

# Isolation and Crystal Structure of $[(C_6H_6)_2GaGaCl_4]_2 \cdot 3C_6H_6$ , a Bis( $\eta^6$ -benzene)gallium(I) Complex<sup>†</sup>

Hubert Schmidbaur,<sup>\*</sup> Ulf Thewalt,<sup>‡</sup> and Theodore Zafiropoulos<sup>§</sup>

Anorganisch-Chemisches Institut, Technische Universität München,  
D 8046 Garching, Federal Republic of Germany

Received April 29, 1983

Under carefully controlled conditions a discrete phase of the composition  $(C_6H_6)_{3.5}Ga_2Cl_4$  can be crystallized from solutions of  $Ga_2Cl_4$  in anhydrous benzene. The complex was characterized by X-ray crystallography. It crystallizes in the triclinic space group  $C_1^1-P\bar{1}$  with lattice constants (at  $-50 \pm 5^\circ C$ ) of  $a = 9.294$  (2) Å,  $b = 10.691$  (3) Å,  $c = 12.791$  (3) Å,  $\alpha = 85.57$  (2)°,  $\beta = 103.15$  (2)°, and  $\gamma = 106.26$  (2)°. The fundamental unit, corresponding to  $Z = 2$ , contains  $(C_6H_6)_2GaGaCl_4 \cdot 1.5C_6H_6$ . The crystal structure can be described as consisting of cyclic centrosymmetrical  $[(C_6H_6)_2Ga^I-Ga^{III}Cl_4]_2$  units and isolated benzene molecules. In the bis(benzene)gallium(I) moieties the two  $\eta^6$ -benzene rings form an interplane angle of  $124.4^\circ$ . Two distorted tetrachlorogallate tetrahedra provide single- or double-bridging chlorine atoms to the Ga(I) centers. The remaining benzene molecules are interstitial solvate components. 1 is the first structurally characterized benzene complex of a univalent group 3A metal. The Ga-C distances range from 3.015 to 3.154 Å (ring B) and from 3.186 to 3.291 Å (ring A). The Ga(I) atom is located 2.758 and 2.926 Å above the ring planes B and A, respectively. The material is closely related to the benzene complexes of Sn(II) and Pb(II) described previously.

## Introduction

The nature of compounds of gallium in the formal oxidation state  $+II^1$  is a classical problem in inorganic and organometallic chemistry.<sup>2</sup> As early as 1932 Klemm and Tilk<sup>3</sup> in their fundamental magnetochemical studies reached the conclusion that materials of the net stoichiometry  $GaX_2$  ( $X = \text{halogen}$ ) may either be present as  $Ga^I Ga^{III} X_4$  mixed-valence species or as  $X_2 Ga-GaX_2$  dimers with covalent metal-metal bonding. Both concepts would account for the diamagnetism observed for all Ga(II) compounds. Klemm and Tilk originally favored the Ga-Ga bonded alternative, which in fact was found later, e.g., in the layer structure of GaS by Hahn and Frank.<sup>4</sup> Detailed Raman,<sup>5,6</sup> infrared,<sup>7</sup> X-ray diffraction,<sup>8</sup> and electrochemical studies<sup>9</sup> have provided conclusive evidence, however, that all gallium dihalides are mixed-valence compounds,  $Ga[GaX_4]$ , both in the crystalline state and in the melt. These unambiguous findings for some time seemed to settle the case once and for all in favor of the  $Ga^I Ga^{III}$  formula, at least for the binary halide systems. The more recent discoveries that complex salts  $M_2^I [Ga_2Cl_6]^{10-13}$  and neutral complexes like  $Ga_2Cl_4 \cdot 2dioxane^{14}$  have, very unexpectedly, the metal-metal bonded  $Ga^{II}-Ga^{II}$  structure have made it quite clear that there may well be a much larger variety of metal-metal bonded species than previously assumed. Kraus and Toonder<sup>15</sup> had postulated an ethane-like structure (Ga-Ga) for the anion  $[Me_3GaGaMe_3]^{2-}$  obtained in the alkali-metal reduction of  $GaMe_3$  ( $Me = \text{methyl}$ ).

Most intriguing to all workers active in the chemistry of low-valent gallium also was the appreciable solubility of  $GaCl_2$  and  $GaBr_2$  in benzene and other aromatic solvents. Physical measurements gave confusing results about the interaction of the solvent molecules with the solute, which is known to be  $Ga^+ GaX_4^-$  in the solid state<sup>8</sup> but might well transform to  $X_2 GaGaX_2$  in solution as in the case of the dioxane complex. The benzene solution of

$GaCl_2$  is nonconducting,<sup>16</sup> whereas fused solvates are good ionic conductors. Molecular weight and dipole moment data are indicative of ion pairs in solution.<sup>17</sup> Vibrational spectra are in agreement with the presence of  $GaCl_4^-$  anions<sup>17</sup> with a symmetry reduced to  $C_{2v}$  or lower, probably forming Cl bridges to the  $Ga^+$  cation,<sup>7</sup> the latter most likely being engaged in bonding to benzene.<sup>18</sup> Phase diagram studies have shown that the system  $GaBr_2/\text{benzene}$  contains the discrete materials  $Ga_2Br_4 \cdot C_6H_6$  and  $Ga_2Br_4 \cdot 3C_6H_6$ .<sup>19</sup> The exact stoichiometries of phases in the system  $GaCl_2/C_6H_6$  do not appear to have been determined, and only a 1:1 complex has been considered throughout the pertinent literature.<sup>7,16-20</sup> Attempts to solve the crystal structure of such a phase, described as at least pseudo-hexagonal ( $a = 11.89$ ,  $c = 30.05$  Å,  $Z \approx 12$ ), have not been successful.<sup>18</sup> A  $C_6H_6 Ga^+$  cation with hexagonal symmetry was inferred as a possible constituent.<sup>7,18</sup> As part of a program in the chemistry of organogallium compounds<sup>21-23</sup>

- (1) de Boisbaudran, L. C. R. *Hebdomadaire des Seances Acad. Sci.* 1881, 93, 294.
- (2) Sheka, I. A.; Chans, I. S.; Mityureva, T. T. "The Chemistry of Gallium"; Elsevier: Amsterdam, London, New York, 1966. Greenwood, N. N. *Adv. Inorg. Chem. Radiochem.* 1963, 5, 91.
- (3) Klemm, W.; Tilk, T. Z. *Anorg. Chem.* 1932, 207, 175.
- (4) Hahn, H.; Frank, G. Z. *Anorg. Chem.* 1955, 278, 333. Schubert, K.; Dorre, E. *Naturwissenschaften* 1953, 40, 604.
- (5) Woodward, L. A.; Garton, G.; Roberts, H. J. *Chem. Soc.* 1956, 3723.
- (6) Woodward, L. A.; Greenwood, N. N.; Hall, J. R.; Worrall, I. J. *J. Chem. Soc.* 1958, 1505.
- (7) Kinsella E.; Chadwick, J.; Coward, J. J. *Chem. Soc. A* 1968, 969.
- (8) Garton, G.; Powell, H. M. *J. Inorg. Nucl. Chem.* 1957, 4, 84.
- (9) Greenwood, N. N.; Worrall, I. J. *J. Chem. Soc.* 1958, 1680.
- (10) Evans, C. A.; Tan, K. H.; Tapper, S. P.; Taylor, M. J. *J. Chem. Soc., Dalton Trans.* 1973, 988.
- (11) Tan, K. H.; Taylor, M. J. *J. Inorg. Nucl. Chem. Lett.* 1974, 10, 267.
- (12) Brown, K. L.; Hall, D. *J. Chem. Soc., Dalton Trans.* 1973, 1843.
- (13) Cumming, H. J.; Hall, D.; Wright, C., as quoted in ref 11.
- (14) Beamish, J. C.; Small, R. W. H.; Worrall, I. J. *Inorg. Chem.* 1979, 18, 220.
- (15) Kraus, C. A.; Toonder, F. E. *J. Am. Chem. Soc.* 1933, 55, 3547.
- (16) Ali, S. M.; Brewer, F. M.; Chadwick, J.; Carton, G. *J. Inorg. Nucl. Chem.* 1959, 9, 124.
- (17) McMullan, R. K.; Corbett, J. D. *J. Am. Chem. Soc.* 1958, 80, 4761.
- (18) Rundle, R. E.; Corbett, J. D. *J. Am. Chem. Soc.* 1957, 79, 757.
- (19) Oliver, J. G.; Worrall, I. J. *Inorg. Nucl. Chem. Lett.* 1967, 3, 575.
- (20) Carlston, R. C.; Griswold, E.; Kleinberg, J. *J. Am. Chem. Soc.* 1958, 80, 1532.

<sup>†</sup> Dedicated to Professor Ernst Otto Fischer on the occasion of his 65th birthday.

<sup>‡</sup> Visiting professor from the University of Ulm, Ulm, West Germany.

<sup>§</sup> A. v. Humboldt Fellow 1983-1984, University of Patras, Patras, Greece.

and other mixed oxidation state organometallics,<sup>24</sup> we have reinvestigated the GaCl<sub>2</sub>/benzene system and report here on the preparation and crystal structure of the most benzene-rich phase Ga<sub>2</sub>Cl<sub>4</sub>·3.5C<sub>6</sub>H<sub>6</sub>. Twenty years ago, the interaction between Ga(I) and benzene was also considered in the pioneering investigations on metal arene complexes carried out in this institute.<sup>25</sup>

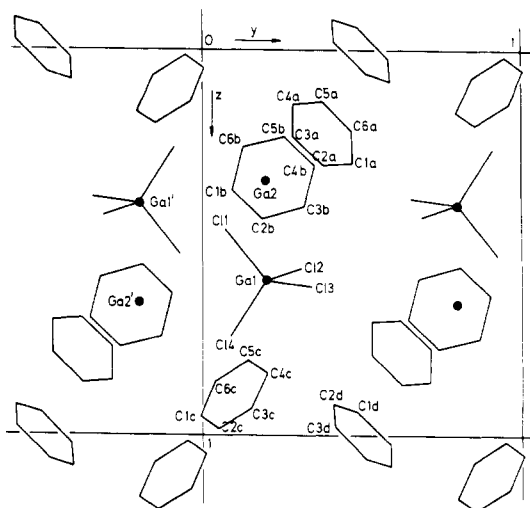
## Experimental Section

**General Data.** All experiments were carried out under an atmosphere of pure and dry nitrogen. Glassware was dried at 140 °C and filled with nitrogen. Benzene was first dried over sodium/acetophenone, distilled from the residues under nitrogen and kept saturated with nitrogen over molecular sieves (4 Å). Gallium metal was a generous gift of Siemens AG, Erlangen (99.999% pure); mercurous chloride was analytical grade (Merck AG, Darmstadt, p.a.).

**Synthesis of Gallium Dichloride.**<sup>20</sup> A 53.38-g sample of Hg<sub>2</sub>Cl<sub>2</sub> (11.3 mmol) was placed in a two-necked flask, which then was evacuated and refilled with nitrogen 3–4 times. Ga metal (7.88 g, 11.3 mmol) then was added dropwise from a heated dropping funnel. An exothermic reaction ensued immediately. The reaction mixture was finally heated to 100 °C for 2 h in order to bring the reaction to completion. After the mixture was cooled to room temperature, 80 mL of benzene was added, which left mercury metal and impurities undissolved. The benzene phase was filtered through a glass frit under nitrogen. A 45.69-g sample of impure mercury was recovered (calcd 45.33 g). Local cooling with dry ice (–78 °C) caused precipitation of a crystalline, colorless material from the benzene solution, which was allowed to proceed further on storing the flask at ca. 15 °C for 2 days. The crystals were filtered and dried in vacuo at 25 °C for 15 h; yield ca. 10 g (63%); mp 170 °C (lit. 172 °C,<sup>9,26</sup> 170 °C,<sup>2,8</sup> 171 °C,<sup>17</sup> 175–176 °C (corr)).<sup>20</sup> Anal. Calcd for GaCl<sub>2</sub> (140.62): Cl, 50.41. Found: Cl, 50.13.

**Growing of Single Crystals of (Ga<sub>4</sub>Cl<sub>5</sub>·4C<sub>6</sub>H<sub>6</sub>)·3C<sub>6</sub>H<sub>6</sub>.** A 2.4-g sample of GaCl<sub>2</sub> (17.1 mmol) was slowly dissolved in 80 mL of benzene with gentle heating and agitation. When the resulting clear colorless solution was kept at temperatures between 15 and 20 °C, large crystals of the new phase separated, which were isolated by decantation. When the material was kept in a flask in the presence of a saturated solution, no benzene was lost and the crystals remained transparent and gave perfectly acceptable diffraction patterns. Crystal drying must not be attempted by lowering the pressure, as any loss of benzene in vacuo leads to phase changes and deterioration of crystal quality. It should be noted that the alleged 1:1 complex Ga<sub>2</sub>Cl<sub>4</sub>·C<sub>6</sub>H<sub>6</sub> is reported<sup>20</sup> to be obtained from GaCl<sub>2</sub> solutions in benzene upon removal of the solvent by pumping at –5 °C. No details are available about the preparative procedure for the crystals used in the previous preliminary X-ray studies<sup>18</sup> on Ga<sub>2</sub>Cl<sub>4</sub>·C<sub>6</sub>H<sub>6</sub>.

**X-ray Crystallographic Study.** Crystals of [(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>Ga·GaCl<sub>4</sub>]<sub>2</sub>·3C<sub>6</sub>H<sub>6</sub> are colorless and transparent and of isometric habitus. A crystal of dimension 0.20, 0.25, and 0.28 mm was mounted under argon at dry ice temperature in a Lindemann glass capillary. All X-ray measurements were made on a Syntex P2<sub>1</sub> diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.71069 Å). The following cell parameters of the triclinic crystal were determined by a least-squares fit of the parameters of the orientation matrix to the setting angles of 15 reflections (at –50 ± 5 °C): a = 9.294 (2) Å, b = 10.691 (3) Å, c = 12.791 (3) Å, α = 85.57 (2)°, β = 103.15 (2)°, and γ = 106.26 (2)°; the space group is P $\bar{1}$  (confirmed by the successful determination and refinement



**Figure 1.** Projection of the crystal structure of [(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>Ga·GaCl<sub>4</sub>]<sub>2</sub>·3C<sub>6</sub>H<sub>6</sub> down the x axis.

of the structure in this space group);  $d_{\text{calcd}} = 1.551 \text{ g cm}^{-3}$  for  $Z = 1$  (referred to the formula [(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>Ga·GaCl<sub>4</sub>]<sub>2</sub>·3C<sub>6</sub>H<sub>6</sub>) and a mol wt. of 1109.30.

**Intensity data:**  $\omega$  scans; scan rate  $\dot{\omega}$  between 1.2 and 29.3° min<sup>-1</sup>, depending on the intensity of a preliminary scan; scan width, 1°; time spent for measuring background intensities at each end of the scan interval, half of scan time; 3731 reflections ( $\pm h, \pm k, \pm l$ ) measured out to  $2\theta_{\text{max}} = 48^\circ$ ; one standard reflection counted after 50 measurements; there was no significant change in its intensity; an empirical correction for absorption was applied ( $\mu = 28.2 \text{ cm}^{-1}$ ) by using  $\phi$  scans for 10 reflections having  $2\theta$  values between 5° and 46° and  $\chi$  settings near 270°; data reduction, intensity  $I = (S - B/\beta)\dot{\omega}$  and  $\sigma(I) = (S - B/\beta^2)^{1/2}\dot{\omega}$  (scan counts, S; total background counts, B; time ratio of total background to scan,  $\beta$ ). The set of 3401 reflections with  $I > 0.7\sigma(I)$  was used in the subsequent calculations;  $F_o = (I/Lp)^{1/2}$  and  $\sigma(F_o) = \sigma(I)/(2F_oLp)$ .

The positions of the gallium atoms were determined from a Patterson synthesis. A subsequent difference Fourier map revealed the positions of the Cl and C atoms. After refinement of the positional and anisotropic thermal parameters of the Ga, Cl, and C atoms, all hydrogen atoms could be located in a  $\Delta F$  map. Least-squares refinement including the H atoms with individual isotropic thermal parameters was continued to convergence at  $R = 0.040$  and  $R_w = 0.041$  ( $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $R_w = \sum (||F_o| - |F_c||) (w)^{1/2} / (\sum |F_o| (w)^{1/2})$  with  $w = 1.855 / (\sigma^2(F) + 0.0004F^2)$ ).

Scattering factors for neutral non-hydrogen atoms were taken from Cromer and Mann<sup>27</sup> and for hydrogen from Stewart.<sup>28</sup> Corrections for  $\Delta f'$  and  $\Delta f''$  were applied.<sup>29</sup> Final positional and thermal parameters are given in Table I. Form of the anisotropic temperature factor:  $U = \exp(-2\pi^2[U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*])$ ;  $U_{ij}$  in Å<sup>2</sup>. Tables of structure factors have been deposited. Programs used: Shelx-76 program package<sup>30</sup> and OTTO (geometry program).<sup>31</sup>

## Results and Discussion

Slow crystallization from saturated benzene solutions of Ga[GaCl<sub>4</sub>] at room temperature affords large, transparent, air-sensitive crystals, the composition of which corresponds to the formula Ga<sub>2</sub>Cl<sub>4</sub>·3.5C<sub>6</sub>H<sub>6</sub> or [(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>Ga·GaCl<sub>4</sub>]<sub>2</sub>·3C<sub>6</sub>H<sub>6</sub> (1) as shown by X-ray diffraction data (below). This phase has not been observed previously, but a stoichiometry Ga<sub>2</sub>Br<sub>4</sub>·3C<sub>6</sub>H<sub>6</sub> has already been reported for the analogous Ga[GaBr<sub>4</sub>]/benzene system.<sup>19</sup> 1 loses

(21) Schmidbauer, H.; Lauteschläger, S.; Milewski-Mahrla, B. *Chem. Ber.* **1983**, 166.

(22) Schmidbauer, H.; Müller, G. *Monatsh. Chem.* **1980**, 111, 1233.

(23) Schmidbauer, H.; Füller, H.-J. *Chem. Ber.* **1977**, 110, 3528. Schmidbauer, H.; Gasser, O.; Krüger, C.; Sekutowski, J. C. *Ibid.* **1977**, 110, 3517. Schmidbauer, H.; Füller, H.-J. *Ibid.* **1974**, 107, 3674.

(24) Schmidbauer, H. *Adv. Inorg. Chem. Radiochem.* **1982**, 25, 239.

(25) Fischer, E. O.; Fritz, H. P.; Manhot, J. Dissertation TU, Munich, 1963.

(26) Beamish, J. C.; Wilkinson, M.; Worrall, I. J. *Inorg. Chem.* **1978**, 17, 2026.

(27) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, 18, 105.

(28) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, 42, 3175.

(29) Cromer, D. T. *Acta Crystallogr.* **1965**, 18, 17.

(30) Sheldrick, G. M. University of Göttingen, Shelx-76 Programsystem.

(31) Thewalt, U. University of Ulm.

Table I. Atomic Parameters for  $[(C_6H_6)_2GaGaCl_4]_2 \cdot 3C_6H_6$ 

atom	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Ga(1)	0.72393 (4)	0.20695 (4)	0.59966 (3)	0.0285 (2)	0.0281 (2)	0.0276 (2)	0.0076 (2)	0.0064 (2)	-0.0004 (2)
Ga(2)	0.39033 (5)	0.20143 (4)	0.34327 (4)	0.0347 (2)	0.0458 (3)	0.0443 (3)	0.0080 (2)	0.0077 (2)	-0.0056 (2)
Cl(1)	0.68247 (11)	0.07797 (10)	0.46624 (8)	0.0477 (6)	0.0388 (5)	0.0383 (5)	0.0097 (4)	0.0091 (4)	-0.0115 (4)
Cl(2)	0.54952 (12)	0.31385 (10)	0.56941 (8)	0.0437 (6)	0.0492 (6)	0.0442 (6)	0.0252 (5)	0.0062 (5)	-0.0048 (5)
Cl(3)	0.94654 (11)	0.34459 (10)	0.61689 (9)	0.0344 (5)	0.0439 (6)	0.0524 (6)	-0.0016 (4)	0.0115 (5)	-0.0098 (5)
Cl(4)	0.70677 (13)	0.09228 (10)	0.74644 (8)	0.0599 (6)	0.0455 (6)	0.0342 (5)	0.0154 (5)	0.0149 (5)	0.0092 (4)
C(1a)	0.6293 (5)	0.4746 (4)	0.2954 (3)	0.053 (3)	0.034 (2)	0.046 (3)	-0.005 (2)	0.013 (2)	-0.008 (2)
C(2a)	0.7095 (4)	0.3821 (4)	0.3023 (3)	0.031 (2)	0.048 (3)	0.046 (3)	-0.003 (2)	0.008 (2)	0.003 (2)
C(3a)	0.6685 (5)	0.2906 (4)	0.2232 (4)	0.042 (2)	0.043 (2)	0.059 (3)	0.011 (2)	0.023 (2)	0.002 (2)
C(4a)	0.5459 (5)	0.2898 (4)	0.1390 (3)	0.049 (3)	0.049 (3)	0.042 (3)	-0.002 (2)	0.015 (2)	-0.017 (2)
C(5a)	0.4665 (5)	0.3814 (4)	0.1325 (4)	0.044 (3)	0.050 (3)	0.045 (3)	0.002 (2)	0.001 (2)	0.001 (2)
C(6a)	0.5079 (5)	0.4737 (4)	0.2109 (4)	0.050 (3)	0.035 (2)	0.056 (3)	0.011 (2)	0.013 (2)	0.004 (2)
C(1b)	0.0601 (5)	0.0999 (4)	0.3622 (4)	0.033 (2)	0.037 (2)	0.084 (4)	0.004 (2)	0.025 (2)	0.006 (2)
C(2b)	0.1179 (5)	0.1958 (5)	0.4367 (4)	0.052 (3)	0.066 (3)	0.048 (3)	0.022 (2)	0.029 (2)	0.011 (2)
C(3b)	0.1579 (5)	0.3240 (4)	0.4051 (4)	0.050 (3)	0.051 (3)	0.048 (3)	0.018 (2)	0.015 (2)	-0.015 (2)
C(4b)	0.1392 (5)	0.3568 (4)	0.2985 (4)	0.053 (3)	0.042 (2)	0.049 (3)	0.027 (2)	0.010 (2)	0.003 (2)
C(5b)	0.0813 (5)	0.2622 (5)	0.2233 (4)	0.049 (3)	0.071 (3)	0.041 (3)	0.036 (2)	0.010 (2)	-0.001 (2)
C(6b)	0.0412 (5)	0.1331 (5)	0.2541 (4)	0.029 (2)	0.058 (3)	0.070 (3)	0.012 (2)	-0.006 (2)	-0.032 (3)
C(1c)	0.2994 (5)	-0.0032 (4)	0.9531 (4)	0.033 (2)	0.043 (3)	0.066 (3)	0.010 (2)	0.003 (2)	0.007 (2)
C(2c)	0.2016 (5)	0.0510 (4)	0.9852 (3)	0.036 (2)	0.058 (3)	0.032 (2)	0.003 (2)	0.004 (2)	0.003 (2)
C(3c)	0.1596 (5)	0.1547 (4)	0.9317 (4)	0.041 (2)	0.042 (3)	0.060 (3)	0.011 (2)	0.010 (2)	-0.009 (2)
C(4c)	0.2150 (5)	0.2047 (4)	0.8421 (4)	0.054 (3)	0.038 (2)	0.059 (3)	0.014 (2)	0.004 (2)	0.005 (2)
C(5c)	0.3150 (6)	0.1500 (5)	0.8088 (4)	0.059 (3)	0.052 (3)	0.052 (3)	-0.001 (2)	0.027 (2)	0.007 (2)
C(6c)	0.3564 (5)	0.0459 (4)	0.8631 (4)	0.038 (2)	0.045 (3)	0.085 (4)	0.010 (2)	0.022 (2)	-0.008 (3)
C(1d)	1.0995 (7)	0.4905 (5)	0.9396 (4)	0.090 (4)	0.048 (3)	0.059 (3)	0.039 (3)	0.042 (3)	0.018 (2)
C(2d)	0.9525 (6)	0.4117 (4)	0.9187 (3)	0.089 (4)	0.035 (2)	0.039 (3)	0.027 (3)	0.014 (3)	0.005 (2)
C(3d)	0.8525 (5)	0.4211 (4)	0.9798 (4)	0.057 (3)	0.041 (3)	0.065 (3)	0.020 (2)	0.013 (2)	0.016 (2)

atom	x	y	z	$U_{11}$ , Å <sup>2</sup>	atom	x	y	z	$U_{11}$ , Å <sup>2</sup>
H(1a)	0.650 (5)	0.537 (4)	0.346 (4)	0.067 (14)	H(6b)	0.001 (6)	0.070 (5)	0.204 (4)	0.071 (15)
H(2a)	0.804 (4)	0.388 (4)	0.354 (3)	0.036 (10)	H(1c)	0.325 (5)	-0.075 (5)	0.988 (4)	0.061 (14)
H(3a)	0.729 (5)	0.221 (4)	0.227 (3)	0.048 (12)	H(2c)	0.166 (5)	0.017 (5)	1.046 (4)	0.071 (14)
H(4a)	0.519 (5)	0.238 (4)	0.083 (4)	0.058 (13)	H(3c)	0.083 (5)	0.185 (4)	0.960 (4)	0.064 (13)
H(5a)	0.381 (5)	0.387 (4)	0.076 (3)	0.051 (12)	H(4c)	0.164 (6)	0.277 (5)	0.797 (4)	0.087 (16)
H(6a)	0.457 (5)	0.531 (4)	0.205 (4)	0.054 (13)	H(5c)	0.357 (5)	0.190 (4)	0.749 (4)	0.051 (13)
H(1b)	0.029 (5)	0.008 (5)	0.383 (4)	0.072 (15)	H(6c)	0.422 (6)	0.005 (5)	0.842 (4)	0.078 (16)
H(2b)	0.129 (5)	0.166 (5)	0.517 (4)	0.071 (14)	H(1d)	1.162 (6)	0.486 (5)	0.896 (4)	0.092 (17)
H(3b)	0.195 (5)	0.397 (4)	0.449 (4)	0.068 (14)	H(2d)	0.912 (6)	0.345 (5)	0.864 (4)	0.077 (16)
H(4b)	0.163 (4)	0.453 (4)	0.275 (3)	0.037 (10)	H(3d)	0.740 (6)	0.371 (5)	0.962 (4)	0.073 (15)
H(5b)	0.078 (5)	0.297 (4)	0.152 (4)	0.062 (14)					

Table II. Bond Distances (Å) and Angles (deg) for  $[(C_6H_6)_2Ga \cdot GaCl_4]_2 \cdot 3C_6H_6$ .

Bond Distances			
Ga(1)-Cl(1)	2.175 (1)	C(4a)-C(5a)	1.370 (7)
-Cl(2)	2.183 (1)	C(5a)-C(6a)	1.375 (6)
-Cl(3)	2.152 (1)	C(6a)-C(1a)	1.372 (6)
-Cl(4)	2.173 (1)	C(1b)-C(2b)	1.363 (7)
Ga(2)-C(1a)	3.247 (4)	C(2b)-C(3b)	1.370 (7)
-C(2a)	3.186 (4)	C(3b)-C(4b)	1.365 (6)
-C(3a)	3.186 (5)	C(4b)-C(5b)	1.359 (6)
-C(4a)	3.222 (5)	C(5b)-C(6b)	1.377 (7)
-C(5a)	3.283 (5)	C(6b)-C(1b)	1.384 (7)
-C(6a)	3.291 (4)	C(1c)-C(2c)	1.353 (7)
-C(1b)	3.015 (5)	C(2c)-C(3c)	1.361 (7)
-C(2b)	3.020 (6)	C(3c)-C(4c)	1.372 (7)
-C(3b)	3.088 (6)	C(4c)-C(5c)	1.382 (8)
-C(4b)	3.154 (5)	C(5c)-C(6c)	1.367 (7)
-C(5b)	3.149 (5)	C(6c)-C(1c)	1.382 (7)
-C(6b)	3.079 (4)	C(1d)-C(2d)	1.368 (7)
C(1a)-C(2a)	1.383 (7)	C(2d)-C(3d)	1.371 (8)
C(2a)-C(3a)	1.376 (6)	C(3d)-C(1d)	1.364 (7)
C(3a)-C(4a)	1.376 (6)		
Bond Angles			
Cl(1)-Ga(1)-Cl(2)	109.3 (1)	C(2b)-C(3b)-C(4b)	120.2 (4)
-Cl(3)	110.5 (1)	C(3b)-C(4b)-C(5b)	120.1 (4)
-Cl(4)	109.6 (1)	C(4b)-C(5b)-C(6b)	120.2 (6)
Cl(2)-Ga(1)-Cl(3)	108.8 (1)	C(5b)-C(6b)-C(1b)	119.7 (4)
-Cl(4)	108.3 (1)	C(6c)-C(1c)-C(2c)	119.6 (4)
Cl(3)-Ga(1)-Cl(4)	110.4 (1)	C(1c)-C(2c)-C(3c)	121.4 (4)
C(6a)-C(1a)-C(2a)	120.0 (4)	C(2c)-C(3c)-C(4c)	119.7 (5)
C(1a)-C(2a)-C(3a)	119.7 (4)	C(3c)-C(4c)-C(5c)	119.2 (4)
C(2a)-C(3a)-C(4a)	120.0 (5)	C(4c)-C(5c)-C(6c)	120.5 (5)
C(3a)-C(4a)-C(5a)	120.2 (4)	C(5c)-C(6c)-C(1c)	119.4 (5)
C(4a)-C(5a)-C(6a)	120.0 (4)	C(3d)-C(1d)-C(2d)	120.7 (5)
C(5a)-C(6a)-C(1a)	120.1 (5)	C(1d)-C(2d)-C(3d)	119.4 (4)
C(6b)-C(1b)-C(2b)	119.4 (4)	C(2d)-C(3d)-C(1d)	119.6 (8)
C(1b)-C(2b)-C(3b)	120.4 (4)		

benzene very rapidly even at room temperature if the partial pressure of benzene is reduced in the atmosphere above the material by purging with nitrogen or argon or under vacuum. Pumping at  $-6^\circ\text{C}$  leads to the composition  $Ga_2Cl_4 \cdot C_6H_6$  (2) of unknown structure.<sup>18</sup> At only slightly elevated temperatures all of the benzene is evaporated and pure  $Ga[GaCl_4]$  remains.<sup>20</sup>

Manipulation of 1 or 2 therefore requires great care and thoroughly controlled conditions. However, single crystals of phase 1 gave very satisfactory X-ray results if the samples were handled in a benzene-saturated inert-gas atmosphere, and reliable structural data have thus become available for this first well-characterized benzene complex of a group 3A element.

The crystal structure (Figure 1) can be described as consisting of centrosymmetrical  $[(C_6H_6)_2Ga \cdot GaCl_4]_2$  units and additional benzene molecules filling the space between such entities. Figure 2 presents a projection perpendicular to the plane occupied by the four gallium atoms. Two of these metal atoms (Ga(1) and Ga(1)'); here and in the following an atom related by symmetry to an atom of the asymmetric unit is indicated by a prime) are surrounded by four chlorine atoms, one of which (Cl(3)) can be referred to as a terminal chlorine, while the other three form either a single bridge (Cl(2) and Cl(4)) or a double bridge (Cl(1)) to the neighboring gallium centers (Ga(2) and Ga(2)', respectively). The  $GaCl_4$  moieties are therefore classified as tetrachlorogallate(III) anions having a multifunctional bridging role for the remaining gallium(I) components.

Apart from the chlorine single or double bridges, both of these Ga(I) centers are engaged in bonding with two benzene molecules each. A projection along the C(6b)-C(3b) vector (a line drawn across one of the benzene rings, Figure 3) shows that the Ga(I) atoms are about equally displaced from the two hydrocarbon rings, the planes of which form an angle of  $124.4^\circ$ .<sup>32</sup> The metal atom is lo-

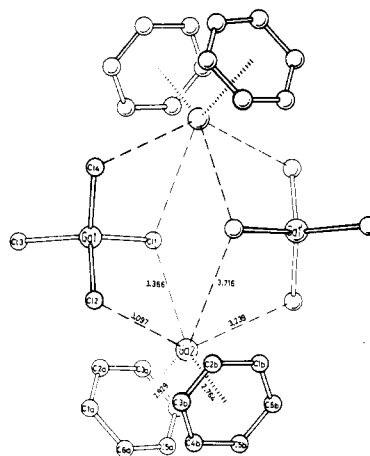
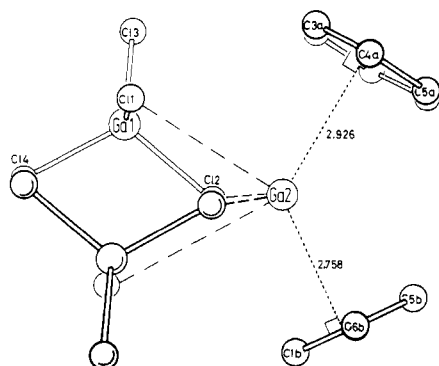


Figure 2. The centrosymmetrical  $[(C_6H_6)_2Ga \cdot GaCl_4]_2$  unit projected perpendicular to the plane of the four Ga atoms. The Ga-Cl distance of 3.716 Å is probably too long as to represent a bonding situation.

cated to a first approximation over the centers of the benzene rings. The line joining Ga(2) with the center of ring A and the normal to ring A form an angle of  $2.8^\circ$ ; the corresponding lines for ring B form an angle of  $3.7^\circ$ . This part of the  $[(C_6H_6)_2Ga \cdot GaCl_4]_2$  unit may thus be addressed as a bis( $\eta^6$ -benzene)gallium(I) cation with the two benzene rings inclined to each other as, e.g., in  $(\pi-C_6H_5)_2TiCl_2$ .

Important bond distances and bond angles are listed in Table II. The Ga(III)-Cl distances range from 2.152 (1) Å for the short "terminal" Ga(1)-Cl(3) bond to 2.173 (1) and 2.183 (1) Å for the single Ga(1)-Cl(4) and Ga(2)-Cl(2)

(32) Equation of least-squares planes (referred to crystal coordinates): ring A,  $5.636x + 4.365y - 8.123z - 3.217 = 0$ ; ring B,  $-9.280x + 3.531y + 2.698z - 0.773 = 0$ . Angle between the planes:  $124.4^\circ$ . Deviation of all C atoms from their plane:  $<0.007\text{Å}$ .



**Figure 3.** View showing the arrangement of ligands around the Ga(I) center.

bridges, respectively, and 2.175 (1) Å for the unsymmetrical double Ga(1)–Cl(1) bridge. As expected, Ga(I)–Cl distances are much larger and well beyond 3.00 Å.

Ga(I) is sharing an edge and a corner, respectively, of two distorted Ga<sup>III</sup>Cl<sub>4</sub> tetrahedra, while the rest of the coordination sphere is capped by the two benzene rings. (The Ga(2)–Cl(1) distance of 3.716 Å probably is too long as to represent a bonding interaction.) The situation is not unlike the structure<sup>8</sup> of (benzene-free) Ga(GaCl<sub>4</sub>), where the tetrahedral Ga(III)–Cl bonds have distances of 2.19 Å, whereas the Ga(I)–Cl distances (in a dodecahedron) are 4 × 3.18 and 4 × 3.27 Å. The Ga(I)–C distances range from 3.186 to 3.291 Å for ring A and from 3.015 to 3.154 Å for ring B. The distances between the Ga atom and the respective ring centers are 2.929 and 2.764 Å. Intrabenzene bond lengths are normal, and in this respect there is, e.g., little difference between benzene rings coordinated to Ga(I) and uncoordinated benzene in the lattice (rings C and D). The Ga(I) atom is located 2.926 and 2.758 Å above rings A and B, respectively. For the Ga(I)–benzene interaction there are no structurally characterized reference compounds, and therefore a discussion of the system 1 has to turn to related species of other post-transition elements.

**Related Benzene Complexes of Other Post-Transition Elements.** The post-transition elements in groups 3A–5A form only weak complexes with aromatic hydrocarbons and the number of compounds known to date is still very limited. Structural information is mainly due to the X-ray investigations by Amma and his collaborators, who have determined the crystal and molecular structures of some classical materials in this series.<sup>33</sup> Like its congener Ga(I), thallium(I) is also known to form benzene complexes, but the structures of the compositions C<sub>6</sub>H<sub>6</sub>·2TlAlCl<sub>4</sub> and (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>·TlAlCl<sub>4</sub><sup>34</sup> have not been deter-

mined. No analogous In(I) compounds have definitely been reported, but preliminary experiments were announced to be positive.<sup>34</sup>

To the best of our knowledge there is no indication of a germanium complex of neutral aromatic hydrocarbons, but both tin(II) and lead(II) give a whole series of coordination compounds with benzene and some of its homologues.<sup>35–38</sup> Molecular structures have been documented for the following stoichiometries: (C<sub>6</sub>H<sub>6</sub>)Sn(AlCl<sub>4</sub>)<sub>2</sub>·C<sub>6</sub>H<sub>6</sub>,<sup>35</sup> (C<sub>6</sub>H<sub>6</sub>)SnCl(AlCl<sub>4</sub>)<sub>2</sub>,<sup>36,37</sup> [1,4-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]SnCl(AlCl<sub>4</sub>)<sub>2</sub>,<sup>37</sup> (C<sub>6</sub>H<sub>6</sub>)Pb(AlCl<sub>4</sub>)<sub>2</sub>·C<sub>6</sub>H<sub>6</sub>,<sup>38</sup> and (C<sub>6</sub>H<sub>6</sub>)U(AlCl<sub>4</sub>)<sub>3</sub>.<sup>39</sup> A U(III) complex<sup>39</sup> was included in this list, because it is structurally closely related to the Pb(II) compound. Analytical and spectroscopic data have been collected for adducts of benzene with low-valent antimony and bismuth chlorides,<sup>34,40</sup> but for these compounds no structural information is available. It thus appears that 1 is the first post-transition-element benzene complex to have two C<sub>6</sub>H<sub>6</sub> rings bonded to the metal. In all cases, however, the metal ions are centered over the hydrocarbon and thus η<sup>6</sup> coordinated. This pattern is different from the structures found for complexes with the late transition elements like Cu<sup>I</sup> or Ag<sup>I</sup>, where η<sup>2</sup> bonding prevails.<sup>41,42</sup>

Typical Sn–C and Pb–C distances range from 3.05 to 3.15 Å in the above Sn(II) and Pb(II) compounds and are not unlike the Ga–C distances found in 1. It seems quite plausible to assume that Sn(II), Pb(II), and Ga(I) have similar ionic (and covalent) radii, though no reliable data are available. The above distances thus are an indication of similar metal–benzene bonding mechanisms. Theoretical models for the post-transition-metal/benzene interaction with the metal in the centered η<sup>6</sup> position have already been considered for Sn(II),<sup>3</sup> Pb(II),<sup>6</sup> U(III),<sup>7</sup> and, also, Ga(I).<sup>7,17,18,25</sup> These approaches were all based on a 1:1 moiety of C<sub>6v</sub> symmetry and, therefore, have to be adapted to the 1:2 entities with the reduced symmetry, C<sub>2v</sub>. This problem will be the subject of a forthcoming paper as more experimental data become available.

**Registry No.** 1, 86884-86-8.

**Supplementary Material Available:** A listing of structure factor amplitudes for [(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>Ga-GaCl<sub>4</sub>]<sub>2</sub>·3C<sub>6</sub>H<sub>6</sub> (15 pages). Ordering information is given on any current masthead page.

(35) Rodesiler, P. F.; Auel, Th.; Amma, E. L. *J. Am. Chem. Soc.* **1975**, *97*, 7405. Lüth, H.; Amma, E. L. *Ibid.* **1969**, *91*, 7515.

(36) Weininger, M. S.; Rodesiler, P. F.; Gash, A. G.; Amma, E. L. *J. Am. Chem. Soc.* **1972**, *94*, 2135.

(37) Weininger, M. S.; Rodesiler, P. F.; Amma, E. L. *Inorg. Chem.* **1979**, *18*, 751.

(38) Gash, A. G.; Rodesiler, P. F.; Amma, E. L. *Inorg. Chem.* **1974**, *13*, 2429.

(39) Cesari, M.; Pedretti, U.; Zazzetta, A.; Lugli, G.; Marconi, W. *Inorg. Chim. Acta* **1971**, *5*, 439.

(40) Daasch, L. W. *Spectrochim. Acta* **1959**, *9*, 726.

(41) Turner, R. W.; Amma, E. L. *J. Am. Chem. Soc.* **1966**, *88*, 3243.

(42) Turner, R. W.; Amma, E. L. *J. Am. Chem. Soc.* **1963**, *85*, 4046; **1966**, *88*, 1877.

(33) Part 24 of a series "Metal Ion-Aromatic Complexes" by Weininger, M. S.; Rodesiler, P. F.; Amma, E. L. *Inorg. Chem.* **1979**, *18*, 751, is a key reference for previous work by these authors.

(34) Auel, Th.; Amma, E. L. *J. Am. Chem. Soc.* **1968**, *90*, 5941.