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SYNTHESIS AND CRYSTAL STRUCTURE OF A MIXED BIS(ARENE)GALLIUM(I) COMPLEX: DIMERIC (η^6-1,2,4,5-TETRAMETHYLBENZENE) (η^6-TOLUENE)GALLIUM(I) TETRACHLOROGALLATE(III)

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Abstract—The title compound (η^6-1,2,4,5-tetramethylbenzene)(η^6-toluene)gallium(I) tetrachlorogallate(III) (**1**) crystallizes from dilute solutions of equimolar quantities of gallium(I) tetrachlorogallate(III) and 1,2,4,5-tetramethylbenzene (durene) in toluene on slow cooling to 0°C. More concentrated solutions yield the 1 : 1 complex (1,2,4,5-$C_6H_2Me_4$)$Ga^+GaCl_4^-$ (**2**). The crystals of compound **1** contain centrosymmetrical dimers, $\{[(\eta^6\text{-}C_6H_2Me_4)(\eta^6\text{-}C_6H_5Me)Ga]GaCl_4\}_2$, in which each gallium(I) centre is hexahapto-bonded to one durene and one toluene molecule. The two aromatic hydrocarbons of these bent-sandwich moieties form an interplane angle of 58°. With a metal-to-ring distance of 2.642 Å, the durene ring is much closer to the Ga^+ atom than the toluene ring (3.039 Å). The Ga^+ atoms are bridged via two slightly distorted $GaCl_4^-$ tetrahedra through contacts with three of the four chlorine atoms. The structure resembles that of the $[(C_6H_6)_2Ga]GaX_4$ complexes with X = Cl, Br.

Salts of the low-valent heavy Group 13 metal cations with counter-ions of low polarizability are unique in showing high solubility in aromatic hydrocarbons.[1] Extensive work in recent years has provided evidence that these phenomena have their origin in the formation of arene complexes of gallium(I), indium(I) and thallium(I), in which the metal is η^6-bonded to the aromatic system, i.e. with the metal positioned exactly above the ring centre in most cases.[2–7] Apart from the 1 : 1 stoichiometry with only one arene in the first coordination sphere of the metal, an increasing number of bent-sandwich complexes with a 2 : 1 ratio of arene-to-metal has been discovered. As a rule, the two aromatic rings show an interplane angle of *ca* 60° in these complexes, with counter-ion contacts of the metal roughly in the plane bisecting the interarene angle. This mode of coordination was first detected for the benzene adducts of $Ga[GaCl_4]$[2] and $Ga[GaBr_4]$,[3] but has meanwhile also been found even in complex networks with donors like the small cyclophanes.[8–9] Compounds of the alternative 1 : 2 stoichiometry arene–metal, with a metal on both sides of a given arene ring, seems to be restricted to the neighbouring elements in Groups 14 and 15.[10] An extreme situation of arene coordination has been reached in the complex of gallium(I) with the large-ring [2,2,2]-paracyclophane, however, where the metal is no less than η^{18}-bonded to the carbon atoms of three benzene rings.[11]

We report here the synthesis and structure determination of a dimeric bent-sandwich gallium(I) complex, in which each metal is η^6-coordinated to two benzene molecules with a different pattern of methyl substitution. This complex is of interest since it allows a direct comparison of metal bonding to ligands with different donor capacity, as determined by the inductive effect of the substituents. There is only one precedent for this situation,[12] with both toluene and hexaethylbenzene present at the gallium(I) centre. The extreme steric crowding at the C_6Et_6 ligand makes this example rather special, however, and a study was therefore initiated with ligand combinations where the steric bulk should play a minor rôle.

SYNTHESIS AND PROPERTIES OF COMPLEXES

Gallium(I) tetrachlorogallate(III) dissolves readily in anhydrous toluene to give a solution probably

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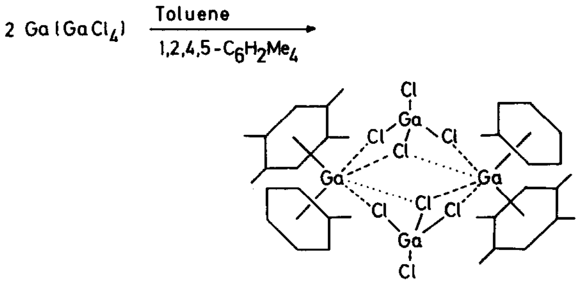
containing toluene complexes of unknown stoichiometry and structure which have not yet been isolated. Ga[$GaCl_4$] can also be dissolved in solutions of 1,2,4,5-tetramethylbenzene (durene) in toluene on heating. Rapid cooling of these mixtures containing high concentrations of durene and the gallium salt to room temperature leads to the separation of a heavy liquid phase which is difficult to crystallize. Slow cooling to *ca* 0°C (refrigerator) gives a fine microcrystalline precipitate which analyses as the 1 : 1 complex of durene and Ga[$GaCl_4$], m.p. 15–16°C. Its structure could not be determined. From dilute solutions in toluene a macrocrystalline product can be crystallized on cooling to 0°C, whose microanalysis data indicate the presence of the title compound with mixed arenes present (m.p. 5°C). The transparent, colourless crystals are extremely hygroscopic, and decomposition starts immediately on contact with air. The black colour developed, thereby, indicates disproportionation to metallic gallium. The ^1H NMR spectrum of benzene solutions shows the resonances of toluene and durene in a 1 : 1 molar intensity ratio.

Experiments with benzene–durene mixtures gave only oily products which were not characterized any further.



DETERMINATION AND DESCRIPTION OF THE CRYSTAL STRUCTURE

A single crystal X-ray diffraction study of the compound confirmed the stoichiometry inferred from analytical and spectroscopic data. Details of the structure determination and crystal data are summarized in Table 1. Selected interatomic distances and angles are presented in Table 2.

The analysis has shown that the complex forms discrete molecules composed of two formula units related by a centre of symmetry (Fig. 1). The packing of the molecules in the unit cell is displayed in Fig. 2. There are no specific contacts between the dimers, and no extra interstitial hydrocarbon—a common phenomenon in Group 13 arene crystal chemistry—could be detected.

The molecular structure of the title compound is very similar to that of the $[(C_6H_6)_2Ga(GaX_4)]_2$ units in the two crystalline phases $[(C_6H_6)_2Ga(GaX_4)]_2 \cdot (C_6H_6)_3$ with X = Cl, Br.[2,3] Apart from the absence of an interstitial hydrocarbon, the main variation stems from the fact that two different arenes are present at each metal(I) centre. The structure thus features two heteroleptic bent-sandwich moieties with interplane angles of 58°, a value typical for this class of compounds.[1]

The most important structural detail is the finding that the metal-to-arene distances are significantly different at each unit, with the durene ring much closer to the metal than the toluene ring (2.642 vs 3.039 Å!). This result is in contrast to expectations on steric grounds (with durene as the more bulky ligand as compared to toluene), and must imply that durene is much more tightly bonded than toluene for electronic reasons.

A simplified molecular orbital description of bonding[1,12] proposes a charge transfer from the arene to the metal, which should be enhanced by electron-donating substituents like methyl groups. This would allow durene to overrule toluene as a donor ligand, especially since its site symmetry is more favourable than that of the toluene competitor (C_{2v} as compared to C_s for durene and toluene, respectively). Along with the differences in metal-to-ring distances, the positioning of the gallium(I)

Table 1. Crystal data and structure solution of the compound $\{[(\eta^6\text{-}1,2,4,5\text{-}C_6H_2Me_4)(\eta^6\text{-}C_6H_5Me)Ga]GaCl_4\}_2$

Formula	$C_{17}H_{22}Ga_2Cl_4$
M_r	507.617
Space group	$P\bar{1}$ (No. 2)
a (Å)	9.821(1)
b (Å)	11.214(1)
c (Å)	11.287(1)
α (°)	90.59(1)
β (°)	115.11(1)
γ (°)	101.56(1)
V (Å^3)	1096.4
Z	2
ρ_{calc} (g cm^{-3})	1.537
μ (Mo-K_α) (cm^{-1})	29.4
T (°C)	−60
Number of measured reflections	4302
Number of unique reflections	4272
Number of observed reflections	3030
Number of refined parameters	208
R^a	0.044
R^b_w	0.037
$\Delta\rho_{final}$ (e/Å^3) (max/min)	+0.64/−0.63

[a] $R = \Sigma(\|F_o\| - \|F_c\|)/\Sigma|F_o|$.

[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$, $w = 1/\sigma^2(F_o)$.

Table 2. Selected bond distances (Å) and angles (°) in the compound $\{[(\eta^6\text{-}1,2,4,5\text{-}C_6H_2Me_4)(\eta^6\text{-}C_6H_5Me)Ga]GaCl_4\}_2$

Ga(1)—Cl(1)	2.173(1)	Ga(2)—Cl(1)	3.259(1)
Ga(1)—Cl(2)	2.162(1)	Ga(2)—Cl(2)	3.109(1)
Ga(1)—Cl(3)	2.160(2)	Ga(2)—Cl(3*)	3.370(2)
Ga(1)—Cl(4)	2.148(2)	Ga(2)—Cl(1*)	3.991(2)
Ga(2)—E(1)$_{\text{tmbz}}$	2.642	Ga(1)—Ga(2)	3.952(5)
Ga(2)—E(2)$_{\text{tol}}$	3.039	Ga(2)—Ga(2*)	6.194(6)
Ga(2)—C(11)	2.971(4)	Ga(2)—C(21)	3.339(5)
Ga(2)—C(12)	2.965(4)	Ga(2)—C(22)	3.216(5)
Ga(2)—C(13)	2.976(4)	Ga(2)—C(23)	3.210(5)
Ga(2)—C(14)	3.022(4)	Ga(2)—C(24)	3.331(6)
Ga(2)—C(15)	3.016(4)	Ga(2)—C(25)	3.445(6)
Ga(2)—C(16)	2.980(4)	Ga(2)—C(26)	3.444(6)
Cl(1)—Ga(1)—Cl(2)	107.0(1)	Cl(2)—Ga(2)—Cl(3*)	131.83(1)
Cl(1)—Ga(1)—Cl(3)	109.1(1)	Cl(1)—Ga(2)—E(1)	109.32
Cl(1)—Ga(1)—Cl(4)	111.3(1)	Cl(1)—Ga(2)—E(2)	143.81
Cl(2)—Ga(1)—Cl(3)	110.7(1)	Cl(2)—Ga(2)—E(1)	109.32
Cl(2)—Ga(1)—Cl(4)	109.2(1)	Cl(2)—Ga(2)—E(2)	94.47
Cl(3)—Ga(1)—Cl(4)	109.5(1)	Cl(3*)—Ga(2)—E(1)	104.47
Cl(1)—Ga(2)—Cl(2)	66.33(1)	Cl(3*)—Ga(2)—E(2)	98.43
Cl(1)—Ga(2)—Cl(3*)	76.46(1)	E(1)—Ga(2)—E(2)	118.67

Interarene angle 58.0.
E : centres of the arenes.

centre above each ring is also not the same, as can be shown by the angles between the normals to the planes and the line connecting the arene centres with the metal (1.3 and 6.7°, respectively). Durene is closer to true η^6-bonding than toluene. It remains an intriguing observation, however, that the benzene molecules in the $(C_6H_6)_2Ga^+GaX_4^-$ complexes show non-equivalent bonding to the metal as judged from significant differences in metal–arene distances in both phases (X = Cl, Br).[2,3] There is no obvious explanation for this deviation from an equivalent interaction, though distortion of the highest

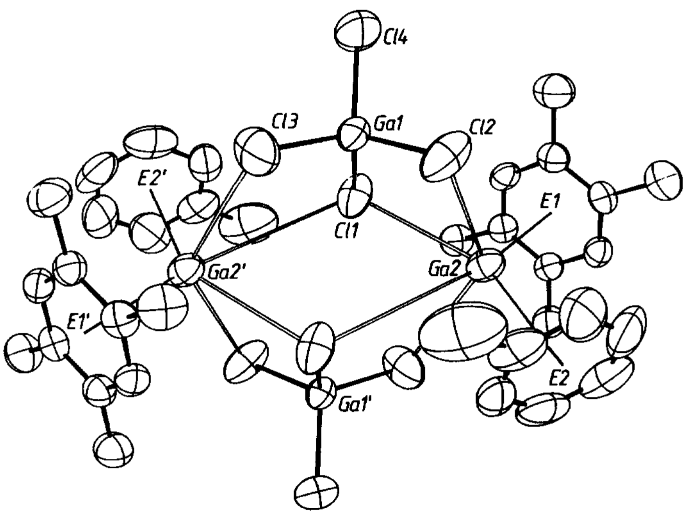


Fig. 1. Molecular structure and atomic numbering of the title compound (ORTEP, 50% probability; the atoms are related by a centre of symmetry).

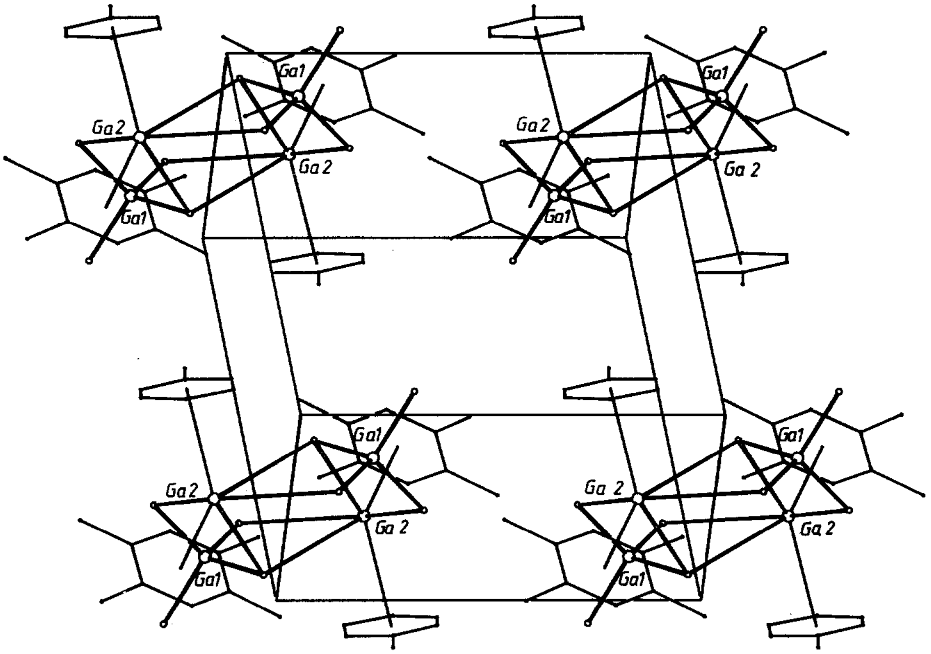


Fig. 2. Molecular packing of the molecules in the unit cell of the title compound (**1**).

symmetry has been shown to be associated with a gain in energy in various related and unrelated species.[13] The complexity of the present systems has discouraged us to produce any more detailed analyses.

The tetramethylbenzene–gallium(I) distance in the title compound (**1**) is the shortest found in bis (arene)gallium(I) complexes, and the toluene–gallium(I) distance is shorter than that in the mixed (toluene)(hexaethylbenzene)gallium(I) complex. These relations show the strengthening influence of an increase in methyl substitution for the *ipso*-ring bonding on one hand, and the weakening effect for the bonding of neighbouring arene ligands on the other. Relatively long C_6H_5Me–Ga^I and C_6Et_6–Ga^I distances (2.960/3.145 Å) in the mixed C_6H_5Me/C_6Et_6 complex appear to be of steric origin,[8] however. 2 : 1 complexes of gallium(I) with penta- or hexamethylbenzene have not yet been observed, probably due to severe steric interactions of the methyl substituents in a bent-sandwich structure.

The two Ga^+ centres of the dimers are bridged by two $GaCl_4^-$ tetrahedra through contacts with all but one of the chlorine atoms at each anion (Fig. 1). Three of these contacts, the distances Cl(2)—Ga(2) (3.109(1) Å), Cl(1)—Ga(2) (3.259(1) Å) and Cl(3)—Ga(2*) (3.370(2) Å) are much shorter than the fourth one, Cl(1)—Ga(2) = 3.991(2) Å, which originates from a bridgehead position of Cl(1). Taking into account only the short contacts, the structure is based on an eight-membered ring with the sequence of atoms Ga(2)—Cl(2)—Ga(1)—Cl(3)—Ga(2*)—Cl(2*)—Ga(1*)—Cl(3*). This pattern is not only present in the bis(benzene)gallium(I) complexes,[2,3] but also in a bis(arene) complex of tin(II) reported recently[14] from this laboratory.

As expected, the $GaCl_4^-$ tetrahedra in the title complex are distorted with minor deviations of the Cl—Ga(1)—Cl angles from the tetrahedral norm, and with a variation of the Ga(1)—Cl distances within narrow limits (Table 2). The non-bridging chlorine atom Cl(4) has the shortest distance to Ga(1) (2.148(2) Å), while Cl(1) with its bridgehead function has the largest (2.173(1) Å).

With Cl(1) considered as a ligand to Ga(2) and Ga(2*), the environment of Ga^+ can be described as distorted octahedral (trigonal-antiprismatic), as indicated by an almost parallel orientation of the planes Cl(1)—Cl(2)—E(1)(centre of durene) and Cl(1*)—Cl(3*)—E(2)(centre of toluene).

EXPERIMENTAL

General

All experiments were carried out under an atmosphere of pure dry nitrogen. Glassware, as well as solvents and reagents, were treated accordingly. Gallium metal was received from Preussag AG and converted to $Ga[GaCl_4]$ by following literature procedures.[15]

(η^6 - 1,2,4,5 - *Tetramethylbenzene*)(η^6 - *toluene*) *gallium*(I) *tetrachlorogallate*(III)

Gallium(I) tetrachlorogallate(III) (1.88 g, 6.68 mmol) and durene (0.9 g, 6.68 mmol) were dissolved in 20 cm^3 of toluene and heated under reflux for 1 h. On slow cooling to 0°C crystallization occurred after a few days. The mother liquor was decanted and the colourless crystalline product dried in a stream of dry nitrogen. Yield 2.58 g (76%), m.p. 5°C.

^{1}H NMR (C_6D_6): $\delta = 2.20$, s, 3H (*Me*Ph); 2.30, s, 12H ($C_6H_2Me_4$); 6.9, m, 5H (Me*Ph*); 7.05, s, 2H ($C_6H_2Me_4$). ^{71}Ga NMR (C_6D_6): $\delta = -680$ ppm rel. $Ga(NO_3)_3$ in aqueous HNO_3, s. $C_{17}H_{22}Ga_2Cl_4$ (507.62): Found: C, 39.7; H, 4.1. Calc. C, 40.2; H, 4.3%.

(η^6 - 1,2,4,5 - *Tetramethylbenzene*)*gallium*(I) *tetrachlorogallate*(III)

A solution of the same components in toluene at higher concentrations (1.40 mol dm^{-3}) yielded a microcrystalline precipitate on cooling to 0°C in *ca* 80% yield (m.p. 15–16°C). $C_{10}H_{14}Ga_2Cl_4$ (415.48): Found: C, 27.2; H, 3.15. Calc. C, 28.9; H, 3.4.

Structure determination of $\{[(\eta^6\text{-}1,2,4,5\text{-}C_6H_2Me_4)(\eta^6\text{-}C_6H_5CH_3)Ga]GaCl_4\}_2$

A suitable crystal was sealed in a capillary under argon at −60°C and mounted on a CAD-4 diffractometer (Mo-K_α radiation, graphite monochromator, $\lambda = 0.71069$ Å). Crystal data and details of the structure determination are summarized in Table 1. The integrated intensities of the reflections were corrected for Lorentz polarization and empirically for absorption effects (relative transmission 0.76–1.00; $(\sin \vartheta/\lambda)_{max} = 0.616$ Å^{-1}, *hkl*: 14, ±14, ±14; ϑ–2ϑ scan, $\Delta\omega = 0.8 + 0.35 \tan \vartheta$). The structure was solved by direct methods (SHELXS-86). Thirteen out of a total of 22 hydrogen atoms could be located in difference Fourier maps, the remainder were calculated at idealized positions. In the refinement with anisotropic displacement parameters the hydrogen atoms were included in constant positions ($U_{iso} = 0.05$ Å^2). The maxima of the residual electron density and the relatively large displacement parameters of the toluene carbon atoms suggested a minor disorder of this molecule, which was too small, however, to justify treatment using a split model. A similar situation was encountered in the structure of $[(\eta^6\text{-}C_6Et_6)(\eta^6\text{-}C_6H_5Me)Ga]Cl_4$.[12] Further crystal structure data have been deposited.*

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