Oxygen Complexes of Triethylenetetraminecobalt(II) in Aqueous Solution[1]

Robert Nakon and A. E. Martell*[2]

Contribution from the Department of Chemistry, Texas A & M University, College Station, Texas 77843. Received June 25, 1971

Abstract: Low-pH equilibrium studies on the oxygenation of the 1:1 Co(II)–triethylenetetramine (trien, L) chelate are reported. Potentiometric titration and Warburg oxygen absorption measurements provide data on the stoichiometry of the oxygen complex in the pH range 4–8 to correspond to the formation of the binuclear complex $Co_2 \cdot O_2 \cdot OH \cdot L_2{}^{3+}$. Acid–base equilibrium is found to be established at a slower rate than oxygen uptake, in agreement with the postulation of a series of equilibria involving the formation of a labile, reversible binuclear oxygen-bridged complex and a somewhat more slowly formed binuclear oxygen-bridged complex containing a second (hydroxo) bridge. Potentiometric equilibrium data are employed to calculate the formation constant, $10^{25.2}$ M^{-3} atm^{-1}, corresponding to the equilibrium quotient $[\text{complex}][\text{H}^+]/[\text{Co}^{2+}]^2[\text{O}_2][\text{L}]^2$.

The resurgence of research activity in the field of synthetic oxygen carriers has led to the discovery of new oxygen complexes which are both reversible and irreversible to molecular oxygen.[3,4] Recent publications by Fallab,[5,6] Miller and Wilkins,[7,8] and Michailidis and Martin[9] have described the composition of kinetics of formation and dissociation of oxygenated complexes of cobalt(II)–polyamine chelates at high pH. Thus far, however, equilibrium studies of the formation constants of these oxygenated species, and the stoichiometry of formation under equilibrium conditions, have not been reported. As the result of extensive equilibrium investigations of these systems that have been carried out in these laboratories for some time, this paper now reports a potentiometric study of the formation of the oxygenated species of the cobalt(II) chelate of triethylenetetramine (1,4,7,10-tetraazadecane, trien, L). The equilibrium constant for the formation of the final oxygenated species is reported and evidence is presented to support the suggestion of the formation of three oxygenated species, two of which are reversible to molecular oxygen, while a third species, which eventually is completely formed as the pH is increased, does not exhibit measurable equilibrium with molecular oxygen.

Experimental Section

Potentiometric Measurements. The experimental method consisted of potentiometric titrations of the tetrahydrochloride salt of triethylenetetramine (trien), in the presence and absence of cobalt(II). The titrations in the presence of cobalt(II) were performed under both nitrogen and oxygen atmospheres. The ionic strengths of the solutions were maintained at 0.10 M by the addition of appropriate amounts of 1 M KNO$_3$ solution. All potentiometric measurements were performed in a jacketed titration cell of 50-ml capacity that was maintained at 25 ± 0.1° by the circulation of water thermostated at this temperature through the outer jacket of the potentiometric cell. A Beckman research model pH meter fitted with glass and calcomel extension electrodes was calibrated on the basis of data tabulated by Harned and Owen[10]

with HCl, NaOH, and acetic acid as standards, so as to allow the direct determination of hydrogen ion concentration instead of the usual $-\log a_{\text{H}}+$.

Warburg Measurements. The stoichiometries of oxygen absorption were measured in a Gilson Model No. 8058 Warburg apparatus. The flasks were paired with a manometer and the constants for each set were determined in the usual manner using triply distilled mercury as the calibrant. Solutions of cobalt(II) and trien base with KNO$_3$ added were added to the side arm and main compartment, respectively, of a Warburg flask. The system was arranged so that when the contents of the side arm was added to the main compartment, the metal to ligand ratio would be 1:1, the pH would be 9, and the ionic strength would be 0.10 M. The Warburg apparatus was then flushed with oxygen and the Warburg flasks were equilibrated at 25 ± 0.1°. The contents of the side arm was then emptied into the main compartment, and the measurement of oxygen absorption at various times was recorded. A blank was run simultaneously to correct for changes in atmospheric pressure.

Reversibility Experiments. Two equimolar and equivolume solutions of 1:1 cobalt(II) to trien at the pH value of interest (*e.g.*, 4.7, etc.) were prepared. One solution was allowed to stand in air, while the other solution was equilibrated with air and then subjected to vigorous and continuous flow of nitrogen. The ultraviolet 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 at pH values from 4.9 to 9 were taken immediately upon addition of alkali metal hydroxide and retaken again after thirty minutes of purging with nitrogen.

Reagents. The source of cobalt was reagent grade (Baker's analyzed) cobalt nitrate. The triethylenetetramine was doubly distilled and recrystallized as the hydrochloride.

Solutions of Co(II) used in the preparation of the complexes employed in experimental runs were standardized by the method of Schwarzenbach.[11] Solutions of triethylenetetramine were standardized by ion-exchange methods using Dowex 50W-X8 cation exchange resin.

Results and Calculations.

Potentiometric Measurements. Potentiometric equilibrium curves for the ligand and for 1:1 molar ratios of Co(II) to trien under both oxygen and nitrogen atmospheres are presented in Figure 1. The ligand titration curve has three buffer zones and two sharp inflection points at $n = 1$ and 2, where n equals moles of base added per mole of ligand present. The last buffer zone continues in the high-pH region, and no inflection is seen. The 1:1 solution titrated under a nitrogen atmosphere has a long buffer zone in the acid region

(1) This work was supported by a research grant, A-259, from the Robert A. Welch Foundation.
(2) Address correspondence to this author.
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(7) F. Miller and R. G. Wilkins, *J. Amer. Chem. Soc.*, **92**, 2687 (1970).
(8) F. Miller, J. Simplicio, and R. G. Wilkins, *ibid.*, **91**, 1962 (1969).
(9) M. S. Michailidis and R. B. Martin, *ibid.*, **91**, 4683 (1969).

(10) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd ed, Reinhold, Princeton, N. J., 1950, p 523.
(11) G. Schwarzenbach, "Complexometric Titrations," Interscience, New York, N. Y., 1957, p 82.

which is terminated by a sharp inflection at $n = 4$. The 1:1 solution titrated under an oxygen atmosphere has a long buffer region in the acid region which is ended by a sharp inflection point at $n = 4.5$. In the latter case, the buffer region is found at much lower pH than that of the 1:1 oxygen-free system, indicating the formation of a very stable oxygen complex. The half-equivalent neutralization value demonstrates the formation of a binuclear complex (or of a higher polynuclear species with even numbers of mononuclear units).

Warburg Measurements. The oxygen uptake curve obtained at pH 9 (not shown) showed very rapid initial absorption of oxygen, followed by much slower absorption. After 15 min, 0.48 mol of oxygen was observed per mole of metal ion or ligand, indicating that 1 mol of oxygen is absorbed per 2 mol of ligand or metal ion.

Reversibility Experiments. The experiments in which oxygen was purged from the 1:1 system by a continuous and vigorous nitrogen flow indicated that there was more than one oxygenated species in solution. In the acidic buffer region nitrogen purging resulted in only partial destruction of the oxygenated species. Even prolonged nitrogen flow through the system did not destroy all of the brown (oxygenated) species. However, there was a reduction in the concentration of the brown species as determined by ultraviolet spectra in the 360–450-mμ region. The amount of oxygenated species destroyed by purging with nitrogen can be regenerated by adding oxygen to the system.

At pH 9, on the other hand, there was essentially no change in the absorption spectra of the oxygenated species under continual nitrogen flow. Even excess ethylenediaminetetraacetic acid did not destroy the oxygenated species at pH 9, in agreement with a previous observation on this system.[7]

Both at the pH range of the acid buffer region of curve O, Figure 1, and at pH 9, the oxygenated species are destroyed by the addition of acid. The oxygenated species can then be regenerated by adding base. Molecular oxygen is released upon acidification, indicating a completely reversible system.

As is the case with the cobalt(II) peptide oxygen-carrying chelates,[12] there is an irreversible side reaction to a probably mononuclear chelate(III) complex. However, in the present case this reaction is unusually slow, taking weeks as compared to hours required in the peptide chelate systems. Bekaroglu and Fallab[13] have also suggested that the irreversible product is a cobalt(III) complex, and considerable attention has been given to the stable, inert products of the side reaction by Michailidis and Martin.[9]

Calculations. Calculation of the protonation constants of the ligand were carried out in the usual manner, the log values obtained being: K_1 9.68; K_2, 9.09; K_3, 6.58; and K_4, 3.28. The equilibrium constants for the Co(II)–trien chelates formed under oxygen and nitrogen atmospheres were calculated with the aid of an IBM 360-67 computer with programs written by one of us (R. N.). The formation constants obtained for the Co(II)–trien complex was log $K^M_{ME} = 10.4 \pm$ 0.1, and for the formation of the μ-hydroxy, μ-oxygen complex, log $K^{M,L,O_2}_{M_2L_2O_2OH,H^+} = 25.2 \pm 0.2$. Calcula-
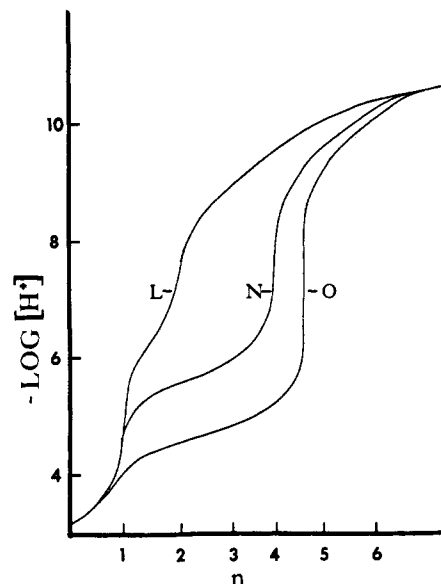

Figure 1. Potentiometric titrations of (L) trien, (N) 1:1 trien to Co(II) solution under a nitrogen atmosphere, (O) 1:1 solution under an oxygen atmosphere.

tions showed that in the buffer region where the oxygenated species is forming, there is essentially no hydrolysis of the Co(II)–trien chelate, ML^{2+}, formed in the absence of oxygen.

Discussion

Metal Chelate Stabilities in the Absence of O_2. The values obtained for the protonation constants of trien and of the formation constant for CoL^{2+} are similar to the literature values reported by Pecsok and coworkers.[14] These equilibrium data and the species involved are well known and need not be discussed further here.

The potentiometric data obtained on the oxygen complex provide information not previously reported by other workers. The stoichiometry under equilibrium conditions demonstrate the formation of the hydroxo binuclear complex as the reversible oxygen carrier in this pH range (5–9). The potentiometric data also yield the stability constant of the oxygen complex, the first one to be reported for this system.

The unusually low pH at which the oxygen complex forms under equilibrium conditions is a striking and significant feature of the 1:1 titration curve presented in Figure 1. The pH of the buffer region (curve O) is far below that of the cobalt(II)–trien curve (curve N), indicating that we are not dealing here with a simple cobalt(II) complex. The coordination of molecular oxygen to such a complex could not increase the stability in the manner indicated. Therefore it seems here that we are dealing with a labile Co(III) complex. The observed titration curve O and the corresponding stability constant calculated for the oxygen complex is reasonable if the complex contains binegative O_2^{2-} coordinated to Co(III). Thus it would be impossible to explain why the addition of a neutral coordinated oxygen would *increase* the affinity of the trien ligand for Co(II) to the extent that results in the dramatic lowering of the buffer region (from L to O) in Figure 1. This

(12) C. Tanford, D. C. Kirk, Jr., and M. K. Chantooni, Jr., *J. Amer. Chem. Soc.*, **76**, 5325 (1954).
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(14) R. L. Pecsok, R. A. Garver, and L. D. Shields, *Inorg. Chem.*, **4**, 477 (1965); G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 974 (1950).

effect is understandable, however, if the oxygen is present as O_2^{2-} and the cobalt is formally in the 3+ state.

The additional 0.5 mol of base needed for the titration under oxygen indicates hydrolysis of the metal ion in the chelate compound and the possible formation of a μ-hydroxo bridge. The fact that such hydroxo complex formation (hydrolysis of coordinated water) occurs is further indication of the increase in valence and binding power of the metal ion that occurs on oxygenation. The pK for hydrolysis of the 1:1 Co^{2+}–trien complex has been reported[7] as 11.2. If the oxygen complex contained Co^{2+}, its pK would be expected to be slightly to somewhat higher than 11.2, because of the more complete coordination of the metal ion in the oxygenated complex.

The structure of the oxygenated complex indicated by I is in general agreement with the formulas suggested
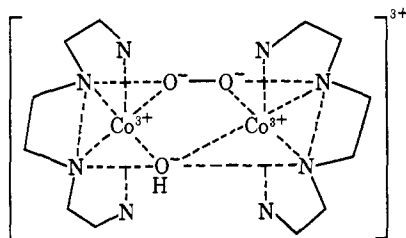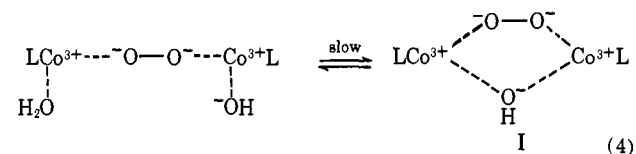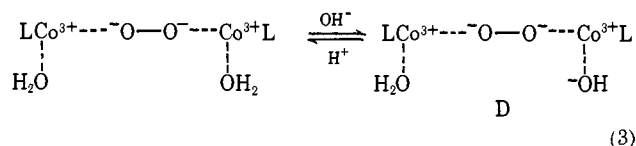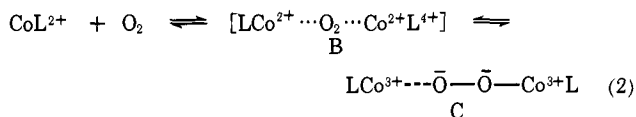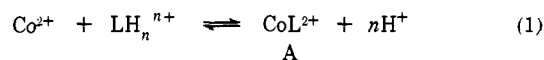

I, bistriethylenetetramine-μ-peroxo-μ-hydroxo-dicobalt(III) ion
(bistriethylenetetramine-μ-oxygen-μ-hydroxo-dicobalt(II) ion)

by other workers.[6,7,9] It differs from that suggested by Fallab,[6] who indicated the bound oxygen as a coordinated oxygen molecule with the O–O axis at right angles to the Co–Co axis. It differs from the stucture illustrated by Miller and Wilkens in actually designating a formal 3+ charge for the metal ions and a 2– charge for the oxygen moiety, although the existence of such a charge distribution was certainly strongly implied and discussed. While Michailidis and Martin[9] did not study the Co(II)–trien–O_2 system, they showed the existence of a similar formula for the oxygenated bisethylenediaminecobalt(II) complex. On the other hand, they stated that the second hydroxo bridge forms only when bidentate ligands are coordinated to cobalt, and in this respect would probably not have predicted a hydroxo bridge for the trien case.

In order that the interpretations of the observations conform to what is known of the range of reaction rates and solution stabilities of Co(II) and Co(III) species, the reaction scheme in eq 1–4 is proposed for the formation of oxygen complexes under equilibrium conditions in acid solution

Combination of the ligand with the Co(II) to give the normal complex A would be relatively fast and quite complete at pH values near 4.7, at which the reversibility of the system is established, as indicated above. It is known that there is no hydrolysis of the Co(II)–trien complex in the vicinity of pH 4.7 or even higher, so that the concentration of hydrolyzed (hydroxo) forms of A would be absent from this system. In analogy to the ammonia complexes of Co(II), association of molecular oxygen with A would give an unstable intermediate B with weak metal–oxygen bonds, as indicated by dotted lines. Lack of stability of this complex is indicated by the titration curve O, which does not show a break before the hydrolysis step from

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

$$CoL^{2+} + O_2 \rightleftharpoons \underset{B}{[LCo^{2+}\cdots O_2\cdots Co^{2+}L^{4+}]} \rightleftharpoons$$

$$\underset{C}{LCo^{3+}\cdots \bar{O}-\bar{O}-Co^{3+}L} \qquad (2)$$

$$\underset{\substack{| \\ H_2O}}{LCo^{3+}\cdots{}^-O-O^-\cdots Co^{3+}L}_{\substack{| \\ OH_2}} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} \underset{\substack{| \\ H_2O}}{LCo^{3+}\cdots{}^-O-O^-\cdots Co^{3+}L}_{\substack{| \\ {}^-OH}}$$

$$D \qquad (3)$$

$$\underset{\substack{| \\ H_2O}}{LCo^{3+}\cdots{}^-O-O^-\cdots Co^{3+}L}_{\substack{| \\ {}^-OH}} \overset{slow}{\rightleftharpoons} \underset{I}{LCo^{3+}\overset{{}^-O-O^-}{\underset{\underset{H}{O^-}}{\diagup\diagdown}}Co^{3+}L} \qquad (4)$$

$n = 4.0$ to 4.5. Although Michailidis and Martin[9] ascribe considerable stability and significance to a low-spin form of B, based on consideration of ligand requirements of other Co(II) oxygen complexes, there is as yet no experimental evidence for the formation of B in appreciable quantities in any of these systems. Electron transfer from B to C takes place rapidly under equilibrium conditions, as explained above. Deprotonation of C to D takes place rapidly, since it does not result in the breaking or forming of bonds in the coordination sphere of the metal. Therefore, the rapidly equilibrating complexes C and D are concluded to be the ones being formed from A in the buffer region of the titration curve. At pH 6 and above very little C is present.

The observation described above of a relatively slow equilibrium following an initial rapid equilibrium is in agreement with the conclusion that I is the final product of the reaction. The closing of a second bridge by elimination of a water molecule from the coordination sphere of the metal ion would be expected to be considerably slower than any of the reactions cited above leading to the formation of species A, B, C, and D. The fact that this reaction is as fast as observed (from 20 sec to $\sim$1 hr in the buffer region of the titration curve) may at first seem surprising. It would be expected to be much faster than most Co(III) substitution reactions, however, in view of the proximity of the hydroxide ion to the reaction site in the ring-closure reaction and the probable ease of interconversion of the robust Co(III) site and the labile Co(II) site, as follows.
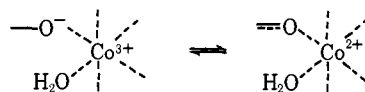
This question has also been considered by Miller and Wilkins,[7] who concluded that the proximity of the bridging hydroxide ion could explain the unusually high substitution rate and cited an analogous Co(III)–ammine complex for which a similar high reaction rate was observed.

According to the mechanisms proposed above, the equilibrium system at low pH has three different oxygenated species, C, D, and I. Since purging with nitrogen produces only partial but rapid destruction of the oxygenated species in the buffer zone of the titration curve, it appears that there are at least two oxy-

genated species in solution, one readily reversible and one not readily reversible to molecular oxygen. Since the dibridged species is formed exclusively at high pH and the high-pH species is essentially irreversible to molecular oxygen, the μ-hydroxo-μ-peroxo species I is proposed as the species which resists deoxygenation in the buffer zone.

The formation of the μ-hydroxo bridge may be the reaction which "locks" in the oxygen and prevents reversibility. The addition of acid will destroy the chelate with the liberation of oxygen, indicating that the μ-hydroxo bridge must be destroyed before oxygen will be liberated. Formation of the second (hydroxo) bridge also explains the slow equilibrium and contributes to the increased stability of the oxygenated species. The difference between the rate of dissociation observed at high and low pH is ascribed to the considerably higher thermodynamic stabilities of the reaction product I and its oxygenated precursor(s) at high pH.

It has been pointed out by McGinnety, et al.,[15] that the closer the O-O distance in the complexed oxygen molecules is to that of molecular oxygen, the greater will be the probability that the oxygen complex will

(15) J. A. McGinnety, N. C. Payne and J. A. Ibers, *J. Amer. Chem. Soc.*, **91**, 6301 (1969).

be reversible to molecular oxygen. For short O-O distances, the oxygen molecule would be only weakly perturbed by the metal ion and would dissociate readily. For long O-O distances, the binding to the metal ion will be strong and the oxygen moiety will resemble a dinegative peroxide ligand. While this situation certainly obtains for solid oxygen complexes, where the equilibrium must be with gaseous oxygen and a less-coordinated metal complex, it is not a necessary condition for reactions in solution. Thus the formation of a structure such as that indicated by I, with a peroxo bridge and the cobalt formally in the 3+ state, does not preclude another state at an accessible level energetically, consisting of a cobalt(II) complex loosely coordinated to free molecular oxygen. The relative energies of these states would be determined primarily by the nature of the ligands bound to the metal ion in the free and oxygenated complexes. The mobility of the equilibrium between these two states would be determined by the energy barrier between these states, which would be determined to some extent by the ligands, but also by the solvent.

Further studies on other polyamine and peptide complexes of cobalt(II) are being undertaken in this laboratory.

An Electron Spin Resonance Study of the Structure of the Polynuclear Copper(II) Chelates of Tetrakis(aminomethyl)methane[1]

T. D. Smith and A. E. Martell

Contribution from the Department of Chemistry, Texas A & M University, College Station, Texas 77843. Received August 6, 1971

Abstract: Electron spin resonance measurements have been made on equivolume water–glycol solutions of the copper(II) chelates of the spiroamine tetrakis(aminomethyl)methane over a wide range of pH and for various mole ratios of metal ion to ligand. When the metal ion to ligand mole ratio is 2:1, the signal at room temperature is almost isotropic at pH 6.0 with little loss of intensity compared to signals observed at lower pH values. This result is notable as the first observed room-temperature spectrum of a binuclear Cu(II) chelate. At 77°K and with increasing pH, the signal becomes less intense and is replaced by a broader signal. At high concentrations of metal ion, a $\Delta M = 2$ signal is observed at low field, demonstrating the presence of the binuclear species. The broad signal centered at about 3000 G together with the low-field signal are interpreted in terms of dipole–dipole coupling of the copper(II) ions in the polynuclear chelate. Solution of a spin Hamiltonian which includes the dipole–dipole interaction makes possible the calculation of the line shapes of the signals due to polynuclear species. The calculations have led to a value of 5.0 Å as the distance between the copper(II) dipoles, which is compatible with the internuclear distance between the copper(II) ions estimated from molecular models.

Recent investigations of the electron spin resonance (esr) spectra of copper(II) chelates has provided useful information on the formation of dimeric species in the liquid phase and frozen solution. These studies have been concerned with the copper(II) chelates of hydroxycarboxylic acids in aqueous and nonaqueous solutions,[2,3] peptides,[4] amino acids,[5] porphyrins,[6]

dialkyl dithiocarbamates,[7] and copper(II) natural products.[8] Frequently other physicochemical evidence has been available to confirm the formation of dimeric species in solution so that little doubt exists concerning the interpretation of the esr results in terms of dimer formation. The results of these studies also indicate

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(6) J. F. Boas, J. R. Pilbrow, and T. D. Smith, *ibid., A*, 721 (1969).

(7) J. R. Pilbrow, A. D. Toy, and T. D. Smith, *ibid., A*, 1029 (1969).

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