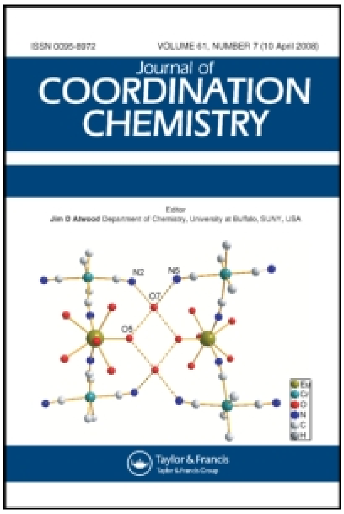

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COMPLEXES OF Al(III) WITH HYDROXYAROMATIC LIGANDS

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In order to assess the aluminium binding ability of humic and fulvic acids, important organic soil constituents, a pH-potentiometric study was made of the proton and aluminium(III) complexes of various bi-, tri- and tetradentate catechol and salicylic acid derivatives at 25°C and at an ionic strength of 0.20 mol dm^{-3} (KCl). The stability data revealed that at low pH the salicylate function, and at high pH the catecholate function, is preferentially bound to the aluminium ion. In the intermediate pH range, mixed hydroxo complexes and other di/oligomeric species are also formed. With an increase of the number of available coordinating sites in the molecule, the tendency to oligomeric complex formation increases, while the tendency to metal ion hydrolysis decreases.

KEY WORDS: Al(III), catechol derivatives, salicylic acid derivatives, stability constants

INTRODUCTION

By acidifying surface waters, acid rain releases metals such as aluminium that are more toxic to aquatic life than the acidity itself.[1] Aluminium leached into the environment does not occur solely as free Al^{3+} and hydroxo complexes, but also forms water-soluble complexes of the different degradation products of larger organic soil constituents such as humic and fulvic acids. Catecholic and salicylic compounds can be regarded as ligands serving as good models of these soil acids. Such phenolic compounds are able to bind metal ions fairly strongly, especially hard ions such as Al^{3+}, to form water-soluble complexes. This complexing contributes to an increase in the concentration of aluminium in soil solutions and natural waters. A question

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relating to the increasing availability of Al(III) as a result of acid rain is its identification as a causative or associative agent in various human disorders.[2,3] In earlier papers we investigated the Al^{3+}-binding ability and strength of certain small biomolecules, such as catecholamines,[4,5] adenine-nucleotides[6] and 2,3-diphosphoglycerate,[7] which occur at rather high concentrations in various body fluids. We now study the interaction of Al^{3+} with different catecholate and salicylate derivatives containing two, three or four phenolate and/or carboxylate binding sites in chelatable positions. Complex formation between Al(III) and catechol has been the subject of a number of investigations,[8–16] all of which indicate the formation of three mononuclear complexes, AlA^{+}, AlA_2^{-} and AlA_3^{3-}, as the main species, and some other mononuclear[15,16] and/or polynuclear[12] mixed hydroxo complexes as minor species. Salicylate is known to form weaker complexes with Al(III) than catecholate[10,15,17] and there is also a higher tendency for mixed hydroxo complex formation and metal ion hydrolysis.[17] Potentially terdentate dihydroxybenzoic acid derivatives, which contain additional phenolate or carboxylate donors besides the catecholate or salicylate chelating sites, have scarcely been studied.[13,18,19]

This paper reports results of a pH-potentiometric study of the equilibrium reactions between Al(III) and catechol (Cat), salicylic acid (Sal), different dihydroxybenzoic acids (DHB), such as 2,X-DHB (X = 3, 4, 5 or 6), 3,4-DHB, trihydroxybenzoic acid (2,3,4-THB) and 2,3-dihydroxyterephthalic acid (2,3-DHTP).

EXPERIMENTAL

The ligands were of the best quality available from Aldrich Chemical Co. and were used without further purification. The purities of the ligands and the exact concentrations of their solutions were checked and measured by the Gran method.[20] An Al^{3+} stock solution was prepared from $AlCl_3.6H_2O$ and its concentration was checked gravimetrically *via* the oxinate. Potentiometric titrations were performed with a Radiometer PHM 64 pH-meter and TTA 80 titration unit equipped with G2040B glass and K4040 calomel electrodes. The ligand concentration was generally 5×10^{-3} mol dm^{-3}, and the ligand to metal mole ratios were 10, 8, 5, 4, 2 and 1 to 1. In the case of 2,3-DHTP, the ligand concentration was 8×10^{-4} mol dm^{-3}, because its poor solubility. At ligand to Al(III) ratios of 8 or greater, no precipitation occurred, but at lower ratios the titration curves could be treated quantitatively only to pH ~5-6 as at these pH values a foam was first formed, which was followed by the development of a fine precipitate. With 2,3-DHTP and 2,3,4-THB, precipitation occurred only at ratios of 1:1 or 1:2 at pH ~7. Within the safe pH range, constancy of pH could be achieved in a reasonable time (1–3 min), and the fit between the experimental (30–40 points/titration) and calculated titration curves was fairly good. For the hydroxo complexes of Al(III), the stability constants (log β) assumed[21] were -5.52 for AlH_{-1}^{2+}, -7.70 for Al_2H_{-2}, -13.57 for $Al_3H_{-4}^{5+}$, -109.1 for $Al_{13}H_{-32}^{7+}$ and -23.46 for AlH_{-4}^{-}. Experiments were performed under an argon atmosphere at 25.0°C, with the ionic strength adjusted to 0.20 mol dm^{-3} with KCl. To convert pH-meter readings to hydrogen ion concentrations the electrode system was calibrated by the method of Irving *et al.*[22]

The concentration stability constants $\beta_{pqr} = [M_pA_qH_r]/[M]^p[A]^q[H]^r$ were calculated from the pH-metric titration curves by means of the PSEQUAD computer program.[23]

RESULTS AND DISCUSSION

As regards the donor group arrangement within the molecules of the ligands studied, 3,4-DHB, which contains a separate carboxylate donor besides the catecholate function, can be regarded as a Cat derivative. For a similar reason 2,X-DHB (X = 4, 5 or 6) may reasonably be assumed to be Sal derivatives, while 2,3-DHB, 2,3,4-THB and 2,3-DHTP contain both catecholate and salicylate functions, and can thus behave and bind metal ions in the same way as both Cat and Sal.

Al(III)-Catechol and Al(III)-3,4-Dihydroxybenzoic Acid Systems

The overall stability constants of the Cat and 3,4-DHB complexes, and some derived equilibrium constants characteristic of various part-processes of complex formation, are tabulated in Table 1. The symbol A designates the 2- species for Cat and the 3- species for 3,4-DHB. The dissociation constant for the very weakly acidic second phenolic hydroxy group could be determined only with much larger uncertainty, in a way described earlier.[24] Taking into consideration the differing ionic strengths, our

Table 1 Protonation constants (log K) and aluminium(III) complex formation constants (log β) for catechol and 3,4-dihydroxybenzoic acid at 25.0 ± 0.1°C and I = 0.20 mol dm^{-3} (KCl).

row		Cat(H_2A)	3,4-DHB(H_3A)
	Proton complexes		
1	OH	13.0(2)	13.0(2)
2	OH	9.28(2)	8.70(1)
3	COOH		4.28(1)
	Al(III) complexes		
4	AlAH		21.09(1)
5	AlA	16.20(2)	16.47(2)
6	AlA_2	29.26(6)	29.38(4)
7	AlA_3	37.95(7)	38.35(5)
8	AlA_2H_{-1}		
9	AlA_2H_{-2}		
10	$Al_2A_2H_{-2}$	24.05(6)	25.03(9)
11	$Al_2A_2H_{-3}$		
	Fitting[a] × 10^3	7.82	7.94
	Number[b]	151	206
12	log K_{AlA_2}	13.06	12.91
13	log(K_{AlA}/K_{AlA_2})	3.14	3.56
14	log K_{AlA_3}	8.69	8.93
15	log(K_{AlA_2}/K_{AlA_3})	4.37	4.98
16	$Al + H_2A = AlA + 2H$	−6.08	−5.23
17	$AlA + H_2A = AlA_2 + 2H$	−9.22	−8.79
18	$AlA_2 + H_2A = AlA_3 + 2H$	−13.59	−12.77
19	$2AlA = Al_2A_2H_{-2} + 2H$	−8.35	−7.91

[a] The average difference between the experimental and the calculated titration curves expressed in cm^3 of the titrant. [b] Number of titration points.

data for the main species AlA, AlA_2 and AlA_3 are in reasonably good agreement with most of the data published so far.[10,12–16] The agreement is exceptionally good with the results of Martell *et al.*,[14,15] especially if one compares the basicity-adjusted stability constants (rows 16–18 in Table 1), which take into account the differences in basicity of the coordinating donor groups. These are −6.08, −9.18 and −13.52 for the mono, bis and tris complexes, respectively.[15] The fit of the experimental titration data, particularly at lower ligand excesses, was improved significantly by the assumption of mixed hydroxo complexes. Practically the same fit was obtained when any of the three previously postulated monohydroxo species, AlA(OH),[16] $Al_2A_2(OH)_2$[20] or $Al_3A_3(OH)_3$,[12] was assumed in the calculation. It is true that pH-potentiometric data are hardly sufficient to distinguish between these monomeric or oligomeric hydroxo complexes. Similarly, as suggested for the catecholamines L-Dopa and tiron,[25] we propose the formation of a bis hydroxo-bridged dimeric species, $Al_2A_2(OH)_2$.

As the data in Table 1 reveal, catechol forms very stable (O^-, O^-)-coordinated chelates with *ortho*-diphenolate oxygens and, at a high enough ligand excess (> 1:6), complex formation can prevent the hydrolysis of Al(III) and precipitation of $Al(OH)_3$ at pH ~6. Formation of the species $Al_2A_2H_{-2}$ (or more precisely $Al_2A_2(OH)_2$) is indicative of the high tendency of Al(III) to undergo hydrolysis. At pH ~8 the precipitate obtained at a lower ligand excess redissolves, through formation of the octahedral, hexacoordinated tris(catecholato) complex AlA_3^{3-} in the case of a threefold or higher ligand excess (see Fig. 1), or formation of the tetrahedral tetrahydroxo complex $Al(OH)_4^-$ at a lower ligand excess.

Because of the presence of a separate carboxylic group in 3,4-DHB, this ligand can also form an (O^-, O^-)-coordinated, protonated 1:1 complex $AlAH^+$, in which

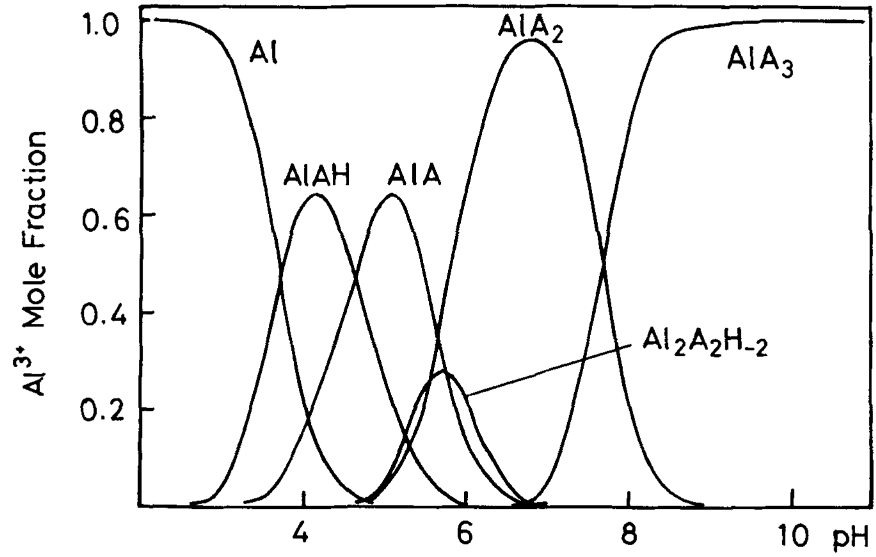


Figure 1 Concentration distribution curves for the complexes formed in the aluminium(III)-3,4-DHB system; $C_{Al} = 0.0005$ mol dm^{-3}, $C_{ligand} = 0.004$ mol dm^{-3}.

the carboxylic group remains protonated (see Fig. 1). This species has a pH of 4.62, similar to that of the free ligand (see Table 1). A comparison of the basicity-adjusted stability constants of Cat and 3,4-DHB reveals the slightly higher stability of the Al(III) complexes of the latter ligand, due to the +I inductive effect of the carboxylate group. The extra negative charge in the 3,4-DHB molecule, on the other hand, results in greater electrostatic hindrance to coordination of the second or third ligand molecule, as indicated by the larger $\log(K_{AlA}/K_{AlA_2})$ and $\log(K_{ALA_2}/K_{ALA_3})$ values. These findings correspond fully to recent conclusions concerning the basic coordination behaviour of the catecholamines.[25]

It is also worthwhile to note that the separate carboxylate in 3,4-DHB cannot compete with the chelating catecholate function in the binding of Al(III) and thus only purely (O^-O^-)-coordinated complexes are formed. The same was found for corresponding VO(IV) complexes.[26] These findings are in contrast, however, with complex-forming ability with copper(II) ion,[27] with which 3,4-DHB exhibited real ambidentate character forming various multinuclear complexes *via* simultaneous metal ion coordination at both the catecholate and the separate carboxylate binding sites.

Al(III)-Salicylic Acid and Al(III)-2,X-Dihydroxybenzoic Acid (X = 4, 5 or 6) Systems

The ligands 2,X-DHB can be regarded as Sal derivatives with an extra separate phenolic hydroxy group within the molecule. Thus, great similarity with one another and with Sal itself can be expected in their Al(III)-binding capabilities. All these ligands contain two protons which dissociate in the measurable pH range, although the DHB derivatives have three acidic functional groups. It has been proved by detailed pH-metric and spectrophotometric measurements,[28] however, that the OH groups *ortho* to the carboxylate in the 2,X-DHB ligands do not dissociate until pH ~13.4, due to the strong intramolecular hydrogen bond between the COO^- and OH groups. In the case of Sal, the dissociation of this phenolic OH could just be detected and determined only with a large experimental error (*c.f.* with pH_{OH} for Cat derivatives in Table 1).

The aluminium(III)-ligand titration curves of these Sal derivatives could be fitted equally well by two speciation models; the difference between the two was that the tris complex AlA_3 (assumed in Ref. 10) could be substituted by a mixed hydroxo complex, AlA_2H_{-1}, or more precisely $AlA_2(OH)$ (assumed in Ref. 17). If both species were assumed simultaneously in the calculation, the tris complex was always rejected. Although in principle the parallel existence of these two species seems to be a reasonable assumption, the formation of the tris complex is less likely; as the log K_{AlA_3} values show, the coordination ability of the third ligand molecule is very ligand dependent and in some cases is even higher than that of the second ligand (see the last row in Table 2). This cannot be explained chemically. Thus we propose the acceptance of Model 1 for all Sal derivatives studied, in agreement with the speciation model suggested by Öhman and Sjöberg[17] for the Al(III)-Sal system.

The speciation diagrams (as an illustration, that for the system Al(III)-2,5-DHB is given in Fig. 2) show that the major species in the acidic pH range in all systems are the mono and bis complexes involving salicylate type, (COO^-, O^-)-coordination, AlA and AlA_2. Because of the acidity differences between Sal and DHB derivatives (see above), the stoichiometries of the complexes of the latter ligands are more precisely $Al(HAH_{-1})$ and $Al(HAH_{-1})_2$, as the separate phenolic OH groups in position X are

Table 2 Protonation constants (log K) and aluminium(III) complex formation constants (log β) for salicylic acid and 2,X-dihydroxybenzoic acid at 25.0 ± 0.1°C and $I = 0.20\,\mathrm{mol\,dm^{-3}}$ (KCl).

row		Sal(H_2A)	2,4-DHB(H_2A)	2,5-DHB(H_2A)	2,6-DHB(H_2A)
	Proton complexes				
1	2-OH	13.4(2)	>14	>14	>14
2	X-OH		8.64(1)	10.06(2)	13.1(2)
3	COOH	2.79(1)	3.09(1)	2.75(1)	1.0(2)
	Al(III) complexes				
	Model I				
4	AlA	13.22(1)	8.71(1)	9.74(1)	12.79(1)
5	AlA_2	23.73(4)	15.03(3)	17.17(4)	23.67(4)
6	$Al_2A_2H_{-2}$	17.9(2)	9.1(3)	11.5(2)	17.2(3)
7	AlA_2H_{-1}	16.60(12)	7.21(11)	9.97(8)	16.46(9)
	Fitting[a] × 10^3	7.87	9.95	13.2	10.7
	Number[b]	115	214	189	190
8	log K_{AlA_2}	10.51	6.32	7.43	10.88
9	log(K_{AlA}/K_{AlA_2})	2.71	2.39	2.31	1.91
10	$Al + H_2A = AlA + 2H$	−2.97	−3.01	−3.07	−1.31
11	$AlA + H_2A = AlA_2 + 2H$	−5.68	−5.40	−5.38	−3.22
12	$Al + HA = AlA + H$	−0.18	0.07	−0.32	−0.31
13	$AlA + HA = AlA_2 + H$	−2.89	−2.32	−2.63	−2.22
14	pK_{AlA_2}	7.13	7.82	7.20	7.21
15	$2AlA = Al_2A_2H_{-2} + 2H$	−8.5	−8.3	−8.0	−8.4
	Model II				
16	AlA	the same as in Model I			
17	AlA_2	the same as in Model I			
18	$Al_2A_2H_{-2}$	the same as in Model I			
19	AlA_3	32.55(14)	18.32(15)	22.98(9)	31.80(15)
	Fitting[a] × 10^3	7.98	10.0	13.4	11.5
20	log K_{AlA_3}	8.82	3.29	5.81	8.13
21	log(K_{AlA_2}/K_{AlA_3})	1.69	3.03	1.62	2.75

[a] The average difference between the experimental and the calculated titration curves expressed in cm^3 of the titrant. [b] Number of titration points.

protonated and the less acidic phenolic OH of the salicylic function is deprotonated and coordinated to Al(III). For this reason, the complex formation constants of Sal and 2,X-DHB derivatives cannot be compared directly. The good agreement of the basicity-adjusted stability constants, however, which take into account the large differences in basicity of the coordinating donor groups, strongly supports the assumption of the formation of complexes with the same (COO^-, O^-)-bonding mode. In 2,6-DHB, the carboxylic group is much more acidic than in the other ligands and its dissociation takes place at much lower pH, below that for any Al(III) complexation. Thus, these Al(III) complex formation processes involve the HA form of the ligand rather than H_2A, and hence the basicity-adjusted formation constants including HA give more comparable data (see rows 12 and 13 in Table 2).

Without a high enough ligand excess (< 1:6), $Al(OH)_3$ precipitates at pH ~6-7 while at above this metal ion to ligand ratio the bis salicylato complexes lose a proton at around pH 7-7.5, a fact which can presumably be ascribed to the ionization of a

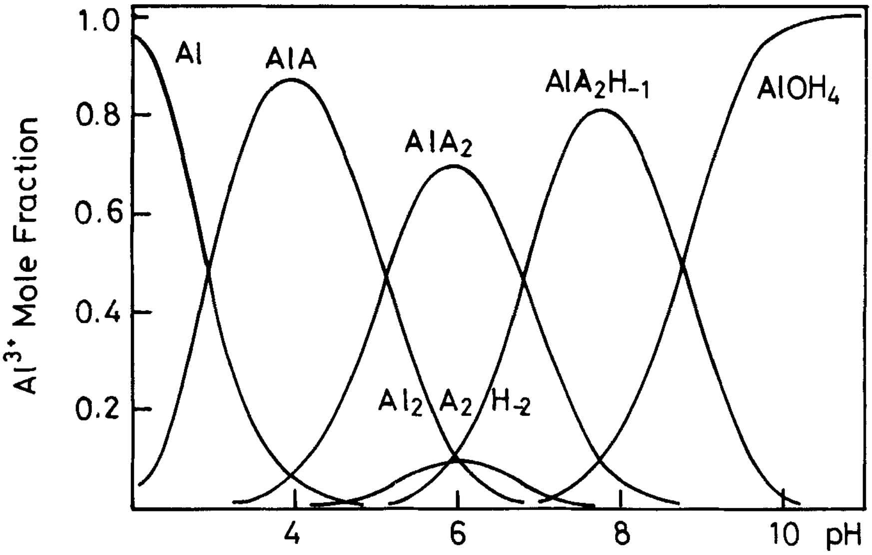


Figure 2 Concentration distribution curves for the complexes formed in the aluminium(III)-2,5-DHB system; $C_{Al} = 0.0005$ mol dm^{-3}, $C_{ligand} = 0.004$ mol dm^{-3}.

coordinated water molecule; dissociation of the non-coordinated phenolic OH of the DHB derivatives would take place only at higher pH. The pK values are 1.5-6 log units higher (*c.f.* rows 2 and 14 in Table 2) and Al(III) ion coordination at the separate salicylate site cannot increase their acidity so much as to allow dissociation in the pH range 7-7.5. Hydroxide ions, however, can displace the coordinated salicylate ligands and through the mixed hydroxo complex $AlA_2(OH)$, finally, the very stable tetrahedral tetrahydroxo complex, $Al(OH)_4^-$, is formed almost exclusively above pH ~10.

Al(III)-Catechol-Salicylic Acid System

Due to the donor atom arrangement, 2,3-DHB, 2,3,4-THB and 2,3-DHTP are typical ambidentate ligands, which can form both salicylate and catecholate-type complexes. To obtain more information on the competitive metal-binding properties of these chelating functions, the mixed ligand system of Cat (A) and Sal (B) with Al(III) was studied. The speciation curves depicted in Figure 3 indicate that at low pH (<5.5) the salicylate (COO^-, O^-)-type complexes AlB and AlB_2 are the dominant species, while at high pH (>8), where proton competition at the catechol site is much weaker, catecholate (O^-, O^-)-type complexes are the main species. In the intermediate pH range, bis and tris mixed ligand complexes are formed at slightly higher concentrations than would be expected on a statistical basis (see the derived equilibrium constants in Table 3, *e.g.*, $\Delta \log \beta_{AlAB} = +0.12$). It can also be seen from Figure 3 that formation of the tris complex containing two Cat and one Sal ligands is much more favoured than that containing two Sal and one Cat (*c.f.* rows 10 and 12 in Table 3). This is in agreement with expectations based on differences in complex-forming properties of the two ligands (see above).

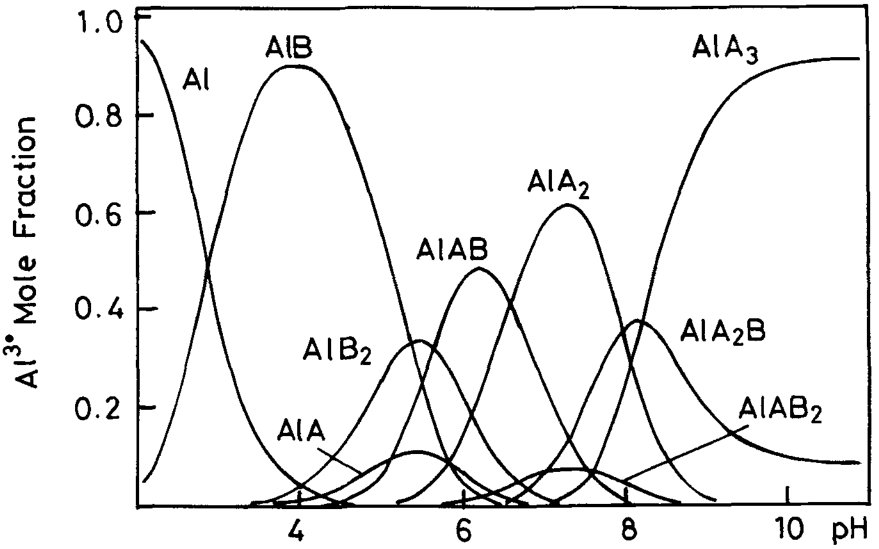


Figure 3 Concentration distribution curves for the complexes formed in the aluminium(III)-Cat(A)-Sal(B) system; $C_{Al} = 0.0005$ mol dm^{-3}, $C_{ligand} = 0.004$ mol dm^{-3}.

Al(III)-2,3-Dihydroxybenzoic Acid, Al(III)-2,3,4-Trihydroxybenzoic Acid and Al(III)-2,3-Dihydroxyterephthalic Acid Systems

Although 2,3-DHB contains three, and 2,3,4-THB and 2,3-DHTP contain four acidic groups, only two of these groups in each ligand lose protons in the measurable pH range, due to the formation of intramolecular hydrogen bonds between the —COO^- and phenolic-OH groups (in 2,3-DHB and 2,3-DHTP) and the two *ortho*-phenolic-OH groups (in 2,3,4-THB). The aluminium(III)-ligand titration curves in Figure 4 indicate that the potentially tetradentate ligands 2,3,4-THB and 2,3-DHTP have a much stronger ability to keep Al(III) in solution than the previously discussed bidentate salicylates and catecholates or the terdentate 2,3-DHB, as no precipitation is observed even at metal ion to ligand ratios of 1:2 or higher. The considerable differences between the titration curves suggest different complex-forming properties of the ligands. When the Al(III)-ligand titration data were evaluated, it was generally found that the assumption of salicylate and/or catecholate-type monomeric complexes was not enough for a fit to the titration curves (especially at a lower ligand excess). The assumption of various polynuclear species, however, improved the fit significantly, *i.e.*, an increase in the number of potential binding sites per molecule increases the tendency to polynuclear complex formation, but decreases the tendency to metal ion hydrolysis.

It was also found that the titration curves of the system Al(III)-2,3-DHTP at different metal ion to ligand ratios exhibited sharp pH jumps (from pH ~4.5 up to pH ~8.5) on liberation of two extra protons per Al(III) independently of the metal ion to ligand ratio. This strongly suggests the dominant formation of a species with the stoichiometry $AlAH_{-2}$. In monomeric form, this would mean the exclusive formation of either catecholate-type (O^-, O^-) complexes or monohydroxo

Table 3 Formation constants (log β) and some derived equilibrium constants for the complexes formed in the Al(III)-Catechol(A)-Salicylic acid(B) mixed ligand system at 25.0 ± 0.1°C and I = 0.20 mol dm^{-3} (KCl).

row		
1	AlAB	26.92(5)
2	$AlAB_2$	35.2(5)
3	AlA_2B	37.12(16)
4	$\Delta \log \beta_{AlAB}$[a]	+0.12
5	AlCat + Sal = AlCatSal	10.72
6	AlSal + Sal = $Al(Sal)_2$	10.51
7	AlSal + Cat = AlSalCat	13.70
8	AlCat + Cat = $Al(Cat)_2$	13.06
9	AlSal + H_2Cat = AlSalCat + 2H	−8.58
10	AlCatSal + Sal = $AlCat(Sal)_2$	8.28
11	$Al(Sal)_2$ + Sal = $Al(Sal)_3$	
12	AlCatSal + Cat = $Al(Cat)_2Sal$	10.20
13	$Al(Cat)_2$ + Cat = $Al(Cat)_3$	8.69
14	AlSalCat + H_2Cat = $AlSal(Cat)_2$ + 2H	−12.08

[a] $\Delta \log \beta_{AlAB} = \log \beta_{AlAB} - 0.5*(\log \beta_{AlA_2} + \log \beta_{AlB_2} + \log 4)$.

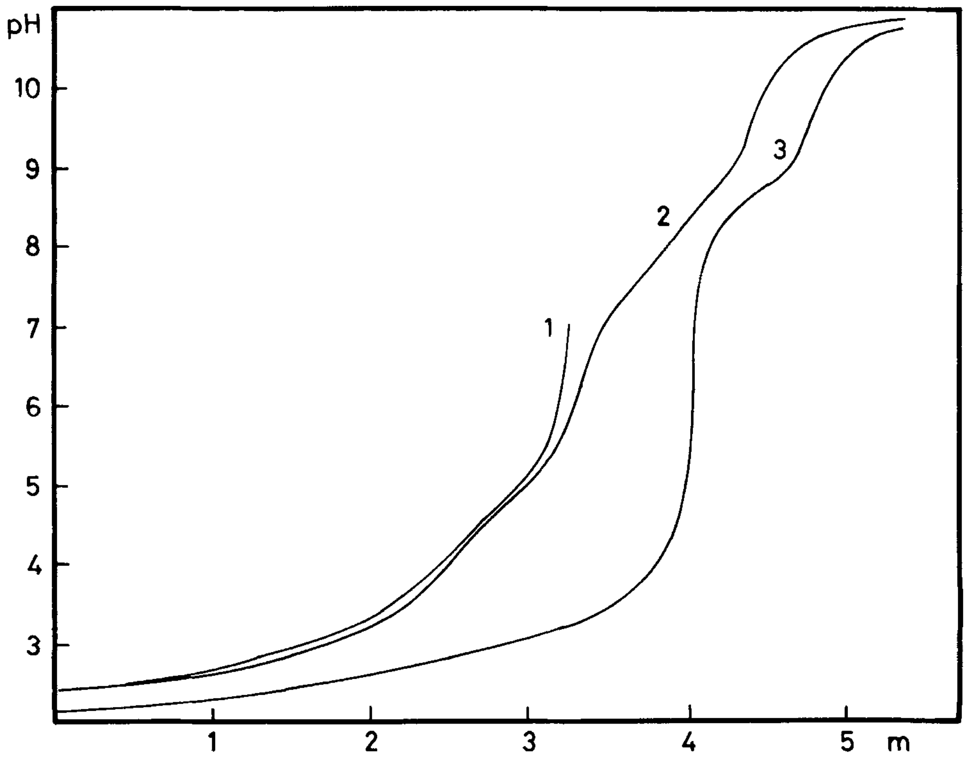


Figure 4 Titration curves for the aluminium(III)-2,3-DHB (1), -2,3,4-THB (2), and -2,3-DHTP (3) systems at a metal to ligand ratio of 2; $C_{ligand} = 0.004$ mol dm^{-3}, m = equivalents of base per mole of ligand.

salicylate-type (COO^-, O^-, OH^-) complexes, both of which are difficult to conceive. At pH 5-6, the salicylate and the salicylate-catecholate mixed bonding modes may be dominant, as can be expected from the speciation curves of the mixed ligand system Al(III)-Cat-Sal (see Fig. 3). On the other hand, a $pK_{AlAH_{-1}}$ of 4.0 would be ~ 1.5 log units smaller than the pK characteristic of the ionization of the first water molecule in the Al^{3+} aquo ion. There is no feasible reason for this large increase in acidity of the coordinated water molecules in the complex $AlAH_{-1}$. However, if dimeric/oligomeric species are assumed, the above stoichiometry can be obtained even through pure salicylate-type coordination. Thus, attempts were made to fit the titration curves with different speciation models assuming the formation of various chain ($Al_2A_2H_{-3}$, $Al_3H_3H_{-5}$) and cyclic ($Al_2A_2H_{-4}$, $Al_3A_3H_{-6}$) polymeric species. The stoichiometry $(AlAH_{-2})_n$, which implies metal ion-induced deprotonation and coordination of both weakly acidic phenolic hydroxy groups, can be achieved only through the formation of cyclic polymers. The best fit to the experimental titration data was obtained with the model given in the first column of Table 4. Although the model involving only dimeric species ($Al_2A_2H_{-3}$, $Al_2H_2H_{-4}$) resulted in practically the same fitting parameter (column 4), the formation of a cyclic dimer cannot be expected for steric reasons. The existence of a similar cyclic trimer was detected in the VO(IV)-2,3-DHTB system and its bonding mode was proved by ESR measurements. The results of the stability constant calculations, together with some derived equilibrium data, are given in Table 5, while the concentration distributions are depicted in Figures 5, 6 and 7. The following conclusions may be drawn from these data and speciation curves.

In the acidic pH range, the salicylate chelating site binds Al(III), due to much weaker proton competition than at the catecholate site. The good agreement of the basicity-adjusted stability constants of AlA and AlA_2 with those of the Sal derivatives

Table 4 Protonation constants (log K) and aluminium(III) complex formation constants (log β) for 2,3-dihydroxyterephtalic acid calculated for different speciation models at 25.0 ± 0.1°C and I = 0.20 mol dm^{-3} (KCl).

Proton complexes						
OH		>14				
COOH		2.89(2)				
COOH		1.93(6)				
Al(III) complexes						
AlA	3.90(12)	4.00(11)	3.94(12)	3.93(16)	3.90(12)	3.92(12)
$AlAH_{-1}$	0.96(3)	0.98(6)	0.98(4)	1.01(6)	1.02(5)	1.02(3)
AlA_2H_{-2}	−0.36(9)					
AlA_2H_{-3}	−8.11(15)	−8.33(17)	−8.10(12)	−8.09(16)	−8.23(17)	−8.30(22)
$AlAH_{-2}$		−3.00(4)				
$Al_2A_2H_{-2}$				−2.50(11)		
$Al_2A_2H_{-3}$	1.36(9)		1.45(9)	1.30(25)		−1.31(9)
$Al_3A_3H_{-5}$	2.27(9)				2.27(25)	2.17(18)
$Al_3A_3H_{-6}$	−2.11(12)		−2.09(12)		−2.16(2)	−2.17(12)
Fitting[a] × 10^3	6.04	8.05	6.60	6.40	6.08	6.06
Number[b]	102	102	102	102	102	102

[a] The average difference between the experimental and the calculated titration curves expressed in cm^3 of the titrant. [b] Number of titration points.

Table 5 Protonation constants (log K) and aluminium(III) complex formation constants (log β) for 2,3-dihydroxybenzoic acid, 2,3,4-trihydroxybenzoic acid and 2,3-dihydroxyterephtalic acid at 25.0±0.1°C and I = 0.20 mol dm^{-3} (KCl).

row		2,3-DHB(H_2A)	2,3,4-THB(H_2A)	2,3-DHTP(H_2A)
	Proton complexes			
1	OH	>14	>14	>14
2	OH	9.87(1)	14	14
3	OH		8.65(1)	
4	COOH	3.32(2)	3.07(1)	2.89(2)
5	COOH			1.93(6)
	Al(III) complexes			
6	AlA	10.32(1)	9.10(2)	3.90(12)
7	AlA_2	18.26(6)	15.94(9)	
8	$AlAH_{-1}$			0.96(3)
9	AlA_2H_{-1}	11.56(8)	10.26(10)	
10	AlA_2H_{-2}	1.74(8)	2.26(24)	−0.36(8)
11	AlA_2H_{-3}			−8.11(15)
12	AlA_3H_{-2}		6.79(12)	
13	$Al_2A_2H_{-2}$	13.62(22)	11.09(17)	
14	$Al_2A_2H_{-3}$	8.87(3)	6.49(5)	1.36(8)
15	$Al_2A_2H_{-4}$		−0.69(15)	
16	$Al_3A_3H_{-5}$			2.27(9)
17	$Al_3A_3H_{-6}$			−2.11(13)
	Fitting[a] × 10^3	15.1	5.67	6.04
	Number[b]	187	112	102
18	log K_{AlA_2}	7.94	6.84	
19	log(K_{AlA}/K_{AlA_2})	2.38	2.26	
20	log $K_{Al(AH_{-1})_2}$			−1.32
21	log($K_{AlAH_{-1}}/K_{AlA_2H_{-2}}$)			2.28
22	$Al + H_2A = AlA + 2H$	−2.87	−2.62	−0.92
23	$AlA + H_2A = AlA_2 + 2H$	−5.25	−4.88	
24	pK_{AlA_2}	6.70	5.68	
25	$pK_{AlA_2H_{-1}}$	9.82	8.00	
26	$pK_{AlA_2H_{-2}}$			7.75
27	$2AlA = Al_2A_2H_{-2} + 2H$	−7.02	−7.11	
28	$pK_{Al_2A_2H_{-2}}$	4.75	4.60	
29	$pK_{Al_2A_2H_{-3}}$		7.18	
30	$AlA + AH_{-1} = AlA_2H_{-1}$	1.24	1.16	
31	$AlA_2H_{-1} + AH_{-1} = AlA_3H_{-2}$		−3.47	
32	log($K_{AlA_2H_{-1}}/K_{AlA_3H_{-2}}$)		4.63	

[a] The average difference between the experimental and the calculated titration curves expressed in cm^3 of the titrant. [b] Number of titration points.

(*c.f.* rows 22 and 23 in Table 5 and rows 10 and 11 in Table 2) proves this assumption quite convincingly. In the case of 2,3-DHTP, as neither of the phenolic hydroxy groups is deprotonated in the measurable pH range, the salicylate-coordinated species have stoichiometries $AlAH_{-1}$ and AlA_2H_{-2}. The complex AlA also has the (COO^-, O^-)-bonding mode, but the other carboxylic function is protonated; $pK_{AlA} = 2.94$, which corresponds well to the pK_{COOH} values of the free ligand (see row 4 in Table 5).

The salicylate-type bis complexes lose a proton, with pK = 6.70 for 2,3-DHB, 5.68 for 2,3,4-THB and 7.75 for 2,3-DHTP. These deprotonation processes, however, are

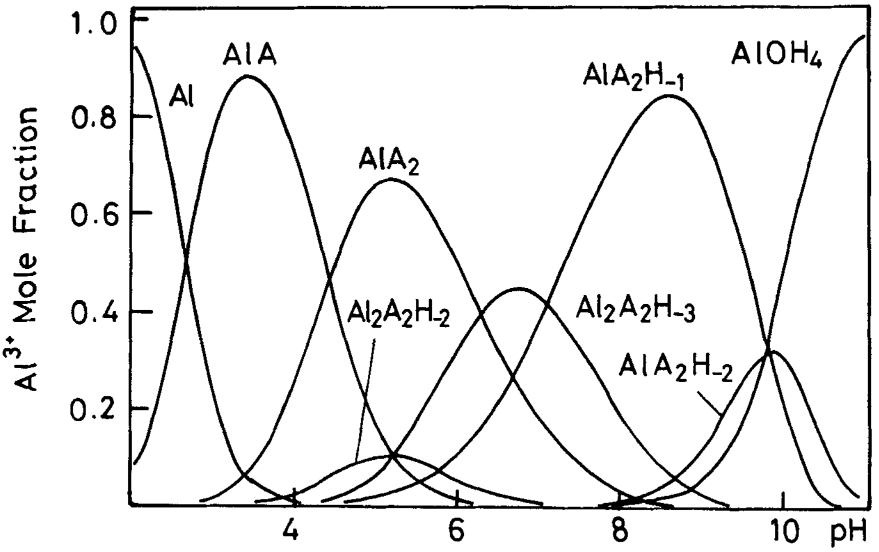


Figure 5 Concentration distribution curves for the complexes formed in the aluminium(III)-2,3-DHB system; $C_{Al} = 0.0005$ mol dm^{-3}, $C_{ligand} = 0.004$ mol dm^{-3}.

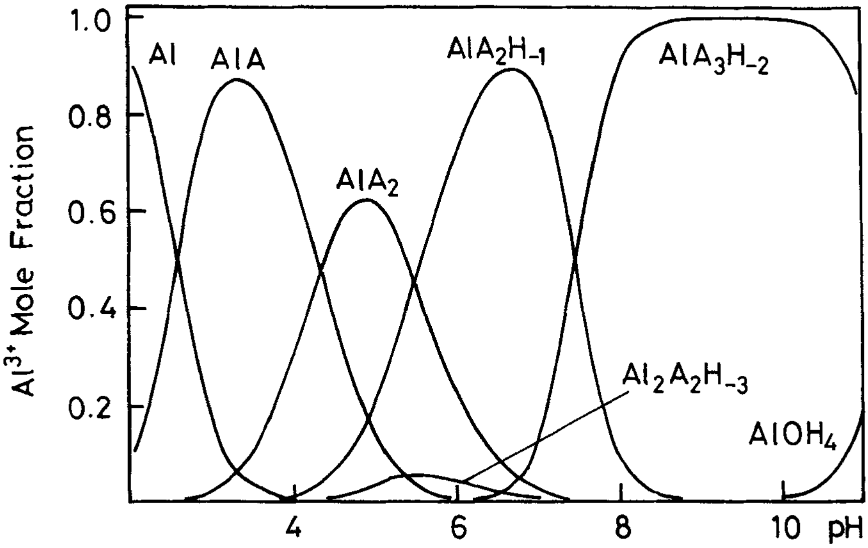


Figure 6 Concentration distribution curves for the complexes formed in the aluminium(III)-2,3,4-THB system; $C_{Al} = 0.0005$ mol dm^{-3}, $C_{ligand} = 0.004$ mol dm^{-3}.

presumably not due to mixed hydroxo complex formation reactions as in the case of the Sal derivatives 2,X-DHB, but are accompanied (at least in part) by a structural rearrangement from the purely salicylate bonding mode to the mixed (COO^-, O^-)(O^-, O^-)-bonding mode. This is supported by the good agreement of the derived

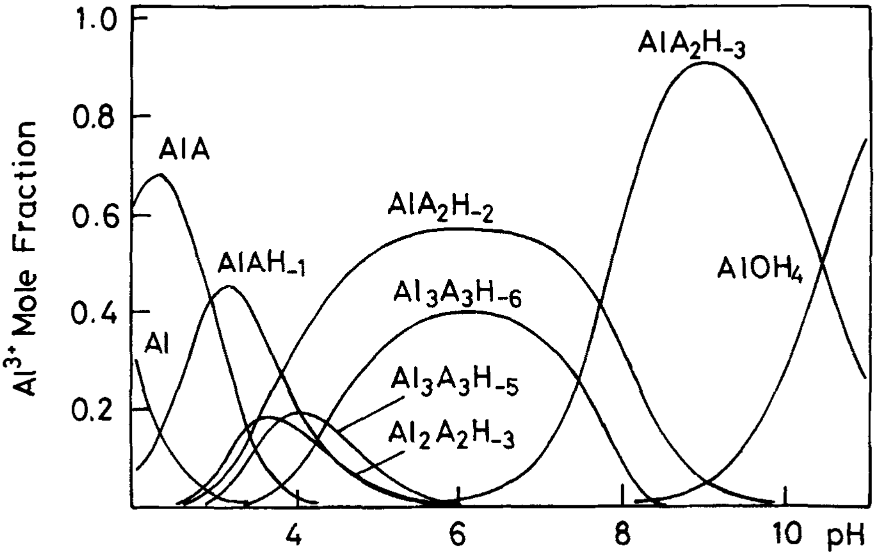


Figure 7 Concentration distribution curves for the complexes formed in the aluminium(III)-2,3-DHTP system; $C_{Al} = 0.0005$ mol dm^{-3}, $C_{ligand} = 0.004$ mol dm^{-3}.

Table 6 Some derived equilibrium constants (log K) characteristic of the formation of complexes containing the mixed (COO⁻, O⁻)(O⁻, O⁻) bonding mode in the systems studied.

row	K* $Al(COO^-, O^-) + H_2(O^-, O^-) = Al(COO^-, O^-)(O^-, O^-) + 2H^+$	
		log K*
1	Sal-Cat: $AlSal + H_2Cat = AlSalCat + 2H^+$	−8.58
2	2,3-DHB: $AlA + HA = AlA_2H_{-1} + 2H^+$	−8.63
3	2,3,4-THB: $AlA + HA = AlA_2H_{-1} + 2H^+$	−7.49
4	2,3-DHTP: $AlAH_{-1} + A = AlA_2H_{-3} + 2H^+$	−9.07
	K⁺ $Al(COO^-, O^-)(O^-, O^-) + H_2(O^-, O^-) = Al(COO^-, O^-)(O^-, O^-)_2 + 2H^+$	
		Log K⁺
5	Sal-Cat: $AlSalCat + H_2Cat = AlSal(Cat)_2 + 2H^+$	−12.08
6	2,3,4-THB: $AlA_2H_{-1} + HA = AlA_3H_{-2} + 2H^+$	−12.17

equilibrium data characteristic of the reaction $Al(COO^-, O^-) + H_2(O^-, O^-) = Al(COO^-, O^-)(O^-, O^-) + 2H^+$ of these ambidentate ligands with the same type of reaction $AlSal + H_2Cat = AlSalCat + 2H^+$ calculated for the mixed ligand system Al(III)-Cat-Sal (see log K* values in Table 6). The somewhat larger equilibrium constant obtained for 2,3,4-THB and the smaller one for 2,3-DHTP than the reference data obtained for the mixed ligand complex AlSalCat can be explained solely by statistical considerations, as 2,3,4-THB has two different catecholate binding sites, while 2,3-DHTP has two different salicylate binding sites. The complex AlA_2H_{-2}

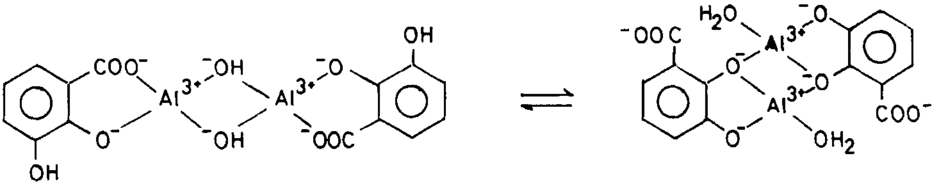
formed in the 2,3-DHB and 2,3,4-THB systems presumably remains of mixed bonding type, as the $pK_{AlA_2H_{-1}}$ values correspond fairly well to the pK_{OH} of the free ligands (*c.f.* rows 2, 3 and 25 in Table 5).

As the pH is raised, there is a marked difference in the metal-binding abilities of these three ligands. This is clearly indicated by speciation diagrams for the Al(III) systems (see Figs. 4-6). In the Al(III)-2,3,4-THB system, where even for statistical reasons there is a higher probability of the catecholate-type coordination of the ligand, a tris complex is formed by catecholate-type coordination of a third ligand molecule. This is strongly supported by the good agreement of the comparable equilibrium data obtained for the mixed ligand complex $AlSal(Cat)_2$ and for the complex AlA_3H_{-2} of 2,3,4-THB (see log K* values in Table 6). On the other hand, with 2,3-DHB and 2,3-DHTP, which have a weaker capability for catecholate-type coordination, as with Sal derivatives, no tris complex is formed; through ligand exchange reactions accompanied by a geometrical change from octahedral to tetrahedral, OH^- ions displace the coordinated ligand molecules and thus the very stable $Al(OH)_4^-$ becomes the dominant species above pH ~10.

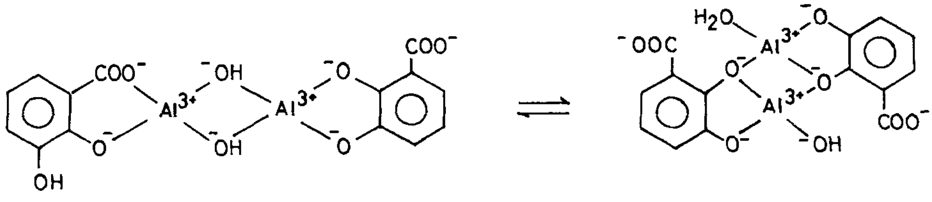
The presence of carboxylate groups in these molecules, and thus their ability to coordinate to Al(III) in a salicylate manner, somewhat weakens the metal-binding ability of 2,3,4-THB and 2,3-DHTP at high pH, as the salicylate-bound ligand is more easily displaceable by OH^-, and the coordination of the first or first two OH^- ions in the octahedral Al(III) complexes seems to greatly promote the geometrical change to tetrahedral and hence formation of the tetrahydroxo species $Al(OH)_4^-$.

In the intermediate pH range, from pH ~4 to pH ~8 (or until precipitation at a low ligand excess), various polymeric complexes presumably containing salicylate or a mixed salicylate-catecholate bonding mode and phenolate or hydroxo bridges (see Schemes 1 and 2) are also formed. It is very difficult, if not impossible, to determine

2,3-DHB

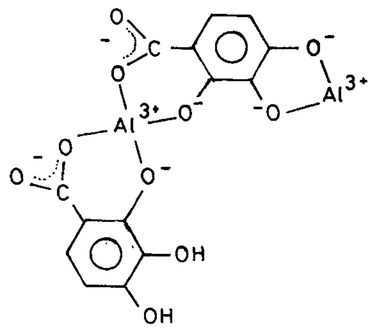


$Al_2A_2H_{-2}$

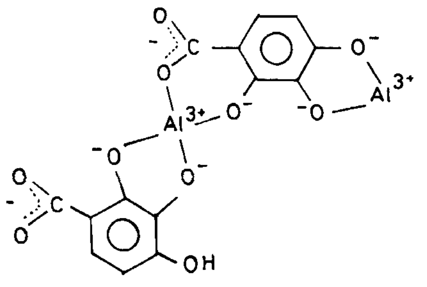


$Al_2A_2H_{-3}$

2,3,4-THB

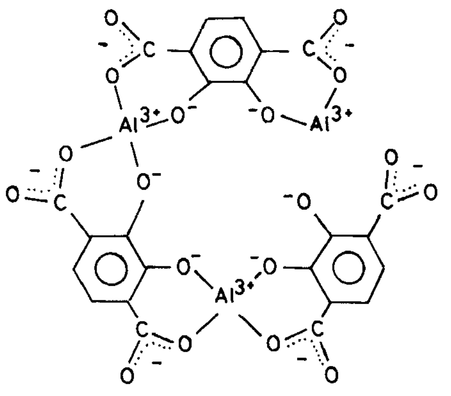


$Al_2A_2H_{-2}$

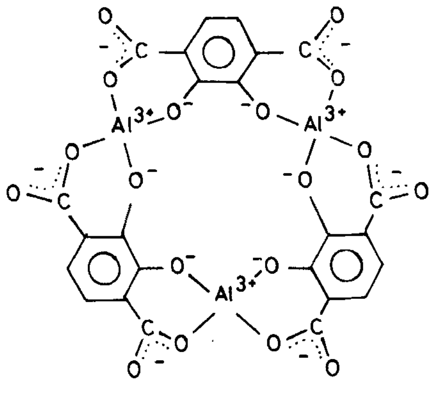


$Al_2A_2H_{-3}$

2,3-DHTP



$Al_3A_3H_{-5}$



$Al_3A_3H_{-6}$

the exact stoichiometries (and stabilities) of these polynuclear species solely from the potentiometric data. For Al(III) and these simple ligands, in which the potential binding sites are very near to each other, spectroscopic measurements can hardly give further information on the bonding modes in the complexes. It can be said, however, that for the terdentate 2,3-DHB the di/oligomerization takes place *via* the formation of mixed hydroxo complexes, while with the tetradentate 2,3,4-THB and 2,3-DHTP the hydrolytic ability of Al(III) is suppressed as the number and binding strength of the available coordinating sites increases.

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REFERENCES

1. R.B. Martin, in, "Aluminium in Chemistry Biology and Medicine," Eds. M. Nicolini, P.F. Zatta and B. Corain, (Cortina International, Verona, 1991).
2. M.R. Wills and J. Savory, *Lancet*, **2**, 23 (1983).
3. C.D. Hewitt, J. Savory and M.R. Wills, *Clinics Lab. Med.*, **10**, 403 (1990).
4. T. Kiss, I. Sóvágó and R.B. Martin, *J. Am. Chem. Soc.*, **111**, 3611 (1989).
5. T. Kiss, I. Sóvágó and R.B. Martin, *Polyhedron*, **10**, 1401 (1991).
6. T. Kiss, I. Sóvágó and R.B. Martin, *Inorg. Chem.*, **30**, 2130 (1991).
7. I. Sóvágó, T. Kiss and R.B. Martin, *Polyhedron*, **9**, 189 (1990).
8. R. Nasaneo, *Acta Chem. Scand.*, **11**, 1308 (1957).
9. V.T. Athavai, L.H. Prabhu and D.G. Vartak, *J. Inorg. Nucl. Chem.*, **28**, 1237 (1966).
10. L. Havelková and M. Bartusek, *Collection Czechoslov. Chem. Comm.*, **34**, 3722 (1969).
11. S.N. Dubey and R.C. Mehrotra, *J. Inorg. Nucl. Chem.*, **26**, 1543 (1964).
12. L. Öhman and S. Sjöberg, *Polyhedron*, **2**, 1329 (1983).
13. R.A. Hancock, S.T. Orszulik, *Polyhedron*, **1**, 313 (1982).
14. R.J. Motekaitis and A.E. Martell, *Inorg. Chem.*, **23**, 18 (1984).
15. A.E. Martell, R.J. Motekaitis and R.M. Smith., *Polyhedron*, **9**, 171 (1990).
16. J.A. Kennedy and H.K.J. Powell, *Aust. J. Chem.*, **38**, 659 (1985).
17. L. Öhman and S. Sjöberg, *Acta Chem. Scand.*, **A37**, 875 (1983).
18. P. Charlet, J.P. Deloume, G. Duc and G. Thomas-David, *Bull. Soc. Chim. France*, 684 (1985).
19. R.N. Soni and K.L. Gupta, *Collection Czechoslov. Chem.*, **36**, 2371 (1971).
20. G. Gran, *Acta Chem. Scand.*, **4**, 599 (1950).
21. L. Öhman and S. Sjöberg, *Acta Chem. Scand.*, **A36**, 47 (1982).
22. H. Irving, M.G. Miles and L.D. Pettit, *Anal. Chim. Acta*, **38**, 475 (1967).
23. L. Zekany and I. Nagypal, in, "Computational Methods for the Determination of Stability Constants," ed. D. Leggett, (Plenum, New York, 1985).
24. T. Kiss and A. Gergely, *Inorg. Chim. Acta*, **36**, 31 (1978).
25. T. Kiss, I. Sovago and R.B. Martin, *J. Am. Chem. Soc.*, **111**, 3611 (1989).
26. M. Jezowska-Bojczuk, H. Kozlowski, A. Zubor, T. Kiss, M. Branca, G. Micera and A. Dessi, *J. Chem. Soc., Dalton Trans.*, 2903 (1990).
27. K. Gerega, H. Kozlowski, T. Kiss, G. Micera, L.S. Erre and F. Cariati, *Inorg. Chim. Acta*, **138**, 31 (1987).
28. T. Kiss, H. Kozlowski, G. Micera and L.S. Erre, *Polyhedron*, **8**, 647 (1989).