(10) L. F. Farnell, E. W. Randall, and E. Rosenberg, *Chem. Commun.*, 1078 (1971).
(11) M. H. Chisholm, H. C. Clark, L. E. Manzer, and J. B. Stothers, *J. Am. Chem. Soc.*, **94**, 5087 (1972).
(12) (a) D. G. Cooper, R. P. Hughes, and J. Powell, *J. Am. Chem. Soc.*, **94**, 9244 (1972); (b) D. G. Cooper and J. Powell, *Inorg. Chem.*, **15**, 1959 (1976); (c) J. Evans and J. R. Norton, *ibid.*, **13**, 3042 (1974).
(13) K. R. Aris, V. Aris, and J. M. Brown, *J. Organomet. Chem.*, **42**, C67 (1972).
(14) (a) C. D. M. Beverwijk and J. P. C. M. Van Dongen, *Tetrahedron Lett.*, 4291 (1972); (b) J. P. C. M. Van Dongen and C. D. M. Beverwijk, *J. Organomet. Chem.*, **51**, C36 (1973).
(15) D. G. Cooper, G. K. Hamer, J. Powell, and W. F. Reynolds, *J. Chem. Soc., Chem. Commun.*, 499 (1973).
(16) R. P. Hughes and J. Powell, *J. Organomet. Chem.*, **60**, 427 (1973).
(17) R. G. Solomon and J. K. Kochi, *J. Organomet. Chem.*, **64**, 135 (1974).
(18) L. Kruczynski, J. L. Martin, and J. Takats, *J. Organomet. Chem.*, **80**, C9 (1974).
(19) W. J. Cherwinski, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1405 (1974).
(20) C. A. Tolman, P. Z. Meakin, D. L. Linder, and J. P. Jesson, *J. Am. Chem. Soc.*, **96**, 2762 (1974).
(21) C. A. Tolman, A. D. English, and L. E. Manzer, *Inorg. Chem.*, **14**, 2353 (1975).
(22) M. H. Chisholm, H. C. Clark, L. E. Manzer, J. B. Stothers, and J. E. H. Ward, *J. Am. Chem. Soc.*, **97**, 721 (1975).
(23) T. Iwayanagi and Y. Saito, *Inorg. Nucl. Chem. Lett.*, **11**, 459 (1975).
(24) L. E. Manzer, *Inorg. Chem.*, **15**, 2354 (1976).
(25) P. W. Clark and A. J. Jones, *J. Organomet. Chem.*, **122**, C41 (1976).
(26) P. Powell and L. J. Russell, *J. Organomet. Chem.*, **129**, 415 (1977).
(27) D. G. Cooper and J. Powell, *Inorg. Chem.*, **16**, 142 (1977).
(28) R. P. Hughes, N. Krishnamachari, C. J. L. Lock, J. Powell, and G. Turner, *Inorg. Chem.*, **16**, 314 (1977).
(29) G. E. Hartwell and P. W. Clark, *Chem. Commun.*, 1115 (1970).
(30) P. W. Clark and G. E. Hartwell, *Inorg. Chem.*, **9**, 1948 (1970).
(31) P. W. Clark, J. L. S. Curtis, P. E. Garrou, and G. E. Hartwell, *Can. J. Chem.*, **52**, 1711 (1974).
(32) P. W. Clark and G. W. Hartwell, *J. Organomet. Chem.*, **96**, 451 (1975).
(33) R. R. Ryan, R. Schaeffer, P. Clark, and G. E. Hartwell, *Inorg. Chem.*, **14**, 3039 (1975).
(34) P. W. Clark and G. E. Hartwell, *J. Organomet. Chem.*, **102**, 387 (1975).
(35) P. W. Clark, *J. Organomet. Chem.*, **137**, 235 (1977).
(36) P. W. Clark and G. E. Hartwell, *J. Organomet. Chem.*, **139**, 385 (1977).
(37) M. Orrico Vischer, J. C. Huffman, and W. E. Streib, *Inorg. Chem.*, **13**, 792 (1974).
(38) G. R. Clark, P. W. Clark, A. J. Jones, and D. Russell, *J. Organomet. Chem.*, **166**, 109 (1979).
(39) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).
(40) G. Winkhaus and H. Singer, *Chem. Ber.*, **99**, 3610 (1966).
(41) A. van der Ent and A. L. Onderdelinden, *Inorg. Chim. Acta*, **7**, 203 (1973).
(42) G. R. Clark and P. W. Clark, *J. Organomet. Chem.*, in press.
(43) See, for example, A. J. Jones, J. A. Elix, and U. Engkaninan, *Aust. J. Chem.*, **29**, 1947 (1976).
(44) R. J. Restivo, G. Ferguson, T. L. Kelly, and C. V. Senoff, *J. Organomet. Chem.*, **90**, 101 (1975).
(45) B. E. Mann, *J. Chem. Soc., Perkin Trans. 2*, 30 (1972).
(46) J.-R. Llinas, E.-J. Vincent, and G. Peiffer, *Bull. Soc. Chim. Fr.*, 3209 (1973).
(47) P. S. Braterman, D. W. Milne, E. W. Randall, and E. Rosenberg, *J. Chem. Soc., Dalton Trans.*, 1027 (1973).
(48) E. D. Becker, "High Resolution N.M.R. Spectroscopy", Academic Press, New York, 1969, p 163.
(49) L. J. Todd and J. R. Wilkinson, *J. Organomet. Chem.*, **77**, 1 (1974).
(50) A. Bright, J. F. Malone, J. K. Nicholson, J. Powell, and B. L. Shaw, *Chem. Commun.*, 712 (1971).
(51) F. Glockling and G. C. Hill, *J. Chem. Soc. A*, 2137 (1971).
(52) R. N. Haszeldine, R. J. Lunt, and R. V. Parish, *J. Chem. Soc. A*, 3711 (1971).
(53) M. A. Bennett, R. N. Johnson, and I. B. Tomkins, *J. Organomet. Chem.*, **118**, 205 (1976).
(54) The averaged value of $\Delta\Delta\delta$(C) includes the values from $[RhCl(C_8H_{12})]_2$ vs. $[IrCl(C_8H_{12})]_2$ and $RhCl(C_2H_4)(PPh_3)_2$ vs. $IrCl(C_2H_4)[P(p\text{-tol})_3]_2$.
(55) M. A. Bennett, P. W. Clark, G. B. Robertson, and P. O. Whimp, *J. Chem. Soc., Chem. Commun.*, 1011 (1972).
(56) M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963).
(57) A. D. Buckingham and P. J. Stephens, *J. Chem. Soc.*, 2747, 4583 (1964).

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μ-Ligand-μ-peroxo-dicobalt(III) Cations

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Potentiometric, ultraviolet–visible, and nuclear magnetic resonance studies of the oxygenation of aqueous solutions of 5:2 and 3:1 molar ratios of ethylenediamine (en) to Co(II) indicate that the equilibrium product is tetrakis(ethylenediamine)-μ-(ethylenediamine)-μ-peroxo-dicobalt(III) (I). The log of the overall formation constant of I is 37.1 (M^{-6} atm^{-1}). Studies also indicate the oxygenation of 2:2:1 and 2:1:3 Co(II) to triethylenetetramine (trien) to ethylenediamine solutions results in the formation of $[Co_2trien(en)(O_2)^{4+}]$ (II) and of I and II, respectively.

Introduction

In biological systems iron(II) (e.g., hemoglobin and myoglobin) or copper(I) (hemocyanin) complexes serve as reversible oxygen carriers for transport and storage of oxygen. Simple low molecular weight metal chelates containing these ions seldom exhibit reversible oxygenation properties.[2] Cobalt(II), however, forms many simple complexes which react reversibly with oxygen to form 1:1 and 2:1 metal complex to oxygen adducts which have been widely studied as models for biological systems.[3] Although two reports[4,5] have invoked μ-ethylenediamine type linkages in μ-peroxo-dicobalt(III) cations, the evidence offered for their existence was not convincing. A third report,[6] however, on the isolation of a salt of the tetrakis(ethylenediamine)-μ-peroxo-μ-(ethylenediamine)-dicobalt(III) cation was more encouraging. We now report potentiometric, ultraviolet–visible, and nuclear magnetic resonance studies of the formation of μ-ethylenediamine bridges in addition to a μ-peroxo bridge in oxygenated Co(II) solutions containing ethylenediamine, diethylenetriamine, and triethylenetetramine. Before designing ligands to hold two Co(II) centers that are favorably disposed for interaction, i.e., to bind 1 mol of O_2, it was necessary to examine the ability of μ-peroxo-dicobalt(III) cations to form μ-ligand bridges.

Experimental Section

Reagents. The hydrochloride salts of ethylenediamine (en), 3-azapentylene-1,5-diamine (diethylenetriamine, dien), and 3,6-diazaoctylene-1,8-diamine (triethylenetetramine, trien) were prepared in the usual manner.[7] Ethanolic water solutions of the ligands were cooled and stirred in a salt–ice bath. Six molar hydrochloric acid was added slowly to the solutions to prevent sudden increases in the temperatures of the solutions. Crystals of the dihydrochloride salt of ethylenediamine and the trihydrochloride of diethylenetriamine precipitated out of solution slowly. Second and third crops of the salts were obtained by successive additions of 95% ethanol. The polyamine salts were recrystallized from water–ethanol solutions three times and then dried.

The triethylenetetramine solution was cooled to 1 °C. The 6 M hydrochloric acid was added very slowly in order to keep the temperature of the solution below 10 °C. This was done to take advantage of the low solubility of the hydrochloride salt of β,β',β''-triaminotriethylamine (tren), a major contaminant of triethylenetetramine.

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Table I. Stability Constants for the Formation of $[Co_2(en)_5(O_2)^{4+}]$

5:2 en:Co(II)			3:1 en:Co(II)		
$[M^{2+}]$, M	[en], M	log (K_{O_2} (M^{-6} atm^{-1}))	$[M^{2+}]$, M	[en], M	log (K_{O_2} (M^{-6} atm^{-1}))
0.006	0.015	37.07 ± 0.12	0.005	0.015	36.96 ± 0.09
0.012	0.030	37.14 ± 0.09	0.010	0.030	37.05 ± 0.10
0.018	0.045	37.05 ± 0.08	0.015	0.045	37.13 ± 0.07

After the hydrochloride salt of tren was removed, the solution was concentrated, and the hydrochloride salt of triethylenetetramine began to precipitate. The tetrahydrochloride salt was then recrystallized three times from water–ethanol solutions and dried.

Solutions of Co(II) and the HCl salts of the polyalkylenepolyamines were standardized via ion-exchange techniques. Aliquots of the metal or hydrochloride salt solutions were passed through Dowex 50W-X8 strongly acidic cation-exchange resin, and the effluent solutions were titrated with standardized NaOH.

Potentiometric Measurements. A Corning 12 Research Model pH meter fitted with a Corning semimicro combination pH electrode or a Corning Digital 112 Research Model pH meter fitted with a Fisher semimicro pH combination electrode was used to determine hydrogen ion concentrations in all potentiometric titrations. The combination electrodes were calibrated in terms of $-\log [H^+]$, according to the procedure of Rajan and Martell,[8] by using HCl and NaOH solutions of known concentrations.

Formation constants were determined from potentiometric data obtained by the bottle method.[9] Appropriate molar ratios of L·*x*HCl to Co(II) and enough 1.0 M KNO_3 to maintain an ionic strength of 0.10 M were added to 2-oz polyethylene bottles. Various amounts of base were added to the bottles while under a constant flow of O_2. The bottles were shaken and O_2 flow was continued for 1 min. The bottles were then sealed with Parafilm M (Marathon Products, Neenah, Wis.) and kept in a water bath at 25 °C for 3–6 h, to ensure that equilibrium had been reached.

Ultraviolet–Visible Spectra. UV–visible spectra of L·*x*HCl–Co(II) solutions were obtained with a Cary 14 spectrophotometer using a matched set of 1-cm quartz cells. The spectra at various pH values were recorded from samples equilibrated in bottles under an oxygen atmosphere (see Potentiometric Measurements).

Nuclear Magnetic Resonance Studies. Proton NMR spectra of aqueous solutions of L·HCl and appropriate ratios of L·*x*HCl to Co(II) (~0.25 M) at various *a* values (*a* = moles of base/mole of metal ion) were obtained on a Varian Associates T-60 spectrometer using 2,2-dimethyl-2-silapentane-5-sulfonate (0.0 ppm to Me_4Si) as an internal standard. Experiments varying the spinning rate (rps) were performed to establish which peaks were sidebands of the HDO resonance (4.8 ppm to Me_4Si). The ^{13}C spectra were recorded on a Varian CFT/20 spectrometer.

Calculations. Formation constants were calculated directly, if possible, by using Bjerrum's method.[10] All constants, however, were also calculated by using a modified form of a least-squares program developed by Sayce.[11] A successful solution to the titration data was considered to be one in which Sayce's[11] "standard deviation in titre", i.e., the theoretical amount of base added compared to the experimental value, was less than 0.015 mL, the accuracy of reading a buret. The experimental error values following the constants are standard deviations in log *K* values as defined by Sayce[11] and not "standard deviations in titre".

Results and Discussion

$Co_2(en)_5(O_2)^{4+}$ Formation. Potentiometric Data. The titration curves for solutions of en·2HCl, 3:1 en·2HCl–Co(II) under both nitrogen (N) and oxygen (O) atmospheres, and 5:2 en·2HCl–Co(II) (A) are shown in Figure 1. The titration curves for en·2HCl and 3:1 en·2HCl–Co(II) were computer generated by using literature values.[12] The 5:2 en·2HCl–Co(II) curve consists of a long buffer zone terminated by an inflection at *a* = 5.0 mol of base/mol of Co(II). The stability constant for the formation of $[Co_2(en)_5(O_2)^{4+}]$ was calculated by Bjerrum's method[10] (eq 1), by use of data from only

$$2Co^{2+} + 5en + O_2 \rightleftharpoons [Co_2(en)_5(O_2)^{4+}] \qquad (1)$$

20–80% of the buffer zone. The constants (Table I) were determined at three different metal ion concentrations to ensure that dimer and not polymer formation was occurring.

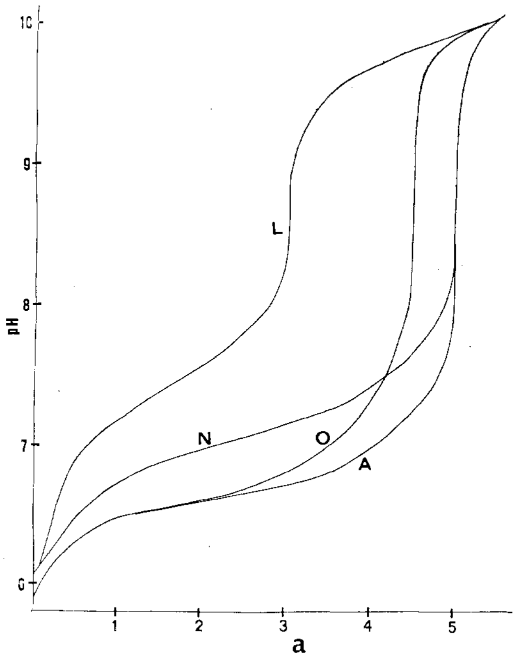


Figure 1. Potentiometric equilibrium curves for 5:2 (A) and 3:1 (O) molar ratios of en·2HCl to Co(II) under an oxygen atmosphere. The free ligand (L) and the 3:1 en·2HCl to Co(II) (N) molar ratio (nitrogen atmosphere) curves are computer drawn on the basis of values in ref 14. Data were obtained at μ = 0.10 (KNO_3), 25 °C, and a ligand concentration of 0.045 M; *a* is moles of base added per mole of Co(II).

The 3:1 en·2HCl–Co(II) system under an oxygen atmosphere consisted of a long buffer zone terminated by a break at *a* = 5.0, corresponding to the titration of 5 protons/Co(II), followed by another buffer zone ending at *a* = 5.5 and a third one terminating at *a* = 6.0. The latter two buffer zones each correspond to the titration of 0.5 proton/Co(II). In the lowest pH buffer region the formation of $[Co_2(en)_5(O_2)^{4+}]$ was presumed to occur, and the formation constants determined by Bjerrum's method[10] at three different metal ion concentrations are listed in Table I. In the latter two buffer regions, uncomplexed en·2HCl was assumed present, and the values obtained for the protonation constants were $K_1 = 10^{9.98\pm0.04}$ M^{-1} and $K_2 = 10^{7.27\pm0.03}$ M^{-1}, in reasonable agreement with literature values ($K_1 = 10^{9.89}$ M^{-1} and $K_2 = 10^{7.08}$ M^{-1} [12]). The potentiometric data indicate that the same oxygen adduct forms in both the 5:2 and 3:1 en·2HCl–Co(II) systems. The observed stoichiometry under equilibrium conditions demonstrates the formation of a μ-ligand binuclear complex as the reversible oxygen carrier in the pH range 6–10. The calculated stability constant, $K^{Co^{2+},en,O_2}_{Co_2(en)_5(O_2)^{4+}} = 10^{37.1}$ M^{-6} atm^{-1}, is similar to that of the bis(tetraethylenepentamine)-μ-peroxo-dicobalt(III) cation,[13] $K^{Co,TEP,O_2}_{Co_2(TEP)_2(O_2)^{4+}} = 10^{38.7}$ M^{-3} atm^{-1}. Since the stability constants of oxygen adducts of (polyalkylenepolyamine)cobalt(II) complexes have been shown[13] to be greatly dependent upon the number of aliphatic amine donor groups bound to Co, the similarity of stability constants for the formation of $[Co_2(en)_5(O_2)^{4+}]$ and $[Co_2(TEP)_2(O_2)^{4+}]$ suggests that there are five nitrogen donors per Co in the $[Co_2(en)_5(O_2)^{4+}]$ cation.

UV–Visible Spectra. The UV–visible spectra for the 5:2 and 3:1 en·2HCl–Co(II) systems were recorded at various *a* values. In the 5:2 system the charge-transfer band, usually found in the 350–360-nm region and characteristic of μ-peroxo-dicobalt(III) complexes,[13,14] increases in absorbance (~358 nm) until a maximum is reached at *a* = 5.0. In the corresponding 3:1 system a maximum absorbance is reached

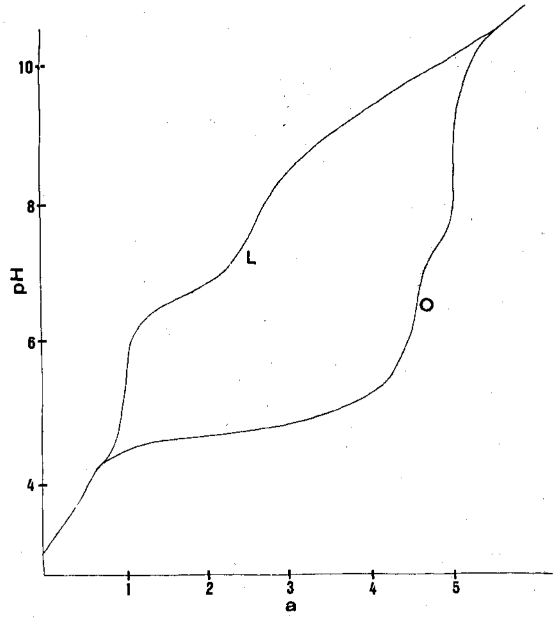


Figure 2. Potentiometric formation curve for 2:2:1 molar ratios of Co(II) to trien·4HCl to en·2HCl at μ = 0.1 M (KNO_3) and 25 °C under an O_2 atmosphere (O) and computer-drawn curve for a 2:1 trien·4HCl to en·2HCl solution (L).[14,19]

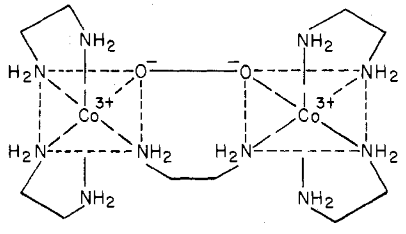
at a = 5.0 (λ_{max} ~357 nm). Further additions of base cause no change in λ_{max} and ϵ_{max} of the band at 358 nm, indicating that formation of the oxygenated species is complete at a = 5.0. However, after a = 5.0, a change in absorbency did occur in the 285-nm region, probably due to absorption by unprotonated en. The λ_{max} and ϵ_{max} values of $[Co_2(en)_5(O_2)^{4+}]$ calculated from data for the 5:2 system are 358 nm and 4100 M^{-1} cm^{-1}, respectively, while those calculated from the 3:1 system are 357 nm and 4100 M^{-1} cm^{-1}, respectively.

The UV–visible spectral data supply further data which indicate the formation of a μ-ligand bridge in addition to a μ-peroxo bridge in both 5:2 and 3:1 en·2HCl–Co(II) systems. Singly bridged μ-peroxo-dicobalt(III) species generally absorb at somewhat higher energies[13,15,16] and show two bands, a high-energy band at ~300–320 nm and a lower energy shoulder at ~380 nm, while spectra of the dibridged μ-peroxo-μ-hydroxo-dicobalt(III) cations usually exhibit a single M → L charge-transfer absorption maximum at ~350–360 nm.[13,15,16]

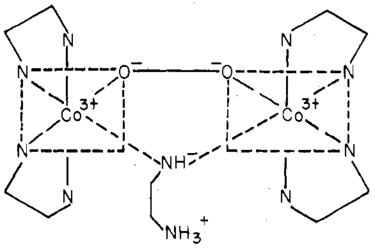
NMR Spectra. Proton NMR spectra of enD_2^{2+} and 5:2 and 3:1 en·2DCl–Co(II) solutions were obtained at various a values (not shown). The proton NMR spectra of enD_2^{2+} and en consist of sharp singlets assigned to absorption by the ethylenic protons at 3.4 and 2.6 ppm, respectively. Addition of Co(II) to a solution of enD_2^{2+} results only in displacement and broadening of the HDO peak and some broadening of the ethylenic proton resonance. Addition of a small amount of base to the Co–en·2HCl solution results in the broadening of the ethylenic proton peak of enD_2^{2+}. Further additions of base result in a disappearance of the peak at 3.4 ppm and the appearance of a broad singlet at 2.6 ppm. The new peak is assigned to the ethylenic protons of en in $[Co_2(en)_5(O_2)^{4+}]$. With the appearance of the 2.6-ppm peak, the water peak concurrently sharpened and moved upfield as higher a values were attained. At a = 5.0, in the 5:2 en·2DCl–Co(II) system, only one broad peak at 2.6 ppm is observed and no peak is observed at 3.4 ppm, the resonance absorption of protonated en, indicating that all the en is coordinated to Co. The position of the HDO resonance at 4.8 ppm indicates the lack of a paramagnetic species in solution. At a = 5.0 in the 3:1 system, two peaks are observed: at 2.6 and 3.4 ppm (sharp) assigned to absorption by the ethylenic protons of en in $[Co_2(en)_5(O_2)^{4+}]$ and uncoordinated protonated en, respectively. The HDO peak is sharp and is located at 4.8 ppm, again indicating the absence of a paramagnetic Co(II) species.

Contrary to a previous report a sharp singlet at ~2.2 ppm was never observed in any of the systems studied. This peak had been assigned as being indicative of the μ-en bridge in the tetrakis(ethylenediamine)-μ-peroxo-μ-(ethylenediamine)-dicobalt(III) cation.[6] For this reason we obtained a ^{13}C NMR spectrum of $[Co_2(en)_5(O_2)^{4+}]$ and observed two peaks at 39.98 and 39.28 ppm, which suggests that the bridging carbon atoms are not magnetically very different from the nonbridging ones.

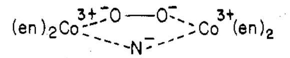
The most probable structure for the $[Co_2(en)_5(O_2)^{4+}]$ cation is I. Another intriguing possibility that has been proposed[17] is II. While both proposed structures are in agreement with potentiometric, acid–base stoichiometric, and UV–visible data, I is preferred on the basis of ^{13}C NMR data. All the carbon atoms are in similar chemical environments in I which is in agreement with the two observed ^{13}C NMR absorptions. The carbon α to the protonated amine group in II would be expected to absorb at a frequency substantially different from that of a carbon α to a deprotonated amine group. However, dibridged species similar to II have been shown[18] to exist for the oxygenated cobalt amine complexes



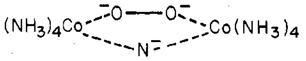
I



II

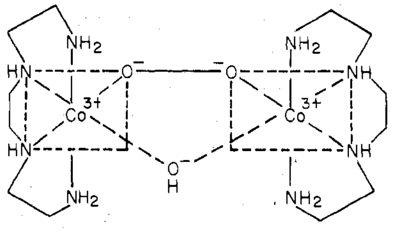


$$(en)_2Co^{3+}\overset{-}{O}{-}\overset{-}{O}Co^{3+}(en)_2 \quad \underset{H_2}{N^-}$$



$$(NH_3)_4Co\overset{-}{O}{-}\overset{-}{O}Co(NH_3)_4 \quad \underset{H_2}{N^-}$$

The 2:2:1 Co(II)–trien–en System. The low pH of complex formation of the first buffer zone (Figure 2) and the inflection at a = 4.5 are strikingly similar to that of the well-studied bis(triethylenetetramine)-μ-peroxo-μ-hydroxo-dicobalt(II) cation (III). Calculations assuming that only III was formed in the low-pH buffer region of Figure 2 yielded a constant of $10^{24.9\pm0.1}$, in good agreement with the literature value[19] of $10^{25.2\pm0.2}$.



III

Further evidence supporting the formation of III in the low-pH buffer region was supplied by the NMR studies. Fully deuterated en and trien exhibited a singlet (3.4 ppm) and a

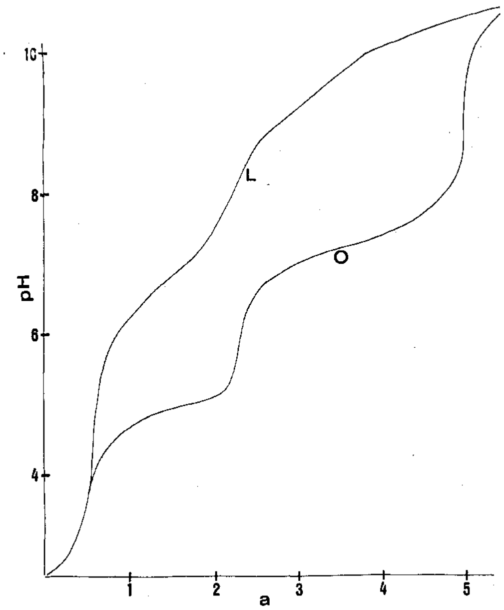


Figure 3. Potentiometric formation curve for 2:1:3 molar ratios of Co(II) to trien·4HCl to en·2HCl at μ = 0.1 M (KNO_3) and 25 °C under an O_2 atmosphere (O) and computer-drawn curve for a 1:3 trien·4HCl to en·2HCl solution (L).[14,19]

multiplet (centered at 3.5 ppm), respectively. At *a* = 4.5, two peaks were observed: a sharp singlet at 3.4 ppm and a broad, ill-resolved peak at ~2.8 ppm, assigned to the ethylenic protons of enD_2^{2+} and $[Co_2(trien)_2(O_2)(OH)^{3+}]$, respectively. Unfortunately, the nuclear spin of Co apparently couples with that of the ethylenic protons of trien to yield a very broad peak. However, the presence of the sharp singlet at 3.4 ppm indicates that no en has reacted, which complements the potentiometric data.

The reaction in the second buffer zone (Figure 2) corresponds to eq 2; i.e., *a* = 0.5 (one proton per two Co centers).

$$[Co_2(trien)_2(OH)(O_2)^{3+}] + enH_2^{2+} \rightleftharpoons [Co_2(trien)_2(en)(O_2)^{4+}] + H_3O^+ \quad (2)$$

The overall formation constant, $K^{Co^{2+},trien,en}_{Co_2(trien)_2(en)(O_2)^{4+}}$, was determined to be $10^{34.2\pm0.2}$, which is similar to that of $[Co(TEP)_2(O_2)^{4+}]$ ($10^{38.7}$[14]) and $[Co_2(en)_5(O_2)^{4+}]$ ($10^{37.1}$), suggesting five aliphatic nitrogen donors per Co. The NMR spectrum at *a* = 5.0 exhibited one broad resonance centered at 2.8 ppm; no sharp bands were observed, indicating the absence of enD_2^{2+} and enD^+ and that the en is coordinated to Co. Unfortunately, we were not able to obtain sufficient resolution to differentiate Co-bound en from trien.

The 2:1:3 Co(II)–trien–en System. The potentiometric formation curve of the 2:1:3 Co(II)–trien·4HCl–en·2HCl system exhibits two buffer regions (Figure 3) terminated by inflections at *a* = 2.25 and 5.0. The low pH value at which complex formation occurs in the first buffer region and the inflection at *a* = 2.25 suggest that III is formed in this region. The titration of the four trien protons (4 protons/trien or 2 protons/Co(II)) and the formation of a μ-hydroxo bridge (0.5 proton/trien or 0.25 proton/Co) yield an inflection at *a* = 2.25. NMR data at *a* = 2.25 showed a broad peak at ~2.8 ppm and a sharp singlet at 3.4 ppm, assigned to the ethylenic protons of bound trien and uncoordinated enD_2^{2+}, respectively. The formation constant of $[Co_2(trien)_2(O_2)(OH)^{3+}]$ was calculated to be $10^{25.1\pm0.1}$ (lit.[19] $10^{25.2\pm0.2}$).

Equations 1 and 2 were found to best fit the potentiometric data of the second buffer region, indicating the formation of both $[Co_2(en)_5(O_2)^{4+}]$ and $[Co_2(trien)_2(en)(O_2)^{4+}]$, with overall formation constants of $10^{37.1\pm0.1}$ M^{-6} atm^{-1} ($10^{37.1}$ from the 5:2 en–Co(II) system) and $10^{34.1}$ M^{-4} atm^{-1} ($10^{34.2}$ from the 2:2:1 Co(II)–trien–en system), respectively. Visible spectral data indicated continued formation of μ-peroxo-dicobalt(II) species throughout the second buffer region as evidenced by a monotonic increase in ϵ_{max} of the ~360-nm band. NMR data at *a* = 5.0 exhibited only a broad peak centered at ~2.8 ppm; no sharp bands attributable to enD_2^{2+} or enD^+ were observed, indicating that all the en in solution was complexed to Co.

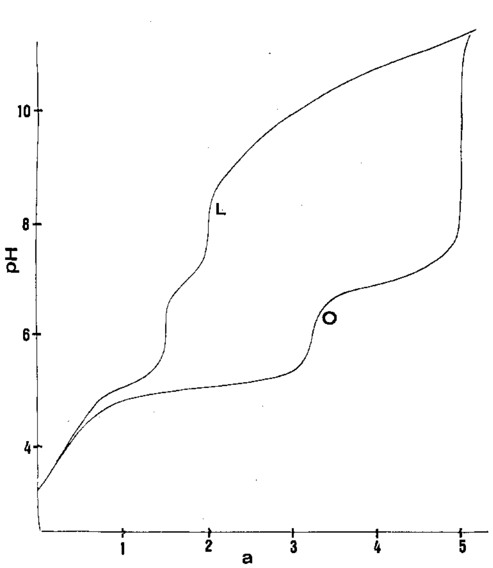


Figure 4. Potentiometric formation curve for 2:1:2 molar ratios of Co(III) to trien·4HCl to dien·3HCl at μ = 0.1 M (KNO_3) at 25 °C under an O_2 atmosphere (O) and computer-drawn curve for a 1:2 trien·4HCl to dien·3HCl solution (L).[14,19]

The 2:1:3 Co(II)–trien–dien System. The potentiometric formation curve for the 2:1:3 Co(II)–trien·4HCl–dien·3HCl system consisted of two buffer zones terminated by inflections at *a* = 3.25 and 5.0 (Figure 4). The low pH value of complex formation and the inflection point at *a* = 3.25 once again indicate the formation of $Co_2(trien)_2(O_2)(OH)^{3+}$. The titration of the protons of trien (2 protons/Co) and μ-OH formation (0.5 proton/trien or 0.25 proton/Co) provide for a total of 2.25 protons/Co. However, the deprotonation of $dienH_3^{3+}$ to $dienH_2^{2+}$ (eq 3) also occurs in this pH region (1 proton/dien,

$$dienH_2^{2+} + H^+ \rightleftharpoons dienH_3^{3+} \quad (3)$$

1 proton/Co) to give the observed inflection at *a* = 3.25. The values calculated on the basis of the formation of III and eq 3 are $10^{25.0\pm0.1}$ (lit.[19] $10^{25.2}$) and $10^{4.31\pm0.03}$ (lit.[14] $10^{4.28}$), respectively. The NMR data at *a* = 3.25 were not particularly helpful since the multiplet at ~3.2 ppm could not be unequivocally assigned to partially protonated dien (partially protonated trien would absorb in the same region).

At *a* = 3.25, the solution appears to contain 2 mol of $dienH_2^{2+}$/mol of unreacted Co^{2+} and III. The formation of $[Co_2(dien)_4(O_2)^{4+}]$ appears likely; however, computer analysis of the potentiometric data yielded no satisfactory constants. Attempts to fit the data to $[Co_2(dien)_3(O_2)^{4+}]$ also failed.

The potentiometric data of the higher pH buffer region are in apparent agreement with reports of the instability of $[Co_2(dien)_4(O_2)^{4+}]$ which reportedly undergoes further reaction to yield $[Co_2(dien)_3(O_2)^{4+}]$ as well as Co(III) products.[4,18] This would explain our inability to find a system of species which would converge in the various computer programs used.

Stabilities of μ-en–μ-O_2 Cations. The formation constants of $[Co_2(en)_5(O_2)^{4+}]$ and $[Co_2(trien)_2(en)(O_2)^{4+}]$ are 1.6 and 4.0 log units smaller than that of $[Co_2(TEP)_2(O_2)^{4+}]$ (no μ-ligand bridge). Since Nakon and Martell[14] have shown that the formation constants of μ-peroxo-dicobalt(III) species are dependent upon the number of aliphatic nitrogen donors, the above indicates that the presence of μ-ligand bridges results in less stable O_2 adducts. This postulate is further supported in comparison with oxygenation constants of μ-peroxo-μ-hydroxo-dicobalt(III) cations. McLendon and Martell[20] have shown that there exists a good direct correlation between the sum of the ligand protonation constants and the oxygenation constant (eq 4). The values for $[Co_2(en)_5(O_2)^{4+}]$ and $[Co_2(trien)_2(en)(O_2)^{4+}]$ fall below the line for that of the μ-peroxo-μ-hydroxo-dicobalt(III) cations, indicating that the presence of μ-en bridges results in a somewhat less stable O_2 adduct.

$$2CoL_x^{y+} + O_2 \rightleftharpoons [Co_2L_{2x}(O_2)^{2y+}] \qquad (4)$$

Finally, the μ-ligand-μ-peroxo-dicobalt(III) complexes are reversible (release O_2) upon the addition of acid both in the acid buffer region and at high pH. Dilute solutions of the μ-en-bridged cations were stable for at least weeks to further reaction to yield mononuclear Co(III) species which are similar to most other (polyalkylenepolyamine)-μ-peroxo-dicobalt(III) cations.[14] However, concentrated solutions of the cations (required for NMR studies) seemed to be less stable, suggesting that further reaction to mononuclear Co(III) cations may occur via an intermolecular pathway or that perhaps the presence of small amounts of unoxygenated Co(II) cations can lead to accelerated rates.

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References and Notes

(1) (a) Presented in part at the 170th National Meeting of the American Chemical Society, Chicago, Ill., 1974. (b) To whom correspondence should be addressed at West Virginia University.
(2) R. D. Gray, *J. Am. Chem. Soc.*, **91**, 56 (1969), and references cited therein.
(3) R. G. Wilkins, *Adv. Chem. Ser.*, **No. 100**, Chapter 6 (1971).
(4) J. Simplicio, Ph.D. Dissertation, State University of New York at Buffalo, 1969.
(5) O. Bekaroglu and S. Fallab, *Helv. Chim. Acta*, **46**, 2120 (1963); S. Fallab, *Chimia*, **21**, 538 (1967).
(6) S. W. Foong, J. D. Miller, and F. D. Oliver, *J. Chem. Soc. A*, 2847 (1969).
(7) D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals", Pergamon Press, New York, 1966.
(8) K. S. Rajan and A. E. Martell, *J. Inorg. Nucl. Chem.*, **26**, 789 (1964).
(9) H. Ackermann and G. Schwarzenbach, *Helv. Chim. Acta*, **32**, 1543 (1949).
(10) J. Bjerrum, "Metal Ammine Formation in Aqueous Solutions", P. Haase and Son, Copenhagen, 1957.
(11) I. G. Sayce, *Talanta*, **15**, 1397 (1968).
(12) L. G. Sillen and A. E. Martell, *Chem. Soc., Spec. Publ.*, **No. 17** (1964); **No. 25** (1971).
(13) G. McLendon, R. J. Motekaitis, and A. E. Martell, *Inorg. Chem.*, **14**, 1993 (1975).
(14) R. Nakon and A. E. Martell, *J. Inorg. Nucl. Chem.*, **34**, 1365 (1972).
(15) C. H. Yang and M. Grieb, *Inorg. Chem.*, **12**, 663 (1973).
(16) P. J. Morris and R. B. Martin, *J. Am. Chem. Soc.*, **92**, 1543 (1970).
(17) G. McLendon, R. J. Motekaitis, and A. E. Martell, personal communication.
(18) F. Miller, J. Simplicio, and R. G. Wilkins, *J. Am. Chem. Soc.*, **91**, 1962 (1969).
(19) R. Nakon and A. E. Martell, *J. Am. Chem. Soc.*, **94**, 3026 (1972).
(20) G. McLendon and A. E. Martell, *Coord. Chem. Rev.*, **19**, 1 (1976).

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Reactions of Coordinated Dinitrogen. 6.[1] Displacement of Coordinated Dinitrogen by Dihydrogen in Low-Valent Molybdenum Complexes

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Bis(dinitrogen) complexes of molybdenum, $Mo(N_2)_2L_2$, where L is a bidentate tertiary phosphine ligand react rapidly in solution with dihydrogen to form MoH_4L_2. Conformation of a tetrahydride rather than a dihydride comes from both ^1H and ^{31}P NMR spectral studies using the specially prepared highly soluble bidentate phosphine ligands $(tol)_2PCH_2CH_2P(tol)_2$, where tol is *m*-tolyl (dmtpe) or *p*-tolyl (dptpe).

Introduction

Early reactions of transition-metal complexes of dinitrogen with dihydrogen resulted in displacement of N_2 by H_2 (e.g., eq 1).[3] These reactions are often reversible. Dihydrogen was reported by Hidai et al. to react with $Mo(N_2)_2(dppe)_2$, **1**, where dppe is $Ph_2PCH_2CH_2PPh_2$, to form a dihydride, $MoH_2(dppe)_2$, **2**, in benzene solution over a 3-day period.[4] On the other hand, in toluene solution a binuclear hydride, $[\textit{trans}\text{-}MoH_2(dppe)]_2(\mu\text{-dppe})$, **3**, was reported to be formed. In benzene solution **3** was converted into **2**, while in toluene solution **2** was converted into **3**. It was stated that these compounds were insufficiently soluble in organic solvents to allow their molecular structure to be determined by NMR spectroscopy. Aresta and Sacco also reported the formation of $MoH_2(dppe)_2$ from the reaction of **1** with dihydrogen.[5] The ^1H NMR spectrum of **2** in C_6D_6 at 60 °C gave a 1:4:6:4:1 quintet centered at τ 13.64 ($J_{P-H} = 30$ Hz) showing four equivalent phosphorus atoms. No spectrum could be obtained below 60 °C because of the poor solubility of **2** in suitable solvents. The stereochemistry of **2** depended upon the solvents, trans being formed in benzene solution and cis in tetrahydrofuran (THF) solution. Compound **2** was also formed by the reduction of $MoCl_4(dppe)$ in benzene solution with sodium and under a dihydrogen atmosphere.[5] Previously, Turio et al. had reported the preparation of **2** by the reduction of molybdenum(III) acetylacetonate with triisobutylaluminum in benzene solution containing dppe.[6] The poor solubility of **2** again precluded NMR studies. In the meantime, Pennella reported the preparation of $MoH_4(dppe)_2$, **4**, by the reduction of $MoCl_4(dppe)$ with an ethanol solution of sodium borohydride containing added dppe.[7] Characterization of **4** relied upon a comparison of the ν(Mo–H) frequency with those of $MoH_4(PMePh_2)_4$ and $MoH_4(PEtPh_2)_4$. The latter two compounds had been characterized by ^1H NMR spectroscopy in which the integration agreed with a formulation of four rather than two hydridic hydrogen atoms per molecule. Once again the poor solubility of the dppe hydride prevented an NMR spectral study.

$$CoH(N_2)(PPh_3)_3 + H_2 \rightleftharpoons N_2 + CoH_3(PPh_3)_3 \qquad (1)$$

Meakin and co-workers reported the first room-temperature ^1H NMR spectrum of **4**, in chlorobenzene.[8] They observed

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