Discussion

The smooth increase in log K^{*}_{MA} with decreasing solvent polarity is similar to trends observed for other polyether ligands [7] and analogous to the effect of solvent polarity on K^{*}_{H1} [4]. The stability constants of the LiA complex are 4–5 fold greater than the NaA complex, in contrast to other carboxylic acid ionophores [1]. The stability of the Li^{+} complex on vesicle membranes is similar to the solution value in 80–85% MeOH–H_2O, as is the case with the protonation constant [4]. This finding suggests a predominantly interfacial location of the complex. However, the discontinuity in log K^{b}_{LiA} indicates that portions of complex penetrate the membrane acyl group region [8].

The present conditions do not allow observation of the 2:1, ionophore:cation, complexes with monovalent cations which were observed in bulk solvent extraction experiments [2]. These higher order complexes may be of greater interest for the transport of monovalent cations by A23187 since preliminary experiments show the rate of A23187-dependent Li^{+} transport into mitochondria is a second order function of the ionophore level.

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Complex Formation in the Al^{3+}–Citrate System

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Aluminium is regarded as a non-essential element for living organisms and has been considered as non-toxic in biological systems. This situation has changed, however, with the suspicion that aluminium is the agent causing dialysis encephalopathy in patients undergoing haemodyalysis with domestic water supplies high in aluminium [1]. Furthermore, the characteristic pathological finding in Alzheimer's disease is an abnormal build-up of aluminium in some regions of the Alzheimer brains [2]. Also, aluminium is implicated as a metal toxic to aquatic life, possibly as the $Al(OH)_2^{+}$ species [3], in acidified lakes and streams.

As the toxicity of a metal is closely related to its speciation, a way to suppress the toxic effect would be to complexate the metal ion into non-toxic, stable chelate species. The aim of the present study is to show this upon stable Al complexes formed with citrate (L^{3-}) ions.

TABLE I. Formation Constants Defined According to the General Equilibria: $pH^{+} + qAl^{3+} + rH_3L \Leftrightarrow (H^{+})_p(Al^{3+})_q(H_3L)_r$; β_{pqr}. The errors given correspond to $3\sigma(\log \beta_{pqr})$.

Complex	p q r	$\log(\beta_{pqr} \pm 3\sigma)$
H_2L^{-}	−1 0 1	−2.769 ± 0.003
H_2L^{2-}	−2 0 1	−6.850 ± 0.003
L^{3-}	−3 0 1	−12.067 ± 0.004
$AlHL^{+}$	−2 1 1	−2.68 ± 0.024
AlL	−3 1 1	−4.925 ± 0.008
AlL_2^{3-}	−6 1 2	−12.53 ± 0.12
$Al_3(OH)_4)_3^{4-}$	−13 3 3	−21.77 ± 0.019

Experimental

The measurements were performed as a series of potentiometric (glass electrode) titrations in 0.6 *M* Na(Cl) at 25 °C. The following concentration ranges were investigated: $0.00025 \leqslant B, C \leqslant 0.016$ *M* (B and C stand for the total concentration of Al^{3+} and H_3L resp.). $-\lg[H^{+}]$ was varied within the limits $2 \lesssim -\lg[H^{+}] \lesssim 8$.

Results and Discussion

An equilibrium analysis of the present system showed that besides a series of mononuclear complexes, *viz.* $AlHL^{+}$, AlL and AlL_2^{3-} a very stable trinuclear complex is formed. Calculations based upon graphical ('core + links' mechanism [4]) as well as least squares computer calculations (LETAGROPVRID [5–7]) showed the composition of this complex to be $Al_3H_{-4}L_3^{4-}$) (tentative composition $Al_3(OH)_4L_3^{4-}$).

Formation constants for the different species are given in Table I.

The stability of $Al_3(OH)_4L_3^{4-}$ implies that with $4 \leqslant -\lg[H^{+}] \leqslant 7$, Al is almost quantitatively bound in this complex (provided $C/B \gtrsim 1$). As a consequence 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$_2$tetren$_2$O$_2^{4+}$ 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.