generally be stronger than for large metal ions which have long M–N bonds. Large metal ions, such as Pb(II) with a M–N length in the vicinity of 2.5–2.7 Å (depending on coordination number), should thus have weak M–N force constants and be tolerant of considerable distortion of the M–N bonds. Thus, the fact that coordination to the trans-I conformer of 12-aneN$_4$ requires the metal to lie some 0.5 Å above the plane of the four nitrogen donor atoms[9] should present no problem. However, for smaller metal ions such as Cu(II), where such distortion of the M–N bonds will be met by strong resistance from the much larger force constants, the requirement of lying well above the plane of the nitrogen donors will cause considerable steric strain. This would lead to a destabilization of the 12- and 13-aneN$_4$ complexes relative to the cyclam complex, where the metal ion lies in the plane of the ligand. Yet another complicating feature which we might consider is that[9] for large metal ions (r° above 2.2 Å) the folded cis-V and trans-I forms of cyclam complex become more stable than the trans-III form, which we have considered here. This, however, serves only to narrow the gap in stability between the 12-aneN$_4$ and cyclam complexes for large metal ions, and there is no need to consider this in any detail either.

Figure 4 thus serves as an excellent, if rather simplified, analysis of the hole-size preference of the tetraaza macrocycles, indicating why it is that larger metal ions tend to prefer the smaller 12-aneN$_4$ macrocycle over cyclam. An important proviso here is that the metal ion should be able to tolerate having its M–N bonds distorted so that it lies some 0.5 Å above the plane of the nitrogen donors, which is likely to be met for all large metal ions.

A reviewer has pointed out that it is not clear that one can speak of hole size when the metal ion lies well out of the plane of the donor atoms, as for 12-aneN$_4$ complexes. What we have shown here and elsewhere[9] is that the tetraaza macrocycles are much more flexible than might have been appreciated. This becomes apparent when we compare the variation in log K_1 produced by varying the number of six- vs. five-membered rings in the open-chain tetraaza ligand along the series trien, 2,3,2-tet, 3,2,3-tet, and 3,3,3-tet (1,4,7,10-tetraazadecane, 1,4,8,11-tetraazaundecane, 1,5,8,12-tetraazadodecane, 1,5,9,13-tetraazatridecane). It is found[17] that the variation in log K_1 along this series parallels, but is often larger than, that along the analogous series of macrocycles from 12- to 15-aneN$_4$. This indicates that the variation in log K_1 along the latter series is related to the presence of five- vs. six-membered rings and is not connected with the presence of a macrocyclic structure. It is thus probably doubly true that we should not speak of hole size in relation to the tetraaza macrocycles. Indeed, our further investigations appear to indicate that the decrease in log K_1 that occurs for large metal ions as six-membered rings are substituted for five-membered rings is a general phenomenon. One of many examples of this effect is found in comparing complexes of EDTA (ethylenediaminetetraacetate) with those of TMDTA (trimethylenediaminetetraacetate). For small metal ions such as Cu(II) or Al(III) there is a small increase in log K_1 in passing from the EDTA complex with its five-membered ring to the TMDTA complex with its six-membered chelate ring.[19] For large metal ions such as Pb(II) or Sr(II) there is a large decrease in stability in making this change, of up to 5 log units.[19] We are at present extending our molecular mechanics calculations to examine this more general phenomenon, in the hope of explaining it and developing it as a tool for controlling selectivity for metal ions on the basis of their size.

Acknowledgment. We thank the Council Research Grants Committee of the University of the Witwatersrand and the Council for Scientific and Industrial Research for generous financial support.

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Synthesis and Electrochemistry of Iron(II) Clathrochelates

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A series of clathrochelates of iron(II) has been prepared from various dioximes (cyclohexanedione dioxime, dimethylglyoxime, and diphenylglyoxime) and boron capping agents (boron halides, borate esters, and boronic acids). New synthetic routes have been developed to introduce various boron substituents (e.g. chloro, bromo, methyl, and hydrido) into these complexes. Cyclic voltammetric studies reveal a pseudoreversible redox couple (Fe(II)/Fe(III)), the potential of which varies over 280 mV as the substituent on the boron cap is changed. The correlation of this potential shift with the Hammett σ_p parameters of the boron substituents has led to a division of the complexes into two groups (group I = Br, Cl, F, OH, OCH$_3$; group II = CH$_3$, H, C$_6$H$_5$, *n*-C$_4$H$_9$). Both groups show essentially linear redox potential behavior within their group with respect to the Hammett σ_p parameters. Attempts to correlate the ^{11}B NMR shifts with the redox potential of the Fe(II)/Fe(III) couple have failed to produce interpretable results. Controlled-potential electrolysis studies have not produced stable Fe(III) species. Decomposition occurs during the course of electrolysis, generating electroactive products as evidenced by very large *n* values (>10). The B–H-capped clathrochelate exhibits remarkable stability in acidic media. Material isolated from refluxing glacial acetic acid (67 h) still possesses a B–H bond as evidenced by infrared studies (ν_{B-H} = 2485 cm^{-1}). ^{11}B NMR studies of this complex reveal a crude doublet centered at −13.76 ppm vs. B(OCH$_3$)$_3$; J_{B-H} = 120 Hz.

Introduction

Clathrochelates, multicyclic ligand systems that completely encapsulate a metal ion, were first proposed by Busch.[1] Recently numerous examples of clathrochelates containing transition-metal ions have been reported.[2-10] Studies of the redox properties of these "cage" complexes have begun to yield much information concerning electron-transfer mechanisms, the stability of novel oxidation states, and the effect of peripheral groups on the redox properties of the central metal ion.[5,8-17]

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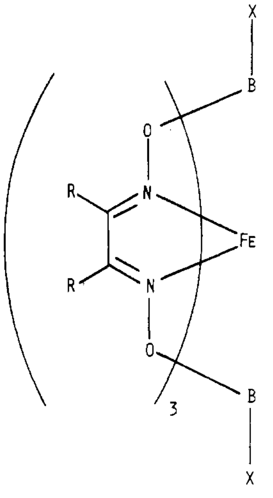
In order to systematically examine the effect of peripheral functional groups on the redox chemistry of the encapsulated metal ion, we chose to study the family of clathrochelates first developed by Rose.[2-4] These complexes are prepared via a template synthesis where the iron serves to orient three dioxime ligands so that they will react with various boron capping agents (boron halides, borate esters, or boronic acids) to produce a ligand cage (I). The framework of these molecules can be systematically altered by varying either the boron capping agent or the dioxime used in the synthesis. In the process of producing this series of complexes for the electrochemical study, new synthetic routes were developed to introduce various substituents at the boron cap. The most unique complex generated contains a boron hydride cap, which has proven to be remarkably unreactive.



I

Experimental Section

Syntheses. The reagents used, with the exception of methylboronic acid,[18] were obtained commercially [$FeBr_2$ (Alfa); diphenylglyoxime (Kodak); all others (Aldrich)] and used as received. The products were dried in vacuo at temperatures >80 °C.

The compounds $Fe(DMG)_3(BF)_2$, $Fe(DMG)_3(BOH)_2$, $Fe(DMG)_3(BOCH_3)_2$, $Fe(DMG)_3(BOC_2H_5)_2$, $Fe(NOX)_3(BF)_2$, $Fe(NOX)_3(BOH)_2$, and $Fe(NOX)_3(BC_6H_5)_2$ were prepared as described in the literature.[2-4] The simplified nomenclature used for the various complexes follows that used by Jackels and Rose.[2]

[Tris(μ-1,2-cyclohexanedione dioximato-*O*:*O*′)dimethyldiborato(2−)-$N,N',N'',N''',N'''',N'''''$]iron(II), [$Fe(NOX)_3(BCH_3)_2$]. A mixture of 0.50 g (2.5 mmol) of $FeCl_2 \cdot 4H_2O$, 1.07 g (7.5 mmol) of cyclohexanedione dioxime, and 25 mL of methanol was stirred for 10 min, producing a deep red solution. A 0.30-g (5.0 mmol) sample of methylboronic acid was added. A red/orange microcrystalline precipitate formed immediately. The product was isolated via suction filtration and washed with a small amount of methanol followed by diethyl ether. The product was dissolved in 20 mL of CH_2Cl_2, and the resulting solution was filtered via gravity and treated with methanol to induce precipitation. Yield: 0.74 g (56%).

Anal. Calcd for $C_{20}H_{30}N_6O_6B_2Fe$: C, 45.50; H, 5.73; N, 15.92. Found: C, 45.67; H, 5.65; N, 15.74.

[Tris(μ-1,2-cyclohexanedione dioximato-*O*:*O*′)dichlorodiborato(2−)-$N,N',N'',N''',N'''',N'''''$]iron(II), [$Fe(NOX)_3(BCl)_2$]. A mixture of 0.50 g of $FeCl_2 \cdot 4H_2O$, (2.5 mmol), 1.07 g of cyclohexanedione dioxime (7.5 mmol), and 50 mL of CH_2Cl_2 was stirred for 45 min. To this mixture was added 10 mL (twofold excess) of 1 M BCl_3 in CH_2Cl_2. The reaction was stirred for 30 min and filtered via suction. The filtrate, treated with 25 mL of methanol, was rotary evaporated at low heat to a volume of 25 mL. The red crystalline product was filtered via suction, washed with ethyl ether, and dissolved in 40 mL of CH_2Cl_2, and the resulting solution was filtered via gravity, treated with 60 mL of methanol, and cooled overnight to 6 °C. The red crystalline product was filtered via suction and washed with ethyl ether. Yield: 0.43 g (30%).

Anal. Calcd for $C_{18}H_{24}N_6O_6B_2Cl_2Fe$: C, 38.07; H, 4.26; N, 14.80; Cl, 12.49. Found: C, 38.11; H, 4.31; N, 14.85; Cl, 12.41.

[Tris(μ-1,2-cyclohexanedione dioximato-*O*:*O*′)dibromodiborato(2−)-$N,N',N'',N''',N'''',N'''''$]iron(II), [$Fe(NOX)_3(BBr)_2$]. A mixture of 0.54 g of $FeBr_2$ (2.5 mmol), 1.07 g of cyclohexanedione dioxime (7.5 mmol), and 50 mL of CH_2Cl_2 was stirred for 90 min. A 5-mL aliquot of 1 M BBr_3 in CH_2Cl_2 was added, causing a solid to precipitate and a dark red oil to separate. After suction filtration, the filtrate was treated with 25 mL of methanol and rotary evaporated to a volume of 10 mL. The red precipitate was isolated via suction filtration and washed with diethyl ether. The product was dissolved in 20 mL of CH_2Cl_2, and the resulting solution was filtered via gravity, treated with 25 mL of methanol, and rotary evaporated to 15 mL. The red crystalline precipitate was filtered via suction and washed with diethyl ether. Yield: 0.28 g (15%).

Anal. Calcd for $C_{18}H_{24}N_6O_6B_2Br_2Fe \cdot CH_2Cl_2$: C, 30.73; H, 3.98; N, 11.32; Br, 21.52. Found: C, 31.41; H, 3.56; N, 11.70; Br, 21.53.

[Tris(μ-1,2-cyclohexanedione dioximato-*O*:*O*′)dimethoxydiborato(2−)-$N,N',N'',N''',N'''',N'''''$]iron(II), [$Fe(NOX)_3(BOCH_3)_2$]. A 125-mL Erlenmeyer flask was charged with 1.0 g (5.0 mmol) of $FeCl_2 \cdot 4H_2O$, 2.13 g (15.0 mmol) of cyclohexanedione dioxime, and 25 mL of methanol. The mixture was stirred for 10 min, treated with 0.62 g (10.0 mmol) of H_3BO_3, and heated to reflux for an additional 10 min. A 0.95-g (2.5 mmol) sample of sodium borate was added slowly to the warm solution. The product was filtered via suction and washed with ethyl ether. The red/orange product was recrystallized from boiling methanol. Yield: 1.2 g (43%).

Anal. Calcd for $C_{20}H_{30}N_6O_8B_2Fe$: C, 42.90; H, 5.40; N, 15.01. Found: C, 43.32; H, 5.17; N, 14.70.

[Tris(μ-1,2-cyclohexanedione dioximato-*O*:*O*′)di-*n*-butyldiborato(2−)-$N,N',N'',N''',N'''',N'''''$]iron(II), [$Fe(NOX)_3(B$-$n$-$C_4H_9)_2$]. A 125-mL Erlenmeyer flask was charged with 0.5 g (2.5 mmol) of $FeCl_2 \cdot 4H_2O$, 1.07 g (7.5 mmol) of cyclohexanedione dioxime, and 50 mL of methanol. A 0.51-g sample of *n*-butylboronic acid was added to the stirred solution, producing an immediate red/orange microcrystalline precipitate. The product, isolated via suction filtration, was washed with a small amount of methanol followed by a small amount of diethyl ether. The complex was dissolved in 50 mL of CH_2Cl_2, and the resulting solution was filtered by gravity and treated with 25 mL of CH_3OH. Removal of the CH_2Cl_2 via rotary evaporation produced a red crystalline product. Yield: 1.0 g (65%).

Anal. Calcd for $C_{26}H_{42}N_6O_6B_2Fe$: C, 51.01; H, 6.92; N, 13.73. Found: C, 51.11; H, 6.81; N, 13.73.

[Tris(μ-1,2-cyclohexanedione dioximato-*O*:*O*′)dihydrodiborato(2−)-$N,N',N'',N''',N'''',N'''''$]iron(II), [$Fe(NOX)_3(BH)_2$]. A mixture of 0.54 g (2.5 mmol) of $FeBr_2$ and 1.07 g (7.5 mmol) of cyclohexanedione dioxime was stirred in 50 mL of acetonitrile (distilled from CaH_2) for 30 min. A 0.19-g (5.0 mmol) sample of $NaBH_4$ was added; stirring was continued for 16 h. The orange solid that formed was isolated via suction filtration, transferred to an Erlenmeyer flask, and stirred in 50 mL of methanol for 30 min. The suspension was filtered via suction, and the orange solid that was isolated was dissolved in 100 mL of methylene chloride. Following gravity filtration, the solution was passed through a column of neutral alumina (Fisher) using methylene chloride as the eluant. The orange band that eluted was collected, treated with 25 mL of methanol, and rotary evaporated until removal of the methylene chloride produced a red crystalline product. The $Fe(NOX)_3(BH)_2$ was isolated via suction filtration and washed with small amounts of methanol and diethyl ether. Yield: 0.15 g (11%). The product was recrystallized by dissolution in 150 mL of chloroform/methanol (5/1), and rotary evaporation to about 20 mL.

Anal. Calcd for $C_{18}H_{26}B_2FeN_6O_6$: C, 43.24; H, 5.24; N, 16.81. Found: C, 43.04; H, 5.44; N, 16.53.

[Tris(μ-2,3-butanedione dioximato-*O*:*O*′)diphenyldiborato(2−)-$N,N',N'',N''',N'''',N'''''$]iron(II), [$Fe(DMG)_3(BC_6H_5)_2$]. A 50-mL Erlenmeyer flask was charged with 0.5 g of $FeCl_2 \cdot 4H_2O$ (2.5 mmol), 0.87 g of dimethylglyoxime (7.5 mmol), and 25 mL of methanol. Warming produced a neat solution, which was treated with 0.61 g (5.0 mmol) of phenylboronic acid. The orange microcrystalline product was filtered via suction and washed with diethyl ether. An adequate recrystallization solvent was not found.

Anal. Calcd for $C_{24}H_{28}B_2FeN_6O_6$: C, 50.22; H, 4.92; N, 14.64. Found: C, 50.07; H, 5.09; N, 14.44.

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[Tris(μ-2,3-butanedione dioximato-*O*:*O*′)dimethyldiborato(2−)-*N*,*N*′,*N*″,*N*‴,*N*⁗,*N*′′′′′]iron(II), $[Fe(DMG)_3(BCH_3)_2]$. A solution of 0.5 g of $FeCl_2 \cdot 4H_2O$ (2.5 mmol) and 0.87 g of dimethylglyoxime (7.5 mmol) in 40 mL of methanol was warmed to approximately 60 °C. A 0.30-g sample of methylboronic acid (5.0 mmol) was added. After being stirred for 1 h, the cool solution yielded a red/orange precipitate, which was filtered via suction and washed with diethyl ether. Yield: 0.50 g. Recrystallization was accomplished by dissolving 200 mg of the product in 200 mL of methylene chloride, filtering the resulting solution and adding 40 mL of methanol. Removal of the methylene chloride by rotary evaporation yielded a red crystalline product.

Anal. Calcd for $C_{14}H_{24}N_6O_6B_2Fe$: C, 37.38; H, 5.38; N, 18.68. Found: C, 36.68; H, 5.41; N, 18.69.

[Tris(μ-1,2-diphenyl-1,2-ethanedione dioximato-*O*:*O*′)dimethyldiborato(2−)-*N*,*N*′,*N*″,*N*‴,*N*⁗,*N*′′′′′]iron(II), $[Fe(DPG)_3(BCH_3)_2]$. A mixture of 0.5 g of $FeCl_2 \cdot 4H_2O$ (2.5 mmol) and 1.8 g of diphenylglyoxime in 50 mL of 1-butanol was heated to boiling. A 0.30-g sample of methylboronic acid was added to the reaction mixture. Heating and stirring were continued for 1 h. After cooling, the solid was filtered via suction and dissolved in about 10 mL of methylene chloride and the resulting solution filtered via gravity. Slow addition of 10 mL of methanol to the filtrate produced a crystalline product, which was isolated via suction filtration and washed with diethyl ether. The compound was recrystallized from methylene chloride/methanol.

Anal. Calcd for $C_{44}H_{36}N_6O_6B_2Fe$: C, 64.27; H, 4.41; N, 10.22. Found: C, 64.18; H, 4.53; N, 10.03.

[Tris(μ-2,3-butanedione dioximato-*O*:*O*′)dihydrodiborato(2−)-*N*,*N*′,*N*″,*N*‴,*N*⁗,*N*′′′′′]iron(II), $[Fe(DMG)_3(BH)_2]$. A 125-mL Erlenmeyer flask was charged with 0.87 g (7.5 mmol) of dimethylglyoxime, 0.54 g (2.5 mmol) of anhydrous ferrous bromide, and 40 mL of acetonitrile (distilled from CaH_2). The mixture was stirred for 30 min, treated with 0.19 g (5.0 mmol) of $NaBH_4$, and stirred for an additional 16 h. The brown reaction mixture was rotary evaporated to dryness, extracted with 250 mL of methylene chloride, filtered via gravity, and passed through a neutral alumina column (CH_2Cl_2 eluant). The yellow band that eluted was collected, treated with 25 mL of methanol, and rotary evaporated to remove the methylene chloride. The dark red crystalline solid that precipitated was filtered via suction and washed with methanol and diethyl ether. Yield: 0.22 g (21%). The compound was recrystallized by rotary evaporation of a methylene chloride/methanol solution.

Anal. Calcd for $C_{12}H_{20}B_2FeN_6O_6$: C, 34.17; H, 4.78; N, 19.92; Fe, 13.24. Found: C, 34.07; H, 4.92; N, 20.02; Fe, 12.62.

Physical Measurements. ^1H NMR spectra were recorded on a Varian T60 spectrometer (60 MHz) using tetramethylsilane as an internal reference, $\delta = 0$. ^{11}B NMR spectra were run at the Northeast Regional NSF-NMR Facility at Yale University on a Brucker WM500 spectrometer (160.47 MHz) using a ^2H lock and trimethylborate as an external reference, $\delta = 0$. The solvent used was $CDCl_3$. Visible and ultraviolet spectra were obtained with a Perkin-Elmer 502 recording spectrophotometer. Infrared spectra were recorded by using KBr pellets and a Perkin-Elmer 281B recording spectrophotometer. Elemental analyses were performed by Galbraith Labs, Inc., Knoxville, TN.

Cyclic voltammetry was performed by using a Bioanalytical Systems CV-1A instrument in conjunction with a Houston Instrument Model 2000 XY recorder. A typical H-cell with a medium-porosity glass frit was used with platinum wires serving as the working and counter electrodes and Ag^0/Ag^+ (0.1 M in CH_3CN) serving as the reference electrode. Acetonitrile (distilled from CaH_2) was used as the solvent and tetra-*n*-butylammonium fluoborate (Fisher; recrystallized three times from water/methanol and dried in vacuo at 105 °C) was used as the supporting electrolyte. Whenever possible the ferrocene/ferrocenium couple was used as an internal reference to correct for reference-electrode deterioration and liquid-junction potentials.[19] Electrolyses were performed by using an Electrosynthesis Co. Model 420A power supply in conjunction with a Model 410 potentiostatic controller. A Model 640 digital coulometer was used to determine *n* values. A three-compartment cell, employing medium-porosity glass frits, a platinum-gauze working electrode, a platinum-wire counter electrode, and a $Ag^0/AgCl$ (in CH_3CN) reference electrode was used for the electrolytic studies. Electrolyses were routinely performed at 200 mV beyond the observed cyclic voltammetric peak.

Results and Discussion

Synthesis. The use of boron trifluoride etherate, boric acid, and borate esters as capping agents to form the desired clathrochelates has been well characterized by Jackels and Rose.[2] Rose also introduced the use of boronic acids as capping agents and alluded to the wide variety of structural types that could be produced by using this synthetic route.[4] These procedures have proven to be very useful in producing many of the clathrochelates used in this study. In addition to the complexes produced by following or paralleling Rose's methods, new synthetic routes were developed to further extend this series of clathrochelates.

The use of 1 M solutions of BCl_3 or BBr_3 in CH_2Cl_2 in place of $BF_3 \cdot O(C_2H_5)_2$ in Rose's synthesis did not produce the desired clathrochelates. Addition of the boron trichloride or the boron tribromide to a solution of dioxime and ferrous chloride tetrahydrate in 1-butanol produced a violent reaction and immediate precipitation of a paramagnetic crystalline solid that defied identification and slowly decomposed on standing. A successful synthesis of $[Fe(NOX)_3(BCl)_2]$ was achieved by using methylene chloride as the solvent, thereby ensuring that the BCl_3 would react with the dioxime instead of the solvent. Parallel attempts to produce $[Fe(NOX)_3(BBr)_2]$ using $FeCl_2 \cdot 4H_2O$ as the starting material produced a material that contained 23.6% of the bromines replaced by chlorines as shown by ^{11}B NMR and verified by elemental analysis. Use of $FeBr_2$ as the iron source produced the desired fully brominated complex. Attempts to synthesize the analogous chloro and bromo compounds using dimethylglyoxime or diphenylglyoxime were unsuccessful because of the poor solubility of these materials in methylene chloride.

The synthesis of $[Fe(NOX)_3(BH)_2]$ follows the generalized equation

$$FeBr_2 + 3NOXH_2 + 2NaBH_4 \xrightarrow{CH_3CN} [Fe(NOX)_3(BH)_2] + 2NaBr + 6H_2(g)$$

It is assumed that the formation of $[Fe(NOXH_2)_3]Br_2$ as an intermediate orients the oxime hydrogens for reaction with the borohydride ion. The possibility of $[Fe(NOXH_2)_3]Br_2$ acting as an intermediate was demonstrated by isolating this tris(dioxime) complex[20] and reacting it in tetrahydrofuran with sodium borohydride to produce $[Fe(NOX)_3(BH)_2]$. Attempts to produce the desired clathrochelate in methanol or butanol or to use a hydrated iron salt resulted in products that contain boron hydrogen bonds (infrared evidence) but are contaminated with B–OH or B–OR capping groups as shown by ^{11}B and/or ^1H NMR. Initially it was hoped that the reactivity of the boron hydrogen bond would allow new functional groups to be introduced at this position, but the lack of reactivity of this bond has all but precluded its use as a synthetic opening (see below). The use of substituted borohydrides such as sodium cyanoborohydride (Alfa) or sodium acetanilidotrihydridoborate (Alfa) in the synthetic scheme described above results in $[Fe(NOX)_3(BH)_2]$ with no evidence supporting retention of the novel substituents.

Characterization of the Clathrochelates. The infrared spectra of the complexes with ligands derived from dimethylglyoxime and cyclohexanedione dioxime have been reported by Rose and coworkers.[2,4] Sahoo and co-workers[7] have characterized the diphenylglyoxime complexes. The new complexes synthesized for this study possess infrared spectra that are virtually identical with those of the previously reported complexes, except for the changes expected from the varied boron substituent, the most dramatic of these being the intense boron hydrogen stretch at 2490 cm^{-1} for $[Fe(NOX)_3(BH)_2]$ and 2495 cm^{-1} for $[Fe(DMG)_3(BH)_2]$. The UV–visible spectra of the complexes were dominated by an intense ($\epsilon = \sim 17000$ L/(mol·cm)) charge-transfer band centered at $\sim 22.5 \times 10^3$ cm^{-1}. The position of the charge-transfer band was not sensitive to variations in the boron substituent.

^1H NMR signals from the dioxime portion of the clathrochelate ligands did not vary significantly from complex to complex; i.e., cyclohexanedione dioxime had two multiplets at ~1.8 and ~2.9 ppm, dimethylglyoxime had one singlet at ~2.4 ppm, and diphenylglyoxime had a multiplet at ~7.3 ppm. The ^1H resonances of the boron substituents are reported in Table I. The methyl

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(20) Anal. Calcd for $C_{18}H_{30}Br_2FeN_6O_6$: C, 32.57; H, 4.56; N, 12.66; Br, 24.08. Found: C, 33.67; H, 4.64; N, 13.17; Br, 24.18.

Table I. ^1H and ^{11}B NMR Resonances[a]

compd	^1H resonance(s) of boron substituent,[b] ppm	^{11}B resonance(s),[c] ppm	^{11}B resonance half-height peak width, ppm
$[Fe(NOX)_3(BF)_2]$		−14.66 (doublet; J_{B-F} = 15 Hz)	0.013
$[Fe(NOX)_3(BCl)_2]$		−11.07	0.029
$[Fe(NOX)_3(BBr)_2]$		−12.19	0.039
$[Fe(NOX)_3(BOH)_2]$	masked by NOX CH_2 resonance at 1.8	−13.52	0.37
$[Fe(NOX)_3(BOCH_3)_2]$	3.55	−13.40	0.45
$[Fe(NOX)_3(BH)_2]$	not observed	−13.76 (doublet; J_{B-H} = 120 Hz)	1.07
$[Fe(NOX)_3(BCH_3)_2]$	0.03	−9.80	1.60
$[Fe(NOX)_3$-$(B$-n-$C_4H_9)_2]$	α-CH_3, broad multiplet 0.6; β- and γ-CH_2, broad multiplet 1.4; CH_3, crude triplet 0.95	−9.59	2.70
$[Fe(NOX)_3(BC_6H_5)_2]$	two multiplets, 7.3 and 7.7	−11.4	2.20
$[Fe(DMG)_3(BH)_2]$	not observed	−13.76 (doublet; J_{B-H} = 125 Hz)	0.73
$[Fe(DMG)_3(BCH_3)_2]$	0.08	−9.64	1.23
$[Fe(DPG)_3(BCH_3)_2]$	−0.2	−22 (very broad)	17.2

[a] The ^1H resonances of the NOX and DMG in clathrochelates of this type have been reported by Rose and co-workers.[2,4] These resonances in the new complexes are essentially unchanged. The phenyl resonances of the DPG complex appear as a complex multiplet centered at 7.3 ppm. [b] $CDCl_3$; Me_4Si internal reference. [c] $CDCl_3$; values are reported vs. $B(OCH_3)_3$, δ = 0.

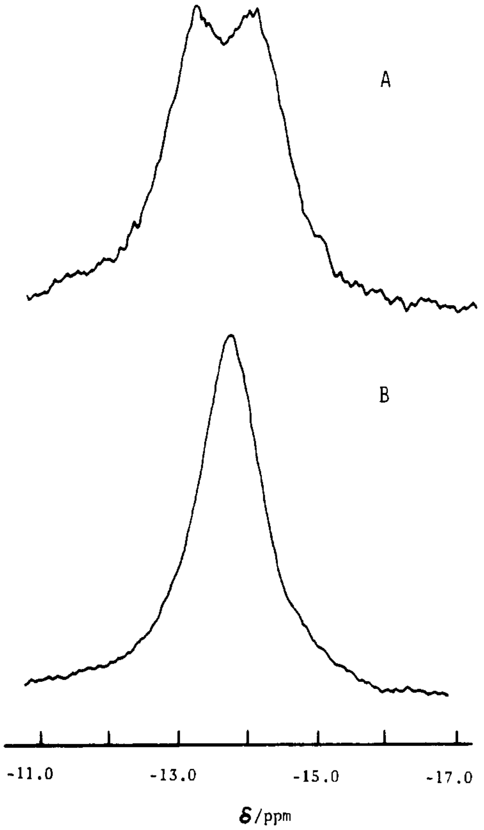

Figure 1. Boron-11 NMR spectrum of $[Fe(NOX)_3(BH)_2]$ vs. external $B(OCH_3)_3$: (A) coupled; (B) proton decoupled.

substituents are deshielded by the boron atom and shifted upfield to a position very nearly overlapping the Me_4Si reference signal. The n-butyl substituent also exhibits an upfield shift (0.6 ppm) for the protons of the methylene group attached to the boron atom. The protons of the β and γ methylenes and the terminal methyl appear in their expected positions. The ^1H resonances of the hydridic protons of $[Fe(NOX)_3(BH)_2]$ and $[Fe(DMG)_3(BH)_2]$ were not observed. This failure is most likely due to large quadrapole broadening by the adjacent boron atom.

The ^{11}B nuclear magnetic resonances are reported in Table I. The chemical shifts observed for the $[Fe(NOX)_3(BX)_2]$ series do not follow a simple pattern. Attempts to correlate the shift with the electronegativity of the adjacent substituent atom fail; e.g., simple Pauling electronegativities[21] predict an order of F > OH = OCH_3 > Cl > Br > C_6H_5 = CH_3 = C_4H_9 > H with the observed order being F > H > OH > OCH_3 > Br > C_6H_5 > Cl > CH_3 > C_4H_9. The use of Mulliken–Jaffe electronegativities[21] does not improve the correlation [OH = OCH_3 (sp^3) > F > Cl > C_6H_5 (sp^2) > Br > CH_3 = C_4H_9 (sp^3) > H]. In both of these attempted correlations the most deviant result is that of the hydrogen substituent. Previous studies on tetravalent boron compounds have established the order BH_4^- > BF_4^- > $B(C_6H_5)_4^-$ > $B(OCH_3)_4^-$ for the magnitude of the ^{11}B NMR chemical shifts, indicating that the anomalous behavior of our B–H compound and the lack of correlation with electronegativities are not without precedent.[22,23] The ordering of the halogens (F > Br > Cl) has also been observed previously in ^{11}B NMR studies with the planar boron trihalides.[22,23]

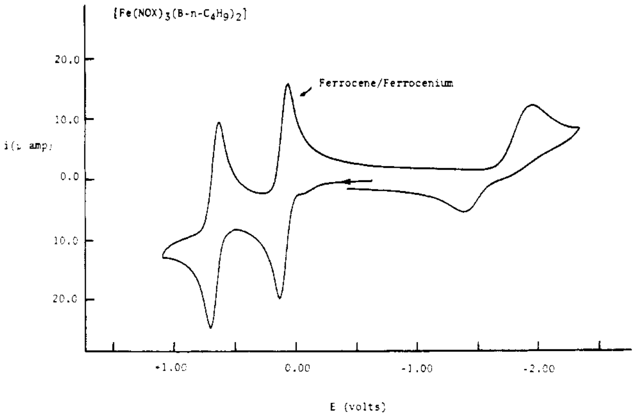

Figure 2. Cyclic voltammogram of $[Fe(NOX)_3(B$-n-$C_4H_9)_2]$ vs. a Ag^0/Ag^+ reference electrode (ferrocene is added as an internal standard).

The sharpness of the observed ^{11}B resonance peaks varies dramatically, with the half-height peak width varying from 0.013

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Table II. Cyclic Voltammetric Data—[Fe(NOX)$_3$(BX)$_2$] Complexes

compd	$(E_{P_{\mathrm{ANOD}}} + E_{P_{\mathrm{CATH}}})/2$,[a] V	peak separation Δ, mV 100 mV/s	300 mV/s
[Fe(NOX)$_3$(BF)$_2$]	0.745	90	100
[Fe(NOX)$_3$(BCl)$_2$]	0.825	70	90
[Fe(NOX)$_3$(BBr)$_2$]	0.850	70	80
[Fe(NOX)$_3$(BOH)$_2$]	0.610	60	75
[Fe(NOX)$_3$(BOCH$_3$)$_2$]	0.640	60	65
[Fe(NOX)$_3$(BH)$_2$]	0.640	60	65
[Fe(NOX)$_3$(BCH$_3$)$_2$]	0.575	65	75
[Fe(NOX)$_3$(B-*n*-C$_4$H$_9$)$_2$]	0.570	70	80
[Fe(NOX)$_3$(BC$_6$H$_5$)$_2$]	0.635	60	65

[a] Vs. ferrocene/ferrocenium internal reference (see ref 19); scan 100 mV/s.

Table III. Cyclic Voltammetric Data—[Fe(DMG)$_3$(BX)$_2$] Complexes

compd	$(E_{P_{\mathrm{ANOD}}} + E_{P_{\mathrm{CATH}}})/2$,[a] V	peak separation Δ, mV 100 mV/s	300 mV/s
[Fe(DMC)$_3$(BF)$_2$]	0.775	70	90
[Fe(DMG)$_3$(BOH)$_2$]	0.620	60	65
[Fe(DMG)$_3$(BOCH$_3$)$_2$]	0.655	75	95
[Fe(DMG)$_3$(BOC$_2$H$_5$)$_2$]	0.650	65	80
[Fe(DMG)$_3$(BH)$_2$]	0.650	70	75
[Fe(DMG)$_3$(BCH$_3$)$_2$]	0.580	60	70
[Fe(DMG)$_3$(BC$_6$H$_5$)$_2$]	*b*		

[a] Vs. ferrocene/ferrocenium internal reference (see ref 19); scan 100 mV/s. [b] Insufficient solubility.

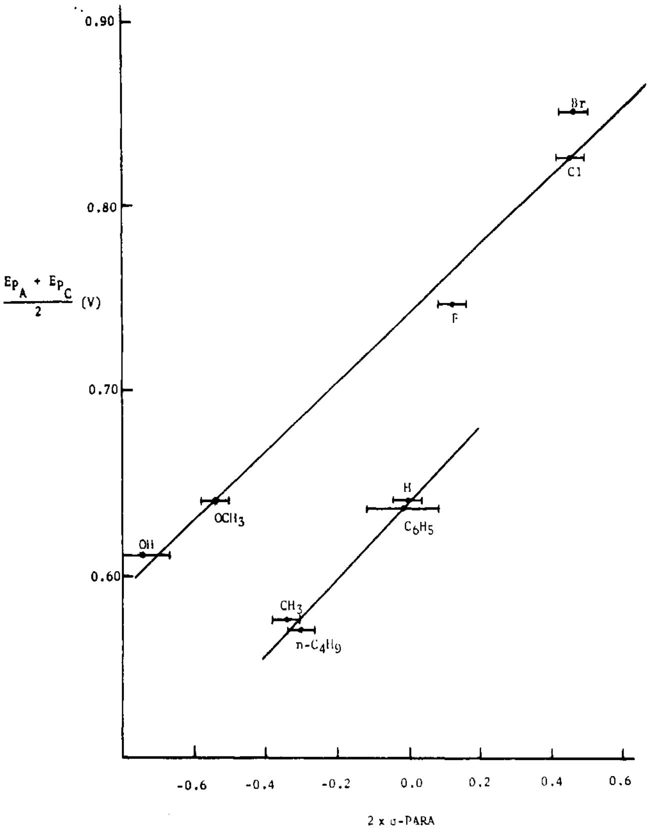

Figure 3. Plot of oxidation potential vs. $2\sigma_p$ for the [Fe(NOX)$_3$(BX)$_2$] series. Uncertainties in $2\sigma_p$ are from ref 32.

(B–F) to 2.70 ppm (B-*n*-C$_4$H$_9$) within the [Fe(NOX)$_3$(BX)$_2$] series. Sharp resonance lines arise from ^{11}B nuclei that exist in environments of spherical charge distribution.[24] This indicates that the fluoro substituent in conjunction with the three oxygens produces the most symmetrical charge distribution around the boron nucleus. In general, it appears that as the substituents become less electronegative the half-height peak width increases.

Electrochemical Studies. A sample cyclic voltammogram is shown in Figure 2. Ferrocene has been added to the sample as an internal standard to correct for liquid-junction potentials and possible variations in the Ag^0/Ag$^+$ (0.1 M in CH$_3$CN) reference electrode.[19,25] Data for the [Fe(NOX)$_3$(BX)$_2$] series and the [Fe(DMG)$_3$(BX)$_2$] series are found in Tables II and III, respectively. The oxidative couple reported is quasi-reversible and is assigned to the Fe$^{\mathrm{II}}$/Fe$^{\mathrm{III}}$ couple. Evidence supporting a metal-centered redox process instead of a ligand-centered process arises from the facts that (1) variations in the ligand system do not greatly affect the position, reversibility, or general appearance of the cyclic voltammetric waves and (2) electrochemical studies of cobalt complexes with identical ligand systems do not produce redox couples other than those that are well established (through electrolytic studies) as being metal centered.[26] Attempts to obtain direct evidence for a metal-centered oxidation via exhaustive electrolysis and isolation of the Fe(III) clathrochelate have not succeeded. The electrolysis experiments all produce *n* values much greater than 1, with values greater than ten times the expected number of coulombs having been recorded. It is believed that these large values result from an ECE mechanism where the Fe(III) clathrochelate produced decomposes into electrochemically active products. The decomposition of the original clathrochelates is verified by cyclic voltammetry of the electrolyzed solutions, which shows the complete disappearance of the original Fe(II)/Fe(III) couple and the generation of a complex voltammogram, which has yet to be interpreted. It should be noted that efforts to produce the Fe(III) clathrochelates through chemical oxidation have also failed.[2,27]

The irreversible reduction observed in Figure 2 is representative of that observed in all of the complexes studied, regardless of ligating system. This reduction, which appears in the potential range −1.5 to −2.2 V [vs. Ag^0/Ag$^+$ (0.1 M in CH$_3$CN)], has not been assigned to a specific redox process.

The data in Tables II and III illustrate the effect of the boron substituent on the position of the Fe(II)/Fe(III) couple. A range of 200 mV is noted for the [Fe(DMG)$_3$(BX)$_2$] series and 280 mV for the more extensive [Fe(NOX)$_3$(BX)$_2$] series. It is presumed that electron-releasing and/or electron-withdrawing mechanisms of the capping substituent alter the electron density in the ligating cage, which in turn alters the electron density at the iron atom. Mössbauer studies by Jackels and Rose[2] verify that the boron substituents affect the electron density at the iron atom with isomer shifts (δ) relative to sodium nitroprusside ranging from 0.42 to 0.32 mm/s (±0.02 mm/s) as the capping substituent is varied from B–F to B–O–*i*-C$_3$H$_7$. This trend is attributed to the greater "elctron-releasing" character of the alkoxy group in comparison to the fluoro group.[2] The electrochemical results loosely follow this trend. The "electron-releasing" alkoxy group should via the σ bonds of the ligand cage provide greater electron density at the iron atom, which in turn should facilitate the loss of an electron and oxidation to Fe(III). This simplistic approach is supported by the electrochemical results, which show that the alkoxy-substituted clathrochelates are oxidized 100–120 mV before the comparable fluoro-substituted complexes.

The substituent effects were examined by using a Hammett treatment.[28-30] Graphs of $(E_{P_{\mathrm{ANOD}}} + E_{P_{\mathrm{CATH}}})/2$ vs. $2\sigma_p$[31,32] for the

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(24) Muetterties, E. L. "The Chemistry of Boron and Its Compounds"; Wiley: New York, 1967; p 159.

(25) Cyclic voltammograms were run in the presence and absence of ferrocene to ensure that the ferrocene had no effect on the electrochemistry of the compound of interest.

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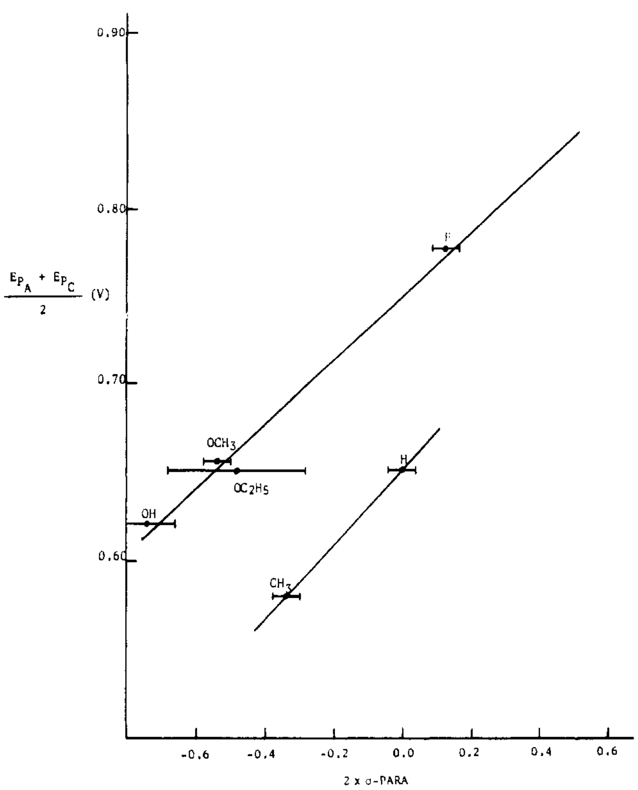

Figure 4. Plot of oxidation potential vs. $2\sigma_p$ for the $[Fe(DMG)_3(BX)_2]$ series. Uncertainties in $2\sigma_p$ are from ref 32.

$[Fe(NOX)_3(BX)_2]$ series and the $[Fe(DMG)_3(BX)_2]$ series are presented in Figures 3 and 4, respectively. The $[Fe(NOX)_3(BX)_2]$ series is divided into two groups by this treatment (group I = Br, Cl, F, OH, OCH_3; group II = H, CH_3, n-C_4H_9, C_6H_5). Both groups show essentially linear behavior within their group with respect to the ordinary Hammett σ_p parameters. The lines generated are parallel within the standard deviation of the data (group I, slope = 0.19 ± 0.02; group II, slope = 0.21 ± 0.01). The smaller $[Fe(DMG)_3(BX)_2]$ series follows an identical pattern (group I = F, OH, OCH_3, OC_2H_5, slope = 0.18 ± 01; group II = H, CH_3, slope = 0.21). The slope can be used as an indication of the sensitivity of the redox potential to the electronic properties of the substituent. Busch and co-workers[29] have observed larger slopes (0.52–0.58) in a similar study of substituent effects in tetraaza macrocycles. The diminished effect of the substituents in this study is most likely due to the fact that the substituent is separated from the reacting center by four σ bonds. Given this separation, the effect although diminished is rather dramatic.

The reasons behind the division of the complexes into two groups are not understood. The obvious feature distinguishing the two groups from each other is the presence of nonbonding electron pairs on the group I substituents. However, the importance of this observation in the overall mechanism of the interaction is open to speculation. In an attempt to explore further this phenomenon a correlation between ^{11}B nuclear magnetic resonance shifts and redox potentials was undertaken. It was expected that shifts in the ^{11}B resonance peak would reflect the electron density at the boron atom. Greater or lesser electron density at the boron atom would be transmitted to the iron atom via the σ-bond network, thereby affecting the Fe(II)/Fe(III) redox potential. No simple correlation was obtained, indicating that the mechanism of interaction involves more than simple electronic considerations.

Table IV. Cyclic Voltammetric Data—Effect of Changing the Dioxime Ligand

compd	$(E_{P_{ANOD}} + E_{P_{CATH}})/2$,[a] V	peak separation Δ, mV 100 mV/s	300 mV/s
$[Fe(NOX)_3(BCH_3)_2]$	0.580	60	70
$[Fe(DMG)_3(BCH_3)_2]$	0.575	65	75
$[Fe(DPG)_3(BCH_3)_2]$	0.775	60	65

[a] Vs. ferrocene/ferrocenium internal reference (see ref 19); scan 100 mV/s.

It is interesting to note that the breadth of the ^{11}B resonance line follows this division of the complexes into two groups, with group I having the narrower lines and group II having the broader lines. The connection between this observation and the electrochemical results is open to interpretation but could involve slight distortions in the tetrahedral geometry of the boron atom altering, via the σ-bond network, the coordination geometry of the nitrogen donors surrounding the iron atom. However, without corroborating structural evidence this approach is purely speculative.

The data cataloging the effect of varying the dioxime portion of the ligand is presented in Table IV. The NOX and DMG ligands do not vary significantly from one another. However, the DPG ligand shifts the redox potential about 200 mV to the positive, making the Fe(III) oxidation state much more inaccessible.

Attempts to synthesize the clathrochelates derived from acetylacetone dioxime[7] to examine the effect of altering the chelate ring size on the Fe(II)/Fe(III) redox potential have failed to produce the desired materials.

Reactivity of the B–H Cap. The $BH(OR)_3^-$ functional group has been shown to be a powerful reducing agent.[33,34] For example, the reaction of acetone with sodium triisopropoxyborohydride in diglyme at 0 °C is complete in seconds.[34] The boron-hydrogen bond in $[Fe(NOX)_3(BH)_2]$ has proven to be remarkably unreactive. Attempts to react $[Fe(NOX)_3(BH)_2]$ with acetone have yielded no reaction after 16 h of reflux.

The acid stability of the complex is even more noteworthy. Studies in concentrated hydrochloric acid indicate that the complex slowly decomposes, producing a pale yellow solution as has been previously reported for similar clathrochelates without hydridic protons.[2] Nonetheless, a suspension of $[Fe(NOX)_3(BH)_2]$ in concentrated HCl that had been stirred for 16 h at 25 °C still yielded a product that contained an intact B–H bond (ν_{B-H} 2485 cm^{-1}). Material isolated from glacial acetic acid after 67 h of reflux still exhibited a strong B–H stretch at 2485 cm^{-1}; however, acetate ester formation is believed to be occurring gradually as evidenced by the appearance of infrared bands typical of esters ($\nu_{C=O}$ 1730 cm^{-1}; ν_{C-O} 1270 cm^{-1}) in the isolated materials.[35] If a longer reflux time is used (165 h) a material can be isolated that contains no B–H stretch in the infrared but does possess the acetate ester bands. Whether the integrity of the ligand cage has been maintained, producing $[Fe(NOX)_3(BOC(=O)CH_3)_2]$, has yet to be established.

Since the infrared and nuclear magnetic resonance studies show the parameters of the clathrochelate's B–H bond to be comparable to other more reactive B–H bonds, it is assumed that the unreactive nature of this bond lies in the steric constraints imposed by the rigid encapsulating ligand. Acid hydrolysis of BH_4^- has been shown to proceed through a five-coordinate BH_5 intermediate prior to loss of H_2, producing trigonal BH_3, which rapidly reacts to produce $B(OH)_4^-$, presumably proceeding through $H_2B(OH)_2^-$ and $HB(OH)_3^-$ intermediates.[36] Analogously, it is unlikely that the rigid clathrochelate ligand would readily distort to form

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pentacoordinate or, even more so, tricoordinate boron intermediates. In a sense the complex can be viewed as containing a "trapped" monohydroborato intermediate resulting from the "hydrolysis" of the starting borohydride.

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Registry No. $[Fe(NOX)_3(BF)_2]$, 66060-48-8; $[Fe(NOX)_3(BCl)_2]$, 97826-20-5; $[Fe(NOX)_3(BBr)_2]$, 97826-21-6; $[Fe(NOX)_3(BOH)_2]$, 66060-49-9; $[Fe(NOX)_3(BOCH_3)_2]$, 91837-84-2; $[Fe(NOX)_3(BH)_2]$, 84242-24-0; $[Fe(NOX)_3(BCH_3)_2]$, 97826-22-7; $[Fe(NOX)_3(B\text{-}n\text{-}C_4H_9)_2]$, 97826-23-8; $[Fe(NOX)_3(BC_6H_5)_2]$, 83356-87-0; $[Fe(DMG)_3(BH)_2]$, 97826-24-9; $[Fe(DMG)_3(BCH_3)_2]$, 97826-25-0; $[Fe(DPG)_3(BCH_3)_2]$, 97826-26-1; $[Fe(DMG)_3(BC_6H_5)_2]$, 97826-27-2; $[Fe(DMG)_3(BF)_2]$, 39060-38-3; $[Fe(DMG)_3(BOH)_2]$, 39060-43-0; $[Fe(DMG)_3(BOCH_3)_2]$, 39060-42-9; $[Fe(DMG)_3(BOC_2H_5)_2]$, 39060-41-8; BCl_3, 10294-34-5; BBr_3, 10294-33-4; H_3BO_3, 10043-35-3; $NaBH_4$, 16940-66-2; methylboronic acid, 13061-96-6; cyclohexanedione dioxime, 29256-75-5; methanol, 67-56-1; *n*-butylboronic acid, 4426-47-5; dimethylglyoxime, 95-45-4; phenylboronic acid, 98-80-6; diphenylglyoxime, 95-45-4.

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Stoichiometry and Kinetics of Oxidation of Dimeric Bis(μ-halo)bis((diamine)copper(I)) Complexes $L_2Cu_2X_2$ by Dioxygen in Aprotic Solvents

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Cryoscopic measurements show that the very soluble complexes formed from reaction of 1 mol of a tetraalkyl diamine $L = R_2N(CH_2)_nNR_2$ (R = methyl, ethyl, propyl, amyl; $n = 2, 3$) with 1 mol of a copper(I) halide (X = Cl, Br) in nitrobenzene are neutral dimeric species, $L_2Cu_2X_2$; solid-state evidence supports their assignment as bis(μ-halo)-bridged species in methylene chloride and nitrobenzene. The complexes rapidly react with dioxygen in these solvents with primary stoichiometry $2L_2Cu_2X_2 + O_2 \rightarrow 2L_2Cu_2X_2O$. Cryoscopic measurements on freshly prepared product solutions identified dimeric oxocopper(II) products, which polymerize and react with additional dioxygen at much lower rates than for copper(I) oxidation. Kinetic data for reduction of dioxygen by large excesses of $L_2Cu_2X_2$ complexes in nitrobenzene and methylene chloride obey the third-order rate law $d[L_2Cu_2X_2O]/dt = k_D[L_2Cu_2X_2]^2[O_2]$. Comparison of the kinetic data for oxidation of a range of $L_2Cu_2X_2$ complexes by dioxygen with corresponding data for tetrameric $N_nCu_4X_4$ and dimeric $N_4Cu_2Cl_2$ complexes (N = a monodentate pyridine; $n = 4, 8$) indicates steric restrictions to electron transfer due to interactions between alkyl substituents of the two $L_2Cu_2X_2$ dimers in the activated complexes for $L_2Cu_2X_2$ oxidation. It is suggested that these steric effects decrease donor–acceptor orbital overlap for electron transfer from copper(I) to dioxygen, but in no case is transfer of the third electron (necessary for breaking of the O–O bond) prevented.

Introduction

Copper(I) halides coordinated by monodentate pyridine ligands, N, can exist in monomeric, dimeric, or tetrameric forms at molar ratios $N/Cu^I_T = 1$ and 2 in aprotic solvents.[1,2] The proportions of such molecular forms depend on the identity of L and the experimental conditions.[2] However, the products of aprotic oxidation of all these species by dioxygen are tetrameric dioxocopper(II) complexes, $L_nCu_4X_4O_2$; in fact, the rate law for oxidation of a halo(pyridine)copper(I) complex is a direct reflection of its molecularity because complete dioxygen reduction occurs in the presence of a large excess of copper(I).[1-3]

Our previous work with pyridine ligands established that a minimum of three electrons must be transferred from copper(I) for irreversible dioxygen reduction.[2] However, consideration of the narrow range of activation parameters for halo(monodentate pyridine)copper(I) oxidation (specifically a second-order rate law with $\Delta H_T^{*} = 2.1\text{–}5.9$ kcal mol^{-1} and $\Delta S_T^{*} = -(35\text{–}48)$ cal deg^{-1} mol^{-1} for $N_nCu_4X_4$ oxidation ($n = 4, 8$; X = Cl, Br) and a third-order rate law with $\Delta H_D^{*} = 0\text{–}1.4$ kcal mol^{-1} and $\Delta S_D^{*} = -(38\text{–}39)$ cal deg^{-1} mol^{-1} for $N_4Cu_2Cl_2$ oxidation)[1,2] strongly suggests that O–O bond breaking is not a significant factor in the activation process. Instead, we favor rate-determining insertion of O_2 into a Cu(X,X)Cu face of tetrameric $N_nCu_4X_4$ structures and have suggested that similar activated complexes are present in aprotic $N_nCu_4X_4$– and $N_4Cu_2X_2$–dioxygen systems when N is a monodentate pyridine ligand.[1-3]

Our recent data for the aprotic oxidation of the bis(μ-bromo)-bridged dimer $L_2Cu_2Br_2$[4] (L = TEED = *N,N,N′,N′*-tetraethylethylenediamine) by dioxygen stand in sharp contrast to the previous findings.[1-3] Although, as expected,[1,2] the rate law for oxidation of this complex in nitrobenzene is second-order in $[(TEED)_2Cu_2Br_2]$, the primary oxidation product is now dimeric, 5-coordinate $(TEED)_2Cu_2Br_2O$.[4] Formation of a dimeric rather than a tetrameric $L_4Cu_4X_4O_2$ product is the apparent result of a strong preference for 5-coordinate centers in oxocopper(II) complexes[1-3] (the symmetrical species $(LCuX)_4O_2$ would be 6-coordinate). This preference may be the origin of quite different activation parameters, $\Delta H_D^{*} = 12.9$ kcal mol^{-1} and $\Delta S_D^{*} = -3$ cal deg^{-1} mol^{-1}, for $(TEED)_2Cu_2Br_2$ oxidation.[4]

In this paper we report the stoichiometry and kinetics of oxidation of other $L_2Cu_2X_2$ complexes by dioxygen in methylene chloride and nitrobenzene. The molecularities of the reactants and products have been established by cryoscopy in nitrobenzene. The ligands, $L = R_2N(CH_2)_2NR_2$ (R = methyl, ethyl, propyl, amyl) and $R_2N(CH_2)_3NR_2$ (R = methyl),[5] and X = Cl or Br have been chosen for three principal reasons. First, we have found in previous work that it is necessary to alkylate primary amine ligands in order to obtain oxocopper(II) products with even moderate oxidative stability.[6] Second, all of the copper(II) products are

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(5) Ligand abbreviations are as follows. (a) Ethylenediamine ligands $L = R_2N(CH_2)_2NR_2$: R = Me, TMED; R = Et, TEED; R = C_3H_7, TPED; R = C_5H_{11}, TAED. (b) $Me_2N(CH_2)_3NMe_2$ = TMPD.

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