Multinuclear Magnetic Resonance Study of the Co-ordination of Aluminium(III) with Glycolic Acid in Aqueous Solution, compared to Co-ordination with Oxalic and Malonic Acid

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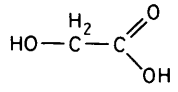
The co-ordination of Al^{III} with glycolic acid in aqueous solution was investigated with the use of ^{1}H, ^{13}C, ^{17}O, and ^{27}Al n.m.r. techniques. High-field ^{27}Al n.m.r. spectroscopy allowed the observation of 1:1, 1:2, 1:3, and polynuclear complexes of Al^{III} with glycolic acid. A gradual shift in the ^{1}H, ^{13}C, and ^{27}Al n.m.r. spectra indicated that ionization of the hydroxy group of co-ordinated glycolate starts at pH 3. ^{17}O N.m.r. measurements showed unambiguously the bidentate co-ordination of oxalic, malonic, and glycolic acid with Al^{III}. Solid-state ^{27}Al 'magic-angle' spinning (m.a.s.) and ^{13}C cross-polarization (c.p.) m.a.s. n.m.r. spectroscopy were employed to study powdered single crystals of a 2:6 aluminium(III)–glycolate complex.

Interest in the aqueous co-ordination chemistry of Al^{III} originates from several research fields. Currently, much research is done on the role of Al^{III} in toxic processes.[1–3] Aluminium might not only be toxic to fish in acidified surface waters, it is also suspect of playing a role in Alzheimer disease.[4–6] On the other hand, aluminium is a valuable element because of its known potential in both homogeneous[7,8] and heterogeneous[9,10] catalysis. Moreover, complexes of Al^{III} with polyhydroxycarboxylates are known for their strong calcium complexing properties.[11,12]

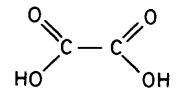
Even in the absence of organic ligands, the aqueous solution chemistry of Al^{III} is complicated because of the tendency to form polynuclear complexes.[13,14] The stoicheiometry and structure of the aluminium(III) species present in hydrolysed solutions is still subject to debate.[15–21] The assignment is hampered by the occurrence of both octahedral and tetrahedral co-ordination of Al^{III} as well. Fortunately, ^{27}Al n.m.r. spectroscopy usually discriminates between octahedrally and tetrahedrally co-ordinated Al^{III}. In aqueous solution octahedral Al^{III} is observed at chemical shifts between −10 and 40 p.p.m., while tetrahedral Al^{III} is found between 60 and 80 p.p.m.[14,22]

In 1973 Toy *et al.*[23] reported a ^{27}Al n.m.r. study on aqueous solutions of Al^{III} and hydroxycarboxylic acids. The ^{27}Al signal, however, was broadened beyond detection as soon as complexation with the ligands occurred. Jaber *et al.*[24] studied the aluminium(III) complexes of oxalic acid using ^{13}C and ^{27}Al n.m.r. spectroscopy. Thanks to the symmetry and the very slow exchange of this ligand, these authors were able to observe 1:1, 1:2, and 1:3 aluminium–oxalate complexes in the n.m.r. spectra. Karlik *et al.*[25] used ^{27}Al n.m.r. spectroscopy to characterise complexes of Al^{III} with lactic acid but broad and overlapping signals made a clear assignment difficult. The ^{27}Al n.m.r. spectrum of malonate complexes has been reported by Greenaway,[26] while Amirhaeri *et al.*[27] reported the ^{13}C n.m.r. chemical shifts of these complexes.

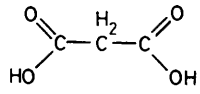
The present paper reports the results of a high-field multinuclear n.m.r. study on the structure of complexes of Al^{III} with glycolic acid (Hga) in aqueous solution, as a function of pH. For comparison, the corresponding complexes of oxalic acid (H_2ox) and malonic acid (H_2mal) were included.



Hga



H_2ox



H_2mal

Experimental

Materials and Methods.—Analytical grade $AlCl_3 \cdot 6H_2O$ (J. T. Baker) and $Al(NO_3)_3 \cdot 9H_2O$ (Merck) were used without further purification. The aluminium(III) content was checked by an ethylenediaminetetra-acetate titration using xylenol orange as the indicator. Oxalic acid dihydrate, malonic acid, and glycolic acid, all analytical grade, were purchased from Merck and used without further purification. The 15% ^{17}O-enriched water was obtained from Rohstoff-Einfuhr, Düsseldorf.

The pH (direct pH-meter reading) of the acidic aluminium(III)–ligand solutions in D_2O was adjusted by adding a concentrated solution of NaOH in D_2O. The pH of the solutions was measured at room temperature, with a calibrated MI 412 microcombination probe from Microelectrodes Inc. All samples were measured within 30 min after preparation. No spectral changes were observed within a day.

Oxygen-17 enrichment of the carboxylic acid groups of malonic and glycolic 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 then was converted into the sodium salt by adding the appropriate amount of NaOH, followed by freeze drying.[28]

The hydrolysed aluminium(III) solution was prepared by adding a concentrated solution of NaOH in D_2O. First, a 0.25 mol dm^{-3} $AlCl_3 \cdot 6H_2O$ solution in D_2O was heated to 90—95 °C. Subsequently, a stepwise addition of the NaOH solution was alternated with vigorous 'vortex' mixing until a clear solution was obtained.[16]

Single crystals of the $Al_2(H_{-1}ga \cdots H \cdots H_{-1}ga)_3Na_3$

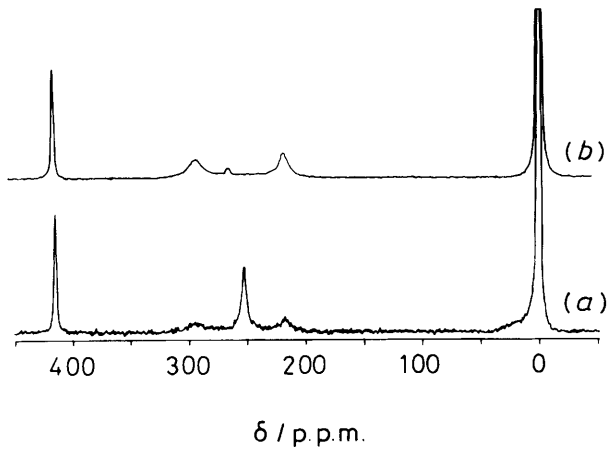


Figure 1. 54.2-MHz ^{17}O N.m.r. spectra of 0.5 mol dm^{-3} $Al(NO_3)_3 \cdot 9H_2O$ and 1.5 mol dm^{-3} oxalic acid (natural abundance) in D_2O at 75 °C: pH 0.6 (*a*) and 6.3 (*b*)

complex were obtained by a liquid-diffusion method.[29] A solution of $AlCl_3 \cdot 6H_2O$ (2.5 g, 0.01 mol) and glycolic acid (2.4 g, 0.03 mol) in water (25 cm^3) was adjusted to pH 4 by adding a concentrated solution of NaOH. Samples of this solution were used for the liquid-diffusion experiments with ethanol as the precipitating solvent.

N.M.R. Measurements.—Proton and ^{13}C n.m.r. spectra were recorded on a Nicolet NT-200 WB and a Varian VXR-400 S spectrometer. The chemical shifts are reported with respect to t-butyl alcohol as internal standard at 1.20 and 31.2 p.p.m., respectively. Linewidths and chemical shifts were determined by fitting the n.m.r. signals with Lorentzian line functions. When necessary, deconvolution was applied.

Oxygen-17 and ^{27}Al n.m.r. spectra were recorded on a Varian VXR-400 S and a Bruker AM-500 spectrometer. The ^{17}O n.m.r. chemical shifts are reported with respect to tap water at 0 p.p.m. as external standard. All ^{27}Al n.m.r. chemical shifts are reported with respect to $[Al(H_2O)_6]^{3+}$ at 0 p.p.m., 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 probehead and ^{27}Al signals from the sample, some spectra were obtained with a magic angle spinning (m.a.s.) probe that was free of ^{27}Al background.

The ^{13}C cross polarization (c.p.) m.a.s. and ^{27}Al m.a.s. n.m.r. spectra were obtained on the Varian VXR-400 S spectrometer. The chemical shifts are reported with respect to $SiMe_4$ and $[Al(H_2O)_6]^{3+}$ respectively, as external standard, both at 0 p.p.m. The ^{13}C c.p.m.a.s. spectrum was obtained with a contact time of 500 μs. The ^{27}Al m.a.s. n.m.r. spectrum was measured with a pulse width of 5 μs, corresponding to a 30° pulse.

Results and Discussion

^{17}O *N.M.R. Spectra of Aqueous Solutions of* Al^{III}.—Until recently, the only way to observe the slowly exchanging water molecules of the $[Al(H_2O)_6]^{3+}$ ion was *via* removal of the signal of the bulk water by adding a shift[30] or relaxation[31] agent. Obviously, the introduction of a second metal ion to the solution is a serious disadvantage in co-ordination chemistry research. High-field ^{17}O n.m.r. spectroscopy was found to allow separate observation of the bulk and Al^{III}-bound water molecules. At room temperature, for a 0.5 mol dm^{-3} solution of $Al(NO_3)_3 \cdot 9H_2O$, the Al^{III}-co-ordinated water molecules are observed as a shoulder to the peak of bulk water.[14–16] Thanks to very slow exchange of co-ordinated and bulk water molecules,[32,33] increase of the temperature causes narrowing of the signals and so at 75 °C two well resolved peaks are observed. The Al^{III}-bound water is observed at 24 p.p.m. Integration of this peak with respect to that of NO_3^- at 417 p.p.m. shows indeed six co-ordinated water molecules.

At pH 12, when the $[Al(OH)_4]^-$ ion is the only species present in solution, no distinct peak of the hydroxide ligands was observed. Probably this is due to extensive exchange broadening or to rapid quadrupolar relaxation.

^{17}O *N.M.R. Spectra of Aqueous Solutions of* Al^{III} *with Oxalic and Malonic Acids.*—Measurements were performed on aqueous solutions (natural abundance) of aluminium(III)–oxalate with a molar ratio metal:ligand (ρ) of 1:3. The resolution of the spectra was improved by increasing the temperature to 75 °C, which causes a reduction of the quadrupolar relaxation rate. The influence of the pH on the ^{17}O n.m.r. spectra is illustrated in Figure 1. At low pH a sharp peak is observed at 253 p.p.m. due to unbound oxalic acid. On both sides a peak is discerned (219 and 295 p.p.m. respectively) which can be assigned to Al^{III}-co-ordinated oxalate. Upon co-ordination the two oxygens in the carboxylate group become inequivalent, giving rise to two peaks of equal intensity. On the basis of the similarity with ^{17}O n.m.r. chemical shifts of esters,[34] the peak at 219 p.p.m. is assigned to the Al^{III}-bonded oxygen of the carboxylate group, while that at 295 p.p.m. is assigned to its carbonyl oxygen. The Al^{III}-bound water is visible as a shoulder to the peak of bulk water.

Upon raising the pH to 6 a strong increase in the amount of Al^{III}-bonded oxalate is observed and, simultaneously, the disappearance of the Al^{III}-bonded waters. The signal of free oxalate at 267 p.p.m. has almost disappeared, which confirms the stoicheiometry of the $[Al(ox)_3]^{3-}$ complex, as has been determined by ^{27}Al and ^{13}C n.m.r., Raman spectroscopy, and potentiometry.[24,35,36] Furthermore, this experiment shows clearly that the structure of the $[Al(ox)_3]^{3-}$ complex in aqueous solution closely resembles the solid-state structure determined by *X*-ray analysis.[37]

Oxygen-17 n.m.r. spectra of aqueous solutions of Al^{III} with malonic acid show the same phenomena as described for oxalic acid. The signals of Al^{III}-bonded malonate are observed at 305 and 229 p.p.m., respectively. The resolution of the spectrum can be enhanced by increasing the temperature to 75 °C, which is indicative of very slow ligand-exchange processes.

^{27}Al *N.M.R. Spectra of Aqueous Solutions of* Al^{III} *and Glycolic Acid.*—In ^{27}Al n.m.r. experiments at a field strength of 4.7 T only a broad resonance due to the aluminium(III)–glycolate complexes was observed. Probably extensive exchange broadening occurs under these conditions. Obviously, these results precluded the assignment of the different complexes. Therefore all further experiments were performed at a field strength of 9.4 or 11.7 T. At these high fields various complexes could be detected. In the Table an overview is given of the observed complexes together with their chemical shifts and linewidths in the ^{27}Al n.m.r. spectrum. Also the pH regions in which the species are observed are indicated. The data were obtained by measuring solutions at $1/8 \leqslant \rho \leqslant 1$.

The influence of the pH on the ^{27}Al n.m.r. spectra of solutions with $\rho = 1/2$ is depicted in Figure 2, while in Figure 3 this is represented schematically. At pH < 1 a large signal of the $[Al(H_2O)_6]^{3+}$ ion is observed at 0 p.p.m. and a small signal at 9 p.p.m. The latter signal is assigned to the octahedral complex $[Al(ga)(H_2O)_4]^{2+}$, in which the glycolate is bound *via* both the carboxylate and hydroxy group. This is confirmed by the ^{17}O n.m.r. spectrum of this solution (see below) which shows two inequivalent oxygens of the carboxylate group. ^{17}O N.m.r. experiments on aluminium(III)–acetate solutions, on the other

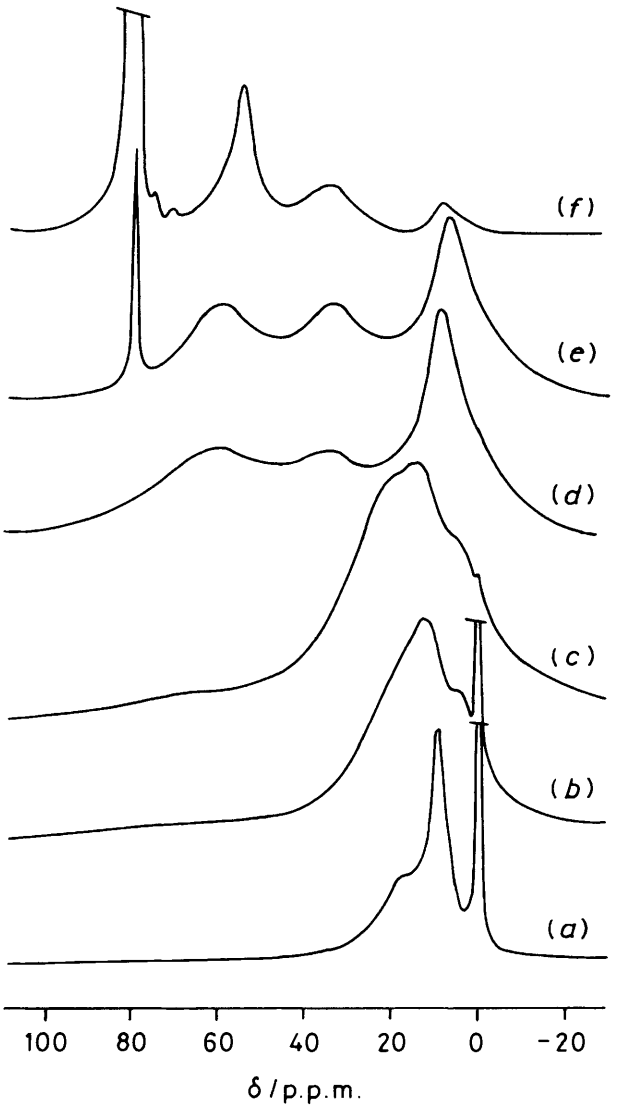


Figure 2. ^{27}Al N.m.r. spectra of 0.25 mol dm^{-3} $AlCl_3 \cdot 6H_2O$ and 0.5 mol dm^{-3} glycolic acid in D_2O at 30 °C, as a function of pH; (*a*) 2.0, (*b*) 3.0, (*c*) 4.0, (*d*) 8.5, (*e*) 10.0, and (*f*) 11.5

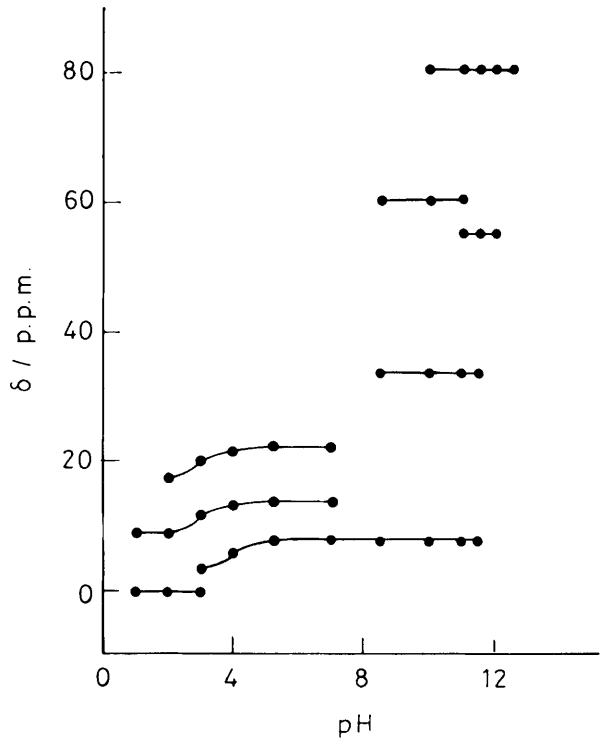
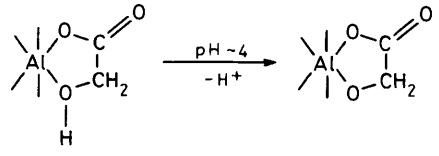


Figure 3. ^{27}Al N.m.r. chemical shifts of 0.25 mol dm^{-3} $AlCl_3 \cdot 6H_2O$ and 0.5 mol dm^{-3} glycolic acid in D_2O at 30 °C, as a function of pH



Scheme 1.

hand, failed to reveal such a phenomenon.[38] Moreover, this is supported by comparing the ^{27}Al chemical shift with that found for acetate as ligand.[19,39] If the glycolate were co-ordinated to the Al^{III} *via* the carboxylate group only one would expect about the same chemical shift as observed for acetate, *i.e.* 4 p.p.m. The larger chemical shift observed for glycolate suggests strain induced by the five-membered ring.[14] Increase of the pH to 2 shows a build up of the 1:1 complex and the appearance of a third signal at 17.5 p.p.m., which is assigned to an octahedral complex $[Al(ga)_2(H_2O)_2]^+$, in accordance with a shift increment of 9 p.p.m. for each bidentate co-ordinated glycolate ligand, as derived above. At pH 3 both signals of the glycolate complexes start to shift to low field, indicating deprotonation of the hydroxy group of glycolate bonded to Al^{III} (Scheme 1). This is in good agreement with the pK_a of this Al^{III}-co-ordinated hydroxy group, which can be estimated to be 3.5 with the use of a previously determined semiempirical relationship.[40] Moreover, this is supported by a simultaneous shift of the ^{13}C and ^{1}H signals to higher frequencies, and also by the structure of a solid aluminium(III)–glycolate complex isolated at this pH, which shows deprotonated hydroxy groups of co-ordinated glycolate (see below). At pH 3, also some aluminium(III)–oligomer is discerned at 3.5 p.p.m. When more NaOH is added to the solution the peaks for the 1:1 and 1:2 complexes as well as that of the oligomer shift to higher frequencies until pH 5 is reached. The shift of the oligomer peak suggests that glycolate is co-ordinated also to the oligomer. Strikingly, all the signals shift by about the same amount, *i.e.* 5 p.p.m., indicating that the same phenomenon occurs in all the complexes: ionization of a hydroxy function of Al^{III}-bonded glycolate.

Apart from the observed shift, the ionization of the hydroxy function is accompanied by an increase in the linewidth for the relevant species (Table). In principle, the linewidth of the signals for the complexes is determined by the quadrupolar relaxation rate and ligand-exchange processes. The quadrupolar relaxation rate may increase because ionization of the hydroxy function of the co-ordinated glycolate causes a change in the electronic symmetry around the aluminium nucleus.[41] On the other hand, the enhanced ligand-exchange rate at pH $\geqslant$ 4, as is observed in ^{17}O, ^{13}C, and ^{1}H n.m.r. spectra, may also cause the observed line broadening.

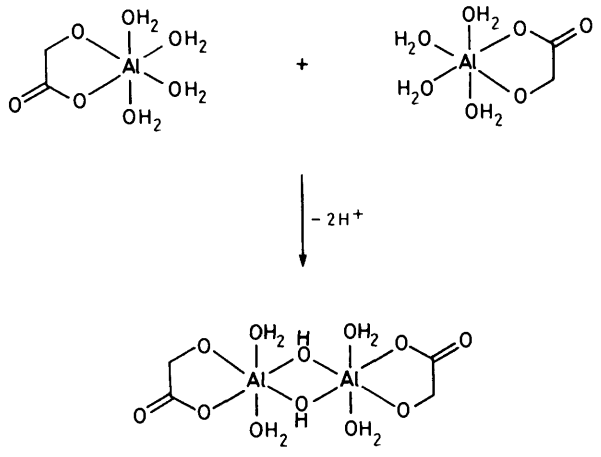
An attempt to improve the resolution of the spectra by changing the sample temperature was unsuccessful. Probably, this is because higher temperatures enhance the ligand-exchange rate and so give rise to exchange broadening, whereas lower temperatures increase the correlation time of the complexes and, consequently, increase the quadrupolar relaxation rate, thus causing line broadening.[42]

At $p = 1/2$, no 1:3 aluminium(III)–glycolate complexes were observed. The concentration of these species are probably low under these conditions and the broad signal of the 1:2

Table. 104.2-MHz ^{27}Al N.m.r. chemical shifts and linewidths of the observed aluminium(III) complexes together with the principal pH region of occurrence

Complex*	Chemical shift (p.p.m.)	Linewidth (Hz)	pH Region
$[Al(H_2O)_6]^{3+}$	0.0	25	<3
$[Al_2(OH)_2(H_2O)_8]^{4+}$	3.5	700	3—4
$[Al_x(OH)_x(H_{-1}ga)_x(ga)_x]$	8.0	1 300	5—11
$[Al(ga)(H_2O)_4]^{2+}$	9.0	400	1—2
$[Al(H_{-1}ga)(H_2O)_4]^{+}$	14.0	1 100	3—5
$[Al(ga)_2(H_2O)_2]^{+}$	17.5	1 400	2—3
$[Al(H_{-1}ga)(ga)(H_2O)_2]$	22.0	2 100	3—6
$[Al(ga)_3]$	27.0	2 200	4—7
$[Al(H_{-1}ga)_3]^{3-}$	34.0	1 600	8—11
$[Al(H_{-1}ga)_2]^{-}$	60.5	2 100	9—11
$[Al(H_{-1}ga)(OH)_2]^{-}$	55.5	700	11—12
$[Al(OH)_4]^{-}$	80.7	70	>11

*ga = $^{-}O_2CCH_2OH$; $H_{-1}ga$ = $^{-}O_2CCH_2O^{-}$.



Scheme 2.

complexes may obscure signals of these species. At lower ρ values (1/5), however, a peak at 27 p.p.m. occurred which is assigned to the complex $[Al(ga)_3]$, in agreement with the proposed ^{27}Al shift increment (9 p.p.m.) for each glycolate.

Above pH 8 the spectra of the samples with ρ = 1/2 change completely. Now, signals arise at 8, 34, and 60.5 p.p.m. The intensity of the oligomer peak at 8 p.p.m. has increased strongly. Probably after ionization of Al^{III}-co-ordinated waters, the 1:1 and 1:2 complexes tend to form oligomers (Scheme 2).

The peak at 34 p.p.m. is ascribed to a 1:3 complex in which probably all three hydroxy groups are ionized (see below). Judged by the chemical shift, the peak at 60.5 p.p.m. is assigned to tetrahedrally co-ordinated Al^{III}, possibly the complex $[Al(H_{-1}ga)_2]^{-}$. When the pH is increased further, not only the signal of $[Al(OH)_4]^{-}$ at 80.7 p.p.m. but also a peak at 55.5 p.p.m. appears. This peak is assigned tentatively to $[Al(H_{-1}ga)(OH)_2]^{-}$. Above pH 12.5, solely the peak at 80.7 p.p.m. remains. It should be noted, however, that the assignment proposed leads to an unexpected order of chemical shifts for the complexes $[Al(OH)_4]^{-}$, $[Al(H_{-1}ga)(OH)_2]^{-}$, and $[Al(H_{-1}ga)_2]^{-}$. If it is assumed that the peak at 55.5 p.p.m. is due to the $[Al(H_{-1}ga)(OH)_2]^{-}$ complex, a chemical shift increment of 25 p.p.m. for each $H_{-1}ga$ ligand would be expected, and then the peak at 34 p.p.m. might be assigned to $[Al(H_{-1}ga)_2]^{-}$. Also species with five-co-ordinated Al^{III}, or polynuclear complexes, cannot be excluded.

^{27}Al N.m.r. spectroscopy was also employed on solutions with ρ = 1. These spectra show a relatively large amount of oligomer in comparison to solutions with ρ = 1/2. Addition of extra ligand to this solution, while maintaining the pH at 4, results in a gradual decrease in the amount of oligomer. At ρ = 1/5 all the oligomer has disappeared and only the peak at 27 p.p.m. remains. Apparently, the excess of glycolate prevents co-ordination of water to the Al^{III} and the consecutive formation of oligomers.

The addition of extra amounts of glycolate to a solution at ρ = 1/2, maintained at pH 8.8, again causes a gradual disappearance of the oligomer. At this pH the peak at 34 p.p.m. remains, which is tentatively assigned to the complex $[Al(H_{-1}ga)_3]^{3-}$. This assignment is supported, however, by comparing the chemical shift of a solid aluminium(III)–glycolate complex (see below).

These experiments demonstrate that excess of glycolate not only may prevent the formation of the oligomer, but also can dissociate the oligomers that are already present in solution.

The Interaction of Glycolate with the Al_{13} *Polyanion.*—The interaction of glycolate with the tridecamer was investigated in an attempt to support the assignment of the peaks at 55.5 and 60.5 p.p.m. in the ^{27}Al n.m.r. spectra. Therefore, a base-hydrolysed solution was made with a molar ratio NaOH:Al^{III} of 2:1. Addition of a small quantity of glycolic acid to this solution (pH 3.3, ρ = 6) caused a strong decrease in the peak at 63 p.p.m. for the central tetrahedral Al^{III} of the Al_{13} polyanion, and the appearance of a signal for the $[Al(ga)(H_2O)_4]^{2+}$ complex at 9 p.p.m. Upon further addition of glycolic acid the peak at 63 p.p.m. disappeared, while the intensities of the signals for the 1:1, 1:2, and polynuclear aluminium(III)–glycolate complexes increased. No other resonances were discerned. The ^{27}Al n.m.r. spectrum of this sample (ρ = 1) shows no difference from those of solutions prepared in the ordinary way, *i.e.* addition of NaOH to an acidic solution of Al^{III} and glycolic acid in D_2O. These results show that glycolic acid is very efficient in destroying the tridecamer. The oligomer, on the contrary, is much more stable towards glycolic acid, as discussed above. These results are in agreement with those reported for acetate as the ligand.[19,39]

^{27}Al *M.A.S. and* ^{13}C *C.P.M.A.S. N.M.R. Spectra of Powdered Single Crystals of* $Al_2(H_{-1}ga \cdots H \cdots H_{-1}ga)_3Na_3$.—[43]* The ^{27}Al m.a.s. n.m.r. spectrum of powdered single crystals $Al_2(H_{-1}ga \cdots H \cdots H_{-1}ga)_3Na_3$ shows a single peak, without fine structure, centred at 25.5 p.p.m. with a linewidth of 620 Hz (Figure 4). Assuming that the linewidth is dominated by the quadrupole interaction, an upper bound of the second-order quadrupole shift can be estimated from the m.a.s. linewidth.[44] Thus an isotropic chemical shift of about 30 p.p.m. is obtained. This value fits well within the results obtained from liquid-state ^{27}Al n.m.r. spectroscopy (see above). This solid, in which the hydroxy groups are half deprotonated, is observed at intermediate chemical shift with respect to the 1:3 aluminium(III)–glycolate with none (27 p.p.m.) and all (34 p.p.m.) hydroxy moieties deprotonated. This solid-state n.m.r. experiment also demonstrates that derivation of the co-ordination number of the aluminium polyhedron from the (corrected) ^{27}Al chemical shift may be ambiguous.[45]

The ^{13}C c.p.m.a.s. n.m.r. spectrum of the powdered single crystals shows only two peaks at 61 and 180 p.p.m. respectively (Figure 5). This points to a preferred facial geometry of the ligands in the solid state.

* Recently, these results were confirmed by a single-crystal *X*-ray analysis which shows 1:3 aluminium(III)–glycolate complexes with a facial geometry. The carboxylate site of the ligand is also co-ordinated to Na, while the hydroxy moieties connect two 1:3 glycolate complexes *via* three short hydrogen bonds to give a binuclear complex.

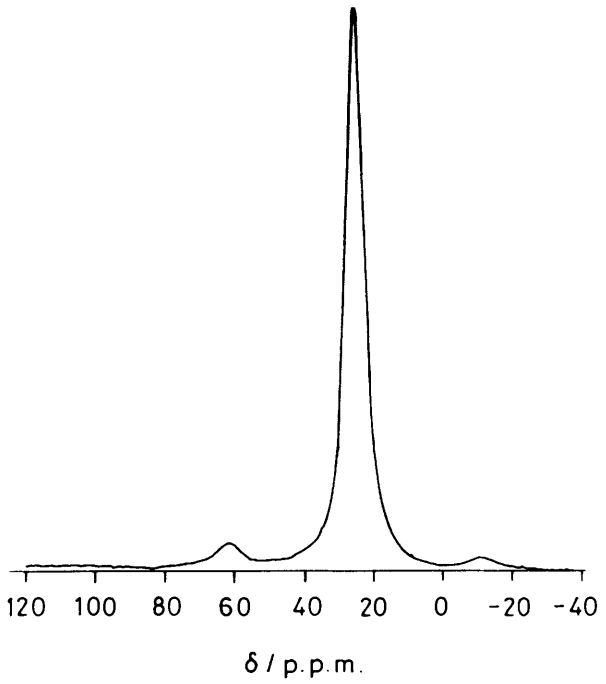


Figure 4. ^{27}Al M.a.s. n.m.r. spectrum of powdered single crystals of $Al_2(H_{-1}ga \cdots H \cdots H_{-1}ga)_3Na_3$ at 30 °C

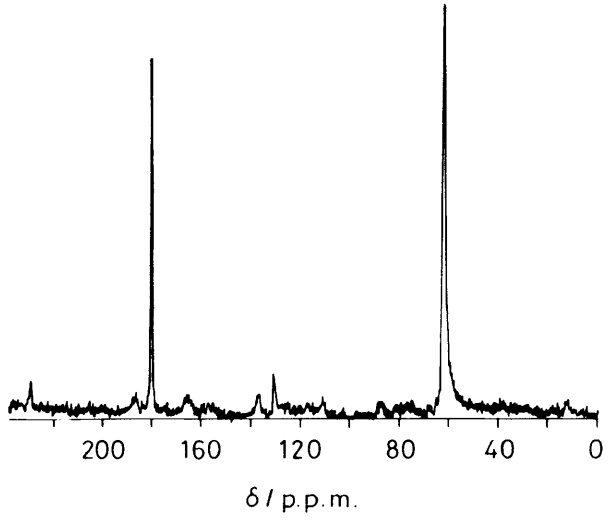


Figure 5. ^{13}C C.p.m.a.s. n.m.r. spectrum of powdered single crystals of $Al_2(H_{-1}ga \cdots H \cdots H_{-1}ga)_3Na_3$ at 30 °C

^{17}O *N.M.R. Spectra of Aqueous Solutions of* Al^{III} *and Glycolic Acid.*—Experiments performed on samples of glycolic acid with a natural abundance of ^{17}O did not reveal any Al^{III}-bonded glycolate. Only a decrease of the signals of unbound glycolic acid and of Al^{III}-co-ordinated water was observed. Therefore, glycolic acid with ^{17}O-enriched carboxylate groups was used. No attempt was made to enrich the hydroxy group of glycolic acid because this signal coincides with the water signal in the ^{17}O n.m.r. spectrum.

The spectra of solutions of Al^{III} and glycolic acid with $p = 1/2$ at 30 °C are shown in Figure 6. They showed a similar splitting of the carboxylate resonance to that observed for oxalic and malonic acid, thus demonstrating bidentate co-ordination *via* the carboxylate and the hydroxy group. Below pH 4, both free and co-ordinated glycolate are observed, indicating slow exchange on the n.m.r. time-scale. Increase of the temperature to 75 °C causes coalescence of the peaks, in contrast to the results obtained for oxalic and malonic acid. This, again, points to a relatively high ligand-exchange rate of the aluminium(III)–glycolate complexes. At pH 4 coalescence occurs of the signals for bonded and free glycolate and above pH 6 only one average peak remains. Apparently, the ligand-exchange rate is relatively high at pH $\geqslant 6$.

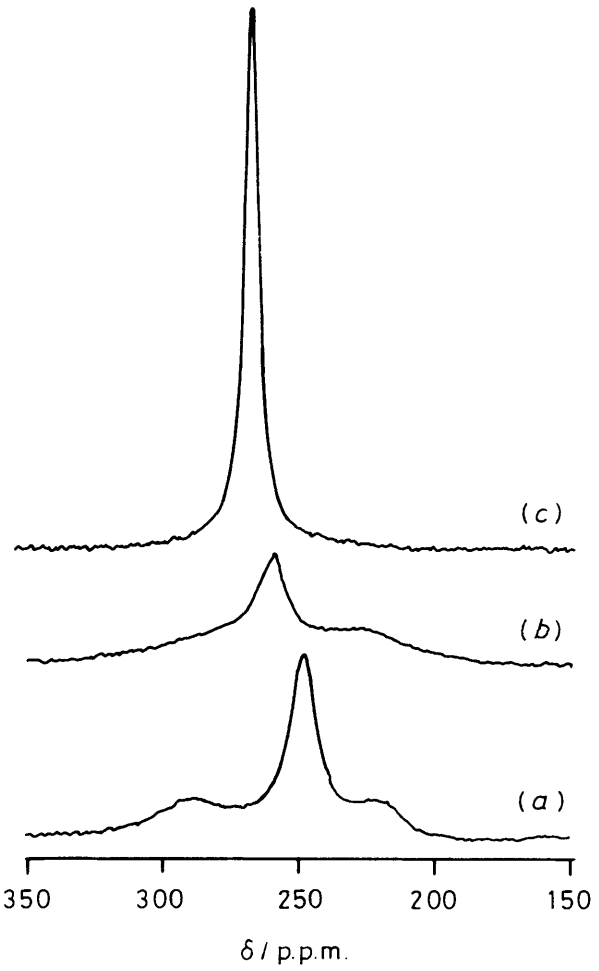


Figure 6. 54.2-MHz ^{17}O N.m.r. spectra of 0.25 mol dm^{-3} $Al(NO_3)_3 \cdot 9H_2O$ and 0.5 mol dm^{-3} glycolic acid (with 5% ^{17}O-enriched carboxylate groups) in D_2O at 30 °C: pH 2.1 (*a*), 4.0 (*b*), and 8.5 (*c*)

Oxygen-17 n.m.r. spectroscopy on solutions with $p = 1$ showed a deviation from the expected 1:1 ratio of the intensities of the two signals of Al^{III}-bonded glycolate. The intensity of the peak at 220 p.p.m., ascribed to the Al^{III}-bonded oxygen of the carboxylate group, is increased upon increase of pH (Figure 7). The ^{27}Al n.m.r. spectra of these samples show a high concentration of the oligomer. Therefore it is suggested that this oligomer consists partly of bridging glycolate ligands (Figure 8). Bridging carboxylate groups are known to occur in many polynuclear metal carboxylates.[46]

^{1}H *N.M.R. Spectra of Aqueous Solutions of* Al^{III} *and Glycolic Acid.*—The influence of the pH on the ^{1}H n.m.r. spectra of solutions with $p = 1/2$ is schematically represented in Figure 9. At pH <2 a small signal to low field of the CH_2 hydrogens is observed, which is assigned to Al^{III}-co-ordinated glycolate without ionization of the hydroxy group. At pH 3 this second signal has increased in intensity and starts coalescing with the signal of free glycolic acid. Probably, this is due to the enhanced ligand-exchange rate at pH values close to the pK_a of glycolic

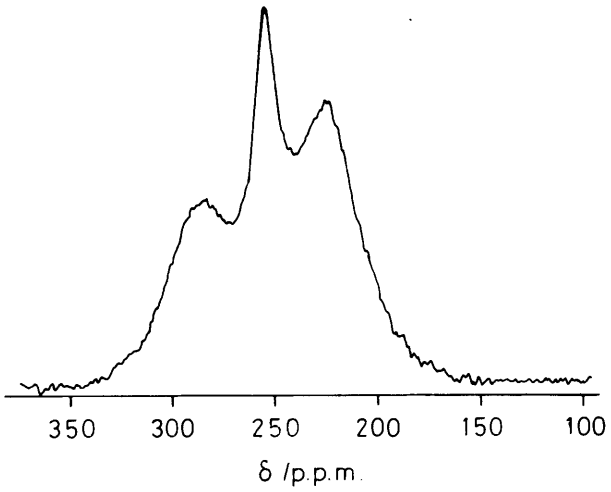


Figure 7. 54.2-MHz ^{17}O N.m.r. spectrum of 0.25 mol dm^{-3} $AlCl_3 \cdot 6H_2O$ and 0.25 mol dm^{-3} glycolic acid (with 5% ^{17}O-enriched carboxylate groups) in D_2O at 30 °C and pH 3.0

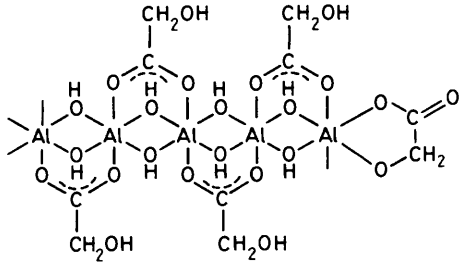


Figure 8. Tentative structure of the polynuclear aluminium(III)–glycolate complex

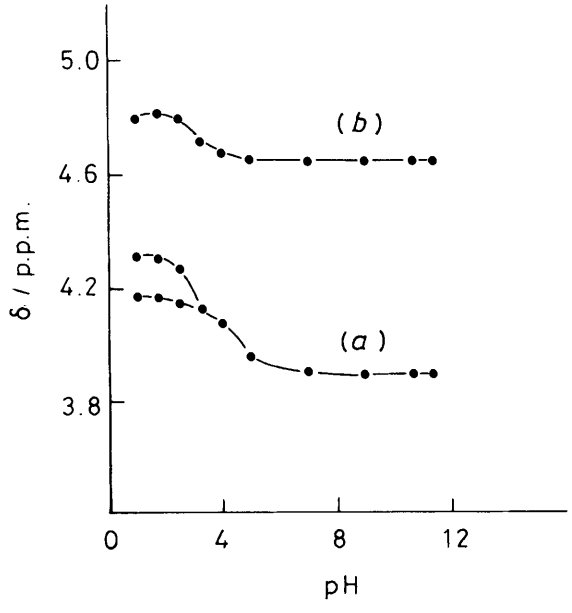


Figure 9. 400-MHz ^1H N.m.r. chemical shifts of 0.25 mol dm^{-3} $AlCl_3 \cdot 6H_2O$ and 0.5 mol dm^{-3} glycolic acid in D_2O at 30 °C, as a function of pH: (*a*) $CH_2O(H)$, (*b*) HDO

acid (3.6).[47] When the pH is increased to 6 a gradual shift of this averaged peak is observed, which may be indicative of ionization of the hydroxy group of co-ordinated glycolate. It should be noted that a solution of glycolic acid in D_2O shows a similar shift in this pH region due to ionization of the carboxylic

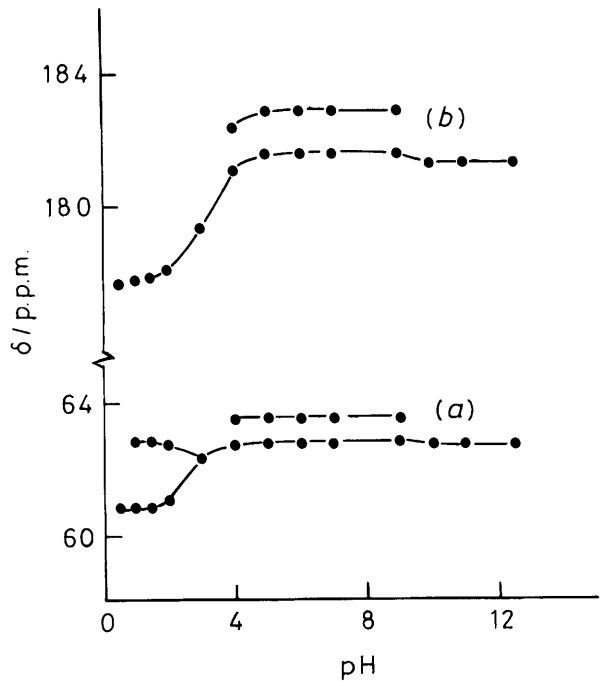


Figure 10. 100.6-MHz ^{13}C N.m.r. chemical shifts of 0.25 mol dm^{-3} $AlCl_3 \cdot 6H_2O$ and 0.5 mol dm^{-3} glycolic acid in D_2O at 30 °C, as a function of pH: (*a*) $-CH_2O(H)$, (*b*) $-CO_2(H)$

acid group. During this pH variation the HDO signal shifts from 4.80 to 4.65 p.p.m., while the linewidth of this peak decreases from 45 to 1.5 Hz. Obviously, this is caused by the lower number of water molecules participating in co-ordination of Al^{III} at pH 6, and by the enhanced exchange rate of the protons of these water molecules.[33] Upon further increase of pH no shift or linewidth change is observed for the signals of both HDO and glycolate. This points to a rapid ligand-exchange rate in this pH region, similar to the results obtained by ^{17}O n.m.r. spectroscopy.

^{13}C N.M.R. Spectra of Aqueous Solutions of Al^{III} and Glycolic Acid.—The results of ^{13}C n.m.r. spectroscopy applied to solutions with $p = 1/2$ are shown in Figure 10. At pH 0.5 the ^{13}C n.m.r. spectra of the aluminium(III)–glycolate solutions show signals with the characteristic chemical shift and linewidth of unbound glycolic acid. At pH 2 an additional peak is observed to low field of the CH_2 peak, which increases in intensity upon raising the pH. This peak is ascribed to Al^{III}-co-ordinated glycolate without ionization of the hydroxy moiety. At pH 3 the peaks for free and complexed glycolic acid coalesce, probably due to the enhanced ligand-exchange rate, as was observed in the ^1H n.m.r. spectra. When the pH is raised further both carbon signals of glycolate show a gradual shift that is completed at pH 5. This shift is ascribed to ionization of the hydroxy group of glycolate, similar to the results found for aluminium(III)–citrate complexes by Gregor and Powell.[48] At this pH, small peaks appear to low field of the two carbon signals of glycolate. The intensity of these peaks increases with pH and higher p values. Above pH 10, however, they disappear. This behaviour is in accord with the intensity changes of the oligomer signal in the ^{27}Al n.m.r. spectrum (see above). Therefore these peaks are ascribed to glycolate participating in the polynuclear complexes.

Conclusion

The combination of ^1H, ^{13}C, ^{17}O, and ^{27}Al n.m.r. techniques

proved to be a powerful tool in the characterization of aluminium(III) complexes with glycolic acid in aqueous solution. At high field ($\geqslant$9.4 T) the observation of several species in the ^{27}Al n.m.r. spectra is no longer restricted to highly symmetric or to extremely slowly exchanging ligands. This seems promising with respect to future research on the co-ordination of Al^{III} in aqueous solution with more complicated hydroxycarboxylic acids, *i.e.* malic, tartaric, and glucaric acid. High-field ^{27}Al n.m.r. in combination with ^{17}O n.m.r. spectroscopy may give a wealth of information about the species present in these solutions.

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