

The observation that the imidazole ring in aqueous solution in the pH range 1–5 can adopt the carbon-bound arrangement and that this form has considerable stability, at least in a kinetic sense, is of substantial interest to considerations of metalloenzyme structure and function. The implication is that histidine residues might be capable of carbon bonding at metal ions in biological media. In terms of similarity in electronic structure to the Ru(II) and Ru(III) systems we have studied, low spin iron(II) and iron(III) in porphyrins could be suggested as potential sites for such binding. It is conceivable that a change in conformation near the metal site or the changes in ligand characteristics that would accompany a nitrogen to carbon bonding re-

organization could play a role in the function of metalloenzymes. These possibilities are entirely speculative at this time, but it will be of interest to learn, as detailed mechanisms of action of metalloenzymes are developed, if carbon-bound histidines play any biological role.

Supplementary Material Available. A listing of proton nmr chemical shift data, positional and thermal parameters, and structure amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-381.

Oxygen Carrier and Redox Properties of Some Neutral Cobalt Chelates. Axial and In-Plane Ligand Effects

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Abstract: Thermodynamic data are reported for the reversible oxygen uptake of several cobalt(II) complexes. A linear correlation was found between the equilibrium constants for oxygen adduct formation and the ease of oxidation of cobalt(II) to cobalt(III), as measured by cyclic voltammetry. It is suggested that this correlation exists because the redox potential of the cobalt chelate is a measure of the electron density on the cobalt, which in turn is the most important parameter in determining the oxygen affinity of the substrates.

The reversible oxygenation of cobalt complexes has posed some striking challenges in our attempt to understand the chemical behavior of heme in myoglobin and hemoglobin. One of the most significant recent achievements was that reported by Hoffman and Petering¹ who reconstituted globin with Co(Pp IX), cobalt(II) protoporphyrin IX, the analog of heme, and found that the resulting coboglobin has oxygen carrier properties similar to hemoglobin.

Since the initial discovery of Tsumaki² that Schiff base complexes of cobalt(II) are oxygen carriers, there has been a continued interest in this property of cobalt complexes.³ However, the recent resurgence of research activity on these systems can be traced to the isolation of one-to-one adducts^{4,5} of the type Co–O₂ and to the use of esr to investigate these systems.^{6–8} Considerable effort has been made to determine the oxygen uptake ability of Co(L)B complexes, where L is a quadridentate chelate group which occupies the equatorial position in the complex and B is a unidentate

ligand in the axial position. Investigations include the effect of the axial base,^{5,9,10} of the equatorial chelate group,^{11–13} and the role of the solvent.¹⁴

From esr results,⁷ approximately 90% of the spin density of the unpaired electron on cobalt(II) is calculated to transfer to oxygen upon formation of the Co(L)B·O₂ adduct. This suggests that the system can be viewed as a superoxide ion attached to cobalt(III), Co^{III}–O₂[–]. On this basis, the reaction of Co(L)B with O₂ may be described as an electron transfer from cobalt(II) to the oxygen molecules. Thus, the ability of these complexes to react reversibly with oxygen should be very closely related to the redox potentials of the systems.¹⁵

This paper reports data which show that there is a direct correlation between the redox potentials of neutral cobalt chelates and their ability to behave as oxygen carriers.

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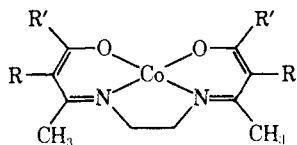
Experimental Section

Materials. All solvents were dried by refluxing over CaH₂ and then distilled and stored under a nitrogen atmosphere.

The liquid amines were reagent grade, stored over NaOH, and distilled prior to use. The solid amine, 4-cyanopyridine, was recrystallized from hexane. Methyl ethyl sulfide and triphenylphosphine were reagent grade and were used without further purification.¹⁶

The reagents, 2,4-pentanedione, benzoylacetone, pyrrole, anisaldehyde, propionic acid, cobaltous chloride hexahydrate, and cobaltous acetate tetrahydrate were reagent grade.

Preparation of Complexes. The structure and symbols of the cobalt compounds prepared for this study are as follows¹⁷



- Co(acacen), R' = CH₃; R = H
 Co(Phacacen), R' = CH₃; R = C₆H₅
 Co(meacacen), R' = CH₃; R = CH₃
 Co(benacen), R' = C₆H₅; R = H
 Co(sacsacen), R' = CH₃; O = S; R = H

The compound 3-phenylacetylacetone was prepared by a modification of the method of Hauser and Adams;¹⁸ 3-methylacetylacetone was obtained by a modification of the method of Taylor, *et al.*¹⁹

Both (acacenH₂)²⁰ and (benacenH₂)²¹ were prepared as described before. The Schiff base, (sacsacenH₂)²² was a gift from Dr. J. L. Corbin of Kettering Scientific Research in Yellow Springs, Ohio.

The ligand, (PhacacenH₂), was prepared by adding 3.5 g of 3-phenylacetylacetone to 60 ml of absolute ethanol followed by 0.6 g of ethylenediamine. The pH of the solution was adjusted to 6 with glacial acetic acid. The solution was refluxed for a few minutes and then evaporated to dryness. The solid residue was recrystallized twice from toluene, filtered, and air-dried, mp 189–190°, yield 2 g.

The Schiff base, (meacacenH₂), was obtained from a solution of 2.2 g of 3-methylacetylacetone and 0.6 g of ethylenediamine in 50 ml of absolute methanol, adjusted to pH 6 with glacial acetic acid. The solution was refluxed for a short time and then evaporated to half volume. Addition of an equal amount of water caused the product to precipitate immediately. The compound was collected, washed with water, and air-dried. The crude product was recrystallized from toluene, filtered, and air-dried, mp 154°, yield 1.6 g.

The porphyrin, (*p*-MeOTPPH₂), was prepared as described by Adler.²³

All of the cobalt(II) compounds were prepared in Schlenk ware in a nitrogen atmosphere. Modifications of literature methods

(16) The following abbreviations will be used throughout this paper: pyridine, py; 1-methylimidazole, *N*-MeIm; 5-chloro-1-methylimidazole; 5-Cl-*N*-MeIm; triphenylphosphine, PPh₃; *n*-butylamine, *n*-BuNH₂; isobutylamine, *i*-BuNH₂; *sec*-butylamine, *sec*-BuNH₂; *tert*-butylamine, *t*-BuNH₂.

(17) Co(acacen), *N,N'*-ethylenbis(acetylacetoniminato)cobalt(II); Co(Phacacen), *N,N'*-ethylenbis(3-phenylacetylacetoniminato)cobalt(II); Co(meacacen), *N,N'*-ethylenbis(3-methylacetylacetoniminato)cobalt(II); Co(benacen), *N,N'*-ethylenbis(benzoylacetiminato)cobalt(II); Co(sacsacen), *N,N'*-ethylenbis(monothioacetylacetoniminato)cobalt(II); Co(*p*-MeOTPP), $\alpha,\beta,\gamma,\delta$ -tetra(*p*-methoxyphenyl)porphyrato-cobalt(II); Co(Pp(IX)DME), protoporphyrin IX dimethyl ester cobalt(II).

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were used to prepare Co(acacen),²⁴ Co(benacen),²¹ and [Co(benacen)py₂]ClO₄.²⁵ The cobalt porphyrin Co(*p*-MeOTPP) was prepared by the method of Walker.⁸

The chelate, Co(Phacacen), was prepared as follows. In order to deprotonate the Schiff base, 1.13 g of (PhacacenH₂) was added to a methoxide ion solution, formed by the addition of 0.24 g of K to 60 ml of methanol. A solution of 0.75 g of Co(C₂H₃O₂)·4H₂O in 25 ml of methanol was added dropwise. The mixed solution was maintained at 40° for 1 hr and then the solvent was removed *in vacuo*. The residue was recrystallized from toluene as bright orange crystals.

The compound Co(meacacen) was prepared by the same method as described above for the phenyl derivative. A reaction mixture of Co(C₂H₃O₂)·4H₂O (0.31 g), 0.32 g of the ligand, and 0.1 g of K was used. The compound was obtained as bright orange plates.

Analyses. Elemental analyses of C, H, and N were performed by H. Beck of this department and are given in Table I.

Table I. Elemental Analyses of Compounds^a

Compound	C _c	C _f	H _c	H _f	N _c	N _f
acacenH ₂	64.29	63.95	8.96	8.89	12.51	12.32
Co(acacen)	51.25	51.20	6.45	6.52	9.96	9.90
PhacacenH ₂	76.60	76.79	7.50	7.42	7.44	7.22
Co(Phacacen)	66.51	66.97	6.05	6.38	6.46	6.34
MeacacenH ₂	66.63	66.20	9.59	9.75	11.10	11.41
Co(Meacacen)	54.37	54.71	7.17	7.22	9.06	9.03
benacenH ₂	75.83	75.93	6.94	7.08	8.04	8.01
Co(benacen)	65.18	65.35	5.47	5.51	6.91	6.84
[Co(benacen)py ₂]ClO ₄	57.97	59.58	4.86	5.22	8.45	8.26
Co(sacsacen)	46.00	45.93	5.79	5.71	8.94	8.84
<i>p</i> -MeOTPPH ₂	78.45	78.64	5.21	5.17	7.62	7.58
Co(<i>p</i> -MeOTPP)	72.86	72.67	4.55	4.39	7.08	7.11

^a C_c, carbon calculated; C_f, carbon found.

Oxygen Uptake Measurements. Oxygen uptake measurements were made in a Pyrex cell (W. Sales Ltd., Deerfield, Ill.) mounted in a dewar. A 45-mm tubular gas ballast was connected to the cell and projected out of the top of the dewar. The path length of the cell was ~4 cm. The cell was so constructed that a slush bath or an ice-salt mixture could completely surround it in the dewar.¹¹ In this manner using organic slushes²⁶ and ice-salt mixtures,²⁷ the temperature of the solutions could be controlled to ±1° during the oxygen uptake equilibrium constant determinations. The temperature of the solution was determined by the potential difference (Leeds and Northrup potentiometer) of a copper-constantan thermocouple referenced at 0.

For a typical experiment, ~3 × 10⁻⁴ mmol of complex was dissolved in 2 mmol of the organic amine and diluted with 15 ml of toluene in the optical cell which had previously been evacuated and filled with nitrogen. The solution was further degassed by repeated evacuation of the cell and refilling with nitrogen. After final evacuation, the solution was cooled with the appropriate slush or ice-salt mixture and the spectrum recorded with a Cary 14 instrument. Then various pressures of oxygen were added, and the spectrum was recorded after each addition.

Pressures of oxygen were added to the solution in two ways:

- (1) when the equilibrium constant was larger than 5 × 10⁻² mm⁻¹, oxygen was added directly by connecting the cell to a vacuum line and adjusting the oxygen pressure using a mercury manometer;
- (2) when the equilibrium constant was smaller than 5 × 10⁻² mm⁻¹, a known aliquot of oxygen was added by filling the volume, V₁, between two stopcocks to a known pressure, P₁, on the vacuum line, then opening the closer stopcock to the gas ballast, V₂, of the cell. The pressure, P₂, was then calculated by simply using the equation, P₁V₁ = P₂V₂.

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Table II. ESR Parameters^a for Some Co(L)B Complexes with Rhombic Spectra

Compound	Base, B	g_x^b	g_y^b	g_z	a_x^{Co}, G	a_y^{Co}, G	a_z^{N}, G
Co(acacen)B	py	2.449	2.236	2.013	47.3	100.0	15.0
Co(Meacacen)B	py	2.470	2.230	2.009	59	104.6	15.3
Co(Phacacen)B	py	2.446	2.237	2.014	52.5	103.0	15.0
Co(sacsacen)B	py	2.443	2.169	2.003		77.6	15.0
Co(<i>p</i> -MeOTPP)B ^f	py	2.312	2.312	2.022		83.3	15.5
Co(benacen) B	py	2.444	2.231	2.014	45.0	98.0	15.0
	<i>n</i> -BuNH ₂	2.428	2.237	2.009	40	96.3	13
	<i>i</i> -BuNH ₂	2.441	2.244	2.012	45	96.0	13
	<i>N</i> -MeIm	2.442	2.257	2.013	44	98	16
	5-Cl- <i>N</i> -MeIm	2.451	2.267	2.013	50	101	15
	<i>sec</i> -BuNH ₂	2.456	2.249	2.007	55	96.0	13
	Piperidine	2.442	2.244	2.013	44	93.5	14
	3,4-Lutidine	2.441	2.248	2.009	45	98	15.5
	4-Picoline	2.442	2.251	2.012	47.5	99	15.5
	py	2.442	2.253	2.012	46	99	15
	CNpy	2.470	2.267	2.013	47	103	16.5
	PPh ₃ ^d	2.319	2.250	1.958		89	
	None ^e	3.114	1.920	2.002			

^a All measurements were made from frozen solutions, $T = 77^\circ K$. Solutions of Co(L)py were 1% py-toluene. Solutions for the axial variations of Co(benacen)B were solvent mixtures of 70% toluene-20% DMF-10% base ($\sim 1 M$) by volume. (Note that the second entry for Co(benacen)py is for the determination from this mixed solvent.) Error limits = $\pm 1\%$ in the final digit. ^b The x and y designations are arbitrarily assigned; these directions are in the Schiff base plane. ^c The spectra are of five-coordinate species. The cobalt parallel hyperfine is split into three components due to interaction with one axial N. ^d The coordination number cannot be exclusively assigned on the basis of the esr spectrum, since there is no hyperfine structure due to the phosphorus ligand. ^e The spectrum is representative of a four-coordinate complex. The g value assignments are made on the basis of B. H. Hoffman, D. L. Diemente, and F. Basolo, *J. Amer. Chem. Soc.*, **95**, 6497 (1973). ^f Our results are in agreement with ref 8.

larography was performed on an instrument built from the following slightly modified components: a Princeton Applied Research Model 373 potentiostat with a triangular wave supplied by a Hewlett-Packard Model 202A function generator. The instrument²⁸ was set to scan a voltage range of 1.0 V in 1-10 sec. The electrode system consisted of a saturated calomel reference electrode, a Brinkmann Instruments hanging drop mercury electrode (for reproducible drop size) or a stationary platinum electrode, and a platinum wire functioned as the third (counter) electrode. Measurements were made at 23° in a closed vessel which was flushed with nitrogen prior to addition of the solution. Contact of the solution to the bridge compartment, which was separated from the reference electrode and solution by two medium glass frits, was made through a glass tube with a capillary tip. The solution was forced up the tube under N_2 pressure. Complex compounds were dissolved in 0.1 M $(CH_3CH_2)_4NClO_4$ solutions. The salt bridge contained 0.1 M $(CH_3CH_2)_4NClO_4$ in the solvent used for electrolysis.

Values of $E_{1/2}$ were obtained from cyclic voltammograms using the expression $E_{1/2} = 1/2(E_p + E_{p/2})$. The "peak" potential, E_p , is the potential at maximum diffusion current and the "half-peak" potential, $E_{p/2}$, is the potential determined at half the maximum diffusion current.

Esr Spectra. ESR spectra were taken on a Varian Associates Model E-4 operating at the X-band frequency. The microwave frequency was measured directly by a Hewlett-Packard x532-B frequency meter. The magnetic field was calibrated with Varian pitch ($g = 2.0027$). For low-temperature liquid-phase spectra, the cavity was cooled by a conventional variable temperature apparatus, using cold nitrogen gas, with a copper-constantan thermocouple ($\pm 1.9^\circ$) placed directly below the sample in the nitrogen steam. Frozen solution spectra were recorded in liquid nitrogen.

Esr samples were prepared in small erlenmeyer flasks (25 ml) equipped with a side-arm to facilitate the deoxygenation of the solutions. The solutions at concentrations between 10^{-3} and $10^{-2} M$ were transferred to the 4-mm quartz esr tubes with a gas-tight syringe. The sample tubes were equipped with Teflon taps and side-arms were fitted with O-ring joints.

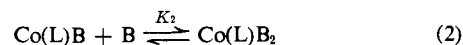
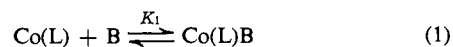
Samples were oxygenated by thawing, thermostating at temperatures between -51.5 and -83.6° (depending on the sensitivity of the sample) while oxygen was bubbled through the solution and freezing immediately. Deoxygenations were carried out by the usual freeze-pump-thaw procedure.

(28) We would like to thank Professor A. L. Allred for the use of the instrument.

Esr parameters of deoxy and oxy complexes are given in Table II and III, respectively. The values obtained are assigned on the basis of Hoffman, *et al.*⁷ There seems to be no correlation between a_{iso} and the ability of the cobalt complexes to react reversibly with oxygen, as previously suggested by Abel, *et al.*²⁹

Results

Coordination Number. The quantitative determination of formation constants for the equilibria



were hampered by very small spectral changes (~ 0.01 - 0.04 absorbance units of the solutions upon addition of bases to solutions of the cobalt complexes). Visible spectral changes were found to cease after the addition of ~ 0.02 ml of base to 20 ml of $\sim 10^{-4} M$ Co(L) in toluene at 25° . These changes were at 360, 365, 365, 470, and 378 nm for Co(acacen)B, Co(Phacacen)B, Co(meacacen)B, Co(benacen)B, and Co(sacsacen)B, respectively. The esr spectra of these solutions were always characteristics (Table II) of five-coordinate species, since the ^{59}Co hyperfine was split into three components due to interaction with only one axially coordinated nitrogen. The compounds studied showed no esr evidence for six-coordination, not even in solutions of neat pyridine. Making use of the small changes in optical densities accompanying the addition of bases to solutions of the cobalt chelates, rough estimates were made of the formation constants of the five-coordinate species examined here and these fall in the range 10^2 - $10^3 M^{-1}$. These formation constants are in accord with those reported for Co(saloph)³⁰ but smaller than those reported for cobalt porphyrins.^{10,31}

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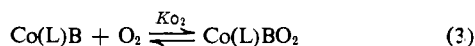
Table III. ESR Parameters^a for Some Co(L)B·O₂ Complexes

Compound	Base, B	g_{\perp}^b	g_{\parallel}	g_{iso}	$A_{\perp},^c$ G	$A_{\parallel},$ G	$a_{iso},^d$ G
Co(acacen)B·O ₂	py	1.998	2.080	2.027	10.4	19.3	13.7
Co(Meacacen)B·O ₂	py	2.007	2.082	2.019	10.9	20.3	14 ^e
Co(Phacacen)B·O ₂	py	1.999	2.084	2.023	9.7	19.3	12.8 ^e
Co(sacsacen)B·O ₂	py	1.997	2.085	2.023	10.4	21.3	14 ^d
Co(<i>p</i> -MeOTPP)B·O ₂ ^f	py	2.002	2.077	2.013	12.0	16.3	10.4 ^e
Co(benacen)B·O ₂	py	1.998	2.077	2.018	10.4	18.3	13 ^e
	<i>n</i> -BuNH ₂	1.999	2.089	2.021	10.7	17.7	13 ^e
	<i>i</i> -BuNH ₂	1.992	2.087	2.026	10.7	18.6	13.3 ^e
	<i>N</i> -MeIm	2.000	2.088	2.024	10.4	18.6	13.1
	5-Cl- <i>N</i> -MeIm	2.000	2.089	2.025	10.7	19.4	13.6
	<i>sec</i> -BuNH ₂	2.000	2.088	2.025	10.2	19.4	13.3
	Piperidine	2.000	2.088	2.025	10.0	19	13.0
	3,4-Lutidine	1.999	2.085	2.024	10.0	19	13.0
	4-Picoline	1.999	2.085	2.024	10.2	19	13.1
	py	2.000	2.085	2.024	10.2	19.2	13.2
	CNpy	1.999	2.085	2.022	11.1	19.2	13.8
	PPh ₃	1.996	2.082	2.024	12.5	15.5	13.5
	C ₂ H ₅ SCH ₃	1.999	2.096	2.022	13.2 ^g	25.8	15.5
	DMF	1.999	2.093	2.025	14.4 ^g	29.4	14.8

^a Parameters for nonisotropic spectra were determined from frozen solutions, $T = 77^\circ\text{K}$. Solutions for Co(L)py were 1% py-toluene. Solutions for the axial variations of Co(benacen)B were solvent mixtures of 70% toluene-20% DMF-10% base ($\sim 1\text{ M}$) by volume. (Note that the second entry for Co(benacen)py is for the determination from this mixed solvent.) Error limits are $\pm 1\%$ in the final digit except as indicated. ^b $g_{\perp} \pm 0.005$. ^c Calculated from $a_{\perp} = \frac{1}{2}(3a_{iso} - a_{\parallel})$, except as indicated. ^d $T = -75 \pm 5^\circ$, except as indicated. ^e $T = -55 \pm 5^\circ$. ^f Our results are in agreement with ref 8. ^g The parameters quoted were obtained from the experimental spectra.

Due to the insolubility of PPh₃ in toluene, it was not possible to determine the formation constant for Co(benacen)PPh₃. However, on the basis of data reported³⁰ for Co(saloph), formation constants of the PPh₃ adducts of such systems are expected to be about ten times smaller than those for amine adducts. Experiments were designed so greater than 95% of the cobalt species in solution was five-coordinate.

Oxygen Uptake. Spectral changes were recorded for solutions of cobalt chelates containing different bases at different partial pressures of oxygen and at different temperatures in order to estimate thermodynamic data for oxygen uptake (eq 3).



Upon contact with oxygen, toluene solutions of Co(L)B underwent spectral changes as a function of oxygen pressure (Figure 1). The spectral changes were immediate upon shaking the solution with oxygen, and the complex Co(L)B·O₂ was stable, as judged by the constancy of the spectra after equilibrium was reached. The total change was reversible and the original spectrum was restored upon evacuating the system to remove oxygen. In order to compensate for a base line drift of the spectrophotometer, the difference in absorbance at two different wavelengths was used to calculate the percentage of oxy and deoxy species present. The wavelengths used for the determinations were 390 and 440 nm for Co(acacen), Co(meacacen), and Co(Phacacen), 400 and 490 nm for Co(sacsacen) and Co(benacen), and 420 and 500 nm for Co(*p*-MeOTPP).

The equilibrium constants were obtained using the Hill relation.

$$Y/(1 - Y) = \frac{(\text{Co(L)B} \cdot \text{O}_2)}{(\text{Co(L)B})} = K_{\text{O}_2} P_{\text{O}_2}^n$$

The slope of the line, experimentally determined from a plot of $\log Y/(1 - Y)$ vs. $\log P_{\text{O}_2}$, ranged from 0.9 to 1.1 but was constrained in all cases to $n = 1.0$, and the

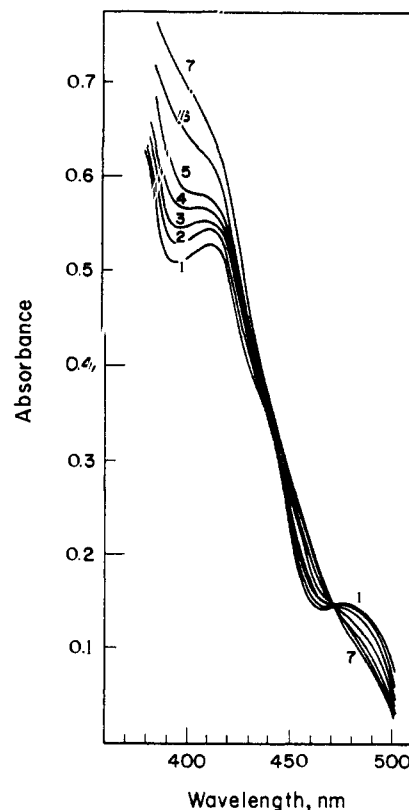


Figure 1. Spectral changes as a function of oxygen pressure for the reversible oxygenation of Co(benacen)CNpy in toluene solutions containing 10^{-2} M CNpy: 1, 0 Torr; 2, 20 Torr; 3, 46 Torr; 4, 95 Torr; 5, 193 Torr; 6, 419 Torr; 7, 766 Torr.

value of $\log K_{\text{O}_2}$ was obtained from the intercept of the best straight line of slope 1.0. Values of $Y/(1 - Y)$ between 0.25 and 4.0 only were used where possible in determining K_{O_2} . A representative Hill plot for the reversible oxygenation of Co(benacen)CNpy in toluene solution at three temperatures.

The equilibrium constants of the compounds studied and the conditions under which these were collected

Table IV. Thermodynamic Data for Reversible O₂ Binding to Co(L)py^a Complexes in Toluene Solution

Compound	Temp, °C	log K _{O₂} , mm ⁻¹	ΔH°, kcal/mol	ΔS°, eu
Co(acacen)py	0	-2.08 ± 0.03		
	-10	-1.53 ± 0.02	-17.3 ± 0.5	-72.7 ± 1.7
	-15	-1.31 ± 0.03		
	-21	-0.90 ± 0.02		
-37.4	-2.12 ± 0.02			
Co(Phacacen)py	-10	-2.12 ± 0.02	-16.3 ± 0.6	-72.5 ± 2.5
	-20.5	-1.54 ± 0.03		
	-31	-0.89 ± 0.03		
	-37.4	-0.58 ± 0.02		
Co(Meacacen)py	-21	-1.74 ± 0.02	-15.6 ± 1.5	-69.5 ± 5.0
	-31	-1.12 ± 0.03		
	-37.4	-0.79 ± 0.02		
	-45	-1.43 ± 0.02		
Co(benacen)py	-21	-2.03 ± 0.03	-16.6 ± 0.8	-75.1 ± 2.6
	-31	-1.38 ± 0.02		
	-37.4	-1.06 ± 0.04		
Co(sacsacen)py ^c	-31	-2.12 ± 0.02	-13.3 ± 0.5	-64.5 ± 2.3
	-45	-1.43 ± 0.02		
	-51.5	-0.98 ± 0.02		

^a In 1.6% pyridine-toluene solution. ^b Standard state of 1 Torr. The values of ΔH° and ΔS° were obtained from a least-squares analysis of the data points. The error limits listed for the thermodynamic data are one standard deviation. A more reasonable confidence level might be two standard deviations. ^c These results are similar to the data reported in ref 39.

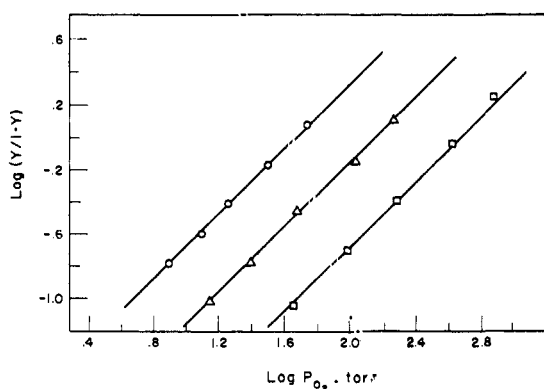


Figure 2. Hill plot of log P_{O₂} vs. log [Co(benacen)(CNpy)O₂] / [Co(benacen)(CNpy)] for the reversible oxygenation of Co(benacen)CNpy in toluene solutions containing 10⁻² M CNpy: ○, T = -37.4°; △, T = -31°; □, T = -21°.

are given in Tables IV and V. Also included in the tables are enthalpy and entropy parameters, which were determined from van't Hoff plots of the type shown in Figure 3.

The change of the equatorial ligand has a pronounced effect on the reversible oxygenations of cobalt complexes. The apparent correlation between ΔH° and the ease of oxygen uptake by Co(L)py complexes was previously pointed out by Tazher, *et al.*,¹² for Co(acacen) and Co(salen) in pyridine, salen = [*N,N'*-ethylenebis(salicylidiminato)]. Accompanying the enthalpy change is also a change in entropy in the same direction, resulting in a free energy change of 1-5 kcal/mol. These thermodynamic changes of ΔH° and ΔS° seem confined to variations in the equatorial plane rather than the axial direction. Little differences in ΔH° and ΔS° are noted as the axial ligands bound to Co(benacen) are varied, even though significant changes in oxygen uptake were found. The ΔH° and ΔS° variations were random, supporting conclusions of Walker for Co(*p*-MeOTPP)B complexes.⁹ Unfortunately, the error limits of ΔH° and ΔS° are too large to make a more detailed analysis of the data.

In the presence of oxygen, toluene solutions of Co(benacen) were stable at -63°, but underwent a very

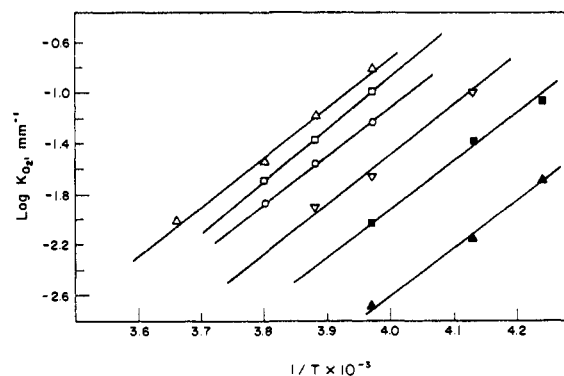


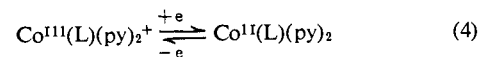
Figure 3. van't Hoff plots for the binding of O₂ to Co(benacen)B in 10⁻² M base-toluene solution: △, *N*-MeIm; □, 5-Cl-*N*-MeIm; ○, piperidine; ▽, 3,4-lutidine; ■, py; ▲, CNpy.

small reversible spectral change at -83°. Under these conditions, the four-coordinate complex can be regarded as quite insensitive to molecular oxygen.

Frozen toluene-DMF glasses of Co(benacen) and CH₃SC₂H₅ gave esr spectra due to the presence of two species, the major component was characteristic of four-coordinate Co(benacen) (Table II) and the minor component was characteristic of a five-coordinate complex. In the presence of oxygen, toluene solutions of Co(benacen) and CH₃SC₂H₅ readily underwent reversible spectral changes at -51° which were associated with the formation of the superoxy species. It seems reasonable that the oxygen was reacting with a small amount of five-coordinated species in solution.³²

Electrochemistry. Redox potentials were determined by cyclic voltammetry. The potential changes for the anodic and cathodic sweeps of the cobalt(II-III) couple were reversible³³ as shown by Figure 4.

The potentials of the Co(L) couples were determined in neat pyridine. The reactions at the electrode surface are believed to correspond to



(32) C. Busetto, F. Cariati, A. Fusi, M. Gallati, F. Marazzoni, A. Pasini, R. Ugo, and V. Valenti, *J. Chem. Soc., Dalton Trans.*, 754 (1973).

(33) R. S. Nicholson and I. Shain, *Anal. Chem.*, 36, 706 (1966).

Table V. Thermodynamic Data for Reversible O₂ Binding to Co(benacen)B Complexes in Toluene Solution

Base, B	Temp, °C	log K _{O₂} , mm ⁻¹	ΔH°, kcal/mol	ΔS°, eu
<i>n</i> -BuNH ₂	-21	-0.75 ± 0.02	-17.4 ± 0.7	-72.3 ± 2.5
	-10	-1.34 ± 0.03		
	0	-1.93 ± 0.04		
<i>i</i> -BuNH ₂	-21	-0.74 ± 0.03	-18.0 ± 0.7	-80.0 ± 3.0
	-10	-1.50 ± 0.05		
	0	-1.95 ± 0.04		
<i>N</i> -MeIm	-21	-0.82 ± 0.02	-17.5 ± 0.5	-73.5 ± 2.0
	-15	-1.18 ± 0.03		
	-10	-1.55 ± 0.03		
	0	-2.00 ± 0.04		
5-Cl- <i>N</i> -MeIm	-21	-0.99 ± 0.03	-17.5 ± 0.6	-74.5 ± 1.8
	-15	-1.38 ± 0.03		
	-10	-1.64 ± 0.04		
<i>sec</i> -BuNH ₂	-21	-1.18 ± 0.02	-17.8 ± 0.9	-76.1 ± 3.0
	-10	-1.90 ± 0.03		
	0	-2.38 ± 0.03		
Piperidine	-21	-1.23 ± 0.03	-16.7 ± 0.7	-71.9 ± 2.4
	-15	-1.57 ± 0.02		
	-10	-1.86 ± 0.03		
3,4-Lutidine	-31	-0.99 ± 0.04	-16.8 ± 0.9	-73.9 ± 2.8
	-21	-1.66 ± 0.02		
	-15	-1.89 ± 0.01		
py	-37.4	-1.06 ± 0.04	-16.6 ± 0.8	-75.1 ± 2.6
	-31	-1.38 ± 0.02		
	-21	-2.03 ± 0.03		
CNpy	-37.4	-1.68 ± 0.04	-16.9 ± 0.7	-77.2 ± 2.5
	-31	-2.15 ± 0.05		
	-21	-2.68 ± 0.06		
PPh ₃	-37.4	-2.41 ± 0.05		
CH ₃ CH ₂ SCH ₃	-51.5	-2.01 ± 0.04		

^a Standard state of 1 Torr. The values of ΔH° and ΔS° were obtained from a least-squares analysis of the data points. The error limits listed for the thermodynamic data are one standard deviation. A more reasonable confidence level might be two standard deviations. All measurements were made in 10⁻² M base-toluene solutions.

since the potentials obtained for Co(acacen) were the same whether starting with Co^{II}(acacen) or Co^{III}(acacen)py₂⁺.³⁴ If the cobalt(II) species were five-coordinated, then the cobalt(II-III) couple would not be reversible. Previous studies³⁵ have shown that as the ligand field strength of the axial ligands go to zero for a quadridentate ligand complex of cobalt(III), the redox potential becomes increasingly more positive. Thus if we assume that the known stable six-coordinated cobalt(III) species is present at the electrode surface, it follows that the less stable and more labile cobalt(II) species may also be six-coordinated. However, it should be noted that for the purpose of the correlation observed in this investigation, all that is required is that the species be of the same coordination number for all of the *E*_{1/2} values recorded.

Redox potentials for Co(benacen) and Co(*p*-MeOTPP) were determined in solutions of acetonitrile and DMF, respectively, which contained known concentrations of base, B. Again the electrochemical reaction for the Co(benacen) system is assigned to the six-coordinated complexes, because Co^{III}(benacen)py₂⁺ was prepared and its redox potential was the same as that obtained by starting with the cobalt(II) complex. By analogy, the potentials of Co(*p*-MeOTPP) are also tentatively assigned to six-coordinate species. Attempts were made to obtain potentials for the Co-(Pp(IX)DME)B systems studied by Ibers and co-workers.^{10,11,14} Unfortunately, redox potentials of the Co(II-III) couples were not observed by cyclic

(34) G. Costa, G. Mestroni, A. Puxeddu, and E. Reisenhofer, *J. Chem. Soc. A*, 870 (1970).

(35) D. P. Rillema, J. F. Endicott, and E. Papaconstatinou, *J. Chem. Soc. A*, 10, 1739 (1970).

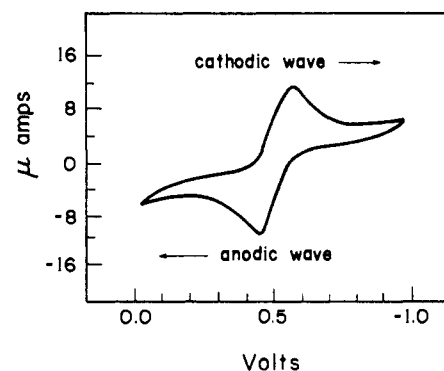
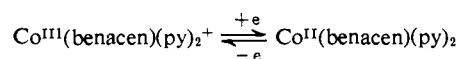


Figure 4. Cyclic voltammogram of Co(benacen) in neat pyridine. The electrochemical reaction corresponds to



voltammetry. This is not understood, but it may account for the lack of literature references on the redox properties of this compound.

The potentials obtained for Co^{II}→III oxidations are given in Tables VI and VII. For the reduction of other tetradentate ligand complexes of cobalt(III), the redox potential was a function of the ligand field strength of the two axial ligands.^{35,36} It seems reasonable to assume that as the ligand field strength goes to zero (five-coordinate), the redox potential will still be a function of the ligand field strength of the remaining axial ligand. Consequently, the relative redox potentials of the six-coordinate species also provide a measure

(36) P. A. Rock, *Inorg. Chem.*, 7, 837 (1968).

Table VI. Comparison of Oxygen Uptake ($\log K_{O_2}$) to Polarographic Half-Wave Potentials ($E_{1/2}$) for Co(benacen)B and Co(*p*-MeOTPP)B Complexes

Base, B	pK_a^a	Co(benacen)		Co(<i>p</i> -MeOTPP)	
		$\log K_{O_2},^b$ mm ⁻¹	$E_{1/2},^{d,e}$ V	$\log K_{O_2},^c$ mm ⁻¹	$E_{1/2},^{d,f}$ V
<i>n</i> -BuNH ₂	10.61 ^g	-0.75	-0.74		
<i>i</i> -BuNH ₂	10.49 ^g	-0.74	-0.73		
<i>N</i> -MeIm	7.25	-0.82	-0.72	-1.72	-0.48
5-Cl- <i>N</i> -MeIm	5.45	-0.99	-0.67	-2.26	-0.24
<i>sec</i> -BuNH ₂	10.56	-1.18	-0.62		
Piperidine	11.3	-1.23	-0.60	-2.28	-0.31
3,4-Lutidine	6.47	-1.66	-0.56	-2.35	-0.22
4-Picoline	5.98			-2.20	-0.23
py	5.27	-2.03	-0.50	-2.46	-0.20
CNpy	1.86	-2.68	-0.35		
PPh ₃		-3.4 ^h	-0.30		

^a From K. Schofield, "Hetero-Aromatic Nitrogen Compounds," Plenum Press, New York, N. Y., 1967, p 146, except as indicated.

^b Measurements were made in 10⁻² M base in toluene solution at -21°. Standard state of 1 Torr. ^c Data from ref 8. Measurements were made in 10⁻²-10⁻³ M base in toluene, solution at -65°. Standard state of 1 Torr. For 5-Cl-*N*-MeIm see correction, *J. Amer. Chem. Soc.*, **95**, 7928 (1973). ^d The solution was 10⁻³ M in complex and 0.1 M in (C₂H₅)₄NCIO₄. $E_{1/2} = \pm 0.01$ V vs. sce. Potential is for anodic wave, Co(II)-Co(III), at the hanging drop mercury electrode. $T = 23^\circ$. ^e Acetonitrile solutions containing 4% base, B, by volume. ^f DMF solutions containing 4% base, B, by volume. ^g "Handbook of Chemistry and Physics," 42nd ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1960-1961, p 1749. ^h Extrapolated from data at -37.5°.

Table VII. Comparison of Oxygen Uptake ($\log K_{O_2}$) to Polarographic Half-Wave Potentials ($E_{1/2}$) for Co(L)py Complexes

Compound	$\log K_{O_2},^a$ mm ⁻¹	$E_{1/2},^b$ V
Co(acacen)py	-0.28	-0.59
Co(Phacacen)py	-0.89	-0.55
Co(Meacacen)py	-1.12	-0.54
Co(benacen)py	-1.36	-0.50
Co(sacacen)py	-2.12	-0.33
Co(<i>p</i> -MeOTPP)py	-3.1	-0.23

^a Standard state of 1 Torr. Measurements were made in 1.6% pyridine-toluene at -31°. ^b Measurements were made in neat pyridine at 23°. The solution was 10⁻³ M in complex and 0.1 M in (C₂H₅)₄NCIO₄. $E_{1/2} = \pm 0.01$ V vs. sce. Potential is for anodic wave, Co(II) → Co(III), at the hanging drop mercury electrode.

of the relative redox potentials of the corresponding five-coordinate systems.

In cases where irreversible potentials were obtained, B = *t*-BuNH₂ and P(Et)₃ with Co(benacen) and B = *N*-MeIm with Co(acacen), irreversible oxygen uptake was also observed. The most oxygen sensitive system studied was Co(benacen)·*n*-BuNH₂ which has a half-wave potential of -0.74 V vs. SCE.

The potential changes from one solvent system to another are remarkably small. For example, the potential of Co(benacen) in pyridine and in 4% pyridine-acetonitrile are the same and there is only 0.03 V difference in potential for Co(*p*-MeOTPP) measured in pyridine and 4% pyridine-DMF solutions.

Half-wave potentials are compared to $\log K_{O_2}$ in Tables VI and VII. The $\log K_{O_2}$ values are given at $T = -21^\circ$ for Co(benacen)B in Table VI, at $T = -65^\circ$ for Co(*p*-MeOTPP) in Table VI, and at $T = -31^\circ$ for Co(L)py in Table VII. The uptake constants are given under these conditions in order to permit a direct comparison with the experimentally measured equilibrium constants. This is more reliable

than adjusting all values to the same temperature, because of the large errors in the enthalpy and entropy terms.

Discussion

Axial Ligands. The principal attention of investigators studying reversible oxygen uptake reactions has been on axial variations of Co(L)B, L = acacen,⁵ Pp(IX)DME,¹⁰ and *p*-MeOTPP.⁹ The bonding properties of the bases, B, used in these investigations change substantially from pure σ bonding (saturated amines) to the σ - and π -bonding properties of substituted pyridines and substituted imidazoles.

Generally the pK_a of the conjugate acid is taken as a measure of the σ -bond strength of the amine. The observed trends (Table VI) in oxygen carrying ability of Co(benacen)B for analogous bases are seen to crudely parallel the pK_a order; thus *n*-BuNH₂ > *i*-BuNH₂; *N*-MeIm > 5-Cl-*N*-MeIm; 3,4-lutidine > py > CNpy. This trend agrees with that previously reported by Crumbliss and Basolo⁵ and by Stynes, *et al.*¹⁰

The butylamines were studied in order to establish the importance of steric factors. The bases, *t*-BuNH₂, *sec*-BuNH₂, *i*-BuNH₂, and *n*-BuNH₂ have similar pK_a 's and these saturated bases can only σ bond, thus any change in the oxygenation ability of Co(benacen)B is expected to result from steric interactions of the base. Experiments show that with *t*-BuNH₂ the complex is only weakly sensitive to oxygen, but it does slowly undergo an irreversible oxidation. The base, *sec*-BuNH₂, is less sterically hindered, but still the steric effects are significant enough to alter the oxygen uptake of Co(benacen)B from that expected when compared with *n*-BuNH₂. For *i*-BuNH₂, little steric effects are noted indicating that the methyl group β to NH₂ has only a minor detrimental influence on the oxygen uptake ability of Co(benacen).

The cyclic, saturated amine, piperidine, which has the highest pK_a and hence the strongest σ -donor bond strength, is less effective in promoting the oxygen affinity of Co(benacen)B than is *n*-BuNH₂. These observations are consistent with the steric hindrance found above for a secondary amine. Furthermore, steric factors previously were suggested for the low oxygen uptake constant of Co(Pp(IX)DME)·piperidine.¹⁰

The other important factor to consider is π bonding. The picture of a cobalt-oxygen adduct as basically⁷ Co(III)-O₂⁻ predicts that the strength of the cobalt-oxygen bond should reflect the extent of back-donation of electrons from the filled 3d_{z²} (or 3d_{yz}) orbital of the cobalt atom into the half-empty π^* orbital of the oxygen moiety. Bases coordinated trans to oxygen will be in direct competition with the oxygen moiety for the three d π electrons of the cobalt atom. Thus, according to the theory, a good π donating base forces more electron density on the cobalt and enhances the π -bonding electron flow from cobalt to oxygen. Furthermore, because of the symmetry of the orbitals involved, the axial ligand can effectively donate its electrons to the d_{z²} or d_{yz} orbitals of cobalt which are the orbitals that π bond to oxygen. It follows that imidazoles, which may be better π donors^{37, 38} than pyridine, have the

(37) (a) W. J. Eilbeck, F. Holms, G. G. Philips, and A. E. Vanderhill, *J. Chem. Soc. A*, 1161 (1967); (b) F. Holms, K. M. Jones, and E. G. Torrible, *ibid.*, 4790 (1961).

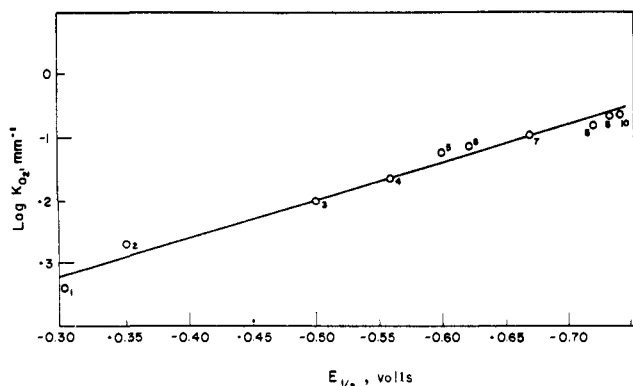


Figure 5. Comparison of oxygen uptake ($\log K_{O_2}$) at -21° for Co(benacen)B to the polarographic half-wave potentials ($E_{1/2}$) for $Co^{II} \rightarrow III$ (benacen)B₂: 1, PPh₃; 2, CNpy; 3, py; 4, 3,4-lutidine; 5, piperidine; 6, *sec*-BuNH₂; 7, 5-Cl-*N*-MeIm; 8, *N*-MeIm; 9, *i*-BuNH₂; 10, *n*-BuNH₂.

greater enhancement on the oxygen carrier ability of Co(benacen) (Table VI). However, the effectiveness of the π donating ability of an axial ligand can be superseded by a strong σ donor, *e.g.*, *n*-BuNH₂ (Table VI).

A linear correlation (Figure 5) exists between the half-wave potential of Co(II \rightarrow III) and the ability of the Co(benacen)B species to react with oxygen. It is interesting to note that on the basis of redox potentials, the π donating bases show the same correlation observed for σ bases. In addition, steric effects cause no problem in the correlation. It would appear that the half-wave potential gives a measure of the electron density on the cobalt as a composite of σ , π , and steric phenomena. Thus, the principal function of the base is to "activate" the cobalt complex by making it a better reducing agent.

An attempt was made to extend these studies to include axial bases of donating atoms other than nitrogen. Only one such system studied was found to give both a reversible electrochemical potential and a reversible oxygen uptake constant. As predicted from the half-wave potential, the oxygen uptake constant of Co(benacen)PPh₃ falls in line with other bases (Figure 5). Again this supports the postulate that the reducibility or electron density on the cobalt chelate is the important parameter in determining its oxygen carrier ability. Examination of Co(*p*-MeOTPP)B complexes also leads to a correlation between $\log K_{O_2}$, as determined by esr measurements,⁹ and $E_{1/2}$ (Figure 6).

Equatorial Ligands. The framework of (acacen) was modified by substitution of different groups on the chelate ring in an effort to test the electronic effect these substituents would have on the oxygen carrier ability of Co(L)py complexes. In terms of oxygen uptake ability (Table VII), a phenyl group on the carbonyl carbon (benacen) proves to be a better withdrawer of electron density from cobalt than a phenyl on the methylene carbon (Phacacen). The methyl group in the 3 position also decreases the ability of reversible oxygenation. This was not expected because the methyl group should contribute electron density to the system and enhance its oxygen affinity. The result

(38) L. M. Epstein, D. K. Straub, and C. Maricondi, *Inorg. Chem.*, **6**, 1720 (1967).

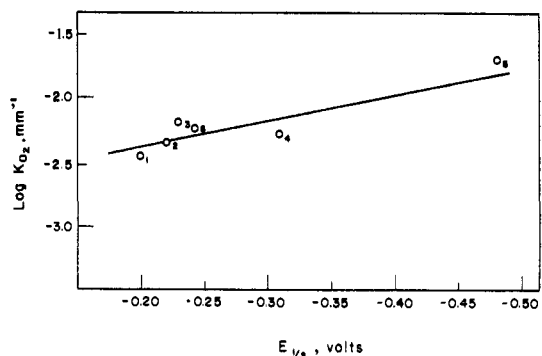


Figure 6. Comparison of oxygen uptake ($\log K_{O_2}$) at -65° to polarographic half-wave potentials ($E_{1/2}$) for $Co^{II} \rightarrow III$ (*p*-MeOTPP)B₂: 1, py; 2, 3, 4-lutidine; 3, 4-picoline; 4, piperidine; 5, *N*-MeIm; 6, 5-Cl-*N*-MeIm.

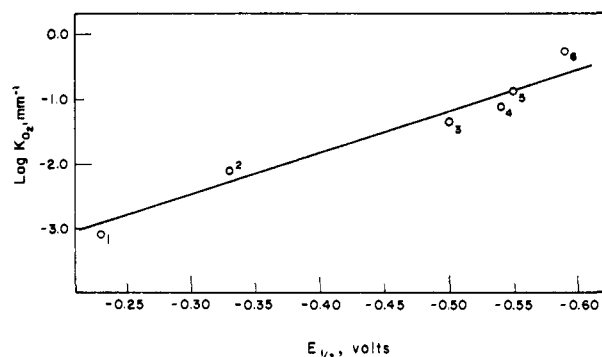


Figure 7. Comparison of oxygen uptake ($\log K_{O_2}$) at -31° for Co(L)py to polarographic half-wave potentials ($E_{1/2}$) for $Co^{II} \rightarrow III$ (L)py₂: 1, Co(*p*-MeOTPP); 2, Co(sacsacen); 3, Co(benacen); 4, Co(meacacen); 5, Co(Phacacen); 6, Co(acacen).

is not understood, but it is in accord with the small change in redox potential (Table VII).

Two other factors are important in ascertaining changes in the equatorial ligands: (1) the nature of the bonding atoms, *i.e.*, electronegativity and π withdrawal properties, and (2) the π delocalization of the metal's electron density over the equatorial ligand. A decrease in electronegativity of the ligand atoms should facilitate the oxygen carrier ability of the complex, whereas π -electron withdrawal from the cobalt should have the opposite effect. In this context, it is important to note that the replacement of O in (acacen) by S in (sacsacen) results in a weaker Co-O₂ bond. Koehler and Cummings³⁹ suggest that the sulfur ligand facilitates electron withdrawal from cobalt by in-plane d-d π back-bonding between cobalt and sulfur. This lowering of electron density on cobalt results in the complex being a less effective oxygen carrier.

The porphyrin ligand is thought to delocalize more electron density from cobalt into the ligand π system, accounting for the lower oxygen uptake ability of cobalt porphyrins compared to Co(acacen).¹¹

Regardless of the mechanism of electron withdrawal from cobalt, the half-wave potentials give a relative measure of the electron density on cobalt. The oxygen uptake ability correlates linearly (Figure 7) with the half-wave potential. This correlation holds in spite of changes such as the framework of the (acacen) ligand, the donor atoms (O, S, and N), and the π delocalization

(39) M. E. Koehler and S. C. Cummings, 165th National Meeting of the American Chemical Society, Dallas, Texas, April 1973.

properties of the quadridentate chelate group (Schiff bases, porphyrins, and macrocycles). The results support the hypothesis that the oxygen carrying ability of metal complexes depends on their ease of oxidation.

Acknowledgment. We would like to thank Professor B. M. Hoffman for discussions about the esr re-

sults and Mr. W. Boberski for his assistance with the electrochemical equipment. We also appreciate the help of Mr. C. B. Cooper, III, with some oxygen uptake determinations, and helpful discussions with Dr. L. M. Engelhardt. This research was supported by a grant from the National Institutes of Health.

Lability of Coordinated Acetonitrile in Nickel(II) Complexes. A Nitrogen-14 Magnetic Resonance Study

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Abstract: The parameters characterizing acetonitrile exchange (where k_{ex} (25°) refers to a single site) in Ni(triol)-(CH₃CN)₃²⁺ and Ni(triam)(CH₃CN)₃²⁺ (all three CH₃CN equivalent in both species) are respectively $k_{\text{ex}} = (1.0 \pm 0.2) \times 10^3 \text{ sec}^{-1}$, $\Delta H^\ddagger = 15.9 \pm 0.8 \text{ kcal mol}^{-1}$, and $\Delta S^\ddagger = 8.7 \pm 2.5 \text{ cal deg}^{-1} \text{ mol}^{-1}$ and $k_{\text{ex}} = (555 \pm 60) \times 10^3 \text{ sec}^{-1}$, $\Delta H^\ddagger = 9.3 \pm 1.0 \text{ kcal mol}^{-1}$, and $\Delta S^\ddagger = -0.9 \pm 3.5 \text{ cal deg}^{-1} \text{ mol}^{-1}$. For Ni(diamol)(CH₃CN)₃²⁺ $k_{\text{ex}} = (180 \pm 20) \times 10^3 \text{ sec}^{-1}$, $\Delta H^\ddagger = 12.0 \pm 1.1 \text{ kcal mol}^{-1}$, and $\Delta S^\ddagger = 5.4 \pm 3.5 \text{ cal deg}^{-1} \text{ mol}^{-1}$ calculated on the assumption that the single observed exchange process pertains to the two equivalent acetonitrile ligands only. The rate parameters for the faster site in Ni(trenol)(CH₃CN)₂²⁺ are $k_{\text{ex}} = (40 \pm 6) \times 10^3 \text{ sec}^{-1}$, $\Delta H^\ddagger = 12.0 \pm 1.2 \text{ kcal mol}^{-1}$, and $\Delta S^\ddagger = 2.8 \pm 4.0 \text{ cal deg}^{-1} \text{ mol}^{-1}$. These data, in conjunction with those for Ni(CH₃CN)₆²⁺ and Ni(tren)(CH₃CN)₂²⁺, indicate that CH₃CN is labilized in six-coordinate Ni(II) species by the groups -NH₂ > N< > -OH ~ CH₃CN in the order of decreasing effectiveness shown. The exchange parameters are discussed in terms of a dissociative mechanism.

The lability of solvent in the first coordination sphere of nickel(II) exhibits a variable but systematic dependence upon the nature of a second ligand in that coordination sphere.¹ This dependence, in conjunction with the recently reported observations of different labilities for the two solvent molecules in Ni(tren)-(solvent)₂²⁺ (where tren = 2,2',2''-triaminotriethylamine and solvent = H₂O² or CH₃CN³), comes tantalizingly close to revealing at least some of the major factors determining solvent lability on nickel(II). It appears that the variation in coordinated solvent lability induced by chelating ligands of similar geometry, but bonding to nickel(II) through different donor atoms, may lead to a better understanding of some of the factors controlling solvent exchange processes. Accordingly CH₃CN exchange studies on the four species, Ni(triol)-(CH₃CN)₃²⁺ (A), Ni(triam)(CH₃CN)₃²⁺ (B), Ni(diamol)(CH₃CN)₃²⁺ (C), and Ni(trenol)(CH₃CN)₂²⁺ (D) (where triol = 2,2-di(hydroxymethyl)-1-propanol, triam = 2,2-di(aminomethyl)-1-propylamine, diamol = 2,2-di(aminomethyl)-1-propanol and trenol = 2,2',2''-trihydroxytriethylamine) shown diagrammatically in Figure 1, are reported. These species were selected on the basis that in both A and B the three CH₃CN ligands are equivalent, and consequently the effect of the oxygen and primary nitrogen chelate donor atoms on the lability of single solvent molecules may be separately discerned, whereas in C the effect of oxygen and primary nitrogen donor atoms may be assessed. Species D

facilitates a comparison of the labilizing effects of oxygen and tertiary nitrogen donor atoms and also bears an obvious geometric similarity to Ni(tren)(CH₃CN)₂²⁺ (E) in which the labilizing effects of primary and tertiary nitrogen atoms may be compared.

Experimental Section

Materials. Redistilled acetonitrile, toluene, and 2,2',2''-trihydroxytriethylamine were dried and stored over Linde 4A molecular sieves. Koch-Light 2,2-di(hydroxymethyl)-1-propanol was recrystallized from benzene and dried under vacuum, and 2,2-di(aminomethyl)-1-propylamine was prepared by a method similar to that of Stetter and Böckmann.⁴ A major by-product of this preparation, 2,2-di(aminomethyl)-1-propanol (diamol), was separated as the dihydrochloride, diamol(HCl)₂, from aqueous solution in which it has a much higher solubility than triam(HCl)₃. Diamol(HCl)₂ was purified by fractional crystallization and was converted to diamol by passing an aqueous solution over an ion-exchange resin (Deacidite FF) in the hydroxide form. Water was removed by azeotropic distillation from benzene to give a benzene solution of diamol. The benzene was removed under vacuum and the diamol, a waxy solid at 25°, was distilled under vacuum. Diamol(HCl)₂ prepared from this product exhibits (in D₂O) ¹H resonances at 4.23 (-CH₂OH), 3.70 (-CH₂NH₂), and 1.65 ppm (-CH₃) downfield from a TMS capillary. *Anal.* Calcd for CH₃C(CH₂OH)(CH₂NH₃Cl)₂: C, 31.42; H, 8.44; N, 14.66. Found: C, 29.91; H, 8.52; N, 14.24. The complex bis(2,2-di(aminomethyl)-1-propylamine)nickel(II) perchlorate was prepared by allowing stoichiometric amounts of triam and nickel(II) perchlorate to react in aqueous solution from which the sparingly soluble lilac product precipitated. The product was washed with water, ethanol, and ether and dried under vacuum. *Anal.* Calcd for Ni(CH₃C(CH₂NH₂)₂)₂(ClO₄)₂: C, 24.41; H, 6.15; N, 17.08. Found: C, 24.48; H, 6.23; N, 16.29.

Spectral Measurements. All solutions were prepared in a dry nitrogen atmosphere. Solutions of Ni(triol)(CH₃CN)₃²⁺, Ni-

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