutely confirm these deductions, we performed an X-ray crystallographic analysis of complex IIIb.

Structure of $[Fe[(CH_2)_5(\text{iminoethyl})_2[16]\text{tetraene-}N_6]](PF_6)_2$ (IIIb). The atom numbering scheme and structure of the clathrochelate complex IIIb are shown in Figure 3. A significant feature of the structure is the unique identification of the cis geometry for the two new rearranged imine donors linked by the pentamethylene chain. The coordination sphere of the iron atom can be seen to consist of a slightly distorted octahedral array of nitrogen donors. The distortion is best viewed as a slight trigonal twist of 5° from ideal O_h symmetry and, as such, is very similar to the 8° twist found for the analogous unbridged complex Id.[1,6] A similar result was found in a crystallographic study[17] of another hexadentate iron(II) clathrochelate but with a larger twist angle of 39°. For low-spin iron(II) complexes, the difference in crystal field stabilization energies between octahedral O_h and trigonal prismatic D_{3h} geometries is negligible,[20] and therefore the molecular symmetry should be governed by ligand steric or electronic requirements. It is interesting to note that most complexes approximating D_{3h} symmetry arise from ligands with unsaturated five-membered chelate rings where conjugation effects strengthen this geometry. In the present complex the unsaturated and un-

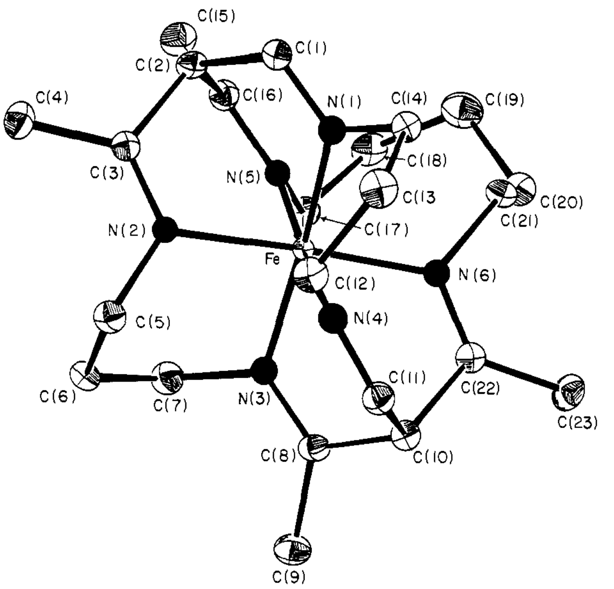

Figure 3. ORTEP plot of $[Fe[(CH_2)_5(\text{iminoethyl})_2[16]\text{tetraene-}N_6]](PF_6)_2$ IIIb. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table IX. Equations of Least-Squares Planes and Distances (Å) of Atoms from the Plane (in Brackets)

plane 1:	Fe, N(2), N(3) $0.879x + 0.453y - 0.156z = 2.507$ [C(5) 0.0736, C(6) −0.016, C(7) −0.763]
plane 2:	Fe, N(1), N(4) $0.272x - 0.045y + 0.957z = 3.525$ [C(12) 0.700, C(13) 0.017, C(14) −0.705]
plane 3:	Fe, N(5), N(6) $-0.467x + 0.844y + 0.267z = 0.767$ [C(17) 0.957, C(18) 0.387, C(19) 0.698, C(20) −0.377, C(21) −0.956]
plane 4:	N(2), C(4), C(2) $0.846x + 0.171y + 0.495z = 4.109$ [C(3) 0.034]
plane 5:	N(5), C(2), C(15) $0.909x - 0.230y - 0.355z = 0.903$ [C(16) 0.014]
plane 6:	N(3), C(9), C(10) $0.956x - 0.232y - 0.185z = 1.510$ [C(8) −0.029]
plane 7:	N(6), C(10), C(23) $-0.036x + 0.612y + 0.789z = 3.431$ [C(22) 0.048]

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[18] Krumholtz, P. *J. Am. Chem. Soc.* **1953**, *75*, 2163.

[19] Rakowski, M. C. Ph.D. Thesis, The Ohio State University, 1974.

[20] Wentworth, R. A. D. *Coord. Chem. Rev.* **1972**, *9*, 171.

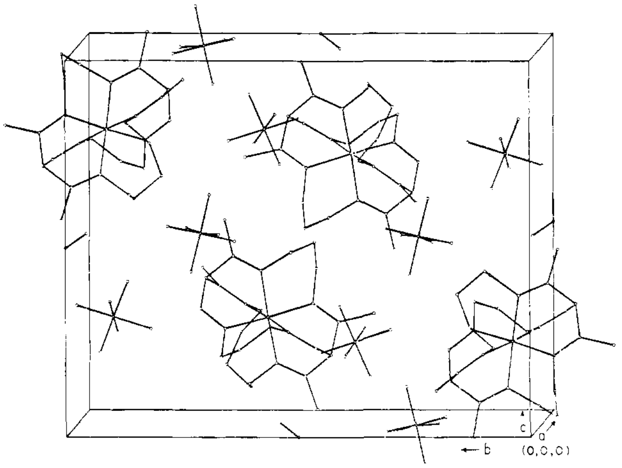


Figure 4. Perspective view of the contents of the unit cell of complex IIIb showing the ion packing and position of the methanol of solvation. Atoms are represented by points for clarity.

conjugated chelate rings present no such constraints, and a geometry close to O_h is observed.

Bond lengths and angles (Table IIIa,b) are closely similar to those reported for complex Id and lie within the expected ranges.[8] The Fe–N bond distances are found to vary somewhat, ranging from 1.93 to 2.02 Å, the longer distances indicating a degree of strain within the chelate rings. The saturated six-membered and eight-membered chelate rings are all found to occupy skew conformations with absolute configuration λλλ(δδδ) (see Table IX). The parent bridged complexes II have been found to give chair or boat conformers of the six-membered rings,[13,14] and it is apparent that during the course of the rearrangement reaction (Scheme II), these rings must undergo a dramatic change of conformation. The δδ, or λλ, configurations of these chelate rings are consistent only with a cis type of complex whereas a λδ configuration would give rise to a trans isomer and so their configurations are probably dictated by the observed cis structure.

The six C=N bonds are localized with bond lengths averaging 1.28 (2) Å, consistent with six isolated imine donor atoms in the coordination sphere. The six Fe–N bonds clearly fall into two groups with the bonds to N(2), N(3), N(5), and N(6) considerably longer (~0.04 Å) than the other two (Table IIIa). The geometry about these atoms is also less sp^2 in character, since whereas imine carbons C(3), C(8), C(16), and C(22) display good planarity with their three neighbors (Table IX), the bond angles in the plane [N(2)–Ĉ(3)–C(4), 131.2°; N(5)–Ĉ(16)–C(15), 103.5°; N(3)–Ĉ(8)–C(9), 127.7°; and N(6)–Ĉ(22)–C(28), 126.8°] all show a considerable deviation away from sp^2 character and are indicative of the steric crowding between the methyl groups C(4), C(15), C(9), and C(23) and the methylene groups C(5), C(17), C(7), and C(21), respectively of the saturated chelate rings. A further manifestation of this effect is seen in the C–C single bond distances from the bridgehead carbons C(2) and C(10) to the imine carbons, which again fall into two groups, those to C(3), C(8), C(16), and C(22) being some 0.03 Å longer than those to C(1) and C(22) (Table IIIa).

The crystal packing diagram (Figure 4) shows the individual clathrochelate ions are flanked by noncoordinated, ordered hexafluorophosphate ions, the major contacts between ions being electrostatic. In addition, a disordered molecule of solvent methanol with site population 0.5 is found to be trapped on a special position of multiplicity 2 ($00^1/_2$) in the crystal lattice but does not appear to interact via hydrogen bonding with any of the major ions.

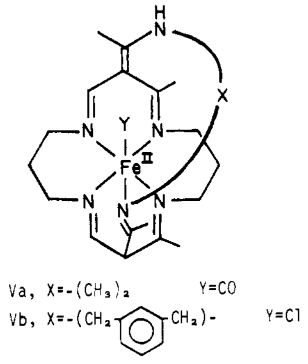
Syntheses and Characterization of Pentadentate Iron(II) Complexes IVb and V. Ligands which have rearranged in a manner similar to that described above but where only one imine group is formed give rise to low-spin pentadentate complexes. The three complexes IVb, Va, and Vb each contain such a pentadentate ligand, but in each case the reason behind the production of such a structure appears to be different.

Table X. Selected IR Data for Pentadentate Ligands

compd	ν_{NH}/ cm^{-1}	C=N, C=C/cm^{-1}	other/cm^{-1}
IVb		1526, 1565, 1607, 1620	
Va	3410	1574, 1620	1989 (ν_{CO})
Vb	3415	1514, 1548, 1620, 1630	

Complex IVb is the compound which one would logically expect to form a pentadentate ligand since it is derived from complex IVa containing *only* one aminoethyl group with a transferable proton. Since such a transfer is essential for rearrangement to occur, only this group can convert to an imine and coordinate, while the piperidylidene substituent is incapable of such a process. The rearranged ligand occupies five coordination sites of the metal ion, and a solvent pyridine molecule is found to occupy the sixth. The structural question then is whether the new imino donor is cis or trans to the pyridine; this will be dealt with below.

With complex Va the reason for the pentadentate ligand is less obvious but is dictated by the mode of synthesis. The precursor complex IIa contains two aminoethyl groups which potentially could rearrange to form a hexadentate complex, and in fact, this is found to occur under most conditions to give IIIa. However, initial exposure of IIa to carbon monoxide produces an unrearranged carbonyl complex as a first product. Subsequent slow rearrangement of the ligand (in the presence of base without heating) can then take place. It is clear that in order to form a hexadentate complex the strongly bound carbon monoxide ligand must be displaced by an impending imino group. This competition of ligands appears to favor the already coordinated carbonyl, and only one imine to metal bond is formed, resulting in a pentadentate ligand. It must be true that while the incoming, rearranging ligand can successfully compete for coordination sites with solvent molecules under these conditions, a carbonyl ligand is too firmly bound to be displaced. Again the question of cis or trans geometry remains.



Va, X=-(CH$_3$)$_2$ Y=CO

Vb, X=-(CH$_2$–C$_6$H$_4$–CH$_2$)- Y=Cl

The third pentadentate ligand occurs in the complex Vb. In this instance, physical or steric limitations prevent both amine nitrogens from becoming coordinated. The inflexible xylene moiety, while permitting the first bond formation, cannot then orientate such that the second amine might also rearrange and bond. The resultant complex completes its coordination sphere with a chloride ion. Due to steric crowding of the cis site the chloride is probably trans to the newly formed imine group. A comparison of the spectral properties of this proposed trans complex with those of complexes IVb and Va may therefore allow some deductions about their geometries also.

Infrared spectra of these complexes, as with the hexadentate ligands above, display a marked complexity of peaks in the azomethine region (Table X), and in each instance, peaks attributable to both C=N and C=C stretches are observed. Complex IVb has no NH stretch as expected, whereas both complexes Va and Vb have amine protons. Complex Va also displays a C=O stretch at 1989 cm^{-1} with $\nu_{^{13}CO}$ at 1946 cm^{-1}, which is of lower energy than any of the iron(II) carbonyl adducts of the parent dry cave ligands.[14] This is probably a consequence of the unrestricted nature of the CO binding site in this complex and the strong π-back-

Table XI. ^{13}C NMR Shifts for Pentadentate Ligand Complexes

compd	δ (Me_4Si reference)
IVb[a]	181.8, 181.5, 180.6, 174.8, 168.9, 162.7, 158.5, 138.2, 125.9, 103.8, 65.8, 62.8, 56.7, 53.9, 52.4, 50.1, 45.9, 40.6, 34.1, 28.0, 27.3, 24.8, 24.6, 23.5, 22.6, 19.8
Va[b]	219.2, 175.9, 173.5, 170.7, 169.5, 166.6, 163.3, 108.5, 65.4, 57.7, 56.8, 52.7, 49.4, 46.7, 43.2, 27.6, 25.6, 24.5, 23.4, 21.7, 20.8

[a] CD_3NO_2 solution. [b] CD_3CN solution.

bonding from iron to CO induced by the basic trans imine group.[14]

The ^1H NMR spectrum of complex IVb shows coupled doublets at 5.75 and 8.03 ppm (^3J = 4.6 Hz), each having the integral of a single proton and corresponding to the H_aH_b pattern of the rearranged portion of the molecule (IVb). A third downfield singlet at 8.40 ppm with single proton integral corresponds to proton H_c of the piperidyl half of the molecule. The rest of the spectrum shows pyridine resonances at 8.71, 7.60, and 7.19 ppm of integral consistent with one pyridine molecule per complex and a total of five singlets due to methyl groups at 3.48, 2.72, 2.66, 2.47, and 2.37 ppm, all consistent with proposed structure IVb. The spectrum compares favorably with that of the pentadentate ligand complex derived from a 15-membered macrocycle and acetonitrile,[9] which contains a *trans*-acetonitrile ligand where δ H_a 5.74, H_b 8.77, and H_c = 8.09, with $^3J_{H_aH_b}$ = 5 Hz.

^{13}C NMR spectra were obtained for complexes IVb and Va and in both instances displayed resonances for every carbon atom in the structure (Table XI) consistent with the proposed lack of symmetry. Complex IVb displays the predicted 26 sharp resonances, and this indicates that the slow dynamic conformational process of the piperidyl ring observed in the Ni^{II} complex[13] is rapid in the Fe^{II} species. The three pyridine resonances at 158.5, 138.2, and 125.9 ppm clearly indicate that the base is coordinated (free pyridine at δ −149.9, 135.3, and 123.5 ppm) and freely rotating. The most striking evidence for the pentadentate nature of the ligand is found in the 65–110 ppm region. Two resonances occur in this region, one at 103.8 ppm (coupled singlet) at the position expected for the γ-carbon of an unrearranged macrocycle[13] and the second at 65.8 ppm (coupled doublet) corresponding to the rearranged protonated γ-carbon (vide supra). Complex Va shows the expected 21 major resonances in a spectrum similar to IVb in that there are again only two resonances in the range 65–110 ppm, corresponding to unrearranged, 108.5 ppm, and rearranged, 65.4 ppm, γ-carbons of a pentadentate ligand. The spectrum also contains a minor component due to a symmetrical hexadentate species such as IIIa produced by the loss of CO and rearrangement of the sixth imine to give a hexaene complex. The carbonyl carbon has a shift of 219.2 ppm and is fairly typical of bound CO in such systems.[14]

The electrochemistry of IVb and Vb show that the Fe^{II}/Fe^{III} couple occurs at considerably more positive potentials than the simple unrearranged chloro complexes but not as positive as the fully rearranged hexaene ligands discussed above (Table VIII). $E_{1/2}$'s for IVb and Vb are −0.185 V and −0.250 V with $E_{3/4} - E_{1/4}$ of 68 and 75 mV, respectively (reference Ag^0/Ag^+ 0.1 M in CH_3CN). As a result, the complexes are slightly less oxygen sensitive than the present species,[14] being stable in air in the solid state but still being unstable in solution.

Conclusions

A new class of clathrochelated metal complex has been produced which extends the series of such compounds from cryptates[2] (crown ether like) and sepulchrates[5] (tris(ethylenediamine)-like) to the tris(bipyridyl)-like structures reported here. Furthermore, these compounds, being produced via a novel route involving base-catalyzed rearrangement of a quadridentate ligand, offer the possibility of producing reversible clathrochelated structures which may be excellent mimics of certain natural enzymic systems in their ability to be dormant until activated by small substrate molecules and/or pH changes (e.g., cytochrome P450). A preliminary investigation of complex IIId has indicated the possibility of reversing the clathro rearrangement by using CO as an incoming nucleophile under appropriate pH conditions. It is clear that this reversibility deserves further study and is a topic of ongoing investigation in these laboratories.

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged.

Registry No. IIa·ClPF$_6$, 80789-33-9; IIb·ClPF$_6$, 80789-35-1; IIc·ClPF$_6$, 80789-37-3; IId·ClPF$_6$, 80789-39-5; IIIa, 80781-40-4; IIIb·0.5CH$_3$OH, 80781-36-8; IIIc, 80781-38-0; IIId, 80781-42-6; IVb, 80781-29-9; Va, 80781-31-3; Vb, 80781-33-5; hexakis(acetonitrile)iron(II) hexafluorophosphate, 34821-77-7.

Supplementary Material Available: Table of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.