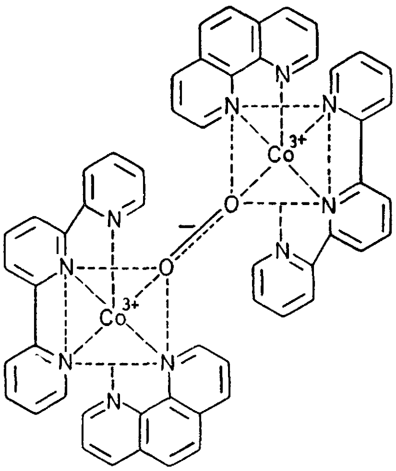
Aquoterpyridine-(1,10-phenanthroline)cobalt(II); a Low pH Oxygen Carrier

By Daniel H. Huchital and Arthur E. Martell*

(*Department of Chemistry, Texas A&M University, College Station, Texas* 77843)

Summary The mixed ligand complex aquoterpyridine-(1,10-phenanthroline)cobalt(II), $Co(tpy)(phen)(OH_2)^{2+}$, readily takes up oxygen at low pH to give an adduct which may rearrange to a mixed ligand cobalt(III) complex or may be readily oxidised to the superoxide.

Interest in oxygen carriers of transition metals has led to many studies concerning the structure, composition, kinetics, and equilibria of these potentially useful species.[1] We report a new mixed ligand cobalt(II) complex which is unique in that it forms an oxygen carrier at low pH.



(I)

The cobalt(II) precursor to the oxygen adduct is the mixed ligand complex of cobalt(II) with terpyridine and 1,10-phenanthroline, $Co(tpy)(phen)(OH_2)^{2+}$. This complex was prepared by the addition of solid $Co(tpy)Cl_2$[2] to a solution containing the 1,10-phenanthroline. Equilibrium and kinetic data for the process were obtained potentiometrically and by stopped-flow studies. The results are $\log K_f$ = 6·53 (potentiometric average of results at pH 2 and pH 3) and 6·56 (stopped-flow $k_f = 2{\cdot}30 \times 10^5\ \text{M}^{-1}\,\text{s}^{-1}$, $k_r = 0{\cdot}063\ \text{s}^{-1}$).

$$Co(tpy)^{2+} + phen \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Co(tpy)(phen)(OH_2)^{2+}$$

$$K_f = k_f/k_r = [Co(tpy)(phen)(OH_2)^{2+}]/[Co(tpy)^{2+}][phen]$$

If solid $Co(tpy)Cl_2$ is added to an oxygen saturated solution of 1,10-phenanthroline, a deep brown solution is obtained. The extent of formation of the oxygen adduct can be determined by measuring the concentration of additional acid released upon its formation compared to that released in the oxygen-free system. The value for $K(O_2)$ for the process is $7{\cdot}06 \times 10^6\ \text{M}^{-2}$.

$$2\ Co(tpy)(phen)(OH_2)^{2+} + O_2 \rightleftharpoons [Co(tpy)(phen)O_2Co(tpy)(phen)^{4+}]$$

$$K(O_2) = [Co(tpy)(phen)O_2Co(tpy)(phen)^{4+}]/[Co(tpy)(phen)(OH_2)^{2+}]^2[O_2]$$

These data are corroborated by stopped-flow experiments on the formation and dithionite ion-promoted dissociation of the oxygen adduct. The rate of formation is second order in $[Co(tpy)(phen)(OH_2)^{2+}]$ and first order in $[O_2]$ under our experimental conditions ($4 \times 10^{-4}\ \text{M} < [Co(tpy)(phen)(OH_2)^{2+}] < 3 \times 10^{-3}\ \text{M}$; $[O_2] = 1{\cdot}29 \times 10^{-4}\ \text{M}$). The third order rate constant obtained is $(8{\cdot}6 \pm 0{\cdot}7) \times 10^5\ \text{M}^{-2}\,\text{s}^{-1}$. The rate constant for the dissociation of the oxygen adduct is $0{\cdot}050\ \text{s}^{-1}$.

The second-order dependence of the concentration of the mixed ligand complex supports the mechanism suggested by Wilkins[3] where the formation of the oxygen adduct is considered to take place *via* a two-step process, *viz.*

$$CoL_n^{m+} + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CoL_nO_2^{m+} \qquad (1)$$

$$CoL_n^{m+} + CoL_nO_2^{m+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (CoL_n)_2O_2^{2m+} \qquad (2)$$

Under pseudo-first order conditions

$$d[O_2\ adduct]/dt = k_1k_2[CoL_n^{m+}][O_2]/(k_{-1} + k_2[CoL_n^{m+}]) = k_{obs}[O_2]$$

With L = dien ($n = 1$), histamine, or histidine ($n = 2$) neither term in the denominator is dominant and rate data were obtained by plotting $[CoL_n^{m+}]/k_{obs}$ *vs.* $1/[CoL_n^{m+}]$. With other polyamine studies by Wilkins and his co-workers only values of k_1 could be obtained as $k_2[CoL_n^{m+}] >> k_{-1}$.

In our system, the second-order dependence on $[Co)(tpy)(phen)(OH_2)^{2+}]$ is the first example of the limiting case where $k_{-1} >> k_2[CoL_n^{m+}]$. The third-order rate constant obtained ($=k_{obs}/[Co(tpy)(phen)(OH_2)^{2+}]^2$) is thus k_1k_2/k_{-1}. The dithionite-promoted dissociation rate constant is thus a measure of k_{-2}. These two rate constants yield an overall equilibrium constant for the O_2 adduct, $K(O_2)$ ($=k_1k_2/k_{-1}k_{-2}$) $= 1{\cdot}7 \times 10^6\ \mathrm{M}^{-2}$.

The oxygen adduct undergoes slow dissociation to a cobalt(III) species. The half-life for dissociation at pH 3 is *ca.* 2 h. The final product is yellow. The spectrum resembles $Co(tpy)_2^{3+}$ and $Co(phen)_2^{3+}$ and is presumed to be $Co(tpy)(phen)(OH)^{2+}$.

A concentrated solution (*ca.* 0·010 M) of the oxygen adduct (pH 2·2) was subjected to chlorine oxidation to form a deep green solution. An e.s.r. spectrum of this solution showed 15 lines indicating a new superoxo binuclear cobalt complex, (I) which is the first mixed ligand complex of this type to be reported.

This work was supported by a research grant from the National Science Foundation.

(*Received*, 30*th July* 1973; *Com.* 1095.)

[1] R. Nakon and A. E. Martell, *Inorg. Chem.*, 1972, **11**, 1002; *J. Inorg. Nuclear Chem.*, 1972, **34**, 1365; *J. Amer. Chem. Soc.*, 1972, **94**, 3026; F. Miller and R. G. Wilkins, *ibid.*, 1970, **92**, 2687; M. S. Michailidis and R. B. Martin, *ibid.*, 1969, **91**, 4683; F. Miller, J. Simplicio, and R. G. Wilkins, *ibid.*, p. 1962.

[2] R. Hogg and R. G. Wilkins, *J. Chem. Soc.*, 1962, 341.

[3] R. G. Wilkins, in 'Bioinorganic Chemistry,' Adv. in Chemistry Series, No. 100, American Chemical Society, 1971.