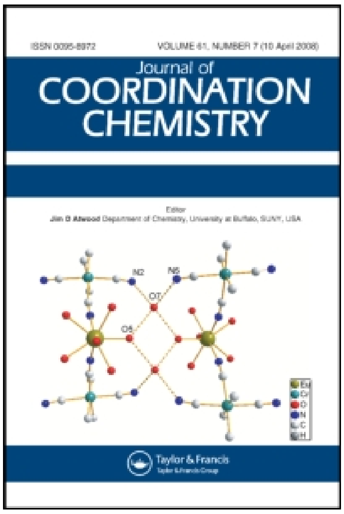

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SHORT COMMUNICATION

Binuclear Chelates as Oxygen Carriers. I. The Reactions of Tetrakis(2-Aminoethyl)*α*,*α*′-Diamino-*p*-Xylene[+]

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INTRODUCTION

Ligands with two multidentate moieties separated by a rigid bridge such as *p*- or *m*-xylene are of considerable interest for the formation of binuclear complexes capable of biscoordination of suitable bridging ligands. The metal ions bound to this type of bis-polyfunctional multidentate ligand would be held apart at a sufficient distance such that the two pairs of donor groups could not coordinate to the same metal ion, and the binuclear complexes would thus be stable relative to other types of coordinate bond arrangement. However, by appropriate adjustment of the size of the ligand backbone, the metal–metal distance would be suitable for bonding a mono- or polyatomic substrate to both metal centers. Binuclear complexes of "wish-bone" ligands of this type may provide interesting models for studying catalytic reactions of biological systems in which concerted catalysis by both metal ions is involved. The first ligand to be synthesized with this idea in mind, P,P,P′,P′-tetra(2-diphenylphosphinoethyl)-α,α -diphospha-p-xylene, was reported by Taqui Khan and Martell[1], and was shown to have a strong tendency toward the formation of binuclear chelates of Ru(II), Rh(I), and Ir(I). A similar bis-tetradentate ligand more recently reported[2], which contains two ter- or quadridentate donor functions (one amino, one oxygen ether and two thio ether), has the same type of *p*-xylene framework and was labelled an "ear-muff" type ligand. Its bis Cu(I) complex was reported by Osborn and coworkers[2] to combine reversibly with dioxygen in the solid state. More recently, the reactions of a mixed tertiary-phosphine–tertiary-arsine ligand having the same *p*-xylene backbone has been reported by Taqui Khan *et al.*[3]

Recently we have reported the synthesis and metal chelate formation constants of the bis-terdentate hexamine, 1,4-bis(bis(2-aminoethyl)aminoethyl) benzene (PXBDE)[4]. The terdentate moieties of the ligand are spaced sufficiently far apart to form binuclear chelates in which each metal ion may combine separately with bidentate auxiliary ligands so as to leave one coordination site open on each metal center. This reaction was found to be perfectly general for all transition metals tried. The bis-pentacoordinated binuclear cobalt(II) chelate is particularly interesting because of its ability to sandwich an oxygen molecule between the two arms of the "wish-bone" chelate structure. This report describes the thermodynamics of oxygenation of the binuclear chelate system $Co_2LL'_2$, in which L is the bis-terdentate "wish-bone" ligand (PXBDE), and L′ is either glycine or ethylenediamine.

RESULTS AND DISCUSSION

Potentiometric equilibrium curves involving the formation of Co(II)-PXBDE mixed ligand systems are shown in Figure 1. The considerable difference in the potentiometric equilibrium curves measured under dioxygen and under dinitrogen indicates strong interaction between dioxygen and the mixed ligand binuclear chelate. Under dioxygen above pH 6 the mixed ligand solutions become dark brown in color and an intense absorbance at 390 nm provides strong evidence for the formation of a binuclear *μ*-dioxygen complex. From the potentiometric equilibrium curves measured under oxygen the logarithms of the stability constants of the dioxygen complexes, defined by Eq. (1),

$$K_{O_2} = \frac{[Co_2L'_2LO_2^{(4+2m)+}]}{[Co_2L'_2L^{(4+2m)+}]P_{O_2}} \tag{1}$$

$K_{O_2} = 10^{6.71}$ $K_{O_2} = 10^{4.68}$
$L' = \text{en}, m = 0$ $L' = \text{gly}, m = -1$

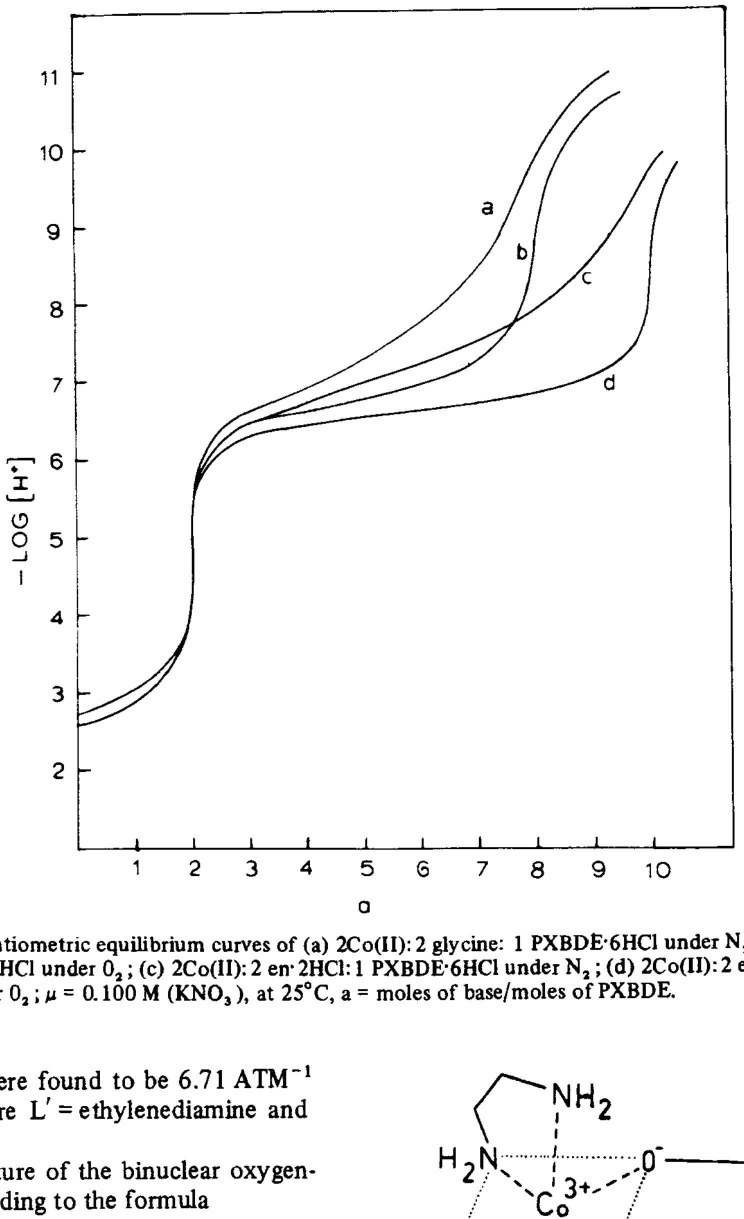
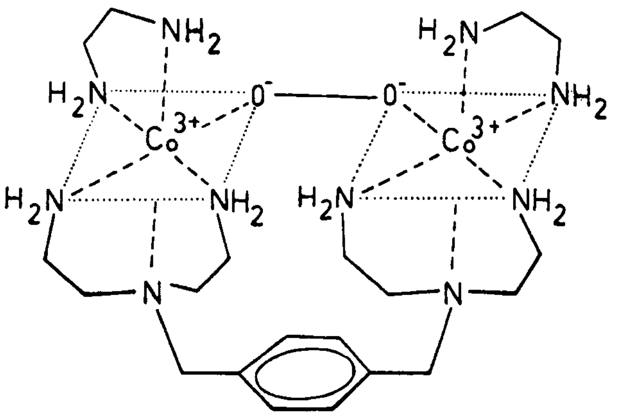


FIGURE 1 Potentiometric equilibrium curves of (a) 2Co(II): 2 glycine: 1 PXBDE·6HCl under N_2; (b) 2Co(II): 2 glycine: 1 PXBDE·6HCl under O_2; (c) 2Co(II): 2 en·2HCl: 1 PXBDE·6HCl under N_2; (d) 2Co(II): 2 en·2HCl: 1 PXBDE·6HCl under O_2; $\mu = 0.100$ M (KNO_3), at 25°C, a = moles of base/moles of PXBDE.

were calculated and were found to be 6.71 ATM^{-1} and 4.08 ATM^{-1} where L′ = ethylenediamine and glycine, respectively.

The monomeric nature of the binuclear oxygenated species, corresponding to the formula $[Co_2L'_2LO_2^{4+}]$, was demonstrated by carrying out similar potentiometric determinations and oxygenation constant calculations under a wide range of initial analytical concentration of metal ion and primary sexadentate (bis-terdentate) ligand in the presence of corresponding concentrations of secondary ligand L′ and excess dioxygen. The calculated values of the formation constants K_{O_2} thus obtained were found to be independent of concentration, and therefore polymerization does not occur in these systems. Consequently the most probable arrangement of coordinate bonds in the dioxygen complex consistent with both spectral and potentiometric



DIOXYGEN COMPLEX FORMED FROM ETHYLENEDIAMINE AND TETRAKIS(2-AMINOETHYL)α,α′-DIAMINO-p-XYLENE (PXBDE) observations involves intramolecular coordination of dioxygen by the binuclear mixed ligand complex in a manner similar to that represented in formula 1.

The equilibrium reactions involved in the formation of these dioxygen complexes are given in equations (1)–(8) and the values of the corresponding equilibrium constants are summarized in Table I. The magnitude of the oxygenation constants is sufficiently high that even though the oxygenation process, expressed by Eq. (1), is not pH dependent, oxygenation of the pentacoordinated cobalt(II) complex begins before it is completely formed in solution. Thus the oxygenation process drives the pH-dependent complex formation reactions and the value of the oxygenation equilibrium constant may be determined by potentiometric measurement of hydrogen ion concentrations.

$$\mathrm{H^+ + H_{\mathit{n}-1}L^{(\mathit{n}-1)+} \rightleftharpoons H_\mathit{n}L^{\mathit{n}+}}$$

$$\mathrm{K}_n^{\mathrm{H}} = \frac{[\mathrm{H}_n\mathrm{L}^{n+}]}{[\mathrm{H}_{n-1}\mathrm{L}^{(n-1)+}]\,[\mathrm{H}^+]} \tag{2}$$

$$\mathrm{H^+ + H_{\mathit{n}-1}L'^{(\mathit{m}+\mathit{n}-1)+} \rightleftharpoons H_\mathit{n}L'^{(\mathit{m}+\mathit{n})+}}$$

$$\mathrm{K}_n'^{\mathrm{H}} = \frac{[\mathrm{H}_n\mathrm{L}'^{(m+n)+}]}{[\mathrm{H}_{n-1}\mathrm{L}'^{(m+n-1)+}]\,[\mathrm{H}^+]} \tag{3}$$

(for glycine, $m = -1$; for ethylenediamine, $m = 0$)

$$\mathrm{Co^{2+} + L + 2H^+ \rightleftharpoons CoH_2L^{4+}}$$

$$\beta_{\mathrm{MH_2L}} = \frac{[\mathrm{CoH_2L^{4+}}]}{[\mathrm{Co^{2+}}]\,[\mathrm{H^+}]^2\,[\mathrm{L}]} \tag{4}$$

$$\mathrm{Co^{2+} + H^+ + L \rightleftharpoons CoHL^{3+}}$$

$$\beta_{\mathrm{MHL}} = \frac{[\mathrm{CoHL^{3+}}]}{[\mathrm{Co^{2+}}]\,[\mathrm{H^+}]\,[\mathrm{L}]} \tag{5}$$

$$\mathrm{2Co^{2+} + L \rightleftharpoons Co_2L^{4+}}$$

$$\beta_{\mathrm{M_2L}} = \frac{[\mathrm{Co_2L^{4+}}]}{[\mathrm{Co^{2+}}]^2\,[\mathrm{L}]} \tag{6}$$

$$\mathrm{2Co^{2+} + L + L'^{(\mathit{m})} \rightleftharpoons Co_2LL'^{(4+\mathit{m})+}}$$

$$\beta_{\mathrm{M_2LL'}} = \frac{[\mathrm{Co_2LL'^{(4+\mathit{m})+}}]}{[\mathrm{Co^{2+}}]^2\,[\mathrm{L}]\,[\mathrm{L'^{(\mathit{m})}}]} \tag{7}$$

$$\mathrm{2Co^{2+} + L + 2L'^{(\mathit{m})} \rightleftharpoons Co_2LL_2'^{(4+2\mathit{m})+}}$$

$$\beta_{\mathrm{M_2LL_2'}} = \frac{[\mathrm{Co_2LL'^{(4+2\mathit{m})+}}]}{[\mathrm{Co^{2+}}]^2\,[\mathrm{L}]\,[\mathrm{L'^{(\mathit{m})}}]^2} \tag{8}$$

TABLE I
Equilibrium data for the PXBDE Co(II)-dioxygen system (μ = 0.100 M ($\mathrm{KNO_3}$); t = 25°C)

Symbol	Log Quotient	Log Value
$\mathrm{K_1^H}$	$\frac{[\mathrm{HL^+}]}{[\mathrm{L}][\mathrm{H^+}]}$	10.06
$\mathrm{K_2^H}$	$\frac{[\mathrm{H_2L^{2+}}]}{[\mathrm{HL^+}][\mathrm{H^+}]}$	9.71
$\mathrm{K_3^H}$	$\frac{[\mathrm{H_3L^{3+}}]}{[\mathrm{H_2L^{2+}}][\mathrm{H^+}]}$	9.11
$\mathrm{K_4^H}$	$\frac{[\mathrm{H_4L^{4+}}]}{[\mathrm{H_3L^{3+}}][\mathrm{H^+}]}$	8.57
$\mathrm{K_5^H}$	$\frac{[\mathrm{H_5L^{5+}}]}{[\mathrm{H_4L^{4+}}][\mathrm{H^+}]}$	1.85
$\mathrm{K_6^H}$	$\frac{[\mathrm{H_6L^{6+}}]}{[\mathrm{H_5L^{5+}}][\mathrm{H^+}]}$	1.2
$\mathrm{K_{MH_2L}^{Co}}$	$\frac{[\mathrm{CoH_2L^{4+}}]}{[\mathrm{Co^{2+}}][\mathrm{H_2L^{2+}}]}$	6.84
$\beta_{\mathrm{M_2L}}$	$\frac{[\mathrm{Co_2L^{4+}}]}{[\mathrm{Co^{2+}}]^2[\mathrm{L}]}$	14.58
$\beta_{\mathrm{M_2LL'}}$	$\frac{[\mathrm{Co_2LL'^{(4+\mathit{m})+}}]}{[\mathrm{Co^{2+}}]^2[\mathrm{L}][\mathrm{L'^{(\mathit{m})}}]}$	18.80 (L′ = en) 18.48 (L′ = gly)
$\beta_{\mathrm{M_2LL_2'}}$	$\frac{[\mathrm{Co_2LL_2'^{(4+2\mathit{m})+}}]}{[\mathrm{Co^{2+}}]^2[\mathrm{L}][\mathrm{L'^{(\mathit{m})}}]^2}$	23.32 (L′ = en) 23.38 (L′ = gly)
$\mathrm{K_{O_2}}$	$\frac{[\mathrm{Co_2LL_2'O_2^{(4+2\mathit{m})+}}]}{[\mathrm{Co_2LL_2'^{(4+2\mathit{m})+}}]P_{\mathrm{O_2}}}$	6.71 (L′ = en) 4.08 (L′ = gly)

The magnitudes of the oxygenation equilibrium constants obtained are compared in Table II with the values of other types of oxygen carriers previously reported. The oxygenation constants are given in terms of the reciprocal dioxygen pressure (in atmospheres) at half oxygenation of the complex, thus allowing direct comparisons of aqueous dioxygen carriers with dioxygen carriers in nonaqueous solutions and in the solid state. The dioxygen affinities of the mixed ligand "wish-bone" cobalt complexes follow the predicted[9] order of basicities of the donor groups of the ligands. Although the formation constant of the mixed ligand glycine complex is slightly higher than that of ethylenediamine the oxygen affinity of the latter is significantly larger, in accord with the fact that ΣpK for ethylenediamine is 16.97, relative to 11.93 for glycine.

The data in Table II also show that the dioxygen affinities of the "wish-bone" cobalt complexes are considerable higher than those of the "picket fence" cobalt complex and the natural oxygen carriers, but considerably lower than those of mononuclear cobalt

TABLE II
Dioxygen affinities of selected complexes

Formulas				
Oxygen-free Complex	Dioxygen Complex	$P_{1/2}^{-1}$ (atm^{-1})	Conditions†	Ref.
Human hemoglobin A, Hb	$Hb \cdot O_2$	4.0×10^2	25°, pH 7.4 tris buffer	6
CoTPivPP(Me_2IM), MLL′	$MLL' \cdot O_2$	8.4×10^{-1}	25°, toluene	7
$Co(TEP)^{2+}$, ML	$(ML)_2 \cdot O_2$	3.4×10^{13}	25°, $\mu = 0.10$	8
$Co_2PXBDE(en)^{4+}$, $M_2LL'_2$	$M_2LL'_2 \cdot O_2$	5.1×10^6	25°, $\mu = 0.10$	*
$Co_2PXBDE(gly)_2^{2+}$, $M_2LL'_2$	$M_2LL'_2 \cdot O_2$	1.2×10^4	25°, $\mu = 0.10$	*

*This work. Abbreviations: TPivPP = tetra(pivaloylphenyl)porphine; Me_2IM = dimethylimidazole; TEP = tetraethylenepentamine. †Aqueous solutions unless otherwise noted.

complexes in which the metal ion is bound in an analogous way to five basic (aliphatic) nitrogen donors. This difference may be due to the inability of the "wish-bone" structure to exactly match the steric requirements of the bridging dioxygen moiety. Further investigation of this question is now in progress.

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