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Effective New Cobalt(II) Dioxygen Carriers Derived from Dimethylglyoxime by the Replacement of the Linking Protons with BF_2^+

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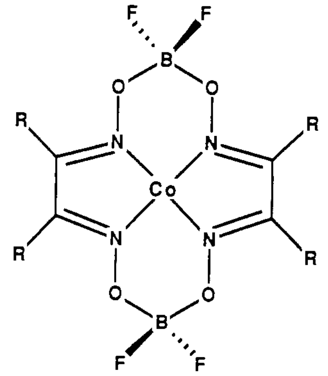
The cobalt(II) complexes of modified dimethylglyoximes in which the linking protons have been replaced by BF_2^+ groups (abbreviated $[Co(R_2GlyoxBF_2)_2]$ (structure I) and Co(*cis*-C10GlyoxBF$_2$)] (structure II)) are effective dioxygen carriers. In contrast to the parent compounds, which have linking protons, $[Co(R_2GlyoxBF_2)_2]$ (R = methyl, phenyl, benzyl, mesityl) and [Co(*cis*-C10GlyoxBF$_2$)] form one-to-one dioxygen complexes of the Pauling type, and in the cases of the ($Me_2glyoxBF_2$) and *cis*-C10GlyoxBF$_2$ complexes, it has been shown that the oxygenation–deoxygenation cycle can be repeated many times without noticeable autoxidation. The equilibrium constants for O_2 adduct formation have been measured for the bridged complex and for the methyl derivative over the temperature range from −20 to 0 °C. The thermodynamic parameters ΔH and ΔS were calculated from the van't Hoff relationship.

Introduction

Their fundamental significance to biochemistry and their great potential for important applications[2] have inspired extensive studies on transition-metal dioxygen carriers,[3] and a number of new families of dioxygen carriers have been discovered recently, including the original Curtis macrocycle,[4] the cobalt and iron cyclidene complexes,[5] the dinuclear cobalt derivatives of Martell,[6] the dinuclear cyclidenes,[7] Kimura's oxo-substituted macrocycles,[8] lacunar and pillared Schiff bases of the acacen type,[9] new salen derivatives,[10] the so-called "fly-over" ligands, which are lacunar salen derivatives,[11] and substituted Goedken macrocycles.[12] The report of Schrauzer and Lee[13] on the dioxygen binding ability of cobaloximes[14] revealed two pathways for the autoxidation of those systems, both of which are examples of well-known processes. The first pathway involves the formation of a (μ-peroxo)dicobalt complex,[15] and the second, the autoxidation of the cobalt atom to the trivalent state, accompanied by the loss of a linking proton and concurrent coordination of a second molecule of an axial base. It has been well established in the case of the dioxygen carriers of iron(II) that inhibiting the mechanisms of autoxidation can produce enormous improvements in dioxygen carriers.[16] On this basis, we have recently been exploring variations of the bis(glyoxime) ligand structures (I and II) and have found unusually simple and effacious new dioxygen carriers. The bridging protons of the bis(dioxime) ligands have been replaced by BF_2^+ groups, an alteration that firms up the macrocyclic structure[17] while removing acidic protons from the vicinity of the O_2 binding site. The parent complex, which has methyl groups as the substituents R (structure I), has been prepared, and its O_2 reactions have been thoroughly characterized. Bulky *rigid riser* groups[18] and bridging groups that might produce cavities[19] have been added in attempts to inhibit the formation of the dinuclear (μ-peroxo)dicobalt species.



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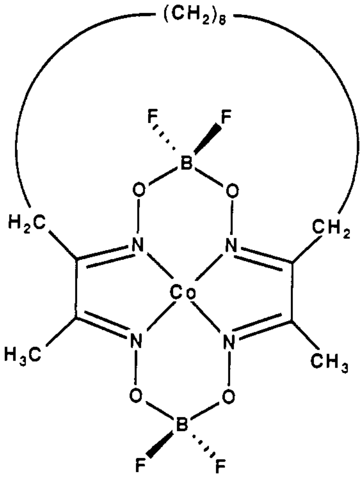

II

Experimental Section

The syntheses of the ligands and of cobalt(III) complexes were performed under the laboratory atmosphere and, when necessary, under a blanket of nitrogen. The oxygen-sensitive complexes of cobalt(II) were prepared and handled in a Vacuum Atmospheres glovebox containing dry nitrogen gas having less than 5 ppm of oxygen. Solvents used in the synthesis of cobalt(II) complexes were dried by using standard techniques, distilled under nitrogen, and degassed under vacuum prior to use.

Physical Measurements. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, or Schwarzkopf Microanalytical Laboratory, Woodside, NY. Infrared spectra were obtained as potassium bromide pellets (1 mg of sample/100 mg of KBr) on a Perkin-Elmer Model 283B infrared spectrometer (4000–200 cm^{-1}), calibrated with polystyrene (ν = 1601.5 cm^{-1}). Routine carbon-13 and proton NMR spectra were recorded on a Bruker WP-250 or a Bruker WP-80 spectrometer operating in the Fourier transform mode at 20.1 MHz. Deuterated solvents were used throughout when obtaining NMR spectra, and all chemical shifts are reported relative to tetramethylsilane,

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usually by direct resonance assignments in the deuterated solvents.

Electron paramagnetic resonance spectra were obtained by using a Varian E-112 spectrometer in the X-band at 9.3 GHz; g tensors are quoted relative to DPPH ($g = 2.0036$), and solution samples were run frozen at 77 K in quartz tubes fitted with a Taperlock stopper unless otherwise noted. Solutions of cobalt(II) complexes were equilibrated with known mixtures of nitrogen and oxygen directly in an EPR tube fitted with a bubbling tube, which was immersed in a temperature-controlled FTS methanol bath and, after the bubbling tube had been pulled out of the solution, frozen with liquid nitrogen.

Electronic spectra were measured on a Varian 2300 spectrophotometer using 1-cm quartz cells. Spectrophotometric studies of the interaction of cobalt(II) complexes with dioxygen were conducted by using a 1-cm gastight quartz cell (from Precision Cells, Inc., Hicksville, NY), fitted with a gas inlet and bubbling tube. Acetonitrile solutions containing 5.56×10^{-4} M complex and a 250-fold excess of axial base were equilibrated with accurately known mixtures of nitrogen and oxygen. Temperature was maintained within 0.2 °C throughout the spectral measurements.

Electrochemical measurements were performed with a Princeton Applied Research Corp. potentiostat–galvanostat, Model 173, equipped with a Model 175 linear programmer, a Model 179 digital coulometer, and a Model 174A polargraphic analyzer. Cyclic voltammetric curves were recorded on a Houston Instruments Model 2000 X-Y recorder. The working electrode for cyclic voltammetry was a glassy-carbon electrode, unless otherwise noted, with potentials measured versus silver wire immersed in 0.1 M tetra-*n*-butylammonium tetrafluoroborate (TBAT) as supporting electrolyte in a glovebox in which the temperature was 25–30 °C under an atmosphere of dry, oxygen-free nitrogen.

Synthesis of Ligands. Glyoxime.[20] *Caution! Glyoxime is reported to be highly flammable and explosive when dry.*[21] A slurry of 20.0 g (0.070 mol) of glyoxal bisulfite (Aldrich Chemical Co.), 10.0 g (0.144 mol) of hydroxylamine hydrochloride, and potassium carbonate (20.0 g, 0.145 mol) in 500 mL of methyl alcohol was brought to reflux. The slurry was allowed to heat at 65 °C for 18 h, and then the hot solution was filtered through Celite. Reducing the volume to 75 mL and cooling to 5 °C overnight resulted in 10.0 g (91%) of glyoxime. Anal. Calcd for $C_2H_4N_2O_2$: C, 27.28; H, 4.58; N, 31.81. Found: C, 27.34; H, 4.72; N, 32.04.

Dichloroglyoxime.[22] Glyoxime (10.0 g, 0.11 mol), suspended in water (200 ml), was stirred with 50 mL of concentrated HCl for 1 min. The mixture was warmed on a hot plate and stirred vigorously until the glyoxime was dissolved. The solution was cooled in an ice bath while a slow stream of chlorine gas was added for 15 min. The mixture was then chlorinated at 0 °C by passing a rapid stream of chlorine through a dispersion disk. After 2 h, the copious precipitate of dichloroglyoxime was filtered with suction, washed with 5 × 100 mL of water, and dried at 120 °C. Yield: 14.3 g, 80.2%. Anal. Calcd for $C_2H_2N_2O_2Cl_2$: C, 15.30; H, 2.57; N, 17.85. Found: C, 15.17; H, 2.75; N, 17.62.

Dimesitylglyoxime. A solution of 1.0 g (0.006 mol) of dichloroglyoxime in 25 mL of tetrahydrofuran (THF) was added, over a period of an hour at 0 °C, to a solution of 26.0 mL of 1.0 M 2-mesitylmagnesium bromide in 50 mL of THF under a blanket of nitrogen. After the addition of dichloroglyoxime, the solution was allowed to warm to room temperature, resulting in a yellow-orange solution. The solvent was removed by rotoevaporation, and the residual paste was added to a cooled (5 °C) solution of water and ammonium chloride. The pasty yellow precipitate was collected and recrystallized from acetic acid. The resulting white powder was collected and washed with water. Anal. Calcd for $C_{20}H_{24}N_2O_2$: C, 74.04; H, 7.46; N, 8.63. Found: C, 74.32; H, 7.19; N, 8.54.

Dibenzylglyoxime. The preparation of this ligand was modeled after the reaction described for the preparation of dimesitylglyoxime. Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 16.13: N, 10.44. Found: C, 71.48; H, 16.31; N, 10.72.

Hexadecane-2,3,14,15-tetraone 3,14-Dioxime.[23] Ethyl acetoacetate (30 g, 0.23 mol) was added with stirring to a solution prepared by the reaction of 4.6 g (0.2 mol) of sodium in 250 mL of absolute ethanol. Decamethylene dibromide (33.0 g, 0.11 mol) was added at reflux temperature. The reaction temperature was maintained until the solution became neutral (12–15 h). Ethanol was removed by rotoevaporation, and a viscous yellow oil, containing a white precipitate (NaBr), was produced. Just enough water was added to the oil to dissolve the precipitate, and the mixture was extracted with ether. The yellow ether layer was washed with water and dried over anhydrous magnesium sulfate. It was then evaporated to a brown viscous syrup. A solution of 16.8 g (0.3 mol) of potassium hydroxide in 120 mL of water was added to the syrup, and hydrolysis was effected at room temperature with constant stirring. The heterogeneous mixture was cooled below 5 °C, and 16.0 g (0.23 mol) of sodium nitrite was added. An aqueous solution of 10% sulfuric acid was added until the color of a potassium iodide/starch solution was retained for at least 15 min when an aliquot of the reaction mixture was added.

With stirring, aqueous potassium hydroxide was added until complete dissolution of all of the solid that had separated upon acidification. The alkaline solution was extracted with ether to remove any unreacted materials. The basic layer was cooled in an ice–salt bath and acidified with 4 M sulfuric acid. The resulting solid was extracted with ether, producing a red-orange solution. The ether extract was washed with an aqueous 2 M sodium carbonate solution until the ether layer became almost colorless. Evaporation of the solvent gave a solid product, which was employed in the next step.

Hexadecane-2,3,14,15-tetraone Tetraoxime.[23] To a mixture of 2.5 g of the tetraone dioxime, 2.0 g of hydroxylamine hydrochloride, 1.5 g of sodium carbonate, and 100 mL of absolute ethanol, water was added slowly to make the mixture homogeneous. The solution was brought to reflux for 10 h and left standing overnight. The white precipitate that formed was filtered and washed with water until no chloride could be detected in the filtrate. Yield: 2.32 g. 84.7%. Anal. Calcd for $C_{16}H_{30}N_4O_4$: C, 56.67; H, 8.84; N, 16.38. Found: C, 56.52; H, 8.72; N, 16.43.

Synthesis of Cobalt Complexes. Chloro(pyridine)bis(dimethylglyoxal dioximato-κ^4*N*)cobalt(III), Co(Me$_2$GlyoxH)$_2$(py)Cl. This compound was prepared by the method of Schrauzer et al.[24]

Chloro(pyridine)bis(2,3-dimesitylglyoxal dioximato-κ^4*N*)cobalt(III), Co(Mes$_2$GlyoxH)$_2$(py)Cl. A solution of 0.500 g (1.54×10^{-3} mol) of dimesitylglyoxal dioxime, 0.078 g (7.70×10^{-4} mol) of triethylamine, and 0.061 g (7.70×10^{-4} mol) of pyridine in 250 mL of tetrahydrofuran was added to a hot solution of 0.183 g (7.70×10^{-4} mol) of cobalt(II) chloride hexahydrate in 250 mL of 95% ethanol. The solution was allowed to cool to room temperature, and a stream of air was bubbled through it for 1 h. When the volume was reduced to 100 mL and the mixture was cooled in a refrigerator overnight, a tan powder formed. This powder was recrystallized from a minimum amount of chloroform, resulting in 0.42 g (66%) of crystalline Co(Mes$_2$GlyoxH)$_2$(py)Cl. Anal. Calcd for C_{45}-

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$H_{51}N_5O_4CoCl\cdot 1.5\,CHCl_3$: C, 55.88; H, 5.29; N, 7.01. Found: C, 56.01; H, 5.17; N, 6.83.

Chloro(pyridine)bis(2,3-dibenzylglyoxal dioximato-κ^4N)cobalt(III), Co(Ben$_2$GlyoxH)$_2$(py)Cl. A solution of 0.600 g (2.24×10^{-3} mol) of dibenzylglyoxal dioxime and 0.176 g (2.24×10^{-3} mol) of pyridine in 200 mL of THF was added to a refluxing solution of 0.266 g (1.12×10^{-3} mol) of cobalt(II) chloride hexahydrate in 200 mL of 95% ethanol. After the two solutions were mixed and cooled to room temperature, a stream of air was allowed to pass through it, and the color subsequently changed from green to yellow-brown. After 1 h, the volume was reduced to ca. 150 mL and a brown powder separated; it was recrystallized from chloroform/ether. Yield: 0.58 g, 73%. Anal. Calcd for $C_{37}H_{35}N_5O_4CoCl$: C, 62.74; H, 4.98; N, 9.89. Found: C, 63.01; H, 5.12; N, 9.64.

Chloro(pyridine)(hexadecane-2,3,14,15-tetraone tetraoxime-κ^4N)cobalt(III), Co(*cis*-C$_{10}$Glyox$_2$H$_2$)(py)Cl. In a three-necked, 2000-mL round-bottom flask, equipped with an air jet and reflux condenser, was placed 1000 mL of 95% ethanol. One syringe was charged with 0.500 g (0.0015 mol) of the decamethylene-bridged ligand and 0.230 g (0.030 mol) of pyridine in 100 mL of THF while the remaining syringe contained 0.36 g (0.0015 mol) of cobalt(II) chloride hexahydrate in 100 mL of 95% ethanol. The two solutions were added to the refluxing reaction mixture over a period of 12 h while a stream of air was passed through the solution. The blue color of the cobalt chloride solution changed to brown upon formation of the complex. The reaction mixture was evaporated to dryness and chromatographed on 50.0 g of silica gel with 9:1 methylene chloride/methanol. The yellow-brown band that eluted was evaporated to dryness and recrystallized from dichloromethane and pentane. Yield: 0.54 g, 70%. Anal. Calcd for $C_{21}H_{33}N_5O_4CoCl$: C, 49.07; H, 6.47; N, 13.62. Found: C, 48.72; H, 6.24; N, 13.97.

Chloro(acetonitrile)(1,1,8,8-tetrafluoro-4,5,11,12-tetramethyl-2,7,9,14-tetraoxa-3,6,10,13-tetraaza-1,8-diboracyclotetradeca-3,5,10,12-tetraene-κ^4N)cobalt(III), Co(Me$_2$GlyoxBF$_2$)(MeCN)Cl. One gram (0.002 mol) of Co(Me$_2$GlyoxH)$_2$(py)Cl was added to 250 mL of freshly distilled acetonitrile, and the resulting solution was brought to reflux. To this solution was added boron trifluoride etherate (1.0 mL) slowly with stirring, which converted the color of the solution from light brown to red. The solvent was removed, and the resulting pink powder was recrystallized from acetonitrile and diethyl ether, resulting in ruby red crystals. Yield: 0.84 g, 74%. Anal. Calcd for $C_{10}H_{15}N_5O_4B_2F_4CoCl$: C, 26.04; H, 3.28; N, 15.18. Found: C, 26.25; H, 3.51; N, 14.97.

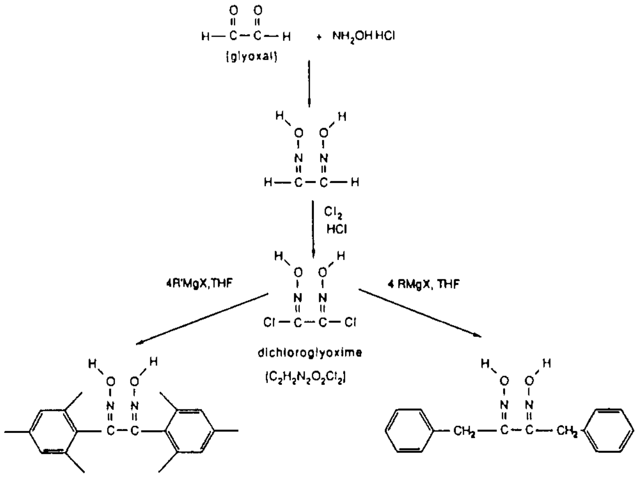
Chloro(acetonitrile)(16,16,22,22-tetrafluoro-13,19-dimethyl-15,17,21,23-tetraoxa-14,18,20,24-tetraaza-16,22-diborabicyclo[10.7.5]tetracosa-1,12,13,18-tetraene-κ^4N)cobalt(III), Co(*cis*-C$_{10}$GlyoxBF$_2$)(MeCN)Cl. The preparation of this compound was accomplished in the same manner as the unbridged compound.

Chloro(acetonitrile)(1,1,8,8-tetrafluoro-4,5,11,12-tetramesityl-2,7,9,14-tetraoxa-3,6,10,13-tetraaza-1,8-diboracyclotetradeca-3,5,10,12-tetraene-κ^4N)cobalt(III), Co(Mes$_2$GlyoxBF$_2$)(MeCN)Cl. A solution of 2.0 g (0.0024 mol) of Co(Mes$_2$GlyoxH)$_2$(py)Cl in 200 mL of acetonitrile was brought to reflux. Boron trifluoride etherate (2.0 mL) was added, and the resulting solution was orange in color. The solvent was evaporated, and the glassy oil that remained was recrystallized from acetonitrile/chloroform. Yield: 0.81 g, 38%. Anal. Calcd for $C_{42}H_{47}N_5O_4B_2F_4CoCl\cdot 2.5CHCl_3$: C, 45.43; H, 4.24; N, 5.95. Found: C, 45.52; H, 4.46; N, 6.17.

Chloro(acetonitrile)(4,5,11,12-tetrabenzyl-1,1,8,8-tetrafluoro-2,7,9,14-tetraoxa-3,6,10,13-tetraaza-1,8-diboracyclotetradeca-3,5,10,12-tetraene)cobalt(III), Co(Ben$_2$GlyoxBF$_2$)$_2$(MeCN)Cl. Boron trifluoride etherate was added to a solution of 1.50 g (0.002 mol) of Co(Ben$_2$GlyoxH)$_2$(py)Cl in 150 mL of acetonitrile. The solution was brought to reflux, and the tan solution turned red. Removal of the solvent and recrystallization of the orange-pink powder from acetonitrile/ether gave 1.20 g (74%) of the desired product. Anal. Calcd for $C_{34}H_{31}N_5O_4B_2F_4CoCl\cdot CH_3CN$: C, 52.09; H, 4.25; N, 10.41. Found: C, 51.84; H, 4.17; N, 10.17.

Bis(acetonitrile)(1,1,8,8-tetrafluoro-4,5,11,12-tetramethyl-2,7,9,14-tetraoxa-3,6,10,13-tetraaza-1,8-diboracyclotetradeca-3,5,10,12-tetraene-κ^4N)cobalt(III), Co(Me$_2$GlyoxBF$_2$)(MeCN)$_2$. A solution of 1.0 g of Co(Me$_2$GlyoxBF$_2$)$_2$(MeCN)Cl in 50 mL of acetonitrile and 10 mL of methanol was prepared in an inert-atmosphere box. A second solution of 0.279 g (1.08×10^{-3} mol) of tetrabutylammonium borohydride in 10 mL of acetonitrile was added to the cobalt solution. A blue-green color was evident at the point of addition along with the formation of a gas (presumably hydrogen), but the color quickly changed to the tan color of cobalt(II). Reduction in volume under reduced pressure resulted in the formation of a tan-orange powder, which was recrystallized from acetonitrile/ether. Yield: 0.512 g, 51%. Anal. Calcd for $C_{12}H_{21}N_6O_4B_2F_4Co$: C, 30.87; H, 3.89; N, 18.00. Found: C, 31.12; H, 3.64; N, 17.64.

Scheme I



Bis(acetonitrile)(16,16,22,22-tetrafluoro-13,19-dimethyl-15,17,21,23-tetraoxa-14,18,20,24-tetraaza-16,22-diborabicyclo[10.7.5]tetracosa-1,12,13,18-tetraene-κ^4N)cobalt(II), Co(*cis*-C$_{10}$GlyoxBF$_2$)(MeCN)$_2$. The preparation of this bridged cobalt(II) complex was accomplished in the same manner as that for the unbridged species.

Bis(acetonitrile)(4,5,11,12-tetrabenzyl-1,1,8,8-tetrafluoro-1,8-dibora-2,7,9,14-tetraoxa-3,6,10,13-tetraazacyclotetradeca-3,5,10,12-tetraene-κ^4N)cobalt(III), Co(Ben$_2$GlyoxBF$_2$)$_2$(MeCN)$_2$. The preparation of this cobalt(II) complex followed the procedure presented for the methyl derivative. Yield: 34%.

Bis(acetonitrile)(4,5,11,12-tetramesityl-1,1,8,8-tetrafluoro-1,8-dibora-2,7,9,14-tetraoxa-3,6,10,13-tetraazacyclotetradeca-3,5,10,12-tetraene-κ^4N)cobalt(III), Co(Mes$_2$GlyoxBF$_2$)$_2$(MeCN)$_2$. The synthesis of this complex followed those previously described for related cobalt(II) complexes. Yield: 45%.

Results

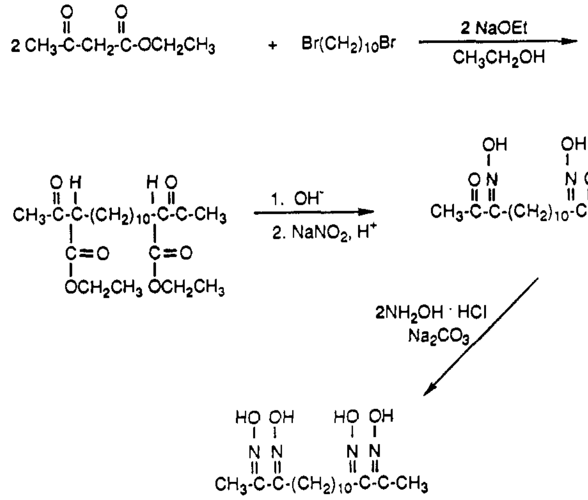
Synthesis and Characterization of the Parent Ligands. α-Dioximes Having Large Substituents. The novel synthetic plan shown in Scheme I was developed for the preparation of disubstituted glyoxime ligands. High yields of unsubstituted glyoxime can be prepared by the reaction of hydroxylamine hydrochloride with the bisulfite adduct of glyoxal in the presence of a proton scavenger (potassium carbonate).[20] *Caution! Glyoxime is reported to be highly flammable and explosive when dry.*[21] In this work, glyoxime was synthesized as needed, and if it was necessary to keep it in the lab, it was stored as a slurry with water. It was not necessary to prepare anhydrous glyoxime except for spectroscopic identification. Recrystallization from THF was found to yield the analytically pure anhydrous compound.

Dichloroglyoxime[22] was prepared by passing chlorine gas through an acidic solution of glyoxime and water. Mass spectral and NMR data confirmed the structure. Electron-impact (EI) mass spectrometry gave a molecular ion peak at 156 amu with additional peaks at 158 and 160 amu, attributable to the isotope distribution of chlorine. The parent ion peak at 121 amu corresponds to the loss of one chlorine atom.

The carbon-13 NMR spectrum displayed a single resonance at 181.2 ppm. This indicates that the two carbon atoms are equivalent, as required for complete chlorination. While it has been reported that the powerful cyanide nucleophile fails to react with dichloroglyoxime,[22] Grignard reagents displaced the chloride and gave the desired disubstituted glyoxime products.

Characterization of Dimesitylglyoxime. Electron-impact mass spectrometry showed a molecular ion peak at m/e 324, and a parent ion peak at 130 amu, which represents a $C_{10}H_{11}$ fragment. The carbon-13 NMR spectrum revealed methyl resonances (confirmed by DEPT) at 19.8 and 20.5 ppm with phenyl resonances at 127.4, 130.7, 134.5, and 136.4 ppm. The peak at 127.4 ppm becomes a doublet in a DEPT experiment, indicating that there is a proton attached to the carbon on the phenyl ring. The other three resonances remained singlets with the peak at 134.5 ppm possessing twice the intensity of the other two. The remaining resonance at 154.8 ppm is assigned to the imine carbon. The proton NMR spectrum reveals four singlets, which integrate to

Scheme II



the ratios 1:2:3:6. Assignments are oxime hydrogens, 11.38 ppm; phenyl hydrogens, 6.38 ppm; *p*-methyl hydrogens, 2.23 ppm; and *o*-methyl hydrogens, 2.14 ppm.

Characterization of Dibenzylglyoxime. The electron-impact mass spectrum showed the expected molecular ion peak at 268 amu. The parent peak in the spectrum is at 91 amu and corresponds to $C_7H_7^+$, the tropilium cation. The carbon-13 NMR spectrum displays six resonances at 155.5, 139.3, 129.8, 128.8, 126.5, and 29.8 ppm. Off-resonance experiments clearly show that the two highest field resonances can be assigned to the imine carbon atom (155.5 ppm) and the tertiary phenyl carbon atom (139.3 ppm). The peaks at 129.8, 128.8, and 126.5 ppm are split into doublets in the off-resonance experiment and are due to the remaining phenyl carbons. The peak at 29.8 ppm becomes a triplet, confirming that it is attributable to the methylene carbon atom. The proton NMR spectrum gave three signals, which integrated to give the ratios 1:5:2 at 10.75, 7.16 and 3.97 ppm. These are assigned to the oxime hydrogens, the phenyl hydrogens, and the methylene hydrogens, respectively.

Synthesis of a Decamethylene-Linked Bis(α-dioxime). In 1970, Retey[23] reported the synthesis and structure of a cis-bridged complex that merited serious attention as a precursor to a possible lacunar complex. To prepare the bis(α-dioxime) ligand, Retey used methyl nitrite at pressures greater than 2 atm. Because of the hazards of this reaction and the relatively low yield it gave, an alternate route was developed (Scheme II). Ethyl acetoacetate was deprotonated with sodium ethoxide in refluxing ethanol and allowed to react with dibromodecane, producing a bis(β-ketoester). Saponification with potassium hydroxide and nitrosation with sodium nitrite produced the α-dioxime of a tetraone. Reaction of this material with 2 equiv of hydroxylamine hydrochloride resulted in the formation of the bridging ligand.

Synthesis and Characterization of Cobalt(III) Complexes of Glyoxime Derivatives. The preparation of cobaloximes in the trivalent state was first accomplished in 1907 by Tsugaev,[25] and these complexes have been of considerable interest as models for vitamin B12. The preparation of the divalent cobalt complexes is not strongly documented, so a systematic method was developed. The cobaloximes were first prepared as their cobalt(III) complexes and the cobalt(III) was used as a template to insert the preferred bridging groups (BF_2^+) into the chelated macrocycle. Since these cobalt(III) complexes are diamagnetic, NMR could be used for their characterization and study. Further, the cobalt(III) complexes, unlike their cobalt(II) counterparts, can be prepared on the bench top and any necessary manipulations, such as chromatography, can be performed in the presence of air.

Synthesis and Characterization of $Co(R_2GlyoxH)_2(B)Cl$. The parent compound in the series is $Co(Me_2GlyoxH)_2(py)Cl$, and it was synthesized according to a literature method.[24] The same procedure was used for the diphenylglyoxime derivative. The yellow-tan crystalline product $Co(Ph_2GlyoxH)_2(py)Cl$ is significantly more soluble in common organic solvents than the dimethylglyoxime derivative. These complexes were characterized by carbon-13 NMR spectral measurements. The preparations of the cobalt(III) complexes of dimesitylglyoxime and dibenzylglyoxime were patterned after earlier procedures.[24] Both the dimesityl and dibenzyl derivatives were characterized by mass spectrometry and NMR spectroscopy. Electron impact failed to give a reasonable spectrum so fast atom bombardment (FAB), employing a matrix known as magic bullet (3:1 dithiothreitol: dithioerythriol), was used.

Table I. Carbon-13 NMR Chemical Shifts for a Series of Difluoroboron-Linked Cobaloximes in Acetonitrile versus TMS[a]

Co-$(Mes_2(GlyoxBF_2)_2$-(MeCN)Cl	Co-$(Ph_2GlyoxBF_2)_2$-(MeCN)Cl	Co-$(Ben_2GlyoxBF_2)_2$-(MeCN)Cl
20.24 (q)	128.27 (d)	31.97 (t)
20.53 (q)	128.52 (d)	126.94 (d)
21.48 (q)	129.31 (d)	128.21 (d)
126.18 (s)	131.33 (s)	128.82 (d)
128.24 (d)	161.52 (s)	137.24 (s)
128.92 (d)		162.74 (s)
139.43 (s)		
139.70 (s)		
163.75 (s)		

[a] q = quartet, t = triplet, d = doublet, and s = singlet in the off-resonance experiment.

For $Co(Mes_2GlyoxH)_2(py)Cl$, the molecular ion peak was found at 820 amu with the parent ion peak at 706 amu. This loss of *m/e* 104 can be accounted for by the removal of pyridine and chloride from the complex. The carbon-13 NMR spectrum showed three peaks in the methyl region, in contrast to the two peaks observed for the free ligand. This indicates that, in the cobalt(III) complex, the methyl groups in the ortho positions are now nonequivalent due to restricted rotation around the C–C bond between the imine carbon atom and the phenyl carbon atom. It also requires the two axial ligands to be different. This is consistent with the proposed structure, wherein chloride and pyridine axial ligands occupy trans positions, above and below the plane of the macrocycle.

The carbon-13 NMR spectrum of the benzyl-substituted ligand in $[Co(Ben_2GlyoxH)_2(py)Cl]$ is, in contrast, similar to that of the corresponding free ligand. Upon coordination to Co(III), the ligand resonances shift slightly but their number is unchanged. Three additional signals due to the presence of the coordinated pyridine molecule are also present. Mass spectral data, using the magic bullet matrix, failed to show the molecular ion peak at 708 amu but did show a very intense peak at 594 amu, which corresponds to the loss of pyridine and chloride as was seen in the dimesityl case.

Template Synthesis and Characterization of Bis(dioximato)-cobalt(III) Complexes Containing Difluoroboron Moieties. When boron trifluoride etherate was added to a refluxing solution containing the cobalt(III) precursor $[Co(Me_2GlyoxH)_2(py)Cl]$, not only was the bridging proton replaced by a BF^{2+} group but the pyridine that was present as an axial base was also replaced by a molecule of acetonitrile. This is a surprising result based on the usual substitutional inertness of cobalt(III).

The preparations of the difluoroboron-linked complexes of the phenyl, mesityl, and benzyl derivatives were modeled after the reaction conditions for the parent methyl complex. The template synthesis of the difluoroboron-linked species again revealed the substitution of acetonitrile for pyridine as the axial base when the reactions were performed in refluxing acetonitrile as evidenced in the carbon-13 NMR spectroscopy. Table I lists the ^{13}C NMR resonances for the cobaloximes prepared. There are no resonances attributable to pyridine, which confirms its replacement by acetonitrile.

The preparation of the difluoroboron-linked *cis*-C10-bridged cobaloxime followed the procedure used for the simpler species. The carbon-13 NMR spectrum again showed no peaks assignable

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(25) Tsugaev, L. *Chem. Ber.* **1907**, *40*, 3498.

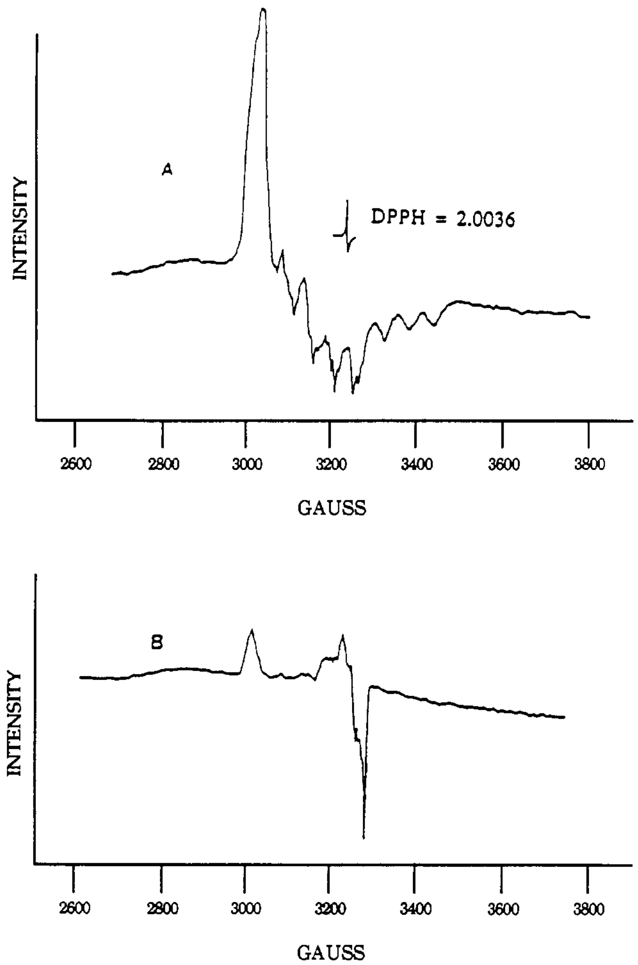

Figure 1. ESR spectra of $Co(Me_2GlyoxBF_2)_2$ in acetonitrile with a 250-fold excess of pyridine at 77 K: (A) before bubbling dioxygen; (B) after bubbling dioxygen at 20 °C.

to pyridine resonances. From the results of the carbon-13 DEPT experiments on the bridged cobaloxime, methyl carbons of the macrocycle are assigned at 13.4 ppm, with methylene groups at 24.4 and 26.2 ppm and an intense peak at 28.2 ppm. The resonances at 166.1 and 161.8 ppm are assigned to the imine carbon atoms, the only quaternary carbons present in the structure. Because of solubility considerations, the NMR spectrum was obtained in acetonitrile, making it impossible to observe an axially bound acetonitrile. The presence of this axial ligand was confirmed by a nitrile stretching vibration at 2315 cm^{-1} in the infrared spectrum. Elemental analyses also confirmed the presence of an acetonitrile molecule.

Preparation of Cobalt(II) Complexes. The preparation of all cobalt(II) complexes was accomplished by reducing the corresponding cobalt(III) complexes with 0.5 mol of tetrabutylammonium borohydride at ambient temperature. Upon addition of the reducing agent, the formation of a transient blue-green species is observed at the point of addition. It has been demonstrated[26] that the addition of 1 mol of borohydride results in the reduction of the cobalt(III) to cobalt(I) in related systems. Thus, the transient blue-green color is attributed to the formation of cobalt(I), which immediately undergoes a comproportionation reaction with cobalt(III) to form the desired 2+ oxidation state of the cobalt ion. This method proved to be advantageous, even though yields were generally 50% or lower, because the cobalt(III) precursors could easily be made and characterized.

Characterization of Cobalt(II) Complexes. Electron Spin Resonance Studies. The cobalt(II) complexes exhibit axial ESR spectra with parallel components displaying eight lines that result from the hyperfine coupling of the unpaired electron in the d_{z^2} orbital to the nuclear spin of cobalt ($I = {}^7/_2$). Nitrogenous axial ligands produce additional fine structure due to the coupling of the nitrogen nuclear spin ($I = 1$). This superhyperfine coupling splits each of the eight cobalt hyperfine signals into three or five lines, depending on whether one or two axial ligands are present. The superhyperfine coupling observed in the ESR spectrum of $[Co(Me_2GlyoxBF_2)_2]$ at 77 K in the presence of excess pyridine (Figure 1) indicates coordination of two axial nitrogens to the cobalt atom. The ESR spectral parameters are $g_{\parallel} = 2.014$ and $g_{\perp} = 2.305$; $A_{\parallel}^{Co} = 105$ G and $A_{\parallel}^{N} = 13$ G.

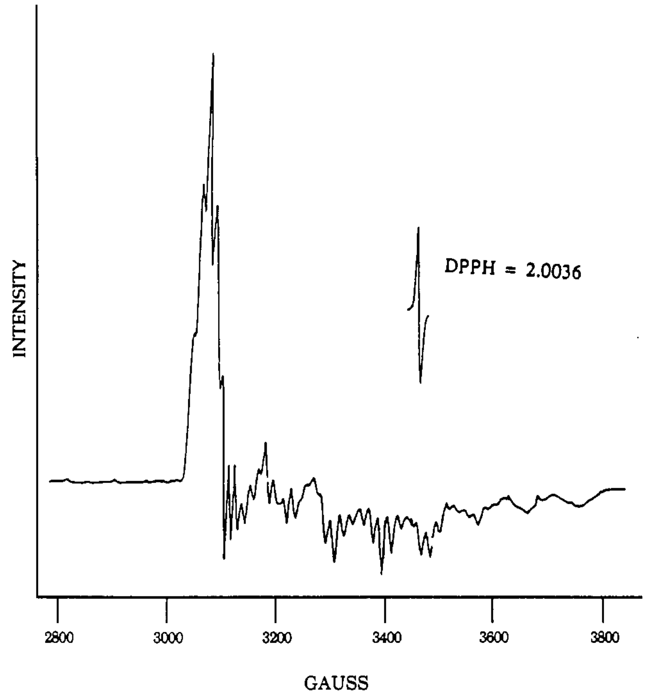

Figure 2. ESR spectrum of $Co(Mes_2GlyoxBF_2)_2$ in acetonitrile with a 250-fold excess of pyridine at 77 K.

Upon exposing the sample to 732 Torr of dioxygen at −10 °C, followed by freezing the sample at the boiling point of liquid nitrogen, one observes a decrease in the intensity of the signals at $g = 2.305$ and the appearance of a signal at $g = 2.01$, which is attributed to the formation of the cobalt dioxygen adduct.

The ESR spectrum of the diphenylglyoxime derivative at 77 K, in acetonitrile containing a 250-fold excess of pyridine, was typical of axial low-spin d^7, and its superhyperfine splitting showed the presence of two axial pyridine ligands, with spectral parameters $g_{\parallel} = 2.00$, $g_{\perp} = 2.25$, $A_{\parallel}^{Co} = 88$ G and $A_{\parallel}^{N} = 17$ G. The ESR spectrum of the same solution after saturation with O_2 at −20 °C and then cooling to 77 K, was essentially unchanged except for minor broadening due to the presence of the dissolved paramagnetic dioxygen. Surprisingly, no indication of O_2 adduct formation was found.

In order to minimize the competition between the axial base and O_2, the same experiment was performed in acetone solution with just 1 equiv of pyridine present. In this case, the familar ESR spectral pattern of a dioxygen adduct appeared; however, the resonance due to the unoxygenated species was also present. Purging with N_2 restored the spectrum of the deoxy complex. The ESR spectrum in acetone with 1 equiv of 1-methylimidazole produces a three-line superhyperfine splitting of the separate components of the parallel branch. In this case, exposure to 745 Torr of dioxygen at −10 °C and cooling to 77 K produces a spectrum that indicates complete oxygenation of the complex.

The ESR spectrum of $Co(Mes_2GlyoxBF_2)_2$ in acetonitrile glass with an excess (250-fold) of pyridine (Figure 2) clearly shows five-line superhyperfine splitting. Further, ESR spectra showed that exposure to dioxygen failed to produce a dioxygen adduct. The ESR spectral parameters were calculated to be $g_{\parallel} = 2.01$ and $g_{\perp} = 2.28$ with $A_{\parallel} = 92$ G.

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[26] (a) Abley, P.; Dockal, E. R.; Halpern, J. *J. Am. Chem. Soc.* **1973**, *95*, 3166. (b) Schrauzer, G. N.; Grate, J. W.; Marihub, A.; Hui, B. X. *Z. Naturforsch, B: Anorg. Chem., Org. Chem.* **1981**, *36B*(10), 1338.

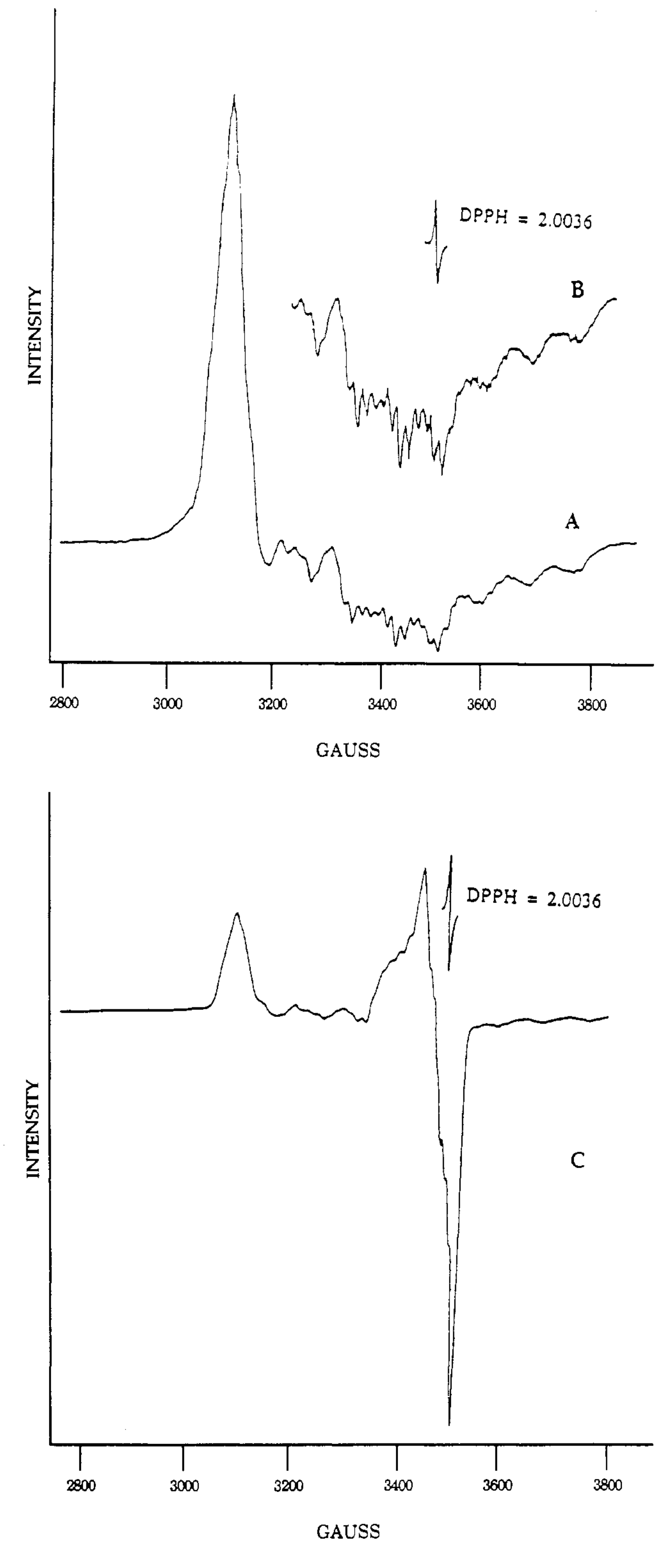

Figure 3. ESR spectra of (A) Co(*cis*-C_{10}GlyoxBF_2)$_2$ in acetonitrile with a 250-fold excess of pyridine; (B) the parallel region, magnified to show the superhyperfine splitting; (C) Co(*cis*-C_{10}GlyoxBF_2)$_2$ after bubbling 100% dioxygen through the solution a −40 °C for 500 s.

The ESR spectrum obtained for the dibenzylglyoxime derivative under the same conditions also displays the five-line splitting in the parallel region, but the splitting is not as pronounced. Bubbling dioxygen through the solution at −40 °C and then freezing the sample to liquid-nitrogen temperature produces a spectrum showing the presence of a dioxygen adduct, but the presence of unoxygenated cobalt(II) is indicated by a strong signal.

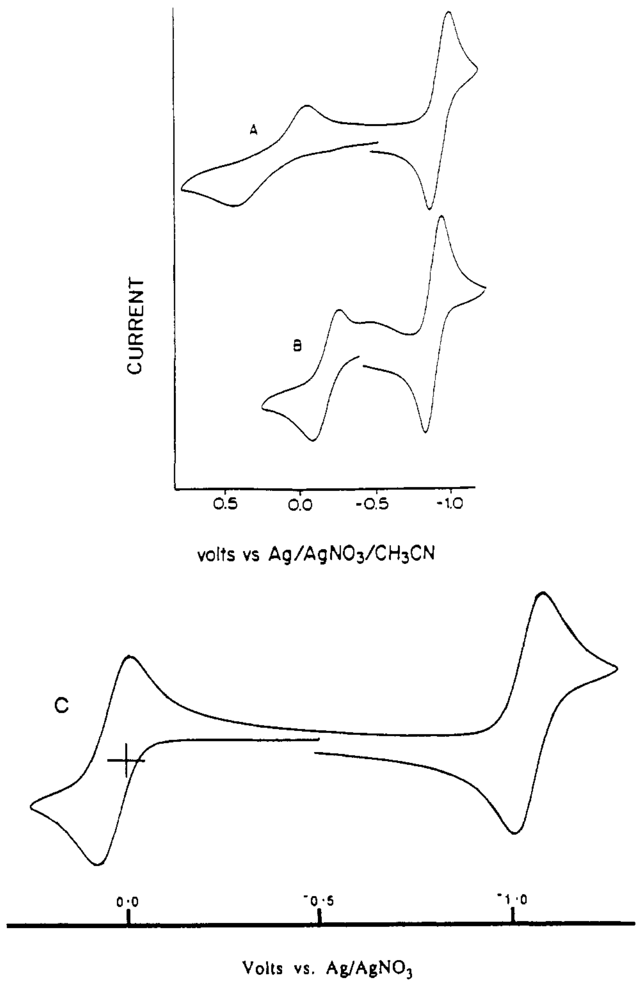

Figure 4. Cyclic voltammograms for Co(Me$_2$GlyoxBF_2)$_2$ in (A) acetonitrile or (B) acetonitrile and pyriline and (C) for Co(Ph$_2$GlyoxBF_2)$_2$ in acetonitrile.

The decamethylene-bridged difluoroboron-linked cobaloxime studied here is a convenient example of a species that might provide some selectivity between axial base binding and O_2 binding. The ESR spectrum was obtained in acetonitrile with an excess of pyridine at −196 °C. As can be seen in Figure 3, the five-line superhyperfine structure is again observed, indicating that there are two axial bases coordinated to the cobalt at liquid-nitrogen temperatures. While this suggests that the bridge is not effective at protecting the metal center from attack of base from one side of the macrocyclic face, it does not fully delineate the chemistry at the higher temperatures where dioxygen titration experiments are usually performed.

After exposure of the sample to dioxygen at −20 °C, the ESR spectrum at 77 K (Figure 3C) reveals the formation of the oxygen adduct with a $g_{\parallel}$ value of 2.01 and also the remnants of the Co(II) signal, as was observed in other cases. This result suggested that the decamethylene bridge in the cis position functions quite similarly to the groups in unbridged cobaloximes. It should be pointed out that a closely similar result was found with the so-called strapped porphyrins.[27]

Electrochemical Properties of the Cobalt(II) Complexes. The cyclic voltammogram of [Co(Me$_2$GlyoxBF_2)$_2$] in acetonitrile (Figure 4A) shows two waves: a quasi-reversible oxidation wave with a peak-to-peak separation (ΔE) of 400 mV, corresponding to the $\mathrm{Co}^{\mathrm{III/II}}$ couple, and a reversible reductive wave with a ΔE of 70 mV, corresponding to the $\mathrm{Co}^{\mathrm{II/I}}$ couple. The large peak-to-peak splitting observed for the $\mathrm{Co}^{\mathrm{III/II}}$ couple can be understood in terms of the changes in coordination number associated with oxidizing cobalt(II) to cobalt(III). In the anodic scan, the five-coordinate cobalt(II) acetonitrile adduct is oxidized at $E_{\mathrm{p,a}} = 0.48$ V vs Ag/AgNO$_3$. Oxidation to cobalt(III) results in formation of the six-coordinate bis(acetonitrile) adduct, which is reduced

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[27] (a) Wijeskera, J.; Paine, J.; Dolphin, D. *J. Am. Chem. Soc.* **1983**, *105*, 6747. (b) Momenteau, M.; Mispelter, J.; Loock, B.; Lhoste, J. J. *J. Chem. Soc., Perkin Trans. 1* **1984**, 61.

Table II. Equilibrium of Constants for the Reversible Oxygenation Reactions in Acetonitrile Solution[a]

ligand	axial base	temp, K	K_{O_2}, Torr^{-1}
Co(Me$_2$GlyoxBF$_2$)$_2$	py	253	0.0145 (3)
		258	0.0101 (2)
		263	0.0056 (1)
		268	0.0038 (1)
		273	0.0019 (1)
Co(Me$_2$GlyoxBF$_2$)$_2$	*N*-MeIm	253	0.206 (4)
		258	0.119 (3)
		263	0.069 (3)
		268	0.041 (2)
		273	0.025 (2)
Co(*cis*-C$_{10}$GlyoxBF$_2$)$_2$	py	258	0.0176 (3)
		263	0.0095 (2)
		268	0.0069 (2)
		273	0.0036 (2)
Co(*cis*-C$_{10}$GlyoxBF$_2$)$_2$	*N*-MeIm	253	0.468 (7)
		258	0.268 (5)
		263	0.151 (4)
		268	0.088 (4)
		273	0.052 (4)

[a] [Complex] = 5.56 × 10^{-4} M with 250-fold excess of axial base.

in the cathodic scan at $E_{p,c} = 0.08$ V. Upon addition of the stronger axial base pyridine (Figure 4B), $\Delta E_{1/2}$ for the Co$^{III/II}$ couple decreases to 100 mV, giving an $E_{1/2}$ of -0.12 V, consistent with having the six-coordinate bis(pyridine) adduct in both the cobalt(II) and cobalt(III) oxidation states. Significantly, the Co$^{II/I}$ couple does not shift upon the addition of pyridine. The sensitivity of the Co$^{III/II}$ couple and the relative insensitivity of the Co$^{II/I}$ couple to the natures of different axial ligands has been noted previously for cobalt macrocyclic complexes.[28]

The cyclic voltammogram for [Co(Ph$_2$GlyoxBF$_2$)$_2$] in acetonitrile (Figure 4C), in contrast to that of the methyl derivative, displays two reversible couples. The Co$^{III/II}$ couple occurs at a potential of 0.036 V vs Ag/AgNO$_3$ with a ΔE of 70 mV. This suggests that no coordination number change accompanies the redox process and is consistent with the ESR results, which showed that the cobalt(II) species is strongly bonded to two axial ligands. Precedent exists for this result in the corresponding diphenylglyoxime derivatives.[29]

Determination of Dioxygen Binding Constants. The measurement of the dioxygen affinities of the cobalt(II) complexes was performed through a titration of various, but progressively increasing, partial pressures of dioxygen. The changes were monitored by UV-vis Spectroscopy. The corresponding equilibrium equation is

$$\mathrm{BLCo} + \mathrm{O_2} \rightleftharpoons \mathrm{BLCo{-}O_2}$$

The equilibrium constants were calculated on the basis of the Ketelaar equation,[30] using the method of Stevens,[31] with a computer program written by Dickerson[32] and modified by Ye.[33] The spectral changes were monitored at 350, 360, 370, and 380 nm. The absorbance increases throughout the region from 450 to 300 nm. The dioxygen binding constants are listed in Table II. These values display standard deviations of less than 10% for each individual determination.

Discussion

The quality of a transition-metal dioxygen carrier may be judged by its affinity for O$_2$, the facility with which various structural parameters provide control over that affinity and the susceptibility of the substance toward competing deleterious reactions.[3,16,18a,34] The most general problem is the proclivity of dioxygen carriers toward autoxidation by the dioxygen molecule they are designed to transport. Therefore, resistance to autoxidation serves as the focus of molecular design, second in importance only to the intrinsic ability to bind O$_2$. Despite the unquestioned fact that they bind O$_2$, the proton-bridged dioxime complexes of cobalt(II) are very poor dioxygen carriers because they are very rapidly autoxidized.

Table III. Dioxygen Equilibrium Binding Constants for Various Pyridine Concentrations in Acetonitrile[a]

K_{O_2}, Torr^{-1}	[pyridine], M	K_{O_2}, Torr^{-1}	[pyridine], M
	A. Co(Me$_2$GlyoxBF$_2$)$_2$		
3.58 × 10^{-3}	9.78 × 10^{-6}	2.38 × 10^{-2}	6.52 × 10^{-3}
5.01 × 10^{-3}	3.50 × 10^{-5}	1.52 × 10^{-2}	1.75 × 10^{-2}
7.98 × 10^{-3}	7.00 × 10^{-5}	1.01 × 10^{-2}	1.00 × 10^{-1}
1.54 × 10^{-2}	3.50 × 10^{-4}	8.05 × 10^{-3}	3.00 × 10^{-1}
2.04 × 10^{-2}	3.18 × 10^{-3}		
	B. Co(*cis*-C$_{10}$GlyoxBF$_2$)$_2$		
4.21 × 10^{-3}	1.00 × 10^{-5}	3.42 × 10^{-2}	6.50 × 10^{-3}
6.17 × 10^{-3}	4.00 × 10^{-5}	2.54 × 10^{-2}	1.80 × 10^{-2}
9.72 × 10^{-3}	8.00 × 10^{-5}	1.76 × 10^{-2}	1.00 × 10^{-1}
2.75 × 10^{-2}	4.00 × 10^{-4}	6.04 × 10^{-3}	3.00 × 10^{-1}
3.04 × 10^{-2}	3.00 × 10^{-3}		

[a] [Complex] = 5.56 × 10^{-4} M.

In the present work, the pathway for irreversible oxidation of the cobalt of bis(dimethylglyoximato)cobalt(II) to the trivalent state in concert with the loss of a hydrogen-bonding proton has been hindered by replacing the offending protons with BF$_2^+$ linking groups that are less supportive of autoxidation. Espenson[17] has reported that the proton-linked species is decomposed in 0.05 M H$^+$ in a matter of minutes whereas the difluoroboron-linked complex, [Co(Me$_2$GlyoxBF$_2$)$_2$], is remarkably resistant to acid hydrolysis, decomposing with a half-life of 5.5 h in 0.05 M H$^+$. The dramatic increase in stability upon formation of the BF$_2^+$-linked macrocyclic complexes provides ample motivation to examine possible dioxygen carriers based on these derivatives. At the same time, we hoped that the new linking groups might provide the necessary steric bulk to hinder the formation of peroxo-bridged dimers. This has indeed proven to be the case, and a new family of dioxygen carriers has been prepared and they are well-behaved from this point of view.

The ligand structures have also been varied to investigate the effects of lacunas and other bulky groups in the vicinity of the coordination sphere of the complex. The structural variations also provide substantial alterations in the electron density of the donor atoms through which the bis(disubstituted glyoximato) ligand systems are bound to the cobalt atom. In a classic paper, Basolo[35] demonstrated a direct correlation between the electrode potential, representing electron density, and the oxygen affinity for a series of unbridged cobalt complexes.

Dioxygen Affinities. For Co(Me$_2$GlyoxBF$_2$)$_2$, the equilibrium constants for dioxygen binding range from 1.80 × 10^{-3} at 0 °C to 1.45 × 10^{-2} at −20 °C, in acetonitrile solution containing a 250-fold excess of pyridine, and the corresponding thermodynamic parameters were estimated to be $\Delta H = -13.7$ kcal/mol and $\Delta S = -61.4$ eu. These values are somewhat lower than would be useful for practical air separation at room temperature.[2c] During the lengthy periods of time required to perform the equilibrium constant determinations, there was no evidence of autoxidation. However, at higher temperatures, autoxidation does occur. Preliminary rate measurements indicate half-lives on the order of hours at room temperature, although the equilibrium constants are too small to give detectable levels of the O$_2$ adduct at that temperature.

Since various reports have indicated that the dioxygen affinities are greater by a factor ranging from 10 to 100 for cobalt(II) complexes having *N*-methylimidazole axial bases when compared to those of pyridine,[3] studies were also carried out with that axial

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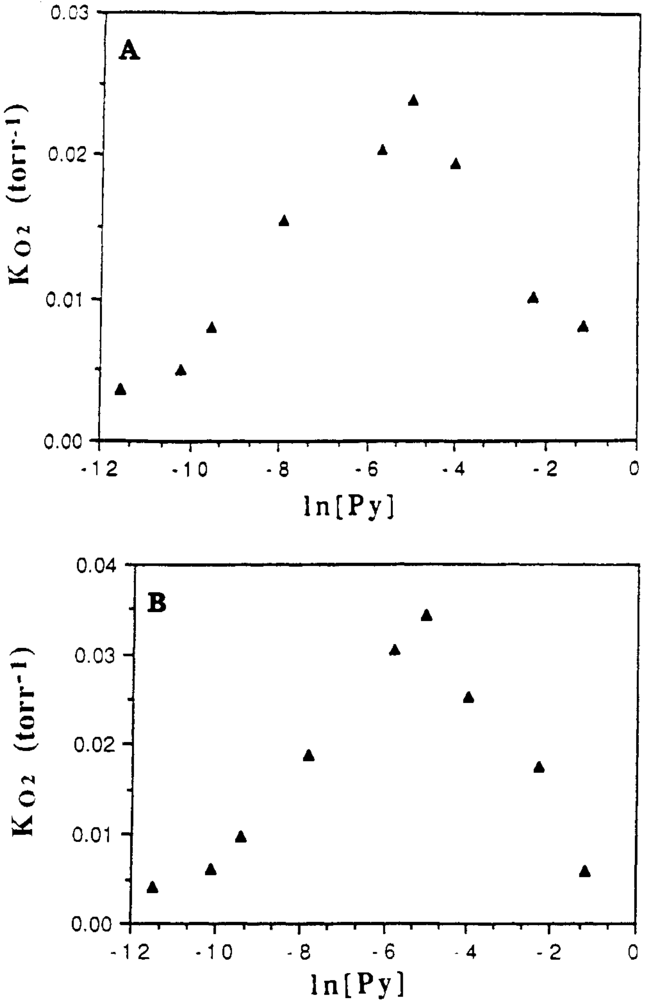

Figure 5. Dependence of the O_2 binding constant on the concentration of pyridine in acetonitrile solution: (A) for $Co(Me_2GlyoxBF_2)_2$; (B) for $Co(\textit{cis}\text{-}C_{10}GlyoxBF_2)_2$.

ligand. The equilibrium constants of the new dioxygen carriers are indeed increased by a factor of 13–16 over those for the corresponding pyridine system at all temperatures measured. As one might expect, the enthalpy change associated with the formation of the dioxygen adduct is greater than that for the pyridine-containing system.

ESR spectral studies have provided evidence that a second mole of axial base coordinates to the cobalt(II) atom of $[Co(Me_2GlyoxBF_2)_2]$ at liquid-nitrogen temperatures. This probably inhibits the binding of oxygen by the complex. This competition has been evaluated by a series of dioxygen affinity measurements at various axial base concentrations (Table III). If only 1 mole of axial base binds and, therefore, a second mole does not compete with O_2 for the sixth site, K_{O_2} should increase with axial base concentration and approach an asymptotically limiting value as saturation of the equilibrium occurs. In the case where a second mole of axial base competes with the O_2 for the sixth coordination site, the equilibrium binding constants should initially increase with increasing axial base concentration and then decrease as, at higher concentrations, axial base competes more successfully with oxygen for the remaining coordination site. Figure 5A graphically confirms the competition between O_2 and pyridine.

Table IV. Thermal Parameters for O_2 Adduct Formation in Acetonitrile Solution

ligand	axial base	ΔH, kcal/mol	ΔS, eu
$(Me_2GlyoxBF_2)_2$	pyridine	−13.7 ± 0.8	−61.4 ± 2.4
	N-methylimidazole	−14.5 ± 1.2	−63.5 ± 1.6
$(\textit{cis}\text{-}C_{10}GlyoxBF_2)_2$	pyridine	−14.6 ± 1.3	−65.2 ± 2.8
	N-methylimidazole	−15.1 ± 2.7	−68.6 ± 3.8

The ESR studies summarized above indicated very low dioxygen affinities for the phenyl, mesityl, and benzyl derivatives, and in these cases, axial ligands compete strongly, thereby decreasing those affinities to still smaller values. Consequently, equilibrium constants have not been determined for those compounds.

Oxygen Affinity of a Lacunar Difluoroboron-Linked Derivative. The presence of a cavity encompassing the O_2 binding site should hinder the competition of large axial bases for that site. While the points of attachments of the bridge to the macrocycle are not the best for the formation of a true lacuna, the ready availability of the *cis*-decamethylene-bridged complex demands that its derivatives be evaluated. It was suspected that the bridge might exert enough steric hindrance to inhibit the formation of a bis(axial base) adduct and still allow oxygen binding.

The equilibrium constants for dioxygen binding were obtained in acetonitrile with both pyridine and *N*-methylimidazole as the axial base and are shown in Table II. Their values are generally about twice those found for the unbridged case for the same axial base and temperature. Thermal parameters are in Table IV. This slight increase in dioxygen affinity probably reflects steric weakening of the binding of the competing large axial base. Data in Table III and Figure 5B show the pyridine dependence of the equilibrium constant. The pattern is the same as that found for the dimethylglyoxime derivative in agreement with the competition between pyridine and O_2 for the second axial binding site. Again, the marginally larger values of the equilibrium constants in the case of the bridged complex might reflect some slight inhibition of the binding of the second axial pyridine. However, any effect is very small, a result consistent with the behavior of the so-called strapped porphyrins.[27]

In summary, the bis(boron difluoride) derivatives of cobaloxime(II) are well-behaved reversible dioxygen carriers, forming adducts of the Pauling type. This is in sharp contrast with the parent complexes, bis(disubstituted glyoximato)cobalt(II), which perform rather poorly. The first several derivatives reported here show relatively low dioxygen affinities, and this is traceable to the electron-withdrawing properties of the bridging groups and in some cases to the substituents. The door is now open for extensive research on an exciting new family of oxygen carriers based on α-dioxime ligands.

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