

noxi radical, forming BQ (reactions 3 and 4).

The "non-Arrhenius" temperature dependence for the oxidation of 2,6-di-*tert*-butylphenol catalyzed by CoTPP indicates the complicated nature of the reaction mechanism. High equilibrium concentrations of the dioxygen CoTPP complex are expected at the lower temperature according to reaction 1. Higher temperatures favor increases in the rates of all subsequent reaction steps but also decrease significantly the equilibrium concentration of the dioxygen complex, which is required for the insertion reaction step 3. The sharp drop in the relative rates of formation of BQ illustrated in Figure 5 indicates that there is an optimal temperature for oxygen insertion in an intermediate temperature range. This temperature seems to be about 40 °C. With increase in temperature, the rate of the coupling reaction increases steadily. While the intrinsic insertion reaction rate also increases, the rate of formation of the insertion product BQ decreases with temperature because of the sharp drop in the solubility of dioxygen with increase in temperature.

It is interesting to note that the type of catalysis observed with Co(II)-TPP differs markedly from that observed with the other transition-metal-TPP complexes investigated (Figures 1 and 2), and it is suggested here that this difference is due to the involvement of dioxygen complexes as intermediates in oxygen insertion. The observed rates of oxidation are much higher with the cobalt catalyst. Also, the latter is the only one that produces a significant amount of quinone. According to reaction 3, a dioxygen complex would appear to be necessary for the oxygen insertion step. While the coupling reaction may

be promoted by dioxygen complexes, there is no requirement that anything but an effective oxidant is needed, so that the coupling reaction may also be catalyzed by one or more of the Co(III) species present in the reaction mixture. Thus, it is seen that higher temperatures promote the coupling reaction but inhibit oxygen insertion relative to coupling (Figure 5) in accordance with the decreased solubility of dioxygen (and consequent decrease in dioxygen complex formation) at higher temperatures. From the well-known relative tendencies of transition-metal complexes toward dioxygen complex formation,²¹ it is apparent that the equilibrium concentrations of dioxygen complexes are orders of magnitude greater for Co(II)-TPP than for the other transition-metal-TPP complexes, thus accounting for the observed differences in the rates of dioxygen insertion to form the benzoquinone derivative. This requirement of dioxygen complexes as intermediates in dioxygen-insertion reactions has also been observed in catalysis of DBP oxygenation with cobalt(II)-polyamine complexes.^{22,23}

Acknowledgment. This research was supported by a research grant (A-259) from the Robert A. Welch Foundation.

Registry No. O₂CoTPP, 37249-49-3; CoTPP, 14172-90-8; Fe(TPP)Cl, 16456-81-8; Mn(TPP)Cl, 32195-55-4; VO(TPP), 14705-63-6; CuTPP, 14172-91-9; 2,6-di-*tert*-butyl-*p*-benzoquinone, 719-22-2; 3,3',5,5'-tetra-*tert*-butyldiphenquinone, 2455-14-3.

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(22) Bedell, S. A.; Martell, A. E. *Inorg. Chem.* 1983, 22, 364.

(23) Bedell, S. A.; Martell, A. E., to be submitted for publication.

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Formation and Stabilities of Cobalt(II) Chelates of *N*-Benzyl Triamine Schiff Bases and Their Dioxygen Complexes

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Received May 11, 1983

Equilibrium constants are reported for the formation of six new Co(II) complexes of tridentate and pentadentate *N*-benzyl triamine ligands and for their reactions with dioxygen in a 70% dioxane-30% water solvent. Procedures for synthesis of the new ligands described involve the formation of Schiff bases of 4-benzyl-diethylenetriamine and 5-benzyl-dipropylenetriamine with salicylaldehyde and pyridine-2-carboxaldehyde and the reduction products of these Schiff bases. Complete equilibrium analysis of these ligand systems requires equilibrium studies of Schiff base components and their interactions with cobalt(II). The relationships between ligand structure and dioxygen affinities of the cobalt complexes are discussed. Stability constants and autoxidation tendencies of the dioxygen complexes indicate that the most satisfactory ligand for oxygen binding and recycling is the 4-benzyl-diethylenetriamine-salicylaldehyde Schiff base.

Introduction

This research report describes the synthesis and study of a number of polyamine-Co(II) dioxygen complexes as models for the design of high polymer oxygen-carrying systems. In order to attach an oxygen carrier to a polystyrene matrix, parasubstituted methylene groups of the phenyl moieties were utilized for the attachment of the coordinating ligands of the appropriate cobalt(II) complexes. For the development of reasonable estimates of the dioxygen affinities of the monomer units of the polymers, it was decided to synthesize and investigate a series of model mononuclear complexes of the type that could be incorporated readily into the polymer. Since it is advantageous to use readily prepared chloromethylated polystyrene, the model ligands should contain a benzyl group

to simulate the steric effects of the point of attachment to the polymer backbone.

Co(saldpt) had been previously attached to polystyrene supports (saldpt = bis(salicylidene)dipropylenetriamine), where it was found to be an active catalyst for the oxidation of alkylphenols.¹ The polymer attachment was through the central secondary nitrogen of dipropylenetriamine (dpt). Further, the polymer-bound Co(saldpt) was shown to reversibly coordinate dioxygen.² It has been suggested that large bulky groups (phenyl and benzyl) attached to the secondary nitrogen of dpt offer considerable steric blockage to the position of attack by dioxygen on Co(saldpt) type complexes.³ Indeed,

(1) Drago, R. S.; Gaul, J.; Zombeck, A.; Straub, D. K. *J. Am. Chem. Soc.* 1980, 102, 1033.

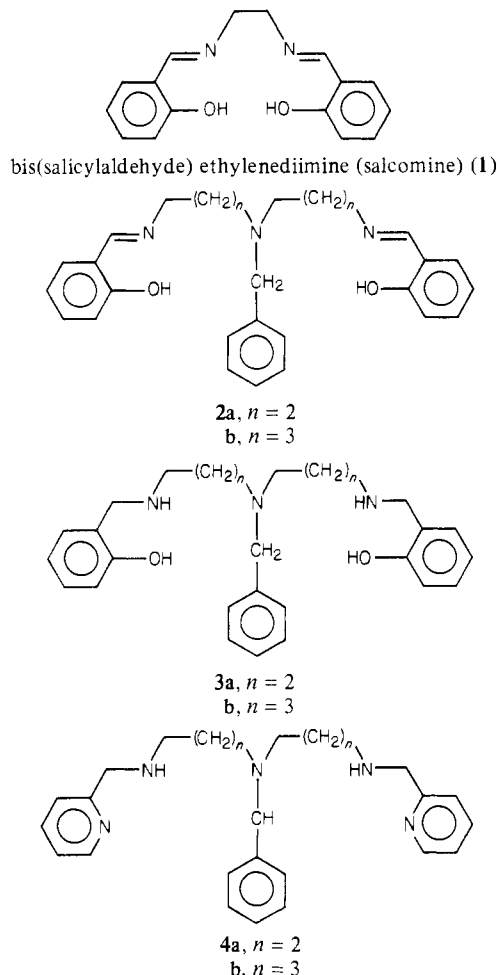
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(3) Niswander, R. H.; Taylor, L. T. *J. Am. Chem. Soc.* 1977, 99, 5935.

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most alkyl- or aryl-substituted cobalt complexes of this type are relatively unreactive toward dioxygen; none would react with oxygen in the solid state.

The types of oxygen carriers selected for this study are the salicylaldehyde Schiff bases similar to the ligand salcomine (1) or related compounds containing pyridine donors in place



of phenolate groups, indicated by 2–4. Because of the fact that these ligands are insoluble in water, it was necessary to determine metal ion and oxygenation equilibria in a mixed aqueous solvent (70% dioxane). The aliphatic triamine was selected because a pentadentate ligand would produce a cobalt complex with the highest possible dioxygen affinity,⁴ and the central secondary nitrogen would provide a convenient point of attachment to a polystyrene polymer.

Experimental Section

Materials. 4-Benzyl-1,7-diphthaloyldiethylenetriamine. The starting material, diphthaloyldiethylenetriamine, was prepared by a method essentially the same as described elsewhere.⁵ To 1 L of isopropyl alcohol was added 1,7-diphthaloyldiethylenetriamine (81.5 g, 0.22 mol), benzyl chloride (41 g, 0.32 mol), and sodium carbonate (23.7 g, 0.22 mol). The mixture was refluxed 18 h and then filtered hot. After the product crystallized, it was collected and washed with ether: yield 89.1 g (88%); mp 133–135 °C.

4-Benzyl-diethylenetriamine. A mixture of 4-benzyl-1,7-diphthaloyldiethylenetriamine (138.7 g, 0.32 mol), 600 mL of 6 M hydrochloric acid, 400 mL of toluene, and 2 g of Adogen 464 were refluxed 5 days. The mixture was cooled and filtered. The toluene was partially removed under an air stream. The aqueous solution was made basic with 6 M NaOH and extracted with dichloromethane. A light yellow oil (66 g) was recovered. This was distilled under

vacuum: yield 30.5 g (50%); bp 120–125 °C (0.5 torr). The NMR spectrum was consistent with the structure.

Bis(salicylidene)-4-benzyl-diethylenetriamine. To 200 mL of ethanol was added 4-benzyl-diethylenetriamine (15 g, 0.08 mol) and freshly distilled salicylaldehyde. The solution was refluxed 18 h. Crystals were collected and washed with hexane: yield 27.1 g (87.1%); mp 54–55 °C. The NMR and IR spectra were consistent with the assigned structure.

Bis(2-hydroxybenzyl)-4-benzyl-diethylenetriamine. Bis(salicylidene)-4-benzyl-diethylenetriamine (5 g, 0.012 mol) was dissolved in 50 mL of absolute alcohol and hydrogenated over 2 g of 10% palladium on carbon at slightly higher than 3 atm of hydrogen. After reaction of the calculated amount of hydrogen, the catalyst was filtered. The solution produced colorless crystals upon standing: yield 2.2 g (44%); mp 102–104 °C. Anal. Calcd for $C_{25}H_{31}N_3O_2$: C, 74.07; H, 7.65; N, 10.37; O, 7.90. Found: C, 73.86; H, 7.86; N, 10.46; O, 8.04.

Bis(2-pyridylmethyl)-4-benzyl-diethylenetriamine Pentahydrochloride. To 100 mL of ethanol were added 4-benzyl-diethylenetriamine (8.9 g, 0.046 mol) and freshly distilled pyridine-2-carboxaldehyde (9.8 g, 0.092 mol). The solution was refluxed 18 h, followed by hydrogenation as described above for bis(2-hydroxybenzyl)-4-benzyl-diethylenetriamine. The filtrate was saturated with dry hydrogen chloride until no additional colorless precipitate formed. The crude pentahydrochloride was recrystallized from 95% ethanol: yield 9.2 g (40%); mp 211–213 °C dec. Anal. Calcd for $C_{23}H_{29}N_5 \cdot 5HCl$: C, 49.52; H, 6.10; N, 12.56; Cl, 32.60. Found: C, 49.79; H, 6.41; N, 12.44; Cl, 31.95.

5-Benzyl-dipropylenetriamine. This compound was prepared by a procedure essentially the same as that described elsewhere.⁶ Although the yield was only 6% the NMR and IR spectra were consistent with the structure; bp 127–130 °C (0.2 torr).

Bis(salicylidene)-5-benzyl-dipropylenetriamine. To 5-benzyl-dipropylenetriamine (2.75 g, 0.012 mol) dissolved in 50 mL of ethanol was added salicylaldehyde (3 g, 0.024 mol). The solution was refluxed 18 h, and the solvent was removed under vacuum. The oil was twice subjected to column chromatography (silica gel) with dichloromethane as eluent; TLC indicated that a single component remained. Both NMR and IR confirmed the assigned structure; yield 2.8 g (57%) of an undistillable oil. Anal. Calcd for $C_{27}H_{31}N_3O_2$: C, 75.52; H, 7.23, N, 9.79. Found: C, 75.26; H, 7.48; N, 9.96.

Bis(2-hydroxybenzyl)-5-benzyl-dipropylenetriamine. To 25 mL of 1.0 M $BH_3 \cdot THF$ was added bis(salicylidene)-5-benzyl-dipropylenetriamine (0.4 g, 0.9 mmol) in 51 mL of THF and two drops of glacial acetic acid. The yellow imine solution immediately decolorized. The solution was refluxed 3 h and then quenched in methanol. Solvent was removed, the residue was refluxed in 3 M HCl, and the resulting solution was cooled and made basic. The mixture was extracted with dichloromethane. The solvent was partially removed, and this solution was eluted through a chromatography column packed with Whatman CF11 cellulose. A green band was collected, which, upon solvent removal, yielded 0.27 g (68%) of a pale green oil. Anal. Calcd for $C_{27}H_{35}N_3O_2$: C, 74.8; H, 8.1; N, 9.7. Found: C, 74.0; H, 8.41; N, 9.2.

Bis(2-pyridylmethyl)-5-benzyl-dipropylenetriamine Pentahydrochloride. This ligand was prepared in a manner similar to that for bis(2-pyridylmethyl)-4-benzyl-diethylenetriamine pentahydrochloride. The yield was 20%, mp 254–256 °C. Anal. Calcd for $C_{25}H_{33}N_5 \cdot 5HCl$: C, 51.24; H, 6.49; N, 11.96; Cl, 30.32. Found: C, 51.56; H, 6.55; N, 11.73; Cl, 29.98.

Other Materials and Standard Solutions. Dioxane utilized was freshly procured as Spectrograde from Aldrich. Its purity for this type of work was calibrated during the preliminary work on tren (tris(aminoethyl)amine) and was found to be satisfactory. Standard base was prepared as a 30% aqueous dioxane solution. It was standardized with use of a linear least-squares fit of Gran's plots for end point determination obtained from titrations of HCl with this base. The water utilized was ion exchanged and doubly distilled (one time from $KMnO_4$).

Equipment and Potentiometric Measurements. A sealed 100-mL capacity, thermostated anaerobic glass vessel was equipped with extension blue-glass pH and calomel reference electrodes, gas inlet and outlet tubes, a magnetic stirrer, and a titrant inlet. The $-\log [H^+]$ readings were obtained with a Corning Model 130 pH meter. The

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titrant was delivered with a Metrohm piston buret, and the temperature was controlled at 25 ± 0.01 °C by circulation of coolant from a Polyscience Poly Temp refrigerated constant-temperature apparatus.

The pH meter was set before each experiment to read $p[H]$ ($= -\log [H]$) directly by using a 70% dioxane solution of known KCl concentration at $\mu = 0.100$ M, which was subsequently titrated with large aliquots of 0.100 M standard KOH in 70% dioxane in order to check the high $p[H]$ readings. The ion product ($K_w = [H][OH]$) was determined for $\mu = 0.1000$ M in 70% dioxane from several series of $[OH]$ and $p[H]$ measurements. It was found to be $10^{-16.00}$.

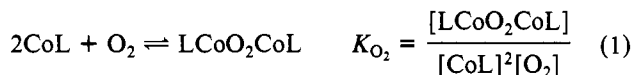
Typically, a test solution for potentiometric measurements was prepared in the following fashion: about 0.10 mmol of the ligand was accurately weighed and placed in the test vessel. Then the requisite amounts of KCl (1.00 M), HCl (0.09681 M), and $CoCl_2$ (0.02686 M) were added. Additional water was added to make 15.00 mL. Finally a 35.00-mL aliquot of dioxane was added, and the solution was sealed with the appropriate connections made as described above. The total volume, calibrated in a separate experiment, was 49.25 mL. After a suitable time for equilibration (i.e. pH drifts <0.001 unit/5 min, usually between 5 min and 1 h) a reading was taken, and an aliquot of titrant was added. The procedure was repeated some 50–60 times for one equilibrium curve.

Computations were carried out with computer programs developed in this laboratory. The requisite protonation constants were determined with FORTRAN program PKAS,⁷ which handles overlapping protonation constants with a high degree of efficiency. Experiments were performed under anaerobic conditions as well as under oxygen, and the data were worked up with the FORTRAN Program BEST,³ which handles potentiometric results for any number of interacting components.

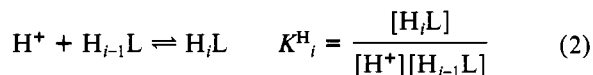
Results and Discussion

The principal method of investigation utilized during the present study that of equilibrium potentiometry. The emf potentials, taken as a function of measured amounts of added standard base, were converted by appropriate calculations to give thermodynamic formation constants describing the ratios of various species present at any given $-\log [H^+]$ value.

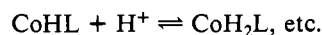
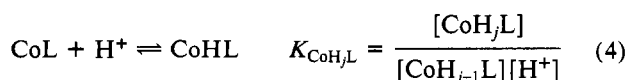
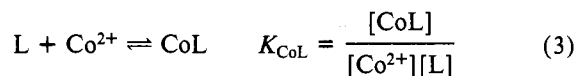
In order to obtain a Co(II) oxygenation constant, K_{O_2} (eq 1), for a new ligand, L, by this method, it is first necessary



to determine two other sets of equilibrium constants: ligand protonation constants and metal–ligand formation constants. In the first experiment the potentials were measured over a wide range of $-\log [H]$ on a millimolar solution of the ligand alone in order to determine the protonation constants, $K_i^{H^+}$ (eq 2). In the second experiment, an anaerobic solution was



prepared containing equimolar amounts of Co(II) and the pentadentate ligand while the potentials were measured over a wide range. These data were then computed to give the metal–ligand and metal–ligand–proton formation constants K_{CoL} and/or K_{CoH_jL} defined in eq 3 and 4. The final oxy-



generation measurements were performed on 1:1 solutions under

Table I. Protonation Constants for Ligands in 70% Dioxane at 25.0 °C and $\mu = 0.100$ M^a

ligand	$\log K_1^{H^+}$	$\log K_2^{H^+}$	$\log K_3^{H^+}$	$\log K_4^{H^+}$	$\log K_5^{H^+}$
tren	10.406	9.673	8.792 (1)		
1	13.77	12.14			
4a	8.44 (1)	6.84 (1)	1.68 (2)		
3a	13.53 (1)	12.52 (2)	8.62 (1)	7.36 (1)	<1
bzdien	9.98 (3)	8.71 (1)			
bzdpt	10.12 (1)	9.12 (3)	5.42 (1)		

^a Values in parentheses are the errors in the last significant digits.

a blanket of O_2 , and the data were obtained in a similar manner.

These measurements are rather facile in aqueous solution, with the standard thermodynamic state chosen as unit molality in an aqueous solvent consisting of 0.100 M KCl or KNO_3 . However, to avoid anticipated aqueous solubility problems, particularly those of the imines, the preliminary solvent system chosen was 70% dioxane–30% water at $\mu = 0.100$ M. In contrast to the well-standardized pure aqueous systems, very little potentiometry has been done previously in 70% dioxane–30% water systems. Of those using aqueous dioxane systems, Harned and Gallon⁹ and Van Uitert et al.¹⁰ provided the most careful measurements. However, the standard state chosen by these investigators was infinite dilution in the solvent.

Thus, in order to calibrate this solvent system for 0.100 M KCl, measurements on a known ligand, tris(aminoethyl)amine (tren), were made in 70% dioxane. The results of the calibration were then utilized for potentiometric measurements on the new ligands studied in the present work.

pK_w in 70% Dioxane. Although Harned and Gallon⁹ reported pK_w in 70% dioxane as 17.86, this value is not valid for solutions at an ionic strength of 0.100 M. Therefore, a determination was made of the ion product constant in the following way: various amounts of standard KOH (in 70% dioxane) were added to a solution containing 0.100 M KCl. The $-\log [H]$ was recorded, while $[OH]$ was calculated from the amount of base added. The product of $[OH]$ and $[H]$ was taken. The mean value obtained in this way for the log concentration product is 16.00 ± 0.05 .

Protonation Constants. Table I lists the protonation constants for tren and the new ligands. The first entry, tren, represents a transition from aqueous systems to 70% aqueous dioxane for a well-known ligand. It was interesting to obtain values (10.41, 9.67, 8.79) surprisingly close to those of tren measured in water (10.14, 9.43, 8.41). The second ligand, **2a**, is an imine for which only the two highest protonation constants could be calculated. Attempts made at lower $p[H]$ values were not possible since hydrolysis of the imine occurred. The pentadentate ligand **3a** possesses four measurable protonation constants: two quite high and two of intermediate strength. Ligand **4a** was found to possess considerably lowered protonation constants (8.44, 6.84, and 1.68) when compared to those of pydien (9.88, 7.04, 3.82, 1.44). pydien, 1,3-bis-(2-pyridyl)-2,5,8-triazanonane, is similar to ligand **4a** except that the 5-benzyl group is not present. Thus, the presence of the central benzyl group in these polyamines in some way exerts a profound influence on the Brønsted basicity of these ligands. Since ligand **4a** was found to oxidize too rapidly in the presence of $Co(II)-O_2$ (vide supra), its investigation was deferred until the kinetics of these ligands will be studied. Likewise ligand **3b** was excluded because some unremovable impurity compromised the accuracy of the data obtained.

Benzyl-diethylenetriamine (bzdien), a constituent of the imine ligand **2a**, is expected to be in equilibrium with free

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Table II. Protonation Constants for Ligands in Water at 25.0 °C, $\mu = 0.100 \text{ M}^a$

ligand	$\log K^{\text{H}}_1$	$\log K^{\text{H}}_2$	$\log K^{\text{H}}_3$	$\log K^{\text{H}}_4$	$\log K^{\text{H}}_5$
tren	10.14	9.43 ^a	8.41 ^a		
4a	8.45	7.23	3.18		
3a	>12	10.55	~8.5	7.51	3.05

^a All errors are 0.01 or lower, except $\log K^{\text{H}}_1$ and $\log K^{\text{H}}_3$ of 3a.

aldehyde and the metal ion and ultimately may become part of an oxygen complex. In the absence of metal ion, from potentiometric equilibrium measurements, the polyamine was found to be characterized by only two protonation constants, 9.98 and 8.71, which are within 0.3 log unit of the corresponding values found for diethylenetriamine (dien) in water;¹¹ however, the third protonation constant is too low to be measurable in 70% dioxane at millimolar concentrations. Perhaps in addition to the large effect of the benzyl group, a lowering of the dielectric constant of the solvent in going from water to 70% dioxane results in sufficient lowering of the solvation of charged ions that triply positively charged species with close packing of the positive charges become much less stable. Thus it appears that the final (i.e., low pH) protonation constants are usually several log units lower in 70% dioxane than in water.

The log (protonation constants) of bzdpt were also determined in 70% dioxane (Table I). The two closely spaced higher constants followed by a much lower constant are consistent with the structure of the triamine. The literature values of dpt itself in water at 25.0 °C, $\mu = 0.100 \text{ M}$, are 10.65, 9.57, 7.72. From this comparison it is also seen that the benzyl substituent as well as the solvent change has the effect of considerably lowering the basicity of the ligand for the third protonation. This lowering is similar to that of the benzyl-diethylenetriamine systems.

The protonation constant of salicylaldehyde was determined in 70% dioxane (0.100 M KNO_3) at 25.0 °C, and was found to be 10.18 ± 0.03 log units. The literature value is 8.13 at 25.0 °C ($\mu = 0.100 \text{ M}$) in water.

Aqueous solution studies were also pursued in an attempt to gain greater accuracy and more reliable equilibrium data. The results are shown in Table II.

Ligand **2a** in water produced a solution that is completely colorless at pH 2.7. The first tinge of yellow was observed at $a = 1$, while at $a = 1.5$ ($a =$ moles of base per mole of compound present) an insoluble yellow imine precipitated. It was not possible to obtain further homogeneous equilibrium data at higher pH because of the insolubility of the ligand.

An analysis of the potentiometric curve of ligand **4a** shows that two of the nitrogens are too weakly basic to be protonated at pH 2. The weakly basic nitrogens are probably those of the two pyridine rings. The successive protonation constants found for the remaining nitrogen donors were quite similar to the protonation constants of **4a** obtained previously in 70% dioxane with the exception of the third constant. In both water and 70% dioxane the fourth and fifth protonation steps were not observed under the reaction conditions employed for potentiometric measurements.

The potentiometric curve of ligand **3a** in the absence of Co(II) in aqueous solution is characterized by three buffer regions separated by two inflections. The protonation constants for this ligand are shown in Table II. The reason for uncertainty in the third constant (~ 8.5) is that the ligand was found to be somewhat insoluble. In order to get this approximate

Table III. Formation Constants of Co(II) Chelates of Ligands in 70% Dioxane at 25.0 °C ($\mu = 0.100 \text{ M}^a$)

ligand	$\log K_{\text{ML}}$	$\log K_{\text{MHL}_n\text{L}}$	$\log \frac{[\text{M}(\text{OH})\text{L}][\text{H}]}{[\text{ML}]}$
tren	14.74 (1)	...	
4a	11.09 (5)	6.64 (5)	-10.00 (5)
3a	22.0 (2)	10.96 (9)	
		6.86 (8)	
		2.00 (4)	
bzdien	9.03 (3)	5.65 (3)	
bzdpt	7.14 (3)	...	-9.40 (3)

^a Values in parentheses are errors in the last significant digits.

constant, the equilibrium data were measured as rapidly as possible to maintain a metastable supersaturated condition. The aqueous protonation constants for **3a** are directly comparable to those measured in 70% dioxane. Because in water its first protonation constant is too high (>12), it could not be determined. The second constant was found to be 2 log units lower than its corresponding value in dioxane. The intermediate $\log K^{\text{H}}$'s in water are similar in magnitude to those in 70% dioxane, while the final one, which was determined at low pH, is measurable in water though probably less accurately than the others.

Bis(salicylidene)diethylenetriamine (saldien) was investigated in a manner similar to that described above for ligand **2a**. This ligand is similar to **2a** except that the 4-benzyl group is missing. It had been hoped that saldien could provide more information than the other imine **2a**, which dissociates in acid solution. Unfortunately, it also has properties that make measurements difficult or impossible: dissociation at low p[H] and precipitation upon addition of base. At $a = 1$ relative to the trihydrochloride, the imine started forming, and at $a = 1.5$ the saldien formed a yellow precipitate, far too insoluble for further investigation.

Cobalt-Ligand Interactions. Table III lists the Co(II) formation constants determined at 25.0 °C and $\mu = 0.100 \text{ M}$ in 70% dioxane. The value of $\log K_{\text{ML}}$ for tren (14.74) compared favorably with 12.7, which is the formation constant measured in aqueous solution. Some of this increase may be due to the increased basicity of the ligand donor groups when one goes from water to 70% dioxane-30% water. However, it is generally well-known that stability constants between metal ions and negative ligands increase markedly as the dielectric constant is lowered, and this behavior is fully understandable on the basis of coulombic effects.

Ligand **4a** ($\log K_{\text{ML}} = 11.09$) was found to be characterized by a value of $\log K_{\text{ML}}$ that is about three orders of magnitude lower than that recorded for the parent pydien ($\log K_{\text{ML}} = 14.73$) in water. Because of the trend established by tren, this difference was expected to be in the opposite direction. A space-filling molecular model shows that the hydrophobic benzyl group can indeed exert a negative steric effect on the structure of the completely formed chelate. This is confirmed by the comparison of their respective $\log K_{\text{MHL}}$'s (2.38 for pydien in water compared with 6.64 for **4a** in 70% dioxane). There really is no immediately available analogue in the literature to compare with the results for **3a**. The seemingly high $\log K_{\text{ML}}$ of 22.02 is a consequence of the high $\text{p}K_a$ values of the ligand, so that the formation of three protonated chelates takes place at lower pH values. These are as follows, in order: MH_3L , MH_2L , and MHL . The equilibria were found to be very slow, indicating that considerable structural modification takes place in each successive chelate deprotonation step. The data also indicate that only at high pH is the chelate in its fully pentacoordinated form, i.e., above pH 10.

Anaerobic potentiometric equilibrium measurements were also attempted for the imine ligand **2a**. Ideally Co(II)-ligand

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interactions should be measured initially at low pH values, where no complex would form. Ligand **2a** was equilibrated at all pH values in order to sort out the stepwise formation of the ligand from bzdien and salicylaldehyde. It was clear that the 1:1 imine forms almost quantitatively, while the 2:1 imine **2a** forms only to an extent of ~50% at 10^{-3} M in 70% dioxane–30% water at 25 °C and pH ~10. This result may affect the two higher pK_a 's calculated for **2a** and presented in Table I. However, it should be recalled that under conditions of low pH, the imine dissociates. Therefore, for the computer to sort out the various equilibria, it was necessary to measure the interaction of the hydrolysis components with Co(II), i.e., that of salicylaldehyde and 4-benzyltriethylenetriamine. Thus, under nitrogen and in the presence of an equimolar quantity of Co(II), two formation constants were found to satisfy the potentiometric curve for bzdien. For bzdien and Co(II), the log formation constant was calculated to be 9.03 while its log protonation constant is 5.65. This latter implies that the protonated chelate is a minor species in solution. For comparison, K_{ML} is 8.0 log units in water for dien-Co(II).

On equilibration of ligand **4a** with Co(II) at a 1:1 molar ratio in water, under nitrogen, a wide buffer region was observed under acidic conditions. Although the mathematical computation was not carried out, the buffer region may be due to the formation of CoL^{2+} , which is evidently a yellow complex.

When Co(II) was added in a 1:1 molar ratio to **3a** in water, there was found to be no tendency for coordination until about pH ~6. At high pH the solubility of the neutral ligand was exceeded. Since the precipitate did not redissolve at still higher pH values, and the solution remained turbid, it is inferred that the neutral chelate, CoL , is also insoluble in the solvent system employed.

Interaction of Dioxygen with Chelates. The first system measured is $tren-Co(II)-O_2$ in 70% dioxane. The formation of the brown $LCoO_2CoL$, $LCoO_2(OH)CoL$ complexes occurred over a wide buffer region spanning about 2 log units and covering 3.5 equiv of base relative to $tren-3HCl$. The midpoint of this region is at about pH 5. The value of $\log K_{O_2}$, the oxygenation constant

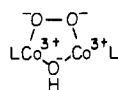
$$K_{O_2} = \frac{[LCoO_2CoL]}{[CoL]^2 P_{O_2}}$$

was found to be 5.91 (± 0.04) while the pK_a for the formation of the dibridged species $\log K^{OH}$

$$K^{OH} = \frac{[LCoO_2(OH)CoL][H^+]}{[CoLO_2CoL]}$$

was calculated to be 6.0 (± 0.04). For comparison with the aqueous studies, only the value of the overall $\log (K_{O_2}K^{OH}) = \log \beta^{OH}$ is available in the literature.¹¹ In water $\log \beta^{OH} = 1.64$ while we find in 70% dioxane a value of -0.08 . The difference reflects cumulative effects introduced by change in solvent.

The formation curve of bzdien was also determined under dioxygen. The characteristic brown color appeared at pH ~6.6 and is in all likelihood associated with the dibridged dioxygen complex indicated by **5**.



5
dibridged dioxygen complex

The complex of **2a** with Co(II) has such a high affinity for oxygen that, even with excess acid present, the solution eventually turns brown in the presence of oxygen. The solution

remained brown from pH ~3 to pH ~12.5. Upon closer scrutiny it became apparent that the dioxygen complex slowly deteriorated in dioxane–water solution through an irreversible process to an inert Co(III) complex. These inferences were based on the visual observation that the deep brown color started fading when experiments became more extended and from the chemical test that addition of large excess of strong acid produced a stable red color.

Ligand **4a** was investigated, but it appeared that a rapid irreversible autoxidation occurs in 70% dioxane. Thus, a brown color never developed under the equilibrium measurement conditions (saturated O_2). However, when a 1:1 Co(II) complex of **4a** was prepared anaerobically and exposed to O_2 , an immediate deep brown color formed, which slowly turned to a permanent pink color. In water, ligand **4a** forms a yellow complex with Co(II). Upon exposure of the yellow solution to air, even at low pH values, the solution turns brown and fades to an amber to pink color within less than 1 h. The potentiometric equilibrium curve of p[H] as a function of base added was determined for this ligand in the presence of a 1:1 molar ratio of Co(II) under dioxygen. Five equivalents of H^+ was released up to the end point, culminating in a very sharp inflection. It is apparent that the ligand under these conditions undergoes rapid oxidation.

In the case of ligand **3a** under O_2 at low pH values, the complexes of the type described above formed in the usual slow fashion. The oxygen complex formed only above pH 10. It may be concluded that the various protonated chelates do not interact with O_2 until the cobalt is sufficiently coordinated by the ligand. Under oxygen in water this Co(II) complex underwent several color changes as the pH was increased: yellow at pH ~2.3, then yellow-green, then olive at pH ~3.3, green at pH 5.2, and finally dark green. The formation of the green complex occurred through pH ~6.5. The brown dioxygen complex forms at much higher pH, ~11, indicating that an essential driving force for dioxygen complex formation is the formation of the hydroxo bridge.

It had been found that for these systems the use of pure water as the solvent has several disadvantages, the primary one being the relatively low solubility of some of the ligands and their cobalt(II) chelates. It was also found that the imine or Schiff base formation equilibria are shifted toward greater dissociation in aqueous solution. Thus, the equilibrium work must be performed in nonaqueous or mixed solvents such as dioxane–water mixtures, which not only provide higher solubility but also drive imine formation equilibrium further toward completion.

Cobalt complexes of ligand **2a** appear to have a higher affinity for oxygen in aqueous dioxane than those of ligand **4a** or **3a**. Complexation with dioxygen by the two latter complexes apparently either is quite slow or is of an irreversible nature.

Equilibrium Measurements of Schiff Base Formation. Figure 1 illustrates and summarizes the experiments that were necessary for the determination of Schiff base formation constants between salicylaldehyde and a typical amine, butylamine. The potentiometric curve for the mixture is seen to be dramatically different from those of the individual components and hence was found to be easily analyzed for the desired equilibrium constants by potentiometric measurement of hydrogen ion concentration.

The *n*-butylsalicylaldehyde–imine system was investigated in order to provide the starting point for bis(imine) formation and protonation constant calculations. This model determination was needed because the number of species present as a function of pH in systems containing 2 mol of salicylaldehyde and 1 mol of triamine is large and literature data could not be found for imine equilibrium reactions in 70% dioxane. The

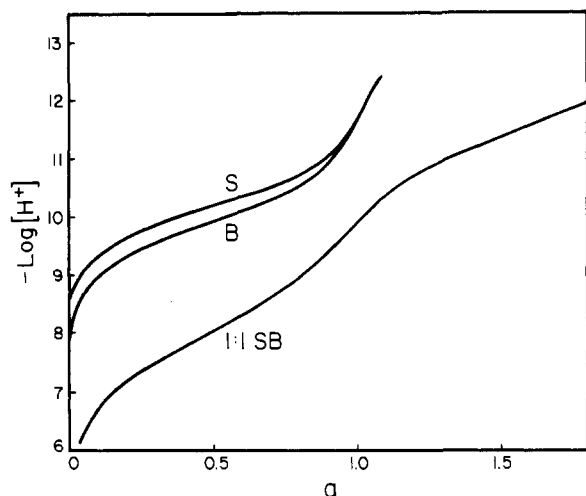
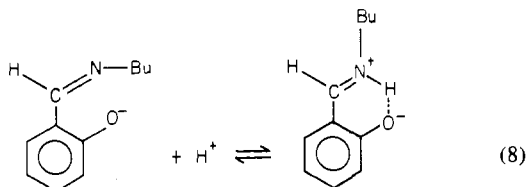
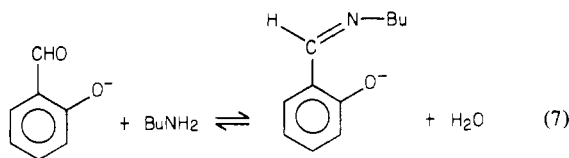
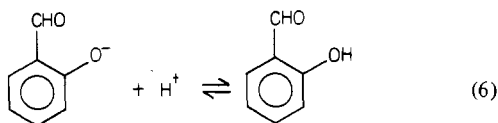
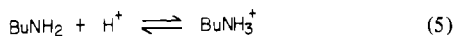


Figure 1. Potentiometric equilibrium curves of 4.69×10^{-3} M salicylaldehyde (S), 3.83×10^{-3} M butylamine (B), and a 1:1 3.83×10^{-3} M mixture of the two ($t = 25.0$ °C; $\mu = 0.100$ M (KNO₃); solvent is 70% dioxane).

equilibria given by eq 5–8 were found to be applicable in the butylamine–salicylaldehyde system.



From the titration of butylamine in 70% dioxane, at 25.0 °C with 0.100 M KOH in 70% dioxane, the log (protonation constant) of butylamine (eq 5) was determined to be 9.92 (± 0.002). In water, this was also determined and was found to be 10.56 (± 0.003). The literature value for aqueous solution at a different ionic strength is 10.64 ($\mu = 0$, at 25.0 °C).¹¹ The protonation constant of salicylaldehyde (eq 6) in 70% dioxane was found to be 10.18 ± 0.03 log units. Equilibrium constants for eq 7 and 8 were calculated by computer simulation of the potentiometric equilibrium curve as a function of pH of a system consisting of a 1:1 mixture of salicylaldehyde and butylamine. The values found are $\log K_{\text{SB}} = 3.24 \pm 0.02$ and $\log K_{\text{SBH}}^{\text{H}} = 11.56 \pm 0.02$ in 70% dioxane. Here $K_{\text{SB}} = [\text{SB}^-]/[\text{Sal}^-][\text{BuNH}_2]$, while $K_{\text{SBH}}^{\text{H}} = [\text{SBH}]/[\text{SB}^-][\text{H}^+]$. The corresponding equilibrium constant for imine base formation in water has been reported by Green and Alexander¹³ to have a much lower value ($\log K_{\text{SB}} = 0.75$). The imine $\text{p}K_{\text{a}}$ in H₂O was found to be similar ($\log K_{\text{SBH}}^{\text{H}} = 12.0$) to that obtained in this investigation for 70% dioxane.

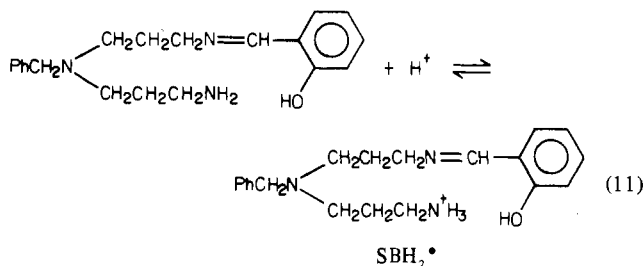
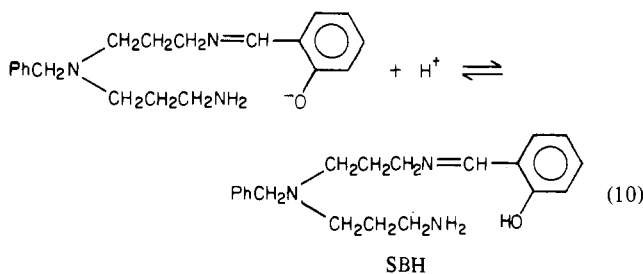
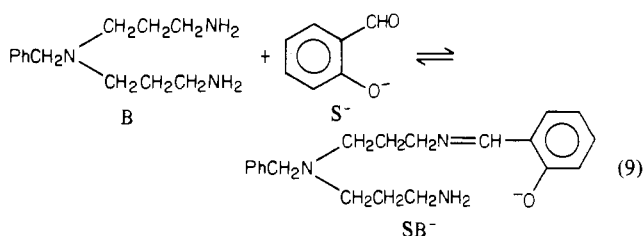
The potentiometric study of the bis(imine) (ligand **2b**) formed by a 2:1 molar ratio of salicylaldehyde to bzdpt involves

Table IV. Equilibrium Constants for Imine Formation between Salicylaldehyde (S) and 4-Benzyl-diethylenetriamine (bzdien) or 5-Benzyl-dipropylenetriamine (bzdpt) in 70% Dioxane at 25.0 °C, $\mu = 0.100$ M KNO₃ (Symbols Defined in Eq 9–14)

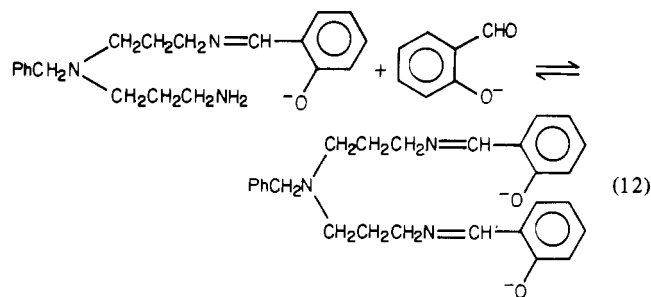
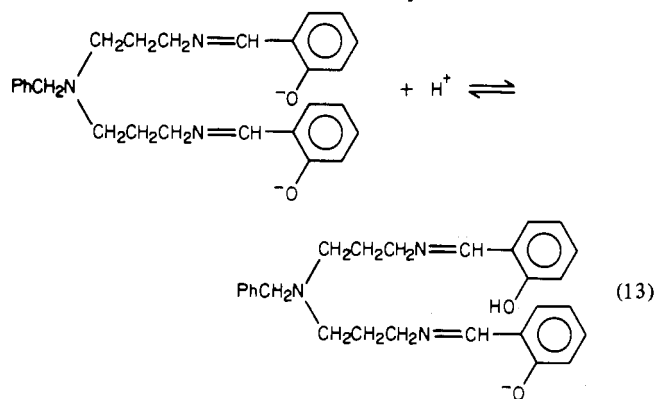
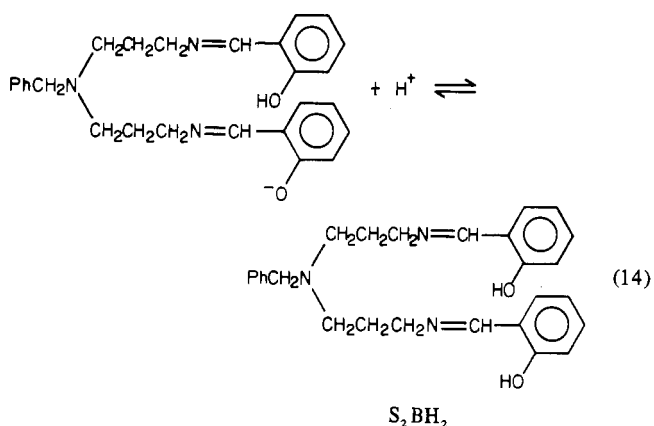
equilibrium quotient	log value		eq
	S-bzdpt ^a	S-bzdien ^b	
$[\text{SB}^-]/([\text{B}][\text{S}^-])$	5.44	2.91	9
$[\text{S}_2\text{B}^{2-}]/([\text{SB}^-][\text{S}^-])$	2.99	3.07	12
$[\text{SBH}]/([\text{SB}^-][\text{H}^+])$	10.88	13.96	10
$[\text{SBH}_2^+]/([\text{SBH}][\text{H}^+])$	8.57	9.93	11
$[\text{S}_2\text{BH}^-]/([\text{S}_2\text{B}^{2-}][\text{H}^+])$	11.33	13.72	13
$[\text{S}_2\text{BH}_2]/([\text{S}_2\text{BH}^-][\text{H}^+])$	10.08	13.36	14

^a σ for the buffer region is 0.05 log unit for recomputation of the pH curve relative to the observed curve. ^b σ for the buffer region is 0.03 log units for recomputing the pH values to the observed curve.

the protonation constant of salicylaldehyde anion (eq 6), the three protonation constants of bzdpt listed in Table I, and eq 9–14.

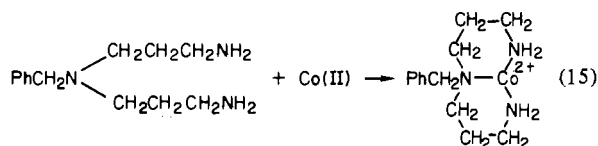


The equilibrium constants governing the concentration of each species have been calculated and are shown in Table IV. Over a range of pH from acidic to alkaline solutions, reaction systems consisting of stepwise imine formation, metal ion coordination by the imine, and eventual coordination of dioxgen by the Co(II) imine chelate are extremely complex, involving many component species with their individual protonation equilibria. Starting at low pH, the salicylaldehyde–5-benzyl-dipropylenetriamine system contains only the protonated forms of the components salicylaldehyde and the benzyl-substituted triamine, with the metal ion partially complexed, as indicated in Figure 2. The first sign of Schiff base (SBH₂) formation occurs at pH 6.5; its concentration reaches a maximum at pH 7.7 and becomes negligible at pH 9.8. The species SBH appears at pH 7.2, reaches its maximum concentration of 22% at pH 9.2, and becomes negligible beyond pH 11.4. SB⁻ appears at pH 9.0 and grows to about 50% by pH 11.4. The species S₂BH₂ appears above pH 6.5, reaches its maximum concentration of 64% at pH 8.8, and then decreases to a relatively low concentration at pH ~11.2. The

 S_2B^{2-}  S_2BH^-  S_2BH_2

species S_2BH^- appears at pH 8.4, reaches its highest concentration (43%) at pH 10.7, and decreases to 18% at pH 10.4. The completely deprotonated imine S_2B^{2-} gradually increases in concentration at high pH, reaching a value of $\sim 31\%$ at pH 11.4. The maximum extent of imine formation for all degrees of protonation occurs between pH 9.1 and 9.8.

The 1:1 bzdpt-Co(II) chelate was studied potentiometrically in the absence of oxygen to obtain its formation constant and under dioxygen in order to determine the oxygenation constant. The logarithm of the formation constant ($\log K_{ML}$) defined by eq 15 was calculated to be 7.14 ± 0.03 . This value is 2



log units less than $\log K_{ML}(\text{bzdien}) = 9.03$ reported in Table III, indicating lower complexation due to larger ring size. At high pH values, the hydrolysis reaction shown by (16) became

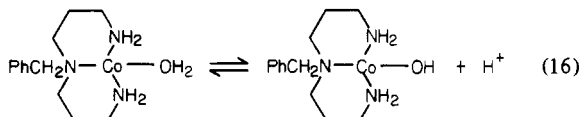


Table V. Species Considered in Calculation of Oxygenation Constants in the bzdien-Salicylaldehyde-Co-O₂ System

no.	log β	composition				H ⁺
		bzdpt	sal	Co(II)		
1	0.0000	1	0	0	0	
2	9.9800	1	0	0	1	
3	18.6900	1	0	0	2	
4	0.0000	0	1	0	0	
5	10.1800	0	1	0	1	
6	0.0000	0	0	1	0	
7	-16.0000	0	0	0	-1	
8	0.0000	0	0	0	1	
9	2.9100	1	1	0	0	
10	16.8700	1	1	0	1	
11	26.7900	1	1	0	2	
12	5.9800	1	2	0	0	
13	19.7000	1	2	0	1	
14	33.0700	1	2	0	2	
15	9.0300	1	0	1	0	
16	14.6800	1	0	1	1	
17	14.1000	2	0	2	-1	
18	48.0000	2	4	2	0	

Table VI. Species Considered in Calculation of Oxygenation Constants in the bzdpt-Salicylaldehyde-Co-O₂ System

no.	log β	composition				H ⁺
		bzdpt	sal	Co(II)		
1	0.0000	1	0	0	0	
2	10.1200	1	0	0	1	
3	19.2400	1	0	0	2	
4	24.6600	1	0	0	3	
5	0.0000	0	1	0	0	
6	10.1800	0	1	0	1	
7	0.0000	0	0	1	0	
8	-16.0000	0	0	0	-1	
9	0.0000	0	0	0	1	
10	5.4400	1	1	0	0	
11	15.8800	1	1	0	1	
12	24.4500	1	1	0	2	
13	8.4300	1	2	0	0	
14	19.7600	1	2	0	1	
15	29.8400	1	2	0	2	
16	7.1400	1	0	1	0	
17	-2.2600	1	0	1	-1	
18	14.4500	2	0	2	-1	
19	49.5000	2	4	2	0	

significant, and its pK_a was found to be 9.40. Under oxygen, the brown binuclear dibridged dioxygen complex was formed according to the equilibrium reaction (17). The overall



equilibrium constant for this oxygenation reaction is defined by $\log K = \log ([M_2L_2O_2(OH)][H^+]/([M]^2[L]^2p_{O_2})) = 14.4 (\pm 0.2)$. An equivalent expression based on the preformed metal-triamine chelate is

$$\log K' = \log \left(\frac{[M_2L_2O_2(OH)][H^+]}{[ML]^2p_{O_2}} \right) = 0.17$$

The formation of this oxygen complex takes place in the p[H] range 6.0–8.0 when $p_{O_2} = 1$ atm.

In a manner analogous to the bzdpt case, the formation and protonation constants for the imine of salicylaldehyde and bzdien have been calculated, and the results are listed in Table IV. The general conclusion that may be drawn from that data in Table IV is that the dien-imine system is more basic (i.e., thus higher metal ion affinity) than is the dpt-imine system.

4-Benzyl-diethylenetriamine was also equilibrated with Co-

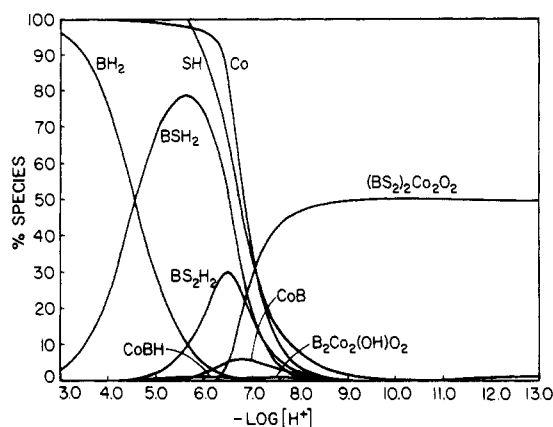


Figure 2. Species distribution diagram for the 4-benzyl-diethylenetriamine (BZ)-salicylaldehyde (S)-cobalt(II)-dioxygen systems ($[BZ] = 2.00 \times 10^{-3}$ M; $[S] = 4.00 \times 10^{-3}$ M; $[Co(II)] = 2.00 \times 10^{-3}$ M; $\mu = 0.100$ M (KNO_3); $t = 25.0$ °C; solvent is 70% dioxane).

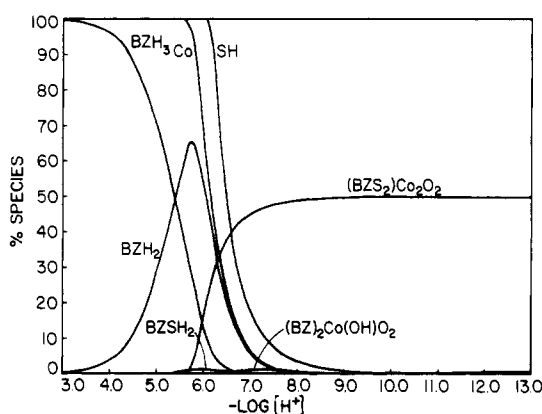


Figure 3. Species distribution diagram of the 5-benzyl-dipropylenetriamine (B)-salicylaldehyde (S)-cobalt(II)-dioxygen system ($[B] = 2.00 \times 10^{-3}$ M; $[S] = 4.00 \times 10^{-3}$ M; $[Co(II)] = 2.00 \times 10^{-3}$ M; $\mu = 0.100$ M (KNO_3); $t = 25.0$ °C; solvent is 70% dioxane).

(II) under oxygen, and the corresponding constant, as defined by eq 17, was determined:

$$\log K = \log \left(\frac{[M_2L_2O_2(OH)][H^+]}{[M]^2[L]^2P_{O_2}} \right) = 14.10 (\pm 0.05)$$

This equilibrium constant may be written in the form

$$\log K' = \log \left(\frac{[M_2L_2O_2(OH)][H^+]}{[ML]^2P_{O_2}} \right) = -3.96$$

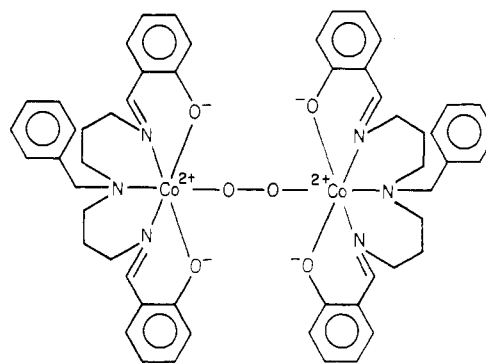
Thus, probably for steric reasons, the affinity for dioxygen of the cobalt complex containing five-membered chelate rings appears to be weaker by 4 orders of magnitude than that of the analogous complex containing six-membered chelate rings.

In 70% dioxane solution, in the presence of Co(II), the dioxygen complexation tendency is so strong, with both salicylaldehyde imines (i.e., bzdpt and bzdien), that it was difficult to prevent some formation of the dioxygen complex even under rigorous anaerobic conditions. Further experiments were carried out in the presence of 1 atm of oxygen. Although it was difficult to obtain precise equilibrium data, because of the sluggishness with which the large number of simultaneously competing reactions adjust themselves, the titration data in the region where brown color forms (pH 6–8) has been analyzed for both ligands **2a** and **2b**. The species considered in the calculation are shown in Tables V and VI, respectively.

The last entry represents the equilibrium quotient given by eq 18. The formula $(SB)_2Co_2O_2$ for the bzdpt ligand may

$$\beta = \frac{[(SB)_2Co_2O_2]}{[Sal]^4[B]^2[Co]^2P_{O_2}} = 10^{48.0 (\pm 0.1)} \text{ (Table V) or } 10^{49.5 (\pm 0.1)} \text{ (Table VI)} \quad (18)$$

be represented by **6**. This seemingly large constant could be



6
monobridged dioxygen complex from Co(II)
of sal-bzdpt Schiff base chelate

more easily compared with oxygenation constants of other complexes if the overall formation constant were known under oxygen-free conditions and were factored out of the quotient of eq 18.

The brown color of the oxygen complex that appeared at low pH was formed from the imine chelate of benzyldiethylenetriamine. However, calculation of the overall stability constant ($\log \beta = 48.0$) for the oxygen complex involving this ligand showed it to be weaker than that of the cobalt bzdpt chelate. More detailed comparisons between the bzdpt and bzdien imine systems cannot be made without the determination of the normal imine-cobalt stability constant.

Figures 2 and 3 show the chemical speciation of the two cobalt Schiff base complexes under dioxygen as a function of pH. The most obvious difference is the substantially larger amounts of partially formed Schiff base in bzdien as contrasted with the results obtained for bzdpt. In the latter case the species are negligible intermediates under O_2 . It is interesting to note that the tendency toward dioxygen complex formation in these systems is very strong, even though formation of the Co(II) complexes of the bis(Schiff bases) is never complete, even at very high pH. Although the stability constants of the oxygen-free complexes must be quite high, lack of completeness of the reaction is ascribed to incomplete formation of the bis(Schiff bases) in solution and the strong proton affinities of the Schiff bases and their components, resulting in competition between protons and metal ions for the ligands. Also, the coordination of Co(II) by the precursors of the Schiff bases provide additional competition. For both the bzdpt and bzdien Schiff base Co(II) chelates, the affinity for dioxygen is so high that the oxygenation reactions go to completion in spite of lack of complete formation of the bis(Schiff base) chelate in the absence of dioxygen. Thus although the bis(Schiff bases) and their Co(II) chelates are highly dissociated in water or water-dioxane solvent systems, Schiff base chelate formation is driven to completion by the subsequent oxygenation reaction. Although this is an unusual phenomenon, a parallel case has been reported by Harris et al.¹⁴ for the binuclear dioxygen complex formed when the bis(glycylglycinato) cobalt(II) complex $[(H_1GG)_4Co_2O_2]$, where HGG represents the gly-

(14) Harris, W. R.; McLendon, G.; Martell, A. E. *J. Am. Chem. Soc.* **1976**, *98*, 8378.

cylglycine. In this case the bis Co(II) complex of the deprotonated dipeptide is not completely formed unless oxygen is present.

Acknowledgment. This research was supported by the Gas Research Institute, Basic Research Department, under Con-

tract 5014-361-0282.

Registry No. 2a, 80525-55-9; 2b, 80525-56-0; 3a, 88057-06-1; 3b, 88057-08-3; 4a, 88057-10-7; 4a·5HCl, 88057-07-2; 4b·5HCl, 88057-09-4; bzdien, 23539-10-8; bzdp, 1555-71-1; 4-benzyl-1,7-dithaloyldiethylenetriamine, 23538-88-7.

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Unusual Structural, Chemical, and Magnetic Properties of Mononuclear Iron(III) Complexes of the Potentially Binucleating Ligand *meso*- $\alpha,\alpha,\alpha,\alpha$ -Tetrakis(*o*-nicotinamidophenyl)porphyrin

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Received October 26, 1982

The preparation and characterization of a series of Fe(III) complexes of the potentially binucleating ligand *meso*- $\alpha,\alpha,\alpha,\alpha$ -tetrakis(*o*-nicotinamidophenyl)porphyrin, FeX(P-N₄), is described (X = Cl, Br, OH, N₃). A crystal structure of FeCl(P-N₄)-CHCl₃·H₂O has been determined. Crystal data: space group *P*2₁/*c*, *a* = 14.739 (6) Å, *b* = 21.924 (7) Å, *c* = 19.524 (6) Å, β = 101.03 (3)°, *Z* = 4, *V* = 6192.4 Å³, 5042 unique reflections, *R* = 0.104. The structure consists of polymeric chains, with the Fe atom of one molecule coordinated to a pyridine N of the nicotinamide unit of a second molecule. The chloride ion occupies the sixth coordination site, inside the "pocket" of the four nicotinamide groups. The Fe is displaced 0.109 (1) Å from the mean plane of the porphyrin toward the Cl⁻. Long Fe-Cl (2.31 (2) Å) and Fe-N_{py} (2.085 (6) Å) distances and an average Fe-N_{porph} distance of 2.042 (8) Å indicate an essentially high-spin Fe, which is accommodated by an *S*₄ ruffling of the porphyrin. Magnetic susceptibility, ESR, and Mössbauer data on solid samples were interpreted as follows: FeCl(P-N₄)-CHCl₃, a mixture of high-spin monomer and high-spin Heisenberg chain, *D* = 10 ± 0.5 cm⁻¹, *E* = 2.25 ± 0.25 cm⁻¹, *J* = -5 ± 0.2 cm⁻¹, fraction of monomer = 0.70 ± 0.02, contributions from spin crossover are also possible; FeBr(P-N₄)-CHCl₃ sample 1, containing hexane of solvation, similar to Cl⁻, *D* = 10 cm⁻¹, *E* = 0.8 cm⁻¹, *J* = -8 cm⁻¹, α = 0.57; FeBr(P-N₄)-CHCl₃, containing no hexane, spin-crossover behavior, *g*(low-spin state) = 2.21, λ (spin-orbit coupling constant of ²T₂ state) = -340 cm⁻¹, ΔE (zero-point energy difference ⁶A₁ - ²T₂) = 80 cm⁻¹, *c*(ratio of vibrational partition functions of the high- and low-spin molecules) = 4.0; FeOH(P-N₄)-CHCl₃, high spin, *D* = 5.3 ± 0.1 cm⁻¹, *E* = 0.05 ± 0.05 cm⁻¹; FeN₃(P-N₄)-CH₃OH, kinetically controlled spin-crossover, parameters for low-temperature high-spin molecules (22.4%) *D* = 5 cm⁻¹ and *E* = 0.02 cm⁻¹, low-spin molecules (77.6%) λ = -340 cm⁻¹, Δ = 1320 cm⁻¹, *V* = 606 cm⁻¹, and κ = 0.83. The solution behavior is more straightforward and resembles that of other 5- or 6-coordinate Fe(III) porphyrins, with respect to UV-visible, ESR, and NMR spectra and ligand binding. The hydroxo complex FeOH(P-N₄) is fully characterized and its properties are compared with those of the closely related μ -oxo oligomer [Fe(P(NO)₄)₂]₂O.

Introduction

A correlation between the structural multiformity exhibited by their iron porphyrin centers and the functional diversity of the hemoproteins has been the underlying objective of many of the more recent studies of the chemistry of simpler, well-defined and characterized ferrous and ferric porphyrins. The synthetic analogue approach has been applied successfully to the resolution of fundamental questions concerning the function-related structure of the oxygen carriers hemoglobin and myoglobin,² the electron-transporting cytochromes *c*³ and *c*'⁴; the oxygenase cytochromes P450,⁵ and as yet with more limited success to cytochrome oxidase.⁶⁻¹²

Our approach^{6,7} to a synthetic model for cytochrome oxidase has involved the synthesis of iron porphyrins containing appended ligand systems capable of binding Cu²⁺ ions. The first such system⁶ incorporated a tetrapyrroline arrangement potentially capable of tetragonal, square-planar, or square-pyramidal coordination to Cu²⁺. Although we have now shown that this binuclear system has restrictions as a model in that magnetic-exchange coupling between the two metal centers is limited,^{6,13,14} interpretation of the physical behavior of these

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