The Structure of Solutions of Gallium(I) Chloride in Benzene†

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The structure of benzene solutions of $Ga[GaCl_4]$ and $Ga[Ga_2Cl_7]$ has been investigated by ^{13}C and ^{71}Ga NMR, Raman spectroscopy and liquid X-ray scattering (LXS). Assignments of the vibrational spectra are based on a reinvestigation of the liquid Ga–$GaCl_3$ system. The results for the $Ga[GaCl_4]$–C_6H_6 system are in agreement with the view that an ion pair between Ga^+ and $GaCl_4^-$, which lowers the symmetry of the $GaCl_4^-$ ion from T_d to C_{2v} or lower, is formed. Spectroscopic effects indicating a complex formation between Ga^+ and benzene are weak. The salt $Ga[Ga_2Cl_7]$ was found to be extremely soluble in benzene (> 50% w/w). The results imply that in such solutions the Ga–Cl_b–Ga bridge in the $Ga_2Cl_7^-$ ion is bent and the ion pairing between Ga^+ and $Ga_2Cl_7^-$ takes place *via* the bridging chloride ion of the latter ion. Results from LXS show that the Ga^{III}–Cl_b distance is remarkably long, 2.85 Å (24% longer than in solid $K[Ga_2Cl_7]$). For this system, ^{71}Ga and ^{13}C NMR as well as Raman spectroscopic results clearly indicate complex formation between Ga^I and benzene.

In contrast to aluminium, gallium readily forms stable compounds in which it resides in oxidation states lower than the group valency, *i.e.* subvalent compounds. It forms stable dihalides with Cl^-, Br^- and I^-, all three of which are easily prepared by reducing molten GaX_3 with stoichiometric amounts of gallium metal or by treating gallium metal with mercury halides.[1] It has long been known[2,3] that all three dihalides must be considered as mixed-valence compounds $Ga^I[Ga^{III}X_4]$, and they have all been structurally determined: Ga_2Cl_4[4,5] and α-Ga_2Br_4[5] are isostructural and both contain Ga^+ quasi-dodecahedrally co-ordinated by slightly distorted tetrahedral GaX_4^- anions, whereas Ga_2I_4[6] and β-Ga_2Br_4[7] have a different structure in which Ga^+ is co-ordinated by the GaX_4^- anions in a trigonal-prismatic fashion. The distances between the Ga^+ centre and the co-ordinated halides are long (> 3.15 Å in the chloride compounds) and the co-ordination is therefore to be considered weak. Such behaviour is expected for weak Lewis bases such as GaX_4^-. Possibly, the most surprising property of the two salt-like[8] subhalides Ga_2Cl_4 and α-Ga_2Br_4 is their high solubility in benzene (7% w/w for Ga_2Cl_4).[9] This anomalous behaviour is even more surprising considering the fact that $K[GaCl_4]$ is virtually insoluble in aromatic solvents despite the fact that the ionic radius for K^+ (1.38 Å) is very similar to that of Ga^+ (1.33 Å).[9] Part of the explanation obviously lies in the ability of Ga^+ to form stable arene complexes, an ability shared by In^+ and Tl^+.[9] Schmidbaur and co-workers[10–15] have reported the isolation and structural determination of a number of gallium(I)–arene complexes, the first of which was $[Ga(C_6H_6)_2{\cdot}GaCl_4]_2{\cdot}3C_6H_6$.[11] In this complex, the gallium(I) ion is co-ordinated to two benzene rings in a 'bent sandwich' fashion and two such entities are linked by two $GaCl_4^-$ units. The bent sandwich co-ordination is a mode preferred by Ga^I in all bis(arene) complexes so far synthesized and attempts to force Ga^I to adopt the ferrocene-type of co-ordination by using paracyclophanes as ligands have so far been unsuccessful.[12,13] An η^6 co-ordination of Ga^I to arene rings with a concomitant co-ordination to $GaCl_4^-$ has been deduced from the IR spectra of solutions of Ga_2Cl_4 in benzene, but details about the structure are lacking.[16,17]

The 'pure' gallium(I) halides, GaX, are found as high-temperature gas-phase species in the vapour above molten Ga_2X_4 solutions[18,19] and in gaseous mixtures of gallium and chlorine.[20] They can also be stabilized in solution at low temperature.[21] Initial reports on the synthesis of 'GaI'[22] were later shown to be erroneous and the compound was, by X-ray diffraction, found to be $Ga_2I_3 = (Ga^+)_2(Ga_2I_6^{2-})$.[6] The corresponding bromide Ga_2Br_3 has also been synthesized and structurally characterized.[23]

The relationship between the structural chemistry of Ga^I and Ga^{II} has been called 'a classic structural problem'.[24] In contrast to Ga^I, Ga^{II} has never been identified as a paramagnetic, monoatomic ion Ga^{2+}. It invariably seems to exist as the dimer Ga_2^{4+} covalently bonded to various ligands.[25] This metal–metal bond was first suggested on the basis of Raman data from the compounds $[NMe_4]_2[Ga_2X_6]$, (X = Cl, Br or I)[26] and the ethane structure proposed for the hexahalogenogallate(II) ions was later confirmed by X-ray crystallography.[27] The Raman band of the chloro-species has been shown to be present also in the spectrum of Ga–Ga_2Cl_4 solutions[28] (Ga is soluble to 1.92 mol % in Ga_2Cl_4[29–31] and to 9.3 mol % in Ga_2Br_4).[32] Solid phases containing the Ga_4^{2+} moiety co-ordinated to dioxane as $Ga_2Cl_4(diox)_2$[33] and $Ga_2Br_4(diox)_2$[34] have been structurally determined and the Ga–Ga bond in both compounds was found to be 2.4 Å, within narrow limits.

The halogenogallate(III) ions $GaCl_4^-$, $Ga_2Cl_7^-$ and $Ga_3Cl_{10}^-$ have been characterized by vibrational spectroscopy,[35–38] potentiometry,[39] voltammetry[40] and phase studies[29,30,41–43] in molten Ga–$GaCl_3$ and MCl–$GaCl_3$ mixtures (M = alkali metal) and solids obtained thereof. The only halogenogallate(III) trimer isolated in the solid state is $Ga_3Br_{10}^-$, which has been crystallized as its rubidium and caesium salts.[44,45] The results for $Ga_2Cl_7^-$ are consistent with a bent or linear Ga–Cl_b–Ga chloride bridge and terminal $GaCl_3$ groups (*i.e.* two apex-sharing $GaCl_4$ quasi-tetrahedra), rendering an ion with C_{2v} symmetry in the solid compound $K[Ga_2Cl_7]$.[46] A staggered D_{3d} symmetry has been suggested on the basis of vibrational spectroscopy for this ion in molten salt solution,[36,47] although some later results indicate that the symmetry is strongly counter-ion dependent.[48] Furthermore, $Ga_2Cl_7^-$ and its aluminium analogue $Al_2Cl_7^-$ have been identified as the chlorometalate species present in the 'red oils' of the Friedel–Crafts system arene–MCl_3–HCl (M = Ga or Al)[48–50] and as anions in Lewis-acidic room-temperature molten salts based on $AlCl_3$[51] and $GaCl_3$.[52,53]

Gallium(I)- and -(II) compounds of the kind described above have recently been shown to be convenient starting points in the

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† Arene Solutions of Gallium Chloride. Part 1.

synthesis of metal–metal bonded cluster compounds of gallium,[54–56] and our own research has indicated that solutions of uni- or tri-valent gallium halides in organic solutions may be a route to other main-group element cluster compounds.[57] With this background in mind, we here report the spectroscopic and structural investigations of some gallium chloride systems in benzene solution. In order to put the spectroscopic assignments for these systems on a solid footing, we also report a reinvestigation of the Ga–$GaCl_3$ system.

Experimental

General.—All handling of the chemicals was carried out in a glove-box containing dry (< 0.5 ppm water) nitrogen. The balance used is accurate to within ± 0.001 g under the actual conditions. All glassware was dried under vacuum at 450 °C prior to use. All measurements except liquid X-ray scattering and EPR spectroscopy (see below) were performed in standard 5 mm NMR tubes which were sealed under vacuum. During the evacuation the samples were cooled to liquid-nitrogen temperature in order to prevent mass loss due to evaporation of the volatile components.

Chemicals.—Benzene (Merck, *p.A.* grade, 'wasserfrei') was pre-dried for several months over activated molecular sieves (4 Å) before being distilled over freshly cut sodium metal and transferred to the glove-box. Mesitylene (Jansen, 99%) was dried over sodium in the glove-box and used as received. The purity of the solvents was checked by gas chromatography (column: Chromosorb P). Only a small (< 1%) peak from an unidentified impurity was detected in benzene, whereas the mesitylene was found to contain about 1% pseudocumene (1,2,4-trimethylbenzene) as the only detectable impurity. Considering the similar boiling points of this impurity (169.3 °C) and mesitylene (164.7 °C) no attempt was made further to purify the solvent by distillation.

Gallium metal and $GaCl_3$ (ALFA chemicals, 99.999% metals basis) were obtained in sealed ampoules, which were cracked open in the glove-box and used as received. Since the vapour pressure of neat $GaCl_3$ is substantial even at room temperature and the vapour was found to attack plastics and vacuum grease, the substance was stored in gas-tight glass flasks with Teflon screwcaps and linings.

Raman Spectroscopy.—Raman spectra were recorded on a Bruker IFS-66/FRA-106 instrument equipped with a liquid-nitrogen-cooled solid-state germanium-diode detector and a low-power Nd/YAG laser (exciting wavelength = 1064 nm). The resolution of the spectra was 4 cm^{-1}. Samples investigated at elevated temperatures were placed inside an electrically heated aluminium block, connected to a PID temperature controller. The furnace keeps the sample temperature constant to within ± 1 °C. Spectra recorded at temperatures higher than 100 °C were obtained by inserting a bandpass filter with a cut-off at 1200 cm^{-1} between the sample and the interferometer in order to prevent excessive black-body radiation from reaching the detector.

NMR Spectroscopy.—The NMR measurements were performed on a Varian Unity 300 MHz spectrometer operating at 299.962 MHz for ^1H, 75.430 MHz for ^{13}C and 91.456 MHz for ^{71}Ga. The spectra were recorded at 20 °C. The ^1H and ^{13}C shifts are given relative to $SiMe_4$, whereas the ^{71}Ga shifts are relative to a solution of $GaCl_3$ in an excess of concentrated hydrochloric acid. Both naturally occurring gallium nuclei are quadrupolar with $I = \frac{3}{2}$; ^{71}Ga was chosen rather than ^{69}Ga since it has been found to be generally easier to observe due to its lower quadrupole moment.[58] A fact with important diagnostic implications is the extremely (considering the quadrupolar nature of the gallium nuclei) sharp and narrow NMR signal from Ga^I in benzene solution and in liquid Ga_2Cl_4.[59] This fact allows ^{71}Ga NMR spectroscopy to be used to distinguish between different oxidation states of gallium in solution, since Ga^{III} generally gives broad signals at higher frequencies and Ga^{II} none at all.[60]

Liquid X-Ray Scattering (*LXS*).—Samples were contained in Lindemann capillaries (Hilgenberg, outer diameter = 1 mm) sealed under vacuum. The intensity of the scattered radiation was recorded on a Siefert GSD θ–θ diffractometer with an EG & G solid-state detector as previously reported in detail.[61] The data treatment and primary data corrections were performed using the KURVLR program,[62] whereas for the least-squares fit of theoretical structure models to the experimental reduced-intensity functions $s{\cdot}i(s)$ the program STEPLR[63] was used. Standard corrections for polarization effects and for spurious peaks in the reduced radial-distribution functions at distances below 1.0 Å were applied.

Synthesis of Ga_2Cl_4.—This compound $Ga[GaCl_4]$ was synthesized by the method of Carlston *et al.*[1]: Hg_2Cl_2 (Merck, *p.A.* grade) was mixed with a stoichiometric amount of gallium metal in a Pyrex ampoule equipped with a narrow neck, which was then evacuated and sealed. The mixture was then heated to 170 °C and kept at this temperature for 1 h (the reaction seems to be instantaneous). The temperature was then increased to 200 °C in order to melt the Ga_2Cl_4 formed and the compound was separated from the liquid mercury by tilting the ampoule slightly and allowing the molten product to flow through its neck into the upper compartment. The ampoule was cooled to room temperature and cracked open in the glove-box and the Ga_2Cl_4 transferred to a glass flask with Teflon seals. The product was colourless both in the liquid and solid state.

Synthesis of Ga_3Cl_7.—Unlike the analogue $K[Ga_2Cl_7]$,[46] the compound Ga_3Cl_7 (= $Ga[Ga_2Cl_7]$) has never been completely structurally characterized, even though the phase diagram of the Ga–$GaCl_3$ system suggests that it is thermodynamically stable[29] (in an older phase study of this system the composition was erroneously stated as Ga_4Cl_9).[30] When a homogeneous Ga–$GaCl_3$ melt with the composition $X_{Ga} = 0.215$ (corresponding closely to the ideal value $X_{Ga} = 0.222$) was quenched a solid was obtained the Raman bands of which are mainly assignable to the $Ga_2Cl_7^-$ moiety (see below). This quenched and powdered melt will be referred to as Ga_3Cl_7.

Results and Discussion

The Liquid Ga–$GaCl_3$ *System.*—This system has previously been subject to Raman spectroscopic studies,[2,28,37] but never over the whole accessible composition range. Our study of the vibrational properties of it was executed in order to facilitate the proper assignment of vibrational spectra and an understanding of the more complex, analogous Ga–$GaCl_3$–arene systems. For this purpose a ^{71}Ga NMR spectroscopic investigation has also been undertaken.

The Raman spectra of the liquid Ga–$GaCl_3$ and MCl–$GaCl_3$ systems (M = alkali metal) are analogous and can readily be interpreted in terms of a stepwise formation of the chlorogallate(III) ions $Ga_nCl_{3n+1}^-$ ($n \leqslant 3$) upon the addition of gallium metal or MCl.[35–37] In addition to such species, the dissolution of gallium metal in $GaCl_3$ produces univalent gallium according to the general reaction (1).

$$2\,Ga + (3n + 1)GaCl_3 \longrightarrow 3\,Ga^+ + 3\,Ga_nCl_{3n+1}^- \quad (1)$$

While assigning bands belonging to chlorogallate(III) anions in the spectra obtained in the Ga–$GaCl_3$ solutions, two trivial assumptions were made: (*a*) The effect of adding increasing amounts of gallium metal to molten $GaCl_3$ is equivalent to gradually decreasing the number *n* in equation (1), therefore an increase in the formal concentration of gallium metal in $GaCl_3$

also increases the Cl : Ga ratio of the chlorogallate(III) complexes present; (*b*) a specific chlorogallate(III) ion $Ga_nCl_{3n+1}^-$ *dominates* in a solution of stoichiometry corresponding to the Cl : Ga ratio of the complex.

Problems encountered in the assignment are due to the overlapping of bands, and to solution equilibria such as (2)–(4).

$$2\,Ga_3Cl_{10}^- \rightleftharpoons 2\,Ga_2Cl_7^- + Ga_2Cl_6 \qquad (2)$$

$$2\,Ga_2Cl_7^- \rightleftharpoons Ga_3Cl_{10}^- + GaCl_4^- \qquad (3)$$

$$2\,Ga_2Cl_7^- \rightleftharpoons Ga_2Cl_6 + 2\,GaCl_4^- \qquad (4)$$

The effect of such equilibria is to mingle bands from a given complex with those of others, even in solutions for which the total stoichiometry corresponds well to that of a specific complex. The problem is especially severe in the region of the spectra corresponding to bending and deformation modes (< 160 cm^{-1}). Assignments to this part of the Raman spectra are thus tentative and less reliable as a diagnostic tool. The Raman spectra of the Ga–$GaCl_3$ system (Fig. 1, Table 1) are quite insensitive to temperature in the range 100–170 °C, and only minor shifts in band positions ($\leqslant 2$ cm^{-1}) and relative intensities are found. In general, the bands are somewhat broadened at higher temperatures. Assignments of bands to $Ga_3Cl_{10}^-$ should be considered as tentative, because of their weak relative intensities and overlap with those of $Ga_2Cl_7^-$ and Ga_2Cl_6. The most substantial spectroscopic proof of the separate existence of $Ga_3Cl_{10}^-$ in this investigation is the fact that the broad shoulder at the high-wavenumber side of the main band in the melt with X(Ga) = 0.154 (close to the value of 0.167, corresponding to the stoichiometry of Ga[Ga_3Cl_{10}]) cannot be explained by considering bands from Ga_2Cl_6 and $Ga_2Cl_7^-$

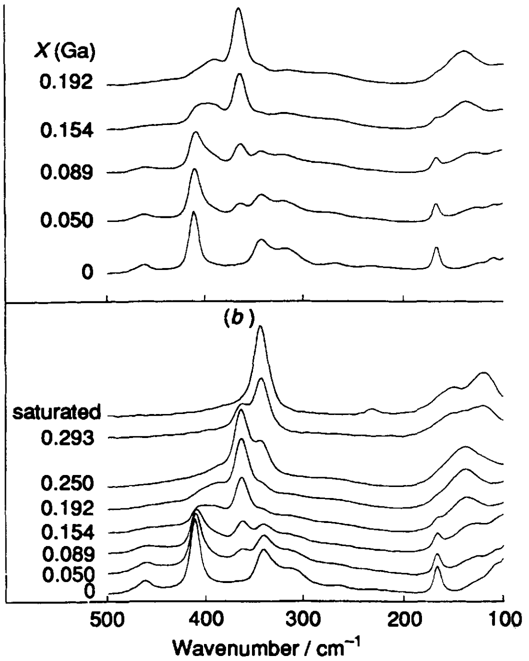

Fig. 1 Raman spectra of the liquid Ga–$GaCl_3$ system at various compositions and (*a*) 100, (*b*) 170 °C

Table 1 Raman bands (cm^{-1}) found in the systems investigated except for those belonging to the solvents; w = weak, m = medium, s = strong, v = very, sh = shoulder, br = broad, asym = asymmetrical, sym = symmetrical, b = bridging, t = terminal. The relative intensity of bands belonging to the Ga–$GaCl_3$ system is given for composition where the band is at maximum intensity. Assignments of bands belonging to Ga_2Cl_6 follow ref. 64; alternative assignments can be found in refs. 36 and 65

	Ga_2Cl_4–C_6H_6					
Ga–$GaCl_3$	Upper phase	Lower phase	Ga_3Cl_7–C_6H_6	Ga–$GaCl_3$–C_6H_6*	Chlorogallate species	Assignment
463m					Ga_2Cl_6	$\nu_{11}(B_{2g})$
≈430w(sh,vbr)			419(sh)	418(sh)	$Ga_2Cl_7^-$	
411s			≈410(sh)		Ga_2Cl_6	$\nu_1(A_g)$
	404m(br)				?	
396m			≈407(sh)		$Ga_3Cl_{10}^-$	$\nu_{asym}[Ga–(Cl_t)_3]$
389m			396w	394m	$Ga_2Cl_7^-$	$\nu_{asym}[Ga–(Cl_t)_3]$
375(sh)	363w	394w 381w 362w			$GaCl_4^-$	$\nu_3(T_2)$
364vs			369s,asym	370s	$Ga_2Cl_7^-$ and $Ga_3Cl_{10}^-$	$\nu_{sym}[Ga–(Cl_t)_3]$
343vs	345vs	345vs	345w	346vs	$GaCl_4^-$	$\nu_1(A_1)$
342m					Ga_2Cl_6	$2\nu_3$
≈320w(br)			317w		$Ga_3Cl_{10}^-$	
319m					Ga_2Cl_6	$\nu_2(A_g)$
≈270w(br)			≈290(sh) ≈280(sh) 264m,asym	260w	$Ga_2Cl_7^-$ and/or $Ga_3Cl_{10}^-$	Ga–Cl_b–Ga stretch
269w					Ga_2Cl_6	$\nu_3 + \nu_4$
234w					Ga_2Cl_6	$\nu_6(B_{1g})$
233mw					$Ga_2Cl_6^{2-}$	Ga–Ga stretch
167s					Ga_2Cl_6	$\nu_3(A_g)$
149m		150(sh)		150(sh)	$GaCl_4^-$	$\nu_4(T_2)$
138 ± 1s			135s		$Ga_2Cl_7^-$	$\delta[Ga–(Cl_t)_3]$
128m					$Ga_3Cl_{10}^-$	
124m(sh)					Ga_2Cl_6	$\nu_7(B_{1g})$
120 ± 1					$GaCl_4^-$	$\nu_2(E)$
109s(sh)					Ga_2Cl_6	$\nu_{12}(B_{2g})$
106m					$Ga_2Cl_7^-$	$\delta[Ga–Cl_t)_3]$
99s					Ga_2Cl_6	$\nu_4(A_g)$

* Saturated with gallium metal.

only. A broad band at about 320 cm^{-1} also seems to belong to $Ga_3Cl_{10}^-$, but this overlaps with a band of Ga_2Cl_6. The intensity of the bands from Ga_2Cl_6 is substantial in melts in which the concentration of $Ga_3Cl_{10}^-$ is maximized. The spectroscopic data clearly suggest that the equilibrium constant for (2) has a quite high value in the system studied.

Apart from the weak, broad feature at 430 cm^{-1} (previously unreported), assigned by us to a $Ga_2Cl_7^-$ band, and the position of the band of $Ga_2Cl_7^-$ at 138 cm^{-1} (previously positioned at 150 cm^{-1}) our assignments are in general agreement with those reported for the CsCl–$GaCl_3$[36] and KCl-$GaCl_3$ systems.[35] Quite surprisingly, they are less in agreement with a previous Raman spectroscopic study of liquid Ga[Ga_2Cl_7],[37] which reports a multitude of bands assigned to $Ga_2Cl_7^-$ not found in our study, as well as bands from Ga_2Cl_6 and $GaCl_4^-$ of much higher intensity than in our spectra. These data were interpreted in terms of a C_{2v} symmetry for the $Ga_2Cl_7^-$ ion, similar to that found in solid KGa_2Cl_7[46] and KGa_2Br_7.[66] This suggestion is in contrast with the D_{3d} symmetry derived from vibrational spectroscopy of $Ga_2Cl_7^-$ in liquid Cs[Ga_2Cl_7],[36] of $Ga_2I_7^-$ in liquid M[Ga_2I_7] (M = Rb or Cs),[67] and also of the analogous $Al_2Cl_7^-$ ion in molten M[Al_2Cl_7] (M = Li, Na, K, Rb or Cs).[68] The apparent anomalies regarding the conformation of $Ga_2Cl_7^-$ in *different* environments may be explained by a dependence of the polarizing power of the counter ion[48] and on crystal-packing effects. However, it clearly cannot be the explanation for the differences in the reported spectra of liquid Ga_3Cl_7. The relatively few bands in our data attributable to $Ga_2Cl_7^-$ suggest a rather high symmetry and thus favour a D_{3d} symmetry over C_{2v}. Thermal blurring of bands and the mere possibility that weak bands are undetected prohibits this statement from being anything but a suggestion, but it should be noted that it is in agreement with the results obtained from quenched solutions (see below).

In a Ga–$GaCl_3$ melt saturated with gallium metal, a peak at 233 cm^{-1} is present, confirming the results of an earlier report.[28] This band is not attributable to any chlorogallate(III) species. Instead it is assigned as the Ga–Ga stretching vibration in the gallium(II) anion $Ga_2Cl_6^{2-}$. This is in agreement with results from a Raman spectroscopic study of the compounds [NR_4][Ga_2X_6] (X = Cl, Br, or I).[69]

The ^{71}Ga NMR spectra of the KCl–$GaCl_3$ system (Fig. 2) only show a broad band at approximately δ + 10 relative to $GaCl_4^-$ in hydrochloric acid. Such broad features are well known to be typical for Ga^{III} in environments of a symmetry less than cubic and are a consequence of the quadrupolar nature of the ^{71}Ga nucleus ($I = \frac{3}{2}$).[58] A further contribution to the line broadening may be the equilibria (2)–(4) between several $Ga_nCl_{3n+1}^-$ species. The gallium resonance from neat $GaCl_3$ cannot be detected, presumably because of severe distortion of the tetrahedral environment of Ga^{III} in the Ga_2Cl_6 units, which are the predominant species in liquid $GaCl_3$.[61] Upfield relative to the gallium(III) resonance, a considerably sharper band which increases in intensity with increasing formal gallium concentration is found in the Ga–$GaCl_3$ system (Fig. 2, Table 2). This peak is readily assigned to the gallium(I) ion, in agreement with the literature.[59] The shielding by the 4s^2 lone pair of Ga^I presumably accounts for both the small linewidth of this band and for its substantial upfield shift.[59] Changes in the composition of the systems cause only minor changes in the position of the two gallium signals. Since the ionic environment around Ga^I changes dramatically in the composition range $0.051 \leqslant X(Ga) \leqslant 0.293$ (according to the Raman investigation from $Ga_3Cl_{10}^-$/Ga_2Cl_6 to $GaCl_4^-$) it may be concluded that the gallium(I) nuclei are insensitive to the nature of the chlorogallate(III) ions surrounding Ga^I in molten salt solutions. At higher X(Ga) the resonance of Ga^{III} is found to narrow as a consequence of the increased concentration of the tetrahedral $GaCl_4^-$ ion (Fig. 2).

A search for a gallium(II) resonance in the gallium-saturated sample was considered pointless because of the low concentration and reports[60] that the resonance from $Ga_2Cl_6^{2-}$ is undetectable even at high concentrations.

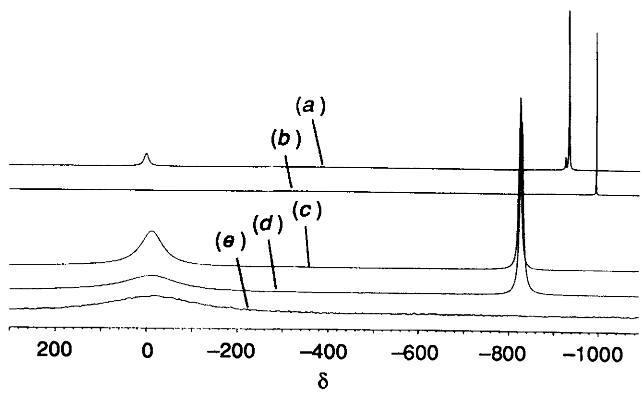

Fig. 2 Gallium-71 NMR spectra for representative systems. Spectra for the Ga–$GaCl_3$ system were recorded at 170 °C, the others at 20 °C. (*a*) Ga_2Cl_4–C_6H_6; (*b*) Ga_3Cl_7–C_6H_6; (*c*) Ga–$GaCl_3$, X(Ga) = 0.30; (*d*) Ga–$GaCl_3$, X(Ga) = 0.25; (*e*) KCl–$GaCl_3$, X(KCl) = 0.25

Table 2 Gallium-71 and ^{13}C NMR shifts for the systems investigated

System	δ(^{13}C)[a]	δ(^{71}Ga^{3+})	δ(^{71}Ga^{+})
Ga–$GaCl_3$, X(Ga) = 0.294	—	−12.7	−824.8
C_6H_6	128.0	—	—
Ga_2Cl_4–C_6H_6 (lower phase)[b]	128.0	−0.3	−933.4
Ga_2Cl_4–C_6H_6 (upper phase)[b]	128.0	Undetectable	−925.9
Ga_3Cl_7–C_6H_6, X(Ga_3Cl_7) = 0.20	129.5	Undetectable	−980.1
Ga–$GaCl_3$–C_6H_6 (saturated in Ga)[c]		0.4	−949.7
Ga–$GaCl_3$–$C_6H_3Me_3$-1,3,5 (saturated in Ga)[c]		Undetectable	−976.8

[a] Values obtained from proton-decoupled spectra. [b] Solution saturated with Ga_2Cl_4. [c] Formal mole fraction of $GaCl_3$ with respect to aromatic = 0.20.

Solid Ga_2Cl_4.—The Raman spectrum of solid Ga_2Cl_4 obtained in this work (Fig. 3, Table 3) is in excellent agreement with that in a previous report.[28] The spectrum has been rationalized as being indicative of a C_2 site symmetry of the $GaCl_4^-$ ions. In addition, the less rigorous approach of site-group analysis[71] (instead of the more elaborate factor-group analysis) was sufficient to explain the structural features. A *weak* coupling between the $GaCl_4^-$ complexes in the unit cell is thus indicated. Using site-group analysis, the Raman-active T_d terms $A_1 + E + 2T_2$ are found to split and give rise to the terms 5A + 4B. These nine terms are sufficient to account for the eight lines found experimentally, if one band is assumed to be hidden by band overlap. The hidden band is most likely a component derived from ν_3, since the full splitting of the ν_2 and ν_4 modes is observed according to the assignments in Table 3.

The Ga_2Cl_4–C_6H_6 *System*.—The Ga_2Cl_4–C_6H_6 system has previously been investigated by ^{71}Ga NMR[59] and IR spectroscopy.[16] Our Raman data are presented in Table 1 and Fig. 3 and the results from ^{13}C and ^{71}Ga NMR spectroscopy are displayed in Table 2. All spectra were obtained from solutions saturated with Ga_2Cl_4. Such solutions are composed of two liquid phases with the greater part of the chloride in the lower, denser phase.[16] No changes in the solvent bands upon dissolution of Ga_2Cl_4 were observed in any of the phases, nor were any bands found at $\geqslant$500 cm^{-1} apart from those which belong to the solvent. The same spectral invariance of the solvent is also observed in the ^{13}C NMR spectra (Table 2), in

Table 3 Raman bands (cm^{-1}) found in the solid systems investigated compared with literature values; for abbreviations see Table 1. For solid compounds containing $GaCl_4^-$ the assignments given are those of the T_d origin of the site-symmetry-split modes

$GaCl_4^-$ (aq) Ref. 70	Ga_2Cl_4(l) This work	Ga_2Cl_4(s) This work	$[Ga(C_6H_6)_2 \cdot GaCl_4]_2 \cdot 3C_6H_6$(s) This work	Assignment
			422w	ν(Ga$^+$–arene)?
			394m	ν(Ga$^+$–arene)?
380w	375w	375mw	383w	$\nu_3(T_2)$
		363w	369m	$\nu_3(T_2)$
346vs	343vs	346vs	345vs	$\nu_1(A_1)$
		172m		$\nu_4(T_2)$
152s	149m	158m	150 (sh)	$\nu_4(T_2)$
		133m		$\nu_4(T_2)$
117s	120s	116 (sh)	118s	$\nu_2(E)$
		112s	105s	$\nu_2(E)$

Ga_3Cl_7(s)			
This work	Ref. 28	Ref. 37	Assignment
		420	
414 (sh)		410	ν_1, Ga_2Cl_6?
406 (sh)	407m		$Ga_3Cl_{10}^-$?
399w			ν_{asym}(Ga–Cl$_3$)
363vs	364vs	367	ν_{sym}(Ga–Cl$_3$)
284m	288m	288	ν(Ga–Cl–Ga)
		279	
		266	
		202	
162m			ν_3, Ga_2Cl_6?
150 (sh)		154	
144m	140m	146	
127m	127m	129	
115s	107m		

which no effect on the benzene signal can be detected upon dissolution of Ga_2Cl_4. There is, therefore, no direct evidence for complex formation between benzene and Ga^I. However, compared with the Ga–$GaCl_3$ system, the chemical shift of Ga$^+$ in the benzene solution is considerably moved upfield, as detected by ^{71}Ga NMR spectroscopy, indicating an increased electron density around Ga$^+$ (Table 2). Bands assigned to distorted $GaCl_4^-$ ions are found in the region < 500 cm^{-1} in the Raman spectra. Five Raman bands are found for the dense phase, but the steep Rayleigh shoulder makes it impossible accurately to assign the spectrum below 150 cm^{-1} and therefore more bands may be hidden in the low-frequency region. The number of bands observed is nevertheless too large to be accounted for by T_d symmetry, which only gives rise to the four bands found in the Ga–$GaCl_3$ system (see above), aqueous solution[70,72] and various molten-salt systems.[2,35,36,73,74] It is therefore concluded that the highest possible symmetry of $GaCl_4^-$ in benzene solution is C_{3v}, corresponding to the shortening or lengthening of *one* of the four Ga–Cl distances. A similar displacement of *two* Ga–Cl distances would thus result in a further lowering of the symmetry to C_{2v}. Since the A_1 mode of $GaCl_4^-$ was found to be weakly IR-active, previous authors[16] assigned a C_{2v} symmetry to $GaCl_4^-$ in this system. They explained the decrease in symmetry of the ion in terms of ion pairing with Ga$^+$, thus giving some support to this previously suggested explanation for the high solubility of Ga_2Cl_4 in aromatics.[75] We agree with this explanation and find that our spectra substantiate the assumption of a C_{2v} symmetry. The three bands at 394, 381 and 362 cm^{-1} are accounted for in this way, since the T_d mode $\nu_3(T_2)$ is split into three components given C_{2v} symmetry ($2A_1 + B_1$). The assumption of C_{3v} symmetry would infer the $\nu_3(T_2)$ term be split into only two modes ($E + A_1$). Furthermore, a distortion to C_{3v} symmetry because of ion pairing would produce a Raman-active symmetric $GaCl_3$ stretching mode analogous to that found for the $Ga_2Cl_7^-$ ion. However, this band is found at 370 cm^{-1} for $Ga_2Cl_7^-$ in benzene (see below). The difference of 8 cm^{-1} between this $Ga_2Cl_7^-$ band and that of $GaCl_4^-$ at 362 cm^{-1} implies that the latter cannot be interpreted as the symmetric $GaCl_3$ stretching mode in a $GaCl_4^-$ ion of C_{3v} symmetry.

The possibility of assigning Raman bands in the low-frequency region to modes involving gallium–arene vibrations also deserves attention. Studies of the η^6-benzene complexes $[M(C_6H_6)(CO)_3]$ (M = Cr, Mo or W) by vibrational spectroscopy[76,77] have reported bands at 312 and 264 cm^{-1} as E and A_1 metal–arene modes, respectively. However, these bands were accompanied by quite large features of the co-ordinated benzene moiety itself in the spectrum, not found in neat benzene. The non-existent changes in the internal benzene bands in our study render the assignment of bands in the low-frequency region to metal–arene interactions less tempting.

Owing to the low concentration of Ga_2Cl_4 in the upper phase, the Raman-scattering ability of this phase is very low and the spectrum obtained is therefore of poor quality (Fig. 3). It is apparent from the spectrum that the same peaks are present in the two phases, except for the broad feature of medium intensity at 404 cm^{-1} which is found only in the upper phase. This feature corresponds to an unassigned band at 402 cm^{-1} reported to be IR-active.[16] However, it must be considered that a band at 410 cm^{-1} found in the IR investigation of the same phase was interpreted as due to a hydrolysis product, together with a band at 363 cm^{-1}. We do not interpret the present band at 404 cm^{-1} in the same way, since we consider it highly improbable that the hydrolysis product would be found only in one of the two phases. Furthermore, the presence of hydrolysis products would give rise to a Raman-active band due to the terminal $GaCl_3$ stretch, of considerably higher intensity, just as observed for the $H_2O \cdot GaCl_3$ and $Et_2O \cdot GaCl_3$ adducts.[78,79]

Solid Ga_3Cl_7.—The Raman[28,37] and IR[37] spectra of crystalline Ga_3Cl_7 have been reported and are compared with our data in Table 3. The relatively few bands observed for $Ga_2Cl_7^-$ in the older of the previous investigations[28] were

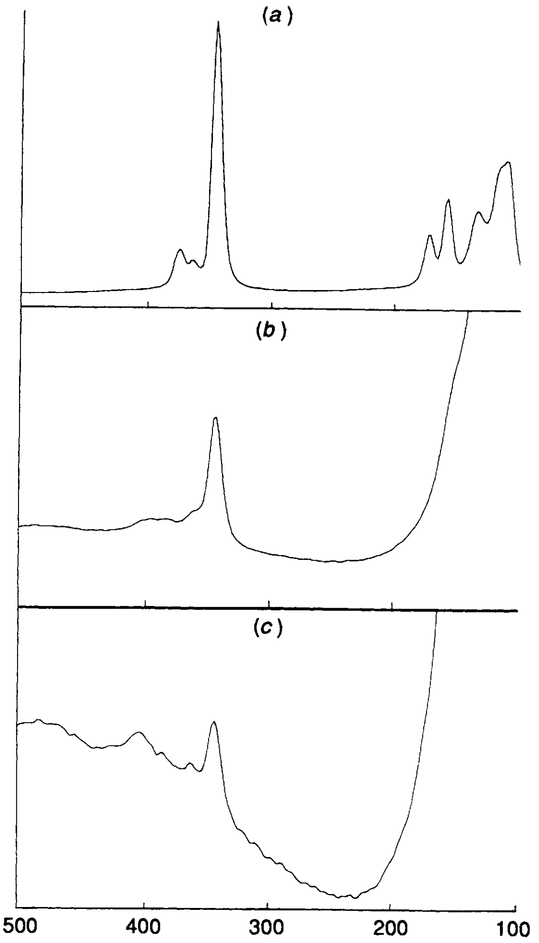

Fig. 3 Raman spectra for the different Ga_2Cl_4-containing systems studied: (a) solid Ga_2Cl_4; (b) Ga_2Cl_4–C_6H_6 (lower phase) and (c) Ga_2Cl_4–C_6H_6 (upper phase)

assumed to indicate a linear Ga–Cl–Ga bridge, rather than a bent one (*i.e.* D_{3d} or D_{3h} symmetry rather than C_{2v} or lower). Our data are in excellent agreement with those of that study. On the contrary, a later paper[37] reports a Raman spectrum with a large number of bands (some of which are assigned to Ga_2Cl_6 and $GaCl_4^-$) not observed by us and states that the spectrum of solid Ga_3Cl_7 is identical to that of KGa_2Cl_7. Since these two compounds are claimed to be isostructural[80] and KGa_2Cl_7 has been shown to contain $Ga_2Cl_7^-$ ions with bent Ga–Cl–Ga bridges and an approximately C_{2v} symmetry,[46] these inconsistencies must be considered. We propose that the differences found are caused by the different modes of preparation of Ga_3Cl_7, and the different degree of crystallization thus obtained in the products. While both Taylor[28] and ourselves have recorded spectra from quenched, homogeneous Ga–$GaCl_3$ mixtures (and obtained very similar results), Chemouni and Potier[37] used a more elaborate route. They treated Ga_2Cl_4 with an excess of liquid Ga_2Cl_6 and then slowly cooled the mixture to room temperature. The latter route presumably produced a more well crystallized product, accounting for the observation of a C_{2v} symmetry of $Ga_2Cl_7^-$ in accordance with the crystallographic results for KGa_2Cl_7. Quenched samples, on the other hand, lead to a structurally less well defined product, thus explaining the observed spectral inconsistencies. We therefore suggest that the spectrum of Ga_3Cl_7 presented in this work represents a frozen image of the structure of $Ga_2Cl_7^-$ in the melt, rather than that in crystallized Ga_3Cl_7. The relatively few bands observed therefore indicate a symmetry higher than C_{2v} in the melt.

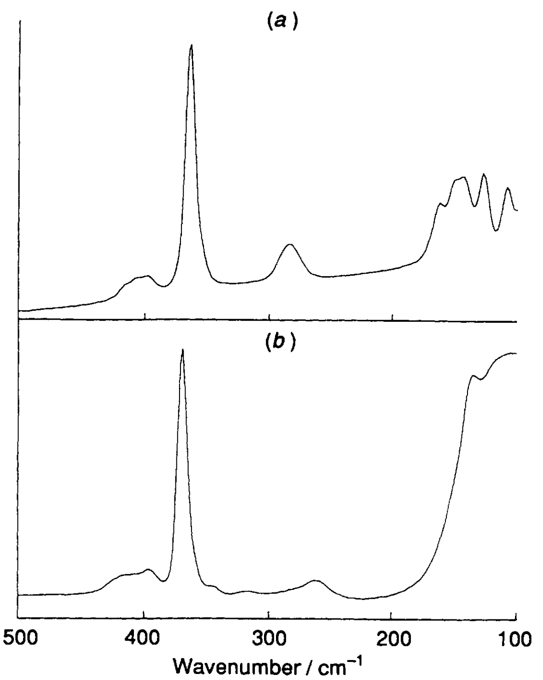

Fig. 4 Raman spectra for the Ga_3Cl_7 systems. The concentration of Ga_3Cl_7 in the benzene solution is 21.5 mol %. (a) solid Ga_3Cl_7; (b) Ga_3Cl_7–C_6H_6

The Ga_3Cl_7–C_6H_6 *System.*—No investigations of the Ga_3Cl_7–C_6H_6 system have been found in the literature, although $Ga_2Cl_7^-$ has been studied by vibrational spectroscopy in the 'red oils' of Friedel–Crafts systems and found to possess a high symmetry in such solutions.[48] Perhaps the most striking feature of the system is the high solubility of this inorganic salt in benzene. The solution investigated has the composition $X(Ga_3Cl_7) = 0.201$, corresponding to 59.6% w/w! The Raman spectrum of this solution in the region < 500 cm^{-1} (Fig. 4, Table 1) displays a number of noteworthy features. First, the band widths are considerably narrower and the resolution consequently higher than in molten-salt systems. This is most probably a thermal effect. Secondly, bands belonging to $Ga_2Cl_7^-$ are relatively more intense than in molten-salt systems, suggesting that the equilibria (3) and (4) are pushed further to the left in benzene solution. The spectrum does not give conclusive evidence for whether equilibrium (3) or (4), or both, are predominant in the liquid. The reasons for this are the problems of properly assigning the $Ga_3Cl_{10}^-$ bands, and the possibility of assigning the band at 317 cm^{-1} to both Ga_2Cl_6 and $Ga_3Cl_{10}^-$. Thirdly, the band positions are considerably shifted as compared to both the molten-salt systems and the quenched sample discussed above. This effect is most profound for bands attributed to the $GaCl_3$ symmetric stretching mode and the Ga–Cl–Ga stretching mode.

The shifts of the band positions carry information about the structure of the species in solution and the nature of the supposed ion pairing between Ga^+ and $Ga_2Cl_7^-$. The substantial shift of the Ga–Cl–Ga mode to lower wavenumber, together with the decreased relative intensity and the more pronounced skew-symmetric character, indicates a weakening of the chloride bridge in $Ga_2Cl_7^-$ (which has been found to be strong in the CsCl–$GaCl_3$ system)[36] in benzene solution and/or a lowering of the overall symmetry of the ion. Two weak shoulders at the high-wavenumber side, characteristic of the skew-symmetry, coincide with bands at 288 and 279 cm^{-1} found in *crystalline* Ga_3Cl_7, although their relative intensities are changed.[37] The splitting of the Ga–Cl–Ga mode is taken as an indication that the Ga–Cl–Ga bridge which is linear in the quenched sample is bent in benzene solution, thereby lowering the overall symmetry of $Ga_2Cl_7^-$. Unfortunately, the total number of bands belonging to $Ga_2Cl_7^-$ in solution cannot be determined, because of the intense Rayleigh shoulder which probably hides weak bands in the region < 150 cm^{-1}. The ^{71}Ga NMR spectroscopic results give further evidence for a low symmetry around Ga in $Ga_2Cl_7^-$ in benzene solutions of Ga_3Cl_7, since no gallium(III) signal is detectable in such solutions. On the other hand, such signals are detectable over the whole concentration range $0.05 \leqslant X(\text{Ga}) \leqslant 0.30$ in the Ga–$GaCl_3$ system. This observation clearly is compatible with the proposition of a linear Ga–Cl–Ga bridge in the latter system, and a bent one in the former. The symmetric $GaCl_3$ stretching mode (at 370 cm^{-1}), however, is not only shifted to *higher* wavenumbers as compared to the quenched melt, but it is also found to be narrower. In addition, no definite new features emerge around this band, other than those readily assigned as $GaCl_4^-$ or $Ga_2Cl_6/Ga_3Cl_7^-$. In light of the results from the $GaCl_4^-$–C_6H_6 systems, we consider these observations to be inconsistent with the assumption that ion pairing takes place by co-ordination of Ga^+ to the terminal chlorides of $Ga_2Cl_7^-$. This conclusion, in turn, leads us to suggest an interaction between the bridging chloride of $Ga_2Cl_7^-$ and Ga^+. Such a co-ordination mode would also conform to the assumed bent, and possibly also weakened, Ga^{III}–Cl–Ga^{III} bridge. A weakened (*i.e.* lengthened) Ga^{III}–Cl–Ga^{III} bridge would also tend to increase the Cl–Ga–Cl angle in the terminal groups of $Ga_2Cl_7^-$, thus tending the conformation of this group *towards* D_{3h} symmetry. The totally symmetric Ga–Cl stretching mode of monomeric, planar (D_{3h}) $GaCl_3$ is found at about 382 cm^{-1} [18,81–83] and the shift of the $GaCl_3$ stretching band towards higher wavenumbers is therefore in agreement with such a view.

In contrast to the Ga_2Cl_4–C_6H_6 systems definite spectral changes arise in both the ^{13}C NMR and Raman spectra of benzene in the solution of Ga_3Cl_7. Such effects are indicative of complex formation between Ga^+ and benzene. The fact that these features are lacking in the former system may well be an effect of the lower Ga^+ concentration, since the observed effects are weak. The ^{13}C resonance is found to move 1.5 ppm downfield (Table 2), indicating the donation of electron density by the aromatic. In the Raman spectrum at $\geqslant 500$ cm^{-1} (Table 4, Fig. 5) the benzene bands are found to shift, broaden and, in the case of the ν_8 band at 1585 cm^{-1} [the ν(C=C), E_{2g} mode],[84] to be accompanied by a low-energy shoulder. A comparison with the solid-state Raman spectra of the so-called Menshutkin complexes (*i.e.* 1:2 complexes between $SbCl_3$ and monoarenes) is illustrative: for the $Sb(C_6H_6)_2Cl_3$ complex the C=C vibrations were found to move to lower wavenumbers as compared to neat benzene, whereas the C–H vibrations displayed the opposite behaviour.[85] This is observed also in the Ga_3Cl_7–C_6H_6 system, although the effects are less prominent. A new, weak band at 1478 cm^{-1}, not present in benzene, is also noteworthy. This band is too high in frequency to be readily attributable to a gallium–arene vibration mode, but may represent a ring-wagging mode of complexed benzene.

To summarize, spectral effects attributable to complex formation are found in both NMR and Raman spectroscopic data, and suggest the formation of a weak gallium(I)-benzene complex in solution. In the ^{71}Ga NMR spectrum of Ga^+ (Table 2) the resonance shifts further upfield as compared to the Ga_2Cl_4–C_6H_6 solution, suggesting that the electron density around the gallium(I) ion is sensitive to the counter ion in solution. Such an effect is not observed in the Ga–$GaCl_3$ system, and this sensitivity is presumably the effect of the different nature

Table 4 Experimental parameters of the LXS study of the Ga_3Cl_7–C_6H_6 system and results from the least-squares fit of a theoretical structure model to the experimental reduced intensity function. Distances (*d*), thermal parameters (*b*) and number of interactions (*n*) are given with one mean error in parentheses. The stoichiometric volume (V_{stoich}) is chosen so as to contain one Ga atom; k = constant applied in the damping function, exp $(-ks^2)$, r_{corr} = distance below which the reduced radial distribution function has been corrected for spurious peaks. Parameters for the benzene contribution were taken from ref. 61 and kept constant in the refinement

Solvent	Benzene	s range (exptl.)	0.200–13.03
Mole fraction, Ga_3Cl_7	0.215	s range (least-squares)	2.5–13.00
Density/g cm^{-3}	1.47	r_{corr}/Å	1.0
Linear absorption (cm^{-1})	29.8	k	0.012
V_{stoich}/Å^3	288		
d(Ga–Cl)/Å	2.160(4)	2.853(25)	3.182(93)
10^3b(Ga–Cl)/Å^2	1.0*	5.5(2.7)	2.4(8.0)
n(Ga–Cl)	2.04(5)	0.63(6)	0.34(7)
d(Cl···Cl)/Å	3.592(12)	5.16*	6.38*
10^3b(Cl···Cl)/Å^2	7.5(1.7)	0.0030*	0.0150*
n(Cl···Cl)	3.94(19)	1.00*	1.00*
d(Ga–C)/Å	3.181(62)	d(Ga···Ga)/Å	4.097(29)
10^3b(Ga–C)/Å^2	10.8(9.1)	10^3b(Ga···Ga)/Å^2	0.0050*
n(Ga–C)	1.77(34)	n(Ga···Ga)	0.27(5)

* Held constant during the refinement.

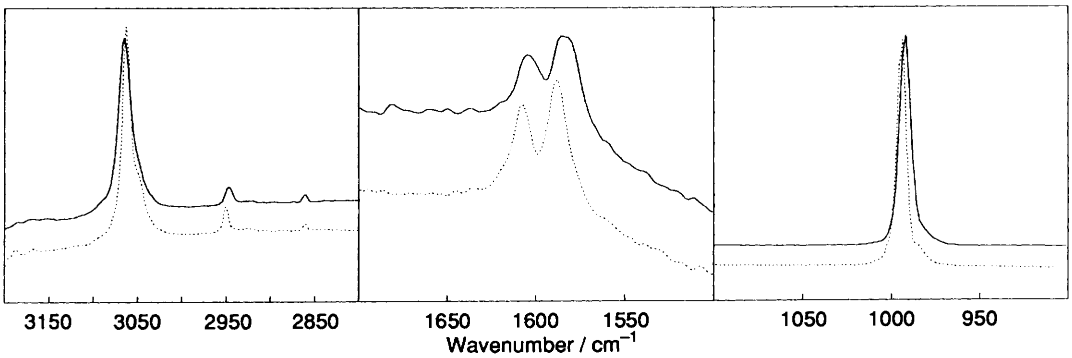

Fig. 5 Raman spectra showing the changes in the benzene vibration modes in a 21.5 mol % Ga_3Cl_7–C_6H_6 solution (solid lines) as compared to neat benzene (dotted lines)

of the ion pairs $Ga^+Ga_nCl_{3n+1}^-$ (n = 1 or 2), rather than the different polarizing effect of $GaCl_4^-$ *vs.* $Ga_2Cl_7^-$ on Ga^I.

In order to gain more insight into the conformation of $Ga_2Cl_7^-$ in benzene solution and the structure of the $Ga^+\cdot Ga_2Cl_7^-$ ion pair, a liquid X-ray scattering study was undertaken. The experimental details are given in Table 4, and the results in Figs. 6 and 7. In analysing LXS data from systems as complicated as the present one careful measures must be taken to avoid overinterpretation. Hints as to the structure given by other methods (such as the spectroscopic data presented above) and relevant solid-state data {in this case the crystal structures of KGa_2Cl_7[46] and the benzene–gallium(I) complex in $[Ga(C_6H_6)\cdot GaCl_4]_2\cdot 3C_6H_6$}[11] are also necessary tools in the hunt for a credible structural model. By visual inspection of the reduced radial-distribution function (Fig. 7) and bearing in mind that the interatomic, intramolecular correlations which are expected to be found are Ga^{III}–Cl (with both terminal and bridging chlorides), Cl • • • Cl, Ga^{III} • • • Ga^{III}, Ga^{III}–C, Ga^I–Cl and Ga^{III}–Ga^I, a few fundamental conclusions may be drawn.

(1) Considering earlier LXS investigations of gallium(III)–chloride systems,[61] the exceptionally sharp peak at 2.16 Å is only attributable to Ga–Cl correlations. The peak does not show a skew-symmetric character, nor does it contain any shoulders. This observation indicates that the next-neighbour Ga–Cl distances in the $Ga_2Cl_7^-$ ion in this system *either* all are very similar (*i.e.* the bridging and terminal Ga–Cl distances are essentially equal) *or* that they have substantially different values. The former explanation is not only unreasonable from a chemical point of view, but is also in conflict with the fact that the magnetic environment around Ga^{III} is of too low a symmetry to allow a ^{71}Ga NMR signal to be detectable. The latter explanation, considered by us as being more credible, allows the peak at 2.16 Å to be assigned to the terminal Ga^{III}–Cl distance (close to the corresponding average distance of 2.14 Å in solid KGa_2Cl_7).

(2) Moving to longer distances in the reduced radial-distribution function, the next peak found is a broad feature at 3.1 Å, which also displays a shoulder at about 2.8 Å assigned to a bridging Ga^{III}–Cl distance. Turning again to the crystal structure of KGa_2Cl_7, it is found that the bridging Ga–Cl distance in this compound is only 2.3 Å. A difference of 0.5 Å is truly exceptional, but all other interatomic correlations are found at even longer distances in the reduced radial-distribution function. Furthermore, a weakening of the Ga^{III}–Cl–Ga^{III} bridge and the highly asymmetric character of the Ga^{III}–Cl distances are also hinted at by the ^{71}Ga NMR and Raman spectroscopic results.

(3) The peak at 3.1 Å is more difficult to analyse properly since it is quite broad and presumably contains contributions from several atom–atom correlations. However, from the crystal structures alluded to above we know that Ga^I–Cl and Ga^I–C distances all fall in the range covered by this broad feature.

(4) The peak at 3.6 Å is assigned to Cl • • • Cl correlations, in agreement with an earlier LXS investigation of Ga^{III}–Cl systems.[61]

(5) The peak at 4.1 Å is a candidate for a Ga^{III} • • • Ga^{III} correlation, consistent with the spectroscopic evidence for a bent Ga^{III}–Cl–Ga^{III} bridge.

Applying the distances suggested above in a structural model and comparing it with the experimental reduced intensity function (Fig. 6) gives quite a satisfactory result. The least-squares refinement of the model to the experimental reduced intensity function converges rapidly and with a convincingly good result (Figs. 6 and 7). The final parameters are shown in Table 4 and the structure proposed in Fig. 8(*a*)

During the refinement it also turned out that the assignment of the very long Ga^{III}–Cl bridging distance is supported not only by the lack of shoulders on the peak at 2.16 Å, but also by the fact that this peak is found to contain only 2.0 Ga–Cl correlations per Ga, not 2.67 which would be the case if the bridging and terminal Ga–Cl distances were equal.

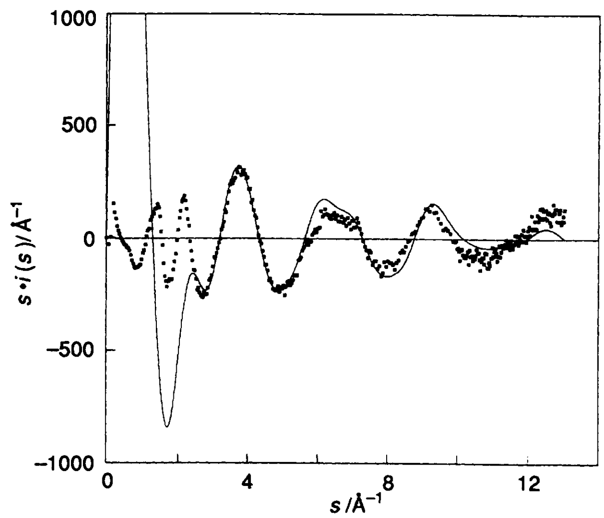

Fig. 6 Experimental reduced intensity function $s \cdot i(s)$ (in units of free electron scattering, *i.e.*, dimentionless) obtained for a 21.5 mol % Ga_3Cl_7–C_6H_6 system compared with the best-fit theoretical structure model (solid line)

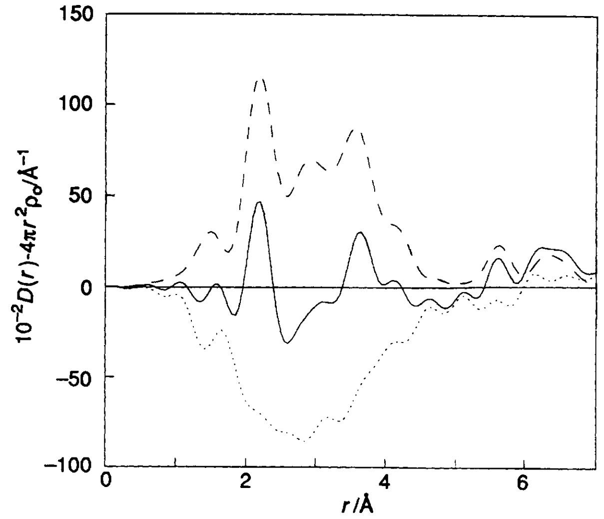

Fig. 7 Reduced radial-distribution function for a 21.5 mol % Ga_3Cl_7–C_6H_6 system (solid line), the best-fit theoretical structure model (dashed line) and the difference (dotted line)

We would like to point out that during the course of this data evaluation a number of other structural models were tried in order carefully to scrutinize the reliability of the exceptionally long bridging Ga–Cl bond found. Two are displayed in Fig. 8(*b*) and 8(*c*). None of these models gave a better fit to the experimental data than did our final results shown in Table 4, nor do they properly account for the spectroscopic observations.

The Ga–$GaCl_3$–C_6H_6 *System*.—During the course of this investigation it was found that solutions of $GaCl_3$ in aromatics readily dissolve substantial amounts of gallium metal. The reasonable assumption that Ga^I is the subvalent gallium species formed is proven by ^{71}Ga NMR spectra, which show a sharp line at < δ–900. This reaction provides an easy route to the *in situ* preparation of Ga^I in arene solutions. A solution of formal composition $Ga : 4GaCl_3 : 16C_6H_6$ produces a Raman spectrum very similar to that discussed for the Ga_3Cl_7–C_6H_6 system. The saturation of a benzene solution of $GaCl_3$ (composition

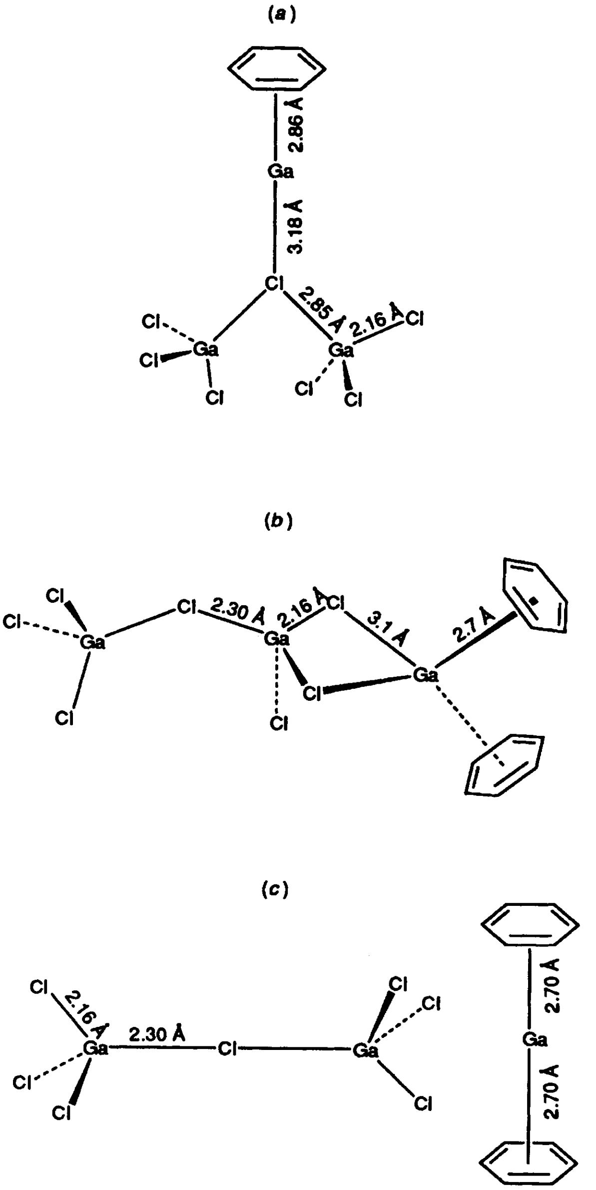

Fig. 8 (*a*) Structure of the $Ga^+\cdot Ga_2Cl_7^-$ ion pair proposed on the basis of the LXS results. The LXS data do not allow for a distinction between a staggered and eclipsed conformation of the terminal $GaCl_3$ units; consequently, the staggered conformation displayed is arbitrarily chosen. Benzene is implied to be η^6-co-ordinated to Ga^I. (*b*) A structure model derived from the solid-state structures presented in refs. 11 and 46. (*c*) A structure model supposing weak ion pairing and a sandwich co-ordination of benzene rings to Ga^+. Models (*b*) and (*c*) (among others) were found to be impossible to refine

$GaCl_3:4C_6H_6$) with gallium metal, on the other hand, yields a solution the spectrum of which contains bands from both $Ga_2Cl_7^-$ and $GaCl_4^-$ (Fig. 9). In addition, a solid phase precipitates. These effects indicate that $Ga_2Cl_7^-$ acts as an oxidizing agent at higher formal gallium-concentrations, yielding Ga^I and $GaCl_4^-$ ions. The lower solubility of Ga_2Cl_4 in benzene as compared to Ga_3Cl_7 then causes the precipitation of a solid phase. The Raman spectrum of the solid compound formed displays bands of $GaCl_4^-$ very close to those of the Ga_2Cl_4–C_6H_6 system (Fig. 9, Table 3) and gives positions of the benzene bands in agreement with those of the Ga_3Cl_7–benzene solution discussed above. These spectral characteristics suggest that the solid phase formed is the previously described benzene complex $[Ga(C_6H_6)_2\cdot GaCl_4]_2\cdot 3C_6H_6$.[11]

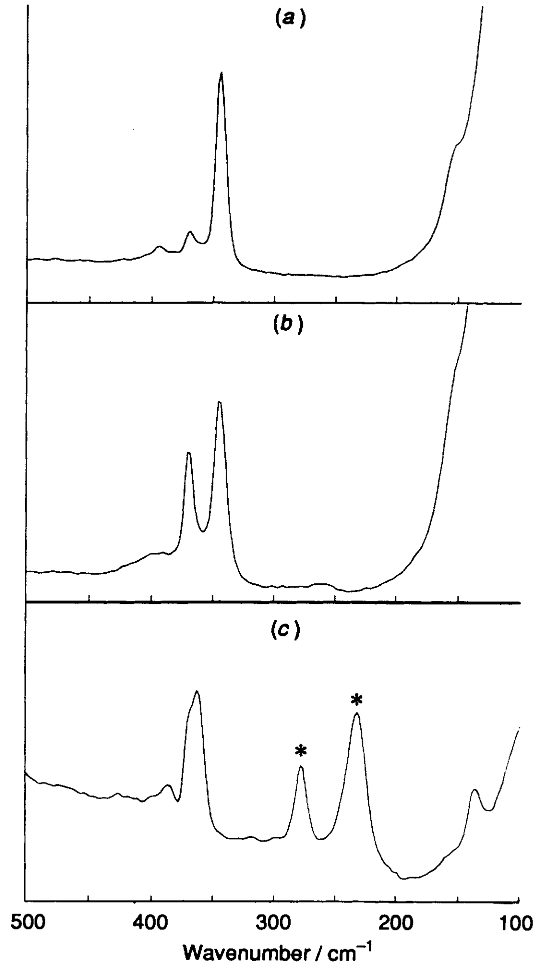

Fig. 9 Raman spectra of Ga–$GaCl_3$–arene systems. Bands denoted by * belong to the arene. (*a*) Ga–$GaCl_3$–C_6H_6 (solid phase); (*b*) Ga–$GaCl_3$–C_6H_6; (*c*) Ga–$GaCl_3$–$C_6H_3Me_3$-1,3,5

The ^{71}Ga NMR spectrum of a solution saturated with Ga (Table 2) displays a gallium(I) signal intermediate in position between those found in the Ga_2Cl_4– and Ga_3Cl_7–C_6H_6 solutions, again suggesting a dependence of the shift of the gallium(I) signal on the chlorogallate(III) environment. In contrast to the solution with X(Ga) = 0.20, a gallium(III) resonance is also observed, because of the presence of $GaCl_4^-$ ions.

The Ga–$GaCl_3$–$C_6H_3Me_3$-1,3,5 *System*.—Saturated solutions of Ga_3Cl_7 and Ga_2Cl_4 in mesitylene at room temperature are found to be of too low concentration in gallium species to allow for a detailed spectroscopic investigation. However, mesitylene solutions of $GaCl_3$ oxidize and dissolve gallium metal, albeit to a much lesser degree than do their benzene analogues. The ^{71}Ga NMR spectrum of a solution saturated with Ga also exhibits a sharp, low-frequency resonance attributable to Ga^I (Table 2). In the Raman spectrum (Fig. 9) a shoulder at 370 cm^{-1} develops adjacent to the $GaCl_3$ stretching vibration of monomeric $GaCl_3$ complexed with mesitylene. The strong complex formation between monomeric $GaCl_3$ and mesitylene (which in part is the subject of Part 2 of this series) presumably inhibits the reduction of Ga^{III} in this system.

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