of XeO_2F_2 can be derived from that of XeF_2 by replacing two free equatorial valence-electron pairs on xenon by two doubly bonded oxygen atoms.

Acknowledgment. We are grateful to Dr. C. J. Schack and R. D. Wilson for their help and to the Office of Naval Research for financial support.

Registry No. $XeO_2F^+AsF_6^-$, 115117-21-0; $[FO_2XeFXeO_2F]^+AsF_6^-$, 13875-06-4; XeO_2F_2, 13875-06-4; AsF_5, 7784-36-3.

Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Potentiometric Determination of the Stabilities of Cobalt(II) Complexes of Polyamine Schiff Bases and Their Dioxygen Adducts

Ramunas J. Motekaitis and Arthur E. Martell*

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Potentiometric measurement of hydrogen ion concentration, previously employed for the determination of oxygenation constants of cobalt(II) complexes in aqueous and mixed aqueous solvents, is now extended to the determination of equilibrium constants for Schiff base ligands and for the determination of oxygenation constants for systems in which the ligands and/or their metal complexes are not completely formed in the absence of dioxygen or in the absence of the cobalt(II) ion. The method is illustrated by the potentiometric measurement of oxygenation constants for solutions in 70% dioxane–30% water (v/v) containing cobalt(II) chloride and the following ligand components: 1, salicylaldehyde and *N*,*N*′-bis(2-aminoethyl)dipicolinic acid diamide; 2, salicylaldehyde and *N*,*N*-bis(2-aminophenyl)methylamine; 3, salicylaldehyde, ethylenediamine, and 4-methylpyridine; and 4, 3-fluorosalicylaldehyde, *o*-phenylenediamine, and 4-methylpyridine. The stability constant and dioxygen affinity are also reported for the cobalt(II) complex of a pentadentate ligand, *N*,*N*-bis(2-((2-hydroxybenzyl)amino)phenyl)methylamine, produced by hydrogenation of the Shiff base formed from salicylaldehyde and *N*,*N*-bis(2-aminophenyl)methylamine. The equilibrium parameters obtained provide all the information necessary to calculate the concentrations of all molecular species present in solution at 25.00 °C and 0.100 M ionic strength as a function of p[H] and solution composition. The results are displayed for each system as distribution curves consisting of species concentration profiles vs p[H] at specific concentrations of solution components.

Introduction

The potentiometric determination of hydrogen ion concentration has long been the technique most frequently employed for the determination of metal ion–ligand stability constants.[1] It is also one of the more accurate techniques for that purpose because of improved methods of data processing and the development of improved equipment for the measurement of hydrogen ion concentration. The application of the method to complex formation requires a mobile equilibrium involving dependence of degree of complex formation on hydrogen ion concentration, under conditions such that the concentrations of all species involved in the equilibrium may be determined accurately. During the past decade, this method has also been employed for the determination of dioxygen affinities (oxygenation equilibrium constants) of cobalt complexes of polyamines, amino acids, and related complexes.[2] Although the oxygenation reaction itself does not usually involve hydrogen ion displacement, dioxygen reacts only with the metal ion complex itself, thus producing a shift of prior hydrogen ion dependent equilibria, so that hydrogen ion concentration is sensitive to the degree of oxygenation.

More recently, it has become apparent that the potentiometric method may be extended one step further—the determination of oxygenation constants of metal complexes that are not formed at all, or not fully formed, in the absence of dioxygen. This experimental technique has now been extended one step further—the determination of oxygenation constants of cobalt(II) complexes for which even the ligand itself is not completely formed in the absence of dioxygen. Several examples of this type of reaction, involving salicylaldehyde–polyamine type Schiff bases, have recently been studied in this laboratory, and several examples of such systems are now presented for the first time in this paper.

Because of the nature of the compounds involved, it was not possible to study these compounds in aqueous systems. The organic components of the ligands, as well as the ligands themselves, are not soluble in water but are soluble in mixtures of water with compatible low dielectric constant solvents such as dioxane and tetrahydrofuran. The water–dioxane system was thoroughly investigated as a medium for potentiometric hydrogen ion concentration measurement up to 70% v/v dioxane by Van Uitert et al.[3] The only previous report of the use of the potentiometric method for the determination of Schiff base formation and cobalt dioxygen complex formation is a paper by Motekaitis et al.[4]

In addition to the improved solubility of the aromatic aldehyde components of the systems under investigation, an advantage of using the dioxane–water mixed solvent lies in the favorable reduction in the dielectric constant of the medium relative to pure water, resulting in more complete formation of the Schiff base. A further advantage is its compatibility with the standard glass electrode (both theoretically and practically) so that the required p[H] measurements may be carried out in a manner similar to that employed in purely aqueous systems.

Experimental Section

Dipicolinic Acid Dimethyl Ester. A 16.7-g (0.100-mol) sample of dipicolinic acid (Aldrich), 100 g of anhydrous methanol (MC/B), and 3.0 g (0.030 mol) of 98% sulfuric acid (Baker) were placed in a flask fitted with a reflux condenser, a magnetic stirrer, and a drying tube. H_2SO_4 was added last, through the condenser. After 2-h reflux, about one-fourth of the volume was evaporated off and the solution was allowed to cool, whereupon a colorless crystalline product was isolated: mp 125–128 °C, 12.2 g (62%). Additional material to a total of 90% was obtained from the mother liquor (lit.[5] mp 121 °C). ^1H NMR ($CDCl_3$), δ: 4.04 (6 H, CH_3); 8.40 (3 H, m, pyridyl).

Preparation of *N*,*N*′-Bis(2-aminoethyl)dipicolinic Acid Diamide Schiff Base. A 9.8-g (0.050-mol) sample of dimethyl 2,6-pyridinedicarboxylate and 50.0 mL (45 g, 0.75 mol) (1:15) of ethylenediamine were refluxed in an Ascarite-protected flask. Two-hour reflux was followed by 10-h storage at room temperature. The reaction mixture was diluted with methanol, filtered, and stored at 0 °C. All volatile materials were then removed by vacuum distillation. The residual oil was found by titration to be nearly pure diamide. ^1H NMR ($CDCl_3$), δ: 3.80 (4 H, sharp multiplet, CH_2NH_2); 7.3 and 6.9 (t's, 4 H, CH_2NHCO, syn and anti); 8.30 (m, 3 H, pyridyl).

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A 3.7-g portion of the diamide was treated with 2.7 g of salicylaldehyde in 40 mL of MeOH, heated for $^1/_2$ h at boiling. Upon cooling, the beautiful yellow microcrystals that formed, mp 205–210 °C (72%), were characterized by NMR spectroscopy and potentiometric titration. ^{1}H NMR ($CDCl_3$), δ: 3.78 (m, 4 H, CH_2N=); 7.25, 7.11, and 6.88 (three multiplets, 8 H, phenol); 8.26 (m, 5 H, pyridyl and =C*H*).

Solution of Pure *N*,*N*′-Bis(2-aminoethyl)dipicolinic Acid Diamide (OPYDIAMIDE). To 0.459 g (1.00 mmol) of Schiff base was added 30.0 mL of 0.100 M HCl. The yellow solid dissolved to form a colorless solution. The solution was then heated with stirring until its volume was reduced to approximately 5 mL (i.e., this process steam-distills off all salicylaldehyde). The solution was transferred to a volumetric flask, and an aliquot of what proved to be the pure trihydrochloride of the diamide was characterized by potentiometric titration.

Other Materials. The synthetic procedures for the preparation of *N*,*N*-bis(2-((2-hydroxybenzyl)amino)phenyl)methylamine and *N*,*N*-bis(2-aminophenyl)methylamine are described elsewhere.[6] Ethylenediamine and *o*-phenylenediamine were employed as the dihydrochlorides, which had been purified before use by recrystallization. The inorganic reagents employed were of the highest purity available (reagent grade).

Solvents and Standard Solutions. The dioxane employed was Spectrograde from Aldrich, further purified by warming with $FeCl_2$ under nitrogen for 10 h, filtering, warming with solid KOH for several hours, filtering, and distilling through a 1.5-cm, 1.5-ft Vigreaux column. The first 20% of the distillate was discarded. The water employed was purified by ion exchange and was doubly distilled (one time from $KMnO_4$). Standard base was prepared from Dilut-it carbonate-free KOH and made up to a 0.1000 M solution in 70% dioxane–30% water solution, v/v. It was standardized with the use of a linear least-squares fit to Gran's plots[7] for end point determination of titrations with standard HCl solution.

Potentiometric Measurements. The sealed 100-mL thermostated double-walled glass reaction vessel was fitted with extension blue glass p[H] and calomel reference electrodes, gas inlet and outlet tubes, a magnetic stirrer, and a titrant inlet. Readings of $-\log [H^+]$ were obtained with a Corning Model 130 pH meter. The titrant was delivered through an immersed capillary tip from a Metrohm piston buret, and the temperature was maintained at 25.00 ± 0.01 °C by circulation of water from a refrigerated constant-temperature bath.

The pH meter–electrode system was calibrated before each experiment to read p[H] (i.e., $-\log [H^+]$) directly by using a 70% dioxane–30% water solution of 0.100 M ionic strength adjusted with KCl and containing 0.0100 M HCl. It was titrated with successive quantities of 0.1000 M KOH in the same solvent so as to obtain p[H] readings both below and above the neutral p[H] value. The ion product constant ($K_w = [H^+][OH^-]$) was found to be $10^{-16.00}$ for this solvent system.

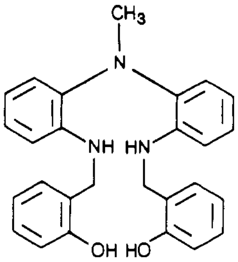
In a typical experiment, a solution containing about 0.10 mmol of ligand or ligand components was placed in the cell. The required amounts of KCl (from a 1.000 M stock solution), HCl (0.1000 M), and $CoCl_2$ (0.0250 M) were added. Additional water was added to a volume of 15.60 mL. Finally, 36.4 mL of dioxane was added, and the reaction vessel was sealed with the appropriate connections described above. The total volume, calibrated in a separate experiment, was 51.22 mL. After a suitable time to establish equilibrium, determined by a p[H] drift of less than 0.001 p[H] unit in 5 min, the p[H] reading was taken and a small volume of standard KOH solution was added. The procedure was repeated so as to provide 50–60 p[H] values for each equilibrium p[H] profile. However, in the determination of oxygenation constants five to eight points were determined in the long equilibrium buffer region.

All computations were carried out with the interactive FORTRAN program BEST,[8] with the aid of a VAX, PDP, or HP 150 computer. Species distribution diagrams were drawn with the aid of a HP 150 II Touchscreen Computer, with the use of the FORTRAN/77 program SPELAZ to generate percentages of species as a function of p[H]. The plotting of these data was carried out on a HP/LASERJET$^+$ driven by the Microsoft GWBASIC program SPEPLOT.

Results

The Co(II) complexes for which dioxygen affinities have been determined by the potentiometric method in this research are indicated by formulas **1–5** (Chart I). The cobalt(II) complexes were not isolated but were formed in solution, and the oxygenation equilibrium constants were measured in each case by the shifts in protonation equilibria resulting from dioxygenation of the ligand, as described above. The oxygenation constants, stability constants of the cobalt(II) complexes, the equilibrium constants of Schiff base formation (where applicable), and the protonation equilibrium constants of the Schiff bases and their components are presented in Tables I–V. It is noted that in only one case, complex **1**, was the pure ligand employed. This was possible because this pentadentate ligand does not dissociate in solution, having been obtained by hydrogenation of the two double bonds of the corresponding Schiff base used to form complex **2**. It is noted that in one case, **2**, the basicity of the polyamine is so low that the 1:1

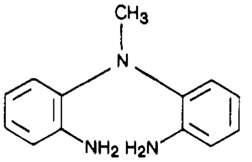
Table I. Equilibrium Constants for *N*,*N*-Bis(2-((2-Hydroxybenzyl)amino)phenyl)methylamine and Co^{2+} in 70% v/v Dioxane–H_2O (t = 25 °C, μ = 0.100 M (KCl))



H_2L

quotient	log value	σ
$[HL]/([H][L])$	13.65	0.003
$[H_2L]/([H][HL])$	12.19	
$[H_3L]/([H][H_2L])$	1.8	
$[H_4L]/([H][H_3L])$	<1.7	
$[CoL]/([Co][L])$	14.21	0.29
$[CoH_2L]/([CoL][H]^2)$	16.20	
$[(CoL)_2O_2]/([Co]^2[L]^2P_{O_2})$	33.08	0.15
or $[(CoL)_2O_2]/([CoL]^2P_{O_2})$	4.65	(alternate expression)

Table II. Equilibrium Constants for a Solution of *N*,*N*-Bis(2-aminophenyl)methylamine, Salicylaldehyde, and Co^{2+} in 70% v/v Dioxane–H_2O[a] (t = 25 °C, μ = 0.100 M (KCl))



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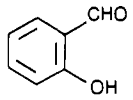
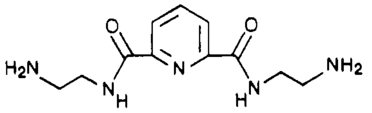


SH

quotient	log value	σ
$[BH]([H][B])$	2.60	0.002
$[BH_2]/([H][BH])$	1.61	
$[SH]/([S][H])$	10.18	
$[CoB]/([Co][B])$	2.84	0.005
$[S_2BCo]/([S]^2[B][Co])$	14.12	0.04
$[(S_2BCo)_2O_2]/([S]^4[B]^2[Co]^2P_{O_2}$	36.54	0.1
or $[(S_2BCo)_2O_2]/([S_2BCo]^2P_{O_2})$	8.30	(alternate expression)

[a] S_2B or SB did not form in this medium.

Table III. Equilibrium Constants for Solutions Containing Salicylaldehyde, Co^{2+}, and *N*,*N*′-Bis(2-aminoethyl)dipicolinic Acid Diamide in 70% v/v Dioxane–H_2O (t = 25 °C, μ = 0.100 M (KCl))



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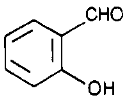

SH

quotient	log value	σ
$[BH]/([H][B])$	9.42	0.011
$[BH_2]/([BH][H])$	8.53	
$[BH_3]/([BH_2][H])$	1.82	
$[SH]/([S][H])$	10.18	
$[HSB]/([B][S][H])$	14.66	0.11
$[H_2S_2B]/([B][S]^2[H]^2)$	27.94	
$[(S_2BCo)_2O_2]/([S]^4[B]^2[Co]^2P_{O_2}$	51.01	0.012

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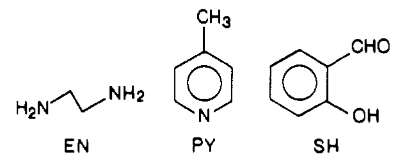
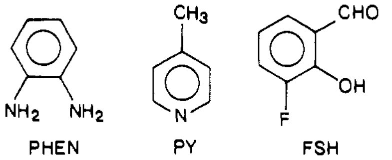
Table IV. Stability Constants of the Salicylaldehyde–Ethylenediamine–4-Methylpyridine–Co^{2+} System in 70% v/v Dioxane–H_2O (t = 25.0 °C, μ = 0.100 M (KCl))



quotient	log value	σ
$[ENH]/([EN][H])$	9.88	0.01
$[ENH_2]/([ENH][H])$	7.37	
$[CoEN]([Co][EN])$	7.36	
$[CoEN_2]/([CoEN][EN])$	6.91	0.01
$[CoEN_3]/([CoEN_2][EN])$	3.55	
$[CoEN_2OH][H]/[CoEN_2]$	−9.44	
$[PYH]([PY][H])$	4.36	0.03
$[SH]([S][H])$	10.18	previously determined
$[SEN]([S][EN])$	3.81	
$[SENH]([SEN][H])$	9.73	
$[SENH_2]/([SENH][H])$	9.25	0.02
$[S_2EN]([SEN][S])$	4.11	
$[S_2ENH]/([S_2EN][H])$	9.55	
$[S_2ENH_2]/([S_2ENH][H])$	9.24	
$[SENCo]/([SEN][Co])$	14.21	
$[SENHCo]/([SENH][Co])$	9.05	
$[S_2ENCo]/([S_2EN][Co])$	14.56	
$[S_2ENCoOH][H^+]/[S_2ENCo]$	−9.93	0.06
$[S_2ENCo(OH)_2][H^+]/[S_2ENCo(OH)]$	−11.12	
$[(S_2ENPYCo)_2O_2]/([S]^4[EN]^2[PY]^2[Co]^2P_{O_2})$	54.02	0.05
or $[(S_2ENPYCo)_2O_2]/([S_2ENCo]^2[PY]^2P_{O_2})$	11.06	(alternate expression)

Table V. Stability Constants of the 3-Fluorosalicylaldehyde–4-Methylpyridine–*o*-Phenylenediamine–Co^{2+} System in 70% v/v Dioxane–H_2O (t = 25.0 °C, μ = 0.100 M (KCl))



quotient	log value	σ
$[PHENH]([PHEN][H])$	4.41	0.01
$[CoPHEN]/([Co][PHEN])$	1.95	0.02
$[PYH]([PY][H])$	4.36	0.03
$[FSH]/([FS][H])$	8.44	0.01
$[CoFS]/([Co][FS])$	3.77	0.02
$[CoFS_2]/([Co][CoFS])$	4.97	0.02
$[FSPHEN]([FS][PHEN])$	2.45	0.03
$[FSPHENH]/([FSPHEN][H])$	7.50	0.03
$[FS_2PHEN]/([FS][FSPHEN])$	2.46	0.03
$[FS_2PHENH]/([FS_2PHEN][H])$	11.23	0.02
$[FS_2PHENH_2]/([FS_2PHEN][H])$	8.41	0.05
$[FS_2PHENH_3]/([FS_2PHENH_2][H])$	3.17	0.04
$[FS_2PHENCo]/([FS_2PHEN][Co])$	14.91	0.02
$[FS_2PHENCoH]/([FS_2PHENCo][H])$	6.94	0.02
$[(FS_2PHENPYCo)_2O_2]/([FS]^4[PHEN]^2[PY]^2[Co^2]P_{O_2})$	38.68	0.07

and 2:1 Schiff bases do not form to an appreciable extent in the absence of metal ion. In another case, **3**, the cobalt(II) complexes of the 2:1 and 1:1 Schiff bases are not sufficiently stable in the absence of dioxygen to be detected by shifts in hydrogen ion concentrations. For each reaction system the components added to form complexes **1**–**5** are indicated in the headings of Tables I–V.

The distribution curves for each system, showing the concentrations of all species formed in solution in measurable concentrations, are presented in Figures 1–5. These graphical plots are simply another way of expressing the equilibrium parameters in Tables I–V but present the results in such a way that the relative stabilities of the complexes formed, and the resulting extent of formation of each complex under varying solution conditions, may be easily seen. The p[H] profiles obtained as primary data are essentially featureless, as is frequently the case for complex multicomponent systems. The species distribution curves provide a more understandable way of presenting the data and are obtained from the constants calculated as described above. These equilibrium constants may readily be converted to the measured p[H] profiles by reversing the calculations employed in their determination.

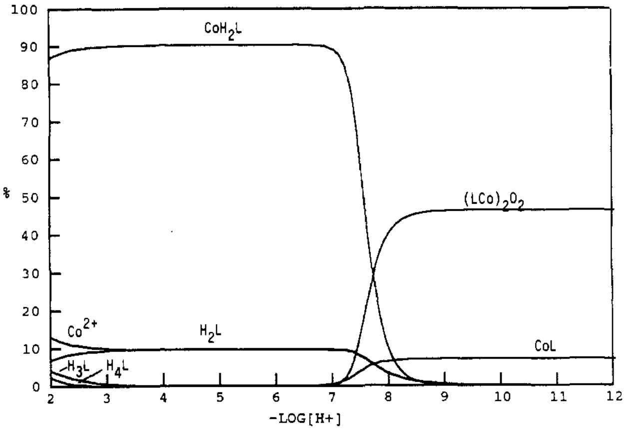


Figure 1. Species distribution as a function of p[H] (−log [H^+]) in aqueous 70% dioxane (μ = 0.100 M (KCl), t = 25.0 °C, P_{O_2} = 1.00 atm). The components consist of *N*,*N*-bis(2-((2-hydroxybenzyl)amino)phenyl)methylamine (L; 2.00 × 10^{-3} M) and Co(II) (2.00 × 10^{-3} M).

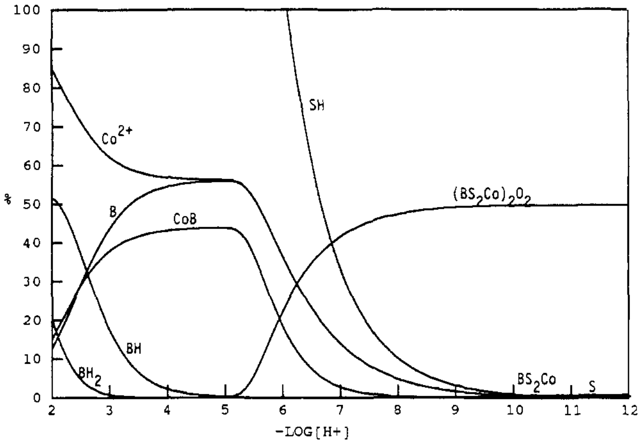


Figure 2. Species distribution as a function of p[H] (−log [H^+]) in aqueous 70% dioxane (μ = 0.100 M (KCl), t = 25.0 °C, P_{O_2} = 1.00 atm). The components consist of *N*,*N*-bis(2-aminophenyl)methylamine (B; 2.00 × 10^{-3} M), salicylaldehyde (SH; 4.00 × 10^{-3} M), and Co(II) (2.00 × 10^{-3} M).

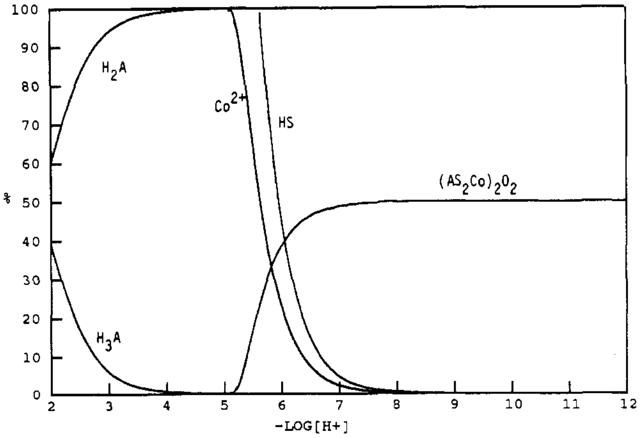


Figure 3. Species distribution as a function of p[H] (−log [H^+]) in aqueous 70% dioxane (μ = 0.100 M (KCl), t = 25.0 °C, P_{O_2} = 1.00 atm). The components consist of *N*,*N*′-bis(2-aminoethyl)dipicolinic acid diamide (A; 2.00 × 10^{-3} M), salicylaldehyde (SH; 4.00 × 10^{-3} M), and Co(II) (2.00 × 10^{-3} M).

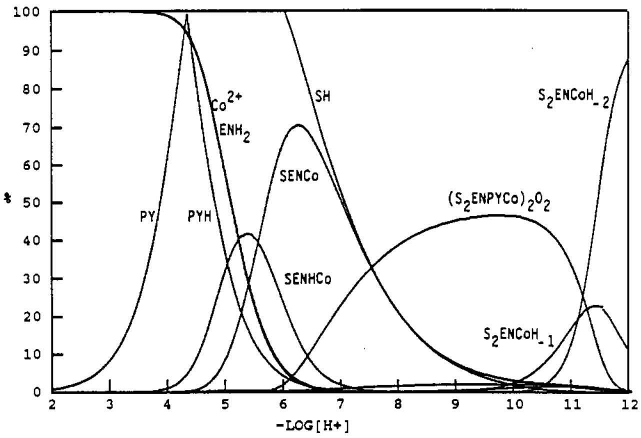


Figure 4. Species distribution as a function of p[H] (–log [H^+]) in aqueous 70% dioxane (μ = 0.100 M (KCl), t = 25.0 °C, P_{O_2} = 1.00 atm). The components consist of ethylenediamine (EN; 2.00 × 10^{-3} M), salicylaldehyde (SH; 4.00 × 10^{-3} M), Co(II) (2.00 × 10^{-3} M), and axial base 4-methylpyridine (PY; 4.00 × 10^{-3} M, 100% excess).

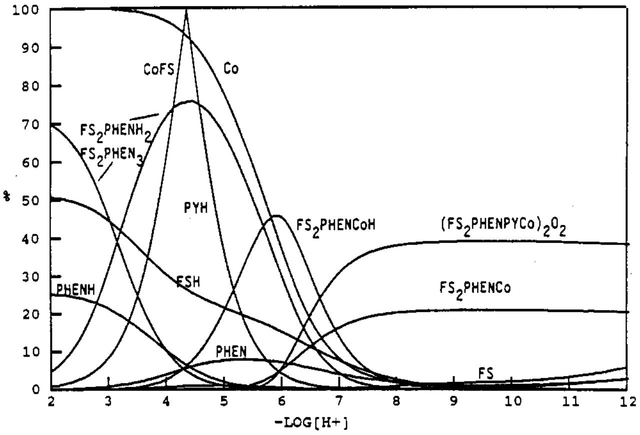


Figure 5. Species distribution as a function of p[H] (–log [H^+]) in aqueous 70% dioxane (μ = 0.100 M (KCl), t = 25.0 °C, P_{O_2} = 1.00 atm). The components consist of *o*-phenylenediamine (PHEN; 2.00 × 10^{-3} M), 3-fluorosalicylaldehyde (FS; 4.00 × 10^{-3} M), Co(II) (2.00 × 10^{-3} M), and axial base 4-methylpyridine (PY; 4.00 × 10^{-3} M, 100% excess).

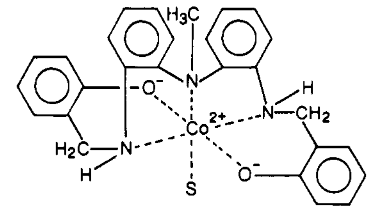
Discussion

Each of the oxygen carriers investigated are described below in the order of increasing complexity of the system. Thus, the pentadentate ligand MHBA provides the least complex system since only protonation and metal ion equilibria of the ligand are involved in formation of the cobalt dioxygen carrier, **1**. In the case of **2** and **3**, two salicylaldehydes combine with a triamine to form the ligand, so that four components are involved in possible metal ion and protonation equilibria. In the case of **4** and **5**, which involves simple diamines, an additional (axial) base is needed to form the oxygen carrier, making five components in the solution under conditions where the oxygen carrier is incompletely formed.

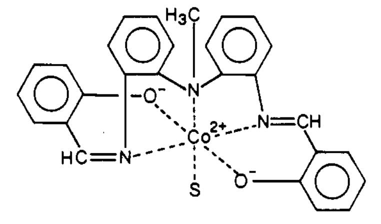
In this investigation it was found that only 2:1 (peroxo-bridged) dioxygen complexes are formed. This finding is consistent with many investigations which show that 1:1 dioxygen (superoxide type) complexes require aprotic solvents having low dielectric constants and steric constraints. The solvent employed in this research contains 30% water, which is equivalent to 68 mol % water. In the course of calculating oxygenation constants, the systems investigated were checked for 1:1 and 2:1 dioxygen complexes and for mixtures of 1:1 and 2:1 dioxygen complexes. Only with 2:1 complexes was it possible to fit the experimental data. It is of course understood that 1:1 adducts are essential intermediates in the formation of 2:1 complexes. However, under the conditions employed in this research, the concentrations of 1:1 complexes present at equilibrium are too low to be measured.

CoMHBA (1). This complex contains the only ligand that is not a Schiff base but that is synthesized by hydrogenation of the Schiff base MBA, described below. This pentadentate ligand contains two basic phenolic donor groups together with three very weakly basic amino groups. The phenolic donors would be expected to dissociate in the absence of metal ion only at very high p[H] values, and the acid dissociation constants having log K values of 12.19 and 13.65 are assigned to these functional groups. Since the pK_w of water in 70% dioxane solution (at μ = 0.100) is 16.00 (0.05), the two protonation reactions can be directly measured potentiometrically. This would not be the case for a purely aqueous solvent, which requires the use of spectrophotometry for the determination of very large protonation constants.[9] For the weakly basic amino groups only one protonation constant was found to be measurable (log K^H = 1.8), while a second is listed only as being less than log K^H = 1.7. These observations are consistent with the chemical structure of the ligand, in that the phenolic dissociation constants are about 1 log unit apart, indicating that they are essentially, but not quite, independent. The protonation reactions of the amino groups are probably highly

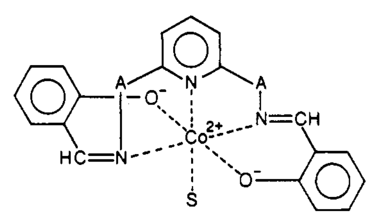
Chart I



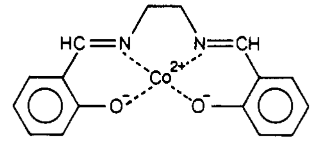
1: [*N*,*N*-bis(2-((2-hydroxybenzyl)amino)phenyl)methylaminato]cobalt(II) (CoMHBA)



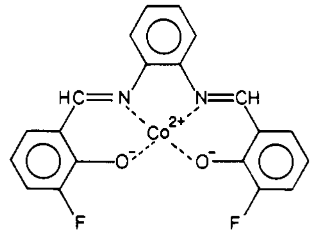
2: [*N*,*N*-bis(2-((2-hydroxybenzylidene)amino)phenyl)methylaminato]cobalt(II) (CoMBA)



3: [*N*,*N*′-bis(2-((2-hydroxybenzylidene)amino)ethyl)-2,6-pyridinedicarboxamidato]cobalt(II) (CoSALOPYDIAMIDE, A = $CONHCH_2CH_2$)



4: bis(salicylaldehyde ethylenediiminato)cobalt(II) (CoSALEN, SALCOMINE)



5: bis(3-fluorosalicylaldehyde *o*-phenylenediiminato)cobalt(II) (Co3FALOPHEN)

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[9] Taliaferro, C. H.; Martell, A. E. *J. Coord. Chem.* **1984**, *13*, 249.

interdependent because they are separated by conjugated bridges, but the low values of these constants preclude accurate measurements for quantitative comparisons.

In the absence of dioxygen, only two reactions with cobalt(II) were found to take place: the formation of the complex CoH_2L^{2+} and its two-proton dissociation to form the normal CoL complex. The simultaneous dissociation of two protons suggests that in the wrapping process, once one phenol becomes coordinated, its conformation is such that the energetics of coordination of the second phenolic oxygen become more favorable than those of the first. The complex formed initially at low p[H], involving only the amino donors, is not very stable, so that a maximum of only 90% coordination occurs. This is in contrast to the 100% formation when the more strongly coordinated groups actually become involved.

When the experiments are performed under aerobic conditions (1 atm of O_2), a single binuclear oxygen complex is formed at and above p[H] 7.5 and persists at higher p[H] values. The formulation of the complex is $Co_2L_2O_2$. The equilibrium distribution curves (Figure 1) show that this oxygen complex contains about 93% of the cobalt, with the remaining cobalt residing in the unoxygenated CoL species.

CoMBA (2). This species is an oxygen-carrying complex formed by the combination of Co(II) with a Schiff base formed from 2 mol of salicylaldehyde and 1 mol of *N*,*N*-bis(2-aminophenyl)methylamine. This is a pentadentate ligand consisting of a central very weakly basic amino group, two imine groups, and two phenolate donors. The methyl group is intended to discourage oxidation of what would otherwise be a secondary amine bound to two aromatic rings.

As expected, the protonation constants show *N*,*N*-bis(2-aminophenyl)methylamine to be extremely weakly basic. The highest log (protonation constant) is only 2.60 log units while the next one is ca 1.6. It is to be recalled that the corresponding protonation constants of MHBA discussed above are similar, 1.8 and less than 1.7. The coordination of Co(II) with *N*,*N*-bis(2-aminophenyl)methylamine is weak, as expected on the basis of the low basicity of the triamine, and is characterized by a 1:1 log (formation constant) of 2.84. The magnitude of this stability constant means that at millimolar concentrations of reactants the complex is largely dissociated at any p[H].

In the absence of dioxygen, the Co(II) ion helps to organize the weakly formed Schiff base as the Co(II) complex. The log of the overall stability constant of 14.12 cannot be readily compared to any analogues because similar complexes do not exist. Its value is really only meaningful in terms of a species distribution computed in the absence of oxygen. The highest concentration of the complex in solution is calculated to be about 95% at p[H] 10, but the solubility product of free Co(II) is certainly exceeded at much lower p[H], so that this degree of complexation would not be achieved. In the presence of oxygen, the Schiff base–Co(II) complex does indeed react with oxygen to give a quantitative conversion to the dioxygen complex by about p[H] 8. That the dioxygen complex concentration does not drop off at high p[H] values may be due to the fact that the computations at high p[H] do not take into account the formation of Schiff base–Co(II)–hydroxo complexes. The log of the overall constant for the formation of the binuclear oxygen complex from its components is 36.54, which is high when one considers the low overall basicity of the donor groups of the Schiff base.

The alternate algebraic expression shown in Table II has a log value of 8.3 and, when compared to oxygenation constants of other complexes, indicates moderately high dioxygen affinity.[10]

CoSALOPYDIAMIDE (3). The triamine ligand *N*,*N'*-bis(2-aminoethyl)-2,6-pyridinedicarboxamide is built around a weakly basic pyridine moiety and contains two widely separated moderately basic terminal primary amino groups attached to the heterocyclic ring through alkylamide functions. The amide groups would not be expected to participate in the coordination of the Co(II) ion. In the absence of metal ions, this ligand possesses successive log (protonation constant) values of 9.42 and 8.53, which involve the highly separated primary amino functions, while the third log (protonation constant) (for the pyridine nitrogen) is 1.82, indicating the electron withdrawal effects of the amide carbonyl in the 2,6-positions. In comparison, as indicated below, 4-methylpyridine has a much higher protonation constant.

In the presence of 1 molar equiv of Co(II), this ligand showed no measurable coordination tendency. This is not surprising, since its structure is characterized by three very widely separated amino groups, the most basic of which are separated by 12 atoms.

The p[H] measurements made it possible to identify two species formed by the reactions of the triamine with salicylaldehyde: the monoprotonated mono(salicylidene Schiff base) and the diprotonated bis(salicyclidene Schiff base). Only overall formation constants for the protonated imines could be calculated since the unprotonated forms were found to be too unstable to be measured reliably. The logarithms of the overall formation constants of the protonated Schiff bases are 14.66 and 27.94. The relative magnitudes of these constants indicate that the Schiff base formation reactions in the absence of metal ions are almost independent of each other.

Under nitrogen, the formation constants of the various Co(II) Schiff base complexes could not be determined because the interactions are too weak and insufficient concentrations are formed in solution. Under oxygen, however, the formation of the binuclear dioxygen complex proceeds completely and was found to be essentially complete at and above p[H] 7. Although the value of 51.01 found for the log (overall formation constant) for the formation of the bis(Schiff base) from its components in their most deprotonated states could not be interpreted on the merits of its magnitude alone, its intrinsic meaning is that this pentacoordinate system wraps around the Co(II) ion in a manner that promotes facile dioxygen complex formation.

CoSALEN (4). The purpose of investigating the SAL–EN–MePy–Co(II)–O_2 system was to calibrate the method and determine the feasibility of the potentiometric technique for a known system (although in a different solvent). Potentiometric studies illustrated for **1**–**3**, above, as well as *N'*-benzyldiethylenetriamine[11] did not involve the incorporation of an axial base. Since this system requires consideration of interactions of up to six components (H^+ ion is the sixth), many preliminary experiments were required to determine the equilibrium constants of the components before the oxygenation constant could finally be determined. This process resulted in the ultimate determination of some 20 equilibrium constants (Table IV), which represent the complete picture of this complex system in 70% dioxane as a function of p[H].

The Co^{II}SALEN dioxygen complex in the solid state has a planar arrangement of the ONNO donors wrapped around the central metal ion with an axial position occupied by a pyridine-like base, which in this case is 4-methylpyridine.[11] On the other hand, in aqueous 70% dioxane, depending on p[H], many cobalt(II) complexes of the components are capable of independent existence.

Ethylenediamine (EN) was studied independently in this solvent and was found to be characterized by log (protonation constant) values of 9.88 and 7.37. In water, the corresponding values are 9.89 and 7.08. Because EN is a bidentate ligand, the successive 1:1, 1:2, and 1:3 metal ion to ligand log (stability constant) values were likewise determined and were found to be 7.36, 6.91, and 3.55. In water these complexes are considerably weaker with corresponding values of 5.6, 4.9, and 3.3. It is interesting to note that in 70% dioxane at high p[H] a hydroxobis(ethylenediamine)cobalt(II) species was found to be present, with a log (protonation constant) of 9.44. In a solvent of low dielectric constant it is not unexpected that charge neutralization through hydroxo complex formation may be preferred over the addition of a neutral ligand.

The apparent basicity of 4-methylpyridine deserves comment. It is well-known that the "hyperconjugative" effect of a methyl

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[10] Niederhofer, E. C.; Timmons, J. H.; Martell, A. E. *Chem. Rev.* **1984**, *84*, 137.

[11] Calderazzo, F.; Floriani, C.; Salzman, J. J. *Inorg. Nucl. Chem. Lett.* **1966**, *2*, 379. Floriani, C.; Calderazzo, F. *J. Chem. Soc. A* **1969**, 946.

substituent feeds electron density into the aromatic ring, thus rendering a methyl-substituted pyridine more basic than the unsubstituted analogue. Indeed, in water it is observed that the log (protonation constant) of pyridine is 5.24,[13] while it increases to 6.04 for 4-methylpyridine. It was therefore surprising to discover that in aqueous 70% dioxane the value of the log (protonation constant) for 4-methylpyridine is only 4.36. Considering the similarity of the behavior of EN in water and in aqueous 70% dioxane as indicated above, the explanation probably lies in the differences in solvation effects of aromatic and aliphatic amines.

Although the acid dissociation constant 10.18 in aqueous 70% dioxane for salicylaldehyde was taken from the literature,[11] its comparison with the aqueous value of 8.13[12] had not been previously made. The solvent effect on the apparent basicity seems to be considerable. Since the stabilities of the salicylaldehyde complexes are generally low and are significant only at high p[H] and only in the absence of other stronger ligands, determination of the formation constants of cobalt(II)–salicylaldehyde complexes was considered unnecessary and therefore was not attempted.

In the absence of Co(II), it was found that initially (i.e. at low p[H]) salicylaldehyde and ethylenediamine form a diprotonated mono(Schiff base) and a diprotonated bis(Schiff base), which possess uniquely different donor groups. The mono(Schiff base) is terdentate with a basic phenol donor at one end and a basic amino group at the other, with a weakly basic imine donor between. The bis(Schiff base) is tetradentate with two adjacent, weak imine donors and two strongly basic phenolate donors. It is the latter complexing agent that is of interest for this research. The log (formation constant) for the completely deprotonated mono(Schiff base) was found to be 3.81 while the log (formation constant) for the addition of the second deprotonated salicylaldehyde was found to be 4.11. The fact that the second value is slightly larger is analogous to a previous observation[11] on an unrelated triamine ligand where the corresponding stepwise formation constants of Schiff bases formed from salicyclaldehyde and 4-benzyl-1,4,7-triazaheptane were reported in 70% dioxane as being 2.91 and 3.07. These examples further illustrate some interesting fundamental observations regarding Schiff base formation energetics and solvent effects. With regard to the latter, a solvent effect on the formation constant of a deprotonated Schiff base would be expected to be about 2.5 log units in favor of the Schiff base in 70% dioxane relative to water. In the present system, however, the pairs of successive protonation constants in aqueous 70% dioxane for the mono- and bis(Schiff base) complexes, respectively, are very similar: 9.73, 9.25 and 9.55, 9.24 log units. The latter difference is exactly one statistical factor, indicating well-separated independent phenolate groups. The former is fortuitous because different types of donor groups are involved.

From anaerobic potentiometric experiments utilizing the components of the Schiff base in the presence of Co(II), a series of interactions between the metal ion, the Schiff base chelates, and H^+ were found to occur. The mono(Schiff base) of EN and salicylaldehyde was found to form a deprotonated (normal) chelate and a monoprotonated chelate. From the size of the chelate log (protonation constant), 5.58, it is difficult to assign the two coordination sites and the remaining protonation site. A tentative suggestion is that one nitrogen and the oxygen are involved in the coordination of Co(II) and that the terminal amino group becomes protonated. The reasoning leading to this conclusion is based on comparison with the log (stability constant) of the Co(II)–EN complex, 7.36, reflecting the two nitrogen donors present. The log (stability constant) for the cobalt(II) complex of the protonated mono(Schiff base) of salicylaldehyde and EN is 9.05, or almost 2 log units higher, whereas a smaller constant would have been anticipated had the coordination of this mono(Schiff base) been through the two amino groups, as in EN. Since the charge on the EN and on the monoprotonated mono(Schiff base) is zero in each, this conjecture seems reasonable. The log (stability constant) of the deprotonated mono(Schiff base) complex was found to be 14.21, indicating coordination of both amino groups and the phenolate oxygen. The log (formation constant) for the Co(II) complex of the bis(Schiff base) is 14.56, reflecting the the balance between the loss of nitrogen basicity due to Schiff base formation and the gain of one additional donor group. The tetradentate bis(Schiff base) complex with Co(II) possesses two axially coordinated water molecules capable of dissociation at high p[H]. It was found that the successive log (acid dissociation constant) values for these are −9.93 and −11.12, giving species of possible importance only at high p[H] values.

Finally, for the SALEN–MePy–Co(II)–O_2 system, aerobic aqueous dioxane potentiometry led to the log (overall formation constant) for the binuclear oxygen complex containing 2 SALEN, 2 MePY, 2 Co(II), and one O_2. The value for this constant is 54.02. This value, together with all of the other equilibrium constants determined, gives a distribution curve that, for the dioxygen complex, begins to form near p[H] 6, reaches a maximum of about 95% at p[H] 10, and then rapidly drops to zero at p[H] 12 because of the formation of hydroxo and dihydroxo chelate complexes.

Co3FSALOPHEN (5). 3-Fluorosalicylaldehyde *o*-phenylenediimine is a tetradentate Schiff base analogous in some ways to fluomine,[14] with the modification that the bridging ethylenediamine found in SALEN and fluomine has been replaced by an *o*-phenylenediimine moiety. Thus, in aqueous dioxane one would expect partial hydrolysis of the imine to 1,2-diaminobenzene and 3-fluorosalicylaldehyde. Hence, these components were investigated first. In order to form a cobalt oxygen complex, it was anticipated that a fifth coordination site be occupied by a pyridine type base, for which 4-methylpyridine was chosen.

To begin with, only one protonation reaction was detected for phenylenediamine. A log (protonation constant) of 4.41 was calculated, but a second protonation step could not be found at p[H] values above 2.5. Apparently, this is also the case in aqueous solution in that only one protonation constant (4.63) has been reported.[8] Potentiometric data measured in aqueous dioxane indicate a tendency for the weak coordination of only 1 mole of 1,2-phenylenediamine/mol of cobalt(II) ion. The log (stability constant) obtained, 1.95, is in accord with the low basicity of the aromatic diamine. No values are currently available for Co(II) in aqueous solution for comparison.

The value for the log (protonation constant) of 3-fluorosalicylate was found to be 8.44. Compared to 10.18, which is the corresponding value for unsubstituted salicylaldehyde, the lowering of log *K* by 2 orders of magnitude is attributed to the electronegativity of the fluoro group in the 3-position. The affinity of the fluorosalicylate anion for Co(II) ions is low, as attested to by the calculated values of 3.77 and 4.97 for the successive log (formation constant) values of 1:1 and 1:2 metal-to-ligand complexes. The increase in successive constants may be ascribed to a coordination change of octahedral Co(II) to a tetragonal structure. Cobalt(II) occurs in a great variety of structural environments. Tetrahedral, pentacoordinate, octahedral, and square-planar structures often result from small perturbations in its ligand field.[15,16]

As for to the SALEN system, both mono- and a bis(Schiff base) complexes were found to be formed, depending on conditions. The completely deprotonated mono(Schiff base) is formed from the deprotonated phenylenediamine and the deprotonated SALEN, characterized by a log (equilibrium constant) of 2.45, while the second fluorosalicylaldehyde adds to the mono(Schiff base) and is characterized by a log (equilibrium constant) of 2.46. The magnitudes of these two values are in line with the reasoning outlined above and are consistent with the reduced basicity of phenylenediamine relative to ethylenediamine. The log (pro-

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[12] Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum: New York, 1977; Vol. 3.

[13] Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum: New York, 1975; Vol. 2.

[14] Wilmarth, W. K.; Aranoff, S.; Calvin, M. *J. Am. Chem. Soc.* **1946**, *58*, 2263.

[15] Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley-Interscience: New York, 1980; pp 768–770.

[16] Rossotti, F. J. C. In *Modern Coordination Chemistry*; Lewis, J., Wilkins, R. G., Eds.; Interscience: London, 1960; pp 38–39.

tonation constant) of the mono(Schiff base) is 7.50, so that the presence of the proton on the phenoxyl anion, hydrogen bonded to the nitrogen (imine), helps to stabilize the Schiff base. In a similar manner the bis(Schiff base) forms both mono- and diprotonated forms with successive log (protonation constant) values of 11.23 and 8.41. A third protonation reaction is half-completed at p[H] 3.17.

The anaerobic cobalt(II) coordination chemistry of this Schiff base is rather simple, in that only two species are formed: a normal complex and a singly protonated complex of the fully formed Schiff base. The log (stability constant) of the 2:1 deprotonated Schiff base and Co(II) is 14.91, while the protonation reaction is characterized by a log (protonation constant) of 6.94. While the normal complex may have a simple planar structure, the monoprotonated complex can be assumed to be protonated at the phenol oxygen on the other fluorosalicylidene moiety, as is the case for protonation of the metal-free Schiff base.

The oxygenation constant determined is much lower than that of CoSALEN. The log (stability constant) is only 38.68, in accordance with the much lower basicity of the ligand. The main difference is in the apparent differences at high p[H] of dioxygen complexes of **4** and **5**. However, the specific mono- and dihydroxylation reactions of the FSALOPHEN Co(II) complex have not been calculated. It is probable, however, that the dioxygen complexes of CoSALEN and Co3FSALOPHEN have similar hydrolytic reactions at high p[H].

Conclusions

While equilibrium potentiometry is used almost routinely to determine the stability constants of metal ions with a variety of basic ligands, this technique has recently been extended in this laboratory to the determination of cobalt(II) Schiff base formation constants of pentadentate ligands and their oxygenation equilibria. The present work goes one step further in showing the method to be applicable to very complicated systems involving Schiff base complex formation and dioxygen equilibria for six components, such as, for example, a phenolic aldehyde, a diamine, a cobalt(II) ion, a substituted pyridine as an auxiliary ligand, dioxygen, and hydrogen ion. The success of this method depends on separate determination of each contributing equilibrium on increasingly complex mixtures, with the final experiment being carried out under oxygen saturation to obtain the oxygenation constant.[17]

Acknowledgment. The work was supported by a cooperative research grant from Dow Chemical Co.

Registry No. OPYDIAMIDE, 115077-75-3; MHBA, 115077-77-5; MBA, 115077-78-6; SALOPYDIAMIDE, 115077-76-4; SALEN, 94-93-9; 3FSALOPHEN, 115077-79-7; O_2, 7782-44-7; dimethyl 2,6-pyridinedicarboxylate, 5453-67-8; 4-picoline, 108-89-4.

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[17] Authors welcome inquiries about the experimental data and the methods employed to convert such data to the equilibrium parameters reported in this paper (409-845-2232).

Contribution from the Department of Chemistry,
University of Western Ontario, London, Ontario N6A 5B7, Canada

Electrochemistry and Spectroscopy of Magnesium Phthalocyanine. Analysis of the Absorption and Magnetic Circular Dichroism Spectra[‡]

Edward Ough, Tebello Nyokong, Katherine A. M. Creber,[†] and Martin J. Stillman[*]

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Absorption, magnetic circular dichroism (MCD), and electrochemical properties are reported for a range of magnesium phthalocyanine (MgPc) complexes in methylene chloride and dimethylacetamide solution. The ligands studied include imidazole, methylimidazole, pyridine, 4-methylpyridine, and cyanide. The major effect of the axial ligation on the spectra is to induce a red shift of each of the bands from the positions recorded for MgPc in methylene chloride. Results of reversible cyclic voltammetry (CV) and differential-pulse voltammetry (DPV) of the MgPc complexes are also reported. Representative $E_{1/2}$ values determined for MgPc in dimethylacetamide (DMA) are 1.11 V (formation of the dication), 0.65 V (the monocation), −0.88 V (the monoanion), and −1.43 V (the dianion) vs SCE. Band deconvolution calculations that couple both the absorption and MCD spectra are reported for each of the complexes studied. The energies of the fitted bands are compared with values reported by Gouterman and co-workers[1,2] from theoretical calculations and with experimental results for ZnPc reported by Nyokong et al.[3] The deconvolution analysis located two degenerate transitions in the 330–400-nm region; it is suggested that the B band lies near 360 nm in a typical phthalocyanine complex. Five degenerate electronic transitions were identified in the spectra of the MgPc complexes in methylene chloride solutions through use of the deconvolution calculations. These transitions are centered on 670 nm (14 900 cm^{-1}), 361 nm (27 600 cm^{-1}), 338 nm (29 600 cm^{-1}), 282 nm (35 500 cm^{-1}), and 246 nm (40 500 cm^{-1}) and correspond to the theoretically predicted Q, B, N, L, and C transitions.

Introduction

The spectral and electrochemical properties of the porphyrins and phthalocyanines have been extensively studied as models of heme proteins and chlorophylls.[1-15] The 18-π-electron system of the porphyrins and phthalocyanines, together with the overlap of orbitals from the central metal, allows for intriguing oxidation and reduction chemistry.[16] A particularly active area of study has been that of the photochemically induced charge-separated species for use as catalysis agents and in solar cells.[17]

While studies of these properties in porphyrins have been facilitated by their high solubility in a variety of solvents, similar studies of phthalocyanines have been hindered by their limited solubility in very few solvents. Attempts to solve the solubility problem by attaching sulfate groups on the outer periphery of the

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[*] To whom correspondence should be addressed.

[†] Present address: Department of Chemistry, Royal Military College, Kingston, Ontario, Canada.

[‡] Contribution No. 399 from the Photochemistry Unit at the UWO.

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