Multinuclear magnetic resonance study of the coordination of aluminium(III) with tartaric acid in aqueous solution

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Abstract

The coordination of Al(III) with (+)-(2*R*,3*R*)-tartaric acid in aqueous solutions at various pH values was investigated with the use of ^{1}H, ^{13}C, ^{17}O and ^{27}Al NMR spectroscopy. High-field ^{27}Al NMR revealed mononuclear 1:1, 1:2, 1:3, and dinuclear 2:2 complexes with both octahedrally and tetrahedrally coordinated Al(III). ^{13}C and ^{27}Al chemical shifts showed that deprotonation of the Al(III) coordinated hydroxy groups of tartrate starts already at pH 1.5. The mononuclear 1:3 complex displayed a remarkable stability and symmetry, which is ascribed to the formation of successive hydrogen bonds. The stereospecific formation of the Al(III) complexes was investigated by comparison with *rac*-(2*R*,3*R*/2*S*,3*S*) and *meso*-(2*R*,3*S*)-tartaric acid.

Introduction

During the last decade general interest in the coordination chemistry of Al(III) with naturally occurring ligands in water has grown rapidly due to its environmental and medical implications. Aluminium toxicity is for instance associated with Alzheimer disease, chronic renal failure, dialysis encephalopathy and fish mortality in acidic surface waters [1].

Already a long tradition exists on the investigation of aqueous Al(III)–tartaric acid solutions. Since 1835, the Al(III)–tartrate system has been the subject of several polarimetric studies [2–6]. A potentiometric study was performed by Motekaitis and Martell [7] but, unfortunately, polynuclear complexes were not considered. Manzurola *et al.* [8] published the formation constants of several dinuclear 'mixed metal' tartrate complexes, and also of a 2:2 Al(III)–tartrate complex. Recently, Marklund and Öhman [9] reported the results of a potentiometric study covering wide metal/ligand ratios and concentration ranges, in which both mono- and polynuclear complexes were taken into account.

Toy *et al.* [10] reported ^{27}Al NMR experiments on Al(III)–*meso*-tartaric acid solutions performed at 8 MHz. At this low field, however, the ^{27}Al NMR signal was broadened beyond detection as soon as coordination with the ligands occurred. Greenaway [11] reported the ^{27}Al NMR spectra of Al(III)–(+)-tartrate solutions. Apart from broad signals, he observed a narrow resonance at 33 ppm at pH > 8, which was assigned tentatively to a symmetric $[Al(H_{-2}ta)_3]^{9-}$ complex (H_2ta = tartaric acid).

Previously, we have reported a multinuclear NMR study on the structure of Al(III)–glycolic acid complexes [12]. The present paper deals with a high-field multinuclear NMR study on the structure of complexes of Al(III) with (+)-tartaric acid in aqueous solution, as a function of pH and at several molar ratios metal:ligand (ρ). The stereospecific formation of Al(III)–tartrate complexes was investigated by including the corresponding complexes of *rac*- and *meso*-tartrate.

Experimental

Materials and methods

Analytical grade $AlCl_3 \cdot 6H_2O$ (J. T. Baker) was used without further purification. The Al(III) content was checked by an EDTA titration using xylenol orange as the indicator. (+)-Tartaric acid (J. T. Baker), *rac*-tartaric acid $\cdot x H_2O$ (Janssen Chimica) and *meso*-tartaric acid (BDH), all analytical grade, were used without further purification. The 15% ^{17}O-enriched water was obtained from Rohstoff-Einfuhr, Düsseldorf.

The pH of the acidic Al(III)–ligand solutions in D_2O was adjusted by adding a freshly prepared concentrated solution of NaOH in D_2O. The pH of the solutions was measured at room temperature, with a calibrated MI 412 micro-combination probe from Microelectrodes Inc. The pH values given are direct meter readings.

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All samples were measured after equilibration for 1 h. No spectral changes were observed within a day, and no irreversible changes of the NMR spectra were observed during variable temperature experiments. The distributions of the species were hardly dependent on the temperature of the samples.

^{17}O enrichment of the carboxylic acid groups of (+)-tartaric acid was accomplished by heating the compound (0.01 mol) for 10 h at 90 °C in 15% ^{17}O-enriched water (1.5 cm^3). The acidic solution was then converted to the sodium salt by adding the appropriate amount of NaOH, followed by freeze drying [13].

NMR measurements

^1H and ^{13}C NMR spectra were recorded on a Varian VXR-400 S spectrometer. The 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.

^{17}O and ^{27}Al NMR spectra were recorded on a Varian VXR-400 S and a Bruker AM-500 spectrometer. The ^{17}O NMR chemical shifts are reported with respect to tap water at 0 ppm as external standard. All ^{27}Al NMR chemical shifts are reported with respect to $[Al(H_2O)_6]^{3+}$ at 0 ppm as external standard. Downfield shifts are denoted as positive. A deconvolution program was used to obtain all the signal characteristics. In order to discriminate between the ^{27}Al background from the probe-head and ^{27}Al signals from the sample, some ^{27}Al NMR spectra were obtained with a 'magic angle' spinning (m.a.s.) probe that was free of ^{27}Al background.

Results and discussion

^{27}Al, ^{17}O, ^{13}C and ^1H NMR spectra of aqueous equimolar solutions of Al(III) and (+)-tartaric acid at pH < 5

^{27}Al and ^{17}O NMR experiments performed at ambient temperature mainly displayed rather broad resonances. In order to improve the resolution of the spectra, the temperature was raised to 90 °C. In this way the quadrupolar relaxation rate decreases as a consequence of decreasing correlation times of the complexes [14]. The influence of pH on the ^{27}Al and ^{17}O NMR spectra of solutions of Al(III) and (+)-tartaric acid with ρ= 1/1 at 90 °C is shown in Figs. 1 and 2, respectively. In Fig. 3, a schematic overview is given of the coordination and deprotonation phenomena of the predominant complexes, as a function of the pH. In Table 1 some characteristic complexes and their ^{27}Al, ^{17}O, ^{13}C and ^1H NMR features are given.

The ^{27}Al NMR spectrum at pH 1.0 (see Fig. 1(a)) shows a large signal due to $[Al(H_2O)_6]^{3+}$ at 0 ppm, and small peaks owing to Al(III)–(+)-tartrate com-

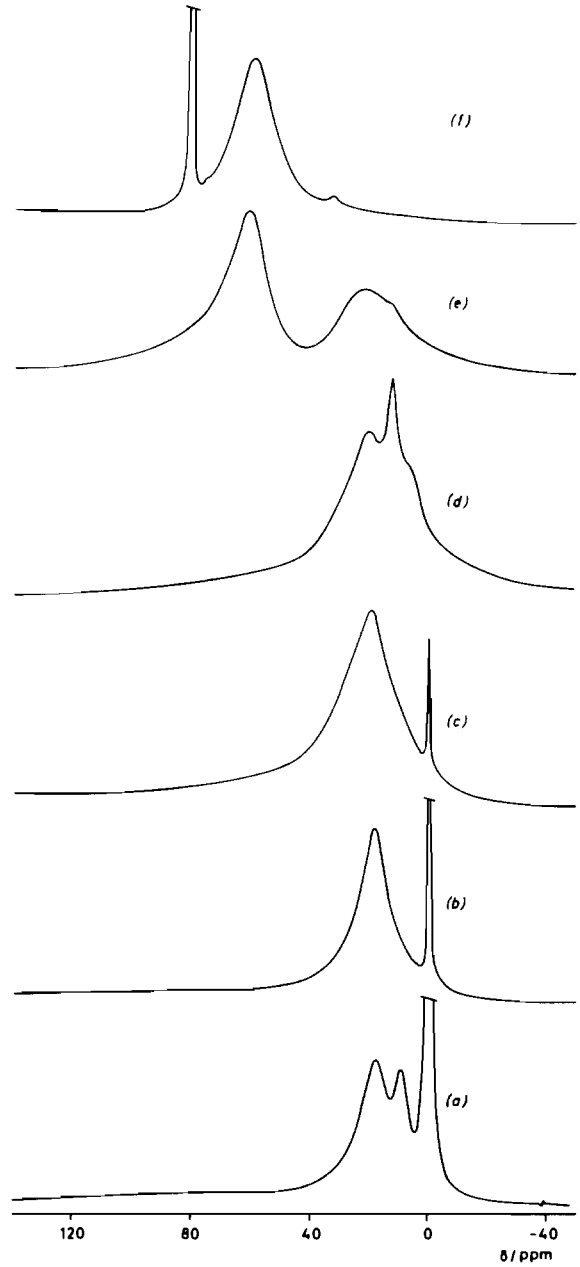

Fig. 1. 104.2-MHz ^{27}Al NMR spectra of 0.25 mol dm^{-3} $AlCl_3 \cdot 6H_2O$ and 0.25 mol dm^{-3} (+)-tartaric acid in D_2O at 90 °C, as a function of pH; (a) 1.0, (b) 2.0, (c) 2.8, (d) 4.4, (e) 10.0, (f) 11.0.

plexes at 9 and 17.5 ppm. On the basis of similarities with the spectra of the corresponding glycolate complex (linewidth, chemical shift) [12], the peak at 9 ppm is assigned to a 1:1 Al(III)–(+)-tartrate complex, $[Al(Hta)(H_2O)_4]^{2+}$, with the metal ion bound to a deprotonated carboxylic acid group and its adjacent hydroxy moiety, thus forming a five-membered ring (see Fig. 3). The chemical shift of the signal at 17.5 ppm is the same as that observed previously for a 1:2 AL(III)–glycolate complex, in which glycolate is bound

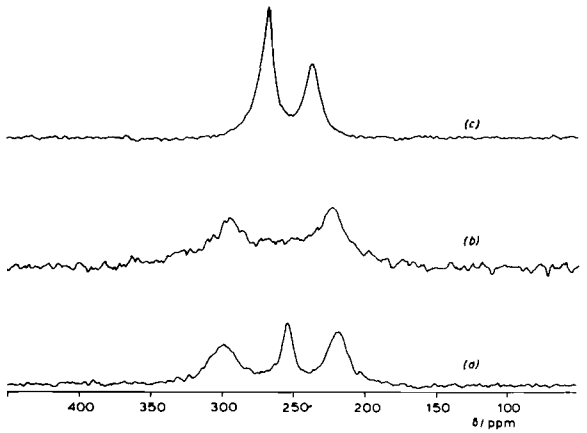

Fig. 2. 54.2-MHz ^{17}O NMR spectra of 0.25 mol dm^{-3} $AlCl_3 \cdot 6H_2O$ and 0.25 mol dm^{-3} (+)-tartaric acid (with 5% ^{17}O enriched carboxylate groups) in D_2O at 90 °C, as a function of pH; (a) 2.0, (b) 4.0, (c) 11.0.

in a didentate fashion. Therefore, we conclude that here, Al(III) is also surrounded by two similarly bound tartrate ligands. The linewidth of the signal of the tartrate complex, however, is much smaller. The ^{27}Al NMR study on Al(III)–glycolate solutions was performed at 30 °C because elevated temperatures decreased the resolution of the spectra by ligand exchange processes, whereas in the present study on tartrate, by contrast, enhanced temperatures increase the resolution of the spectra drastically, which is indicative of relatively low exchange rates. Therefore, we assign this signal to the relatively rigid dinuclear $[Al_2(ta)_2(H_2O)_4]^{2+}$ complex, see Figs. 3 and 4, rather than a mononuclear 1:2 complex $[Al(Hta)_2(H_2O)_2]^+$ (Fig. 5), for which higher ligand exchange rates should be expected.

The *n*:*n* stoichiometry of this complex was confirmed by the signal intensities in the ^{13}C spectrum of the sample at pH 2.0, which contained according to ^{27}Al NMR predominantly the concerned complex, see Fig. 1(b). The ^{27}Al NMR spectrum of an equimolar solution at 0.020 M displays the same characteristics, which denotes a relatively high stability of the 2:2 complexes. This is in line with the conclusions of the potentiometric study of Marklund and Öhman, that the 2:2 complex

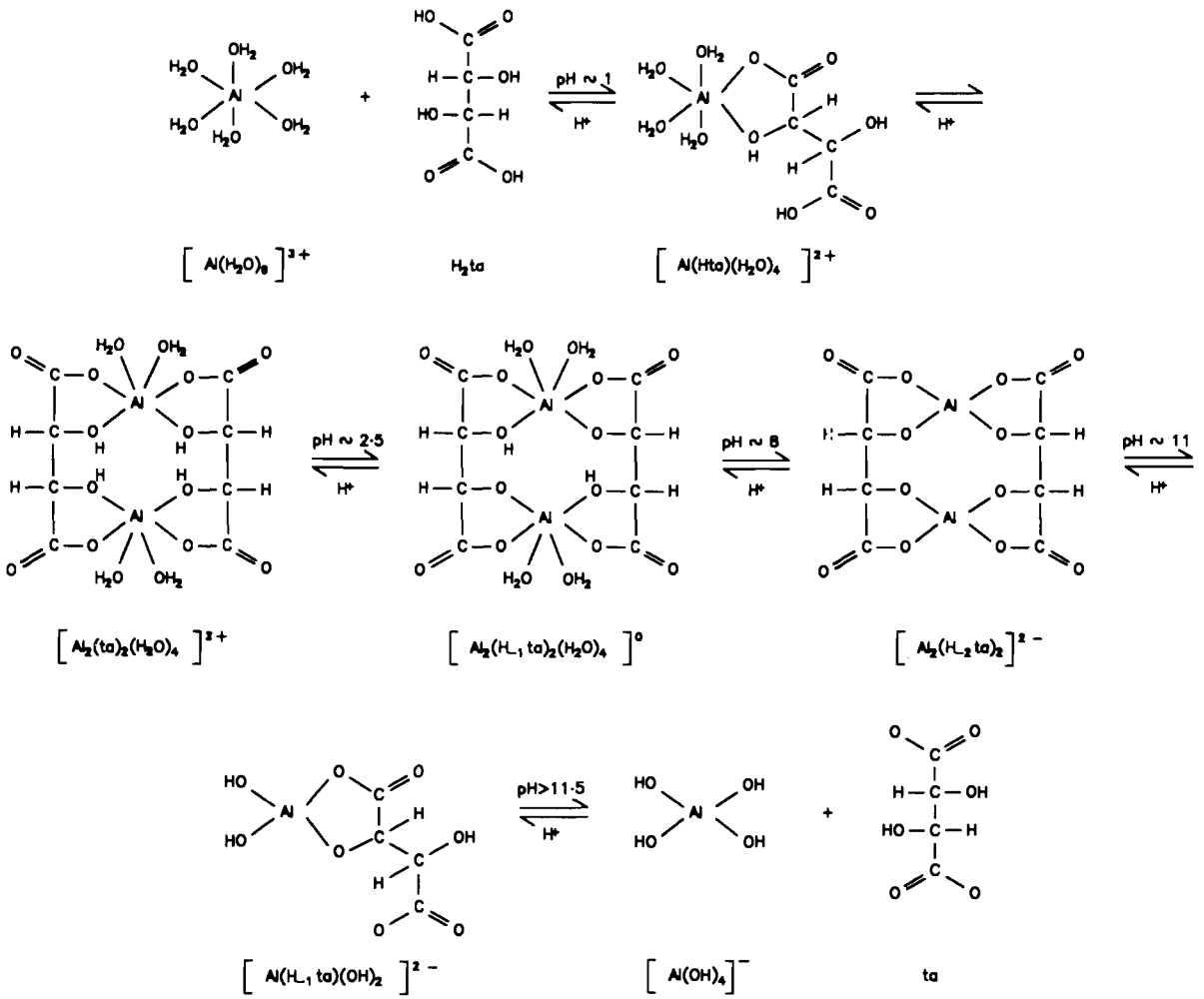

Fig. 3. Schematic overview of the coordination and deprotonation phenomena of the complexes, as a function of pH.

TABLE 1. Overview of characteristic Al(III)–tartrate complexes and their ^{27}Al, ^{17}O, ^{13}C and ^{1}H NMR features

Complex[a]	^{27}Al NMR[b]		^{13}C NMR [$\Delta\delta$] (ppm)[c]				^{17}O NMR (ppm)[b]		^{1}H NMR (ppm)[c]
	δ (ppm)	$\Delta\nu_{1/2}$ (Hz)	COO–Al	HCO–Al	HCO(H)	COO^-	*COO*–Al	CO*O*–Al	
$[Al_2(H_{-1}ta)_2(H_2O)_4]^0$	21	800	180.6[d]	76.1[d]			299	219	4.57[e]
$[Al(H_{-1}ta)_3]^{6-}$	33	600	185.2 [5.4]	77.1 [1.9]	77.1 [1.9]	182.3 [2.5]	265	235	4.31; 4.13
$[Al_2(H_{-2}ta)_2]^{2-}$	60	1400	185.0 [5.2]	78.4 [3.2]			268	239	4.26

[a] $H_{-1}ta = {}^-O_2CCHOHCHO^-CO_2^-$; $H_{-2}ta = {}^-O_2CCHO^-CHO^-CO_2^-$. [b] At 90 °C. [c] At 30 °C; $\Delta\delta = \delta$(complex) $- \delta$(free ligand). [d] See also Fig. 4. [e] At pH 3.5.

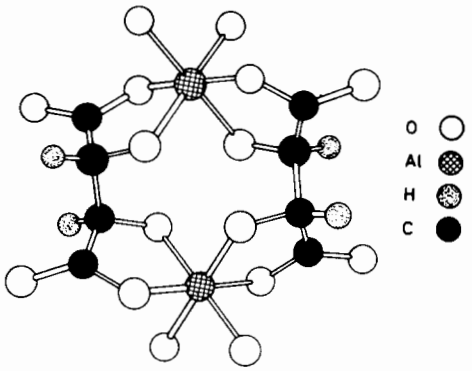

Fig. 4. Representation of the 2:2 Δ,Δ Al(III)–(+)-tartrate complex, with octahedrally coordinated Al(III). Alcoholic hydrogens are omitted for clarity.

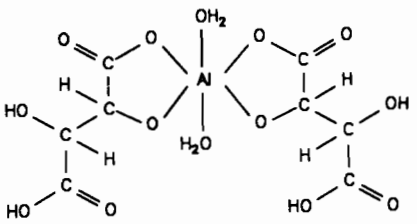

Fig. 5. Schematic representation of the $[Al(Hta)_2(H_2O)_2]^+$ complex. Other isomers are possible.

is predominant at millimolar concentrations [9]. Similar 2:2 metal–tartrate complexes have been reported for As(III), Sb(III), Ni(II), Cu(II), Cr(III), Mo(VI), W(VI) and V(V) [15–22].

Increase of the pH to 2.8 causes a gradual increase of the amount of 2:2 complexes and the appearance of relatively broad shoulders at both sides of the signal of these complexes. These shoulders are ascribed to a small amount of mononuclear 1:2 Al(III)–(+)-tartrate complexes, $[Al(Hta)_2(H_2O)_2]^+$ (Fig. 5), for which on the basis of the phenomena observed for the corresponding 1:2 Al(III)–glycolate complexes [12], broadening by extensive ligand exchange processes should be expected. Increase of the pH to 4.4 induces a gradual shift of the Al(III)–(+)-tartrate complexes from 17.5 to 21 ppm. Previously, we have shown that a shift of this magnitude is caused by deprotonation of a coordinated hydroxy group of the ligand [12]. Therefore, we conclude that a 2:2 $[Al_2(H_{-1}ta)_2(H_2O)_4]^0$ complex is formed, see Fig. 3.

In addition minor species with peaks at 7.0 and 12.5 ppm are observed. The latter signal has a remarkable small linewidth which suggests a symmetric surrounding of the Al(III) nucleus [23]. Its ^{27}Al NMR chemical shift may be dissected into a contribution of 14 ppm of a deprotonated 'glycolate-like' moiety and −1 ppm of a second unstrained carboxylate group [24]*. Accordingly, the signal is tentatively assigned to a polynuclear Al(III)–(+)-tartrate complex in which Al(III) is coordinated with two carboxylate groups and one hydroxy moiety, but a mononuclear 1:1 Al(III)–(+)-tartrate complex with the ligand bound tridentately to the metal ion via two carboxylate groups and one deprotonated hydroxy moiety, cannot be excluded. It should be noted that Marklund and Öhman conclude from a potentiometric study, that the mononuclear complex would immediately aggregate to the more stable 2:2 complex [9]. The peak observed at 7.0 ppm is assigned tentatively to a hydroxide bridged oligomeric Al(III)–(+)-tartrate species, because the complex is broken down with decreasing ρ values.

The pronounced presence of 2:2 Al(III)–(+)-tartrate complexes is supported by ^{17}O, ^{13}C and ^{1}H NMR experiments. At pH 2.0, the ^{17}O NMR spectrum of a solution of Al(III) and (+)-tartrate in a molar ratio of 1:1 (Fig. 2.), shows at 254 ppm a sharp peak of non-coordinated carboxylic acid groups of (+)-tartaric acid, while on both sides broad signals are discerned (219 and 299 ppm, respectively), which are assigned to Al(III) coordinated carboxylate groups of (+)-tartrate. Upon coordination the two oxygens of the carboxylate group become inequivalent, thus causing two

*The contribution of an unstrained carboxylate group was derived from the ^{27}Al chemical shift of the 1:3 Al(III)–maleic acid complex (−2.5 ppm) [24].

signals of equal intensity to appear. The signal at 219 ppm is assigned to the Al(III) bonded oxygen, while that at 299 ppm is attributed to the carbonyl oxygen, analogous to glycolic, oxalic and malonic acid as ligand [12]. Upon increasing the pH the intensity of the signal of free (+)-tartrate carboxylate groups decreases, and at pH 4 exclusively signals for Al(III) coordinated carboxylate groups are observed. This is consistent with the conclusion from the ^{27}Al NMR spectrum that highly stable 2:2 complexes are predominant under these conditions.

The ^{13}C NMR spectra recorded of 1:1 Al(III)–(+)-tartrate solutions reveal in this pH region (1–4), apart from the free ligand signals, only two narrow signals originating from the proposed 2:2 Al(III)–(+)-tartrate complex, see Fig. 6*. Probably, the C–O(H) groups are equivalent due to fast exchange of the protons, thus yielding a complex with effective D_2 symmetry. Fast exchange of C–O(H) protons might occur via a hydrogen

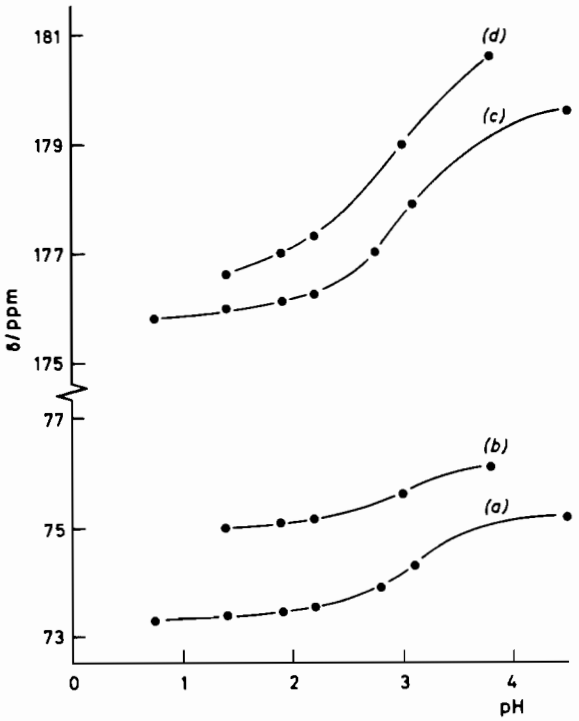

Fig. 6. ^{13}C NMR chemical shifts of the free (+)-tartrate (a) *C*OH, (c) CO_2(H), and of the 2:2 Al(III)–(+)-tartrate complex (b) *C*O(H)–Al, (d) CO_2–Al, of a solution with 0.25 mol dm^{-3} $AlCl_3 \cdot 6H_2O$ and 0.25 mol·dm^{-3} (+)-tartaric acid in D_2O at 30 °C, as a function of pH.

*The ^{13}C NMR experiments on the 2:2 complexes were performed at 30 °C instead of 90 °C, because at the latter temperature, the carboxylate resonance of the complex coalesces with that of the free ligand, due to fast exchange on the ^{13}C NMR timescale at this temperature. The peaks of the free ligand are somewhat broadened, probably because of exchange with 1:1 and 1:2 complexes that are present at low amounts, as determined by ^{27}Al NMR spectroscopy.

bond between two 'half' deprotonated hydroxy groups, as was reported for a dinuclear ditartrate-bridged Cr(III) complex [25]. This effective D_2 symmetry of the complex is supported by the ^{1}H NMR spectra, which display one singlet for the 2:2 complex. From Fig. 6 it is apparent that both the signals of the free (+)-tartrate and the resonances of the 2:2 complex shift to higher frequencies at increasing pH. Evidently, the signals of the free ligand shift due to deprotonation of the carboxylic acid groups ($pK_{a1}=2.8$; $pK_{a2}=4.0$ [26]). The $\Delta\delta$ ($\Delta\delta=\delta$(complex)$-\delta$(free ligand)) value (1.6) of the signal of the C–OH group of the 2:2 Al(III)–(+)-tartrate complex at pH 1.5 is comparable with the $\Delta\delta$ value (1.9) of the C–OH signal of the 1:2 Al(III)–glycolate complex with intact hydroxy groups [12]. This points to the presence of a $[Al_2(ta)_2(H_2O)_4]^{2+}$ complex (Fig. 3). The pH jump of the chemical shifts of the 2:2 complex, at pH 2–4, must be due to ionization of Al(III) coordinated hydroxy groups of (+)-tartrate, hence to gradual deprotonation of the $[Al_2(ta)_2(H_2O)_4]^{2+}$ to the $[Al_2(H_{-1}ta)_2(H_2O)_4]^0$ complex, see Fig. 3. These conclusions are supported by the recent potentiometric study on Al(III)–(+)-tartrate solutions of Marklund and Öhman [9], which also indicates the predominance of dinuclear complexes, and a maximum concentration of the $[Al_2(H_{-1}ta)_2(H_2O)_4]^0$ species around pH 4. The higher acidity of the Al(III) coordinated hydroxy group of (+)-tartrate ($pK_a \sim 2.5$) compared to that of glycolic acid ($pK_a \sim 3.5$ [12]) must be due to the higher stability of the rigid polydentate Al(III)–(+)-tartrate complex.

^{27}Al, ^{17}O, ^{13}C and ^{1}H NMR spectra of aqueous equimolar solutions of Al(III) and (+)-tartaric acid at pH > 5

In the pH region 5 to 10, the ^{27}Al NMR spectra alter dramatically, a large peak emerges at 60 ppm, while the signals at about 10–30 ppm are distinctly reduced in intensity and become featureless (Fig. 1(e)). Also, a small signal for $[Al(OH)_4]^-$ is observed at 80 ppm. These observations are indicative of a gradual changeover of octahedrally coordinated Al(III) into tetrahedrally coordinated Al(III), though five-coordinated Al(III) cannot be excluded [27]. At pH 11.0, the signal at 60 ppm dominates the ^{27}Al NMR spectrum of the equimolar Al(III)–(+)-tartrate solution. This chemical shift is the same as that for a 1:2 Al(III)–glycolate complex in which tetrahedral Al(III) is bound by two glycolate ligands with deprotonated hydroxy groups [12]. The linewidth of the Al(III)–(+)-tartrate complex, however, was again strongly reduced by increasing the sample temperature to 90 °C, thus pointing to slow ligand exchange processes. The *n:n* stoichiometry of this complex was confirmed by the signal intensities in the ^{13}C spectrum of the sample at

pH 11.0, which contained according to ^{27}Al NMR predominantly the concerned complex, see Fig. 1(f). Therefore, again a 2:2 Al(III)–(+)-tartrate complex is proposed but now with two tetrahedrally coordinated Al(III) ions and two (+)-tartrate ligands with both hydroxy groups deprotonated: $[Al_2(H_{-2}ta)_2]^{2-}$ (Figs. 3 and 7).

The proposed structure is supported by ^{13}C NMR which shows, besides very small amounts of free ligand, only two (narrow) signals at 185.0 and 78.4 ppm, respectively (Table 1), which is compatible with the D_2 symmetry of the complex. The ^{13}C chemical shift of the signals of the 2:2 complex is independent of pH, demonstrating that indeed no further deprotonation of coordinated hydroxy groups occurs. Therefore, it can be concluded that all four hydroxy groups of the (+)-tartrate complex corresponding to the signal at 60 ppm in the ^{27}Al NMR spectrum are deprotonated. The ^{1}H NMR spectra confirm the high symmetry of the tetrahedral 2:2 complex: only one singlet is observed for the four (equivalent) methine protons of (+)-tartrate (Table 1)*.

The ^{17}O NMR spectrum of the solution at pH 11.0 shows a large peak at 268 ppm, and a small one at 239 ppm, see Fig. 2. The latter signal is assigned to the Al(III) coordinated oxygen of the carboxylate group, while the signal at 268 ppm can be explained by fast exchange, on the NMR time-scale, between the carbonyl oxygen of the 2:2 Al(III)–(+)-tartrate complex and the carboxylate signal of some free ligand. Variable temperature experiments support this rationale.

The potentiometric study of Marklund and Öhman on Al(III)–(+)-tartrate solutions also establishes the existence of a 2:2 complex with all (+)-tartrate hydroxy groups deprotonated [9]. The octahedral structure proposed by these authors, however, is unlikely on the basis of the ^{27}Al chemical shift, which is characteristic of tetrahedrally coordinated Al(III) [27].

On further addition of NaOH to the solution, the Al(III)–(+)-tartrate complexes are broken down gradually under the formation of $Al(OH)_4^-$, as witnessed by the signal at 80 ppm in the ^{27}Al NMR spectrum. In addition, a small signal appears at 55 ppm in the ^{27}Al NMR spectrum, analogously to what was observed for glycolate as ligand. Therefore this signal was assigned to the 1:1 tetrahedral Al(III)–(+)-tartrate complex $[Al(H_{-1}ta)(OH)_2]^{2-}$ (Fig. 3), though five-coordinated Al(III) cannot be excluded. At pH > 11.5, only the $[Al(OH)_4]^-$ signal at 80 ppm persists.

^{27}Al, ^{17}O, ^{13}C and ^{1}H NMR spectra of aqueous 1:3 Al(III)–(+)-tartaric acid solutions

^{27}Al NMR experiments were also performed on solutions with $\rho = 1/3$ at 90 °C. In Fig. 8, some characteristic ^{27}Al NMR spectra are shown. At pH 1.2, besides the $[Al(H_2O)_6]^{3+}$ signal at 0 ppm, peaks are detected at 9 and 17.5 ppm, which are assigned to 1:1 and 2:2

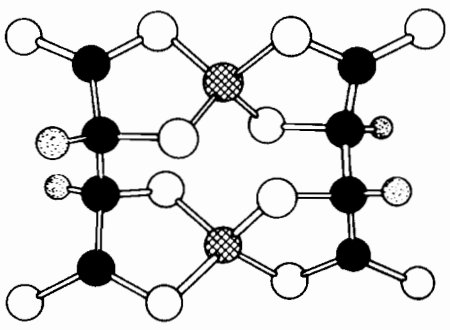

Fig. 7. Representation of the 2:2 (*S*,*S*) Al(III)–(+)-tartrate complex with tetrahedrally coordinated Al(III).

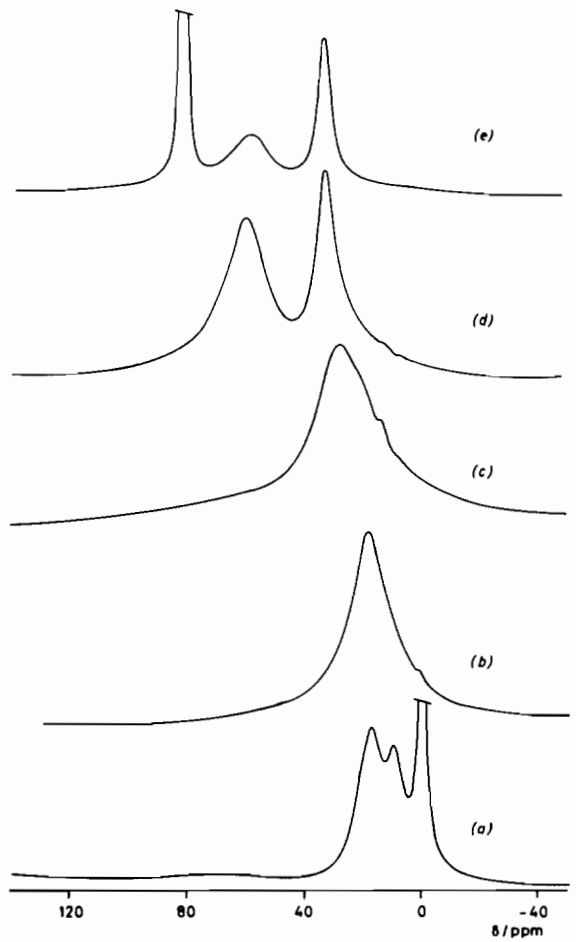

Fig. 8. 104.2-MHz ^{27}Al NMR spectra of 0.25 mol dm^{-3} $AlCl_3 \cdot 6H_2O$ and 0.75 mol dm^{-3} (+)-tartaric acid in D_2O at 90 °C, as a function of pH; (a) 1.2, (b) 2.0, (c) 4.4, (d) 10.0, (e) 12.5.

*Recently, the 2:2 stoichiometry of the complex was confirmed by displacing half the amount of Al(III) by Ga(III), which results in the formation of three different 2:2 complexes: Al–Al, Al–Ga and Ga–Ga [28].

Al(III)–(+)-tartrate complexes, respectively, *vide supra*. At pH 2.0, the signal of the 2:2 complexes is still distinctly present, notwithstanding the presence of excess ligand over metal, which points to a relatively high stability of these complexes in comparison to the mononuclear ones. This is in agreement with the results of the potentiometric study of Marklund and Öhman, which displays the predominance of 2:2 complexes even at tenfold excess ligand over metal [9]. At pH 4.4 the signal for the 2:2 Al(III)–(+)-tartrate complexes is less prominent. Probably, it is obscured by the signals for mononuclear 1:1, 1:2 and 1:3 Al(III)–(+)-tartrate complexes, which are broadened at elevated temperatures, *vide supra*. At pH 10.0, the spectra become less complicated. Now a remarkable sharp signal is observed at 33 ppm, as well as the signal at 60 ppm. The latter signal is due to the 2:2 Al(III)–(+)-tartrate complex with tetrahedral Al(III), see above. The signal at 33 ppm has been reported also by Greenaway [11], who assigned it tentatively to a $[Al(H_{-2}ta)_3]^{9-}$ complex. However, the ^{27}Al chemical shift of the signal at 33 ppm is comparable with that of a 1:3 Al(III)–glycolate complex in which all hydroxy groups are deprotonated [12]. From ^{13}C NMR spectra in combination with ^{27}Al NMR spectra of solutions with several ρ values, a stoichiometry of 1:3 was derived for the Al(III)–(+)-tartrate complex at 33 ppm in the ^{27}Al NMR spectrum. The observed linewidth of this complex is hardly dependent on temperature, whereas the ^{27}Al signal of the analogous 1:3 Al(III)–glycolate complex was broadened by exchange processes at elevated temperatures. This points to a relatively low ligand exchange rate in the present case. Moreover, the small linewidth is indicative of a highly symmetrical complex [23]. The ^{13}C NMR spectrum of the solution with $\rho = 1/3$ at pH 10.0 shows, at 30 °C, apart from the signals of some free (+)-tartrate and (+)-tartrate in $[Al_2(H_{-2}ta)_2]^{2-}$ complexes, peaks at 185.2, 182.3 and 77.1 ppm due to the 1:3 complex, see Table 1, Upon increase of the temperature to 90 °C the ^{13}C signals of this complex coalesce with that of the free ligand. This behaviour contrasts with that of the dinuclear $[Al_2(H_{-2}ta)_2]^{2-}$ complexes (Fig. 7) which do not exhibit any exchange effects in ^{13}C NMR spectra, see above. Therefore, a mononuclear 1:3 Al(III)–(+)-tartrate complex is proposed. Moreover, it should be mentioned that the signal at 33 ppm is not observed in the ^{27}Al NMR spectra of Al(III)–(−)-malic acid [28] and Al(III)–*meso*-tartaric acid solutions, *vide infra*. On the basis of all these observations we conclude that the 1:3 complex has the structure schematically depicted in Fig. 9.

In this $[Al(H_{-1}ta)_3]^{6-}$ complex, the *facial* geometry of the (+)-tartrate ligands together with the *Λ* configuration [29] permits the formation of three successive (interligand) hydrogen bonds between coordinated and deprotonated hydroxy groups and non-coordinating hydroxy groups, which leads to a stabilized and symmetrical (C_3) mononuclear 1:3 Al(III)–(+)-tartrate complex. The proposed structure is supported by the ^1H and ^{13}C NMR data. The carboxylate resonances show a $\Delta\delta$ value of 5.4 and 2.5 (see Table 1). The former $\Delta\delta$ value corresponds with that observed in the $[Al_2(H_{-2}ta)_2]^{2-}$ complex, a complex with fully deprotonated carboxylate and hydroxy groups. The latter $\Delta\delta$ value is attributed to the non-coordinated carboxylate group of the (+)-tartrate ligand. The occurrence of a single broadened ^{13}C signal for the six methine carbons of the 1:3 complex is probably caused by fast ligand exchange on the NMR time-scale: upon lowering the temperature to 2 °C, two distinct signals were observed. The ^1H NMR spectra reveal, at 30 °C, two broad signals ($\Delta\nu_{1/2} = 5.7$ Hz) of equal intensity due to the 1:3 complex, denoting non-equivalent methine protons that are broadened by the exchange effects mentioned above. Upon lowering the temperature to −0.5 °C sharpening of the signals occurred and the vicinal coupling constant could be determined to be 2.0 Hz, which suggests a conformational preference of the bound ligand, almost equal to that observed in non-coordinated tartrate [30]. With use of an empirically generalized Karplus equation [31], which accounts for substituent effects, it can be calculated that the measured vicinal coupling constant corresponds with a dihedral angle of either 65 or 125 °. The former angle is in accordance with a (staggered) conformation of the tartrate ligand that is favourable for hydrogen bond formation (see Figs. 9 and 10).

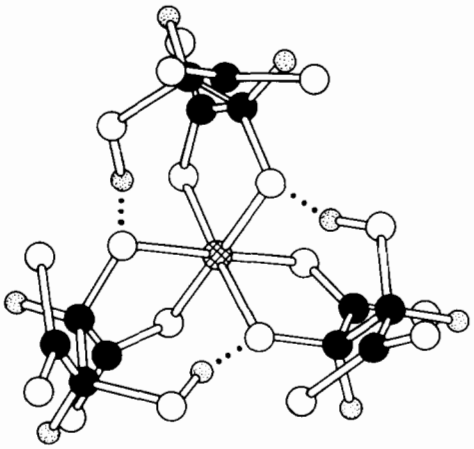

Fig. 9. Representation of the *Λ-fac* 1:3 Al(III)–(+)-tartrate complex. Hydrogen bonds are indicated by dotted lines.

The *Λ* configuration of the 1:3 Al(III)–(+)-tartrate complex implies a left-handed helix, which may have a profound effect on the rotation angle of polarized light. This effect is actually reported by Delsal [5], Yeu Ki Heng [4] and Frei [6]. Under the conditions that we observe the signal at 33 ppm in the ^{27}Al NMR

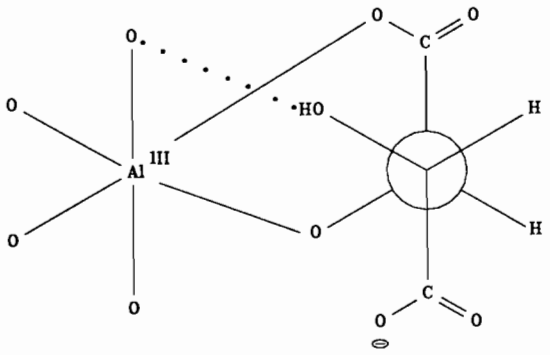

Fig. 10. Conformation of the tartrate ligand in the *Λ-fac* 1:3 Al(III)–(+)-tartrate complex. The hydrogen bond is indicated by a dotted line.

spectrum, these authors observed a dramatic increase of the rotation angle. Moreover, the maximum was observed at a ratio Al:tartrate:NaOH of 1:3:9 which is in agreement with the structure we propose. A similar structure was suggested for a 1:3 Cr(III)–(+)-tartrate complex, on the basis of circular dichroism and potentiometric measurements [32].

At pH > 11.0 the signals at 33 and 60 ppm in the ^{27}Al NMR spectrum decrease gradually, while the intensity of the signal of the $[Al(OH)_4]^-$ complex at 80 ppm exhibits a steady increase. Also a minor peak at 55 ppm shows up, which is assigned to a tetrahedral $[Al(H_{-1}ta)(OH)_2]^{2-}$ complex, see above. At still higher pH values the peak at 80 ppm remains and is broadened. No evidence however was found for the presence of $[Al(H_{-2}ta)_2]^{5-}$ or $[Al(H_{-2}ta)(OH)_2]^{3-}$ complexes in which the (+)-tartrate is bound to the metal exclusively via the two deprotonated hydroxy groups as has been reported for B(III)–tartrate complexes [33]. Probably, these complexes are rather instable, or are imperceptible due to fast exchange with $[Al(OH)_4]^-$ complexes.

^{27}Al, ^{13}C and ^{1}H NMR spectra of aqueous solutions of Al(III) and rac-tartaric acid

Aqueous solutions of Al(III) with *racemic* mixtures of tartrate were also studied in order to establish possible stereospecific effects in the formation of the Al(III)–tartrate complexes. At $\rho = 1/1$, 90 °C and between pH 1 and 3, essentially the same ^{27}Al NMR spectra were obtained as for the pure (+)-tartrate enantiomer. Obviously, no constraints are imposed on the formation of 'mixed' 1:2 complexes (Fig. 5) i.e. complexes with both (+) and (−)-tartrate ligands. Furthermore, these 'mixed' 1:2 complexes are expected to have the same ^{27}Al characteristics as the (+),(+) or (−),(−) complexes, thus being indistinguishable by ^{27}Al NMR. On the other hand, the formation and stability of the 2:2 complexes is presumably strongly dependent on the configuration of the (tetradentate) ligand. However, not only the ^{27}Al NMR characteristics of the 2:2 complex at about 20 ppm resemble those of the optically pure ligand, but also the ^{13}C and ^{1}H NMR results are identical. 'Mixed' Al(III)–tartrate complexes have a lower symmetry (C_2) and therefore distinctive spectra may be expected. In the hypothetically most favourable 'mixed' 2:2 complex with tetradentate ligands (Δ, Δ), as was determined by Tapscott [34], one tartrate ligand is fixed in a nearly eclipsed conformation, and this complex has short O–O and Al–Al distances, leading to severe non-bonded repulsions. Probably, this explains the absence of 'mixed' 2:2 complexes and the preferred stereospecific formation of (+),(+) and (−),(−) octahedral 2:2 Al(III)–tartrate complexes.

In the pH range 4–9, the ^{27}Al NMR spectra of the *racemic* solutions with $\rho = 1/1$ resemble those obtained for (+)-tartrate apart from a unprecedented peak at 21 ppm with a linewidth of only 350 Hz. Due to the relatively low concentration (< 10% at various ρ values), characterization by ^{13}C and ^{1}H NMR failed. The complex however must embody at least two tartrate ligands of different chirality, together with one or more equivalent Al(III) ions. The small linewidth of the ^{27}Al NMR signal at this temperature insinuates a highly symmetrical complex with slow exchange phenomena. Also, complexes with additional hydroxide ligands cannot be excluded at this pH.

At pH > 10.5 the ^{27}Al NMR spectra of the *racemic* mixture again resemble those of (+)-tartrate, i.e. signals are observed at 60 and 80 ppm. The presence of a signal at 60 ppm together with the analogous ^{13}C and ^{1}H results with respect to (+)-tartrate, demonstrates the stereospecific formation of enantiomeric (+),(+) and (−),(−) 2:2 complexes with tetrahedrally coordinated Al(III), since formation of a 'mixed' version is impossible, as was concluded from molecular models.

rac-Tartrate solutions with $\rho = 1/3$ display again almost the same spectra as their optically pure counterpart, apart from a new (small) signal at −2.5 ppm (pH 3), which is ascribed to 'mixed' tartrate complexes of relatively low stability. The ^{27}Al chemical shift and linewidth of the signal at −2.5 ppm correspond namely to a (strain-free) coordination of Al(III) with carboxylate groups [24] and, moreover, a similar peak is much more prominent in spectra of Al(III)–(−)-malic acid solutions [28], i.e. ligands which lack a second hydroxy group. Therefore, here the signal is assigned to 'mixed' complexes with tridentate ligands, in which only one hydroxy group per ligand is coordinated.

At pH 4–9 again the narrow signal at 21 ppm is detected, see above. At pH > 10.5, the ^{27}Al NMR spectra of the *racemic* mixture are similar to those of (+)-tartrate, i.e. peaks are observed at 33, 60 and 80 ppm. The presence of the signal at 33 ppm implies the

stereospecific formation of *facial* 1:3 Λ (+),(+),(+) and Δ (−),(−),(−) complexes, since 'mixed' complexes are incapable of forming the successive hydrogen bonds that are required for a comparative stability and symmetry. The stereospecific formation of the complex is confirmed by the ^{13}C and ^{1}H NMR data, which are identical to those of the (+) enantiomer.

^{27}Al, ^{13}C and ^{1}H NMR spectra of aqueous solutions of Al(III) and meso-tartaric acid

Solutions of Al(III)–*meso*-tartrate with $\rho = 1/1$ at 90 °C, display at pH 1.0, in contrast to the results obtained with optically pure and *rac*-tartrate solutions, merely signals of 1:1 Al(III)–*meso*-tartrate complexes at 9 ppm in the ^{27}Al NMR spectrum. This observation clearly establishes the instability of 2:2 Al(III)–*meso*-tartrate complexes at low pH. This instability was already predicted from molecular models because of non-bonded repulsions between opposing hydroxy and carboxylate groups [34]. At pH 4.0, however, the number of species has greatly enhanced. Numerous peaks are detected in the ^{27}Al NMR spectrum besides a significant signal at 20 ppm, which would suggest the presence of a 2:2 complex. However, ^{13}C NMR experiments failed to reveal signals typical of 2:2 complexes. Probably, the ^{27}Al signal at 20 ppm is due to a different (polynuclear) complex. At pH 10, ^{27}Al NMR shows a minor signal at about 60 ppm, and this peak is on the basis of a comparison of chemical shift and linewidth with those of the corresponding glycolate complexes, assigned to a tetrahedral 1:2 Al(III)–*meso*-tartrate complex $[Al(H_{-1}ta)_2]^{3-}$ (Fig. 11).

The absence of 2:2 Al(III)–*meso*-tartrate complexes with tetrahedrally coordinated Al(III) is obvious from molecular models, the complex cannot be constructed. Also, no indication was observed for the presence of symmetrical 1:3 complexes analogous to those observed for (+)-tartaric acid. Probably this is due to an unfavourable *gauche* conformation that the ligand has to adopt to form the hydrogen bond.

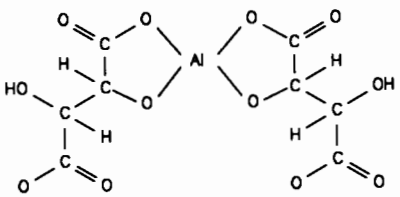

Fig. 11. Schematic representation of the $[Al(H_{-1}ta)_2]^{3-}$ complex.

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