Synthesis and Characterization of Iron and Cobalt Clathrochelate Complexes Derived from Oxime–Hydrazone Ligands

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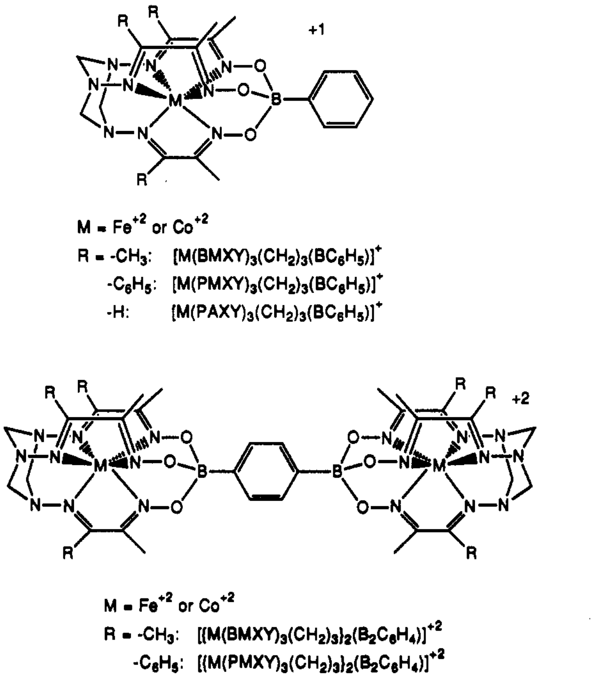
The synthesis of an extended series of mononuclear and binuclear iron complexes based on oxime–hydrazone ligands is reported. In addition, the syntheses of the first examples of cobalt clathrochelate complexes utilizing oxime–hydrazone ligands are presented. The structures of the new complexes are established through elemental analysis and NMR spectral characterization. Cyclic voltammetric and electrolytic studies illustrate that the oxidation of the iron to the +3 state does not produce a stable complex; however, the cobalt complexes are shown to be stable in both the +2 and the +3 oxidation states. Electrochemical studies of the binuclear complexes indicate that the two metal centers are effectively separated from one another and are noninteractive.

Introduction

Clathrochelate complexes, metal complexes in which the metal ion is completely encapsulated in a ligand cage, have proven to be valuable reagents in studies which examine outer sphere electron transfers.[1-11] Other investigators have begun to explore the use of these substitution inert complexes as electrocatalytic mediators.[12,13] Since many important chemical and biochemical processes involve multiple electron transfers, we have been investigating synthetic routes to clathrochelate systems which contain more than one metal ion.[14,15]

Numerous approaches have been taken to incorporate multiple metal sites into a clathrochelate-based molecule. Hendrickson, Gagne, Sinn, and co-workers[16,17] have developed a clathrochelate system in which two metal ions are encapsulated within a single ligand cage derived from the condensation of 2 mol of 2,2′,2″-triaminotriethylamine and three moles of 2-hydroxy-5-methylisophthalaldehyde. Drago and Elias[18] and Chaudhuri and co-workers[19] have utilized tris(dioximato) complexes as bridging ligands which are "capped" by metal complexes to produce trinuclear species in which the central metal ion is encapsulated.



M = Fe^{+2} or Co^{+2}
R = $-CH_3$: $[M(BMXY)_3(CH_2)_3(BC_6H_5)]^+$
$-C_6H_5$: $[M(PMXY)_3(CH_2)_3(BC_6H_5)]^+$
$-H$: $[M(PAXY)_3(CH_2)_3(BC_6H_5)]^+$

M = Fe^{+2} or Co^{+2}
R = $-CH_3$: $[\{M(BMXY)_3(CH_2)_3\}_2(B_2C_6H_4)]^{+2}$
$-C_6H_5$: $[\{M(PMXY)_3(CH_2)_3\}_2(B_2C_6H_4)]^{+2}$

Figure 1. Schematic representations of the complexes and shorthand notation used in the text.

Similarly, iron and cobalt tris(dioximato) complexes which are capped by tin chloride groups have been studied by Rose and Boston[20] and Voloshin and co-workers.[21,22] Wherland and co-workers[23] have synthesized a tris(dioximato)cobalt clathrochelate which is capped by ferrocenylboronate groups thereby producing a trimetallic complex.

The focus of this paper is to discuss a series of clathrochelate complexes which is based on an oxime–hydrazone ligand system.[14,15] This clathrochelate system utilizes the boronic acid/oxime capping reaction developed by Rose and co-workers[24,25]

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and the formaldehyde/hydrazone capping reaction pioneered by Goedken and co-workers[26,27] in a two-step reaction sequence. A two-step approach allows a diboronic acid capping group to be used to link two clathrochelate complexes covalently while avoiding the formation of polymeric side products.

Experimental Section

Materials. The 2,3-butanedione oxime hydrazone (BMXY) was prepared by the reaction of 2,3-butanedione monoxime (Aldrich) with an excess of hydrazine hydrate in ethanol as described previously.[28] The 1-phenyl-1,2-propanedione 2-oxime 1-hydrazone (PMXY) was prepared by utilizing 1-phenyl-1,2-propanedione 2-oxime (Alrich) in the reaction with hydrazine hydrate. The pyruvic aldehyde 1-oxime 2-hydrazone (PAXY) was prepard in a similar fashion by beginning with pyruvic aldehyde 1-oxime.[29] Benzene-1,4-diboronic acid was prepared as described previously.[30] All other reagents were obtained commercially ($FeBr_2$, Strem; all others, Aldrich Chemical Co.) and used as received.

The preparations of [phenyl[[3,3′,3″-(*s*-triazine-1,3,5(2*H*,4*H*,6*H*)-triyltrinitrilo)tris(2-butanone) trioximato](3−)-$O^2,O^{2'},O^{2''}$]borato(1−)]-iron(1+) hexafluorophosphate(1−), $[Fe(BMXY)_3(BC_6H_5)(CH_2)_3]PF_6$, and [*μ*-[*μ*-*p*-phenylenebis[[3,3′,3″-(*s*-triazine-1,3,5(2*H*,4*H*,6*H*)-triyltrinitrilo)tris(2-butanone) trioximato](3−)-$O^2,O^{2'},O^{2''}$]diborato(2−)]]diiron(2+) bis[hexafluorophosphate(−1)], $[\{Fe(BMXY)_3(CH_2)_3\}_2B_2C_6H_4](PF_6)_2$ have been described previously.[14]

[Phenyl[[1,1′,1″-(*s*-triazine-1,3,5(2*H*,4*H*,6*H*)-triyltrinitrilo)tris(1-phenyl-2-propanone) trioximato](3−)-$O^2,O^{2'},O^{2''}$]borato(1−)]iron(1+) Hexafluorophosphate(1−), $[Fe(PMXY)_3(BC_6H_5)(CH_2)_3]PF_6\cdot H_2O$. A 0.76-g sample (4,3 mmol) of 1-phenyl-1,2-propanedione 2-oxime 1-hydrazone (PMXY) was dissolved/suspended in 50 mL of absolute ethanol, and the mixture was outgassed with nitrogen. A 0.31-g (1.4-mmol) sample of ferrous bromide was added. The mixture was stirred under nitrogen until a brown solution was produced. The brown solution was treated with 0.18 g (1.4 mmol) of phenylboric acid and stirred for an additional 2 h. The air-stable orange solid which precipitated was filtered *via* suction and washed with ethanol followed by ethyl ether. The yield of partially capped intermediate, $[Fe(PMXY)_3BC_6H_5]Br$, was 0.82 g (78%).

The entire yield of partially capped intermediate was suspended in 50 mL of acetonitrile and treated with 4 mL (12-fold excess) of a formaldehyde solution (37% in H_2O) followed by one drop of concentrated hexafluorophosphoric acid (60% in H_2O). The dark purple solution was stirred for 18 h. A 1.0-g sample of ammonium hexafluorophosphate in 25 mL of ethanol was added and the mixture was rotary evaporated to near dryness. The residue was redissolved in a minimum of acetonitrle and passed down a neutral alumina column (Brockmann activity III) using 1/1 acetonitrile/methylene chloride as the eluent. The first purple band to elute was collected, rotary evaporated to one-half its volume and treated with 30 mL of a 1/1 ethanol/water mixture. Further rotary evaporation yielded a crystalline product which was filtered *via* suction, washed with water, and dried *in vacuo* at 78 °C. Yield: 0.55 g (46%; overall). Anal. Calcd for $C_{36}H_{37}N_9O_4BFePF_6$: C, 49.62; H, 4.27; N, 14.47. Found: C, 49.96; H, 4.15; N, 14.53.

[*μ*-[*μ*-*p*-[Phenylenebis[[1,1′,1″-(*s*-triazine-1,3,5(2*H*,4*H*,6*H*)-triyltrinitrilo)tris(1-phenyl-2-propanone) trioximato](3−)-$O^2,O^{2'},O^{2''}$]diborato-(2−)]]diiron(2+) Bis[hexafluorophosphate(1−)], $[\{Fe(PMXY)_3(CH_2)_3\}_2(B_2C_6H_4)](PF_6)_2\cdot 2H_2O$. A 0.76-g sample (4.3 mmol) of 1-phenyl-1,2-propanedione 2-oxime 1-hydrazone (PMXY) was dissolved/suspended in 50 mL of absolute ethanol. After the mixture was outgassed with nitrogen, 0.31 g (1.4 mmol) of ferrous bromide was added. As the ferrous bromide dissolved an orange-brown suspension was produced. A 0.12-g sample (0.7 mmol) of benzene-1,4-dibonoic acid was added to the mixture, and the mixture was stirred for 2 h while the nitrogen atmosphere was maintained. The orange solid was filtered *via* suction and washed with a small portion of ethanol followed by ethyl ether. The yield of partially capped complex, $[\{Fe(PMXY)_3\}_2B_2C_6H_4](Br)_2$, was 1.0 g (97%).

The entire yield of $[\{Fe(PMXY)_3\}_2B_2C_6H_4](Br)_2$ was suspended in 50 mL of acetonitrile, and the suspension was treated with 5 mL (15-fold excess) of a formaldehyde solution (37% in H_2O). One drop of concentrated hexafluorophosphoric acid (60% in H_2O) was added as a catalyst. The resulting dark purple solution was stirred for 15 h. The solution was treated with 1.0 g (6.1 mmol) of ammonium hexafluorophosphate in 25 mL of ethanol, and the mixture was rotary evaporated to near dryness. The residue was dissolved in a minimum of acetonitrile and passed down a neutral alumina column (Brockmann activity III) using 1/1 methylene chloride/acetonitrile as the eluent. The first purple band to elute was collected and rotary evaporated to half its original volume. The solution was treated with 15 mL of a 1/1 ethanol/water mixture and rotary evaporated. The dark purple crystalline product was filtered *via* suction, washed with a small amount of ethanol followed by ethyl ether, and dried *in vacuo* at 78 °C. Yield: 250 mg (21%; overall). Anal. Calcd for $C_{66}H_{68}N_{18}O_8B_2Fe_2P_2F_6$: C, 47.62; H, 4.12; N, 15.15. Found: C, 47.63; H, 4.12; N, 14.81.

[Phenyl[[1,1′,1″-(*s*-triazine-1,3,5(2*H*,4*H*,6*H*)-triyltrinitrilo)tris(2-propanone) trioximato](3−)-$O^2,O^{2'},O^{2''}$]borato(1−)]iron(1+) Hexafluorophosphate(1−), $[Fe(PAXY)_3(BC_6H_5)(CH_2)_3]PF_6$. A 0.50-g sample (5.0 mmol) of pyruvic aldehyde 1-oxime 2-hydrazone (PAXY) was dissolved in 25 mL of absolute ethanol, and the solution was outgassed with nitrogen. A 0.35-g (1.6-mmol) sample of ferrous bromide, followed by 0.20 g (1.6 mmol) of phenylboric acid, was added to the outgassed solution. As the phenylboric acid dissolved in air-stable red-orange crystalline product formed. The monocapped intermediate, $[Fe(PAXY)_3(BC_6H_5)]Br$, was filtered *via* suction and washed with a small amount of ethanol followed by ethyl ether. Yield: 0.45 g (52%).

A 0.45-g sample of the intermediate was dissolved/suspended in 25 mL of acetonitrile and treated with 2 mL (10-fold excess) of a formaldehyde solution (37% in H_2O). One drop of concentrated hexafluorophosphoric acid was added as a catalyst. The dark red solution which developed was filtered *via* gravity, and the filtrate was treated with 0.5 g (3.0 mmol) of ammonium hexafluorophosphate in 10 mL of ethanol. The mixture was rotary evaporated to half its original volume and treated with 20 mL of a 1/1 ethanol/water mixture. Further rotary evaporation produced a red crystalline solid which was filtered *via* suction, washed with a small amount of ethanol followed by ethyl ether, and dried *in vacuo* at 78 °C. Yield: 280 mg (27%; overall). Anal. Calcd for $C_{18}H_{23}N_9O_3FeBPF_6$: C, 34.58; H, 3.71; N, 20.17. Found: C, 34.68; H, 3.73; N, 20.25.

[Phenyl[[3,3′,3″-(*s*-triazine-1,3,5(2*H*,4*H*,6*H*)-triyltrinitrilo)tris(2-butanone) trioximato](3−)-$O^2,O^{2'},O^{2''}$]borato(1−)]cobalt(1+) Tetrafluoroborate(1−), $[Co(BMXY)_3(BC_6H_5)(CH_2)_3]BF_4\cdot H_2O$. A 1.00 g (8.7 mmol) sample of 2,3-butanedione 2-hydrazone 3-oxime (BMXY) was dissolved/suspended in 25 mL of acetonitrile, and the mixture was outgassed with nitrogen. A 0.38-g (2.9-mmol) sample of anhydrous cobalt(II) chloride was added, and the mixture was stirred under nitrogen until the cobalt chloride dissolved. At this point a 0.36-g (2.9-mmol) sample of phenylboric acid was added, and the mixture was stirred for 2 h, producing a brown/orange solution/suspension as the phenylboric acid dissolved. The suspension was treated with 3 mL (approximately a 4-fold excess) of a formaldehyde solution (37% in water) which had been outgassed with nitrogen and was stirred for an additional 2 h. The reaction mixture was exposed to the air, and the mildly air-sensitive purple crystals were filtered via suction and washed with a small amount of ethanol followed by ethyl ether. The entire yield was dissolved in a minimum amount of methanol under a blanket of nitrogen and treated with 2.5 g (7.6 mmol; approximately a 3-fold excess) of tetrabutylammonium tetrafluoroborate in 50 mL of methanol. The mixture was rotary evaporated to yield a dark purple crystalline solid. The solid was filtered *via* suction and washed with a small amount of methanol followed by ethyl ether. To obtain analytically pure samples the complex was purified further by column chromatography. The purple solid was dissolved in a minimum of acetonitrile and was passed down a neutral alumina column (Brockmann activity III) using 1/1 (V/V) acetonitrile/methylene chloride as the eluent. The initial purple band to elute was collected, rotary evaporated to half its initial volume, and treated with ethanol (added in a 1/1 ratio to the remaining solution). Continued rotary evaporation produced a purple crystalline solid, which was collected *via* suction filtration, washed with a small volume of absolute ethanol followed by ethyl ether, dried *in vacuo* at 78 °C, and stored under nitrogen. Yield: 140 mg (8%). Anal. Calcd for $C_{21}H_{31}N_9O_4B_2F_4Co$: C, 40.03; H, 4.96; N, 20.00. Found: C, 40.49; H, 4.87; N, 20.12.

[Phenyl[[3,3′,3″-(*s*-triazine-1,3,5(2*H*,4*H*,6*H*)-triyltrinitrilo)tris(2-butanone) trioximato](3−)-$O^2,O^{2'},O^{2''}$]borato(1−)]cobalt(2+) Bis[tetrafluoroborate(1−)], $[Co(BMXY)_3(BC_6H_5)(CH_2)_3](BF_4)_2$. A 270-mg sample (0.44 mmol) of $[Co(BMXY)_3(BC_6H_5)(CH_2)_3]BF_4$ was dissolved in 30 mL of acetonitrile and oxidized by a dropwise addition of a solution of excess nitrosonium tetrafluoborate in acetonitrile. The oxidation of the cobalt(II) species was monitored biamperometrically. When the end point was reached (zero current), 10 mL of absolute ethanol was added

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to the solution to quench any unreacted nitrosonium ions. The solution was rotary evaporated to half its initial volume and treated with an additional 25 mL of absolute ethanol. Further rotary evaporation of the solution produced a red/orange crystalline solid, which was filtered *via* suction, washed with a small amount of absolute ethanol followed by ethyl ether, and dried in vacuo at 78 °C. Yield: 220 mg (71%). Anal. Calcd for $C_{21}H_{29}N_9O_3B_3F_8Co$: C, 36.10; H, 4.18; N, 18.03. Found: C, 35.84; H, 4.31; N, 17.70.

[Phenyl[[1,1′,1″-(*s*-triazine-1,3,5(2*H*,4*H*,6*H*)-triyltrinitrilo)tris(1-phenyl-2-propanone) trioximato](3–)-$O^2,O^{2'},O^{2''}$]borato(1–)]cobalt(1+) Tetrafluoroborate(1–), $[Co(PMXY)_3(BC_6H_5)(CH_2)_3]BF_4{\cdot}H_2O$. A 1.54-g sample (8.7 mmol) of 1-phenyl-1,2-propanedione 2-oxime 1-hydrazone (PMXY) was dissolved/suspended in 70 mL of acetonitrile. After the system was outgassed with nitrogen, 0.38 g (2.9 mmol) of anhydrous cobalt(II) chloride was added. When the cobalt(II) chloride and undissolved PMXY dissolved, 0.36 g (2.9 mmol) of phenylboric acid was added to the red solution. The solution gradually turned a murky purple/brown as stirring under nitrogen was continued for 6 h. At this point 4 mL (approximately a 6-fold excess) of a formaldehyde solution (37% in H_2O) which had been outgassed with nitrogen was added. The mixture was stirred overnight under a nitrogen atmosphere.

The dark purple solution was exposed to the air and treated with 1.5 g (13.6 mmol; approximately a 5-fold excess) of sodium tetrafluoborate in 10 mL of water, and the solution was rotary evaporated to remove the acetonitrile. After the residual water was decanted from the solid residue, the solid was redissolved in a minimum volume of acetonitrile and passed through a neutral alumina column (Brockmann activity III) using 1/1 (v/v) acetonitrile/methylene chloride as the eluent. The first dark purple band was collected, and the solution was rotary evaporated to dryness. The residue was redissolved in 5/1 (v/v) methanol/water and rotary evaporated to yield a black crystalline material, which was filtered *via* suction, washed with a small amount of ethanol followed by ethyl ether, dried *in vacuo* at 78 °C, and stored under nitrogen. Yield: 600 mg (26%). Anal. Calcd for $C_{36}H_{37}N_9O_4B_2F_4Co$: C, 52.96; H, 4.57; N, 15.44. Found: C, 52.81; H, 4.34; N, 15.80.

[Phenyl[[1,1′,1″-(*s*-triazine-1,3,5(2*H*,4*H*,6*H*)-triyltrinitrilo)tris(1-phenyl-2-propanone) trioximato](3–)-$O^2,O^{2'},O^{2''}$]borato(1–)]cobalt(2+) Bis[tetrafluoroborate(1–), $[Co(PMXY)_3(BC_6H_5)(CH_2)_3](BF_4)_2$. A 500-mg sample (0.63 mmol) of $[Co(PMXY)_3(BC_6H_5)(CH_2)_3]BF_4$ was dissolved in 100 mL of acetonitrile and oxidized by a dropwise addition of a solution of excess nitrosonium tetrafluobrate in acetonitrile. The oxidation of the cobalt(II) species was monitored biamperometrically. When the end point was reached (zero current), 25 mL of absolute ethanol was added to the solution to quench any unreacted nitrosonium ions. The solution was rotary evaporated to produce a gelatinous product. The gel was redissolved by the addition of a minimum amount of acetonitrile, and the solution was cooled in a refrigerator overnight. The fibrous precipitate that formed was isolated *via* suction filtration, triturated under ethyl ether to extract the persistently held solvents, filtered a second time, and washed with ethyl ether. The product was dried *in vacuo* at 78 °C. Yield: 160 mg (29%). Anal. Calcd for $C_{36}H_{35}N_9O_3B_3F_8Co$: C, 48.85; H, 3.99; N, 14.24. Found: C, 48.40; H, 4.57; N, 14.16.

[μ-[μ-*p*-Phenylenebis[[1,1′,1″-(*s*-triazine-1,3,5(2*H*,4*H*,6*H*)-triyltrinitrilo)tris(1-phenyl-2-propanone) trioximato](3–)-$O^2,O^{2'},O^{2''}$]diborato-(2–)]]dicobalt(2+) Bis[tetrafluoborate(1–)], $[\{Co(PMXY)_3(CH_2)_3\}_2(B_2C_6H_4)](BF_4)_2{\cdot}2H_2O$. A 1.54-g sample of PMXY (8.7 mmol) was dissolved/suspended in 50 mL of acetonitrile, and the mixture was outgassed with nitrogen. A 0.38-g (2.9-mmol) sample of anhydrous cobalt(II) chloride was added, and the mixture was stirred under nitrogen until the cobalt(II) chloride dissolved to produce a red solution. The reaction mixture was treated with 0.24 g (1.4 mmol) of benzene-1,4-diboronic acid and was stirred for 18 h under a nitrogen atmosphere. The resultant dark purple solution was treated with 4 mL (12-fold excess) of a formaldehyde solution (37% in H_2O), and the mixture was stirred for an additional 2 h. The solution was exposed to air, treated with 1.5 g (4.6 mmol) of tetra-*n*-butylammonium tetrafluoborate in 25 mL of ethanol, and rotary evaporated to near dryness. The residue was redissolved in acetonitrile and passed down a neutral alumina column (Brockmann activity III) using 1/1 acetonitrile/methylene chloride as the eluent. The second purple band (the first band appears to be due to a mononuclear impurity) to elute from the column was collected and rotary evaporated to half its initial volume. An equal volume of 1/1 methanol/water containing 0.5 g of sodium tetrafluoborate was added to the solution, and the mixture was rotary evaporated to produce a black solid. If this solid was found to be impure by TLC (neutral alumina plates; 1/1 methylene chloride/acetonitrile), the above chromatographic separation was repeated to produce pure material. The black solid was filtered *via* suction and washed with water, a small amount of ethanol, and diethyl ether. The product was dried *in vacuo* at 78 °C. Yield: 20 mg (0.9%). Anal. Calcd for $C_{66}H_{68}N_{18}O_7B_4F_8Co_2$: C, 50.99; H, 4.41; N, 16.22. Found C, 51.09; H, 4.05; N, 16.37.

Physical Methods. ^1H and ^{13}C NMR spectra were recorded using an IBM NR/80 FT Spectrometer (AF series). Acetnitrile-d_3 and dimethyl sulfoxide-d_6 were used as the solvent and tetramethylsilane was used as the reference. When necessary, distortionless enhanced polarization transfer (DEPT) techniques were used to aid in the assignment of ^{13}C resonances. Visible and UV spectra were obtained using a Milton Roy Spectronic 3000 diode array spectrometer with acetonitrile as the solvent. Infrared spectra were recorded using KBr pellets and a Mattson Polaris FT-IR spectrometer. Elemental analyses were performed by Galbraith Labs, Inc., Knoxville, TN.

For all electrochemical measuremnets, acetonitrile (Aldrich, anhydrous, 99+%) which had been outgassed with purified nitrogen was used as the solvent and tetra-*n*-butylammonium tetrafluoborate[31] was used as the supporting electrolyte. Cyclic voltammetry was performed using a Bioanalytical Systems (BAS) CV-1A instrument coupled to a Houston Instrument 2000 XY recorder. A 20-mL cylindrical cell was used in conjunction with a platinum disk (1.6-mm diameter) working electrode, a platinum-wire counter electrode, and a saturated sodium chloride calomel electrode (SSCE).[32] Electrolyses were performed using an Electrosynthesis Company (ESC) power unit (No. 420) coupled with an ESC potentiostatic controller (No. 410). A 30-mL H-cell was used with a platinum-gauze working electrode, a platinum-wire counter electrode, and a silver/silver chloride reference electrode (BAS). A glass frit separated the working electrode compartment from the counter electrode compartment. Coulometric measurements were made with an ESC digital coulometer (No. 640). Biamperometric end points were measured using two spherical platinum electrodes and an applied potential of 200 mV. Current was measured by using a Keithley 168 autoranging digital multimeter.

Results and Discussion

Synthesis and Stability of the Complexes. The synthesis of clathrochelate complexes using oxime–hydrazone ligands utilizes two different means of "capping" the ligand cage. Initially, the oxime end of the molecule is closed off using the oxime–boronic acid capping reaction developed by Rose.[24,25] It is assumed that the labile nature of Fe(II) and Co(II) complexes allows the three chelating oxime–hydrazone ligands to orient themselves so that the desired "tripodal" hexadentate ligand can be formed on reaction with the boronic acid. Finally, the hydrazone end of the molecule is "capped" by using the hydrazone–formaldehyde capping reaction pioneered by Goedken.[26,27] The overall reaction sequence for an iron complex based on the 2,3-butanedione oxime hydrazone ligand (BMXY) is as follows:

$$FeBr_2 + 3BMXY + R\text{–}B(OH)_2 \rightarrow [Fe(BMXY)_3(B\text{–}R)]Br + HBr + 2H_2O$$

$$[Fe(BMXY)_3(B\text{–}R)]Br + 3H_2CO + PF_6^- \rightarrow [Fe(BMXY)_3(CH_2)_3(B\text{–}R)]PF_6 + 3H_2O + Br^-$$

The use of excess formaldehyde in the final closure step is necessary to prevent the formation of significant amounts of partially capped materials. The small amounts of partially capped materials produced in this reaction even in the presence of large excesses of formaldehyde must be removed from the desired product by column chromatography.

The use of a bifunctional chelate (oxime-hydrazone) which requires a two-step capping sequence to form the clathrochelate allows for the use of diboronic acids as bridging groups between two clathrochelate cages.[14] This synthetic advantage has been exploited to produce binuclear iron complexes in which two

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(31) Sawyer, D. T. *Experimental Electrochemistry for Chemists*, John Wiley and Sons: New York, 1974.

(32) The ferrocene/ferrocenium couple occurs at a potential of +0.405 V under the described experimental conditions.

Table I. ^{1}H Nuclear Magnetic Resonance Data for the Fe(II) and Co(III) Complexes

	chem shifts (ppm vs. TMS)[a]			
complex	methyl	"R"	methylene	capping group
$[Fe(BMXY)_3(CH_2)_3(BC_6H_5)]PF_6$	2.48 (s)	2.52 (s)	5.22 (d) 3.51 (d) (J = 13 Hz)	7.37 (m) 7.76 (m)
$[Fe(PMXY)_3(CH_2)_3(BC_6H_5)]PF_6$	2.46 (s)	7.55 (br)	5.15 (d) 3.80 (d) (J = 13 Hz)	7.40 (m) 7.95 (m)
$[Fe(PAXY)_3(CH_2)_3(BC_6H_5)]PF_6$	2.46 (s)	8.35 (s)	5.34 (d) 3.65 (d) (J = 13 Hz)	7.40 (m) 7.82 (m)
$[\{Fe(BMXY)_3(CH_2)_3\}_2(B_2C_6H_4)](PF_6)_2$	2.49 (s)	2.54 (s)	5.23 (d) 3.52 (d) (J = 13 Hz)	7.82 (s)
$[\{Fe(PMXY)_3(CH_2)_3\}_2(B_2C_6H_4)](PF_6)_2$	2.47 (s)	7.56 (br)	5.14 (d) 3.83 (d) (J = 13 Hz)	7.98 (s)
$[Co(BMXY)_3(CH_2)_3BC_6H_5)](BF_4)_2$	2.62 (s)	2.77 (s)	5.44 (d) 3.82 (d) (J = 13 Hz)	7.45 (m) 7.84 (m)
$[Co(PMXY)_3(CH_2)_3(BC_6H_5)](BF_4)_2$	2.53 (s)	7.66 (s)	4.94 (d) 3.75 (d) (J = 13 Hz)	7.48 (m) 7.85 (m)

[a] Solvent: CD_3CN; "R" group is bonded to the azomethine carbon at the hydrazone end of the molecule.

clathrochelate cages are linked by a 1,4-phenyldiboronate group. Numerous attempts to produce the analogous binuclear cobalt complexes have met with limited success. A large number of side products are produced in the reaction and the instability of the cobalt complexes does not readily allow the necessary column chromatography to be performed successfully. The problem of numerous impurities coupled with the low yields of the reaction (and in the case of the BMXY complex, extremely low solubility) thus far has limited the investigation of these binuclear cobalt complexes to an elelctrochemical study of $[\{Co(PMXY)_3(CH_2)_3\}_2(B_2C_6H_4)](BF_4)_2$.

The cobalt(II) complexes are reasonably air stable in the solid form. After exposure to air for 1 week the samples contain small amounts of decomposition products detectable *via* thin layer chromatography (neutral alumina; 1/1 acetonitrile/methylene chloride). Acetonitrile solutions of the cobalt(II) complexes are sufficiently stable to allow for spectral and electrochemical measurements to be made without the need for inert atmosphere sample handling techniques. Acetonitrile solutions show slight decomposition, measured *via* deterioration of the complex's UV-Visible spectrum, over a period of 5 days. Methanolic solutions show dramatically increased air sensitivity, undergoing complete decomposition over the same five day period.

The mononuclear Co(III) complexes show remarkably different stabilities as the solvent system is varied. The Co(III) complexes of both the BMXY and the PMXY ligand systems are stable in acetonitrile. However, the Co(III) complex $[Co(BMXY)_3(CH_2)_3(BC_6H_5)](BF_4)_2$ rapidly decomposes in dimethyl sulfoxide, giving a ^{1}H NMR spectrum that is broadened by a paramagnetic species, a UV–visible spectrum similar to that of the cobalt(II) complex (see Table III) and a cyclic voltammogram with numerous irreversible and quasi-reversible waves that bears little resemblance to that of the original complex. Contrary to this behavior, the complex $[Co(PMXY)_3(CH_2)_3(BC_6H_5)](BF_4)_2$ does not exhibit any spectral or electrochemical evidence of decomposition in dimethyl sulfoxide. This stability of $[Co(PMXY)_3(CH_2)_3(BC_6H_5)](BF_4)_2$ in DMSO could be due to a steric effect resulting from the phenyl substituents inhibiting attack by the DMSO. Steric constraints appear to be more significant in determining the stability of this complex than its redox activity because in examining the electrochemical potentials of the complexes, the cobalt(III) state in $[Co(PMXY)_3(CH_2)_3(BC_6H_5)](BF_4)_2$ is actually less accessible by 70 mV (see Table IV) than the analogous BMXY complex, thereby making it a stronger oxidizing agent.

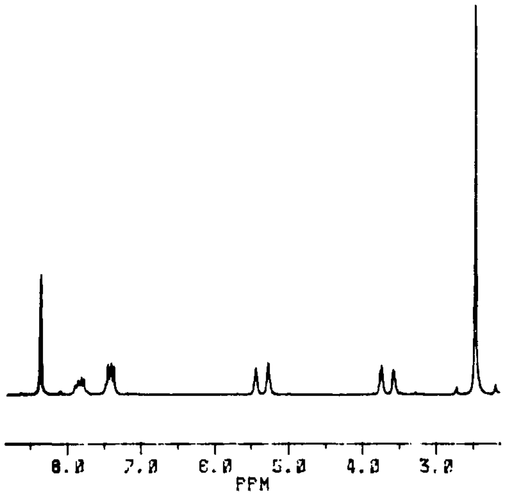

Figure 2. ^{1}H NMR spectrum of $[Fe(PAXY)_3(CH_2)_3(BC_6H_5)]PF_6$ in CD_3CN (TMS reference).

Nuclear Magnetic Resonance Spectra. The ^{1}H nuclear magnetic resonance data for the Fe(II) and Co(III) complexes are presented in Table I. The signature signals for this class of complexes are the pair of doublets (4.9–5.5 and 3.5–3.9 ppm; J = 13 Hz) which are the result of the geminal coupling of the methylene protons on the 1,3,5-triazacyclohexane capping group. This large AB splitting pattern, which is identical to that observed by Goedken in the dihydrazone-based clathrochelate complex,[26,27] arises because the fixed conformation of the 1,3,5-triazacyclohexane capping group locks the methylene protons into nonequivalent axial and equatorial sites. The proton signals arising from the phenylboronate capping group in the mononuclear complexes appear as a pair of multiplets in the 7.35–7.95 ppm region. This is in contrast to the resonances due to the protons in the phenyldiboronate bridging group of the binuclear complexes which appear as a singlet in the 7.8–8.0 ppm region.

The ^{13}C magnetic resonance spectra illustrate the high degree of symmetry found in these complexes (see Table II). The peaks found furthest downfield are due to the pair of azomethine carbons. Using distortionless enhanced polarization transfer techniques (DEPT) with the $[Fe(PAXY)_3(CH_2)_3(BC_6H_5)]PF_6$ complex, the resonance at 159.1 ppm can be assigned unambiguously to the azomethine carbon furthest from the boronate cap. By comparison, it is assumed that the signals furthest downfield in the

Table II. ^{13}C Nuclear Magnetic Resonance Data for the Fe(II) and Co(III) Complexes

	chem shifts (ppm vs. TMS)[a]				
complex	methyl	"R"	methylene	capping groups	C=N
$[Fe(BMXY)_3(CH_2)_3(BC_6H_5)]PF_6$	14.1	17.7	75.7	128.6 129.0 132.8	154.5 168.9
$[Fe(PMXY)_3(CH_2)_3(BC_6H_5)]PF_6$	15.6	129.6[b] 130.3 131.4 133.0	76.7	128.3[b] 129.0 132.7	155.2 170.4
$[Fe(PAXY)_3(CH_2)_3(BC_6H_5)]PF_6$	14.1		78.1	128.6 129.4 132.8	153.0 159.1
$[\{Fe(BMXY)_3(CH_2)_3\}_2(B_2C_6H_4)](PF_6)_2$	14.1	17.7	75.7	132.0	154.4 168.9
$[\{Fe(PMXY)_3(CH_2)_3\}_2(B_2C_6H_4)](PF_6)_2$	15.6	129.6[b] 130.3 131.5 133.0	76.7	131.9[b]	155.1 170.4
$[Co(BMXY)_3(CH_2)_3(BC_6H_5)](BF_4)_2$	15.6	21.2	76.3	128.6 130.2 132.7	163.9 183.3
$[Co(PMXY)_3(CH_2)_3(BC_6H_5)](BF_4)_2$	17.7	130.1[b] 130.7 131.4 134.3	76.1	129.0[b] 130.1 132.8	164.4 181.0

[a] Solvent: CD_3CN. "R" group is bonded to the azomethine carbon at the hydrazone end of the molecule. [b] Phenyl carbons are tentatively assigned on the basis of comparisons made within this family of complexes.

Table III. Electronic Spectral Data for the Complexes[a]

complex	$\lambda_{MAX}(\epsilon)$[b]
$[Fe(BMXY)_3(CH_2)_3(BC_6H_5)]PF_6$	20 200 (1.5×10^4), 37 800 (1.8×10^4)
$[Fe(PMXY)_3(CH_2)_3(BC_6H_5)]PF_6$	19 700 (2.2×10^4), 37 500 (3.0×10^4)
$[Fe(PAXY)_3(CH_2)_3(BC_6H_5)]PF_6$	20 600 (1.2×10^4), 37 900 (1.5×10^4)
$[\{Fe(BMXY)_3(CH_2)_3\}_2(B_2C_6H_4)](PF_6)_2$	20 300 (2.7×10^4), 37 500 (3.0×10^4)
$[\{Fe(PMXY)_3(CH_2)_3\}_2(B_2C_6H_4)](PF_6)_2$	19 600 (3.8×10^4), 37 000 (6.3×10^4)
$[Co^{II}(BMXY)_3(CH_2)_3(BC_6H_5)]BF_4$	18 900 (5.4×10^3), 25 000 (7.0×10^3)
$[Co^{III}(BMXY)_3(CH_2)_3(BC_6H_5)](BF_4)_2$	20 000 (sh), 29 200 (8.3×10^3)
$[Co^{II}(PMXY)_3(CH_2)_3(BC_6H_5)]BF_4$	18 300 (6.7×10^3), 24 100 (9.8×10^3)
$[Co^{III}(PMXY)_3(CH_2)_3(BC_6H_5)](BF_4)_2$	18 900 (sh); 24 900 (1.4×10^4)

[a] Solvent: CH_3CN. [b] λ_{MAX} in cm^{-1}; ϵ in $M^{-1}\ cm^{-1}$.

other complexes are due to the analogous carbons in those molecules and that the signal more upfield is due to the azomethine carbon nearest the boronate cap. Additional evidence supporting these assignments lies in the fact that in the iron complexes the resonances of the azomethine carbons to which the "R" groups are attached have chemical shifts that vary over a range of 159.1–170.4 ppm; whereas the resonances of the other azomethine carbons, which in every case have a methyl substituent, have chemical shfits that fall within a 2.2 ppm range.

In all of the complexes the capping methylene resonance (75.7–78.1 ppm) is readily assigned using DEPT techniques. The phenyl carbon resonances for the phenylboronate capping groups all fall within the range of 128.3–132.8 ppm. It should be noted that the resonance of the phenyl carbon attached to the boron atom is not observed due to the fact that the boron nuclear spins are not decoupled from the carbon nuclear spin, which results in a highly split and broadened signal which is further reduced in intensity by the fact that it experiences no nuclear Overhauser enhancement.

The remaining signals in the ^{13}C spectra are attributed to the carbons in the "R" groups or the methyl groups bonded to the azomethine carbons.

Electronic Spectra. The electronic spectra of the iron complexes (see Table III) are dominated by an intense charge transfer band in the region from 19 600 to 20 600 cm^{-1}. This band is located between the comparable band (22 000 cm^{-1}) reported by Rose[24] for the tris(dioxime)/boronic acid-capped clathrochelate and that reported by Goedken[26] (19 100 cm^{-1}) for the tris(dihydrazone)/formaldehyde-capped clathrochelate. This intermediate behavior is expected for complexes which incorporate three oxime nitrogens and three hydrazone nitrogens into the coordination sphere of the iron. Also observable at higher energy (37 000–37 900 cm^{-1}) in the electronic spectra of the iron complexes is an intense band most likely due to a $\pi \rightarrow \pi^*$ transition within the ligand.

The general pattern of the electronic spectra of the cobalt(II) complexes consists of two bands in the visible region (roughly 18 000–19 000 and 24 000–25 000 cm^{-1}). On oxidation to cobalt(III) the two peaks are replaced by a shoulder (18 000–20 000 cm^{-1}) and a peak at a higher energy (24 000–30 000 cm^{-1}). These general patterns are similar to those found in spectra reported by Wherland[4] and Rose[20,33] for cobalt(II) and cobalt(III) complexes of the tris(dioxime)clathrochelate ligand system. In all cases the absorbance bands resulting from the tris(dioxime) complexes occur at slightly higher energy than the comparable bands for the oxime–hydrazone complexes.

Electrochemical Studies. Cyclic voltammetric data for the complexes are presented in Table IV. Most of the iron complexes undergo a quasireversible oxidation to Fe(III) and a quasireversible reduction to what is nominally an Fe(I) state. The oxidation potentials of the iron complexes become more anodic as the "R" substituent on the clathrochelate is varied from $-CH_3$ to $-C_6H_5$. This anodic shift is reminiscent of the 200 mV shift observed in the tris(dioximato) clathrochelate system on varying the chelating ligand from dimethylglyoxime to diphenylglyoxime.[25] The oxidation wave of the $[Fe(PAXY)_3(CH_2)_3(BC_6H_5)]PF_6$ complex is unique in that it is completely irreversible and has an "*n*" value greater than 1. This behavior is most likely due to an ECE process wherein, following the initial electron transfer, a rapid chemical reaction occurs involving the reactive C–H bond on the azomethine carbon (the only site that has been altered in the PAXY system) to produce an electrochemically active species.

The cyclic voltammetric waves observed for the binuclear complex, $[\{Fe(BMXY)_3(CH_2)_3\}_2(B_2C_6H_4)](PF_6)_2$, are practically

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(33) Boston, D. R.; Rose, N. J. *J. Am. Chem. Soc.* **1968**, *90*, 6859.

Table IV. Cyclic Voltammetric Data[a]

complex	$E_{1/2}$ (V)[b]	ΔE_p (mV)	current ratio[c]
$[Fe(BMXY)_3(CH_2)_3(BC_6H_5)]PF_6$	+1.14	75	0.83
	−1.02	90	0.79
$[Fe(PMXY)_3(CH_2)_3(BC_6H_5)]PF_6$	+1.29	75	0.90
	−0.89	75	0.90
$[Fe(PAXY)_3(CH_2)_3(BC_6H_5)]PF_6$	+1.45[d]	irr	
	−0.84	85	0.77
$[\{Fe(BMXY)_3(CH_2)_3\}_2(B_2C_6H_4)](PF_6)_2$	+1.14	70	0.88
	−1.04	90	0.89
$[\{Fe(PMXY)_3(CH_2)_3\}_2(B_2C_6H_4)](PF_6)_2$	+1.25	50	1.3
	−0.89	80	0.83
$[Co(BMXY)_3(CH_2)_3(BC_6H_5)]BF_4$	+0.26	65	0.99
	−0.67	65	0.87
$[Co(PMXY)_3(CH_2)_3(BC_6H_5)]BF_4$	+0.34	65	1.0
	−0.50	65	0.96
$[\{Co(PMXY)_3(CH_2)_3\}_2(B_2C_6H_4)](BF_4)_2$	+0.31	55	1.3
	−0.51	80	0.90

[a] Solvent: 0.10 M tetra-*n*-butylammonium tetrafluoborate in acetonitrile. Reference: saturated sodium chloride calomel electrode. Platinum disk working electrode. Scan rate: 100 mV/s. [b] $E_{1/2} = (E_{Pa} - E_{Pc})/2$. [c] i_{Pc}/i_{Pa} for oxidations; i_{Pa}/i_{Pc} for reductions. [d] Irreversible oxidation; E_P is reported.

identical to those observed for the analogous mononuclear complex. This similarity between the waveforms is expected for the special case in which the redox centers of the binuclear complexes do not interact. Similar results have been observed in systems with non-interacting redox centers that have been investigated by Bard and Anson,[34] Taube,[35] Ciampolini and Fabrizzi,[36] and Lever.[37] In contrast, the oxidative wave observed in the cyclic voltammetry of the binuclear complex, $[\{Fe(PMXY)_3(CH_2)_3\}_2(B_2C_6H_4)](PF_6)_2$, is very different in appearance from that of the analogous mononuclear complex or that of the other binuclear iron complex, $[\{Fe(BMXY)_3(CH_2)_3\}_2(B_2C_6H_4)](PF_6)_2$, having much more pointed peak profiles and an overall asymmetrical shape as evidenced by a peak current ratio, i_{pc}/i_{Pa}, of 1.3 *versus* a ratio of 1.0 for the mononuclear complex.[38] The peak separation of 50 mV is close to the theoretical separation of 42 mV predicted for a reversible simultaneous two-electron transfer; however, the peak separation varies greatly from 36 to 70 mV as the scan rate is varied from 25 to 300 mV/s. As a result, this atypical wave-form shape appears to be due to adsorption of the relatively large binuclear clathrochelate complex on the electrode surface rather than a simultaneous two-electron transfer.

Although the Fe(III) complexes appear to be stable on the cyclic voltammetric time scale, attempts to produce Fe(III) complexes *via* exhaustive electrolysis have not proven to be successful. For example, a typical oxidative electrolysis at a potential 200 mV more anodic than the $E_{1/2}$ of the Fe(II)/Fe(III) couple would produce an "*n*" value at least four times larger than the predicted value of 1 (the experiments were terminated before the current reached an equilibrium value). A cyclic voltammogram of this electrolyzed solution would show numerous irreversible couples, indicating that an almost complete decomposition of the clathrochelate complex had occurred. This lack of stability for the Fe(III) complexes is comparable to that observed for the clathrochelate complexes based on the dioximato ligand system.[25]

The mononuclear cobalt complexes are stable and are able to be isolated in both the +2 and +3 oxidation states. Cyclic voltammetric studies of the cobalt complexes reveal quasireversible/reversible waves for the cobalt(III)/cobalt(II) and cobalt(II)/cobalt(I) redox couples. As in the case of the iron complexes both redox couples are shifted anodically as the ligand substituent is changed from methyl to phenyl. Electrolytic studies of the cobalt(III)/cobalt(II) couple produce "*n*" values approaching the expected value of 1 electron per complex (0.95–0.96). Cyclic voltammograms before and after electrolysis are essentially the same and they are identical to those of the chemically synthesized Co(II) and Co(III) complexes, indicating that the integrity of the complexes is maintained during electrolytic cycles of the +2/+3 oxidation states.

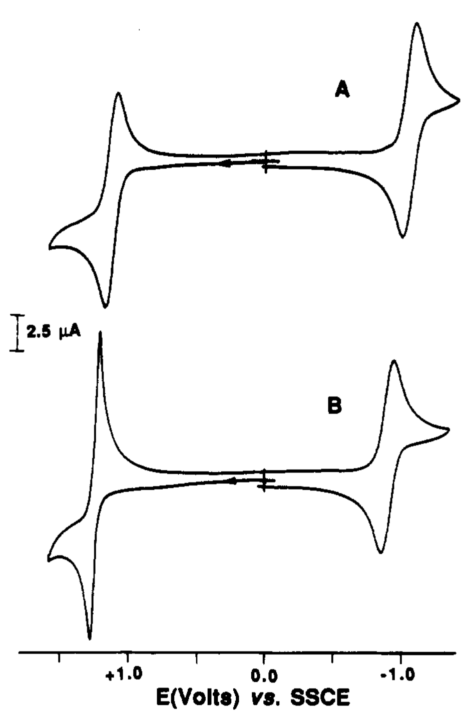

Figure 3. Comparison of the cyclic voltammograms of the binuclear iron complexes: (A) $[\{Fe(BMXY)_3(CH_2)_3\}_2(B_2C_6H_4)](PF_6)_2$ (concentration: 0.93 mM); (B) $[\{Fe(PMXY)_3(CH_2)_3\}_2(B_2C_6H_4)](PF_6)_2$; (concentration: 0.88 mM).

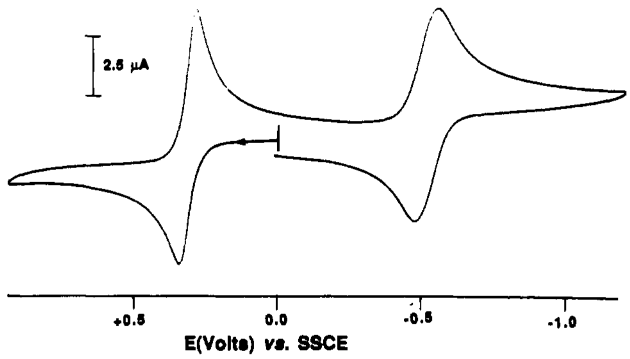

Figure 4. Cyclic voltammogram of the binuclear cobalt complex $[\{Co(PMXY)_3(CH_2)_3\}_2(B_2C_6H_4)](BF_4)_2$ (concentration: 0.48 mM).

The cyclic voltammetric wave describing the behavior of the Co(III)/Co(II) couple of the binuclear cobalt complex, $[\{Co(PMXY)_3(CH_2)_3\}_2(B_2C_6H_4)](BF_4)_2$, is identical in shape to that observed for the oxidation of the analogous iron complex. Due to adsorption of the complex on the electrode surface, the peak profiles have more pointed shapes and the waveform is asymmetric with i_{Pc}/i_{Pa} equal to a value of 1.3. In addition the peak separations vary in a comparable fashion to that observed for the iron complex. As the scan rate is increased from 25 to 300 mV/s, the peak separation also increases from 48 to 70 mV. Attempts to produce the binuclear Co(III) species by exhaustive electrolysis have been limited by the adsorption of the oxidized complex on the electrode

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(34) Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, *100*, 4248.

(35) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278.

(36) Ciampolini, M.; Fabbrizzi, L.; Perotti, A.; Poggi, A.; Seghi, B.; Zanobini, F. *Inorg. Chem.* **1987**, *26*, 3527.

(37) Nevin, W. A.; Hempstead, M. R.; Liu, W.; Leznoff, C. C.; Lever, A. B. P. *Inorg. Chem.* **1987**, *26*, 570.

(38) Calculated by using the semiempirical procedure reported by: Nicholson, R. S. *Anal. Chem.* **1966**, *38*, 1406.

surface. The transfer of electrons becomes very slow and eventually stops entirely before reaching the expected "*n*" value of 2 electrons per molecule.

Concluding Remarks. This study continues our examination of the synthesis of mononuclear and binuclear iron clathrochelates based on oxime–hydrazone ligands. In addition, the first examples of cobalt clathrochelate complexes based on oxime–hydrazone ligands have been synthesized. Spectral characterization has been presented to establish the structures of these new iron and cobalt species. Electrochemical results have shown that oxidation of the iron clathrochelates to the Fe(III) state does not produce stable complexes. However, the Co(III) oxidation state is readily accessible, thereby defining a Co(III)/Co(II) couple that is both chemically and electrochemically reversible. Electrochemical studies of both the iron and the cobalt binuclear complexes are consistent for systems with two equivalent noninteractive redox sites per molecule.

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