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Contribution from the Chemistry Department,
The Ohio State University, Columbus, Ohio 43210

Synthesis and Characterization of New Cobalt Dioxygen Carriers Based on a Familiar Macrocyclic Ligand

Sharlene J. Dzugan and Daryle H. Busch*

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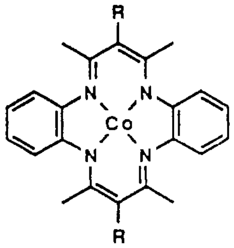
A new family of cobalt dioxygen carriers has been produced by modifications of the known macrocyclic ligand that is prepared by the condensation of 2,4-pentanedione with *o*-phenylenediamine. Acylation of the α-carbon with benzoyl and perfluorinated benzoyl and acetyl groups is readily accomplished, and the bisacylated products have been isolated in high yields. The cobalt(II) complexes of these macrocyclic ligands exhibit relatively high dioxygen affinities. Furthermore, a range of dioxygen affinities spanning 2 orders of magnitude can be achieved by a judicious choice of acylating agent; at 5 °C in toluene with excess pyridine, K_{O_2} = 1.12 (5), 0.11 (1), and 0.0075 (4) Torr^{-1}, respectively, for the benzoyl, trifluoroacetyl, and perfluorobenzoyl derivatives. While the dioxygen carriers are slowly oxidized by O_2, the ligand appears to remain intact.

Introduction

The impetus for the preparation and study of transition-metal complexes capable of transporting dioxygen comes primarily from the wide range of applications that have been envisioned. These include internal medicine and small devices, the commodity gas market, and basic fuel production.[1] While natural systems (i.e., hemoglobin and myoglobin) employ an iron(II) porphyrin moiety at the active center, many synthetic cobalt(II) systems have been prepared and investigated.[1-11] Cobalt systems are particularly attractive because their dioxygen affinities are generally lower (~2 orders of magnitude) and thus reversible dioxygen binding is easier to achieve.[12] Concomitant with this lower affinity, activation of the dioxygen molecule that results in autoxidation processes should occur to a much lesser extent. Unlike the case for iron, formation of cobalt(III) oxide does not provide so threatening a thermodynamic driving force for decomposition. Also, the 1:1 cobalt-dioxygen adducts give characteristic ESR signals, which greatly facilitates their study. Despite studies that have extended over more than 50 years, the structural relationships determining the dioxygen affinities, the rates of addition and dissociation of dioxygen, and the rates and mechanisms of autoxidation are not completely understood. It is equally true that ideal dioxygen carriers have not yet been designed and synthesized.

Herein we report the preparation of a new class of macrocyclic cobalt(II) dioxygen carriers of general structure I that exhibit a wide range of dioxygen affinities. The cobalt(II) complexes are prepared by template reactions on nickel(II) or by direct acylation of the cobalt(II) starting material (R = H).[13,14] Cobalt(II) complexes of the unacylated macrocycle (R = H) have been shown to undergo a strongly exothermic ligand autoxidation reaction, producing a ketone at one of the methine positions. The cobalt metal center is also oxidized to cobalt(III).[15]


I

Studies in these laboratories and others have shown that replacement of the hydrogen atom by an acyl group serves to inhibit the autoxidation of cobalt(II) complexes having this particular kind of chelate ring.[16-18] In the case of the linear tetradentate Schiff bases formed between β-diketones and diamines, the acyl substituents produce dramatic electrochemical results. The Co^{III}/Co^{II} couple is completely irreversible in the complex with the unsubstituted ligand, while it becomes highly reversible in the complex with the diacylated ligand.[18] It has been concluded that the acyl groups prevent ligand oxidation in these compounds.

Experimental Section

Physical Measurements and Procedures. Infrared spectra were obtained with KBr pellets on a Perkin-Elmer 283B infrared spectrophotometer in the range 4000-250 cm^{-1}. Ultraviolet and visible spectra were obtained on a Varian 2300 spectrophotometer interfaced to an IBM PC computer. ^{1}H, ^{13}C, and ^{19}F NMR spectra were measured on a Bruker AM-250 FT spectrometer at 250.113, 62.896, and 75.300 MHz, respectively. ESR spectra were measured on a Varian E-112 spectrometer in the X-band at 9.3 GHz on frozen glasses (-196 °C), and the *g* values are quoted relative to external DPPH (*g* = 2.0036). Electron impact mass spectra were obtained by using a VG 70-250S mass spectrometer, and fast atom bombardment mass spectra were obtained with a Kratos MS-30 spectrometer. The dioxygen binding measurements were obtained by the method of Stevens.[19] Dioxygen titrations were performed on toluene solutions containing 10^{-4} M cobalt complex and 10^{-2} M pyridine. The cell temperature and dioxygen pressures were controlled as described earlier.[20] Electrochemical measurements were carried out as reported previously.[21] Air-sensitive samples were prepared in a Vacuum Atmo-

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* To whom correspondence should be addressed at the Chemistry Department, The University of Kansas, Lawrence, KS 66045-0046.

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spheres inert-atmosphere box under dioxygen-free dinitrogen. All solvents were reagent grade and were dried by recommended procedures[22] and distilled under N_2 before use.

Syntheses. (5,7,12,14-Tetramethyl-2,3:9,10-dibenzo-1,4,8,11-tetraazacyclotetradeca-2,4,6,9,11,13-hexaenato(2−)-κ^4N)nickel(II), [Ni(Me$_4$Bzo$_2$[14]hexaenatoN$_4$)], and the Free Ligand, [H$_2$(Me$_4$Bzo$_2$[14]hexaenatoN$_4$)] (R, X = H). These complexes were prepared and purified by the previously published methods.[13]

[Cu(Me$_4$Bzo$_2$[14]hexaenatoN$_4$)] (R, X = H). This complex was made according to the literature procedure by mixing stoichiometric amounts of the free ligand and copper acetate tetrahydrate in a 1:2 (v:v) hot methanol/acetonitrile solution. On cooling, the brown crystalline material was collected by filtration and washed with methanol. The IR spectrum was essentially identical with that of the nickel complex.

[Co(Me$_4$Bzo$_2$[14]hexaenatoN$_4$)] (R, X = H). This complex was synthesized as described for the copper complex, except all manipulations were carried out in an inert-atmosphere box. The green product was isolated by filtration. The IR spectrum was also similar to those of the nickel and copper complexes, and the mass spectrum featured the molecular ion peak at *m/e* 401 amu.

(5,7,12,14-Tetramethyl-6,13-dibenzoyl-2,3:9,10-dibenzo-1,4,8,11-tetraazacyclotetradeca-2,4,6,9,11,13-hexaenato(2−)-κ^4N)nickel(II), [Ni(Me$_4$Bz$_2$Bzo$_2$[14]hexaenatoN$_4$)], and the Free Ligand, [H$_2$(Me$_4$Bz$_2$Bzo$_2$[14]hexaenatoN$_4$)] (R = Benzoyl; X = H). These complexes were prepared by acylation and subsequent demetalation of the [Ni(Me$_4$Bzo$_2$[14]hexaenatoN$_4$)] complex following literature procedures.[14]

[Co(Me$_4$Bz$_2$Bzo$_2$[14]hexaenatoN$_4$)] (R = Benzoyl; X = H). This dark green compound was synthesized by mixing the free ligand, [H$_2$(Me$_4$Bz$_2$Bzo$_2$[14]hexaenatoN$_4$)], and cobalt(II) acetate tetrahydrate in methanol/acetonitrile (1:2) under an inert atmosphere.

Bis(pyridine)(5,7,12,14-tetramethyl-6,13-dibenzoyl-2,3:9,10-dibenzo-1,4,8,11-tetraazacyclotetradeca-2,4,6,9,11,13-hexaenato(2−)-κ^4N)cobalt(III) Iodide, [Co(Me$_4$Bz$_2$Bzo[14]hexaenatoN$_4$)(py)$_2$]I$_x$ (R = Benzoyl; X = H). A large excess (2.0 mL) of pyridine was added to a suspension of 0.10 g of [Co(Me$_4$Bz$_2$Bzo$_2$[14]hexaenatoN$_4$)] in 10 mL of absolute ethanol. An excess of I_2 was added. The solution immediately turned blood red, and dark red-black crystal were collected after refrigeration. The complex was recrystallized from neat pyridine to give block-shaped single crystals. (^{1}H NMR (CD_3CN): 1.98 ppm (s), 12 H; 6.5–9.5 ppm (multiplets), 24 H. ^{13}C NMR (CD_3CN): 21.39, 120.72, 122.69, 123.79, 125.00, 126.49, 127.88, 128.14, 128.74, 133.41, 137.59, 139.74, 140.52, 147.86, 152.55, 154.36, 157.04, 197.38 ppm.)

(5,7,12,14-Tetramethyl-6,13-bis(perfluorobenzoyl)-2,3:9,10-dibenzo-1,4,8,11-tetraazacyclotetradeca-2,4,6,9,11,13-hexaenato(2−)-κ^4N)nickel(II), [Ni(Me$_4$Pfbz$_2$Bzo$_2$[14]hexaenatoN$_4$)], and the Free Ligand, [H$_2$(Me$_4$Pfbz$_2$Bzo[14]hexaenatoN$_4$)] (R = Perfluorobenzoyl; X = H). These substances were synthesized by minor variations of the procedure used for the benzoyl derivative mentioned above. In a typical preparation of the nickel complex, 0.870 g (2.17 × 10^{-3} mol) of [Ni(Me$_4$Bzo$_2$[14]hexaenatoN$_4$)] was suspended in 100 mL of benzene. The solution was heated to reflux, and approximately 50 mL of benzene was removed by distillation. This served to dry the glassware by azeotropic removal of water. Then, 0.91 mL (6.5 × 10^{-3} mol) of triethylamine was added to the reaction mixture. A 1.00-g amount (4.34 × 10^{-3} mol) of perfluorobenzoyl chloride was then added dropwise, and the reaction mixture was heated at reflux under N_2 for several hours. A white crystalline product, triethylamine hydrochloride, formed on the sides of the reaction vessel within minutes, and the solution color gradually changed from deep emerald green to a dark red-green. The reaction mixture was cooled to room temperature and stirred overnight under N_2. This complex is substantially more soluble in common organic solvents than its unfluorinated counterpart. After the reaction mixture had cooled, the triethylamine hydrochloride was removed by filtration; all of the nickel complex remained in solution. The red-green solution was evaporated to dryness and washed with water and a saturated sodium bicarbonate solution. The solid was then recrystallizd from methylene chloride/diethyl ether to give a purple-red crystalline compound in 78.2% yield. (^{1}H NMR ($CDCl_3$): 2.09 ppm (s), 12 H; 6.71 ppm (m), 8 H. ^{13}C NMR ($CDCl_3$): 20.30, 228.6,[23] 122.34, 123.63, 125.26, 135.7,[23] 139.7,[23] 142.4,[23] 144.5,[23] 146.96, 156.86, 187.89 ppm. ^{19}F NMR: −164.88 ppm (m), 2 F; −156.36 ppm (t), 1 F; −146.35 ppm (m), 2 F.)

The free ligand was easily prepared by removal of the nickel in acetone with HCl in the same manner as was reported for the benzoyl complex.

Table I. Electrochemical Potentials for the Cobalt(II/III) Couples[a]

substituent[b]	$E_{1/2}$(Co(II/III)), V	$(E_p{}^C - E_p{}^A)/2$, V
benzoyl	1.23	0.097
F*-benzoyl	1.462	0.120
F*-acetyl	1.406	0.098

[a] $E_{1/2}$ versus cobaltocene/cobaltocenium(0/1+). [b] F* designates a perfluorinated group.

The demetalation of the perfluorinated benzoyl species proceeds more rapidly than in the unfluorinated case, yielding a bright yellow-orange crystalline product. The conditions utilized in the demetalation process do not deacylate the macrocycle. (^{1}H NMR ($CDCl_3$): 2.13 ppm (s), 12 H; 7.05 ppm (m), 4 H; 7.21 ppm (m), 4 H; 15.08 ppm (s), 2 H. ^{13}C NMR ($CDCl_3$): 20.53, 111.95, 119.8,[23] 125.06, 125.81, 135.6,[23] 136.28, 139.6,[23] 141.6,[23] 144.0,[23] 145.6,[23] 166.66, 181.94 ppm.)

[Co(Me$_4$Pfbz$_2$Bzo$_2$[14]hexaenatoN$_4$)] (R = Perfluorobenzoyl; X = H). The cobalt(II) complex was prepared in the inert-atmosphere box by mixing the free ligand, [H$_2$Me$_4$Pfbz$_2$Bzo$_2$[14]hexaenatoN$_4$)], and cobalt acetate tetrahydrate in 1:2 (v:v) methanol/acetonitrile. The brown powder was isolated by filtration.

(5,7,12,14-Tetramethyl-6,13-bis(trifluoroacetyl)-2,3:9,10-dibenzo-1,4,8,11-tetraazacyclotetradeca-2,4,6,9,11,13-hexaenato(2−)-κ^4N)nickel(II), [Ni(Me$_4$Tfa$_2$Bzo$_2$[14]hexaenatoN$_4$)] (R = Trifluoroacetyl; X = H). This complex was acylated by the procedure described above for the perfluorobenzoyl complex, except trifluoroacetic anhydride was used instead of the acyl chloride. The resulting acylate nickel complex forms Kelly green crystals that dissolve in chloroform to give a cherry red solution. (IR: ν(C=O) 1720 cm^{-1}. ^{1}H NMR ($CDCl_3$): 2.26 ppm (s), 12 H; 6.95 ppm (m), 8 H.)

[Cu(Me$_4$Tfa$_2$Bzo$_2$[14]hexaenatoN$_4$)] and [Co(Me$_4$Tfa$_2$Bzo$_2$[14]hexaenatoN$_4$)] (R = Trifluoroacetyl; X = H). These two complexes were prepared by the procedure described above by acylation of [Cu(Me$_4$Bzo$_2$[14]hexaenatoN$_4$)] and [Co(Me$_4$Bzo$_2$[14]hexaenatoN$_4$)], respectively. Once again, all cobalt(II) species were handled under an inert atmosphere. The resulting copper complex is green, while the cobalt species is brownish green. The IR spectra feature strong absorbances at 1718 an 1724 cm^{-1} for the copper and cobalt complexes, respectively. This is attributed to the C=O stretching vibration. The mass spectrum of the cobalt(II) complex shows the molecular ion peak at *m/e* 593 amu as the major component.

Bis(pyridine)(5,7,12,14-tetramethyl-6,13-bis(trifluoroacetyl)-2,3:9,10-dibenzo-1,4,8,11-tetraazacyclotetradeca-2,4,6,9,11,13-hexaenato(2−)-κ^4N)cobalt(III) iodide, [Co(Me$_4$Tfa$_2$Bzo$_2$[14]hexaenatoN$_4$)(py)$_2$]I$_x$ (R = Trifluoroacetyl; X = H). This complex is prepared by the same procedure used for the benzoyl derivative, [Co(Me$_4$Bz$_2$Bzo$_2$[14]hexaenatoN$_4$)(py)$_2$]I$_x$. (^{13}C NMR (CD_3CN): 23.33, 114.38, 117.50, 119.05, 124.35, 126.09, 126.69, 136.91, 140.69, 141.01, 148.71, 150.82, 154.07, 154.68, 161.93, 188.05, 188.59 ppm.) The fragment due to the cation is observed in the FAB mass spectrum (*m/e* 751 amu).

Results

The nickel(II) complexes of structure I were easily prepared by reaction of the macrocyclic starting material (R = H) with acyl chlorides or anhydrides in benzene with an excess of triethylamine. The yields of the reactions generally exceed 80%, and the complexes have been characterized by NMR techniques. In the case of the aroyl derivatives, the nickel complexes are readily demetalated with anhydrous HCl in acetone, yielding the neutral free ligand (M = H_2). The cobalt(II) complexes are then easily prepared by reaction of the acylated free ligands with cobalt(II) acetate tetrahydrate in methanol/acetonitrile (1:2, v:v) under nitrogen in the inert-atmosphere box. In contrast, attempts to demetalate the nickel(II) complex of the trifluoroacetyl-substituted ligand with anhydrous HCl or *p*-toluenesulfonic acid were unsuccessful. Under these conditions the complex preferentially deacylates before demetalation. The copper(II) trifluoroacetyl species is also easily synthesized, but the free ligand could not be isolated because the usual procedure for demetalation failed (treatment with H_2S). Consequently, the cobalt(II) complex of the unsubstituted macrocycle (R = H) was prepared in the inert-atmosphere box and this species was then acylated directly with trifluoroacetic anhydride. The complex was characterized by mass spectral analysis and, after iodine oxidation to the bis(pyridine)cobalt(III) adduct, by NMR techniques.

The electrochemical potentials for the cobalt(II/III) couples were determined in methylene chloride with 0.1 M TBAP sup-

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(23) A broad multiplet due to ^{19}F splitting.

Table II. ESR Parameters[a]

	benzoyl	F*-benzoyl	F*-acetyl
	Unoxygenated Complexes		
g_1	2.483	2.450	2.433
g_2	2.273	2.270	2.350
g_3	2.002	1.999	2.024
$A_\parallel$	106.4	107.5	93.2
	Oxygen Adducts		
$g_\parallel$	2.091	2.078	2.081
$g_\perp$	1.998	1.944	2.002
$A_\parallel$, G	19.9	18.9	16.1
$A_\perp$	12.9	10.5	11.8

[a] F* designates a perfluorinated group.

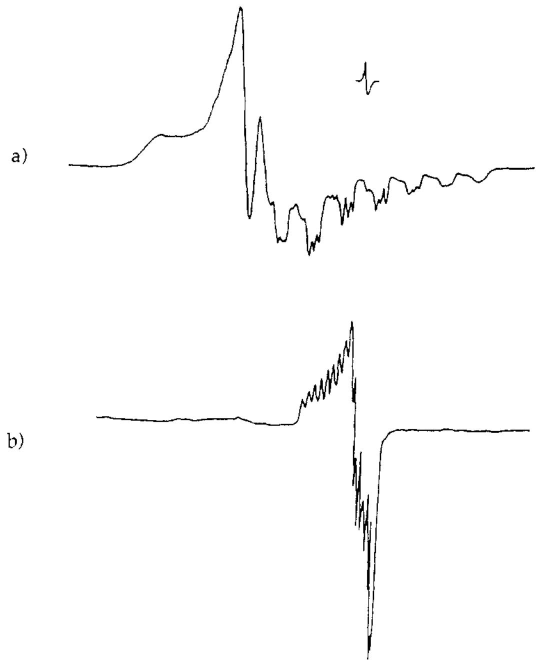

Figure 1. ESR spectra at 77 K of [Co(Me$_4$bzo$_2$bz$_2$hexaenatoN$_4$)] in toluene containing a large excess of pyridine: (a) unoxygenated; (b) after exposure to air.

porting electrolyte, versus the cobaltocene/cobaltocenium(0/1+) couple, and the results are presented in Table I.

ESR spectra of the unoxygenated cobalt(II) complexes were measured at 77 K on frozen toluene solutions containing an excess of pyridine. All of the spectra exhibit a rhombic distortion from idealized axial symmetry, with their perpendicular branches split into two components, g_1 and g_2. Also, in the presence of excess pyridine, the eight-line hyperfine splitting in the parallel branches (g_3) are further split into three or five lines by coupling of the cobalt(II) center with one or two axially coordinated pyridine nitrogen atoms, respectively.

Exposure of these solutions to oxygen at room temperature followed by refreezing to 77 K results in the formation of the 1:1 cobalt–dioxygen adduct as evidenced by typical ESR spectra. They feature eight-line hyperfine splitting in both the $g_\parallel$ and $g_\perp$ branches and familiar values for the tensors and coupling constants. The g-tensor values and the hyperfine coupling constants, A, for both the unoxygenated and oxygenated complexes are presented in Table II. Figures 1 and 2 show the ESR spectra of the unoxygenated (a) and oxygenated (b) benzoyl and perfluorobenzoyl complexes, respectively.

The dioxygen binding constants were determined on toluene solutions of the complexes in the presence of excess pyridine, which served as the axial base. The results are reported in Table III.

Discussion

ESR Spectra of the Unoxygenated and Oxygenated Cobalt Complexes. ESR spectroscopy has unequivocally identified the 1:1 dioxygen adducts of these complexes. This powerful technique also discloses the presence of competing complex-forming processes.

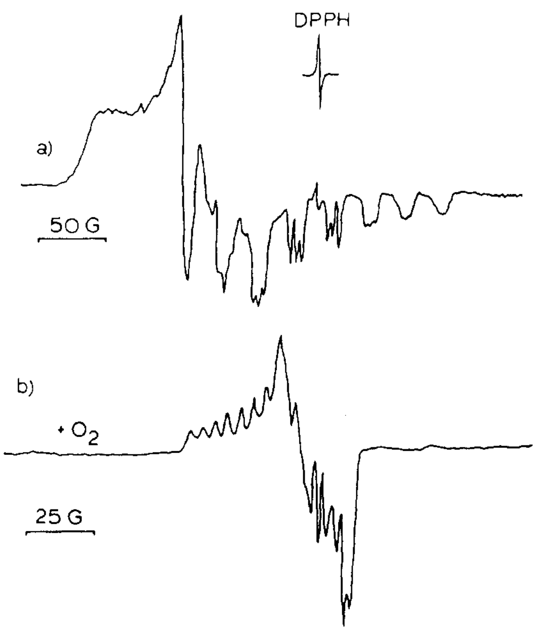

Figure 2. ESR spectra at 77 K of perfluorobenzoyl-substituted cobalt complex in toluene containing a large excess of pyridine: (a) unoxygenated; (b) after exposure to air.

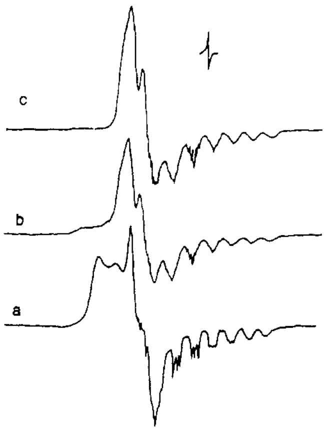

Figure 3. ESR spectral changes upon increasing the concentration of pyridine (a < b < c) in a solution of the trifluoro-substituted cobalt complex in toluene at 77 K.

Table III. K_{O_2} Values for the Cobalt Macrocyclic Complexes (Torr^{-1})[a]

T, °C	benzoyl	F*-benzoyl	F*-acetyl
−21		0.089 (2)	
−15		0.044 (3)	1.58 (2)
−10			
−5		0.0150 (8)	0.46 (9)
5	1.12 (5)	0.0075 (4)	0.11 (1)
10	0.60 (7)		
15			0.58 (6)
20	0.23 (2)		
28	0.074 (5)		
35	0.050 (6)		

[a] F* designates a perfluorinated group.

For both of the benzoyl systems, a three-line superhyperfine splitting pattern is observed for the unoxygenated cobalt(II) complex. This clearly indicates that the geometry about the cobalt center is five-coordinate, with only one axially bound pyridine molecule. In contrast, the trifluoroacetyl derivative coordinates two pyridine molecules at higher concentrations. This is shown in Figure 3, where spectrum c, recorded at higher pyridine con-

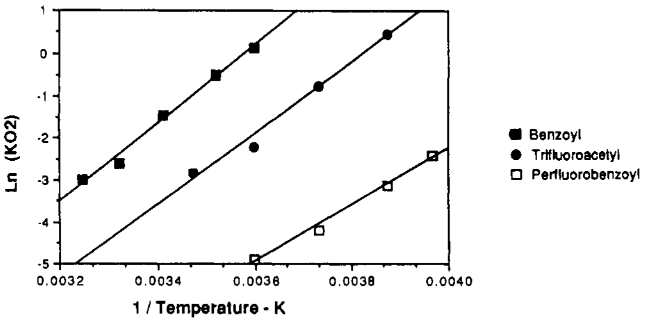

Figure 4. van't Hoff plots for cobalt–dioxygen complexes. $\ln K_{O_2} = -\Delta H/RT + \Delta S/R$

Table IV. Thermodynamic Values for the Cobalt–Dioxygen Adduct Formation

benzoyl	$-18._9$	$-67._6$	0.996
F*–benzoyl	$-13._4$	$-58._1$	0.996
F*-acetyl	$-16._8$	$-64._3$	0.933

[a] F* designates a perfluorinated group.

centrations, displays a five-line superhyperfine splitting, but at lower concentrations spectrum a has a three-line splitting pattern and additional signals indicate that the geometry about the metal center is much more rhombically distorted. The fact that the less bulky trifluoroacetyl substituent favors the six-coordinate species over the arguably more electron-withdrawing perfluorobenzoyl substituent may be taken as evidence that steric factors are important in determining the coordination numbers of the metal ions in these systems, at least with large ligands like pyridine.

The spectrum of the unoxygenated perfluorobenzoyl complex was recorded at 10 times higher gain than was necessary for the oxygen adduct. However, this disparity in signal strength was not observed for the trifluoroacetyl and benzoyl complexes. While the graphical areas of the plotted ESR signals for a given set of experiments should be the same before and after oxygenation, the oxygen adduct signal is generally much more narrow and should display a much greater amplitude. Consequently, signal shape permits observation of the oxygen adduct spectrum at much lower gains than those required for the corresponding deoxy systems, under simple conditions. This is observed for the perfluorobenzoyl adduct. In contrast, the absence of increased signal intensity upon oxygenation of the other complexes suggests that significant portions of them exist as ESR-silent species under the conditions of these experiments. The most likely possibilities are formation of a μ-peroxo species or some other cobalt(III) compound, probably a bis(pyridine) complex. Perhaps, as suggested earlier, the greater bulk of the perfluorobenzoyl groups inhibits the tendency of the molecule to form a μ-peroxo species and/or prohibits the formation of a six-coordinate bis(pyridine)cobalt(III) complex.

Dioxygen Titrations of the Cobalt(II) Complexes. The data reported in Table III clearly show that the dioxygen affinity can be tuned by variations in the acyl substituent. For the complexes studied here, the benzoyl derivative has the highest dioxygen affinity, while that of the trifluoroacetyl complex is 1 order of magnitude lower. The perfluorobenzoyl species has the lowest dioxygen affinity; its K_{O_2} value is approximately 150 times lower than that of the benzoyl derivative at the same temperature. Thus, attaching strongly electron-withdrawing fluorine substituents significantly lowers the dioxygen affinity. The temperature dependence of K_{O_2} provides the thermal parameters, and the results suggest that the observed variations in the O_2 affinities arise from the enthalpy term. van't Hoff plots of $\ln K_{O_2}$ versus $1/T$ are presented in Figure 4, and ΔH and ΔS values are listed in Table IV.

Bubbling dioxygen through a toluene/pyridine solution of the cobalt benzoyl complexes produces a color change from forest green to red. Figure 5 shows the spectra obtained at various partial pressures of O_2 for a 10^{-4} M toluene solution of the complex, at 6 °C, to which a 100-fold excess of pyridine has been added.

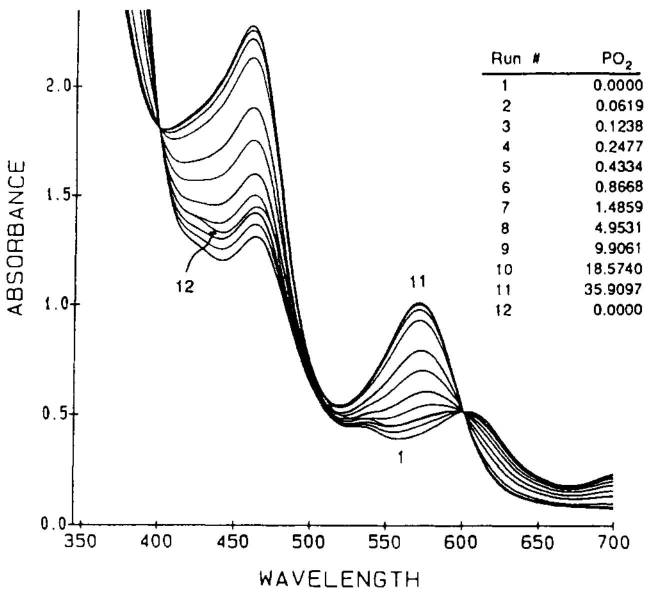

Figure 5. Dioxygen spectral titration for [Co(Me$_4$bzo$_2$bz$_2$hexaenatoN$_4$)] at 279 K in toluene/pyridine solution.

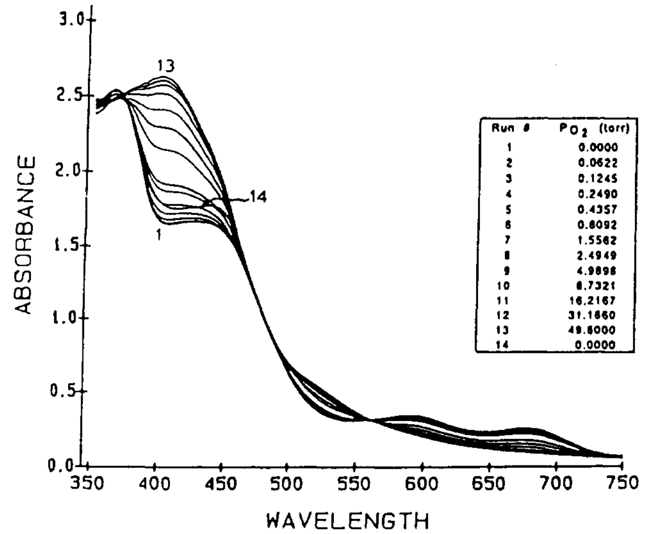

Figure 6. Dioxygen spectral titration for [Co(Me$_4$(CF$_3$CO)$_2$bz$_2$hexaenatoN$_4$)] at 278 K in toluene/pyridine solution.

Purging the system with N_2 for 30 min does not completely deoxygenate the complex. Further, at 20 °C, isosbestic behavior is lost at dioxygen pressures below 1 Torr. Both of these observations are probably indications that 2:1 binding occurs at these rather low oxygen concentrations. This second equilibrium should become competitive as the relative concentration of free cobalt(II) is increased by the diminished concentration of O_2.[24] In fact, this constitutes a kind of autoxidation that can be reversed in some cases by the addition of higher pressures of oxygen.

Exposure of solutions of the trifluoroacetyl complex to dioxygen under similar conditions produces the spectra shown in Figure 6. Once again, the dioxygen binding is not completely reversible. Also, this system loses some of its isosbestic behavior at the lower wavelengths. The lack of complete reversibility for these two systems is consistent with the ESR experiments that show a loss of some of the complex to ESR-silent species upon oxygenation. Reproducibility of the equilibrium measurements suggests that these effects are mainly due to competing equilibria rather than time-dependent processes.

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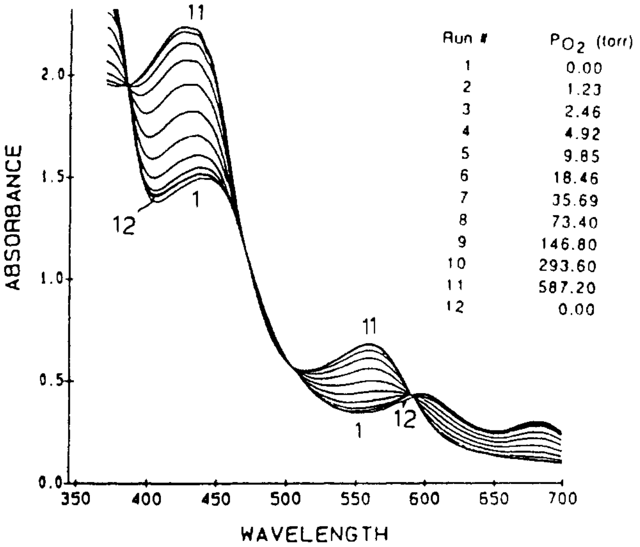

Figure 7. Dioxygen spectral titration for [$Co(Me_4(C_6F_5CO)_2bz_2hexaenatoN_4)$] at 258 K in toluene/pyridine solution.

Figure 7 presents the spectra obtained at various partial pressures of O_2 at −15 °C for the perfluorobenzoyl derivative. The spectra have clean isosbestic points at 385 and 590 nm. Purging with N_2 for 20 min reverses the oxygenation process almost completely.

The decomposition of the perfluorobenzoyl complex was monitored at −5 and 15 °C for 10^{-3} M toluene solutions containing 100-fold excess of pyridine. The complex was fully oxygenated, and the decay of the bands at 425 and 555 nm was monitored. The half-life for decay is about 10 h at 5 °C, but the decomposition rate was not the same for the two wavelengths. The decay only approximates a simple exponential function and is therefore not a simple first-order process. At 15 °C, the complex decomposes with a half-life of at least 2 h, and the wavelength dependence is more pronounced. These preliminary observations indicate that these new oxygen carriers are subject to irreversible autoxidation processes. In this way they are comparable to most other dioxygen carriers. Further, the decomposition process appears to be complicated, but its nature could only be revealed by more detailed studies.

Electrochemical Behavior of the Macrocyclic Cobalt Complexes. The cobalt couples are quasi reversible with $(E_p^C - E_p^A)/2$ values that are less than 120 mV. This strongly supports the view that the autoxidation processes do not involve ligand oxidation, a result of considerable importance. For many purposes, the ability of the oxygen carrier to function can be restored by the addition of reducing agents, so long as the ligand is not oxidized.

The benzoyl complex is the most cathodic and thus should exhibit the highest dioxygen affinity,[25] as has indeed been observed. The trend is as expected for the trifluoroacetyl and the perfluorobenzoyl complexes.

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Contribution from the Laboratoire de Synthèse et d'Electrosynthèse Organométallique Associé au CNRS (UA 33),
Faculté des Sciences "Gabriel", Université de Bourgogne, 6 Boulevard Gabriel, 21100 Dijon, France,
and Department of Chemistry, University of Houston, Houston, Texas 77204-5641

Disulfur and Diselenium Titanium(IV) Porphyrins: Synthesis and Characterization of (P)Ti(η^2-S_2) and (P)Ti(η^2-Se_2), Where P is One of Several Different Porphyrin Rings. Crystal Structure of (5,10,15,20-Tetra-*p*-tolylporphinato)perthiotitanium(IV)

R. Guilard,*[,1a] C. Ratti,[1a,b] A. Tabard,[1a] P. Richard,[1a] D. Dubois,[1b] and K. M. Kadish*[,1b]

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The synthesis and characterization of various disulfur and diselenium titanium(IV) porphyrins are presented. Each compound was synthesized by one of two methods. The first involves an oxidative addition of Cp_2TiS_5 or Cp_2TiSe_5 to (P)TiF under an inert atmosphere and leads to the corresponding (P)Ti(η^2-S_2) or (P)Ti(η^2-Se_2) derivative, where P is the dianion of octaethylporphyrin (OEP), tetraphenylporphyrin (TPP), tetra-*p*-tolylporphyrin (TpTP), tetra-*m*-tolylporphyrin (TmTP), tetramesitylporphyrin (TMP), or tetrakis(*p*-(trifluoromethyl)phenyl)porphyrin (TpCF$_3$PP). The same series of complexes was also obtained by a substitution reaction involving (P)TiF$_2$ and either Cp_2TiS_5 or Cp_2TiSe_5. Each disulfur and diselenium compound was characterized by mass spectrometry and IR, UV-visible, and ^{1}H NMR spectroscopies as well as by electrochemistry. The crystal structure of (TpTP)Ti(η^2-S_2) was determined by X-ray diffraction (monoclinic, $P2_1/n$, a = 14.688 (2) Å, b = 14.822 (2) Å, c = 19.308 (4) Å, β = 90.51 (2)°, Z = 4, $R(F_o)$ = 0.047, $R_w(F_o)$ = 0.0494). The S_2 entity is "side-on" bonded to the titanium atom. The S–S bond length is 2.042 (2) Å, the two Ti–S bond lengths are 2.283 (2) and 2.311 (2) Å, and the mean Ti–N bond length is 2.10 (2) Å.

Introduction

Numerous organometallic compounds containing transition-metal–chalcogen bonds have been characterized.[2] Chalcogen atoms may bind metals in a large variety of bridging geometries or they may act as terminal ligands.[2,3] Metalloporphyrins containing oxo or peroxo axial ligands have been well characterized,[4-20] but little data[21-25] are available for porphyrins with sulfur or

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