J. Am. Chem. Soc. 1980, 102, 6014-6019

is that $Li(t\text{-}BuO)_2AlH_2$, $Li(t\text{-}BuO)_3AlH$, and $LiAlH_4$ are in slow equilibrium according to eq 2. Confirmation of this suggestion was sought by approaching the equilibrium from the opposite direction. If this equilibrium is present, one should be able to start with a solution of $Li(t\text{-}BuO)_3AlH$ and add $LiAlH_4$ to reestablish the equilibrium. Spectrum G in Figures 2–4 was obtained in just such a manner. To a solution of $Li(t\text{-}BuO)_3AlH$ (spectrum E in Figures 2, 4, and 5) was added a solution of $LiAlH_4$ so that the new molar ratio was 1.7. Note that in the ^{27}Al spectrum (Figure 2) the broad singlet −21.9 ppm from $LiAlH_4$ is gone and that in the ^{13}C spectrum (Figure 4) the singlet for $Li(t\text{-}BuO)_3AlH$ is nearly gone while the singlet for $Li(t\text{-}BuO)_2AlH_2$ has reappeared.

From the ratio of the integrated areas of the methyl singlets in the ^{13}C spectrum one can obtain the ratio R_C:

$$2[Li(t\text{-}BuO)_3AlH]/3[Li(t\text{-}BuO)_2AlH_2] = R_C \qquad (3)$$

The ^{27}Al spectra of solutions containing *tert*-butyl alcohol/$LiAlH_4$ molar ratios between 0.5 and 2.0 consist of a broad singlet due to $Li(t\text{-}BuO)_2AlH_2$ and $Li(t\text{-}BuO)_3AlH$ with a quintet from $LiAlH_4$ imposed upon it. Using the instruments computer, one may subtract the $LiAlH_4$ quintet from the spectra to obtain just the broad singlet whose area is proportional to the concentration of $Li(t\text{-}BuO)_2AlH_2$ plus $Li(t\text{-}BuO)_3AlH$; the resulting broad singlets are shown in Figure 3. In this way one may determine the ratio R_{Al}:

$$\frac{[LiAlH_4]}{[Li(t\text{-}BuO)_2AlH_2] + [Li(t\text{-}BuO)_3AlH]} = R_{Al} \qquad (4)$$

Together, these ratios allow the calculation of the equilibrium constant

$$K_{eq} = \frac{[Li(t\text{-}BuO)_3AlH]^2[LiAlH_4]}{[Li(t\text{-}BuO)_2AlH_2]^3} \qquad (5)$$

Combining eq 3–5 one can obtain

$$K_{eq} = (3/2R_C)^2 R_{Al}(3/2R_C + 1) \qquad (6)$$

The data in Table I indicate an equilibrium constant of 2.2×10^{-2}.

Conclusions

We find that for molar ratios for *tert*-butyl alcohol/$LiAlH_4$ up to 2 the major *tert*-butoxyaluminate in solution is $Li(t\text{-}BuO)_2AlH_2$ and that it is in a slow equilibrium with $LiAlH_4$ and $Li(t\text{-}BuO)_3AlH$. If $Li(t\text{-}BuO)AlH_3$ is present, its concentration must be low compared to the $Li(t\text{-}BuO)_2AlH_2$ concentration. Clearly the *tert*-butoxyaluminate system is not as simple a system as some have thought it to be.

Acknowledgments. The support of the Department of Chemistry at The University of Toledo is gratefully acknowledged. We thank Professors J. Fry and J. Gano for helpful discussion.

Hydrogen-Bonding Interactions Involving Metal-Bound Dioxygen

Russell S. Drago,* J. Patrick Cannady, and Kenneth A. Leslie

Contribution from the School of Chemical Sciences,
University of Illinois, Urbana, Illinois 61801. *Received May 21, 1980*

Abstract: In this article the equilibrium constant and enthalpy for formation of the dioxygen adduct of the bis(salicylideniminato-3-propyl)methylaminocobalt(II) complex (CoSMDPT) are reported in methylene chloride solution (−9.8 kcal mol^{-1}). When small amounts of 2,2,2-trifluoroethanol (TFE) are added, extra stabilization of the dioxygen adduct is found. The measured enthalpy for adduct formation increases to −11.8 kcal mol^{-1}. Infrared frequency shift studies of the O–H stretching vibration indicate that TFE undergoes a hydrogen-bonding interaction with the coordinated dioxygen. An enthalpy-frequency shift, $\Delta\nu$OH, relation provides an estimate of a 6.6 kcal mol^{-1} hydrogen bond strength. This is one of the few instances in which a clear-cut reaction of the coordinated dioxygen is shown. This interaction suggests an explanation for the high oxygen affinities of such systems as cobalt myoglobin and CoTpivPP·MeIm compared to cobalt(II) protoporphyrin IX dimethyl ester.

Introduction

The reversible binding of dioxygen in biological systems and interest in the activation of dioxygen by metal ions in biological as well as commercial processes have led to extensive activity in the area of metal–dioxygen systems.[1-5] Results from this laboratory[2-4] have led to the formulation of the spin-pairing model for dioxygen binding. The metal–dioxygen bonding interaction is viewed as resulting from a pairing up of the spins (bonding) of metal electrons with unpaired electrons in the π^* orbital of dioxygen. An EPR analysis indicates that partial negative charges on the bound O_2 of some cobalt complexes vary from 0.1 to 0.8 depending upon the ligands bound to the metal.[3]

Several important questions remain to be answered in the areas of dioxygen binding and activation. The question of dioxygen activation is very intimately connected with the reactivity and nucleophilicity of bound O_2. However, very little chemistry involving metal-bound dioxygen has been reported. The 1:1 dioxygen adduct (referred to as a superoxo complex) can react with a second cobalt(II) complex forming a 2:1 adduct (referred to as a μ-peroxo complex).[1b] The cobalt(II)-catalyzed oxidation of phenol has been proposed to involve a mechanism in which phenol hydrogen bonds to the coordinated dioxygen in the course of undergoing a hydrogen-atom abstraction to produce the phenoxy radical.[6] A better appreciation for the factors influencing the reactivity of bound O_2 is essential to the understanding of the catalytic activation of this molecule.

A widely held view of the nature of the bound dioxygen consideres it to be a superoxide ion that is bound ionically to the cobalt.[1a,c] The superoxide ion has been shown to be a potent nucleophile.[7] Quantitative information about the basicity or

---

(1) For a review of early work see (a) F. Basolo, B. M. Hoffman, and J. A. Ibers, *Acc. Chem. Res.*, **8**, 384 (1975), and references cited therein; (b) L. Vaska, *ibid.*, **9**, 175 (1976); (c) J. P. Collman *ibid.*, **10**, 265 (1977); (d) G. McLendon and A. E. Martell, *Coord. Chem. Rev.*, **19**, 1 (1976).

(2) R. S. Drago, T. Beugelsdijk, J. A. Breese, and J. P. Cannady, *J. Am. Chem. Soc.*, **100**, 5374 (1978).

(3) B. S. Tovrog, D. J. Kitko, and R. S. Drago, *J. Am. Chem. Soc.*, **98**, 5144 (1976).

(4) R. S. Drago, *Inorg. Chem.*, **18**, 1408 (1979).

(5) For a theoretical analysis see B. H. Huynh, D. A. Case, and M. Karplus, *J. Am. Chem. Soc.*, **99**, 6103 (1977), and references cited therein.

(6) A. Nishinago, H. Tomita, T. Shimizu, and T. Matsuura in "Fundamental Research in Homogeneous Catalysis", Vol. 2, Y. Ishii and M. Tsutsui, Eds., Plenum Press, New York, 1978, and references cited therein.

0002-7863/80/1502-6014$01.00/0

nucleophilicity of the cobalt-bound dioxygen is important to distinguish this alternative view from the spin-pairing description.

The enthalpies of binding O_2 to cobalt(II) in cobalt myoglobin and in the cobalt(II) picket fence porphyrin Co(TpivPP)(N-MeIm) (in toluene and the solid state) are 2–3 kcal mol^{-1} larger than the enthalpy of binding O_2 to cobalt(II) protoporphyrin IX dimethyl ester in toluene. The differences have been attributed[8] to solvation of the flat porphyrins by toluene in their deoxy form and an absence of this effect in CoMb and CoTpivPP(N-MeIm). The higher affinity of cobalt for O_2 in the solid-state complex of imidazole–polystyrene bound CoTPP was offered as support for the toluene solvation model.[8] Recently[9] we have commented upon the fact that these data are not directly comparable to solution data. Stabilization by a hydrogen-bonding interaction of the bound O_2 with a nearby proton donor in CoMb and in CoTpivPPP(N-MeIm) was also considered as an explanation but considered less likely.[8]

All of the above considerations provide strong motivation to investigate the potential for hydrogen bonding to the metal-bound dioxygen. Such an experiment with a typical four-coordinate cobalt(II) complex is hampered by the influence that hydrogen bonding to the axial base can have on the two-step equilibria for dioxygen binding:

$$CoL_4 + B \rightleftharpoons CoL_4B$$

$$CoL_4B + O_2 \rightleftharpoons CoL_4B{\cdot}O_2$$

The Co(II) complexes of linear pentadentate Schiff base ligands, which are also capable of binding dioxygen reversibly, do not require an additional donor molecule for dioxygen binding and as a result are ideal for studies of hydrogen bonding to metal-bound dioxygen. These adducts have been thoroughly investigated in solution by EPR and NMR techniques.[3,10,11] Severable isolable dioxygen complexes have been reported[11] of the type $[Co(x\text{-}SDPT)]_2{\cdot}O_2{\cdot}S$ and $[CoSMDPT]_2O_2{\cdot}2C_6H_6$, where SDPT = bis(salicylideniminato-3-propyl)amine, x denotes substitution of the salicylaldehyde ring, S = solvent such as acetone, benzene, tetrahydrofuran, or acetonitrile, and SMDPT = bis(salicylidenimiato-3-propyl)methylamine. Complexes with isopropyl and phenyl substituents on nitrogen instead of methyl were markedly unreactive toward dioxygen. Based on these observations and on the X-ray crystallographic determination of the structure of $(CoSDPT)_2{\cdot}O_2{\cdot}C_6H_5CH_3$,[12] a structure for the monomeric dioxygen adduct of CoSMDPT was proposed in which the dioxygen ligand is trans to one of the phenolic oxygen atoms and cis to the amine nitrogen.[11] As yet, no definitive structural report of an isolated, simple 1:1 CoSMDPT·O_2 adduct has yet appeared. Furthermore, thermodynamic data for dioxygen binding to these complexes have not been reported.

The purpose of this study is thus to attempt to quantitatively determine (1) the oxygen affinity of a linear pentadentate Co(II) Schiff's base complex as a function of the presence of hydrogen-bonding interactions provided by solvent, added Lewis acid, or both, (2) the strength of the hydrogen-bonding interaction, and (3) the extent to which this interaction contributes to the overall stability of the cobalt–dioxygen complex.

Experimnetal Section

Synthesis of CoSMDPT. CoSMDPT was prepared by an adaptation of a reported procedure:[13] 5.0 g of *N*-methyl-*N*,*N*-bis(3-aminopropyl)amine (MDPT, Columbia Organic Chemicals) was dissolved in 30 mL of EtOH which had been deoxygenated by an Ar purge, and the solution transferred to a dropping funnel. All operations were carried out under a blanket of Ar. To this solution was added 8.3 g of salicylaldehyde. This yellow solution was added dropwise to a solution of 8.6 g $Co(CH_3CO_2)_2{\cdot}4H_2O$ in 30 mL of deoxygenated (Ar purge) EtOH. The resulting brown reaction mixture was refluxed for 2 h with stirring. The mixture was allowed to cool to room temperature, and the crystalline, brown product filtered (Schlenk tube), washed three times with anhydrous Et_2O, and dried in vacuo.

Anal. Calcd for $CoC_{21}H_{25}N_3O_2$ (mol wt 410.4): C, 61.45; N, 10.24; H, 6.09; Co, 14.39. Found: C, 60.88; N, 10.27; H, 5.95; Co, 14.64.

Materials and Sample Preparation. Salicyladehyde and 2,2,2-trifluoroethanol (Gold Label) were purchased from Aldrich and used as received. MPDT was purchased from Columbia Organic Chemicals Co., Inc., and used as supplied. All other materials were usual reagent grade materials.

Toluene for use in the spectroscopic work (visible, EPR, and NMR) was distilled from CaH_2 under Ar. C_6D_6 (≥99.5% isotope purity) was purchased from Merck Sharp and Dohme Canada Ltd. and degassed by three freeze–pump–thaw cycles prior to being used in the NMR experiments. Methylene chloride was dried by refluxing over CaH_2, distilled under an argon atmosphere, and degassed prior to use by the freeze–pump–thaw technique. Carbon disulfide (Baker "Analyzed") was dried over 3 Å molcecular sieves and degassed by freeze–pump–thawing for use in the high-pressure infrared experiments.

Spectroscopic Apparatus and Procedure. Cobalt containing EPR and NMR solutions were prepared volumetrically in a nitrogen-filled inert atmosphere drybox and the sample tubes stoppered and sealed with parafilm. No evidence of oxygen contamination was seen (that is, no cobalt(II) dioxygen adducts formed) in EPR spectra run on these samples.

EPR spectra were obtained on a Varian E-9 X-band spectrometer with temperature variation provided by heating a stream of cold nitrogen gas. ^1H NMR spectra were recorded at 60 MHz on a Varian T-60 spectrometer and at 90 MHz on a Varian EM-390 spectrometer. ^{19}F spectra were obtained on a Varian EM-390 spectrometer equipped with an ^{19}F and Joule-Thompson temperature control system.

Electronic spectra were obtained on a Cary 14-A scanning spectrophotometer with Infrasil optics. Low temperatures were obtained with a circulating methanol bath cooled by dry ice. Equilibrium constants for oxygen binding were obtained by using a specially designed and constructed high-pressure stainless steel cell described elsewhere.[2]

Infrared spectra were recorded on a Perkin-Elmer 457 spectrometer, a Beckman IR-12 spectrometer, and a Perkin-Elmer 283 spectrometer. Samples were run as solutions in NaCl cavity cells or as Nujol mulls between KBr plates.

High-pressure infrared spectra were obtained on a Perkin-Elmer 283 spectrometer. The high-pressure reactor and infrared cell have been described in the literature.[14]

The CoSMDPT solutions were prepared and transferred into the stainless steel reactor vessel in the inert atmosphere box. The infrared cell was loaded from this system. Windows for the cell were made of KRS-5 (Harshaw Chemical Co). Pressures up to 1200 psi of oxygen or argon were added to the cooled reactor vessel and the solution was allowed to equilibrate. No pressure leaks were observed in the cell as long as the total pressure in the systm was greater than 200 psi.

Calculation of Dioxygen Binding Constants. Equilibrium constants for the formation of the one-to-one CoSMDPT·O_2 complex were obtained by evaluation of the changes of the electronic absorption spectrum of the solutions of CoSMDPT in the wavelength region 300–550 nm as a function of oxygen pressure over the solutions. The difference between the molar absorbance of CoSMDPT·O_2 and the molar absorbance of CoSMDPT, $(\epsilon_{CoO_2} - \epsilon_{Co})$, and the equilibrium constant for binding dioxygen, k_{O_2}, were fit by an iterative least-squares fitting procedure, which uses as the convergence criterion the minimization of the sum of the squared errors of the calculated and observed absorbance changes at any wavelength.

Since the data do not permit an accurate evaluation of the consecutive equilibria involved in the O_2 binding studies in solutions containing TFE, this was formulated as a 1:1 equilibrium. A reported infrared frequency shift relation is employed to produce the enthalpy for the second step.

Results and Discussion

Thermodynamics of Dioxygen Binding to CoSMDPT. 1. Toluene as Solvent. On exposure to increasing pressures of O_2, toluene solutions of CoSMDPT exhibit changes in the visible spectrum characteristic of the coordination of dioxygen. In addition, intense spectral changes due to a charge-transfer interaction

---

(7) J. San Fillippo, Jr., C-I. Chern, and J. S. Valentine, *J. Org. Chem.*, **40**, 1678 (1975).

(8) J. P. Collman et al., *J. Am. Chem. Soc.*, **100**, 2761 (1978).

(9) R. S. Drago and J. Gaul, *Inorg. Chem.* **18**, 2010 (1979).

(10) R. H. Niswander and L. T. Taylor, *Inorg. Nucl. Chem. Lett.* **12**, 399 (1976); R. H. Niswander and L. T. Taylor, *J. Magn. Reson.*, **26**, 491 (1977).

(11) R. H. Niswander and L. T. Taylor, *J. Am Chem. Soc.*, **99**, 5935 (1977).

(12) L. A. Lindblom, W. P. Schaefer, and R. E. Marsh, *Acta Crystallogr., Sect. B*, **27**, 1461 (1971).

(13) L. Sacconi and I. Bertini, *J. Am. Chem. Soc.*, **88**, 5180 (1966).

(14) T. A. Ballinitine and C. D. Schmulbach, *J. Organomet. Chem.*, **164**, 381 (1978).

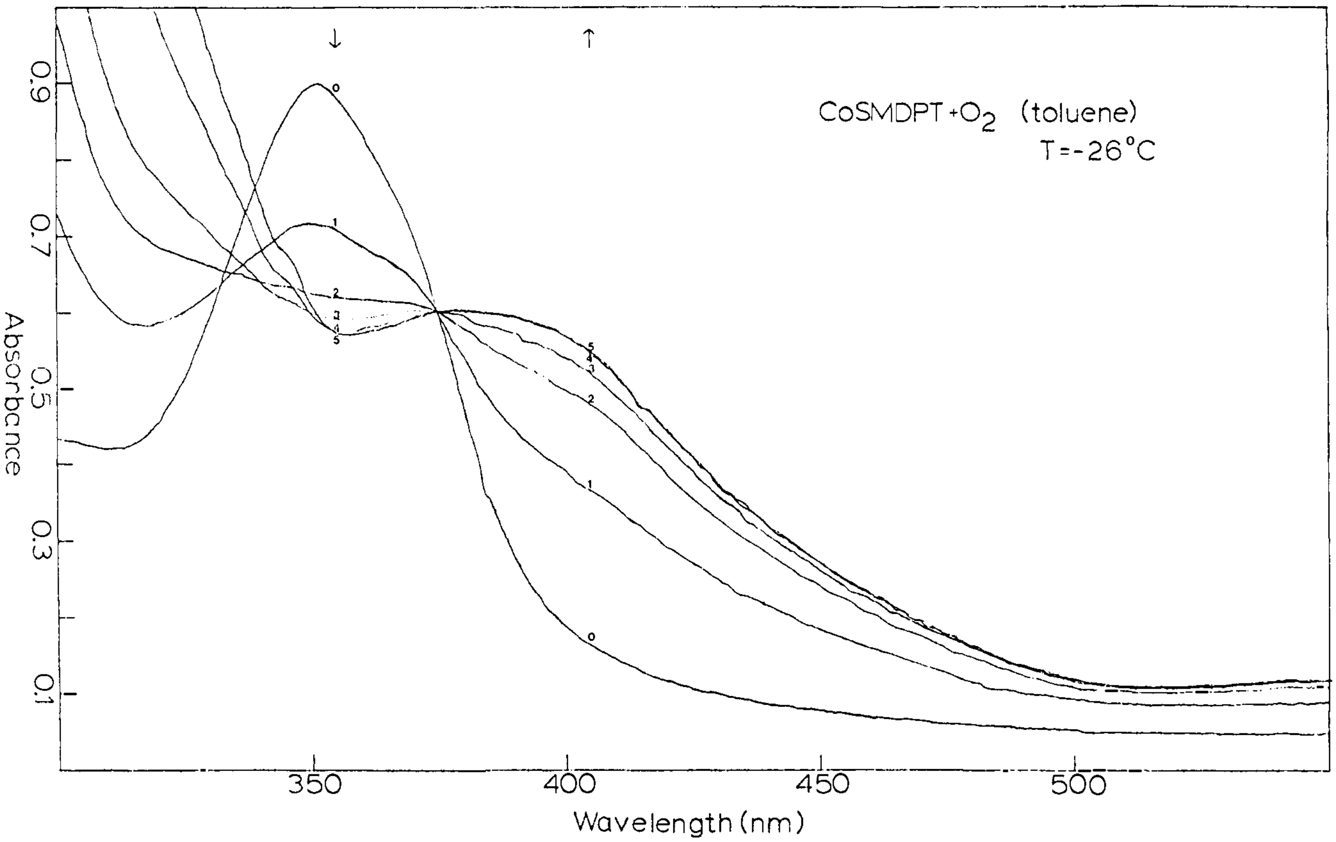

Figure 1. Electronic spectra of CoSMDPT in toluene as a function of oxygen pressure over the solution: (0) 0.000, (1) 0.885, (2) 3.947, (3) 8.438, (4) 22.73, (5) 48.38 atm O_2.

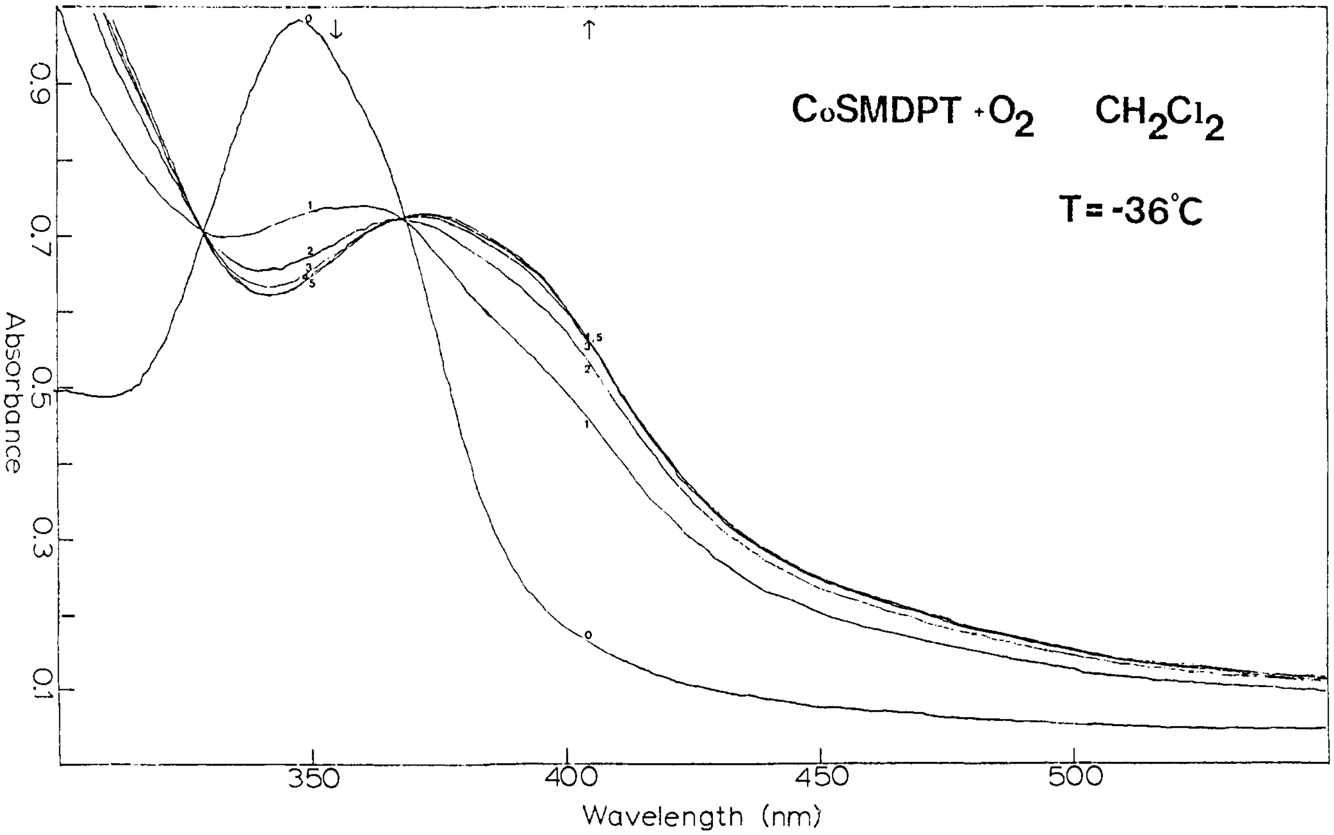

Figure 2. Electronic spectra of CoSMDPT in methylene chloride solution at −36 °C as a function of oxygen pressure over the solution: (0) 0.000, (1) 0.3401, (2) 1.224, (3) 4.694, (4) 15.58, (5) 40.75 atm O_2.

between O_2 and the solvent are evident in the 300–350-nm region. This complication prevents the observation of the low-wavelength isobestic point (vide infra); however, the higher wavelength isosbestic point is maintained through the experiment.

Upon adduct formation, the maximum at 352 nm due to CoSMDPT decreases in intensity. At the same time, a new, broad

Table I. Spectrophotometric and Equilibrium Data for Dioxygen Binding to CoSMDPT in Toluene

run	P_{O_2}, atm	$A - A^0$	K	$\epsilon_{CoO_2} - \epsilon_{Co}$[a]	K_{eq}, atm^{-1} [a]	MSD[b]/ CSD[c]	t, °C	[Co] total[d]	[TFE][d]
1	0.885	0.201	1.226	5734 ± 72	1.2 ± 0.1	1.31	−29	0.000 41	0.000 00
2	3.947	0.308	0.994						
3	8.438	0.351	1.143						
4	22.73	0.379	2.122						
5	48.38	0.380	1.142						
1	0.408	0.113	0.974	5741 ± 83	1.0 ± 0.1	1.32	−31	0.000 42	0.000 84
2	1.089	0.208	1.014						
3	2.654	0.284	0.946						
4	8.370	0.340	0.711						
5	21.16	0.384	1.408						
6	42.26	0.393	2.294						
1	0.408	0.059	0.698	3754 ± 27	0.7 ± 0.02	1.30	−26.5	0.000 43	0.005 41
2	1.089	0.118	0.733						
3	2.722	0.170	0.652						
4	10.14	0.234	0.724						
5	27.49	0.252	0.697						
6	55.59	0.259	0.740						

[a] Error limit is marginal standard deviation. [b] MSD = marginal standard deviation. [c] CSD = conditional standard deviation. [d] Concentration units are mol/L.

Table II. Equilibrium Data for CoSMPDT in CH_2Cl_2

P_{O_2}, atm	$A - A^0$	K	$\epsilon_{CoO_2} - \epsilon_{Co}$[a]	K_{eq}, atm^{-1} [a]	MSD[b]/ CSD[c]	t, °C
2.177	0.245	1.137	5534 ± 35	1.174 ± 0.062	1.42	−12
5.442	0.302	1.321				
12.24	0.321	1.141				
25.65	0.333	1.181				
0.2721	0.139	2.363	5873 ± 71	2.560 ± 0.180	1.30	−26
0.8842	0.249	2.652				
2.245	0.311	3.134				
4.762	0.332	3.005				
13.95	0.342	1.857				
0.3401	0.294	8.062	6634 ± 32	8.250 ± 0.387	1.22	−36
1.224	0.369	9.355				
4.694	0.393	10.180				
15.58	0.397	6.032				

[a] Error limit is marginal standard deviation. [b] Marginal standard deviation. [c] Conditional standard deviation. [d] [Co] 0.000 37, −12 °C; [Co] 0.000 36, −26 °C; [Co] 0.000 36, −36 °C.

peak at 380 nm appears. Figure 1 shows spectra obtained at −26 °C. The spectrophotometric and equilibrium data are summarized in Table I. Data in this table were taken at a wavelength of 405 nm. Also in this table are the data for runs done in toluene with a twofold and a 13-fold excess of trifluoroethanol. In all cases, the spectrophotometric titrations have been carried out to at least 99% conversion of CoSMDPT to the O_2 adduct. Because of the high saturation factor obtained in these experiments, the variable which is best fit is the change in molar absorbtivities.

Equilibrium constants, K, have been calculated by reported[2] procedures. As can be seen from Table I, values of K obtained in this fashion tend to bracket the value of the equilibrium constant obtained in the least-squares fitting, K_{eq}. The ratio of the marginal standard deviation to the conditional standard deviation (MSD/CSD) is seen to be very low, nearly unity. This relationship and the small relative size of the marginal standard deviations are indications[15] that the systems under study are well behaved and, in these experiments, well characterized.

The magnitudes of the equilibrium constants for the reversible binding of dioxygen reported here are found to be larger than most of those observed at similar temperatures in the LCoPPIXDME system, where L is an axial base molecule and PPIXDME is protoporphyrin IX dimethyl ester (K ranges from 0.020 for L = tetrahydrothiophene to 4.20 for L = 1-methylimidazole).[2] Of the systems studied, only when L is 1-methylimidazole is the equilibrium constant for the binding of dioxygen greater than the values reported here in toluene solvent.

The effect of the presence of trifluoroethanol on the dioxygen binding equilibrium to CoSMDPT in toluene is to decrease the oxygen binding affinity at temperatures near −30 °C. The reason for this behavior is difficult to determine because of the complex series of equilibria involved in this solvent. An O_2 pressure dependent behavior of the "UV tail" of the spectrum of neat toluene is observed in the spectral region of interest, when run as a blank under the same conditions as those employed in the experiments. A complex between TFE and toluene is expected on the basis of a reported phenol–benzene complex.[16] Thus the calculated binding constants for TFE solutions could be meaningless and are not reported. Because of the complications cited above, further characterization of the thermodynamic data for this system in toluene was not undertaken.

2. Methylene Chloride As Solvent. At low temperatures spectral changes characteristic of reversible binding of dioxygen are observed for methylene chloride solutions of CoSMDPT very similar to those described in Figure 1. One noticeable difference, however, is the absence of the low-wavelength charge-transfer band for O_2 in this solvent. A shift of the free CoSMDPT absorption maximum to a slightly lower wavelength occurs in CH_2Cl_2 and a second isobestic point is observed. Table II summarizes the spectrophotometric and equilibrium data for dioxygen binding to CoSMDPT in methylene chloride, in the absence of TFE. Data were gathered at −12, −26, and −36 °C. At each of these three temperatures, the system exhibited well-behaved characteristics, i.e., well-defined isobestic points (at 329 and 368 nm) that were maintained throughout the experiments, which typically lasted 12 h each. As was the case for the experiments performed in toluene, excellent fits for $\epsilon_{CoO_2} - \epsilon_{Co}$ and K_{eq} were obtained for

---

(15) R. M. Guidry and R. S. Drago, *J. Am. Chem. Soc.*, **95**, 6645 (1973).

(16) R. S. Drago, L. B. Parr, and C. S. Chamberlain, *J. Am. Chem. Soc.*, **99**, 3203 (1977).

Table III. Spectrophotometric and Equilibrium Data for Dioxygen Binding to CoSMPDT in CH_2Cl_2/TFE[a]

run	P_{O_2}, atm	$A - A^0$	K	$\Delta\epsilon$	K_{eq}	MSD/ CSD	t, °C
1	0.1361	0.052	2.986	3128 ± 20	2.740 ± 0.099	1.26	−12
2	0.6803	0.119	2.694				
3	1.701	0.149	2.508				
4	5.034	0.173	3.145				
5	12.93	0.179	2.810				
6	29.93	0.182	3.157				
1	0.2041	0.152	11.72	3666 ± 16	12.06 ± 0.43	1.31	−25.5
2	0.4083	0.180	12.40				
3	0.6805	0.194	13.22				
4	3.402	0.209	9.36				
5	6.873	0.214	19.95				
6	27.90	0.214	4.91[b]				
1	0.2041	0.179	26.32	3611 ± 7	26.05 ± 0.74	1.25	−37.5
2	0.6803	0.200	23.85				
3	1.633	0.208	29.44				
4	13.61	0.212	47.66[b]				

[a] [Co] 0.000 35, [TFE] 0.005 20, −12.0 °C; [Co] 0.000 35, [TFE] 0.005 15, −25.5 °C; [Co] 0.000 35, [TFE] 0.005 15, −37.5 °C. [b] Statistical considerations indicated that these data should be discarded from the van't Hoff analysis.

each of the temperatures employed, as is evidenced by the small ratio of the marginal standard deviation to the conditional standard deviation, as well as by the low relative magnitudes of the marginal standard deviations of both $\epsilon_{CoO_2} - \epsilon_{Co}$ and K_{eq}.

The observed value of the dioxygen equilibrium binding constant at temperature near −26 °C in CH_2Cl_2 solvent is increased over that found for this system in toluene ($K_{O_2}(CH_2Cl_2) = 2.56$, $K_{O_2}(\text{toluene}) = 1.16$). There have been several suggestions that solvents of high polarity increase oxygen affinity[1a] and this could explain this result. However, the possibility exists that a hydrogen-bonding interaction with the coordinated dioxygen adduct could enhance the dioxygen affinity. The hydrogen bonding would amount to a specific solvation of the adduct, stabilizing the adduct and increasing the amount of cobalt oxygenated. Specific hydrogen bonding interactions of the solvent CH_2Cl_2 with various bases have been establiehsed.[17] In order to investigate this possibility a small amount of the strong[18] hydrogen-bonding acid trifluoroethanol (TFE, 0.005 M) was added to the CH_2Cl_2 solution and the equilibrium constants for dioxygen binding were redetermined.

While slightly more than a twofold increase was observed in K_{eq} at or near −26 °C upon switching from toluene to methylene chloride, an increase of nearly 400% is caused by the presence of 0.005 M TFE in methylene chloride at −26 °C. We interpret this stabilization as resulting from a specific hydrogen bonding interaction of the alcohol with the dioxygen adduct. Application of the van't Hoff equation to the data in Tables II and III yields the following values of the enthalpy, ΔH, and entropy, ΔS, of adduct formation: $\Delta H_{noTFE} = -9.8 \pm 0.11$ kcal/mol; $\Delta H_{TFE} = -11.6 \pm 0.12$ kcal/mol; $\Delta S_{noTFE} = -37.2$; $\Delta S_{TFE} = -42.0$.

The error limits given are standard deviations of the fit from a nonweighted least-squares fit of the data listed under the columns entitled K and T in Tables II and III.

3. Infrared Studies. The interaction of a hydrogen-bonding alcohol with a Lewis base results in a characteristic decrease in frequency and increase in $\Delta\nu_{1/2}$ for the band assigned to the O–H stretching vibration.[19] The magnitude of the shift has been correlated with the enthalpy of formation of the hydrogen-bonded adduct.[19] Thus, it was of considerable interest to investigate the infrared spectra of these solutions to ascertain the cause of the extra stabilization observed when TFE was added to the system. Since the equilibrium constant for oxygen binding is rather small, high pressures were required to form enough O_2 adduct to detect a hydrogen-bonded OH peak. A specially built high-pressure infrared cell and reactor were used as described in the Experimental Section. Oxygen pressures up to 1000 psi were used to ensure formation of the adduct. Since no reference cell was used and the cell path was 2–4 mm, overtones were observed in the 3500–3000-cm^{-1} region when CD_2Cl_2 was used as the solvent. This required a shift in solvent to CS_2.

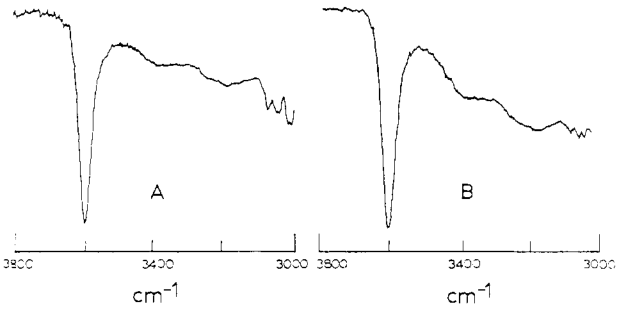

Figure 3. IR spectrum of OH stretching region for (A) 0.01 M NiSMDPT/0.05 M TFE and (B) 0.01 M CoSMDPT/0.05 M TFE in CS_2 under 1000 psi Ar at 15 °C.

A series of spectra were obtained. The OH stretching vibration of 0.05 M TFE in CS_2 occurred at 3610 cm^{-1} at 15 °C. The frequency did not change with pressure in the range 200–1000 psi. Bands at 2920 and 2800 cm^{-1} from CS_2 were observed but there is no evidence for self-association of the TFE at this concentration and temperature. Solutions of 0.01 M NiSMDPT in CS_2 showed no absorption in the 4000–3100-cm region.

The spectrum of the OH stretching region for 0.05 M TFE/0.01 M NiSMDPT in CS_2 is shown in Figure 3. The absorptions in the 3100–3000-cm^{-1} range can be attributed to C–H stretching vibrations of the ligand and TFE. The free TFE ν_{O-H} band occurs at 3600 cm^{-1} with two broad shifted bands occurring at 3380 and 3180 cm^{-1}. These bands do not change with changing Ar pressure or with the addition of high pressure of O_2. The absorptions are assigned to TFE hydrogen bonding to basic sites on the Schiff base ligand. Solutions of CoSMDPT were prepared in an inert atmosphere box and the infrared cell was flushed with several milliliters of solution to make sure that the spectrum observed was totally free from O_2. At 800 psi of Ar the spectrum (Figure 3B) has absorptions from free TFE at 3600 cm^{-1} and of the two shifted bands at 3380 and 3180 cm^{-1}, identical with that obtained for NiSDPT. We can only speculate about the identity of the hydrogen-bonding sites. The nitrogen from the coordinated imine is one possibility as are the phenolic oxygens and the benzene rings. Phenolic oxygen lone pairs have been shown to behave as good Lewis bases[20] and the benzene ring π cloud presents another source

---

[17] R. S. Drago, J. A. Nusz, and R. C. Courtright, *J. Am. Chem. Soc.*, **96**, 2082 (1974).

[18] A. D. Sherry and K. F. Pucell, *J. Phys. Chem.*, **74**, 3535 (1970).

[19] R. S. Drago, N. B. O'Bryan, and G. C. Vogel, *J. Am. Chem. Soc.*, **92**, 3924 (1970).

[20] N. B. O'Bryan, T. O. Maier, I. C. Paul, and R. S. Drago, *J. Am. Chem. Soc.*, **95**, 6640 (1973); K. A. Leslie, R. S. Drago, G. D. Stucky, D. J. Kitko, and J. A. Breese, *Inorg. Chem.* **18**, 1885 (1979).

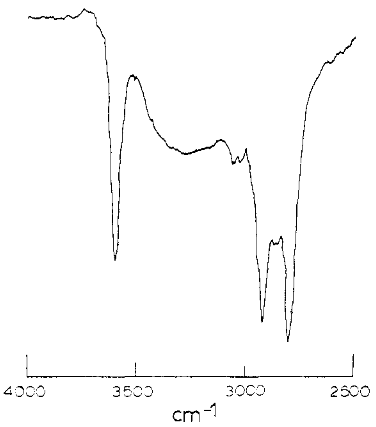

Figure 4. IR spectrum of 0.01 CoSMDPT/0.05 M TFE in CS_2 under 1000 psi O_2 at 15 °C.

of electron density. Two distinct OH stretching vibrations have been observed when phenol hydrogen bonds to anisole.[21] The $\Delta\nu_{OH}$ of 59 cm^{-1} and $\Delta\nu_{OH}$ of 164 cm^{-1} have been assigned[21] to interactions with the benzene ring and an oxygen lone pair, respecitvely. Larger shifts would be expected in this complex because of the larger negative charge on the Schiff base ligand than on anisole.

When a 0.01 M solution of CoSMDPT that is 0.05 M in TFE is oxygenated at 1000 psi, the spectrum in Figure 4 results (at ~15 °C). The free TFE is seen at 3600 cm^{-1}. A new single broad band is observed at 3280 cm^{-1} that is not present in either the NiSMDPT·TFE spectrum, at 1000 psi of O_2, or the nonoxygenated CoSMDPT·TFE spectrum. Thus the new O–H band must involve the dioxygen adduct. Based on the values for K_{O_2} (Table II) 90–95% of the CoSMDPT should be oxygenated at the conditions of our experiment. Since this band appears only under conditions when the O_2 adduct can form, the shift is due to hydrogen bonding of the TFE to the dioxygen adduct. The next question involves the nature of the hydrogen bonding to the adduct. Since coordination of the O_2 withdraws electron density from the cobalt[2] making it a stronger Lewis acid, the ligand functional groups are expected to be weaker Lewis base sites (if they change at all) in the O_2 adduct than in the cobalt(II) complex. Thus the new O–H band and the added stabilization cannot arise from hydrogen bonding to the SMDPT ligand in the oxygenated adduct. We propose that TFE is hydrogen bonding to the terminal oxygen of the bound dioxygen molecule. Of the two oxygen atoms in O_2, ^{17}O EPR indicates[22] that the terminal oxygen has more of the unpaired electron density on it.

The following relationship has been reported[18] for TFE Lewis acid–base adducts: where ΔH is the enthalpy of the interaction

$$-\Delta H(0.2) = 0.0121\Delta\nu_{OH} + 2.7$$

in kcal/mol, and $\Delta\nu_{OH}$ is the observed frequency shift of the OH stretch in cm^{-1}.[23] The shift of 320 cm^{-1} due to the dioxygen adduct represents an enthalpy of −6.6 kcal/mol. This is to be compared to the 1.8 kcal mol^{-1} stabilization observed when TFE is added to CH_2Cl_2 solutions of this adduct. The discrepancy arises because of the 1:1 formulation of the equilibrium, for a two-step system: O_2 binding to cobalt and TFE incompletely complexing to the bound dioxygen. The 1:1 formulation supports the proposed stabilization. However, the spectral overlap of the O_2 adduct and the hydrogen-bonded O_2 adduct does not permit an independent evaluation of the hydrogen-bonding stabilization from the electronic spectrum. Fortunately, the $\Delta\nu_{OH}$ vs. ΔH relation provides this data and indicates a 6 kcal mol^{-1} hydrogen bonding interaction of TFE to the bound O_2.

Investigation of the O–O stretching vibration, ν_{O_2}, was also considered. There is extensive absorption from the ligands in this region. This complication coupled with the insensitivity[4] of this vibration to the charge on the bound O_2 (HO_2, O_2^-, and most cobalt–O_2 adducts have ν_{O_2} around 1145 ± 50 cm^{-1}) discouraged pursuit of this line of investigation.

There are several interesting implications of these results. The donor strength of the terminal oxygen in the O_2 adduct toward TFE is comparable to that of the oxygen in *N*,*N*-dimethylacetamide (DMA) ($-\Delta H$ of the TFE–DMA adduct is 6.3 kcal mol^{-1}). The superoxide ion is a potent nucleophile[7] and anions are generally strong hydrogen-bonding bases. Thus, the reactivity of the coordinated O_2 is not that of an ion-paired (90% ionically bound[1]) superoxide ion but more like that of a bound O_2 fragment with fractional (0.5 e$^-$) electron density transferred into it.[3]

The other implication of this hydrogen-bonding interaction involves the potential contribution of this effect to the enhanced binding affinity at 25 °C of cobalt myoglobin ($p_{1/2}O_2 = 57$ Torr), coboglobin ($p_{1/2}O_2 = 45$ Torr), and Co(TpivPP)·N-MeIm ($p_{1/2}O_2 = 61$ Torr) relative to CoPPIXDME–N–MeIm ($p_{1/2}O_2 = 10^4$ Torr). In the high-affinity systems a potential Lewis acid, hydrogen-bonding group is within bonding distance of the terminal O_2. In the picket fence porphyrin (TpivPP) an amide N–H group is nearby, while in cobalt myoglobin and coboglobin a distal imidazole is within weak hydrogen bonding range. In these systems, weak hydrogen bonds (in the 1–2 kcal mol^{-1} range) are expected. This enthalpy is not large enough to overcome the entropy associated with bringing a separate Lewis acid and Lewis base together in solution at room temperature. However, in the high-affinity systems listed above, the acid site is held in the appropriate position for interaction by the geometrical constraints of the ligand and protein. Thus we feel that these hydrogen-bonding interactions provide a very reasonable explanation for the enhanced dioxygen binding in the high-affinity proteins and picket fence systems relative to Co(PPIXDE)·1-MeIm.

Acknowledgments. The authors acknowledge the financial support of this research by the National Science Foundation.

---

[21] B. B. Wayland and R. S. Drago, *J. Am. Chem. Soc.*, **86**, 5240 (1964).

[22] D. Getz, E. Melamud, B. L. Silver, and Z. Dori, *J. Am. Chem. Soc.*, **97**, 3846 (1975).

[23] Since this relationship was derived using CCl_4 as the solvent, it was not apparent whether it would work when CS_2 was the solvent. The Lewis bases acetonitrile, diethyl ether, dimethylformaide, dimethyl sulfoxide, and pyridine were used to check whether the adduct frequencies obtained in CCl_4 matched those obtained in CS_2. In all cases the frequency in CS_2 matched that determined in CCl_4, allowing the frequency shift equation to be used to predict the solvation minimized enthalpies.

[24] M. E. Jacox and D. E. Milligan, *J. Mol. Spectrosc.*, **42**, 495 (1972).