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Preliminary communication

Structural characterization of a dialkylgallium cation: X-ray crystal structure of $[Me_2Ga(^tBuNH_2)_2]Br$

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Abstract

The X-ray crystal structure of $[Me_2Ga(^tBuNH_2)_2]Br$ (**1**) has been determined. The compound was prepared in a 51% yield *via* the reaction of t-$BuNH_2$ with Me_2GaBr in Et_2O solution. The solid state of **1** consists of $[Me_2Ga(^tBuNH_2)_2]^+$ cations and bromide anions. The gallium cation adopts a highly distorted tetrahedral geometry with Me(1)–Ga–Me(2) and N(1)–Ga–N(2) angles of 121.5(5) and 95.6(3)°, respectively.

In 1933, Kraus and Toonder reported the preparation of a diammoniate of dimethylgallium chloride [1]. No structural details were available at that time; however, several years later Coates [2] proposed an ionic formulation for this compound, $[NH_4][Me_2Ga(Cl)NH_2]$. Following recognition of the formula $[H_2B(NH_3)_2][BH_4]$ for the diammoniate of diborane [3], Shriver and Parry [4] postulated that the structure of the diammoniate of dimethyl gallium chloride is $[Me_2Ga(NH_3)_2]Cl$. The postulation of the existence of the cation $[Me_2Ga(NH_3)_2]^+$ was supported by analogy with the ethylenediamine complex $[Me_2Ga(en)]Cl$. Strong evidence for such an ionic formulation for the latter stemmed from a molecular weight determination and from the observation of facile metathesis reactions. Subsequently, convincing evidence has been presented for the presence of the cation $[Me_2Ga(H_2O)_2]^+$ in acidic aqueous solutions [5]. The purpose of the present communication is to report the first definitive structural evidence for a solvated dimethylgallium cation.

Dimethylgallium bromide (prepared *in situ*) was treated with two equivalents of $^tBuNH_2$ in Et_2O solution at 25°C. Removal of the solvent left a white residue of

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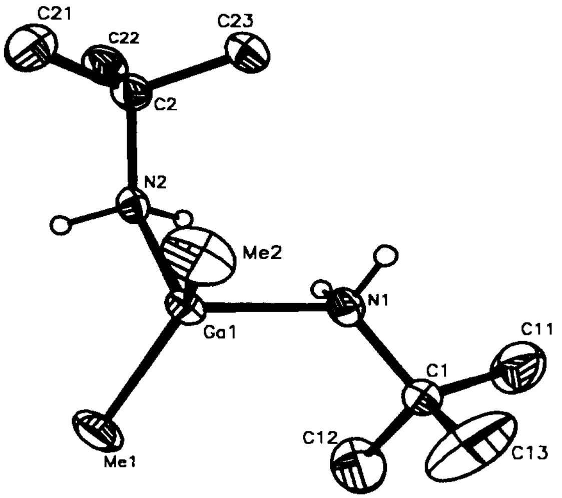

Fig. 1. ORTEP view of 1. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ga–N(1) 2.045(7), Ga–N(2) 2.034(8), Ga–Me(1) 2.00(1), Ga–Me(2) 1.97(1); Me(1)–Ga–N(1) 112.8(4), Me(2)–Ga–N(1) 106.0(4), Me(1)–Ga–N(2) 102.0(4), Me(2)–Ga–N(2) 116.5(4), N(1)–Ga–N(2) 95.6(3), Me(1)–Ga–Me(2) 121.2(5).

composition $[Me_2Ga(^tBuNH_2)_2]Br$ which was recrystallized from hexane at −25°C *. Crystals of **1** suitable for X-ray diffraction were grown from a pentane solution which was held at −25°C for a period of three weeks.

The X-ray analysis ** confirms that the solid state of **1** comprises an array of $[Me_2Ga(^tBuNH_2)_2]^+$ cations (Fig. 1) and bromide anions. The shortest interionic contacts are those between Br^- and the N–H protons (range 2.59–2.75 Å). The Ga $\cdots$ Br distance is > 3.6 Å and therefore falls outside the range anticipated for

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* For 1: m.p. 81–83°C. Anal. Found: C, 37.05; H, 8.42; N, 8.30. $C_{10}H_{28}N_2GaBr$ calcd.: C, 36.85; H, 8.66; N, 8.59%.

** Crystal structure analysis of $[Me_2Ga(^tBuNH_2)_2]Br$ (1). Crystal data: $C_{10}H_{28}N_2GaBr$, $M = 325.96$, monoclinic, space group $P2_1/c$, $a = 9.113(2)$, $b = 10.209(1)$, $c = 17.323(5)$ Å, $\beta = 104.94(2)°$, $V = 1557.21(6)$ Å^3. $Z = 4$, $D_c = 1.352$ g cm^{-3}, $F(000) = 676$, $\mu(\text{Mo-}K_\alpha) = 42.95$ cm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.71069$ Å.

A block shaped colorless crystal (0.09×0.15×0.18 mm) was mounted in a glass capillary (0.5 mm diameter) under an inert atmosphere. The final lattice parameters were determined from 25 reflections with 2θ between 20 and 25° accurately centered on an Enraf–Nonius CAD-4 diffractometer. During the data collection, the intensities of three monitored reflections decreased by < 2%. No correction was applied. Data for 3017 unique reflections were input into the SHELX program system [12].

The position of the gallium atom was determined from a Patterson map and subsequent difference Fourier maps permitted the location of all non-hydrogen atoms. Refinement of all the atoms with isotropic thermal parameters converged at a conventional R value of 0.09. Treatment of the gallium, nitrogen and methyl carbon atoms with anisotropic thermal parameters led to the reduction of the R value by about 3%. Hydrogen atoms were placed in calculated positions (except for the amino hydrogens which were located from a difference map) and allowed to 'ride' upon the appropriate atom.

Refinement converged at $R = 0.056$ and $R_w = 0.060$ for 1607 reflections having $F > 6\sigma(F)$ using the weighting scheme, $w = [(\sigma F)^2 + 0.000625F^2]^{-1}$. The largest parameter shifts in the final cycles of refinement were less than 0.01 of their estimated standard deviations.

covalent interaction. The most surprising feature of the structure is the large C–Ga–C angles (121.2(5)°) in the cation. Previous studies have revealed that the C–metal–C angles in the unsolvated cations $[Me_2In]Br$ [6] and $[Me_2Tl]Cl$ [7] are 180°. The approach of two monodentate amine molecules (ideally at the tetrahedral angle) to a $[Me_2Ga]^+$ moiety is anticipated to result in a progressive decrease in the C–Ga–C angle from 180 to 109.5°. This might lead to the conclusion that in the case of **1**, the approach of the amines along the reaction coordinate had been arrested. However, such a conclusion is not borne out by the Ga–N bond lengths. While there is no precedent for a cationic Ga–N bond length, it is noteworthy that the Ga–N bond length in **1** (2.039(8) Å, equal within experimental error) is significantly shorter than those in other trialkylamine adducts: $Me_3Ga \cdot N(^tBu)H_2$ 2.12(1) Å [8]), $2(Me_3SiCH_2)_3Ga \cdot NMe_2CH_2CH_2NMe_2$ (2.241(9) Å [9]) and $Me_3Ga \cdot N_4C_6H_{12}$ (2.138(9) Å [10]). On the other hand, the average Ga–C bond length in **1** (1.98(1) Å) is very similar to those in the foregoing neutral amine adducts. The N–Ga–N angle in **1** is also of interest. Despite the steric bulk of the amine ligands, this angle is rather small (95.6(3)°). In part, steric repulsion between the amines is diminished by the adoption of a mutually *trans* disposition of the ^tBu groups. In contrast to $[^tBu_2Ga(\mu\text{-NHPh})]_2$ and $^tBu_3Ga \cdot NH_2Ph$ [11], there is no evidence for close interactions between the N–H hydrogens and the gallium atoms.

The ^1H NMR spectrum of **1** in C_6D_6 displays resonances at δ 0.98 (s, 18H, ^{t}Bu-N) and δ 0.19 (s, 6H, *Me*-Ga). The Me–Ga resonance for **1** is slightly deshielded in comparison with that reported for $[Me_2Ga(H_2O)_2]^+$ (δ −0.30 [5b]; δ −0.26 [5d]). Finally, no spectroscopic evidence was found for solution equilibria such as that shown in eq. 1.

$$[Me_2Ga(^tBuNH_2)_2]Br \rightleftharpoons Me_2GaBr(^tBuNH_2) + {}^tBuNH_2 \qquad (1)$$

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References

1 C.A. Kraus and F.E. Toonder, Proc. Natl. Acad. Sci. U.S., 19 (1933) 298.
2 G.E. Coates, Organo Metallic Compounds, Methuen and Co. Ltd., John Wiley and Sons Inc., New York, N.Y., (1960) 147.
3 D.R. Shultz and R.W. Parry, J. Am. Chem. Soc., 80 (1958) 4.
4 D.F. Shriver and R.W. Parry, Inorg. Chem., 1 (1962) 835.
5 (a) M.E. Kenney and A.W. Laubengayer, J. Am. Chem. Soc., 76 (1954) 3839; (b) R.S. Tobias, M.G. Sprague and G.E. Glass, Inorg. Chem., 7 (1968) 1714; (c) L. Pellerito and R.S. Tobias, Inorg. Chem., 9 (1970) 953; (d) O.T. Beachley, Jr., R.U. Kirss, R.J. Bianchini and T.L. Royster, Organometallics, 6 (1987) 724.
6 E.D. Hausen, K. Mertz, J. Weidlein and W. Schwarz, J. Organomet. Chem., 93 (1975) 291.
7 H.D. Hausen, E. Veigel and H.-J. Guder, Z. Naturforsch., Teil B, 29 (1974) 269.
8 D.A. Atwood, R.A. Jones, A.H. Cowley, S.G. Bott and J.L. Atwood, J. Organomet. Chem., submitted.
9 R.B. Hallock, W.E. Hunter, J.L. Atwood and O,.T. Beachley Jr., Organometallics, 4 (1985) 547.
10 H. Krause, K. Sille, H.D. Hausen and H. Weidlein, J. Organomet. Chem., 235 (1982) 253.
11 D.A. Atwood, R.A. Jones, A.H. Cowley, S.G. Bott and J.L. Atwood, Polyhedron, 10 (1991) 1897.
12 G.M. Sheldrick, SHELX. A System of Computer Programs for X-ray Structure Determination, Cambridge, UK, 1976.