814. *Nuclear Magnetic Resonance Studies with the Gallium-71 Isotope*

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The ^{71}Ga nuclear magnetic resonance signals of a series of symmetrical gallium ions have been located at 20 Mc./sec. and fields of about 15·4 kilogauss. Chemical shifts over a range of 1367 p.p.m. were noted with resonance line-widths between 90 and 6000 c./sec. A ^{71}Ga n.m.r. study of the system gallium trichloride–hydrochloric acid indicates that there is a critical concentration of acid below which the tetrachlorogallate anion is increasingly replaced by the hexa-aquogallium cation $[Ga(H_2O)_6]^{3+}$ together with some intermediate species. Similar results are reported for the bromide and iodide systems though the latter shows less tendency to form intermediate species.

Solutions and melts of gallium dichloride and dibromide have also been examined and the results confirm the presence of two types of gallium. The ^{71}Ga resonance positions of the species GaH_4^-, $Ga(OH)_4^-$, and Et_2OGaCl_3 are also reported.

This paper reports the first extensive investigation of compounds of gallium by nuclear magnetic resonance using the ^{71}Ga isotope. Most previous n.m.r. work with gallium has been carried out on solids [1] but Rice and Pound during their determination of the ratio of the nuclear magnetic moments of the gallium isotopes [2] measured the positions of the ^{69}Ga and ^{71}Ga resonances in a solution of gallium trichloride in 6M-hydrochloric acid. They obtained a line-width of 440 c./sec. for the ^{71}Ga signal and attributed this to magnetic field inhomogeneity. They noted that the lines broadened and weakened if the hydrochloric acid concentration was reduced, but offered no explanation of this effect. As both the gallium isotopes have large quadrupole moments it seems likely that line broadening would be caused by a reduction in symmetry at the nucleus due to structural changes, and the present work was undertaken, in part, to study the nature of these changes and the factors governing them. Present knowledge of the species present in aqueous acid solutions of gallium halides comes from Raman spectroscopy. Thus the spectrum of a solution of gallium metal in concentrated hydrochloric acid shows [3] that the gallium is present as the tetrachlorogallate anion, $GaCl_4^-$. Similar work on the corresponding bromide system [4] established the presence of the tetrabromogallate anion. Little is known about the nature of the ions present at lower concentrations of acid.

A second area of study was the investigation of resonance signals from the species present in the dihalides. Gallium dichloride has been shown by Raman spectroscopy,[5] by *X*-ray studies,[6] and by chemical reactions in benzene [7] to be gallium(I) tetrachlorogallate(III), $Ga^+GaCl_4^-$, and the dibromide has been shown [8] to be $Ga^+GaBr_4^-$. Since the gallium in these dihalides exists in two oxidation states, n.m.r. spectroscopy with the ^{71}Ga nucleus should indicate the presence of two types of gallium. This is of particular importance in solution since Raman spectroscopy gives no information about the monatomic ion Ga^+.

EXPERIMENTAL

Nuclear magnetic resonance of ^{71}Ga was observed at 20 Mc./sec. with field strengths in the region of 15·4 kilogauss using an A.E.I. type RS2 spectrometer. Studies were retricted to

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[1] R. G. Shulman, B. J. Wyluda, and H. J. Hrostowski, *Phys. Rev.*, 1958, **109**, 808; D. J. Oliver, *Phys. and Chem. Solids*, 1959, **11**, 257.

[2] M. Rice and R. V. Pound, *Phys. Rev.*, 1955, **99**, 1036.

[3] L. A. Woodward and A. A. Nord, *J.*, 1956, 3721.

[4] L. A. Woodward and A. A. Nord, *J.*, 1955, 2655.

[5] L. A. Woodward, G. Garton, and H. L. Roberts, *J.*, 1956, 3723.

[6] G. Garton and H. M. Powell, *J. Inorg. Nuclear Chem.*, 1957, **4**, 84.

[7] R. C. Carlson, E. Griswold, and J. Kleinberg, *J. Amer. Chem. Soc.*, 1958, **80**, 1532.

[8] L. A. Woodward, N. N. Greenwood, J. R. Hall, and I. J. Worrall, *J.*, 1958, 1505.

^{71}Ga because this nuclide has the lower quadrupole moment of the two naturally occurring isotopes and this should give narrower and more intense signals. This, and the greater signal strength per nucleus arising from its greater magnetic moment, should more than compensate for its lower abundance (39·8%).

Sample tubes of 9 mm. diameter were used for measurements at room temperature (25°). Melts were studied at approximately 170—200° in 5 mm. tubes sealed below the holder to eliminate problems due to sublimation. Failure to do this resulted in loss of sample to cooler parts of the tube together with continuous drift in the conditions of bridge balance due to the changing mass of sample in the detector coil. The samples were not spun as the resonances were all broad.

The signals were weak and were best observed with maximum radiofrequency power ($H_1 \sim 3$ milligauss). It was possible to record signals from some species in the absorption mode and line-widths as low as 90 c./sec. were obtained for $GaCl_4^-$. In view of the known attainable homogeneity of the magnet in other experiments at comparable field strengths it is unlikely that the observed line-width is due to magnetic inhomogeneity but rather that it is approaching the natural line-width of the species. For broader resonances it was found essential to observe the derivative signal by using field modulation (23 c./sec.) and an audiofrequency phase-sensitive detector. Eventually all signals were recorded in this way to ensure comparability of line positions. For the stronger signals from the 9 mm. tubes, the magnetic field was swept using the repetitive sweep facility which gave a sweep rate of about 12 c./sec. per second. This sweep rate is quite fast for this type of work and care had to be taken that filter time constants were not made so large as to displace the lines noticeably. Typical values were 0·3 sec. for the 90 c./sec. line of $GaCl_4^-$ and 6·0 sec. for the 600 c./sec. line of $[Ga(H_2O)_6]^{3+}$. In addition, the modulation level was kept as low as possible consistent with receiving a good signal to avoid over-broadening the lines. No advantage was found in using the flux stabiliser since the long-term drift even without it was small and easily corrected for. Line positions were measured on the cathode ray tube graticule which was calibrated with sidebands of the $GaCl_4^-$ absorption line. The derivative of this line was then used as standard, all other samples being compared by substitution. The standard was measured before and after each sample to compensate for any drift. The accuracy is about ±2% for shifts up to 300 p.p.m. For weak signals, particularly those from the 5 mm. tubes, it was necessary to use a mechanically driven sweep with a maximum sweep rate of 2·4 c./sec. per second. This enabled much longer filter time constants to be used with consequent improvement in signal : noise ratio. With this technique, line positions were determined by the voltage derived from the sweep circuit, which was in turn calibrated against the cathode ray tube graticule. No corrections were made for magnetic susceptibility differences.

Gallium trichloride,[9] tribromide,[10] and tri-iodide [11] were prepared and purified as previously described. Solutions of the trihalides in the corresponding acids were prepared by dissolving the halide in the minimum quantity of acid, dividing this into equal aliquot portions, and adding varying amounts of acid and water to each to give a series of 2·5 ml. samples each containing 0·3 g. of gallium, but with various concentrations of acid, which were later determined accurately by analysis. Gallium perchlorate was prepared by dissolving a known weight of gallium metal in heated aqueous 75% perchloric acid.[12] The product was obtained as a white free-flowing powder after filtration from the cooled solution and heating under vacuum at 125° to remove excess of perchloric acid solution. Gallium trichloride–diethyl ether was prepared by condensing a slight excess of diethyl ether on freshly sublimed gallium trichloride, and removal of excess of ligand under vacuum at 0°.[13] Pure liquid complex was used for measurements. A solution containing the tetrahydroxygallate anion $Ga(OH)_4^-$ was prepared by dissolving gallium trichloride in concentrated sodium hydroxide solution.[14] Gallium dibromide [15] and dichloride [16] were prepared as reported previously and samples were sublimed

[9] N. N. Greenwood and K. Wade, *J.*, 1956, 1527.

[10] N. N. Greenwood and I. J. Worrall, *Inorg. Synth.*, 1960, **6**, 31.

[11] N. N. Greenwood and I. J. Worrall, *J. Inorg. Nuclear Chem.*, 1957, **3**, 357.

[12] L. S. Foster, *Inorg. Synth.*, 1946, **2**, 26.

[13] P. G. Perkins, Thesis, Nottingham University, 1958.

[14] B. N. Ivanov-Emin, L. A. Nisel'son, and L. E. Larionova, *Russ. J. Inorg. Chem.*, 1962, **7**, 266; B. N. Ivanov-Emin and Ya. I. Rabovic, *J. Gen. Chem.* (*U.S.S.R.*), 1944, **14**, 781.

[15] N. N. Greenwood and I. J. Worrall, *Inorg. Synth.*, 1960, **6**, 33.

[16] N. N. Greenwood and I. J. Worrall, *J.*, 1958, 1680.

into carefully dried tubes. Solutions were made by condensing benzene on freshly sublimed dihalide, stringent precautions being taken to eliminate moisture from all sources. It was found possible to prepare a solution of the dichloride which remained supersaturated indefinitely at 25° and gave strong signals. The dibromide formed a two-phase system consisting of a clear and a yellow phase. The yellow phase contained all the dihalide but tended to solidify during measurements so that partial results only could be obtained.

Lithium gallium hydride was prepared as reported previously [17] at a solution strength of about 50%.

Gallium was determined gravimetrically by 8-hydroxyquinoline and halogens by precipitation with silver nitrate.

RESULTS

Aqueous Solutions.—Typical spectra for gallium trichloride dissolved in various concentrations of aqueous hydrochloric acid are shown in Figure 1. As the normality of the acid falls the strong sharp peak due to $GaCl_4^-$ broadens and moves to high field and a second broad signal appears at higher fields still. The former resonance moves to higher field and decreases in intensity with decrease in acid concentration. The higher field signal, which was absent from solutions in 6·05 and 7·3M acid, remains stationary but increases in intensity as the solution becomes less acid. Its position was about 257 p.p.m. upfield from the $(GaCl_4)^-$ signal, invariably near the position of the siganl from aqueous gallium perchlorate $[Ga(H_2O)_6]^{3+}$ and with the same peak-to-peak line width. A graph of line position *versus* acid concentration is shown in Figure 2 which indicates that the sharp resonance due to $GaCl_4^-$ broadens and starts to move below a molarity of about 4·5. The line position then varies linearly with molarity until at 1·65M it becomes hardly distinguishable from the stationary signal from $[Ga(H_2O)_6]^{3+}$. The corresponding data for the systems $GaBr_3$–HBr and GaI_3–HI are shown in Figure 3. The bromide behaves in the same way as the chloride system, but with the $GaBr_4^-$ signal shifted 188 p.p.m. upfield from $GaCl_4^-$. The iodide on the other hand shows only two fixed resonances with no real indication of other species which are dependent on the concentration of acid. The line at high field is presumably due to GaI_4^- and is 707 p.p.m. upfield from $GaCl_4^-$.

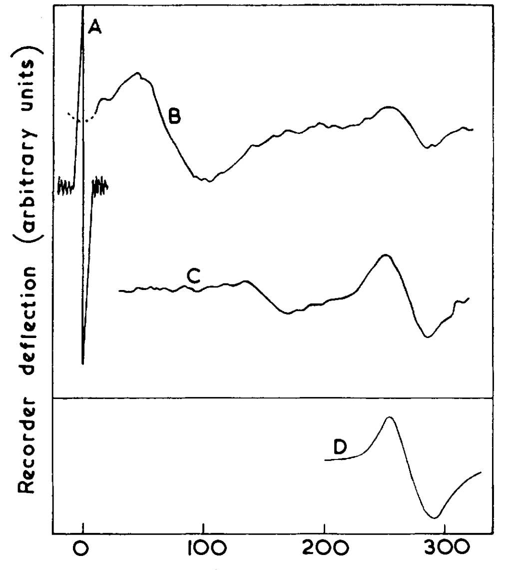

FIGURE 1. ^{71}Ga n.m.r. traces for $GaCl_3$–HCl mixtures and for aqueous gallium perchlorate
A, 6·05M-HCl. *B*, 3·62M-HCl. *C*, 2·5M-HCl. *D*, Gallium perchlorate.

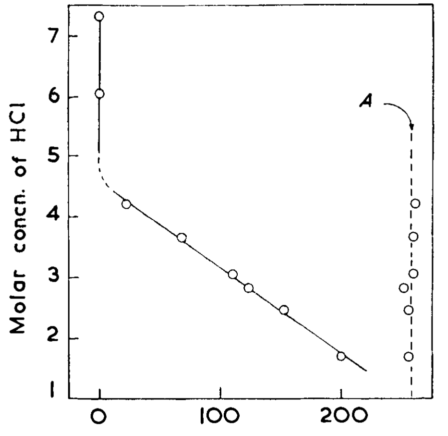

FIGURE 2. N.m.r. line positions for $GaCl_3$–HCl mixtures
A, Gallium perchlorate line position.

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[17] N. N. Greenwood, A. Storr, and M. G. H. Wallbridge, *Inorg. Chem.*, 1963, **2**, 1036.

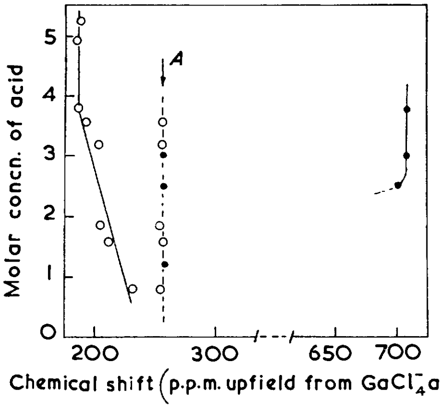
The presence of a resonance signal which is dependent on the concentration of acid in the chloride and bromide systems can be explained if the species $GaCl_4^-$ and $GaBr_4^-$ are in fast equilibrium with other species which have their resonances at higher field. These cannot include $[Ga(H_2O)_6]^{3+}$ since the signal from this ion appears separately and its position does not depend on the acid strength though its intensity does. This indicates that $[Ga(H_2O)_6]^{3+}$ is in slow equilibrium with the rest of the system and that the resonance with variable position is due to some new ionic species such as $[GaCl_n(H_2O)_{6-n}]^{(3-n)+}$ which are intermediate in composition between $GaCl_4^-$ and $[Ga(H_2O)_6]^{3+}$. The equilibrium can be formulated

$$GaCl_4^- \overset{\text{fast}}{\rightleftharpoons} [GaCl_n(H_2O)_{6-n}]^{(3-n)+} \overset{\text{slow}}{\rightleftharpoons} [Ga(H_2O)_6]^{3+}$$
$$\text{where } 4 \geqslant n \geqslant 1.$$

The minimum separation between the resonances associated with $[Ga(H_2O)_6]^{3+}$ and the intermediate species is about 30 p.p.m. implying that the lifetime of the hexa-aquo-ion is greater than about 2 millisec.

The lack of evidence for intermediate species in the iodide system is of interest since $[Ga(H_2O)_6]^{3+}$ and GaI_4^- are obviously in equilibrium. The rate of exchange between them must be slow with a lifetime greater than about 0·1 millisecond but the lifetime of any intermediate species must be negligibly short compared with this time and the interconversion of forms perhaps occurs directly.

FIGURE 3. N.m.r. line positions for $GaBr_3$–HBr ○ and GaI_3–HI ● mixtures *A*, Gallium perchlorate line position.



An interesting feature of these results is that the changes all take place in strongly acid solutions. This suggests that the equilibrium positions are determined by the concentration of halide ions rather than by the concentration of hydrogen ions, which presumably merely serve to keep the gallium in solution. This hypothesis was tested by measuring changes in spectra due to changes in chloride concentration for the system $GaCl_3$–HCl–$MgCl_2$ in which the gallium and acid concentrations were kept constant, the acid concentration being 2·5M. As shown in Figure 4 addition of magnesium chloride to increase the chloride ion concentration moved the mobile resonance downfield as expected though it was not quite possible to reach the $GaCl_4^-$ resonance position even with a total chloride ion concentration of 6M. It is likely that the chloride ion activity was reduced by ion-pair formation and ionic strength effects.

Since fast exchange is postulated in the systems described above, a confirmatory experiment was carried out on a sample made by dissolving gallium tribromide in concentrated (8M) hydrochloric acid to give a solution of similar concentration in gallium to those used above. The spectrum was a single sharp line intermediate in position between those for the ions $GaCl_4^-$ and $GaBr_4^-$. The relative sharpness of the line indicates rapid exchange rather than a single intermediate species, such as $GaCl_2Br_2^-$, which would be expected to give a broad line.

Gallium Dihalides.—A solution of gallium dichloride in benzene showed two resonances. One was weak and broad and occurred some 34 p.p.m. upfield from the $GaCl_4^-$ resonance in aqueous hydrochloric acid solutions; the other was strong and sharp and occurred 942 p.p.m. upfield from the aqueous $GaCl_4^-$ resonance. The low-field line, though broad, is assigned to $GaCl_4^-$ and the high-field peak to Ga^+. The high symmetry of the monatomic ion ensures a narrow line and the large increase in screening results from the loss of paramagnetic effects associated with chemical bonding.

Gallium dibromide in benzene also showed a strong, sharp resonance at high field due to the Ga^+ cation, though this was 33 p.p.m. ($\pm 2\%$) to low field of the same resonance in the solution of the dichloride. It was not possible to observe the $GaBr_4^-$ line owing to problems arising from the rate of solidification of the solute from concentrated solutions, but this indicates that the resonance was not sharp.

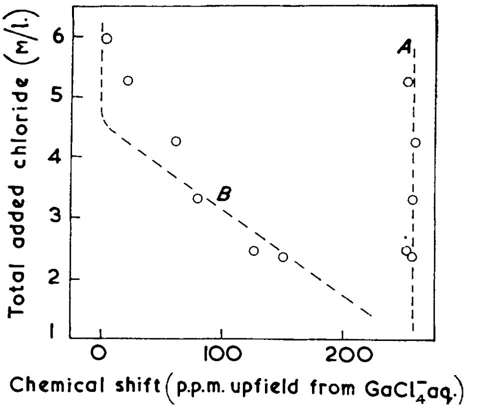


FIGURE 4. N.m.r. line positions for $GaCl_3$–$MgCl_2$–HCl mixtures
A, Gallium perchlorate line position.
B, Line from Figure 2.

Surprisingly, a quite different picture was obtained in the melts. The dichloride showed a peak near the aqueous $GaCl_4^-$ position, but about 60 p.p.m. upfield while the Ga^+ line was sharp, but was shifted 192 p.p.m. downfield from its position in solution. In contrast, the dibromide signals were both very broad and were detected only with difficulty. The low-field peak was in the correct region for $GaBr_4^-$ but the Ga^+ peak was shifted still further downfield by 240 p.p.m.

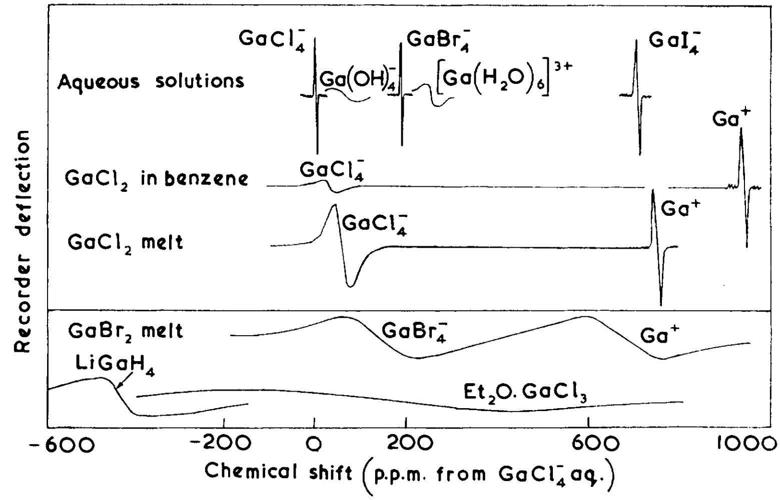


FIGURE 5. Comparative line shapes and positions for ^{71}Ga resonances (the vertical scale for the lower section is $\times 10$)

In addition to the above data, single resonances were detected for the ion GaH_4^- in an ethereal solution of lithium gallium hydride and for the liquid 1 : 1 complex of diethyl ether with gallium trichloride. These were very broad and weak. The ^{71}Ga resonance for the ion $Ga(OH)_4^-$ has also been observed in a solution of gallium trichloride in aqueous sodium hydroxide.

The various line positions measured in this work are summarised in Table 1 and some of the line shapes are shown in Figure 5.

TABLE 1

^{71}Ga Chemical shifts

Species	Environment	Shift (p.p.m. from $GaCl_4^-$ aq.)
GaH_4^-	$LiGaH_4$ in Et_2O solution	425 *
$GaCl_4^-$	6M-Aqueous HCl	0
$GaCl_4^-$	$GaCl_2$ in benzene	34
$GaCl_4^-$	$GaCl_2$ melt	60
$Ga(OH)_4^-$	Concentrated aqueous alkali	65
Et_2OGaCl_3	Pure liquid	120
$GaBr_4^-$	$GaBr_2$ melt	130
$GaBr_4^-$	5M-Aqueous HBr	188
$[Ga(H_2O)_6]^{3+}$	Aqueous gallium perchlorate or dilute aqueous acid	257
GaI_4^-	3M-Aqueous HI	707
Ga^+	$GaBr_2$ melt	670
Ga^+	$GaCl_2$ melt	750
Ga^+	$GaBr_2$ in benzene	909
Ga^+	$GaCl_2$ in benzene	942

* Downfield. The remaining values are upfield from $GaCl_4^-$.

DISCUSSION

The total range of chemical shifts observed is 1367 p.p.m. and this falls correctly in the sequence[18] $B < Al < Ga < Tl$. The chemical shifts in the GaX_4^- ions indicate an increase in screening along the series X = H, Cl, Br, or I. This sequence is similar to that found for the earlier members of Group III, boron[19] and aluminium.[20] The large chemical shifts are consistent with the view that screening in compounds of the heavier elements is determined primarily by the paramagnetic bonding term.[18] There is thus a decrease in paramagnetic screening in the sequence $H > Cl > Br > I$. In the case of Ga^+, where there is no chemical bonding the paramagnetic effect should be zero, and as expected this resonance appears at the highest field position.

The widths of the resonances show some interesting features. Since ^{71}Ga has an electric quadrupole moment, rapid relaxation can occur in an asymmetrical environment due to interaction of the moment with fluctuating electrical field gradients at the nucleus. This leads to considerable line broadening as observed with gallium in $Et_2O \rightarrow GaCl_3$. Similar line broadening occurs for ethereal solutions of lithium gallium hydride and this may indicate some asymmetry at the gallium atom due to subsidiary bonding of the GaH_4^- ion with the solvent and probably also with the cation. In aqueous solution the resonances of $GaCl_4^-$, $GaBr_4^-$, and GaI_4^- are all narrow (~100 c./sec.) as expected for ions of this symmetry. For $Ga(OH)_4^-$ and $[Ga(H_2O)_6]^{3+}$ the resonances are much broader (~600 and 300 c./sec., respectively) though the symmetry of the former is the same as that of the halide complexes and the octahedral symmetry of the latter would also be expected to lead to a narrow line. This broadening suggests that there is some hydrogen bonding between the solvent and the ions $Ga(OH)_4^-$ and $[Ga(H_2O)_6]^{3+}$. The ions will therefore to some extent be fixed within the solvent structure so that the local correlation time of molecular motion will be increased leading to an increased rate of quadrupolar relaxation. The effectiveness of this process would be reduced by ligand exchange, but for $[Ga(H_2O)_6]^{3+}$ the results show that exchange is slow. The halide ions on the other hand have been shown to undergo rapid exchange so that any tendency for the bonded ligands to associate with the solvent cannot be transmitted to the gallium.

The same mechanism also accounts for the increased line widths of the intermediate species which appear at the lower concentrations of acid in the gallium trichloride and tribromide solutions. Co-ordination of water or hydroxyl would lead to hydrogen bonding

[18] C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, 1963, **40**, 1714.
[19] H. Landesman and R. E. Williams, *J. Amer. Chem. Soc.*, 1961, **83**, 2663.
[20] D. E. O'Reilley, *J. Chem. Phys.*, 1960, **32**, 1007.

and the rate of exchange of ligands might decrease as less free Cl^- or Br^- became available in solution.

In addition, the extra ligands lower the symmetry around the gallium and this also broadens the line. Species such as $H_2O \rightarrow GaCl_3$ would be expected to have a line width similar to that of $Et_2O \rightarrow GaCl_3$ and would not be visible under the conditions of the experiment.

The Ga^+ resonance is sharp both in the molten dichloride and in benzene solutions. By contrast, the $GaCl_4^-$ resonances in these two samples are much broader than in aqueous acid and are shifted slightly upfield, possibly indicating some association of the $GaCl_4^-$ ion with benzene. This result is surprising since it is thought [7,21] that the benzene which crystallises with the dichloride and dibromide from solution is associated with the Ga^+ ion rather than the anions. However, the dynamic exchange possible in solution could well affect the n.m.r. spectra and one cannot necessarily infer the structure of crystalline phases from the spectrum of the supernatant liquid.

The n.m.r spectrum of molten gallium dibromide is quite different in appearance to that of the molten dichloride. The lines for both Ga^+ and $GaBr_4^-$ are broadened to such an extent that asymmetric species are indicated. Viscosity effects can be ruled out since the sample was held at 200°, at which temperature the dynamic viscosity is only 4 cP.[16] Variation in viscosity is also unlikely to have influenced line-widths in solution since there appeared to be little overall variation in the visocity of the solutions used. A more quantitative treatment of line-widths will be presented at a later stage.

We thank Mr. W. A. Campbell for help with the chemical analyses, the D.S.I.R. for an equipment grant, and the European Office of Aerospace Research, U.S.A.F., for financial support (to A. S.).

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[*Received, January 8th,* 1965.]

[21] R. E. Rundle and J. D. Corbett, *J. Amer. Chem. Soc.*, 1957, **79**, 757.