Thermodynamic Studies on (Thio iminato)cobalt(II) Oxygen Carriers and the Effect of Chelate Ring Substituents

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Abstract: Thermodynamic studies on the oxygenation of Co(sacsacen) in nonaqueous solutions containing 1.8% py, DMF, and MeIm have been completed. Stability of the six-coordinate, 1:1 type oxygen adduct increases by 28% as the Lewis base is changed from py to MeIm. The stability of Co(sacsacen)·MeIm·O$_2$ can be increased an additional 20% by using CH$_3$CN instead of toluene or DMF as the solvent. The enthalpy of formation of Co(sacsacen)·MeIm·O$_2$ in CH$_3$CN is -18.5 ± 1.7 kcal/mol and represents the most stable system here studied. This adduct is only slightly more stable than Co(acacen)·py·O$_2$ in toluene. Clearly, it takes a combination of more polar solvent and stronger Lewis base to overcome the destabilizing influence of the in-plane sulfur ligand. Adducts in the series Co(Xbensacen)·py·O$_2$ and Co(Xbenacen)·py·O$_2$, where X = *p*-Cl, *p*-Br, *p*-CH$_3$, *p*-CH$_3$O, and H, exhibit stability orders of Cl > Br > CH$_3$ ≳ CH$_3$O ≫ H, ($\Delta(\Delta H^\circ) = -5.2 \pm 1.0$ kcal/mol, and Cl ≃ Br > CH$_3$O ≃ CH$_3$ ≃ H, $\Delta(\Delta H^\circ) = -1.1 \pm 1.0$ kcal/mol, respectively. The trends observed for ring substituents and magnitude of $\Delta(\Delta H^\circ)$ in the thio imine system are explained in terms of resonance contributions through π bonds.

Introduction

Over the past several years, it has been demonstrated that a number of metal ions in controlled ligand environments will combine reversibly with dioxygen.[2-6] Monomeric oxygen adducts, mainly of the first row transition metals in which the combination ratio of metal ion to dioxygen is 1:1, are of the greatest biological interest.[7] Complexes with Cr,[8] Mn,[9] Fe,[10-13] Co,[2,14] Zn,[15] and most recently Ru[16] have been investigated as prototypes for hemoglobin and myoglobin; however, the greatest proclivity for reversibly oxygen binding rests with synthetic oxygen carriers containing Co(II) and Fe(II) ions. The most extensively studied of the Co(II) oxygen carriers are square-planar complexes with N$_4$ and N$_2$O$_2$ ligands. Typical examples include the cobaltoporphyrins,[17-22] Co(II) complexes with synthetic tetraaza macrocyclic ligands,[23] and salicylaldiminato-[24-28] and (keto iminato)cobalt(II) complexes.[29-33] All of the aforementioned complexes form 1:1 adducts with dioxygen in nonaqueous donor solvents or in nonaqueous solutions containing added Lewis base.

The obvious advantage in working with carefully designed model systems is that the complexity of the active molecule can be held within reasonable limits and modified systematically. In this way, cause and effect relationships can be monitored by using such techniques as X-ray structure analysis, EPR and IR spectral studies, magnetic and redox studies, and thermodynamic and kinetic measurements.

Results of such studies have shown that at least four factors effect oxygen reactivity. These include (1) the type of tetradentate ligand used, (2) the particular ring substituents and donor atoms present in the tetradentate ligand, (3) the Lewis base (ancillary ligand), and (4) the solvent. In general, the most stable oxygen adducts form in polar solvents when the Co(II) ions are in electron-rich environments, i.e., bound to Lewis bases which exhibit both σ and π donating character and to tetradentate ligands which afford minimal opportunity for electron delocalization onto chelate rings. Although it may at first appear paradoxical, the stability of the oxygen adducts also parallels the ease of oxidation to Co(III).[22,23] This is easily rationalized when it is realized that a buildup of electron density on the d^7 Co(II) ion will tend to raise the energy of the d$_{z^2}$ orbital containing the odd electron and thus facilitate its transfer. The oxygenation reactions are therefore best viewed as oxidative additions.

A few years ago, we reported[34] the synthesis of Co(II) and other divalent metal complexes, Ia, containing the tetradentate,
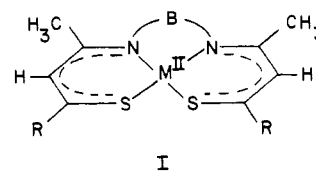
I

Ia, M(sacsacen): B = -(CH$_2$)$_2$-, R = CH$_3$
b, M(sacsacpn): B = -CH$_2$CH(CH$_3$)-, R = CH$_3$
c, M(sacsactn): B = -(CH$_2$)$_3$-, R = CH$_3$
d, M(sacsacchxn): B = -C$_6$H$_{10}$-, R = CH$_3$
e, M(bensacen): B = -(CH$_2$)$_2$-, R = C$_6$H$_5$
f, M(Xbensacen): B = -(CH$_2$)$_2$-, R = *p*-XC$_6$H$_4$ (where X = Cl, Br, CH$_3$, CH$_3$O, and H)

thio imine ligand, N,N'-ethylenebis(monothioacetylacetone imine), sacsacenH$_2$.[35] Following those initial reports, the synthetic procedures have been extended and modified to allow the preparation of a variety of thio imine ligands and complexes incorporating different substituent groups,[36-39] Ib-e. We were particularly interested in investigating the oxygen reactivity of the new Co(II) complexes since the structurally similar N,N'-ethylenebis(acetylacetone iminato)cobalt(II) species, Co(acacen), and related (keto iminato)cobalt(II) complexes were known to combine reversibly with dioxygen.[29-31]

Early studies in our laboratory[40,41] as well as by Basolo and co-workers[33] confirmed that Co(sacsacen) combined reversibly with dioxygen in toluene in the presence of pyridine according to the equilibrium depicted in Figure 1. The enthalpy of adduct formation in this case (-13.3 ± 0.5 kcal/mol,[33] -12.0 ± 0.3 kcal/mol (this work)) shows that the thio iminato complex forms a much less stable oxygen adduct than Co(acacen)·py·O$_2$ ($\Delta H^\circ = -17.3 \pm 0.5$ kcal/mol).[33]

In order to find out if sulfur donors bonded to the Co(II) ion always decreased oxygen reactivity, and if so, why this occurs, we have obtained additional thermodynamic data on the oxygenation of Co(sacsacen) as a function of solvent and different Lewis bases. We have also completed thermodynamic studies on oxygen adducts formed in the series Co(Xbensacen)·py·O$_2$ and Co(Xbenacen)·py·O$_2$, where X = *p*-Br, Cl, CH$_3$, CH$_3$O, and H. In all cases, adduct stabilities are markedly dependent on the nature of the Lewis base, solvent, and *p*-phenyl substituent.

Experimental Section

Materials. Solvents for the thermodynamic studies were purified either by refluxing over CaH$_2$ (toluene and acetonitrile, CH$_3$CN) or
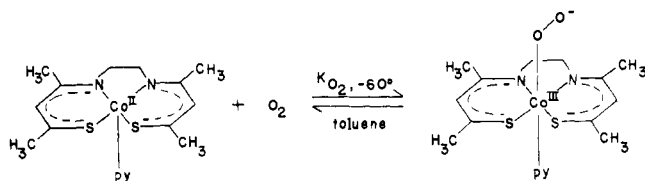
Figure 1. Oxygenation of Co(sacsacen)·py in toluene at low temperatures.

CaO (*N,N*-dimethylformamide, DMF) and then distilled and stored under dry nitrogen. Pyridine, py, and 1-methylimidazole (MeIm) were refluxed over and then distilled from KOH. All solvents and bases were degassed by the freeze-pump-thaw method immediately before use.

Syntheses. The structure and abbreviations of the Co(II) complexes prepared for this study are shown below.[42] The ligand, benacenH₂,
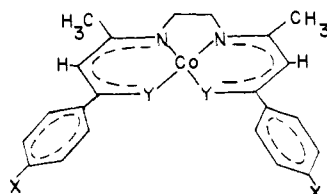
X, *p*-phenyl substituent	Y = O, keto iminato complexes	Y = S, thio iminato complexes
H	Co(benacen)	Co(bensacen)
CH₃	Co(CH₃benacen)	Co(CH₃bensacen)
CH₃O	Co(CH₃Obenacen)	Co(CH₃Obensacen)
Br	Co(Br(benacen))	Co(Br(bensacen))
Cl	Co(Cl(benacen))	Co(Cl(bensacen))

and its Co(II) complex were prepared by literature methods.[33,43] Synthesis and characterization of the remaining new ligands and complexes are reported elsewhere.[39] All Co(II) complexes used gave correct elemental analyses as formulated and exhibited μ_{eff} = 2.19–2.28 B.M. Dried solid samples could be handled in air for brief periods without noticeable oxidation.

Oxygen Uptake Measurements. Oxygenation studies were carried out in custom-made low-temperature cells, either Pyrex or quartz (Kontes-Martin, Ltd.), which were mounted in dewars so that the cell chambers (~7.5 cm long) could be completely surrounded by a slush bath of the desired temperature. Temperatures were monitored to ±1° by means of a chromel-alumel thermocouple fitted into a well which protruded into one side of the sample chamber. Potential differences were determined with a Keithley Model 160 digital multimeter. An ice-water bath served as the reference junction. Slush baths were prepared according to the method reported in Shriver.[44] The following compounds were used to attain the required temperatures (°C): chloroform, −63.5°; 3:1 carbon tetrachloride/chloroform, −57°; ethyl malonate, −51.5°; chlorobenzene, −45°; anisole, −37.4°; bromobenzene, −30.8°; and benzyl alcohol, −15.9°. Temperatures of −7 and 0 °C were achieved using a 9% salt/ice mixture and distilled water/ice bath, respectively.

In a typical measurement, ~8 × 10⁻⁴ mmol of cobalt complex was placed in the cell, the cell was degassed, and the sample was dried under vacuum overnight. The cell was refilled with dry nitrogen and 28 ml of solvent and ~6 mmol of base (0.3–0.5 ml) were added through a serum cap by means of gas-tight syringes. The resulting solution was further degassed by repeated evacuation of the cell and refilling with nitrogen. After final evacuation, the solution was chilled to the desired temperature and the spectrum was recorded. Various pressures of oxygen were added to the solution by connecting the cell to a vacuum line and adjusting the pressure using a mercury manometer. The spectrum was recorded after each oxygen addition.

Thermodynamic Measurements. Spectral changes during oxygenation were recorded on a Cary Model 14 recording spectrophotometer at three to five different temperatures and at oxygen pressures which ranged from 0 to 760 torr. Spectral changes occurred immediately upon the addition of oxygen and were constant after 10–20 min of mild stirring. The total change was reversible and the original spectrum could be restored by evacuating the system; however, some decom-

Table I. Wavelengths Used in Spectral Analysis

complex	base	solvent	wavelength, λ (nm)
Co(sacsacen)	py	toluene	380
Co(sacsacen)	DMF	toluene	380
Co(sacsacen)	MeIm	toluene	490
Co(sacsacen)	MeIm	DMF	490
Co(sacsacen)	MeIm	CH₃CN	490
Co(benacen)	py	toluene	550
Co(CH₃benacen)	py	toluene	550
Co(CH₃Obenacen)	py	toluene	550
Co(Br(benacen))	py	toluene	490
Co(Cl(benacen))	py	toluene	490
Co(Xbensacen)	py	toluene	530
X = CH₃, CH₃O, Br, Cl, H			

position occurred when the oxygenated solutions were allowed to stand at room temperature for extended periods. The wavelengths used in calculation of the thermodynamic parameters are listed in Table 1. These wavelengths were chosen because they showed the largest differences in absorbance for the oxy and deoxy species present. In those cases where complete oxygenation was not observed even at the lowest temperature (−63.5 °C), the value of A_{oxy} was obtained by extrapolating a plot of A_{obsd} vs. P_{O_2} to infinite pressure.

Data Treatment. Equilibrium constants were determined using the Hill equation:

$$K_{O_2} = \frac{[Co(L)B \cdot O_2]}{[Co(L)B]P_{O_2}{}^n} = \frac{Y}{(1-Y)P_{O_2}{}^n}$$

$$\log K_{O_2} = \log \frac{Y}{1-Y} - n \log P_{O_2}$$

The slopes of the straight lines obtained from least-squares plots of log $[Y/(1-Y)]$ vs. log P_{O_2} ranged from 0.9 to 1.1 but were constrained in all cases to $n = 1.0$ for determination of K_{O_2}. van't Hoff plots of log K_{O_2} vs. $1/T$ were used to calculate $\Delta H°$, while $\Delta G°$ and $\Delta S°$ values at 20 °C, standard state of 1 torr, were determined from the relationships $\Delta G° = -2.303RT \log K_{O_2}$ and $\Delta G° = \Delta H° - T\Delta S$.

Results

All of the complexes studied take up and release molecular oxygen reversibly in solutions containing small amounts of Lewis bases. Concentrated solutions of the five-coordinate, Co(lig)·B species, are brownish red to orange-red. Adduct formation causes a color change from red to brownish black. At the dilute concentrations used in the visible spectral study, these color changes were not discernible to the eye but were easily followed on the Cary 14 spectrophotometer.

The visible spectrum of Co(sacsacen)·MeIm during oxygenation in toluene is shown in Figure 2 and is typical of the spectral changes observed. The spectrum of nonoxygenated Co(sacsacen)·MeIm is characterized by three absorption bands at 490, 428, and 380 nm. Upon oxygenation, the bands at 428 and 490 diminish in intensity and eventually disappear while the band at 380 broadens and grows in intensity and a weak shoulder appears at 542 nm. The EPR spectrum of the oxygenated species in toluene solution exhibits an eight-line pattern which confirms the 1:1 nature of the adduct.[33,40,41]

Thermodynamic data obtained for Co(sacsacen)·B·O₂ as a function of solvent and Lewis base are presented in Table II. The stability of Co(sacsacen)·B·O₂ in toluene, as reflected in more negative enthalpy values, increases in the order py < DMF < MeIm. When the Lewis base is held constant and the solvent is changed, the stability of the oxygen adduct increases in the order toluene < DMF < CH₃CN. The most stable of the systems studied is Co(sacsacen)·MeIm·O₂ in CH₃CN.

Modifying the substituents on the chelate rings of the Schiff base ligands also affects the stability as is evident from the

Table II. Thermodynamic Data for the Reaction Co(sacsacen)·B + O$_2$ $\overset{K_{O_2}}{\rightleftharpoons}$ Co(sacsacen)·B·O$_2$ for Different Lewis Bases and Solvents[a]

solvent	Lewis base	temp, °C	log K_{O_2}, mm^{-1}	$\Delta H°$,[b] kcal/mol	$\Delta S°$,[b] eu
toluene	py	−63.5	−0.93 ± 0.02		
		.−51.5	−1.60 ± 0.03	−12.0 ± 0.3[c]	−61.5 ± 1.2
		−45	−1.95 ± 0.03		
toluene	DMF	−63.5	−0.90 ± 0.02		
		−57	−1.31 ± 0.03	−14.1 ± 0.4	−71.3 ± 1.4
		−51.5	−1.73 ± 0.03		
		−45	−2.08 ± 0.02		
toluene	MeIm	−51.5	−1.19 ± 0.03		
		−45	−1.60 + 0.02	−15.4 ± 0.6	−75.0 ± 2.3
		−45	−1.57 ± 0.03		
		−37.4	−2.10 ± 0.03		
DMF	MeIm	−51.5	−0.72 ± 0.05[d]		
		−45.0	−1.12 ± 0.02	−16.1 ± 0.6	−75.6 ± 2.1
		−37.4	−1.60 ± 0.02		
		−30.8	−2.00 ± 0.02		
CH$_3$CN	MeIm	−30.8	−1.00 ± 0.02		
		−23.0	−1.44 ± 0.05	−18.5 ± 1.7	−80.9 ± 6.0
		−23.0	−1.65 ± 0.06		
		−15.9	−1.97 ± 0.02		

[a] In 1.8% base/solvent solution. Standard state of 1 torr. [b] At 20 °C. [c] Reference 33 lists $\Delta H° = -13.3 \pm 0.5$, $\Delta S° = -64.5 \pm 2.3$. [d] Omitted from van't Hoff plot.
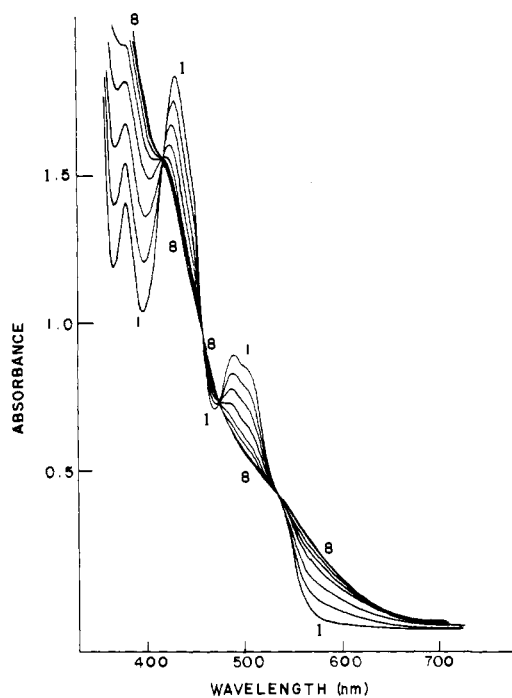
Figure 2. Visible spectra of Co(sacsacen)·MeIm·O$_2$ in toluene at −45 °C at various stages of oxygenation: (1) no oxygen; (2) 8 torr O$_2$; (3) 24 torr O$_2$; (4) 58 torr O$_2$; (5) 131 torr O$_2$; (6) 290 torr O$_2$; (7) 633 torr O$_2$; (8) 760 torr O$_2$.

Figure 3. van't Hoff plots for the binding of O$_2$ to Co(Xbenacen) in 1.8% pyridine–toluene solution: (a) X = Cl, (b) X = Br, (c) X = CH$_3$, (d) X = CH$_3$O, (e) X = H.

thermodynamic data reported in Table III for the Co(X-benacen)·py·O$_2$ and Co(Xbensacen)·py·O$_2$ complexes, where X = H, *p*-Me, *p*-MeO, *p*-Cl, and *p*-Br. The van't Hoff plots obtained in these calculations are shown in Figures 3 and 4. In the (thio iminato)cobalt(II) systems, oxygen adduct stability increases substantially with the addition of substituents in the para position on the phenyl ring. This effect is illustrated dramatically by the difference in steepness of the slopes of the lines in Figure 4. The relative order of adduct stability is H ≪ CH$_3$O ≲ CH$_3$ < Br < Cl. Substituent effects appear to be less important for the corresponding keto iminato complexes and the order is H ≃ CH$_3$ ≃ CH$_3$O < Br ≃ Cl. The overall change in $\Delta H°$ for adducts in the Co(Xbensacen)·py·O$_2$ series is −5.2 kcal/mol, whereas in the Co(Xbenacen)·py·O$_2$ systems

it is only −1.1 kcal/mol, a value which almost falls within the rather large, ±1.0 kcal/mol error limits of the measurements.

Discussion

Until this report, only one Co(II) complex with an N$_2$S$_2$ ligand, namely Co(sacsacen)·py in toluene, was known to bind molecular oxygen in a reversible manner.[33,40,41] The fact that five new (thio iminato)cobalt(II) complexes also exhibit this property indicates that such complexes must be considered as a new class of synthetic oxygen carrier. It is likely that other N$_2$S$_2$ ligands may also activate metal ions toward oxygenation. The stability of oxygen adducts formed from thio iminato complexes is, in general, less than those from their keto iminato counterparts; however, this fact should be useful in identification of the chemical and electronic factors which effect oxygen reactivity of metal ions in both controlled and natural ligand environments.

Table III. Thermodynamic Data for Reversible O_2 Binding to Co(L)·py[a] Complexes in Toluene Solution

compound	temp, °C	log K_{O_2}, mm^{-1}	$\Delta H°$,[b] kcal/mol	$\Delta S°$,[b] eu
Co(benacen)·py	−23	−1.05 ± 0.02		
	−15.9	−1.45 ± 0.03	−16.2 ± 0.3	−69.6 ± 1.2
	−7	−1.90 ± 0.02		
	0	−2.25 ± 0.02		
Co(CH₃Obenacen)·py	−23	−1.01 ± 0.03		
	−15.9	−1.39 ± 0.02	−16.5 ± 0.4	−70.6 ± 1.4
	−7	−1.88 ± 0.01		
	0	−2.22 ± 0.04		
Co(CH₃benacen)·py	−23	−1.01 ± 0.04		
	−15.9	−1.37 ± 0.07	−16.3 ± 0.8	−69.8 ± 2.8
	−7	−1.87 ± 0.07		
	0	−2.20 ± 0.02		
Co(Br(benacen))·py	−23	−0.87 ± 0.02		
	−15.9	−1.25 ± 0.02	−17.1 ± 0.4	−72.4 ± 1.6
	−7	−1.77 ± 0.05		
	0	−2.12 ± 0.01		
Co(Cl(benacen))·py	−23	−0.73 ± 0.04		
	−23	−0.82 ± 0.02		
	−15.9	−1.22 ± 0.02	−17.3 ± 0.7	−72.8 ± 2.6
	−15.9	−1.16 ± 0.04		
	−7	−1.69 ± 0.05		
	0	−2.05 ± 0.02		
Co(bensacen)·py	−63.5	−1.78 ± 0.02		
	−51.5	−2.22 ± 0.02	−8.05 ± 0.30	−46.5 ± 1.2
	−45	−2.47 ± 0.03		
Co(CH₃Obensacen)·py	−63.5	−1.34 ± 0.02		
	−51.5	−2.08 ± 0.04	−10.8 ± 0.6	−57.6 ± 2.3
	−45	−2.22 ± 0.03		
	−37.4	−2.62 ± 0.02		
Co(CH₃bensacen)·py	−63.5	−0.97 ± 0.02		
	−51.5	−1.62 ± 0.04	−11.2 ± 0.3	−57.8 ± 1.0
	−45	−1.93 ± 0.02		
	−37.4	−2.26 ± 0.02		
Co(Br(bensacen))·py	−63.5	−0.76 ± 0.02		
	−51.5	−1.46 ± 0.02	−12.1 ± 0.4	−61.1 ± 1.3
	−45	−1.74 ± 0.03		
	−37.4	−2.18 ± 0.03		
Co(Cl(bensacen))·py	−63.5	−0.62 ± 0.02		
	−51.5	−1.35 ± 0.02	−13.3 ± 0.4	−66.3 ± 1.6
	−45	−1.68 ± 0.04		
	−37.4	−2.19 ± 0.03		

[a] In 1.8% pyridine–toluene solution. Standard state of 1 torr. [b] At 20 °.

In studying the (thio iminato)cobalt(II) complexes, it was deemed important to show at the outset that no unusual solvent or Lewis base interactions were involved in the oxygenation process. Thus, oxygenation of Co(sacsacen) was studied in two additional solvents (DMF and CH₃CN) and with two additional Lewis bases (DMF and MeIm).[45] When the data listed in Table II are compared with those of similar Schiff base and porphyrin complexes, reported in Table IV, it appears that solvent and Lewis base effects are essentially the same in all. For example, enthalpies of formation calculated for Co(sacsacen)·B·O₂ increase by ~28% as B is changed from py to MeIm. A similar percentage increase is observed in the Co(PpIXDME)·B·O₂ series, while the change reported for Co(benacen)·B·O₂ is in the same direction but only 8%. In all cases, the increase in stability imparted by MeIm is attributed to its combined σ and π donating properties which increase the electron density on the metal ion.

The effect of solvent in stabilizing oxygen adducts of the (thio iminato)cobalt(II) complexes is illustrated by the 20% increase in magnitude of the negative enthalpy of formation of Co(sacsacen)·MeIm·O₂ as the solvent is changed from toluene to acetonitrile. Similar increases in stability observed for Co(PpIXDME)·B·O₂ adducts have been attributed to an increase in solvent dielectric constant which favors formation of the polar, superoxo-type adducts, CoL·B·O₂⁻.[46] Evidence

for the existence of Co(III)-O₂⁻ species has been provided by numerous EPR studies,[14,17,31,46] and our data are in agreement with this interpretation.

It is interesting to note that the most stable oxygen adduct in the sacsacen series is Co(sacsacen)·MeIm·O₂ in CH₃CN ($\Delta H° = -18.5 \pm 1.7$ kcal/mol). This is slightly more stable than Co(acacen)·py·O₂ in toluene ($\Delta H° = -17.3 \pm 0.5$ kcal/mol)[33] but it obviously takes a combination of more polar solvent and stronger Lewis base to overcome the destabilizing influence of the in-plane sulfur atoms. The rather general destabilizing effect of the tetradentate, thio imine ligand environment is shown in the results of thermodynamic measurements on oxygen adducts in the structurally related Co(X-bensacen) and Co(Xbenacen) series of complexes.

The most stable Co(Xbensacen)·py·O₂ species is some 20% less stable than the least stable of the Co(Xbenacen)·py·O₂ adducts, and the overall range in stability reflects a difference of 53%. The most surprising aspect of this study is the trend in stability observed as a function of the *p*-phenyl substituent. For Co(Xbenacen)·py·O₂, $\Delta(\Delta H°) = -1.1 \pm 1.0$ kcal/mol with Cl ≃ Br > CH₃O ≃ CH₃ ≃ H; and for Co(Xbensacen)·py·O₂, $\Delta(\Delta H°) = -5.2 \pm 1.0$ kcal/mol with Cl > Br > CH₃ ≳ CH₃O ≫ H. Clearly, ring substituent effects are much larger and more important in the thio imine systems. Furthermore, the trends observed cannot be explained simply on
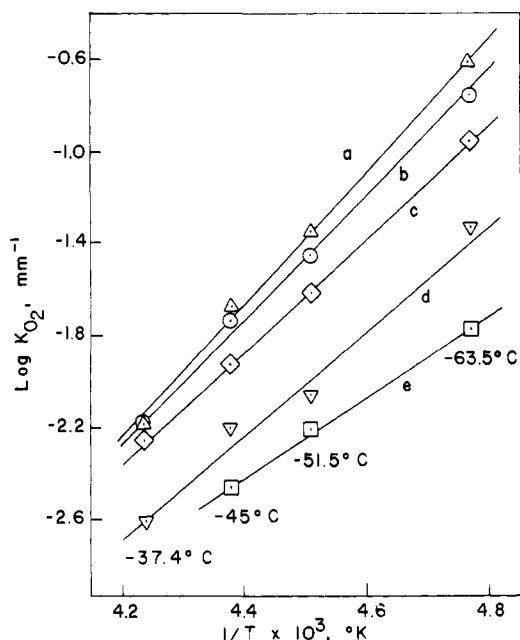
Figure 4. van't Hoff plots for the binding of O_2 to Co(Xbensacen) in 1.8% pyridine-toluene solution: (a) X = Cl, (b) X = Br, (c) X = CH_3, (d) X = CH_3O, (e) X = H.
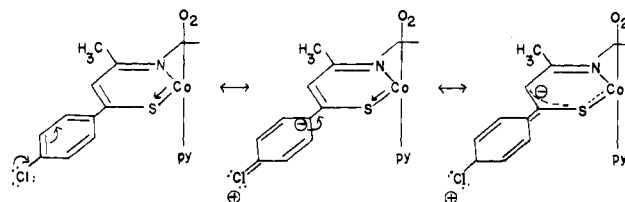

Figure 5. Proposed electronic contribution to cobalt ion via resonance interaction.

Table IV. Thermodynamic Data for Reversible Oxygen Binding by Various Cobalt(II) Complexes in Toluene Solutions

compound	$\Delta H°$,[a] kcal/mol	$\Delta S°$,[a] eu	ref
Co(acacen)·py	-17.3 ± 0.5	-72.7 ± 1.7	33
Co(benacen)·py	-16.6 ± 0.8	-75.1 ± 2.6	33
Co(benacen)·MeIm	-17.5 ± 0.3	-73.5 ± 2.0	33
Co(PpIXDME)·py	-9.2 ± 0.6	-53 ± 2	19
Co(PpIXDME)·DMF[b]	-11.0 ± 0.6	-59 ± 2	19
Co(PpIXDME)·MeIm[b]	-11.8 ± 0.6	-59 ± 2	19

[a] Standard state of 1 torr, 20 °C. All measurements were made in 10^{-2} M base-toluene solutions. [b] Oxygenation of these two complexes in DMF has also been studied.[46] Half-oxygenation pressures for Co(PpIXDME)·MeIm in toluene vs. DMF are 417 vs. 12.6 torr which corresponds to a change in ΔG of 1.7 kcal/mol at -23 °C, favoring oxygenation in DMF. The half-oxygenation pressure for Co(P-pIXDME)·DMF in DMF is 40 torr.

the basis of inductive effects and Hammett–Taft parameters.[47]

We had anticipated that *p*-methyl and *p*-methoxy substitution would increase the stability due to electron donation through the σ framework while *p*-bromo and *p*-chloro substitution might reduce the stability as a result of electron withdrawal. Instead, all substituents enhance stability with the greatest contribution being made by the Cl and Br species. These data can be explained, at least in part, by the dominance of π effects (resonance interactions) over σ effects (inductive contributions). Differences in solvation may also play a part.

The fact that all of the thio imine systems are less stable than their keto imine counterparts suggests that the sulfur atoms are poorer σ donors than the keto oxygen atoms. This is perhaps not unexpected since the charge density on sulfur will be less owing to its larger size, and since the σ electron pairs of sulfur are less directed in space than those of oxygen. In addition to the σ interactions, we propose that the sulfur donors can drain electron density from the cobalt ion via a π-backbonding interaction between filled d_{xz} and d_{yz} orbitals on the metal and empty d orbitals on the sulfurs. This type of metal–ligand bonding would provide a mechanism for the transmittal of resonance effects from the *p*-phenyl substituents to the active metal site. This type of electronic contribution is illustrated in Figure 5. π-Donation by the para substituent should increase the electron density in the chelate ring and reduce the π-backbonding between Co and sulfur, thereby increasing the electron density on the cobalt ion. Dipole moment studies on Ni(*p*-Br(benacpn)), Cu(*p*-Br(benacpn)), and M(tfacpn) systems support this type of interaction.[48] We would expect that the methoxy substituent should also be able to participate in this type of resonance as well as serve as an electron donor through the σ framework; therefore, we cannot explain the unusually low stability of Co(CH_3Obensacen)·py·O_2.

To our knowledge, no other thermodynamic studies of *p*-phenyl substituted Schiff base oxygen carriers have been performed, although Walker[22] has studied the oxygenation of para X-substituted tetraphenylporphyrin complexes of Co(II) in toluene. In the examples reported, where X = CH_3O, CH_3, H, F, Cl, CN, and NO_2, equilibrium constants paralleled the

Hammett σ parameters, with Co(*p*-CH_3OTPP)·py·O_2 being the most stable adduct. In these complexes, only σ effects should be important since the phenyl rings are not coplanar with the porphyrin ring owing to steric interactions. In contrast to this, the X-ray structure of Co(benacen)·py·O_2 shows that the phenyl rings are essentially coplanar with the Co–N_2O_2 plane.[32] Thus, resonance contributions via extensive π interactions are more probable for the Co(Xbensacen)·B·O_2 systems. This hypothesis gains support from the fact that the enthalpies of formation for the Co(Xbensacen)·py·O_2 adducts lie in the same range as those reported for porphinatocobalt(II) complexes where extensive π-bonding is known to be present.[46]

We are continuing our investigations into the (thio iminato)cobalt(II) systems to further define the role of sulfur and its effect on oxygen reactivity. EPR studies on pyridine and oxygen adducts of the Co(Xbensacen) and Co(Xbenacen) complexes have been completed[49] and the *g* values and coupling constants appear to support increased covalency and π-backbonding in the sulfur complexes. These studies will be reported in a forthcoming paper.[50] We are also engaged in the preparation of a series of *m*-phenyl substituted Co(Xbenacen) and Co(Xbensacen) derivatives. Trends in the oxygen adduct stability of the latter complexes should either confirm or refute the π-resonance hypothesis since π-resonance contributions should be minimized in the new systems while solvation effects should remain unchanged.

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Mixed Valence Interactions in Di-μ-oxo Bridged Manganese Complexes. Electron Paramagnetic Resonance and Magnetic Susceptibility Studies

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Abstract: EPR examination of the class II (deeply trapped) mixed valence complexes $[(bpy)_2MnO_2Mn(bpy)_2]^{3+}$ (the bipyridyl(III,IV) dimer) and its phenanthroline analogue in acetonitrile solution verifies that these complexes possess inequivalent Mn ions at room temperature. Isotropic hyperfine structure for two Mn ions is resolved with $A_1 = 167 \pm 3$ G and $A_2 = 79 \pm 3$ G for both complexes. The hyperfine pattern with $|A_1| \simeq 2|A_2|$ and the small g anisotropy are consistent with high-spin Mn(III) antiferromagnetically coupled to Mn(IV), producing an $S = \frac{1}{2}$ ground state. At room temperature a rate of less than 10^8 s^{-1} is estimated for the thermally activated intramolecular electron transfer, consistent with an upper limit of 10^6 s^{-1} calculated from Hush's theory. The magnetic susceptibility of the (III,IV) complexes is characteristic of a strongly antiferromagnetically coupled $S = (2, \frac{3}{2})$ pair. The temperature dependence of the data was in good agreement with the isotropic Heisenberg exchange Hamiltonian $H = -2JS_1S_2$, yielding $J = -150 \pm 7$ cm^{-1} for the bipyridyl(III,IV) dimer and $J = -134 \pm 5$ cm^{-1} for the phenanthroline analogue.

Introduction

Since the 1964 reviews of Hush,[1] Allen and Hush,[2] and Robin and Day,[3] mixed valence compounds have received considerable attention, prompted in some part by interest in synthesis of new conducting materials and the occurrence of

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mixed valence complexes in biology, notably the ferredoxins. One of the most interesting properties of a mixed valence compound is the extent of electron delocalization, expressed as an electron delocalization rate. The classification scheme of Robin and Day[3] divides mixed valence compounds into three groups—those exhibiting no delocalization (class I), those with complete electron delocalization (class III, the molecular ion case), and those with intermediate delocalization (class II).