portion of 2,2'-$(B_5H_8)_2$ was then condensed into the reactor. The flask was allowed to warm from −78 to −30 °C over several hours while the solution was stirred. The flask was then frozen at −196 °C, and the amount of H_2 gas above the reaction mixture was measured and found to be 0.96 mmol, a 91% yield assuming monodeprotonation of the 2,2'-$(B_5H_8)_2$. Similar reactions employing methyl- and butyllithium in place of KH produced methane and butane, indicating that deprotonation also occurred with those species.

Reaction of K-2,2'-$(B_5H_7)(B_5H_8)$ and Me_3SiCl. An equimolar amount of Me_3SiCl was added to a dimethyl ether solution of K-2,2'-$(B_5H_7)(B_5H_8)$. The mixture was warmed slowly from −78 to −40 °C. The dimethyl ether was then removed by pumping on the reaction mixture overnight at −40 °C. The residues were extracted with C_6H_6 and were transferred by syringe to a −10 °C cold-finger sublimator. After removal of the solvent under high vacuum, a small amount of oil condensed on the cold finger. The ^{11}B NMR spectrum of the oil showed a large pattern of overlapping resonances at −12 ppm and three doublets of approximate intensity 3:2:1 at −51.1, −48.6, and −44.8 ppm, respectively. The −44.8 ppm resonance appears to represent a μ-Me_3Si-substituted 2,2'-$(B_5H_8)_2$, while the −48.6 ppm resonance represents a basal–terminal Me_3Si-substituted 2,2'-$(B_5H_8)_2$.[13] The −51.1 ppm resonance represents the apical boron atom of the unsubstituted cage in the (Me_3Si)-2,2'-$(B_5H_7)(B_5H_8)$ mixture. On treatment of the oil with diethyl ether, the resonance at −44.8 ppm decreased in intensity while the intensity of the resonance at −48.6 ppm increased. The ^{11}B NMR spectrum of the final product had resonances of intensity 1:1 at −48.6 and −51.1 ppm and a complex pattern of overlapping resonances at −12 ppm. These data suggest that the final product was a basal–terminal Me_3Si-substituted 2,2'-$(B_5H_8)_2$ derivative.

Deprotonation of 1,2'-$(B_5H_8)_2$. A 1.2-mmol portion of methyllithium in hexane solution was transferred by syring into a small pump-through reactor equipped with a Teflon-coated stirbar. After the hexane was removed under high vacuum, 0.5 mL of diethyl ether was condensed onto the methyllithium at −196 °C and 0.59 mmol of 1,2'-$(B_5H_8)_2$ was condensed into the reactor. The flask was allowed to warm from −78 to −35 °C while the reaction mixture was stirred. The solution was frozen, and the evolved methane was measured. A 0.4-mmol portion of methane formed during the reaction. The flask was again allowed to warm from −78 to −25 °C, the solution was refrozen, and the reactor was checked for methane. A small quantity of methane was observed; however, the total quantity of methane evolved was less than 1 equiv of the borane starting material. No attempt was made to characterize the presumed anionic intermediate.

Reaction of Li-1,2'-$(B_5H_8)(B_5H_7)$ and DCl. A 1.2-mmol portion of DCl (2 equiv based on 1,2'-$(B_5H_8)_2$ starting material) was condensed into the diethyl ether solution of Li-1,2'-$(B_5H_7)(B_5H_8)$. The flask was warmed to near room temperature while the solution was stirred. The products were distilled through a −22 °C U-trap into a −196 °C U-trap. A 0.055- g portion of white solid was isolated in the −22 °C U-trap. The solid was identified by ^{11}B NMR spectroscopy as the 1,2'-$(B_5H_7D)(B_5H_8)$. Yield: 0.44 mmol (75% based on borane added).

The $^1H\{^{11}B\}$ NMR spectrum of the product was identical with the spectrum of a similar sample of 1,2'-$(B_5H_8)_2$ except for variations in the intensity of resonances in the region characteristic of bridging protons. For the three resonances at −2.12, −2.43, and 2.70 ppm, the normal intensity ratio at 2:2:4 (respectively) was altered to approximately 2:2:3 in the new product. An integration of the ^1H NMR spectrum of the new material indicated that the terminal proton to bridge-proton ratio was 8:7. The ^2H NMR spectrum of the product had a single resonance at −2.74 ppm.

Reaction of 1,2'-$(B_5H_8)_2$ and 2,2'-$(B_5H_8)_2$ with HCl. A catalytic amount of $AlCl_3$ was transferred into an NMR pump-through reactor. A small amount of 2,2'-$(B_5H_8)_2$ and approximately 3.0 mmol of C_6H_6 were condensed into the tube. The sample was thawed and refrozen at the bottom of the tube. A tenfold excess of HCl was condensed into the NMR tube. The sample was sealed and allowed to warm to room temperature. No change in the ^{11}B NMR spectrum of the sample was observed after several days at ambient temperature. Heating at 65 °C for several days also produced no change in the spectrum of the sample.

1,2'-$(B_5H_8)_2$ (0.18 mmol) and HCl (0.18 mmol) were condensed into a small reactor containing a catalyst amount of $AlCl_3$. The flask was sealed and warmed at 60 °C for 1 day. The reaction was opened, and the contents were distilled through a −63 °C U-trap into a −196 °C U-trap. A small amount of liquid isolated in the −63 °C U-trap was identified as a 2-ClB_5H_8 by ^{11}B NMR spectroscopy. The contents of the −196 °C U-trap were identified as B_5H_9 by ^{11}B NMR spectroscopy. Yield: 0.14 mmol (78%). No unreacted 1,2'-$(B_5H_8)_2$ was recovered.

Acknowledgment. This research was funded in part by grants, including departmental instrument grants, from the National Science Foundation.

Registry No. I, 87937-19-7; II, 87937-20-0; III, 80786-88-5; IV, 80786-89-6; V, 82544-59-0; 2,2'-$(B_5H_8)_2$, 28775-81-7; 1,2'-$(B_5H_8)_2$, 31831-99-9; $AlBr_3$, 7727-15-3; $AlCl_3$, 7446-70-0; K-2,2'-$(B_5H_7)(B_5H_8)$, 87884-33-1; Me_3SiCl, 75-77-4; 2,2'-$(B_5H_8)_2$ (Me_3Si derivative), 87901-27-7; Li-1,2'-$(B_5H_8)(B_5H_7)$, 87884-34-2; 1,2'-$(B_5H_7D)(B_5H_8)$, 87937-23-3; Ph_3As, 603-32-7; 2-ClB_5H_8, 19469-14-8; B_5H_9, 19624-22-7.

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Complexes of Aluminum(III) with Hydroxy Carboxylic Acids

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The reactions of the Al(III) ion with citric acid, tartaric acid, gluconic acid, saccharic acid, glyceric acid, bis(hydroxyethyl)glycine, and catechol were studied by potentiometric methods. The equilibrium data were processed with the Fortran computer program BEST. By taking into account all of the known hydrolytic aluminum(III) species, problems associated with previous investigations were avoided. Detailed computations at various ratios of ligands to aluminum(III) now provide a comprehensive description of the Al(III) complexes formed in solution, and formation constants are reported for the various complex species involved. It was found that Al(III) has a very strong tendency toward displacement of protons from the hydroxyl groups of hydroxy acids, a property that previously has not been fully recognized.

Introduction

The Al(III) ion has a strong tendency to undergo complex hydrolytic reactions,[1] and consequently quantitative studies of its reactions in aqueous solution have lagged far behind those of most other common divalent and trivalent metal ions. It is, therefore, not surprising that, except for a few phenolic and multidentate polyamino polycarboxylic acids, quantitative studies[2] of aluminum(III) complexes have been carried out

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(1) Baes, C. F.; Mesmer, R. E. "The Hydrolysis of Cations"; Wiley: New York, 1976.

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only at low pH ($\lesssim 3$) where hydrolytic species are generally absent. In previous investigations, equilibrium data have been determined for the coordination of Al^{3+} with IDA (iminodiacetic acid), NTA (nitrilotriacetic acid), HIDA (((hydroxyethyl)imino)diacetic acid), EDTA (ethylenediaminetetraacetic acid), CDTA (cyclohexanediaminetetraacetic acid), DTPA (diethylenetriaminpentaacetic acid), TTHA (triethylenetetraminehexaacetic acid), several pyridine carboxylates, several phosphonic acids, several dicarboxylic acids, salicylic acid, several catechols (including Tiron, chromotropic acid), acetylacetone, ascorbic acid, and acetohydroxamic acid.[2] From these limited studies, some empirical trends emerge. It appears that with polyamino polycarboxylates, aluminum(III) is capable of forming the normal (ML) complex, as well as protonated complexes. Also, these complexes have been considered to be converted to hydroxo complexes in the pH range of about 5–8. However, these data were measured long ago, before computer-assisted calculations of complex systems were generally feasible. Because of the simplified treatment of data that was employed earlier, hydrolysis and olation reactions were not included in the computation of the equilibrium constants. In recent work on gallium(III),[3-5] it was found that there had been a tendency to ascribe the formation of species such as $ML(OH)_2$ to regions of potentiometric data where in reality the metal ion was dissociating from the ligand to form gallate and free ligand. In view of the fact that the pK_a for reaction 1 is 5.3, it is surprising that published values[2] of

$$Al^{3+} + H_2O \rightleftharpoons AlOH^{2+} + H^+ \qquad (1)$$

$$AlL^{n+} \rightleftharpoons AlLOH^{(n-1)+} + H^+ \qquad (2)$$

analogous hydrolysis constants for coordinated Al^{3+} in multidentate complexes (eq 2) are 5.09 for NTA, 4.89 for HEDTA, 5.83 for EDTA, 7.82 for CDTA, and 5.2 for EGTA. The EDTA vs. CDTA discrepancy is striking, while the values reported for the remaining examples appear much too low. For comparison $\log K^{H}_{FeOH} = 2.5$,[2] while $\log K^{H}_{FeEDTA(OH)}$ is 7.49,[2] 5 orders of magnitude higher. The Fe(III) values are fairly dependable, indicating that the Al(III) values must be way out of line.

While phenolic ligands such as catechol, salicylic acid, and chromotropic acid appear to be especially suited to coordination of Al(III) in that they form 1:1, 2:1, and 3:1 complexes characterized by large overall β values, the remaining several dozen studies reported in the literature show very little consistency.

The purpose of the present work is to define the quantitative interaction between the Al^{3+} ion and complexing ligands containing polyhydroxy aliphatic donor groups such as are found in the well-known ligands tartaric acid and other hydroxy carboxylic acids. When approximate computation methods (i.e., by including all pertinent equilibria) are avoided, it is possible for the first time to provide an accurate description of the aqueous coordination chemistry of Al(III) for this series of ligands.

Experimental Section

Potentiometry. The apparatus consisted of a custom-designed, thermostated 80-mL capacity all-glass vessel. It was fitted with a cover having a 50-mm "O"-ring seal, through which were inserted blue glass and calomel extension electrodes, a delivery tube for a Metrohm piston buret, and inlets and outlets for prepurified nitrogen. Each experiment was preceded by standardization of the pH meter, which was calibrated to display $-\log [H^+]$ directly through the use of dilute standard HCl and KOH solutions. The system was maintained at an ionic strength of $\mu = 0.10$ M with KNO_3 as a supporting electrolyte ($[KNO_3]_0 = 0.1000$).

Table I. Protonation Constants (25.0 °C, $\mu = 0.1000$ (KNO_3))

ligand	log of protonation constants	σ^a	lit.[b] values
citric acid	5.710, 4.389, 3.025	0.0015	5.66, 4.34, 2.90
tartaric acid	3.930, 2.794	0.0012	3.96, 2.82
gluconic acid	3.439	0.0013	3.48
saccharic acid	3.964, 3.174	0.0008	
glyceric acid	3.32	0.008	3.54
	3.24[c]	0.016[c]	
bicine[d]	8.093, 1.658	0.0055	
catechol	9.220[e]	0.0015	13.0, 9.24

[a] σ = standard deviation fit in log units for reproducing 90% of the titration curve. [b] Reference 2. [c] Glyceric acid was retitrated after adding acid. The differing results indicate a mixture of compounds resulting from self-condensation. [d] Bicine is *N,N*-bis(2-hydroxyethyl)glycine. [e] High pK_a of catechol was not determined.

In general, a given experimental run consisted of obtaining many equilibrium data points throughout the pH range between 2.0 and 11.0 as a function of millimoles of standard KOH added by means of the piston buret through a fine capillary tip immersed in the solution. Concentrations of reactants in the experimental solutions were of the order of 10^{-3} M for each component. All ligands were investigated at 1:1, 2:1, and 3:1 ratios to metal ion. Catechol was additionally studied at a 10:1 ratio to Al^{3+}. Equilibration times allowed between increments were variable; in cases where $-\log [H^+]$ drift continued beyond about 4 h, it was concluded that a second phase was present and the data thus obtained were not employed in equilibrium computations.

Computations. All computer calculations were performed with the program PKAS[6] for overlapping protonation constants and accurate determination of the equivalent weights of the ligands, the program BEST[7] for the refinement of metal ion–ligand interaction constants, and the program SPE for the determination of species distributions. SPE employs the algorithm taken from BEST but has been adapted to our VAX 11/780 computer system for graphical display of the species program. For systems containing Al(III), allowance was made in the computations for the presence of $AlOH^{2+}$, $Al(OH)_2^+$, $Al(OH)_3$, $Al_2(OH)_2^{4+}$, $Al_3(OH)_4^{5+}$, and $Al(OH)_4^-$.[2]

Reagents. An Al(III) solution was prepared from reagent grade crystalline $AlCl_3 \cdot 6H_2O$ and was standardized by titration with the disodium salt of EDTA. All ligands, except glyceric acid, were crystalline monopotassium salts or acids. All other reagents were reagent grade.

Procedure. The general procedure employed for the study of the ligands identified above with Al^{3+} was adapted from the method described in the literature.[4]

Results and Discussion

The ligands studied in this work are listed in Table I, together with the successive protonation constants obtained. Glyceric acid is known to be an unstable substance and as such proved to be not useful in these studies. The refinement in the present work to standard deviations on the order of 0.001 log unit represents virtually the limit of accuracy achievable with the potentiometric equipment employed. Although the agreement with literature values is close, the small differences are at least in part due to the more accurate nature of the present computational techiques compared to the graphical or approximate methods used by workers years ago. The slightly higher σ for bicine arises from the 4–5 log unit potential jump in the middle of the titration curve. The values obtained are believed to be "accurate" in the third decimal place. Therefore they have not been rounded off to the two-

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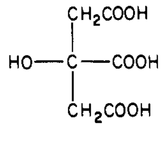
(6) Motekaitis, R. J.; Martell, A. E. *Can. J. Chem.* **1982**, *60*, 168.
(7) Motekaitis, R. J.; Martell, A. E. *Can. J. Chem.* **1982**, *60*, 2403.

Table II. Stability Constants of Al^{3+} with Hydroxy Carboxylic Acids (μ_0 = 0.100 M (KNO_3), 25.0 °C)

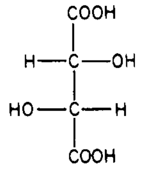
ligand	type	quotient, Q	log Q
citric acid	H_3L	$[AlL]/[Al^{3+}][L^{3-}]$	7.98
		$[AlHL^+]/[AlL][H^+]$	2.94
		$[AlH_{-1}L^-][H^+]/[AlL]$	−3.31
gluconic acid	HL	$[AlL^{2+}]/[Al^{3+}][L^-]$	1.98
		$[AlH_{-1}L^+][H^+]/[AlL^{2+}]$	−2.87
		$[AlH_{-3}L^-][H^+]^2/[AlH_{-1}L^+]$	−9.29
saccharic acid	H_2L	$[AlLH_{-1}L][H^+]/[Al^{3+}][L^{2-}]$	1.57
		$[AlH_{-2}L^-][H^+]/[AlH_{-1}L]$	−3.76
bicine	HL	$[AlHL^{3+}]/[Al^{3+}][HL]$	3.38
		$[AlH_{-2}L][H^+]^3/[AlHL^{3+}]$	−13.72
tartaric acid	H_2L	$[AlH_{-1}L][H^+]/[Al^{3+}][L^{2-}]$	1.18
		$[AlH_{-2}L^-][H^+]/[AlH_{-1}L]$	−5.15
		$[AlL_2{}^-]/[Al^{3+}][L^{2-}]^2$	7.65
		$[AlH_{-1}L_2{}^{2-}][H^+]/[AlL_2{}^-]$	−3.72
		$[AlH_{-3}L_2{}^{4-}][H^+]^2/[AlH_{-1}L_2{}^{2-}]$	−12.67
		$[AlH_{-4}L_3{}^{7-}][H^+]^3/[Al^{3+}][L^{2-}]^3$	−15.92
		$[AlH_{-5}L_3{}^{8-}][H^+]/[AlH_{-4}L_3{}^{7-}]$	−10.89
		$[AlH_{-6}L_3{}^{9-}][H^+]/[AlH_{-5}L_3{}^{8-}]$	−12.7
catechol	L	$[AlH_{-2}L^+][H^+]^2/[Al^{3+}][L]$	−6.08
		$[AlH_{-4}L_2{}^-][H^+]^2/[AlH_{-2}L^+][L]$	−9.18
		$[AlH_{-6}L_3{}^{3-}][H^+]^2/[AlH_{-4}L_2{}^-]$	−13.52
		$[AlH_{-3}L_2]/[AlH_{-4}L_2{}^-][H^+]$	6.03
		$[AlH_{-5}L_3{}^{2-}]/[AlH_{-6}L_3{}^{3-}][H^+]$	8.01

digit convention practiced by most workers in this field.

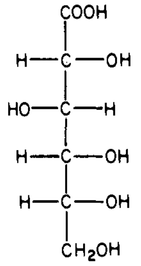
The ligands investigated in this work are represented by **1**–**7**.



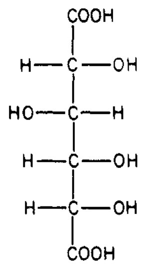
1, citric acid



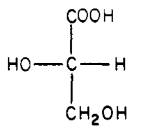
2, L-tartaric acid



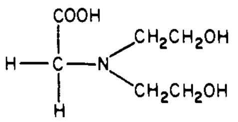
3, D-gluconic acid



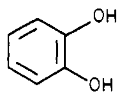
4, D-saccharic acid



5, D,L-glyceric acid



6, bicine



7, catechol

Metal Complexes of Al(III). The most significant finding in this work is the tendency of Al^{3+} toward the displacement of aliphatic hydroxyl protons from the various ligands in which they are in positions favorable for metal ion coordination. Although this property is well established in the complex chemistry of Fe(III) and is in effect exploited in various commercial applications involving alkaline gluconate etching and cleaning preparations, it has not previously been quantitatively described in the chemical literature. Table II is a list of the quantitative results of Al(III) complexation discussed in detail below.

Citric Acid, H_3L. The potentiometric equilibrium curve for the 1:1 Al^{3+}–citric acid system (Figure 1) is unusual in that at low pH it shows the neutralization of one more proton than the three available from the carboxylic acid groups. Since this reaction is complete well below the pH value for the first hydrolysis step of the uncoordinated (aquo) Al^{3+} ion (−log $K^{-H^+}{}_{AlOH^{2+}}$ = 5.30), the deprotonation must be associated with the hydroxyl group of the citric acid. The complex formation region of the curve was found to involve a protonated chelate as well as the normal complex. Hence citric acid, in the presence of aluminum(III), is explained by the macroscopic equilibra (3)–(5). Furthermore the potentiometric curves for

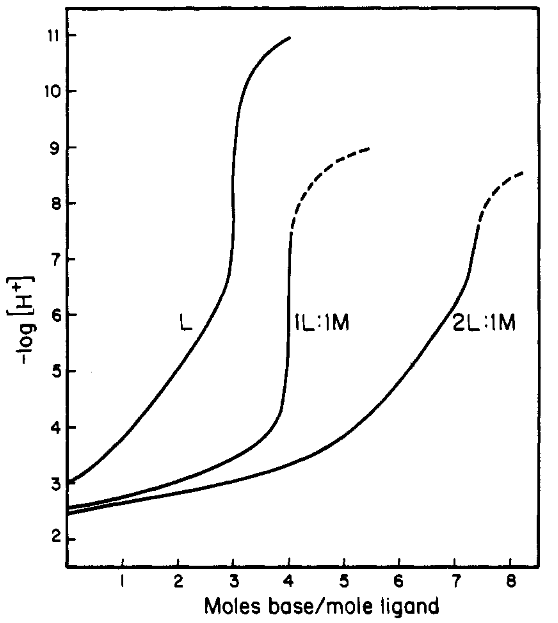


Figure 1. Potentiometric equilibrium curves for citric acid (T_L = 1.978 × 10^{-3} M), citric acid + Al^{3+} (T_L = T_M = 2.010 × 10^{-3} M), and 2(citric acid) + Al^{3+} (T_L = 4.200 × 10^{-3} M, T_M = 2.012 × 10^{-4} M). Broken lines indicate the presence of a solid phase.

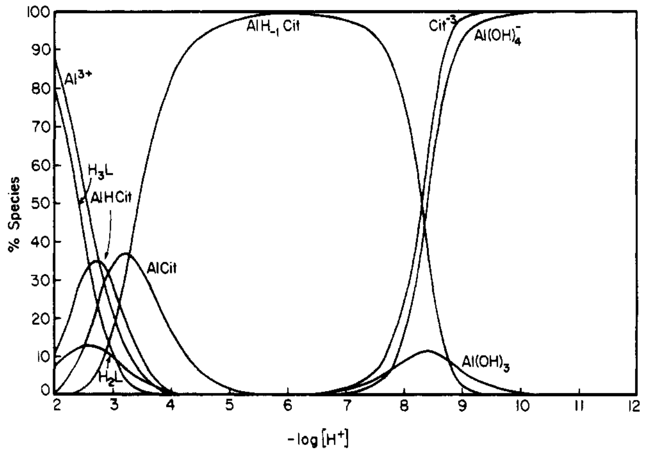


Figure 2. Distribution of major species as a function of −log [H^+] for a 1:1 molar ratio of citric acid to Al(III) (total analytical concentration of each component 2.00 × 10^{-3} M).

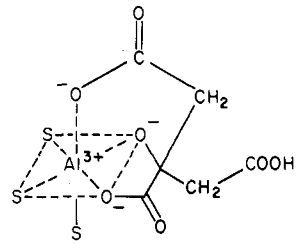
$$Al^{3+} + L^{3-} \rightleftharpoons AlL \qquad K = 10^{7.98} \qquad (3)$$

$$AlL + H^+ \rightleftharpoons AlHL^+ \qquad K = 10^{2.94} \qquad (4)$$

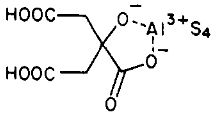
$$AlL \rightleftharpoons AlH_{-1}L^- + H^+ \qquad K = 10^{-3.31} \qquad (5)$$

2:1 and 3:1 molar ratios of citrate to aluminum(III) are also explained quantitatively by these three equilibria. The potential plateau between a = 4 and a = 7 is neatly explained by the excess citrate present. There is no need to invoke any 2:1 or 3:1 species. The species distribution pH diagram in Figure 2 not only points out the interplay of the above equilibria but illustrates the very important interference of Al(III) hydrolysis. The computation was carried out with the assumption that the $Al(OH)_3$ phase remains supersaturated. Nevertheless, above pH 9.0, none of the citrate remains coordinated to the Al(III), since $Al(OH)_4^-$ becomes the thermodynamically preferred species. Similar diagrams for the 2:1 and 3:1 systems also show that, above neutral pH, citrate would be totally released and Al(III) would distribute itself between $Al(OH)_3$ solid and $Al(OH)_4^-$ depending on the alkalinity of the solution.

The magnitude of log K_{ML} (7.98) seems surprisingly large, since ordinary carboxylic acids such as acetic acid possess log K_{ML} values of $\sim$1.5. Thus, the log K_{ML} of Al with citrate is >3.5 orders of magnitude larger than three isolated acetic acid ligands. Certainly such a large chelate effect is not expected with three seven-membered rings. The answer could be sought in Coulombic terms where the affinity of two highly oppositely charged particles would indeed be expected to exert strong mutual attraction. That this is not the case is supported by consideration of available data for tricarballylic acid and acetic acid. The normal stability constants for the tripositive La^{3+} with acetate, tricarballylate, andcitrate are 1.82, 3.71, and 7.63 log units, while the chelate protonation constant for lanthanium(III) carballylate is 4.61 log units. The corresponding values for the divalent Zn^{2+} ion are 1.1, 1.60, and 4.98 while that for the carballylate chelate protonation is 5.13. The increases (3.9 log units for La^{3+} and 3.4 log units for Zn^{2+}) are much higher than can be explained by carboxylate coordination alone and strongly suggest the involvement of the alkoxide group as a strong coordinating donor. Thus, the only bonding arrangement that explains the observed stabilities involves the simultaneous formation of a "protonated" carboxyl group and a deprotonated metal ion-coordinated hydroxyl group to form the chelate (tautomer) ML (**8**) as a major microscopic constituent. Also, in the case of Al(III) it seems that the species "MHL" is really a "diprotonated–deprotonated chelate", represented by **9**. These interpretations are further supported by the more clearly interpretable examples shown below for the remaining ligands.



8, ML



9, MHL^+

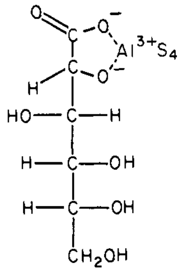
Gluconic Acid, HL. A solution containing a 1:1 molar ratio of gluconic acid to Al(III) was shown to require 4 mol of base to complete the formation part of the curve. However, above pH 5, computations could not be carried out because of the formation of a precipitate of $Al(OH)_3$. Since the deprotonation reactions occur at pH values below the logarithm of the hydrolysis constant of the Al^{3+} ion, they must be assigned to one proton from the carboxyl group and three protons from hydroxyl groups on nonadjacent carbon atoms. The nonadjacent conclusion is based on the small ionic radius of Al^{3+} and the best small cavity obtainable from examination of CPK molecular models of structures capable of forming aluminum(III) chelates. Hence the acid–base coordination reactions of Al(III) and gluconic acid are explained by postulating three species that are formed in accordance with eq 6–8. The magnitude of log K_{ML} compares favorably to those of ordinary carboxylic acid compounds such as propionic acid (log K_{ML} = 1.7). The first hydroxyl group dissociation from this minor constituent gives rise to a major species $MH_{-1}L^+$. It was found that $MH_{-2}L$ does not possess enough stability to be important relative to the strong tendency to form $MH_{-3}L^-$. The potentiometric data taken on a solution containing a molar ratio of ligand to metal of 3:1 is explained by the presence of the same three species, and it was found that there is no need to introduce the 2:1 complex as an important constituent in these systems.

$$Al^{3+} + L^- \rightleftharpoons AlL^{2+} \qquad \log K = 1.98 \qquad (6)$$

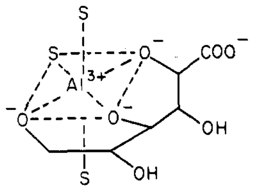
$$AlL^{2+} \rightleftharpoons AlH_{-1}L^+ + H^+ \qquad \log K = -2.87 \qquad (7)$$

$$AlH_{-1}L^+ \rightleftharpoons AlH_{-3}L^- + 2H^+ \qquad \log K = -9.29 \qquad (8)$$

The coordinate bonding schemes consistent with the above data for $AlH_{-1}L^+$ and $AlH_{-3}L^-$ can be represented by **10** and **11**. The geometry of the 2,4,6-cavity is particularly amenable toward metal complex formation in that the ionized hydroxyl oxygens point directly toward three corners of a square plane. Sterically there is ample room for the formation of a 2:1 complex, a fact that may be the chemical basis for the applications of concentrated gluconic acid and its derivatives for aluminum etching, and the solubilization of calcium and magnesium deposits at very high pH.



10, $AlH_{-1}L^+$



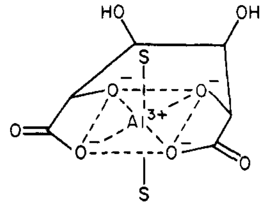
11, $AlH_{-3}L^-$

Saccharic Acid, H_2L. In the coordination of Al(III), this ligand was shown to release two protons in addition to the carboxyl protons, resulting in a pronounced inflection in the potentiometric curve at a = 4. The ultimate stoichiometry of the 1:1 complex formed is therefore $MH_{-2}L^-$. At slightly lower pH values a species $MH_{-1}L$ forms, while the normal complex ML^+ was shown to be absent. The Al(III) complex formation equilibria are therefore given by

$$Al^{3+} + L^{2-} \rightleftharpoons AlH_{-1}L + H^+ \qquad \log K = 1.57 \qquad (9)$$

$$AlH_{-1}L \rightleftharpoons AlH_{-2}L^- + H^+ \qquad \log K = -3.76 \qquad (10)$$

It is concluded that the structure of $AlH_{-1}L$ is that of a bidentate chelate involving a terminal carboxylate and its adjacent ionized hydroxyl, while the doubly deprotonated species can be represented schematically by **12**.



12, $AlH_{-2}L^-$ (S = solvent (H_2O))

A 1:1 solution of this ligand maintains Al(III) in solution up to pH 7, while above pH 10 essentially all of the Al(III) reverts to the aluminate form. It was also shown from equilibrium studies at higher ratios of ligand to metal that no 2:1 or higher species are formed.

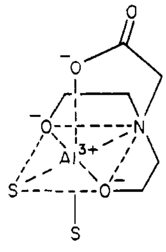
Indirectly the behavior of saccharic acid as a ligand for Al(III) seems to corroborate the suggestion given above for 2,4,6-binding of gluconic acid to Al(III). If the adjacent position were found to be bound in the former case, then at least three hydroxyls could have been dissociated in the latter case. Also, since saccharic acid possesses two α-hydroxyls, this ligand is more acidic and hence the formation of two five-membered chelate rings is made possible by the arrangement shown.

N,N-Bis(2-hydroxyethyl)glycine (Bicine), HL. This ligand was included because of its structure, which involves two hydroxyethyl groups on the glycine moiety, and the fact that it is known to strongly complex Fe(III) at high pH. Because the ligand is dipolar and the protonation constant of the acetate group is very low, this ligand forms a MHL species with Al(III) at pH values below 4. This complex then readily reverts upon addition of more base to $MH_{-2}L$ at higher pH, with the concomitant release of two protons from the hydroxyethyl groups. Above pH 5 significant $Al(OH)_3$ forms, rendering the system unsuitable for further equilibrium calculations. Neither the normal chelate species ML^{2+} nor the complex $MH_{-1}L^+$ was found in this system. Thus, potentiometric data provide evidence for only two significant complexes for this ligand with Al(III):

$$Al^{3+} + HL \rightleftharpoons AlHL^{3+} \qquad \log K = 3.38 \qquad (11)$$

$$AlHL^{3+} \rightleftharpoons AlH_{-2}L + 3H^+ \qquad \log K = -13.72 \qquad (12)$$

The coordinate bonding represented by **13** involves strong coordination by the two dissociated aliphatic hydroxy groups, moderately strong coordination by the acetate group, and perhaps weaker coordination by the intermediate basic nitrogen donor.



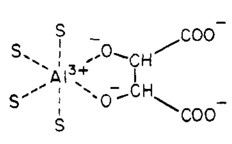
13, $AlH_{-2}L$

Tartaric Acid, H_2L. The significant species identified in the complex Al(III)–tartaric acid system, which was studied at various ligand to metal ratios, are $MH_{-1}L$, $MH_{-2}L^-$, ML_2^-, $MH_{-3}L_2^{-4}$, $MH_{-4}L_3^{-7}$, $MH_{-5}L_3^{-8}$, and $MH_{-6}L_3^{-9}$. The normal chelate ML does not form in detectable amounts. Instead, the more stable $MH_{-1}L$ complex is formed initially and increases in concentration with pH up to a maximum at pH 4.1. In a subsequent hydroxyl deprotonation step $MH_{-2}L^-$ is formed.

$$Al^{3+} + L^{2-} \rightleftharpoons AlH_{-1}L + H^+ \qquad \log K = 1.18 \qquad (13)$$

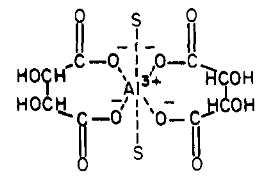
$$AlH_{-1}L \rightleftharpoons AlH_{-2}L^- + H^+ \qquad \log K = -5.15 \qquad (14)$$

The nature of the metal–ligand binding in $AlH_{-2}L^-$ is indicated by **14**.

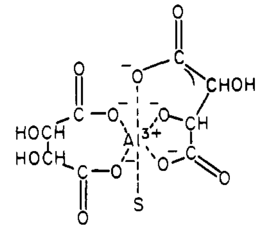


14, $AlH_{-2}L^-$ (H_2L = tartaric acid, S = solvent)

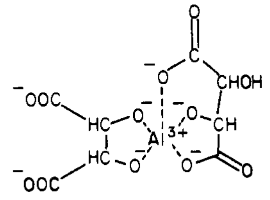
For a 2:1 molar ratio of ligand to metal ion, the complex ML_2^- does form and its concentration increases with pH to a maximum value of about 24% of the metal ion present at pH 3.2. While it appears somewhat unusual in that large, relatively unstable chelate rings are involved, the complex indeed probably has the coordinate bonding indicated by **15** in which carboxylate groups are the only donors supplied by the ligand. A single deprotonation to form $AlH_{-1}L_2^{2-}$ (**16**) was next observed. The intermediate complex $AlH_{-2}H_2^{3-}$ does not form on further deprotonation, probably because of steric hindrance of the donor groups of the ligand near or in the coordination sphere of the metal ion. The triple hydroxyl-deprotonated species $MH_{-3}L_2^{4-}$ (**17**) reaches 65% formation at pH 8.4 and probably has the coordinate bonds shown below. The complex $MH_{-4}L_2^{5-}$, if it does form, is a minor constituent, the presence of which may be masked either by the more dominant species $Al(OH)_3$ from pH 7.0 to 9.5 or $Al(OH)_4^-$ at higher pH values.



15, AlL_2^- (H_2L = tartaric acid, S = solvent)



16, $AlH_{-1}L_2^{2-}$ (H_2L = tartaric acid, S = solvent)



17, $AlH_{-3}L_2^{4-}$ (H_2L = tartaric acid, S = solvent)

The significant equilibria involving 2:1 species are given by eq 15–17.

$$Al^{3+} + 2L^{2-} \rightleftharpoons AlL_2^- \qquad \log K = 7.65 \qquad (15)$$

$$AlL_2^- \rightleftharpoons AlH_{-1}L_2^{2-} + H^+ \qquad \log K = -3.72 \qquad (16)$$

$$AlH_{-1}L_2^{2-} \rightleftharpoons AlH_{-3}L_2^{4-} + 2H^+ \qquad \log K = -12.67 \qquad (17)$$

Analysis of the 3:1 equilibrium data showed the absence of 3:1 complexes with from zero to one dissociated hydroxy group per ligand, ML_3^{3-}, $MH_{-1}L_3^{4-}$, $MH_{-2}L_3^{5-}$, and $MH_{-3}L_3^{6-}$. This result is not surprising since the major 2:1 complex present at the onset of 3:1 complex formation is $MH_{-3}L_2^{4-}$ (**17**), which already has three alkoxide groups bound to the Al(III) ion. However, the $MH_{-4}L_3^{7-}$, $MH_{-5}L_3^{8-}$, and $MH_{-6}L_3^{9-}$ species do definitely form but at progressively higher pH values. Species $MH_{-4}L_3^{7-}$ maximizes at pH 10.2 while the other two keep increasing as more alkali-metal hydroxide is added. The solution structure of $MH_{-4}L_3^{7-}$ probably involves one tartaric acid coordinated to the Al^{3+} ion through both deprotonated hydroxyls, while the remaining tartrates are attached to one each of a carboxylate and a deprotonated hydroxyl group. The species $MH_{-6}L_3^{9-}$ is obviously a symmetrical octahedral complex while $MH_{-5}L_3^{8-}$ has a structure between those of the other two high-pH complexes. The equilibrium constants for the formation of these complexes are defined by eq 18–20.

$$Al^{3+} + 3L^{2-} \rightleftharpoons AlH_{-4}L_3^{7-} + 4H^+ \qquad \log K = -15.92 \qquad (18)$$

$$AlH_{-4}L_3^{7-} \rightleftharpoons AlH_{-5}L_3^{8-} + H^+ \qquad \log K = -10.89 \qquad (19)$$

$$AlH_{-5}L_3^{8-} \rightleftharpoons AlH_{-6}L_3^{9-} + H^+ \qquad \log K = -12.7 \qquad (20)$$

Catechol, L. Catechol is best described as a neutral ligand because it possesses one extremely high pK_a, the value of which can not be known with certainly. Therefore its successively deprotonated forms would be represented by $H_{-1}L^-$ and $H_{-2}L^{2-}$, thus maintaining a parallel relationship to the other hydroxyl group containing ligands discussed above.

Because its measurable pK_a is 9.22 and complex formation was complete near pH 8, relatively large excesses of ligand were used in some of the measurements without the danger of overwhelming the system with catecholate buffer. The predominant species that are successively formed in a 3:1 system in overlapping steps are $MH_{-2}L^+$ (maximum concentration at pH 4.7), $MH_{-4}L_2^-$ (maximum concentration at pH 6.5–7.1), and finally $MH_{-6}L_3^{3-}$ (forms completely above pH 8.5). The minor species detected are $MH_{-3}L_2$ and $MH_{-5}L_3^{2-}$. In a 1:3 Al–ligand mixture, $MH_{-3}L_2$ reaches a maximum concentration of 44% at pH 5.8 and $MH_{-5}L_3^{2-}$ peaks at 25% at pH 8.1.

"Normal" stability constants based on a ligand formulation of H_2L could not be computed per se, because of the lack of a precise value of the high pH dissociation constant, but the quantitative overall equilibrium constants (for proton displacement) were calculated and are given in the protonation and deprotonation equations (21)–(25). Although the assignment of probable arrangements of coordinate bonds for each of the five species is straightforward, the detection of protonated chelate complexes was unexpected. The relative ease of formation of 2:1 and 3:1 complexes at lower pH values, when compared to tartaric acid that also contains adjacent hydroxyl groups, is in part due to the more acidic nature of the hydroxyl groups of catechol.

$$Al^{3+} + L \rightleftharpoons AlH_{-2}L^{+} + 2H^{+} \qquad \log K = -6.08 \tag{21}$$

$$AlH_{-2}L^{+} + L \rightleftharpoons AlH_{-4}L_2^{-} + 2H^{+} \qquad \log K = -9.18 \tag{22}$$

$$AlH_{-4}L_2^{-} + L \rightleftharpoons AlH_{-6}L_3^{3-} + 2H^{+} \qquad \log K = -13.52 \tag{23}$$

$$AlH_{-4}L_2^{-} + H^{+} \rightleftharpoons AlH_{-3}L_2 \qquad \log K = 6.03 \tag{24}$$

$$AlH_{-6}L_3^{3-} + H^{+} \rightleftharpoons AlH_{-5}L_3^{2-} \qquad \log K = 8.01 \tag{25}$$

One of the most interesting and unexpected results of this investigation is that for all of the hydroxy ligands studied no hydroxo Al(III) complexes are formed as the pH is increased. The first ionization constant of the aquo Al(III) ion is $10^{-5.30}$, which on first principles implies that ligand coordination would decrease the tendency of the remaining coordinate water molecules to hydrolyze, thus giving lower ionization constants. This would imply that coordinated mononuclear aluminum complexes would certainly not be expected to polarize and ionize coordinated water below pH ~5.3. On this basis, previously suggested structures such as that proposed by Patnaik and Pani[8] involving $Al(OH)(H_{-1}L)^{2-}$ formulation for citrate are probably incorrect. Because of the magnitude of the pK's involved, the only source of protons beyond the acid carboxyl groups must come from the ligand hydroxyl groups. For the aluminum(III) citrate system, the presence of a protonated chelate at low pH is also a novel finding, which had not been considered by previous workers.

It is interesting to note that, in one case, the potentiometric data resulted in the postulation of fewer Al(III) complexes than had been suggested by other methods. Thus, Frei[9] studied tartaric acid and Al^{3+} by optical rotation measurements and postulated the presence of 22 discrete $Al_xH_y(OH)_z(H_{-1})_v$ species: six with a 1:1 molar metal to ligand ratio, seven with a 1:2 ratio, and nine with a 2:1 ratio. By contrast, in this work it was found necessary to introduce only two 1:1, three 1:2, and three 1:3 Al(III) to ligand species to explain the potentiometric results over a wide range of conditions.

In general, it is preferable to postulate the minimum number of species necessary to explain the equilibrium data. In doing so it is essential to avoid the temptation of increasing the number of individual species in a system, and the associated equilibrium constants, so as to produce a slightly better fit. Where to draw the line is sometimes a matter of judgment and chemical intuition. In the case of aluminum(III) tartrate, only one microscopic technique, used by one investigator, has been employed to suggest a larger number of complex species than those suggested in the present work. Until more microscopic evidence becomes available to corroborate the existence of additional complex species, the simpler system suggested here should be preferred. It is quite possible that higher molar ratios of metal ion to ligand than those employed in the present work could lead to the formation of binuclear complexes, especially at high metal ion (and metal complex) concentrations.

The problem that exists with the investigation of catechol is that the value of the high pK_a cannot be determined accurately at low ionic strengths. Thus, previous workers[10] calculated stabilities that were highly dependent on the value of this constant. However, in the approach employed in this work, catechol is treated as a neutral dihydroxy compound (L) while in its complexes the ligand is considered a doubly deprotonated species ($H_{-2}L$), thus avoiding the inherent inaccuracy of the stability constant calculations that would be necessary if the ligand were considered H_2L and to have a formulation of L^{2-} in its complexes. In addition to the expected 1:1, 1:2, and 1:3 normal chelates ($AlH_{-2}L$, $AlH_{-4}L_2$, and $AlH_{-6}L_3$), which were also noted by others, two new protonated species were identified, as indicated above. The other ligands studied have not been previously investigated with Al(III), and comparisons with the literature are therefore impossible.

In order to study these complexes further, more work needs to be done at higher alkalinities and therefore at higher ionic strength. Also, further confirmation of the proposed binding sites should be made. Studies such as ^{13}C and ^{1}H NMR should provide additional microscopic structural information of the high-pH species of interest, while additional potentiometric studies at higher concentrations of complexes at high pH would provide a fuller quantitative evaluation of the equilibrium processes of the Al(III) complexes of the ligands described in this investigation.

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