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Multinuclear NMR studies of mixtures of aluminium and gallium trihalides in benzene

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The ^{27}Al and ^{71}Ga NMR spectra of mixtures of M_2X_6 and M_2Y_6 (M = Al, Ga; X ≠ Y = Cl, Br or I) in benzene are reported. All these systems show rapid inter-halogen exchange, and in some cases stable intermediates $M_2X_nY_{6-n}$ can be characterised spectroscopically. In particular, the results are used to identify the predominant species present in solutions prepared by mixing (i) Al_2Br_6 and Ga_2Cl_6, and (ii) Al_2I_6 and Ga_2Br_6, in benzene in various mole ratios. The expected $M_2X_3Y_3$ intermediates are found for M = Al or Ga, X ≠ Y = Cl, Br, but with other mixed halide systems, unsymmetric structures predominate, and possible reasons for this are discussed. The experimental results are in agreement with thermodynamic predictions, and with arguments based on maximizing the M–X, Y electronegativity differences.

The trihalides of the Group 13 elements form a large number of addition compounds, which have been extensively studied because of their intrinsic importance in the field of coordination chemistry. The thermodynamic stabilities of these adducts differ widely, and a number of attempts have been made to establish stability sequences, both in terms of the properties of the metallic elements, and of the different donor elements involved. In the case of aluminium and gallium, the metal clearly has a substantial effect on the stabilities, since complexes of the latter with sulfur as the donor site are more strongly bonded than those with oxygen and nitrogen donors, while the converse is true for the trihalides of aluminium. Similarly, it is known that in competition between aluminium and gallium trihalides with hard donors, the lighter element forms the stronger complexes, whereas the opposite applies with sulfur donors. Some of the difficulties implicit in these relationships have been discussed elsewhere.[1,2]

Most of the reported experimental studies of adduct formation have involved infrared spectroscopy, proton NMR, conductivity measurements, or thermochemical methods. The present paper is part of a series of investigations of such systems through the application of multinuclear NMR spectroscopy, using both ^{27}Al and ^{71}Ga chemical shifts to investigate changes at the coordinated metal atom as a result of complex formation. The dearth of spectroscopic information on the parent Lewis acids is surprising; there is a shortage of reliable data for the aluminium trihalides, and an apparent absence of results for gallium triiodide. In this paper, we report NMR studies of these typical hard and soft acids, and of the halogen exchange reactions which can occur in solutions of these trihalides in benzene.

Experimental

General

Benzene was freshly distilled from CaH_2 before use. Aluminium(III) chloride (Fluka, AG, Buchs SG puriss. Grade, anhydrous) was used as supplied; $AlBr_3$ and AlI_3 (Alfa Products) were freshly distilled before use. Gallium(III) chloride and bromide were prepared by reacting the metal with halogen.[3,4]

NMR spectroscopy

The ^{27}Al and ^{71}Ga NMR spectra were recorded by the techniques described earlier. Chemical shifts for ^{27}Al are relative to $[Al(H_2O)_g]^{3+}_{aq}$ for which $\delta(^{27}Al) = 0$, and for ^{71}Ga, to $[Ga(H_2O)_6]^{3+}_{aq}$, for which $\delta(^{71}Ga) = 0$. The reproducibility of δ and the half-width ($\omega_{1/2}$) values was established by the methods used in previous work.[4,5]

Solution preparation

Samples for NMR investigation were prepared in an atmosphere of dry argon, using weighed quantities of both trihalide and benzene placed directly into NMR tubes. Concentrations are expressed throughout as wt% (*i.e.* weight of solute (g) per 100 g of solution), and as molality; the latter leads to the initial $AlX_3 : GaY_3$ mole ratios for mixed halide systems. All samples were subsequently treated for 1 h in an ultrasonic bath at room temperature, and then sealed, after which each was heated to 60° for 15 min. to ensure equilibration. In the case of ^{27}Al NMR measurements (Fig. 1A–C) the spectra were recorded at this temperature to allow direct comparison with previous studies of $AlCl_3$ in benzene.[5] For the results in Fig. 2A, the ^{71}Ga spectrum is that of a sample held at 40 °C, since at this temperature it was possible to get good signal : noise ratios; below this the limited solute solubility made the results unreliable. All other results refer to solutions at room temperature (*ca.* 23 °C).

When homogeneous solutions of AlX_3 and GaY_3 (X = Br, I; Y = Cl, Br) in benzene were mixed, precipitation occurred. In order to establish the equilibrium solute concentrations in the samples used for NMR study, identical mixtures were analysed by chelatometric titration. These results, and the composition of the initial reaction mixture, are given in Tables 1 and 2, and the relevant spectra are shown in Figs. 1 and 2.

In addition to the AlX_3/GaY_3 studies, we recorded the ^{27}Al

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Table 1 Solutions of $AlBr_3$ and $GaCl_3$ in benzene: experimental data appropriate to Fig. 1

Spectrum (Fig. 1)	Initial wt%	$[GaCl_3]$/M	Initial $AlBr_3$: $GaCl_3$ mole ratio	Final equilibrium concentration/wt% Ga	Final equilibrium concentration/wt% Al	Equilibrium Al : Ga mole ratio
A	14.5	0.82	1 : 3	0.06	5.6	1 : 36
B	12.0	0.68	1 : 2	0.06	4.7	1 : 30
C	10.0	0.57	1 : 1	0.08	4.0	1 : 19
D	6.0	0.34	1.8 : 1	0.55	2.4	1 : 17
E	5.0	0.28	2.6 : 1	1.2	2.1	1.5 : 1

Table 2 Solutions of AlI_3 and $GaBr_3$ in benzene; experimental data appropriate to Fig. 2

Spectrum (Fig. 2)	Initial wt%	$[GaBr_3]$/M	Initial AlI_3 : $GaBr_3$ mole ratio	Final equilibrium concentration/wt% Al	Final equilibrium concentration/wt% Ga	Equilibrium Al : Ga mole ratio
A	4.1	0.13	3.1 : 1	1.1	0.12	24 : 1
B	6.3	0.20	2 : 1	1.1	0.20	14 : 1
C	10.3	0.33	1 : 0.9	0.95	1.8	1.4 : 1
D	19.3	0.62	1 : 2.1	0.80	4.3	0.48 : 1
E	21.0	0.68	1 : 3	0.60	4.7	0.33 : 1

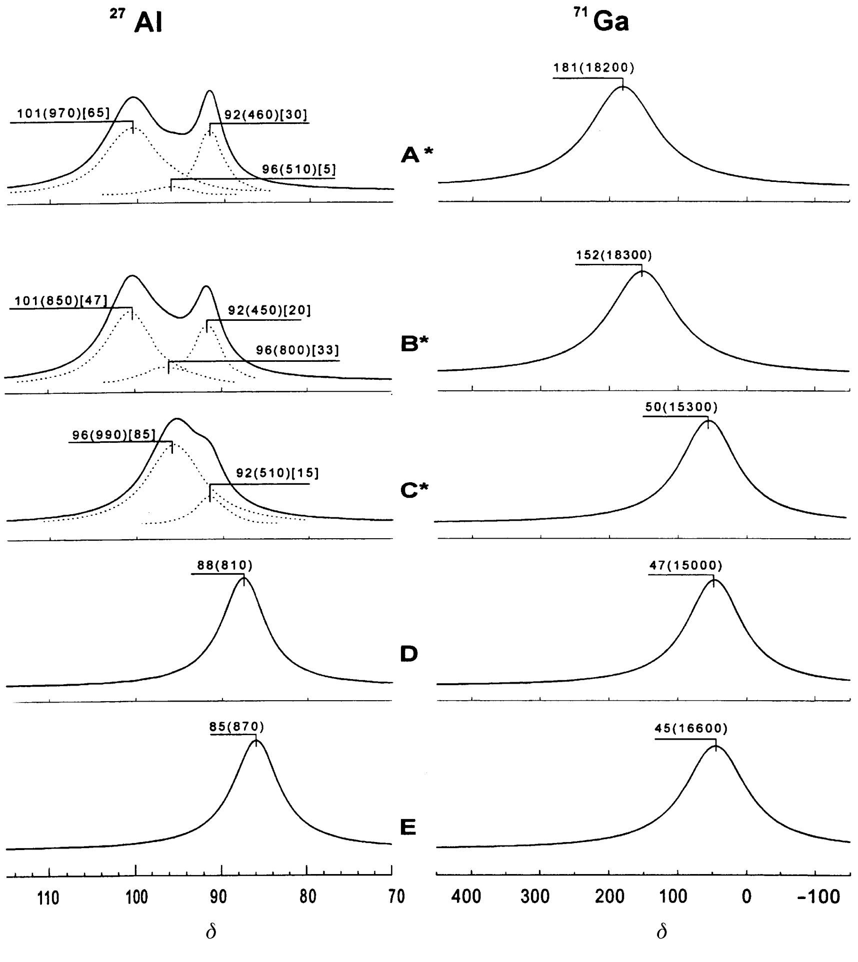


Fig. 1 ^{27}Al and ^{71}Ga NMR spectra of mixtures of Al_2Br_6 and Ga_2Cl_6 in benzene at room temperature. A–E refer to data in Table 1. Numbers given δ, halfwidth $\omega_{1/2}$ (Hz), percentage intensity. Asterisks identify solutions for which ^{27}Al spectra were recorded at 60 °C after 30 min heating.

spectra of heterogeneous mixtures of $AlCl_3/AlBr_3$ and $AlCl_3/AlI_3$ (*i.e.*, saturated solutions) in benzene (δ, $\omega_{1/2}$), with the results shown in Figs. 3 and 4, and of homogeneous benzene solutions of $AlBr_3/AlI_3$ (Fig. 6). The corresponding ^{71}Ga NMR spectra of homogeneous solutions of $GaCl_3/GaBr_3$ and $GaBr_3/GaI_3$ in the same solvent are illustrated in Figs. 7 and 8.

Results and discussion

Thermodynamic considerations

The halogen exchange reaction between trihalides of aluminium and gallium [eqn. (1)] can be considered in terms of the

$$AlX_3 + GaY_3 \longrightarrow AlY_3 + GaX_3 \qquad (1)$$

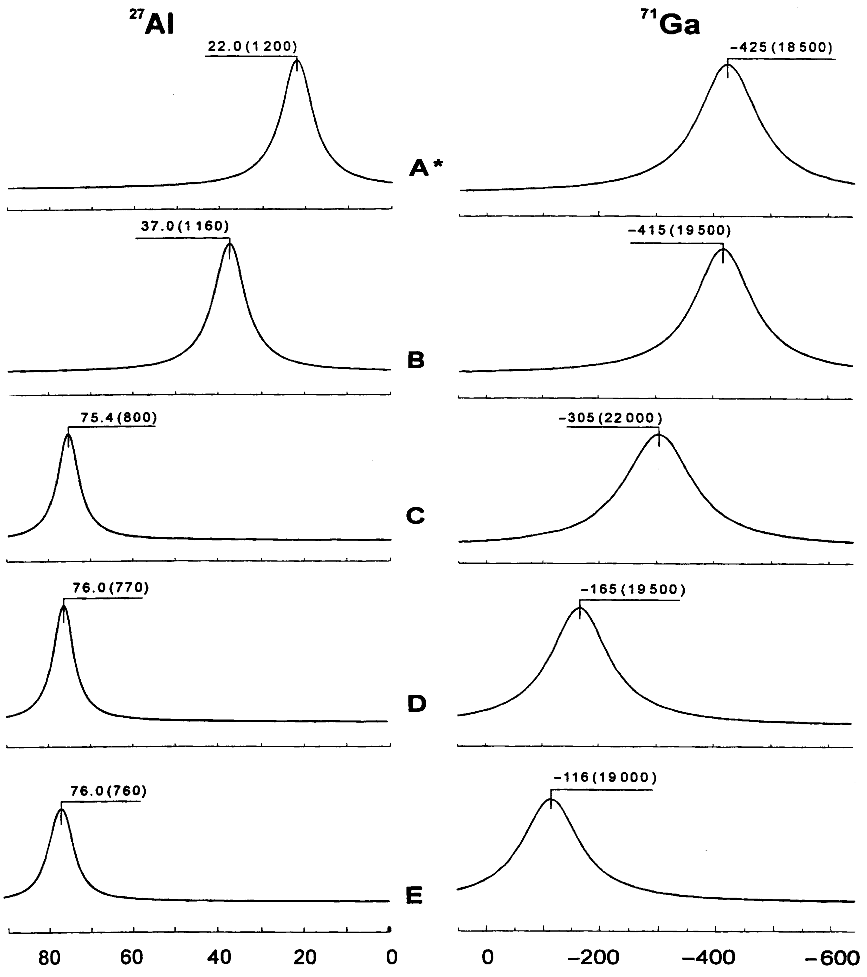


Fig. 2 ^{27}Al and ^{71}Ga NMR spectra of benzene solutions of $GaBr_3$ and AlI_3 at room temperature; labels refer to data in Table 2. For A, the Ga spectrum was recorded at 40 °C.

Table 3 Standard enthalpies of formation (ΔH°_f)[a] and calculated enthalpies of reaction (ΔH°_r) for the process $AlX_3(s) + GaY_3(s) \rightarrow AlY_3(s) + GaX_3(s)$ (all in kJ mol^{-1})

	$-\Delta H^\circ_f(s)$				
	AlX_3	GaY_3	AlY_3	GaX_3	$-\Delta H^\circ_r$
X = Br Y = Cl	511	524	705	386	56
X = I Y = Br	309	386	511	239	55

[a] ΔH°_f values from ref. 6.

hard–soft acid–base concept, in which case the exchange will be expected to proceed spontaneously so as to favour hard–hard interactions. A more quantitative approach employs the standard enthalpies of formation of the appropriate trihalides; two such sets of data are presented in Table 3. One qualification to this treatment is that the ΔH°_f values are for the solids, but it is reasonable to assume that the overall differences in the enthalpies of solution in benzene will not change the final conclusion substantially; the neglect of entropy changes is also insignificant, since $T\Delta S$ for these reactions at 25 °C is of the order of 0.5 kJ mol^{-1}.[6] The $-\Delta H^\circ_f$ results clearly predict that the exchange reactions [eqns. (2) and (3)] will proceed in the direction

$$AlBr_3 + GaCl_3 \longrightarrow AlCl_3 + GaBr_3 \qquad (2)$$

and

$$AlI_3 + GaBr_3 \longrightarrow AlBr_3 + GaI_3 \qquad (3)$$

A third predictor is the electronegativity differences. From the values Cl 3.16, Br 2.96, I 2.66, Al 1.16, Ga 1.81, the function $(\chi_Y - \chi_{Al})^2 + (\chi_X - \chi_{Ga})^2$ has the values 3.94 (X = Br, Y = Cl), 3.65 (X = Cl, Y = Br), 2.5 (X = I, Y = Br) and 2.44 (X = Br, Y = I), and the direction of the reaction should correspond to a maximization of this function.[7]

Since we are dealing with reactions in the non-polar solvent benzene, the solute species will be written in the remainder of this paper as the dimers M_2X_6.[1] In such terms, it follows that a reaction between a moles Al_2Br_6 and b Ga_2Cl_6, with $a \leq b$, should give a mixture whose ^{27}Al NMR spectrum will be of Al_2Cl_6 alone, while the ^{71}Ga spectrum will be that of a mixture of Ga_2Cl_6 and Ga_2Br_6. Similarly, when $a > b$, the ^{27}Al spectrum will be that of a mixture of Al_2Cl_6 and Al_2Br_6, with a ^{71}Ga spectrum uniquely that of Ga_2Br_6. Analogous predictions can be made for the Ga_2Br_6/Al_2I_6 system, and we return to these below. This analysis implies that in some cases the experimental spectra will be of mixtures of $M_2X_6 + M_2Y_6$ for both nuclei, and we therefore first discuss the ^{27}Al and ^{71}Ga spectra of such mixtures, before returning to the systems considered in Tables 1 and 2, and the corresponding spectra in Figs. 1 and 2.

Al_2X_6/Al_2Y_6 systems

The ^{27}Al NMR spectra of saturated benzene solutions of mixtures of $Al_2Cl_6 + Al_2Br_6$ and $Al_2Cl_6 + Al_2I_6$ are summarized in Figs. 3 and 4 respectively; these show $\delta(^{27}Al)$ and $\omega_{1/2}$,

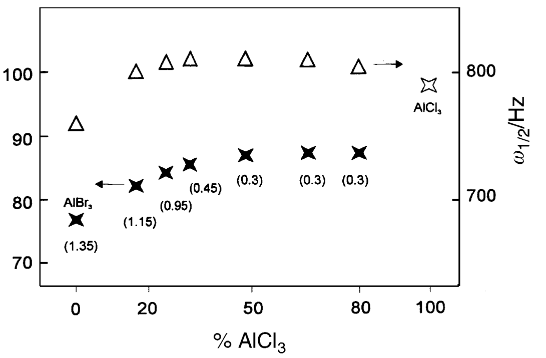


Fig. 3 ^{27}Al NMR spectra of saturated benzene solutions of mixtures of Al_2Cl_6 + Al_2Br_6; triangles show $\omega_{½}$, and crosses $\delta(^{27}Al)$, as a function of the initial mole fraction of Al_2Cl_6. Numbers in parentheses are the equilibrium Al concentrations (wt%).

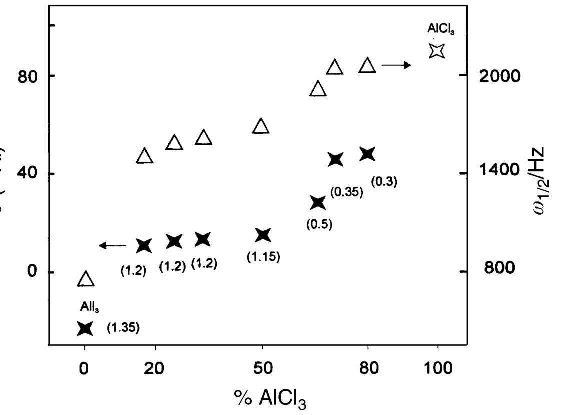


Fig. 4 ^{27}Al NMR spectra of saturated benzene solutions of Al_2Cl_6 + Al_2I_6; symbolism as in Fig. 3.

Table 4 ^{27}Al and ^{71} Ga NMR chemical shifts[a] for M_2X_6 and MX_4^- in non-aqueous solvent

	Al	Ref.	Ga	Ref.
M_2Cl_6	98	5	222	3
M_2Br_6	78	4	45	4
M_2I_6	−24	9	−425	[b]
MCl_4^-	103	8,10	250	3, 11, 12
MBr_4^-	80	8	63	11, 12
MI_4^-	−27	8	−455	11, 12

[a] In ppm; ^{27}Al relative to $[Al(H_2O_6]^{3+}_{aq}$ for which $\delta(^{27}Al) = 0$; ^{71}Ga relative to $[Ga(H_2)_6]^{3+}_{aq}$ for which $\delta(^{71}Ga) = 0$. [b] This work; see Fig. 8.

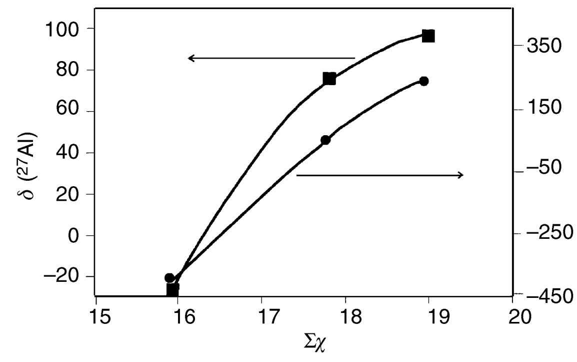


Fig. 5 ^{27}Al and ^{71}Ga chemical shifts as a function of total ligand electronegativity in M_2X_6 (M = Al, Ga; X = Cl, Br, I).

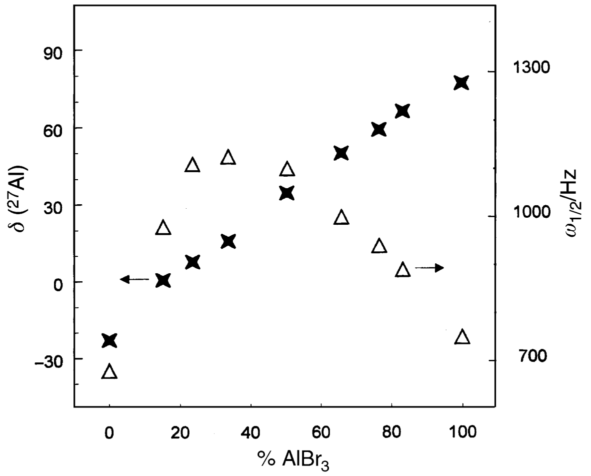


Fig. 6 ^{27}Al NMR spectra of solutions of Al_2Br_6 + Al_2I_6 in benzene (total Al concentration 1.0 wt%); symbolism as in Fig. 3.

and the analytically determined Al content, all as a function of the initial composition. In both cases, δ for Al_2Cl_6 is that determined previously[5] as 98 ppm; the half-width is very large, and is not shown in either figure. In contrast to the $AlCl_4^-/AlBr_4^-$ system, which shows resonances from all five possible $AlCl_nBr_{4-n}^-$ anions,[8] only one resonance is observed in Al_2Cl_6/Al_2Br_6 mixtures, indicating that the solute species are in rapid chemical exchange relative to the ^{27}Al NMR time scale. The results for $\delta(^{27}Al)$ show significant deviation from the monotonic dependence on composition, and there is a distinct plateau at 88 ± 1 ppm in the range 30–80 mol% Al_2Cl_6. We identify this as the chemical shift of $Al_2Cl_3Br_3$, which is apparently the thermodynamically stable compound of highest chlorine content, with a solubility in benzene corresponding to [Al] = 0.3 wt%. A similar conclusion can be reached from the plateau in the $\omega_{½}$ plot.

A confirmation of this assignment can be obtained from Fig. 5, in which the chemical shifts for Al_2X_6 and Ga_2X_6 are shown as a function of the total ligand electronegativity $\Sigma\chi$; the sources of the chemical shifts for these molecules, and for MX_4^- anions, are given in Table 4. For these latter species, as for other halogen derivatives of the Group 13 elements, [8–14] monotonic curves similar to those in Fig. 5 have been constructed. The value of $\delta(^{27}Al) = 88$ derived from Fig. 3 corresponds to $\Sigma\chi = 18.3$; the derived value for $Al_2Cl_3Br_3$ is 18.36, supporting the above assignment of the species present at the plateau in Fig. 3.

Fig. 4 refers to the Al_2Cl_6 + Al_2I_6 system, and we note here that the δ and $\omega_{½}$ values for Al_2I_6 in benzene are for a saturated solution whose concentration is 1.35 wt%. A distinct plateau can be seen, corresponding to $\delta(^{27}Al) = 16 \pm 1$, or $\Sigma\chi = 16.1$; the calculated value for Al_2I_5Cl is 16.46. There is a less well-defined feature at $\delta = 44$; the derived value of $\Sigma\chi = 16.7$ corresponds to $Al_2I_4Cl_2$ (calculated value 16.96), although the steepness of the curve in this region on Fig. 5 places some uncertainty on this conclusion. In contrast to the Al_2Cl_6/Al_2Br_6 system in which $Al_2Cl_3Br_3$ apparently predominates over a wide concentration range, these mixed iodo–chloro complexes only exist over narrow ranges, although their solubility is high (≈1.2 and ≈0.3 wt% Al respectively). The half-width plots also show plateaux at the same concentrations as the δ values, in keeping with the existence of such mixed halide complexes.

Unlike those mixtures in which Al_2Cl_6 is a constituent, the Al_2Br_6 + Al_2I_6 system produces homogeneous solutions over the whole composition range. Fig. 6 presents the $\delta(^{27}Al)$ and $\omega_{½}$ results for solutions containing 1.0 wt% Al. The chemical shifts of these mixtures show an almost linear dependence on composition, so that no unique thermodynamically stable mixed species can be identified. On the other hand, there is a maximum in the $\omega_{½}$ dependence on composition at 33% $AlBr_3$. The corresponding chemical shift is 16 ppm, which by interpolation in Fig. 5 corresponds to Al_2BrI_5 (derived $\Sigma\chi = 16.3$, calculated value 16.26). The dependence of line-width on the

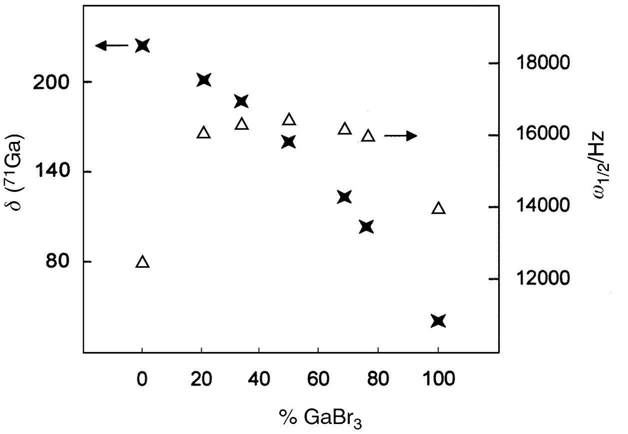


Fig. 7 ^{71}Ga NMR spectra of solutions of Ga_2Cl_6 + Ga_2Br_6 in benzene (total Ga concentration 1.5 wt%); symbolism as in Fig. 3.

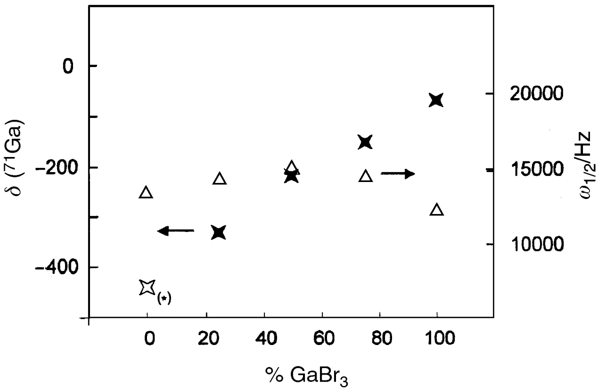


Fig. 8 ^{71}Ga NMR spectra of solutions of Ga_2Br_6 + Ga_2I_6 in benzene (total Ga concentration 1.5 wt%); symbolism as in Fig. 3.

composition indicates that the rate of halogen exchange is close to the intermediate rate between the Al_2Br_6 and Al_2I_6 environments. In this region, the line-width depends on the rate of exchange, on the composition, on the transverse relaxation times and on the radio frequency used,[15] and on the composition of the binary mixture, involving as it does all the exchanging sites, including the intermediates. The effect of quadrupolar coupling relaxation is believed to be negligible in these systems. For $AlBr_3/AlI_3$, for example, the ^{27}Al spin–spin relaxation time $T2$ is less than $T1$ by a factor of 2–4, and the spectral changes observed are therefore reasonably discussed in terms of chemical exchange.

Ga_2X_6/Ga_2Y_6 systems

We have studied mixtures of Ga_2Cl_6 + Ga_2Br_6 and Ga_2Br_6 + Ga_2I_6 in benzene, with the results shown in Figs. 7 and 8. These homogeneous solutions all contained 1.5 wt% Ga, with the exception of pure Ga_2I_6 for which a saturated solution at room temperature had a concentration of 0.8 wt%. In each case, there is a smooth dependence of δ(^{71}Ga) on composition, but $\omega_{1/2}$ shows a clear maximum. For the chloride–bromide system, this occurs at the equimolar composition, and the corresponding $\delta = 173$ implies that the predominant species at this point is either $Ga_2Cl_3Br_3$ ($\Sigma\chi = 18.36$) or $Ga_2Cl_4Br_2$ ($\Sigma\chi = 18.56$), since the derived value from Fig. 5 is 18.5. Analogous arguments for the bromide–iodide mixtures give the maximum in $\omega_{1/2}$ also at the equimolar point, with $\delta = -220$, and $\Sigma\chi = 16.6$; $\Sigma\chi$ for $Ga_2Br_3I_3$ and $Ga_2Br_2I_4$ are 16.86 and 16.56 respectively, slightly favoring the latter composition for the most stable species.

The maxima in the line-width–composition dependence again indicate that the rate of halogen exchange is close to the intermediate exchange rate region, as in the Al_2Br_6 + Al_2I_6 case. A comparison of the data reveals that for Ga_2Cl_6 + Ga_2Br_6, the maximum $\omega_{1/2}$ (16.5 kHz) is 15–35% greater than the values for Ga_2Cl_6 (12.5 kHz) and Ga_2Br_6 (14.0 kHz). In the aluminium system noted above, this factor is about 40%, indicating that the exchange is faster in the gallium halides.

Al_2Br_6/Ga_2Cl_6 systems

It is now possible to examine the spectra in Fig. 1 in the light of the above discussion. The ^{27}Al spectra in Fig. 1A and B are almost identical to those discussed in a previous paper[5] and show the presence of the hydrolysis products of Al_2Cl_6, which were identified earlier as the ionic species $HAlCl_4$ ($\delta = 101$) and $H[HOAlCl_3]$ ($\delta = 96$) as aggregates, and the neutral dimer $[HOAlCl_2]_2$ ($\delta = 92$). In keeping with this earlier discussion, there is also a broad unresolved resonance from the small quantity of dissolved Al_2Cl_6, although the solubility of this substance in benzene at room temperature is very low. The Al concentration in these two solutions (0.06 wt%; Table 1) is close to that found for a solution prepared by equilibrating $AlCl_3$ and nominally anhydrous benzene,[5] and represents the sum of these various Al/Cl/OH solutes. The hydrolysis products are of decreasing significance as the Al concentration rises, being marginal in Fig. 1C and negligible in Figs. 1D and E. The series of ^{27}Al NMR spectra show that with increasing total solute concentration (Table 1), the dilute solution of Al_2Cl_6 and hydrolysis products gives way to a much more concentrated solution apparently containing only one species (Fig. 1E) for which $\delta(^{27}Al) = 86 \pm 1$. This can be identified on the basis of the discussion above as $Al_2Cl_3Br_3$, which as noted earlier is significantly more soluble than Al_2Cl_6.

The ^{71}Ga NMR spectra in these solutions (Figs. 1A–E) show no evidence of hydrolysis products, presumably because any H_2O impurity reacts preferentially at the more electropositive aluminium(III) sites. Only one ^{71}Ga resonance is observed in each case, with the chemical shift changing from 181 ppm in Fig. 1A to *ca.* 45 ppm in Fig. 1E. The higher value can be ascribed to $Ga_2Cl_4Br_2$ ($\Sigma\chi = 18.6$; calculated value 18.56), while the lower is clearly Ga_2Br_6 (see Table 4, and ref. 4).

These findings are in good agreement with the predictions made above for a mixture of *a* Al_2Br_6 and *b* Ga_2Cl_6. When $b > a$ (Figs. 1A and B), the only aluminium species detected is essentially Al_2Cl_6, and its hydrolysis products, while gallium is present as a mixture of Ga_2Cl_6 and Ga_2Br_6, co-existing in rapid equilibration with $Ga_2Cl_4Br_2$ as the thermodynamically most stable species. For $a > b$ (Figs. 1D and E), aluminium is present as $Al_2Cl_3Br_3$, presumably in fast exchange with very small quantities of Al_2Cl_6 and Al_2Br_6, while the only gallium halide in this system is Ga_2Br_6.

Al_2I_6/Ga_2Br_6 system

Both aluminium and gallium exhibit only one signal under all conditions studied (see Table 2 for concentration range). For ^{27}Al, $\delta = 22$ (Fig. 2A) when this element is in large excess; Al_2BrI_5 was identified earlier as the stable complex in Al_2Br_6/Al_2I_6 mixtures with $\delta = 16$. Increasing the Ga : Al mole ratio (Figs. 2B–E), and hence the Br : I ratio, causes the maximum to move to lower field, with the chemical shift becoming constant at 76 ± 1 ppm, which immediately identifies the solute as Al_2Br_6 (*cf.* Table 4). The half-width (760 Hz) is close to that for a 1% solution of Al_2Br_6 in benzene (*cf.* Fig. 3 and ref. 4).

The ^{71}Ga NMR chemical shifts from $\delta = -425$ in Fig. 2A (*cf.* $\delta = -425$ for Ga_2I_6, Table 4) to −116 ppm at the highest Ga concentrations (Fig. 2E). Interpolation from Fig. 5 identifies this as $Ga_2Br_3I_3$ (see above).

The nature of these spectra is such that no reliable equilibrium constants could be derived for eqns. (2) and (3). It appears that K_2 and K_3 are of similar magnitude, in keeping with the thermodynamic data in Table 3, but the only conclusion must be that the results agree qualitatively with these predictions.

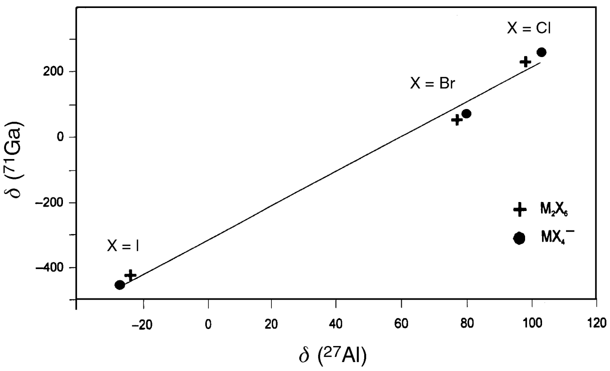


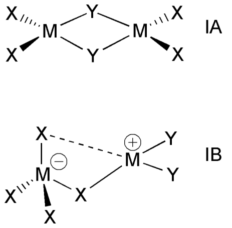
Fig. 9 Correlation of ^{27}Al and ^{71}Ga chemical shifts in M_2X_6 (in benzene solution) and MX_4^- (in chloroform). Data from Table 4.

Correlations between $\delta(^{27}Al)$ and $\delta(^{71}Ga)$

As noted earlier, Table 4 presents literature data for the chemical shifts of M_2X_6 and MX_4 derivatives of aluminium and gallium. In both series, the range of chemical shifts is clearly greater for ^{71}Ga, and the linear relationship shown in Fig. 9 ($y = 5.2x - 316$; $r = 0.995$) establishes that this is greater by a factor of *ca.* 5.3. This correlation also serves to confirm our earlier[5] assignment of $\delta(^{27}Al) = 98$ for Al_2Cl_6 in benzene.

The structure of mixed halide solutes

In five of the mixed halide systems reported in this work, we have identified solute species of the type $M_2X_nY_{6-n}$, the specific entities being $Al_2Cl_3Br_3$, Al_2ClI_5, $Al_2Cl_2I_4$, Al_2BrI_5, $Ga_2Cl_3Br_3$ (or $Ga_2Cl_4Br_2$), $Ga_2Br_2I_4$ and/or $Ga_2Br_3I_3$. It is clear that the symmetrical $M_2X_3Y_3$ species are not formed exclusively, and indeed in most cases there is no evidence for their existence. Give that monomeric MX_3 molecules are of negligible importance in non-aqueous solutions, the question of the structure of these mixed halide complexes must be discussed in terms of dimers. These can be of two related types. The classical approach is to write a neutral halide-bridged form of (say) $X_2M(\mu\text{-}Y)_2MX_2$, in which case the predominance of compounds with high iodine content is explained through the form **IA** (Scheme 1). The alternative approach is based on a series of reports which show that singly-bridged bipolar structures must be considered as significant in non-aqueous solution. For aluminium, NMR studies[5] on this point are supported by Raman spectroscopy of Al_2Br_6 in aromatic solvents,[16] while for Ga_2X_6, NMR spectra,[4] vapour pressure measurements,[17] and electron spin resonance spectroscopy[18] all support the structure shown as Fig. 1B. In this case, the predominance of iodine in the complex is explained by the charge distribution, with a coordinatively saturated MI_4^- moiety stablizing the MY_2^+ group, which is itself then a favourable site for solvation. This may explain the enhanced solubility observed in the $AlCl_3/AlBr_6$ system. Equally, the availability of the MY_2 site may enhance the rate of halogen exchange in these systems. Further studies of this problem are underway.



Scheme 1

Acknowledgements

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