# Oxygenation of a Cobalt(II)–Dioxime Complex

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## Abstract

The ligand 4,4,9,9-tetramethyl-5,8-diazadodecane-2,11-dione dioxime ($LH_2$) forms cobalt(II) complexes $[Co(LH)(H_2O)_2]^+$ and $[Co(LH)(H_2O)OH]$; the stabilities of these complexes have been determined in aqueous solution at 25°C ($I = 0.10$ M NaCl). The hydroxo complex $[Co(LH)(H_2O)OH]$ reacts with dioxygen to give the non-labile oxygen adduct $[(HO)(HL)CoO_2Co(LH)(OH)]$ in aqueous solution: this reaction has been followed by polarographic oxygen sensor.

The oxygenation reactions of cobalt(II) complexes of amines, amino acids, porphyrins, oximes and Schiff bases have been studied.[1] E.s.r. studies establish that in coordination there is an electron transfer from the cobalt to the oxygen molecule.[1–3] Because of this electron transfer, coordination of oxygen by amine and amino acid complexes requires a minimum of three nitrogen atoms coordinated to the cobalt[4,5] while the square-planar porphyrin and Schiff base complexes require coordination of either a suitable ligand molecule or donor solvent molecule in the fifth coordination site.[1,6,7]

Cobalt(II) forms complexes $[Co(LH)(H_2O)_2]^+$ and $[Co(LH)(H_2O)OH]$ with the ligand 4,4,9,9-tetramethyl-5,8-diazadodecane-2,11-dione dioxime ($LH_2$).
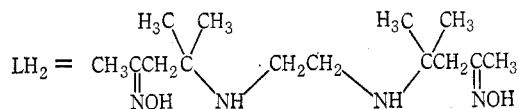


The stability constants for the formation of $[Co(LH)(H_2O)_2]^+$ and $[Co(LH)(H_2O)OH]$ have been determined in aqueous solution at 25°C ($I = 0.10$ M NaCl). Whereas $[Co(LH)(H_2O)_2]^+$ shows little oxygen affinity, $[Co(LH)(H_2O)OH]$, which forms at pH >9, takes up oxygen quantitatively to give a non-labile 2 : 1 adduct $[(HO)(HL)CoO_2Co(LH)(OH)]$.

[1] Wilkins, R. G., in 'Bioinorganic Chemistry' Adv. Chem. Ser. No. 100 (American Chemical Society: Washington 1971).
[2] Hoffman, B. M., and Petering, D. H., *Proc. Nat. Acad. Sci. U.S.A.*, 1970, **67**, 637.
[3] Hoffman, B. M., Diemonte, D. L., and Basolo, F., *J. Am. Chem. Soc.*, 1970, **92**, 61.
[4] Michailidis, M. S., and Martin, R. B., *J. Am. Chem. Soc.*, 1969, **91**, 4683.
[5] Kee, T.-S., and Powell, H. K. J., *J. Chem. Soc., Dalton Trans.*, 1975, 2023.
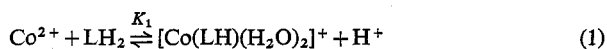[6] Floriani, C., and Calderazzo, F., *J. Chem. Soc. A*, 1969, 946.
[7] Stynes, D. V., Stynes, H. C., James, B. R., and Ibers, J. A., *J. Am. Chem. Soc.*, 1973, **95**, 1796.

## Experimental

The synthesis of the ligand,[8] and a description of the titration cell and the methods for $[H^+]$-calibrations have been reported.[9] Titrations of NaOH against solutions of ligand dihydroperchlorate $(4 \cdot 5 \times 10^{-4}$ M), $HClO_4$, cobalt dichloride $(4 \cdot 1 \times 10^{-4}$ M) and NaCl $(I = 0 \cdot 10$ M) gave a buffer region at pH $6 \cdot 3$–$7 \cdot 3$, and a marked inflexion (end-point) at pH $7 \cdot 5$–$9 \cdot 5$, followed by a second buffer region at pH $> 9 \cdot 8$. The end-point titre corresponded to the completion of the reaction

$$LH_4{}^{2+} + 3OH^- + Co^{2+} \rightarrow [Co(LH)(H_2O)_2]^+ + 3H_2O$$
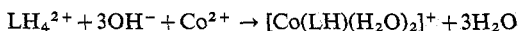
(plus $LH_4{}^{2+} + OH^- \rightarrow LH_3{}^+ + H_2O$ for the excess ligand present). The data were best interpreted in terms of the single equilibrium reactions

$$Co^{2+} + LH_2 \overset{K_1}{\rightleftharpoons} [Co(LH)(H_2O)_2]^+ + H^+ \tag{1}$$

$$[Co(LH)(H_2O)_2]^+ + OH^- \overset{K_{OH}}{\rightleftharpoons} [Co(LH)(H_2O)OH] \tag{2}$$

for the respective buffer regions. Results were calculated for three titrations from 7–9 data points in each of the two buffer regions defined by $\bar{n}_L = 0 \cdot 12$–$0 \cdot 7$ and $\bar{n}_{OH} = 0 \cdot 2$–$0 \cdot 6$. Average values were $\log K_1 = -0 \cdot 58 \pm 0 \cdot 06$ and $\log K_{OH} = 3 \cdot 32 \pm 0 \cdot 04$.

Oxygenation of the cobalt complexes was studied by use of a Beckman 39550 polarographic oxygen electrode and Beckman 100802 Fieldlab oxygen analyser. Electrode calibration and the titration cell have been described.[5] A solution of cobalt dichloride $(0 \cdot 302$ M) was added incrementally to an air-saturated buffered solution of the ligand in the air-tight titration cell kept at constant temperature. The formation of cobalt complexes was determined from the measured pH and the stoichiometry of the solutions, and the formation of oxygen adducts was determined from the decrease in $[O_2]_{aq}$.

Solutions containing $[Co(LH)(H_2O)OH]$ (pH $> 9$) developed a deep amber colour and at pH $10 \cdot 7$ oxygen uptake was quantitative, at $0 \cdot 5$ mole $O_2$ per mole of $[Co(LH)(H_2O)OH]$. In contrast to many analogous dioxygen adducts of cobalt(II)[5] addition of edta to a solution of the adduct did not cause release of oxygen ($[Co(edta)]^{2-}$ is not oxygen-sensitive up to pH $11 \cdot 6$);[10] neither was there evidence for the formation of a stable cobalt(III)–edta complex ($\lambda_{max}$ 576 nm).[11] On acidification only 10% of the coordinated oxygen was released in 30 min; changes in the absorption spectrum indicated a slow reaction which was complete in c. 24 h. In this period 50% of the initial complex decomposed to cobalt(II) (determined as $[Co(NCS)_4]^{2-}$ in 50% acetone solution). Because the adduct is non-labile it was not possible to calculate an equilibrium constant for its formation.

## Discussion

Coordination between cobalt(II) and the dioxime $LH_2$ occurs in the pH range $6 \cdot 3$–$7 \cdot 3$ to give a single complex $[Co(LH)(H_2O)_2]^+$, equation (1); in this complex an oxime-oximato ligand is coordinated to the metal ion. In contrast, with copper(II) two species, $[Cu(LH_2)]^{2+}$ and $[Cu(LH)]^+$, are formed in the pH range $2 \cdot 0$–$5 \cdot 0$. The dioxime complex $[Cu(LH_2)]^{2+}$ represents more than 20% of total metal at pH $2 \cdot 55$–$3 \cdot 8$ with a maximum concentration (46% of total metal) at pH $3 \cdot 1$.[8] The complex $[Cu(LH)]^+$ is related by proton dissociation:

$$[Cu(LH_2)]^{2+} \rightleftharpoons [Cu(LH)]^+ + H^+ \qquad \log K = -3 \cdot 24$$
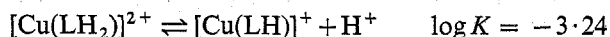
Coordination of the dioxime to a divalent transition metal ion lowers p$K$ for the oxime group from $12 \cdot 3$ to $3 \cdot 24$. The coordination of the ligand to cobalt(II) occurs at pH $\geqslant 3 \cdot 24$, so that ligand coordination and (oxime) proton dissociation appear
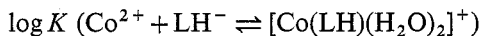
[8] Fraser, J. W., Hedwig, G. R., Powell, H. K. J., and Robinson, W. T., *Aust. J. Chem.*, 1972, **25**, 747.
[9] Hedwig, G. R., and Powell, H. K. J., *Anal. Chem.*, 1971, **43**, 1206.
[10] Kee, T.-S., and Powell, H. K. J., unpublished data.
[11] Yalman, R. G., *J. Phys. Chem.*, 1961, **65**, 556.

to occur in one step, reaction (1); i.e. the concentration of a species $[Co(LH_2)(H_2O)_2]^{2+}$ is immeasurably small. If we assume a value of $12\cdot3$ for $\log K$ ($LH^- + H^+ \rightleftharpoons LH_2$) then

$$\log K \ (Co^{2+} + LH^- \rightleftharpoons [Co(LH)(H_2O)_2]^+)$$

is $11\cdot7$ compared with $22\cdot1$ for copper(II).

The value of $\log K_{OH}$ ($3\cdot32$) is similar to that for the other polyamine hydroxo complex reported for cobalt(II)[12] ([Co(L)OH]$^+$, L = 4-(3-aminopropyl)-4-azaoctane-1,8-diamine; $\log K_{OH} = 2\cdot99$).

Oxygenated solutions of $[Co(LH)(H_2O)_2]$ (pH $6\cdot5$–$7\cdot5$) developed a slight yellow colour, indicating limited oxygen uptake. In contrast, solutions containing the hydroxo species $[Co(LH)(H_2O)OH]$ developed a deep amber colour, and oxygen uptake was quantitative to give the adduct $[(HO)(HL)CoO_2Co(HL)(OH)]$. This adduct differs from that for bis(dimethylglyoximato)cobalt(II)[13] and many amine and amino acid complexes[1,5] in being non-labile; there was no detectable release of oxygen on treatment with edta and only partial, slow release on treatment with acid.

Absorption spectra measured for fresh alkaline solutions of the oxygen adduct did not exhibit the charge-transfer bands (between 300 and 400 nm) which are characteristic of adducts formed by cobalt(II) amine and amino acid complexes.[4,5,14] The spectrum has a shoulder at 510 nm ($\varepsilon$ c. 370 mol$^{-1}$ l. cm$^{-1}$) which is in the range reported for peroxo complexes of the type $[X(cyclam)CoO_2Co(cyclam)X]$, where X and $O_2$ are trans and cyclam is 1,4,8,11-tetraazacyclotetradecane.[15] The absorption spectrum was unchanged after 50 h.

The role of the hydroxide ion in enhancing coordination of cobalt(II) to dioxygen parallels the role of the ligand or solvent molecule coordinated in the fifth donor position for oxygen-sensitive square-planar complexes of iron(II)[16] and cobalt(II),[1,6,7] including haemoglobin and coboglobin.[2]

[12] Dei, A., Paoletti, P., and Vacca, A., *Inorg. Chem.*, 1968, **7**, 865.
[13] Schrauzer, G. N., and Lee, L. P., *J. Am. Chem. Soc.*, 1970, **92**, 1551.
[14] Stadtherr, L. G., Prados, R., and Martin, R. B., *Inorg. Chem.*, 1973, **12**, 1814.
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[16] Collman, J. P., Gagne, R. R., Halbert, T. R., Marchon, J. C., and Reed, C. A., *J. Am. Chem. Soc.*, 1973, **95**, 7868.