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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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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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:

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

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

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

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