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Dioxygen Affinities of Synthetic Cobalt Schiff Base Complexes

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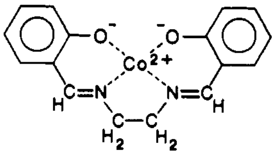
The synthesis and dioxygen affinities of six cobalt(II) Schiff base complexes in diglyme solution in the presence of excess aromatic bases are reported. The cobalt(II) chelates investigated are (bis(salicylaldehyde) tetramethylethylenediiminato)cobalt(II) (CoSALTMEN), (bis(salicylaldehyde) *o*-phenylenediiminato)cobalt(II) (CoSALOPHEN), (bis(2-hydroxyacetophenone) ethylenediiminato)cobalt(II) (CoαCH$_3$SALEN), (bis(3,5-dichlorosalicylaldehyde) *o*-phenylenediiminato)cobalt(II) (Co35ClSALOPHEN), (bis(3-methoxysalicylaldehyde) *o*-phenylenediiminato)cobalt(II) (Co3MeOSALOPHEN), and the parent compound, (bis(salicylaldehyde) ethylenediiminato)cobalt(II). Axial bases employed are pyridine, 4-methylpyridine, 4-(dimethylamino)pyridine, and 4-cyanopyridine. In the solvent medium employed the Schiff base chelates combine with only one axial base; no 2:1 adducts were observed. Electron-withdrawing substituents on the Schiff bases were found to decrease the affinity of the cobalt Schiff base for dioxygen. Equilibrium dioxygen uptake measurements over a range of temperatures provide values of $\Delta H°$ and $\Delta S°$ of oxygenation that fall in the range −6 to −13 kcal mol^{-1} for $\Delta H°$ and −30 to −52 cal deg^{-1} mol^{-1} for $\Delta S°$ and are in line with values reported for analogous dioxygen complexes in the literature.

Introduction

The potential attractiveness of carrying out dioxygen–dinitrogen separation by chemical means has long been recognized, but suitable methods have not yet been carried to the point where they are sufficiently cost effective to be adopted by industry. The cobalt(II) chelate of "salen", labeled "salcomine" has been investigated for its ability to chemically absorb dioxygen when used in the solid state,[1] but dioxygen-separation processes based on this type of compound have encountered problems because of gradual degradation upon dioxygen cycling resulting in loss of capacity.[1,2] The cobalt(II) chelate of bis(3-fluorosalicylaldehyde) ethylenediimine, called "fluomine", shows the best performance thus far,[3-5] undergoing as many as 3500 sorption–desorption cycles before about 40% of the material becomes inert. In addition to the degradation reaction, there is a problem in preparing active solid fluomine dioxygen carriers that are reproducible from one batch to the next. The preparative method is primarily a recipe, and the differences in the structures and compositions of active and inactive solids are not known.[4-6]

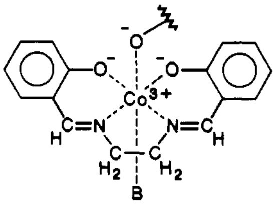
The use of dioxygen carriers in solution is attractive because solutions make possible more complete contact with the gaseous mixture through the use of countercurrent packed columns or multiplate distillation-type towers. Solid–gas equilibria on the other hand require gas-permeable solids or adsorption of the material on porous supports. In such systems the achievement of complete solid–gas equilibrium is frequently difficult. Oxygen carriers in solution suffer from the problem that oxidative degradation to inert complexes seems to occur more rapidly in solution than in the solid state and that the degradation reaction is highly concentration dependent, increasing rapidly at high concentrations of the complexes.[7]

Dioxygen carriers studied in the past include metal complexes of Schiff bases, porphyrins, and macrocyclic ligands. The Co(II) Schiff base chelate that has been studied most extensively is (bis(salicylaldehyde) ethylenediiminato)cobalt(II) (**1**). The ligands in such dioxygen carriers are usually tetra- or pentadentate, and in the case of Co(II), the resulting complex may have wide variations in structure, composition, and dioxygen affinity. Dioxygen-binding complexes based on Fe(II), Cu(I), Ni(II), and Mn(II) have been reported,[8-11] but chelates of Co(II) offer the greatest promise for oxygen production because of the wide range of stabilities of cobalt dioxygen complexes and the correspondingly wide range of structures and properties available.



1 (CoSALEN, salcomine)

Four-coordinate Co(II) chelates such as that shown in **1** do not by themselves bind oxygen strongly, but their adducts with suitable monodentate Lewis bases readily bind oxygen under suitable conditions of temperature and oxygen pressure,[12,13] as a result of the additional stabilization of the Co(II)–dioxygen bond through increase in electron density at the metal center provided by the axial base. The dioxygen ligand binds in a position trans to the axial base (formula **2**).



2

dioxygen complex of salcomine (half of molecule shown)

The axial bases (B) that promote oxygenation of **1** may be aliphatic or aromatic amines. Pyridine and substituted pyridines are most frequently employed.

This paper describes the synthesis of new cobalt dioxygen complex systems related to **1** that are potentially useful for di-

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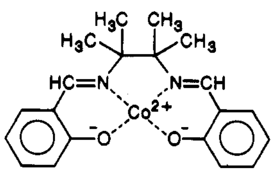
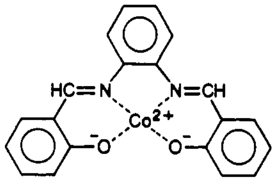
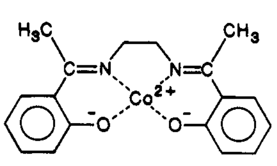
Chart I. Structures of the Cobalt Complexes Prepared



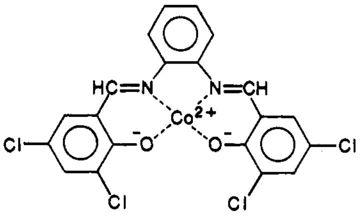
3 (CoSALTMEN)



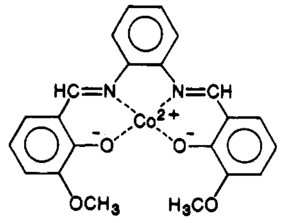
4 (CoSALOPHEN)



5 (CoαCH$_3$SALEN)



6 (Co35ClSALOPHEN)



7 (Co3MeOSALOPHEN)

oxygen separation processes, i.e., capable of recycling the oxygenation–deoxygenation reactions without appreciable loss through oxidative degradation of the coordinated ligands or permanent oxidation of the central metal ion. The ligand design employed consists of substitution of electronegative groups on the aromatic rings to deactivate them toward electron-seeking oxidative attack, methylation of the ethylene bridge, considered sensitive to oxidation, or replacement of the bridge with an aromatic ring. The dioxygen affinities, which are expected to be reduced by these changes in the ligands, are to be adjusted by varying the donor properties of the axial base indicated in **2**, substituted with electron-withdrawing or -releasing groups. The solvent medium, diethylene glycol methyl ether (diglyme) was selected because of its wide liquid range (>200 °C), as well as for its solvating properties, thus simplifying the adjustment of dioxygen affinities through temperature variation. Thermodynamic parameters for dioxygen complex formation in solution are reported and compared with the values available for analogous complexes.

Experimental Section

Materials. Pyridine and 4-picoline were purified by refluxing them with NaOH for 15 h. They were then distilled and stored over 4A molecular sieves. Diglyme (diethylene glycol methyl ether) was purified by distillation over Na metal. Ethylenediamine was refluxed over NaOH for 11 h; sodium metal was added, and it was refluxed for 2 h and then distilled.

The following compounds were all reagent grade and were used without further purification: cobalt acetate ($CoAc_2 \cdot 4H_2O$, Fisher Scientific Co.); salicylaldehyde (MCB); *o*-vanillin, 4-cyanopyridine, 4-(dimethylamino)pyridine, *o*-phenylenediamine, 3,5-dichlorosalicylaldehyde, 2,3-dinitro-2,3-dimethylbutane, and 2-hydroxyacetophenone (Aldrich Co.).

Structures of the prepared cobalt complexes **3**–**7** may be found in Chart I.

1,1,2,2-Tetramethylethylenediamine was prepared by a modification of the method of Sayre.[14] The product was a colorless liquid that showed no impurities by NMR.

Bis(salicylaldehyde) tetramethylethylenediimine (SALTMEN) was prepared by the method of Averill and Broman.[15] A 1.6-g sample of 1,1,2,2-tetramethylethylenediamine was dissolved in 6 mL of MeOH. This solution was then mixed with 3.3 g of salicylaldehyde. The yellow precipitate, which separated out, was collected off and washed with ether, and after recrystallization from ethanol, 3.0 g of yellow product was obtained. Its melting point was 117 °C, in agreement with the literature value (117 °C[15]).

^{1}H NMR: δ 1.4 (s, 12 H, CH_3), 6.6–7.4 (m, 8 H, phenyl), 8.4 (s, 2 H, =CH), 14.0 (br, s, 2 H, OH).

(Bis(salicylaldehyde) tetramethylethylenediiminato)cobalt(II) (CoSALTMEN) (3) was prepared by a modification of the method of Baker et al.[16] A 3.2-g sample of SALTMEN was dissolved in a mixture of 10 mL of pyridine and 10 mL of MeOH. A solution containing 2.45 g of $CoAc_2 \cdot 4H_2O$ in 25 mL of water was prepared and mixed with the SALTMEN solution and stirred for 20 min. The product was then filtered off and washed with water and then with ethyl alcohol. The material was first dried over P_2O_5 for 24 h and then dried at 170–180 °C at a pressure of 2 Torr for 3 h. The weight of the red orange product obtained was 3.1 g.

Anal. Calcd for $C_{20}H_{22}N_2O_2Co$: Co, 15.46. Found: Co, 15.3.

(Bis(salicylaldehyde) *o*-phenylenediiminato)cobalt(II) (CoSALOPHEN) (4) was synthesized by a modification of the method of Marzilli et al.[17] A 2.0-g sample of salicylaldehyde was mixed with 0.90 g of *o*-phenylenediamine and stirred for 10 min. The reaction mixture heated up and became viscous. The mixture was allowed to stand for 15 min and was then poured with vigorous stirring into 40 mL of 95% ethanol. The solid mass that formed was filtered off with a large Büchner funnel and air-dried at 40 °C for 12 h. The yellow product (2.3 g) was recrystallized from ethanol. The product, bis(salicylaldehyde) *o*-phenylenediimine (SALOPHEN), which weighed 1.36 g, had a melting point of 167–168 °C (lit. 166 °C[18]).

^{1}H NMR: δ 6.6–7.4 (m, 12 H, phenyl), 8.6 (s, 2 H, =CH), 13.2 (s, 2 H, OH).

A 1.5-g sample of SALPOHEN was mixed with 1.25 g of $CoAc_2 \cdot 4H_2O$ and refluxed in 400 mL of MeOH for 1 h. The mixture was then cooled and filtered, and the resulting CoSALOPHEN was washed with MeOH and ether and dried under vacuum at 100 °C. The brown CoSALOPHEN obtained weighed 1.3 g (73%).

Anal. Calcd for $C_{20}H_{14}N_2O_2Co$: Co, 15.79. Found: Co, 15.5.

(Bis(salicylaldehyde) ethylenediiminato)cobalt(II) (CoSALEN) (1). From 2.44 g of salicylaldehyde and 0.60 g of ethylenediamine, 1.55 g of yellow Schiff base was obtained (mp 128–129 °C; lit. 125–126 °C[19]).

^{1}H NMR: δ 4.1 (s, 4 H, CH_2), 6.8–7.6 (m, 8 H, phenyl), 8.5 (s, 2 H, =CH), 13.3 (br, s, 2 H, OH).

CoSALEN (salcomine) was synthesized by the method of Bailes and Calvin.[20]

Anal. Calcd. for $C_{16}H_{14}N_2O_2Co$: Co, 18.11. Found: Co, 17.8.

(Bis(2-hydroxyacetophenone) ethylenediiminato)cobalt(II) (CoαCH$_3$SALEN) (5) was prepared by a modification of the method of Lancashire et al.[21] To a solution containing 5.5 g of 2-hydroxyacetophenone in 25 mL of ethanol was added 1.20 g of ethylenediamine. After the solution was heated and stirred for approximately 10 min, a yellow product precipitated. The precipitate was filtered and washed with ethanol and after being dried weighed 5.1 g. The αCH$_3$SALEN (5.1 g) was recrystallized from ethanol to give a final yield of 4.1 g. The melting point of the product was determined to be 202–203 °C.

^{1}H NMR: 2.5 (s, 6 H, CH_3), 4.1 (s, 4 H, CH_2), 6.7–7.7 (m, 8 H, phenyl), 13.9 (s, 2 H, OH).

To a solution of 4.1 g of αCH$_3$SALEN dissolved in 40 mL of boiling pyridine was added a solution of 3.5 g of $CoAc_2 \cdot 4H_2O$ dissolved in 30 mL of water. The mixture was then stirred and cooled to room temperature. The red precipitate was filtered off, washed with water and then ethanol, and dried under vacuum at 100 °C. The CoαCH$_3$SALEN obtained weighed 0.80 g.

Anal. Calcd. for: $C_{18}H_{18}N_2O_2Co$: Co, 16.68. Found: Co, 16.3.

(Bis(3,5-dichlorosalicylaldehyde) *o*-phenylenediiminato)cobalt(II) (Co35ClSALOPHEN) (6). A 2.3-g sample of 3,5-dichlorosalicylaldehyde was dissolved in 35 mL of ethanol, and the solution was mixed with a solution of 0.65 g of *o*-phenylenediamine in 20 mL of ethanol. This mixture was then stirred for approximately 10 min, and an orange product precipitated. After the reaction mixture stood for 20 min, it was

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Table I. Thermodynamic Constants for Dioxygen Binding to Cobalt Schiff Base Complexes in 2-Methoxyethyl Ether as Solvents

complex	base	t, °C	log K_{O_2}, mm^{-1}	$P_{1/2}$, mm	$P_{1/2}^{-1}$, mm^{-1}	$10^{-2}K^{B}_{1}$, M^{-1}	$\Delta H°$,[b] kcal/mol	$\Delta S°$,[c] eu	oxygen complex
CoSALOPHEN, 0.012 M	4-Mepy, 1 M	0.5	−2.07	1.2×10^2	8.5×10^{-3}	3	−10.3	−47	1:1
		10	−2.37	2.3×10^2	4.3×10^{-3}				
		25	−2.74	5.5×10^2	1.8×10^{-3}				
	4-CNpy, 1 M	0.5	−2.27	1.8×10^2	5.5×10^{-3}	2	−8.4	−41	1:1
		10	−2.51	3.2×10^2	3.1×10^{-3}				
		25	−2.82	6.6×10^2	1.5×10^{-3}				
	py, 2 M	0.5	−2.22	1.7×10^2	6.0×10^{-3}	2	−9.1	−43	1:1
		15	−2.60	4.0×10^2	2.5×10^{-3}				
		25	−2.81	6.5×10^2	1.6×10^{-3}				
	DMAP, 0.4 M	25	1.04			4			2:1
CoSALTMEN, 0.014 M	4-Mepy, 2 M	0.5	−3.4	3×10^3	4×10^{-4}	4	−6	−40	1:1
		15	−3.6	4×10^3	3×10^{-4}				
		25	−3.8	6×10^3	2×10^{-4}				
CoαCH$_3$SALEN, 0.010 M	4-Mepy, 3 M	0.5	−1.31	20	4.9×10^{-2}	1	−13.4	−55	1:1
		5	−1.50	32	3.2×10^{-2}				
		10	−1.68	48	2.1×10^{-2}				
Co3MeOSALOPHEN, 0.012 M	4-Mepy, 2 M	0.5	−2.23	1.7×10^2	5.9×10^{-3}	3	−6.9	−35	1:1
		15	−2.52	3.3×10^2	3.0×10^{-3}				
		25	−2.68	4.8×10^2	2.1×10^{-3}				
CoSALEN, 0.010 M	4-Mepy, 2 M	0.5	1.58	2.6	0.38	1	−10.3	−30	2:1
		10	1.30	5.0	0.20				
		25	0.91	12	0.093				
Co35ClSALOPHEN, 0.010 M	4-Mepy, 0.04 M	0.5	0.52	30	0.033	1	−10.7	−37	2:1
		5	0.38	42	0.024				
		10	0.23	59	0.017				

[a] The K_1^B values were determined from the visible spectra. [b] ΔH values were obtained from the van't Hoff plots (illustrated in Figure 3). [c] ΔS was calculated from the equations $\Delta G° = -RT \ln K_{O_2}$ and $T\Delta S° = \Delta H° - \Delta G°$.

filtered and the precipitate was washed with ethanol and ether. The 35ClSALOPHEN obtained weighed 1.65 g (60%). It was further purified by refluxing with 1.0 L of MeOH for 1 h. The hot MeOH solution was filtered and allowed to stand overnight. The purified 35ClSALOPHEN, which crystallized out, weighed 1.0 g and had a melting point range of 214–215 °C. A 400-mg sample of this purified material was dissolved in 40 mL of diglyme at 65 °C. A solution of CoAc$_2$ (220 mg) in 25 mL of water was then rapidly poured into the diglyme solution, and the resulting mixture was stirred for 1 h at room temperature. The brown solid material was filtered off and was washed with water and then with ethanol. After being dried under vacuum at 100 °C for 4 h, the product weighed 220 mg (49%).

Anal. Calcd for $C_{20}H_{10}N_2O_2Cl_4Co{\cdot}0.4H_2O$: C, 46.35; H, 2.10; N, 5.41. Found: C, 46.74; H, 2.38; N, 5.59.

(Bis(3-methoxysalicylaldehyde) *o*-phenylenediiminato)cobalt(II) (Co3MeOSALOPHEN) (7). A solution of 3.04 g of vanillin in 25 mL of ethanol was mixed with a solution of 1.08 g of *o*-phenylenediamine in 25 mL of ethanol. The mixture was stirred, and after about 10 min an orange product precipitated. The solid was filtered off, and the precipitate was washed with ethanol. The product obtained weighed 2.5 g (67%). The 3MeOSALOPHEN was then recrystallized from ethanol, and 1.8 g of purified material with a melting point of 172–173 °C was obtained.

^{1}H NMR: δ 3.9 (s, 6 H, CH$_3$), 6.9–7.3 (m, 10 H, phenyl), 8.7 (s, 2 H, =CH), 13.2 (s, 2 H, OH).

One gram of this product was dissolved in 120 mL of boiling ethanol, and 0.67 g of $CoAc_2{\cdot}4H_2O$ in 25 mL of water was added to the ethanol solution. The resulting mixture was stirred for 1 h at room temperature. The precipitate was then filtered off and was washed with water and ethanol. The Co3MeOSALOPHEN was then dried under vacuum at 100 °C, and the final weight was 0.65 g (57%).

Anal. Calcd for $C_{22}H_{18}N_2O_4Co{\cdot}0.5H_2O$: C, 59.73; H, 4.33; N, 6.33. Found: C, 60.10; H, 4.10; N, 6.46.

Proton NMR spectra were recorded with an EM-390 spectrometer in deuteriochloroform. The resonances are reported in ppm relative to tetramethylsilane (Me$_4$Si) as standard. C, H, and N analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Cobalt analyses were carried out by oxidizing the cobalt chelate with hot concentrated nitric acid and then using a colorimetric method of analysis described by Snell and Snell.[22] Visible spectra were recorded with a Perkin-Elmer 553 spectrophotometer.

Oxygen uptake measurements were made with a gas volumetric apparatus illustrated in Figure 1, which is a modified version of that described by Calderazzo and Cotton.[23] A 25-mL graduated gas buret was fitted with a mercury leveling bulb and was connected through a T-bore stopcock to a 100-mL 2-neck flask containing a magnetically activated stirring bar. The flask was connected to vacuum and gas inlet lines through a 3-way stopcock. A mercury manometer was connected to the gas line between the 3-way and T-bore stopcocks. The reaction flask and buret were enclosed with jackets through which water was rapidly circulated from a constant-temperature bath. The temperature was adjusted between 0 and 50 °C with variations within ±0.05 °C.

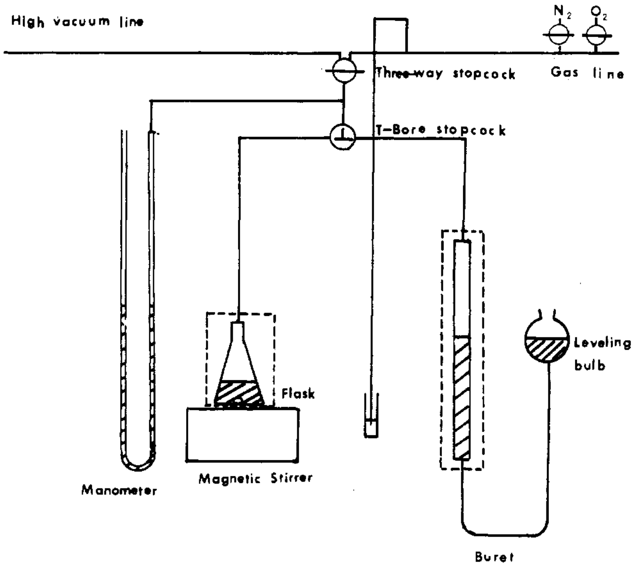

Figure 1. Sketch of the gas volumetric apparatus.

The total volume of the gas buret, the reaction flask, and the connecting tubing was measured by standard methods. Solubilities of dioxygen and dinitrogen in the solvent (diglyme) were measured at the various temperatures employed in order to make appropriate corrections on the gas absorption measurements. Over the range of temperatures used in this research it was found that the vapor pressure of the solvent was negligible.

In a typical run, 30 mL of diglyme saturated with air and 100–170 mg of dioxygen carrier sealed in a thin-walled vial were carefully added to the flask. The entire apparatus was thermostated at a preselected temperature. The flask was filled with dry air, and its pressure was then

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reduced to a lower predetermined value by exhausting part of the air via the vacuum line. Then pure dinitrogen was introduced from the gas supply line, and the total pressure of the gas was brought back to atmospheric pressure. From the pressure measurements, known volumes, and the corrections mentioned above, the partial pressures of dioxygen and dinitrogen in the mixture were calculated. The vial containing the dioxygen carrier was crushed with the stirrer to begin the absorption of dioxygen. The gas in the buret was transferred to the reaction flask several times during the dioxygen absorption to assure uniform composition of the gas remaining in the system. From the stoichiometry of the reaction, determined by dioxygen uptake, and the (corrected) partial pressure of dioxygen at equilibrium, the oxygenation constant was calculated.

Dioxygen Equilibria. The equilibria of interest in this investigation are the following:

addition of axial base

$$\mathrm{CoL} + \mathrm{B} \rightleftharpoons \mathrm{CoLB} \qquad K^{\mathrm{B}}_1 = \frac{[\mathrm{CoLB}]}{[\mathrm{CoL}][\mathrm{B}]} \tag{1}$$

$$\mathrm{CoLB} + \mathrm{B} \rightleftharpoons \mathrm{CoLB_2} \qquad K^{\mathrm{B}}_2 = \frac{[\mathrm{CoLB_2}]}{[\mathrm{CoLB}][\mathrm{B}]} \tag{2}$$

oxygenation

$$\mathrm{CoLB} + \mathrm{O_2} \rightleftharpoons \mathrm{CoLBO_2} \qquad K_{\mathrm{O_2}} = \frac{[\mathrm{CoLBO_2}]}{[\mathrm{CoLB}][\mathrm{O_2}]} \tag{3}$$

$$2\mathrm{CoLB} + \mathrm{O_2} \rightleftharpoons (\mathrm{CoLB})_2\mathrm{O_2} \qquad K'_{\mathrm{O_2}} = \frac{[(\mathrm{CoLB})_2\mathrm{O_2}]}{[\mathrm{CoLB}]^2[\mathrm{O_2}]} \tag{4}$$

In order to distinguish between 1:1 and 2:1 dioxygen complex formation (eq 3 and 4), the oxygenation constants were determined as a function of dioxygen pressure. The stoichiometry of dioxygen uptake, as well as the calculations of the oxygenation constants, provided the needed information. In order to determine the nature of the stoichiometry of axial base adducts formed (eq 1 and 2), the oxygenation constants were determined at constant dioxygen pressure, but with varying concentrations of axial base, B. If the complex $\mathrm{CoLB_2}$ were predominant in solution, or if it formed to any considerable extent, an increase in the concentration of axial base (always in large excess) would result in a decrease in dioxygen uptake.

Axial Base. The axial bases employed (B in eq 1–4) are as follows, pyridine, 4-picoline, 4-cyanopyridine, and 4-(dimethylamino)pyridine. All were obtained from Aldrich and were reagent grade.

Thermodynamic constants, $\Delta H°$ and $\Delta S°$, for the oxygenation process (eq 3 and 4) were determined in the usual way from the variation of $K_{\mathrm{O_2}}$ and $K'_{\mathrm{O_2}}$ over a range of temperatures.

Results and Discussion

The effect of axial base concentration on dioxygen absorption was measured, and a tabulation of the data obtained is available as supplementary material. In all examples shown the axial base concentration is 1 or 2 orders of magnitude higher than that of the cobalt chelate, so that in most cases the formation of the axial base adduct was complete or nearly complete. Because one axial base is necessary for the chelates investigated to combine with dioxygen, plus the fact that combination of the cobalt(II) chelate with two axial bases to form an octahedral complex would prevent reaction with dioxygen, the extent of dioxygen uptake provides a convenient probe for indicating the stoichiometry of the cobalt(II) chelate present in solution (i.e., CoLB or $\mathrm{CoLB_2}$, eq 1 and 2). Three possible effects on dioxygen uptake as a function of increase in axial base concentration would be expected: (1) increase in dioxygen uptake; (2) no increase in dioxygen uptake; (3) a decrease in dioxygen uptake. These effects reflect, respectively, (1) incomplete formation of CoLB, (2) complete formation of CoLB, and (3) partial to complete conversion of CoLB to $\mathrm{CoLB_2}$. The results in Table I indicate complete or nearly complete formation of the 1:1 adduct, CoLB, in nearly all cases. There seems to be a possibility that the 1:1 adduct was not completely formed in the cases of CoαCH$_3$SALEN and CoSALEN at the lower concentrations of axial base. The behavior of Co35ClSALOPHEN is not clear in view of the fact that the lower concentration of axial base produced the highest dioxygen uptake, even at a 1:1 molar ratio, while on the other hand, much higher concentrations of axial base produced a lowering of dioxygen uptake. This type of behavior requires further investigation.

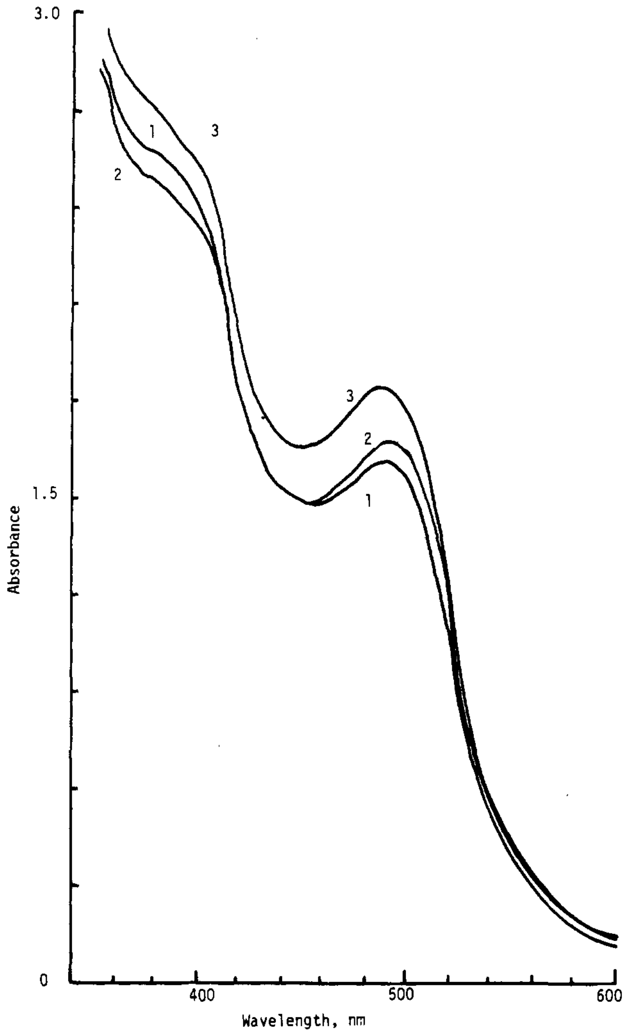

Figure 2. Spectral changes accompanying the addition of 4-picoline and $\mathrm{O_2}$ to a diglyme solution containing CoSALOPHEN: (1) spectrum of 4.0×10^{-4} M CoSALOPHEN; (2) spectrum of the solution with 0.10 M 4-picoline added; (3) spectrum of the solution after saturation with $\mathrm{O_2}$.

The formation constants of the 1:1 adducts of the six cobalt(II) chelates with the axial bases are presented in Table I. Because of the fact that under the conditions employed in this investigation the 1:1 adducts were almost completely formed, the corresponding stability constants, defined by eq 1 and 2, are only approximate. Another factor contributing to the low accuracy of determination of the formation constants involving the axial base is the small shift in absorbance observed when the tetradentate Schiff base complex is converted to the pentacoordinated complex containing the axial base adduct (eq 1), indicated in Figure 2 for the combination of CoSALOPHEN with 4-methylpyridine. Even combination of this complex with dioxygen is seen in Figure 2 to result in only a modest increase in absorbance. For this reason the oxygenation constants were measured (much more accurately) by the quantities (volumes) of dioxygen absorbed at equilibrium, as described in the Experimental Section. The uncertainties in the determination of the axial base formation constants (eq 1) had no influence on the accuracy of determination of the oxygenation constants, because the oxygenation equilibria were measured under conditions such that the 1:1 axial base adducts were completely formed.

The oxygenation constants of the pentadentate complexes of the 1:1 adducts of the Schiff base complexes are listed in Table I (eq 3 and 4). It is seen that no definite pattern exists with respect to the relative electron-donating effects of the Schiff base ligands and the relative electron-donating effects of the axial base. The presence of electron-donating and electron-withdrawing substituents of the Schiff base ligands would be expected to have con-

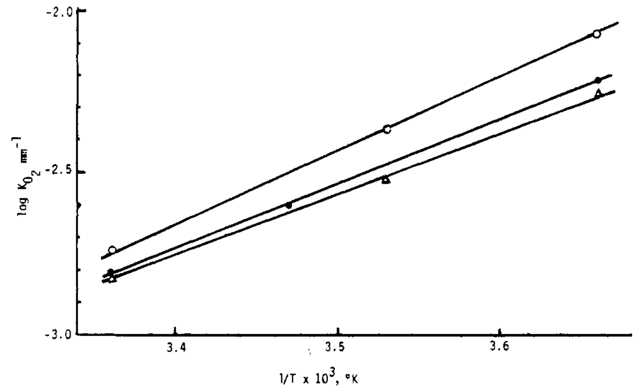

Figure 3. van't Hoff plots for the binding of O_2 to Co(SALOPHEN)B: (○) in 1.0 M 4-picoline–diglyme solution; (●) in 2.0 M py–diglyme solution; (△) in 1.0 M 4-CNpy–diglyme solution [CoSALOPHEN] = 0.010 M.

siderable influence on dioxygen affinity. That this is not the case is seen from the magnitudes of the oxygenation constants and is probably partly due to the fact that the axial base affinity increases as the electron-releasing effects of the Schiff base ligands decrease. Thus the substituent effects on the aromatic rings are mitigated by the presence of the axial ligand, which binds more effectively when the donor properties of the Schiff bases decrease. Because of the lack of correlation between ligand basicity and dioxygen affinity, a principle that has been well established for other types of cobalt dioxygen complexes,[13] it appears that the variations observed are mainly the result of the steric effects of the substituents on dioxygen affinity.

The values of the thermodynamic constants listed in Table I do present discernible trends based on ligand donor effectiveness. Thus for CoSALOPHEN, the dioxygen binding energies, as measured by the enthalpy changes, increase in the order 4-CNpy < py < 4-Mepy, which is the order of increasing basicity of the axial base. The high binding energy observed with DMAP cannot be compared with the others because a binuclear dioxygen complex is formed. The large increase in stability in this case is probably due to the formation of two coordinate bonds to dioxygen as well as to the stronger bonding resulting from a stronger electron-donating axial base.

The entropy values are all strongly negative, as would be expected from comparable values of other complexes described previously,[13] because of the large negative entropy effect resulting from the loss of translational motion of the dioxygen. An additional major effect contributing to negative entropy is the loss of vibrational and partial rotational freedom of the ligands resulting from the increase in coordinate bond strength in converting a cobalt(II) complex to one in which the metal ion is more highly charged (formally written as cobalt(III)). This effect may be seen in the case of the three very similar CoSALOPHEN complexes, with entropy changes becoming increasingly negative in the order 4-CNpy < py < 4-Mepy, which is also the order of increasing coordinate bond energy. Another example of this effect is the dioxygen complex formed from CoαCH$_3$SALEN and 4-Mepy, which has the highest bond energy of the 1:1 dioxygen complexes investigated and also the most negative entropy change.

In conclusion, the results of this study indicate the feasibility of several variations of ligand structure on the dioxygen-carrying properties of cobalt(II) Schiff base chelates—the replacement of the ethylene bridge by more oxidation-resistant *o*-phenylene and tetramethylethylene groups, increase in the oxidation resistance of the aromatic rings by substitution with electronegative groups, and the use of electron-releasing and electron-attracting substituents on the axial base. With all of the structural variations employed for the nine complexes listed in Table I, the oxygenation equilibria were found to occur in a convenient range of temperatures and pressures for the determination of oxygenation constants and for the planning of recycling experiments by the use of temperatures and dioxygen pressures not very far from ambient. In addition, variation of axial base basicity was found to have appreciable and predictable affects on dioxygen affinity. On the basis of these results, it is planned to further stabilize the ligand against oxidative attack by fluorine substitution. Another variation in ligand structure planned for the extension of this research will be to attach the axial base covalently to the Schiff base ligand, thus preventing loss of axial base during long-term recycling tests.

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Supplementary Material Available: Table of data showing the effect of axial base concentration on dioxygen absorption (1 page). Ordering information is given on any current masthead page.