TABLE I. Oxygenation Constants and 2,6-Di-t-butylphenol Oxidation Rate Constants.

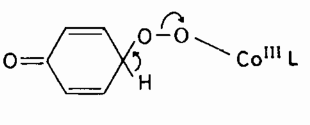
Ligand, L[a]	$\log K_{O_2}$[b]	k_{obs}[b]	k_1[c]	k_2[d]
tetren	15.8[e]	0.67	0.24	0.43
pydien	11.4[e]	3.7	1.6	2.1
tattd	8.4[f]	1.1	0.65	0.45

[a] Ligand abbreviations defined in text. [b] $K_{O_2} = [M_2L_2O_2]/(ML)^2[O_2]$. [c] Defined by eqn. (2). [d] Defined by eqn. (3). [e] Ref. 1. [f] Ref. 2.

The oxidation reactions were run with a steady state concentration of dioxygen complex. It was noted, however, that when the supply of dioxygen was cut off, the reaction rate for bq formation was slowed considerably even though most of the dioxygen complex was still present. On the other hand, the oxygen insertion reaction does not occur at all in the absence of the dioxygen complex. These observations, and temperature coefficient data, indicate that the reactive dioxygen complex is probably the mononuclear superoxo species governed by the equilibrium:

$$M_2L_2O_2 + O_2 \rightleftharpoons 2MLO_2$$

The results lend support to the concept that the mechanism of oxygen insertion involves the intermediate 1, in accordance with suggestions of Nishinaga [3] and Drago [4] for other dioxygen complex systems.



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Comparison of Electrochemical Behaviour of Cobalt and Molybdenum as Binding Sites for Dioxygen in Model Chelates for Oxygen Carriers and Oxygenases

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Complexing to a transition metal ion seems to be one of the most general methods to circumvent the low kinetic reactivity of triplet O_2 in biological systems. Direct comparison of the behaviour of different metal centres in a model system and model reaction can be very useful for unravelling different mechanisms of activation, which are dependent on the nature of the metal and its coordination sphere.

Following our previous work on the electrochemical behaviour of end-on co-ordinated molecular oxygen to cobalt atom in oxygen carriers, we have investigated with the same techniques the side-on co-ordination of O_2 to molybdenum in peroxo complexes. In both types of coordination the oxygen activation is measured by the displacement of the reduction potentials towards less cathodic values as compared with the free molecular oxygen in the same solvent.

In the presence of suitable acceptors and in aprotic solvents some cobalt chelates are active in the electrocatalytic generation of $O_2^{\overline{\cdot}}$. In aqueous acid solutions the same type of cobalt chelates lead to the electrocatalytic generation of H_2O_2. On the other hand it does not appear that end-on coordination to the cobalt atom weakens the O–O bond enough to catalyse oxidation reactions of biological interest. Investigations of the side-on co-ordination of O_2 in a series of molybdenum peroxide complexes show that again the reduction is displaced toward less cathodic potential as compared with free O_2 in the same solvent.

As an important difference from the behaviour of cobalt–di-oxygen adducts, H_2O_2 is not generated by reaction of co-ordinated dioxygen with H^+ but is reversibly released from the peroxide function in alkaline solution. Moreover, in the presence of suitable substrates the cleavage of the O–O bond and the transfer of atomic oxygen is observed, and can be monitored by electrochemical techniques.

The above differences are substantiated by identification of products of simple model reactions and by thermodynamic and kinetic parameters of chemical reactions coupled with electron transfer. The results may explain the different role of the metal ion and of the coordination sphere in oxygen carriers and monooxygenases.