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Preliminary communication

Unusual intramolecular hydrogen bonding in $\text{Cy}_2\text{GaBrNH}_2\text{Ph}$. The first structurally characterized dialkyl gallium halide primary amine adduct

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Abstract

The aniline adduct of dicyclohexyl gallium bromide $\text{Cy}_2\text{GaBrNH}_2\text{Ph}$ (**1**) provides the first example of a structurally characterized dialkyl gallium halide primary amine adduct. X-ray crystallographic data indicate the possibility of an intramolecular hydrogen bond between the bromide and a hydrogen of the amine group ($\text{H} \cdots \text{Br} = 2.48 \text{ \AA}$).

Our interest in bonding between the elements of Groups 13 and 15 has led us to prepare and structurally characterize several dialkyl gallium halide mono-amine adducts of general formula $\text{R}_2\text{GaXNH}_2\text{R}'$ where R and R' = alkyl or aryl and X = Cl, Br, I. This communication describes the synthesis and X-ray structure of $\text{Cy}_2\text{GaBrNH}_2\text{Ph}$ (**1**) (Cy = cyclohexyl). This compound was prepared by the reaction of Cy_2GaBr and NH_2Ph in diethylether at low temperature.

Crystals suitable for X-ray crystallography were grown from a concentrated toluene solution at -30°C . The crystals are monoclinic: $a = 13.526$, $b = 6.456$, $c = 22.267 \text{ \AA}$, $\beta = 99.64^\circ$, $U = 1917 \text{ \AA}^3$, $Z = 4$, $D_c = 1.423 \text{ g/cm}^3$, space group $P2_1/n$. The unit cell contains four molecules and there is one molecule per asymmetric unit. Diffraction data were collected using an Enraf–Nonius CAD-4 diffractometer using $\text{Mo-K}\alpha$ radiation. Data were collected to $2\theta = 35^\circ$ and 1311 unique observed reflections ($F > 6\sigma(F)$) from a total of 2925 were used in the refinement. The position of the gallium atom was determined from a Patterson map and subsequent difference Fourier maps allowed the location of all non-hydrogen atoms which were refined anisotropically. The hydrogen atoms were located and allowed to ride on their respective atoms with fixed isotropic thermal parameters. The result was a conventional R value of 0.0453 with $R_w = 0.0560$.

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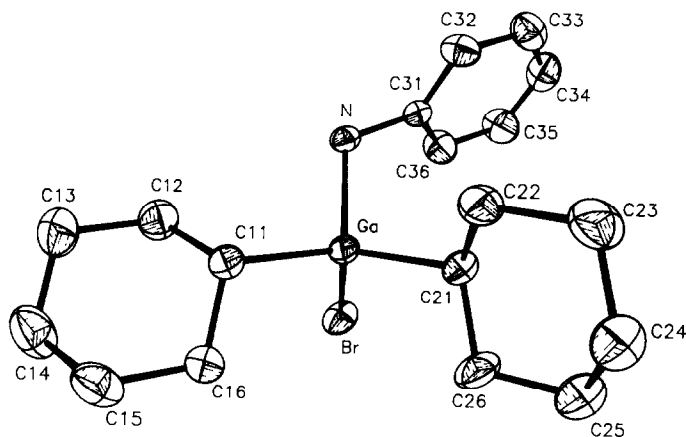


Fig. 1. ORTEP view of $\text{C}_2\text{GaBrNH}_2\text{Ph}$ (**1**) with hydrogen atoms omitted for clarity. Selected bond lengths (\AA) and angles ($^\circ$): Ga–Br 2.444(1), Ga–N 2.107(7), Ga–C(11) 1.981(9), Ga–C(21) 1.968(9); Br–Ga–N 95.8(2), Br–Ga–C(11) 107.7(3), Br–Ga–C(21) 109.5(3), C(11)–Ga–C(21) 124.9(4), Ga–N–C(31) 117.0(5).

The molecule exhibits an extremely distorted tetrahedral geometry around the central gallium atom. An interesting feature of the molecule is the presence of an intramolecular hydrogen bond between the bromine atom and a hydrogen atom of the amine group. This type of intramolecular bonding has been seen before in transition metal species [1]. However, this is the first instance where such an interaction has been seen for a main group compound. The solution spectroscopic information (IR and ^1H NMR) does not support the presence of this interaction. This may be due to solvation effects which result in the breaking of these weak interactions [2]. In compound **1** the Ga–Br distance is 2.444(1) \AA while the H(2)–Br distance is 2.48 \AA . This may be compared to van der Waals radii for H and Br, 1.8 \AA and 1.2 \AA , respectively. This intramolecular bonding may also account for the significant compression in the Br–Ga–N angle (95.8(2) $^\circ$). This leaves the C(11)–Ga–C(21) angle to open up to 124.9(4) $^\circ$. The other angles are close to tetrahedral (Br–Ga–C(11) 107.7(3) $^\circ$, N–Ga–C(11) 106.7(3) $^\circ$, N–Ga–C(21) 108.2(3) $^\circ$). The Ga–N bond length (2.107(7) \AA) is somewhat shorter than the values found for $\text{Ga}(\text{2-C}(\text{SiMe}_3)_2\text{C}_5\text{H}_4\text{N})_2\text{Cl}$ (2.22 \pm 0.04 \AA) [3] and $\text{GaMe}_2\text{Cl} \cdot \text{C}_{12}\text{H}_8\text{N}_2$ (2.119 and 2.433 \AA) [4] which may indicate the presence of a partial positive charge on gallium. This effect is most dramatic in the cationic fragment $[\text{Me}_2\text{Ga}(\text{NH}_2(\text{t}\text{Bu}))_2]^+$ with Ga–N bond lengths of 2.039(8) [5]. The Ga–C bond lengths are standard at 1.981(9) \AA and 1.968(9) \AA as compared to 1.96 \pm 0.01 \AA for the Ga–C bond lengths in the phenanthroline adduct $\text{GaMe}_2\text{Cl} \cdot \text{C}_{12}\text{H}_8\text{N}_2$ [4]. The intramolecular hydrogen bonding does not affect the N–H bond lengths to any appreciable extent (N–H(1) = 1.000 and N–H(2) = 0.990 \AA). Also the Ga–N–H bond angles are tetrahedral at 107.0 $^\circ$ (H(1)) and 108.0 $^\circ$ (H(2)). The only distortion of the nitrogen geometry is the Ga–N–C(31) angle of 117.0(5) $^\circ$ which probably reflects steric interactions between the N–phenyl and Ga–cyclohexyl groups.

This complex may represent the isolation of an intermediate in the formation of the corresponding dialkyl gallium di-adducted cationic species of general formula

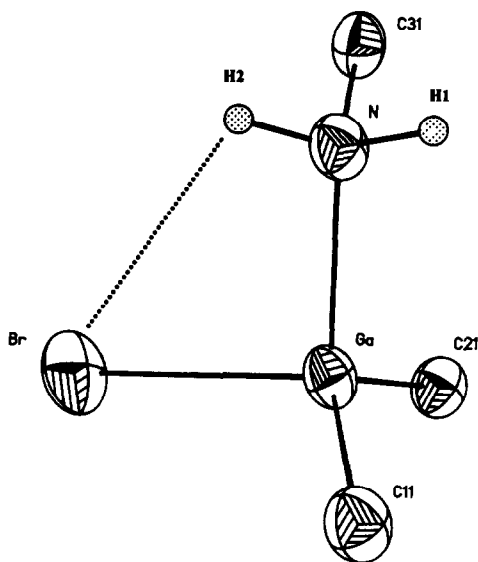


Fig. 2. Intramolecular hydrogen bonding in **1** with relevant bond lengths (Å) and angles (°): N–H(1) 1.00, N–H(2) 0.99, Br–H(2) 2.48; Ga–N–H(1) 107, Ga–N–H(2) 108, H(1)–N–H(2) 109.

$[\text{R}_2\text{Ga}(\text{NH}_2\text{R}')_2]^+$. The intramolecular hydrogen–bromide bond in **1** would facilitate the formation of the cation in two ways. First, the $\text{H}^{\delta+} \cdots \text{Br}^{\delta-}$ dipolar interaction makes the displacement of the bromide anion more favorable. Second, the wide alkyl–gallium–alkyl angle resulting from the previous interaction makes the attack of a second mole of amine more sterically favorable. Further studies into this reaction mechanism are currently in progress.

*Cy*₂GaBr(NH₂Ph)

Two equivalents of *Cy*MgCl in Et₂O (38.62 mmol, 18.39 ml, 2.1 *M* soln.) were added to a stirred, –78°C, solution of GaBr₃ (5.98 g, 19.31 mmol) in Et₂O. The resulting mixture was allowed to warm to 25°C and then stirred for 12 h before cooling to –78°C and addition of 1.2 equivalents of NH₂Ph (23.17 mmol, 2.11 ml). This mixture was allowed to warm to 25°C and then stirred 12 h before solvents were removed *in vacuo*. The residue was extracted with toluene (50 ml) and filtered. The filtrate was concentrated (25 ml) and cooled to –30°C for 7 days to afford colorless square crystals of **1** (m.p. 72–74°C), yield 92% based on Ga. ¹H NMR (300 MHz, toluene-*d*₈ (ppm)): 6.8, 6.6, 6.4 (5H, m, *N-Ph*), 3.4 (2H, b, *N-H*), 1.8–1.3 (22H, m, *Ga-Cy*). MS (70 eV, 25°C): *m/z*, 93, NH₂Ph; 153, GaCy; 236 (100%), GaCy₂; 316, GaCy₂Br. IR (cm⁻¹, *nujol*): 3200(s), 3110(s), 1200(w), 1095(s), 1000(s), 875(m), 798(s), 750(m), 740(s), 650(m). Microanalysis: Found: C, 69.15; H, 9.82; N, 4.01. C₁₈H₂₉BrGaN calc.: C, 69.87; H, 9.45; N, 4.52%.

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