and HBMA are low enough for exchange of the In(III) with intracellular binding sites to occur, while for the other ligands this exchange does not occur and so the intact complex is cleared.

Acknowledgment. This work was supported by a research grant, CA42925, from the National Cancer Institute, National Institutes of Health, U.S. Public Health Service. We acknowledge with thanks the contribution of Yizhen Sun, who synthesized the three new ligands described here. Syntheses of these ligands have been described elsewhere.[5,8]

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Equilibrium Studies and Molecular Recognition in the Catechol- and TIRON-Bridged Binuclear Cobalt(II) 1,4,7,13,16,19-Hexaaza-10,22-dioxacyclotetracosane Dioxygen Complexes

Bruno Szpoganicz, Ramunas J. Motekaitis, and Arthur E. Martell*

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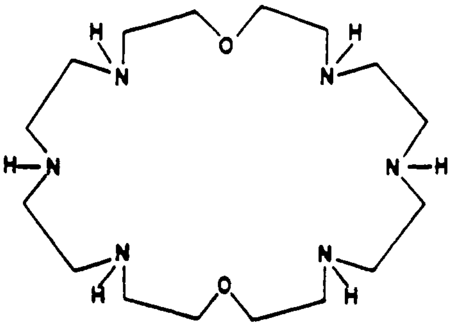
Catechol and TIRON bridge two cobalt centers in the cavity of the macrocyclic 1,4,7,13,16,19-hexaaza-10,22-dioxacyclotetracosane (BISDIEN) dicobalt dioxygen complex, forming five species in each case. In addition to the doubly bridged μ-peroxo, μ-catecholate (or TIRON) complex, mono- and diprotonated forms, as well as monohydroxo and dihydroxo species, have been detected. Under anaerobic conditions catecholate and 3,5-disulfocatecholate anions also bridge the two cobalt(II) centers, stabilizing the binuclear array. Both monobridged complexes add a second, hydroxo, bridge at high pH. The 3,5-disulfocatecholate-bridged complex forms mono- and diprotonated species at low pH. These dinuclear complex systems are characterized by potentiometric titration and UV–vis spectrophotometric measurements. Equilibrium constants for all major complexes formed are reported, and the results are presented in the form of distribution diagrams showing the concentrations of individual complex species as a function of p[H]. Coordinate bonding modes suggested for these complexes show the proposed oxidant (μ-peroxo) and the proposed substrate (μ-catechol or μ-TIRON) in very close proximity, and thus, facile oxidation of the substrates is expected. The dianion of hydroquinone does not bridge the two cobalt centers through its phenolate oxygen donors, apparently reacts with the dinuclear cobalt dioxygen complex through one of its phenolate groups only, and seems to replace the hydroxo bridge in the (μ-peroxo)(μ-hydroxo)dicobalt–BISDIEN dioxygen complex. Reaction with hydroquinone occurs at room temperature to give the inert binuclear cobalt(III)–BISDIEN complex.

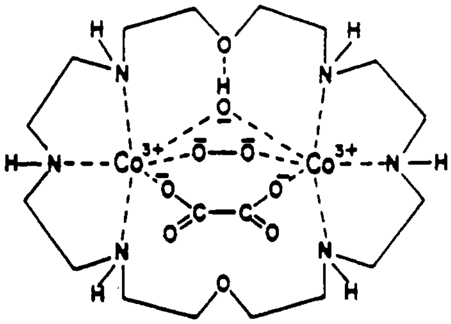
Introduction

The macrocyclic ligand 1,4,7,13,16,19-hexaaza-10,22-dioxacyclotetracosane (BISDIEN, **1**) has been shown to form binuclear complexes with first-row transition-metal ions, which in turn bind secondary anions as bridging groups.[1-3] In this case, the binuclear metal complexes are themselves the hosts, and the bridging anions are the guests. This secondary bridging type of anion binding has been labeled cascade complex formation by Lehn.[3] Examples of secondary anionic guests in binuclear BISDIEN complexes are hydroxide ion, imidazolate anion, and peroxide, for which quantitative binding constants have been reported.[2] In addition, the crystal structure of an imidazolate-bridged binuclear copper(II)–BISDIEN complex has been reported by Lippard and coworkers.[4,5] Whithout the stabilizing bridging bifunctional anions, the dicobalt–BISDIEN complex is somewhat unstable and decomposes at high pH to form cobalt(II) hydroxide.



1 (BISDIEN)

Recently, the formation and redox reactions of the oxalato- and peroxo-bridged dicobalt–BISDIEN dioxygen complex (**2**) was reported.[6] This is the first example of oxidation of a substrate coordinated to two metal centers in a macrocycle where the oxidizing agent, dioxygen, is also bound to the two cobalt centers in the same macrocyclic complex. That result suggested the investigation of reactions of other reducing bifunctional substrates capable of acting as bridging donors in the binuclear (μ-peroxo)dicobalt–BISDIEN complex. In this work, equilibrium studies of complexes involving coordinated anions of catechol and TIRON as bridging groups are described and briefly contrasted with the complexes formed by hydroquinone in the same binuclear system.



2 ((μ-hydroxo)(μ-peroxo)(μ-oxalato)dicobalt–BISDIEN complex)

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(1) Coughlin, P. K.; Lippard, S. J.; Martin, A. E.; Bulkowski, J. R. *J. Am. Chem. Soc.* **1980**, *102*, 7616.

(2) Motekaitis, R. J.; Martell, A. E.; Lecompte, J. P.; Lehn, J.-M. *Inorg. Chem.* **1983**, *22*, 609.

(3) Lehn, J.-M. *Pure Appl. Chem.* **1980**, *52*, 2441.

(4) Coughlin, P. K.; Dewan, J. C.; Lippard, S. J.; Watanabe, E.; Lehn, J.-M. *J. Am. Chem. Soc.* **1979**, *101*, 265.

(5) Coughlin, P. K.; Martin, A. E.; Dewan, J. E.; Watanabe, E.; Bulkowski, J. R.; Lehn, J.-M.; Lippard, S. J. *Inorg. Chem.* **1984**, *23*, 1004.

(6) Martell, A. E.; Motekaitis, R. J. *J. Am. Chem. Soc.* **1988**, *110*, 8059.

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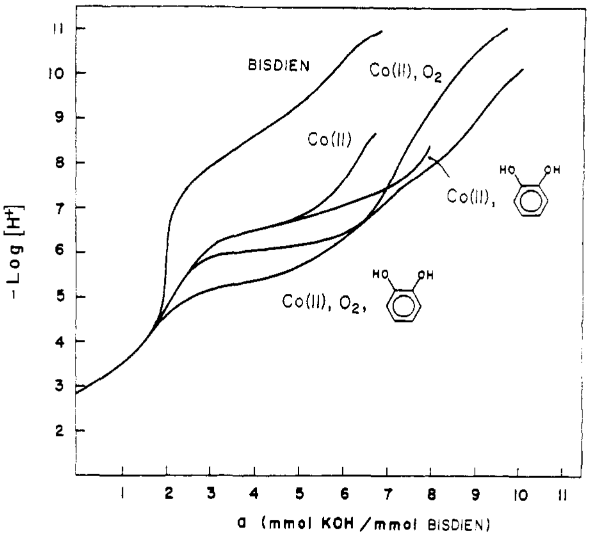

Figure 1. Potentiometric p[H] profiles for solutions containing 2.50×10^{-3} M BISDIEN; BISDIEN and 5.00×10^{-3} M of Co(II), in the presence and the absence of dioxygen; and BISDIEN and Co(II) with 2.50×10^{-3} M of catechol in the presence and the absence of dioxygen. $T = 25.0$ °C, and $\mu = 0.100$ M (KCl).

Experimental Section

Materials. The BISDIEN·6HBr employed was provided by I. Murase and was synthesized by a modification of the method previously described.[7,8] 1,2-Dihydroxybenzene (catechol), 1,4-dihydroxybenzene (hydroquinone), 1,2-dihydroxy-3,5-disulfobenzene disodium salt monohydrate (TIRON), potassium chloride (supporting electrolyte), and cobalt(II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) were reagent grade materials and were used without further purification. The stock solution of cobalt(II) was standardized by titration with EDTA with murexide as the indicator.[9] Carbonate-free solutions of 0.100 M KOH were prepared from Dilut-it ampules and were standardized by titration with potassium acid phthalate.

Potentiometric Equilibrium Measurements. Potentiometric studies of BISDIEN in the absence and presence of cobalt(II), dioxygen, catechol, and TIRON were carried out with a Corning Model 150 research pH meter fitted with blue-glass and calomel reference electrodes calibrated with standard HCl and KOH solutions to read $-\log [H^+]$ directly. Samples of about 0.10 mmol of BISDIEN, catechol, and TIRON, and 0.10 and 0.20 mmol of Co(II) were diluted with 40 mL of doubly distilled water in a sealed thermostated vessel at 25.00 ± 0.05 °C. The experimental solutions, adjusted to 0.100 M in ionic strength by addition of KCl, were titrated with 0.1000 M standard CO_2-free KOH. The ternary systems containing BISDIEN, Co(II), and catechol or TIRON were studied at molar ratios of 1:2:1, with 0.10 mmol of BISDIEN, 0.20 mmol of Co(II), and 0.10 mmol of catechol or TIRON. Potentiometric studies were carried out with 50 mL of experimental solution, with the BISDIEN at approximately 2.0×10^{-3} M. All systems were studied under anaerobic conditions, established by a stream of purified argon, to exclude oxygen and CO_2, and under dioxygen saturation maintained by a stream of purified oxygen.

Spectrophotometric Studies. Uv-visible measurements were carried out with a Perkin-Elmer Model 533 Fast Scan spectrophotometer, equipped with a thermostated cell compartment attached to a refrigerated constant-temperature bath with a variable-temperature control to maintain the temperature at 25.0 °C. Matched flow cells of 1.000-cm path length were used throughout, with the reference containing 0.100 M KCl. Samples of about 0.0096 mmol of BISDIEN, 0.0192 mmol of Co(II), and 0.0096 mmol of catechol or TIRON were diluted to 100 mL of solution in a sealed thermostated vessel at 25.00 ± 0.05 °C equipped with outlets leading to the spectrophotometer flow cell driven by a peristaltic pump. The p[H] values of solutions were adjusted by addition of small volumes of 2 M KOH or 6 M HCl with a Gilmont microburet attached to a thermostated vessel. The experimental vessel was fitted with pH and reference electrodes, gas inlet and outlet tubes, and suitable connections to narrow bore tubing passing through the peristaltic pump. With this arrangement, absorbance may be measured with variations of pH, added KOH, gas, and temperature. The electrodes were calibrated by the same procedure as describe above for potentiometric measurements, and the ionic strengths of solutions were adjusted to 0.100 M by the addition of KCl.

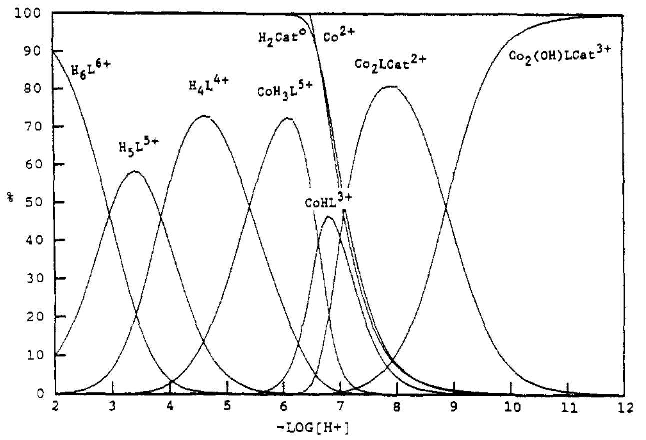

Figure 2. Species distribution curves for a solution containing 2.50×10^{-3} M BISDIEN, 5.00×10^{-3} M Co(II), and 2.50×10^{-3} M catechol under anaerobic conditions. $CoL(OH)Cat^{3+}$ is the μ-catechol, μ-hydroxo binuclear Co(II)–BISDIEN complex and Co_2LCat^{2+} is the μ-catechol binuclear Co(II)–BISDIEN complex. $CoHL^{3+}$ and CoH_3L^{5+} are the mono- and triprotonated species of binuclear Co(II)–BISDIEN complexes, and Co^{2+} is the aqueous Co(II) ion. H_2Cat^0 is the diprotonated catechol, and H_4L^{4+}, H_5L^{5+}, and H_6L^{6+} are the tetra-, penta-, and hexaprotonated forms of BISDIEN.

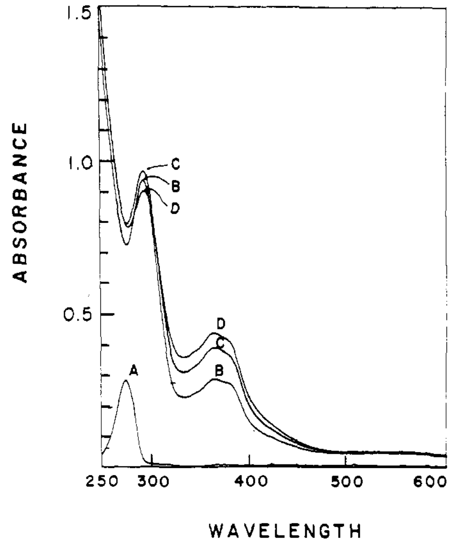

Figure 3. UV–vis absorption spectra of a solution initially containing 0.960×10^{-4} M BISDIEN, 1.920×10^{-4} M Co(II), and 0.960×10^{-4} M catechol under anaerobic conditions at the following p[H] values: (A) p[H] 3.87; (B) p[H] 9.06; (C) p[H] 10.23; (D) p[H] 11.33. $T = 25.0$ °C, and $\mu = 0.100$ M (KCl).

The experimental solution employed for spectrophotometric work with hydroquinone contained 20.7 mg (0.0244 mmol) of BISDIEN, 10.00 mL of 1.00 M KCl, 2.25 mL of 0.02151 M (0.0488 mmol) $CoCl_2$, and 87.75 mL of water to make 100.0 mL of test solution.

Computations. The protonation constants and Co(II)-binding constants of BISDIEN have been reported earlier.[2] The equilibrium constants in the systems BISDIEN–Co(II) in the presence and absence of oxygen, and in the ternary systems of BISDIEN–Co(II)–catechol and BISDIEN–Co(II)–TIRON in the presence and absence of dioxygen, were calculated with the aid of the program BEST.[10] The input for the program BEST consists of millimoles of each component, the titration variables, the initial estimates of equilibrium constants of each species thought to be formed from the solution components, and the experimentally determined profiles of p[H] vs base added. The program em-

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(7) Lehn, J.-M.; Pine, S. H.; Watanabe, E.; Willard, A. K. *J. Am. Chem. Soc.* **1977**, *99*, 6766.

(8) Comarmond, J.; Plumeré, P.; Lehn, J.-M.; Agnus, Y.; Louis, R.; Weiss, R.; Kahn, O.; Morgenstern-Badarau, I. *J. Am. Chem. Soc.* **1982**, *104*, 6330.

(9) Schwarzenbach, G.; Flaschka, H. *Complexometric Titration*; Methuen Co. Ltd.: London, 1969; p 244.

(10) Motekaitis, R. J.; Martell, A. E. *Can. J. Chem.* **1982**, *60*, 2403.

Table I. Logarithms of Stability Constants and Protonation Constants for Ternary Species of Co(II) Complexes of BISDIEN and a Bridging Ligand (Catechol or TIRON) at 25.00 °C and μ = 0.100 M (KCl)[a]

H_2X (bridging ligand)	log ($[LCo_2X]/[Co]^2[L][X]$)	log ($[HLCo_2X]/[LCo_2X][H^+]$)	log ($[H_2LCo_2X]/[HLCo_2X][H^+]$)	log ($[LCo_2(OH)X][H^+]/[LCo_2X]$)
catechol	25.75			−8.88
TIRON	26.42	7.73	6.48	−9.68

[a] Logarithmic values for other equilibrium constants determined in this work were as follows: log ($[CoL]/[Co][L]$) = 10.35; log ($[CoHL]/[Co][HL]$) = 8.74; log ($[CoH_2L]/[Co][H_2L]$) = 5.28; log ($[CoH_3L]/[Co][H_3L]$) = 4.74; log ($[Co_2L]/[Co]^2[L]$) = 13.45.

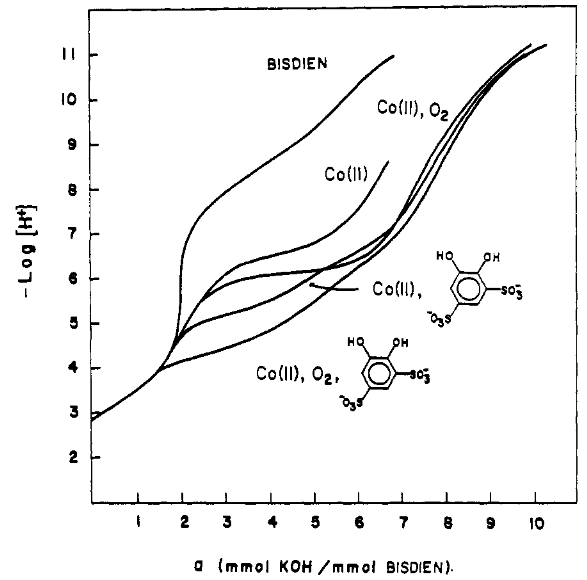


Figure 4. Potentiometric p[H] profiles of solutions with concentrations and conditions identical with those of Figure 1, with TIRON in place of catechol.

ploys mass balance equations for all species present at each increment of base added and solves for the concentration of hydrogen ion, which is compared to the experimental value. The fitting process is minimized with respect to weighted least-squared minimization between observed and calculated p[H$^+$]. Further details about the method of calculation have been described elsewhere.[11]

Results and Discussion

Species Formed in the Co(II)-BISDIEN System. Potentiometric equilibrium curves of BISDIEN in the absence of and in the presence of 1 or 2 molar equiv of Co(II) under argon were determined by the potentiometric method described in the Experimental Section, and the 1:2 (dinuclear) system is illustrated in Figure 1. While detailed discussion of such curves may be found in specialized works such as ref 11, the generalized interpretations of the data plotted in Figure 1 (and Figure 4) is as follows. Each curve plotted represents a separate experiment. The shape of a given curve provides qualitative information on solution stoichiometry and provides suggestions for possible species present. The top curves shown in Figures 1 and 4 reveal that hexaprotonated BISDIEN becomes dissociated in two buffer regions near pH 3.5 and near pH 9. The steep break in the curve indicates no chemistry is going on in that pH range (i.e., pH ~4–7). The experiment for which Co(II) is present yields a curve which is distinctly lower than that of BISDIEN alone yet coincident with it before $a = 2$. This result indicates that only when $a > 2$ does the cobalt ion form a complex (or complexes) with the ligand. The curve ends abruptly, indicating the experiment could not be carried out past pH 8 since $Co(OH)_2$ precipitates out of solution. The equilibrium constants calculated from the potentiometric data are listed in Table I. The overall formation constants β_n for the protonated and unprotonated 1:1 BISDIEN–Co(II) complexes are defined by eq 1, and they are related to the formation constant of the unprotonated complex β_0, by eq 2, while β_0 is defined by eq 3, and the successive protonation steps $K_1, K_2, ..., K_n$ are defined by eq 4. A description and suggested conformation of un-, mono-, and diprotonated species of 1:1 Co(II)–BISDIEN complexes have been described previously.[2] In this work, the triprotonated species of the 1:1 BISDIEN–Co(II) complex was detected, while it was not found in an earlier investigation.[2] This difference may be due to the presence of bromide ion in the present study, since the BISDIEN compound used is a hexabromide salt, while the supporting electrolyte in the previous study contained perchlorate, without bromide, as the supporting electrolyte anion. The "population" of the triprotonated mononuclear species would be increased in the present study because of the stabilizing effect of the bromide ion, as shown in **3**. In this coordinate bonding arrangement, one Co(II) ion is pictured as coordinated to three nitrogens on one side of the macrocycle, and a bromide ion is coordinated to the positively charged nitrogens in the other half of the BISDIEN ligand.

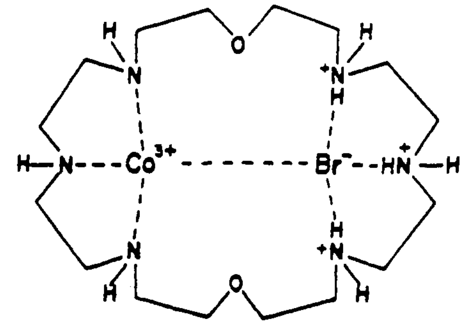
$$Co^{2+} + L + nH^+ \rightleftharpoons CoH_nL^{2+n} \qquad \beta_n = \frac{[CoH_nL^{2+n}]}{[Co^{2+}][L][H^+]^n} \tag{1}$$

$$\beta_n = \beta_0 K_1 K_2 ... K_n \tag{2}$$

$$Co^{2+} + L \rightleftharpoons CoL^{2+} \qquad \beta_0 = \frac{[CoL^{2+}]}{[Co^{2+}][L]} \tag{3}$$

$$CoH_{n-1}L^{2+n-1} + H^+ \rightleftharpoons CoH_nL^{2+n}$$

$$K_n = \frac{[CoH_nL^{2+n}]}{[CoH_{n-1}L^{2+n-1}][H^+]} \tag{4}$$



3

Formation of the 2:1 Co(II)–BISDIEN complex was also investigated and its formation constant is defined by eq 5.

$$2Co^{2+} + L \rightleftharpoons Co_2L^{4+} \qquad \beta_{Co_2L}{}^{2} = \frac{[Co_2L^{4+}]}{[Co^{2+}]^2[L]} \tag{5}$$

Catechol-Bridged Binuclear Co(II)–BISDIEN. The potentiometric equilibrium curve involving the formation of μ-catecholate-bridged binuclear Co(II)–BISDIEN complexes is shown in Figure 1, and the equilibrium constants defined by eqs 6 and 7

$$2Co^{2+} + L + Cat^{2-} \rightleftharpoons Co_2LCat^{2+}$$

$$\beta = \frac{[Co_2LCat^{2+}]}{[Co^{2+}]^2[L][Cat^{2-}]} \tag{6}$$

$$Co_2LCat^{2+} \rightleftharpoons Co_2(OH)LCat^+ + H^+$$

$$K = \frac{[Co_2(OH)LCat^+][H^+]}{[Co_2LCat^{2+}]} \tag{7}$$

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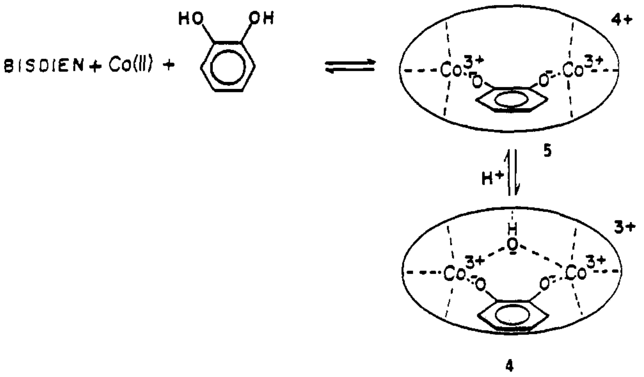
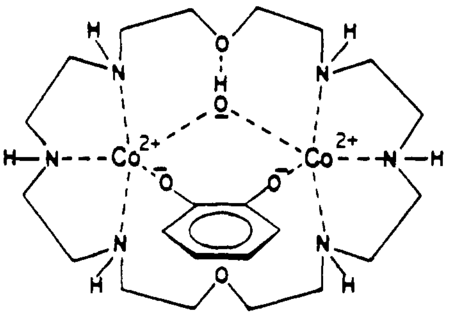
[11] Martell, A. E.; Motekaitis, R. J. *Determination and Use of Stability Constants*; VCH Publishers: New York, 1988.

Scheme I. Catechol-Bridged Binuclear Co(II)–BISDIEN Complexes



are reported in Table I. In the presence of catechol (anaerobically), the formation buffer regions (Figure 1) extend to $a = 8$ indicating eight protons lost in the formation of the ultimate complex (six lost from the ligand and two lost in the binding of the catechol groups). L is the completely deprotonated form of BISDIEN, Co^{2+} is the free aquo cobalt(II) ion, and Cat^{2-} is the completely deprotonated form of catechol. In the calculations of these constants, allowance was made for all of the other coordination and protonation equilibria of the species present, including equilibrium constants for the formation of Co(II)–BISDIEN complexes discussed above and the equilibrium constants for the formation of Co(II)–catechol complexes, which were taken from the literature.[12]

Formation of the μ-hydroxo, μ-catecholate complexes of binuclear Co(II)–BISDIEN is defined by eq 7. The proposed coordinate bonding in this compound, **4**, shows the catecholate dianion bridging the two cobalt(II) ions in the macrocyclic cavity and a hydroxide ion also bridging the two metal centers and probably hydrogen-bonded to one of the two ether oxygens of the macrocyclic ring.

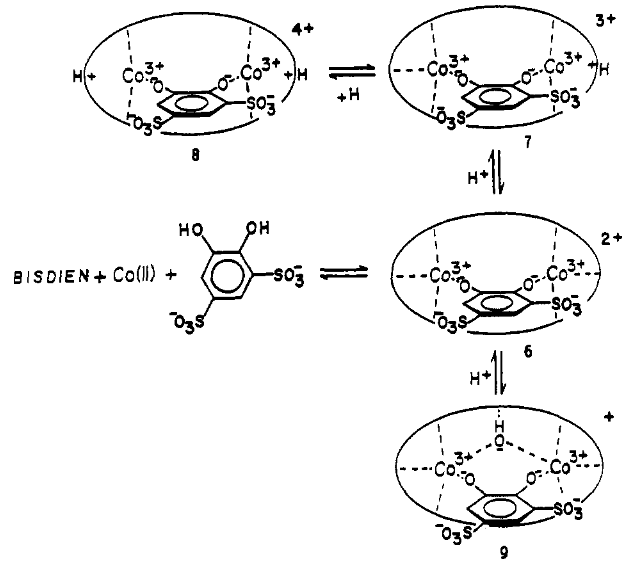


4

Scheme I suggests that protonation of **4** probably occurs on the bridged hydroxide ion resulting in **5**, with water molecules filling the remaining coordination sites of the cobalt(II) ions. Species **5** is 78.6% formed at p[H] 8.0 and decreases in concentration at higher p[H] when the proportion of the μ-hydroxo species **4** increases (Figure 2). That species is 99.6% formed at p[H] 12.0.

The UV–vis spectra of a species of catechol-bridged binuclear Co(II)–BISDIEN are shown in Figure 3, at several p[H] values. The spectrum at p[H] = 3.87 (curve A) is the same as that of catechol in the acid region. It has a maximum absorbance at 275 nm. The absorbance peak shifts to 300 nm as the catechol coordinates to the metal centers as shown by curves B, C, and D in Figure 3. The absorption band in the 360–380-nm range is probably due to a dioxygen impurity, which led to formation of (μ-peroxo)(μ-catecholato)dicobalt(III)–BISDIEN complexes that absorb in this region and that will be described below.

Scheme II. TIRON-Bridged Binuclear Co(II)–BISDIEN Complexes



TIRON-Bridged Dinuclear Co(II)–BISDIEN Complex. The potentiometric p[H] profile for the Co(II)–BISDIEN–TIRON dinuclear complex system is shown in Figure 4. The equilibrium constants for complexes formed are listed in Table I and are defined by eqs 8–10, where Tir^{4-} is the completely deprotonated

$$2Co^{2+} + L + Tir^{4-} \rightleftharpoons Co_2LTir^0$$

$$\beta = \frac{[Co_2LTir^0]}{[Co^{2+}]^2[L][Tir^{4-}]} \qquad (8)$$

$$Co_2H_{n-1}LTir^{n-1} + H^+ \rightleftharpoons Co_2H_nLTir^{n+}$$

$$K = \frac{[Co_2H_nLTir^{n+}]}{[Co_2H_{n-1}LTir^{n-1}][H^+]} \qquad (9)$$

$$Co_2LTir^0 \rightleftharpoons Co_2(OH)LTir^- + H^+$$

$$K = \frac{[Co_2(OH)LTir^-][H^+]}{[Co_2LTir^0]} \qquad (10)$$

form of TIRON. Two protonated species are formed and are defined by eq 9, where $n = 1$ and 2. As with the catechol system, a μ-hydroxo, μ-TIRON binuclear Co(II)–BISDIEN complex analogous to **4** (eq 10) and a singly bridged complex analogous to **5** (eq 8) are formed. The reaction sequence involving the equilibrium equations (8)–(10) is illustrated by Scheme II. Protonation of **9** yields **6** with loss of the hydroxo bridge. For the two protonated species, **7** and **8**, the protonation sites are tentatively assigned to be on the nitrogens of the macrocyclic ring. The existence of these protonated forms was not predicted, and structural information is needed before the coordinate bonding in these complexes can be understood.

Species **6** reaches its maximum stability at p[H] 8.6 where it is 84.0% formed (Figure 5), and the μ-hydroxo-bridged species (**7**) is perhaps the most stable of all TIRON complexes and is 96.7% formed at p[H] 11.7. The monoprotonated species (**8**) reaches a maximum of 44.1% formation at p[H] 7.3 and the diprotonated form is 75% formed at p[H] 6.3.

Figure 6 shows a family of absorbance curves for solutions containing a 1:2:1 molar ratio of BISDIEN:Co(II):TIRON under argon at several p[H] values. A is the absorbance curve of TIRON at the same p[H] value, which has a peak at 292 nm. This absorbance peak shifts to 325 nm as TIRON coordinates to the two Co(II) ions in the macrocyclic cavity (curves B–E).

Hydroquinone-Bridged Binuclear Co(II)–BISDIEN Complex. The potentiometric equilibrium curve obtained for a 1:2:1 molar ratio of BISDIEN:Co(II):hydroquinone could not be explained without invoking the participation of one hydroquinone molecule per BISDIEN per two Co(II) ions. The stoichiometry of this

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[12] Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum Press: New York, 1989; Vol. 6.

Table II. Logarithms of Equilibrium Constants for the Formation of Co(II) Complexes of BISDIEN and a Bridging Ligand (Catechol or TIRON) in Aqueous Solution, at 25.00 °C and $\mu = 0.100$ M (KCl)[a]

H_2X	log $([LCo_2O_2X]/[LCo_2X]P_{O_2})$	log $([HLCo_2O_2X]/[LCo_2O_2X][H^+])$	log $([H_2LCo_2O_2X]/[HLCo_2O_2X][H^+])$	log $([LCo_2O_2(OH)X][H^+]/[LCo_2O_2(OH)X])$	log $([LCo_2O_2(OH)X][H^+]/[LCo_2O_2(OH)X])$
catechol	4.05	7.76	6.42	−3.88	−9.48
TIRON	3.74	7.59	6.87	−5.87	−11.92

[a] Logarithmic values for other equilibrium constants determined in this work were as follows: log $([LCo_2O_2(OH)][H^+]/[LCo_2]P_{O_2}) = -3.35$ (−3.19); log $([LCo_2O_2(OH)_2][H^+]/[LCo_2O_2(OH)]) = -8.30$ (−8.25); log $([LCo_2O_2(OH)_3][H^+]/[LCo_2O_2(OH_2)]) = -9.8$ (−9.45). The numbers in parentheses are logarithmic values reported for the same constants in ref 2.

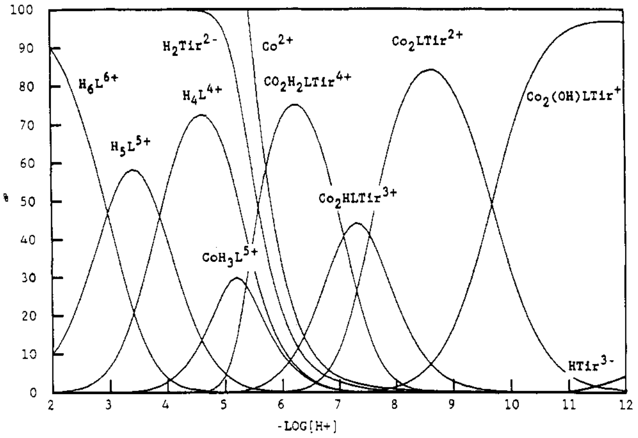


Figure 5. Species distribution curves for a solution containing 2.50×10^{-3} M BISDIEN, 5.00×10^{-3} M Co(II), and 2.50×10^{-3} M TIRON under anaerobic conditions. $Co_2(OH)LTir^+$, Co_2LTir^{2+}, Co_2HLTir^{3+} and $Co_2H_2LTir^{4+}$ are the μ-hydroxo, μ-TIRON binuclear Co(II)–BISDIEN complex and protonated species. Co^{2+} is the free aqueous Co(II) ion, and CoH_3L^{5+} is the triprotonated form of the binuclear Co(II)–BISDIEN complex. $HTir^{3-}$ and H_2Tir^{2-} are the mono- and diprotonated forms of TIRON, and H_4L^{4+}, H_5L^{5+}, and H_6L^{6+} are the tetra-, penta-, and hexaprotonated forms of BISDIEN.

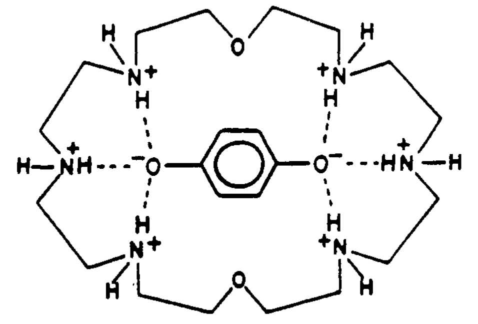
μ-hydroquinone complex was found to be represented by the formula Co_2(BISDIEN)(hydroquinone)(H_{-1}) where H_{-1} represents the proton dissociated from a bridging phenoxide donor group. The formation reaction for this unusual complex is shown in eq 10a with a calculated log equilibrium constant of 5.51.

$$HQH_{-1}^- + LCo^{4+} \rightleftharpoons LHQH_{-1}Co_2^{3+}$$

$$K' = \frac{[LHQH_{-1}Co_2^{3+}]}{[HQH_{-1}^-][Co_2L^{4+}]} \qquad (10a)$$

This hydroquinone-bridged complex forms to the extent of 65% before the system disproportionates, as expected, by precipitation of one of the Co(II) ions as the hydroxide, $Co(OH)_2$, and the formation of Co(BISDIEN). During the formation of the bridged complex, the color of the solution changes gradually from dull pink to a yellowish hue.

Prior investigation of BISDIEN with hydroquinone in the absence of Co(II) showed absolutely no interaction of the guest-host type such as



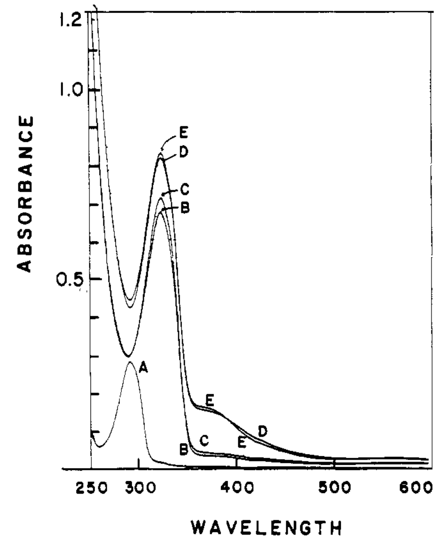


Figure 6. UV–vis absorption spectra of a solution containing 0.960×10^{-4} M BISDIEN, 1.920×10^{-4} M Co(II), and 0.960×10^{-4} M TIRON under anaerobic conditions, at the following p[H] values: (A) p[H] 3.95; (B) p[H] 6.22; (C) p[H] 7.28; (D) p[H] 8.66; (E) p[H] 10.96. $T = 25.0$ °C, and $\mu = 0.100$ M (KCl).

Oxygen Complexes. The dioxygen complexes formed in the catechol- and TIRON-bridged binuclear Co(II)–BISDIEN dioxygen complexes are illustrated in Scheme III, and the equilibrium constants for the dioxygen-containing species, defined by eqs 11–14, were determined from potentiometric data (Figure 1

$$Co_2LX + O_2 \rightleftharpoons Co_2O_2LX \qquad K_{O_2} = \frac{[Co_2O_2LX]}{[Co_2LX]P_{O_2}} \qquad (11)$$

$$H_{n-1}Co_2O_2LX + H^+ \rightleftharpoons H_nCo_2O_2LX$$

$$K_n^H = \frac{[H_nCo_2O_2LX]}{[H_{n-1}Co_2O_2LX][H^+]} \qquad (12)$$

$$Co_2LX + O_2 \rightleftharpoons Co_2O_2(OH)LX + H^+$$

$$K_{O_2} = \frac{[Co_2O_2(OH)LX][H^+]}{[Co_2LX]P_{O_2}} \qquad (13)$$

$$Co_2O_2(OH)LX \rightleftharpoons Co_2(OH)_2LX + H^+$$

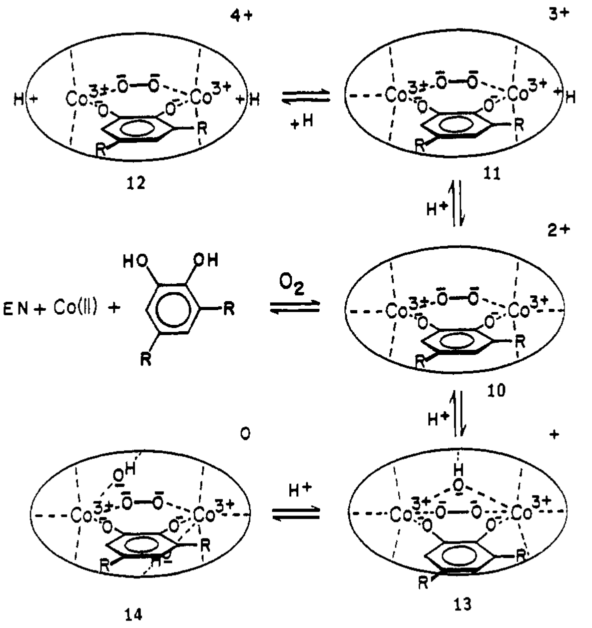
$$K^H = \frac{[Co_2(OH)_2LX][H^+]}{[Co_2O_2(OH)LX]} \qquad (14)$$

X is the bridging ligand catechol or TIRON

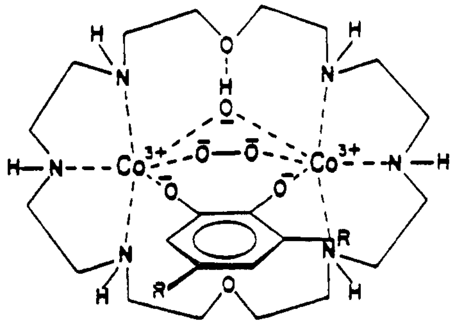
and Figure 4), and they are reported in Table II. Figures 1 and 4 show the experiments where catechol is absent, but oxygen is present. This forms an extremely long buffer region with an initial upward break at $a = 7$ followed by two additional deprotonations to $a = 9$. From this result the brown dioxygen complex and its two hydroxo forms have been inferred. Finally, the lowest curve demonstrates the formation of BISDIEN–dioxygen catechol species, since this curve is distinct with its own break at $a = 9$ (six from BISDIEN plus two from catechol plus one from hydroxo) consistent with structure **13**.

Each species in Scheme III differs in degree of protonation. Protonation of the μ-catechol and the μ-TIRON, μ-peroxo binuclear Co(II)–BISDIEN complexes **10** yields **11** and **12**. Also,

Scheme III. Catechol- or TIRON-Bridged Binuclear Co(II)-BISDIEN Dioxygen Complexes



10 can be interpreted as resulting from the protonation of the μ-catechol, (or μ-TIRON) μ-hydroxo, and μ-peroxo binuclear Co(II)-BISDIEN complex **13**. This protonation step is considered as occurring on the hydroxo bridge. The dihydroxo species (**14**) has one hydroxo ligand coordinated to each metal center, and both ligands are probably hydrogen-bonded to an ether oxygen of the macrocyclic ring. Protonation of one hydroxo ligand of **14** would produce a coordinated water molecule, which is then displaced by the other hydroxo group, which is now considered to bridge the two Co^{3+} ions as in **15** (a more detailed representation of structure **13** of Scheme III). It is important to note that the oxidant (peroxo bridge) and a substrate (catechol or TIRON) are very close, as was the case in an analogous complex in which the oxidation of oxalate was studied.[6] The species distribution curves of the catechol-Co(II)-BISDIEN dioxygen system are shown in Figure 7a,b. The dihydroxo species (**14**, Scheme III) predominates at p[H] values above 11.0 (Figure 7a). The relative concentration of this species decreases as the p[H] decreases while the concentration of the monohydroxo species (**13**) increases, reaching a maximum at p[H] 8.8, at which it is 72.1% formed. Protonation of this species yields complex **10**, which is 36.2% formed at p[H] 7.9. Two other protonated species (**11** and **12**) are formed at lower p[H] values, and they are 62% and 63% formed at p[H] values 7.1 and 5.9, respectively.



15 (R = H or SO_3^-)

The conditions employed for the species distribution curves shown in Figure 7b resemble closely the conditions (lower concentration) used to obtain the UV-vis spectra. The concentrations of species **11** and **12** (Scheme III) are much lower in Figure 6b compared to those in Figure 6a. The degree of formation of **10** is also lower, but **13** and **14** show only a small decrease in degree of formation. The family of absorbance curves in Figure 8 shows two intense charge-transfer absorption bands very close to each other for the catechol-bridged binuclear Co(II)-BISDIEN dioxygen complexes, with maxima at 365 and 376 nm. The absorption peak at 275 nm of curve "A" is due to catechol itself. The p[H] value of that solution was 3.83. At this p[H] value, no dioxygen complex is formed and catechol is not complexed.

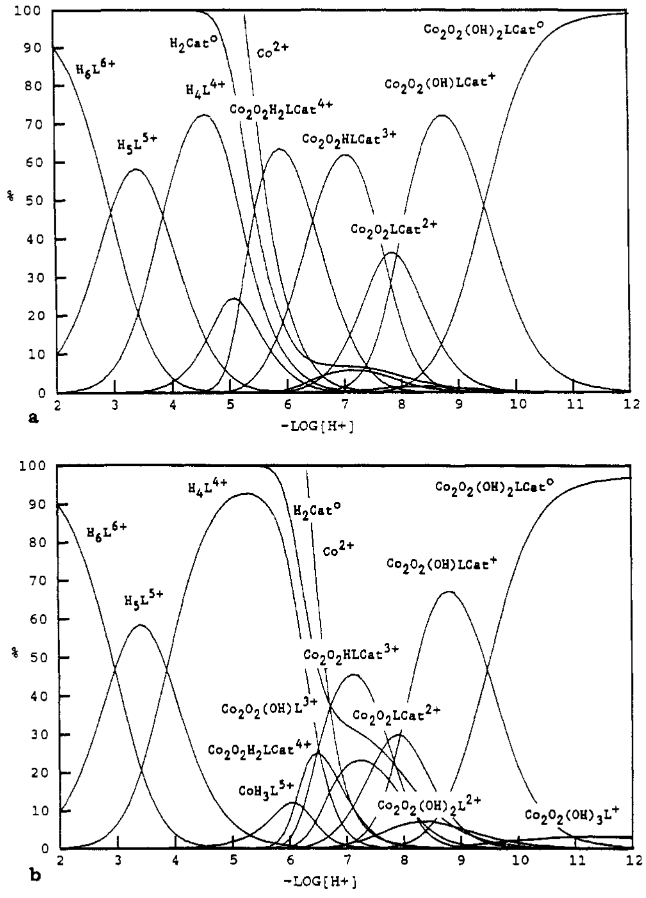


Figure 7. (a) Species distribution curves of the 1:2:1 BISDIEN-Co(II)-catechol system under oxygen as a function of -log [H^+], for a solution initially containing 2.50 × 10^{-3} M catechol under oxygen (P_{O_2} = 1 atm). T = 25.0 °C, and μ = 0.100 M (KCl). (b) Species distribution curves of the 1:2:1 BISDIEN-Co(II)-catechol system under oxygen (P_{O_2} = 1 atm) with initial concentrations of BISDIEN, Co(II), and catechol at $^1/_{26}$th their concentrations in part a.

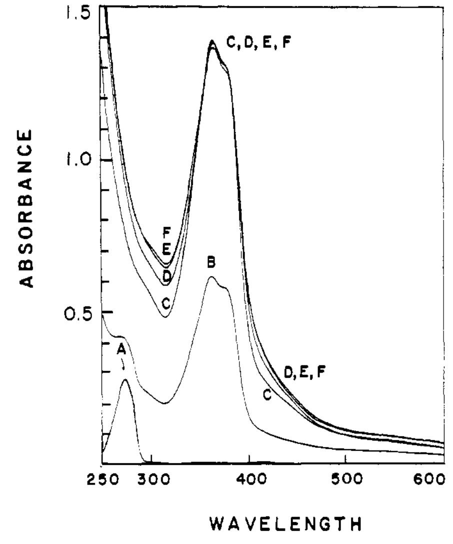


Figure 8. UV-vis absorption spectra of a solution initially containing 0.960 × 10^{-4} M of bisdien, 1.920 × 10^{-4} M Co(II), and 0.960 × 10^{-4} M catechol under oxygen (P_{O_2} = 1 atm) at the following p[H] values: (A) p[H] 3.83; (B) p[H] 6.15; (C) p[H] 7.20; (D) p[H] 8.56; (E) p[H] 9.37; (F) p[H] 10.57. T = 25.0 °C, and μ = 0.100 M (KCl).

Table III. Molar Absorbance (ϵ) of Binuclear Co(II)-BISDIEN Oxygen Complexes Measured at 25.0 °C and μ = 0.100 M (KCl)

oxygen complexes	$10^{-4}\epsilon$, L cm^{-1} mol^{-1}	λ_{max}, nm
$[Co_2O_2(OH)L]^{3+}$	0.321	380
$[Co_2O_2(OH)_2L]^{2+}$	0.395	363
$[Co_2O_2(OH)_3L]^{+}$	0.375	366
$[Co_2O_2LCat]^{2+}$	2.10	365
$[Co_2O_2(OH)LCat]^{+}$	1.5	365
$[Co_2O_2(OH)_2LCat]^{0}$	1.5	365
$[Co_2O_2HLCat]^{3+}$	2.0	365
$[Co_2O_2H_2LCat]^{4+}$	2.0	365
$[Co_2O_2LTir]^{0}$	1.1	324
$[Co_2O_2(OH)LTir]^{-}$	1.2	324
$[Co_2O_2HLTir]^{+}$	1.0	324
$[Co_2O_2H_2LTir]^{2+}$	1.0	324

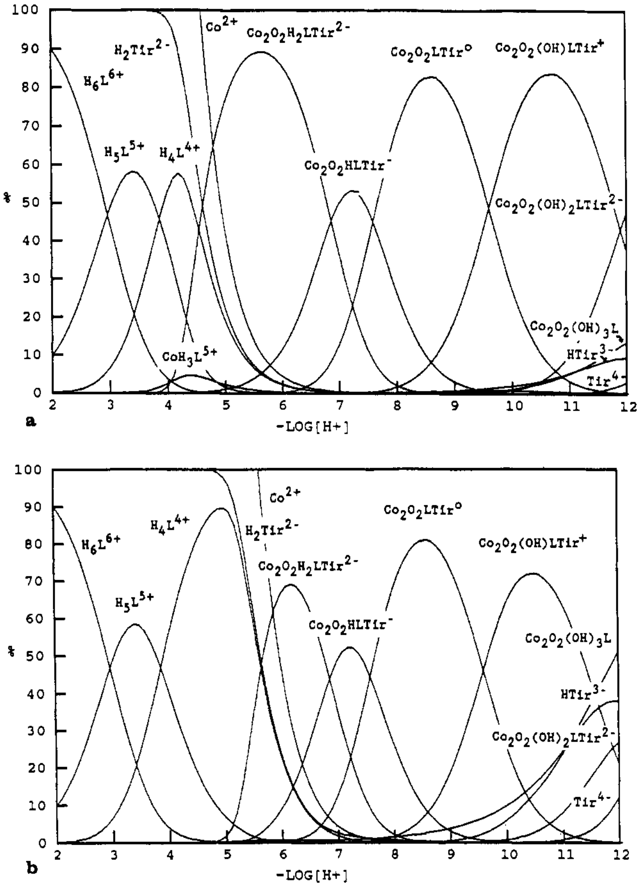


Figure 9. (a) Species distribution curves of the 1:2:1 BISDIEN-Co(II)-TIRON system under dioxygen as a function of $-\log [H^+]$, for a solution initially containing 2.50×10^{-3} M BISDIEN, 5.00×10^{-3} M Co(II), and 2.50×10^{-3} M TIRON under oxygen (P_{O_2} = 1 atm). T = 25.0 °C and μ = 0.100 M (KCl). (b) Species distribution curves of the 1:2:1 BISDIEN-Co(II)-TIRON system under oxygen (P_{O_2} = 1 atm) with initial concentrations of BISDIEN, Co(II), and TIRON at $^1/_{26}$th their concentrations in part a.

The UV-vis spectrum of a 10^{-4} M solution of catechol showed the same absorption peak at 275 nm at p[H] 5.62, indicating that the peak at 275 nm on curve A in Figure 8 is due to the completely protonated form of catechol. The molar absorbances of each catechol-bridged binuclear Co(II)-BISDIEN dioxygen complex were determined with the aid of Figures 7b and 8 and are reported in Table III.

Species distribution curves for TIRON-bridged binuclear Co(II)-BISDIEN dioxygen complexes are shown in Figure 9a,b. The μ-TIRON, μ-hydroxo, and μ-peroxo binuclear Co(II)-BISDIEN complex (**13**) (Scheme III) predominates above p[H] 9.5 until near p[H] 12.0, where the degree of formation of the dihydroxo species becomes higher (Figure 9a). Protonation of the μ-hydroxo species yields **10** (Scheme III), which is 82.9% formed at p[H] 8.6. The two other protonated species are formed at lower p[H] values; species **11** is 53.1% formed at p[H] 7.2, and **12** is 89.2% formed at p[H] 5.6. Figure 9b shows the species distribution curves for the TIRON-bridged binuclear Co(II)-BISDIEN dioxygen complexes where the initial concentration of the reagents are the same as those employed for UV-visible studies. Comparison of Figure 9b with Figure 9a shows that the degree of formation of the most protonated species, **12** (Scheme III), decreases significantly, and it starts to form only at p[H] about 5.0 while in Figure 9a the same species starts to form at about p[H] 4.0. On the other hand, the degrees of formation of species **10** and **11** (Scheme III), show only minor decreases. Above p[H] 11, competition between species **14** and the peroxo trihydroxo complex without the TIRON bridge favor the latter. In other words, the hydroxide ion displaces TIRON from bridging the two metal centers.

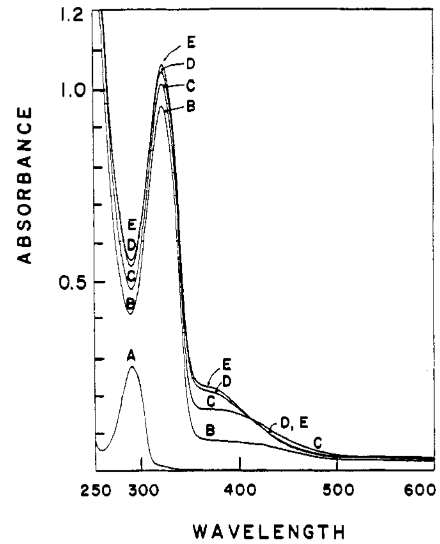


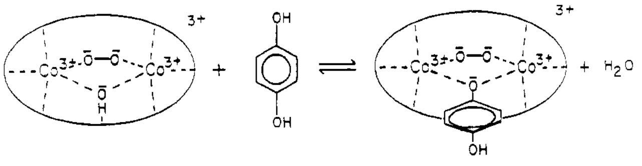
Figure 10. UV-vis spectra of a solution initially containing 0.960×10^{-4} M BISDIEN, 1.920×10^{-4} M Co(II), and 0.960×10^{-4} M TIRON under oxygen (P_{O_2} = 1 atm) at the following p[H] values: (A) p[H] 3.88; (B) p[H] 6.48; (C) p[H] 7.70; (D) p[H] 9.36; (E) p[H] 10.50. T = 25.0 °C, and μ = 0.100 M (KCl).

The family of absorbance curves in Figure 10 shows an intense charge-transfer absorption band with maxima at 324 nm. The absorption peak at 272 nm (curve A) is due to free TIRON. The p[H] of that solution was 3.88, and at this p[H] value TIRON is uncomplexed. The UV-vis spectra of a 10^{-4} M solution of TIRON at p[H] 3.71 showed the same absorption peak at 272 nm. The molar absorbance of each species was determined with the aid of Figure 10 and is reported in Table III.

In contrast to the catechols,, the hydroquinone molecule is too readily oxidized to allow accurate equilibrium measurement of its coordination to the dinuclear BISDIEN-cobalt(II) system in the presence of dioxygen. Potentiometric equilibrium measurements failed in the sense that not even approximate equilibrium was achieved. Downward drift in p[H] was continuous, and thus computations could not be carried out. Nevertheless, approximate room-temperature kinetics were determined in order to characterize the quaternary system (BISDIEN-hydroquinone-Co(II)-dioxygen). Additional preliminary kinetic experiments were performed on the ternary system BISDIEN-Co(II)-dioxygen in order to understand the background reactions in the absence of hydroquinone.

The procedure employed was to preform the oxygen complex as completely as possible, quickly remove the free dioxygen in solution, and then add the hydroquinone to determine whether it reacts with the preformed dioxygen complex. The rate of the formation of the dioxygen complex is quite slow, as it takes over 4 h at pH 7 to become essentially fully formed at 0.244 mM concentration. The electronic spectrum at pH 7.1 possesses the characteristic intense charge-transfer band at 380 nm with a molar absorbance of 0.83 cm^{-1} M^{-1}. Previous calculations[2] indicated

Scheme IV. Formation of the (μ-Hydroquinonato)cobalt Dioxygen Complex



16 **17**

that, under these conditions, the predominating dioxygen complex present in solution is $Co_2O_2(OH)L^{3+}$.

The reversible loss of dioxygen under the conditions employed occurs too rapidly to maintain a fixed concentration of the dioxygen complex. Thus, when argon is used to flush out the free dioxygen from the system, the spectral absorbance peak drops at a steady rate with the concomitant increase in p[H], as the hydroxide ion is released in the deoxygenation process

$$Co_2O_2(OH)L^{3+} \rightleftharpoons Co_2L^{4+} + O_2 + OH^-$$

This equilibrium is driven to the right upon removal of oxygen at an observed rate of approximately 0.02 absorbance units/h. Subsequent addition of oxygen completely restores the spectrum with a concomitant drop in pH to its original value (7.1). Thus the drop in absorbance is due to simple dissociation of the dioxygen complex, and irreversible degradation does not occur under these conditions at a measurable rate. Since the p[H] value employed is nearly 3 log units below the numerical value of the lower log protonation constant of hydroquinone and therefore the free hydroquinone present is totally protonated and not readily susceptible to uncatalyzed oxidation by free dioxygen, it was decided that, in the initial experiment, the free dioxygen would not be purged out of the solution. When 0.33 mmol of hydroquinone was added, the peak at 380 nm increased some 5% in intensity over a period of about 10 min, but no new absorbance bands were observed. A second addition of 0.66 mmol of hydroquinone after 1 h did not change the spectrum; nevertheless, a very gradual decrease in the intensity of the 380-nm peak was observed. The gradual decrease is a continuation of the decrease observed after the original addition of hydroquinone.

The suspected reaction is consistent with the formation of a hydroquinone–μ-phenoxo bridge in place of the μ-hydroxo bridge originally present in the dioxygen complex. One would not expect p[H] changes in this replacement reaction, because the displaced hydroxide corresponds to the hydrogen ion dissociated from the bridging hydroquinone (Scheme IV). The chromophores in **16** and **17** are similar, and one would not expect much change in absorbance when the replacement occurs. In this complex, the hydroquinone is slowly oxidized in a process that takes many hours at room temperature. The observed rate was such that the absorbance rose by about 8% during a 4-h period of time. All of the free dioxygen was then replaced by argon, but the slow reaction accompanied by gradual color change to deep amber continued for at least 20 h. The fact that the reaction continued after the dioxygen supply had been eliminated and was replaced by argon indicates that internal oxidation was taking place. No attempt was made to determine the products of this reaction.

Similar results were also obtained at p[H] 9.1, at which the maximum concentration of the dioxygen complex $Co_2O_2(OH)_2L^{2+}$ is expected.[2] For these experiments it was considered necessary to first remove the excess dioxygen initially, since hydroquinone undergoes autoxidation at this p[H]. The charge-transfer band of the dioxygen complex formed under these conditions absorbs at 362 nm. After the removal of oxygen, successive absorbance measurements showed that the rate of deoxygenation via spontaneous dissociation of oxygen was detectable but was much slower than at pH 7.1.

When hydroquinone was added anaerobically to the oxygen-free solution at pH 9.1, there was a rapid decrease in absorbance, indicating the rapid loss of the dioxygen complex. The observed drop in absorbance from 0.640 to 0.496 units corresponding to a 20% decrease in the dioxygen complex concentration over a 10-min period of time. The reaction could not be followed further since a solid-phase separation started taking place. Loss of coordinated dioxygen would destabilize the dinuclear complex of BISDIEN, and in the absence of a bridging group, precipitation of one of the cobalt centers as cobalt hydroxide would be expected at pH 9.1. Alternatively, the precipitate could be quinone produced in the redox reaction. As these qualitative experiments indicate, hydroquinone does not seem to be a suitable substrate for the dicobalt–BISDIEN dioxygen complex system, and this conclusion is in accord with the fact that for steric reasons it cannot serve as a bridging group involving both phenolate oxygens between the two cobalt centers.

It may be added that increase in cavity size to accommodate the hydroquinone by the use of a larger macrocyclic ring would probably result in difficulties in binding dioxygen as a bridging peroxo group.

Conclusions

Characterization of the species present in the BISDIEN–Co(II)–dioxygen–catechol and in the BISDIEN–Co(II)–dioxygen–TIRON systems has been accomplished by potentiometric and UV–vis studies now makes possible the selection of the most suitable conditions for kinetic studies of the expected redox reaction of coordinated (bridging) catechol and TIRON with coordinated dioxygen in the cavity of the dinuclear cobalt complex with macrocyclic BISDIEN. The close proximity of the oxidant and reductant, as well as their simultaneous coordination to the two metal centers, is expected to lead to a facile redox reaction. In fact, preliminary kinetic runs have revealed that oxidations of catechol and of TIRON in these systems do occur. Kinetic studies involving the use of UV–vis absorbance techniques are now in progress, and the results will be described in a subsequent publication.

Acknowledgment. This work was supported by the Office of Naval Research.