

# Aluminium-27 and $^{71}\text{Ga}$ NMR studies of the solution chemistry of $\text{Ga}[\text{AlCl}_4]$ and related compounds

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The non-aqueous solution chemistry of  $\text{GaAlCl}_4$  has been investigated by  $^{27}\text{Al}$  and  $^{71}\text{Ga}$  NMR spectroscopy. In dilute solution in benzene, the solute species are of the form  $\{[\text{R}_n\text{Ga}]^+[\text{Cl}_x\text{AlCl}_{4-x}]^-\}_m$  ( $\text{R}$  = arene;  $x = 1-3$ ,  $n$ ,  $m$  undetermined), while in concentrated solutions the dominant interactions involve aggregates of ion pairs. Dilute solutions of the salt in *n*-heptane have also been studied, together with *n*-heptane–benzene mixtures, solutions of  $\text{GaAlCl}_4$  and  $\text{Ga}_2\text{Cl}_6$  in *n*-heptane, solutions of  $\text{GaAlBr}_4$  and  $\text{GaAlI}_4$  in benzene, and mixed  $\text{GaAlCl}_4$ – $\text{GaAlBr}_4$  systems. The hydrolysis of  $\text{GaAlCl}_4$  in benzene is shown to involve reaction at both Ga and Al centres.

The +I and +II oxidation states of gallium and indium represent a relatively unexplored area of Main Group chemistry, and in particular the structures of these species in both solid and solution phases raise some interesting problems.<sup>1,2</sup> A number of these are illustrated by the behaviour of the so-called gallium dihalides. The crystalline state of ‘ $\text{GaCl}_2$ ’ clearly contains  $\text{Ga}^+$  and  $\text{GaCl}_4^-$  ions, with the cation co-ordinated by eight chlorides of the surrounding anions,<sup>3</sup> and a similar situation holds for ‘ $\text{GaI}_2$ ’.<sup>4</sup> There are no simple solid binary compounds in which the Ga–Ga bonds have been identified, but adducts such as  $\text{Ga}_2\text{X}_4(\text{diox})_2$  ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ ;  $\text{diox} = 1,4$ -dioxane) show this feature,<sup>5</sup> as do the anionic complexes<sup>2,6</sup>  $\text{Ga}_2\text{X}_6^{2-}$ . It has been argued elsewhere<sup>1</sup> that a crucial factor in stabilizing Ga–Ga and similar M–M bonds is the prevention of intramolecular halide transfer through co-ordinative saturation at the metal centres.

Gallium dihalides are appreciably soluble in aromatic solvents, and the solvation of the  $\text{Ga}^+$  cation is believed to play a significant role in this respect. Studies of these solutions by previous workers, using  $^{71}\text{Ga}$  NMR spectroscopy, are discussed below. The compounds which are produced on crystallization reveal a fascinating range of structures,<sup>7</sup> and the differing modes of co-ordination are reminiscent of those reported for the substituted cyclopentadienyl derivatives of indium(I). It is significant that analogous  $\text{MR}^+$  ( $\text{R}$  = arene) and  $\text{MCp}$  molecules ( $\text{M} = \text{Ga}$  or  $\text{In}$ ) are isoelectronic.<sup>2</sup>

The related  $\text{GaAlX}_4$  compounds<sup>8,9</sup> have received less attention than the  $\text{Ga}_2\text{X}_4$  systems. The ionic nature of  $\text{Ga}[\text{AlCl}_4]$  has been confirmed by vibrational spectroscopy<sup>10</sup> and X-ray crystallography;<sup>11</sup> the latter studies identified eight-co-ordination of  $\text{Ga}^+$ , with Ga–Cl distances corresponding to a  $6 + 2 + 1$  interaction. We now report NMR studies of such compounds, mainly for  $\text{X} = \text{Cl}$  and  $\text{Br}$ , using  $^{27}\text{Al}$  and  $^{71}\text{Ga}$  MNR spectroscopy. The results refer to both aromatic and aliphatic solvents, and are discussed in terms of solvation and ion-multiplet interactions. Comparisons are made with earlier work on  $^{71}\text{Ga}$  spectroscopy of  $\text{Ga}_2\text{X}_4$  compounds in solids, melts and aromatic solvents.<sup>7,12</sup>

## Experimental

The compound  $\text{GaAlCl}_4$  was prepared by the literature method,<sup>8</sup> involving the reaction of elemental aluminium with  $\text{GaCl}_3$ . The composition was confirmed analytically (Found: Ga, 28.8; Al, 11.8. Calc. for  $\text{AlCl}_4\text{Ga}$ : Ga, 29.2; Al, 11.3%). Analogous reactions yielded  $\text{GaAlBr}_4$  and  $\text{GaAlI}_4$ . The

preparation and analysis of  $\text{Ga}_2\text{Cl}_6$  followed methods described previously.<sup>13</sup> All solvents were purified before use by distillation from calcium hydride.

Samples for NMR studies were prepared in an atmosphere of dry nitrogen: concentrations are stated as wt. %, *i.e.* weight of solute (g) per 100 g of solution. Spectra were recorded on a Varian 500 instrument operating at a frequency of 152.34 MHz for  $^{71}\text{Ga}$ , and 130.24 MHz for  $^{27}\text{Al}$ . Resonance frequencies refer to  $\delta = 0$  for  $^{71}\text{Ga}$  in  $[\text{Ga}(\text{H}_2\text{O})_6]^{3+}$ , and for  $^{27}\text{Al}$  in  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ . Each value quoted is the average of at least six measurements, following the techniques described earlier.<sup>13,14</sup> The experimental errors on the reported values are better than in our previous work because of the relatively sharp resonances observed for  $^{71}\text{Ga}$ . The determination of  $T_1$  involved an  $180-t-90^\circ$  inversion recovery pulse sequence, and pulse width measurements were a regular feature of such studies, as were integral scale measurements.

We noted an interesting effect in the solutions of  $\text{GaAlCl}_4$ . Over the course of 6 months, during which the samples were stored at ambient temperature, the half-widths of the  $^{71}\text{Ga}$  resonance decreased systematically by *ca.* 60%, while those for  $^{27}\text{Al}$  increased by *ca.* 30%. In contrast, the chemical shifts for both nuclei were invariant over this same period. All the (averaged) values in Table 1 are for measurements taken at the end of this period, when changes over 1 month did not exceed 5%. We take these effects to be evidence of slow equilibration processes in such solutions. The values in Table 2 are for solutions kept for a few days at 60 °C before the spectra were recorded; under these circumstances, the differences in  $w_2$  did not exceed 15% between successive measurements.

## Results and Discussion

### General

As noted above, the crystal structures of  $\text{Ga}_2\text{Cl}_4$ ,  $\text{Ga}_2\text{I}_4$  and  $\text{GaAlCl}_4$  have been established. All involve co-ordination of  $\text{Ga}^+$  by halides of the  $\text{MX}_4^-$  anion, and some important parameters are given in Table 3. There is also information on the crystalline derivatives of the complexes of  $\text{Ga}_2\text{X}_4$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) with aromatic molecules, carefully reviewed by Schmidbaur.<sup>7</sup> A mononuclear  $[(\eta^6\text{-R})\text{Ga}]^+$  unit has been identified in  $\text{Me}_6\text{C}_6\text{Ga}_2\text{Br}_4$ , in which  $\text{Ga}^+$  is also co-ordinated by five bromine atoms; this  $\eta^6$ -co-ordination of the aromatic ligand is in keeping with species such as  $\text{CpM}$  ( $\text{M} = \text{In}$  or  $\text{Tl}$ ) and

**Table 1** Aluminium-27 and  $^{71}\text{Ga}$  NMR data for benzene solutions of  $\text{GaAlCl}_4^a$ 

Concentration	$^{27}\text{Al}$						$^{71}\text{Ga}$					
	20 °C			80 °C			20 °C			80 °C		
	$\delta$	$w_{1/2}^1$	$T_1$	$\delta$	$w_{1/2}^1$	$T_1$	$\delta$	$w_{1/2}^1$	$T_1$	$\delta$	$w_{1/2}^1$	$T_1$
1.1 <sup>b</sup>	103	190	1.7	103	130	2.8	-675	130	4.0	-656	300	4.1
1.8 <sup>b</sup>	103	260	1.4	103	180	2.3	-680	120	3.9	-656	300	4.6
3.5 <sup>c</sup>	103	200	2.1	103	150	3.4	-678	100	3.8	-654	270	5.7
22.7 <sup>c</sup>	103	140	2.8	103	95	4.7	-696	70	7.8	-674	200	8.0
36.5 <sup>d</sup>	103	120	2.9	103	90	4.9	-697	80	7.0	-674	155	9.2
46.6 <sup>d</sup>	102	180	2.2	102	115	3.9	-695	80	6.8	-675	145	11.0

<sup>a</sup> All values are averaged from six measurements (see Experimental section); concentration in wt. %,  $\delta$  in ppm,  $w_{1/2}^1$  in Hz,  $T_1$  in  $10^{-3}$ s. <sup>b</sup> Dilute solution. <sup>c</sup> Solutions from two-phase system; see Experimental section. <sup>d</sup> Heavy phase of two-phase system.

**Scheme 1**

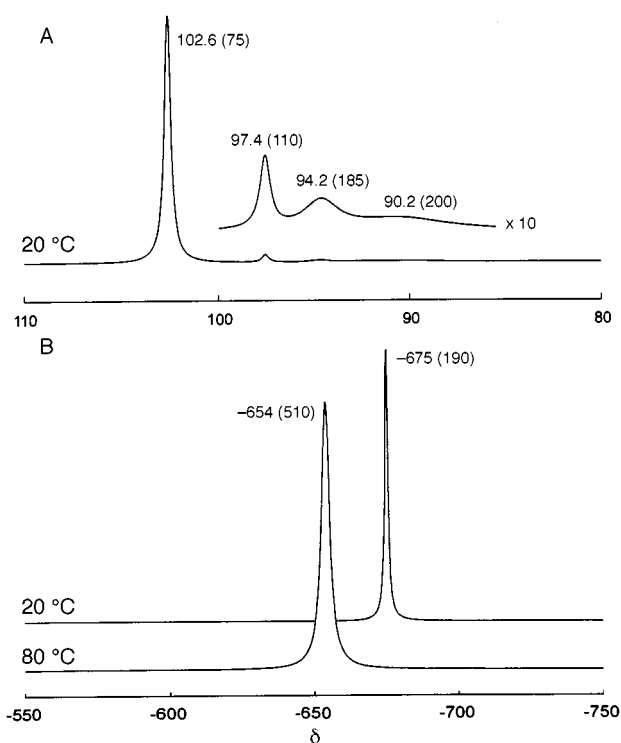
$[\text{CpSn}]^+$ , and has been explained at various levels of sophistication in terms of overlap of metal and ring  $\pi$  orbitals. The relative simplicity of  $\text{Me}_6\text{C}_6\cdot\text{Ga}_2\text{Br}_4$  gives way to more complex structures as the donor strength of the aromatic ligand, and the size of the halide, decrease, so that the solid state of  $\text{C}_6\text{H}_6\cdot\text{Ga}_2\text{Cl}_4$  is based on  $\{[(\text{C}_6\text{H}_6)_2\text{Ga}]\text{GaCl}_4\}_2$  units. In all cases, co-ordination involves both aromatic and halide ligands. The crystal structure results do not directly identify the species present in the solution phase, but do emphasize the necessity of considering both solvation by the aromatic solvent, and cation-anion interactions, in interpreting the NMR results.

The existence of Ga-Al bonded species in these solutions can be ruled out for a number of reasons. Firstly, the structural results noted earlier<sup>11</sup> demonstrate the eight-fold co-ordination of  $\text{Ga}^+$  by chloride ligands of  $\text{AlCl}_4^-$  in the solid state. Secondly, the difference in the electronegativities of Ga and Al means that intramolecular halide transfer will favour the dissociation shown in Scheme 1, in the absence of co-ordinative saturation. Finally, this sequence will be enhanced by the solvation of  $\text{Ga}^+$  by the aromatic solvent. We therefore restrict the discussion to  $\text{Ga}^+\cdots\text{R}$  and  $\text{Ga}^+\cdots\text{AlX}_4^-$  interactions.

Before discussing our results, we should note the relevant results for  $\text{Ga}_2\text{X}_4$  systems. Akitt *et al.*<sup>12</sup> based their  $^{71}\text{Ga}$  NMR values for  $\text{Ga}_2\text{Cl}_4$  on  $\delta(\text{GaCl}_4^-) = 0$ , but recalculation to  $[\text{Ga}(\text{H}_2\text{O})_6]^{3+} = 0$  gives  $\delta(^{71}\text{Ga}) = -692$  for  $\text{Ga}^+$  in benzene solution, and  $\delta -500$  for  $\text{Ga}^+$  in molten  $\text{Ga}_2\text{Cl}_4$  at 200 °C. Schmidbauer<sup>7</sup> reports  $\delta -596$  for  $\text{Ga}^+$  in crystalline  $\text{Ga}[\text{GaCl}_4]$ , in which  $\text{Ga}^+$  is co-ordinated by eight chlorides. Dilute solutions of this salt in benzene or toluene gave  $\delta -659$  and  $-668$  respectively, while in the light and heavy phases obtained with benzene, toluene or *p*-xylene  $\delta -669$  to  $-674$  for the light phases, and  $-687 \pm 1$  for the heavy phases (see below).

### Solutions in benzene

**The light phase.** Except at low concentrations (*i.e.*, below  $\approx 3.5\%$  at 20 °C), mixtures of benzene and  $\text{GaAlCl}_4$  resolve into two liquid phases at room temperature, and above. Similar behaviour has been reported for  $\text{Ga}_2\text{X}_4$  systems.<sup>7</sup> The NMR spectra were recorded separately for each phase, and the results are discussed accordingly. In most cases, the spectra refer to sample separated by centrifugation, but the results recorded at two levels for unseparated systems were essentially identical to the former. Typical spectra are shown in Fig. 1, and the concen-



**Fig. 1** Aluminium-27 (A) and  $^{71}\text{Ga}$  (B) NMR spectra of light phase solution of  $\text{GaAlCl}_4$  in benzene;  $\text{GaAlCl}_4$  concentration  $< 3.5$  wt. %. Chemical shifts are in ppm; values in parentheses are the half-widths, in Hz, and refer to a freshly prepared solution

tration and temperature dependencies of the chemical shifts are summarized in Table 1.

The upper (*i.e.* light) phase solutions contain  $\text{GaAlCl}_4$  in the range 1.1–3.5 wt. %; in terms of the quantity of benzene available for solvation of  $\text{Ga}^+$ , the corresponding  $\text{C}_6\text{H}_6:\text{Ga}$  mol ratios are in the range 85–270. The  $^{27}\text{Al}$  chemical shift in such phases is essentially temperature and concentration independent, and the value of  $\delta$  103 immediately identifies the species present as  $\text{AlCl}_4^-$ . The half-widths of the signals are of the order of a few hundred Hz, whereas in basic solvents of high relative permittivity, unassociated  $\text{AlCl}_4^-$  gives much smaller values, with a low of 3 Hz being reported.<sup>15,16</sup> Similarly, the relaxation times ( $T_1$ ) are in the order of  $10^{-3}$  s, to be compared with values of  $\approx 10^{-2}$  s for the free anion. Throughout this series of measurements,  $T_2$  for  $^{27}\text{Al}$  is equal to or smaller than  $T_1$  (typically  $T_2 \approx 90\text{--}100\%$   $T_1$ ), indicating that quadrupolar relaxation dominates for this nucleus in such media at ambient temperature. The differences become larger at 80 °C, where  $T_2 \approx 60\text{--}90\%$   $T_1$ , which may be due to a scalar contribution to  $T_2$  caused by relaxation of the halogen nuclei of  $\text{AlCl}_4^-$ .

The width of the  $^{27}\text{Al}$  resonance at 20 °C may be due to changes in the magnitude of the field gradient at this nucleus, or

to an increase in the correlation time of the fluctuation of the field gradient. Changes in these parameters can be interpreted in terms of (i) increasing aggregation of the solute, (ii) distortion of the  $T_d$  symmetry of the  $\text{AlCl}_4^-$  anion due to solvation and/or ion-pairing effects, or (iii) chemical exchange between differing modes of co-ordination of the anion to  $\text{Ga}^+$ . In the  $\text{Ga}_2\text{Cl}_4$ -benzene system, infrared spectroscopy<sup>17</sup> has been used to demonstrate a lowering of the symmetry of the anion from  $T_d$  to  $C_{3v}$  or  $C_{2v}$  upon dilution, with the explanation being in terms of ion-pair formation. The changes in half-width with increasing concentration are not monotonic in the present system, and it may well be that all these factors must be taken into account; for example, the constancy of  $w_2$  for  $^{27}\text{Al}$  resonance in increasingly concentrated solutions of  $\text{NaAlEt}_4$  in *m*-xylene was explained as a peculiar and accidental combination of changes in correlation time (which should be affected by aggregation due to increasing concentration), and a lowering of the average electric field gradient at the Al nucleus as aggregation occurs.<sup>17</sup>

At 20 °C, the chemical shifts for  $^{71}\text{Ga}$  in these solutions are almost independent of concentration within a few ppm, in contrast to the changes from  $\delta -650$  to  $-670$  for gallium(III) in solutions of  $\text{Ga}_2\text{Cl}_4$  in benzene over approximately the same concentration range.<sup>7</sup> The half-widths show a slight decrease with increasing concentration of  $\text{GaAlCl}_4$ , all of which implies a well defined environment for the  $\text{Ga}^+$  ion. The effect of raising the temperature is quite marked, with a change in  $\delta$  of about 20 ppm to lower field over the range 20–80 °C, and this is again in contrast to the temperature independence reported for the  $\text{Ga}_2\text{Cl}_4$ -benzene system;<sup>7</sup> similarly  $w_2$  decreases with increasing temperature in the latter case, whereas the opposite is true for the present work.

While the interaction of the  $\text{AlCl}_4^-$  anions with  $\text{Ga}^+$  must be important, the crystal-structure evidence suggests that weak solvation by benzene may also be significant and this may contribute to the diamagnetic shielding of the Ga nucleus. Changes in the anisotropy and magnetic susceptibility of benzene will also contribute to the observed temperature effects. The interaction of both benzene and  $\text{AlCl}_4^-$  with  $\text{Ga}^+$  discussed above implies that the solute species can be formulated as  $\{[\text{R}_n\text{Ga}]^+[\text{Cl}_x\text{AlCl}_{4-x}]^-\}_m$  ( $x = 1-3$ ,  $n$  and  $m$  cannot be defined); writing the anion as  $[\text{Cl}_x\text{AlCl}_{4-x}]^-$  implies that the number of chlorides co-ordinated to  $\text{Ga}^+$  from a given  $\text{AlCl}_4^-$  may vary with the conditions. The time-averaged values of  $n$  and  $m$  cannot be derived from the present studies. In more concentrated (but still dilute) solution, the possibility of the association of ion-pairs into higher aggregates will increase with solute concentration. At 80 °C in the most dilute solution, at the  $^{27}\text{Al}$  signal sharpens slightly and for  $^{71}\text{Ga}$  broadens; increasing Brownian motion of the ions will cause a weakening of the interaction of  $\text{AlCl}_4^-$  with  $\text{Ga}^+$ , leading to a higher average symmetry for the anion at higher temperatures.

**The heavy phase.** In these solutions, the  $\text{GaAlCl}_4$  concentration of 22.7–46.6 wt. % corresponds to  $\text{C}_6\text{H}_6$ :Ga mol ratios between 10.8 and 3.6. The  $^{27}\text{Al}$  chemical shift is again invariant at  $\delta 103$ , and independent of temperature, but the half-widths are significantly smaller than in the lighter phase, and increasing temperature produces further sharpening of the signal. The chemical shift of the  $^{71}\text{Ga}$  resonance is more negative than in the dilute solutions, the signals are narrower, and the values of the spin-relaxation times ( $T_1$ ) are approximately twice as high. With increasing temperature, the signal shifts to lower field by *ca.* 20 ppm, and the differences between  $T_2$  and  $T_1$  increase. In general, the resonances for the lower phase are shifted by about 20 ppm to higher field relative to the upper phase (Table 1), and are independent of concentration within experimental error.

At the concentrations studied, interactions between anion and cation, and ion-pair aggregation, must be very significant. At ambient temperature, a sharpened  $^{27}\text{Al}$  signal at constant

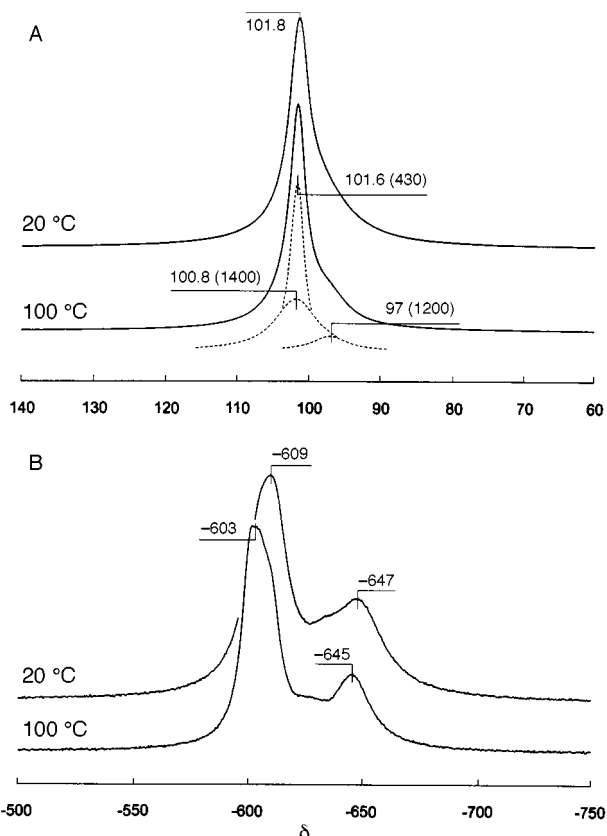
$\delta$  implies that the packing of anions around the cation is stereochemically more efficient than in the dilute solutions, and the  $^{71}\text{Ga}$  resonance is also sharper than in dilute solution. While these results do not identify the solute structure unambiguously, they imply an increasingly ordered arrangement, in which interaction with  $\text{AlCl}_4^-$  results in efficient shielding of the  $^{71}\text{Ga}$  nucleus and a shift of  $\delta$  to a more negative value, as observed. The temperature effect is in the same order as in dilute solution.

The most concentrated solution studied contained 46.6 wt. %  $\text{GaAlCl}_4$ , with a  $\text{C}_6\text{H}_6$ :Ga mol ratio of 3.6:1, and under these conditions the liquid phase will contain highly ordered aggregates of  $\text{Ga}^+ \cdots \text{AlCl}_4^-$  ion pairs. This will result in tight packing, and an increased average distortion of the  $\text{AlCl}_4^-$  symmetry, as evidenced by the  $^{27}\text{Al}$  line-width, but should have little effect on the already strong shielding of Ga. Increasing temperature (*i.e.*, increased molecular motion) will lead to some loosening of this structure, and hence  $w_2$  decreases for  $^{27}\text{Al}$  and increases for  $^{71}\text{Ga}$ . Infrared studies of the heavy phase of the  $\text{Ga}_2\text{Cl}_4$  benzene system also showed that increasing concentration lowered the symmetry of the  $\text{GaCl}_4^-$  anion.<sup>17</sup> Finally, we note that the chemical shifts for  $\text{Ga}^+$  in  $\text{Ga}[\text{AlCl}_4]$  and  $\text{Ga}[\text{GaCl}_4]$  in benzene are very similar, suggesting that the nature of the  $\text{Ga}^+ \cdots \text{Cl}^-$  interaction is almost independent of the central metal of the anion. In these concentrated solutions, which are approaching those from which crystallization of solvated  $\text{GaMX}_4$  occurs, interaction of benzene with  $\text{Ga}^+$  may become sufficiently strong to bring about changes in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, but no such effects were detected.

The NMR results do not of themselves explain the existence of two phases at  $\text{GaAlCl}_4$  concentrations above *ca.* 3.5% at 20 °C. The  $^{71}\text{Ga}$  chemical shifts for phases in chemical equilibrium with each other ( $\delta -678$ ,  $-696$  at 20 °C: see Table 1) show that  $\text{Ga}^+$  has significantly different shielding in the two solutions, while the  $^{27}\text{Al}$  results give identical chemical shifts for  $\text{AlCl}_4^-$ , and only small variations in  $w_2$  [and this latter parameter is difficult to interpret with certainty (see above)]. The formation of two phases may be an indication of significant changes in the degree of solvation of  $\text{Ga}^+$  by benzene, and the emergence of the heavy phase may signal the absence of sufficient benzene to allow the formation of  $[\text{R}_n\text{Ga}]^+$  species, which can exist only in the dilute (light) phase.

### Solutions in *n*-heptane

Although it is generally assumed that  $\text{M}_2\text{X}_4$  compounds are only soluble in aromatic solvents,  $\text{GaAlCl}_4$  is in fact slightly soluble in *n*-heptane. A saturated solution at room temperature contains *ca.* 0.57 wt. %  $\text{GaAlCl}_4$  ( $\approx 24$  mmol  $\text{L}^{-1}$ ), which is sufficient for the study of both  $^{27}\text{Al}$  and  $^{71}\text{Ga}$  NMR spectroscopy, and Fig. 2 illustrates the spectra obtained in a typical experiment. Careful deconvolution shows that the  $^{27}\text{Al}$  signal at  $\delta 102$  at 20 °C shifts very slightly on raising the temperature to 100 °C, at which point this main resonance is accompanied by a small shoulder at *ca.*  $\delta 97$ , barely perceptible at 20 °C. This shoulder is assigned to a small quantity of hydrolysis product (see below), originating from traces of residual moisture in the system. The  $^{71}\text{Ga}$  spectra at both 20 and 100 °C (Fig. 2) reveal the existence of at least two  $\text{Ga}^+$  environments, which are undergoing slow chemical exchange. In such solutions, strong solvation can be of little significance, and the solvent presumably acts as a dispersing agent for the electrolyte, and given the low relative permittivity, aggregation of the ions must be a major factor. The line-width of the  $\text{AlCl}_4^-$  signal shows that this anion is in a symmetrical environment. Two possible models seem reasonable. The first is that despite the visual evidence, there are in fact two admixed phases present (*cf.* Schmidbaur<sup>7</sup> on  $\text{Ga}_2\text{Cl}_4$ -benzene systems), in which case the two  $^{71}\text{Ga}$  resonances arise from these different phases. The second is that the ions are assembled into stable aggregates such as micelles, in which  $\text{Ga}^+$  ions are



**Fig. 2** Aluminium-27 (A) and  $^{71}\text{Ga}$  (B) NMR spectra of a saturated solution of  $\text{GaAlCl}_4$  in *n*-heptane;  $\text{GaAlCl}_4$  concentration 0.57 wt. %. Numbers have the same significance as in Fig. 1

found in different environments on the micelle surface and in the interior. The lack of a significant temperature effect on either  $^{27}\text{Al}$  or  $^{71}\text{Ga}$  resonance suggests a measure of stability for these aggregates, whatever their structure.

### Mixed benzene–*n*-heptane solutions

Solutions of  $\text{GaAlCl}_4$  in mixtures of benzene and *n*-heptane were prepared by mixing the three components. Analysis showed that the gallium content of the resultant saturated solution was 0.17 wt. % at 20 °C, corresponding to 24 mmol  $\text{L}^{-1}$   $\text{GaAlCl}_4$ , and the benzene: $\text{GaAlCl}_4$  mol ratios were calculated on this basis. The results for the two solutions studied are: I initial quantities 1.2 mmol  $\text{GaAlCl}_4$ , 0.11 mmol  $\text{C}_6\text{H}_6$  ( $\approx 0.01$  mL), 2 mL *n*-heptane; calculated mol ratio  $\text{C}_6\text{H}_6$ : $\text{GaAlCl}_4 = 2.3$  in the resultant solution. II initial quantities 1.1 mmol  $\text{GaAlCl}_4$ , 0.60 mmol  $\text{C}_6\text{H}_6$  ( $\approx 0.06$  mL), 2 mL *n*-heptane; calculated mol ratio  $\text{C}_6\text{H}_6$ : $\text{GaAlCl}_4 = 12.0$ .

The spectra are shown in Fig. 3. The most striking feature, compared with Fig. 2A, is the very considerable increase in the line-widths of the  $^{27}\text{Al}$  resonance for both solutions I and II ( $\nu_2 \approx 2000$  Hz), indicating very significant departures from  $T_d$  symmetry for the  $\text{AlCl}_4^-$  anion. There is little change with temperature, or with benzene concentration. Other noteworthy features are the evidence of slight hydrolysis, shown by shoulders at *ca.*  $\delta$  97, and the presence of a broad resonance at  $\delta$  114 in solution I at 20 °C, of unknown origin (Fig. 3A and 3B).

The  $^{71}\text{Ga}$  spectra of these solutions are complex. For solution I at 20 °C (Fig. 3C) a rather broad resonance at  $\delta -670$  is accompanied by two others at  $\delta$  *ca.*  $-640$  and  $-608$ , corresponding to those seen in *n*-heptane solution (*cf.* Fig. 2B). With increasing temperature this shifts to lower field, until at 100 °C a resonance at  $\delta -625$  is the dominant feature. Multi-component spectra are also found in the case of solution II (Fig. 3D). The strongest resonance at 20 °C occurs at  $\delta -690$ , with minor features at  $\delta -670$  and  $-605$ ; with increasing

temperature, the first two coalesce into a dominant resonance at  $\delta -640$  at 100 °C, at which temperature the only other resonance detected is at  $\delta -610$ . The  $\delta -690$  signal is close in frequency to that for the concentrated solutions in benzene, but the temperature dependence, which is similar to that in benzene solutions, and the presence of other resonances, suggests that we are dealing with a mixture of species in equilibrium, including those present in pure *n*-heptane. The relative importance of these clearly depends on temperature, and on the benzene:*n*-heptane ratio, and they may therefore include  $[\text{R}_n\text{Ga}]^+$ , ion pairs, aggregates and the micelles postulated above.

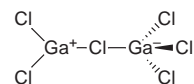
### Addition of $\text{Ga}_2\text{Cl}_6$ to solutions in *n*-heptane

One advantage of studying solutions of  $\text{GaAlCl}_4$  in *n*-heptane is that the effect of adding other reagents can be investigated. No changes were detected when either  $\text{BCl}_3$  or  $\text{CH}_2\text{Cl}_2$  was added to a saturated solution of  $\text{GaAlCl}_4$  (mol ratio total Cl: $\text{Ga}$  varied from 10 to 100) at room temperature, and raising the temperature did not alter this situation. On the other hand, the addition of  $\text{Ga}_2\text{Cl}_6$  gave rise to interesting effects. Following the methodology used for solutions I and II above, solutions of following compositions were prepared: III initial quantities 1.4 mmol  $\text{GaAlCl}_4$ , 0.3 mmol  $\text{Ga}_2\text{Cl}_6$ , 1.5 mL *n*-heptane; calculated mol ratio  $\text{Ga}_2\text{Cl}_6$ : $\text{GaAlCl}_4 = 8.3$  in resultant solution. IV initial quantities 1 mmol  $\text{GaAlCl}_4$ , 1.4 mmol  $\text{Ga}_2\text{Cl}_6$ , 1.5 mL *n*-heptane; calculated mol ratio  $\text{Ga}_2\text{Cl}_6$ : $\text{GaAlCl}_4 = 38.8$ .

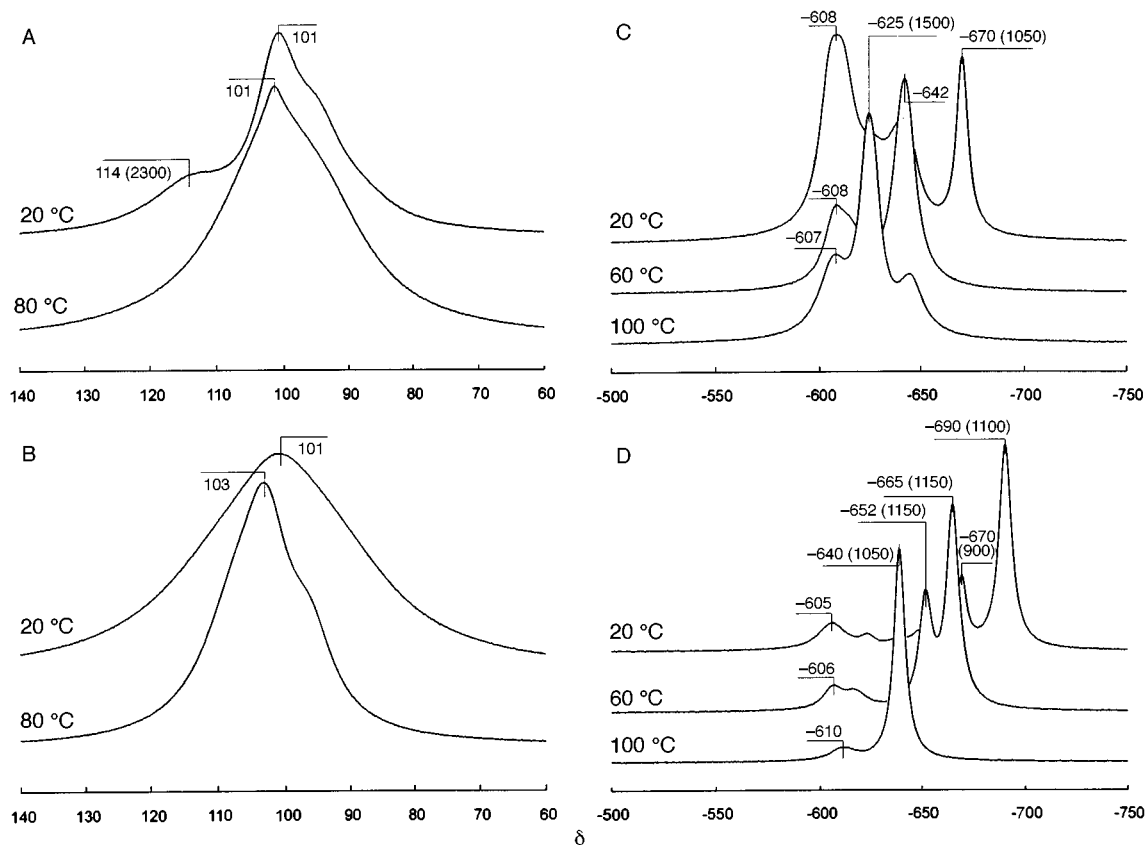
As in the earlier studies, the  $^{27}\text{Al}$  spectrum (Fig. 4A) consists of a single strong  $\text{AlCl}_4^-$  resonance whose frequency is invariant with temperature, although the signal narrows significantly at 80 °C. Solutions III and IV gave essentially identical  $^{27}\text{Al}$  spectra. Once again we note the presence of a small quantity of an unidentified product, which in the deconvoluted spectrum at 20 °C gives rise to the shoulder at  $\delta$  99.5.

The  $^{71}\text{Ga}$  spectra of solutions III and IV show, as expected, a new feature due to the presence of gallium(III) species, which at 20 °C gives rise to a broad resonance at  $\delta$  231, moving to  $\delta$  225 at 100 °C, and narrowing significantly in the case of solution IV (Fig. 4B). The  $\text{Ga}^+$  region of the spectrum for solution III at 20 °C has resonances at  $\delta -610$  and  $-645$ , with a new sharp signal appearing at  $\delta -600$  at 100 °C (Fig. 4C). Solution IV, containing more  $\text{Ga}_2\text{Cl}_6$ , has a series of  $^{71}\text{Ga}$  resonances in this region; the two absorptions at  $\delta -608$  and  $-640$  at 20 °C gives way to one sharp resonance at  $\delta -594$  at 100 °C (Fig. 4D). As with all the other temperature effects for this system, the changes are completely and rapidly reversible, indicating species in rapid equilibrium with each other.

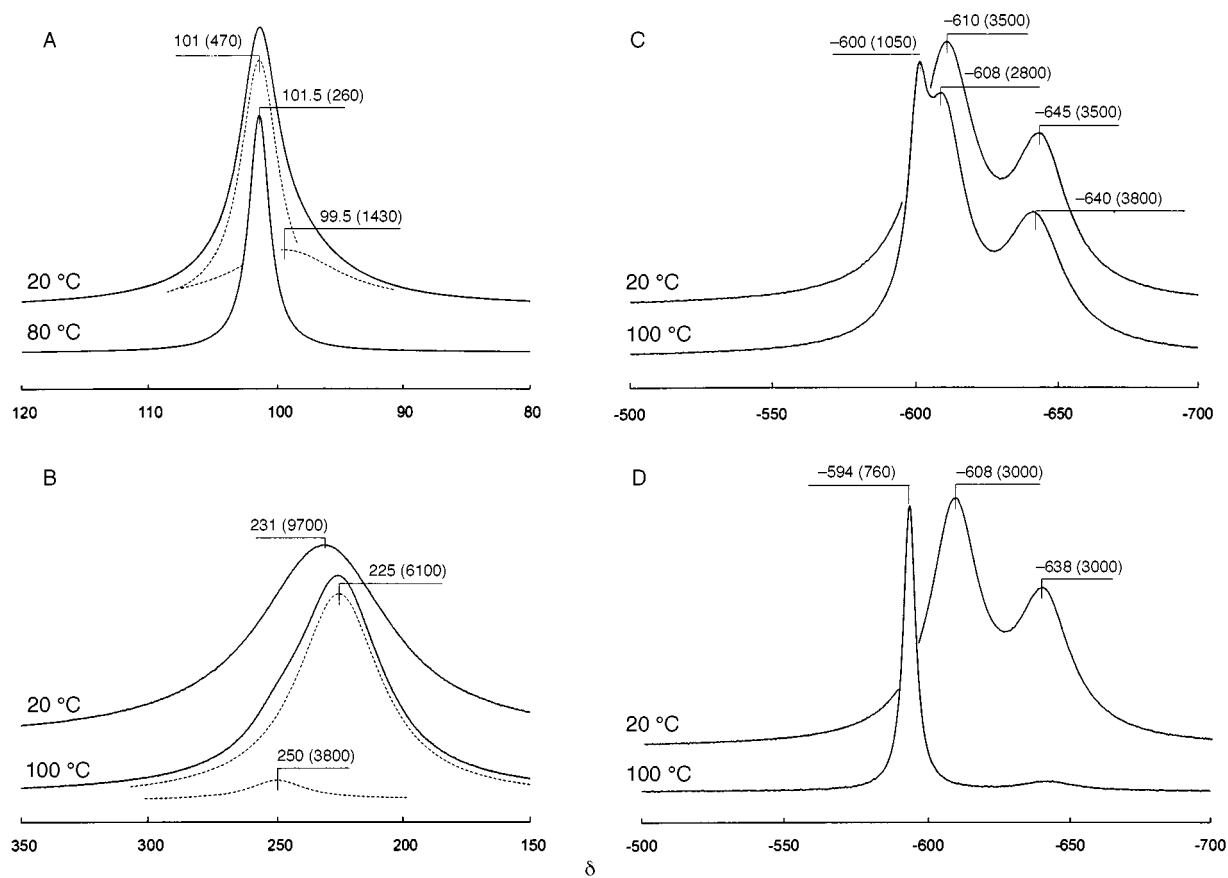
The interaction between  $\text{GaAlCl}_4$  and  $\text{Ga}_2\text{Cl}_6$  in *n*-heptane can be understood in terms of the potential of  $\text{Ga}_2\text{Cl}_6$  for polarisation into either the ion-pair  $\text{GaCl}_2^+ \cdots \text{GaCl}_4^-$  (see below), or the partially opened dimer which we designate the half-open structure. The importance of this latter tautomer in adduct formation has been discussed elsewhere.<sup>14</sup>



The spectrum of  $\text{Ga}_2\text{Cl}_6$  in *n*-heptane (and in benzene)<sup>15</sup> is a broad singlet at  $\delta$  222 and in solution IV at ambient temperature this shifts to  $\delta$  231. At 100 °C, we observed a new signal at  $\delta$  250, corresponding to the proposed  $\text{GaCl}_4^-$  moiety of the half-open structure (*cf.*  $\text{GaCl}_4^-$  in  $\text{CH}_2\text{Cl}_2$ ,  $\delta$  250).<sup>15</sup> The spectrum of solution III (Fig. 4C) shows that the signals from  $\text{Ga}^+$  in *n*-heptane are little affected by the presence of small quantities of  $\text{Ga}_2\text{Cl}_6$  at 20 °C, or 100 °C, but further addition of the trihalide eventually results in the appearance of a single sharp resonance at  $\delta -594$  at 100 °C (Fig. 4D). The difference between this value and that for the half-open  $\text{Ga}_2\text{Cl}_6$  is 845 ppm, almost identical to that for the difference between the  $\text{Ga}^+$



**Fig. 3** Aluminium-27 (A,B) and  $^{71}\text{Ga}$  (C,D) NMR spectra of saturated solutions of  $\text{GaAlCl}_4$  in benzene-*n*-heptane mixtures. Spectra A and C are for solution I, and B and D for solution II; see text for details. Numbers have the same significance as in Fig. 1



**Fig. 4** Aluminium-27 (A) and  $^{71}\text{Ga}$  (B,C,D) NMR spectra, showing the effect of adding  $\text{Ga}_2\text{Cl}_6$  to saturated solutions of  $\text{GaAlCl}_4$  in *n*-heptane. Spectra A,B and C are for solution III, and spectrum D for solution IV; see text for details of composition. Numbers have the same significance as in Fig. 1

**Table 2** Gallium-71 and <sup>27</sup>Al NMR results for benzene solutions of GaAlBr<sub>4</sub>, GaAlI<sub>4</sub>, and GaAlCl<sub>4</sub> + GaAlBr<sub>4</sub> mixtures<sup>a</sup>

Compound	Concentration	<sup>27</sup> Al		<sup>71</sup> Ga			
		20 °C		20 °C		80 °C	
		δ	w <sub>2</sub> <sup>1</sup>	δ	w <sub>2</sub> <sup>1</sup>	δ	w <sub>2</sub> <sup>1</sup>
GaAlBr <sub>4</sub>	6	—	—	-635	270	-617	600
GaAlBr <sub>4</sub>	28	78	180	-654	230	-627	710
GaAlI <sub>4</sub> <sup>b</sup>	3	—	—	-552	550	-515	1200
GaAlCl <sub>4</sub> + GaAlBr <sub>4</sub> <sup>c</sup>	10.5 + 22.2	90	170	-672	120	-650	440

<sup>a</sup> Concentration in wt. %, δ in ppm, w<sub>2</sub><sup>1</sup> in Hz. <sup>b</sup> Saturated solution. <sup>c</sup> Apparently one-phase solution.

and GaCl<sub>4</sub><sup>-</sup> resonances in solid Ga<sub>2</sub>Cl<sub>4</sub>.<sup>7</sup> On the other hand, the value of δ -594 for Ga<sup>+</sup> implies a deshielded cation, and these results can be accommodated in terms of co-ordination of both AlCl<sub>4</sub><sup>-</sup> and half-open Ga<sub>2</sub>Cl<sub>6</sub> around Ga<sup>+</sup> in such a way as to give eight-co-ordination of Ga<sup>+</sup> by Cl<sup>-</sup> from both anions. Since these processes occur in pure *n*-heptane, there can be no aromatic solvation, and the resonance at δ -594 therefore identifies the limiting case of chloride co-ordination in solution; the chemical shift is in fact identical to that for Ga<sup>+</sup> in crystalline Ga[GaCl<sub>4</sub>], in keeping with the eight-co-ordinate structure proposed.

#### Other GaAlX<sub>4</sub> systems

Table 2 shows the results of the investigation of <sup>27</sup>Al and <sup>71</sup>Ga spectra of benzene solutions of GaAlX<sub>4</sub> (X = Br or I), and of mixtures of GaAlCl<sub>4</sub> and GaAlBr<sub>4</sub> in this solvent. The <sup>27</sup>Al spectrum of GaAlBr<sub>4</sub> was only observed in the higher concentration, for which the resonance at δ 78 confirms the presence of the AlBr<sub>4</sub><sup>-</sup> anion.<sup>15,16</sup> The line-width is similar to the values for AlCl<sub>4</sub><sup>-</sup> at similar concentrations (*cf.* Table 1). Change in the <sup>71</sup>Ga resonance with concentration and increasing temperature, are similar to those for GaAlCl<sub>4</sub>, although the absolute values are to lower field by about 40 ppm. For GaAlI<sub>4</sub>, the limited solubility (3% at 20 °C) meant that only <sup>71</sup>Ga resonances were observed, and here the values are some 130–140 ppm downfield from those in GaAlCl<sub>4</sub> solutions; the temperature effect is more pronounced than in the GaAlCl<sub>4</sub> and GaAlBr<sub>4</sub> systems.

Table 2 shows a considerable dependence of the chemical shift of <sup>71</sup>Ga on the type of anion, with a low-field shift difference of about 100 ppm from AlCl<sub>4</sub><sup>-</sup> to AlI<sub>4</sub><sup>-</sup>. This indicates a marked paramagnetic shift contribution arising from the orbital angular momentum introduced by the interaction of halogen electron density with the outer filled 3d orbitals of Ga<sup>+</sup> in the tightly bound ion-solute species. Since the electron density of the halogen involved in this interaction depends on the polarisability of the atom, the contribution to the shift decreases in the sequence I > Br > Cl, and the magnitude of the paramagnetic shifts of <sup>71</sup>Ga serves as an indication of the strength of the donor interactions at the metal centre.

It is also interesting to note that the <sup>71</sup>Ga resonances of Ga<sup>+</sup> in GaAlCl<sub>4</sub>-GaAlBr<sub>4</sub> systems at both 20 and 80 °C are almost identical to those for this cation in GaAlCl<sub>4</sub> in dilute solutions, which implies that the closeness of approach of the halide ligands of AlX<sub>4</sub><sup>-</sup> (or AlX<sub>2</sub>Y<sub>2</sub><sup>-</sup>) is an important factor in the shielding of the cation. This concept can be extended by comparing the present data with those for Ga[GaX<sub>4</sub>] salts<sup>7</sup> in the manner shown in Table 3. Within the scant data available, there is a monotonic relationship between δ(<sup>71</sup>Ga) for a given salt in solution and the closest approach of X (of MX<sub>4</sub><sup>-</sup>) to the Ga<sup>+</sup> ion in the solid state. This does not mean that the same forces govern the structures in solid and solution phases, but rather that the closeness of approach of MX<sub>4</sub><sup>-</sup> to Ga<sup>+</sup> is important

**Table 3** Summary of structural data on Ga[MX<sub>4</sub>] salts; distances in Å

Compound	r(M-X)		r(Ga <sup>+</sup> ...X)		Ref.
	Average	Range	Average	Closest approach	
Ga[GaCl <sub>4</sub> ]	2.19	3.18–3.27	3.23	3.18	3
Ga[GaI <sub>4</sub> ]	2.557	3.281–3.820	3.54	3.281	4
Ga[AlCl <sub>4</sub> ]		3.101–3.858	3.36	3.101	8

in determining the extent of the shielding of the cation by surrounding anions.

The spectra of a solution containing both GaAlCl<sub>4</sub> and GaAlBr<sub>4</sub> (mol ratio 1 : 1.21) are also instructive. The <sup>27</sup>Al resonance is at δ 90, close to that reported for AlCl<sub>2</sub>Br<sub>2</sub><sup>-</sup> in CH<sub>2</sub>Cl<sub>2</sub> and in acetone (δ 92–94),<sup>15</sup> showing that in benzene, as in other solvents, rapid halide exchange occurs between the two AlX<sub>4</sub><sup>-</sup> anions. For <sup>71</sup>Ga, the resonance at δ -672 is close to that for a dilute solution of GaAlCl<sub>4</sub> in benzene (*cf.* Table 1), but this value is probably better understood as the average of the signals of the initial components [GaAlCl<sub>4</sub> δ -696, GaAlBr<sub>4</sub> δ -654 (both values for the heavy phases), weighted mean δ -673].

#### Hydrolysis studies

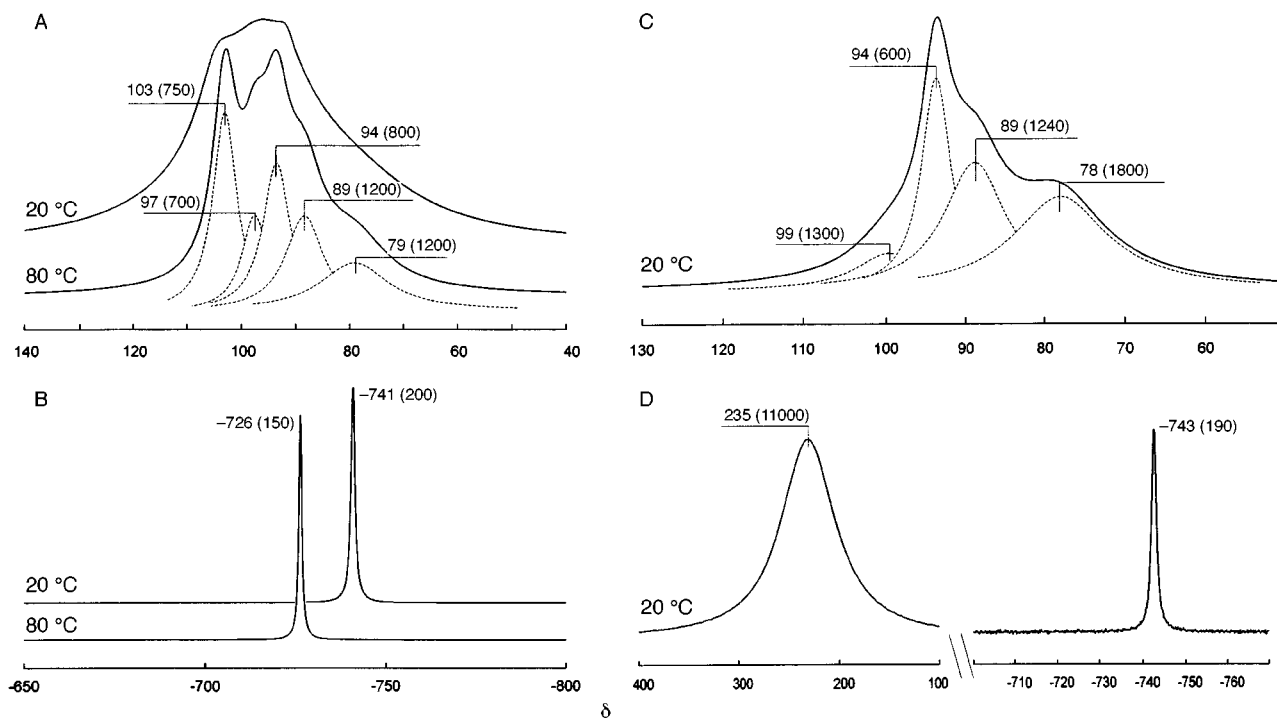
We have noted earlier a number of spectra in which weak resonances were assigned to hydrolysis products, and it therefore seemed sensible to investigate this by the deliberate addition of water to solutions of GaAlCl<sub>4</sub> in benzene (22.7 wt. %). Fig. 5 shows the <sup>27</sup>Al and <sup>71</sup>Ga NMR spectra of a solution with the mol ratio Al:H<sub>2</sub>O = 0.33 : 1. Broad <sup>27</sup>Al peaks are observed at both 20 and 80 °C, and the latter has been deconvoluted to a series of five individual peaks at δ 103, 97, 94, 89 and 79 (Fig. 5A). The same features emerge from the treatment of the spectrum found after increasing the water content (Al:H<sub>2</sub>O = 1.6 : 1) except that at 20 °C, the original signal at δ 103 is absent (Fig. 5C). These results also explain the presence of minor shoulders in the <sup>27</sup>Al spectra of systems noted above (*e.g.* Fig. 1); the sum of the intensities in this latter case is no more than 3% of the total. More importantly, hydrolysis is only a minor effect in the overall scheme of interactions in non-aqueous solutions of GaAlCl<sub>4</sub> in the concentration and temperature range used in this work.

In the solution of lower water content, the <sup>71</sup>Ga spectrum shows the characteristic resonance of Ga<sup>+</sup>, at δ -741 (20 °C) and -726 (80 °C) (Fig. 5B), shifted significantly from the signal seen for a water-free solution at the same salt concentration (see Table 1; δ -696 and -674). At the higher water content (Fig. 5D), the δ -743 resonance is still apparent, but an additional very broad resonance appears at δ +235, indicating the formation of gallium(III) species (*cf.* Ga<sub>2</sub>Cl<sub>6</sub> in benzene; δ 222). The <sup>71</sup>Ga chemical shift in GaCl<sub>4</sub><sup>-</sup> is in the region δ 223–252, depending on the solvent;<sup>13</sup> a range of chemical shifts has been reported for aqueous solution (δ 240–275) and [Ga(OH)<sub>4</sub>]<sup>-</sup> gives a broad resonance at δ 220.<sup>15,16</sup> Any hydrolysis scheme must therefore incorporate change at both Al and Ga centres.

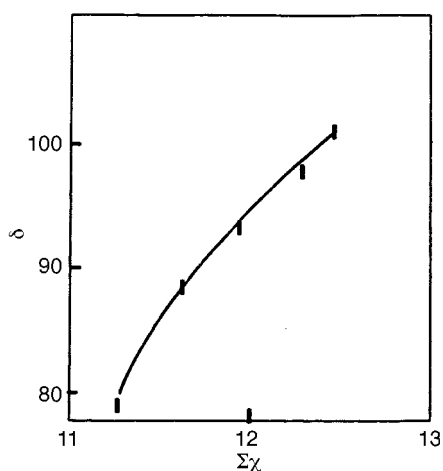
It is known that Ga<sub>2</sub>X<sub>4</sub> can be hydrolyzed according to equation (1) with the eventual formation of gallium(III)



hydroxide and gallium metal.<sup>18,19</sup> The <sup>27</sup>Al spectra of solutions of GaAlCl<sub>4</sub> containing added water indicate a similar series of processes; Fig. 5A and 5C show that a series of new signals develop in the region predicted for [Al(OH)<sub>4-n</sub>Cl<sub>n</sub>]<sup>-</sup> species. This argument is supported by considering the frequencies of these signals as a function of the total electronegativity of these ligands, assuming that all the species in question have the same



**Fig. 5** Aluminium-27 (A,C) and  $^{71}\text{Ga}$  (B,D) NMR spectra of a solution of  $\text{GaAlCl}_4$  in benzene, ca. 23 wt. %, treated with  $\text{H}_2\text{O}$ . For A and B, mol ratio  $\text{H}_2\text{O}:\text{Al} = 0.3$ ; for C and D,  $\text{H}_2\text{O}:\text{Al} = 1.6$ . Numbers have the same significance as in Fig. 1



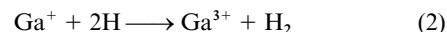
**Fig. 6** Dependence of  $\delta(^{27}\text{Al})$  as a function of  $\Sigma\chi$  for  $[\text{Al}(\text{OH})_x\text{Cl}_{4-x}]^-$ ; chemical shift values from Fig. 5

stereochemistry and co-ordination number. Various attempts have been made in the past to estimate the electronegativity of OH, and values ranging from 2.3 to 3.9 have been proposed.<sup>20</sup> For the present purpose, it is only necessary to have internally consistent values for both OH and Cl, and we use the Pauling electronegativities,  $\chi(\text{OH}) = 2.82$  and  $\chi(\text{Cl}) = 3.16$ . The relationship between  $\Sigma\chi$  and  $\delta(^{27}\text{Al})$  (values from Fig. 5A), shown in Fig. 6, has the monotonic form found in several similar plots for mixed halide complexes of Main Group elements. We therefore assign the  $^{27}\text{Al}$  chemical shifts of these species as  $[\text{Al}(\text{OH})\text{Cl}_3]^- = \delta$  97,  $[\text{Al}(\text{OH})_2\text{Cl}_2]^- = 94$ ,  $[\text{Al}(\text{OH})_3\text{Cl}]^- = 89$  and  $[\text{Al}(\text{OH})_4]^- = 79$  (all in ppm). The last value compares well with  $\delta + 80$  from previous studies.<sup>16</sup>

This leaves no doubt that hydrolysis involves the formation of  $[\text{Al}(\text{OH})\text{Cl}_3]^-$  and that the minor features seen in Fig. 1, *etc.* are indeed due to small quantities of related products. Ligand exchange between the various aluminium anions is slow on the NMR time-scale. The other spectral changes in Fig. 5B show that the  $^{71}\text{Ga}$  resonance in the  $\text{Ga}^+$  region is about 45 ppm to higher field than in benzene solutions of  $\text{GaAlCl}_4$  at similar

concentrations, so that the presence of OH ligands in the anion results in stronger shielding at the cation.

The very broad signal (Fig. 5D) seen for higher water content solution at  $\delta$  235 clearly indicates the presence of gallium(III) complexes, presumably formed by the reaction of  $\text{Ga}^+$  with water or HCl [equation (2)] followed by complexation and



ligand exchange to give  $\text{GaCl}_4^-$ ,  $[\text{Ga}(\text{OH})\text{Cl}_3]^-$ , *etc.* The involvement of  $[\text{Al}(\text{OH})_n\text{Cl}_{4-n}]^-$  complexes in this scheme would explain the non-statistical distribution of these anions in Fig. 5. For  $^{71}\text{Ga}$ , the chemical shifts<sup>13</sup> for the relevant molecules are  $\text{GaCl}_4^-$   $\delta$  252,  $\text{Ga}_2\text{Cl}_6$  221,  $[\text{Ga}(\text{OH})_4]^-$  220, and a mixture of gallium(III) species in rapid exchange readily explains the broad resonance observed at  $\delta$  235 (20 °C) (Fig. 5D).

## Conclusion

The  $^{27}\text{Al}$  and  $^{71}\text{Ga}$  NMR spectra of solutions of  $\text{GaAlX}_4$  in benzene, *n*-heptane and mixtures of these solvents are affected by concentration, temperature and the presence of  $\text{Ga}_2\text{Cl}_6$ . Solvation of  $\text{Ga}^+$  or  $\text{Al}^+$  by benzene, and interaction with  $\text{AlX}_4^-$  anions, are important factors in understanding the results. In the absence of benzene, the aggregation of ion pairs is important. The quadrupolar relaxation of  $^{27}\text{Al}$  is governed predominantly by the local electronic environment.

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