Spectroscopic Investigation of Concentrated Solutions of Gallium(III) Chloride in Mesitylene and Benzene†

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The metal–arene interaction in concentrated binary mixtures of $GaCl_3$ and mesitylene or benzene has been investigated using multinuclear (^1H, ^{13}C, ^{71}Ga) NMR, Raman and UV/VIS spectroscopy as well as liquid X-ray scattering. The effects of hydrolysis and radiolysis of such mixtures have also been studied using UV/VIS, EPR and IR spectroscopy. Gallium(III) chloride has been found to be monomeric in mesitylene and to form η^6 complexes with this arene. A structural determination of this complex in solution yielded a Ga–C distance of 2.20 Å and a $GaCl_3$ moiety with C_{3v} symmetry and Ga–Cl distances of 2.10 Å. In benzene, $GaCl_3$ exists as a mixture of the $Cl_2Ga(\mu\text{-}Cl)_2GaCl_2$ dimer and one or several other species, containing terminal $GaCl_3$ groups of C_{3v} symmetry, *e.g.* the dimer isomer $Cl_2Ga(\mu\text{-}Cl)GaCl_3$ and monomeric $GaCl_3$. The complex with benzene is weaker than with mesitylene and the co-ordination mode cannot be unambiguously elucidated. Hydrolysis of the $GaCl_3$–C_6H_6 system produced a darkly coloured precipitate showed by IR spectroscopy to be a mixture of poly(*p*-phenylene) and other polymeric species, probably *meta*-substituted, chlorinated and hydroxylated polyphenylenes. On the basis of ^{71}Ga NMR results, it is suggested that the formation of this polymer proceeds *via* protonated Wheland intermediates, rather than direct oxidation of benzene by Ga^{III}. Radiolysis of the mixtures of $GaCl_3$ with mesitylene and benzene yielded radicals, according to EPR spectroscopy. In benzene solution the formation of radicals is accompanied by reduction of Ga^{III} to Ga^I. No formation of solid polymers could be detected.

While the structural, thermodynamic and spectroscopic properties of metal–arene complexes of *soft* main-group acceptors such as the univalent ions of the third group (Ga^I, In^I and Ti^I),[1,2] Sn^{II},[3,4] Pb^{II},[5] Sb^{III} (refs. 6–10) and Bi^{III} (refs. 10 and 11) have been structurally investigated in considerable detail, the exact nature of arene complexes of *hard* acceptors such as Ga^{III} and Al^{III} is still to a great extent unknown. The interpretation of available data seems to range from the opinion raised in a recent review that the effects observed spectroscopically in mixtures of arenes and MR_3 (M = Al^{III} or Ga^{III}, R = alkyl or halide) acceptors, and thus the complexes formed, are *weak*[12] to the somewhat older statement that the ions in question are such good electron acceptors that the interactions between these and arenes are so *strong* that they *inevitably* lead to reactions of the aromatic moiety in the form of polymerization or decomposition.[5] Solid-state data for such complexes are also scarce and no direct structural determinations seem to have been performed except for that of the benzene complex $Al_2Br_6{\cdot}C_6H_6$, in which the metal–arene interaction was found to be very weak.[13] Very recently, a bis(hexamethylbenzene) complex of the hard transition-metal ion Ti^{IV}, $[Ti(C_6Me_6)_2Cl_3][Ti_2Cl_9]$, has also been structurally investigated and the arene molecules found to be η^6-bound to the titanium(IV) centre.[14]

A survey of the existing literature displays confusing manifold suggestions as to the nature of the complexes between hard donors and arenes in solution as well as the structures of the halides themselves (*i.e.* whether they are di- or mono-meric in solution) and the possible side-reactions taking place in such binary systems. However, turning, for a moment, away from the $GaCl_3$–arene systems to the similar, and better studied, $AlBr_3$–arene mixtures it is apparent that the confusion prevailing in the older work has been considerably attenuated by more recent findings. Schümann and Perkampus[15,16] performed detailed investigations of the low-frequency part of the Raman spectra of these systems and found that the doubly bromide-bridged $Br_2Al(\mu\text{-}Br)_2AlBr_2$ species well known from the solid structure of $AlBr_3$[17] is in equilibrium with the monobridged $Br_2Al(\mu\text{-}Br)AlBr_3$ isomer in arene solution at lower temperatures. The Raman data were also used to calculate the equilibrium constant for reaction (1) for a number of arenes, RH.[18] Infrared

$$RH{\cdot}Br_2Al(\mu\text{-}Br)AlBr_3 \longrightarrow Br_2Al(\mu\text{-}Br)_2AlBr_2 + RH \quad (1)$$

spectra of a large number of arene–MX_3 (M = Al or Ga, X = Cl or Br) systems with poly-[19] and mono-cyclic arenes[20] were rationalized by the same authors in previous work as indicating RH–Al^{III} bonds of σ type. In addition, recent work has suggested that in the presence of the more basic methylbenzenes (*e.g.* mesitylene) the bridge in the $Br_2Al(\mu\text{-}Br)AlBr_3$ isomer may break up and the Br_2Al^+ fragment subsequently forms a π complex with the arene.[21] This scenario has not been considered for the $GaCl_3$–arene systems, for which IR spectroscopic data in the low-frequency range are rather fragmentary,[22,23] Raman data are lacking and much of the older literature reports very contradictory results from cryoscopy,[24,25] mid-IR spectroscopy,[20,26–28] dipole-moment measurements[23,25] and calorimetry.[25,29] In benzene solution, $GaCl_3$ has been suggested to be either dimeric[22] or to exist as an equilibrium between the monomer and dimer.[24] The complexes (if any)[27] formed between the halide and arenes have been suggested to be both of π[23,25,29] and σ type.[20,26]

In this study we have used various spectroscopic methods (multinuclear NMR, EPR, UV/VIS and Raman spectroscopy) as well as liquid X-ray scattering (LXS) in an attempt to clarify the metal–arene interactions in mixtures of benzene or mesitylene and gallium(III) chloride. Such mixtures are advantageous model systems in this respect, since the halide is extremely soluble in aromatics (> 50 mol % in benzene, > 20 mol % in mesitylene), which makes the concentration of gallium species present in solution high enough to enable their detection and characterization with great accuracy by spectroscopic methods.

Like their aluminium analogues, gallium(III) chloride and bromide are covalent, low-melting compounds (the melting

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† Arene solutions of Gallium Chloride. Part 2.[1]

point of $GaCl_3$ is 78 °C). The structure of $GaCl_3$ has been studied in the solid,[30] liquid[31] and gas phase[32] and it has been shown to consist of Ga_2Cl_6 dimers (D_{2h} symmetry) of edge-sharing $GaCl_4$ tetrahedra, analogous to the Al_2Br_6 dimers mentioned above.

In contrast to Al^{III}, the strong Lewis acidity of Ga^{III} is combined with a tendency to be reduced to Ga^{I}. Gallium(III) chloride can therefore simultaneously act *both* as a powerful halide-ion acceptor *and* as a mild oxidizing agent. Furthermore, the high solubility in arenes of both gallium(III) chloride and the reduction product most often encountered, the mixed-valence chloride $Ga^{I}[Ga^{III}Cl_4]$, make $GaCl_3$ ideal for various organic syntheses, *e.g.* Friedel–Crafts reactions and oxidation of polyarenes.[33] The high solubility of salts of Ga^{III} and Al^{III} in aromatics is further exemplified by the $M_2Cl_7^-$ ions, which have been found to be present in the 'red oils' of the Friedel–Crafts systems Arene–HCl–MCl_3 (M = Ga[34] or Al).[35] The formation of soluble halogenoaluminates also accounts for the high solubility of alkali-metal halides in arene–$AlBr_3$ systems.[36]

While evaluating spectroscopic data from binary mixtures of metal halides in arenes possible side reactions involving the aromatic moiety must be taken into account. These include Scholl-type reactions (*i.e.* polymerization of arenes),[37] halogenation[38–40] and isomerization or transalkylation.[41–43] All these possible side-reactions complicate the analysis of data from metal halide–arene systems. Furthermore, the possible role of water and/or HCl as co-catalysts in the reactions mentioned above has been pointed out again and again and it is quite possible that the inconsistent data regarding the nature of the arene–Ga^{III}/Al^{III} complexes which appear in the literature are caused by traces of water. In this paper we therefore also report the results from hydrolysis and radiolysis studies of the $GaCl_3$–arene systems.

Experimental

General.—All chemicals and procedures for sample preparation were as described in Part 1 of this series.[1] This also applies to the NMR and Raman measurements. In order to impede radiolysis, all samples were stored in the dark in between measurements, except when otherwise stated.

Liquid X-Ray Scattering.—Sample preparation and data evaluation were as previously described.[1,31] However, corrections for multiple scattering effects were applied in the data evaluation.

UV/VIS Spectroscopy.—The spectra were recorded with the samples enclosed in 5 mm NMR tubes on a Guided Wave 260 fibre-optics spectrometer specially designed for oxygen- and moisture-sensitive samples contained in cylindrical sample tubes at ambient and elevated temperatures. By calibration against aqueous nitrate solutions of Cu^{II}, Cr^{III} and Ni^{II} enclosed in conventional 1.00 mm cuvettes, the effective path length of the NMR tubes was determined to be 0.44 ± 0.01 cm. Since UV/VIS spectroscopy constitutes only a minor part of this article, details about the experimental set-up will be given in a forthcoming publication.[44]

EPR Spectroscopy.—The EPR spectra were recorded on the upgrade version 3220-200SH of a Bruker ER-200D instrument with samples contained in quartz cells. The samples were prepared just prior to the experiment and sealed with a rubber stopper. Radiolysis experiments were performed by irradiating the sample with a 50 W high-pressure mercury lamp.

Infrared Spectroscopy.—The IR spectrum of the polymer formed in the $GaCl_3$–benzene–water system was recorded on a Nicolet 20SXC FT-IR spectrometer with the sample as a KBr pellet (1 : 100 ratio).

Results and Discussion

The $GaCl_3$–C_6H_6 *System.*—Since it was considered plausible that this system is thermodynamically unstable, spectroscopic data were collected from freshly prepared samples (less than 2 d after their preparation). Results from samples investigated after prolonged standing and radiolysis/hydrolysis are also reported below.

The Raman spectrum of neat, liquid $GaCl_3$[1,45–47] shows bands only below 500 cm^{-1} and bears a close resemblance to those of the $GaCl_3$–benzene solutions in this work (Fig. 1, Table 1). Pronounced exceptions are the bands at 140, 367 and 393 cm^{-1} and the inversion of the relative intensities of the $2\nu_3$ and ν_2 bands of Ga_2Cl_6. In contrast to the other Ga_2Cl_6 bands, the ν_2 band is also substantially shifted as compared with neat Ga_2Cl_6. It is thus possible that this band in the benzene system is *not* a Ga_2Cl_6 band. *A priori*, bands not attributable to Ga_2Cl_6 may be assigned in four different ways: (1) from a hydrolysis product [*e.g.* $GaCl_3(OH)^-$]; a weak IR band at 363 cm^{-1} in $GaCl_3$–benzene solution has been explained in this way;[22] (2) from chlorogallate(III) ions; such ions have previously been found to exist in the 'red oils' of Friedel–Crafts systems MCl_3–arene–HCl (M = Al[35] or Ga)[34] and are thus soluble in aromatics; (3) from monomeric $GaCl_3$ in equilibrium with Ga_2Cl_6; (4) from an isomer of Ga_2Cl_6 (*e.g.* Cl_2Ga–Cl–$GaCl_3$) which has been inferred by Raman spectroscopy of the $AlBr_3$–benzene system and discussed in the Introduction.

The first explanation is rendered improbable not only because of the care taken during sample preparation, but also by noting that the deliberate addition of even minute amounts of water to the solutions results in a profound discolouration and rapid (within days) formation of a solid precipitate (see below). The samples investigated here were, on the contrary, colourless or (for the highest $GaCl_3$ concentrations) faintly yellow. No precipitation was found even after prolonged standing (> 2 months), although a discolouration of the solutions is apparent on this time-scale.

Formation of chlorogallate(III) ions, on the other hand, requires either addition of or liberation of chloride ions from a redox reaction involving $GaCl_3$ and benzene. Considering the polymerization reactions between benzene and other oxidizing

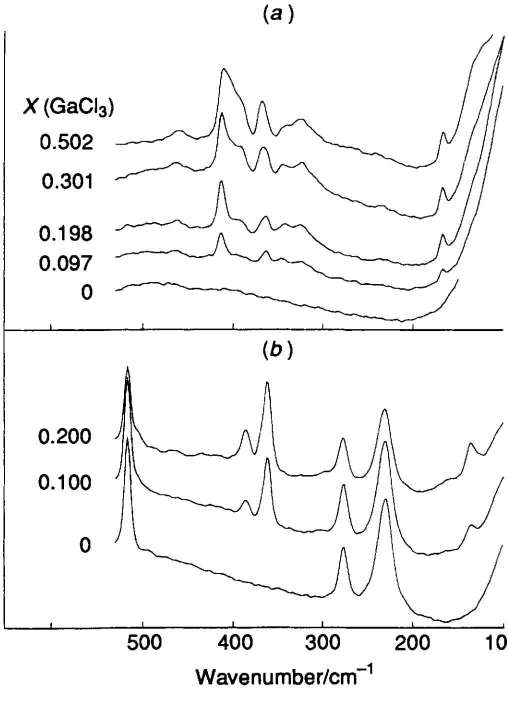

Fig. 1 Raman spectra of the $GaCl_3$–benzene (*a*) and –mesitylene (*b*) systems at different concentrations of $GaCl_3$

Table 1 Raman bands (cm^{-1}) of the systems investigated compared with literature data; solvent bands are omitted; w = weak, m = medium, s = strong, v = very, sh = shoulder, br = broad. For 1 : 1 L·$GaCl_3$ adducts with $GaCl_3$ moieties of C_{3v} symmetry, solid-state far-IR data are for 15 different complexes with O-, S- and N-donors;[49] values are the averages of these systems with limits of error given as the standard deviation from the mean. These results are compatible with Raman data, since all vibration modes of C_{3v} symmetry are both IR and Raman active

$GaCl_3$–C_6H_6 This work	$GaCl_3$–$C_6H_3Me_3$-1,3,5 This work	Ga_2Cl_6 (liquid) Ref. 1	$GaCl_3$ (D_{3h}, gas, 500 °C) Ref. 48	L·$GaCl_3$ (C_{3v}) Ref. 49	Assignment
970w	992 (sh)				'Ga–C' (see text)
	506 (sh)				'Ga–C' (see text)
463w		463m			Ga_2Cl_6, $\nu_{11}(b_{2g})$
			462w (br)		$GaCl_3$, $\nu_3(e')$
413s		411s			Ga_2Cl_6, $\nu_1(a_g)$
393 (sh)	387w			396 ± 7	$GaCl_3$, ν_s
			382s		$GaCl_3$, $\nu_1(a_1')$
367m	363s			359 ± 2	$GaCl_3$, ν_{asym}
344m		342m			Ga_2Cl_6, $2\nu_3$
Obscured		319mw			Ga_2Cl_6, $\nu_2(a_g)$
325m	300 (sh)				'Ga–C' (see text)
168m		167m			Ga_2Cl_6, $\nu_3(a_g)$
	160 (sh)			153 ± 3	$GaCl_3$, δ
140 (sh)	138w			134 ± 3	$GaCl_3$, δ
			130m (br)		$GaCl_3$, $\nu_4(e')$
109s (sh)		119 (sh)			Ga_2Cl_6, $\nu_{12}(b_{2g})$

metal halides,[38,50,51] the latter possibility cannot be ruled out. To check this hypothesis, ^{71}Ga NMR spectra were recorded. The ^{71}Ga NMR spectra of Ga^I in aromatics normally exhibit narrow, sharp signals.[1,52] However, in the present system no gallium resonance could be detected in samples protected from light. This result discredits the view that the bands are assignable to chlorogallate(III) ions formed during a reduction of Ga^{III} to Ga^I by benzene. A reduction to Ga^{II}, on the other hand, is not considered to be detectable by ^{71}Ga NMR spectroscopy, since the resonances of this species are too broad.[53] Also, the formation of Ga^{II} is less likely from a chemical viewpoint. Furthermore, the very strong Raman band from the Ga–Ga stretch in the invariably metal–metal bonded gallium(II) dimers found between 230 and 240 cm^{-1} for all gallium(II) chloride compounds so far investigated by vibrational spectroscopy[54–57] is *not* found in this study.

The possibility that a Friedel–Crafts system involving HCl and chlorogallate(III) ions is formed because of acidic impurities can be discarded by the mere fact that protic impurities result in the formation of a solid polymer (see below). As already mentioned, no such formation was observed. In accord with previous dipole[25] data we thus conclude from the present Raman spectroscopic data that an equilibrium between Ga_2Cl_6 and $GaCl_3$ *and/or* Ga_2Cl_6 dimer isomers is manifest in benzene over the whole concentration range investigated.

The bands at 140, 367 and 393 cm^{-1} agree very well with those found for various L·$GaCl_3$ adducts of N-, O- and S-donors in which the $GaCl_3$ moiety has C_{3v} symmetry.[49,58,59] However, in benzene solution, these bands need not correspond to a $GaCl_3$ monomer, but may also be assigned to a terminal $GaCl_3$ group of C_{3v} symmetry in a hypothetical monobridged Cl_2Ga–Cl–$GaCl_3$ dimer. Apart from the band at 325 cm^{-1} overlapping the $\nu_2(Ga_2Cl_6)$ mode discussed above, the spectra do not show *strong* bands attributable to further modes in such a species. A diffuse feature at about 230 cm^{-1} is close to the position expected for a Ga–Cl–Ga vibration.[1] Furthermore, a shoulder at 400 cm^{-1} is manifest, and it seems to increase in intensity with increasing concentration of $GaCl_3$. Still weaker bands may of course have escaped detection, and the situation is further complicated by the fact that bands due to gallium(III)–arene modes are expected to occur in the same spectral range. For the η^6-benzene complexes $[M(C_6H_6)(CO)_3]$ (M = Cr, Mo or W) of C_{3v} symmetry, bands found at 312 and 264 cm^{-1} were assigned to E and A_1 (metal–arene), respectively.[60,61] In reasonable agreement with this study, it is thus possible to assign the bands of 325 and 400 cm^{-1} in our study to gallium–arene vibrations of either E or A_1 symmetry. Attempts to determine the polarization character of these bands by performing depolarized Raman spectroscopy proved inconclusive, because of the low scattering power of $GaCl_3$ in benzene.

We thus conclude that our Raman data are inconclusive as to the nature of the gallium(III) solute in benzene, but that they unambiguously show that Ga_2Cl_6 of D_{2h} symmetry is not the sole species present. Furthermore, the species (one or several) in equilibrium with the D_{2h} dimer contains a $GaCl_3$ group of C_{3v} symmetry. A previous LXS investigation of the $GaCl_3$–C_6H_6 system displayed only a monomeric $GaCl_3$ unit with C_{3v} symmetry, but it was suggested that this result was a consequence of the radiolytically induced splitting of the dimer.[31] *If* monomeric $GaCl_3$ is assumed to be present in this system, the deviation from the D_{3h} symmetry adopted by $GaCl_3$ in the gas phase suggests a specific interaction between the monomer and benzene in solution. In this context it is interesting that trialkylgallium (which is monomeric in solution irrespective of solvent)[62] has a vanishing dipole moment in inert (non-donating) solvents such as heptane, but high ones in solvents with donor capacity (*e.g.* benzene).[63] These results indicate complex formation between Ga^{III} and benzene and a concomitant change in the GaX_3 monomer symmetry from D_{3h} to C_{3v} in solvents with donating properties.

Considering the high concentrations of $GaCl_3$, the change in the benzene spectra at $\geqslant 500$ cm^{-1} upon the addition of $GaCl_3$ is remarkably small. It consists only of the gradual build-up of a new, weak band at about 970 cm^{-1} [Table 1, Fig. 2; exact position slightly dependent on $X(GaCl_3)$] close to the strongest benzene band at 994 cm^{-1}, which is assigned to the 'ring breathing' mode $A_{1g}[\nu(C–C)]$.[64] The band is unlikely to be a Raman-forbidden band of benzene being observable in the most concentrated solutions because of symmetry lowering of the benzene molecules. Benzene does not have an IR absorption in this region except for a very weak band at 985 cm^{-1}.[63,65] It is therefore reasonable to assign the band to the A_{1g} benzene mode in complexed benzene. Literature data neither support nor discredit this assignment. Raman spectra of solid Menschutkin complexes (*i.e.* η^6-arene complexes with $SbCl_3$) only show small shifts (a couple of wavenumbers) in the C=C bands belonging to the aromatic,[66] whereas the interaction between $AlBr_3$ and alkenes or cycloalkenes produces a low-energy shift of the C=C stretching vibration of 50–70 cm^{-1}.[67] The same effect is found for the η^6-benzene complexes $[M(C_6H_6)(CO)_3]$ (M = Cr, Mo or W) mentioned above. The A_{1g}[ν(C–C)] mode of benzene is, in these cases, found to shift substantially to lower wavenumber ($\leqslant$40 cm^{-1}) when benzene acts as a ligand.

In our earlier LXS study of the $GaCl_3$–C_6H_6 system no Ga–C distances could be detected.[31] This result discredits the view that benzene forms π complexes with $GaCl_3$ and indirectly suggests a σ type of complex (as in the recently structurally characterized complex $[SiEt_3{\cdot}C_6H_5Me]^+$),[68] in which the Ga–C contribution to the intensity function may well be too low to be detectable. However, this line of reasoning is not sufficient to eliminate the possibility that a π complex of low hapticity is formed. Such co-ordination modes are found in arene complexes of Cu^I and Ag^I, where η^2 co-ordination prevails.[69,70] Gallium-71 NMR spectroscopy does not clarify the picture since no signals at all can be detected. The small dependence of the ^{1}H and ^{13}C shift of benzene on the concentration of $GaCl_3$ (Table 2) is indicative of a *weak* interaction between benzene and $GaCl_3$. The absence of splitting in ^{13}C NMR spectra of the aromatic carbons does not unambiguously suggest an equivalence of these nuclei (*i.e.* an η^6 co-ordination mode), since the concomitant line broadening [$w_{\frac{1}{2}}$ = 10 and 80 Hz for $X(GaCl_3)$ = 0 and 0.50, respectively] suggests a rapid aromatic exchange.

The UV/VIS spectra of freshly prepared $GaCl_3$–C_6H_6 solutions (Fig. 3) only show a steeply rising UV absorption edge. The transition responsible for this intense band is too far out in the UV to be detectable with the experimental set-up used. Such an absorption is expected for this system from the UV/VIS spectroscopic characteristics of solid adducts between $AlCl_3$ and methylated benzene derivatives. In such systems an increase in donor strength (*i.e.* an increased number of methyl substituents)[71] was found to shift the absorption to longer wavelengths.[72] *p*-Xylene, the least-substituted benzene derivative investigated, was found to have an absorption maximum at 364 nm. Although the data are somewhat inconsistent, the same trend has also been reported for $AlCl_3$ adducts with polycyclic arenes, which have been assumed to have σ-complex character.[73–75]

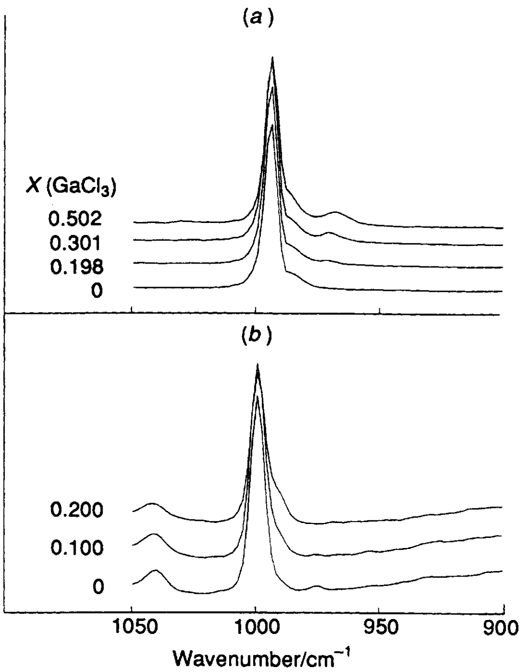

Fig. 2 Effect of the concentration of $GaCl_3$ on the most intense benzene (*a*) and mesitylene (*b*) Raman bands

To conclude, the spectroscopic and structural data discussed above suggest a weak σ-complex formation between benzene and monomeric $GaCl_3$ of C_{3v} symmetry and/or the dimer isomer of Cl_2Ga–Cl–$GaCl_3$. Both species are satisfying from a structural point of view, since Ga^{III} in both cases retains its (quasi-) tetrahedral co-ordination. Suggested structures are displayed in Fig. 4.

Mesitylene.—The structure of neat mesitylene was determined by LXS in order to provide a good structure model for the subsequent $GaCl_3$–$C_6H_3Me_3$-1,3,5 investigation (below) and the results are presented in Figs. 5 and 6 and in Table 3. Owing to the low linear absorbance of mesitylene, only data in the range $s \leqslant 10.31$ Å^{-1} could be recorded. This limitation severely complicates the data evaluation, in particular because mesitylene contains a large number of different carbon–carbon interactions in the relatively narrow range 1.4–2.9 Å. However, the best structural model obtained by a least-squares fit to the experimental data agrees well with standard bond lengths in hydrocarbons as well as with the geometrical restrictions of the molecule and previous electron diffraction data.[76]

The $GaCl_3$–$C_6H_3Me_3$-1,3,5 *System*.—Spectroscopic data were collected in the same way as for the benzene systems, *i.e.* only freshly prepared samples were used. In contrast to the benzene systems, the $GaCl_3$–$C_6H_3Me_3$-1,3,5 solutions are yellow even when freshly prepared. This is caused by an intense UV absorption edge with a low-energy shoulder at 450 nm (Fig. 3).

Although solvent bands interfere, it is clear that the Raman spectra of $GaCl_3$–$C_6H_3Me_3$-1,3,5 at $\leqslant$500 cm^{-1} (Fig. 1, Table 1) show *no* bands attributable to Ga_2Cl_6. Instead, the four bands from a $GaCl_3$ unit of C_{3v} symmetry are displayed, along with a weak shoulder at 300 cm^{-1}, which we assign to a gallium–arene vibration in accordance with the discussion above. The $GaCl_3$ bands are shifted to lower wavenumber as compared to the benzene system. At $\geqslant$500 cm^{-1} the effects on the lines belonging to the solvent are considerably more pronounced than those found for benzene, suggesting the formation of a stronger gallium(III)–arene complex (Figs. 1 and

Table 2 Representative ^{71}Ga, ^{1}H and ^{13}C NMR shifts for the systems investigated. The ^{13}C shifts given are obtained from ^{1}H-decoupled spectra. For the mesitylene system, the ^{13}C shifts are those observed for the α-carbon; $|J|_{C-H}$ is given for aromatic carbons/protons

System	$X(GaCl_3)$	δ(^{1}H)	δ(^{13}C)	$\lvert J\rvert_{C-H}$/Hz	δ(^{71}Ga)
$GaCl_3$–C_6H_6	0	7.16	128.0	158.2	—
	0.50	6.74	129.2	131.8	Undetectable
$GaCl_3$–$C_6H_3Me_3$-1,3,5	0	6.51, 2.04	136.3	154.3	Undetectable
	0.20	6.36, 1.92	140.2	151.4	Undetectable
$GaCl_3$–C_6H_6 (hydrolysed)[a]	0.20	7.02	127.7	158.5	7, very broad
$GaCl_3$–$C_6H_3Me_3$-1,3,5 (hydrolysed)[a]	0.20	6.49, 2.01	136.6	155.3	6, very broad
$GaCl_3$–C_6H_6 (radiolysed)[b]	0.50	6.62	128.9	117.1	−996.7, narrow
$GaCl_3$–$C_6H_3Me_3$-1,3,5 (radiolysed)[b]	0.20	6.36, 1.92	140.2	153.3	Undetectable

[a] Samples left for about 3 weeks in contact with a separate water phase in the sample tubes. The water phase was removed just prior to measurement. [b] Samples radiolysed with a 60 W tungsten lamp for 1 week before measurement.

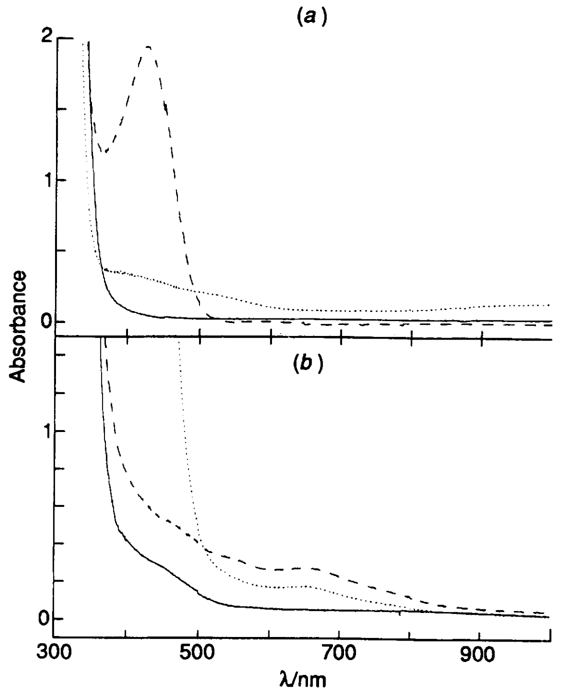

Fig. 3 The UV/VIS spectra of 10 mol % $GaCl_3$–C_6H_6 solution (*a*) and of a 2 mol % $GaCl_3$–$C_6H_3Me_3$-1,3,5 solutions (*b*) freshly prepared with dry solvents (solid lines), radiolysed for 1 week (dashed lines) and prepared using water-saturated solvents (dotted lines). The spectra have been normalized to an optical pathlength of 1.00 cm. The neat solvents were used as references

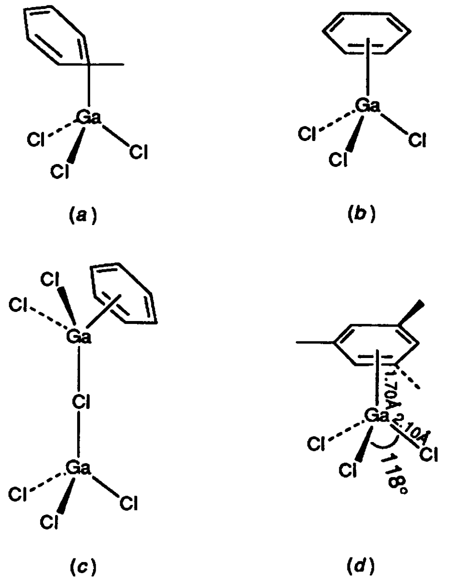

Fig. 4 Proposed structures for the $GaCl_3$–C_6H_6 complex, (*a*)–(*c*), and the structure of the $GaCl_3$–$C_6H_3Me_3$-1,3,5 complex from the LXS investigation, (*d*). A σ complex of benzene with the Cl_2Ga–Cl–$GaCl_3$ dimer is also possible, but not depicted

2). The peaks at 517 and 999 cm^{-1} [assigned to the δ(C–C–C)(E′) and ν(C–C–C)(A_1′) modes, respectively],[77,78] contain prominent shoulders (at 506 and 992 cm^{-1}, respectively) which emerge when $GaCl_3$ is added. We assign these bands to the corresponding vibrational modes in mesitylene complexed with $GaCl_3$. Shifts in the ν(C–C–C)(A_1′) mode of mesitylene to lower wavenumber upon formation of the compounds $[M(C_6H_3Me_3\text{-}1,3,5)(CO)_3]$ (M = Cr, Mo or W) have been reported,[61] and such effects are in agreement with those of the benzene analogues discussed above. The ^{71}Ga NMR spectra are, as in the corresponding benzene systems, uninformative since no signal can be detected. However, ^{13}C NMR spectra reveal a substantial shift in the α-C resonance in mesitylene following the addition of $GaCl_3$ (Table 2), again suggesting gallium(III)–arene complex formation. Other carbon resonances are much less affected by the addition of $GaCl_3$. In agreement with this observation, a previous ^{13}C NMR investigation of the $AlBr_3$–$C_6H_4Me_2$-*m* system reported that upon addition of

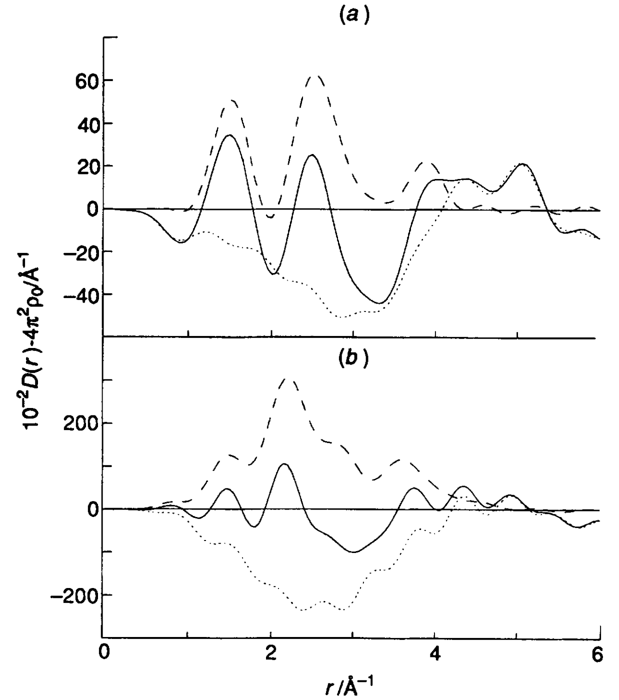

Fig. 5 Reduced radial-distribution functions for mesitylene (*a*) and 20 mol % $GaCl_3$–$C_6H_3Me_3$-1,3,5 (*b*) (solid lines), the best-fit theoretical structure models (dotted lines) and the difference (dashed lines)

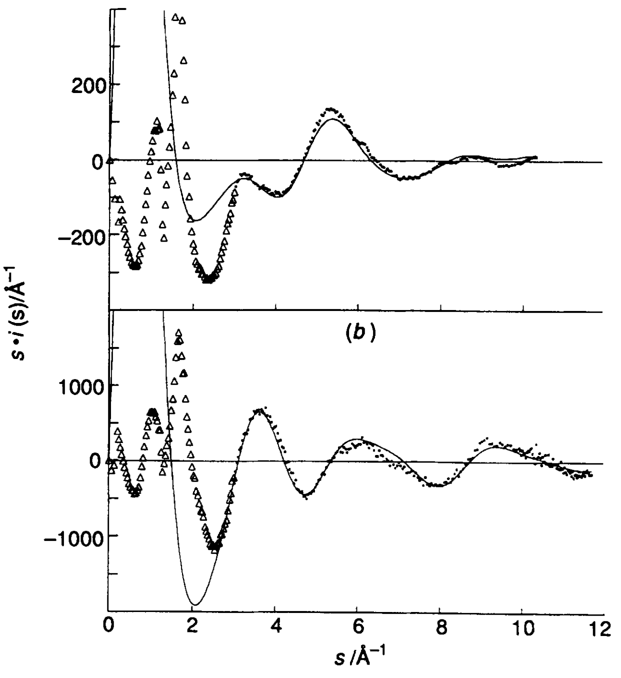

Fig. 6 Reduced intensity functions for mesitylene (*a*) and 20 mol % $GaCl_3$–$C_6H_3Me_3$-1,3,5 (*b*) and the best-fit theoretical structure model (solid lines). Experimental points depicted as triangles have not been used in the least-squares fit

Table 3 Experimental parameters and results from the LXS study of mesitylene and $GaCl_3$–$C_6H_3Me_3$-1,3,5 or –C_6H_6. Stoichiometric volume (V_{stoich}) chosen so as to contain one gallium atom or one mesitylene molecule in the $GaCl_3$–arene and the mesitylene systems, respectively. Distances (d), thermal parameters (b) and number of interactions (n) are given with one mean error in parentheses; μ = linear absorptivity; exptl = experimental; r_{corr} = distance below which the reduced intensity function has been corrected for spurious peaks; k = constant in the damping function, exp $(-ks^2)$; C(1) = carbon in methyl group, C(2) = α-carbon, C(3) = β-carbon

Solvent	Mesitylene	Mesitylene	Benzene
Mole fraction of $GaCl_3$	0	0.20	0.50
Ref.	This work	This work	31
Density/g cm^{-3}	0.8652	1.061	1.510
μ/cm^{-1}	0.519	9.20	32.3
V_{stoich}/Å^3	230.7	1028	280.4
s range (exptl.)	0.200–10.31	0.200–11.68	0.200–13.00
s range (least squares)	3.0–10.31	3.0–11.67	4.0–13.0
r_{corr}/Å	0.80	1.0	0.90
k	0.012	0.012	0.008
d[C(1)–C(2)]/Å	1.588(22)	1.588*	—
10^3b[C(1)–C(2)]/Å^2	5.3(1.8)	5.3*	—
n[C(1)–C(2)]	5.1(5)	20.4*	—
d[C(2)–C(3)]/Å	1.425(5)	1.425*	1.425*
10^3b[C(2)–C(3)]/Å^2	3.8(7)	3.8*	3.5*
n[C(2)–C(3)]	11.6(3)	46.4*	10.56*
d[C(2)–C(2′)/C(1)–C(3)]/Å	2.485(13)	2.485*	2.428*
10^3b[C(2)–C(2′)/C(1)–C(3)]/Å^2	4.9(9)	4.9*	4.8*
n[C(2)–C(2′)/C(1)–C(3)]	20.3(5)	81.2*	11.58*
d[C(2)–C(3′)]/Å	2.891(20)	2.891*	2.764*
10^3b[C(2)–C(3′)]/Å^2	2.7(2.9)	2.7*	12*
n[C(2)–C(3′)]	6.4(6)	25.6*	5.46*
d[C(1)–C(2′)]/Å	3.845(26)	3.845*	—
10^3b[C(1)–C(2′)]/Å^2	14(4)	14*	—
n[C(1)–C(2′)]	8.0(8)	32.0*	—
d(Ga–Cl$_t$)/Å	—	2.102(7)	2.196(4)
10^3b(Ga–Cl$_t$)/Å^2	—	1.0*	1.8(4)
n(Ga–Cl$_t$)	—	2.9(1)	2.49(6)
d(Cl···Cl)/Å	—	3.609(17)	3.658(12)
10^3b(Cl···Cl)/Å^2	—	2.8(2.2)	3.7(1.3)
n(Cl···Cl)	—	2.7(3)	3.3(3)
d(Ga–C)/Å	—	2.200(2)	—
10^3b(Ga–C)/Å^2	—	5.1(1.6)	—
n(Ga–C)	—	6.4(5)	—

* Held constant during the refinement.

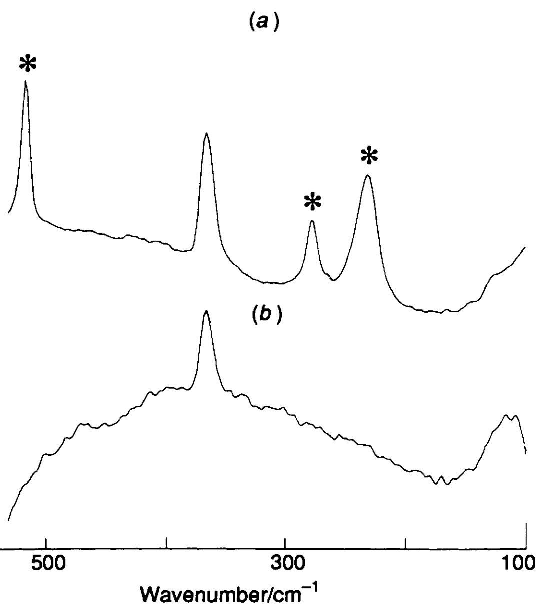

Fig. 7 Raman spectra of hydrolysed 20 mol % $GaCl_3$–$C_6H_3Me_3$-1,3,5 (a) and 20 mol % $GaCl_3$–C_6H_6 (b) solutions. Bands belonging to the arene are denoted *

metal halide the resonances of the methylated carbons were shifted more than those of secondary ones.[78] A preferred interaction of $GaCl_3$ with the methylated α-carbon of mesitylene is also what should be expected from the increased electron density there, caused by the inductive effect of the methyl groups.

Evidence that Raman bands found in the $GaCl_3$–$C_6H_3Me_3$-1,3,5 system are assignable to *monomeric* $GaCl_3$ units of C_{3v} symmetry (rather than to a terminal $GaCl_3$ group in a dimer isomer) is given by LXS. This system turns out to be far less sensitive to radiolysis by X-rays than does the benzene analogue, and only a slight darkening of the sample can be detected during the course of the measurement (8 d). No feature indicative of a specific Ga–Ga correlation is found in the radial-distribution function (Fig. 5) of a solution of 20 mol % $GaCl_3$ in mesitylene, which suggests an absence of appreciable amounts of dimers in the system. The best structural model (Table 3), obtained by a least-squares fit to the experimental reduced intensity function (Fig. 6), contains approximately six Ga–C interactions per gallium at a distance of 2.20 Å. This bond distance must be considered as somewhat uncertain, since the Ga–C interaction is overlapped by the stronger Ga–Cl peak. The value d(Ga–C) = 2.20 Å (giving a distance of 1.70 Å between Ga^{III} and the ring centre) may be compared with the average value d(Ga^I–C) = 3.01 Å in the solid gallium(I) complex $Ga(C_6H_3Me_3\text{-}1,3,5)_2{\cdot}GaCl_4$.[79]

The data are thus much more clear-cut for the mesitylene system than for the corresponding benzene one. There seems to be little doubt that mesitylene, in solution, forms a 1 : 1 η^6 complex with a $GaCl_3$ monomer of C_{3v} symmetry (Fig. 4).

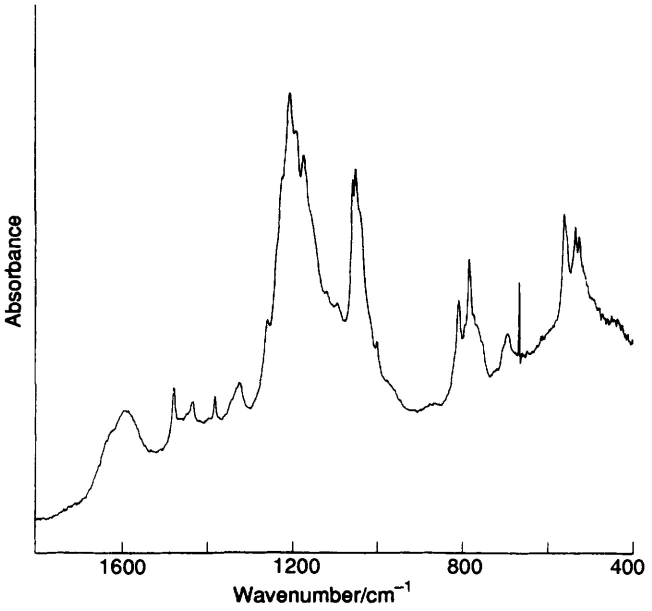

Fig. 8 The IR absorption spectrum of the polyarene produced by hydrolysing a $GaCl_3$–C_6H_6 solution

Table 4 Infrared absorptions in the range 400–1800 cm^{-1} for the polyphenylene obtained by hydrolysis of a $GaCl_3$–C_6H_6 solution. Weak bands are omitted unless diagnostically important

Band	Assignment
526m	
536m	
558 (sh)	
562m	
668s, sharp	CO_2 in sample compartment
695w	Ring puckering
760 (sh)	C–H deformation in monosubstituted rings
784m	C–Cl stretch
793m	C–Cl stretch
809m	C–H out-of-plane deformation in *para*-disubstituted rings
1041s	C–H in-plane deformation in *para*-disubstituted rings
1051s	
1056s	
1156 (sh)	
1174s	See text
1193s	
1207s	
1224 (sh)	
1260 (sh)	
1436w	C–C deformation
1481mw	
1593m (br)	C=C stretch

Hydrolysis.—The rate and extent of hydrolysis of dissolved $GaCl_3$ are greatly dependent on which of the two solvents is used. The benzene solutions fume in moist air and hydrolyse violently in contact with water, HCl gas being liberated, whereas mesitylene solutions do not produce visible amounts of HCl gas even if provoked by the addition of liquid water. This suggests a large difference in the co-ordination and concomitant stabilization of $GaCl_3$ in the two solvents. Upon hydrolysis the Raman spectra of both the benzene and mesitylene systems (Fig. 7) change dramatically as compared to the unhydrolysed systems and only a single Ga–Cl band at 366 cm^{-1} survives in either solvent. This behaviour has previously been observed for benzene solutions by IR spectroscopy and thus the band is also IR active.[22] At the same time the Raman bands assigned to the gallium(III)–benzene/mesitylene interaction disappear, suggesting a breaking of the arene–gallium(III) bonds. The band of 366 cm^{-1} is thus caused by a hydrolysis product, presumably $GaCl_3(OH)^-$.[22] Weak ^1H NMR signals at δ 4.13 and 4.10 in the benzene and mesitylene systems, respectively, are found in the hydrolysed solutions. The shifts differ significantly from those obtained from the neat solvents saturated with water (δ 4.31 and 4.77 in benzene and mesitylene, respectively). The ^{13}C and ^1H NMR spectra gave no evidence for the formation of either protonated arenes, oligomeric species or isomerization products of mesitylene, even after exposure to liquid water for $\geqslant 3$ weeks. Recently hydrolysed samples do not exhibit any ^{71}Ga NMR resonances, but upon standing ($\geqslant 3$ weeks) a broad, weak feature at approximately δ 10 relative to $GaCl_4^-$ in HCl(aq) develops. This peak most probably appears because of a slow halide-transfer process in which the chloride ions of the initially formed hydrolysis product to a small extent redistribute to give minute concentrations of chlorogallate(III) ions (*e.g.* $GaCl_4^-$) of high enough symmetry to allow the NMR signal to be detected. Halide-transfer processes involving Ga^{III} have been reported to be slow in non-aqueous solvents.[53] Upon standing, hydrolysed benzene solutions produce a flocculent precipitate. This precipitate, dark brown while in solution, is black when filtered off and dried. An attempt to record a Raman spectrum of the dried precipitate failed because of the very dark colour. However, the IR spectrum of the substance as a KBr pellet was recorded (Fig. 8) and the main bands and their assignments are presented in Table 4. Bands from poly(*p*-phenylene) are found in the IR spectrum. This is the main product formed when benzene is polymerized by oxidation or catalysis with metal halides such as $MoCl_5$,[51] $FeCl_3$,[50] $AlCl_3$–$CuCl_2$ (the Kovacic route),[80] or by polycondensation of a Grignard reagent (the Yamamoto route).[81] The C–H out-of-plane deformation mode (at 809 cm^{-1} in our spectrum), typical of *para*-disubstituted phenyls, is sensitive to the average chain length of polyl(*p*-phenylene) and has been found to shift towards lower wavenumbers when the chain length increases.[82] The band is found at 806.9 and 805.7 cm^{-1} for samples prepared by the Kovacic and Yamamoto routes, respectively.[82] By the position of the band we can thus deduce that the chain length in our sample is considerably shorter than in poly(*p*-phenylene) synthesized by the aforementioned routes. Furthermore, the group of intense absorptions found in our sample at about 1200 cm^{-1} is not attributable to this compound and the same is true of the band at 784 cm^{-1}. The former bands are in the region characteristic of hydroxylated phenyls and it is thus assumed that they are indicative of OH groups in the polymer, most likely as terminating groups. However, the molar ratio between terminal OH groups and arene fragments may be assumed to be quite low. The very high intensity of the bands thus renders the explanation insufficient. Presumably, other functional groups contribute to this assembly of bands as well. The band at 784 cm^{-1} may be caused by a substantial degree of *meta* substitution and/or the presence of chlorinated products. The position of the band is in agreement with both these assignments. Bands at this position in doped poly(*p*-phenylene) have also been assigned to perylene-like structure defects.[83] It seems clear that the product is a complex mixture of various polymeric species and that the $GaCl_3$–water system is a poor route to poly(*p*-phenylene). Further characterization of the product was not pursued.

No signal attributable to Ga^I was detected in the hydrolysed samples. This demonstrates that the $GaCl_3$-promoted polymerization of benzene with water as co-catalyst does not involve an oxidation of benzene by the metal ion. Most probably the process proceeds *via* a protonated Wheland arene intermediate. In UV/VIS spectroscopy of $GaCl_3$–C_6H_6 samples prepared by using water-saturated benzene as solvent (Fig. 3), hydrolysis products are manifested as two low-energy shoulders on the UV absorption edge at 420 and 520 nm. Protonated benzene has previously been shown to absorb at 332 nm in Al_2Br_6–HBr solution.[84] Our bands are thus not readily attributable to such a species. On the contrary, the positions of the bands seem to suggest that they arise from protonated, aromatic oligomers.[85] Protonated biphenyl, for instance, absorbs at 440 nm in HF–BF_3 solution.[86]

In hydrolysed $GaCl_3$–C_6H_3Me-1,3,5 solutions a greatly increased UV absorption and new bands at about 550 and 660 nm are found (Fig. 3). As in the benzene systems, the relatively long wavelengths involved suggest that protonated, oligomeric species are present. However, the intense UV absorption may be caused by protonated mesitylene, which absorbs at 355 nm in HF–BF_3 solution.[86]

Radiolysis.—Even if kept in the dark, the $GaCl_3$–C_6H_6 system slowly turns yellow (fresh solutions are colourless or, in the case of the most concentrated samples, very faintly yellow) over a period of several weeks. The $GaCl_3$–$C_6H_3Me_3$-1,3,5 solutions are yellow even when freshly prepared because of the intense charge-transfer transitions discussed above and the colour remains unchanged if the samples are kept in the dark. The rate of the colour change in the benzene solutions is greatly increased by the action of radiation (be it X-rays or visible light). The mesitylene is likewise affected as is apparent from the deepening of the yellow colour, which ultimately produces opaque solutions. Fig. 3 shows UV/VIS spectra recorded from radiolysed solutions of $GaCl_3$ in benzene and mesitylene. Radiolysis was effected by using light from a tungsten lamp. Since weak EPR signals at *g* about 2 are recorded from samples of both systems radiolysed with a mercury lamp, the UV/VIS bands emerging upon radiolysis may be attributed to radiolytically produced aromatic radicals or to oligomers or condensed aromatic species formed by a dehydrocoupling proceeding *via* a radical mechanism. In both the benzene and the mesitylene systems at least one UV/VIS absorption band seems to be present in *both* the radiolysed and hydrolysed solutions. This fact suggests that the radiolytic and the hydrolytic decompositions of the solutions have at least one reaction product in common.

Two EPR signals (both centred at *g* about 2) are detected in the radiolysed mesitylene solutions, whereas benzene only produces one. All peaks are weak, broad and without fine structure even at -70 °C and are thus inconclusive as to the nature of the radicals. The signal from the $GaCl_3$–C_6H_6 system was persistent even after the lamp had been switched off, and the same is true for one of the mesitylene signals. In the $GaCl_3$–C_6H_6 solutions the radiolysis also produces a small but narrow ^{71}Ga NMR signal at $\delta -996$, readily assigned to Ga^I, suggesting that Ga^{III} oxidizes benzene during radiolysis. For the same solutions the ^1H and ^{13}C NMR spectra contain no signals attributable to oligomeric benzene or mesitylene species and likewise no signals indicative of any isomerization or transalkylation of mesitylene. The most plausible conclusion therefore seems to be that the deepening colour is caused by radicals formed by a slow oxidation of benzene by Ga^{III} and that this mechanism is slightly different in the two solvents. The fact that no gallium(I) signal can be detected in the latter system may be a consequence of the slower reaction and the therefore lower concentration of Ga^I (below the limit of detection). Interestingly, in the absence of water no precipitation takes place in radiolysed $GaCl_3$–C_6H_6 solutions even after exposure to visible light for several months, although radicals are present. It is inferred that water is a necessary co-catalyst for polymer formation in this system.

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