# Synthesis and Characterization of Iron Clathrochelate Complexes Derived from Oxime–Hydrazone Ligands and Capped by Ferrocenylborate and 1,1'-Ferrocenediyldiborate

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The synthesis and characterization of a series of iron clathrochelate complexes based on oxime–hydrazone ligands and capped with ferrocenylboronic acid to produce dimetallic species is reported. The first example of a metal complex which uses 1,1'-ferrocenediyldiboronic acid as a capping/bridging agent between two clathrochelate complexes to form a novel trimetallic species is also presented. The redox chemistry of these multiple metal systems is examined by cyclic voltammetry and controlled-potential electrolysis. The generation of stable mixed-valent ($Fe^{2+}/Fe^{3+}$) species by exhaustive electrolysis and their subsequent characterization by UV–visible spectroscopy and cyclic voltammetry is discussed.

## Introduction

Clathrochelate complexes have proven to be valuable reagents in studying outer-sphere electron-transfer reactions.[1–11] In addition, their usefulness as electron-transfer mediators in electrocatalytic reaction schemes has begun to be explored.[12,13] Since many chemical and biological processes involve multiple electron transfers, we have been investigating synthetic routes to produce clathrochelate-based systems with multiple redox centers.[14]

Wherland and co-workers have recently synthesized a cobalt clathrochelate complex that is capped by two ferrocenylborate groups.[15] This trimetallic complex has been shown to possess very interesting redox properties with significant interactions between the metal centers. We have been able to adapt the use of a ferrocenylborate capping group to our system of clathrochelate complexes based on oxime–hydrazone ligands (Figure 1).[14] The use of the bifunctional oxime–hydrazone ligand allows us to use diboronic acids as bridging groups between two clathrochelate cages. The use of 1,1'-ferrocenediyldiboronic acid produces a unique metal complex wherein a ferrocene group forms the bridge between two iron clathrochelate complexes (Figure 1). In this paper the synthesis and characterization of these novel dimetallic and trimetallic species will be presented.

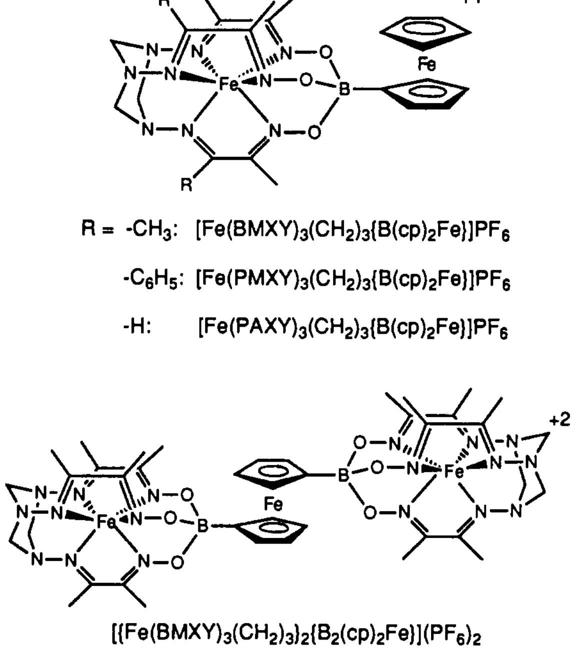

**Figure 1.** Schematic representations of the complexes and shorthand notation used in the text.

## Experimental Section

**Materials.** Ferrocenylboronic acid and 1,1'-ferrocenediyldiboronic acid were prepared as described previously.[16,17] 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 desribed previously.[18] The 1-phenyl-1,2-propanedione 2-oxime 1-hydrazone (PMXY) was prepared by utilizing 1-phenyl-1,2-propanedione 2-oxime (Aldrich) in the reaction with hydrazine hydrate. The pyruvic aldehyde 1-oxime 2-hydrazone (PAXY) was prepared in a similar fashion by beginning with pyruvic aldehyde 1-oxime.[19] All other reagents were obtained commercially [$FeBr_2$(Strem); all others (Aldrich)] and used as received.

**[Ferrocenyl[[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-)–Acetonitrile, [$Fe(BMXY)_3(CH_2)_3\{B(cp)_2Fe\}$]$PF_6\cdot CH_3CN$.**[20] A 0.50-g sample (4.3 mmol) of 2,3-butanedione oxime hydrazone (BMXY) was dissolved in 15 mL of absolute ethanol, and the mixture

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(1) Anderson, K. A.; Wherland, S. *Inorg. Chem.* **1991**, *30*, 624.
(2) Murgia, M A.; Wherland, S. *Inorg. Chem.* **1991**, *30*, 139.
(3) Gribble, J.; Wherland, S. *Inorg. Chem.* **1989**, *28*, 2859.
(4) Borchardt, D.; Wherland, S. *Inorg. Chem.* **1986**, *25*, 901.
(5) Borchardt, D.; Wherland, S. *Inorg. Chem.* **1984**, *23*, 2537.
(6) Bernhard, P.; Sargeson, A. M. *Inorg. Chem.* **1987**, *26*, 4122.
(7) Bakac, A.; Espenson, J. H.; Creaser, I. I.; Sargeson, A. M. *J. Am. Chem. Soc.* **1983**, *105*, 7624.
(8) Creaser, I. I.; Sargeson, A. M.; Zanella, A. W. *Inorg. Chem.* **1983**, *22*, 4022.
(9) Dubs, R. V.; Gahan, L. R.; Sargeson, A. M. *Inorg. Chem.* **1983**, *22*, 2523.
(10) Doine, H.; Swaddle, T. W. *Inorg. Chem.* **1991**, *30*, 1858.
(11) Rudgewick-Brown, N.; Cannon, R. D. *J. Chem. Soc., Dalton Trans.* **1984**, 479.
(12) Lay, P. A.; Mau, A. W. H.; Sasse, W. H. F.; Creaser, I. I.; Gahan, L. R.; Sargeson, A. M. *Inorg. Chem.* **1983**, *22*, 2349.
(13) Houlding, V.; Geiger, T.; Kolle, U.; Gratzel, M. *J. Chem. Soc., Chem. Commun.* **1982**, 681.
(14) Belinski, J. A.; Squires, M. E.; Kuchna, J. M.; Bennett, B. A.; Grzybowski, J. J. *J. Coord. Chem.* **1988**, *19*, 159.
(15) Murgia, M. A.; Borchardt, D.; Wherland, S. *Inorg. Chem.* **1990**, *29*, 1982.
(16) Epton, R.; Marr, G.; Rogers, G. K. *J. Organomet. Chem.* **1978**, *150*, 93.
(17) Nesmejanow, A. N.; Ssasonowa, W. A.; Drosd, V. N. *Chem. Ber.* **1960**, *93*, 2717.
(18) Forster, M. O.; Dey, B. B. *J. Chem. Soc.* **1912**, *101*, 2234.
(19) Newbold, G. T.; Sharp, W.; Spring, F. S. *J. Chem. Soc.* **1951**, 2679.
(20) Evidence for the acetonitrile of solvation in this complex is found in the infrared spectrum (CN stretch at 2253 $cm^{-1}$) and in the $^1H$ NMR spectrum (singlet; 3H; 2.06 ppm *vs* TMS; solvent DMSO-$d_6$).

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was sparged with nitrogen. Solid ferrous bromide (0.31 g; 1.4 mmol) was added, and the mixture was stirred under a nitrogen atmosphere until a dark red solution was achieved. Under a positive flow of nitrogen a 0.33-g sample (1.4 mmol) of ferrocenylboronic acid was added and the mixture was stirred for 2 h. The air-stable red/orange crystalline solid that formed was isolated *via* suction filtration, washed with a small amount of ethanol followed by diethyl ether, and air dried. Yield of the intermediate, $[Fe(BMXY)_3\{B(cp)_2Fe\}]Br$, was 430 mg (46%).

The entire yield of $[Fe(BMXY)_3\{B(cp)_2Fe\}]Br$ was dissolved/suspended in 25 mL of acetonitrile and treated with 1.5 mL (10-fold excess) of a formaldehyde solution (37% in $H_2O$). One drop of concentrated hexafluorophosphoric acid was added, and the dark red/purple solution that resulted was stirred for 18 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 a volume of 10 mL. An additional 25 mL of ethanol was added, and rotary evaporation was continued until a red/orange product formed. The product was purified by dissolving it in a minimum of acetonitrile and passing it down a neutral alumina column (Brockmann activity III) using 1/1 acetonitrile/methylene chloride as the eluent. The first band to elute was collected, rotary evaporated to half its original volume, treated with 25 mL of ethanol, and rotary evaporated further to produce a red crystalline product. The product was isolated *via* suction filtration, washed with a small amount of ethanol followed by diethyl ether, and dried *in vacuo* at 78 °C. Yield: 150 mg (14%, overall). Anal. Calcd for $C_{27}H_{36}N_{10}O_3BFe_2PF_6$: C, 39.73; H, 4.45; N, 17.16. Found: C, 39.30; H, 4.79; N, 17.44.

**[Ferrocenyl[[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-)–Water, $[Fe(PMXY)_3(CH_2)_3\{B(cp)_2Fe\}]PF_6 \cdot H_2O$.** The intermediate, $[Fe(PMXY)_3\{B(cp)_2Fe\}]Br$, was prepared by using a procedure identical to that employed in synthesizing the analogous BMXY complex. The yield of the intermediate was 620 mg (48%).

The entire yield of the intermediate was suspended in 25 mL of acetonitrile and treated with 2.0 mL (11-fold excess) of a formaldehyde solution (37% in $H_2O$). One drop of concentrated hexafluorophosphoric acid was added, and the dark purple solution was stirred for 32 h. The solution was treated with 1.5 g (9.2 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 the solution was passed down a neutral alumina column (Brockmann activity III) using 1/1 acetonitrile/methylene chloride as the eluent. The initial purple band was collected in 5–10-mL fractions. The fractions which prove to be pure by thin-layer chromatography (alumina; 1/1 acetonitrile/methylene chloride) were combined, and the combined solutions were rotary evaporated to near dryness. The residue was dissolved in a minimum of acetonitrile and treated with 1.0 g (6.1 mmol) of ammonium hexafluorophosphate in 30 mL of ethanol. Rotary evaporation of this solution produced a purple crystalline solid which was isolated *via* suction filtration, washed with ethanol followed by diethyl ether, and dried *in vacuo* at 78 °C. Yield: 300 mg (21%, overall). Anal. Calcd for $C_{40}H_{41}N_9O_4BFe_2PF_6$: C, 49.05; H, 4.22; N, 12.87. Found: C, 49.11; H, 4.36; N, 13.21.

**[Ferrocenyl[[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-), $[Fe(PAXY)_3(CH_2)_3\{B(cp)_2Fe\}]PF_6$.** The intermediate, $[Fe(PAXY)_3\{B(cp)_2Fe\}]Br$, was prepared by using a procedure identical to that employed in synthesizing the analogous BMXY complex. The yield of the intermediate was 490 mg (48%).

A 400-mg sample (0.63 mmol) of the intermediate was dissolved/suspended in 25 mL of acetonitrile and treated with 2.0 mL (13-fold excess) of a formaldehyde solution (37% in $H_2O$). One drop of concentrated hexafluorophosphoric acid was added, producing a dark red solution which was stirred for 2 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 acetonitrile/methylene chloride as the eluent. The first red/orange band that eluted was collected and rotary evaporated to dryness. The residue was dissolved in a minimum of acetonitrile and treated with 0.5 g (3.0 mmol) of ammonium hexafluorophosphate in 20 mL of ethanol. The red/orange crystals which formed on cooling the solution were isolated *via* suction filtration, washed with a small amount of ethanol followed by diethyl ether, and dried *in vacuo* at 78 °C. Yield: 120 mg (26%). Anal. Calcd for $C_{22}H_{27}N_9O_3Fe_2BPF_6$: C, 36.05; H, 3.71; N, 17.20. Found: C, 36.10; H, 4.03; N, 17.41.

**[$\mu$-[($\mu$-1,1′-Ferrocenediyl)bis[[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-)], $[\{Fe(BMXY)_3(CH_2)_3\}_2\{B_2(cp)_2Fe\}](PF_6)_2$.** A 0.50-g sample (4.3 mmol) of BMXY was dissolved in 20 mL of absolute ethanol, and the solution was sparged with nitrogen. Solid ferrous bromide (0.31 g; 1.4 mmol) was added, and the mixture was stirred until a brown solution was produced. While a nitrogen atmosphere was maintained, 0.20 g (0.7 mmol) of 1,1′-ferrocenediyldiboronic acid was added. The mixture was stirred for an additional 2 h. The air stable red/orange precipitate that formed was isolated *via* suction filtration, washed with a small amount of ethanol followed by diethyl ether, and air dried. The yield of the intermediate, $[\{Fe(BMXY)_3\}_2B_2(cp)_2Fe]Br_2$, was 410 mg (50%).

The entire yield of the intermediate was dissolved/suspended in 30 mL of acetonitrile and treated with 3 mL (18-fold excess) of a formaldehyde solution (37% in $H_2O$). After the addition of one drop of concentrated hexafluorophosphoric acid, the mixture was stirred for 18 h. A 1.0 g (6.1 mmol) sample of ammonium hexafluorophosphate in 20 mL of ethanol was added, and the mixture was rotary evaporated to near dryness. The residue was redissolved in a minimum of acetonitrile and passed down a neutral alumina column (Brockmann activity III) using 1/1 acetonitrile/methylene chloride as the eluent. The first red/orange band that eluted was collected, rotary evaporated to half its initial volume, and treated with 0.50 g (3.0 mmol) of ammonium hexafluorophosphate in 25 mL of ethanol. Further rotary evaporation coupled with cooling overnight produced a red crystalline product which was isolated *via* suction filtration, washed with a small amount of ethanol followed by diethyl ether, and dried *in vacuo* at 78 °C. Yield: 120 mg (13%, overall). Anal. Calcd for $C_{44}H_{56}N_{18}O_6B_2Fe_3P_2F_{12}$: C, 35.22; H, 4.14; N, 18.48. Found: C, 35.34; H, 4.51; N, 18.54.

**Physical Methods.** $^1H$ and $^{13}C$ NMR spectra were recorded using an IBM NR/80 FT spectrometer (AF series). DMSO-$d_6$ was 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 measurements, acetonitrile (Aldrich, anhydrous, 99+%) which had been sparged with purified nitrogen was used as the solvent and tetra-*n*-butylammonium tetrafluoborate[21] 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). Electrolyses were performed using an Electrosynthesis Co. (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 electroode (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).

## Results and Discussion

**Synthesis.** 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.[22,23] It is assumed that the labile nature of Fe(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.[24,25] The

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(21) Sawyer, D. T.; Roberts, J. L. *Experimental Electrochemistry for Chemists*; John Wiley and Sons: New York, 1974.

(22) Johnson, J. N.; Rose, N. J. *Inorg. Synth.* **1978**, *17*, 139.

(23) Robbins, M. K.; Naser, D. W.; Heiland, J. L.; Grzybowski, J. J. *Inorg. Chem.* **1985**, *24*, 3381.

(24) Goedken, V. L.; Peng, S.-M. *J. Chem. Soc., Chem. Commun.* **1973**, 62.

**Table I.** $^1$H Nuclear Magnetic Resonance Data

| complex | chem shifts (ppm vs TMS)[a] methyl | "R" | methylene | ferrocene |
|---|---|---|---|---|
| $[Fe(BMXY)_3(CH_2)_3\{B(cp)_2Fe\}PF_6$ | 2.47 (s) | 2.51 (s) | 5.39 (d), 3.62 (d) ($J$ = 13 Hz) | 4.34 (m), 4.25 (m), 4.13 (s) |
| $[Fe(PMXY)_3(CH_2)_3\{B(cp)_2Fe\}]PF_6$ | 2.39 (s) | 7.55 (br) | 4.93 (d), 3.57 (d) ($J$ = 13 Hz) | 4.40 (m), 4.27 (m), 4.18 (s) |
| $[Fe(PAXY)_3(CH_2)_3\{B(cp)_2Fe\}]PF_6$ | 2.52 (s) | 8.66 (s) | 5.56 (d), 3.80 (d) ($J$ = 13 Hz) | 4.42 (m), 4.30 (m), 4.19 (s) |
| $[\{Fe(BMXY)_3(CH_2)_3\}_2\{B_2(cp)_2Fe\}](PF_6)_2$ | 2.49 (s) | 2.54 (s) | 5.41 (d), 3.64 (d) ($J$ = 14 Hz) | 4.37 (br), 4.18 (br) |

[a] Solvent: DMSO-$d_6$. "R" group is bonded to the azomethine carbon at the hydrazone end of the molecule.

**Table II.** $^{13}$C Nuclear Magnetic Resonance Data

| complex | chem shifts (ppm vs TMS)[a] methyl | "R" | methylene | ferrocene | C═N |
|---|---|---|---|---|---|
| $[Fe(BMXY)_3(CH_2)_3\{B(cp)_2Fe\}]PF_6$ | 13.2 | 18.9 | 74.0 | 71.2, 68.5, 67.8 | 167.3, 152.4 |
| $[Fe(PMXY)_3(CH_2)_3\{B\{cp\}_2Fe\}]PF_6$ | 14.9 | 131.9<br>130.0<br>129.2<br>128.3 | 74.8 | 71.1, 68.6, 67.8 | 168.1, 153.1 |
| $[Fe(PAXY)_3(CH_2)_3\{B(cp)_2Fe\}]PF_6$ | 14.6 |  | 77.6 | 72.5, 69.8, 69.0 | 159.8, 152.1 |
| $[\{Fe(BMXY)_3(CH_2)_3\}_2\{B_2(cp)_2Fe\}](PF_6)_2$ | 13.2 | 16.8 | 73.9 | 71.1, 69.6 | 167.2, 152.2 |

[a] Solvent: DMSO-$d_6$. "R" group is bonded to the azomethine carbon at the hydrazone end of the molecule.

overall reaction sequence for a 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 closure 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 the trimetallic species $[\{Fe(BMXY)_3(CH_2)_3\}_2\{B_2(cp)_2Fe\}](PF_6)_2$, which links two clathrochelate cages with a 1,1′-ferrocenediyldiborate group.

**Nuclear Magnetic Resonance Spectra.** The $^1$H nuclear magnetic resonance data are presented in Table I. The signature signals for this class of complexes are the pair of doublets (4.9–5.6 and 3.5–3.8 ppm; $J$ = 13–14 Hz) which are the result of the geminal coupling of the methylene protons on the 1,3,5-triazacyclohexane capping group (Figure 2). This large AB splitting pattern, which is identical to that observed by Goedken in the dihydrazone-based clathrochelate complex,[24,25] arises because the fixed conformation of the 1,3,5-triazacyclohexane capping group locks the methylene protons into axial and equatorial sites.

The signals arising from the ferrocene protons on the cyclopentadienide rings fall between the pair of methylene doublets and appear as either a singlet and a pair of multiplets for the ferrocenylborate with a single appended clathrochelate cage or a pair of broad multiplets for the 1,1′-ferrocenediyldiborate with two appended clathrochelate cages.

The $^{13}$C magnetic resonance spectra illustrate the high degree of symmetry found in these complexes (Table II). The peaks found furthest downfield are due to the pair of azomethine carbons. Using distortionless enhanced polarization transfer techniques (DEPT) with the $[Fe(PAXY)_3(CH_2)_3\{B(cp)_2Fe\}]PF_6$ complex, the resonance at 159.8 ppm can be unambiguously assigned to the azomethine carbon furthest from the appended ferrocene. By comparison, it is assumed that the signals furthest downfield in the other complexes are due to the analogous carbons in those molecules and that the signal in the range 152.1–153.1 ppm is due to the azomethine carbon nearest the appended ferrocene. Additional evidence supporting these assignments lies in the fact that the resonances of the azomethine carbons to which the "R" groups are attached have chemical shifts that vary over a range 159.8–168.1 ppm, whereas the resonances of the other azomethine carbons which in every case have a methyl substituent have chemical shifts that fall within a 1.0 ppm range.

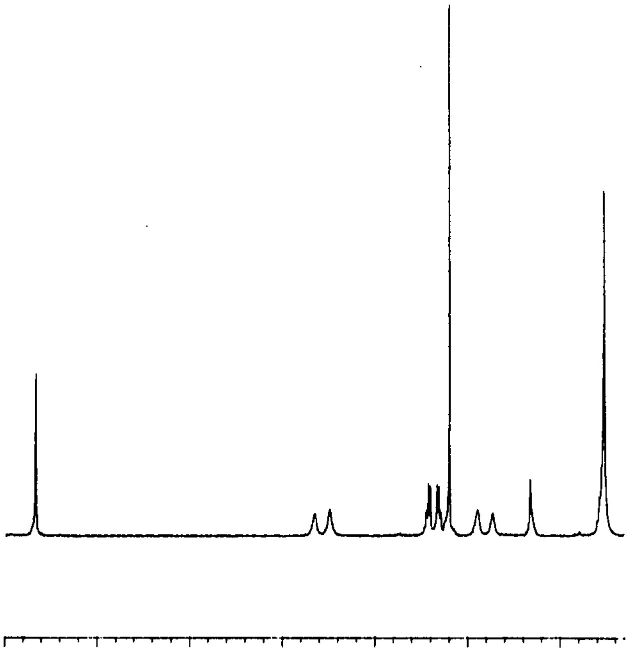

**Figure 2.** $^1$H NMR spectrum of $[Fe(PAXY)_3(CH_2)_3\{B(cp)_2Fe\}]PF_6$. (The peak at 3.3 ppm is due a trace of water in the DMSO-$d_6$).

In all of the complexes the capping methylene resonance (73.9–77.6 ppm) is readily distinguished from the nearby ferrocenyl carbon signals (67.8–72.5 ppm) using DEPT techniques (Figure 3). It should be noted that the resonance of the ferrocenyl 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.

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(25) Goedken, V. L. *Inorg. Synth.* **1980**, *20*, 87.

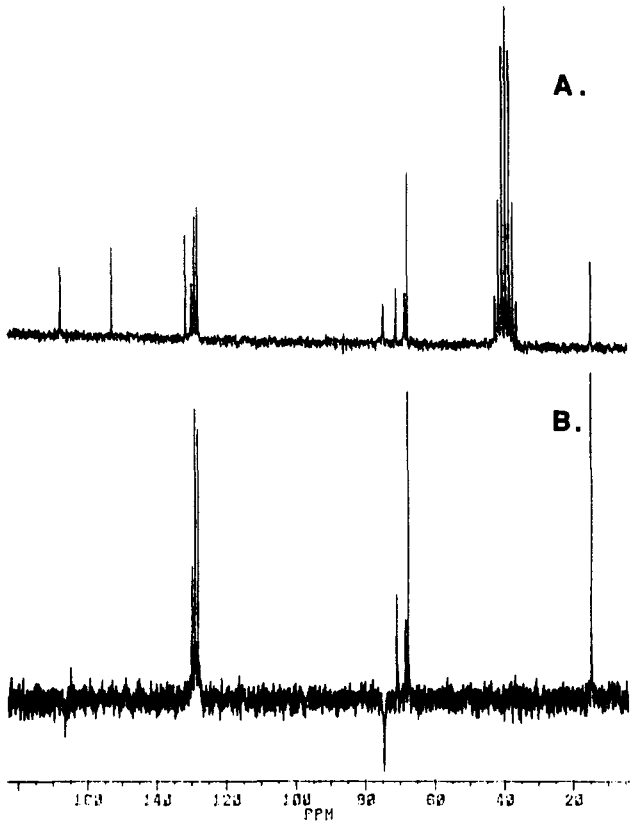

**Figure 3.** (A) $^{13}C$ NMR of $[Fe(PMXY)_3(CH_2)_3\{B(cp)_2Fe\}]PF_6$ in DMSO-$d_6$. (B) DEPT NMR spectrum of $[Fe(PMXY)_3(CH_2)_3\{B(cp)_2Fe\}]PF_6$ with 135° pulse angle. (Quaternary carbon signals disappear; methylene carbon signals are inverted.)

**Table III.** Electronic Spectral Data$^a$

| complex | $\lambda_{MAX}$ ($\epsilon$)$^b$ |
|---|---|
| $[Fe(BMXY)_3(CH_2)_3\{B(cp)_2Fe\}]PF_6$ | 20 300 (12 000),<br>38 300 (14 000) |
| $[Fe(PAXY)_3(CH_2)_3\{B(cp)_2Fe\}]PF_6$ | 20 600 (10 000),<br>38 000 (16 000) |
| $[Fe(PMXY)_3(CH_2)_3\{B(cp)_2Fe\}]PF_6$ | 19 800 (19 000),<br>37 600 (29 000) |
| $[\{Fe(BMXY)_3(CH_2)_3\}_2\{B_2(cp)_2Fe\}](PF_6)_2$ | 20 400 (24 000),<br>37 900 (28 000) |

$^a$ Solvent = $CH_3CN$. $^b$ $\lambda_{MAX}$ in $cm^{-1}$; $\epsilon$ in $M^{-1}$ $cm^{-1}$.

The remaining signals in the $^{13}C$ spectra are readily accounted for by the carbons in the "R" groups or the methyl groups bonded to the azoomethine carbons.

**Infrared and Electronic Spectra.** The infrared spectra of the clathrochelate complexes are very similar to those of previously reported complexes of this type with differences being attributable to either the ferrocenylborate cap or the changes in the chelating ligand's backbone.[14] The most distinctive infrared absorption band for the ferrocenylborate capping group is the C–H stretch observed in the region 3085–3095 $cm^{-1}$ for all of the complexes.

**Table IV.** Cyclic Voltammetric Data$^a$

| complex (concn) | $E_{1/2}$ (V)$^b$ | $\Delta$ (mV) | current ratio$^c$ |
|---|---|---|---|
| $[Fe(BMXY)_3(CH_2)_3\{B(cp)_2Fe\}]PF_6$ | +1.15 | 80 | 0.73 |
| ($6.0 \times 10^{-4}$ M) | +0.32 | 65 | 1.0 |
| | −1.05 | 70 | 0.91 |
| $[Fe(PMXY)_3(CH_2)_3\{B(cp)_2Fe\}]PF_6$ | +1.38$^d$ | irr | |
| ($1.3 \times 10^{-3}$ M) | +0.33 | 65 | 1.0 |
| | −0.90 | 70 | 0.87 |
| $[Fe(PAXY)_3(CH_2)_3\{B(cp)_2Fe\}]PF_6$ | +1.6$^d$ | irr | |
| ($1.0 \times 10^{-3}$ M) | +0.33 | 65 | 1.0 |
| | −0.88 | 75 | 0.70 |
| $[\{Fe(BMXY)_3(CH_2)_3\}_2\{B_2(cp)_2Fe\}](PF_6)_2$ | +1.16 | 90 | 0.76 |
| ($1.7 \times 10^{-3}$ M) | +0.23 | 70 | 1.0 |
| | −1.08 | 95 | 0.91 |

$^a$ Solvent: 0.1 M tetra-*n*-butylammonium tetrafluoborate in $CH_3CN$. Reference: Saturated sodium chloride calomel electrode. Working electrode: Platinum disk. Scan Rate: 100 mV/s. $^b$ $E_{1/2} = (E_{Pa} - E_{Pc})/2$. $^c$ Current ratio: $i_{Pc}/i_{Pa}$ for anodic waves; $i_{Pa}/I_{Pc}$ for cathodic waves. $^d$ Irreversible wave; anodic peak potential is reported.

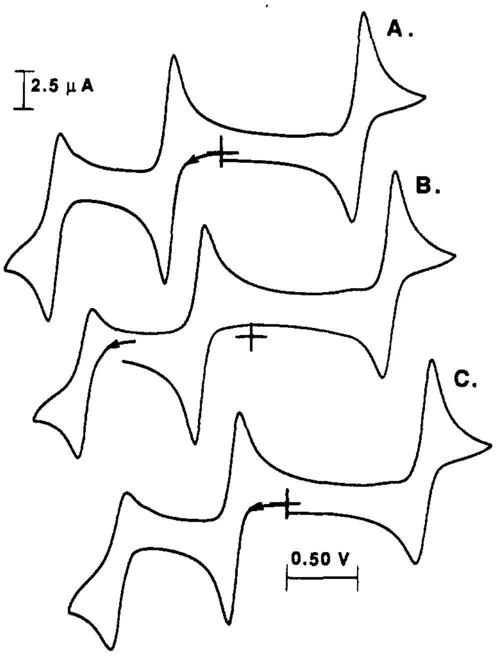

**Figure 4.** Cyclic voltammetric study of $[Fe(BMXY)_3(CH_2)_3\{B(cp)_2Fe\}]PF_6$ before and after electrolyses: (A) initial solution, 1.4 mM; (B) after electrolytic oxidation at +0.75 V (mixed-valent species); (C) after electrolytic rereduction at −0.20 V.

The electronic spectra of the complexes are dominated by an intense charge-transfer band in the region 19 800–20 600 $cm^{-1}$ (Table III). As noted previously, the energy of this band lies between that of comparable bands for Rose's dioxime-based iron clathrochelate complexes (22 000 $cm^{-1}$)[22,23] and Goedken's dihydrazone-based iron clathrochelate complex (19 100 $cm^{-1}$).[24,25] Additional absorbances at higher energies are attributable to $\pi \rightarrow \pi^*$ transitions within the conjugated $\pi$-system of the ligand. It is notable that the trimetallic complex $[\{Fe(BMXY)_3(CH_2)_3\}_2\{B_2(cp)_2Fe\}](PF_6)_2$ has an electronic spectrum which is essentially identical to that of the dimetallic complex $[Fe(BMXY)_3(CH_2)_3\{B(cp)_2Fe\}]PF_6$, with the molar absorptivities of the bands attributable to the clathrochelate groups being doubled as would be expected for a complex that has two clathrochelate moieties per molecule as opposed to one.

**Electrochemical Studies.** Cyclic voltammetric studies (Table IV) of the dimetallic complexes reveal a reversible one-electron oxidation of the ferrocenyl iron at 0.32–0.33 V *versus* the saturated sodium chloride calomel electrode (SSCE). Electrolytic oxidation of the ferrocenyl iron at a potential of +0.75 V produces a mixed-valence complex which is stable in solution. Cyclic voltammograms of the solution before and after electrolysis indicate that the integrity of the complexes is maintained as the ferrocenyl iron is cycled between the +2 and +3 oxidation states (Figure 4). These results also indicate that the redox potentials associated with the encapsulated iron are not affected by the oxidation state of the ferrocenyl iron; i.e., there is no apparent interaction between the two iron centers in the molecule. Coulometric measurements during these electrolytic experiments reveal "*n*" values approaching the expected value of one electron per molecule ($n = 0.93$–$0.99$). The color change of the solutions during the oxidative electrolyses is minimal. This result is initially surprising considering the fact that ferrocenylboronic acid undergoes a dramatic color change from pale yellow [$\lambda_{MAX}$ 22 600 cm$^{-1}$ (130 M$^{-1}$ cm$^{-1}$)] to blue [$\lambda_{MAX}$ 16 000 cm$^{-1}$ (330 M$^{-1}$ cm$^{-1}$)] on oxidation.[26] However, examination of the electronic spectra of the oxidized complexes reveals that the intense charge-transfer band associated with the encapsulated iron (molar absorptivity 10 000–24 000 M$^{-1}$ cm$^{-1}$) overwhelms the minor changes in the visible spectrum caused by the oxidation of the ferrocenyl iron. Close examination of the electronic spectra of the oxidized species uncovers a shoulder located at 16 100 cm$^{-1}$ (700 M$^{-1}$ cm$^{-1}$) on the low energy side of the charge-transfer band which corresponds well with the band observed in the oxidized ferrocenylboronic acid. This result also correlates well with the 16 100-cm$^{-1}$ band observed by Wherland and co-workers in their fully oxidized cobalt clathrochelate complex with two appended ferrocenes.[15] Changes also occur in the ultraviolet region of the spectrum on oxidation of the ferrocenyl iron with the $\pi \rightarrow \pi^*$ band at approximately 38 000 cm$^{-1}$ increasing in intensity. This increase in intensity in the UV region also correlates well with the changes observed in the electronic spectrum of ferrocenylboronic acid upon oxidation. No intervalence transfer bands were observed for the mixed-valent species in the near-infrared region out to the limit of the instrument used (900 nm). Attempts to isolate the mixed-valence species after either exhaustive oxidative electrolysis or chemical oxidation with nitrosonium tetrafluoborate have yet to be successful in producing pure materials.

The other redox couples observed for these dimetallic complexes are quite comparable to those couples observed for other iron(II) clathrochelate complexes of the oxime–hydrazone ligand system.[14] The [Fe(BMXY)$_3$(CH$_2$)$_3${B(cp)$_2$Fe}]PF$_6$ complex has a one-electron quasi-reversible couple at +1.15 V *versus* SSCE, which is assigned to the oxidation of the encapsulated iron(II). This is nearly identical to the oxidative couple observed in the [Fe(BMXY)$_3$(CH$_2$)$_3$(BC$_6$H$_5$)]PF$_6$ complex, which has a phenyl group in place of the ferrocenyl group.[14] The analogous couples in both the "PMXY" complex and the "PAXY" complex are irreversible with more than one electron being transferred in what is most likely an ECE mechanism involving eventual oxidation of the ligand and destruction of the complex. Attempts to electrolytically produce a fully oxidized species have lead to irreversible results with decomposition of the complex. A one-electron quasi-reversible reduction is also observed in all of these complexes in the range –0.88 to –1.05 V. It is likely that this is a metal-centered rather than a ligand-centered reduction since cobalt complexes of analogous ligands do not have reductions that occur at the same potential.[26]

Cyclic voltammetric studies of the trimetallic complex, [{Fe(BMXY)$_3$(CH$_2$)$_3$}$_2${B$_2$(cp)$_2$Fe}](PF$_6$)$_2$, reveal results that are very similar to those observed for the dimetallic species (Figure 5). The ferrocenyl iron undergoes a reversible one-electron reduction at a lower anodic potential, +0.23 V *versus* SSCE. This potential is 90 mV less anodic than the comparable oxidation in the dimetallic complexes and 220 mV less anodic than the oxidation of ferrocenylboronic acid itself ($E_{1/2}$ = 0.45 V *versus* SSCE).[26] This trend indicates that as the number of tetrahedral borate groups appended to the ferrocene moiety are increased, the electron density at the iron increases, making it easier to remove an electron and generate the ferrocenium species.

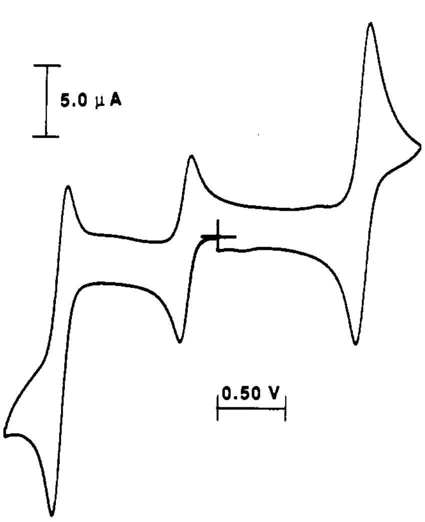

**Figure 5.** Cyclic voltammogram of the trinuclear species [{Fe(BMXY)$_3$(CH$_2$)$_3$}$_2${B$_2$(cp)$_2$Fe}](PF$_6$)$_2$ (0.65 mM).

The two-electron oxidative and reductive waves of the encapsulated Fe(II) species have shapes that match that of the one-electron oxidative wave of the ferrocenyl iron; however, the size of the waves is twice that of the one-electron wave. This result is expected for systems containing identical, noninteracting electroactive centers and has been observed in systems studied by Bard and Anson,[27] Taube,[28] Ciampolini and Fabrizzi,[29] and Lever.[30]

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(26) Grzybowski, J. J. Unpublished results.

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

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

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

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