quence of this, the citrate ligand could be an appropriate candidate for eliminating toxic Al species and to avoid abnormal buildups of aluminium in human tissues.

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R23

Thermodynamic Studies of the Reaction of Addition of Molecular Oxygen to Co(II) Complexes. The Co(II)–Tetraethylenepentamine–O_2 System in Aqueous Solution at 25 °C

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As part of a systematic study on oxygen carrier complexes [1, 2], we carried out a calorimetric study on the system Co(II)–tetraethylenepentamine-(tetren)–O_2. Tetren is a pentadentate ligand wich forms a monobridged oxygenated complex of Co(II), more similar to mononuclear peroxo complexes, interesting models of biological O_2 carriers, than the μ-hydroxo-μ-peroxo dibridged complexes usually formed in oxygenated aqueous solution of Co(II) and azotate ligands.

Our calorimetric experiments, carried out by adding Co(II) stock solution to O_2-saturated solutions containing an excess of tetren, or by bubbling O_2 into Co(tetren)$^{2+}$ aqueous solutions, produced for the binding of O_2 to Co(tetren)$^{2+}$ an enthalpy change $\Delta H^{\mathrm{CoL}}_{\mathrm{Co_2L_2O_2}} = -179.0 \pm 1.5$ kJ·mol^{-1}. This value is very large compared with the enthalpy changes obtained in the formation of mononuclear species ($\Delta H^{\mathrm{CoL}}_{\mathrm{CoLO_2}}$ values usually range from −40 to −65 kJ·mol^{-1} [3]) starting from the non-oxygenated parent complex, and compared with the enthalpy changes measured for the formation of dibridged μ-hydroxo-μ-peroxo complexes ($\Delta H^{\mathrm{CoL}}_{\mathrm{Co_2L_2O_2OH}} \cong -112$ kJ·mol^{-1} for L = 2en [2] or L = trien [1] starting from non-oxygenated tetrazotate complexes of Co(II). The entropy for the binding of O_2 to the $Co_2tetren_2O_2^{4+}$ complex is negative and its magnitude, when considerations are made of the characteristics of the reactions of O_2 addition, is: (*i*) very large when compared with those associated with the formation of binuclear dibridged complexes, (*ii*) small when compared with those associated with the formation of mononuclear oxygenated species.

These findings allow a first approach to a comparison among the various types of cobalt oxygen carrier complexes in water. Other data are however necessary in order to attain a significant picture of the situation and to correlate the thermodynamic behaviour of these compounds in water to their structures.

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R24

Catalysis of Oxidation of Di-t-butylphenol by μ-Peroxodicobalt(III) Complexes

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The oxidation of 2,6-di-t-butylphenol (dbp) by molecular oxygen is catalyzed by the μ-peroxodicobalt(III) complexes formed from tetraethylenepentamine (tetren), bis(picolyl)diethylenetriamine (pydien), and 1,4,10,13-tetraaza-7-thiatridecane (tattd). The oxygenation equilibrium constants of the cobalt(II) complexes of these ligands, and the observed rate constants, are presented in Table I. The rates of formation of the oxidative coupling product 3,3′,5,5′-tetra-t-butyldiphenoquinone (dpq) and the partial oxygen insertion product 2,6-tetra-t-butylbenzoquinone (bq) are shown to be first order with respect to the concentrations of both the cobalt–dioxygen complex (designated 'cat' for catalyst) and the phenol. The following rate expressions apply to this system:

$$-\frac{[\mathrm{dbp}]}{\mathrm{dt}} = k_1[\mathrm{cat}][\mathrm{dbp}] + k_2[\mathrm{cat}][\mathrm{dbp}] \qquad (1)$$

$$\frac{\mathrm{d[bq]}}{\mathrm{dt}} = k_1[\mathrm{cat}][\mathrm{dbp}] \qquad (2)$$

$$\frac{\mathrm{d[dpq]}}{\mathrm{dt}} = \frac{k_2}{2}[\mathrm{cat}][\mathrm{dbp}] \qquad (3)$$

It is interesting to note that the observed rate was lowest for the most stable dioxygen complex.

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

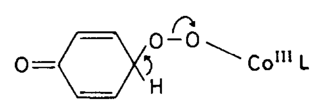
Ligand, L[a]	$\log K_{O_2}$[b]	k_{obs}[b]	k_1[c]	k_2[d]
tetren	15.8[e]	0.67	0.24	0.43
pydien	11.4[e]	3.7	1.6	2.1
tattd	8.4[f]	1.1	0.65	0.45

[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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R25

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.