Co-ordination of Oxygen by Cobalt(II)–L-Ornithinate and –DL-2,3-Diaminopropanoate Complexes in Aqueous Solution †

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The oxygenation of cobalt(II) bis(DL-2,3-diaminopropanoate) and bis(L-ornithinate) complexes has been studied in aqueous solution at 25 °C. Equilibrium constants are reported for protonation of the two ligands, and for formation of the complexes $[CoL]^+$, $[Co(HL)]^{2+}$, and $[CoL_2]$ (HL = DL-2,3-diaminopropanoic acid) and $[Co(HL)]^{2+}$, $[Co(HL)_2]^{2+}$, and $[Co(HL)L]^+$ (HL = L-ornithine). Equilibrium data for oxygenation of the DL-2,3-diaminopropanoate complex $[CoL_2]$ ($\log K_{O_2}$ 8.90 ± 0.08, $\log K_{O_2,OH}$ 12.13 ± 0.14) and the L-ornithine complex $[Co(HL)L]^+$ ($\log K_{O_2}$ 7.17 ± 0.12) have been obtained by use of a polarographic oxygen analyser.

SOME cobalt(II) complexes with amine, amino-acid, or peptide ligands can reversibly oxygenate to give 2 : 1 adducts $[L_nCoO_2CoL_n]$.[1-3] The chemical properties of these adducts have been reviewed.[4] In an earlier paper [5] equilibrium and (calorimetric) enthalpy data for oxygenation of cobalt(II) bis(histidinate), bis(histamine), and bis(ethylenediamine) were reported. Subsequent papers have reported data for the oxygenation of Co^{II} complexes with 3,6-diazaoctane-1,8-diamine,[6] 3-azapentane-1,5-diamine and 3,6,9-triazaundecane-1,11-diamine,[7] histidine, ornithine, 2,3-diaminopropanoic acid, and 2,4-diaminobutanoic acid,[8] and 'mixed' 1,10-phenanthroline and terpyridyl ligands.[9]

This paper presents the results from a detailed study of the cobalt(II)–L-ornithine (2,5-diaminopentanoic acid) and –DL–2,3-diaminopropanoic acid complexes. Equilibrium constants are reported for the formation of metal–ligand species and for the oxygenation of metal–bis(ligand) species. These two ligands were considered because in earlier work [8] on them (*i*) the oxygenation reactions were studied under conditions where formation of a single cobalt(II)–bis(ligand) complex was assumed (erroneously) to be complete, (*ii*) it was implied that ornithine (HL) acted as a tridentate ligand to give 100% of an oxygen-sensitive species $[CoL_2]$, whereas equilibrium studies (*e.g.* A. Albert, *Biochem. J.*, 1952, **50**, 690) had established that ornithine acts predominantly as a bidentate α-aminocarboxylate ligand {to give $[Co(HL)_2]^{2+}$}, and (*iii*) oxygen uptake was determined with Warburg apparatus and, in our experience, this is much less reliable than the polarographic oxygen analyser.

EXPERIMENTAL

Materials.—L-Ornithine hydrochloride and DL-2,3-diaminopropanoic acid hydrochloride (Sigma) were used without further purification. The molarity of standard solutions of these ligands was determined by Gran analysis [10] on ligand hydrochloride–NaOH titrations. Stock solutions of cobalt dichloride (B.D.H., AnalaR) were acidified and analysed by precipitation of cobalt as $[Co(py)_4(NCS)_2]$ (py = pyridine).[11]

pH Measurements.—pH Data were obtained from potentiometric titrations with the apparatus and $[H^+]$-calibration method described previously.[12]

Oxygen Measurements.—The concentration of dissolved oxygen was determined with a Beckman 39550 polarographic oxygen electrode and Beckman Fieldlab oxygen analyser 100802 which were calibrated against air-saturated,[13] nitrogen-saturated, and mixtures of air- and nitrogen-saturated water. A linear calibration was achieved. Oxygen-uptake experiments were made in a jacketed cell maintained at 25.0 ± 0.1 °C. The cell, total capacity 65 cm^3, had no air space above the solution and was air tight except for a capillary venting tube. The oxygen sensor, two syringe needles, and a micro combination reference electrode–pH electrode (Titron Instruments, type 121BB) passed into the solution through entry ports in the lid of the cell. In a typical run the cell was filled with ligand solution (acidic), and this solution was air saturated. The solution pH was then adjusted to *ca.* 10 by addition of NaOH, before incremental addition of cobalt dichloride titrant from a Gilmont micrometer syringe. Complex species were formed, as noted by a decrease in solution pH. Oxygen uptake occurred rapidly and was complete within the response time of the membrane sensor (90 s). The concentration of adduct formed was equated to the decrease in concentration of O_2(aq) in solution. The composition of the solution in equilibrium with the adduct was determined from the measured pH and the stoicheiometry of reaction.

RESULTS AND CALCULATIONS

Representative pH data from the titration of NaOH against solutions of (*i*) 2,3-diaminopropanoic acid hydrochloride and NaCl (I = 0.10M) ‡ and (*ii*) ornithine hydrochloride and NaCl (I = 0.020M) are in Supplementary Publication No. SUP 21454 (7 pp.) § The stepwise protonation constants in Table 1 were computed from derived $\bar{n}_H$(obs.) ¶ –pH data by use of the least-squares procedure

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† No reprints available.

‡ 1M = 1 mol dm^{-3}.

§ For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1974, Index issue (items less than 10 pp. are supplied as full-size copies).

¶ $\bar{n}_H$ = Average number of protons bound per ligand molecule.

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[13] R. Battino and H. L. Clever, *Chem. Rev.*, 1966, 395.

Table 1

Equilibrium constants for stepwise protonation of diaminocarboxylates at 25 °C

Amino-acid	log K_1	log K_2	log K_3 [a]
DL-2,3-Diaminopropanoic acid [b]	9.407 ± 0.004	6.702 ± 0.004	1.33
2,3-Diaminopentanoic acid [c] (ornithine)	10.506 ± 0.012	8.70 ± 0.01_5	1.98

[a] Ref. 14. [b] I = 0.10M-NaCl; average from two titrations. [c] I = 0.020M-NaCl; average from two titrations.

described previously.[12] A literature [14] value was assumed for each K_3 (for protonation of the carboxylate group; the accuracy of this value does not affect any of the calculations involved in this work). The protonation constants were determined for duplicate titrations from *ca.* 24 data points in the range $\bar{n}_H$ = 0.17—1.85 (2,3-diaminopropanoic acid) or 0.53—1.89 (ornithine); R factors [15] of *ca.* 0.3—0.5% were achieved and there were no systematic trends in the residuals, [16] $\bar{n}_H$(obs.) — $\bar{n}_H$(calc.).

Table 2

Logarithms of equilibrium constants for formation of cobalt(II)–amino-acid complexes at 25 °C

Reaction	Amino-acid			
	DL-2,3-Diaminopropanoic [a]	L-2,5-Diaminopentanoic (ornithine) [b]	2,6-Diaminohexanoic (lysine) [c]	Glycine [d]
$Co^{2+} + L^- \xrightleftharpoons{K_1} [CoL]^+$	6.55 ± 0.01			5.07 ± 0.01
$[CoL]^+ + L^- \xrightleftharpoons{K_2} [CoL_2]$	5.18 ± 0.01			3.97 ± 0.02
$Co^{2+} + HL \xrightleftharpoons{K_3} [Co(HL)]^{2+}$	2.91 ± 0.02	3.48 ± 0.06	3.87	
$[Co(HL)]^{2+} + HL \xrightleftharpoons{K_4} [Co(HL)_2]^{2+}$		2.96 ± 0.06	3.20	
$[Co(HL)]^{2+} + L^- \xrightleftharpoons{K_5} [Co(HL)L]^+$		3.42 ± 0.10		

[a] This work, I = 0.10M-NaCl; average from two titrations. [b] This work, I = 0.020M-NaCl; mean ± standard deviation from five titrations. [c] Ref. 14; I = 0.15M-K[NO$_3$]. [d] J. R. Brannan, H. S. Dunsmore, and G. H. Nancollas, *J. Chem. Soc.*, 1964, 304; I = 0.0M.

For the study of metal–ligand complexes the ligand solution (pH *ca.* 3.5) was placed in the titration cell [12] and thoroughly flushed (30 min) with N_2 [scrubbed through vanadium(II) chloride solution] before addition of cobalt(II) chloride solution in a single aliquot portion from a micrometer syringe; titration with NaOH followed, with continuous N_2 flushing. For titration of NaOH against solutions of cobalt dichloride (2.00×10^{-3}M), 2,3-diaminopropanoic acid hydrochloride (4.97×10^{-3}M), and NaCl (I = 0.10M) the pH against titre curves showed a buffer region, pH 5.5—7.5, followed by a marked inflexion (end-point) at pH 8.0—10.0. The end-point titre corresponded to addition of 4 mol of hydroxide per mol of cobalt (*i.e.* the reaction $2H_2L^+ + Co^{2+} + 4OH^- \longrightarrow CoL_2 + 2H_2O$; HL = 2,3-diaminopropanoic acid) plus 1 mol of hydroxide per mol of excess of ligand (the end-point for the titration $H_2L^+ + OH^- \longrightarrow HL + H_2O$ was observed at pH 7.6—8.5). When data from the buffer region were interpreted in terms of reactions (1) and (2) only [1] the derived constants K_1 and

$$Co^{2+} + L^- \xrightleftharpoons{K_1} [CoL]^+ \qquad (1)$$

$$[CoL]^+ + L^- \xrightleftharpoons{K_2} [CoL_2] \qquad (2)$$

K_2 carried a significant error (*ca.* 7—14%) and the least-squares fit between c_H(obs.) and c_H(calc.) (c_H = total ionisable acid) was poor at low pH. Inclusion of a third reaction, (3), in the least-squares calculation reduced the R

$$Co^{2+} + HL \xrightleftharpoons{K_3} [Co(HL)]^{2+} \qquad (3)$$

factor from 1.9 to 0.3%, and reduced the least-squares error on K_1 and K_2 to 1 and 2% respectively. Values of log K_1, log K_2, and log K_3 are given in Table 2.

Titration of NaOH against solutions of cobalt dichloride, ornithine hydrochloride, and NaCl (I = 0.020M) having a ligand to metal ratio < 5 : 1 led to precipitation of basic cobalt(II) salts (pH *ca.* 8.5) after an initial buffer (complex-formation) reaction. By use of a 10 : 1 ratio of ligand to metal the solutions were stable up to pH 11. Calculations based on titrations against 2 : 1 solutions (c_L 8.0×10^{-3}M) gave an approximate log K_3 value of 3.65 from the pH range 5.7—7.8 ($\bar{n}_L$ < 0.75). Least-squares analysis of data from triplicate titrations against 10 : 1 solutions (c_L 1.55×10^{-2}M) and titrations against 8 : 1 and 7 : 1 solutions (c_L 1.35×10^{-2}M) gave the constants K_3, K_4, and K_5 [reactions (3), (4), and (5)]. An R factor of 0.2—0.5% was achieved from 24—30 data points (pH 5.8—10.2). There was no evidence of formation of [CoL$_2$] up to pH 10.2; attempts to include

$$[Co(HL)]^{2+} + HL \xrightleftharpoons{K_4} [Co(HL)_2]^{2+} \qquad (4)$$

$$[Co(HL)]^{2+} + L^- \xrightleftharpoons{K_5} [Co(HL)L]^+ \qquad (5)$$

this species in the refinement led to a negative parameter. Attempts to analyse the data in terms of equilibrium constants K_3, K_4, and K_6 [reaction (6)] gave $K_6 > K_4$ and K_3 (an unacceptable solution) and a very poor least-squares fit. Log K values are given in Table 2. For both ligands,

$$[Co(HL)_2]^{2+} + HL \xrightleftharpoons{K_6} [Co(HL)_3]^{2+} \qquad (6)$$

distribution curves for the metal–ligand species present during a titration are given in the Figure, and pH data from representative titrations are given in SUP 21454.

Oxygenation of the cobalt(II)–2,3-diaminopropanoic acid complexes was studied at pH *ca.* 6.0, 8.0, 10.0, and 10.7. The complex [CoL$_2$] alone was oxygen sensitive (negligible O_2 uptake at pH 6.0; see Figure). Because of the high

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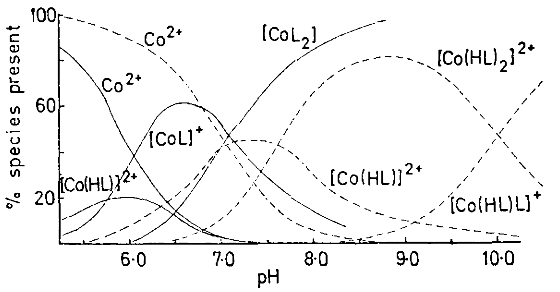
stability of the oxygen adduct it was necessary to work at low $[O_2]_0$ so that the equilibrium concentration of $[CoL_2]$ was significant and could be calculated accurately from known log K values, the measured pH, and expressions for solution composition. In a typical titration cobalt dichloride (0.302M) was added incrementally to a solution of ligand (4.97×10^{-3}M) and NaCl ($I = 0.10$M) at a given pH and with $[O_2]_0$ *ca.* 1.0×10^{-4}M. Titrations were completed as rapidly as possible (20—30 min) to minimise the effect of irreversible oxidation of Co^{II} to Co^{III}. Measurement of $[O_2]_{eq}$ was reproducible within ± 1%. Plots of log $[CoL_2]$ against log [adduct]/$[O_2]$ had a gradient of 0.5, as required for a 2 : 1 cobalt: O_2 adduct. Proton-balance studies, which determine α in the equation $Co^{2+} + H_{\bar{n}_H}L + O_2 \longrightarrow \frac{1}{2}$ adduct $+ (2\bar{n}_H + \alpha)H^+$ established that the adduct is $[L_2CoO_2CoL_2]$ at pH 8.0 (α *ca.* 0), and that a mixture of μ-dioxygen and μ-dioxygen-μ-hydroxo-species is present at pH 10.0 (α *ca.* 0.33). Because of the effect of hydrolysis a meaningful proton balance could not be made at higher pH but it was inferred that the dibridged species would predominate at pH 10.7. The value of K_{O_2} [pH 8.0, reaction



Distribution curves for cobalt(II)–2,3-diaminopropanoic acid, Co^{2+} : HL ratio 1 : 2.5 (——), and cobalt(II)–ornithine, Co^{2+} : HL ratio 1 : 10 (— — —). Percentages of species present are relative to the total metal-ion concentration

$$2[CoL_2] + O_2 \xrightleftharpoons{K_{O_2}} [L_2CoO_2CoL_2] \qquad (7)$$

(7)] was calculated from $K_{O_2} = ([O_2]_0 - [O_2]_{eq})/([O_2]_{eq}[CoL_2]^2)$, while the value of $K_{O_2,OH}$ [pH 10.7, reaction (8)] was given by $K_{O_2,OH} = K_{O_2}/[OH^-]$.

$$2[CoL_2] + O_2 + OH^- \xrightleftharpoons{K_{O_2,OH}} [L_2Co(O_2)(OH)CoL_2]^- \qquad (8)$$

The cobalt(II)-ornithine system was oxygen sensitive only in the pH range where $[Co(HL)L]^+$ existed in solution (*i.e.* pH > 9; at pH 8.5 themeasured O_2 uptake was negligible, in agreement with previous work [8]). Titrations of cobalt dichloride solution into ornithine solutions (pH *ca.* 10.1—9.7) were carried out as above, except with $[O_2]_0$ *ca.* 2.6×10^{-4}M. Values of K_{O_2} for the two ligands are given in Table 3 and data from representative titrations are in SUP 21454.

It is to be noted that the choice of different ionic strengths for studies on the two ligand systems relates to an attempt (initially) to use literature values of log K [reactions (1)—(4)] in the determination of K_{O_2}; these values proved to be unsatisfactory for the calculation of solution composition in oxygenation studies, and therefore were redetermined.

DISCUSSION

Protonation.—Protonation constants for 2,3-diaminopropanoic acid have been determined previously at 25 °C by Michailidis and Martin [1] (log K_1 9.50, log K_2 6.70; $I = 0.5$M-KCl) and by Hay and Morris [17] (log K_1 9.51, log K_2 6.79; ' practical constants ', $I = 0.1$M-KCl; calculation procedure not cited) but cannot be compared directly with those reported here for 0.10M-NaCl. Protonation constants have been reported for ornithine (log K_1 10.67, log K_2 8.65, log K_3 1.98; $I = 0.02$M) but the experimental method was not given.[18] For each ligand the terminal amino-group will be the more basic and K_1 refers to its protonation. The K_1 values increase as the methylene chain between the terminal amino-nitrogen and the α-aminocarboxylate group increases in length, *e.g.* log $K_1 = 9.41$, 10.28 ($I = 0.025$M), 10.51, and 10.54 ($I = 0.1$M-Na[ClO$_4$]) respectively for 2,3-diaminopropanoic, 2,4-diaminobutanoic,[19] 2,5-diaminopentanoic (ornithine), and 2,6-diaminohexanoic acid (lysine).[14] For the two latter ligands log K_1 is similar to that for protonation of a primary alkylamine ($MeNH_2$ 10.64, $EtNH_2$ 10.63; $I = 0.0$M) [20] and that for protonation of the corresponding monoaminocarboxylic acids (γ-aminobutanoic acid 10.56, 6-aminohexanoic acid 10.80; $I = 0.0$M);[20] this indicates

TABLE 3

Equilibrium constants for formation of dioxygen adducts by cobalt(II)–amino-acid complexes at 25 °C

Ligand, HL	Reactive complex	log K_{O_2} [a]	Reaction conditions [b]
DL-2,3-Diaminopropanoic acid	$[CoL_2]$	12.3 ± 0.14 [c,d] (log $K_{O_2,OH}$)	0.10M-NaCl, pH 10.7
		8.90 ± 0.08 [c]	0.10M-NaCl, pH 8.0
		7.96 [e]	30 °C; Warburg, pH 8.7
L-2,5-Diaminopentanoic acid (ornithine)	$[Co(HL)L]^+$	7.17 ± 0.12 [c,d]	0.020M-NaCl, pH 9.7—10.1
		5.43 [e]	30 °C; Warburg
2,6-Diaminohexanoic acid (lysine)	$[Co(HL)_2]^{2+}$?	5.18 [f]	pH 7.8—8.6
Histidine	$[CoL_2]$	6.63 ± 0.05 [g]	
		5.82 [e]	30 °C; Warburg
		5.57 [h]	26 °C; Warburg

[a] $K_{O_2} = [\text{Adduct}]/[\text{Co(ligand)}_n]^2[O_2]$. [b] Polarographic measurement unless stated otherwise. [c] This work. [d] Mean ± standard deviation of results from five titrations. [e] Ref. 8. [f] Ref. 28, assumes cobalt species is $[CoL_2]$, but potentiometric data (A. Albert, *Biochem. J.*, 1952, **50**, 690) establishes $[Co(HL)_2]^{2+}$ as the predominant species. [g] Ref. 5. [h] Recalculated (ref. 5) from published data (ref. 3).

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[17] R. W. Hay and P. J. Morris, *Austral. J. Chem.*, 1968, **21**, 1073.

[18] R. L. Rebertus, *Diss. Abs.*, 1954, 1917.

[19] A. Albert, *Biochem. J.*, 1952, **50**, 690 (published values at 20 °C, log K_1 10.44, log K_2 8.24, corrected to 25 °C assuming $\Delta H_1 = 54.8$ and $\Delta H_2 = 52.8$ kJ mol^{-1}).

[20] J. J. Christensen, R. M. Izatt, D. P. Wrathall, and L. D. Hansen, *J. Chem. Soc.* (*A*), 1969, 1212.

significant diminution of inductive effects[21] with increasing (methylene) chain length.

The log K_2 values (Table 1) show a similar trend (6.70, 8.08, 8.70, and 9.06 respectively), reflecting the diminishing inductive effect of the terminal ammonium group. It is of interest that the log K_2 values for (amino) protonation of $\overset{+}{N}H_3[CH_2]_xCH(NH_2)CO_2^-$ are only *ca.* 0.3—0.9 log units smaller than for protonation of the analogous diamines $\overset{+}{N}H_3[CH_2]_xCH_2NH_2$ (log K_2 7.10,[22] 8.98,[23] and 9.49[24] at $I = 0.1$M for $x = 1$, 2, and 3); this bears out the small inductive effect associated with the α-carboxylate group.

Cobalt Complexes.—Michailidis and Martin[1] reported equilibrium constants for the formation of L-2,3-diaminopropanoic acid complexes $[CoL]^+$ and $[CoL_2]$ (HL = 2,3-diaminopropanoic acid; log K_1 6.2, log K_2 5.0; 25 °C, $I = 0.5$M-KCl). They did not observe the formation of the protonated species reported here for the racemic ligand, $[Co(HL)]^{2+}$, although Hay and Morris[17] noted formation of the complexes $[CuL]^+$, $[CuL_2]$, $[Cu(HL)]^{2+}$, and $[Cu(HL)L]^+$; $[Co(HL)]^{2+}$ is a minor species (for the ligand : metal ratio used here), its concentration reaching a maximum of 21% of the total metal present at pH 5.95. In contrast for copper, where the complexes form at lower pH, the $[M(HL)]^{2+}$ species is more dominant, rising to 60% of the total copper concentration at pH 3.6.[17] Comparison of log K_1 and log K_3 for the cobalt complexes indicates that co-ordination of the second five-membered (diamino) chelate ring adds 3.6 log units to the stability constant, in contrast with a value of 5.15 (log K_1—log K_3)[17] for the analogous copper–amino-acid complexes.

Ornithine is a strongly basic ligand and, in the absence of metal ions, removal of the last proton from the conjugate acid will not be significant unless the pH > 9.5. Further, its second (diamino) chelate ring is seven membered and will not add greatly to complex stability.[25] Therefore it is not surprising that $[Co(HL)_2]^{2+}$ is the dominant species in a 10 : 1 ligand : metal titration (Figure) and that $[Co(HL)L]^+$ [reaction (5)] does not exceed 10% of the total metal concentration until pH > 9.2. Results from least-squares calculations did not support the existence of the species $[CoL]^+$. Comparison of log K_5 and log K_4 indicates that co-ordination of an additional seven-membered (diamino) chelate ring adds only *ca.* 0.3—0.6 log units to the stability constant for the α-aminocarboxylate complex.

The sequence of K values for formation of mono (α-aminocarboxylate) complexes, 2,3-diaminopropanoic acid (K_3) < ornithine (K_3) < lysine (K_3) < glycine (K_1) [also the K values for the bis(α-aminocarboxylate) complexes with the last three ligands], reflects the base-weakening effect which the terminal amino-group has on the co-ordinating power of the α-aminocarboxylate function.[17]

Oxygen Adducts.—In the formation of 2 : 1 adducts the co-ordinating oxygen molecule may displace either (*i*) a co-ordinated carboxylate group [*e.g.* as in bis(histidinato)-cobalt(II)[4]] or amine group {*e.g.* as in $[Co(en)_3]^{2+}$}[26] or (*ii*) a co-ordinated solvent molecule {*e.g.* as in $[Co(en)_2(OH_2)_2]^{2+}$}[1] (en = ethylenediamine). Formation of the highly co-ordinated oxygen-sensitive Co^{II} complexes is usually complete only in alkaline solution, and in cases where this complex is four-co-ordinate with respect to the ligand [*e.g.* L = 2 en, 2 histamine, or 3,6-diazaoctane-1,8-diamine] a μ-dioxygen-μ-hydroxo-structure may result.[1,4-7]

Stadtherr *et al.*[27] suggested that the 2 : 1 oxygen adduct formed by bis(L-2,3-diaminopropanoate)cobalt(II) is dibridged at pH > 9 [and has an u.v. absorption maximum at 358 nm (pH 11.4)], in contrast to the monobridged species formed at lower pH which has absorption maxima at 315 and 385 nm (pH 8.7). That is at high pH the remaining carboxylate group attached to each metal centre in the dioxygen adduct is displaced by a bridging hydroxo-group.[27] In the present work proton-balance studies have established the same general result for the racemic ligand. Absorption spectra recorded on fresh solutions of the dioxygen adduct established u.v. maxima at 310 and 385 nm (ε *ca.* 10 000 and 8 000 l mol^{-1} cm^{-1}) at pH 8.0 for the monobridged adduct, and at 359 (ε *ca.* 6 500) at pH 10.0 and at 357 nm (ε *ca.* 7 700 l mol^{-1} cm^{-1}) at pH 10.7 for the dibridged adduct. Equilibrium constants (Table 3) for formation of the monobridged (K_{O_2}) and dibridged adducts ($K_{O_2,OH}$) were calculated from oxygen-uptake measurements at pH 8.0 and 10.7 respectively.

For the bis(ornithinate) complex it was not possible to study the oxygenation over such a wide pH range, and because of the large buffering effect of excess of ligand in solution it was not possible to achieve a definitive proton-balance study.[5] It was inferred, solely from lower residuals in mass-balance summations, that the oxygenation at pH 10.0 follows reaction (9) rather than (10). The oxygen adduct formed at pH 10.0 had

$$2[Co(HL)L(OH_2)]^+ + O_2 \rightleftharpoons [L(LH)CoO_2Co(HL)L]^{2+} + 2H_2O \quad (9)$$

$$2[Co(HL)L(OH_2)]^+ + O_2 + H^+ \rightleftharpoons [(LH)_2Co(O_2)(OH)Co(HL)_2]^{3+} + H_2O \quad (10)$$

a u.v. absorption maximum at 313 nm and a shoulder near 410 nm; this two-band spectrum is consistent with previous assignments[27] for a monobridged adduct. The observation that the ornithine complex $[Co(HL)L]^+$ is oxygen sensitive, whereas $[Co(HL)_2]^{2+}$ is not, is consistent with previous findings that oxygen-sensitive complexes require at least three co-ordinated nitrogen atoms.[1]

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The reversibility of the oxygenation reactions was estimated by polarographic measurement of oxygen released on decomposing the adduct with (*i*) dilute acid at pH *ca.* 2.5 and (*ii*) ethylenediaminetetra-acetate at pH *ca.* 6.5. For the 2,3-diaminopropanoate complex 100% of the co-ordinated oxygen was released in 15—20 min from a solution of the adduct which had been aged for 20 min (*cf.* Michailidis and Martin report a half-life of 24 h for irreversible oxidation of the 2,3-diaminopropanoate adduct). Under similar conditions oxygen release from the ornithinate adduct was *ca.* 65—85%; the acid-stable Co^{III} decomposition product had an absorption maximum at 542 nm (ε *ca.* 120 l mol^{-1} cm^{-1}). Both these results are at variance with those of Munakata[8] who reported from studies under similar conditions that the ornithinate complex is 100% reversibly oxygenated whereas the 2,3-diaminopropanoate is not (85—96% oxygen release on acidification).

Equilibrium data for cobalt(II)-amino-acid oxygenation reactions are collected in Table 3. The data for lysine may be in doubt because Sokol *et al.*[28] assumed that the dominant cobalt species in a metal–ligand solution is $[CoL_2]$ (which has four N donors co-ordinated, and probably is oxygen sensitive), whereas the dominant species at pH *ca.* 8 is probably $[Co(HL)_2]^{2+}$ (see footnote *f*, Table 3), and this species (two N donors co-ordinated) is not likely to be oxygen sensitive.[1] It is likely that the 'correct' value for K_{O_2} is higher than that reported. Similarly the result reported for ornithine at 30 °C is in doubt. Munakata[8] assumed that all the cobalt–amino-acid complex in solution (pH 9—10) was oxygen sensitive. This complex was assumed to be $[CoL_2]$, but the present work establishes the cobalt species as $[Co(HL)]^{2+}$, $[Co(HL)_2]^{2+}$, and $[Co(HL)L]^+$ and only $[Co(HL)L]^+$, which represents *ca.* 7—45% of the total cobalt at pH 9—10, is oxygen sensitive.

As yet there are insufficient reliable equilibrium data published for cobalt(II)-amino-acid complexes to enable precise deductions about factors affecting the stability of the oxygen adducts. However, if log $\beta_n([CoL_n])$ is taken as a measure of the donor power of the ligand, and if this in turn relates to the ability of the cobalt to donate electron density to the oxygen,[4] then it is seen that the value of K_{O_2} for the histidinate adduct is anomalously low with respect to those for ornithine and 2,3-diaminopropanoic acid (*cf.* log β_n 11.9,[14] 6.9, and 11.7 respectively). The (apparent) high oxygen affinity of the histidinate complex, and its early discovery as an oxygen-sensitive species, probably relate to the properties of the ligand {(*i*) tridentate, with log K ($[CoL_2]$) = 5.1, (*ii*) pK(HL) only 6.1} which favour complete formation of the $[CoL_2]$ complex at low pH in solutions not containing a large excess of ligand.

[5/344 *Received, 18th February, 1975*]

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