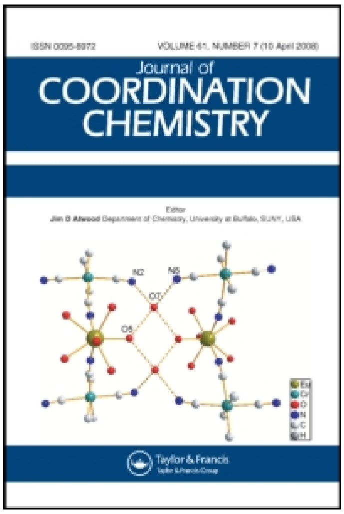

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article McLendon, G. and Martell, A. E.(1975) 'OXYGEN COMPLEX FORMATION BY COBALT(II)-TRIS (2-AMINOETHYL) AMINE ', Journal of Coordination Chemistry, 4: 4, 235 — 241

To link to this Article: DOI: 10.1080/00958977508075906

URL: http://dx.doi.org/10.1080/00958977508075906

J. Coord. Chem.
1975, Vol. 4, pp. 235–241

OXYGEN COMPLEX FORMATION BY COBALT(II)-TRIS (2-AMINOETHYL) AMINE[+]

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(*Received December 19, 1974*)

The reversible oxygenation of the Co(II) complex of tris(2-aminoethyl)amine (TREN, L) has been studied in some detail. The equilibrium constant $K_{O_2} = 10^{26.92}$ M^{-2} atm^{-1}, corresponding to the quotient $[H^+][L_2Co_2(O_2)(OH)^{3+}]/[Co^{2+}]^2[L]^2 P_{O_2}$ was determined by potentiometric equilibrium measurements of hydrogen ion concentration. Values for the thermodynamic constants, $\Delta H^\circ = -63 \pm 9$ kcal/mole and $\Delta S^\circ = -100 \pm 15$ cal/deg. mol, were calculated from the temperature dependence of the equilibrium constant. Oxygen stoichiometry, measured with a polarographic sensor, indicated the formation of a binuclear (peroxo bridged) complex, and the potentiometric equilibrium data indicated the presence of a second, μ-hydroxo, bridge. Measurement of the kinetics of the fast reaction between the cobalt(II)-TREN complex and dioxygen gave the value of the second order rate constant for the formation of the dioxygen complex as $k_1 = 2.8 \times 10^{+3}$ sec^{-1} mol^{-1}. The first order rate constant for the decomposition of the dioxygen complex measured by stopped-flow was found to be $k_{-2} = 0.7$ sec^{-1}. Kinetic and equilibrium data are discussed with respect to the probable structure and mechanism of formation of the dioxygen complex, and are compared with similar data previously reported for analogous complexes. The oxygen complex reported is unique with respect to its extremely slow rate of conversion to inert cobalt(III) complexes.

INTRODUCTION

A number of recent papers[1–6] have helped to delineate the nature of the interesting interactions between cobalt(II) chelate complexes and molecular oxygen. In particular, the reaction of dioxygen with the cobalt(II) complex of the polyamine triethylenetetraamine (TRIEN) has been studied in some detail.[7–9] For the non-linear isomer of TRIEN, tris-(2-aminoethyl)amine (TREN), such studies are lacking, in spite of its interesting geometry and characteristics.

Grieb and Yang[10,11] have recently reported the synthesis, isolation, and partial characterization of the peroxo-bridged complex, $Co_2L_2O_2{}^{4+}$, L = TREN, and of the doubly-bridged μ-hydroxo complex, $Co_2L_2(O_2)(OH)^{3-}$, but no quantitative studies of the equilibrium or kinetics of complex formation were carried out. As the result of detailed studies in this laboratory, equilibrium measurements, thermodynamic data, stoichiometric data, esr spectra, and reaction kinetics involving the dioxygen complexes of cobalt(II) and TREN are now presented.

EXPERIMENTAL

Materials

All chemicals used were reagent grade. TREN was recrystallized, as the tetrahydrochloride salt by the method of Mann and Pope,[12] giving a satisfactory melting point (168°, d). The cobalt(II) solutions were standardized by titration with EDTA.

Methods

Stoichiometry of oxygen uptake was measured using a polarographic oxygen sensor (Yellow Springs Instrument Co.), calibrated with aqueous solutions saturated with air and pure oxygen.

Potentiometric equilibrium studies involving the use of a Beckman research pH meter fitted with extension glass and calomel electrodes were carried out on the tetrahydrochloride salt of TREN in the presence and in the absence of cobalt(II). Oxygenation equilibria were measured by potentiometric measurements of 1:1 molar ratios of metal ion and ligands in solutions saturated with argon, air, and pure oxygen. These measurements were performed in a jacketed cell in which the temperature was maintained at 25 ± 0.1°, and the ionic strength maintained at 0.100 M by the addition of potassium nitrate. The potentiometric pH equipment was calibrated in terms

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[†] This research was supported by a grant, No. 259, from The Robert A. Welch Foundation.

of hydrogen ion concentration by the titration of standard hydrochloric acid solution with standard sodium hydroxide in the ionic medium specified above, as described previously.[7]

Measurements

Reversibility experiments were performed using the method of Nakon and Martell.[7] Absence (or presence) of an irreversible rearrangement or decomposition to a cobalt(II) complex was determined with a Cary Model 14 spectrophotometer by observing changes as a function of time of intensities of absorption of the charge-transfer band of the oxygen complex in the 350–355 nm region.

Kinetics of the rapid interaction of the cobalt(II)-TREN complex with dioxygen were measured with a Durrum stopped flow fast reaction spectrophotometer set at 352 nm. A solution of a 1:1 molar ratio of cobalt(II) and TREN was mixed with an aqueous solution of oxygen or air at a predetermined pH with a molar ratio of complex to oxygen of 10–20:1. The temperature was maintained at 25.0° and the ionic strength was regulated at 0.10 μ by the addition of potassium nitrate.

Esr spectra were obtained on a Varian E6S epr spectrometer. The spectrum was obtained after bubbling chlorine gas through a low pH solution of the complex.

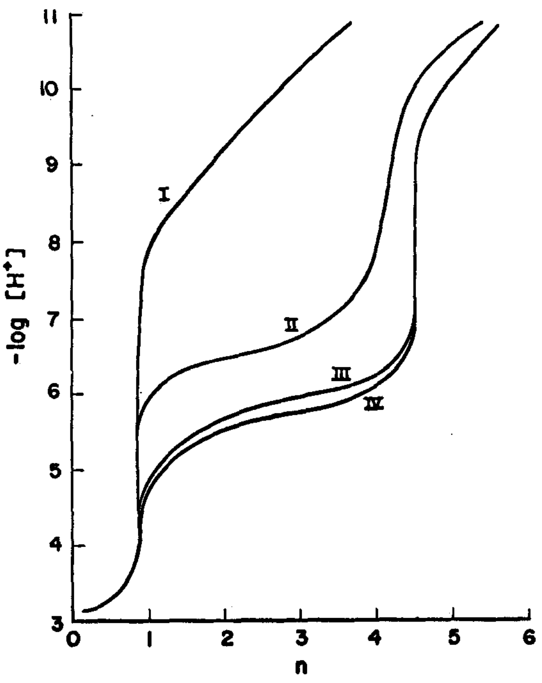


FIGURE 1 Potentiometric equilibrium curves for the cobalt(II)-TREN-dioxygen system: I, ligand H_4L^{4+} only; II, 1:1 molar ratio of TREN to Co(II) under argon; III, 1:1 molar ratio of TREN to Co(II) under air; IV, 1:1 molar ratio of TREN to Co(II) under pure dioxygen.

RESULTS AND CALCULATIONS

Potentiometric equilibrium curves for the ligand (L), ligand and cobalt(II) under an argon atmosphere and ligand and cobalt(II) under pure oxygen or under air, are presented in Figure 1. The ligand curve has a sharp inflection at $n = 1$ (n = moles of added base per mole of ligand) with no other sharp breaks readily apparent. The cobalt–TREN curve obtained under an inert atmosphere has a long buffer zone terminated by a sharp inflection at $n = 4$ corresponding to the formation of the cobalt(II) complex, CoL^{2+}. The equilibrium curves obtained under oxygen and air show a buffer region at much lower pH than that obtained under oxygen-free conditions, indicating formation of a quite stable oxygen complex. The inflection point at $n = 4.5$ further indicates formation of a μ-hydroxo binuclear complex, presumably of the well-known binuclear oxygen-bridged type.

Values for the successive ligand protonation constants $K_1 = 10^{10.14\pm0.02}$, $K_2 = 10^{9.43\pm0.03}$, $K_3 = 10^{8.45\pm0.02}$, $K_4 = 10^{2.60\pm0.05}$, were computed from potentiometric data, using a program written by Dr. R. J. Motekaitis of these laboratories. Values of the equilibrium constants for complex formation under inert atmosphere $K_{ML} = 10^{12.69\pm0.04} = [ML^{2+}]/[M^{2+}][L]$ and for oxygen complex formation $K_{O_2} = 10^{26.92\pm0.03} = [H^+][M_2L_2O_2(OH)^{3+}]/[M]^2[L]^2P_{O_2}$ were determined from potentiometric data analyzed with an IBM 360-65 computer using programs written by George McLendon.

Equilibrium measurements carried out at different temperatures were employed to calculate ΔH, using the Gibbs Helmholtz equation for the equilibrium constant $K_{O_2} = [M_2L_2O_2OH^{3+}][H^+]/[M^{2+}]^2[L]^2P_{O_2}$, the following hermodynamic constants were calculated:

$$\Delta G = -13.5 \pm 0.1 \text{ kcal mole}^{-1}$$

$$\Delta H = -63 \pm 10 \text{ kcal mole}^{-1}$$

$$\Delta S = -100 \pm 15 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

Stoichiometric experiments utilizing the polarographic oxygen meter showed 0.50×10^{-3} mmole oxygen were absorbed in two minutes on addition of

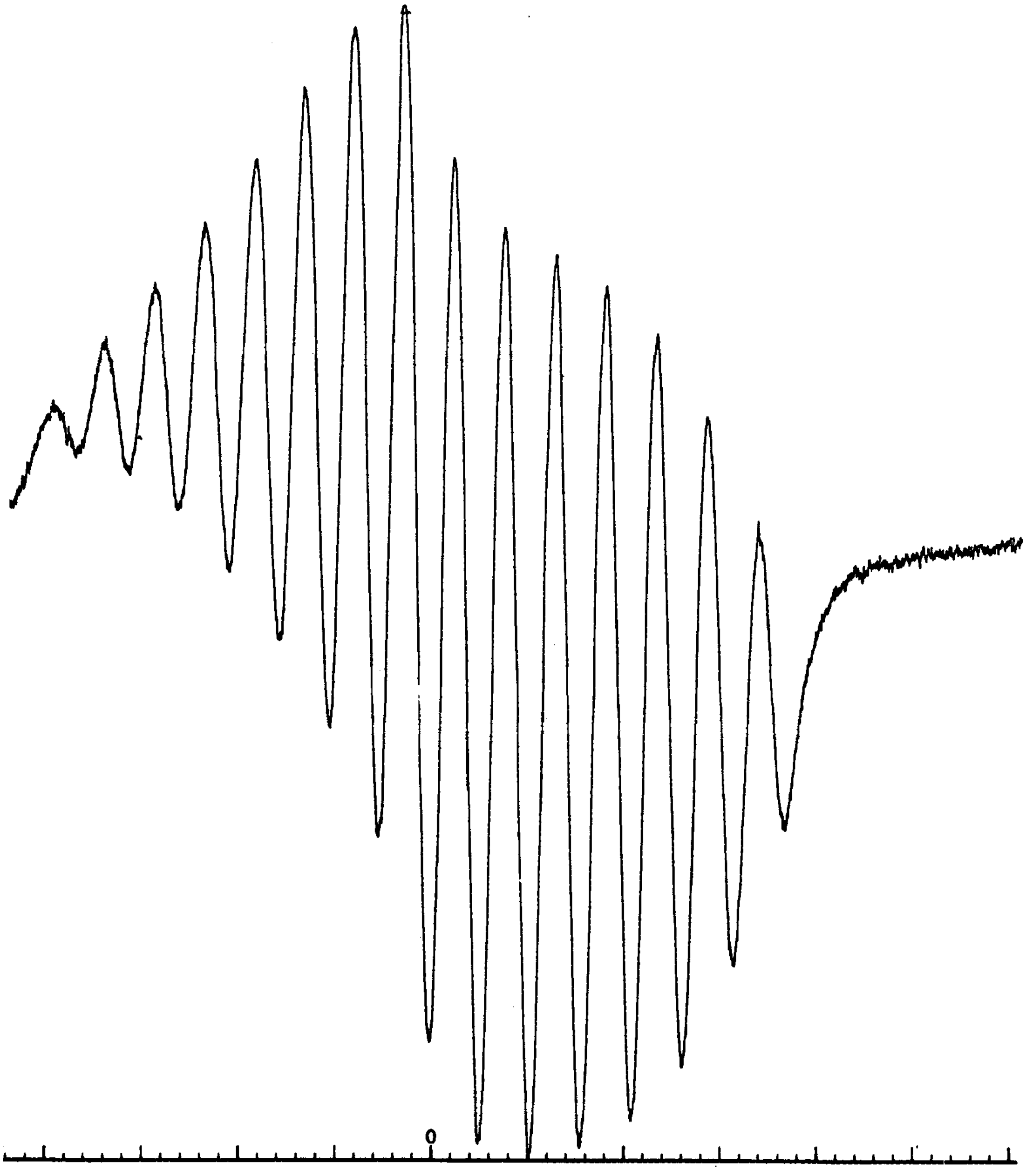


FIGURE 2 Esr spectrum of $Co_2(TREN)_2O_2(OH)^{4+}$; t ≅ 25°; $\mu = 0.3$.

1×10^{-3} mmole Co^{2+}([TREN] = $[Co^{2+}]$ = 1×10^{-3} M). This result agrees with the formation of a 2:1 complex as postulated by Grieb,[9] and is in line with the kinetic and potentiometric data presented here.

The esr spectrum obtained on the superoxide shows 15 lines with a peak separation of ~10 gauss. The spectrum is typical of a binuclear superoxo-bridged complex with ca. 90% of the free electron density on the dioxygen linkage, and supports our assignment of the oxygen adduct as a binuclear peroxo bridged complex.

The rapid interaction of the cobalt(II)-TREN complex with oxygen showed excellent pseudo first order kinetics. Data evaluated by the method of Wilkins[5,8] gave for the limiting second order rate constants $k_1 = 2.8 \times 10^3$ sec^{-1} mol^{-1}, and for the reverse reaction with HCl, $k_{-2} = 0.7$ sec^{-1}.

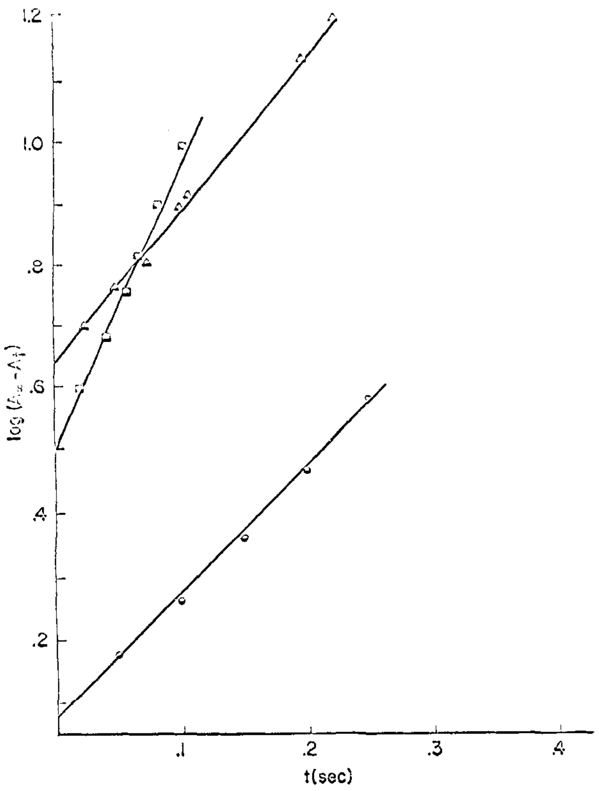


FIGURE 3 Pseudo first order dependence of oxygen complex formation on [CoTREN]; I [CoTREN] = 2.3×10^{-3}, $k_{obs} = 5.8$ sec^{-1}; II [CoTREN] = 4.1×10^{-3}, $k_{obs} = 11.5$ sec^{-1}; III [CoTREN] = 1.5×10^{-3}, $k_{obs} = 4.6$ sec^{-1}; $[O_2] = 1.2 \times 10^{-4}$ for I, II, III; $k_1 = k_{obs}/[CoTREN] = 2.8 \times 10^3$. (I = ▲, II = ■, III = ●)

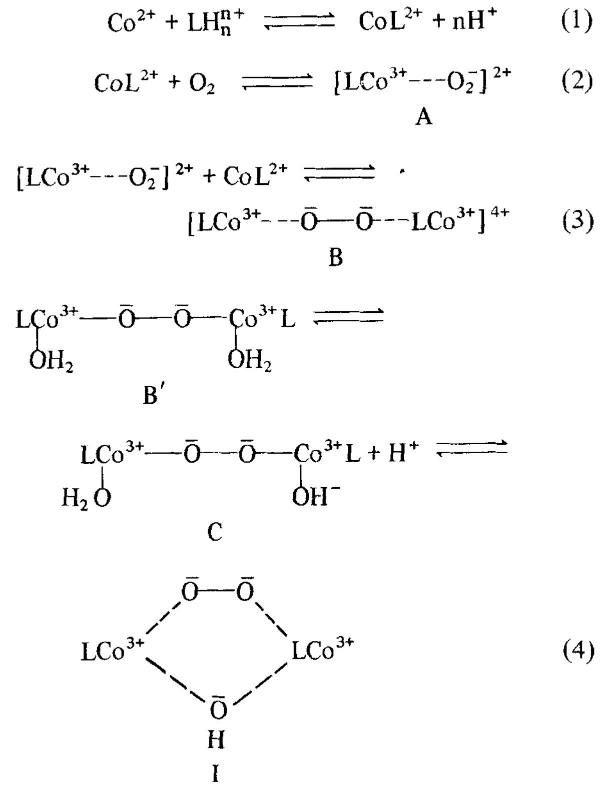
DISCUSSION

The values obtained for the protonation constants of TREN are in excellent agreement with those reported by Schwarzenbach[13] when corrected to 25°C. The value reported here for the cobalt(II)-TREN formation constant also correlates well with the results of Schwarzenbach[13] and Paoletti.[14]

The potentiometric data obtained under equilibrium conditions for the formation of the oxygen complex are rather interesting. Polarographic stoichiometric data indicate formation of a binuclear complex, presumably of the peroxo bridged type. The half equivalent neutralization value, combined with the unusually long equilibration times required for pH stabilization, indicate formation of a μ-hydroxo bridge, as in similar polyamine systems.[2,7]

The anomalously low pH values obtained under conditions of oxygen complex formation compared to the observed pH values for the simple cobalt(II)-TREN complex formed under an inert atmosphere, suggest the formation of a labile cobalt(III)-peroxo complex, rather than a simple cobalt(II)–oxygen complex.

Data are consistent with the following reaction scheme proposed by Nakon and Martell[7] for a similar system.



$$Co^{2+} + LH_n^{n+} \rightleftharpoons CoL^{2+} + nH^+ \quad (1)$$

$$CoL^{2+} + O_2 \rightleftharpoons \underset{A}{[LCo^{3+}---O_2^-]^{2+}} \quad (2)$$

$$[LCo^{3+}---O_2^-]^{2+} + CoL^{2+} \rightleftharpoons \underset{B}{[LCo^{3+}---\bar{O}—\bar{O}---LCo^{3+}]^{4+}} \quad (3)$$

$$\underset{B'}{L\underset{OH_2}{Co^{3+}}—\bar{O}—\bar{O}—\underset{OH_2}{Co^{3+}}L} \rightleftharpoons$$

$$\underset{C}{L\underset{H_2O}{Co^{3+}}—\bar{O}—\bar{O}—\underset{OH^-}{Co^{3+}}L} + H^+ \rightleftharpoons$$

$$\underset{I}{LCo^{3+}\overset{\bar{O}—\bar{O}}{\underset{\underset{H}{\bar{O}}}{\diamond}}LCo^{3+}} \quad (4)$$

Such a scheme is similar to that proposed by Wilkins on the basis of kinetic data and is in line with our observation of a half equivalent neutralization value ($n = 4.50$) implying the instability of intermediate complexes A and B relative to complex I.

Such a scheme also agrees with our observation that even at low pH not all of the oxygen complex is destroyed as determined spectrally by monitoring the band at 352 nm. Intermediates such as B and C might be expected to be stable at low pH, thus rationalizing this observation. Formation of the final product I is consistent with the slow equilibration observed at higher pH.

The value determined for the equilibrium constant of oxygen complex formation is somewhat higher for the TREN-cobalt(II) system than for the isomeric TRIEN-cobalt(II) system

$$\log K_{O_2}\ (\text{TREN}) = 26.92 \pm 0.03;$$
$$\log K_{O_2}\ (\text{TRIEN}) = 25.22 \pm 0.04^{7}$$

as might be predicted from the higher basicity of TREN.

Correcting for ligand basicity to allow a parallel comparison of equilibria involving only the oxygenation reaction of the metal ligand complex, one can formulate a different equilibrium constant

$$K'_{O_2} = \frac{[M_2L_2O_2OH][H^+]}{[ML]^2[O_2]}$$

For the equilibrium constant as written, the stability of the metal ligand complex is taken into account, and the value of log K'_{O_2} for the $Co_2(TREN)_2O_2OH$ complex becomes 4.41 ± 0.02. Similarly computed, the values of the equilibrium constant for DTMA[16]† and TRIEN are log K_{O_2} = 2.39 and 8.0, respectively. The values of DTMA and TREN are orders of magnitude lower than that of TRIEN and may reflect the structural similarity of the complexes of the former two ligands. Further, the lower value of the constant may explain why the $Co_2L_2O_2OH$ complex is completely reversible where L = DTMA and TREN, but not when L = TRIEN.

This exceptional stability of the cobalt–TREN oxygen complex is further enhanced by the lack of appreciable conversion of the complex to irreversible cobalt(III) complexes. Monitored spectrally, the complex shows no significant degradation in basic solution for over a month (some conversion is observed, however, over a 3-month period). By contrast most cobalt(II)-dipeptide oxygen carriers degrade quite rapidly (e.g., for the glycylglycine cobalt oxygen carrier a red cobalt(III) complex is formed irreversibly and completely within two hours).

Values reported in the literature for ΔS for cobalt oxygen complexes formed with other polyamines are relatively large and negative. Nancollas *et al.*[15] have attributed the highly negative entropy values for such reactions to formation of new charge centers in the complex, involving the transfer of charge from cobalt(II) to oxygen, and the increased interaction of the new charged centers with solvent molecules. For the reaction as written, the values of ΔH and ΔS are much larger in magnitude than those reported for similar systems with histidine or ethylenediamine as the chelating ligand. In order to compare these values, it is necessary to correct our overall reaction for the exothermic formation of the Co–TREN chelate (ΔH = 10.6 ± 0.15 per mole[14]). This correction gives a value $\Delta H = 42 \pm 9$ kcal per mole. Further the equilibrium constants used in these calculations employ the partial pressure of oxygen, P_{O_2} rather than oxygen concentration, which changes with the changing solubility of oxygen in water as a function of temperature.

It is uncertain how much of the observed differences between our values $\Delta H = 42 \pm 9$ kcal and reported values for the histidine and other systems ($\Delta H \cong 30$ kcal) is due to this discrepancy and how much may be ascribed to the inherently higher stability of the TREN complex. We are undertaking calorimetric studies to resolve this question.

Kinetic parameters (Table I) were obtained by the method of Wilkins.[2,6,8] The values given for the limiting second order rate constant, k_1, and the rate of decomposition k_{-2}, compare interestingly with those previously reported by Wilkins for similar systems. Values are compared in Table I for the reaction sequences (4) and (5) (charges omitted for clarity):

$$\text{CoL} + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{CoLO}_2 \qquad (4)$$

$$\text{CoLO}_2 + \text{CoL} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{Co}_2\text{L}_2\text{O}_2 \qquad (5)$$

The interesting constancy exhibited by these values has been interpreted by Wilkins[6] as arising from the similarity in such complexes of H_2O replacement by O_2 dominated by H_2O exchange. The relatively lower value of k_1 for the formation of the cobalt(II)-TREN oxygen complex relative to the cobalt(II)-TRIEN analog may reflect specific orientation requirements for oxygen complexes, which are more difficult to meet when the metal ion is bound

TABLE I
Kinetic parameters for the formation and dissociation of cobalt (II)-oxygen complexes at 25°C

System	k_1 M^{-1} sec^{-1}	k_{-2} sec^{-1}
Co-TRIEN-O_2	25.0×10^3	0.46^a
Co-L-histidine-O_2	3.5×10^3	0.47
Co-DTMA-O_2[16]	3.0×10^3	0.62
Co-TREN-O_2	2.8×10^3	0.70

[a] At 4°C.

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† DTMA = diethylenetriaminemonoacetic acid (2-aminoethylglycine).

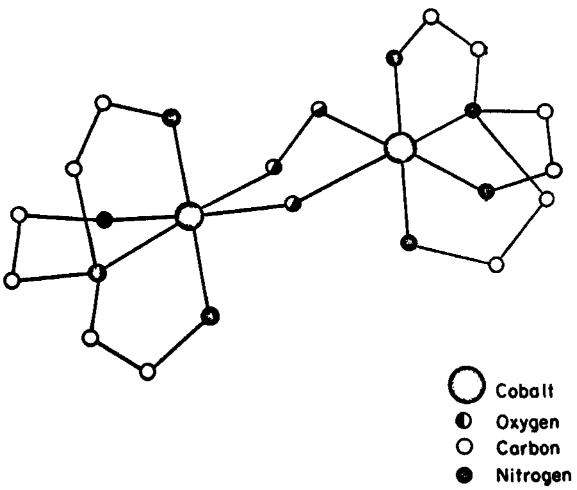

FIGURE 4 Probable structure of the oxygen complex ($Co_2TREN_2O_2OH^{3+}$).

to the tripod-like TREN ligand (Figure 4). This concept is in accord with the large negative value of the entropy of oxygen complex formation, as noted above.

The similar values of k_1 and k_{-2} for the formation of the cobalt(II)-TREN and DTMA oxygen complexes reflect their structural similarity. These values also offer support for the multi-stage mechanism given in equations (1)–(3).

As TREN and other ligands with similar stereochemical requirements are known to favor five coordination[17] with cobalt(II) (under nitrogen atmosphere) the similar kinetic values for oxygenation of the TREN-Co(II) and S-DTMA-Co(II) chelates may reflect either oxidative addition to a five-coordinate complex, or a modified rate of ligand exchange in five coordinate *vs.* six coordinate complexes.

Wilkins[18] has recently reported the addition of oxygen to a tetrahedral cobalt(II) complex with a rate constant remarkably similar to that of the octahedral complex, thus supporting the possibility that complexes of different stereochemistry can interact with molecular oxygen at quite similar rates. Since the generally accepted mechanism for such oxygenation involves H_2O replacement by O_2 in the rate limiting step, dominated by H_2O exchange, it may be that the rate of ligand exchange for a five coordinate *vs.* an octahedral complex is reflected in the rate data, probably followed by a rapid rearrangement to octahedral symmetry. Alternately the oxygenation might be looked at as an oxidative addition, although in this case a much larger rate difference might be expected.

In any event, if five coordination is assumed, the TREN-Co(II) case is the first reported example of the interaction of a five coordinate polyamine complex with molecular oxygen. This possibility, in conjunction with the desirable properties of ready reversibility and slow or nonexistent irreversible oxidation make the Co(II)-TREN system an interesting system for further study.

ACKNOWLEDGEMENTS

The authors thank Dr. Leonard Mohrmann for measuring the esr spectrum and Dr. R. J. Motekaitis for helpful discussions.

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NOTE ADDED IN PROOF

In an unpublished study, Bogdansky and Wilkins[19] have described the oxygenation of Co(II)-TREN in terms of several hydrolyzed octahedral forms, assuming the five-coordinate species to be oxygen inactive. The present results could be so interpreted if a rapid conformational pre-equilibrium can be assumed to occur between the octahedral and trigonal bipyrimidal species.