Kinetics and mechanism of the reactions of the Al_{13} Keggin oligomer, $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$, with a series of phenolic ligands

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The kinetics and mechanism of the reactions of the Keggin oligomer, $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ (Al_{13}), with a series of phenol based ligands have been investigated using the stopped-flow technique. Ligands studied include catechol, chorogenic acid, L-dopa, gallic acid, gallic acid methyl ester, maltol, and salicylic acid. A mechanism is proposed that is consistent with the kinetic data. Formation of the initial bond is the rate determining step and subsequent breakdown of the Al_{13} oligomer is rapid.

Aluminium occurs ubiquitously in the environment in the form of silicates, oxides and hydroxides, combined with other elements such as sodium and fluorine and as complexes with organic matter. It has only one oxidation state (+3) in nature; therefore, its transport and distribution in the environment depend only upon the stabilities of its complexes and the kinetics of its substitution reactions. It is a small cation that is highly charged and in the absence of competing ligands is readily hydrolysed in aqueous solution.

Until recently aluminium and its salts were described as non-absorbable compounds causing little or no physiological harm. As a result, these salts were widely used in medicine and food. Aluminium salts are commonly used as reactants for coagulation-flocculation in the treatment of drinking water supplies.[1] However, the discovery of a possible correlation between aluminium consumption and Alzheimer's disease led to a renewed interest in the coordination chemistry of aluminium.[2]

In aqueous solutions Al(III) is known to form species of the type $Al_x(OH)_y^{(3x-y)+}$ where (x, y) vary from (1, 0) for the Al^{3+} ion, to (13, 32) for the so-called "Keggin" structure,[3] named after its discoverer.[4] While a relatively large number of species may be formed on hydrolysis of aqueous solutions of aluminium(III), Öhman and Forsling suggested that up to pH 4.2, only the following species need be considered:[5]

$$Al^{3+} + H_2O = Al(OH)^{2+} + H^+, \beta_{-11} = 10^{-5.52}$$

$$3Al^{3+} + 4H_2O = Al_3(OH)_4{}^{5+} + 4H^+, \beta_{-43} = 10^{-13.57}$$

$$13Al^{3+} + 32H_2O = Al_{13}O_4(OH)_{24}{}^{7+} + 32H^+, \beta_{-3213} = 10^{-109.2}$$

The composition of the Keggin structure may be written as $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, however, the representation $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ is more descriptive of the structure. This tridecamer has previously been characterised crystallographically.[6] The structure consists of a central tetrahedral AlO_4 unit containing the 4 μ_4-O sites, which is surrounded by 12 AlO_6 octahedra. There are 12 η^1-OH_2 sites and two distinct sets of 12 μ_2-OH at the shared edges of the AlO_6 octahedra.

The present work is concerned with the complex formation reactions of the polynuclear species, $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ (Al_{13}), or Keggin species. This polynuclear species can be considered as the smallest possible "aluminium-oxide particle". The charge density on the Al_{13} ion is in the same range as a fully protonated oxide-mineral surface. Using 0.53 nm as the approximate radius of the Al_{13} ion, the + 7 charge is distributed across a spherical area to yield $\approx$ 2 proton charges per nm^2 with the average charge on each Al^{3+} ion equal to 0.54 units.[7]

The decomposition of Al_{13} follows the stoichiometry in eqn. (1):

$$[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+} + 32H^+ \rightarrow 13Al^{3+} + 40H_2O \quad (1)$$

This reaction has a $\Delta G°$ value of -240 kJ mol^{-1} at 25 °C and $I = 0.01$ mol dm^{-3},[8] and may be catalysed by protons, complexing ligands or solid surfaces. It has been indicated, however, that the Al_{13} Keggin species has a half-life of several hundred hours at pH 5 at 25 °C.[9]

The concentration of dissolved aluminium in the environment depends critically on pH. Where the pH changes quickly, polynuclear aluminium species may be formed in relevant concentrations. For example, if acidic solutions of greater than 10^{-5} mol dm^{-3} total Al(III) are neutralised to a pH value between 5 and 6, Al_{13} formation is possible.[10] It was always believed that Al_{13} only existed in solutions hydrolysed in the laboratory but Bradley *et al.* demonstrated, using ^{27}Al NMR studies of soil samples, that the Al_{13} ion is present in the natural environment and in the samples studied actually comprised up to 30% of the aluminium that was detectable by NMR.[11] A probable pathway for the formation of Al_{13} in natural systems might involve the dissolution of Al(III)-bearing minerals in acidic water followed by transport of the dissolved Al(III) species and mixing with a less acidic body of water.

Polyphenols occur widely in nature[12] and aluminium(III) complexes of such ligands have high stability. In this paper we report the results of our studies of the kinetics and mechanism of the reactions of Al_{13} with simple phenols such as catechol, chlorogenic acid, L-dopa, gallic acid, gallic acid methyl ester, maltol and salicylic acid. These ligands are suitable model compounds for naturally occurring polyphenols.

Results

Fig. 1 shows the structures of the ligands used in this investigation. Solutions of the Al_{13} oligomer and Al^{3+} containing identical total concentrations of aluminium(III) were reacted with an excess of the ligands and the final spectra compared. It was found that the final absorbances of both solutions were

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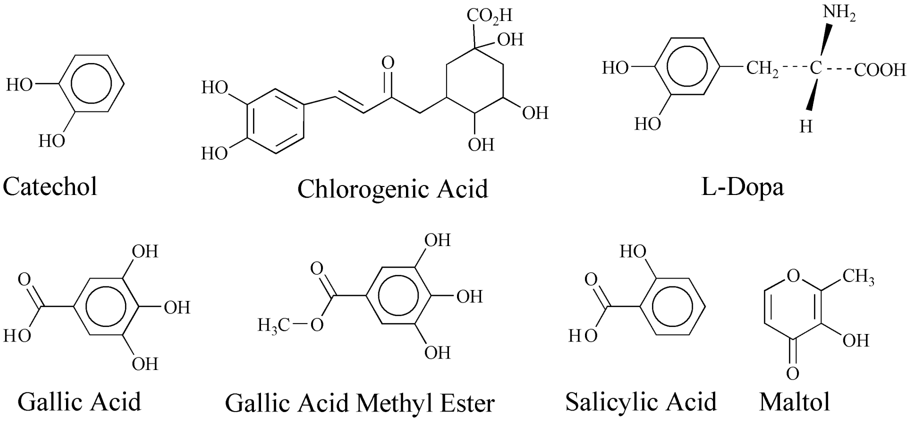


Fig. 1 Structures of the ligands used.

identical within experimental error. This confirmed that complete degradation of the Al_{13} Keggin oligomer occurred when it was reacted with an excess of ligand.

When solutions of the Al_{13} oligomer containing a total aluminium(III) concentration of 0.5 mM were reacted with a pseudo-first-order excess of catechol, L-dopa, salicylic acid, maltol, or chlorogenic acid, an absorbance change was observed, which consisted of a single exponential. Global analysis[13] of spectral kinetic data clearly showed that only two absorbing species contributed to the spectral changes, the ligand and the aluminium(III) complex formed during the reaction. The kinetic data are shown in Table 1. When gallic acid methyl ester was the ligand, the absorbance changes consisted of two exponentials, with the majority of the absorbance change being accounted for by the slower of the two exponentials. The amplitude of the faster reaction did not allow the calculation of reliable rate constants. For all of the above ligands, k_{obs} is adequately described by eqn. (2):

$$k_{obs} = k_a + k_b[\text{ligand}] \tag{2}$$

A typical plot of k_{obs} against ligand concentration is shown in Fig. 2.

When Al_{13} was reacted with gallic acid, a single reaction was observed. However, k_{obs} did not display a linear dependence on gallic acid concentration, as seen in Fig. 3. For this ligand, the kinetic data in Table 1 were analysed in terms of eqn. (3):

$$k_{obs} = k_a + k_b[\text{ligand}] + k_c[\text{ligand}]^2 \tag{3}$$

This gave values of 0.253 ± 0.04 s^{-1}, 628 ± 11 dm^3 mol^{-1} s^{-1} and 38400 ± 700 dm^6 mol^{-2} s^{-1} for k_1, k_2 and k_3, respectively. Fig. 3 shows the plot for the experimental data and the calculated line and the fit is excellent. Except at the lowest gallic acid concentration, the contribution of the k_2 pathway to k_{obs} is small.

The general mechanism proposed to account for the kinetic data is shown in Scheme 1 where HO–OH represent the phenolic ligand. It is broadly similar to the mechanism proposed for ligand promoted dissolution of slightly soluble oxides and silicates[14] and is also consistent with the Eigen–Wilkins–Tamm[15] mechanism for complex formation. The first step involves the formation of an outer-sphere complex in which the incoming ligand enters the second coordination sphere of the Al_{13} species. The second step involves loss of the axial water molecule from an aluminium atom, following which the ligand is bound in a mono-dentate fashion. Step three involves a rapid ring-closure step. This is followed by expulsion of a six-coordinated aluminium(III) species following which the remainder of the oligomer rapidly dissociates. For this mechanism, when the entering ligand L is present in pseudo-first-order excess, k_{obs} has the form of eqn. (4):

$$k_{obs} = \frac{k_1 k_2 k_3 K_o[\text{L}]}{k_{-1}(k_{-2} + k_3) + k_2 k_3} \tag{4}$$

Eqn. 4 predicts that a plot of k_{obs} against [L] should be a straight line with a slope of $k_1k_2k_3K_o$ $\{k_{-1}(k_{-2}+k_3)+k_2k_3\}$ and zero intercept. Table 1 and Fig. 2 show that this is broadly consistent with the experimental results. With the exception of gallic acid, plots of k_{obs} against ligand concentration yield good linear plots with small intercepts. The magnitudes of the intercepts differ by less than a factor of four in the case

Table 1 Kinetic data for the reaction of ligands with Al_{13} in aqueous solution at 25 °C, I = 1.0 mol dm^{-3} NaCl. $[Al]_{total}$ = 0.5 mM

	10^3[H$^+$]/mol dm^{-3}	k_{obs}/s^{-1}
Chlorogenic acid	2.50	1.24
	5.00	2.41
	7.50	3.72
	10.0	4.72
	12.5	6.04
Catechol	2.50	0.242
	5.00	0.316
	7.50	0.373
	10.0	0.427
	12.5	0.482
Gallic acid methyl ester (GAME)	2.50	0.580
	5.00	0.920
	7.50	1.56
	10.0	1.91
	12.5	2.55
L-Dopa	2.50	0.173
	5.00	0.274
	7.50	0.347
	10.0	0.434
	12.5	0.517
Maltol	2.50	0.348
	5.00	0.563
	7.50	0.859
	10.0	1.11
	12.5	1.28
Salicylic acid	2.50	0.337
	5.00	0.624
	7.50	0.992
	10.0	1.25
	12.5	1.51
Gallic acid	2.50	0.606
	5.00	1.59
	7.50	2.93
	10.0	4.60
	12.5	7.10

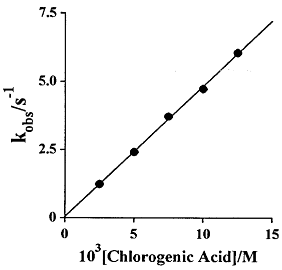


Fig. 2 Plot of k_{obs} against ligand concentration for reaction of chlorogenic acid with Al_{13}. $[Al]_{total} = 0.5$ mM, pH = 4.3, $\lambda = 425$ nm.

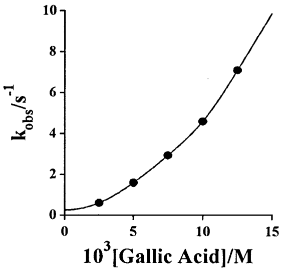
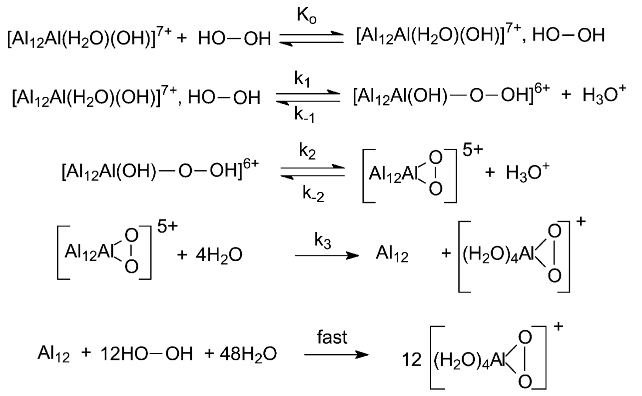


Fig. 3 Plot of k_{obs} against ligand concentration for reaction of gallic acid with Al_{13}. $[Al]_{toal} = 0.5$ mM, pH = 4.3, $\lambda = 320$ nm.



Scheme 1

of the ligands where k_{obs} exhibits a linear dependence on ligand concentration, this corresponds to a difference of only 3.7 kJ in $\Delta G^\ddagger$. This suggests that the reaction giving rise to this step is relatively independent of the nature of the ligand. As outlined in the introduction, there are distinct classes of μ_2-OH groups and these have been shown to have different labilities. We suggest that the intercepts in the plots of k_{obs} against ligand concentration have their origin in the dissociation of one of the less labile bridging hydroxyl groups to produce a labile species that then undergoes rapid reaction to yield the final product.

The second-order dependence of k_{obs} on gallic acid concentration could have a number of origins. For example, it could involve the formation of a gallic acid outer-sphere complex having two gallic acid molecules in the second coordination sphere. Alternatively, it could arise from simultaneous attack by the incoming ligand at two coordinated water sites. It is not possible to experimentally differentiate between these possibilities.

Discussion

The rate coefficients for exchange of the twelve, terminal, coordinated water molecules on the complex at 298 K are $k_{ex} = 1100 \pm 300$ s^{-1}, $\Delta H^\ddagger = 53 \pm 12$ kJ mol^{-1} and $\Delta S^\ddagger = -7 \pm 25$ J mol^{-1} K^{-1} and fall within the range measured for dissolved aluminium monomers.[16] The water exchange rate constants for $[Al(H_2O)_6]^{3+}$ and $[Al(H_2O)_5(OH)]^{2+}$ have been found to be 1.3 s^{-1} [17] and 3.1×10^4 s^{-1},[18] respectively. Thus, while Al_{13} is considerably more labile than Al^{3+} it is less labile than $[Al(H_2O)(OH)]^{2+}$. While a volume of activation, $\Delta V^\ddagger$, is only available for $[Al(H_2O)_6]^{3+}$ (+5.7 cm^3 mol^{-1}),[17] given the small size of the Al^{3+} ion, it may be reasonably assumed that water exchange at any aluminium(III) centre has considerable dissociative character.

Chemical surface processes control dissolution kinetics of most slightly soluble oxides. It is largely admitted that organic acids significantly increase the dissolution of sparingly soluble oxides and that the dissolution rate is controlled by the rate of surface chemical reactions. A reaction of this type consists of the attachment of the ligands at the surface sites, where they polarise and weaken the critical metal–oxygen bonds. The detachment of the reacting surface metal species proves to be the rate-limiting step. The reaction also consists of the transport of the detached metal complex into the bulk solution and the regeneration of the initial active site by fast protonation reactions. If the system is far away from equilibrium, the back reaction can be neglected.

Previous studies of adsorption mechanisms of organic acids on crystallised metal oxides and hydroxides have shown that adsorption does not take place uniformly on the crystal surface.[19] These observations strongly suggest that surface density of ligand and soluble metal concentration are not sufficient parameters to understand the mechanisms underlying dissolution phenomena and a more accurate description of the reacting system is necessary. Similar to the dissolution of metal hydroxides, the process of decomposition of Al_{13} has been considered as a "surface-controlled" process where the proton and the ligand-promoted processes are treated independently and parallel to each other. The twelve octahedral Al(III) centres of Al_{13} that surround the tetrahedral Al(III) centre each have one terminal water molecule and as such resemble the surface step sites in aluminium hydroxides. Al_{13} may be considered as a model oxide mineral with a homogeneous surface in which complexation only takes place at the surface sites.

A useful model has been proposed[20] where the influence of several surface species (including water, protons, hydroxide ions and other inorganic ligands) on dissolution rates is expressed as independent parallel reaction mechanisms, eqn. (5):

$$R_{net} = R_{H+} + \sum R_{Ligand} \qquad (5)$$

where the overall reaction rate R_{net} (mol $h^{-1}m^{-2}$) contains contributions from proton promoted (R_{H+}) and ligand-promoted (R_{Ligand}) dissolution. It has been demonstrated that the effect of various surface species on dissolution is a function of their surface concentration, eqn. (6):

$$R_{Ligand} = k_{L_i}[\equiv ML_i] \qquad (6)$$

so that for each ligand i, the rate of ligand-promoted dissolution is a function of the rate constant $k_{Ligand}(h^{-1})$ and the surface concentration of metal organic surface complexes $[\equiv M\text{–}L_i]$ (mol m^{-2}).

The rate law for proton-promoted assisted decomposition of Al_{13} is given by eqn. (7):[9]

$$k_H = k_{1H}[H^+] + k_{2H}[H^+]^2 \qquad (7)$$

where $k_{1H} = 0.0333$ dm^3 mol^{-1} s^{-1} and $k_{2H} = 2.59$ dm^6 mol^{-2} s^{-1}.

At the pH of the current investigation, the proton-promoted dissociation reaction would have a half-life of *ca.* 116 h. It is clear from the data in Table 1 that the contribution of the proton-promoted dissociation of Al_{13} is insignificant and may be discounted in any discussion of the mechanism.

In a previous investigation Amirbahman *et al.* investigated the mechanism of the ligand-promoted decompostion of Al_{13}.[14] However, in their experiments they always had an excess of Al^{3+} over ligand. Combining the highest concentration of ligand (1.3×10^{-3} mol dm^{-3}) with the highest and lowest Al_{13} concentrations used, one obtains ligand/Al^{3+} ratios of 0.39 and 0.66, respectively. The experiments consisted of mixing the Al_{13} and the ligand *in situ* and then observing the influence of hydrogen ion concentration on the rate of decomposition. Their modelling experiments were interpreted in terms of eqn. (8)–(10) [their eqn. (12)–(14)]:

$$R_L = -k_{La}[Al_{13}L^{5+}] \quad (8)$$

$$R_L = -k_{La}K_{Al_{13}-L}[Al_{13}{}^{7+}][L^{2-}] \quad (9)$$

$$k_{La} = k_{L1}[H^+] + k_{L2}[H^+]^2 \quad (10)$$

where R_L is the rate of ligand-promoted decomposition of Al_{13}, K_{Al13-L} is the stability constant of the Al_{13}–ligand complex, and k_{L1} and k_{L2} represent terms first- and second-order in hydrogen ion concentration, respectively.

The values of $k_{L1}K_{Al13\text{-}L}$ varied over *ca.* five orders of magnitude while the values of $k_{L2}K_{Al13\text{-}L}$ varied by *ca.* seven orders of magnitude. Previous work by Sullivan *et al.*[21] showed that for water exchange on Al(III)–salicylate and Al(III)–sulfosalicylate complexes, a linear relationship existed between log $k_{exchange}$ and the basicity of the coordinated ligand as expressed by a Lewis basicity index (BI) given by eqn. (11):

$$BI = (pK_{a1} + pK_{a2})/2 \quad (11)$$

where pK_{a1} and pK_{a2} are the pK_a values of the groups coordinated to the metal. The higher the basicity index, the more rapid the rate of water exchange. For most of the ligands studied, Amirbahman *et al.* also found a good correlation between the basicity of the ligand and the rate of decomposition. However, the more acidic ligands gave rise to more rapid rates of decomposition. They ascribed this to the fact that ring closure rather than solvent exchange was rate determining.

The experiments described here differ substantially from those described by Amirbahman *et al.* Firstly, a minimum of a five-fold excess of ligand over total Al^{3+} concentration was used. Secondly, the kinetic measurements determined the rate of reaction of the ligand with the Al_{13} moiety, rather than its rate of decomposition following complex formation as described by Amirbahman *et al.* Previous work by Sullivan *et al.*[21] and Casey *et al.*[22] show that the coordination of a ligand to a metal significantly labilises the remaining water molecules such that attack by a second ligand should be more rapid. Incorporation of a second ligand results in even greater labilisation of the solvent.[22] Thus, in the current work where the ligand is always in excess, it is to be expected that the binding of the first ligand will be rate determining. The mechanism outlined in Scheme 1 is in accord with this hypothesis.

Whereas the Amirbahman data could be interpreted in terms of the basicity of the ligands, the current data show no dependence on the basicity of the ligands as indicated by their pK_a values. The rate constants for salicylic acid (BI = 9.3), maltol (BI = 8.5), gallic acid (BI = 8.44) and gallic acid methyl ester (BI = 11) are all within a factor of 2. That this is so is hardly surprising in view of the fact that the data are readily interpreted in terms of the modified Eigen–Wilkins–Tamm mechanism outlined in Scheme 1.

Catechol and L-dopa have the slowest rates of reaction with Al_{13}. These are the two ligands having the highest basicity indices, 11.1 and 11.6, respectively. Thus, under the experimental conditions of the present work, the uncomplexed ligands are fully protonated. Previous work has shown that in general protonated ligands are relatively poor entering groups.[23,24] This is due to: (1) strong intramolecular hydrogen bonds, which convert the protonated ligand into a poor entering group and (2) the energetics of proton release from a unidentate intermediate, which may slow down the rate of ring closure (proton-controlled ring closure). Furthermore, in the case of such ligands, it has been shown that complex formation can be viewed as metal catalysed proton transfer.[25] It is to be expected that those ligands having the highest basicity indices would be most affected by these factors.

Examination of the data in Table 2 shows that the second-order rate constants for the slowest (catechol) and the fastest (chlorogenic acid) reactions differ by a factor of *ca.* 20. The higher rate constant for chlorogenic acid is consistent with the data obtained for its reaction with iron(III)[26] where it was also found to be the most reactive phenol-based ligand in complex formation reactions. For complex formation reactions that proceed by an interchange-dissociative mechanism (I_d) of the Eigen–Wilkins–Tamm type, eqn. (12)[27] usually gives a good approximation of the rate of complex formation k_f.

$$k_f = (3/4)k_sK_o \quad (12)$$

In eqn. (12), k_s is the solvent exchange rate constant and K_o is the outer-sphere association constant. The statistical factor 3/4 represents the fact that not every dissociation of a solvent molecule will lead to complex formation.

Arising from this, the dimensionless parameter R, given by eqn. (13):

$$R = (4/3)k_f/k_sK_o \quad (13)$$

is often used to evaluate the 'normality' of complex formation reactions. If substitution is 'normal', R should have a value close to unity. A reasonable suggestion is that in the case of Al_{13}, every loss of water from any of the 12 η^1-OH_2 sites will lead to complex formation such that the 3/4 statistical factor may be dropped and $k_f = k_sK_o$. Given that the water exchange rate constant (k_s) on Al_{13} is 1100 s^{-1} [16] and that the outer-sphere equilibrium constant (K_o) for reaction of an uncharged ligand is 0.3 mol^{-1} dm^3, a normal rate constant for reaction of Al_{13} with an uncharged ligand may be calculated to be 330 dm^3 mol^{-1} s^{-1}.

Table 2 shows the ratio of k_2(expt)/k_2(calc) for all the ligands with the exception of gallic acid, which did not show simple second-order kinetics. It is clear that the rates of complex formation of Al_{13} with salicylic acid, maltol, gallic acid methyl ester and chlorogenic acid are all relatively 'normal'

Table 2 Summary of kinetic data for reaction of ligands with Al_{13} in aqueous solution at 25 °C and I = 1.0 M NaCl

Ligand	λ/nm	k_1/s^{-1}	k_2/dm^3 mol^{-1} s^{-1}	k_2(expt)/k_2(calc)
Catechol	293	0.19 ± 0.004	23.0 ± 0.8	0.07
L-Dopa	250	0.094 ± 0.001	33.3 ± 0.7	0.10
Salicylic acid	340	0.050 ± 0.003	119 ± 3.4	0.36
Maltol	340	0.11 ± 0.02	96.6 ± 0.6	0.29
GAME	320	0.042 ± 0.004	192 ± 6.8	0.58
Chlorogenic acid	425	0.098 ± 0.068	489 ± 16.2	1.48
Gallic acid	320		$k_{obs} = 0.253 + 61.4[L] + 3.86 \times 10^4[L]^2$	

based on the criteria outlined above. This is similar to the results obtained for reaction of $Al(OH)^{2+}$ with a series of ligands.[28] Given that the rates of exchange of the less reactive and more reactive hydroxyl groups on Al_{13} are 1.6×10^{-5} and 1.6×10^{-2} s^{-1}, respectively,[16] this is a rather surprising result. However, it has been argued that only a single proton is required to delocalise an electron pair from a μ_4-O group and apparently a single weakened μ_4-O group completely destabilises the Al_{13} species. Such protonation could be readily achieved during step 3 of the mechanism shown in Scheme 1. This would also explain why only a single reaction step is observed as all the Al(III) species released would contain at least one coordinated OH group and the rate of solvent exchange on $[Al(H_2O)_5(OH)]^{2+}$ is 3.1×10^4 s^{-1};[18] this is considerably greater than that on the Al_{13} species.

The fact that the rate constants for reaction of Al_{13} with salicylic acid and maltol are similar provides an insight into the manner in which an incoming ligand views the aluminium(III) centre. At the pH of the investigations, the carboxyl group of salicylic acid ($pK_a = 2.81$) would be almost completely dissociated. Using the Eigen–Fuoss equation[29] to calculate the outer-sphere association constant, it is readily shown that if it appears to the attacking ligands as a +7 centre, then the rate constant for reaction of Al_{13} with salicylic acid monoanion should be *ca.* 40 times greater than its rate of reaction with maltol. Alternatively, if it is assumed that the positive charge on Al_{13} is distributed over all 13 aluminium atoms and the aluminium centre is viewed as having an effective charge of +0.54, the rate constants should be broadly similar as is observed.

The rate constant for reaction of Al_{13} with salicylic acid is *ca.* 5 times greater than the rate of reaction with catechol. Based on their infrared spectroscopy data, Molis *et al.* have reported that salicylate forms only a monodentate complex with Al_{13}.[19] However, Amirbahman *et al.* have argued that decomposition of Al_{13} can only be brought about by ligands bound in a bidentate fashion.[14] The mechanism in Scheme 1 is consistent with this hypothesis. The origin of the enhanced rate constant for salicylic acid must lie in the greater ability of the carboxylic acid group to promote dissociation of the Al_{13} oligomer. It is interesting to note that despite the fact that maltol ($pK_a = 8.5$) is fully protonated at the pH of the investigations, its reactivity is very similar to that of salicylic acid.

Conclusion

Removal of aluminium(III) from the Al_{13} oligomer is quantitative under the conditions of the current experiments. In view of the fact that apart from the reaction with gallic acid, only a single exponential is observed, it appears that removal of the first aluminium is rate determining and that subsequent reactions are rapid. This is also confirmed by global analysis of spectra-kinetic data, which clearly shows that only two absorbing species are involved, namely the ligand and the resulting aluminium(III) complex. It has been shown that Al_{13} is considerably more labile than Al^{3+} with respect to its reactions with phenol based organic ligands. The results show that in the presence of organic ligands of the type investigated in this work, Al_{13} may not be very stable in the environment as its decomposition is clearly promoted by their presence.

Experimental

Solutions of aluminium trichloride, prepared from $AlCl_3$ (Aldrich), were standardised by addition of an excess of standardised EDTA, followed by back titration with a standard solution of Zn^{2+}(aq) prepared from $ZnSO_4 \cdot 7H_2O$ using Solochrome Black indicator. The Al_{13} oligomer was prepared in a temperature-controlled reaction vessel as described by Furrer *et al*:[9] 25 mL of 2 mol dm^{-3} NaCl was placed in the vessel and diluted with 18 mL of distilled water; 2 mL of 0.125 mol dm^{-3} $AlCl_3$ was then added and pH adjusted to a value of 2.0 utilising perchloric acid (Riedel-de Haën). Aluminium(III) does not form any complexes with Cl^-.[30] Addition of 5 mL of 0.1 mol dm^{-3} NaOH neutralised the solution to a final pH value of 4.3. The temperature was raised to 45 °C and allowed equilibrate for 1 h, in order to accelerate the formation of the Al_{13} oligomer. The resulting solution produced 5 mM total Al(III) in 1 mol dm^{-3} NaCl. Because of its symmetric structure, the dissolved Al_{13} species is detectable by ^{27}Al-NMR spectroscopy and exhibits a sharp peak at 62.5 ppm with respect to the mononuclear hexaquo ion.[31] The solution was then buffered by addition of 0.05 mol dm^{-3} piperazine-*N*,*N*′-bis(4-butanesulfonic acid), pipbs.[32] This resulted in a negligible change in pH on reaction with the ligands.

Solutions of catechol (BDH), chlorogenic acid (Fluka), L-dopa (Aldrich), gallic acid (H_3ga, Aldrich) and gallic acid methyl ester (H_2game, Aldrich) were all made up from deoxygenated stock solutions in 1 mol dm^{-3} NaCl and pH adjusted to a value of 4.3 using perchloric acid as the source of hydrogen ions. Spectroscopic investigations showed that over the time-span of the experiments (*ca.* 1 h), no decomposition was evident in solutions maintained at pH 4.3. Solutions of the polyphenols obeyed Beer's law over the concentration range used in the experiments, thus confirming the absence of oligomerisation.

The complex formation reactions were studied with the ligand in pseudo-first-order excess with a total aluminium(III) concentration of 0.5 mM. A Hi-Tech SF-20 stopped-flow apparatus was employed for most of the kinetic analysis. This was interfaced to a PC and rate constants were calculated from the experimental absorbance data using the Olis KINFIT routines,[33] employing *ca.* 500 data points. Time-dependent spectra were acquired using a Hewlett Packard 8453A diode array spectrophotometer equipped with a Hi-Tech SFA-20 rapid kinetics accessory. Global analysis was carried out using SPECFIT/32®,[13] which is based on the published work of Maeder and Zuberbühler.[34]

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