approach *a* of 0.7 nm (corresponding to the metal cation separated from the ligand by one solvent molecule), and the literature values of ϵ and κ,[34] the volume change accompanying the outer-sphere association can be calculated as $\Delta V_{os}^0 = +2.3$ cm^3 mol^{-1} at 228 K, +2.6 cm^3 mol^{-1} at 238 K, +3.0 cm^3 mol^{-1} at 264 K, and +5.0 cm^3 mol^{-1} at 298 K. For the two ligands with −1 charge, it seems therefore reasonable to subtract these calculated values from $\Delta V_f^\ddagger$ to obtain the activation volume corresponding to the interchange step, $\Delta V_I^\ddagger$, displayed in parentheses in Table II.

The overall picture emerging from Table II is that a dissociative activation mode is the rule in DMF throughout the series of cations studied. On the basis of the present data, it is not possible to decide whether the mechanisms are dissociative interchanges for all cations or if a changeover from dissociative interchange mechanisms (I_d) to a limiting dissociative mechanism (D) takes place along the series. This latter proposition would confirm the earlier conclusion to a limiting dissociative mechanism proposed for Ni^{2+}, based on DMF exchange data.[35] It would not be in contradiction with the observations in water, methanol, and acetonitrile, in which easier bond-making capabilities displace the spectrum of mechanisms into an I_a–I_d changeover.

Acknowledgment. We thank Prof. J. Barthel for valuable discussions and Dr. G. Laurenczy for help in the computer calculations. The Swiss National Science Foundation (Grant 2.854-0.85) is thanked for financial support, and the Herbette Foundation, for equipment supply.

Registry No. **1**, 77038-70-1; **2**, 392-74-5; Mn(DMF)$_6^{2+}$, 39016-85-8; Co(DMF)$_6^{2+}$, 34409-32-0; Fe(DMF)$_6^{2+}$, 62126-14-1.

Supplementary Material Available: Listings of observed first-order rate constants and calculated forward and reverse rate constants (Tables SI–SVII) and equilibrium measurements (Table SVIII) (8 pages). Ordering information is given on any current masthead page.

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(34) The only solvent-specific parameters in eq 11 are ϵ, measured between 213 and 393 K (Bass, S. J.; Nathan, W. I.; Meighan, R. M.; Cole, R. H. *J. Phys. Chem.* **1964**, *68*, 509), and κ, which has only been experimentally determined between 288 and 308 K (Easteal, A. J.; Woolf, L. A. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 2821) but can be estimated at the very low temperatures of our experiments by using a simple linear extrapolation of the literature data.

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New Synthetic Cobalt Schiff Base Complexes as Oxygen Carriers

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The synthesis and dioxygen affinities of ten new cobalt Schiff base complexes and two new cobalt complexes obtained by reduction of Schiff bases are reported and compared in a common solvent with two well-known parent Schiff base complexes and six Schiff base complexes recently reported. The cobalt(II) Schiff base complexes investigated are (bis(3-fluorosalicylaldehyde) ethylenediiminato)cobalt(II) (CoFLUOMINE), (bis(3-methoxysalicylaldehyde) ethylenediiminato)cobalt(II) (Co3MeOSALEN), (bis(3-fluorosalicylaldehyde) *o*-phenylenediimato)cobalt(II) (Co3FSALOPHEN), disodium (bis(5-sulfosalicylaldehyde) *o*-phenylenediiminato)cobaltate(II) (Co5SO$_3$NaSALOPHEN), (bis(2-hydroxyacetophenone) *o*-phenylenediiminato)cobalt(II) (CoαCH$_3$SALOPHEN), (bis(3-fluorosalicylaldehyde) tetramethylethylenediiminato)cobalt(II) (Co3FSALTMEN), (bis(3-methoxysalicylaldehyde) tetramethylethylenediiminato)cobalt(II) (Co3MeOSALTMEN), (*N*,*N*′-bis(salicylidene)-2,6-bis(aminomethyl)pyridinato)cobalt(II) (CoSALMP), (*N*,*N*′-bis(salicylidene)-2,6-bis(aminoethyl)pyridinato)cobalt(II) (CoSALEP), (*N*,*N*′-bis(2-hydroxybenzyl)-2,6-bis(aminoethyl)pyridinato)cobalt(II) (CoBHBEPTY), (*N*,*N*′-bis(salicylidene)bis(2-aminophenyl)methylaminato)cobalt(II) (CoMBA), and (*N*,*N*′-bis(2-hydroxybenzyl)bis(2-aminophenyl)methylaminato)cobalt(II) (CoMHBA). Oxygenation equilibria were measured by monitoring gaseous oxygen uptake by the cobalt(II) complexes in bis(2-methoxyethyl) ether (diglyme) as solvent. The seven tetradentate Schiff base complexes were studied in the presence of large excess (ca. 50 times) concentrations of 4-methylpyridine. The substitution of methyl groups on the Schiff bases (α-substitution, acetophenone derivatives) increases the affinity for dioxygen but also increases the rate of degradation. Fluorine substitution on the aromatic rings of the Schiff bases increases the affinity of the complexes for dioxygen by promoting 2:1 (binuclear) dioxygen complex formation. Sulfonation of the aromatic rings of the Schiff base seems to increase the rate of degradation of the cobalt dioxygen complexes studied. Methoxy groups on the aromatic rings of the Schiff bases tend to increase the affinity of the cobalt(II) complex for dioxygen and favor 1:1 dioxygen complex formation. Combination of dioxygen with the cobalt(II) complexes of the pentadentate Schiff bases seems to be partially inhibited by steric effects, which are relieved by hydrogenation of the ligands. The cobalt(II) complexes of reduced ligands have much higher affinities for dioxygen than do the complexes of the corresponding Schiff bases.

Introduction

Of the dioxygen carriers that have been studied as potential reagents for oxygen separation and transport, the cobalt(II) complexes of Schiff bases, such as bis(salicylaldehyde) ethylenediimine (salcomine) and its analogues, have been the first and the most extensively investigated.[1] The potential usefulness of such dioxygen carriers has long been recognized, in view of the fact that the separation factor for the removal of oxygen from a mixture of inert gases (N$_2$, CO, CO$_2$, etc.) is 100%. However dioxygen separation processes based on this type of complex formation have suffered from the fact that all dioxygen complexes synthesized thus far undergo degradation reactions to inert compounds incapable of carrying dioxygen.[2,3] The cobalt(II) complex of bis(3-fluorosalicylaldehyde) ethylenediimine (fluomine) shows the best performance achieved thus far,[3-5] with up to 3500 oxygenation–deoxygenation cycles before about 40% of the complex becomes inert. Although a variety of cobalt(II) dioxygen carriers have been investigated,[1,6] including several salcomine analogues,

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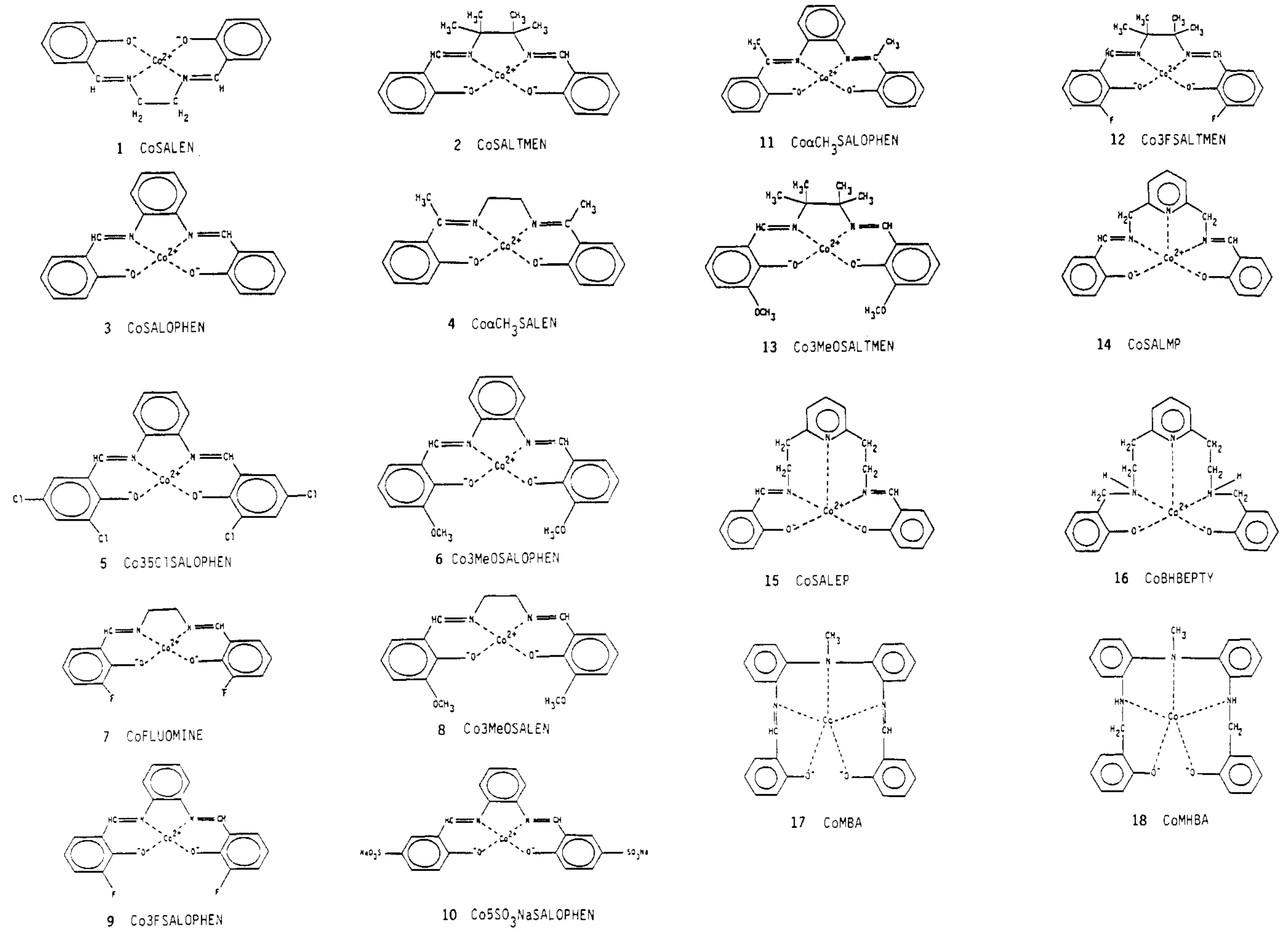
Chart I. Structural Formulas of the Co(II) Oxygen Carriers



1 CoSALEN

2 CoSALTMEN

3 CoSALOPHEN

4 CoαCH$_3$SALEN

5 Co35ClSALOPHEN

6 Co3MeOSALOPHEN

7 CoFLUOMINE

8 Co3MeOSALEN

9 Co3FSALOPHEN

10 Co5SO$_3$NaSALOPHEN

11 CoαCH$_3$SALOPHEN

12 Co3FSALTMEN

13 Co3MeOSALTMEN

14 CoSALMP

15 CoSALEP

16 CoBHBEPTY

17 CoMBA

18 CoMHBA

there has not yet been a sufficiently broad study of cobalt Schiff base complexes to establish structure–activity guidelines that may be used to design oxygen carriers having the most suitable properties for dioxygen separation.

It is the purpose of this paper to report the results of studies of dioxygen affinities and oxygen-carrying properties of cobalt(II) Schiff base complexes having a wider variation of ligands than had been available previously. Ten Schiff bases that represent modifications of the structure of the parent ligand bis(salicylaldehyde) ethylenediimine have been synthesized, their cobalt(II) complexes have been prepared, and the dioxygen affinities have been measured in bis(2-methoxyethyl) ether (diglyme) solution. Seven of these are tetradentate Schiff bases, while three are pentadentate. Two of the latter have been hydrogenated to provide ligands that are more flexible and more basic than the original Schiff bases. The cobalt(II) complexes of these new ligands, the five complexes recently described, and the parent cobalt(II) Schiff base oxygen carrier, salcomine (**1**), provide a total of eighteen cobalt(II) oxygen carriers for comparison of dioxygen affinities and resistance to degradation with the structures of the ligands.

Cobalt(II) complexes of the tetradentate Schiff bases such as **1** do not bind dioxygen sufficiently without a basic monodentate ligand that coordinates the Co(II) in the position trans to the dioxygen. 4-Methylpyridine (4-picoline) was employed as the axial base for all tetradentate ligands in this investigation. An axial base was not employed with the pentadentate chelating agents.

Experimental Section

Materials (Reagents, Ligands, and Cobalt(II) Complexes). Diethylene glycol dimethyl ether (diglyme) was purified by storage and distillation over sodium metal. Ethylenediamine was refluxed over solid NaOH for 10 h; sodium metal was added, and the solvent was refluxed for a further 2 hr and then distilled. 4-Methylpyridine (Aldrich) was refluxed over solid NaOH for 15 h, distilled, and stored over 4-Å molecular sieves. Cobalt(II) acetate ($CoAc_2{\cdot}4H_2O$, Fisher Scientific Co.) was reagent grade and was used without further purification.

Structural formulas of the cobalt(II) complexes synthesized and studied in this investigation are illustrated in Chart I (formulas **7–18**), together with the formulas of the oxygen carriers described earlier.[7] Synthetic procedures for complexes **7–18** are the following:

CoFLUOMINE ((Bis(3-fluorosalicylaldehyde) ethylenediiminato)cobalt(II)) (7) was prepared by the method of Bailes and Calvin.[8]

Co3MeOSALEN ((Bis(3-methoxysalicylaldehyde) ethylenediiminato)cobalt(II)) (8) was prepared by the method of Bailes and Calvin.[8]

Co3FSALOPHEN ((Bis(3-fluorosalicylaldehyde) *o*-phenylenediiminato)cobalt(II)) (9). 3-Fluorosalicylaldeyde was prepared by the method of Ferguson et al.[9] A 1.2-g sample of 3-fluorosalicylaldehyde was dissolved in 25 mL of MeOH, and the solution was mixed with 0.46 g of *o*-phenylenediamine in 15 mL of MeOH. The reaction was stirred for 10 min, and the yellow Schiff base precipitated. After the mixture was allowed to stand for 1 h, the solid was filtered off and washed with ethanol. The crystalline product (3FSALOPHEN) weighed 1.2 g (81%). Recrystallization from MeOH gave material with a melting point of 156–157 °C. ^1H NMR ($CDCl_3$–Me_4Si): 6.7–7.3 (m, 10 H, phenyl), 8.6 (s, 2 H, =CH), 13.1 ppm (s, 2 H, —OH).

A 1.0-g sample of 3FSALOPHEN was dissolved in 30 mL of boiling 95% ethanol. The solution was then mixed with 0.71 g of $Co(Ac)_2{\cdot}4H_2O$ in 20 mL of hot water. The reaction mixture was stirred for 10 min and then allowed to stand at room temperature for 1 h. The precipitate was filtered off and washed with water. The product was dried under vacuum at 100 °C for 4 h. Yield: 86% (1.0 g).

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Anal. Calcd for $C_{20}H_{12}N_2F_2O_2Co$: C, 58.68; H, 2.96; N, 6.85; Co, 14.40. Found: C, 58.61; H, 3.20; N, 7.02; Co, 14.3.

Co5SO$_3$NaSALOPHEN (Disodium (Bis(5-sulfosalicylaldehyde) *o*-phenylenediiminato)cobaltate(II)) (10). A 2-g amount of 5-sulfosalicylaldehyde[10] was dissolved in 9 mL of water and 1.5 mL of pyridine, and then the solution was combined with 0.48 g of *o*-phenylenediamine and 1.1 g of $CoAc_2{\cdot}4H_2O$. The mixture was stirred for 1 h under nitrogen and allowed to stand for 48 h. The product was obtained as a brown precipitate, which was washed successively with ethanol and ethyl ether. It was recrystallized from methanol and dried under reduced pressure at 170 °C. Yield: 60% (1.4 g).

The IR test of the product shows a peak at 1540 cm^{-1} for N=C, and at 1200, 1100, and 1040 cm^{-1}, there are three peaks for SO_3^-. The fact that the 1651-cm^{-1} peak had vanished shows that the product does not contain 5-sulfosalicylaldehyde. UV–vis spectroscopy shows a peak at 327 cm^{-1} for the Schiff base.

Anal. Calcd for $C_{20}H_{12}N_2O_8S_2Na_2Co$: Co, 10.2. Found: Co, 10.0.

αMeSALOPHEN (Bis(2-hydroxyacetophenone) *o*-phenylenediimine) (11). A 4.02-g sample of 2-hydroxyacetophenone was mixed with 1.52 g of *o*-phenylenediamine in a sublimation tube, and the reaction was carried out at 120 °C for 10 h under vacuum (30–40 Torr). After the reaction mixture was cooled to room temperature, 20 mL of MeOH was added, and the mixture was stirred for 10 min. The yellow product that precipitated from the resulting solution was filtered off and washed with MeOH. The product weighed 1.1 g (23%). The αMeSALOPHEN was recrystallized from MeOH, and 0.8 g of purified material with a melting point of 149–150 °C was obtained. ^1H NMR: 2.3 (s, 6 H, $-CH_3$), 6.6–7.6 (m, 12 H, phenyl), 14.2 ppm (s, 2 H, –OH).

Anal. Calcd for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85; N, 8.13. Found: C, 76.72; H, 6.02; N, 8.12.

Co3FSALTMEN ((Bis(3-fluorosalicylaldehyde) tetramethylethylenediiminato)cobalt(II)) (12) was prepared by the method of Avdeef and Schafer.[11]

Co3MeOSALTMEN ((Bis(3-methoxysalicylaldehyde) tetramethylethylenediiminato)cobalt(II)) (13) was prepared by the method of Baker et al.[12]

CoSALMP ((*N*,*N'*-Bis(salicylidene)-2,6-bis(aminomethyl)pyridinato)cobalt(II)) (14). A mixture of 2,6-bis(bromomethyl)pyridine (2 g), potassium phthalimide (2.1 g), and DMF (10 mL) was heated (90–100 °C) for 22 h. After cooling, it was poured into 40 mL of crushed ice and allowed to stand for 1 h until precipitation was complete. The precipitate was filtered off, washed with water until no bromide remained in the filtrate, and then dried in 60 °C for 24 h. A 3.0-g sample of 2,6-bis(phthalimidomethyl)pyridine was obtained. The product was added to 16 mL of absolute EtOH, and then 0.7 mL of hydrazine was added. The mixture was refluxed for 12 h. After it was cooled, 6 N HCl was added to the mixture, to bring the pH to 1. The mixture was refluxed for 1 h and allowed to stand overnight. The precipitate was filtered off, washed with water until neutral (pH 6), and vacuum evaporated to remove the EtOH and water. The residue of phthaloylhydrazide was filtered off and washed with water. The filtrate was evaporated almost to dryness. A 4-mL portion of 50% NaOH solution was slowly added to the hydrochloride salt, and the mixture was extracted with $CHCl_3$. The $CHCl_3$ phase was taken out and filtered, and the filtrate was dried with anhydrous $MgSO_4$ for 2 h. The clear $CHCl_3$ solution of the diamine was vacuum-evaporated to remove $CHCl_3$. Bis(aminomethyl)pyridine, 0.96 g, was obtained. Yield: 88%. ^1H NMR: 7.1–7.7 (m, 3 H, pyridine), 3.9 (s, 4 H, $-CH_2$), 2.0 ppm (s, 4 H, $-NH_2$).

A 0.91-g amount of 2,6-bis(aminomethyl)pyridine was dissolved in 15 mL of MeOH, and the solution was mixed with 1.65 g of salicylaldehyde. This mixture was then stirred and allowed to stand for 2 h. The yellow precipitate was filtered out and washed with ether. The product obtained weighed 2.5 g (75%). SALMP, bis(salicylaldehyde) 2,6-bis(iminomethyl)pyridine, was then recrystallized from EtOH, and 2.08 g of purified material with a melting point of 114–115 °C was obtained.

Anal. Calcd for $C_{21}H_{19}N_3O_2$: C, 73.03; H, 5.54; N, 12.17. Found: C, 73.08; H, 5.71; N, 12.25.

A solution of 232 mg of NaOH in 2 mL of water was added to 1.0 g of SALMP in 25 mL of hot EtOH. This solution was then mixed with 724 mg of $CoAc_2{\cdot}4H_2O$ in 65 mL of water. After the mixture was stirred for 2 h, the precipitate was filtered out and washed with water. The product was then dried under vacuum at 150 °C for 4 h. The CoSALMP obtained weighed 0.58 g. Yield: 50%.

Anal. Calcd for $C_{21}H_{17}N_3O_2Co$: Co, 14.65. Found: Co, 14.4.

CoSALEP ((*N*,*N'*-Bis(salicylidene)-2,6-bis(aminoethyl)pyridinato)cobalt(II)) (15). 2,6-Bis(bromomethyl)pyridine hydrobromide was prepared by a modification of the method of Baker et al.[13] A 25-g amount of 2,6-pyridinedimethanol and 48% aqueous hydrobromic acid (250 mL) were refluxed for 4 h. The reaction mixture was distilled under reduced pressure to remove most of the solvent, and the mixture was refrigerated for 4 h. The product was filtered off and washed with a small amount of cold water. The material was dried over P_2O_5 under vacuum at room temperature for 24 h. The weight of the colorless product obtained was 40 g. Yield: 84%.

2,6-Bis(cyanomethyl)pyridine was prepared by a modification of the method of Baker et al.[12] A mixture of 2,6-bis(bromomethyl)pyridine hydrobromide (10 g), potassium cyanide (8.5 g), and water was heated on a water bath for 5 h. After the mixture was cooled, 50 mL of water was added and the product was extracted with $CHCl_3$. The organic phase was dried with anhydrous $MgSO_4$. The solvent was removed under reduced pressure and dried at 50 °C under vacuum for 2 h. The 3.6-g sample of 2,6-bis(cyanomethyl)pyridine obtained was recrystallized from ethanol to give a final yield of 3.0 g (66%).

A 250-mL three-necked round-bottomed flask equipped with a reflux condenser, magnetic stirring bar, and pressure-equalizing dropping funnel was evacuated and refilled with dry N_2 three times and then flushed with dry N_2 for 10 min. A 2-g sample of 2,6-bis(cyanomethyl)pyridine was then added. A 100-mL portion of 1 M BH_3THF solution was added dropwise to the flask over a 60-min period. The reaction mixture was stirred at room temperature for 12 h. The red precipitate was hydrolyzed by careful dropwise addition of 12 mL of water followed by 10 mL of 6 N HCl. When the addition was complete, the THF was removed by distillation at atmospheric pressure until a temperature of 85–90 °C was reached. This forced complete hydrolysis of the borane amine complex and ensured formation of the amine hydrochloride. The amine was isolated by adding 16 mL of 50% NaOH and extraction with $CHCl_3$. The organic phase was dried with anhydrous $MgSO_4$ for 12 h. After the solvent was removed, 1.2 g of 2,6-bis(aminoethyl)pyridine was obtained as a yellow oil. Yield: 57%. ^1H NMR: 1.7 (s, 4 H, $-NH_2$), 2.9 (m, 4 H, $-CH_2$), 3.1 (m, 4 H, $-CH_2$), 7.0–7.5 ppm (m, 3 H, pyridine).

A 1.2-g sample of 2,6-bis(aminoethyl)pyridine was dissolved in 15 mL of MeOH. The solution was then mixed with 1.85 g of salicylaldehyde. The reaction mixture was stirred and allowed to stand for 4 h under refrigeration. The yellow solid that formed was filtered off and washed with ether. The resulting product was dried under vacuum at 120 °C for 4 h. The yellow Schiff base, 2,6-bis(aminoethyl)pyridine (SALEP) obtained weighed 1.6 g (59%). After recrystallization from ethanol, 1.2 g of SALEP was obtained. Its melting point was 140–141 °C.

A solution of 257 mg of NaOH in 2 mL of water was added to 1.2 g of SALEP in 60 mL of hot ethanol. This solution was then mixed with 803 mg of $CoAc_2{\cdot}4H_2O$ in 25 mL of water with stirring, followed by 100 mL of water. After the mixture was stirred for 2 h, the precipitate was filtered and washed with water. The product was then dried under vacuum at 100 °C for 4 h. The CoSALEP obtained weighed 0.62 g (23%).

Anal. Calcd for $C_{23}H_{21}N_3O_2Co{\cdot}5H_2O$: C, 62.87; H, 5.05; N, 9.56; Co, 13.41. Found: C, 62.37; H, 5.27; N, 9.57; Co, 13.4

CoBHBEPTY ((*N*,*N'*-Bis(2-hydroxybenzyl)-2,6-bis(aminoethyl)pyridinato)cobalt(II)) (16). A 1.0-g sample of SALEP prepared as described above in 100 mL of EtOH was placed in a 500-mL flask. The flask was flushed with dry N_2 for 10 min, and about 1 g of Pd–C was added to the solution. The flask was successively evacuated and refilled with N_2 three times and refilled with H_2 at a pressure of 40 psi. After the flask was shaken for 24 h, the reaction mixture was filtered off and the filtrate was evaporated off to remove the solvent; a 0.7-g sample of light yellow oil (BHBETPY) was obtained. Yield: 69%. ^1H NMR measurement shows that the hydrogenation reaction was complete because the 8.2 ppm CH=N peak had vanished.

A solution of 212 mg of NaOH in 2 mL of water was added to 1.08 g of BHBEPTY in 20 mL of hot MeOH. The resulting solution was then mixed with 662 mg of $CoAc_2{\cdot}4H_2O$ in 50 mL of H_2O. After the mixture was stirred for 2 h, the precipitate was filtered out and washed with water. The product was then dried under vacuum at 120 °C for 4 h. The weight of the brown CoBHBEPTY obtained was 0.62 g (54%).

Anal. Calcd for: $C_{23}H_{25}N_3O_2Co$: Co 13.29. Found: Co, 13.3.

CoMBA ((*N*,*N'*-Bis(salicylidene)bis(2-aminophenyl)methylaminato)cobalt(II)) (17). A mixture of 13.8 g (0.1 mol) of *o*-nitroaniline, 27 g (0.10 mol) of *o*-iodonitrobenzene, 7.0 g (0.66 mol) of anhydrous sodium

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carbonate, and a small amount of anhydrous cuprous chloride was heated to 200 °C (bath temperature) for 4 h. The reaction mixture was cooled and was treated with boiling water to remove the inorganic salt. The insoluble brown-black residue was extracted with chloroform and the extract dried with anhydrous sodium sulfate and evaporated under reduced pressure to near dryness. The crude product was recrystallized from absolute ethanol. The orange needlelike crystalline 2,2′-dinitrodiphenylamine obtained weighed 11.2 g (43%); mp 170–172 °C (lit.[14] 171 °C).

To a 50-mL three-neck flask was added 1.86 g (0.0072 mol) of 2,2′-dinitrodiphenylamine. In a mortar, 2.2 g of potassium hydroxide pellets (Fisher P-250, containing 15% water) as covered with 8 mL of acetone and was ground to a fine powder. The suspension was transferred to the flask, and 8 mL of more acetone was added. The reaction mixture was heated to boiling, and after slow addition of methyl sulfate (3 mL), boiling was continued under reflux for 5 min. The reaction mixture changed from deep violet to brown. The hot suspension was poured into 80 mL of water, and the yellow-orange precipitate was collected and washed with absolute ethanol. This crude product was recrystallized from ethanol. Golden crystalline *N*-methyl-2,2′-dinitrophenylamine was obtained: yield 89%; mp 146–147 °C (lit.[15,16] 147.5–148.5 °C).

To a suspension of 2 g of *N*-methyl-2,2′-dinitrophenylamine and 30 mL of glacial acetic acid was added zinc dust in small portions with vigorous shaking until the solution became nearly colorless. The zinc salt and unreacted zinc dust were removed by filtration and washed with 30 mL of water. The filtrate and washings were combined and poured into 300 mL of water. The acetic acid solution was neutralized with ammonia to about pH 6, and a gray shiny precipitate was formed. After being vacuum dried at room temperature under P_2O_5 for 16 h, 1.0 g of *N*-methyl-2,2′-diaminophenylamine was obtained. Yield: 64%. This product was pure enough for preparation of the following Schiff base.

To 100 mL of petroleum ether (bp range 60–80 °C) was added 1.0 g of the reduced product, and the solution was heated at reflux for 1–2 h. The hot solution was then filtered. After the cooled filtrate was allowed to stand near 0 °C for 16 h, 0.74 g of pale purple triamine was obtained: yield 74%; mp 127–129 °C (lit.[17] 127.5–128.5 °C). ^{1}H NMR ($CDCl_3$): 3.0 (s, 3 H, *N*-methyl), 3.7 (b, 4 H, $-NH_2$), 6.7–7.0 ppm (m, 8 H, aromatic) ^{13}C NMR ($CDCl_3$): 40.0 ppm (*N*-methyl); 115.9, 118.8, 122.1, 124.8 ppm (aromatic); 136.5, 140.6 ppm (nonprotonated aromatic).

A mixture of 1.06 g (0.005 mol) of *N*-methyl-2,2′-diaminodiphenylamine and 1.21 g (0.010 mol) of salicylaldehyde was heated to 100–105 °C for 2–3 h. The water that was produced from the reaction and condensed near the neck of the flask was removed. The cooled reaction mixture was dissolved in about 40 mL of hot absolute ethanol, which was filtered hot and was allowed to stand at ca. 0 °C for 16 h. After filtration, the yellow *N*-methyl-*N*,*N*-bis(2-(salicylidenamino)phenyl)amine, MBA, that crystallized out was washed with ethanol and ethyl ether and air-dried. A 1.6-g amount was obtained. Another 0.28 g of dark brown product was collected from the concentrated filtrate. Both yellow and dark brown product had identical ^{1}H NMR spectra: yield 85%; mp 133–135 °C. ^{1}H NMR ($CDCl_3$): 3.3 (s, 3 H, *N*-methyl), 6.7–7.2 (m aromatic), 8.2 (s, 2 H, —CH═N—), 12.7 ppm (s, 2 H, phenolic —OH). ^{13}C NMR ($CDCl_3$): 41.6 ppm (*N*-methyl); 117.1, 118.8, 120.3, 122.4, 123.7, 127.2 ppm (aromatic); 119.4, 143.2, 144.0, 161.0 ppm (nonprotonated aromatic); 162.9 (—CH═N—).

Anal. Calcd for $C_{27}H_{23}N_3O_2$: C, 76.96; H, 5.46; N, 9.98. Found: C, 76.74; H, 5.39; N, 9.85.

A solution of 0.91 g of $CoAc_2{\cdot}4H_2O$ in 100 mL of hot water was added to 1.45 g of MBA in 140 mL of boiling MeOH. The reaction mixture was stirred for 30 min and filtered, and the precipitate was washed with water. The product was then dried under vacuum at 100 °C for 4 h. The brown product obtained weighed 1.3 g (79%).

Anal. Calcd for $C_{27}H_{21}N_3O_2Co$: Co, 12.32. Found: Co, 12.1.

CoMHBA ((*N*,*N′*-Bis(2-hydroxybenzyl)bis(2-aminophenyl)methylaminato)cobalt(II)) (18). A suspension of 2.2 g of MBA, prepared as described above, in 15 mL of absolute ethanol was reduced with sodium borohydride. When the reaction was complete, the solvent was removed under reduced pressure, and the product was extracted with chloroform from alkaline aqueous solution. The chloroform solution was dried with magnesium sulfate. The concentrated chloroform solution was loaded on the top of 30 g of a silica gel column (grade 60, 230–400 mesh, 60 Å, column size 35/40 mm) and eluted with 15-mL batches of chloroform. Every collection was examined by TLC. The collections with one spot of $R_f = 0.3$ developed with 95:5 v/v $CHCl_3$/MeOH were combined and concentrated. After the solvent was removed under reduced pressure, 2 g of sticky brown oil was obtained. After the crude product was recrystallized twice from petroleum ether (30–60 °C), 1.0 g of pale yellow solid (MHBA) was obtained: yield 45%; mp 63–65 °C. ^{1}H NMR ($CDCl_3$): 3.0 (s, 3 H, $-N-CH_3$), 4.1 (s, 4 H, benzyl $-CH_2-$), 4.4 (b, 2 H, NH), 6.8–7.3 (m, 16 H, aromatic), 7.6 ppm (b, 2 H, phenolic OH). ^{13}C NMR ($CDCl_3$): 40.8 ppm (*N*-methyl); 47.9 ppm (benzyl $-CH_2-$); 114.4, 116.7, 120.3, 120.4, 125.6, 129.2, 129.3, 121.9 ppm (aromatic); 123.6, 138.4, 141.5, 156.5 ppm (nonprotonated aromatic).

A solution of 0.208 g of NaOH in 1 mL of water was added to 1.08 g of MHBA in 40 mL of MeOH. This solution was then mixed with 0.64 g of $CoAc_2{\cdot}H_2O$ in 20 mL of water with stirring, and a light gray product precipitated. After the mixture was stirred for 30 min, the precipitate was filtered out and washed with water. The product was then dried under vacuum at 100 °C for 4 h. Yield: 89% (1.1 g).

Anal. Calcd for $C_{27}H_{25}N_3O_2Co$: Co, 12.22. Found: 12.0.

Analytical Methods. Proton NMR spectra were obtained with a Varian EM-390 spectrometer, with deuteriochloroform as solvent. The resonances are reported in ppm relative to tetramethylsilane. Elemental C, H, and N analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Cobalt analyses were carried out by oxidizing the sample with hot concentrated nitric acid and by using a colorimetric method described by Snell and Snell.[18]

Dioxygen Uptake and Equilibria. The stoichiometry and equilibrium constants of the oxygenation of the cobalt complexes were measured by determining the volume of gaseous dioxygen taken up by the complexes in diglyme solution, and the pressure of dioxygen gas at equilibrium, with the apparatus described previously.[7] The pertinent equilibrium expressions are

$$\mathrm{CoL} + \mathrm{B} \rightleftharpoons \mathrm{CoLB} \qquad K^{\mathrm{B}}_1 = \frac{[\mathrm{CoLB}]}{[\mathrm{CoL}][\mathrm{B}]} \tag{1}$$

$$\mathrm{CoLB} + \mathrm{O_2} \rightleftharpoons \mathrm{CoLBO_2} \qquad K_{\mathrm{O_2}} = \frac{[\mathrm{CoLBO_2}]}{[\mathrm{CoLB}]P_{\mathrm{O_2}}} \tag{2}$$

$$2\mathrm{CoLB} + \mathrm{O_2} \rightleftharpoons (\mathrm{CoLB})_2\mathrm{O_2} \qquad K'_{\mathrm{O_2}} = \frac{[(\mathrm{CoLB})_2\mathrm{O_2}]}{[\mathrm{CoLB}]^2P_{\mathrm{O_2}}} \tag{3}$$

where complexes are expressed in terms of molarities. The dioxygen concentrations are expressed as partial pressures in Torr, of gaseous dioxygen in equilibrium with the liquid phase, assuming that Henry's law holds, thus eliminating the necessity of calculating solubilities of dioxygen in diglyme at various temperatures. The constants K^{B}_1 apply only to the tetradentate Schiff base complexes. Large excesses (ca. 50:1) of the monodentate axial base (4-methylpyridine) were employed to assure complete formation of the 1:1 adduct. Under the conditions of the experiments, no 2:1 complexes with axial base were formed, as was true in the previous study.[7] In some cases degradation of the dioxygen complexes was too rapid to allow accurate determination of the oxygenation constant. Mainly because of this complication, special care was taken to make sure that equilibrium was reached when the quantity and pressure of dioxygen uptake were measured. Details are given below.

In order to distinguish between 2:1 (μ-peroxo) and 1:1 (superoxo) dioxygen complex formation, oxygenation constants were measured at more than one oxygen pressure. The quantity of dioxygen taken up, the concentration of the cobalt(II) complex in solution, and the pressure of dioxygen at equilibrium provided the necessary information.

Thermodynamic constants $\Delta H°$ and $\Delta S°$ for the oxygenation reactions corresponding to eq 2 and 3 were calculated in the usual way from the variation of $K_{\mathrm{O_2}}$ and $K'_{\mathrm{O_2}}$ over a range of temperatures.

Assurances that Oxygenation Equilibria Were Attained. In a typical experiment, 30–50 mL of solvent, which had been saturated with air, the requisite excess of axial base, where required, and 100–200 mg of dioxygen carrier sealed in a thin-walled vial were carefully added to the reaction flask. The entire apparatus was thermostated at a preselected temperature. The flask was filled with dry air, and its pressure was then reduced to a lower predetermined value by exhausting part of the air via the vacuum line. Then pure nitrogen was introduced from the gas supply line, and the total pressure of the gas was brought back to atmospheric pressure. The flask was then disconnected from the vacuum and gas supply line and connected to the gas buret. The buret was then read, and the vial containing the dioxygen carrier was crushed with the stirrer to begin the absorption of dioxygen. The gas in the buret was transferred to the reaction flask several times during the dioxygen absorption to assure uniform composition of the gas remaining in the system. After

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Table I. Equilibrium Constants and Thermodynamic Constants for Oxygenation of Cobalt(II) Complexes of Tetradentate and Pentadentate Ligands[a]

complex	base	t, °C	stoichiometry of O_2 complex	log K_{O_2}; 1:1, mm^{-1}; 2:1, mm^{-1} M^{-1}	$P_{1/2}$, mm	ΔH°, kcal/mol	ΔS°, eu	ref
CoSALEN (**1**), 0.010 M	4-Mepy, 2 M	0.5	2:1	1.58	2.6	−10.3	−30	7
		10		1.30	5.0			
		25		0.91	12			
CoSALTMEN (**2**), 0.014 M	4-Mepy, 2 M	0.5	1:1	−3.4	3×10^3	−6	−40	7
		15		−3.6	4×10^3			
		25		−3.8	6×10^3			
CoSALOPHEN (**3**), 0.012 M	4-Mepy, 1 M	0.5	1:1	−2.07	1.2×10^2	−10.3	−47	7
		10		−2.37	2.3×10^2			
		25		−2.74	5.5×10^2			
	4-CNpy, 1 M	0.5	1:1	−2.27	1.8×10^2	−8.4	−41	
		10		−2.51	3.2×10^2			
		25		−2.82	6.6×10^2			
	py, 2 M	0.5	1:1	−2.22	1.7×10^2	−9.1	−43	
		15		−2.60	4.0×10^2			
		25		−2.81	6.5×10^2			
	DMAP, 0.4 M	25	2:1	1.04	7.6			
CoαCH$_3$SALEN (**4**), 0.010 M	4-Mepy, 3 M	0.5	1:1	−1.31	20	−13.4	−55	7
		5		−1.50	32			
		10		−1.68	48			
Co35ClSALOPHEN (**5**), 0.010 M	4-Mepy, 0.04 M	0.5	2:1	0.52	30	−10.7	−37	7
		5		0.38	42			
		10		0.23	59			
Co3MeOSALOPHEN (**6**), 0.012 M	4-Mepy, 2 M	0.5	1:1	−2.23	1.7×10^2	−6.9	−35	7
		5		−2.52	3.3×10^2			
		25		−2.68	4.8×10^2			
CoFLUOMINE (**7**), 0.0040 M	4-Mepy, 0.34 M	0	2:1	2.19	1.6	−22	−71	
		10		1.58	6.6			
		20		0.98	26			
Co3FSALOPHEN (**9**), 0.0022 M	4-Mepy, 0.14 M	−10	2:1	2.64	1.0	−18.4	−58	
		−5		2.40	1.8			
		0		2.10	3.6			
Co3MeOSALTMEN (**13**), 0.0056 M	4-Mepy, 0.80 M	0	1:1	−2.34	2.2×10^2	−5.6	−31	
		5		−2.42	2.6×10^2			
		10		−2.49	3.1×10^2			
CoBHBETPY (**16**), 0.0097 M		0	2:1	1.03	9.6	−12.0	−39	
		5		0.87	14			
		10		0.70	21			
CoMBA (**17**), 0.026 M		0	1:1	−3.8	6×10^3			
CoMHBA (**18**), 0.0095 M		0	1:1	−2.65	4.5×10^2			

[a] Bis(2-methoxyethyl) ether solvent; 4-methylpyridine axial base employed with tetradentate ligands.

every successive 5-min interval the buret was read until equilibrium had apparently been reached.

At the beginning the dioxygen was rapidly absorbed; then the change in volume became smaller and smaller and finally became constant. Then the experiment was repeated at the same temperature but with a different pressure of oxygen. If the oxygenation constant was found to be unchanged for three sets of measurements of dioxygen pressure and volume of dioxygen taken up, equilibrium was assumed to have been reached.

In order to determine reaction stoichiometry (in addition to conformity with eq 2 or 3), the oxygenation reaction was carried out at much higher dioxygen pressure than that used for the equilibrium measurements. The volume of dioxygen taken up under these conditions then corresponded to the 1:1 or 2:1 stoichiometry of dioxygen complex formation.

For all of the oxygen carriers successfully measured (i.e., excepting those undergoing rapid degradation) the time required to reach equilibrium, for each set of pressure–volume uptake measurements, was less than 1 h.

Results and Discussion

The stoichiometry of the dioxygen complexes formed and their oxygen constants (eq 2 and 3) are presented in Table I. Several of the cobalt(II) complexes described in the Experimental Section are not listed in Table I for one reason or another. Co3FSALTMEN (**12**) seems to form a mixture of 1:1 and 2:1 dioxygen complexes. When the partial pressure of dioxygen is changed, the calculated oxygenation constant also changes. The Schiff base of the pyridine-containing pentadentate ligand SALEP forms a cobalt complex, **15**, which does not absorb oxygen under the conditions employed in this research. The corresponding cobalt complex of SALMP, **14**, absorbs dioxygen slowly, but it undergoes irreversible oxidation sufficiently rapidly to preclude equilibrium measurements. Similarly, CoαMeSALOPHEN (**11**) absorbs oxygen slowly at 0 °C, but it undergoes irreversible oxidation at that temperature and the oxygenation constant could not be determined.

Because of difficulty in the synthesis of the cobalt complex of αMeSALOPHEN, the oxygenation reaction of the complex was carried out without isolating it. A 100-mg sample of αMeSALOPHEN and 74.5 mg of CoAc$_2$·4H$_2$O were added to 30 mL of 3 M 4-Mepy diglyme solution in a 100-mL reaction flask that was filled with dry air. The reaction temperature was kept at 0 °C. After the reaction proceeded for 30 min all the solid dissolved and the solution changed from brown to nearly black. The oxygenation rate was very slow. After the oxygenation reaction was carried out for 8 h the complex had absorbed 3.2 mL of oxygen and the absorption of oxygen still continued, showing that the dioxygen complex undergoes irreversible oxidation.

Compound Co5SO$_3$NaSALOPHEN is itself inactive toward oxygen. When it was mixed with 4-Mepy under pure oxygen, it absorbed oxygen slowly. After 16 h this compound absorbed more than 100% oxygen, indicating that at 25 °C the compound[11] exhibits an irreversible redox process.

Compound Co3MeOSALEN absorbs oxygen at 25 °C and forms a mixture, because when the pressure of the oxygen is changed, the oxygenation constant also changes. A rough approximation for the formation of the 1:1 dioxygen complex gives log K of −2.8 at 0 °C in the presence of 1 M 4Mepy, which is lower than the 1:1 oxygenation constant of the analogous complex, Co3MeOSALOPHEN.

In general, it is seen from the thermodynamic data in Table I that the driving force for dioxygen complex formation is the highly favorable enthalpy of reaction, corresponding to coordinate-bond formation, not only for the metal–dioxygen bond but also for the coordinate bonds between the metal ion and the ligand donor atoms. The increase in the electropositive nature of the metal ion on oxygenation results in strengthening of its coordinate bonds, thus contributing considerably to the exothermicity of the reaction. All entropies of oxygenation are seen to be negative, a general characteristic for all oxygenation processes. The observed decrease of entropy is considered derived from two sources: (1) the loss of translational entropy of the oxygen molecule when it becomes bound and (2) the increase in rigidity of the ligand due to strengthening of the coordinate bonds, and consequent loss of vibrational and partial rotational freedom of the ligand.

Increasing the temperature seems to favor 2:1 complex formation (peroxo-bridged binuclear dioxygen complex). With bis(methylamino)pyridine as an axial base the CoSALOPHEN complex, **3**, forms a 2:1 complex at 25 °C; however, at 0 °C it forms a 1:1 complex.[7]

A review of the literature revealed that very little work has been carried out previously on the determination of oxygenation constants of cobalt Schiff bases complexes in solution. Surprisingly, there are no reports of oxygenation constants of CoFLUOMINE (**7**) in any solvent, although its solid–gas equilibrium has been very thoroughly investigated. Of the oxygen carriers for which oxygenation constants are reported in this paper, only in the case 3MeOSALTMEN has a solution oxygenation constant been reported by others. Baker et al.[12] reported the oxygenation constant $\log K_{O_2} = -2.0$), which is somewhat larger than the value reported in Table I, but this seems reasonable in view of the fact that it was measured at a lower temperature (−10 °C) and in the presence of a much stronger base. Also the solvent employed, γ-butyrolactone, was different. The only other comparisons that can be made with work in the literature involve the parent complex, **1**, which was described in both ref 7 and 12. Although the cobalt complex of 3MeOSALEN was described in both papers, only a very rough approximate value was measured in this work, because the constant was found to be concentration dependent, probably indicating a mixture of 1:1 and 2:1 dioxygen complexes. Baker et al.,[12] however, reported the 1:1 constant without comment. In our hands, and in diglyme solution, the parent complex **1** forms a 2:1 complex and therefore cannot be compared with the 1:1 constant reported by Baker et al.[12] For CoSALTMEN, the oxygenation constant found here for diglyme solution at 0.5 °C is very small, ca. −3.5, while the value reported[12] for DMAC solution at 5 °C is similar, ca. −3.4. These low values, which seem to be lower than those of any other cobalt Schiff base complexes reported, may indicate steric effects resulting from the distortion from planarity of the ligand by the four methyl substituents on the ethylene bridge.

All of the 23 oxygenation constants reported thus far for cobalt Schiff bases in solution are found in ref 7 and 12 and in this paper. They involve 16 Schiff bases, measured in five different solvents, with four different Schiff bases, and at several temperatures. In 12 cases, the temperature variation of the oxygenation constant was determined (this work and ref 7). When one considers the wide variation in the magnitude of the oxygenation constants reported, the presence of obvious steric effects, and the fact that the formation of 2:1 vs 1:1 constants is not yet predictable, it becomes apparent that at the present time there are insufficient data to develop dependable structure–stability relationships for these dioxygen complex systems.

The rates of degradation to inert complexes were appreciable for several complexes as noted above. A surprise was the observed degradation of CoFLUOMINE in diglyme solution, in view of the fact that the solid material may be recycled hundreds of times while maintaining most of its dioxygen carrier capacity. It is suggested that the mobility of dioxygen complexes in solution greatly facilitates degradation reactions to form inert complexes, implying that such degradation processes are bimolecular in nature. Similar effects have been observed for cobalt–dioxygen complexes with polyamine ligands in aqueous solution. Thus, the dioxygen complex of Co–DTMA (diethylenetriaminemonoacetic acid)[19] is stable for weeks in 10^{-3} solution but decomposes rapidly at 10^{-1} M concentration.

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Cyclic Voltammetry of Mono- and Diiron(II) Cyclopentadienyl Complexes of Thianthrene and Related Heterocycles

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Electrochemical studies of mono- and diiron cyclopentadienyl complexes of thianthrene (TH), phenothiazine, and diphenylene dioxide at a platinum electrode in MeCN and CH_2Cl_2 solutions containing tetra-*n*-butylammonium hexafluorophosphate are reported. At fast scan rates (above 10 V/s) at an ultramicroelectrode (25-μm diameter) in MeCN, the diiron complexes show two Nernstian one-electron reduction waves. The small separation of the reduction waves (180 mV for the TH complex) is attributed to a moderate through-space interaction of the two Fe(cp) centers in the dimer. At slower scan rates, some decomposition of the reduced complex is observed; the chemical step involves cleavage of the Fe–arene bond to form the free arene and a solvated $cpFe^{I}$ species. This $cpFe^{I}$ species reacts with added CO to produce $(cpFe(CO)_2)_2$, disproportionates to form ferrocene and FeCO, or reduces the TH complex in homogeneous solution. Digital simulations of the electrochemistry are presented in support of the assigned mechanism. The monoiron TH complex displays similar reactions, with the $TH(Fe^{I}cp)$ species more stable in CH_2Cl_2 than in MeCN solutions.

Introduction

We report here the electrochemical studies of mono- and diiron cyclopentadienyl complexes of thianthrene, phenothiazine, and diphenylene dioxide. These diarenes have structures analogous to anthracene, with the exception that positions 9 and 10 (i.e., the heteroatomic sites) are saturated. Coordination of the arenes to iron occurs through one (monoiron systems) or both (diiron systems) of the arene rings (Figure 1).

There have been numerous studies of (η^6-arene)(η^5-cyclopentadienyl)iron(II) complexes that focus on electronic properties.[1-5] Unlike other iron(II) complexes, specifically the fer-

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