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Short Ga ··· H–N distances in gallium amine and amide complexes

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Abstract

The reaction of Cy_2GaCl with LiNHR in diethylether at −78°C produces the dinuclear primary amido bridged complexes $[Cy_2GaNHR]_2$ (R ≡ Ph (**1**), ^tBu (**2**)) with high yields. The addition of the secondary amines tetramethylpiperidine (TMPH) and $^iPr_2NH$ to $GaCl_3$ in toluene at −78°C produces the adducts $TMPH \cdot GaCl_3$ (**3**) and $^iPr_2NH \cdot GaCl_3$ (**4**) with a yield of more than 80%. Compounds **1**–**3** were characterized through single-crystal X-ray diffractometry. The solid state structures of **1** and **2** feature planar Ga_2N_2 four-membered rings. Interestingly, compounds **1**–**3** feature short Ga ··· H–N distances, which are 2.113 Å, 2.33 Å and 2.28(9) Å for **1**, **2** and **3** respectively.

1. Introduction

We have previously reported the alkyl gallium primary amine complexes, $^tBu_3Ga \cdot NH_2Ph$ [1], $Me_3Ga \cdot NH_2(^tBu)$ [2], $[^tBu_2GaNHPh]_2$ [1] and $[Me_2GaNH(^tBu)]_2$ [2]. In the solid state these molecules were found to have short Ga ··· H–N distances in the range 2.1–2.4 Å, well within the sum of the van der Waals radii for gallium and hydrogen (3.1 Å) [3]. Other, structurally characterized examples are the dimeric molecules $[Me_2GaNHDipp]_2$ (Dipp ≡ $2,6{}^iPr_2\text{-}C_6H_3$), and $[Me_2GaNH(1\text{-}Ad)]_2$ (1-Ad ≡ 1-adamantyl) and $[Me_2GaNHPh]_2$ [4]. As part of our continuing interest, and in order to elucidate the nature of these short Ga ··· H–N distances, we have prepared $[Cy_2GaNHPh]_2$ (**1**) and $[Cy_2GaNH(^tBu)]_2$ (**2**), two compounds which differ only in the type of alkyl on nitrogen. The effect of the alkyl group is seen in a decrease in the Ga ··· H–N distance on going from $HN(^tBu)$ to HNPh. This introduces the possibility that the acidity of the amine group may dictate the Ga ··· H distance. In order to explore this phenomenon further the secondary amine adducts $TMPH \cdot GaCl_3$ (**3**) (TMPH ≡ tetramethylpiperdine and $^iPr_2NH \cdot GaCl_3$ (**4**) were also prepared. The structure of **3** confirmed the presence of a short Ga ··· H–N distance of 2.28(9) Å. This hydrogen was located crystallographically and was refined as an independent atom in the structure solution. We note that other structurally characterized amine adducts of $GaCl_3$ are limited to the tertiary amine complex $Me_2Si(NMe_2)_2 \cdot GaCl_3$ [5].

2. Results and discussion

2.1. Synthesis and characterization of $[Cy_2GaNHR]_2$ (R ≡ Ph (1), ^tBu (2))

Compounds **1** and **2** were prepared by the reaction of the lithium amide with dicyclohexyl gallium chloride at low temperature in Et_2O and tetrohydrofuran (THF). They can be isolated with high yields by recrystallization in ether or hexane. For both compounds the *Cy*–Ga ^1H NMR resonances are manifested as a series of multiplets in the range δ 0.80–1.2 ppm. The *Ph*N groups for **1** are manifested as a broad multiplet centered at δ 6.8 ppm, while the *^tBu*N groups of **2** are seen as a singlet at δ 1.45 ppm. Interestingly, the N–H resonances and the ν_{N-H} infrared stretches were not observed for **1** and **2**.

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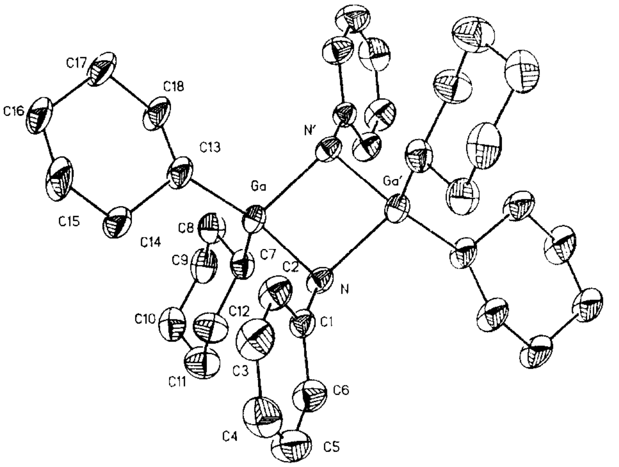

Fig. 1. Molecular structure and atom numbering scheme for $[Cy_2GaNHPh]_2$ (**1**).

TABLE 1. Positional parameters for **1**

Atom	x	y	z	U_{eq}
Ga	0.13928(12)	0.02880(12)	0.40386(11)	0.0484(5)
N	0.0310(8)	0.0382(8)	0.5976(7)	0.045(4)
C(1)	0.1128(10)	0.0232(10)	0.7004(9)	0.046(4)
C(2)	0.2093(12)	0.1826(12)	0.7265(11)	0.062(5)
C(3)	0.2873(14)	0.2382(14)	0.8249(12)	0.076(7)
C(4)	0.2770(15)	0.149(2)	0.9011(13)	0.080(7)
C(5)	0.182(2)	0.009(2)	0.8800(13)	0.082(8)
C(6)	0.1012(13)	0.0665(13)	0.7774(11)	0.066(6)
C(7)	0.1132(11)	0.2470(11)	0.3201(10)	0.055(5)
C(8)	0.1514(14)	0.2839(13)	0.1723(11)	0.067(6)
C(9)	0.1363(14)	0.4522(14)	0.1173(12)	0.077(6)
C(10)	0.2270(14)	0.4976(14)	0.1727(13)	0.076(7)
C(11)	0.184(2)	0.464(2)	0.3188(14)	0.089(9)
C(12)	0.200(2)	0.2959(14)	0.3764(13)	0.076(7)
C(13)	0.3355(11)	0.1634(13)	0.3718(11)	0.062(5)
C(14)	0.4825(12)	0.157(2)	0.3933(14)	0.084(7)
C(15)	0.6238(13)	0.314(2)	0.3686(15)	0.099(8)
C(16)	0.6484(12)	0.340(2)	0.2353(14)	0.085(7)
C(17)	0.5047(13)	0.3387(15)	0.2097(14)	0.085(7)
C(18)	0.3634(12)	0.1838(14)	0.2346(12)	0.076(6)
NH	0.0611(6)	0.0618(6)	0.5637(4)	0.06

2.2. X-ray structures of 1 and 2

Molecules of **1** and **2** crystallize in the triclinic space group $P\bar{1}$. Figures 1 and 2 show the molecular geometry and atom numbering scheme; positional parameters are given in Tables 1 and 2; selected bond lengths and angles are given in Tables 3 and 4 for **1** and **2** respectively. Molecules **1** and **2** are nitrogen-bridged dimers having a center of inversion and planar Ga_2N_2 four-membered rings. The Ga–N bond lengths for **1** and **2** are similar at 2.038(7) Å and 2.01(1) Å. It is interesting to note that the more sterically hindered **2** features the slightly shorter bond length, since the trend is for more sterically crowded molecules to show longer distances. A summary of some selected bond lengths and angles in other dimeric and trimeric complexes is given in Table 5. The Ga–N–Ga′ and N–Ga–N′ angles in compounds **1** and **2** are nearly identical at 95.4(6)°, 96.5(2)° and 84.4(3)°, 84.6(6)° respectively. This serves to demonstrate the structural similarity between the two molecules. That the Ga–N–Ga′ angle for these compounds is larger than the N–Ga–N′ angle is a general trend seen for primary amido complexes. This may reflect the difference in steric requirements for two alkyl groups on gallium compared with one on nitrogen.

The nitrogen–hydrogen atoms for both compounds were found on difference Fourier maps. Attempts to refine these hydrogen atoms separately led to unrealistic values for the thermal parameters. Thus these atoms were constrained to "ride" upon the nitrogen and

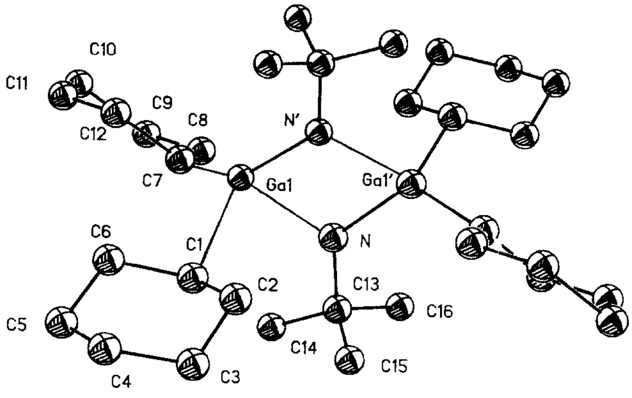

Fig. 2. Molecular structure and atom numbering scheme for $[Cy_2GaNH(^tBu)]_2$ (**2**).

TABLE 2. Positional parameters for **2**

Atom	x	y	z	U_{eq}
Ga	0.1815(2)	0.1043(2)	0.5306(2)	0.040(8)
N	0.024(1)	−0.125(1)	0.485(1)	0.050(5)
NH	−0.047(1)	−0.106(1)	0.520(1)	0.080()
C(1)	−0.008(2)	−0.269(2)	0.384(2)	0.057(15)
C(2)	−0.084(2)	−0.271(2)	0.227(2)	0.062(14)
C(3)	0.174(2)	−0.249(2)	0.447(2)	0.080(27)
C(4)	−0.134(2)	−0.419(2)	0.381(2)	0.067(14)
C(11)	0.395(2)	0.197(2)	0.734(2)	0.054(9)
C(12)	0.382(2)	0.116(2)	0.834(2)	0.062(15)
C(13)	0.547(2)	0.203(2)	0.991(2)	0.072(20)
C(14)	0.712(2)	0.238(2)	0.995(2)	0.074(31)
C(15)	0.730(2)	0.319(2)	0.895(2)	0.064(28)
C(16)	0.565(2)	0.233(2)	0.739(2)	0.065(23)
C(21)	0.218(3)	0.174(2)	0.381(2)	0.122(19)
C(22)	0.117(4)	0.211(4)	0.283(3)	0.248(69)
C(23)	0.172(3)	0.297(3)	0.196(2)	0.125(21)
C(24)	0.293(3)	0.258(4)	0.165(3)	0.186(79)
C(25)	0.389(4)	0.213(4)	0.260(3)	0.234(19)
C(26)	0.333(2)	0.128(2)	0.347(2)	0.094(15)

TABLE 3. Selected bond lengths (Å) and angles (°) for **1**

Distances			
Ga–N	2.038(7)	N–C(1)	1.41(1)
Ga–C(7)	1.98(1)	C(1)–C(2)	1.41(1)
Ga–C(13)	2.020(9)	C(1)–C(6)	1.35(2)
C(2)–C(3)	1.36(2)	C(3)–C(4)	1.35(2)
C(4)–C(5)	1.40(2)	C(5)–C(6)	1.41(2)
C(7)–C(8)	1.49(2)	C(7)–C(12)	1.49(2)
C(8)–C(9)	1.53(2)	C(9)–C(10)	1.50(3)
C(10)–C(11)	1.48(2)	C(11)–C(12)	1.53(2)
C(13)–C(14)	1.56(2)	C(13)–C(18)	1.50(2)
C(14)–C(15)	1.57(2)	C(15)–C(16)	1.49(2)
C(16)–C(17)	1.51(2)	C(17)–C(18)	1.56(2)
N–NH	1.00	Ga–NH	2.114
Angles			
N–Ga–C(7)	103.3(4)	N–Ga–C(13)	127.2(4)
C(13)–Ga–N	115.3(4)	C(1)–N–Ga	123.9(5)
C(2)–C(1)–C(6)	118(1)	C(2)–C(1)–N	121(1)
C(6)–C(1)–N	121.9(8)	C(3)–C(2)–C(1)	119(1)
C(4)–C(3)–C(2)	123(1)	C(5)–C(4)–C(3)	120(1)
C(6)–C(5)–C(4)	117(2)	C(1)–C(6)–C(5)	123(1)
C(8)–C(7)–C(12)	113(1)	C(8)–C(7)–Ga	115.9(9)
C(12)–C(7)–Ga	109.3(7)	C(9)–C(8)–C(7)	112(1)
C(10)–C(9)–C(8)	113(1)	C(11)–C(10)–C(9)	111(1)
C(12)–C(11)–C(10)	112(1)	C(7)–C(12)–C(11)	113(1)
C(14)–C(13)–C(18)	111.5(9)	C(14)–C(13)–Ga	112.3(9)
C(18)–C(13)–Ga	108.4(7)	C(15)–C(14)–C(13)	107(1)
		C(17)–C(16)–C(15)	114(1)
C(16)–C(15)–C(14)	111(1)	C(17)–C(16)–C(17)	110(1)
C(18)–C(17)–C(16)	109(1)		
NH–Ga–C(7)	100.0	Ga–N–NH	80.2
NH–N–C(1)	151.6	Ga–N–Ga′	95.4(6)
		N–Ga–N′	84.4(3)

TABLE 4. Selected bond lengths (Å) and angles (°) for **2**

Distances			
Ga–Ga	3.017(3)	Ga–C(11)	1.99(1)
Ga–N	2.01(1)	N–N′	2.75(2)
Ga–C(21)	2.01(2)	C(1)–C(2)	1.54(2)
N–C(1)	1.51(2)	C(1)–C(4)	1.51(2)
C(1)–C(3)	1.54(2)	C(12)–C(13)	1.52(2)
C(11)–C(16)	1.55(2)	C(14)–C(15)	1.50(2)
C(13)–C(14)	1.51(2)	C(21)–C(22)	1.33(2)
C(15)–C(16)	1.51(2)	C(22)–C(23)	1.51(3)
C(21)–C(26)	1.57(2)	C(24)–C(25)	1.35(3)
C(23)–C(24)	1.57(3)	N–H	1.00
C(25)–C(26)	1.51(2)	Ga–H	2.33
Angles			
N–Ga–N′	84.6(6)	N–Ga–C(11)	106.6(6)
N–Ga–C(21)	122.2(7)	C(11)–Ga–C(21)	117.6(7)
Ga–N–Ga′	95.4(6)	Ga–N–C(1)	127.2(9)
N–C(1)–C(2)	109(1)	N–C(1)–C(3)	106(1)
C(2)–C(1)–C(3)	110(1)	N–C(1)–C(4)	111(1)
C(2)–C(1)–C(4)	111(1)	C(3)–C(1)–C(4)	110(1)
C(11)–C(12)–C(13)	114(1)	C(12)–C(13)–C(14)	112(1)
C(13)–C(14)–C(15)	111(1)	C(14)–C(15)–C(16)	114(2)
C(11)–C(16)–C(15)	112(1)	Ga–C(21)–C(22)	126(1)
Ga–C(21)–C(26)	114(1)	C(22)–C(21)–C(26)	117(1)
C(21)–C(22)–C(23)	123(2)	C(22)–C(23)–C(24)	112(2)
C(23)–C(24)–C(25)	117(2)	C(24)–C(25)–C(26)	124(2)
C(21)–C(26)–C(25)	111(1)	NH–N–Ga	95.3
		NH–N–C(1)	134.2

refined with fixed isotropic thermal parameters [7*]. The hydrogen atoms project symmetrically above and below the Ga_2N_2 plane at N–Ga–NH angles of 80.2° and 95.4° for **1** and **2** respectively. This places the hydrogen atom 2.11 Å from the gallium atom for **1**, and 2.33 Å for **2**. The shorter distance in **1** may be the result of a stronger dipole that is formed between the more acidic $H^{\delta+}$ (of PhNH compared with ${}^tBuNH$) and the electron density of the Ga_2N_2 four-membered ring. A correlation between amide acidity and narrowed Ga–N–H angles and shortened Ga ··· H distance can be seen in Table 5.

To the best of our knowledge there appears to be no precedent for this type of interaction for the heavier main group elements. Of related interest are H^+–

TABLE 5. Comparison of bond lengths and angles for alkyl gallium primary amide and amine complexes

Compound	Ga ··· H (Å)	Ga–N (average) (Å)	Ga–N–Ga′ (°)	N–Ga–N′ (°)	Reference	Ga–N–H (°)
$[Me_2GaNH({}^tBu)]_2$	2.390	2.011(1)	95.3(3)	84.8(2)	[2]	108.0
$[{}^tBu_2GaNHPh]_2$	2.037	2.06(4)	96.5(2)	83.5(3)	[1]	71.2
$[Cy_2GaNHPh]_2$ (**1**)	2.113	2.038(7)	95.6(3)	84.4(3)		80.2
$[Cy_2GaNH({}^tBu)]_2$ (**2**)	2.33	2.01(1)	95.4(6)	84.6(6)		95.4
$[{}^tBu_2GaNH_2]_3$	2.45	2.017(2)	134.5(3)	106.4(1)	[6]	
$[Me_2GaNHPh]_2$	– ^{a}	2.039(3)	93.6(1)	86.4(1)	[4]	107(4)
$[Me_2GaNHDipp]_2$	– ^{a}	2.024(11)	94.2(4)	83.6(4)	[4]	91(4)
$[Me_2GaNH(1\text{-}Ad)]_2$	– ^{a}	2.031(3)	94.7(1)	85.3(1)	[4]	101(3)
$Me_3Ga–NH_2({}^tBu)$	2.52	2.12(1)	–	–	[2]	104.0
${}^tBu_3Ga \cdot NH_2Ph$	2.42	2.246(9)	–	–	[1]	87.0
$TMPH \cdot GaCl_3$ (**3**)	2.28(9)	2.050(7)	–	–	–	
$Me_2Si(NMe_2)_2 \cdot GaCl_3$	–	2.003(5)	–	–	[5]	–

^{a} These values were not reported.

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* Reference number with an asterisk indicates a note in the list of references.

aromatic interactions in organic moieties which have been the subject of recent experimental and theoretical studies. The shortest of these, between the hydrogen of a water molecule and the centroid of a benzene ring in a calixarene (2.38 Å), is comparable with those in **1** and **2** [8]. Further studies are in progress to determine what role these weak interactions may play in heavier main group chemistry.

2.3. Synthesis and characterization of TMPH · $GaCl_3$ (3) and $^iPr_2NH \cdot GaCl_3$ (4)

In order to explore further the nature of close Ga · · · H–N distances the secondary amine adducts of $GaCl_3$ (**3** and **4**) were studied. These compounds were prepared by the addition of the amine to $GaCl_3$ at a low temperature in toluene or benzene. The use of THF or Et_2O as solvent leads to the formation of the solvent · $GaCl_3$ adducts. Both compounds can be crystallized as colorless crystalline solids from non-polar solvents. The NMR spectra of **3** and **4** show resonances that are shifted slightly up-field compared with the resonances for the free amine. Thus the N–H groups are manifested as broad singlets for **3** and **4** at δ 2.43 ppm and 2.51 ppm respectively. In the IR spectrum the ν_{N-H} absorbances are at 3175 cm^{-1} and 3191 cm^{-1} for **3** and **4** respectively. These values are very similar to those found for free TMPH (3186.36 cm^{-1}) and $^iPr_2NH$ (3191.29 cm^{-1}). The slight shift down-field can be attributed to a weakening of the N–H bond on nitrogen coordination to gallium. Thus, spectroscopically, the presence of a Ga · · · H–N interation may be too weak to be detected.

2.4. X-ray structure of 3

In order to probe further the nature of the bonding in secondary amine adducts of $GaCl_3$, an X-ray crystal structure analysis was conducted on **3**. Molecules of **3** crystallize in the monoclinic space group $P2_1/n$ with four molecules in the unit cell. An ORTEP view of **3** with the atom numbering scheme is shown in Fig. 3, while key bond distances, angles and fractional coordinates are given in Tables 6 and 7.

Molecules of **3** are manifested as a Lewis acid–Lewis base adducted complex. The structure shows the gallium atom to be in a tetrahedral environment with the largest deviations found in the Cl–Ga–N angles, resulting from the steric effects of the TMP *o*-methyl groups. The Ga–N distance (2.050(7) Å) corresponds closely to that found for $Me_2Si(NMe_2)_2 \cdot GaCl_3$ (2.003(5) Å) [5]. The distances seen for **3** and the adducts in Table 5 show a close correlation between steric bulk and increasing Ga–N distance.

The nitrogen-hydrogen atom in **3** was located from difference Fourier maps and then refined as an indi-

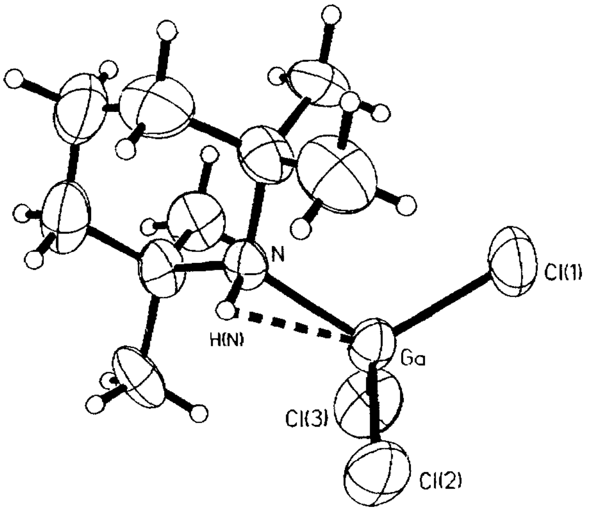


Fig. 3. Molecular structure and atom numbering scheme for TMPH · $GaCl_3$ (**3**).

TABLE 6. Positional parameters for **3**

Atom	*x*	*y*	*z*	U_{eq}
Ga	0.8602(1)	−0.0620(1)	0.7316(1)	0.047(1)
Cl(1)	0.7091(4)	0.0720(2)	0.6812(2)	0.080(1)
Cl(2)	0.7914(4)	−0.1265(2)	0.8738(2)	0.072(1)
Cl(3)	1.0840(4)	0.0149(3)	0.7523(2)	0.088(1)
N	0.8437(8)	−0.1994(6)	0.6436(5)	0.038(2)
NH	0.8244(103)	−0.2442(72)	0.6959(60)	0.062(31)
C(1)	0.6980(11)	−0.2057(8)	0.5677(7)	0.051(4)
C(11)	0.5549(12)	−0.1922(10)	0.6296(8)	0.082(5)
C(12)	0.7001(13)	−0.1185(8)	0.4861(7)	0.068(4)
C(2)	0.6894(14)	−0.3200(9)	0.5202(8)	0.075(5)
C(3)	0.8373(16)	−0.3542(9)	0.4759(8)	0.087(6)
C(4)	0.9682(14)	−0.3536(8)	0.5567(8)	0.073(5)
C(5)	0.9979(10)	−0.2428(8)	0.6078(7)	0.049(3)
C(51)	0.1107(1)	−0.2598(8)	0.7033(7)	0.063(4)
C(52)	0.1066(1)	−0.1621(8)	0.5362(7)	0.063(4)

TABLE 7. Selected bond lengths (Å) and angles (°) for **3**

Distances			
Ga–Cl(1)	2.175(3)	Ga–Cl(2)	2.161(3)
Ga–Cl(3)	2.151(3)	Ga–N	2.050(7)
N–NH	0.895(87)	N–C(1)	1.547(11)
N–C(5)	1.544(12)		
Angles			
Cl(1)–Ga–Cl(2)	110.2(1)	Cl(1)–Ga–Cl(3)	102.5(1)
Cl(2)–Ga–Cl(3)	111.0(1)	Cl(1)–Ga–N	116.0(2)
Cl(2)–Ga–N	100.2(2)	Cl(3)–Ga–N	117.2(2)
Ga–N–NH	93.3(54)	Ga–N–C(1)	115.1(5)
NH–N–C(1)	106.1(54)	Ga–N–C(5)	115.8(5)
NH–N–C(5)	104.4(56)	C(1)–N–C(5)	117.6(6)

vidual atom. The refinement resulted in a Ga ··· H–N distance of 2.28(9) Å. This is similar to the distance seen in compound **1** (2.33 Å). As for compounds **1** and **2** the Ga–N–NH angle is 93.3(54)° which appears to position the hydrogen atom in a bridging capacity with respect to the N and Ga atoms. However, in this case, the steric effects of the TMP group, seen in a wide C–N–C angle (117.6(6)°), may explain the narrower Ga–N–NH angle.

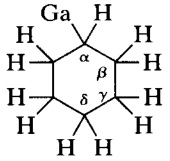
Two types of Ga ··· H–N interaction have been described in this paper. The first appears motivated by an attraction between a N–$H^{\delta+}$ and the electron density present in a Ga_2N_2 four-membered ring. As seen in Table 5, the shorter Ga ··· H distances appear in compounds which feature relatively acidic amide groups. The second type of short Ga ··· H distances occurs in monomeric adducts of trisubstituted gallium(III) with primary and secondary amines. However, in this case there is no recognizable electronic motivation or solution spectroscopic indications of a Ga ··· H interaction, and the short Ga ··· H distance may be attributed to steric effects.

3. Experimental section

All reactions were performed under oxygen-free nitrogen or under vacuum using Schlenk line or dry-box techniques. Toluene, hexane and diethylether were distilled from sodium–benzophenone under nitrogen prior to use. Aniline and t-butyl amine were dried over molecular sieves and then distilled from calcium hydride before use. The instruments used were as follows: IR, Perkin–Elmer 1330, Digilab FTS-40; NMR, GE QE-300, ^1H, 300.17 MHz. Mass spectral analyses, EI and CI, were recorded on a Bell and Howell 21-491 instrument. Elemental Analysis (C, H and N) were carried out with a Perkin–Elmer 3100 analyzer. IR spectra were run as Nujol mulls using KBr plates. NMR spectra were recorded in C_6D_6, toluene-d_8, or $CDCl_3$ and are in parts per million referenced to Me_4Si (0.0 ppm). All NMR solvents were dried over 4 Å molecular sieves prior to use. Melting points were obtained in sealed capillaries under argon (1 atm) and are uncorrected. Elemental analyses on all compounds (C, H and N) were satisfactory.

3.1. Synthesis of $[Cy_2Ga(\mu\text{-}NHPh)]_2$ (1)

To a stirred diethylether solution of Cy_2GaCl (4.43 g, 18.17 mmol) prepared according to the method in the literature [9] was added, at −78°C, a solution of LiNHPh, prepared from the reaction of ^{t}BuLi (9.0 ml, 2.02 M, 18.17 mmol) with NH_2Ph (1.66 ml, 18.17 mmol). The reaction mixture was allowed to warm to 25°C and then heated to 60°C for 5 h before solvent removal and extraction–filtration in hexane (200 ml). The hexane solution was concentrated (25 ml) and then cooled to −30°C for 5 days to afford colorless microcrystalline **1** (melting point (m.p.), 101–103°C; yield, 5.00 g (83.9%)). X-ray quality crystals were grown from a diethylether solution cooled to −30°C for 2 weeks. ^1H NMR (C_6D_6): 7.08 (t, 1H, *Ph*–N), 6.99 (t, 2H, *Ph*–N), 6.80 (d, 2H, *Ph*–N), 1.57 (m, 2H, δ-CH_2), 1.03 (m, 4H, γ-CH_2), 0.88 (m, 4H, β-CH_2), 0.75 (m, 2H, α-CH) ppm. The labelling scheme for the cyclohexyl hydrogen atoms is shown below. (MS) (EI, 70 eV): 654 (M^+).



3.2. Synthesis of $[Cy_2Ga(\mu\text{-}NH(^tBu))]_2$ (2)

To a stirred diethyl ether solution of Cy_2GaCl (6.70 g, 24.69 mmol) prepared according to the method in the literature [9] was added, at −78°C, a solution of $LiNH(^tBu)$, prepared from the reaction of ^{t}BuLi (12.2 ml, 2.02 M, 24.65 mmol) with $NH_2(^tBu)$ (2.59 ml, 24.65 mmol). The reaction mixture was allowed to warm to 25°C and then heated to 60°C for 4 h before solvent removal and extraction–filtration in hexane (200 ml). The hexane solution was concentrated (30 ml) and then cooled to −30°C for 7 days to afford colorless crystalline **2** (m.p., 95–97°C; yield, 6.5 g (85.6%)). X-ray quality crystals were grown from a diethyl ether solution cooled to −30°C for 30 days. ^1H NMR (C_6D_6): δ 1.45 (s, 9H, ^{t}*Bu*–N), 1.32 (m, 4H, δ-CH_2), 1.11 (m, 4H, γ-CH_2), 1.01 (m, 4H, β-CH_2), 0.95 (m, 1H, α-CH) ppm. MS (EI, 70 eV): 614 (M^+).

3.3. Synthesis of $TMPH \cdot GaCl_3$ (3)

To a stirred solution of $GaCl_3$ (0.013 mol, 2.29 g) in benzene (50 ml) at −78°C was added one equivalent of TMPH (0.013 mol, 1.84 g) in benzene (10 ml). The reaction mixture was allowed to warm to 25°C over 2 h and then stirred at that temperature for 6 h before the solvent was removed *in vacuo* and the resulting pale-red solid extracted in toluene (100 ml) and filtered. The filtrate was concentrated (30 ml) and then stored at −30°C for 2 weeks to afford **3** as football-shaped crystals (m.p. 170–173°C; yield, 3.92 g (95%). ^1H NMR (C_6D_6): δ 2.43 ((br), 1H, H–N), 1.340 (s, 12H, Me_2C), 1.106 (s(br), 6H, CH_2) ppm. MS (CI, CH_4): 316 (M^+ + H).

3.4. Synthesis of $^iPr_2NH \cdot GaCl_3$ (4)

To a stirring solution of $GaCl_3$ (4.00 mmol, 0.70 g) in toluene (15 ml), at −78°C, was added one equiva-

TABLE 8. Crystal data, details of intensity measurement and structure refinement for $[Cy_2Ga(\mu\text{-}NHPh)]_2$ (**1**), $[Cy_2Ga(\mu\text{-}NH({}^tBu))]_2$ (**2**) and TMPH · $GaCl_3$ (**3**)

Compound	**1**	**2**	**3**
Formula	$C_{36}H_{56}N_2Ga_2$	$C_{32}H_{64}N_2Ga_2$	$C_9H_{19}Cl_3NGa$
Mass	656.29	616.31	317.34
Crystal dimensions (mm × mm × mm)	0.05 × 0.08 × 0.10	0.06 × 0.06 × 0.09	0.2 × 0.3 × 0.6
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	9.736(1)	9.951(1)	8.640(2)
b (Å)	9.852(1)	10.079(1)	12.311(2)
c (Å)	10.962(1)	11.048(1)	13.187(3)
α (°)	71.297(1)	98.36(1)	90
β (°)	70.207(1)	116.52(1)	94.51(3)
γ (°)	63.306(1)	114.24(1)	90
V (Å^3)	865(5)	827(5)	1398.3(7)
D_c (g cm^{-3})	1.286	1.245	1.507
Z	1	2	4
Radiation	Mo Kα	Mo Kα	Mo Kα
Total reflections	3039	2034	1821
Total observations	2907	1341	1254
Sigma test	$F_o > 6\sigma(F)$	$F_o > 6\sigma(F)$	$F_o > 4.0\sigma(F)$
Number of parameters	72	163	133
Weighting scheme, g in $[(\sigma F)^2 + gF^2]^{-1}$	0.000625	0.000625	0.0008
Final R	0.0770	0.0736	0.0597
Final R_w	0.1008	0.0905	0.0543

lent of ${}^iPr_2NH$ (4.00 mmol, 0.56 ml). The reaction mixture was allowed to warm to 25°C over 1 h and then stirred at that temperature for 1 h before concentration (5 ml). Cooling of this solution to −30°C for 12 h afforded colorless crystals of **4** (m.p. 85–86°C, yield, 0.92 g (85%)). ^{1}H NMR (C_6D_6): δ 3.11 (br, 2H, C–H), 2.51 (br, 1H, H–N), 0.89 (br, 12H, $(CH_3)_2$) ppm. MS(CI, CH_4): 276 ($M^+ + H$).

4. X-ray experimental data

Details of crystal data and a summary of intensity data collection parameters for **1**, **2** and **3** are given in Table 8. The crystals were mounted in thin-walled glass capillaries and sealed under argon. Unit-cell parameters were obtained by centering 25 reflections having 2θ values between 22 and 26°. For **1** and **2**, data were collected on an Enraf–Nonius CAD-4 diffractometer at $2\theta = 2$–$50°$ using graphite-monochromated Mo Kα radiation. The data for **3** were collected on a Siemens R3m/v diffractometer. Intensity data were recorded in the usual manner [10]. The intensity standards for each data collection indicated a decrease in intensity of less than 2% over the course of data collection, and no correction was applied, unless otherwise indicated. Calculations for **1** and **2** were performed on a Microvax 3100 computer using SHELX software [11]. The calculations for **3** were performed on an IBM PC using the Siemens SHELXTL PLUS software package. For each structure, the data were corrected for Lorentz and polarization effects. The observed structure factors of equivalent reflections were averaged. The structures were solved by direct and Patterson methods with successive interpretation of difference Fourier maps, followed by least-squares refinement. Data with intensities less than $3.0\sigma(I)$ and with $\sin\theta/\lambda$ less than 0.10 were excluded, and weighting schemes of $[(\sigma F)^2 + 0.000625F^2 = {}^{-1}$ for **1** and **2** and of $[(\sigma F)^2 + 0.0008F^2]^{-1}$ for **3** were used in the final stages of the refinement.

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