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Equilibrium studies of 1,2-diaminobenzene and 3,4-diaminobenzoate anion with dinuclear cobalt(II) 1,4,7,13,16,19-hexaaza-10,22-dioxacyclotetracosane ☆

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Abstract

1,2-Diaminobenzene and 3,4-diaminobenzoate bridge two cobalt centers in the cavity of the macrocycle 1,4,7,13,16,19-hexaaza-10,22-dioxacyclotetracosane (OBISDIEN), under both anaerobic and aerobic conditions, stabilizing the binuclear array. Under dioxygen μ-peroxo μ-hydroxo bridges are also formed at p[H] values above 6. These dinuclear complex systems were 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 species as a function of p[H]. Coordinate bonding modes suggested for these supramolecular complexes show the proposed oxidant (a μ-peroxo group) and the substrate (μ-1,2-diaminobenzene or μ-3,4-diaminobenzoate) in close proximity, and thus facile oxidation of the substrates is expected.

Keywords: Equilibrium studies; Cobalt complexes; Macrocyclic ligand complexes; Diamine complexes

1. Introduction

OBISDIEN, 1,4,7,13,16,19-hexaaza-10,22-dioxacyclotetracosane, forms cascade complexes involving first-row transition metal ions such as Co^{2+}, Cu^{2+} and Zn^{2+}, and secondary anionic guests [1–4]. Examples of secondary anionic guests in dinuclear OBISDIEN complexes are hydroxide ion, imidazolate anion, peroxide, oxalate, ketomalonate, phosphonousformate, malonate, ethylenediamine, glycine, catecholate, and the anion derived from TIRON, for which quantitative binding constants have been reported [1,4–10]. The formation and redox reactions of the oxalato- and peroxo-bridged dicobalt–OBISDIEN dioxygen complexes have been reported [4]. In that system, oxalate is coordinated to two cobalt centers in the cavity of the OBISDIEN macrocycle, and the oxidizing agent, dioxygen, is also bound to the same two cobalt centers [9]. In the present work, equilibrium studies of complexes involving coordinated aryl diamines — 1,2-diaminobenzene and 3,4-diaminobenzoic acid — as bridging groups (bifunctional substrates) are described.

2. Experimental

2.1. Materials

The OBISDIEN·6HBr employed was synthesized by the method described in the literature [11,12]. 1,2-Diaminobenzene, 3,4-diaminobenzoic acid, potassium chloride (supporting electrolyte), methanol 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 (ethylenediaminetetraacetic acid) with murexide as indicator [13]. Carbonate-free solutions of 0.100 M KOH were prepared from Baker Dilut-It ampules and were standardized by titration against standard potassium acid phthalate purchased from Sigma.

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2.2. *Potentiometric equilibrium measurements*

Potentiometric studies of OBISDIEN in the absence and presence of cobalt(II), dioxygen, 1,2-diaminobenzene and 3,4-diaminobenzoic acid were carried out with a Micronal model B-375 research pH meter fitted with blue-glass and Ag–AgCl reference electrodes calibrated with standard HCl and KOH solutions to read $-\log[H^+]$ directly [14]. Samples of about 0.10 mmol of OBISDIEN diluted to 40 ml with distilled water or 50% water–methanol solution were placed in a sealed thermostated vessel at 25.00 ± 0.05 °C. The experimental solution of OBISDIEN·6HBr alone, adjusted to 0.100 M ionic strength by addition of KCl, was titrated with 0.100 M standard CO_2-free KOH until the p[H] reached about 11. To conserve ligand the solution was then brought to a p[H] value near 3 by adding standard HCl, and 0.20 mmol of Co(II) was added. The solution containing OBISDIEN and Co(II) was then titrated with standard KOH solution until the p[H] was about 8.5, and again standard HCl was added to adjust the solution to near p[H] 3. About 0.10 mmol of 1,2-diaminobenzene was dissolved in water, and 0.10 mmol of 3,4-diaminobenzoic acid was dissolved in 50% water–methanol. The ternary solutions containing OBISDIEN, Co(II) and 1,2-diaminobenzene dihydrochloride or 3,4-diaminobenzoic acid were then studied potentiometrically at molar ratios of 1:2:1 with 0.10 mmol of OBISDIEN, 0.20 mmol of Co(II), and 0.10 mmol of 1,2-diaminobenzene dihydrochloride (Sigma) or 3,4-diaminobenzoic acid (Aldrich). 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.

2.3. *Spectrophotometric studies*

UV–Vis measurements were carried out with a Perkin-Elmer Lambda 19 Fast Scan spectrophotometer, equipped with a thermostated cell compartment to maintain the temperature at 25.0 °C. Samples of solutions of about 0.010 mmol of OBISDIEN, 0.0191 mmol of Co(II), and 0.010 mmol of 1,2-diaminobenzene or 3,4-diaminobenzoic acid were diluted to 100 ml in a sealed thermostated vessel at 25.00 ± 0.05 °C, equipped with blue-glass and Ag–AgCl reference electrodes calibrated as described above. Initially Co(II) and OBISDIEN were added, the p[H] was adjusted, and the Co(II)–OBISDIEN dioxygen complexes were allowed to form during about 3–4 h. After that 1,2-diaminobenzene or 3,4-diaminobenzoic acid was added and 1,2-diaminobenzene or 3,4-diaminobenzoate bridged dinuclear Co(II)–OBISDIEN dioxygen complexes were completely formed in 1 h at the appropriate p[H]. The vessel was maintained under oxygen saturation by a stream of purified oxygen to allow complete formation of dioxygen complexes. The p[H] values of the experimental solutions were adjusted by adding small volumes of 2 M KOH or HCl with a Gilmont microburet attached to the vessel. The ionic strengths of solutions were adjusted to 0.100 M by the addition of KCl. About 3.5 ml of these solutions were transferred to a quartz cell of 1.000 cm path length, with the reference containing 0.100 M KCl.

2.4. *Computations*

The protonation constants of OBISDIEN and equilibrium constants in the systems OBISDIEN–Co(II) in the presence and absence of oxygen have been reported earlier [1].

For the ternary systems OBISDIEN–Co(II)–1,2-diaminobenzene and OBISDIEN–Co(II)–3,4-diaminobenzoic acid in the presence and absence of dioxygen, equilibrium constants were calculated from potentiometric p[H] data with the aid of the program BEST [14]. BEST utilizes the number of millimoles of each component, the titration variables, the initial estimates of equilibrium constants of each species thought to be

Table 1
Logarithms of stability constants of Co(II) complexes of OBISDIEN and the bridging ligands 1,2-diaminobenzene or 3,4-diaminobenzoic acid at 25.00 ± 0.05 °C and $\mu = 0.100$ M (KCl) measured under argon [a]

S bridging substrate	log		
	$\frac{[LCo_2S]}{[Co]^2[L][S]}$	$\frac{[LCo_2(OH)S][H^+]}{[LCo_2S]}$	$\frac{[LCo_2(OH)_2S][H^+]}{[LCo_2(OH)S]}$
1,2-Diaminobenzene	25.29	−8.23	−8.89
3,4-Diaminobenzoic acid	23.58	−8.59	−9.79

[a] S = aryl diamine. Logarithms of other equilibrium constants determined in this work are: $\log[HPD]/[H][PD] = 4.65(4.63)$; $\log[HDBA]/[H][DBA] = 5.74(4.75)$; $\log[H_2DBA]/[HDBA][H] = 3.57(3.69$; $\log[CoPD]/[PD][Co] = 11.24$; $\log[CoHPD]/[CoPD][H] = 4.96$; $\log[CoDBA]/[DBA][Co] = 9.81$; $\log[CoHDBA]/[CoDBA][H] = 5.81$; $\log[CoH_2DBA]/[CoHDBA][H] = 4.41$; $\log[CoL]/[Co][L] = 9.74(9.73)$; $\log[CoHL]/[CoL][H] = 7.57(7.58)$; $\log[CoH_2L]/[CoHL][H] = 6.02(5.97)$; $\log[Co_2L]/[Co][CoL] = 12.41(12.43)$. PD = 1,2-diamonobenzene(*o*-phenylenediamine); DBA = 3,4-diamonobenzoic acid; L = OBISDIEN. The log values in parentheses are from the literature [1,10].

formed from the solution components, and the experimentally determined profiles of p[H] versus solution composition. The program sets up mass balance equations for all species present at each increment of base added and solves for the concentration of each species present. The species introduced are those taken from known chemistry, those shown to be present by spectrophotometric evidence and those that can be justified on the basis of established principles of coordination chemistry in solution.

3. Results and discussion

The protonation constants for the aryl diamines were determined and compared with the values reported in the literature (Table 1) [15]. The one log unit difference for the first protonation constant for 3,4-diaminobenzoate is explained by the solvent used in this work (50% methanol–water solution). The pK_w of this solution was determined to be 14.005.

3.1. Species formed in the Co(II)–OBISDIEN system

Potentiometric equilibrium curves of OBISDIEN in the absence and presence of 2 equivalents of Co(II) under argon were determined by the potentiometric method described in Experimental. The generalized interpretation of the data plotted in Fig. 1 is as follows. Each curve plotted represents a separate experiment. The shape of a given curve provides qualitative information on solution stoichiometry and suggests possible species present. The curves shown in Fig. 1 (and Fig. 2) reveal that hexaprotonated OBISDIEN possesses a sharp inflection at $a=2$ (where a = moles of base added per mole of ligand), followed by an extensive buffer region from $a=2$ to $a=6$. The experiment for which Co(II) is present yields a curve that is distinctly lower than that of OBISDIEN alone, yet coincident with it before $a=2$. This result indicates that only when $a>2$ does cobalt ion form a complex (or complexes) with the ligand. The curve ends abruptly, indicating the experiment could not be carried out past p[H] 8 since $Co(OH)_2$ precipitates out of solution. The equilibrium constants for the 1:1 and 1:2 OBISDIEN–Co(II) complexes were determined previously [1]. The ligand alone and in the presence of cobalt(II) behaves similarly in 50% methanol (Fig. 2).

3.2. 1,2-Diaminobenzene- and 3,4-diaminobenzoate-bridged dinuclear Co(II)–OBISDIEN complexes

The anaerobic potentiometric equilibrium curves for the formation of μ-1,2-diaminobenzene- and μ-3,4-diaminobenzoate-bridged dinuclear Co(II)–OBISDIEN complexes are shown in Figs. 1 and 2, respectively.

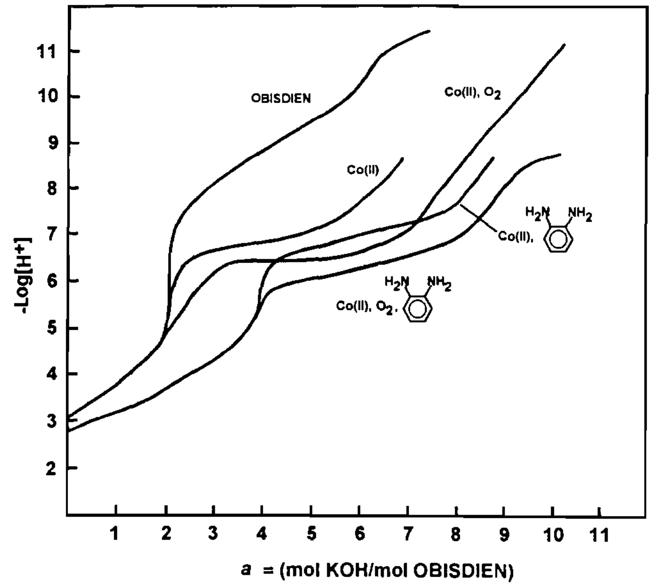


Fig. 1. Potentiometric p[H] profiles for solutions containing 2.51×10^{-3} M OBISDIEN alone; 1.75×10^{-3} M OBISDIEN and 3.34×10^{-3} M Co(II) in the absence of dioxygen; 1.55×10^{-3} M OBISDIEN and 2.96×10^{-3} M Co(II) in the presence of dioxygen; 1.25×10^{-3} M OBISDIEN, 2.39×10^{-3} M Co(II) and 1.26×10^{-3} M 1,2-diaminobenzene dihydrochloride in the absence of dioxygen; and 1.13×10^{-3} M OBISDIEN, 2.15×10^{-3} M Co(II) and 1.14×10^{-3} M 1,2-diaminobenzene dihydrochloride in the presence of dioxygen; $t=25.00\pm0.05$ °C and $\mu=0.100$ M.

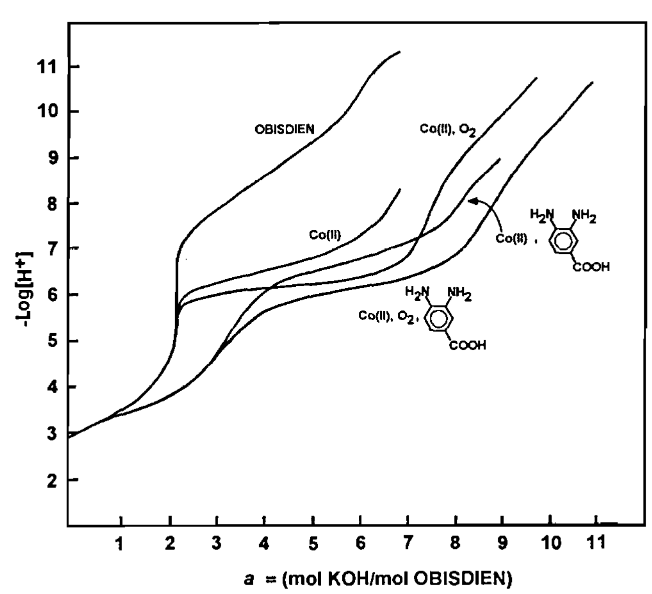


Fig. 2. Potentiometric p[H] profiles for 50% vol. methanol/water solutions containing 2.67×10^{-3} M OBISDIEN alone; 1.86×10^{-3} M OBISDIEN and 3.34×10^{-3} M Co(II) in the absence of dioxygen; 1.58×10^{-3} M OBISDIEN and 2.84×10^{-3} M Co(II) in the presence of dioxygen; 1.22×10^{-3} M OBISDIEN, 2.18×10^{-3} M Co(II) and 1.14×10^{-3} M 3,4-diaminobenzoic monohydrochloride acid in the absence of dioxygen; and 1.10×10^{-3} M OBISDIEN, 1.97×10^{-3} M Co(II) and 1.03×10^{-3} M 3,4-diaminobenzoic monohydrochloride acid in the presence of dioxygen; $t=25.00\pm0.05$ °C and $\mu=0.100$ M.

The curves show inflections close to $a=4$ and $a=8$. The uptake of base up to $a=8$ is due to the neutralization of six protons of OBISDIEN·6HBr plus two protons of the diamines. The utilization of base above $a=8$ is due to the formation of the hydroxo species. The equilibrium constants defined in Eqs. (1)–(3) are reported in Table 1. L is the completely deprotonated form of OBISDIEN, Co^{2+} is the free aquo cobalt(II) ion, and S is aryl diamine. In the calculation of these constants allowance was made for all of the other coordination and protonation equilibria of all the species present, including equilibrium constants for the formation of Co(II)–OBISDIEN dioxygen complexes [1], and the stability constants of the Co(II)–diamine complexes (Table 1). The interaction of bromide ion as well as the complex species which it forms was also considered [16]. The changes shown are valid for the neutral diamine.

$$2Co^{2+} + L + S \rightleftharpoons Co_2LS^{4+};$$

$$\beta = \frac{[Co_2LS^{4+}]}{[Co^{2+}]^2[L][S]} \tag{1}$$

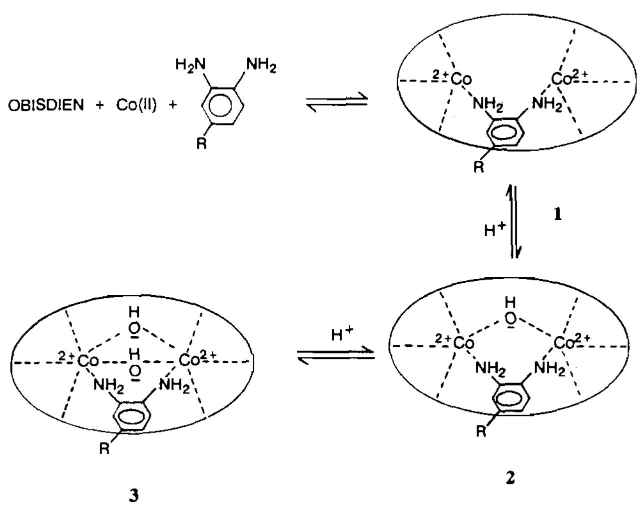
$$Co_2LS^{4+} \rightleftharpoons Co_2(OH)LS^{3+} + H^+;$$

$$K = \frac{[Co_2(OH)LS^{3+}][H^+]}{[Co_2LS^{4+}]} \tag{2}$$

$$Co_2(OH)LS^{3+} \rightleftharpoons Co_2(OH)_2LS^{2+} + H^+;$$

$$K = \frac{[Co_2(OH)_2LS^{2+}][H^+]}{[Co_2(OH)LS^{3+}]} \tag{3}$$

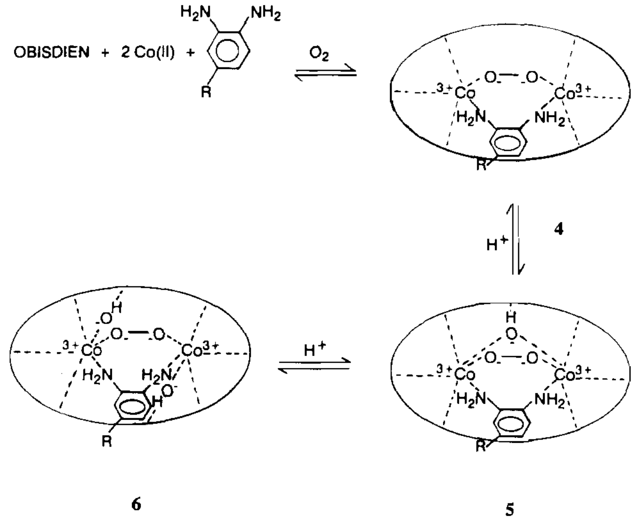
Scheme 1 suggests that first and second protonations of **3** and **2** probably occur on bridged hydroxide ions, resulting in **1**, with water molecules filling the remaining coordination sites of the cobalt(II) ions. The μ-1,2-diaminobenzene-bridged dinuclear Co(II)–OBISDIEN complex, species **1**, is 56% formed at p[H] 7.5 and decreases in concentration at higher p[H], while the proportion of the μ-hydroxo species **2** increases to reach a maximum of 44% formation at p[H] 8.5 (Fig. 3). The dihydroxo species **3** is 95% formed at p[H] 11.8. Species formed for the μ-3,4-diaminobenzoate-bridged dinuclear Co(II)–OBISDIEN system are also indicated in Scheme 1. The distribution of the species formed in the μ-3,4-diaminobenzoate-bridged dinuclear Co(II)–OBISDIEN system are shown in Fig. 4. The dihydroxo species is 80% formed at p[H] 12.0; the monohydroxo species reaches a maximum concentration at p[H] 9.2, where it is 39% formed; and species **1** (Scheme 1) is 48.6% formed at p[H] 7.7.



Scheme 1. 1,2-Diaminobenzene (R=H) or 3,4-diaminobenzoate (R=COO⁻) bridged dinuclear Co(II)–OBISDIEN complexes.

3.3. Oxygen complexes

The dioxygen complexes formed in the 1,2-diaminobenzene- and 3,4-diaminobenzoate-bridged dinuclear Co(II)–OBISDIEN dioxygen complexes are illustrated in Scheme 2, and the equilibrium constants for the dioxygen-containing species, defined in Eqs. (4)–(6) and determined from potentiometric data (Figs. 1 and 2), are reported in Table 2. Figs. 1 and 2 show the p[H] profiles where the aryl diamine is absent, but oxygen is present. These conditions produce a 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. The lowest curve in Fig. 1 demonstrates the formation of the dinuclear cobalt complex containing OBISDIEN, dioxygen and 1,2-diaminobenzene. This curve is distinct, with its own break at $a=9$ (six from OBISDIEN·6HBr plus two from 1,2-diaminobenzene plus one from hydroxide bridging),



Scheme 2. 1,2-Diaminobenzene (R=H) or 3,4-diaminobenzoate (R=COO⁻) bridged dinuclear Co(II)–OBISDIEN dioxygen complexes.

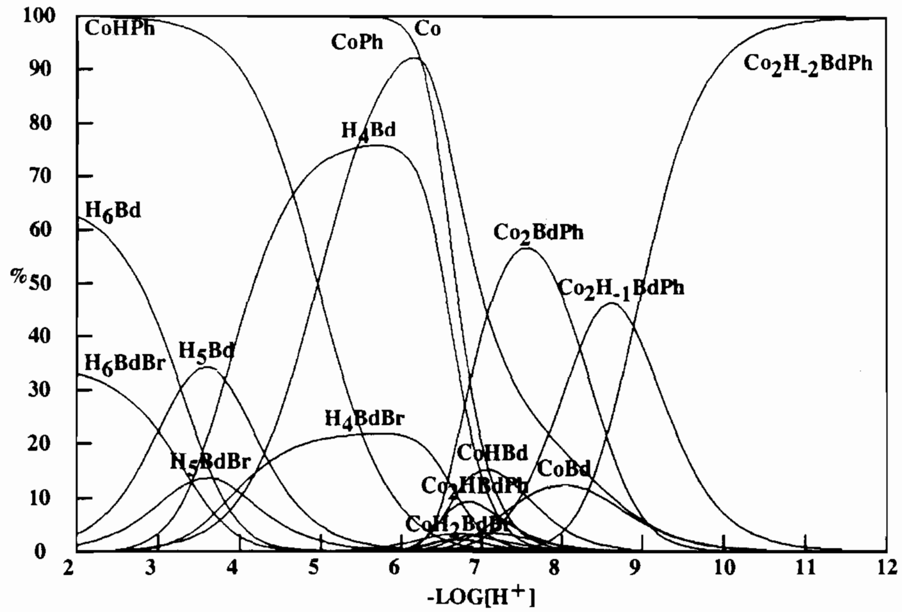


Fig. 3. Species distributions for a solution containing 1.00×10^{-3} M OBISDIEN (Bd), 2.00×10^{-3} M Co(II) and 1.00×10^{-3} M 1,2-diaminobenzene (Ph) under anaerobic conditions in aqueous solution containing 6.00×10^{-3} M Br^-. % is percentage of a species present, with 1.00×10^{-3} M OBISDIEN set at 100%. H_{-1} and H_{-2} represent OH^- and $(OH^-)_2$, respectively.

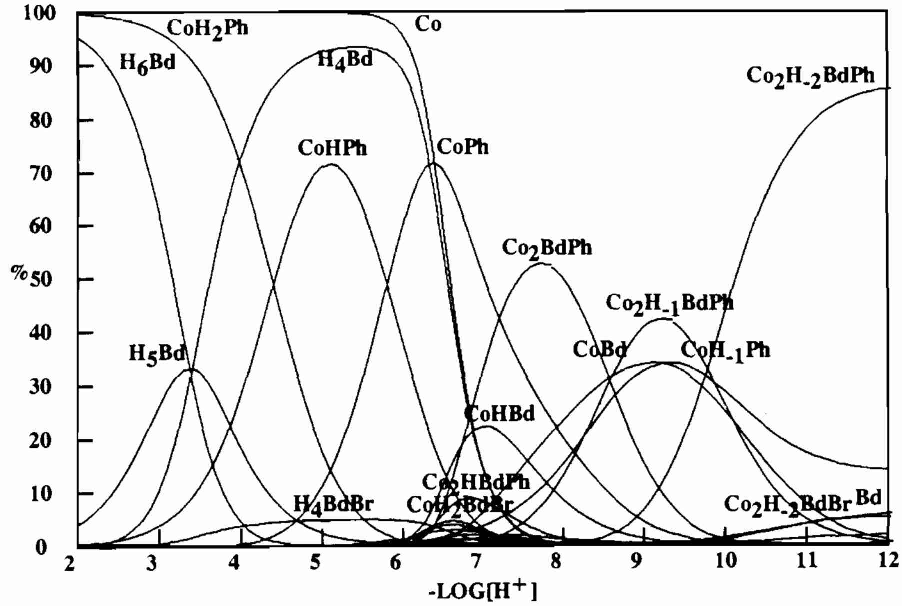


Fig. 4. Species distributions for a 50% vol. methanol/water solution containing 1.00×10^{-3} M OBISDIEN (Bd), 2.00×10^{-3} M Co(II) and 2.00×10^{-3} M 3,4-diaminobenzoic acid (Ph) under anaerobic conditions in aqueous solution at 25.0 °C containing 6.00×10^{-3} M bromide. % is percentage of a species present, with 1.00×10^{-3} M OBISDIEN set at 100%. H_{-1} and H_{-2} represent OH^- and $(OH^-)_2$, respectively.

consistent with formula 5. Finally, the lowest curve in Fig. 2 demonstrates the formation of the dinuclear cobalt complex of the OBISDIEN-μ-dioxygen-μ-3,4-diaminobenzoate complex (Scheme 2).

$$Co_2LS + O_2 \rightleftharpoons Co_2O_2LS;$$

$$K(O_2) = \frac{[Co_2O_2LS]}{[Co_2LS]P(O_2)} \qquad (4)$$

$$Co_2O_2LS \rightleftharpoons Co_2O_2(OH)LS + H^+;$$

$$K'(O_2) = \frac{[Co_2O_2(OH)LS][H^+]}{[Co_2O_2LS]} \qquad (5)$$

$$Co_2O_2(OH)LS \rightleftharpoons Co_2O_2(OH)_2LS + H^+;$$

$$K''(O_2) = \frac{[Co_2O_2(OH)_2LS][H^+]}{[Co_2O_2(OH)LS]} \qquad (6)$$

Table 2

Logarithms of equilibrium constants for the formation of Co(II) dioxygen complexes of OBISDIEN and a bridging ligand (1,2-diaminobenzene or 3,4-diaminobenzoic acid) at 25.00±0.05 °C and $\mu=0.100$ M (KCl)

S bridging ligand	log		
	$\frac{[LCo_2O_2S]}{[LCo_2S]P(O_2)}$	$\frac{[LCo_2O_2(OH)S][H^+]}{[LCo_2O_2S]}$	$\frac{[LCo_2O_2(OH)_2S][H^+]}{[LCo_2O_2(OH)S]}$
1,2-Diaminobenzene	2.88	−7.44	−7.73
3,4-Diaminobenzoic acid	2.82	−7.06	−9.05

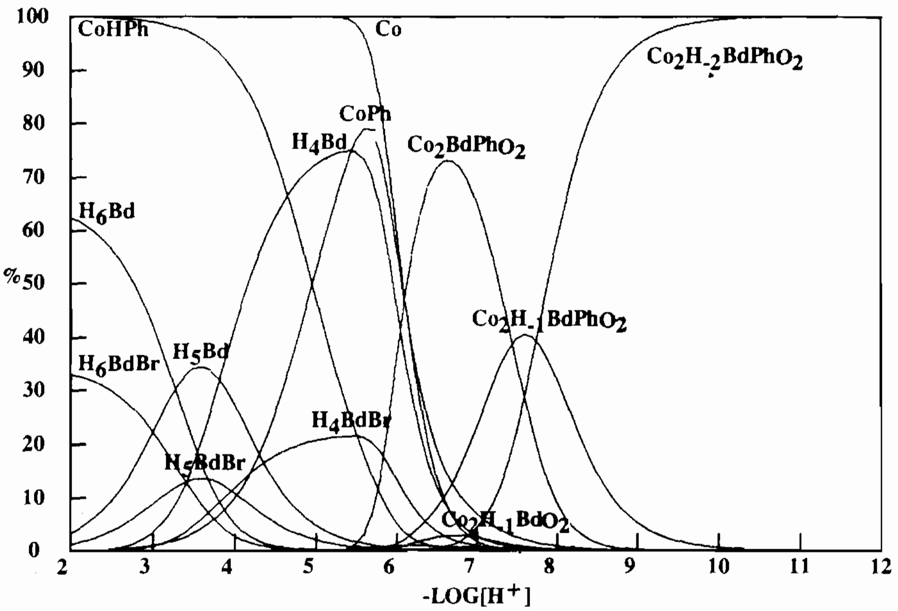
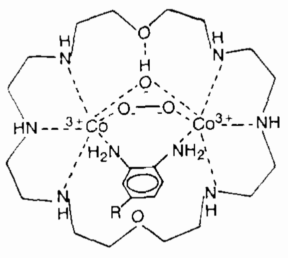


Fig. 5. Species distribution curves of the 1:2:1 OBISDIEN–Co(II)–1,2-diaminobenzene system under oxygen as a function of $-\log[H^+]$, for a solution initially containing 1.00×10^{-3} M OBISDIEN, 2.00×10^{-3} M Co(II) and 1.00×10^{-3} M 1,2-diaminobenzene (Ph) under oxygen ($P(O_2)=1.00$ atm) in 50% methanol; $t=25.00\pm0.05$ °C, and $\mu=0.100$ M (KCl). % is percentage of a species present, with 1.00×10^{-3} M OBISDIEN set at 100%. H_{-1} and H_{-2} represent OH^- and $(OH^-)_2$, respectively.

The species in Scheme 2 differ from the species in Scheme 1 in having a greater tendency toward hydroxo complex formation, because oxygenation causes an increase in the charge of the metal ions. The hydroxo species, **6**, has two hydroxo ligands coordinated to each metal center, and both hydroxo groups are probably hydrogen bonded to an ether oxygen of the macrocyclic ring. Protonation of one hydroxo ligand of **6** would produce a coordinated water molecule, which is then displaced by the other hydroxo group, which is now considered to bridge the metal centers as in **7** (shown in Scheme 3, a more detailed representation of compound **5** of Scheme 2).

Species distribution curves for 1,2-diaminobenzene-bridged dinuclear Co(II)–OBISDIEN dioxygen complexes are shown in Fig. 5. The dihydroxo, μ-1,2-diaminobenzene, μ-peroxo dinuclear Co–OBISDIEN complex, **6** (Scheme 2), predominates above p[H] 9.8. Protonation of this species yields the monohydroxo species **5** (Scheme 2), which reaches a maximum of 35% at p[H] 7.6. Protonation of this species yields **4** (Scheme 2), and this complex is 69% formed at p[H] 6.6.



7 R = H or CO_2^-

Scheme 3. Structure of compound **7**.

Fig. 6 shows the species distribution curves for the 3,4-diaminobenzoate-bridged dinuclear Co–OBISDIEN dioxygen system. Species **4** is 57% formed at p[H] 6.5, and the monohydroxo species **5** reaches a maximum concentration of 72% at p[H] 8.1. The dihydroxo species is 87.0% formed at p[H] 10.29 and decreases slightly at higher p[H].

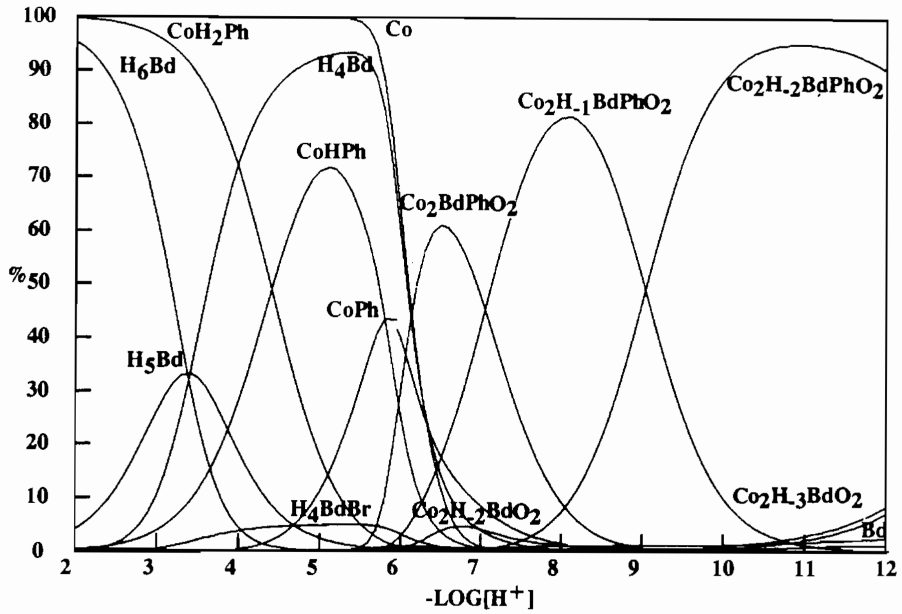


Fig. 6. Species distribution curves of the 1:2:1 OBISDIEN–Co(II)–3,4-diaminobenzoic acid system under oxygen as a function of $-\log[H^+]$, for a solution initially containing 1.00×10^{-3} M 3,4-diaminobenzoic acid under oxygen ($P(O_2)=1.00$ atm) in 50% methanol; $t=25.00\pm0.05$ °C and $\mu=0.100$ M (KCl). % is percentage of a species present, with 1.00×10^{-3} M OBISDIEN set at 100%. H_{-1}, H_{-2} and H_{-3} represent OH^-, $(OH^-)_2$ and $(OH^-)_3$, respectively.

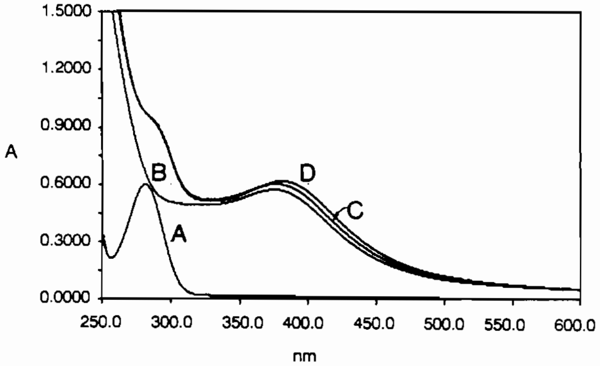


Fig. 7. UV–Vis spectra of solutions containing 1.103×10^{-4} M total OBISDIEN species, 1.913×10^{-4} M total Co(II) and 1.104×10^{-4} M total 1,2-diaminobenzene under oxygen ($P(O_2)=1.00$ atm) at the following p[H] values: A, 3.34; B, 7.52; C, 6.68; D, 7.53; $t=25.0$ °C and $\mu=0.100$ M (KCl).

The family of absorbance curves in Fig. 7 shows an intense charge-transfer absorption band for the (μ-peroxo)(μ-hydroxo)(μ-1,2-diaminobenzene) dinuclear Co(II)–OBISDIEN complex, with a maximum at 380 nm and a shoulder at about 290 nm, the latter from the coordinated 1,2-diaminobenzene (curve D) at p[H] 7.53. Curve C shows the intense charge-transfer absorption band due to the (μ-peroxo)(μ-1,2-diaminobenzene) dinuclear Co(II)–OBISDIEN complex at p[H] 6.68, with a maximum at 376 nm and a shoulder at about 290 nm, the latter of which is also due to coordinated 1,2-diaminobenzene. The absorption peak at 282 nm of curve A is that of 1,2-diaminobenzene in the same solution but at p[H] 3.34. At this p[H] no dioxygen complex is formed. The UV–Vis spectrum of a 10^{-4} M solution of 1,2-diaminobenzene shows a similar absorption peak at 282 nm at p[H] 3.42, indicating that the peak at 282 nm on curve A in Fig. 7 is due to the monoprotonated 1,2-diaminobenzene. Curve B is due to the dinuclear Co(II)–OBISDIEN dioxygen complex without 1,2-diaminobenzene, with a maximum at 376 nm. This maximum increases slightly as 1,2-diaminobenzene becomes coordinated to the metal centers of the dinuclear Co(II)–OBISDIEN dioxygen complex, forming the (μ-peroxo)(μ-1,2-diaminobenzene) dinuclear Co(II)–OBISDIEN complex, and shifts a little to 380 nm as the μ-hydroxo species is formed. The absorbance curve for the dihydroxo species is not shown.

The family of absorbance curves in Fig. 8 shows an intense charge-transfer absorption band due to dinuclear Co(II)–OBISDIEN dioxygen complexes (curve B) and two bands due to 3,4-diaminobenzoate-bridged dinuclear Co–OBISDIEN dioxygen complexes (curves C and D). Curve C is due to (μ-peroxo)(μ-3,4-diaminobenzoate) Co(II)–OBISDIEN complex, since this is the major species at p[H] 6.49 (see Fig. 6). Absorption band C shows a maximum at 388 nm and another at 304.8 nm, the latter due to the coordinated diamine. Curve D is due to the (μ-peroxo)(μ-hydroxo)(μ-3,4-diaminobenzoate) dinuclear Co(II)–OBISDIEN complex at p[H] 8.1 (see Fig. 6). The absorption band for the dihydroxo species is not shown. Absorption curve D shows maxima at 382 and 304 nm, the latter being due to the coordinated diamine. The absorption peaks at 310 and 277 nm of curve A are due to 3,4-diaminobenzoate in solution at p[H] 4.07, because at this p[H] the dioxygen complex is not formed. The UV–Vis

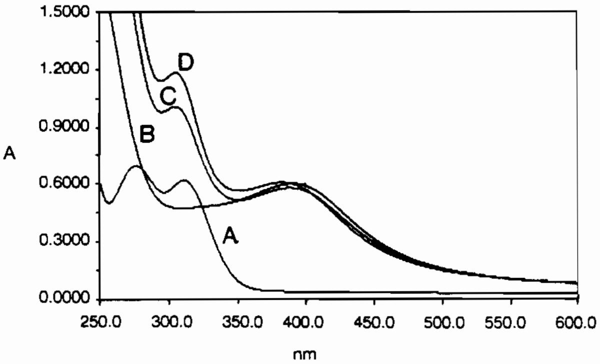


Fig. 8. UV–Vis spectra of 50% vol. methanol/water solutions containing 1.104×10^{-4} M total OBISDIEN, 1.913×10^{-4} M total Co(II) and 1.106×10^{-4} M total 3,4-diaminobenzoic acid under oxygen ($P(O_2)=1.00$ atm) at the following p[H] values: A, 4.07; B, 7.53; C, 6.49; D, 8.13; $t=25.0$ °C and $\mu=0.100$ M (KCl).

spectrum of a 10^{-4} M solution of 3,4-diaminobenzoate shows the same absorption peaks at p[H] 4.07, indicating that the peaks at 310 and 277 nm on curve A in Fig. 8 are due to 3,4-diaminobenzoate.

4. Conclusions

The 1,2-diaminobenzene-bridged dinuclear Co(II)–OBISDIEN dioxygen complexes and the 3,4-diaminobenzoate dinuclear Co(II)–OBISDIEN dioxygen complexes were characterized by potentiometric and UV–Vis spectrophotometric studies. The species distributions of these systems now make possible the selection of the most suitable conditions for kinetic studies of the expected redox reaction between the bridging 1,2-diaminobenzene and 3,4-diaminobenzoate with coordinated dioxygen (μ-peroxo) in the cavity of the dinuclear cobalt complex of macrocyclic OBISDIEN. The close proximity of the oxidant (the μ-peroxo group) and the reductant (the aryl diamine), as well as their simultaneous coordination to the same two metal centers, is expected to lead to a redox reaction at an elevated temperature. Kinetic studies are in progress, and the results will be described in a subsequent publication.

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