# Coordination of Oxygen by Cobalt(II) Complexes in Aqueous Solution. A Calorimetric Study[1]

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**Abstract:** The oxygenation of cobalt(II)–bis(histidinate), –bis(histamine), and –bis(ethylenediamine) complexes has been studied in aqueous solutions at 25.0°. Enthalpy changes have been determined calorimetrically and equilibrium data obtained by use of a polarographic oxygen analyzer. The reactions $2CoL_n(aq) + O_2(aq) \rightleftharpoons (CoL_n)_2 \cdot O_2(aq)$ are characterized by large negative enthalphy and entropy changes. For L = histidinate and ethylenediamine, $\Delta H = -30.1 \pm 1.3$ and $-29.4 \pm 0.6$ kcal $mol^{-1}$, $\Delta S = -70 \pm 5$ and $-49 \pm 4$ eu, respectively. These data are discussed in relation to the oxidation and coordination reactions involved.

In biological systems the reversible oxygen-carrying complexes responsible for transport and storage of oxygen are complex species of iron(II) (*e.g.*, hemoglobin and myoglobin) or copper(I) (hemocyanin) in which the metal ion and coordinated prosthetic group are embedded within a hydrophobic protein matrix.[2] In simple low molecular weight complexes, these ions seldom show reversible oxygenation properties.[3] However, the cobalt(II) ion forms many simple complexes which react reversibly with oxygen to form 1:1 or 2:1 complex oxygen adducts, and following the pioneering work of Calvin, *et al.*,[4] and Hearon, *et al.*,[5] these have been widely studied as model compounds for the biological systems.

Early studies established the formation of 2:1 adducts with cobalt(II) complexes containing (a) amino acids,[5-7] (b) dipeptides,[6,8] (c) polyamines and ammonia,[5,6,9-13] and (d) bis(salicylaldehyde)ethylenediamine and related ligands.[4,14,15] Oxygen affinity was observed for solids, *e.g.*, (d), and aqueous solutions, although for complexes with few polarizable donor atoms in the ligand a nonaqueous electron-donor solvent is required to enhance the electron-donor properties of the cobalt(II) Lewis base.[14,15] On the basis of magnetic susceptibility,[5] electronic absorption, CD spectra,[3] and proton affinity of the O–O bridge,[16] these complexes are generalized as essentially cobalt(III) species linked by a peroxide group, $Co^{III}L_n$–$(O_2{}^{2-})$–$Co^{III}L_n$. X-Ray studies[17,18] have shown the bridge to be nonlinear and nonplanar (*cf.* $H_2O_2$), but bond lengths are not fully consistent with a peroxy structure and the complexes have a greater lability toward decomposition with acid,[6,7,9] EDTA,[7,9,10] dithionite,[7] and temperature or pressure variation[10,19,20] than expected for a cobalt(III) species. The oxygen-carrying capacity of these complexes decreases with time as irreversible oxidation to mononuclear cobalt(III) complexes occurs. For some ligands this is very rapid (*e.g.*, diethylenetriamine, glycylglycinamide), while for others it is quite slow (*e.g.*, histamine, ethylenediamine).[5]

Recent studies have characterized 1:1 adducts with "coboglobin" and the dimethyl ester of cobalt(II) protoporphyrin IX,[21] Co(acacen)B[22] (acacen = bis(acetylacetonato)ethylenediimine, B = *N*,*N*-dimethylformamide, pyridine, etc), *N*,*N*′-ethylenebis(3-methoxysalicylidineiminato)cobalt(II),[14] and *N*,*N*′-iminodi-*n*-propylbis(salicylideneiminato)cobalt(II) in the solid state[4] and certain solvents,[22] dimethylglyoxime[23] and vitamin $B_{12r}$.[24] With the exception of coboglobin and vitamin $B_{12r}$, the adducts form only in nonaqueous solution and may be rapidly decomposed and oxidized by traces of water.[22,23] These compounds are paramagnetic, and esr studies suggest that 80–90% of the odd-electron density is transferred to the oxygen to give a cobalt(III) superoxo species with a bent Co–O–O link.[21,25] From kinetic studies, a 1:1 adduct has been postulated as a reactive intermediate in the formation of 2:1 adducts[7,9-11] and this has been confirmed by esr for cobalt(II)–polyamine systems.[26]

The object of this research has been to determine thermodynamic data for selected oxygenation reactions. Thermodynamic data have been determined for the reaction of $O_2(aq)$ with the cobalt(II)–bis(histidinato), –bis(ethylenediamine), and –bis(histamine) (log $K$ only) complexes in aqueous solution at 25°. Hitherto, the

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only published calorimetric data on such systems were concerned with salicylaldehydeethylenediiminecobalt(II) complexes in the solid state.[4]

## Experimental Section

Histidine and histamine dihydrochloride (Nutritional Biochemical Corp.) were used without further purification. Ethylenediammonium chloride was prepared from the free base (Fisher) and recrystallized from 20% aqueous 2-propanal. Stock cobalt chloride (Fisher, reagent grade) solutions were acidified and analyzed by precipitation of cobalt as $Co(pyridine)_4(NCS)_2$. Titrations were done in a jacketed cell maintained at 25.00 ± 0.05° and with no air space above the solution. Titrant was added from a Gilmont micrometer buret, and the partial pressure of dissolved oxygen was determined with a Beckman 39550 polarographic oxygen electrode and Beckman Fieldlab oxygen analyzer 100800 calibrated against air-saturated and oxygen-saturated water; measurement of $p_{O_2}$ was reproducible to *ca.* 2%. The calorimeter was similar to one described previously.[27]

## Results

For L = histidinate, the concentration quotient $K_{O_2}$ was determined from titration of 0.2927 *M* $CoCl_2$

$$2CoL_2 + O_2 \rightleftharpoons CoL_2 \cdot O_2 \cdot CoL_2 \qquad K_{O_2}, \Delta H_{O_2}$$

with histidine solution (200 ml, $[L^-] = 1.985 \times 10^{-2}$ *M*, $[HL] = 2.15 \times 10^{-3}$ *M*) containing dissolved oxygen ($[O_2]_{initial} = 2.6\text{–}6.4 \times 10^{-4}$ *M*). Under these conditions formation of bis(histidinato)cobalt(II) species from hexaquocobalt(II) is complete. A plot of log $[CoL_2]$ against log $[adduct]/[O_2]$ for several titrations had a slope of 0.5 (Figure 1), as required for a 2:1 cobalt:$O_2$ adduct; the intercept gave $^1/_2 \log K_{O_2} = 3.315 \pm 0.025$. Typical titration results are given in Table I.

Table I. Representative Data for the Titration of Cobalt(II) into Oxygenated Histidine Buffer Solution,[a] 25.0°

$$Co^{2+} + 2L^- \longrightarrow CoL_2$$

$$2CoL_2 + O_2(aq) \rightleftharpoons (CoL_2)_2O_2\ (K_{O_2})$$

| $10^3[cobalt]_{total}$, *M* | $10^3[O_2]$, *M*[b] | $10^{-6}K_{O_2}$, $M^{-2}$ [c] |
|---|---|---|
| 0.000 | 1.055 | |
| 0.519 | 0.90 | 4.05 |
| 0.742 | 0.82 | 4.05 |
| 1.037 | 0.705 | 4.38 |
| 1.334 | 0.60 | 4.28 |
| 1.628 | 0.495 | 4.34 |
| 1.923 | 0.39 | 4.69 |
| 2.220 | 0.31 | 4.36 |

[a] For solution composition, see Results section. [b] ±2%. [c] $K_{O_2} = [adduct]/[O_2][CoL_2]^2 = ([O_2]_{initial} - [O_2]_{eq})/([O_2]_{eq}([Co]_{total} - 2[adduct])^2)$.

For L = ethylenediamine, titrations of $CoCl_2$ solution into oxygenated ethylenediamine solution (*I* = 1 *M* KCl) confirmed that a 2:1 adduct is formed and the reaction goes to completion ($K_{O_2}$ large). The ethylenediamine solutions were buffered (initial concentrations, $[enH^+] = 9.90 \times 10^{-3}$ *M*, $[enH_2^{2+}] = 6.60 \times 10^{-3}$ *M*; pH 7.63) so that the pH varied between 7.63 and 7.15 during titrations. At lower pH the oxygenation reaction is slow because the concentration of the reactive species[9] $Co(en)_2(H_2O)_2^{2+}$ is small, while at high pH the reaction is complicated by the presence of $Co(en)_3^{2+}$, which leads to the formation of μ-dioxygen-μ-ethylenediamine-dicobalt(II) tetra(ethylenediamine).[16] (At pH 7.63 and total ligand $1.65 \times 10^{-2}$ *M*, $[CoL_3]/[CoL_2] = 7 \times 10^{-3}$.) Proton balance studies indicated that 0.5 mol of protons per mole of cobalt was liberated in excess of that expected from complex formation.

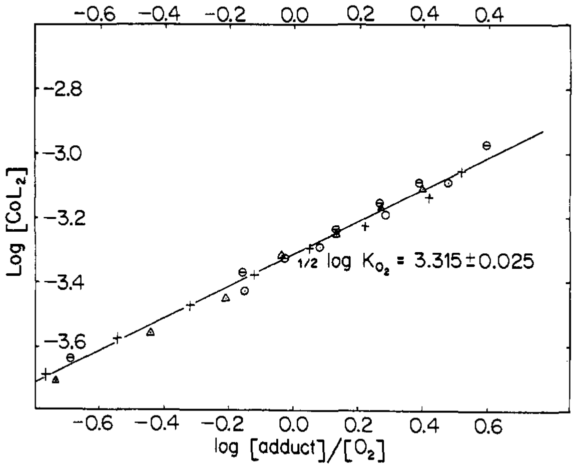
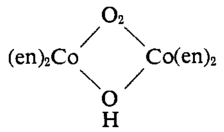


Figure 1. A plot of log $[adduct]/[O_2]$ against log $[CoL_2]$ for the reaction $2CoL_2(aq) + O_2(aq) \rightleftharpoons (CoL_2)_2O_2(aq)$ at 25.0°, L = histidinate. The indicated slope = 2.0 and the intercept yields $1/2 \log K_{O_2} = 3.315 \pm 0.025$.

$$Co^{2+} + enH^+, enH_2^{2+}\ (\bar{n} = 1.40) + O_2 \longrightarrow \text{adduct} + (1.40 + \alpha)H^+$$

Average α = 0.489, 0.480, and 0.507 for three titrations. Titrations involved addition of small concentrations of cobalt(II) (up to a total of $1.2 \times 10^{-3}$ *M*) into the above ethylenediamine buffer solution at pH 7.63 and back-titration to constant pH with standard alkali. The result suggests the formation of a μ-dioxygen-μ-hydroxy species



as observed by Michailidis and Martin[6] at pH 9–10.

For L = histamine, $K_{O_2}$ was too large to determine accurately using polarographic oxygen analysis. $CoCl_2$, 0.2972 *M*, was titrated into oxygenated histamine buffer solutions (total histamine $4.0 \times 10^{-2}$ *M*, pH 7.9 to 7.6). The [adduct] was determined spectrophotometrically ($\epsilon_{371\ nm} = 5420 \pm 50$) and $[O_2]$ was determined using the oxygen analyzer or maintained constant by bubbling air into the solution through a glass frit. $[CoL_2]$ was determined from mass-balance equations for total acid and cobalt(II) by use of the measured pH ($p[H^+] = pH - 0.113$ at *I* = 0.13 *M* using a univalent ion activity coefficient calculated from the extended Debye–Hückel equation proposed by Davies[28]) and the known ligand proton dissociation[29] and complex formation concentration quotients.[30] Data are given in Table II.

The enthalpy change $\Delta H(CoL_2)$ for the reaction

$$2\text{histidinate}\ (L^-) + Co^{2+} \rightleftharpoons CoL_2$$

was determined as −11.59 ± 0.15 kcal $mol^{-1}$ (average of four values with standard deviation) by titration of 0.2972 *M* $CoCl_2$ into the calorimeter containing 150 ml of the histidine solution prepared as described above.

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**Table II.** Data for the Titration of Cobalt(II) into Oxygenated Histamine Buffer[a] Solution, 25.0°

| $10^4$[cobalt]$_{total}$, $M$ | $10^8$[H$^+$], $M$ | $10^4$[adduct], $M$ | $10^4$[O$_2$], $M$ | $10^4$[L], $M$ | $10^5$[CoL$_2$], $M$ | $10^{-8}K_{O_2}$, $M^{-2}$ |
|---|---|---|---|---|---|---|
| 1.605 | 1.884 | 0.540 | 2.22 | 2.65 | 2.89 | 2.91 |
| 2.79 | 2.34 | 1.014 | 2.03 | 2.12$_5$ | 3.80 | 3.44 |
| 4.28 | 2.90 | 1.508 | 1.87 | 1.69 | 5.61 | 2.56 |
| 5.47 | 3.36 | 1.850 | 1.78 | 1.44 | 7.22 | 2.00 |
| 1.78 | 1.73 | 0.627 | 2.56 | 2.93 | 3.03 | 2.66 |
| 3.27 | 2.26 | 1.235 | 2.56 | 2.20 | 4.04 | 2.96 |
| 5.05 | 2.95 | 1.970 | 2.56 | 1.66 | 4.90 | 3.20 |
| | | | | | | $K_{O_2}$ = (2.95 ± 0.35) × $10^8$ |

[a] [histamine]$_{total}$ = 3.99$_5$ × $10^{-2}$ $M$, [acid]$_{total}$ = 4.016 × $10^{-2}$ $M$, $I$ = 0.13 (KCl); for other details see Results section.

**Table III.** Enthalpy Data for the Reaction $2CoL_2(aq) + O_2(aq) \rightleftharpoons (CoL_2)_2O_2$ (L = Histidinate, Ethylenediamine) in Aqueous Solution, 25.0°

L = Histidinate[a]

| $10^3$[cobalt]$_{total}$, $M$[a] | $10^4$[O$_2$], $M$ | $10^4$[adduct], $M$ | $-Q$, cal | $-Q_{corr}$,[b] cal | $-\Delta H_{O_2}$, kcal mol$^{-1}$ |
|---|---|---|---|---|---|
| 2.528 | 3.03 | 8.56 | 7.916 | 3.476 | 29.0 |
| 1.974 | 4.52 | 6.86 | 6.665 | 2.966 | 28.8 |
| 1.516 | 5.76 | 5.26 | 5.172 | 2.332 | 29.6 |
| 1.086 | 6.67 | 3.64 | 3.681 | 1.646 | 30.1 |
| 0.988 | 6.73 | 3.25 | 3.207 | 1.357 | 27.8 |
| 0.890 | 7.10 | 2.90 | 3.078 | 1.413 | 32.5 |
| 0.890 | 7.10 | 2.90 | 3.045 | 1.380 | 31.7 |
| 0.791 | 7.63 | 2.70 | 2.711 | 1.232 | 30.4 |
| 0.791 | 8.23 | 2.59$_5$ | 2.618 | 1.138 | 29.2 |
| 0.653 | 8.08 | 2.04$_5$ | 2.200 | 0.979 | 31.9 |
| | | | | | Av 30.1 ± 1.3 |

L = Ethylenediamine[c]

| $10^3$[cobalt]$_{total}$,[d] $M$ | $-Q$, cal | $-Q$(CoL$_2$),[e] cal | $-Q$(dil),[f] cal | $-Q_{corr}$, cal | $-\Delta H_{O_2}$, kcal mol$^{-1}$ |
|---|---|---|---|---|---|
| 0.790$_5$ | 3.464 | 1.654 | 0.103 | 1.707 | 28.7 |
| 0.631 | 2.778 | 1.320 | 0.083 | 1.385 | 29.2$_5$ |
| 0.514 | 2.271 | 1.072 | 0.068 | 1.131 | 29.2 |
| 0.595 | 2.636 | 1.241 | 0.078 | 1.317 | 29.4$_5$ |
| 0.553 | 2.488 | 1.155 | 0.073 | 1.260 | 30.2$_5$ |
| | | | | | Av 29.6 ± 0.6 |

[a] 150 ml of histidinate solution in calorimeter; [L$^-$] = 1.985 × $10^{-2}$ $M$, [HL] = 2.15 × $10^{-3}$ $M$; titrant 0.2972 $M$ CoCl$_2$. [b] This term corrected for heat of dilution of titrant,[31] protonation of histidinate by acid in titrant,[32] and formation of CoL$_2$; *e.g.*, $Q$ = −2.200 and corrections were −0.084, −0.001, and −1.136 cal, respectively. [c] Ethylenediamine buffer, 150 ml; initial concentrations, [LH$^+$] = 9.90 × $10^{-3}$ $M$, [LH$_2^{2+}$] = 6.60 × $10^{-3}$ $M$; titrant 0.2972 $M$ CoCl$_2$. [d] [Adduct] = $^1/_2$[cobalt]$_{total}$. [e] $Q$ for $Co^{2+}(aq) + 2en(aq) \rightarrow Co(en)_2(H_2O)_2^{2+}(aq)$. Data from M. Ciampolini, P. Paoletti, and L. Sacconi, *J. Chem. Soc.*, 4553 (1960). [f] Heat of dilution of CoCl$_2$ titrant[31] plus −0.002 cal for protonation of ethylenediamine by acid in titrant.

Prior to the experiment the calorimeter and contents were flushed thoroughly with N$_2$ freed from oxygen by means of vanadous chloride scrubbers. The measured heat change (*ca.* 2.3 cal) was corrected for dilution of the titrant (*ca.* 0.15 cal)[31] and protonation of the histidinate ion by acid in the titrant (*ca.* 0.002 cal).[32]

For L = histidinate, $\Delta H_{O_2}$ was determined from single-addition titrations of CoCl$_2$ solution into oxygen-saturated histidine solution (as above) in an O$_2$ atmosphere. The cooling curve was followed for *ca.* 5 min; then the calorimeter contents were quickly removed and the dissolved oxygen was determined. Transfer of oxygen to or from the solution was negligible in the time interval from the addition of CoCl$_2$ to measurement of oxygen concentration. A manometric analysis indicated that complete equilibration between the gas and liquid phases required more than 2 hr under the stirring conditions used in the calorimeter. For each experiment, [adduct] was calculated from $K_{O_2}$, [O$_2$], and total cobalt concentration. The observed heat changes $Q$ (2.2–7.9 cal) were corrected as above and for the heat of formation of CoL$_2$ (*ca.* 0.5$Q$). For L = ethylenediamine, the oxygenation reaction is complete ($K \sim 7 \times 10^{10}$;[16] degree of adduct formation >99%) and a titration procedure was adopted, using the buffer solutions described above. Data are given in Table III.

## Discussion

**Equilibrium Constants.** $K_{O_2}$(histidinate), (4.24 ± 0.5) × $10^6$ $M^{-2}$, is smaller than the value 6.0 × $10^6$ $M^{-2}$ extrapolated for 25° from the data of Simplicio and Wilkins.[7] In a manometric study, Hearon, *et al.*,[5] reported $K_{O_2}$ = 2.30 × $10^6$ at 26° using a graphical analysis of data. However, these results are questionable, since the number of moles of O$_2$ absorbed is greater than one-half the number of moles of cobalt at $P_{O_2}$ = 0.974 and 0.195 atm and 14°. From their data we cal-

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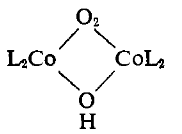
(32) J. L. Meyer and J. E. Bauman, *J. Amer. Chem. Soc.*, **92**, 4210 (1970).

**Table IV.** Comparison of Thermodynamic Data for Oxygenation and Nitrogenation Reactions, Substrate + $O_2$ (or $N_2$) $\rightleftharpoons$ Adduct, 25.0° (1 *M* standard state for gas)

| Substrate | Physical state | Log *K* | $\Delta G$, kcal mol$^{-1}$ | $\Delta H$, kcal mol$^{-1}$ | $\Delta S$, cal deg$^{-1}$ mol$^{-1}$ |
|---|---|---|---|---|---|
| 2:1 Adducts, $(ML_n)_2 \cdot O_2$ | | | | | |
| $CoL_2$ (L = histidinate) | A;[a] $I = 0.02\ M$ | $6.63 \pm 0.05$[b] | $-9.05 \pm 0.07$ | $-30.1 \pm 1.3$ | $-70 \pm 5$ |
| $CoL_2(H_2O)_2^{2+}$ (L = histamine) | A; $I = 0.13\ M$ KCl | $8.47 \pm 0.05$ | $-11.55 \pm 0.07$ | | |
| $CoL_2(H_2O)_2^{+}$ (L = ethylenediamine)[c] | A; $I = 1.0\ M$ KCl | $10.84 \pm 0.3$ | $-14.8 \pm 0.4$ | $-29.4 \pm 0.6$ | $-49 \pm 4$ |
| $CoL_2(H_2O)_2^{2+}$ (L = ethylenediamine)[d] | A; $I = 1.0\ M$ KCl | | $-10$ | $-29.4$ | $-65$ |
| Co(Salen)[e] | Solid | | $-1.6$ | $-19.1$ | $-59$ |
| Co(3-MeO-Salen)[e] | Solid | | $-1.45$ | $-19.1$ | $-59$ |
| Co(3-EtO-Salen)[e] | Solid | | $-3.5$ | $-18.9$ | $-52$ |
| 2:1 Adduct $(ML_n)_2 \cdot N_2$ | | | | | |
| $Ru(NH_3)_5(H_2O)^{2+}$[f] | A; $I = 0.1\ M$ NaCl | | $-11.4$ | $-21.2 \pm 2.8$ | $-33 \pm 10$ |
| 1:1 Adducts, $ML_n \cdot O_2$ | | | | | |
| Co(acacen)py[g] | Pyridine solvent | | $-6.45$ | $-15.0$ | $-29$ |
| Myoglobin[h] | A; pH 8.5 | | | $-15.3 \pm 0.4$ | $-37.5 \pm 1.0$ |
| Hemoglobin (ox)[i] | A; pH 9.1 | | | $-13.2$ | |
| Hemoglobin (human)[j] | A; pH 7 | | | $-13.4$ | |
| 1:1 Adduct, $ML_n \cdot N_2$ | | | | | |
| $Ru(NH_3)_5(H_2O)^{2+}$[f] | A; $I = 0.1\ M$ NaCl | | $-6.2$ | $-10.1 \pm 1.4$ | $-13 \pm 5$ |

[a] $O_2(aq)$ + substrate in aqueous solution. [b] All values from this work are the mean ± standard deviation from the mean. [c] The reaction product is



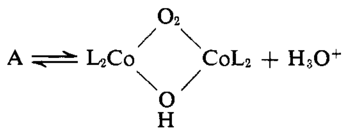
[d] Calculated for the product $L_2(H_2O)Co \cdot O_2Co(H_2O)L_2$ (see Discussion). [e] Reference 4; Salen = bis(salicylaldehyde)ethylenediimine. [f] J. N. Armor and H. Taube, *J. Amer. Chem. Soc.*, **92,** 6170 (1970), substrate + $N_2 \rightleftharpoons$ dinitrogen adduct. [g] From M. H. Keyes, M. Falley, and R. Lumry, *ibid.*, **93,** 2035 (1971), and G. Amiconi, M. Brunori, E. Antonini, G. Tauzher, and G. Costa, *Nature* (*London*), **228,** 549 (1970). [h] Keyes, Falley, and Lumry; see footnote *g*. Calculated for 1 *M* standard state for oxygen.[31] [i] F. W. Roughton, *Biochem. J.*, **29,** 2604 (1935). [j] A. J. Splittgerber, Ph.D. Dissertation, University of Colorado, 1968. For hemoglobin, $\Delta H$ is the mean value for oxygenation of the four heme groups.

culate $K_{O_2} = (3.7 \pm 1.5) \times 10^5\ M^{-2}$ at 26°. $K_{O_2}$(histamine), $(2.95 \pm 0.35) \times 10^8\ M^{-2}$ (Table III), agrees with the value $(2.9 \times 10^8)$ from kinetic data.

**Enthalpy and Entropy Data.** $\Delta H(CoL)_2$ compares with Williams' value[33] of $-12.25 \pm 0.08$ kcal mol$^{-1}$ in 3 *M* $NaClO_4$, and falls into the expected sequence with values for Ni, Cu, Zn(II), *viz.*, $-16.6 \pm 0.5$, $-21.3 \pm 0.6$, and $-11.7 \pm 0.3$ kcal mol$^{-1}$, respectively, 0.1 *M* $KNO_3$.[34]

$\Delta H_{O_2}$(histidinate) contrasts with the temperature coefficient value, $-38$ kcal mol$^{-1}$.[5] A recalculation from Simplicio's temperature coefficient data[16] yields $\Delta H_{O_2} = -30.6 \pm 3.0$ kcal mol$^{-1}$. For L = ethylenediamine, the measured $\Delta H_{O_2}$ corresponds to the following reactions

$$2CoL_2(H_2O)_2^{2+} + O_2(aq) \rightleftharpoons \underset{A}{CoL_2(H_2O){-}O_2{-}CoL_2(H_2O)} + 2H_2O \qquad \Delta H^1_{O_2}$$



$\Delta H_{ol}$

$$LH^+ + H_3O^+ \rightleftharpoons LH_2^{2+} + H_2O \qquad \Delta H_{LH_2}$$

$$\Delta H_{O_2} = \Delta H^1_{O_2} + \Delta H_{ol} + \Delta H_{LH_2}$$

For ligand protonation, $\Delta H_{LH_2} = -11.1$ kcal mol$^{-1}$ and $\Delta S_{LH_2} = -5.8$ cal deg$^{-1}$ mol$^{-1}$.[35] Data for the olation reaction are not readily estimated, but reference to somewhat analogous reactions

$$Co(NH_3)_5(H_2O)^{3+} + H_2O \rightleftharpoons Co(NH_3)_5(OH)^{2+} + H_3O^+$$

(proton dissociation, $\Delta H = +9.0$ kcal mol$^{-1}$, $\Delta S = +2.9$ cal deg$^{-1}$ mol$^{-1}$)[36] and

$$2Fe^{3+} + 4H_2O \rightleftharpoons (Fe(OH)_2Fe)^{4+} + 2H_3O^+$$

(diolation, $\Delta H = +10.0$ kcal mol$^{-1}$, $\Delta S = +20$ cal deg$^{-1}$ mol$^{-1}$)[37] suggests that $\Delta H_{ol}$ and $\Delta S_{ol}$ will be positive and about +10 kcal mol$^{-1}$ and +10 to +20 cal deg$^{-1}$ mol$^{-1}$, respectively. If this is valid, then for the first reaction $\Delta H^1_{O_2} \sim \Delta H_{O_2} \sim 29$ kcal mol$^{-1}$ and $\Delta S^1_{O_2} \sim \Delta S_{O_2} - 15$ cal deg$^{-1}$ mol$^{-1}$ = $-65$ cal deg$^{-1}$ mol$^{-1}$, values which are close to those for the histidine system.

The observed enthalphy and entropy values are compared in Table IV with data for similar reactions, involving the formation of dinitrogen and $\mu$-dinitrogen-ruthenium(II) complexes,[38] the formation of $\mu$-dioxygen-cobalt(II) complexes in the solid state,[4] and the for-

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mation of 1:1 oxygen adducts by hemoglobin[39,40] and myoglobin.[41] The most striking feature of the energetics of all these reactions is the large negative $\Delta H$ and $\Delta S$ values. For the cobalt(II) systems, consideration of a simple energy cycle involving an oxidation (1) and subsequent coordination (2) reaction shows that the origin of the large negative $\Delta H^1{}_{\mathrm{O_2}}$ lies in the strongly

$$\underset{2(-54.5)}{2\mathrm{Co(en)_2(H_2O)_2{}^{2+}(aq)}} + \underset{(-2.8)}{\mathrm{O_2(aq)}} + \underset{(0)}{2\mathrm{H^+(aq)}} \longrightarrow \underset{2(-51.1)}{2\mathrm{Co(en)_2(H_2O)_2{}^{3+}(aq)}} + \underset{(-45.7)}{\mathrm{H_2O_2(aq)}} \tag{1}$$

$$\Delta H = -36.1 \text{ kcal mol}^{-1}$$

$$\underset{2(-51.1)}{2\mathrm{Co(en)_2(H_2O)_2{}^{3+}(aq)}} + \underset{(-45.7)}{\mathrm{H_2O_2(aq)}} \longrightarrow \underset{(-4.6)}{\mathrm{adduct(aq)}} + \underset{(0)}{2\mathrm{H^+(aq)}} + \underset{2(-68.3)}{2\mathrm{H_2O(l)}} \tag{2}$$

$$\Delta H = +6.7 \text{ kcal mol}^{-1}$$

exothermic reduction of $\mathrm{O_2(aq)}$ to $\mathrm{H_2O_2(aq)}$ (reaction 1). In these two reactions the heats of formation of reactants and products[31] are given in parentheses. $\Delta H_f$($\mathrm{Co(en)_2(H_2O)_2{}^{3+}}$) was estimated from data[31] for $\mathrm{Co(en)_2(H_2O)_2{}^{2+}}$, $\mathrm{Co(en)_3{}^{2+}}$, and $\mathrm{Co(en)_3{}^{3+}}$, and $\Delta H_f$(adduct) was calculated from $\Delta H^1{}_{\mathrm{O_2}}$ for the reaction.

Upon coordination, the oxygen molecule will lose its translational, rotational, and much of its vibrational entropies ($\Delta S_f(\mathrm{O_2(aq)}) = 26.5$ cal deg$^{-1}$ mol$^{-1}$).[31] New charge centers are generated as charge is transferred from cobalt to oxygen ($2\mathrm{CoL}_n{}^{2+} + \mathrm{O_2} \rightarrow \mathrm{L}_n\text{-}\mathrm{Co}^{3+}\cdots(\mathrm{O_2})^{2-}\cdots\mathrm{CoL}_n{}^{3+}$) and the interaction of these with solvent molecules will contribute to the observed negative $\Delta H$ and $\Delta S$.

The enthalpy and entropy changes for oxygenation of hemoglobin (mean values) and myoglobin are approximately equal to those for formation of the 1:1 cobalt:$\mathrm{O_2}$ adduct and half the values for formation of the 2:1 cobalt:$\mathrm{O_2}$ adducts (Table IV). However, comparison of these data does not permit inference about the bonding of $\mathrm{O_2}$ in the hemoproteins. This latter bonding is accompanied by significant conformational (tertiary and quaternary) changes in the protein molecule.[42] In the hemoproteins the coordinated $\mathrm{O_2}$ is sheathed by a hydrophobic protein environment, in contrast to a solvent sheath of water or pyridine for the cobalt systems studied. The sensitivity of $\Delta H$ and $\Delta S$ to changes in conformation and environment is seen by comparison of data for hemoglobin and myoglobin: $\Delta\Delta H°$ $(=\Delta H(\mathrm{Hb}) - 4\Delta H(\mathrm{Mb})) = -18.3$ kcal mol$^{-1}$ and $\Delta\Delta S° = -40$ eu.[41]

The enthalpy data (Table IV) for the formation of dinitrogen and dioxygen adducts refer to different elements and do not differentiate the bonding properties for the two diatomics. The suggested bonding scheme for $\mathrm{N_2}$ coordination, as in $[\mathrm{Ru(NH_3)_5N_2}]\mathrm{X_2}$, considers $\mathrm{N_2}$ as a $\sigma$ donor and (predominantly) a $\pi$ acceptor (*cf.* CO).[43] The M–N–N system is linear and the importance of $\pi$ back-bonding is inferred from the effect on the (coordinated) N–N stretching frequency of variation in the $\pi$-acceptor properties of the ligands coordinated to the metal.[43] $\pi$ donation from the metal into the $\mathrm{N_2}$ antibonding orbitals causes an increase in the N–N length ($\mathrm{N_2}$, 1.098 Å; $[\mathrm{Ru(NH_3)_5N_2}]\mathrm{Cl_2}$, 1.12 Å) and thus a reduction in the nitrogen–nitrogen bond order from 3.0 ($\mathrm{N_2}$) to *ca.* 2.6 (relative to data for $\mathrm{N_2}$, $\mathrm{N_2O}$, and $\mathrm{HN_3}$).[44] This change in bond order corresponds to a net transfer of 0.8 electron from ruthenium to $\mathrm{N_2}$ antibonding orbitals.

In contrast, the M–O–O and M–O–O–M systems are nonlinear.[17,18,21,25] The O–O bond length increases on coordination ($\mathrm{O_2(g)}$, 1.21 Å; $[(\mathrm{H_2O})(\text{F-Salen})\mathrm{Co\cdot O_2\cdot Co}(\text{F-Salen})]_2$, 1.31 Å;[45] $(\mathrm{Co(Salen)DMF})_2\cdot\mathrm{O_2}$, 1.35 Å;[18] and $([\mathrm{Co(NH_3)_5\cdot O_2}](\mathrm{SO_4})_2$, 1.47 Å;[17] *cf.* $\mathrm{H_2O_2}$, 1.48 Å), and there is a corresponding decrease in bond order (2.0, 1.35, 1.25, 1.05, and 1.0, respectively: values for adducts interpolated from data[46] for $\mathrm{O_2{}^+}$, $\mathrm{O_2}$, $\mathrm{O_2{}^-}$, and $\mathrm{O_2{}^{2-}}$). The change in bond order corresponds to transfer of *ca.* 0.65–0.95 electron for each cobalt to the dioxygen group, and the amount of transfer increases with increased polarizability of the ligand donor groups. Esr studies have shown that *ca.* 90% of the odd-electron density is transferred from cobalt ($\mathrm{d^7}$, low spin) onto the spin-paired oxygen molecule in bis(acetylacetonato)ethylenediiminecobalt(II):$\mathrm{O_2}$ adducts.[25]

Therefore, although the nitrogen atom has a much smaller electron affinity than the oxygen atom,[47] $\mathrm{N_2}$ and $\mathrm{O_2}$ act as Lewis acids of similar strength in these compounds.

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