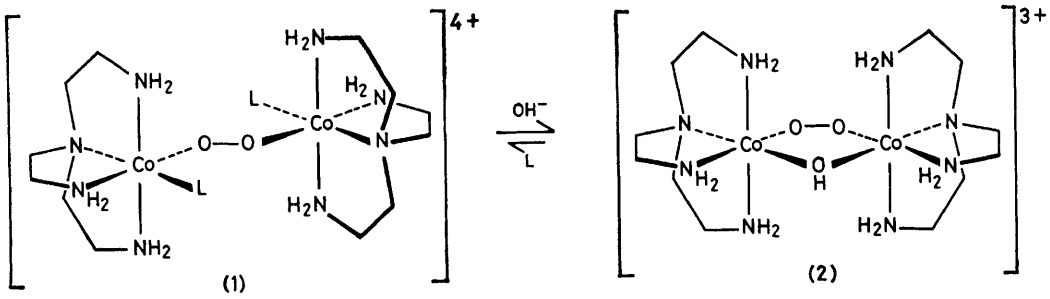
Oxygen-18 Exchange of μ-Peroxo-dicobalt(III) Complexes

By SILVIO FALLAB, HORST-PETER HUNOLD, MARCEL MAEDER, and PAUL R. MITCHELL*
(*Institute of Inorganic Chemistry of the University of Basel, Spitalstrasse* 51, *CH*-4056 *Basel, Switzerland*)

Summary The rate of exchange of oxygen-18 in [(tren)(MeNH$_2$)Co(μ-^{18}O$_2$)Co(tren)(MeNH$_2$)]$^{4+}$ (**1b**) ($t_{\frac{1}{2}}$ *ca.* 700 s) [tren = tris-(2-aminoethyl)amine] has been found to be the same as both the rate of decomposition by acids to cobalt(II) and O$_2$, and the rate of formation of [(tren)Co(μ-O$_2$,μ-OH)Co(tren)]$^{3+}$ from (**1b**) in neutral or alkaline

solution, indicating that a cobalt(II) complex is a common intermediate; the rate of exchange of $[(tren)Co(\mu\text{-}O_2,\mu\text{-}OH)Co(tren)]^{3+}$ is very much slower.

THE reactivity of μ-peroxo-dicobalt(III) complexes formed by oxidative addition of O_2 to cobalt(II) species has attracted the interest of many groups of workers.[1-4] Complexes of the type $L_5CoOOCoL_5$ (L = amine) can undergo either (i) heterolytic dissociation leading to mononuclear cobalt(III) species or (ii) decomposition to cobalt(II) species with reductive elimination of O_2. The latter reaction is usually very much faster than the former indicating that a homolytic cleavage of the Co–O co-ordinate bond is kinetically preferred to the normal ligand-substitution process. We have now found that cobalt(II) is an intermediate in the reaction of one peroxo-bridged complex to give another using complexes labelled with $^{18}O_2$.

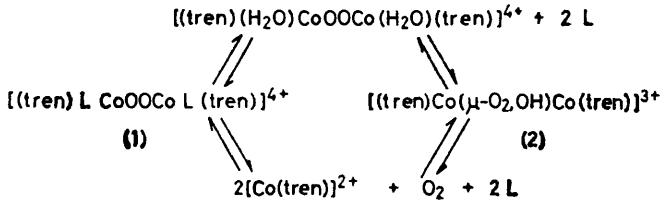


a; L = NH_3

b; L = $MeNH_2$

μ-Peroxo-bis[amine-tris-(2-aminoethyl)aminecobalt(III)] (**1a**) loses ammonia to give[4] the corresponding μ-hydroxo-μ-peroxo-complex (**2**) with a half-life of 450 s at 25 °C. Similarly, the related complex (**1b**) also forms (**2**), at a rate which is lower by a factor of 2.

The structures of the singly bridged peroxo-complex[4] (**1a**), and of the hydroxo-bridged complex[5] (**2**), have been determined by *X*-ray crystallography, and show no unusual features which could account for the high reactivity of (**1**).



SCHEME

Two possible mechanisms have been proposed[4] for the reaction (**1a**) → (**2**). (i) Substitution of NH_3 with retention of the binuclear Co–O–O–Co framework followed by fast deprotonation of co-ordinated H_2O and formation of a hydroxo-bridge. This would seem at first sight the simplest and most probable mechanism, although the reaction is very much faster than is normal for a substitution at cobalt(III). (ii) Decomposition of the binuclear complex to give labile cobalt(II) followed by reoxygenation which at low $[NH_3]$ leads predominantly to the μ-hydroxo-complex (**2**).

In order to clarify the situation we prepared the complexes (**1b**) and (**2**), labelled with $^{18}O_2$, which were analysed for $^{18}O_2$ by decomposing them in dilute perchloric acid at pH *ca.* 1·5, and isolating the oxygen liberated in a high-vacuum system, followed by mass spectroscopic analysis. We found that stirring $[(tren)(MeNH_2)Co^{18}O_2(tren)(MeNH_2)]^{4+}$ under $^{16}O_2$ gave $[(tren)Co(\mu\text{-}^{16}O_2,\mu\text{-}OH)Co(tren)]^{3+}$. Within experimental error, the half-life of exchange is the same as that of formation of the hydroxo-bridged complex (**2**), implying that the rate-determining step is the same for both reactions. Although the formation of (**2**) is inhibited† by the presence of 1 M methylamine buffer, the exchange of $^{18}O_2$ takes place at the same rate in 1 M methylamine as in 1 M KCl. Although the reverse reaction (**2**) → (**1b**) is possible in the presence of 1 M methylamine, it is far too slow ($t_{\frac{1}{2}} \geqslant 2 \times 10^4$ s) to account for the observed exchange.

Since in the absence of a high concentration of monodentate ligand the conversion of (**1**) into (**2**) is virtually complete, the μ-hydroxo-species is obviously much more stable thermodynamically than (**1**); moreover the kinetics of decomposition in neutral or slightly alkaline solution show that the hydroxo-bridged complex (**2**) is also more stable kinetically than (**1a**) or (**1b**). In agreement with this the exchange of $^{18}O_2$ in (**2**) has been found to be much slower: the half-life is of the order of 5×10^4 s.

It is therefore clear that the predominant pathway for the reaction (**1**) → (**2**) involves complete breakdown of the Co–O–O–Co framework to reform a cobalt(II) species, and that the reaction is rapid because of the ready accessibility of the rapid cobalt(II) equilibria. It may be assumed that the slower pathway is that involving direct substitution of cobalt(III).

It has long been known[6] that the formation of the hydroxo-bridge is the rate-determining step in the formation of, for example, $[(trien)Co(\mu\text{-}O_2,\mu\text{-}OH)Co(trien)]^{3+}$

† The reaction (**1**) → (**2**) is inhibited by the monodentate amine: $k_{obs} = a + b/(1 + c[NH_3]^2)$ [for (**1a**) → (**2**), $a = 1{\cdot}2 \times 10^{-5}$ s^{-1}, $b = 1{\cdot}4 \times 10^{-3}$ s^{-1}, and $c = 930$ l^2 mol^{-2}, in 0·1 M KCl at pH 10; for (**1b**) → (**2**), $a = 7{\cdot}5 \times 10^{-6}$ s^{-1}, $b = 7{\cdot}5 \times 10^{-4}$ s^{-1}, and $c = 115$ l^2 mol^{-2}, in 1 M KCl at pH 10·7]. The rate law can be interpreted by the two possible reaction paths outlined in the Scheme. The rate of the amine-independent pathway is clearly very much slower than that of the amine-dependent pathway. The kinetics alone do not permit an unambiguous choice between the two mechanisms mentioned in the Scheme.

[trien = $(H_2NCH_2CH_2NHCH_2)_2$] in alkaline solution. The reverse of this, the opening of the hydroxo-bridge, rather than the redox reaction to cobalt(II) and oxygen, is clearly the rate-determining step in the $^{18}O_2$ exchange of (**2**), which proceeds at a rate much more like that of cobalt(III) complexes.

Thus, if the reactivity of these complexes may be taken as typical, the chemical lability of singly bridged μ-peroxo-complexes depends ultimately on the availability of a rapid intramolecular redox reaction; a further bridging group decreases the likelihood of such a redox process.

(*Received*, 28*th January* 1981; *Com.* 098.)

[1] A. G. Sykes and J. A. Weil, *Prog. Inorg. Chem.*, 1970, **13**, 1.
[2] G. McLendon and A. E. Martell, *Coord. Chem. Rev.*, 1976, **19**, 1.
[3] L. G. Stadtherr and R. B. Martin, *Inorg. Chem.*, 1973, **12**, 1810.
[4] U. Thewalt, M. Zehnder, and S. Fallab, *Helv. Chim. Acta*, 1977, **60**, 867.
[5] M. Zehnder, U. Thewalt, and S. Fallab, *Helv. Chim. Acta*, 1976, **59**, 2290.
[6] F. Miller and R. G. Wilkins, *J. Am. Chem. Soc.*, 1970, **92**, 2687.