Raman Spectra of Aqueous Solutions of Hydrolysed Aluminium(III) Salts

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The hydrolysis of aluminum salts in aqueous solution has been studied by Raman spectroscopy. Evidence for the occurrence of the ion $[Al_{13}O_4(OH)_{24}(OH_2)_{12}]^{7+}$ in solutions containing a formal $[OH^-]:[Al^{3+}]$ ratio of 2.5 :1 is provided by comparisons with the spectra of crystalline compounds containing this ion. The presence of other polymeric species in less highly hydrolysed solutions cannot be confirmed.

EXCEPT in very dilute solution and at low degrees of hydrolysis, hydrolysed solutions of aluminium(III) salts contain polymeric species.[1] The degree of aggregation depends on the formal ratio $m = [OH^-] : [Al^{3+}]$, although (especially at higher values of m) equilibrium may be attained only slowly. At high degrees of hydrolysis (m *ca.* 2.5) a variety of evidence [2-10] points to the formation of a complex containing *ca.* 13 aluminium atoms per molecule. This complex is generally considered to be the cation $[Al_{13}O_4(OH)_{24}(OH_2)_{12}]^{7+}$, whose structure (Figure 1) was established by X-ray measurements [5] on the crystalline derivatives $Na[Al_{13}O_4(OH)_{24}(OH_2)_{12}(XO_4)_4]$ (X = S or Se). Evidence of the structural identity of the solution and the crystalline species is, however, limited. Low-angle X-ray scattering data for solutions [6] indicate an ion with a radius of gyration equal to the expected value for the species. Aluminium-27 n.m.r. observations [8,10] show the presence of a tetrahedrally co-ordinated aluminium atom in an environment of zero (or near-zero) field gradient, as required for the central atom of the ' Al_{13} ' cluster.

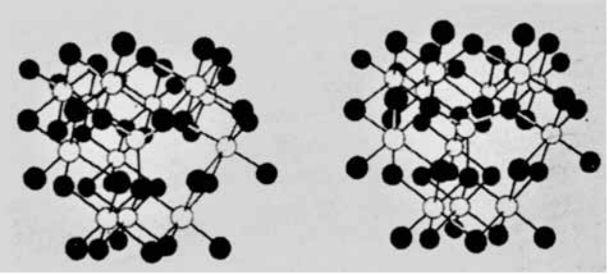

FIGURE 1 The $[Al_{13}O_4(OH)_{24}(OH_2)_{12}]^{7+}$ ion (stereoscopic pair): ○ = aluminium, ● = oxygen

We now present Raman spectroscopic data on the above crystalline compounds and on hydrolysed aqueous solutions of m *ca.* 2.5. The observations support the view that the solutions contain the same polymeric ion as is present in the crystals. Observations on solutions of lower degrees of hydrolysis were less fruitful in identifying other polymers.

EXPERIMENTAL

Solutions.—The Raman spectra are weak, and for this reason solutions of high concentration were required. Because of often reported differences of properties of nominally identical solutions prepared in different ways, highly hydrolysed solutions were prepared by three methods. (*i*) By prolonged reflux of aluminium powder (0.1 mol, added gradually) with dilute hydrochloric acid (0.05 mol) in the presence of a drop of mercury. The resulting solution was concentrated to *ca.* 6 mol dm^{-3} on a rotary evaporator. (*ii*) By precipitation of aluminium hydroxide, by controlled mixing of aluminium chloride and sodium carbonate solutions in a continuous-flow apparatus at pH 6.4, followed by dissolution of the precipitate in concentrated HCl, under reflux, to give a $[Cl^-]:[Al^{3+}]$ ratio of 0.50 : 1. After equilibrating at the boiling point for 0.5 h, the solution was concentrated to $[Al^{3+}] = 6$ mol dm^{-3}. (*iii*) From commercial ' aluminium chlorohydrate ', $Al_2Cl(OH)_5$ (which is prepared by reaction of aluminium metal with aluminium chloride). Material of typical analysis (Al, 24.9; Cl, 16.8 w/w%) as a spray-dried powder (I.C.I. Ltd.) was dissolved to give $[Al^{3+}] = 6$ mol dm^{-3} and equilibrated for 5 h at 80 °C.

Solutions were analysed for aluminium present in the form of colloidal or dispersed solid matter by filtration through ' Millipore ' filters. The proportions of aluminium in the form of low-molecular-weight (*i.e.* mono- and dimeric) and high-molecular-weight material were estimated by Turner's method [11] which is based on differences in the rates of reaction with quinolin-8-ol. The results (see Table 1) show relatively little variation between solutions prepared by the three methods and suggest that, for these solutions at least, the composition is not markedly dependent on the method of preparation.

Solids.—The compound $[Al_2(OH)_2(OH_2)_8][SO_4]_2$ and the compounds containing the $[Al_{13}O_4(OH)_{24}(OH_2)_{12}]^{7+}$ cation were prepared as well defined crystals by the methods of Johansson and his co-workers.[4,5,12] Analyses for Al, Cl$^-$,

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[1] See, for example, N. I. Eremin, Yu. A. Volokhov, and V. E. Mironov, *Russ. Chem. Rev.*, 1974, **43**, 92.

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[11] R. C. Turner, *Canad. J. Chem.*, 1969, **47**, 2521.

[12] G. Johansson, *Acta Chem. Scand.*, 1962, **16**, 403.

$[SO_4]^{2-}$, and $[SeO_4]^{2-}$ agreed well with the published data. Attempts to prepare periodate and tellurate derivatives of the ' Al_{13} ' cation by analogous methods were unsuccessful, gelatinous precipitates being obtained in each case.

Spectra.—Raman spectra were recorded on a Spex ' Ramalab ' instrument, with excitation at 488.0 or 514.5 nm from a Coherent Radiation Laboratories model 52 MG laser. Multipassing of the laser beam through the solution samples was necessary to produce spectra of satisfactory intensity. Polarisation data were obtained by the use of a half-wave plate in the incident beam. Solids were examined as pellets, with a combination of spherical and cylindrical lenses in the laser beam to minimise the incident power density.[13] Infrared spectra were recorded in CsBr discs on a Perkin-Elmer model 457 spectrophotometer.

TABLE 1

Analytical data for hydrolysed aluminium chloride solutions

	Method		
	(*i*)	(*ii*)	(*iii*)
$[OH^-] : [Al^{3+}]$	2.49	2.45	2.48
% Al as (monomer + dimer)	4.1	5.7	6.0
% Al as polymer	93.3	90.3	90.0
% Al as solid >25 nm	2.6	4.0	4.0

RESULTS AND DISCUSSION

The $[Al_{13}O_4(OH)_{24}(OH_2)_{12}]^{7+}$ *Ion.*—Raman spectra of solutions prepared by methods (*i*)—(*iii*) were indistinguishable. The spectrum of a freshly prepared solution of $Al_2Cl(OH)_5$ was essentially identical with the spectra of equilibrated solutions, but the band intensities were slightly lower. The solution spectrum and spectra of the sulphate and selenate salts of the ' Al_{13} ' cation are shown in Figure 2. For the crystalline compounds, bands of the oxo-anions unfortunately obscured regions of the cation spectra. However, the regions so obscured were different for the two salts, and so it is possible to make a fairly complete comparison between the solution spectrum and the cation bands of the solids. There were small differences in band position (Table 2) and intensity which can reasonably be attributed to a change of state or change of anion, but it is clear that the cation spectra are essentially identical. Of particular importance is the fact that several of the Raman bands in the solution spectrum were highly polarised. In fact, within the accuracy of measurement, all the bands indicated as polarised (Table 2) had $\rho \approx 0$. Symmetry considerations require $\rho = 0$ only for totally symmetric

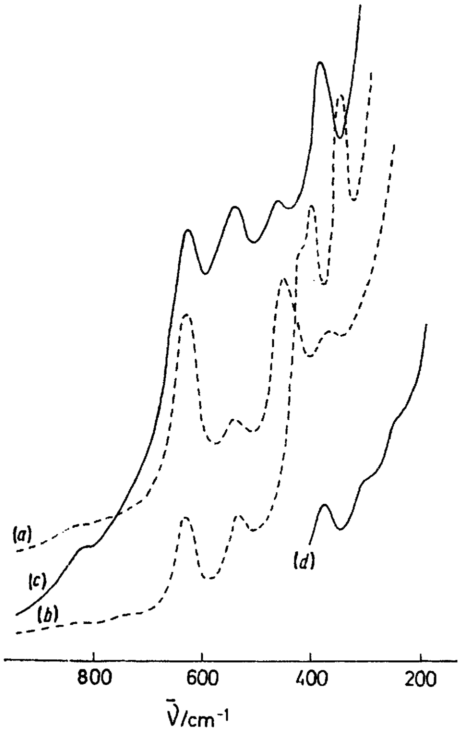

FIGURE 2 Raman spectra: (*a*) solid $Na[Al_{13}O_4(OH)_{24}(OH_2)_{12}(SO_4)_4]$; (*b*) solid $Na[Al_{13}O_4(OH)_{24}(OH_2)_{12}(SeO_4)_4]$; (*c*) and (*d*) a solution (6 mol dm^{-3} in Al) of $AlCl(OH)_5$. Spectrum (*d*) was recorded at one third of the gain used for (*c*)

TABLE 2

Raman and infrared spectra (cm^{-1}) of solids and solutions containing the $[Al_{13}O_4(OH)_{24}(OH_2)_{12}]^{7+}$ cation

Raman				Infrared		
Sulphate (solid) *	Selenate (solid) *	Aluminium chlorohydrate (solution)	Aluminium chlorodeuterate (solution)	Sulphate (solid) *	Selenate (solid) *	Aluminium chlorohydrate (solid)
		248w, pol		298w, sh	298w, sh	
		295w, pol		310m	310m	300w
	(345s)			375m	370w	368w
375m		380s, pol	362s		(410m)	
	(402s)			490m	490mw	480w
	(422m, sh)			550w, sh	540w	530w, sh
(452s)				(612ms)		
		452m, dp	452m		630m, br	618m, br
546m	542m	542s, pol	530s	730ms	725ms	770ms
(618s)					(882s)	
	625ms	625s, pol	625s	975w		970w, br
		835w, dp	835w		1 020w, br	
					1 110mw	1 090ms
				(1 115s, br)		
				1 420vw	1 418w	1 420vw

w = weak, m = medium s = strong, v = very, sh = shoulder, pol = polarized, dp = depolarized.

* Bands attributed to the sulphate and selenate anions are enclosed in parentheses.

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vibrations of molecules of spherical symmetry. Some molecules of lower symmetry exhibit modes with ρ *ca.* 0, but it would be unusual to find such a molecule with several modes having very low ρ values. This observation alone points to the presence of a species both of considerable size (for only then can there be several totally symmetric vibrations) and of spherical (or near-spherical) symmetry. Some confirmation that the solution spectrum originates from a single species and not from a mixture of different ions in equilibrium is provided by dilution experiments. Spectra were obtained from solutions [prepared by method (*i*)] spanning the concentration range 2—7 mol dm^{-3}. (At concentrations <2 mol dm^{-3} the spectra became very weak.) No variations in relative intensities within these spectra could be discerned.

The i.r. spectra may be similarly compared. Data for the crystalline sulphate and selenate and for amorphous $AlCl(OH)_5$ are given in Table 2. The cation spectra were again essentially identical. The combined spectral evidence therefore points to the conclusion that hydrolysed solutions of *m ca.* 2.5 contain the 'Al_{13}' complex cation as the major constituent. It may be inferred that the ion is also present with little structural modification in solid $AlCl(OH)_5$.

Partial band assignments may be made as follows. The vibrational representation (T_d symmetry: OH and OH_2 groups treated as single atoms) is $\Gamma_{vib} = 9A_1 + 4A_2 + 13E + 16F_1 + 22F_2$. Five A_1 modes were observed in the Raman spectrum. Since, for molecules of spherical symmetry, A_1 bending modes are expected to be weak,[14,15] we assign the observed A_1 bands to stretching vibrations (*i.e.* to vibrations of predominantly bond-stretching character). A solution of $AlCl(OD)_5$, prepared from the chlorohydrate by repeated dissolution and evaporation with D_2O, gave the Raman bands in Table 2. The two lowest-frequency modes observed for the chlorohydrate were not seen in the spectrum of the chlorodeuterate. The two bands showing significant frequency shifts must be associated with motions of OH or OH_2 groups. We assign the band at 542 cm^{-1} to Al–OH_2 vibration and the band at 380 cm^{-1} to Al–OH–Al vibration. The relatively higher intensity of the latter band may be correlated with the fact that there are 48 $(Al–O)_b$ bonds in the molecule compared to only 12 $(Al-O)_t$ bonds. The remaining bands were insensitive to deuterium substitution and the extent of involvement of the peripheral oxygens is probably small. We offer a tentative assignment of the band at 625 cm^{-1}: because of its relatively high frequency, which must in part reflect the magnitudes of the force constants involved, it might reasonably be assigned to stretching of the tetrahedral group of four bonds attached to the central aluminium atom of the cluster.

Solutions having m < 2.5.—The Raman spectrum of a freshly prepared solution of $AlCl_3$ showed bands at 525 p, (ν_1, A_{1g}), 440 dp (ν_2, E_g), and 330 dp cm^{-1} (ν_5, F_{2g}), consistent with the octahedral $[Al(OH_2)_6]^{3+}$ ion, in agreement with previous observations.[16] N.m.r.,[10] sedimentation,[7] and pH [7,9] data suggest that solutions having *m ca.* 1.0 contain an appreciable concentration of the dimer $[Al_2(OH)_2(OH_2)_8]^{4+}$. This ion is present in the crystalline derivative $[Al_2(OH)_2(OH_2)_8][SO_4]_2$, the Raman spectrum of which showed only a single band, 530 cm^{-1}, attributable to the cation, any other bands being obscured by relatively strong anion bands or by the Rayleigh background. The spectrum of a solution of formal composition $AlCl_2(OH)$ showed bands at 540p, 410 (dp or weakly polarised), and 340dp cm^{-1}. Because of the similarity to the spectrum of the monomer, it is not possible to infer the presence of other species. It has been suggested [10] that solutions in the range $1.5 < m < 2.0$ might contain a high concentration of an octameric species. The Raman spectra of such solutions are difficult to interpret because of band overlap, but may reasonably be accounted for as superpositions of spectra of a monomer (or dimer) and the tridecamer. Thus they offer no firm support for the occurrence of an intermediate polymer.

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