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Mononuclear and Dinuclear Cobalt Complexes and its Dioxygen Adduct with a New 24-membered Hexaaza Macrocyclic Ligand

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Dinucleating 24-membered hexaazadiphenol macrocyclic ligand 3,6,9,17,20,23-hexaaza-29,30-dihydroxy-13,27-dimethyl-tricyclo[23,3,1,1^{11,15}] triaconta-1(29), 11,13,15(30),25,27-hexaene (L or BDBPH), is prepared by the $NaBH_4$ reduction of the Schiff base obtained from [2+2] template condensation of 2,6-diformyl-p-cresol with diethylenetriamine. The ligand maintains dinuclear integrity for cobalt (II) while facilitating the formation of bridging phenolate dicobalt cores. Potentiometric equilibrium studies indicate that a variety of protonated, mononuclear and dinuclear cobalt (II) complexes form from p[H] 2 through 11 in aqueous solution. The protonation constants of this ligand and stability constants of the 1:1, 1:2 ligand: cobalt(II) complexes were determined in KCl supporting electrolyte ($\mu = 0.100$ M) at 25°C. The mechanism for the formation of dinuclear dioxygen cobalt(II) complexes is also described. The stability constants of mononuclear and dinuclear cobalt complexes were determined under nitrogen. Preliminary results show that the dinuclear dioxygen cobalt (II) complexes do not catalyze hydroxylation of adamantane in the presence of H_2S as *two-electron reductant.*

Keywords: Cobalt complex; Macrocycle ligand; Mononuclear complex; Dinuclear complex; Dioxygen adduct

INTRODUCTION

Dinuclear peroxo centers have been the subject of continuing investigation because of their relevance as structural models for the active sites in several metalloproteins [1]. Dinucleating macrocyclic ligand, tetraazadiphenol macrocycle and its derivatives capable of binding two metal ions in close proximity have received particular attention [2–5]. Recently, Wang *et al.*, reported the synthesis of two macrocyclic ligands: 24-membered Schiff-base hexaazadiphenol macrocycle (24BPyBC) and its hydrogenated form, 15, 31-dimethyl-3, 11, 19, 27-33, 35-hexaazapentacyclo[27.3.1.1^{5,9}1.^{13,17}1.^{21,25}]-hexatriaconta-5,7,9(33),13,15,17(34),21,23,25(35), 29, 31, 1(36)-dodecaene-34, 36-diol (24RBPyBC) [6]. The dinuclear dioxygen iron complex of 24RBPyBC was found to catalyze the hydroxylation of hydrocarbons with O_2 in the presence of H_2S [7].

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In this paper, a new 24-membered ligand 3,6,9,17,20,23-hexaaza-29,30-dihydroxy-13,27-dimethyl-tricyclo[23,3,1,$1^{11,15}$]triaconta-1(29),11,13,15(30),25,27-hexaene (L or BDBPH) has been synthesized and compared with the analogous ligand, 24RBPyBC. This new ligand has more flexible donor groups in the side chain than 24RBPyBC, which can provide a larger cavity for dinuclear centers. Also the amino groups are more basic groups than pyridine nitrogen, and may allow metal–metal spatial distances and coordination geometry to vary from one intermediate to the next.

The direct functionalization of saturated hydrocarbons usually requires extreme reaction conditions (*i.e.*, high temperature, high pressure, strongly electrophilic or radical reagents) and gives mixtures of products including polyfunctional compounds [8]. The oxidation of saturated hydrocarbons under mild conditions is an intellectually stimulating and industrially important objective of current relevance. Many biological systems are able to hydroxylate non-activated hydrocarbon bonds. Of particular interest are the mono-oxygenases of which cytochrome P450(cP450) constitutes the most studied group. It consists of a family of isozymes, which are active in the oxidation of numerous drugs, xenobiotics and endogenous compounds [9,10]. Among these transformations, the attractive model of hydroxylation of saturated hydrocarbons, such as GIF systems [11] proposed by the Barton group, strongly support a $Fe^{V}=O$ species, which probably acts as a hydrogen abstractor to give a discrete carbon radical [12]. In our system, we use molecular oxygen, pyridine, the designed and synthesized macrocyclic ligand and ferrous ions, in the presence of a two-electron reductant (H_2S) for facile oxygenation of adamantane.

Our former studies have demonstrated that dinuclear dioxygen iron (II) complex of this ligand also shows the effectively catalytic hydroxylation of adamantane and cyclohexane. But its cobalt dioxygen complex does not show similar activity, though dioxygen cobalt complexes formed easily and can easily be degraded to metal-centered or ligand-centered products. Cobalt (III) dioxygen complexes having easily oxidizable ligands are converted to the corresponding inert cobalt (II) complexes with concomitant release of hydrogen peroxide. In some cases easily oxidizable coordinated ligands undergo oxidative dehydrogenation [13].

In this paper we studied the stabilities of mononuclear, and dinuclear Co (II) complexes and homodinuclear Co (II) dioxygen complexes of BDBPH. The potentiometric method was employed successfully to determine formation constants that govern the interaction between the metal ion and ligand, and to determine the distribution of species present in the solution as a function of p[H].

EXPERIMENTAL

Materials

Dinucleating 24-membered hexaazadiphenol macrocyclic ligand, 3,6,9,17,20,23-hexaaza-29,30-dihydroxy-13,27-dimethyl-tricyclo [23,3,1,$1^{11,15}$] triaconta-1(29),11,13,15(30),25,27-hexaene (L or BDBPH), was prepared by the $NaBH_4$ reduction of the Schiff base obtained from [2 + 2] template condensation of 2,6-diformyl-p-cresol (supplied by Aldrich Chemical Co.) with diethyltriamine (redistilled before use). All other reagents used in the synthetic work were obtained in high purity from Aldrich Chemical Co. and were used without further purification.

The macrocyclic ligand was titrated. Six equivalents of hydrobromic acid were found to be bound to six amino groups. The fully protonated form of BDBPH is designated as H_8L^{6+} including two phenolic protons. Octa-, hepta-, hexa-, penta-, tetra-, tri-, di- and mono-protonated, and fully deprotonated forms of the ligand are designated as H_8L^{6+}, H_7L^{5+}, H_6L^{4+}, H_5L^{3+}, H_4L^{2+}, H_3L^{+}, H_2L, HL^{1-} and L^{2-}, respectively. The cobalt stock solution for potentiometric study was reagent grade nitrate made up with doubly distilled water and standardized by cation exchange hydrogen techniques. CO_2-free 'Dilute-it' ampoules of KOH were obtained from J. T. Baker Inc. KOH solutions (about 0.1 M) were prepared in doubly distilled water and standardized. The extent of carbonate accumulation ($\leq 1.8\%$) was checked periodically by titration with a standard HCl solution.

Potentiometric Determinations

A Corning Model 250 pH digital meter fitted with a blue-glass electrode and a calomel reference electrode was calibrated with standard dilute strong acid at 0.10 M ionic strength to read hydrogen concentration directly so that the measured quantity was $-\log [H]^+$, designated as p[H]. Hydrogen ion activities (pH) were not used in this research. The experimental solution was contained in a 75 mL jacketed glass cell thermostated at 25.00 ± 0.05°C by a circulating constant-temperature water bath. Potentiometric p[H] measurements and computation of the protonation constants and the stabilities of the cobalt complexes were carried out by procedures described in detail elsewhere [14]. The p[H] measurements were made at ionic strength 0.10 M adjusted with KCl. All systems were investigated under anaerobic conditions; oxygen and carbon dioxide were excluded from the reaction mixture by maintaining a slight positive pressure of purified argon gas in the reaction vessel. The oxygenation reaction was carried out under the 1.00 atm purified oxygen bubbled into the reaction vessel. The equilibrium constants were determined with the program BEST. The species distribution diagrams were calculated from equilibrium constants with the help of program SPE and plotted with SPEPLOT developed by Martell *et al.* [14] The p[H] range of accurate measurements was considered to be 2–12. The log K_w for the aqueous system, defined as $-\log([H^+][OH^-])$ at the ionic strength employed, was found to be −13.78.

UV Spectrophotometric Studies

UV-Vis measurements were carried out with a Beckman DU-640B spectrophotometer. Samples of solutions of about 0.008 mmol of ligand and 0.016 mmol of Co(II) were diluted to 50 mL in a sealed vessel thermostated at 25°C, and equipped with blue-glass and Ag-AgCl reference electrodes calibrated as described previously. Initially Co(II) and BDBPH were allowed to react with dioxygen for about 3 h. The vessel was maintained under oxygen saturation by a stream of purified oxygen to allow the complete formation of dioxygen complexes. The p[H] values of the experimental solutions were adjusted by addition of 0.1 M KOH. The ionic strengths of solutions were adjusted to 0.1 M by the addition of KCl. About 3.5 ml of these solutions were transferred to a quartz cell of 1.00 cm path length. The reference cell contained 0.1 M KCl solution.

O_2-uptake Experiment

The O_2-uptake measurement was carried out on the reaction of ligand (0.0948 mmol) and $Co(SCN)_2 \cdot 6H_2O$ (0.1896 mmol) in acetonitrile (20 ml) at room temperature. The volume of O_2 consumed during the oxygenation reaction was determined to be 2.20 mL directly from the O_2 consumption using a manometer designed for the small-scale reaction. Thus, the stoichiometry of O_2 : Co was calculated to be 1 : 2.11.

RESULTS AND DISCUSSIONS

Potentiometric Studies

Ligand

The fully protonated species is designated as H_8L^{6+} and the fully deprotonated species as

L^{2-}. LogK_n^H values of eight successive stepwise protonation constants of the ligand used in this paper are 11.90, 11.04, 10.03, 9.47, 7.13, 4.49, 3.57 and 3.30 ($K_n^H = [H_nL^{(n-2)+}]/[H_{n-1}L^{(-3)+}][H^+]$, $n = 1,2,3,4,5,6,7$, and 8) and are in good agreement with previous work, especially in last six constants [15]. When the $p[H] < 2$, the ligand exists in the fully protonated form, H_8L^{6+}. As the p[H] is increased, the ligand loses its protons from amino nitrogens to become H_7L^{5+}, H_6L^{4+} H_5L^{3+}, H_4L^{2+}, H_3L^+ and H_2L species respectively. When the p[H] is above 9.5, one of the two phenolic hydroxygens begins to be deprotonated to form HL^{-1}, which reaches its maximum concentration (56.8%) at p[H] 11.5. The neutral ligand H_2L reaches its maximum concentration at $p[H] = 10.6$ (61%). Under more alkaline conditions, the two phenol groups deprotonate to the free ligand dianion L^{-2} ($p[H] > 12$). The first phenolate dissociation overlaps with the latter amino dissociation steps.

Stability of Mononuclear Cobalt(II) Complex

The stability constants involving protonated and deprotonated Co(II) species are shown in Table I. For mononuclear systems, only one major species [CoL] was present with a log stability constant of 13.35. The [CoL] species makes its appearance only above pH 10. Even in a 1:1 system, the dinuclear species were found to dominate: $[Co_2H_2L]^{4+}$, $[Co_2HL]^{3+}$, and $[Co_2L]^{2+}$. In the 1:1 system the dinuclear species of $[Co_2H_2L]^{4+}$ was minor, but the other two dinuclear species: $[Co_2HL]^{3+}$ and $[Co_2L]$ reached the highest values 49.8% and 21.1% at $p[H] = 6.1$ and 10.8, respectively.

TABLE I Stepwise stability constants for the L-Co(II) system [$\mu = 0.10$ M (KCl), 25°C, under Argon]

Stepwise quotient, K	BDBPH Log K[a]	OBISDIEN Log K	BISBAMP Log K
$[CoL]/[Co][L]$	13.35	9.73	9.05
$[CoHL]/[CoL][H]$		7.58	7.12
$[CoH_2L]/[CoHL][H]$		5.97	–
$[CoL]/[Co(OH)L][H]$	–	–	9.97
$[Co_2L]/[CoL][Co]$	11.12	2.7	3.00
$[Co_2HL]/[Co_2L][H]$	10.32	–	–
$[Co_2H_2L]/[Co_2HL][H]$	5.69	–	–
$[Co_2L]/[Co_2(OH)L][H]$		–	7.90

[a] Estimated error = ± 0.02 ~ 0.04; – species not found.

TABLE II Stepwise stability constants for the L-Co(II) systems [$\mu = 0.10$ M (KCl), 25°C, in the presence of O_2]

Stepwise quotient, K	Co LogK[a]	Co/O-BISDIEN LogK
$[Co_2L(O_2)]/[Co_2L]PO_2$	13.29	–
$[Co_2L(O_2)]PO_2/[Co_2L(O_2)(OH)][H]$	–	3.29
$[Co_2L(O_2)(OH)]/[Co_2L(O_2)(OH)_2][H]$	–	−8.25
$[Co_2L(O_2)(OH)_2]/[Co_2L(O_2)(OH)_3][H]$	–	−9.36

[a] Estimated error = ± 0.02 ~ 0.04; – species not found.

The formation constant of $\mathrm{logK}_{[CoL]}$ is 13.35 which is larger than that of OBISDIEN (L′), $\mathrm{logK}_{[CoL']} = 9.73$ or BISBAMP [16]. Because these two ligands have different structure though they have the same side chains with same six amine nitrogen donors, BDBPH has two phenolic heads in the 24-membered macrocyclic skeleton, which increases the affinity to metal ions compared with the ether oxygen in OBISDIEN.

The stability constants of this ligand have been determined with several other metal ions by Shangguan *et al.* [15] ($\mathrm{logK}_{[FeL]/[Fe][L]} = 33.85$, $\mathrm{logK}_{[CuL]/[Cu][L]} = 24.50$, $\mathrm{logK}_{[ZnL]/[Zn][L]} = 17.72$, $\mathrm{logK}_{[CdL]/[Cd][L]} = 14.28$ and $\mathrm{logK}_{[MnL]/[Mn][L]} = 11.58$). BDBPH shows higher affinity to Fe(III), Co(II) and Cu(II) ions. The stability constant of Co(II) complexes with fully deprotonated BDBPH, [CoL] is slightly higher than that of Mn(II) yet slightly lower than Zn(II) and Cd(II). In 1:1 solution, because of the ligand's tendency toward 2:1 Co:L complex formation. [CoL] begins to form from $p[H] > 10$ and to dominate when the p[H] is higher than 11, then reaches its highest concentration at $p[H] = 11.9$ (69%). The species distribution based on stability

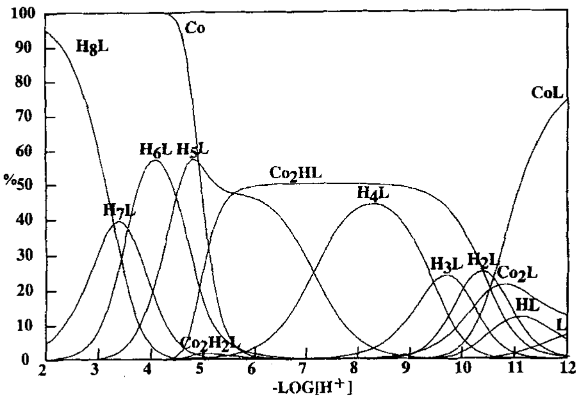


FIGURE 1 Species distribution diagram for the L-Co(II) (1 : 1) system as a function of p[H] under argon (% = Percentage of species distribution in solution, T_{Co} = 0.00176 M, T_L = 0.00176 M).

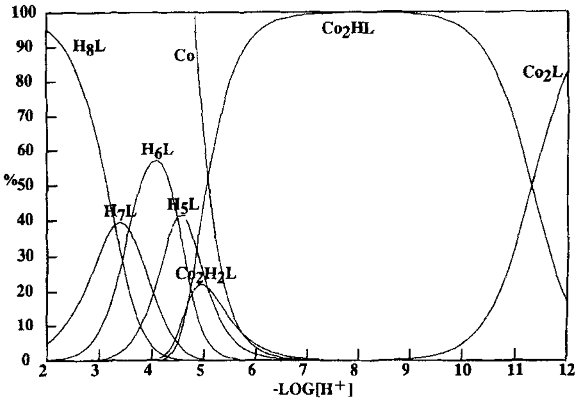


FIGURE 2 Species distribution diagram for the L-Co(II) (1 : 2) system as a function of p[H] under argon (% = Percentage of species distribution in solution, T_L = 0.00163 M, T_{Co} = 0.00326 M).

constants is calculated and demonstrated in Figure 1.

Stabilities of Cobalt(II) Dinuclear Complexes

The potentiometric titration of 1 : 2 molar ratio of $Co(II)-H_8L^{6+}$ likewise shows that 2 : 1 Co : L complexes are preferred. The first formed species is diprotonated dinuclear complex, $[Co_2H_2L]^{4+}$, as a minor component. The maximum concentration of it appears at p[H] = 5.0 with 22%. A very stable monoprotonated dinuclear species-$[Co_2HL]^{3+}$ follows in the p[H] range 6 to 10 at or near 100%, which finally reverts to the dinuclear species $[Co_2L]^{2+}$ above pH 11. This neutral dinuclear Co(II) complex was not prone to deprotonate to form hydroxo species. The stepwise stability constants of 2 : 1 Co(II) complex with fully deprotonated BDBPH, Co_2L, is 11.12, which is somewhat lower than $Fe(III)_2L$ ($\log_{[Fe_2L]/[Fe][FeL]} = 15.03$) When the second Co(II) enters into the macrocyclic cavity and forms bridged oxo dinuclear complexes, it is expected that each metal center still has a vacant coordination site, so hydroxo species could be possible. However such species were not found.

The species distribution diagram based on the stability constants is shown in Figure 2.

Oxygenation and Stability of Dinuclear Complexes

From titration experiments under 1 atm of purified oxygen it is clear that a single dinuclear species $[Co_2LO_2]^{2+}$ is formed. Formation of oxygen complexes is slow and it takes 1–2 h to reach each equilibrium point. Oxygen complexes start to appear at p[H] 3.2. The oxygen species-$[Co_2LO_2]^{2+}$ reach its highest concentration 100% when the p[H] increases to 5.3. There does not seem to be evidence for any other dioxygen species. Figure 3 shows the complete species distribution in this system under oxygen.

Formula (1) represents the oxygenation equilibrium and has the value log $K_{O_2} = 13.29$. This cannot be directly compared with the oxygenation constant of Co-OBISDIEN because of unusual OH^- stoichiometry. These differences can be accounted for by taking into account the existence of two phenolate heads in this ligand. Meanwhile, in Co-OBISDIEN-oxygen system, the species $[Co_2L'O_2]^{4+}$ (L′ = OBISDIEN) is never more than a minor constituent in solution. This

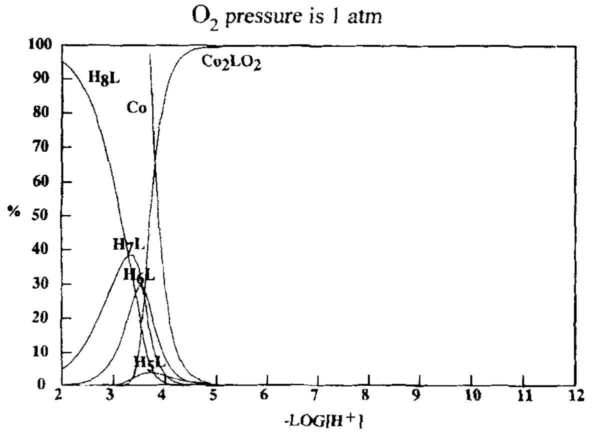


FIGURE 3 Species distribution diagram for the L-Co(II) (1 : 2) system as a function of p[H] under oxygen (% = Percentage of species distribution in solution, $T_L = 0.00208$ M, $T_{Co} = 0.00418$ M).

is ascribed to low stability resulting form steric effects and the strong tendency of the dinuclear Co(II) complex to combine with bridging hydroxide ions, which take up the coordination sites that would otherwise be occupied by the bridging peroxo group of the dioxygen complexes. The bridging groups and the basic nitrogen donor groups of the dioxygen complex of Co-OBISDIEN initially formed account for only five of the required six coordination of the metal ion. The sixth position is probably occupied by water molecules, their dissociation in the dioxygen complex, results in the formation of a dihydroxo- complexes. But the BDBPH can serve as an octadentate (N_6O_2) ligand when the bridging dinuclear complexes formed. The oxygen molecule can enter into the cavity to support the sixth coordination as a monodentate ligand in the formation of μ-peroxo complex. In $BDBPHCo_2O_2$, the stoichiometric ratio O_2 : Co for the formation of oxygen adducts was also determined to be 1 : 2 by manometry in separate experiments.

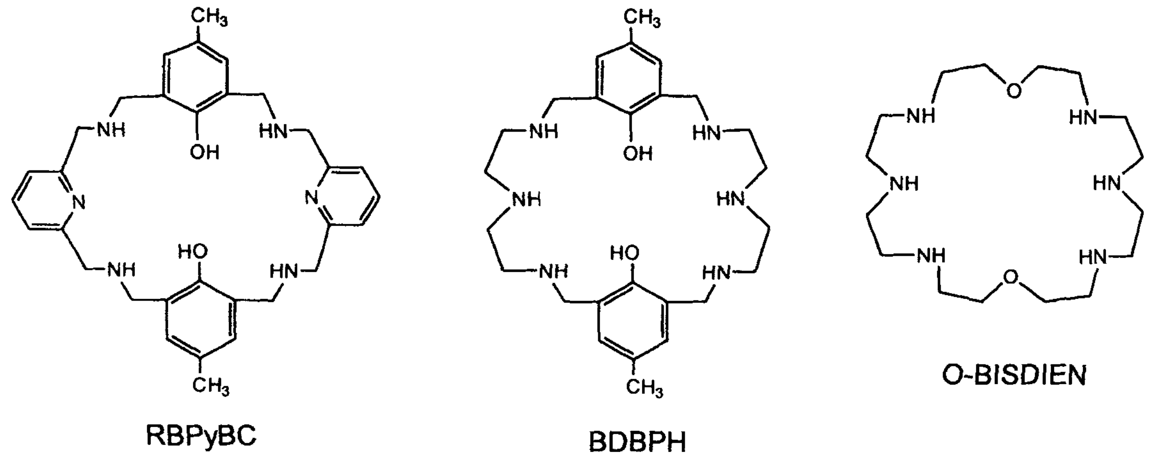
$$Co_2L + O_2 \rightleftharpoons Co_2\,LO_2$$

$$K_{O_2} = \frac{[Co_2LO_2]}{[Co_2L]P_{O_2}} = 10^{13.29} \qquad (1)$$

UV Spectrum of Dinuclear Dioxygen Complexes

Figure 4 shows the visible spectra of 2 : 1 Co(II) – H_8L^{6+} under 1 atm oxygen. The absorption band at 390 nm can be assigned to the charge transfer from ligand to metal (LMCT, $\pi^* - d_{z^2}$) with formation of the dinuclear dioxygen complex, and the intensity is increased with p[H] [13d].

In our former report, dinuclear ferrous complexes can catalyze the oxidation of alkane.



RBPyBC

BDBPH

O-BISDIEN

CHART 1

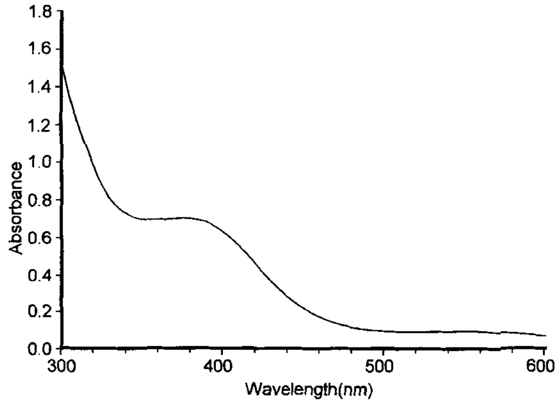


FIGURE 4 UV spectra of dinuclear cobalt complex in the presence of oxygen (water solution, $T_{Co} = 6.52 \times 10^{-5}$ M, $T_L = 3.26 \times 10^{-5}$ M).

When we ran the reaction under similar experimental conditions, the cobalt dioxygen complexes did not show any catalytic activity to oxidize saturated substrates (adamantane or cyclohexane).

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