

are due to protonation at an oxime oxygen is further supported by the results of an X-ray crystallographic study of $[\text{Co}(\text{dmgH})(\text{dmgH}_2)(\text{C}_2\text{H}_5)(\text{Cl})]\text{H}_2\text{O}^6$ and $[\text{Co}(\text{dmgH})(\text{dmgH}_2)(i\text{-C}_3\text{H}_7)(\text{Cl})]\text{H}_2\text{O}^{20}$. Both protonated compounds are observed to have one intramolecular dimethylglyoxime O—O distance greater than the other. This is consistent with protonation at an oxime oxygen resulting in cleavage of the intramolecular O—H...O bond with concomitant elongation to the nonbonded O—O distance. The N—O bond distances at this proposed site of protonation are longer than that observed in the same molecule where protonation has not occurred and the intramolecular O—H...O hydrogen bond is still intact.^{6,20}

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Registry No. $[\text{Co}(\text{dmgH})(\text{dmgH}_2)(\text{CH}_3)(\text{Cl})]\text{H}_2\text{O}$, 53516-27-1; $\text{Co}(\text{dmgH})(\text{dmgH}_2)(\text{CH}_3)(\text{Cl})$, 53495-31-1; $\text{Co}(\text{dmgH})(\text{dmgH}_2)(\text{C}_2\text{H}_5)(\text{Cl})$, 53432-72-7; $\text{Co}(\text{dmgH})(\text{dmgH}_2)(n\text{-C}_3\text{H}_7)(\text{Cl})$, 53432-73-8; $\text{Co}(\text{dmgH})(\text{dmgH}_2)(i\text{-C}_3\text{H}_7)(\text{Cl})$, 53432-74-9; $\text{Co}(\text{dmgH})(\text{dmgH}_2)(\text{C}_6\text{H}_{11})(\text{Cl})$, 53432-75-0; $\text{Co}(\text{dmgH})(\text{dmgH}_2)(\text{CN})_2$, 53537-51-2; $[\text{AsPh}_4][\text{Co}(\text{dmgH})_2(\text{CN})_2]$, 43065-09-4; $\text{Co}(\text{dmgH})_2(\text{CH}_3)(\text{H}_2\text{O})$, 25360-55-8; $\text{Co}(\text{dmgH})_2(\text{C}_2\text{H}_5)(\text{H}_2\text{O})$, 26025-30-9; $\text{Co}(\text{dmgH})_2(i\text{-C}_3\text{H}_7)(\text{H}_2\text{O})$, 30974-89-1; $\text{Co}(\text{dmgH})_2(n\text{-C}_3\text{H}_7)(\text{H}_2\text{O})$, 28182-23-2; $\text{Co}(\text{dmgH})_2(\text{C}_6\text{H}_{11})(\text{H}_2\text{O})$, 52970-74-8; $[\text{AsPh}_4][\text{Co}(\text{dmgH})_2(\text{SCN})_2]$, 39494-95-6; $\text{Co}(\text{dmgH})(\text{dmgH}_2)(\text{SCN})(\text{CN})$, 53495-32-2; $[\text{AsPh}_4][\text{Co}(\text{dmgH})_2$

$(\text{SCN})(\text{CN})]$, 53432-71-6; $\text{Co}(\text{dmgH})_2(\text{CN})(\text{py})$, 23318-65-2; $\text{Co}(\text{dmgH})_2(\text{CH}_3)$, 36609-02-6; $\text{Co}(\text{dmgH})(\text{dmgHD})(\text{CH}_3)(\text{Cl})$, 53432-66-9.

References and Notes

- (1) The term cobaloxime is used to describe any bis(dimethylglyoximate) complex of cobalt(III). The symbol *dmgH* represents the dimethylglyoxime monoanion $(\text{CH}_3\text{C}(\text{=NO})\text{C}(\text{=NOH})\text{CH}_3)^-$ and *dmgH*₂ neutral dimethylglyoxime $(\text{CH}_3\text{C}(\text{=NOH})\text{C}(\text{=NOH})\text{CH}_3)$. This symbolism differs from that used in ref 6.
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Five- and Six-Coordinate Complexes of Iron(II) and -(III) with a Macrocyclic Tetradentate Ligand

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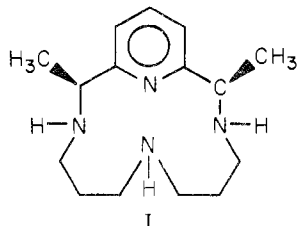
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Iron(II) and iron(III) complexes have been prepared with the 14-membered macrocyclic tetradentate ligand *meso*-2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (abbreviated *ms*-CRH). The iron(II) derivatives include both high-spin and low-spin six-coordinate complexes and a series of high-spin five-coordinate complexes related in structure to deoxyhemoglobin. The iron(III) derivatives are all high-spin and six-coordinate. All complexes were characterized by infrared and visible spectra, magnetic susceptibilities, molar conductivity, elemental analyses, and Mössbauer spectra. Assignments of the probable structures of a number of these complexes are based on the results of the Mössbauer spectral studies.

Introduction

During the last several years, many synthetic macrocyclic ligands have been prepared and their metal complexes characterized.^{2,3} The similarities between these synthetic ligand systems and such naturally occurring macrocyclic ligands as the porphyrins lend special significance to the study of those of iron. We report here the synthesis and characterization of the complexes of iron with the synthetic macrocyclic ligand *meso*-2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (*ms*-CRH, I). Previous studies with nickel and cobalt have revealed the rich chemistry of this ligand.⁴⁻⁷



The six-coordinate complexes of both iron(II) and iron(III) were found to be predominantly high spin in electronic configuration, the only exception being a low-spin dithiocyanatoiron(II) derivative. A series of five-coordinate high-spin iron(II) complexes has also been isolated and their configurations assigned on the basis of their distinctive Mössbauer spectra.⁸ These compounds and certain other synthetic iron(II) porphyrin derivatives^{9,10} are of special interest because they are among the first synthetic complexes which have the high-spin, five-coordinate structure that has been assigned to deoxyhemoglobin and deoxymyoglobin. Prior to the discovery of the synthetic high-spin pentacoordinate complexes, there was some tendency to treat the natural products as being unique in coordination structure. Indeed, it now appears that such configurations are not rare.

Experimental Section

Materials. 2,6-Diacetylpyridine (Aldrich Chemical Co.) was recrystallized before use from ethanol, and 3,3'-diaminodipropylamine (Aldrich Chemical Co.) was used as supplied. The iron(II) salts were obtained from Alfa Inorganics Inc. and used as supplied. Solvents termed dry and degassed were dried over molecular sieves for several days before being refluxed under nitrogen for 1 hr. The syntheses

Table I. Elemental Analyses and Approximate Yields of Iron-*ms*-CRH Complexes

Compd	Approx yield, %	Theory					Found				
		C	H	N	X	Fe	C	H	N	X	Fe
[Fe(<i>ms</i> -CRH)Cl]Cl	70	46.3	6.68	14.4	18.2	14.4	45.60	6.48	14.10	18.99	14.1
[Fe(<i>ms</i> -CRH)Br]Br	70	37.6	5.24	11.75	33.4	11.70	37.31	5.16	11.68	33.25	11.5
[Fe(<i>ms</i> -CRH)I]I	70	31.6	4.55	9.82	44.4	10.0	32.04	4.32	10.05		10.1
[Fe(<i>ms</i> -CRH)Cl]PF ₆	80	36.37	5.33	11.32	7.22		36.18	5.26	11.23	7.11	
[Fe(<i>ms</i> -CRH)Br]PF ₆	80	32.89	4.76	10.23	14.64		33.17	4.79	10.31	14.72	
[Fe(<i>ms</i> -CRH)I]PF ₆	70	30.55	4.63	9.37	21.63		30.52	4.40	9.49	21.52	
[Fe(<i>ms</i> -CRH)(N ₃) ₂]	40	44.75	6.46	34.80			44.11	6.32	35.43		
[Fe(<i>ms</i> -CRH)OAc]PF ₆	40	39.08	5.56	10.72			39.25	5.91	11.12		
[Fe(<i>ms</i> -CRH)(NCS) ₂]	50	47.0	5.99	19.3			47.29	6.14	19.02		
[Fe(<i>ms</i> -CRH)Cl ₂]ClO ₄	80	36.83	5.12	11.46			36.49	5.17	10.97		
[Fe(<i>ms</i> -CRH)Cl ₂]BF ₄	80	37.80	5.35	11.76			37.88	5.38	11.58		
[Fe(<i>ms</i> -CRH)Br ₂]ClO ₄	80	31.17	4.33	9.70			31.40	4.47	9.37		
[Fe(<i>ms</i> -CRH)Br ₂]BF ₄	80	31.87	4.43	9.92			31.87	4.65	9.89		

were carried out either in a controlled-atmosphere glove box or under a blanket of nitrogen on the bench top.

Measurements. Visible and near-infrared absorption spectra were obtained on a Cary Model 14-R recording spectrophotometer. The solvents used were dry and degassed methanol, nitromethane, and acetonitrile. Solution spectra were recorded using Teflon-stoppered cells, immediately after preparation of the solutions under nitrogen, and then repeated 30 min later. For determination of extinction coefficients, weighings were made on the solids in the atmosphere and the samples were quickly transferred to the drybox where the solutions were prepared. Infrared spectra were obtained on a Perkin-Elmer Model 337 recording spectrometer using Nujol mulls between KBr disks and also using potassium bromide pellets. The conductances were determined with an Industrial Instruments Inc. conductivity bridge. The solid-state magnetic moments were determined at room temperature under 35 Torr of helium gas by the Faraday method.¹¹ The diamagnetic correction for *ms*-CRH was measured and found to be -110×10^{-6} cgsu. Diamagnetic corrections for the other ligands and counterions were made by using Pascal's constants. Elemental analyses were performed by Chemalytic's Inc. and by Galbraith Laboratories Inc. Analytical results are listed in Table I. ⁵⁷Fe Mössbauer spectra were obtained with a conventional constant-acceleration spectrometer operated in the time mode, with a ⁵⁷Co(Cu) source. Experiments were performed with both source and absorber at room temperature. The spectrometer was calibrated with a sodium nitroprusside standard; Fe₂O₃ and iron metal were employed as secondary standards. Isomer shifts and quadrupole splittings were determined by inspection with an accuracy of ± 0.01 mm/sec. The absorber thickness was normally less than 75 mg/cm² of the compound.

meso-2,12-Dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]-heptadeca-1(17),13,15-triene Monohydrate, CRH·H₂O. The free ligand was prepared from its nickel complex by the method of Melnyk.¹² The synthesis involves the preparation of [Ni(*ms*-CRH)](ClO₄)₂ by the original method.⁴ The procedure for stripping the ligand from the Ni(II) follows. Six equivalents of KCN is added to a warm (65°) aqueous solution of [Ni(*ms*-CRH)](ClO₄)₂ and the resulting solution is made very strongly alkaline with concentrated NaOH (~1 lb of solid NaOH needed for the treatment of 30 g of Ni(II) complex in 800 ml of water). Under such conditions the ligand is easily stripped from the Ni(II) ion. In the warm solution it exists as a yellowish oil which floats to the top of the solution. When left standing in an ice bath for a few hours or at room temperature overnight, the ligand solidifies to a cake and is mechanically removed from the reaction mixture. The crude solid ligand is powdered and then dissolved in Et₂O. The Et₂O solution is treated with activated carbon and filtered through a sintered-glass funnel to give a colorless Et₂O filtrate. After the evaporation of Et₂O the pure white ligand is obtained.

Fe(*ms*-CRH)X₂ (Where X = Cl, Br, or I). All syntheses of iron(II) complexes were carried out in the absence of air. Care must be taken to be sure the iron(II) salts are pure. One-hundredth mole of the appropriate anhydrous iron(II) salt was dissolved in hot absolute ethanol (50 ml). This was added to a solution containing 0.01 mol of *ms*-CRH·H₂O dissolved in absolute ethanol. The volume was reduced and the solution allowed to stand undisturbed for several hours. Crystalline materials were isolated by filtration, recrystallized from absolute ethanol, and dried *in vacuo*.

[Fe(*ms*-CRH)X]PF₆ (Where X = Cl, Br, or I). Five-tenths

millimole of the appropriate Fe(*ms*-CRH)X₂ complex was dissolved in a minimum volume of hot absolute ethanol. To the resulting yellow solution was added a filtered solution containing 1.5 g of LiPF₆ in 30 ml of absolute ethanol. The volume was reduced until cloudiness developed and the solution was allowed to stand undisturbed. Yellow crystalline products were obtained and recrystallized from absolute ethanol and dried *in vacuo*.

[Fe(*ms*-CRH)(N₃)₂]. Five-tenths millimole of Fe(*ms*-CRH)Br₂ was dissolved in hot absolute ethanol (40 ml). To this solution was added 1.5 g of NaN₃ dissolved in 30 ml of 1:1 ethanol-water mixture. The volume was reduced and the solution cooled. The solution was allowed to stand several hours undisturbed. At the end of this time, yellow-orange crystals were isolated by filtration, washed with an ethanol-ether mixture, and dried *in vacuo*.

[Fe(*ms*-CRH)(NCS)₂]. Five-tenths millimole of Fe(*ms*-CRH)Br₂ was dissolved in hot ethanol (40 ml). To this was added 1.5 g of LiSCN dissolved in 30 ml of hot absolute ethanol. The volume was reduced and the solution was cooled. Deep brown crystals of the product precipitated; the product was isolated by filtration, washed with an ethanol-ether mixture, and dried *in vacuo*.

[Fe(*ms*-CRH)X₂]Y (Where X = Cl or Br and Y = ClO₄⁻ or BF₄⁻). One millimole of the appropriate Fe(*ms*-CRH)X₂ complex was dissolved under nitrogen in warm (40°) absolute ethanol. To the yellow solution was added 0.5 ml of concentrated HY dropwise. Air was then bubbled through the yellow solution for several minutes. An immediate color change was observed. The chloride-containing solution became a deeper yellow, while that containing bromide became a deep red. Allowing the solutions to cool slowly gave crystalline products, which were filtered, washed with an ethanol-ether mixture, and dried *in vacuo*.

[Fe(*ms*-CRH)OAc]PF₆. *ms*-CRH·H₂O (3.6 mmol) was dissolved in 100 ml of hot absolute ethanol and 3.6 mmol of anhydrous ferrous acetate was added to the solution. The solution turned green and 2.0 g of NH₄PF₆ was added. After heating for an additional hour, the solution was filtered. The volume of the filtrate was reduced to 25 ml and the filtrate was allowed to stand undisturbed for several hours. A green crystalline product was obtained and recrystallized from absolute ethanol and dried *in vacuo*.

Results and Discussion

The nickel(II),⁴ cobalt(III),⁵ and copper(II)⁶ complexes with the ligand *ms*-CRH have been extensively studied. Previous work has shown that this ligand can act as a tetradentate chelate in two ways, with all four nitrogens in a single plane or with the folded CRH occupying four adjacent sites, leaving two cis sites for other ligands. In the cases of the nickel and copper complexes only the planar mode of coordination has been observed, but for cobalt(III) both the *cis*- and *trans*-diacido complexes have been characterized.^{5,7} These earlier observations have greatly facilitated the stereochemical assignments for the newly synthesized complexes of iron. In all cases except one, it is assumed that the additional ligand or ligands occupy axial sites with the iron atom positioned within or elevated slightly out of the plane defined by the four donor atoms of the macrocycle.

The synthesis of these iron complexes is complicated by the fact that iron(II) has an extreme tendency to react with water

Table II. Some Physical Properties of $\text{Fe}(\text{ms-CRH})^{2+}$ $\text{Fe}(\text{ms-CRH})^{3+}$ Complexes

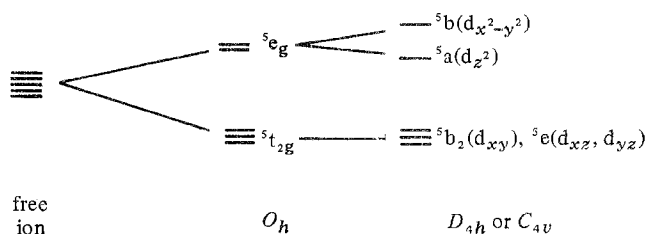
Compd	Color	μ_{eff}^a	ΔM^b		N-H str ^d	C=N str ^d
			Me-OH	Me-NO ₂ ^c		
$[\text{Fe}(\text{ms-CRH})\text{Cl}]\text{Cl}$	Yellow	5.20	110	66	3215 3155	1597 1575
$[\text{Fe}(\text{ms-CRH})\text{Br}]\text{Br}$	Yellow	5.11	107	68	3215 3185	1597 1575
$[\text{Fe}(\text{ms-CRH})\text{I}]\text{I}$	Yellow	5.05	114	55	3185 3155	1597 1575
$[\text{Fe}(\text{ms-CRH})\text{Cl}]\text{PF}_6$	Yellow	4.95	86.3	3290	1590	
$[\text{Fe}(\text{ms-CRH})\text{Br}]\text{PF}_6$	Yellow	5.11	89.5	3279	1560	
$[\text{Fe}(\text{ms-CRH})\text{I}]\text{PF}_6$	Yellow	5.20	88.4	3265	1590	
$[\text{Fe}(\text{ms-CRH})(\text{N}_3)_2]$	Orange	5.50	50	3236	1597 1580	
$[\text{Fe}(\text{ms-CRH})\text{OAc}]\text{PF}_6$	Green	5.11	94	75	3279 3175	1600 br
$[\text{Fe}(\text{ms-CRH})(\text{NCS})_2]$	Red-black	0.8	27	3195	1597 1575	
$[\text{Fe}(\text{ms-CRH})\text{Cl}_2]\text{ClO}_4$	Yellow	5.79	119	3226	1603 1580	
$[\text{Fe}(\text{ms-CRH})\text{Cl}_2]\text{BF}_4$	Yellow	5.85	103	3241	1605 1580	
$[\text{Fe}(\text{ms-CRH})\text{Br}_2]\text{ClO}_4$	Red	5.76	117	3216	1605 1580	
$[\text{Fe}(\text{ms-CRH})\text{Br}_2]\text{BF}_4$	Red	5.73	116	3215	1605 1580	

^a At 25°; units BM. ^b All solutions $\sim 10^{-3} M$; units $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$. ^c Molar conductance obtained in purified MeNO_2 under N_2 atmosphere. ^d Units cm^{-1} .

to form hydrous oxides. In addition, the solutions of all of these complexes are very sensitive to air as evidenced by immediate color changes upon exposure. This sensitivity to both water and oxygen lowers the yields and gives rise to impure materials with spuriously high magnetic susceptibilities unless much care is exercised during synthesis and purification of the products. On the other hand, the dry solids are stable in the air for periods of several hours. Analyses and yields are reported in Table I.

The infrared spectra of these complexes (Table II) show the presence of the unaltered ligand in each case. The N-H stretching mode appears as a sharp doublet in all cases, while the characteristic doublet due to the pyridine ring changes slightly from complex to complex. However, neither the N-H nor the pyridine doublet appears to depend in a regular way on oxidation state, spin state, or the coordination number of the iron atom.

The Iron(II) Complexes. The infrared spectrum of the complex $[\text{Fe}(\text{ms-CRH})(\text{NCS})_2]$ has a strong doublet at 2101 and 2114 cm^{-1} ($\text{C}\equiv\text{N}$, str) and a doublet of moderate intensity at 815 and 801 cm^{-1} ($\text{C}-\text{S}$ str), that are typical of N-bonded thiocyanate.¹³ The magnetic susceptibilities of the dithiocyanate derivative (Table II) show it to be low spin and its residual moment of 0.8 BM is only slightly greater than is normally found for temperature-independent paramagnetism in low-spin d^6 systems.¹⁴ The low electrolyte molar conductivity (Table II) of the dithiocyanato derivative supports six-coordination for this complex. The electronic spectrum of the dithiocyanato derivative exhibits bands at 15.6 and 20.4 kK in the mull spectrum, while only one band at 21.5 kK appears in its chloroform solution spectrum. The low-energy band in the mull spectrum is weak and attempts to observe it using very concentrated solutions were unsuccessful. While low-spin d^6 metal ion spectra have been studied extensively for cobalt(III)¹⁵ and for some iron(II) complexes,¹⁶ attempts to apply these results in order to assign the band (or bands) and determine ligand field parameters is not justified here.

Chart I. Tetragonal Splitting Pattern for High-Spin Iron(II)

Two high-spin six-coordinate iron(II) derivatives are found among the complexes of the subject ligand. The diazido- and the monoacetato complexes both have magnetic susceptibility values (Table II) typical of high-spin iron(II). The conductivity of the diazido complex has a particularly high value in nitromethane (50 mhos) for a nonelectrolyte.¹⁷ This suggests that a solvolysis equilibrium occurs wherein one anion is either displaced by solvent or lost outright to produce a mixture of five-coordinate and six-coordinate structures. The $[\text{Fe}(\text{ms-CRH})\text{OAc}]\text{PF}_6$ complex has a magnetic moment of 5.11 BM, somewhat lower than that for the diazido complex, and the monoacetato complex also behaves as a univalent electrolyte in nitromethane, as expected. This is consistent with the assumption that the acetate is coordinated in a bidentate fashion, forcing the ligand into a folded conformation. Both of these compounds exhibit a broad "d-d" band in the region 10,000–11,500 cm^{-1} . This band shows none of the splitting which is expected for high-spin iron(II) in ligand fields of less than O_h symmetry. It is assumed that this transition is due to a $5T_{2g} \rightarrow 5E_g$ transition and that the broadness of the band is due to some splitting of the $5E_g$ excited state. It is reasonable to suggest that the anions are coordinated to the iron(II) above and below the plane defined by the metal and the macrocyclic ligand in $[\text{Fe}(\text{ms-CRH})(\text{N}_3)_2]$, whereas the $[\text{Fe}(\text{ms-CRH})\text{OAc}]\text{PF}_6$ complex is presumed to have a cis structure. Examples of such structures are well known.^{5,7,14} These structural assignments are supported by the Mössbauer spectra for the two materials (*vide infra*).

The complexes $\text{Fe}(\text{ms-CRH})\text{X}_2$ and $[\text{Fe}(\text{ms-CRH})\text{X}]\text{PF}_6$, where X is a halide ion, are all pale yellow crystalline solids. The dihalo complexes exhibit molar conductances in nitromethane which are slightly lower than is normal for uni-univalent electrolytes, whereas the halo-hexafluorophosphate complexes all exhibit molar conductance values that are typical of uni-univalent electrolytes and this is consistent with their formulation as containing five-coordinate complexes. The low conductances for the dihalo complexes in nitromethane may be indicative of ion pairing in solution and do not confirm either five- or six-coordination. The molar conductance values for the dihalo complexes in methanol are typical of uni-univalent electrolytes but are not indicative of five-coordination, since the six-coordinate species $[\text{Fe}(\text{ms-CRH})(\text{MeOH})\text{X}]^+$ could exist.

The solid-state magnetic moments of these complexes are all in the range 4.95–5.23 BM (the spin-only value for high-spin iron(III) is 4.90 BM). These values are consistently lower than that of the six-coordinate *trans*-diazido complex ($\mu_{\text{eff}} = 5.50$ BM). The consistently lower magnetic moments are consistent with five-coordination in the solid state for these six complexes. The presence of only one axial ligand in a square-pyramidal coordination sphere would generate a greater splitting of the $5T_2$ state (of O_h parentage),¹⁸ thereby reducing the orbital contribution to μ_{eff} .

The electronic spectra of the complexes $\text{Fe}(\text{ms-CRH})\text{X}_2$ reveal a broad transition at 10.7–11.3 kK. No "d-d" absorptions were observed at lower energies in either methanol solution or solid mulls. The spectra of the complexes $[\text{Fe}(\text{ms-CRH})\text{X}]\text{PF}_6$ exhibit two broad weak "d-d" transitions

Table III. Electronic Spectra $\text{Fe}^{\text{II,III}}(\text{ms-CRH})\text{X}_n^{m+}$ Complexes

Compd	"d-d" bands, ^a kK	Charge transfer, kK
[Fe(<i>ms</i> -CRH)Cl]Cl	10.7 ^b (6) 11.3 ^c	31.0 sh
[Fe(<i>ms</i> -CRH)Br]Br	10.7 ^b (6) 11.3 ^c	26.4 sh
[Fe(<i>ms</i> -CRH)I]I	11.3 ^b (7) 11.4 ^c	27.8 sh
[Fe(<i>ms</i> -CRH)Cl]PF ₆	10.8 ^d (4) ~4.9 (~3)	
[Fe(<i>ms</i> -CRH)Br]PF ₆	11.0 ^d (5) ~4.5 (~4)	
[Fe(<i>ms</i> -CRH)I]PF ₆	11.4 ^d (5) ~4.2 (~5)	
[Fe(<i>ms</i> -CRH)(N ₃) ₂]	11.7 ^d (55)	
[Fe(<i>ms</i> -CRH)OAc]PF ₆	11.6 ^b (10)	18.5 sh
[Fe(<i>ms</i> -CRH)(NCS) ₂]	21.5 ^e (190) 15.6, ^c 20.4 ^c	
[Fe(<i>ms</i> -CRH)Cl ₂]ClO ₄		30.7 (2050)
[Fe(<i>ms</i> -CRH)Cl ₂]BF ₄		30.7 (2180)
[Fe(<i>ms</i> -CRH)Br ₂]ClO ₄		30.7 (2000)
[Fe(<i>ms</i> -CRH)Br ₂]BF ₄		30.7 (1800)

^a Numbers in parentheses are extinction coefficients. ^b Methanol solution. ^c Solid-state spectra in Nujol mull. ^d Nitromethane solution. ^e Chloroform solution.

near 5.0 and 11.0 kK with molar extinction coefficients on the order of 5 (Table III). These two absorption bands are assigned to transitions to the ⁵A₁ and ⁵B₁ states derived from the splitting of the ⁵E spectroscopic term in a tetragonal ligand field (Chart I).

The position of the low-energy band is dependent upon the axial ligand field strength, while the higher energy band is primarily dependent upon the constant "in-plane" macrocyclic ligand field. The spectra of the haloheptafluorophosphate series are compatible with the presumed five-coordination. Their spectra show a splitting of the ⁵E state on the order of 6–7 kK, while the separation of ⁵B₁ and ⁵A₁ states in known six-coordinate tetragonal iron(II) complexes is usually of the order of 3.0 kK.¹⁹ The presence of a single axial ligand would lead to a larger expected splitting of the ⁵E state than that of the usual six-coordinate tetragonal complexes and this has been observed in a related series of complexes.²⁰

The Iron(III) Complexes. The iron(III) complexes of *ms*-CRH were synthesized from previously prepared iron(II) complexes. The appropriate iron(II) complex is dissolved in a minimum amount of dry, oxygen-free ethanol under an inert atmosphere; acid is added and oxidation is achieved by bubbling air through the solution. The crystalline dichloro (yellow) and dibromo complexes (red) are stable in air and soluble in a number of common polar solvents. They have the high-spin electronic configuration, as evidenced by their magnetic moments (5.7–5.9 BM, Table II). In methanol they are uni-univalent electrolytes. This is consistent with their formulation as six-coordinate cationic species [Fe(*ms*-CRH)X₂]⁺.

Mössbauer Spectra. In Table IV are listed the Mössbauer parameters for some of the new iron complexes. The isomer shift values (δ), which are sensitive to both the oxidation state and the spin state of the iron,²¹ were found to be in agreement with the structural assignments made on the basis of the magnetic susceptibility, conductivity, and electronic spectral data. The second parameter listed is the quadrupole splitting (ΔE_q). The ΔE_q values of a number of the complexes have been very useful in the determination of their structures in the solid state. For transition metal complexes there are two factors which contribute to ΔE_q : (a) the dissymmetry of the electron density about the nucleus and (b) the dissymmetry of the ligand field. Hence, the more nonspherical the electron density and/or the greater the ligand field dissymmetry, the larger the

Table IV. Mössbauer Spectra of Iron-*ms*-CRH Complexes

Compd	Spin state <i>S</i>	δ , ^a mm/sec	ΔE_q ,
			mm/sec
[Fe(<i>ms</i> -CRH)Cl]Cl ^b	2	1.11	3.72
[Fe(<i>ms</i> -CRH)Br]Br ^b	2	1.12	3.84
[Fe(<i>ms</i> -CRH)I]I ^b	2	1.08	3.84
[Fe(<i>ms</i> -CRH)Cl]PF ₆	2	1.075	3.85
[Fe(<i>ms</i> -CRH)Br]PF ₆	2	1.063	3.91
[Fe(<i>ms</i> -CRH)I]PF ₆	2	1.051	3.77
[Fe(<i>ms</i> -CRH)(N ₃) ₂]	2	1.24	1.68
[Fe(<i>ms</i> -CRH)OAc]PF ₆	2	1.19	2.40
[Fe(<i>ms</i> -CRH)(NCS) ₂]	0	0.71	0.67
[Fe(<i>ms</i> -CRH)Cl ₂]BF ₄	⁵ / ₂	0.59	0.66
[Fe(<i>ms</i> -CRH)Br ₂]BF ₄	⁵ / ₂	0.61	0.55

^a All values with respect to sodium nitroprusside. ^b From ref 23.

quadrupole splitting, provided the two contributions have like signs.²²

For the complexes [Fe(*ms*-CRH)X]PF₆, characterization as five-coordinate high-spin iron(II) derivatives is confirmed by the ΔE_q values. These are in the range 3.77–3.91 mm/sec, which is characteristic of five-coordinate high-spin iron(II), as demonstrated for [Fe(*ms*-CRH)X]X and broad series of related complexes in a previous communication.⁸ For comparison normal high-spin six-coordinate iron(II) compounds have ΔE_q values in the range from 1.7 to 3.0 mm/sec,²³ and those of so-called ionic salts range from 2.5 to 3.5 mm/sec.²⁴ The large ΔE_q values for the five-coordinate complexes are assumed to be caused by large contributions of like sign from both the nonspherical electron distribution and the ligand field dissymmetry. The contribution to ΔE_q from the dissymmetry of the d-electron population will depend on the nature of the ground state. Under a tetragonal distortion the ⁵T₂ state (*O_h*) is split into ⁵B₂ and ⁵E states. The magnitudes of the contributions to ΔE_q from a 3d electron in either a ⁵B₂ or ⁵E ground state are equal, but the electric field gradients associated with the two states are of opposite signs. The magnetically perturbed Mössbauer spectrum of a five-coordinate high-spin iron(II) complex,²⁵ [Fe(1,7-CT)Cl]ClO₄ (1,7-CT = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1(14),7-diene), has recently been reported. The results of this study imply that the ground state is the ⁵B₂, contrary to the ordering of the one-electron d orbitals expected from crystal field theory for both the square-pyramidal and the trigonal-bipyramidal geometries. From this result, it is assumed that the structurally analogous high-spin five-coordinate complexes [Fe(*ms*-CRH)X]X and [Fe(*ms*-CRH)X]PF₆ also have a ⁵B₂ ground state.

The ΔE_q values were unambiguously indicative of five-coordination in the solid state for a number of these new complexes that were otherwise difficult to characterize with regard to structure and coordination number. For example, the haloalide derivatives were practically insoluble in the weak donor solvent nitromethane; as a result, their conductivities were inconclusive with regard to coordination number.

The [Fe(*ms*-CRH)OAc]PF₆ derivative provides another example for which the Mössbauer results are extremely useful. The ΔE_q value (2.40 mm/sec) is too low for the compound to be five-coordinate but is in the range normally found for high-spin six-coordinate iron(II).^{21,23} Thus, the Mössbauer data and molar conductivity provide evidence for a six-coordinate complex containing a tetradentate folded macrocyclic ligand and a bidentate acetate.

The ΔE_q values for the remaining two six-coordinate iron(II) complexes and the two six-coordinate iron(III) complexes are all consistent with the assignments made based on magnetic susceptibilities, conductivities, and electronic spectra. The ΔE_q value for high-spin pseudooctahedral [Fe(*ms*-CRH)(N₃)₂] (1.68 mm/sec) is considerably smaller than those for the high-spin five-coordinate complexes and is typical of that of

a high-spin six-coordinate iron(II) derivative. The ΔE_q for low-spin pseudooctahedral $[\text{Fe}(ms\text{-CRH})(\text{NCS})_2]$ (0.67 mm/sec) is typical of low-spin iron(II) derivatives,^{21,23} the low ΔE_q value resulting from the spherically symmetric filled t_{2g} (O_h) orbitals. For the high-spin iron(III) derivatives $[\text{Fe}(ms\text{-CRH})X_2]\text{BF}_4$ the ΔE_q values are typically small^{21,23} because of the spherical symmetry of the half-filled 3d shell.

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Registry No. $[\text{Fe}(ms\text{-CRH})\text{Cl}]\text{Cl}$, 31122-39-1; $[\text{Fe}(ms\text{-CRH})\text{Br}]\text{Br}$, 31122-40-4; $[\text{Fe}(ms\text{-CRH})\text{I}]\text{I}$, 31122-41-5; $[\text{Fe}(ms\text{-CRH})\text{Cl}]\text{PF}_6$, 53537-54-5; $[\text{Fe}(ms\text{-CRH})\text{Br}]\text{PF}_6$, 53537-56-7; $[\text{Fe}(ms\text{-CRH})\text{I}]\text{PF}_6$, 53537-58-9; $[\text{Fe}(ms\text{-CRH})(\text{N}_3)_2]$, 53432-27-2; $[\text{Fe}(ms\text{-CRH})\text{OAc}]\text{PF}_6$, 53432-29-4; $[\text{Fe}(ms\text{-CRH})(\text{NCS})_2]$, 53432-30-7; $[\text{Fe}(ms\text{-CRH})\text{Cl}_2]\text{ClO}_4$, 53466-54-9; $[\text{Fe}(ms\text{-CRH})\text{Cl}_2]\text{BF}_4$, 53466-55-0; $[\text{Fe}(ms\text{-CRH})\text{Br}_2]\text{ClO}_4$, 53466-57-2; $[\text{Fe}(ms\text{-CRH})\text{Br}_2]\text{BF}_4$, 53466-58-3; $[\text{Ni}(ms\text{-CRH})](\text{ClO}_4)_2$, 53537-60-3.

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Interaction of Ethylenediaminetetraacetatocobaltate(II) with Ferricyanide and Monosubstituted Ferricyanide Ions. I. $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_5\text{P}(\text{C}_6\text{H}_5)_3^{2-}$

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A deep purple cyanide-bridged intermediate is formed between $\text{Co}^{\text{II}}\text{EDTA}$ and either $\text{Fe}(\text{CN})_6^{3-}$ or $\text{Fe}(\text{CN})_5\text{P}(\text{C}_6\text{H}_5)_3^{2-}$. The equilibrium and rate constants for the formation of the intermediate and the rate constant for the decomposition of the intermediate at 30°, pH 6.00 ($\text{EDTA}-\text{NaOH}$), and $I = 0.26 M$ ($\text{EDTA}-\text{NaClO}_4$) are $201 M^{-1}$, $3.8 \times 10^4 M^{-1} \text{sec}^{-1}$, and $1.74 \times 10^{-2} \text{sec}^{-1}$ for $\text{Fe}(\text{CN})_6^{3-}$ and $1,490 M^{-1}$, $2.0 \times 10^4 M^{-1} \text{sec}^{-1}$, and $2.10 \times 10^{-3} \text{sec}^{-1}$ for $\text{Fe}(\text{CN})_5\text{P}(\text{C}_6\text{H}_5)_3^{2-}$. Activation parameters and thermodynamic data are also reported. The results indicate that the charge and size of the substituent group and the net driving force all influence the stability and rate of formation of the intermediates in these reactions.

The first example of the inner-sphere reaction of a cobalt(II)-chelate complex was reported by Adamson and Gonick¹ in 1963. A purple intermediate was observed in the oxidation of ethylenediaminetetraacetatocobaltate(II), $\text{Co}^{\text{II}}\text{EDTA}$, with hexacyanoferrate(III), $\text{Fe}(\text{CN})_6^{3-}$. On the basis of magnetic and spectrophotometric measurements, it was concluded that the intermediate was the bridged-binuclear successor complex, viz., a $\text{Co}^{\text{III}}-\text{NC}-\text{Fe}^{\text{II}}$ species. This intermediate was shown to decompose slowly to the products of the reaction, $\text{Co}^{\text{III}}\text{EDTA}$ and $\text{Fe}(\text{CN})_6^{4-}$.

Huchital and Wilkins² later reported results for the formation of the intermediate in this reaction using the more sophisticated stopped-flow and T-jump techniques. These workers found that a second intermediate could form via the oxidation of the first intermediate by excess $\text{Fe}(\text{CN})_6^{3-}$, producing a $\text{Co}^{\text{III}}-\text{NC}-\text{Fe}^{\text{III}}$ species. The rate of formation of this intermediate was about 50-100 times slower than for the first intermediate. More recently Huchital and coworkers³ extended these studies to other cobalt(II)-chelate systems. Rate and equilibria data were discussed with regard to the

stereochemistry of the chelate and the effects of substitution on the chelate ring on the stability of the intermediate.

In order to understand more fully the factors at play in these redox reactions, we have investigated the oxidation reactions of $\text{Co}^{\text{II}}\text{EDTA}$ in which the oxidants are a monosubstituted ferricyanide ion, $\text{Fe}(\text{CN})_5\text{X}^{2-}$. The cases in which X is NH_3 , H_2O , and $\text{P}(\text{C}_6\text{H}_5)_3$ have been examined. Of primary interest here are the effects of the charge and size of the substituent group and the number of cyano groups available for bridge formation. We report here on the oxidation of $\text{Co}^{\text{II}}\text{EDTA}$ by $\text{Fe}(\text{CN})_5\text{P}(\text{C}_6\text{H}_5)_3^{2-}$ at $I \approx 0.26 M$ and pH 6.00. Results are also presented for the $\text{Co}^{\text{II}}\text{EDTA}$ reaction with ferricyanide ion, reexamined under the above solution conditions.

Experimental Section

Materials. NaClO_4 (BDH Chemicals), $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{Co}(\text{N}_3)_2 \cdot 6\text{H}_2\text{O}$ (Baker and Adamson), NaOH (Corco Chemicals), and $\text{Na}_2\text{H}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$ (Fisher) were all reagent grade chemicals and were used without further purification. $\text{Na}_2\text{Fe}(\text{CN})_5\text{P}(\text{C}_6\text{H}_5)_3$ was prepared as the dihydrate by the method of Nast and Krieger.⁴ The results of the atomic absorption analysis for iron content and the