

Study of the Thermodynamics of Base and Dioxygen Binding to the Cobalt(II) Schiff Base Complex Co(4,6-CH₃Osal-4-CF₃oph)

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A study of the thermodynamics of base and dioxygen binding to the cobalt(II) Schiff base complex Co(4,6-CH₃Osal-4-CF₃oph), formed by condensation of 4,6-dimethoxysalicylaldehyde with a 4-(trifluoromethyl)-*o*-phenylenediamine, is reported. The results are compared with those reported for porphyrin complexes to evaluate the effect that variation in the *cis* ligands of the dioxygen adduct has on the cobalt-O₂ bond strength. Even though oxygen is more electronegative, the N₂O₂ ligand set of the Schiff base leads to a less acidic cobalt(II) center than the N₄ ligand set of the porphyrin. Consistent with predictions of the spin-pairing model, in analogous base adducts the less acidic Schiff base complex binds dioxygen more strongly than the porphyrin complex.

Introduction

Earlier work from this laboratory¹ has shown that the binding of dioxygen by metal complexes can be viewed as a pairing of the unpaired π^* electrons of dioxygen with metal electrons. This spin-pairing model offered an alternative interpretation² of the EPR spectra based on spin polarization. The spin-pairing model explains many facets¹ of metal-dioxygen complexes. It provides a rationale for the observed³ enthalpies of dioxygen binding as the axial base is varied for a series of substituted cobalt(II) porphyrin complexes and also led to the proposal^{1c,3} of a potential energy storing model for hemoglobin cooperativity.

Although the influence of axial base variations on the metal-dioxygen bond strength ($-\Delta H$) is well documented,³ the influence of varying the *cis* ligands is still an open question. The spin-pairing model predicts that any effect that raises the energy of the essentially metal-based molecular orbital which contains the unpaired electron in the five-coordinate adduct will increase the strength of oxygen binding and the electron transfer into O₂. The strength ($-\Delta H$) of dioxygen binding to base adducts of cobalt(II) Schiff base complexes is information needed to test this prediction. Accurate enthalpy data for both the binding of Lewis bases to a four-coordinate Schiff base complex and the enthalpy of binding O₂ to the resulting five-coordinate adducts are needed in poorly basic, nonpolar solvents so comparison can be made with the porphyrin data.

The correct choice of the system to investigate is critical to attaining this objective. Complexes related to (*N,N'*-ethylenebis(acetylacetonate)iminato)cobalt(II), abbreviated Co(acacen), have been studied,⁴ but because of the small spectral changes upon base addition these are a poor choice if other than a very crude estimate of the equilibrium constant is desired. Literature estimates of the error limits on these systems are often grossly underestimated for reasons previously discussed,^{3b} and problems with reported data⁴ can be appreciated when one compares enthalpies on the same system and finds⁴ them differing by 4.5 kcal mol⁻¹ with error limits of 0.5 kcal mol⁻¹. Under these and reported^{3b} circumstances and in view of the considerations below, one must question any reported⁴ conclusions comparing porphyrin and Schiff base complex binding to dioxygen.

Small spectral changes preclude¹ the use of Co(salen) derivatives, where salen = *N,N'*-ethylenebis(salicylideneaminato).⁵ Use of the saloph ligand system (formed by the condensation of salicylaldehyde with *o*-phenylenediamine) leads to measurable spectral changes in both base-binding and dioxygen-binding studies.⁶ However, due to the poor solubility of Co(saloph) in toluene, this system is also a poor choice. A more soluble derivative of Co(saloph) was synthesized and used in this study. This ligand system is formed by the condensation of 4,6-dimethoxysalicylaldehyde with 4-trifluoromethyl-*o*-phenylenediamine. The cobalt(II) complex, abbreviated as Co(4,6-CH₃Osal-4-CF₃oph), has

a solubility in toluene that is sufficient for this investigation.

The need for quantitative information on the basicity of bound O₂ has taken a new significance with the demonstration of the ability of some of these cobalt(II) complexes to effectively catalyze the selective oxidation of organic substrates.⁷ Both the rates of oxidation and catalyst lifetime are dramatically affected by ligand variation. The enthalpy of O₂ binding is also needed for the interpretation of changes in the O-O stretching frequency⁸ in various cobalt(II) adducts of O₂.

Experimental Section

Purification of Bases and Solvents. Considerable care was taken to use pure bases and solvents in this work. Our procedures have been described earlier.¹⁵ All solvents and all bases were dried, distilled, and degassed by the freeze-pump-thaw method and then transferred to an inert-atmosphere box. All transfers of bases were made under N₂. Precautions were taken to avoid oxygen during distillation and storing of solvents. Toluene-*d*₈ was obtained from Aldrich (Gold Label) and was used without further purification.

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Synthesis of Compounds. 3,4-Diaminobenzotrifluoride. A procedure similar to that of Whalley¹⁰ was used. A 7.0-g sample of 4-amino-3-nitrobenzotrifluoride (ROC/RIC Chemical or Aldrich), purified by double sublimation under vacuum, and 3.0 g of 5% Pd/C were placed in a 250-mL Parr pressure bottle, which was then flushed with argon. Under a stream of argon, 100 mL of methanol was added. The bottle was pressurized to 50 psi with hydrogen, and the solution was stirred. Three fillings over a 6-h period were required for complete reaction. The suspension was filtered, and methanol was removed by rotary evaporation. The crude beige product was then vacuum sublimed, yielding a white compound with a melting point of 59–60 °C in 92% yield. Anal. Calcd for C₇H₇N₂F₃: C, 47.73; H, 4.01; N, 15.90; F, 32.36. Found: C, 47.27; H, 3.97; N, 15.76; F, 31.61.

***N,N'*-Bis(4,6-dimethoxysalicylidene)-4-(trifluoromethyl)-*o*-phenylenediamine, H₂-4,6-CH₃Osal-4-CF₃oph.** 3,4-Diaminobenzotrifluoride (0.8 g) was dissolved in 25 mL of methanol. 4,6-Dimethoxysalicylaldehyde (Aldrich Chemical, 1.65 g) was dissolved in 75 mL of hot methanol. The two solutions were combined, and the resultant solution was refluxed for 12 h to ensure that the Schiff base condensation reached completion. The solution was reduced to 25 mL and allowed to cool. An orange crystalline solid was isolated and dried in vacuo. Mp: 180–182 °C. Yield: 1.32 g (58%). Anal. Calcd for C₂₃H₂₃N₂F₃O₆: C, 59.92; H, 4.60; N, 5.55; F, 11.30; O, 19.03. Found: C, 59.47; H, 4.54; N, 5.38; F, 11.03.

[*N,N'*-Bis(4,6-dimethoxysalicylidene)-4-(trifluoromethyl)-*o*-phenylenediaminato]cobalt(II), Co(4,6-CH₃Osal-4-CF₃oph). Cobalt acetate tetrahydrate (1.63 g) was dissolved in 100 mL of methanol, and the solution was purged with argon for 1 h. To 100 mL of methanol was added 2.39 g of 4,6-dimethoxysalicylaldehyde. A 1.16 g sample of 3,4-diaminobenzotrifluoride was added to the red-orange solution, yielding a dark orange solution, which was transferred to a pressure-equalizing dropping funnel. The aldehyde-amine solution was purged for 45 min with argon. This solution was then added dropwise over a period of 1 h to the refluxing cobalt acetate solution. A red-brown microcrystalline product began to form as the ligand solution was added. The reaction mixture was refluxed for 3 h and then allowed to cool to room temperature. The red-brown crystalline product was collected on a Schlenk frit, washed with deoxygenated methanol, and dried in vacuo (49% yield). Anal. Calcd for C₂₅H₂₁N₂F₃O₆Co: C, 53.49; H, 3.77; N, 5.00; F, 10.15; O, 17.10; Co, 10.50. Found: C, 53.60; H, 3.65; N, 4.85; F, 9.96; O, 17.41; Co, 10.50.

Physical Measurements. Electron paramagnetic resonance spectra were obtained on a IBM-Bruker ER 200 D spectrometer and a Varian Model E-9 spectrometer operating at ca. 9.1 GHz and equipped with a Hewlett-Packard frequency counter. The field was calibrated by using either a Varian weak pitch sample with $g = 2.0027$ or a powdered sample of DPPH with $g = 2.0036$.

Spectra were run in 4-mm-o.d. quartz tubes fitted with o-ring joints. The sample solutions were prepared in an inert-atmosphere box. The quartz tubes were filled and closed off with Teflon needle valves attached to o-ring joints. The samples were then degassed by the freeze-pump-thaw method on a vacuum line. Samples used for base-binding spectra were closed off with a torch to keep any trace of oxygen from entering the tube. The samples used for obtaining dioxygen adduct spectra were oxygenated by opening the Teflon needle valves and performing freeze-thaw cycles in the air.

Solid-state magnetic susceptibilities were determined on a 70-mg sample of the free acid by using a superconducting SQUID susceptometer. The data were recorded over the 10–300 K temperature range. Calibration and operating techniques are described elsewhere.⁹ The magnetic susceptibility data, corrected for diamagnetism by using Pascal's constants, are presented in Table A1 of the supplementary material.

Attempts to measure the magnetic properties of the free acid in solution with the vibrating magnetometer have been unsuccessful because the solubility of the free acid is very low ($\sim 10^{-4}$ M in toluene), and an elaborate airtight sample container is required to prevent the free acid from coordinating oxygen. The sample container partially obscures the magnetic response of the solution. The resulting low signal to noise ratio precludes an accurate magnetic measurement.

Magnetic moments in solution were determined by applying the Evans method with Me₄Si on the JEOL FX-100 spectrometer and using the correction for field direction on the Varian XL-200 superconducting spectrometer. Allowances were made for the variation of the volume of the solution with temperature and for the effects of excess ligand. Diamagnetic corrections were made by using Pascal's constants.

Equilibrium Measurements. 1. Base Binding. The equilibrium constant for the reaction $\text{Co(4,6-CH}_3\text{Osal-4-CF}_3\text{oph)} + \text{base} \rightleftharpoons \text{Co(4,6-CH}_3\text{Osal-4-CF}_3\text{oph)}\cdot\text{base}$ was determined for the Lewis bases 1-methylimidazole, pyridine, tetrahydrothiophene, and dimethyl sulfoxide. Spectrophotometric titrations were carried out by using electronic ab-

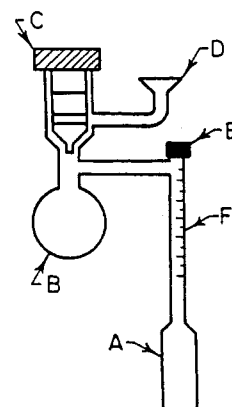


Figure 1. Sample cell for visible spectra of O₂-sensitive compounds: (A) 0.5-cm path length quartz cell; (B) 10-mL round-bottom flask for solution degassing; (C) high-vacuum Ace Teflon stopcock; (D) no. 9 o-ring joint for vacuum line and manifold connection; (E) serum cap; (F) Pyrex graduated pipet.

sorption spectra recorded with a Cary 14-R1 spectrophotometer in the visible region. The enthalpy of base binding to the cobalt complex, ΔH_B , was determined by a van't Hoff analysis of the temperature dependence of the equilibrium constant.

Due to the high affinity of the Co(4,6-CH₃Osal-4-CF₃oph) system for oxygen in basic solution, extreme care had to be taken in order to obtain accurate equilibrium constants. A 5–6 mL aliquot of the cobalt stock solution (prepared under N₂) was added to the round bottom-flask, B, of the apparatus shown in Figure 1, and valve C was closed. The cell was then removed from the inert-atmosphere box and degassed by using the freeze-pump-thaw method. The apparatus was next filled to a positive pressure of argon. The quartz cell, A, was filled by tipping the assembly and allowing solution to flow from B. After equilibration at room temperature (usually 15 min), an initial volume reading was made by using the calibrated pipet, F. The cell was allowed to reach thermal equilibrium in a Varian constant-temperature chamber in the spectrometer.

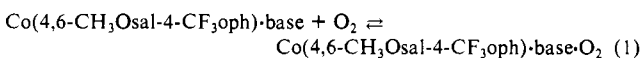
The temperature of the chamber was controlled by two methods. For temperatures from 15 to 60 °C, a Braun Thermoboy constant temperature (± 0.2 °C) bath was used. For temperatures less than 15 °C, a Forma Temp Jr. circular bath filled with methanol was used. The lowest temperature that could be obtained and held for a 6-h period was -10 ± 0.5 °C. The cell compartment was continually flushed with nitrogen at temperatures less than 10 °C. The temperature of the cell was monitored by means of a digital thermometer.

Once the visible spectrum was recorded, the cell was removed and attached to a manifold by means of the o-ring joint. Addition of base was made through the serum cap with a Pressure-Lok syringe. The base was mixed into the solution by convection currents produced by placing the cell bottom directly on a hot plate. Solutions were stable for 6–7 h from the time of degassing before signs of oxidation appeared.

For several bases (Me₂SO, THF, CH₃CN) spectral changes in the visible region that result from adduct formation were not enough to accurately determine equilibrium constants. Since changes in the ¹⁹F NMR spectrum of Co(4,6-CH₃Osal-4-CF₃oph) do occur upon addition of pyridine and Me₂SO, ¹⁹F NMR could be used to determine equilibrium constants. The raw shift data for the pyridine and Me₂SO titrations are presented in Tables A2 and A3 of the supplementary material. A solution of the cobalt complex in perdeuterated toluene was prepared in an inert-atmosphere box and base added via syringe. The NMR tubes were capped with serum stoppers, Freon vapor was injected as a standard, and each cap was wrapped with Parafilm, as a further precaution. The ¹⁹F NMR for each set of samples was run at two or four temperatures. Typically, 1000 scans were taken, and the signal appeared 40–50 ppm upfield of the Freon resonance.

The pyridine adduct was investigated by the NMR method and the equilibrium constants obtained were compared with the results from the UV-vis method. In calculating equilibrium constants, dilution effects from the added base were assumed to be additive. A solvent density correction was also made.¹⁰

2. Dioxygen Binding. Spectrophotometric titration was used to determine the equilibrium constant for dioxygen binding, K_{O_2} , for the reaction



The absorbance of the oxygenated complex in the visible region was

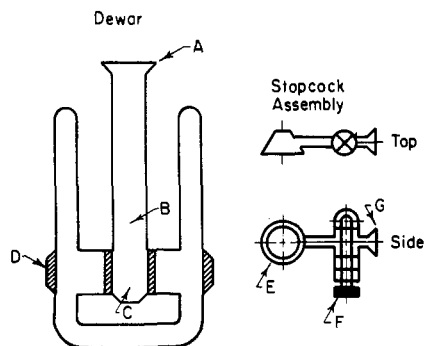


Figure 2. Low-temperature all-quartz optical Dewar assembly: (A) o-ring joint; (B) solution cell; (C) stir bar well; (D) optical quartz windows; (E) o-ring joint (same size as A); (F) high-vacuum Ace Teflon stopcock; (G) no. 9 o-ring joint.

monitored as a function of oxygen pressure over the sample solution.

A low-temperature quartz optical Dewar (Figure 2) and a Pyrex Dewar of similar design were used. The solution cell, B, was completely surrounded by a slush bath of desired temperature.^{11,12} The cell was designed to be loaded in an inert-atmosphere box, degassed on a vacuum line, and subjected to a fixed O₂ pressure by adding O₂ to the line. The Cary sample compartment is equipped with a small magnetic stirrer. Absorbance change at one wavelength indicated that between 30 and 75 min were needed for equilibration.

Calculations. Spectrophotometrically, the equilibrium constant and change in molar absorptivity ($\Delta\epsilon$) between the complex and the free acid were calculated by using

$$K^{-1} = \frac{A - A_0}{b(\Delta\epsilon)} - [\text{acid}]_0 - [\text{base}]_0 + \frac{[\text{acid}]_0[\text{base}]_0}{A - A_0} b(\Delta\epsilon) \quad (2)$$

where $[\text{acid}]_0$ is the initial acid concentration, $[\text{base}]_0$ is the initial base concentration, b is the path length in cm, A_0 is the initial absorbance of the free acid, and A is the absorbance of the complex. For a series of base concentrations, a best K and best $\Delta\epsilon$ can be calculated by using a least-squares technique. The computer program used for this purpose and the error analysis have already been described.¹³ The procedure for calculating K 's from the isotropic shift has been reported.¹⁴

In order to obtain a more meaningful estimate of the error in the enthalpies, the best K and best $\Delta\epsilon$ (or the isotropic shift, $\Delta\omega$) are determined for each temperature. The best $\Delta\epsilon$ (or $\Delta\omega$) is then substituted into eq 3 (or its NMR equivalent) along with the measured absorbance values

$$K^{-1} = P_{\text{O}_2} \frac{[A]_0 b(\Delta\epsilon)}{A - A_0} - 1 \quad (3)$$

and concentrations to calculate a K for each measurement. These K 's are then used in the van't Hoff analysis to calculate $-\Delta H$.

Thermodynamic data for O₂ binding was calculated by using the reported¹⁵ modified form of the equilibrium constant expressing (eq 3). In this equation, P_{O_2} is the pressure of O₂ above the solution. $[A]_0$ is the initial concentration of acid [in this case Co(4,6-CH₃Osal-4-F₃oph)-base], b is the path length of the cell, A is the absorbance of the oxygenated species, A_0 is the absorbance of the initial acid concentration, and $\Delta\epsilon$ is the difference in molar absorptivity between the oxygenated and non-oxygenated complexes.

Results

A typical spectral titration for the formation of a 1:1 base adduct of Co(4,6-CH₃Osal-4-CF₃oph) is illustrated in Figure 3. The isosbestic point is consistent with the presence of only two absorbing species and indicates that oxidation of the complex has not occurred. The raw spectral data are presented in Tables A4–A6 of the supplemental material. The calculated equilibrium constants are given in Table I. The enthalpies of adduct formation are summarized in Table II.

A typical change in the electronic spectrum accompanying dioxygen binding to the 1:1 base adducts is illustrated in Figure 4. The isosbestic point supports the existence of only two absorbing species. Raw data for the spectral titration with O₂ are presented in Tables A7–A9 of the Supplemental Material. Values of the equilibrium constants at each temperature could be obtained from these spectral changes. The enthalpies of dioxygen binding to Co(4,6-CH₃Osal-4-CF₃oph)-base for the bases 1-MeIm, py, and THTP were obtained from a van't Hoff analysis of the equilibrium constants and are listed in Table III. The corre-

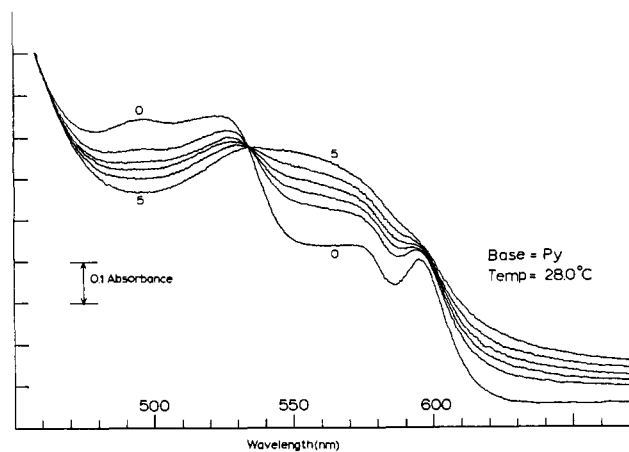


Figure 3. Spectrophotometric titration of Co(4,6-CH₃Osal-4-CF₃oph) with pyridine in toluene at 28.0 °C. Concentrations are listed in Table A5.

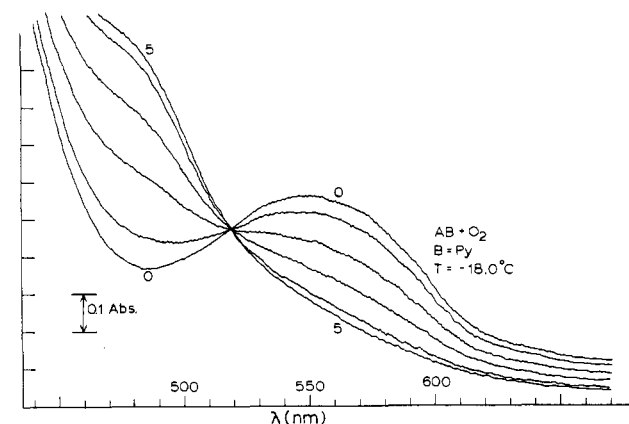


Figure 4. Spectrophotometric titration of Co(4,6-CH₃Osal-4-CF₃oph)-py with O₂ in toluene at -18.0 °C. Concentrations and pressures are listed in Table A8.

sponding dioxygen enthalpies for CoPPIXDME-base³ are also given for comparison.

The temperature range over which the O₂ binding studies can be carried out is limited. At lower temperatures the isosbestic point does not exist, probably due to the existence of 1:1 and 2:1 base adducts of the cobalt complex. EPR studies of frozen glasses indicated that pyridine and 1-methylimidazole form a 1:1 adduct at an equimolar ratio of complex to base but formed 2:1 adducts at lower temperatures at a 3–4:1 molar ratio. In a toluene solution of 50% tetrahydrothiophene, the predominant adduct in the frozen glass was the 1:1 adduct. At higher temperatures irreversible oxidation of the cobalt occurs.

EPR spectra, similar to those described earlier,^{1a} were obtained for the dioxygen adducts. The spectral parameters are summarized in Table IV, along with the electron transfer values (ET) calculated from our reported^{1a} analysis of the cobalt hyperfine splitting constants. EPR spectra were not observed for Co(4,6-CH₃Osal-4-CF₃oph) in a 3:2 v/v toluene-CH₂Cl₂ mixture at liquid-nitrogen temperatures or for solutions containing 10% (v/v) CH₃CN, 25% Me₂SO, or 100% THF at liquid nitrogen temperatures.

Figure 5 illustrates the inverse magnetic susceptibility of the free acid Co(4,6-CH₃Osal-4-CF₃oph) plotted as a function of temperature. The nearly linear appearance of the plot suggests the normal behavior of a paramagnet. The effective magnetic moment (at 300 K, $\mu_{\text{eff}} = 2.25 \mu_B$) is consistent with the one unpaired electron per cobalt(II) ion of a low-spin electronic configuration. Since normal paramagnetic behavior was indicated, the data were analyzed according to the Curie-Weiss law

$$\chi = \frac{Ng^2\mu_B^2S(S+1)}{k(T-\Theta)} + \text{TIP} \quad (4)$$

Table I. Equilibrium Data for Base Binding

$K,^a \text{ atm}^{-1}$	best $K (b, c), \text{ atm}^{-1}$	$\Delta\epsilon (b, c)$	MSD/CSD ^d	temp, °C
1-Methylimidazole				
883, 864	855 (26, 13)	3233 (29, 15)	1.9	19.4
835, 818				
437, 441	440 (3.6, 2.0)	3216 (6.9, 3.8)	1.8	30.1
444, 433				
301, 306	302 (6.4, 3.7)	3358 (18, 10)	1.7	40.0
302, 286				
326				
218, 202	209 (5.5, 3.5)	3372 (22, 14)	1.6	51.4
211, 208				
224, 196				
Pyridine				
152, 154	157 (5.6, 2.9)	2941 (32, 16)	1.9	18.7
165, 151				
161, 155				
102, 96.9	101 (3.6, 1.5)	2677 (33, 14)	2.4	28.0
104, 101				
100				
78.1, 73.8	77.4 (3.7, 1.6)	1599 (26, 12)	2.3	37.8
80.9, 78.5				
74.8				
44.3, 45.6	45.7 (1.2, 0.4)	2156 (20, 7.4)	2.7	47.0
46.7, 44.7				
46.0				
Tetrahydrothiophene				
4.22, 4.40	4.53 (0.30, 0.13)	2982 (74, 32)	2.3	-1.7
4.64, 4.82				
4.22				
3.80, 3.66	3.72 (0.07, 0.03)	2700 (18, 8.3)	2.2	5.0
3.73, 3.79				
3.64				
2.84, 2.78	2.83 (0.09, 0.04)	2630 (33, 13)	2.5	9.8
2.84, 2.94				
2.72				
2.10, 2.18	2.14 (0.08, 0.03)	2453 (38, 12)	3.2	19.7
2.10, 2.15				
Me ₂ SO				
3.836, 4.379, 4.640	4.090 (0.641, 0.280)	13.87 (0.795, 0.347)	2.29	-13.3
3.409, 4.066				
3.365, 3.411, 3.804	3.427	11.79	2.45	-2.8
3.013, 3.552				
2.726, 2.761, 2.867	2.760	10.20	2.70	9.0
2.610, 2.794				
2.415, 2.185, 2.371	2.330 (0.137, 0.0464)	8.912 (0.235, 0.799)	2.95	19.7
2.301, 2.418				

^a From the simultaneous determination of K and $\Delta\epsilon$. ^b Marginal standard deviation. ^c Conditional standard deviation. ^d Ratio of marginal standard deviation to conditional standard deviation;¹² ratio is the same for K and $\Delta\epsilon$. ^e K values used in van't Hoff analysis; see text.

Table II. Thermodynamics of Base Binding to Cobalt Complexes

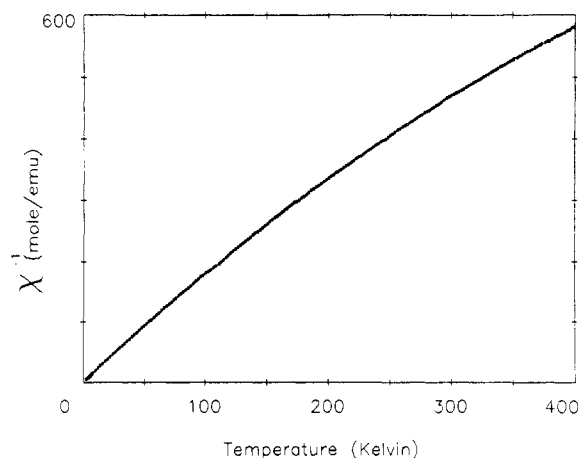
base	Co(4,6-CH ₃ Osal-4-CF ₃ oph) ^{b,c}	
	CoPPIXDME ^{a,c} - ΔH , kcal/mol	- ΔH , kcal/mol - ΔS , eu
1-MeIm	9.6 (1.0)	8.1 (0.4) 14.5 (1.2)
py (NMR)	8.9 (0.4)	7.8 (0.4) 17.4 (1.2)
THTP	6.0 (0.5)	5.6 (0.3) 17.8 (1.2)
Me ₂ SO (NMR)		2.6 (0.05) 7.4 (0.2)

^a Values taken from ref 3. ^b This work was performed by visible spectroscopy unless otherwise indicated in parentheses after the name of the base. ^c Standard deviation is in parentheses.

Table III. Enthalpy of Dioxygen Binding to Co(4,6-CH₃Osal-4-CF₃oph)-base

base	- ΔH , kcal/mol	- ΔS , eu	- ΔH , ^a kcal/mol
1-MeIm	11.6 (0.5)	37.1 (2.0)	10.0 (0.3)
py	10.9 (1.2)	38.7 (4.8)	8.0 (0.7)
THTP	4.42 (0.38)	10.6 (1.7)	7.6 (1.2)

^a Experimentally determined enthalpies for CoPPIXDME from ref 3.

**Figure 5.** Temperature dependence of the magnetic moment of Co(4,6-CH₃Osal-4-CF₃oph).

where all of the parameters have their usual meaning and TIP represents the temperature-independent paramagnetism of low-spin cobalt(II). The line drawn through the points is the best fit of the magnetic data to eq 4 for an electron spin $S = 1/2$. The fitted

Table IV. EPR Parameters for Dioxygen Adducts of Cobalt Complexes

base	Co(4,6-CH ₃ Osal-4-CF ₃ oph)·base ^c							CoPPIXDME ^d	
	g_{\parallel} (±0.003)	g_{\perp} (±0.01)	g_{iso} (±0.003)	$-A_{\parallel}^a$ (±0.2)	$-A_{\perp}^{a,b}$	$-A_{\text{iso}}^a$ (±0.2)	α^2	ET	ET
Pip	2.082	2.00	2.025	15.2	9.2	11.2	0.205	0.59	
1-MeIm	2.086	2.01	2.028	16.0	9.1	11.4	0.230	0.54	0.43
py	2.072	2.00	2.019	16.4	8.8	11.3	0.250	0.50	0.47
THTP	2.078	2.00	2.020	18.7	10.2	13.0	0.275	0.45	0.58

^a A values in 10^{-4} cm⁻¹. ^b $A_{\perp} = 3/2(A) - A_{\parallel}/2$. ^cSpectra run in 3:2 (v/v) toluene-CH₂Cl₂. ^dThe corresponding values for CoPPIXDME in toluene were taken from ref 3.

parameters are $g = 2.32$, $\Theta = -0.506$ K, and $\text{TIP} = 0.00045$ amu/mol.

Evans susceptibility measurements give a magnetic moment of $3.7 \mu_{\text{B}}$ at 27 °C for a 0.67 M solution of Me₂SO and 10^{-4} M Co(4,6-CH₃Osal-4-CF₃oph) in toluene. The poor solubility of the low-spin pure complex in toluene led to an unobservable shift and precluded a determination of the magnetic moment of the free acid. Since the pyridine adduct gave results similar to the free acid, we conclude it is low spin.

Discussion

Acidity of the Cobalt Center in Co(4,6-CH₃Osal-4-CF₃oph). The enthalpies of base binding to Co(4,6-CH₃Osal-4-CF₃oph), calculated from the temperature dependence of K (Table II), were measured in toluene to minimize solvation effects and to provide data comparable to that for the porphyrin system. The bases employed provide a wide range of $C_{\text{B}}/E_{\text{B}}$ ratios.¹⁶ The enthalpies of base adduct formation (Table II) for Co(4,6-CH₃Osal-4-CF₃oph) can be fit to

$$-\Delta H = E_{\text{A}}E_{\text{B}} + C_{\text{A}}C_{\text{B}} \quad (5)$$

Values of $E_{\text{A}} = 3.64$ (0.27) and $C_{\text{A}} = 0.54$ (0.03) result. The enthalpy of Me₂SO adduct formation is too low to provide a consistent fit with the nitrogen donors and THTP and was not included in this fit. These values are to be compared with those for the cobalt(II) protoporphyrin IX dimethyl ester: $E_{\text{A}} = 4.44$; $C_{\text{A}} = 0.58$. The porphyrin system is the stronger acid toward all bases, for both the E and C parameters are larger.

Two explanations were considered to account for the anomalous behavior of this acid with the complete set of donors. The first is that the acid exists as a dimer or higher aggregate and that certain bases cleave the dimer, while others do not. In the former case the equilibrium is described by $\text{A}_2 + 2\text{B} \rightleftharpoons \text{B} \cdot \text{A}_2 \cdot \text{B}$. Dimeric cobalt Schiff base complexes have been isolated whose X-ray crystal structures demonstrate close interaction between the cobalt on one molecule and the coordinating oxygen on another molecule.¹⁷

EPR results are also consistent with this dimerization model. A dimeric form of the acid could be diamagnetic due to antiferromagnetic interaction of the cobalt centers. For Me₂SO, THF, and CH₃CN, no EPR signal was seen, and these bases may not be able to break apart the dimer. For the strong nitrogen and sulfur donors, an EPR signal is seen, and the dimer could be cleaved upon adduct formation. However, this explanation is ruled out on the basis of our results. The spectrophotometric titration data fit an $\text{A} + \text{B} \rightleftharpoons \text{AB}$ equilibrium well but do not fit an $\text{A}_2 + 2\text{B} \rightleftharpoons 2\text{AB}$ equilibrium nearly as well, and the molecular weight determination of Co(4,6-CH₃Osal-4-CF₃oph) at room temperature by the Signer method¹⁸ indicates that the species is present as a monomer. Finally, aggregation would be more extensive in the solid than in solution and there is no evidence of extensive association in the solid from the susceptibility results.

The second explanation involves complications in understanding the acid-base chemistry that arises from differences in the electronic configuration of the free acid and the different adducts.^{19,21}

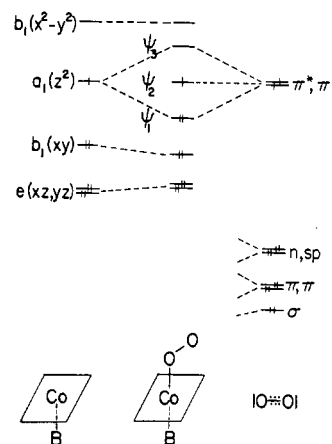


Figure 6. Molecular orbital model for the coordination of dioxygen to cobalt(II) complexes.

The temperature dependence of the magnetic susceptibility of the free acid in the solid state was investigated and is consistent with a low-spin doublet ground state. No antiferromagnetic coupling is evident in the sample, and there is no abrupt spin crossover, as would be expected for a system in which the ground state changes from high spin to low spin with temperature. There is precedence for the existence of both low-spin²² and high-spin²³ five-coordinate Schiff base adducts. Evans susceptibility indicates that this situation occurs in our system. One set of E_{A} and C_{A} values would be needed for the acid reacting with bases to form low-spin adducts and a second set for reactions that form the "high-spin" adducts. The term "high spin" could refer to a Boltzmann population of quartet and doublet states. In the high-spin adduct, occupancy of the $d_{x^2-y^2}$ orbital leads²⁴ to metal-Schiff base donor atom differences that are ~ 0.1 Å greater than in the low-spin adduct for which the $d_{x^2-y^2}$ orbital is vacant. This, coupled with different amounts of 4s mixing into the cobalt acceptor orbital, would cause the two spin states to behave as different adducts and require a different set of E_{A} and C_{A} values to describe their acid-base chemistry. We propose that pyridine, *N*-methylimidazole, and tetrahydrothiophene yield low-spin complexes while the Me₂SO adduct either has a quartet ground state or a doublet-quartet Boltzmann distribution, leading to weakly bound adducts. This is consistent with the EPR studies. Low-spin adducts of cobalt(II) are generally EPR active while high-spin adducts are generally EPR silent near liquid-nitrogen temperatures. Thus, obtaining EPR spectra of the pyridine, *N*-methylimidazole, tetrahydrothiophene, and piperidine adducts indicates low-spin complexes. The lack of an EPR spectrum at liquid-nitrogen temperatures for the dimethyl sulfoxide, tetrahydrofuran, and acetonitrile adducts indicates that these adducts are high spin either as 1:1 or possibly²⁵ 2:1 complexes. Our

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reported E_A and C_A values will work only for low-spin adducts.

Dioxygen Binding to Cobalt-Base Adducts. The spin-pairing model¹ for dioxygen binding, Figure 6, involves the unpaired electron of low-spin cobalt(II) (shown for simplicity as residing in d_{z^2}) pairing up with an electron in an oxygen π^* orbital to form a σ molecular orbital, Ψ_1 , which contains the two spin-paired electrons, and a σ^* molecular orbital Ψ_3 . The remaining π^* orbital is orthogonal to both Ψ_1 and Ψ_3 and becomes the essentially oxygen-based molecular orbital, Ψ_2 , containing the unpaired electron. The conclusion that the unpaired electron resides in this molecular orbital is confirmed by the evaluation of the ^{17}O anisotropic hyperfine coupling constant,²⁶ which showed that 0.4e and 0.6e were present on the bound and terminal oxygen atoms. If minor overlap with other orbitals is neglected, Ψ_1 , Ψ_2 , and Ψ_3 have the form

$$\begin{aligned}\Psi_3 &= \beta(d_{z^2}) - \alpha(\pi_1^*) \\ \Psi_2 &= \pi_2^*(a(2p_1) + b(2p_2)) \\ \Psi_1 &= \alpha(d_{z^2}) + \beta(\pi_1^*)\end{aligned}$$

where $\beta = (1 - \alpha^2)^{1/2}$. When $\alpha = 0$ and $\beta = 1$, the complex can be described as an ionically bound superoxide, $[(d^6)\text{Co}]O_2^-$. If $\alpha = 1$ and $\beta = 0$, the complex can be described as $[(d^8)\text{Co}]O_2^+$. For $\alpha = \beta = (0.5)^{1/2}$, $[(d^7)\text{Co}]O_2$ will describe the complex.

In the CoPPIXDME series, an increase of axial base strength increases the enthalpy of dioxygen binding.³ This was readily rationalized³ with the spin-pairing model. The electron in d_{z^2} of the five-coordinate cobalt(II) complex is stabilized in the Ψ_1 molecular orbital of the O_2 adduct. The higher the energy of the d_{z^2} orbital is driven by a strong axial base, the more its electron becomes stabilized when the O_2 adduct is formed. One notes that this trend is also maintained when the axial base is varied in the Schiff base series. The enthalpy of O_2 binding to the tetrahydrothiophene adduct is surprisingly small. Good isosbestic point behavior and dioxygen binding reversibility were found for this system. However, the value for the entropy indicates the existence of unusual effects in this system that are not understood, so we would be hesitant to compare this enthalpy with others.

The comparison of dioxygen binding to $\text{Co}(4,6\text{-CH}_3\text{Os}al\text{-}4\text{-CF}_3\text{oph})\text{-}N\text{-MeIm}$ with that for $\text{CoPPIXDME}\text{-}N\text{-MeIm}$ indicates that the cobalt metal orbital energies are at a higher energy in the former complex. This would be consistent with a weaker acidity of $\text{Co}(4,6\text{-CH}_3\text{Os}al\text{-}4\text{-CF}_3\text{oph})$ because of a greater inductive effect from the Schiff base ligand than from the porphyrin. Even though oxygen is more electronegative than nitrogen, the poorer acidity of $\text{Co}(4,6\text{-CH}_3\text{Os}al\text{-}4\text{-CF}_3\text{oph})$ than CoPPIXDME and the stronger dioxygen binding to both the pyridine and 1-methylimidazole adducts of $\text{Co}(4,6\text{-CH}_3\text{Os}al\text{-}4\text{-CF}_3\text{oph})$ suggests that more electron density is placed on the cobalt by the Schiff base ligand than by the porphyrin. The negative charge on the anion may be more effectively delocalized in the porphyrin than in the Schiff base, rendering the former a power donor.^{4c} Alternatively, delocalization of metal electron density into the porphyrin ring may be occurring to increase the partial positive charge on the cobalt and lower the energy of the d-orbital manifold in the porphyrin complex. The comparison of these complexes shows that inductive transfer of electron density to the metal by variation of the ligands cis to the dioxygen has a pronounced effect on dioxygen binding. These findings parallel the trend reported by Basolo et al.⁴ of increasing $\log K$ with $E_{1/2}$. However, $\log K$ has now been replaced by a more reliable measure of bond strength ($-\Delta H$) and $E_{1/2}$ has been replaced by a more direct measure of the cobalt positive charge than $E_{1/2}$, the acidity of the metal center.

EPR Studies of the Dioxygen Adducts. Of all the physical techniques used to study the dioxygen adducts of cobalt(II) complexes, EPR has been the most widely used. The intensity of the O_2 adduct signal and its characteristic features makes EPR an extremely easy method for determining if a five-coordinate cobalt(II) complex has bound dioxygen. In most cases,²⁷⁻²⁹ the

anisotropic spectra of five-coordinate low-spin cobalt(II) complexes are characterized by g_{\perp} (g_x, g_y) in the range 2.2-2.5, g_{\parallel} (g_z) \approx 2.0, and A_z in the range $(80-110) \times 10^{-4} \text{ cm}^{-1}$. The intense signal due to the corresponding O_2 adduct of these complexes has a reversal of g values ($g_{\parallel} \approx 2.1$, $g_{\perp} \approx 2.0$) and a reduction in A_{\parallel} to a value of $(15-30) \times 10^{-4} \text{ cm}^{-1}$.

The 1:1 base adducts of $\text{Co}(4,6\text{-CH}_3\text{Os}al\text{-}4\text{-CF}_3\text{oph})$ listed in Table III form reversible O_2 adducts at low temperature. When the solution was warmed to a temperature in the range -80 to -40 °C, an isotropic signal for the O_2 adduct can be obtained. Corresponding EPR parameters for the O_2 adducts of $\text{Co}(4,6\text{-CH}_3\text{Os}al\text{-}4\text{-CF}_3\text{oph})\text{-}base$ are listed in Table IV. The values for A_{\perp} were calculated from measured values of A_{\parallel} and A_{iso} .

The procedure for calculating metal to dioxygen electron transfer (ET) values from the EPR parameters has been reported earlier.¹ Smith and Pilbrow^{30a} in an excellent review of the interpretation of the EPR spectra of O_2 adducts conclude that "a formidable amount of evidence now points to a spin pairing model". These authors point out additional reasons to those we report¹ that render the ET values semiquantitative at best. Thus, our discussion focuses on trends in similar families or in the comparison of complexes with very different ET values. The data in Table IV show that the value for A_{\parallel} decreases as the axial base strength increases, and therefore the value for ET increases. As discussed earlier, as the axial base strength increases the energy of the " d_{z^2} " orbital³¹ is raised. This causes Ψ_1 to contain more oxygen character and less cobalt character. In other words, α^2 decreases, and the fraction of an electron transferred from cobalt to the dioxygen fragment increases. This trend in the ET value as the basicity of the axial ligand increases is that expected from the spin pairing model. The CoPPIXDME series³ does not exhibit this trend, illustrating the need for a more quantitative analysis before small differences can be reliably interpreted.³³ An overall range of electron transfer from 0.1e to 0.8e has been reported, and adducts of both $\text{Co}(4,6\text{-CH}_3\text{Os}al\text{-}4\text{-CF}_3\text{oph})$ and CoPPIXDME have values around 0.5e as would be expected for adducts to cobalt centers with comparable partial positive charges.

Infrared Studies of the Dioxygen Adducts. As mentioned in earlier work,^{1,3} the O-O stretching frequency is quite insensitive to variation in the axial base in a given series of O_2 adducts. Recent results³² show that the variation of the axial base over a pK_B range of 9 orders of magnitude resulted in a less than 25-cm^{-1} variation in the O-O stretching frequency.^{32c} In other series^{32b} a variation of 5 orders of magnitude in pK_B resulted in a 3-cm^{-1} change. The changes that do occur are consistent with predictions of the spin-pairing model; enhanced basicity leads to more electron transfer which in turn leads to a lower O-O stretching frequency. The ν_{O-O} values when the axial base is held constant in the series $\text{Co}(\text{TPP}) \sim \text{Co}(\text{J-en}) > \text{Co}(\text{acacen})$ (TPP refers to tetraphenylporphyrin and acacen refers to the Schiff base derived from ethylenediamine and acetylacetone while J-en refers to the acetyl derivative of the latter) can now be explained with our demonstration of stronger dioxygen binding to Schiff base type complexes than to porphyrins. The weaker base binding and stronger dioxygen binding to the former indicate more extensive electron

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donation from the Schiff base ligand and a higher energy d_{z^2} orbital. More electron transfer and a lower ν_{O-O} is expected for the Schiff base. The electron-withdrawing acetyl groups result in less electron density being placed on the cobalt; a weaker metal- O_2 adduct is predicted to form, and a higher O-O stretching frequency would result.

The largest differences in ν_{O-O} are observed when one compares the O_2 adducts of the free four-coordinate cobalt complex with those of the five-coordinate complexes. In solution, O_2 adducts of the four-coordinate complexes do not form at room temperature. In the Co(J-en) series,^{32b} for Co(J-en) $\cdot O_2$ in a matrix occurs at 1260 cm^{-1} while that for the pyridine adduct occurs at 1143 cm^{-1} . The ν_{O-O} for Co(TPP) $\cdot O_2$ occurs at 1278 cm^{-1} and the pyridine adduct has a ν_{O-O} value of 1144 cm^{-1} . A significant fact has been overlooked³² in the interpretation of these results. The ground state for many square-planar cobalt(II) complexes has the unpaired electron in the d_{xz} , d_{yz} set. Spin pairing of this electron with the π -antibonding electrons of O_2 results in a weaker interaction since the four-coordinate complexes do not readily form O_2 adducts in solution. Alternatively, if promotion of the electron to a largely d_{z^2} orbital is required for spin pairing, this energy must come from the Co- O_2 bond for there is no axial base to provide this energy. A higher O-O stretch is expected to accompany the weaker binding of O_2 to many four-coordinate Schiff base complexes.

Clearly, the spin-pairing model provides a valuable tool for correlating a wide variety of results on O_2 binding. If the formal

positive charge on the metal is reduced, stronger O_2 binding, more electron transfer into O_2 , and a lower O-O stretch result in a fashion readily understood by qualitative molecular orbital arguments.

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Registry No. 1-MeIm, 616-47-7; py, 110-86-1; THTP, 110-01-0; H₂-4,6-CH₃Osai-4-CF₃oph, 107960-11-2; Co(4,6-CH₃Osai-4-CF₃oph), 106904-68-1; Co(4,6-CH₃Osai-4-CF₃oph) \cdot pip $\cdot O_2$, 108007-43-8; Co(4,6-CH₃Osai-4-CF₃oph) \cdot 1-MeIm $\cdot O_2$, 108007-44-9; Co(4,6-CH₃Osai-4-CF₃oph) \cdot py $\cdot O_2$, 108007-45-0; Co(4,6-CH₃Osai-4-CF₃oph) \cdot THTP $\cdot O_2$, 108007-46-1; Me₂SO, 67-68-5; Co(4,6-CH₃Osai-4-CF₃oph) \cdot 1-MeIm, 108007-42-7; Co(4,6-CH₃Osai-4-CF₃oph) \cdot py, 107985-21-7; Co(4,6-CH₃Osai-4-CF₃oph) \cdot THTP, 107985-22-8; O₂, 7782-44-7; Co(4,6-CH₃Osai-4-CF₃oph) \cdot Me₂SO, 107985-23-9; 3,4-diaminobenzotrifluoride, 368-71-8; 4,6-dimethoxysalicylaldehyde, 708-76-9; 4-amino-3-nitrobenzotrifluoride, 400-98-6.

Supplementary Material Available: Tables of data pertaining to the physical measurements involved in this work including magnetic susceptibility data (Table A1), ^{19}F NMR data (Tables A2 and A3), UV-vis spectrophotometric data (Tables A4-A6), and spectrophotometric titration data (Tables A7-A9) (10 pages). Ordering information is given on any current masthead page.

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Absorption, Emission, and Photophysical Properties of Copper(I) Pyrazole Complexes and Their Carbonyl Adducts

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This work examines the electronic and photophysical properties of copper(I) pyrazole complexes. All two-, three-, and four-coordinate copper(I) pyrazole complexes investigated have strong MLCT electronic transitions in the UV region, and these transitions are affected by the ligand environment around the metal ion. Excitation at 77 K into the MLCT transitions produces visible emissions that are from $^3d-\pi^*$ excited states. Copper(I) pyrazole complexes with a phenolate donor have lower energy MLCT absorption and emission transitions relative to those of Cu(N)_x⁺ complexes. The binding of carbon monoxide to the three-coordinate and phenolate complexes shifts the electronic transitions to higher energy while the emission (from a $^3d-\pi^*$ excited state) is found at lower energy. This has been explained by proposing that the Cu(I)-CO complexes have a low-energy electronic transition that is so weak it cannot be clearly resolved in the absorption spectrum. The intense absorption transitions resulting from the aromatic amino acid side chains will severely limit the possibility of observing MLCT transitions for most copper(I) proteins; nevertheless, such transitions are present and this work suggests that they may be useful for probing the metal ion site properties in those proteins. This is illustrated in comparing the present results with the spectroscopic properties of carbonylhemocyanin (HcCO).

The importance of copper(I) centers at the active sites of a number of proteins is well documented,² but investigations of those sites have been hindered because the d^{10} Cu(I) ion is invisible to many spectroscopic methods used to study metalloproteins. Excited-state properties associated with the metal ion may provide a way to circumvent the problem, since at least three copper proteins display luminescent emission when irradiated at around 300 nm: hemocyanin,³ tyrosinase,⁴ and metallothionein (MT).⁵

Corequisite with investigating the spectroscopic properties of copper(I) sites in proteins is the need to study the analogous properties in well-defined synthetic copper(I) complexes. Although such complexes exhibit no ligand field transitions that are usually found in the visible spectra of transition-metal complexes, there are a large number of systems with intensely absorbing Cu(I) chromophores. Recent studies have revealed many aspects of copper(I) photochemistry and photophysics, which include emission from intraligand or metal-to-ligand charge-transfer excited states,^{6,7} dual emission occurring from two distinct excited

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