

# Multinuclear magnetic resonance study of the interaction of aluminium(III)–(+)-tartrate complexes with additional metal ions in aqueous solution

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## Abstract

The interaction of Al(III)–(+)-tartrate complexes with alkali, alkaline earth, transition and Group 13 metal ions in aqueous solution has been studied with use of  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{17}\text{O}$  and  $^{27}\text{Al}$  NMR spectroscopy. For comparison, some Ga(III)–(+)-tartrate complexes were included. Dinuclear ditartrate-bridged complexes are favored in tartrate solutions of Al(III) and Ga(III), whereas dinuclear tritartrate-bridged complexes are preferred in tartrate solutions of Al(III) with alkali and alkaline earth metal ions. The strong alkaline earth metal ion complexing properties are reflected by the high sequestering capacities which were determined by titration procedures.

## Introduction

By far the most commonly observed geometry of metal ion tartrate complexes is the dinuclear structure with two bridging tartrate ligands. Dinuclear ditartrate-bridged complexes have been reported for (+), *rac* and *meso* tartaric acid with a tetrahedral, square planar, trigonal bipyramidal or a octahedral coordination of the metal ions or metalloids [1–8]. Heterodinuclear ditartrate-bridged structures have been reported for As(III)–Sb(III) and Fe(III)–Gd(III) [9–11]. Formation constants have also been determined for ditartrate complexes of U(VI) and Al(III), Fe(III), In(III) and Cu(II) [12].

The metal-ion coordinating ability of borate esters of polyhydroxycarboxylates and their amino and oxime derivatives has been studied quite extensively [13–17]. It appears that borate links two polyhydroxycarboxylates, usually via binding of threo-diol functions, under the formation of good metal ion coordinating sites. Aqueous solutions of Al(III) with D-glucaric acid are also known for their Ca(II) complexing properties [15, 18].

Recently, we have reported on a multinuclear magnetic resonance study of the coordination of Al(III) with tartaric acid in aqueous solution as a function of pH [19]. High field NMR revealed the presence of 1:3

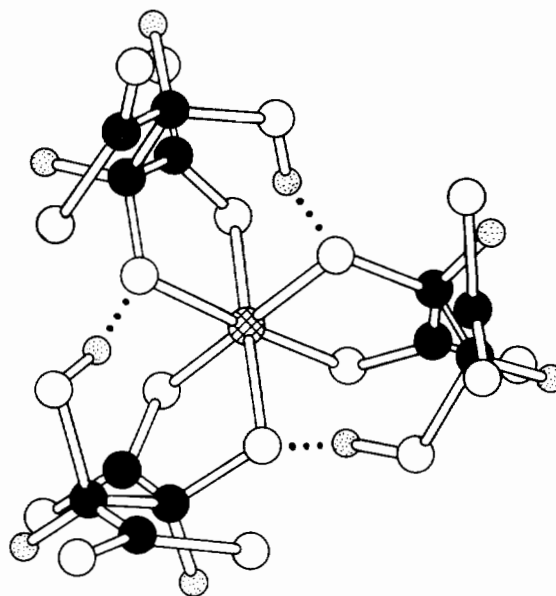


Fig. 1. Schematic representation of the 1:3 metal–(+)-tartrate complex, viewed along the threefold axis. Hydrogen bonds are indicated by dotted lines.

Al(III)–(+)-tartrate (Fig. 1) and 2:2 Al(III)–(+)-tartrate complexes (Fig. 2) at pH 9–12.\*\*

Molecular models of the 1:3 complex show that the three non-coordinated carboxylate groups of the complex are oriented in such a way that they create a potential coordination site for a second metal ion

\*\*The occurrence of five-coordinated Al(III), however, cannot be excluded.

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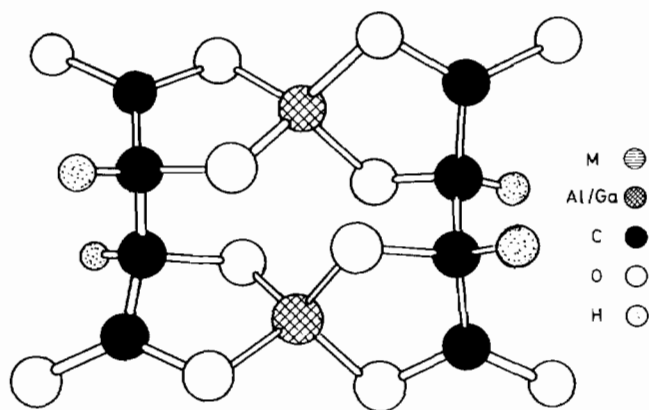


Fig. 2. Schematic representation of the dinuclear 2:2 metal-(+)-tartrate complex.

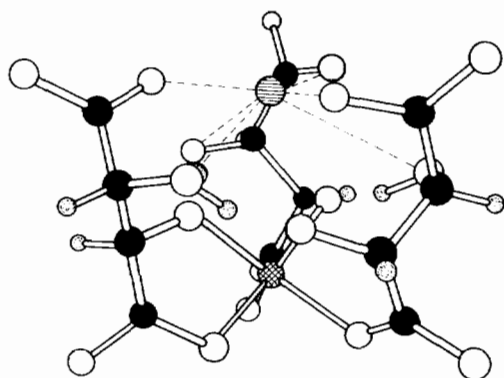


Fig. 3. Schematic representation of the 1:3 metal-(+)-tartrate complex with a coordinated second metal ion (M).

(Fig. 3). Therefore, we have investigated the influence of additional metal ions i.e. Li(I), Na(I), K(I), Rb(I), Cs(I), Mg(II), Ca(II), Sr(II), Ba(II), Mn(II), Cu(II), Zn(II), Cd(II), Y(III), La(III), Al(III), Ga(III) and In(III), on the relative stability of the Al(III)-tartrate complexes. For comparison, some Ga(III)-(+)tartrate complexes are also included in this study.

## Experimental

### Materials and methods

Analytical grade (+)-tartaric acid (J. T. Baker),  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  (J. T. Baker) and  $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  (Janssen Chimica) were used without purification. The metal-ion content of the metal salts was determined by ICP-atomic emission spectroscopy (Al(III)) or by an EDTA titration (Ga(III)). All other metal ions were used as their analytical grade chloride salts, apart from the alkali metal ions which were used as their hydroxides. The  $^{17}\text{O}$  enrichment of the carboxylic acid groups of (+)-tartaric acid was accomplished as described previously [19].

The NMR samples for the metal-ion complexation experiments were prepared by the addition, under stirring, of one mole equivalent of metal ion (relative to Al(III) or Ga(III)) dissolved in 0.33 ml  $\text{D}_2\text{O}$ , to 0.67 ml of a stock solution of 1:3 Al(III)-(+)tartrate or Ga(III)-(+)tartrate (0.25 M  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  or  $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  in  $\text{D}_2\text{O}$ , pH 10.0). The stability constants of the complexes were determined at constant ionic strength.

The pH of the solutions was adjusted by the addition of a concentrated solution of NaOH (analytical grade) in  $\text{D}_2\text{O}$ , except for the alkali metal-ion experiments in which the corresponding hydroxides were used to attain pH 10. The pH of the solutions was measured at room temperature, with a calibrated micro-combination probe purchased from Aldrich. The pH values given are direct meter readings. All samples were measured after equilibration for at least 1 h. No spectral changes were observed within a week.

The Ca(II), Sr(II) and Ba(II) complexing capacities were determined by a modified Wilham and Mehlretter titration procedure [20]. Therefore, a stock solution of 1:3 Al(III)-tartrate at pH 11.0, which was 2% (wt./wt.) in disodium (+)-tartrate was prepared. Sodium carbonate was used as an indicator for Ca(II) instead of sodium oxalate, since the latter resulted in the precipitation of aluminium oxalate upon standing. For Sr(II) and Ba(II), sodium carbonate and sodium sulfate were used as indicator, respectively, yielding sharp turbidity points. The endpoint was defined as the point where the turbidity did not disappear within 2 min.

### NMR measurements

All NMR spectra were recorded on a Varian VXR-400 S spectrometer. The  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts are reported with respect to the methyl signal of *t*-butyl alcohol as internal standard at 1.2 and 31.2 ppm, respectively. The concentrations of the complexes were determined by addition of a weighted amount of *t*-butyl alcohol to the samples followed by integration of the  $^1\text{H}$  NMR signals. The  $^{27}\text{Al}$  NMR chemical shifts are reported with respect to  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  at 0 ppm, as external standard. Downfield shifts are denoted as positive. The  $^{17}\text{O}$  NMR chemical shifts are reported with respect to tap water at 0 ppm, as external standard.

## Results and discussion

### Characterization of the Al(III)-(+)tartrate and Ga(III)-(+)tartrate complexes with use of multinuclear NMR spectroscopy

Previously, we have shown that the predominant species in an aqueous solution of Al(III) and (+)-tartrate, with a molar ratio of 1:3 at pH 9–12, are the mononuclear 1:3 complex and the dinuclear 2:2 complex [19]. The 1:3 complex has a *A fac* configuration [21]

and is stabilized by successive hydrogen bonds between the non-coordinated hydroxy groups and the coordinated and deprotonated hydroxy groups (see Fig. 1). This complex has  $C_3$  symmetry, whereas the 2:2 complex has  $D_2$  symmetry. The exchange between the Al(III) complexes is slow on the NMR time scale. Their NMR characteristics are given in Table 1.

Aqueous solutions with a molar ratio of 1:3 Ga(III)–tartrate have  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra, which are very similar to the Al(III)–tartrate samples, see Table 1. Therefore, it is concluded that isostructural Ga(III)–tartrate species are formed. This is supported by the occurrence of the heterodinuclear 2:2 complexes in the presence of Al(III), and the complexation of alkaline earth metal ions by the 1:3 complex, see below. Unfortunately, characterization of the complexes by  $^{71}\text{Ga}$  NMR failed due to excessive linewidths, probably as the result of the fast quadrupolar relaxation of this nucleus.

Upon introduction of additional metal ions to the Al(III)–tartrate samples, small shifts were observed of the signals of the 1:3 complex in the  $^{27}\text{Al}$ ,  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra ( $<3$ ,  $<1$  and  $<0.2$  ppm, respectively), indicating that the exchange between the mononuclear and the heterodinuclear complexes is fast on the NMR time scale. In Fig. 4 this is illustrated for the  $^1\text{H}$  and  $^{13}\text{C}$  NMR signals of the 1:3 Al(III)–tartrate complex upon stepwise addition of Ba(II).

No changes were observed in the chemical shifts of the 2:2 complexes. These complexes were, in the presence of Ga(III), converted into new heterodinuclear 2:2 complexes, which were in slow exchange with the homonuclear ones. In most cases the introduction of additional metal ions caused a drop of the pH and an increase of the molar ratio of the 1:3 Al(III)–tartrate species and the 2:2 Al(III)–tartrate complexes. In Fig. 5 the concentration of the 1:3 Al(III)–tartrate complex is given as a function of the amount of Ba(II) added. The 1:3 complex attains a maximum concentration after addition of about one mole equivalent of Ba(II) with respect to Al(III), which is indicative of the formation of a 1:1 adduct of the 1:3 complex with Ba(II).

The interaction of the 1:3 Al(III)–tartrate and Ga(III)–tartrate complex with additional metal ions can be understood by inspection of the structure of the 1:3 complex, Fig. 1. The *facial* geometry of the ligands together with the  $A$  configuration of the Al(III) ion results in the alignment of the non-coordinated carboxylate groups. These preoriented carboxylate groups thus create a second coordination site. From  $^{27}\text{Al}$ ,  $^{13}\text{C}$  and  $^1\text{H}$  NMR data, it can be concluded that the conformation of the complex is conserved upon coordination of the second metal ion. Therefore, we assume that a 2:3 heterodinuclear tritartrate-bridged complex is formed, that is schematically displayed in Fig. 3. The metal ion is coordinated to each carboxylate and hydroxy group, thus maintaining the  $C_3$  symmetry of the complex and the hydrogen bonding network. The hydrogen bonded hydroxy groups probably play an essential role in the metal-ion complexing properties of the 1:3 complex, which is supported by the absence of these properties in the corresponding Al(III)–(–)-malate complex.

The suggested structure of the metal-ion coordinating 1:3 complex (Fig. 3) is supported by the  $^{17}\text{O}$  NMR spectrum (Fig. 6) of a 1:3 Al(III)–tartrate solution with one mole equivalent of the strongly coordinating Ba(II) added. The high concentration of the 1:3 complex under these conditions, *vide infra*, allows the characterization of this particular species. Three  $^{17}\text{O}$  NMR signals are discerned for the complex. The signal at 265 ppm is assigned to the two oxygens of the carboxylate groups coordinated to Ba(II), which are isochronous due to fast rotation of the carboxylate group. The signal at 231 ppm is assigned to the Al(III) bonded oxygen, and the shoulder at 277 ppm to the carbonyl group of the Al(III) coordinated carboxylate group. The oxygens of the Al(III) coordinated carboxylate group are inequivalent due to slow rotation. This phenomenon has also been observed for Al(III) complexes with oxalate, glycolate and tartrate [19, 22].

The decrease of the pH upon addition of a second metal ion to the 1:3 Al(III)–tartrate solution is related to the hydrolytic behavior and ratio charge/radius of

TABLE 1.  $^{13}\text{C}$  and  $^1\text{H}$  NMR chemical shifts and vicinal coupling constants of 1:3 and 2:2 tartrate-bridged complexes in  $\text{D}_2\text{O}$  at 30 °C, pH 10

Complex	Metal ions		$^{13}\text{C}$ NMR (ppm)				$^1\text{H}$ NMR (ppm)		
	$M_1$	$M_2$	COO– $M_1$	HCO– $M_1$	HCO– $M_2$	COO– $M_2$	HCO– $M_1$	HCO– $M_2$	$^3J(\text{H,H})$ (Hz)
1:3	Al	Na	185.2	77.1	77.1	182.3	4.31	4.13	1.8 <sup>a</sup>
1:3	Ga	Na	184.8	77.1	76.4	182.2	4.35	4.20	<sup>b</sup>
2:2	Al	Al	185.0	78.4	78.4	185.0	4.26	4.26	
2:2	Al	Ga	185.1	78.8	77.5	184.3	4.29	4.28	2.0
2:2	Ga	Ga	184.4	77.9	77.9	184.4	4.32	4.32	

<sup>a</sup>Determined at 2.0 °C. <sup>b</sup>Broadened doublet.

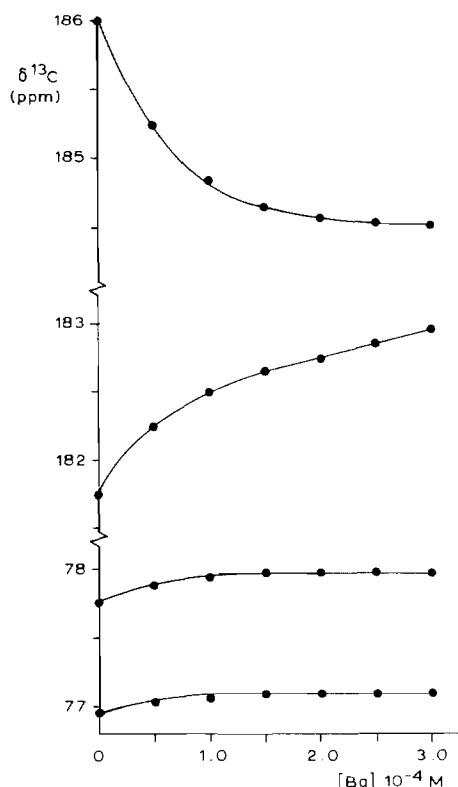
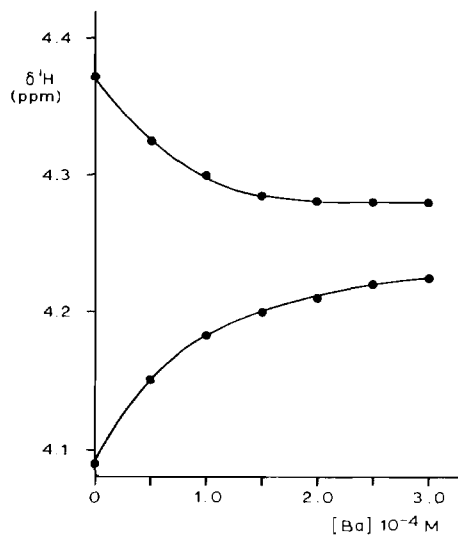


Fig. 4.  $^1\text{H}$  (top) and  $^{13}\text{C}$  (bottom) NMR chemical shifts of the 1:3 Al(III)-(+)–tartrate complex as a function of the amount of Ba(II) added to a solution of 0.25 M  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , 0.75 M (+)-tartaric acid, and 2.25 M CsOH in  $\text{D}_2\text{O}$  at 30 °C, pH 10.

the metal ion involved. Brown *et al.* have developed an equation that correlates the hydrolytic behavior of cations to their ionic radius, charge and electronic structure [23]. Their  $g_1(z/r^2 + g_2)$  values describe the influence of electronic effects on the charge of the metal ion, and therefore may be regarded as an ‘extended electrostatic model’ for the metal ions involved.

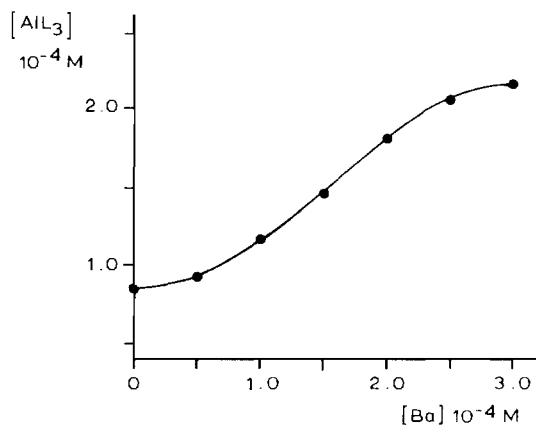


Fig. 5. Influence of Ba(II) on the concentration of the 1:3 Al(III)-(+)–tartrate complex ( $\text{AlI}_3$ ) as determined by integration of  $^1\text{H}$  NMR signals. Conditions as given in Fig. 4.

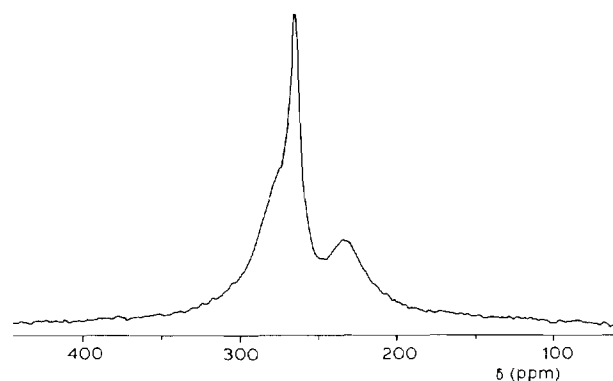


Fig. 6.  $^{17}\text{O}$  NMR spectrum of 0.25 M  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , 0.75 M (+)-tartaric acid (with 5%  $^{17}\text{O}$ -enriched carboxylate groups), and 0.25 M  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  in  $\text{D}_2\text{O}$  at 90 °C, pH 10.

On basis of their influence on the 1:3 Al(III)–tartrate solutions the metal ions can be classified into four groups of increasing acidity, which will be discussed in the following paragraphs.

#### Interaction with alkali metal ions

An aqueous solution of 1:3 Al(III)-(+)–tartaric acid at pH 10.0 displays in the  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra, by virtue of slow exchange phenomena, distinct peaks coming from free non-coordinated ligands, ligands in 2:2, and ligands in 1:3 complexes. Therefore, an illustrative way to study the influence of the alkali metal ions on the composition of the solution, is by monitoring the change of the relative intensities of the signals of the complexes. The signals that exhibit an increase of intensity, point to the most favored, hence stable, dinuclear complex. In order to study the generally observed weak interaction of the alkali metal ions with (negative) oxygen donor containing ligands [24], the metal ions were added as their hydroxides to attain

pH 10.0. The molar ratio alkali ion/Al(III) in the samples was 9\*.

In Fig. 7, the composition of the 1:3 Al(III)–tartrate solutions is given as a function of the metal ions involved. The concentration of the 1:3 Al(III)–tartrate species obtains a maximum in a solution prepared with K(I). Both solutions with Li(I) and Cs(I) show a significant lower amount of the 1:3 species. This dependence of the composition of the solution on the added second metal ion, suggests a specific interaction of that metal ion with the non-coordinated carboxylate groups of the 1:3 Al(III)–tartrate complex. This is supported by the linewidth of the  $^{23}\text{Na}$  signal of the sample prepared with Na(I), which is 45 Hz, whereas the  $^{23}\text{Na}$  resonance of an equimolar solution of NaCl has a linewidth of only 8 Hz. Addition of one equivalent of Ba(II) results in a reduction of the linewidth from 45 to 22 Hz, which suggests displacement of the Na(I) by the more strongly coordinated Ba(II), *vide infra*. Similar phenomena were observed for the  $^7\text{Li}$  and  $^{87}\text{Rb}$  linewidths.

The maximum concentration of the 1:3 complex in the presence of K(I) can be explained in terms of steric crowding of the ligand and the affinity of the metal ions for negative oxygen donor containing ligands [24]. The metal ion acidity (i.e. the affinity of the metal ion for the  $\text{OH}^-$  ion) of the alkaline metal ions, which is related to their radius, decreases in the order  $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$ . Accordingly, the binding constants of the alkaline metal ions with open chain ligands

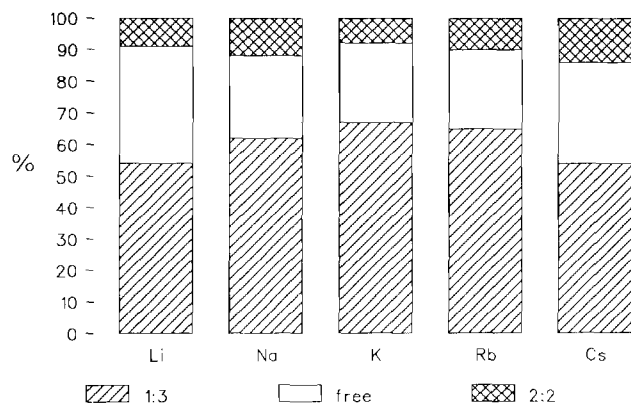


Fig. 7. Influence of alkali metal ions on the relative amounts of non-coordinated ligand, and ligand present in the 2:2 and 1:3 Al(III)–(+)-tartrate complexes. Determined from  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 0.25 M  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , 0.75 M (+)-tartaric acid, and 2.25 M alkali metal hydroxides in  $\text{D}_2\text{O}$  at 30 °C, pH 10.

\*An attempt to determine the composition of the Al(III)–tartrate solution in the absence of alkali metal ions by using tetraalkylammoniumhydroxides failed. The amount of 1:3 complexes present in solution was distinctly reduced but unprecedented signals showed up in the  $^{13}\text{C}$  NMR spectrum. No conclusions were drawn from these experiments, but it demonstrates that the alkali metal ions play a significant role in the stability of the Al(III)–tartrate complexes.

(e.g. (+)-tartaric acid) decrease in the same order [25]. The steric crowding in the 1:3 complex, however, will be strongly dependent on the size of the second metal ion that is coordinated in the cavity that is formed by the three preoriented non-coordinated carboxylate groups. Apparently, the size of K(I) (1.38 Å) leads to the sterically most efficient complex [23, 24, 26]. By integration of the  $^1\text{H}$  NMR signals and with use of the material balances (1) and (2) and eqn. (3), the stability constant of the dinuclear complex was estimated at  $\log \beta_{1:3} \sim 4$ .

$$C_{\text{Al}} = [\text{free}] + [\text{AlL}_3] + 2[\text{Al}_2\text{L}_2] \quad (1)$$

$$C_{\text{L}} = [\text{free}] + 3[\text{AlL}_3] + 2[\text{Al}_2\text{L}_2] \quad (2)$$

$$\beta_{1:3} = [\text{AlL}_3]/[\text{Al}][\text{L}]^3 \quad (3)$$

$$\beta_{2:2} = [\text{Al}_2\text{L}_2]/[\text{Al}]^2[\text{L}]^2 \quad (4)$$

#### Interaction with alkaline earth metal ions

The interaction of the 1:3 Al(III)–tartrate and 1:3 Ga(III)–tartrate complex with alkaline earth metal ions was studied by monitoring the change of signal intensities in the  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra of the free non-coordinating ligand, the ligand in 2:2, and the ligand in the 1:3 complex. Figures 8 and 9 display the composition of the 1:3 Al(III)–tartrate and 1:3 Ga(III)–tartrate solutions, respectively, after addition of one mole equivalent of the alkaline earth metal ions.

Comparison of Figs. 8 and 9 shows that already in the absence of alkaline earth metal ions the composition of the Ga(III)–tartrate solution differs considerably from the Al(III) one. The 1:3 Ga(III)–tartrate solution has a relatively low amount of 1:3 complexes, and somewhat more of the 2:2 complexes. By integration of the  $^1\text{H}$  NMR signals and with use of the material balances

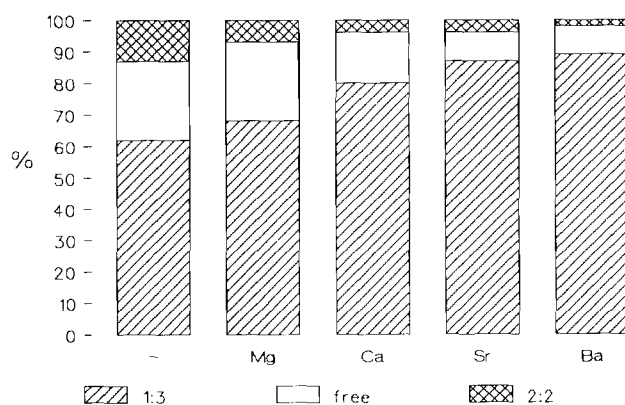


Fig. 8. Influence of alkaline earth metal ions on the relative amounts of non-coordinated ligand, and ligand present in the 2:2 and 1:3 Al(III)–(+)-tartrate complexes. Determined from  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 0.25 M  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , 0.75 M (+)-tartaric acid, and 0.25 M alkaline earth metal chloride salts in  $\text{D}_2\text{O}$  at 30 °C, pH 10.

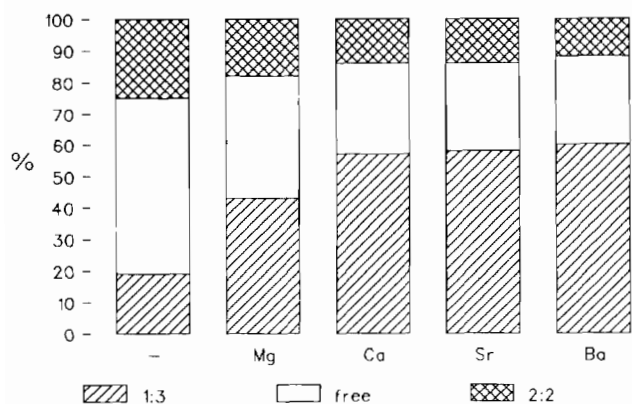


Fig. 9. Influence of alkaline earth metal ions on the relative amounts of non-coordinated ligand, and ligand present in the 2:2 and 1:3 Ga(III)-(+)-tartrate complexes. Determined from  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 0.25 M  $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ , 0.75 M (+)-tartaric acid, and 0.25 M alkaline earth metal chloride salts in  $\text{D}_2\text{O}$  at 30 °C, pH 10.

(1) and (2) and eqn. (4), the stability constants of the complexes could be estimated. The binding constants of the 2:2 complexes of Al(III) and Ga(III) appear to be of comparable strength,  $\log \beta \sim 5$ , whereas the binding constant of the 1:3 Ga(III) complex ( $\log \beta \sim 2$ ) is significantly lower than that of the 1:3 Al(III) complex ( $\log \beta \sim 4$ ). The lower binding constant of the 1:3 Ga(III)-tartrate complexes compared to the Al(III) ones is unexpected from the higher acidity and larger ionic radius of Ga(III) [23]\*. Generally, a higher metal ion acidity leads to a higher affinity for negative oxygen donors, while a larger ionic radius may prevent steric crowding of the ligand [24]. However, the interligand hydrogen bonds of the 1:3 complex, which contribute significantly to the stability of the 1:3 complex [19], may become less favorable due to steric strain, hence result in a lower stability of the complex.

Addition of Mg(II), Ca(II), Sr(II) and Ba(II) to the Al(III)-tartrate and Ga(III)-tartrate solution leads to a gradual increase of the 1:3 complexes, see Figs. 8 and 9. The increase of 1:3 Ga(III)-tartrate complexes is less prominent than observed for the Al(III)-tartrate solutions. This may be attributed to the intrinsic lower stability of the 1:3 Ga(III)-tartrate complexes, see above. The acidity of the alkaline earth metal ions, and consequently their binding strength with negative oxygen donors containing ligands, decreases in the order  $\text{Mg} > \text{Ca} > \text{Sr} > \text{Ba}$ . However, a reverse order of stability of the alkaline earth complexes of the 1:3 species is observed:  $\text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$ , see Fig. 8. This may be ascribed to enhanced steric crowding with decreasing ionic radii [24, 26]. The observed highest affinity for

Ba(II) is in line with the results found for the alkali metal ions, where K(I) has the highest affinity for the 1:3 species. Both ions have namely about equal ionic radii, 1.36 Å (K(I)) and 1.38 Å (Ba(II)) [26]. By integration of the  $^1\text{H}$  NMR signals and with use of the material balances (1), (2) and (5) and eqn. (6), the stability constant of the dinuclear complex was estimated at  $\log \beta_{1:3 \cdot \text{Ba}} \sim 6$ .

$$C_{\text{Ba}} = [\text{free}] + [\text{AlL}_3] \quad (5)$$

$$\beta_{1:3 \cdot \text{Ba}} = [\text{AlL}_3 \cdot \text{Ba}] / [\text{Ba}][\text{Al}][\text{L}]^3 \quad (6)$$

In order to illustrate the alkaline earth metal ion complexing properties of the 1:3 Al(III)-tartrate complex, the complex was submitted to titration procedures from which the sequestering capacities were calculated [20]. The results for Ca(II), Sr(II) and Ba(II) are given in Table 2. The sequestering capacities of the 1:3 Al(III)-tartrate complex are compared to that of a (+)-tartrate solution, which is equimolar in tartrate. In accordance with the NMR results described above, the alkaline earth metal ion sequestering capacity of the 1:3 Al(III)-tartrate solution increases in the order  $\text{Ca} < \text{Sr} < \text{Ba}$ . A solution of 1:3 Al(III)-tartrate sequesters 1.3 mol of Ca(II) and even 2.1 mol of Ba(II), Table 2.  $^{27}\text{Al}$ ,  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra did not show any indication of a structural change of the 1:3 complex on going from one equivalent to two equivalents of Ba(II) sequestered. Therefore we assume that one Ba(II) is coordinated to the 1:3 complex as depicted in Fig. 3, whereas the second Ba(II) is bound by the three carboxylate groups at the opposite site of the complex. The result is a very high sequestering capacity of the 1:3 Al(III)-tartrate complex: 65 g Ba(II)/100 g tartrate.

#### Interaction with transition metal ions

The transition metal ions Mn(II), Cu(II), Zn(II), Y(III), Cd(II) and La(III) have moderate acidity ( $31 < g_1(z/r^2 + g_2) < 50$ ). Addition of these metal ions to a solution of 1:3 Al(III)-tartrate at pH 10 gives rise to a considerable decrease of the pH ( $5.7 < \text{pH} < 7.3$ ). From  $^{27}\text{Al}$  and  $^{13}\text{C}$  NMR it can be concluded that the 1:3 complex is still present as an important species under these conditions, whereas in the absence of additional metal ions the pH region of occurrence of the 1:3 complex is restricted to pH 9–12. This points

TABLE 2. Ca(II), Sr(II) and Ba(II) sequestering capacities of the 1:3 Al(III)-tartrate complex compared to tartrate, in mole metal ion/mole 1:3 complex, at 25 °C and pH 11.0

	Ca(II)	Sr(II)	Ba(II)
Al(III)-tartrate	1.3	1.5	2.1
Tartrate	0.5	0.06	0.05

\*The  $g_1(z/r^2 + g_2)$  value for Ga(III) (84.9) was calculated with use of the equations given in ref. 23. The used ionic radius of Ga(III) is the value suggested by Brown *et al.* (0.68 Å) [23].

to a considerably stabilizing influence of these metal ions under these circumstances. Increase of the pH to its initial value (pH 10), nonetheless, causes the decomposition of the 1:3 complex. At this pH the added cations are capable of deprotonation of  $\alpha$ -hydroxy groups of tartrate [27], which may lead to substitution of the Al(III) ion. The  $^{13}\text{C}$  NMR spectra of these solutions display numerous signals, which illustrates the decomposition of the symmetrical 1:3 complex into many different species with a low symmetry. No attempt was made to reveal the structures of these complexes. Addition of Cu(II) and Mn(II) led to excessive broadening of the  $^{27}\text{Al}$  and  $^{13}\text{C}$  signals of the 1:3 complex which is attributed to fast paramagnetic relaxation.

#### Interaction with Group 13 metal ions

Addition of the highly acidic cations Al(III), Ga(III) and In(III) ( $67 < g_1(z/r^2 + g_2) < 85$  (see footnote on p. xx) leads to a strong decrease of the pH ( $5.1 < \text{pH} < 3.9$ ). At these low pH values the 1:3 and tetrahedral 2:2 complexes are decomposed and only mononuclear 1:1 and 1:2, and octahedral 2:2 complexes are observed in the  $^{27}\text{Al}$  NMR spectra, i.e. spectra similar to that reported previously for an equimolar Al(III)-(+)tartrate solution are recorded [19]. Apparently, 'mixed' Ga(III)/Al(III) complexes are formed, probably because these ions are about isosteric. Adjustment of the pH to its initial value (pH 10) results again in the formation of the 1:3 complexes and tetrahedral 2:2 complexes, see below.

In contrast, addition of In(III) results in the preservation of the 1:3 species, and formation of a small amount of octahedral 2:2 complexes, as was determined with  $^{27}\text{Al}$  NMR. After adjustment of the pH to 10, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra recorded of the sample, however, no longer showed characteristic signals for the 1:3 and 2:2 complexes. Moreover, aqueous 1:3 In(III)-tartrate solutions exhibited anomalous spectra compared to aqueous Al(III) and Ga(III)-tartrate solutions, see below. Therefore, the In(III)-tartrate complexes were not included in this study.

The compositions of 1:3 Al(III)-tartrate and 1:3 Ga(III)-tartrate solutions at pH 10 are represented in Fig. 10(a) and (b), respectively. The 1:3 Al(III)-tartrate solution in the absence of additional metal ions contains a substantial higher amount of 1:3 complexes than the 1:3 Ga(III)-tartrate solution, which was attributed to the intrinsic higher stability of the 1:3 Al(III)-tartrate complex. Addition of one equivalent of Al(III) to the 1:3 Al(III)-tartrate solution and one equivalent of Ga(III) to the 1:3 Ga(III)-tartrate solution results in a strong increase of the amount of homodinuclear 2:2 complexes, which is obviously caused by the decrease of the molar ratio metal/ligand. In the obtained 2:3 Al(III)-tartrate solution still a significant amount of

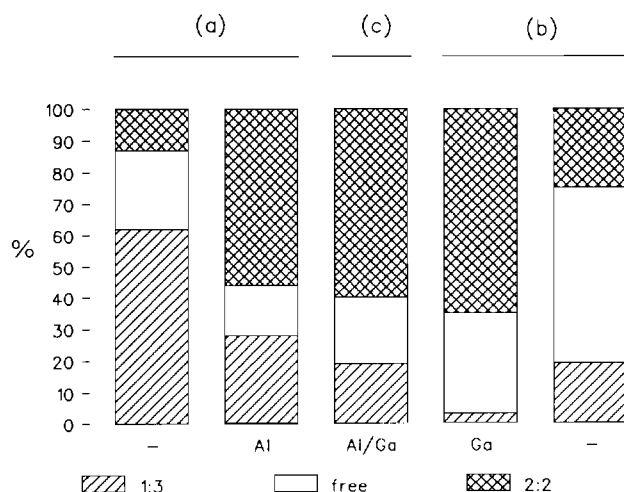


Fig. 10. Influence of Al(III) and Ga(III) on the relative amounts of non-coordinated ligand, and ligand present in the 2:2 and 1:3 tartrate complexes. (a) Al(III)-(+)tartrate solution, (b) Ga(III)-(+)tartrate solution, (c) 'mixed' 1:1 Al(III)-Ga(III) solution. Determined from  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 0.25 M  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  (a) or 0.25 M  $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  (b), 0.75 M (+)-tartaric acid, and 0.25 M  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  or  $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  in  $\text{D}_2\text{O}$  at 30 °C, pH 10.

the 1:3 complexes is present, whereas in the 2:3 Ga(III)-tartrate solution the 1:3 complexes have nearly vanished. This is in line with the intrinsic lower stability of the 1:3 Ga(III)-tartrate complex.

Addition of one mole equivalent of Ga(III) to the Al(III)-tartrate solution and one mole equivalent of Al(III) to the Ga(III)-tartrate solution (Fig. 10(c)), results in the occurrence of heterodinuclear 2:2 complexes. The exchange between the homodinuclear and heterodinuclear 2:2 complexes is slow on the NMR time scale, which is probably a consequence of the high rigidity of the 2:2 complexes. Therefore, the total concentration of 2:2 complexes can be dissected into contributions for the Al-Al, Al-Ga and Ga-Ga complexes, which all have characteristic chemical shifts (Table 1). From  $^{13}\text{C}$  and  $^1\text{H}$  NMR integrations a molar ratio of 16:53:31 was determined of these 2:2 complexes, which suggests an almost statistical distribution of the metal ions. This is in agreement with the comparable stability constants of the Al-Al and Ga-Ga 2:2 complexes, see above.

In contrast to the results with the alkaline earth metal ions, Al(III) and Ga(III) induce a strong decrease of the 1:3 complexes present in solution. This behavior can be rationalized by assuming that upon coordination of Al(III) or Ga(III) by the 1:3 complex, deprotonation of the hydrogen bonded hydroxy groups will occur. The resulting increase of coulombic repulsion in the 1:3 complex may lead to the expulsion of one tartrate ligand. The net result is a 2:2 complex, with tetrahedrally coordinated Al(III).

## Conclusions

Introduction of additional metal ions to Al(III) or Ga(III) (+)-tartrate solutions may have a profound effect on the composition of the solutions. Dinuclear ditartrate-bridged complexes are preferred in the presence of Al(III) and Ga(III), whereas the dinuclear tritartrate-bridged complex is adopted in the presence of alkaline earth metal ions. Particularly, Ba(II) shows a high affinity for the 1:3 complex as is reflected by the high sequestering capacity of 65 g Ba(II)/100 g tartrate.

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