# Reaction of Cobalt(II) Macrocyclic Tetra-amine Complexes with Dioxygen

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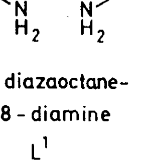
Low-pH equilibrium and kinetic studies on the oxygenation of $[CoL]^{2+}$ complexes containing 12- ($L^2$), 13- ($L^3$), and 14-membered (isomeric, $L^4$ and $L^5$) fully saturated macrocyclic tetra-amines are reported. The ring size strongly influences the stability of the oxygenated products. The relative stability is connected with the stoicheiometry of the oxygenated complex, $[(CoL)_2(O_2)(OH)]^{3+}$ for $L^2$ and $L^3$ and $[(CoL)_2(O_2)]^{4+}$ for $L^5$, which has been elucidated by potentiometric titration and polarographic measurements. The results for the macrocyclic systems are compared with a linear tetra-amine system ($L^1$). The cyclic nature of the macrocycles, while serving to raise the $[CoL]^{2+}$ stability, markedly lowers the $O_2$ affinity of the complexes. Rates for the reaction of $Co^{2+}$, L, and $O_2$ in acetate buffers (yielding the dioxygen adducts) are first order in $[Co^{2+}]$ and also in [L], but are independent of $[O_2]$, indicating that the formation of $[CoL]^{2+}$ is the slowest step in the $O_2$ uptake. The separate reaction of $[CoL]^{2+}$ with $O_2$ is first order in $[CoL^{2+}]$ and also in $[O_2]$, with the second-order rate constants being *ca.* $10^4$ times faster than those for the formation of $[CoL]^{2+}$ under comparable conditions. The presence of the macrocyclic ligand slows down (by *ca.* $10^2$ times) the overall rate of $O_2$ uptake compared with linear tetra-amine systems.

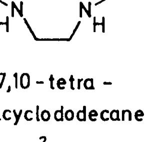
THE interaction of molecular oxygen with cobalt(II) chelates has received much attention recently,[1,2] complexes of both 2 : 1 and 1 : 1 stoicheiometries being possible. The dioxygenation is generally,[1-3] but not universally,[4] viewed as a reversible internal redox reaction where the $Co^{2+}$ is formally oxidized to $Co^{3+}$ and the $O_2$ formally reduced to peroxide $O_2^{2-}$ (in 2 : 1 complexes) or superoxide $O_2^-$ ion (in 1 : 1 complexes). Of the two, the μ-peroxo-complexes are generally more stable and preferred unless inhibited sterically[5] or by use of low temperatures[6] and non-aqueous solvents.[7]

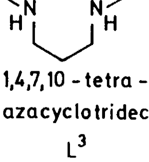
A second (μ-hydroxo-) bridge is spontaneously formed in aqueous solutions whenever a site *cis* to the dioxygen bridge is readily available, serving to tightly ' lock-in ' the peroxo-oxygen and shift the equilibrium in favour of dioxygen complex formation.[8-12] With certain complexes this olation process occurs at a slower rate than the preceding oxygenation, probably because it involves a substitution reaction on metal ions of partial $Co^{3+}$ character.[9,13]

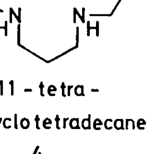
The oxygenation mechanisms are extensively documented for polydentate chelates ranging from fully saturated linear ligands represented by $L^1$ (refs. 9 and 13) to fully unsaturated macrocycles such as porphyrins.[1,3,7,14] However, an intermediate system of saturated macrocycles seems to have been overlooked except for a 14-membered tetra-amine $L^5$.[15,16] We have thus begun a study of the reaction of $O_2$ with cobalt(II) complexes of tetra-amine macrocycles including 12- ($L^2$), 13- ($L^3$), and 14-membered rings (two isomers, $L^4$ and $L^5$) so as to test whether the previous conclusions may be extended and to show up possible new effects. Particularly instructive would be a comparison with a linear tetra-amine $L^1$ system, which might reveal any special $O_2$-uptake qualities that derive from the cyclic nature of macrocyclic ligands. The use of the macrocyclic homologues would allow simplified mechanistic studies since any variation in equilibrium or kinetic parameters is defined and elaborated almost solely by a single source, the ring size. Earlier studies with $Co^{3+}$ showed that, while larger macrocycles (*e.g.* $L^5$) preferentially form planar *trans*-octahedral complexes,[17,18] the smaller ones (*e.g.* $L^2$) cannot attain planarity and adopt folded *cis* configurations.[19-21] It is thus readily conceivable that the ring size affects the stereochemical course of oxygenation of cobalt(II) complexes [involving partial transformation to cobalt(III) complexes].

Herein we report the formation of stable oxygenated complexes using $L^2$, $L^3$, and $L^5$ systems in aqueous solutions, along with corresponding equilibrium and rate constants. The oxygenated species of another isomer $L^4$ of a 14-membered macrocycle decomposes more rapidly to $Co^{3+}$ and quantitative measurements were not made. As an important basis, the present study includes measurement of $[CoL]^{2+}$ complex stability, the first systematic investigation of macrocyclic chelation of $Co^{II}$. It is found that the complex stability varies with the cyclic nature of $L^2$—$L^5$. The present work constitutes part of a program to examine the effect of ligand


3,6-diazaoctane-1,8-diamine
$L^1$


1,4,7,10-tetra-azacyclododecane
$L^2$


1,4,7,10-tetra-azacyclotridecane
$L^3$


1,4,7,11-tetra-azacyclotetradecane
$L^4$

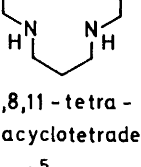

1,4,8,11-tetra-azacyclotetradecane
$L^5$

TABLE 1

Equilibrium constants for $[CoL]^{2+}$ complex formation and for the oxygenation of $[CoL]^{2+}$ in aqueous solution [a]

| Ligand | $K_{CoL}$ | $K_{O_2,OH}$ [b] | $K_{O_2}$ [c] | $\log K_{O_2,OH}'$ [d] or $\log K_{O_2}'$ [e] | $\log K_i$ (mixed protonation constant) [f] |
|---|---|---|---|---|---|
| $L^1$ | $(4.3 \pm 0.6) \times 10^{10}$ | $(1.3 \pm 0.2) \times 10^{28}$ | | $6.9 \pm 0.1$ [d] | 9.73, 9.12, 6.65, 3.68 [g] |
| $L^2$ | $(6.2 \pm 1) \times 10^{13}$ | $(2.8 \pm 0.4) \times 10^{28}$ | | $0.8 \pm 0.1$ [d] | 10.51, 9.49, 1.6, 0.8 |
| $L^3$ | $(1.9 \pm 0.3) \times 10^{14}$ | $(6.7 \pm 1) \times 10^{29}$ | | $1.2 \pm 0.1$ [d] | 10.90, 9.91, 1.6, 0.9 |
| $L^4$ | $(8.2 \pm 1.2) \times 10^{10}$ | | | | 10.81, 9.74, 3.03, 0.9<br>(11.05, 9.98, 3,3. 1.0) [h] |
| $L^5$ | $(5.1 \pm 0.8) \times 10^{12}$ | | $(1.2 \pm 0.2) \times 10^{27}$ | $1.7 \pm 0.1$ [e] | 11.23, 10.30, 1.5, 0.8 |

[a] All values determined at 35 °C and $I$ 0.20 mol $dm^{-3}$ unless otherwise noted. [b] Defined by equation (18); units of $dm^9$ $mol^{-3}$. [c] Defined by equation (30); units of $dm^{12}$ $mol^{-4}$. [d] Calculated from equation (36); units of $dm^3$ $mol^{-1}$. [e] Calculated from equation (37), units of $dm^6$ $mol^{-2}$. [f] Average deviations are ±0.02 for $\log K_1$ and $K_2$, and ±0.05 for $\log K_3$ and $K_4$. [g] Literature values at 25 °C and $I$ 0.5 mol $dm^{-3}$ (R. Barbucci, L. Fabbrizzi, P. Paoletti, and A. Vacca, *J.C.S. Dalton*, 1973, 1963) were corrected using the given thermodynamic parameters. [h] At 25 °C.

cyclization and of ring size on metal-complex formation and on the reactivities of the resulting complexes.[20,22-34]

## EXPERIMENTAL

Macrocyclic tetra-amines were generally prepared according to the method of Richman and Atkins.[35] The linear tetra-amine $L^1$ was doubly distilled and recrystallized as the hydrochloride. The protonation constants used for calculations are listed in Table 1. Stock solutions of cobalt(II) were prepared from analytical grade chloride salts and standardized by the method of Schwarzenbach.[36] Potentiometric [32,34] and polarographic apparatus [22,23] were as those used previously.

*Potentiometric Measurements.*—The ligand hydrochloride salts ($1.5 \times 10^{-3}$ mol $dm^{-3}$) were titrated potentiometrically with standard sodium hydroxide solution in the presence of equimolar cobalt(II), and the $-\log[H^+]$ (pH) values were recorded 20 min after addition of each increment of base. The titrations were performed under both nitrogen [passed through chromium(II) sulphate solution in 1N $H_2SO_4$] and oxygen (passed through Ascarite) atmospheres. The solubility of $O_2$ in water used was taken from the literature: 2.7 (2.3) $\times 10^{-4}$ mol $dm^{-3}$ at 25(35) °C.[37] Solutions were adjusted to 0.20 mol $dm^{-3}$ ionic strength by addition of $Na[ClO_4]$ and maintained at $35.0 \pm 0.1$ °C.

*Reversibility Experiments.*—Two equimolar and equivolume solutions of cobalt(II) and macrocycle (1 : 1) in acetate buffer ($L = L^2$ and $L^3$) or in lutidine buffer ($L = L^5$) were prepared. One solution was allowed to stand in air, while the other was equilibrated with air and then subjected to a vigorous and continuous flow of nitrogen. The visible spectra were then taken of both solutions in contact with air and under nitrogen, respectively. Another type of experiment was performed in which the spectra of oxygenated 1 : 1 solutions ($L = L^2$ and $L^3$) were taken immediately upon addition of acid.

*Kinetic Measurements.*—Two sets of $O_2$-uptake rates were measured with a stopped-flow apparatus by observing the increase in absorbance at 370 nm at $I$ 0.2 mol $dm^{-3}$ and 25 °C. One is the rate for the reaction of $Co^{II}$, L ($=L^2$ or $L^3$), and $O_2$ all in acetate buffer solutions. No decomposition to $Co^{3+}$ was seen (spectrophotometrically). The rate constants were determined by the initial-gradient method.

The other set comprised the rate of $O_2$ uptake by $[CoL]^{2+}$

TABLE 2

Typical initial-rate data for the reaction of $Co^{II}$ with macrocyclic tetra-amine in aerobic conditions to form oxygen adducts at 25 °C and $I$ 0.2 mol $dm^{-3}$

| Ligand | $10^3[Co^{2+}{}_T]_0$ | $10^3[L_T]_0$ | $10^3[MeCO_2^-]_0$ | $10^3[O_2]_0$ | pH | $10^2 k_{obs.}$ | $k_{obs.}\beta_{MeCO_2}/K_{Co(O_2OMe)}[MeCO_2^-]$ |
|---|---|---|---|---|---|---|---|
| | mol $dm^{-3}$ | | | | | $dm^3$ $mol^{-1}$ $s^{-1}$ | $dm^3$ $mol^{-1}$ $s^{-1}$ |
| $L_2$ | 2.0 | 2.5 | 100 | 0.27 | 5.35 | 1.65 | $3.64 \times 10^{-2}$ |
| | 4.0 | 2.5 | 100 | 0.27 | 5.35 | 1.61 | |
| | 10.0 | 2.5 | 100 | 0.27 | 5.35 | 1.63 | |
| | 4.0 | 5.0 | 100 | 0.27 | 5.35 | 1.70 | |
| | 4.0 | 7.5 | 100 | 0.27 | 5.35 | 1.60 | |
| | 2.0 | 2.5 | 50 | 0.27 | 5.35 | 1.10 | $3.77 \times 10^{-2}$ |
| | 2.0 | 2.5 | 150 | 0.27 | 5.35 | 1.85 | $3.54 \times 10^{-2}$ |
| | 2.0 | 2.5 | 200 | 0.27 | 5.35 | 2.06 | $3.71 \times 10^{-2}$ |
| | 2.0 | 2.5 | 100 | 0.27 | 4.81 | 1.35 | |
| | 2.0 | 2.5 | 100 | 0.27 | 5.01 | 1.75 | |
| | 2.0 | 2.5 | 100 | 0.27 | 5.63 | 2.24 | |
| | 2.0 | 2.5 | 100 | 0.068 | 5.35 | 1.63 | |
| | 2.0 | 2.5 | 100 | 0.135 | 5.35 | 1.68 | |
| | 2.5 | 1.58 | 100 | 0.27 | 5.55 | 4.00 | |
| | 5.0 | 1.58 | 100 | 0.27 | 5.55 | 3.93 | $8.68 \times 10^{-2}$ |
| | 7.5 | 1.58 | 100 | 0.27 | 5.55 | 3.95 | |
| | 10.0 | 1.58 | 100 | 0.27 | 5.55 | 3.89 | |
| | 10.0 | 3.16 | 100 | 0.27 | 5.55 | 3.95 | |
| | 10.0 | 6.32 | 100 | 0.27 | 5.55 | 3.88 | |
| | 5.0 | 1.58 | 50 | 0.27 | 5.55 | 2.60 | $8.90 \times 10^{-2}$ |
| | 5.0 | 1.58 | 200 | 0.27 | 5.55 | 4.83 | $8.70 \times 10^{-2}$ |
| | 5.0 | 1.58 | 100 | 0.27 | 5.11 | 3.28 | |
| | 5.0 | 1.58 | 100 | 0.27 | 5.30 | 3.60 | |
| | 5.0 | 1.58 | 100 | 0.27 | 5.93 | 5.90 | |
| | 5.0 | 1.58 | 100 | 0.068 | 5.55 | 3.89 | |
| | 5.0 | 1.58 | 100 | 0.135 | 5.55 | 4.00 | |

which was prepared in $N_2$ by mixing $Co^{2+}$ ($10^{-2}$—$10^{-3}$ mol $dm^{-3}$) with L (5—7% in excess) in acetate ($L = L^2$ and $L^3$) or lutidine buffer ($L = L^5$) and allowing the mixture to equilibrate for 1 h. The concentration of $[CoL]^{2+}$ used was always in large excess over that of $O_2$ and excellent pseudo-first-order kinetics were observed. Typical rate data are shown in Tables 2 and 3.

TABLE 3

Typical kinetic data for the reaction of $[CoL]^{2+}$ with $O_2$ at 25 °C and $I$ 0.2 mol $dm^{-1}$ to give oxygen adducts

| $10^3[CoL^{2+}]$ | $10^3[O_2]$ | $10^3$[Buffer] | pH | $10^{-2}k_2$ |
|---|---|---|---|---|
| | mol $dm^{-3}$ | | | $dm^3$ $mol^{-1}$ $s^{-1}$ |
| $L^2$ | | $MeCO_2^-$ | | |
| 1.25 | 0.135 | 100 | 5.30 | 6.97 |
| 2.50 | 0.135 | 100 | 5.30 | 7.20 |
| 5.00 | 0.135 | 100 | 5.30 | 7.00 |
| 7.50 | 0.135 | 100 | 5.30 | 7.19 |
| 2.50 | 0.068 | 100 | 5.30 | 7.05 |
| 2.50 | 0.034 | 100 | 5.30 | 6.95 |
| 2.50 | 0.135 | 100 | 5.62 | 7.00 |
| 2.50 | 0.135 | 100 | 5.04 | 6.95 |
| 2.50 | 0.135 | 100 | 4.83 | 6.97 |
| 2.50 | 0.135 | 200 | 5.30 | 7.04 |
| 2.50 | 0.135 | 50 | 5.30 | 7.01 |
| $L^3$ | | $MeCO_2^-$ | | |
| 1.25 | 0.135 | 100 | 5.20 | 8.25 |
| 2.50 | 0.135 | 100 | 5.20 | 8.25 |
| 5.00 | 0.135 | 100 | 5.20 | 8.29 |
| 2.50 | 0.068 | 100 | 5.20 | 8.20 |
| 2.50 | 0.034 | 100 | 5.20 | 8.43 |
| 2.50 | 0.135 | 100 | 5.58 | 8.31 |
| 2.50 | 0.135 | 100 | 4.83 | 8.20 |
| 2.50 | 0.135 | 200 | 5.20 | 8.19 |
| 2.50 | 0.135 | 50 | 5.20 | 8.20 |
| $L^5$ | | Lutidine | | |
| 2.50 | 0.135 | 100 | 7.00 | 1.06 |
| 1.25 | 0.135 | 100 | 7.00 | 1.05 |
| 2.50 | 0.135 | 50 | 7.00 | 1.06 |
| 2.50 | 0.068 | 100 | 7.00 | 0.95 |
| 2.50 | 0.135 | 100 | 6.50 | 1.07 |
| 2.50 | 0.135 | 100 | 7.50 | 1.01 |

## RESULTS AND CALCULATIONS

*Potentiometric Measurements under* $N_2$ *Atmosphere*.—The equilibrium curves under $N_2$ represent overlapping equilibria defined by (1) and (2). The hydrolysis of $Co^{2+}$(aq) can be neglected in light of the reported value of $K_{OH}(=[Co(OH)^+]/[Co^{2+}][OH^-])$ ($\log K_{OH} = 3.96$ at 25 °C) [38] and the pH range $4 < pH < 8$) studied.

$$H_{i-1}L^{(i-1)+} + H^+ \rightleftharpoons H_iL^{i+}; \quad K_i = [H_iL^{i+}]/[H_{i-1}L^{(i-1)+}][H^+] \qquad (1)$$

$$Co^{2+} + L \rightleftharpoons [CoL]^{2+} \quad K_{ML} = [CoL^{2+}]/[Co^{2+}][L] \qquad (2)$$

The total concentrations of ligand, $c_L$, and of cobalt ion, $c_M$, are expressed by (3) and (4), respectively. The sum of

$$c_L = [ML^{2+}] + [L]_F \qquad (3)$$

$$c_M = [ML^{2+}] + [M^{2+}] \qquad (4)$$

$$[L]_F = [L] + [HL^+] + \ldots + [H_4L^{4+}] \qquad (5)$$

the hydrogen-ion and sodium-ion (from Na[OH]) concentrations, $\alpha$, at titration point $a$ is given by (6) which can be rewritten as (7) by using the definitions (8)—(10). A combination of (4) and (7) leads to (10), and substitution of (10) into (3) gives (11). Combination of (10) and (11)

$$\alpha = [H^+] + ac_L = 4[L] + 3[HL^+] + 2[H_2L^{2+}] + [H_3L^{3+}] + 4[ML^{2+}] \qquad (6)$$

$$\alpha = 4[ML^{2+}] + [L]_F\beta_H/(\alpha_H)_L \qquad (7)$$

$$(\alpha_H)_L = [L]_F/[L] = 1 + [H^+]K_1 + [H^+]^2K_1K_2 + [H^+]^3K_1K_2K_3 + [H^+]^4K_1K_2K_3K_4 \qquad (8)$$

$$\beta_H = 4 + 3[H^+]K_1 + 2[H^+]^2K_1K_2 + [H^+]^3K_1K_2K_3 \qquad (9)$$

$$[ML^{2+}] = \{\alpha(\alpha_H)_L - \beta_H[L]_F\}/4(\alpha_H)_L \qquad (10)$$

$$[L]_F = \frac{(\alpha_H)_L(4c_L - \alpha)}{4(\alpha_H)_L - \beta_H} \qquad (11)$$

$$[ML^{2+}] = \frac{\alpha(\alpha_H)_L - c_L\beta_H}{4(\alpha_H)_L - \beta_H} \qquad (12)$$

$$[M^{2+}] = \frac{(\alpha_H)_L(4c_M - \alpha) - \beta_H(c_M - c_L)}{4(\alpha_H)_L - \beta_H} \qquad (13)$$

$$\frac{K_{ML}}{(\alpha_H)_L} = \frac{[ML^{2+}]}{[M^{2+}][L]_F} \qquad (14)$$

affords (12) from which, with (4), one obtains (13). Substituting (11)—(13) into equation (14), which is readily derivable from (2), one finally gets equation (15).

$$K_{ML} = \frac{[\alpha(\alpha_L)_H - c_L\beta_H][4(\alpha_H)_L - \beta_H]}{[(\alpha_H)_L(4c_M - \alpha) - \beta_H(c_M - c_L)](4c_L - \alpha)} \qquad (15)$$

Under the buffer conditions of $4 < pH < 8$, it is apparent that $2(\alpha_H)_L = \beta_H$ for a macrocyclic system. Hence, when $c_M = c_L$, (15) is simplified to (16). Plots of $(\alpha_H)_L$ against

$$K_{ML} = \frac{2(\alpha_H)_L(\alpha - 2c_L)}{(4c_L - \alpha)^2} \qquad (16)$$

$(4c_L - \alpha)^2/(\alpha - 2c_L)$ are linear and pass through the origin for all the macrocyclic systems $L^2$—$L^5$. Values of $K_{ML}$ were thus determined from the gradients.

For the $L^1$ system, where $2(\alpha_H)_L \neq \beta_H$, equation (17) was used to determine $K_{ML}$. The stability constant obtained

$$K_{ML} = \frac{[\alpha(\alpha_H)_L - \beta_Hc_L][4(\alpha_H)_L - \beta_H]}{(4c_L - \alpha)^2(\alpha_H)_L} \qquad (17)$$

was $\log K_{CoL} = 10.6$ (at 35 °C) in satisfactory agreement with a literature value of 10.4 (at 25 °C).[9] (The value at 35 °C will not be greatly different, as seen from the reported [39] $\Delta H = -13.9$ kcal $mol^{-1}$ and $\Delta S = 14.5$ cal $K^{-1}$ $mol^{-1}$.) *

*Potentiometric Measurements under* $O_2$ *Atmosphere*.—The titration curves measured under $O_2$ differ from those under $N_2$. The lower pH of the buffer regions and the half-equivalent neutralization values (as shown by inflections at $a = 4.5$) for the $L^2$ and $L^3$ systems are common with $L^1$ (ref. 9) and other systems,[1b,11] suggesting the formation of similar hydroxo-containing $O_2$-bridged complexes, $[(CoL)_2(O_2)(OH)]^{3+}$.

$$2M^{2+} + 2L + O_2 + H_2O \rightleftharpoons [(ML)_2(O_2)(OH)]^{3+} + H^+; \quad K_{O_2,OH} = \frac{[(ML)_2(O_2)(OH)^{3+}][H^+]}{[M^{2+}]^2[L]^2[O_2]} \qquad (18)$$

The equilibrium constants defined by (18) were calculated as follows. $\alpha$ defined as above is given here by (19). Total

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* Throughout this paper: 1 cal = 4.184 J.

concentrations of $Co^{2+}$ and L are as in (20) and (21). Equation (19) may be rewritten as (22) using the definitions given in the preceding section, and appropriate combinations of (18)—(22) as before give the solutions (23)—(25).

$$\alpha = 4[\mathrm{L}] + 3[\mathrm{HL^+}] + 2[\mathrm{H_2L^{2+}}] + [\mathrm{H_3L^{3+}}] + 9[(\mathrm{ML})_2(\mathrm{O_2})(\mathrm{OH})^{3+}] \quad (19)$$

$$c_{\mathrm{M}} = 2[(\mathrm{ML})_2(\mathrm{O_2})(\mathrm{OH})^{3+}] + [\mathrm{M^{2+}}] \quad (20)$$

$$c_{\mathrm{L}} = 2[(\mathrm{ML})_2(\mathrm{O_2})(\mathrm{OH})^{3+}] + [\mathrm{L}]_{\mathrm{F}} \quad (21)$$

$$\alpha = 9[(\mathrm{ML})_2(\mathrm{O_2})(\mathrm{OH})^{3+}] + \{[\mathrm{L}]_{\mathrm{F}}\beta_{\mathrm{H}}/(\alpha_{\mathrm{H}})_{\mathrm{L}}\} \quad (22)$$

$$[(\mathrm{ML})_2(\mathrm{O_2})(\mathrm{OH})^{3+}] = \frac{\alpha(\alpha_{\mathrm{H}})_{\mathrm{L}} - \beta_{\mathrm{H}}c_{\mathrm{L}}}{9(\alpha_{\mathrm{H}})_{\mathrm{L}} - 2\beta_{\mathrm{H}}} \quad (23)$$

$$[\mathrm{L}]_{\mathrm{F}} = \frac{9(\alpha_{\mathrm{H}})_{\mathrm{L}}c_{\mathrm{L}} - 2\alpha(\alpha_{\mathrm{H}})_{\mathrm{L}}}{9(\alpha_{\mathrm{H}})_{\mathrm{L}} - 2\beta_{\mathrm{H}}} \quad (24)$$

$$[\mathrm{M^{2+}}] = \frac{(\alpha_{\mathrm{H}})_{\mathrm{L}}(9c_{\mathrm{M}} - 2\alpha) + 2\beta_{\mathrm{H}}(c_{\mathrm{L}} - c_{\mathrm{M}})}{9(\alpha_{\mathrm{H}})_{\mathrm{L}} - 2\beta_{\mathrm{H}}} \quad (25)$$

$$\frac{K_{\mathrm{O_2,OH}}}{(\alpha_{\mathrm{H}})_{\mathrm{L}}{}^2} = \frac{[(\mathrm{ML})_2(\mathrm{O_2})(\mathrm{OH})^{3+}][\mathrm{H^+}]}{[\mathrm{M^{2+}}]^2[\mathrm{L}]_{\mathrm{F}}{}^2[\mathrm{O_2}]} \quad (26)$$

$$K_{\mathrm{O_2,OH}}[\mathrm{O_2}][9(\alpha_{\mathrm{H}})_{\mathrm{L}}c_{\mathrm{L}} - 2\alpha(\alpha_{\mathrm{H}})_{\mathrm{L}}]^2[(\alpha_{\mathrm{H}})_{\mathrm{L}}(9c_{\mathrm{M}} - 2\alpha) + 2\beta_{\mathrm{H}}(c_{\mathrm{L}} - c_{\mathrm{M}})]^2 = [\alpha(\alpha_{\mathrm{H}})_{\mathrm{L}} - \beta_{\mathrm{H}}c_{\mathrm{L}}][9(\alpha_{\mathrm{H}})_{\mathrm{L}} - 2\beta_{\mathrm{H}}]^3[\mathrm{H^+}](\alpha_{\mathrm{H}})_{\mathrm{L}}{}^2 \quad (27)$$

Substituting (23)—(25) into (26), derived from (18), one finally gets equation (27).

Under the weakly acidic buffer conditions and at $c_{\mathrm{L}} = c_{\mathrm{M}}$, equation (27) is simplified to (28), as is (15) to (16). Plots of

$$K_{\mathrm{O_2,OH}}[\mathrm{O_2}]\,\frac{(9c_{\mathrm{L}} - 2\alpha)^4}{(\alpha - 2c_{\mathrm{L}})[\mathrm{H^+}]} = 5^3(\alpha_{\mathrm{H}})_{\mathrm{L}}{}^2 \quad (28)$$

$(9c_{\mathrm{L}} - 2\alpha)^4$ against $(\alpha - 2c_{\mathrm{L}})(\alpha_{\mathrm{H}})_{\mathrm{L}}{}^2[\mathrm{H^+}]$ are linear passing through the origin. The $K_{\mathrm{O_2,OH}}$ value for the $L^1$ system at 35 °C was estimated by using equation (29).

$$K_{\mathrm{O_2,OH}}[\mathrm{O_2}] = \frac{[\alpha(\alpha_{\mathrm{H}})_{\mathrm{L}} - \beta_{\mathrm{H}}c_{\mathrm{L}}][9(\alpha_{\mathrm{H}})_{\mathrm{L}} - 2\beta_{\mathrm{H}}]^3[\mathrm{H^+}]}{(9c_{\mathrm{L}} - 2\alpha)^4(\alpha_{\mathrm{H}})_{\mathrm{L}}{}^2} \quad (29)$$

With the $L^5$ system, the 1 : 1 solution exhibited a titration curve under $O_2$ at higher pH than that under $N_2$. In each case the inflection point occurred at 4 equivalents of the metal complex. If one postulates the formation of an $O_2$-monobridged complex, $[(\mathrm{CoL})_2(\mathrm{O_2})]^{4+}$, expressed by equilibrium (30) at the buffer region $a = 2$—4, $\alpha$ is represented by (31). A final equation (32) is obtained by a similar

$$2\mathrm{M^{2+}} + 2\mathrm{L} + \mathrm{O_2} \rightleftharpoons [(\mathrm{ML})_2(\mathrm{O_2})]^{4+}$$

$$K_{\mathrm{O_2}} = \frac{[(\mathrm{ML})_2(\mathrm{O_2})^{4+}]}{[\mathrm{M^{2+}}]^2[\mathrm{L}]^2[\mathrm{O_2}]} \quad (30)$$

$$\alpha = 8[(\mathrm{ML})_2(\mathrm{O_2})^{4+}] + \{[\mathrm{L}]_{\mathrm{F}}\beta_{\mathrm{H}}/(\alpha_{\mathrm{H}})_{\mathrm{L}}\} \quad (31)$$

$$K_{\mathrm{O_2}}[\mathrm{O_2}]\,\frac{(8c_{\mathrm{L}} - 2\alpha)^4}{(\alpha - 2c_{\mathrm{L}})} = 4^3(\alpha_{\mathrm{H}})_{\mathrm{L}}{}^2 \quad (32)$$

treatment and rearrangement as above. Plots of $(8c_{\mathrm{L}} - 2\alpha)^4/(\alpha - 2c_{\mathrm{L}})$ against $(\alpha_{\mathrm{H}})_{\mathrm{L}}{}^2$ are linear.

All the formation constants determined are summarized in Table 1.

*Polarographic Measurements of* $O_2$ *Uptake*.—A reduction wave of $O_2$ ($3.0 \times 10^{-4}$ mol dm$^{-3}$) in aqueous solution (25 cm$^3$) containing $Co^{2+}$ ($2.0 \times 10^{-3}$ mol dm$^{-3}$) and $MeCO_2^-$ ($10^{-2}$ mol dm$^{-3}$) at pH 5.48, $I$ 0.2 mol dm$^{-3}$, and 20 °C (where the complexation with $L^3$ can occur with or without $O_2$) exhibited a wave height of 8.5 cm (corresponding to 1.70 μA). Addition of $L^3 \cdot 4HCl$ (9.0 mg) lowered the $O_2$ reduction wave height (after 40 min of equilibration) to 4.8 cm (= 0.96 μA). The diminution due to $O_2$ uptake by $[CoL]^{2+}$ is thus calculated as $(3.0 \times 10^{-4}) \times (8.50 - 4.80)/8.50 = 1.3 \times 10^{-4}$ mol dm$^{-3}$. Meanwhile, the concentration of CoL–$O_2$ adduct formed is calculated from an absorbance of 0.50 at 370 nm, which corresponds to $2.6 \times 10^{-4}$ mol dm$^{-3}$ based on the apparent molar absorbance of $1.9 \times 10^3$. It is thus concluded that the stoicheiometry of $[CoL]^{2+}$ to $O_2$ in the oxygen complex is 2 : 1. The same technique also provided a 2 : 1 stoicheiometry for the $L^2$ and $L^5$ (in lutidine buffer) systems.

*Reversibility Measurements*.—The cobalt(II)–dioxygen adducts with $L^2$ and $L^3$ were allowed to stand in solution at pH 5.7 at 20 °C for 1 week. No diminution of the absorption intensity at 360 nm ($L^2$) and 370 nm ($L^3$) was observed. Upon acidification to pH 5, the brown colour of the $O_2$ complex faded to the pink of $Co^{II}$ and gaseous $O_2$ was evolved nearly quantitatively with no $[CoL]^{3+}$ formation (from visible spectra). Raising the pH and bubbling $O_2$ through the solution resulted in reformation of the complex with an identical spectrum (wavelength and intensity). Acidification below pH 4.5 caused partial (irreversible) decomposition to $[CoL]^{3+}$ ($\lambda_{\mathrm{max.}}$ 510 nm).

In the acetate buffers (pH *ca.* 5.5) the vigorous $N_2$ purging resulted in only partial (*ca.* 30% for $L^2$ and $L^3$, *ca.* 25% for $L^1$ under the same conditions) destruction of the oxygenated species. Even a prolonged $N_2$ flow did not destroy all of the brown oxygenated species. The process was then reversed by bubbling $O_2$ through the solution to give quantitative regeneration of the $O_2$ adducts with $L^2$ and $L^3$ (with $L^1$ *ca.* 90% of the $O_2$ adduct was regenerated). This cyclic process was repeated several times without any changes in absorption intensities.

With $L^5$, the $O_2$ adduct (lutidine buffer) is relatively unstable and irreversible oxidation to $[CoL]^{3+}$ started to occur in 30 min, as detected from the visible spectrum ($\lambda_{\mathrm{max.}}$ 365 and 500 nm). With $L^4$, the irreversible oxidation of the brown $O_2$ adduct occurred even more rapidly.

*Kinetics of* $O_2$ *Complexation*.—*Reactions between cobalt*(II) *and* L *in the presence of* $O_2$. In acetate buffers ($4.8 < \mathrm{pH} < 6$), the predominant form of the ligands is $H_2L^{2+}$ and cobalt(II) ion is present as $Co^{2+}$(aq), $[Co(O_2Me)]^+$, and $[Co(O_2CMe)_2]$ with the hydrolysis of $Co^{2+}$(aq) being negligible. At a given pH and $[MeCO_2^-]$, the observed rates are first order in $[Co^{2+}{}_{\mathrm{T}}]_0$ and first order in $[L_{\mathrm{T}}]_0$, but are independent of $[O_2]_0$. The second-order rate constants $k_{\mathrm{obs.}}$ at constant pH increase as $[MeCO_2^-]$ increases in proportion to $K_{\mathrm{Co(O_2CMe)}}[\mathrm{MeCO_2^-}]/\beta_{\mathrm{MeCO_2}}$ (see Table 2), which indicates that $[Co(O_2CMe)]^+$ is a reactive species of cobalt. $\beta_{\mathrm{MeCO_2}}$ is defined as in equation (33). The

$$\beta_{\mathrm{MeCO_2}} = [\mathrm{Co^{2+}}]_{\mathrm{F}}/[\mathrm{Co(aq)^{2+}}] = 1 + K_{\mathrm{Co(O_2CMe)}}[\mathrm{MeCO_2^-}] + K_{\mathrm{Co(O_2CMe)_2}}K_{\mathrm{Co(O_2CMe)_2}}[\mathrm{MeCO_2^-}]^2 \quad (33)$$

values for $K_{\mathrm{Co(O_2CMe)}}$ ($=10^{0.97}$ dm$^3$ mol$^{-1}$) and $K_{\mathrm{Co(O_2CMe)}}$-$K_{\mathrm{Co(O_2CMe)_2}}$ ($=10^{1.10}$ dm$^6$ mol$^{-2}$) were taken from ref. 40 and corrected to $I = 0.2$ mol dm$^{-3}$.

At constant $[MeCO_2^-]$, $k_{\mathrm{obs.}}$ increases as the pH increases, according to relation (34). Plots of $k_{\mathrm{obs.}}(\alpha_{\mathrm{H}})_{\mathrm{L}}/[\mathrm{H^+}]K_1$

$$k_{\mathrm{obs.}}(\alpha_{\mathrm{H}})_{\mathrm{L}} = k_{\mathrm{H}}[\mathrm{H^+}]K_1 + k_{2\mathrm{H}}[\mathrm{H^+}]^2K_1K_2 \quad (34)$$

against $[H^+]$ are linear with a finite value of the intercept for both the $L^2$ and $L^3$ systems. The rate constants $k_{\mathrm{H}}$ for monoprotonated L and $k_{2\mathrm{H}}$ for diprotonated L were thus determined graphically.

*Reaction between* $[\mathrm{CoL}]^{2+}$ *and* $O_2$. Examination of the kinetic data showed that the rate was first order in $[\mathrm{CoL}^{2+}]$

$$\mathrm{d}[O_2\ \text{adduct}]/\mathrm{d}t = k_2[\mathrm{CoL}^{2+}][O_2] \qquad (35)$$

and so the rate law (35) holds. The values of $k_2$ were independent of pH and of buffer concentration. All the kinetic results are listed in Table 4.

TABLE 4

Rate constants ($\mathrm{dm^3\ mol^{-1}\ s^{-1}}$) for the formation of oxygen adducts at 25 °C and $I$ 0.2 mol $\mathrm{dm^{-3}}$

| Ligand | $k_{\mathrm{H}}$ | $k_{2\mathrm{H}}$ | $k_2$ |
|---|---|---|---|
| $L^2$ | $(2.5 \pm 0.5) \times 10^2$ | $(2.5 \pm 0.4) \times 10^{-2}$ | $(7.1 \pm 1) \times 10^2$ |
| $L^3$ | $(4.2 \pm 0.8) \times 10^2$ | $(2.9 \pm 0.5) \times 10^{-2}$ | $(8.2 \pm 1.2) \times 10^2$ |
| $L^5$ | | | $(1.1 \pm 0.2) \times 10^2$ |

## DISCUSSION

*Protonation Constants and Metal-ion Equilibria.*—This is the first report of the protonation constants for $L^4$. A comparison of $K_i$ with other macrocycles (see Table 1) indicates a general trend in basicities of macrocyclic tetra-amines. More interesting is a comparison with isomeric $L^5$, which possesses a higher symmetry arrangement. The lower $K_1$ and $K_2$ values for $L^4$ are ascribable to its asymmetric ring framework, which probably hinders intramolecular hydrogen bonding facilitating accommodation of one or two protons into the macrocycle.[41]

Potentiometric equilibrium curves for 1 : 1 mol ratios of ligand to $\mathrm{Co^{II}}$ under $N_2$ show that attainment of the acid–base equilibrium in the presence of $\mathrm{Co^{II}}$ is very slow at 25 °C (requiring *ca.* 40 min for each increment of Na[OH] titrant), and we had to employ a higher temperature of 35 °C (the time required decreased to 20 min). As discussed later, this behaviour may be explained in terms of the very slow interaction of cobalt with free macrocyclic amines. The proton-releasing complex formation is seen commencing at $a = 2$ for macrocyclic systems and at $a = 1$ for linear systems, with an ultimate release of four protons from each complex molecule formed. The calculation of $K_{\mathrm{CoL}}$ indicates the formation of 1 : 1 $[\mathrm{CoL}]^{2+}$ complexes.

Two results are immediately obvious from the log $K_{\mathrm{CoL}}$ data given in Table 1. One is the cyclization effect which enhances complex stability by orders of 3—4. Similar orders of the ' macrocyclic effect '[42] were found for $\mathrm{Cu^{II}}$,[22] $\mathrm{Zn^{II}}$,[28] $\mathrm{Cd^{II}}$,[28] and $\mathrm{Pb^{II}}$.[28] The second result is that the ring size is sensitive to the complex stability in the sequence, 13 > 12 > 14 > 14 (isomeric). Somewhat similar ring-size effects and stability sequences were reported for $\mathrm{Cu^{II}}$.[22,23,25,27] The preference of the 13-membered ring by $\mathrm{Co^{II}}$ is noteworthy in view of the fact that the smaller sized $\mathrm{Co^{III}}$ fits best the larger 14-membered $L^5$ in planar configuration.[17] One may thus infer some distorted co-ordination geometry around $\mathrm{Co^{II}}$.

*Oxygenation Equilibria.*—Oxygenation of cobalt(II) complexes of macrocycles in aqueous solutions (at appropriate pH in buffers) leads to formation of dicobalt μ-peroxo-complexes. This is verified spectrally by the appearance of brown L→Co charge-transfer bands[1b] at 360 (*ca.* 2 300), 370 (*ca.* 1 900), 370, and 370 nm (ε *ca.* 2 400 $\mathrm{dm^3\ mol^{-1}\ cm^{-1}}$) for $L^2$, $L^3$, $L^4$, and $L^5$ systems, respectively. Oxidation of the μ-peroxo-complexes to $[\mathrm{CoL}]^{3+}$ can be detected visibly by the red absorption at 490—510 nm. Of the macrocyclic tetra-amines tested, $L^2$ and $L^3$ form the most stable $O_2$ adducts (as described in Results). Their stability allowed accurate determination of equilibrium constants. The $O_2$ adduct with $L^5$ is less stable, narrowly surviving the equilibrium study: a gradual conversion into $[\mathrm{CoL}]^{3+}$ proceeded (*ca.* 10% in total) during the potentiometric titration under $O_2$. For other macrocycles such as $L^4$ or 1,4,8,12-tetra-azacyclopentadecane (15-membered ring) the irreversible oxidation is much faster, precluding the use of the present analytical methods.

The polarographic study indicated the uptake of 1 mol of $O_2$ by 2 mol of cobalt(II) chelate with the macrocycles $L^2$, $L^3$, and $L^5$. The potentiometric data provide the stoicheiometry of the binuclear hydroxo-complex (with $L^2$ and $L^3$) or of the binuclear non-hydroxo-complex (with $L^5$). The validity of our calculations may be found in the occurrence of the same stoicheiometry $[(\mathrm{CoL})_2(O_2)(OH)]^{3+}$ for $L^1$,[9] and of a stoicheiometry $[(\mathrm{CoL})_2(O_2)]^{4+}$ for $L^5$, in agreement with the qualitative observation by Bosnich *et al.*[15] who isolated *trans*-$[(H_2O)\mathrm{LCoO_2CoL}(OH_2)]^{4+}$ by mixing $\mathrm{Co^{2+}}$ and $L^5$ in aqueous solutions under aerobic conditions.

The relative instability of the $O_2$ adduct with $L^5$ can now be immediately explained by the stoicheiometry lacking hydroxo-bridging. The smaller macrocycles $L^2$ and $L^3$ have no choice but to adopt a folded *cis* configuration around the oxygenated cobalt ion, which leaves a suitable position for the second hydroxo-bridge to reinforce the peroxo-bridge. In contrast, the larger $L^5$ would like to encircle cobalt by use of a planar *trans* geometry even at the sacrifice of hydroxo-bridging. The presence of the hydroxo-bridges in the $O_2$ adducts of $L^2$ and $L^3$ explains the facts that purging with $N_2$ produces only partial (*ca.* 30%) destruction in acetate buffers and that lowering the solution pH leads to quantitative liberation of $O_2$. Similar observations were made for $L^1$ by Nakon and Martell.[9]

The lower pH values at which the oxygenation of linear chelates occurs under equilibrium conditions (relative to $[\mathrm{CoL}]^{2+}$ formation curves in $N_2$) have been rationalized in terms of the oxygen complexes containing binegative $O_2^{2-}$ co-ordinated to $\mathrm{Co^{3+}}$.[9] The increased effective charge ($\mathrm{Co^{3+}}$ character) of the metal would enable it to compete more effectively with protons for the nucleophilic ligands.[1b] Then, the smaller pH depreciation of the buffer regions upon oxygenation of the macrocyclic $L^2$ and $L^3$ systems suggests less $\mathrm{Co^{3+}}$ character in their $O_2$ adducts, which may further be translated into a weaker oxygen affinity of the macrocyclic with respect to a linear system such as $L^1$. This is supported by a comparison (see Table 1) of the oxygenation constants $K_{O_2,OH}'$ defined and calculated as in (36).* The sources of the unusually low $K_{O_2,OH}'$ values

$$K_{O_2,OH}' = \frac{[(ML)_2(O_2)(OH)^{3+}][H^+]}{[ML^{2+}]^2[O_2]} = \frac{K_{O_2,OH}}{(K_{ML})^2} \qquad (36)$$

for $L^2$ and $L^3$ may be steric factors such as crowding or strain which are non-existent with the $L^1$ system.

The most puzzling result with the $L^5$ titration was the position of the buffer zone measured in an $O_2$ atmosphere, which is above the one measured in $N_2$. This is opposite to the expectation based on the internal oxidative addition of $O_2$.[1b] We have no immediate explanation for this phenomenon. To assess the value $K_{O_2}$ obtained, a more convenient format $K_{O_2}'$ as described by (37) was calculated for comparison with the reported $K_{O_2}'$ values of other peroxo-monobridged complexes.[1b,12,43,44]

$$K_{O_2}' = \frac{[(CoL)_2(O_2)^{4+}]}{[CoL^{2+}]^2[O_2]} = \frac{K_{O_2}}{(K_{CoL})^2} \qquad (37)$$

The value of 47 dm$^6$ mol$^{-2}$ (at 35 °C) for the $L^5$ system † was unexpectedly small: *e.g.* $10^{15.8}$ (at 25 °C) for the 3,6,9-triazaundecane-1,11-diamine system [44] (as a typical linear saturated penta-amine) or $10^{4.2}$ dm$^6$ mol$^{-2}$ (at 25 °C) for the bisbipyridine system [12] (as a typical linear unsaturated tetra-amine).

*Kinetics of* $O_2$ *Uptake.*—A most remarkable difference in the kinetics of $O_2$ uptake between the linear $L^1$ and the macrocyclic $L^2$—$L^5$ systems was initially observed in titrations, where the equilibration time (at 35 °C) after each increment of Na[OH] titrant was *ca.* 20 s for $L^1$, but *ca.* 20 min for macrocycles (*e.g.* $L^2$). The following kinetic study shows that the slow rates of $O_2$ uptake by the macrocyclic systems are ascribable to the extremely slow $[CoL]^{2+}$ chelate formation.

The potentiometric titration results showed that, using $L^2$ or $L^3$, the macrocyclic complexes $[CoL]^{2+}$ and their oxygen adducts can be formed in acetate buffers. Mixtures of $Co^{2+}$, $L^2$ (or $L^3$), and $O_2$ in acetate buffers developed a brown colour. Stopped flow measurements of the appearance of the peak at 360—370 nm gave excellent second-order (first order in $[Co^{2+}]$ and first order in $[L_T]$) kinetics for the $O_2$-adduct formation. This implies a slow formation of $[CoL]^{2+}$ followed by a rapid oxygenation. Thus the first set of kinetic data concerns only the mechanism of $[CoL]^{2+}$ formation.

The analysis of the observed second-order rate constants has led to a reaction scheme identical to that previously found for the macrocycle complexation of bivalent metal ions such as $Cu^{2+}$,[22,23,25,27] $Zn^{2+}$,[28] $Cd^{2+}$,[28] or $Pb^{2+}$ in acetate buffers.[28] The reactive macrocycle species $HL^+$ and $H_2L^{2+}$ and metal-ion species $[M(O_2CMe)]^+$ involved are all similar and need not be discussed further. The value of the rate constant $k_H$ or $k_{2H}$ for the present $Co^{2+}$ reaction is $10^2$—$10^3$ times smaller than the corresponding one for other bivalent metal ions. This is in parallel with the relative $k_{H_2O}$ (water-exchange rate constant) value of $Co^{2+}$ which is *ca.* $10^2$—$10^3$ times smaller than those for the other metal ions.[45] Involvement of water exchange in the rate-determining step has been cited for macrocycle complex formation with metal ions.[22,23,25,27,28,46,47] Further, the present $k_H$ value ($4.2 \times 10^2$ dm$^3$ mol$^{-1}$ s$^{-1}$) with $L^3$ is almost comparable to the rate constant of $1.8 \times 10^2$ dm$^3$ mol$^{-1}$ s$^{-1}$ reported for the $[CoL]^{2+}$ formation reaction between $Co^{2+}$ and monoprotonated 12,12-dimethyl-1,4,7,10-tetra-azacyclotridecane.[47] Assuming minor effects of the acetate anion attached to $Co^{2+}$ (which is really the case with $Cu^{2+}$) [23,27] and of the dimethyl substituents on $L^3$, the agreement is excellent. These facts strongly support $[CoL]^{2+}$ complex formation as the rate-determining step for oxygen uptake by the macrocyclic tetra-amine systems in acetate-buffered pH regions.

The rates of $O_2$ uptake by preformed $[CoL]^{2+}$ chelates in acetate buffers ($L^2$ and $L^3$) or in lutidine buffers ($L^5$) have been studied separately. Examination of the kinetic data showed that the reactions are first order in $[CoL^{2+}]$ and first order in $[O_2]$ for all the macrocycles investigated, *i.e.* the same rate law applies whether the final μ-peroxo-products contain a hydroxo-group (with $L^2$ and $L^3$) or not ($L^5$). The observed rates of oxygenation seem to refer to the formation of the 1 : 1 $[CoL]^{2+}$–$O_2$ species which then rapidly reacts with another $[CoL]^{2+}$ to give the μ-peroxo-species. Another interpretation of the rate law, as invoked for $O_2$ uptake by cobalt porphyrin systems,[6] may be that a unimolecular distortion of the 1 : 1 cobalt–oxygen species is rate-limiting. The hydroxo-bridge formation process for $L^2$ and $L^3$ systems appears to be rapid with respect to the μ-peroxo-formation in view of the rate law which is independent of pH in the examined range (4.8—6). The second-order rate constant $k_2$ for $L^5$ is also independent of pH from 6.5 to 7.5. One cannot totally ignore some interaction of lutidine (used as buffer) at the axial position of the planar $L^5$ complex,* which may affect the rate of oxygenation for the $L^5$ system.

The reaction of $[CoL]^{2+}$ with $O_2$ occurs *ca.* $10^4$ times faster than the prior formation of $[CoL]^{2+}$, which is illustrated by comparison of the second-order rate constants $k_2$ with $k_{obs.}$, as expressed in (34), under the same conditions: for $L^2$, $k_2 = 7.0 \times 10^2$, $k_{obs.} = 2.2 \times 10^{-2}$ (both in dm$^3$ mol$^{-1}$ s$^{-1}$) at pH 5.62; for $L^3$, $k_2 = 8.3 \times 10^2$, $k_{obs.} = 3.9 \times 10^{-2}$ at pH 5.55 (see Tables 2 and 3). It is now clear that the slow formation of macrocyclic chelates $[CoL]^{2+}$ determined the longer equilibrating time for the titrations in an $O_2$ atmosphere.

While the $[CoL]^{2+}$ formation limits the oxygenation of the macrocyclic systems, this step would not affect the rate of $O_2$ uptake by the linear $L^1$ counterpart. Rather,

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* Our log $K_{O_2,OH}'$ value of 6.8 (at 35 °C) for $L^1$ is fairly close to that of 6.1 (at 25 °C) reported by McLendon and Martell,[43] which gives support to our calculations.

† Our value disagrees with the $10^{8.1}$ dm$^6$ mol$^{-2}$ (at 25 °C) reported by McLendon and Mason.[16]

* Cobalt(II) porphyrin exhibits some interaction with γ-collidine in toluene (F. A. Walker, *J. Amer. Chem. Soc.*, 1973, **95**, 1150.

the kinetics[9,13] indicate two stages: first, the second-order reaction of $[CoL]^{2+}$ with $O_2$ to give peroxo-monobridged intermediates, and secondly, slower first-order transformation of the monobridged species to the dibridged μ-peroxo-μ-hydroxo-product. Reported second order rate constants for the reaction of $O_2$ are $2.5 \times 10^4$ $dm^3$ $mol^{-1}$ $s^{-1}$ with $[CoL^1(OH_2)_2]^{2+}$ and $2.8 \times 10^5$ $dm^3$ $mol^{-1}$ $s^{-1}$ with $[CoL^1(OH_2)(OH)]^+$, 30—300 times larger than those for the reaction of $O_2$ with the macrocyclic system. Steric crowding blocking the $H_2O$ exchange may retard the oxygenation of the macrocyclic chelates.

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REFERENCES

[1] (*a*) F. Basolo, B. M. Hoffman, and J. A. Ibers, *Accounts Chem. Res.*, 1975, **8**, 384; (*b*) G. McLendon and A. E. Martell, *Co-ordination Chem. Rev.*, 1976, **19**, 1.

[2] R. Wilkins, *Adv. Chem. Ser.*, 1971, **100**, 111.

[3] J. P. Collman, J. Brauman, T. Halbert, and K. Suslich, *Proc. Nat. Acad. Sci. U.S.A.*, 1976, **73**, 3333.

[4] B. S. Tovrog, P. J. Kitko, and R. S. Drago, *J. Amer. Chem. Soc.*, 1976, **98**, 5144.

[5] J. P. Collman, J. I. Brauman, K. M. Doxsee, T. R. Halbert, S. H. Hayes, and K. S. Suslick, *J. Amer. Chem. Soc.*, 1978, **100**, 2761.

[6] D. V. Stynes, H. C. Stynes, J. A. Ibers, and B. R. James, *J. Amer. Chem. Soc.*, 1973, **95**, 1142; F. S. Molinaro, R. G. Little, and J. A. Ibers, *ibid.*, 1977, **99**, 5628.

[7] A. L. Crumbliss and F. Basolo, *J. Amer. Chem. Soc.*, 1970, **92**, 55; B. M. Hoffman, D. Diemente, and F. Basolo, *ibid.*, p. 61.

[8] A. Zuberbuhler, T. Kaden, and F. Koechlin, *Helv. Chim. Acta*, 1971, **54**, 1502.

[9] R. Nakon and A. E. Martell, *J. Amer. Chem. Soc.*, 1972, **94**, 3026.

[10] L. G. Stadther, R. Prados, and R. B. Martin, *Inorg. Chem.*, 1973, **12**, 1814.

[11] G. McLendon, D. T. MacMillan, M. Harikaran, and A. E. Martell, *Inorg. Chem.*, 1975, **14**, 2322.

[12] R. F. Boguchi, G. McLendon, and A. E. Martell, *J. Amer. Chem. Soc.*, 1976, **98**, 3202.

[13] F. Miller and R. G. Wilkins, *J. Amer. Chem. Soc.*, 1970, **92**, 2687.

[14] F. S. Molinaro, R. G. Little, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1977, **99**, 5628 and refs. therein.

[15] B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, 1966, **5**, 1514.

[16] G. McLendon and M. Mason, *Inorg. Chem.*, 1978, **17**, 362.

[17] D. H. Busch, *Accounts Chem. Res.*, 1978, **11**, 392 and refs. therein.

[18] T. F. Lai and C. K. Poon, *Inorg. Chem.*, 1976, **15**, 1562 and refs. therein.

[19] J. P. Collman and P. W. Schneider, *Inorg. Chem.*, 1966, **5**, 1380.

[20] Y. Iitaka, M. Shina, and E. Kimura, *Inorg. Chem.*, 1974, **13**, 2886.

[21] M. Sarther and E. L. Blinn, *Inorg. Chem.*, 1976, **15**, 3083.

[22] M. Kodama and E. Kimura, *J.C.S. Chem. Comm.*, 1975, 326; *J.C.S. Dalton*, 1976, 116.

[23] M. Kodama and E. Kimura, *J.C.S. Chem. Comm.*, 1975, 891; *J.C.S. Dalton*, 1976, 1720.

[24] M. Kodama and E. Kimura, *Bull. Chem. Soc. Japan*, 1976, **49**, 2465.

[25] M. Kodama and E. Kimura, *J.C.S. Dalton*, 1976, 2335.

[26] M. Kodama and E. Kimura, *J.C.S. Dalton*, 1976, 2341.

[27] M. Kodama and E. Kimura, *J.C.S. Dalton*, 1977, 1473.

[28] M. Kodama and E. Kimura, *J.C.S. Dalton*, 1977, 2269.

[29] M. Kodama and E. Kimura, *J.C.S. Dalton*, 1978, 104.

[30] M. Kodama and E. Kimura, *J.C.S. Dalton*, 1978, 247.

[31] M. Kodama and E. Kimura, *Inorg. Chem.*, 1978, **17**, 2446.

[32] M. Kodama and E. Kimura, *J.C.S. Dalton*, 1978, 1081.

[33] M. Kodama and E. Kimura, *Inorg. Chem.*, 1978, **17**, 3716.

[34] M. Kodama and E. Kimura, *J.C.S. Dalton*, 1979, 325.

[35] J. E. Richman and T. J. Atkins, *J. Amer. Chem. Soc.*, 1974, **96**, 2268.

[36] G. Schwarzenbach, 'Complexometric Titrations,' Interscience, New York, 1957, p. 82.

[37] Chemical Handbook of Japan (Kagaku-binran),' Chem. Soc. Japan, Maruzen, 1973, p. 571.

[38] J. A. Bolzen and A. J. Aruia, *Electrochim. Acta*, 1962, **7**, 589.

[39] P. Paoletti and A. Vacca, *J. Chem. Soc.*, 1964, 5051.

[40] S. K. Siddhanta and S. N. Banerjee, *J. Indian. Chem. Soc.*, 1958, **35**, 323.

[41] B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, 1965, **4**, 1102.

[42] D. K. Cabbiness and D. W. Margerum, *J. Amer. Chem. Soc.*, 1969, **91**, 6540.

[43] G. McLendon and A. E. Martell, *J.C.S. Chem. Comm.*, 1975, 223.

[44] W. R. Harris, I. Murase, J. H. Timmons, and A. E. Martell, *Inorg. Chem.*, 1978, **17**, 889.

[45] M. Eigen, *Pure Appl. Chem.*, 1963, **6**, 105.

[46] L. Hertli and T. A. Kaden, *Helv. Chim. Acta*, 1974, **57**, 1328.

[47] W. Steinmann and T. A. Kaden, *Helv. Chim. Acta*, 1975, **58**, 1358.