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Primary amide and amine complexes of gallium and indium: X-ray crystal structures of $[Me_2Ga(\mu\text{-}NH(^tBu))]_2$, $Me_3Ga \cdot NH_2(^tBu)$ and $Me_3In \cdot NH_2(^tBu)$.

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Abstract

The reaction of Me_2GaCl with $LiNH(^tBu)$ in diethylether at −78°C produces the dinuclear primary amido-bridged complex $[Me_2Ga(\mu\text{-}NH(^tBu))]_2$ (**1**) in 76% yield. The $^tBuNH_2$ adducts $Me_3M \cdot NH_2(^tBu)$, M = Ga (**2**), in (**3**), have been prepared in quantitative yield by the reactions of Me_3M with $^tBuNH_2$ in toluene at −78°C. The X-ray structure of **1** reveals that the Ga_2N_2 core is planar and that the ^tBu–N groups adopt an *anti* configuration. The solid state structures of **2** and **3** feature approximately tetrahedral nitrogen and metal geometries. In both compounds staggered arrangements are observed for the metal methyl groups and the nitrogen t-butyl groups. However, in **3** the arrangement is distorted so that no internal symmetry is present. In **2** the staggered geometry is symmetrical as indicated by the presence of a minor plane which contains the bonded atoms C(5), Ga, N, C(1) and C(2).

Introduction

The recent interest in compounds featuring bonds between the Group 13 and 15 elements is attributable to the potential of these compounds to serve as precursors to III/V (13/15) compound semiconductor materials [1]. Amine adducts and amido complexes of gallium and indium alkyls are well known [2]; however, relatively little structural information is available for these classes of compound [3]. Recently we reported the syntheses and X-ray analyses of $^tBu_3Ga \cdot NH_2Ph$ and $[^tBu_2Ga(\mu\text{-}NHPh)]_2$ [4]. To our knowledge, these compounds represent the first structurally characterized examples of a $^tBu_3Ga$ adduct and an alkyl gallium

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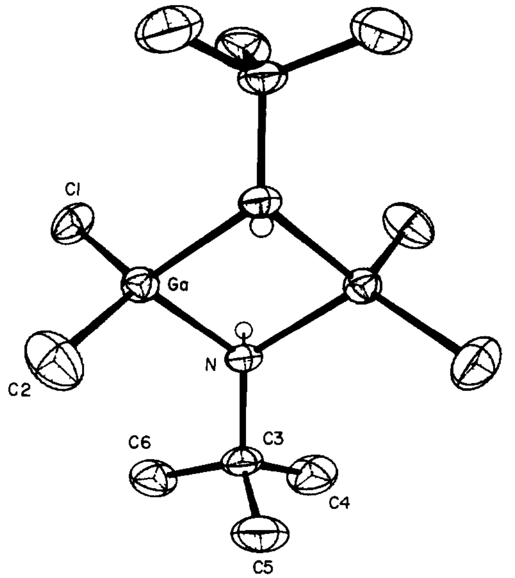

Fig. 1. View (ORTEP) of 1 showing the atom numbering scheme. Hydrogen atoms on carbon omitted for clarity.

primary amido complex, respectively. Of related interest are the compounds $[Cl_2GaN(H)SiMe_3]_2$ [5], $[Br_2GaN(H)SiMe_3]_2$ [6] and $[Me_2GaN(H)Dipp]_2$ [7]. The focal point of interest in these compounds was the possibility of close N–H $\cdots$ Ga interactions. In order to explore this phenomenon further, we have now prepared and performed X-ray analyses on $[Me_2Ga(\mu\text{-}NH(^tBu))]_2$ (**1**) and $Me_3M \cdot NH_2(^tBu)$ (M = Ga (**2**), In (**3**)).

Results and discussion

Synthesis and characterization of $[Me_2Ga(\mu\text{-}NH(^tBu))]_2$ *(1)*

The reaction of Me_2GaCl(prepared *in situ*) with $LiNH(^tBu)$ in diethyl ether at −78°C, followed by warming to 25°C, produces $[Me_2Ga(\mu\text{-}NH(^tBu))]_2$ (**1**) in 76% yield. Colorless, crystalline **1** is stable in air for up to 12 h. The spectroscopic data for **1** are in accord with the solid-state X-ray structure (*vide infra*). Thus both the EI (70 eV) and CI (CH_4) mass spectra of **1** exhibit a peak at m/z 329 which corresponds to the dimer minus methyl. No peaks attributable to the monomer were detectable under these conditions. The ^1H NMR spectrum comprises only two sharp singlets at δ −0.08 (12 H, Me–Ga) and δ 0.98 (18 H, ^{t}Bu–N) thus indicating a symmetrical structure. No N–*H* resonance was detected.

X-Ray crystal structure of 1

Crystals of **1** suitable for X-ray structural analysis were obtained from hexane solution after prolonged storage at −30°C. An ORTEP view of **1** is shown in Fig. 1 and pertinent crystallographic data are presented in Table 1. Some key bond lengths and the positional parameters are compiled in Tables 2 and 3, respectively.

Table 1

Crystal data and details of intensity measurements and structure refinement

	$Me_2GaNH_2(^tBu)$ (1)	$Me_3GaNH_2(^tBu)$ (2)	$Me_3InNH_2(^tBu)$ (3)
Formula	$C_{12}H_{32}N_2Ga_2$	$C_7H_{20}NGa$	$C_7H_{20}NIn$
M	343.84	187.96	232.90
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/m$	$P2_1$
a (Å)	6.799(1)	6.413(1)	6.5954(8)
b (Å)	12.184(1)	10.720(1)	19.844(2)
c (Å)	10.870(1)	8.443(1)	8.581(3)
α (°)	90	90	90
β (°)	95.34(8)	110.12(6)	111.60(3)
γ (°)	90	90	90
U (Å^3)	896.5(6)	545(5)	570.60(5)
Z	2	2	2
D_c (g cm^{-1})	1.279	1.150	1.345
$F(000)$	360	200	232
μ (cm^{-1})	29.92	24.66	19.8
hkl range	$h = 0-8$ $k = 0-15$ $l = -12 \rightarrow 12$	$h = 0-8$ $k = 0-12$ $l = -11 \rightarrow 11$	$h = 0-8$ $k = 0-14$ $l = -11 \rightarrow 10$
Total no. of reflections	1833	1140	1500
No. of unique reflections	1691	1078	1388
Significance test	$F_o > 6\sigma(F_o)$	$F_o > 6\sigma(F_o)$	$F_o > 5\sigma(F_o)$
No. of observed reflections	1105	703	938
No. of refined parameters	73	49	72
Weighting scheme parameter g in $1/[\sigma^2(F_o) + gF_o^2]$	0.000625	0 000625	0 000625
Final R	0.0468	0.0670	0.052
Final R_W	0.0595	0.0741	0.069

The observation of a dimeric structure for **1** is in keeping with the structures that have been found for other group 13 dialkyl amido compounds [8]. Individual molecules of **1** reside on a twofold axis of symmetry and there are no short intermolecular contacts. The dimeric structure causes the bond angles within the planar Ga_2N_2 core to be highly strained (84.8(2)° for N–Ga–N′ and 95.3(3)° for Ga–N–Ga′). This angle strain would be reduced in a cyclohexane-like trimeric

Table 2

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

Atoms	Distance	Atoms	Angle
Ga–N	2.012(4)	N–Ga–N′	84.8(2)
Ga–C(1)	1.978(7)	Ga–N–Ga′	95.3(3)
Ga–C(2)	1.968(7)	C(1)–Ga–C(2)	118.4(3)
N–C(3)	1.513(7)	Ga–N–C(3)	124.7(4)
N–H(1)	1.020	N–Ga–C(1)	107.3(2)
Ga· ·H(1)	2.390	N–Ga–C(2)	117.2(3)
		Ga–N–H(1)	108.0
		C(3)–N–H(1)	103.0

Table 3

Atomic coordinates for adducts **1**

Atom	x	y	z
Ga	0.4096(1)	0.61113(5)	0.49208(6)
N	0.4264(6)	0.4837(4)	0.6103(4)
C(1)	0.128(1)	0.6304(6)	0.4324(7)
C(2)	0.566(1)	0.7424(6)	0.5411(7)
C(3)	0.4596(9)	0.4939(6)	0.7493(5)
C(4)	0.434(2)	0.3826(6)	0.8043(7)
C(5)	0.667(1)	0.5379(7)	0.7872(7)
C(6)	0.306(1)	0.5706(7)	0.7913(7)

structure in which the bond angles are approximately tetrahedral. However, in such a structure the steric repulsion between the nitrogen t-butyls and gallium methyls would be increased significantly. It is only when sterically less demanding substituents (*e.g.* Me, Et) are employed that trimerization is observed [9]. Structural preferences are therefore governed by steric rather than electronic effects. The Ga–N bond distances within the inner core are equivalent within experimental error (2.011(4) and 2.012(4) Å). This is a common feature of the M_2E_2 cores of dimers (M = Group 13 element; E = Group 15 element) and can be attributed to mixing of two canonical forms [1]. The Ga–N bond distance in **1** is comparable to those in $[{}^t\mathrm{Bu}_2\mathrm{Ga}(\mu\text{-NHPh})]_2$ (2.103(9) and 2.018(9) Å), the only structurally characterized primary amido gallium dimer [4]. The geometries at gallium and nitrogen are approximately tetrahedral; however, there is a wide scatter of bond angles (Table 1). The nitrogen hydrogen atoms of **1** project symmetrically above and below the Ga_2N_2 plane in keeping with the C_2 rotational axis present along the Ga–Ga′ vector. The Ga $\cdots$ H distance of 2.39 Å in **1** is considerably larger than that in $[{}^t\mathrm{Bu}_2\mathrm{Ga}(\mu\text{-NHPh})]_2$ (2.037 Å [4]). This may be a consequence of the lower acidity of a ^{t}BuNH group compared with a PhNH group which in turn would result in the dipolar interaction between N–$H^{\delta+}$ and the Ga_2N_2 ring being smaller.

Synthesis and characterization of $Me_3M \cdot NH_2({}^tBu)$ (M = Ga (2), In (3))

The adducts of t-butyl amine with trimethylgallium and trimethylindium were prepared by addition of the amine to stirred solutions of the metal trialkyl in toluene at −78°C. The reaction mixtures were allowed to warm to 25°C and stirred for a further 24 h at that temperature. Compounds **2** and **3** are white crystalline solids that exhibit extreme air sensitivity. Both compounds can be purified by vacuum sublimation (for **2**, 65–67°C (10^{-3} Torr); for **3**, 72°C (10^{-3} Torr)). Monitoring of the reaction mixtures by ^{1}H NMR spectroscopy indicated that **2** and **3** are the only products. As expected, the chemical shifts of the $Me_3M \leftarrow L$ resonances (**2**, δ −0.30 (s); **3** δ −0.18 (s)) are slightly downfield of those due to the free metal trialkyl (Me_3Ga, δ 0.031 (s); Me_3In, δ 0.028 (s)). Likewise the protons on the β-carbon of the complexed t-butyl amine (**2**, 0.63 (s); **3**, 0.56 (s)) are also shifted downfield relative to those of the parent amine (δ 1.0 (s)). The N–H protons are manifested as a broad peak ($W_{1/2}$ = 10 Hz) centered at δ 1.26 in the case of **3**. No N–H resonance was detected for **2**.

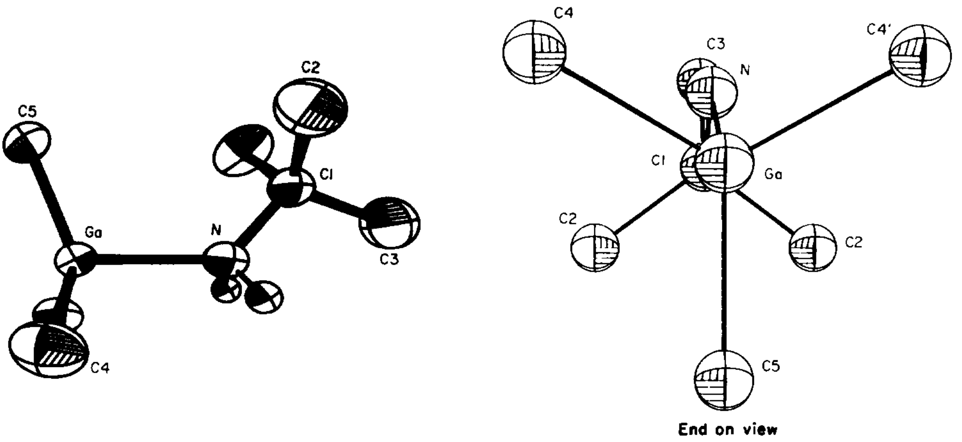

Fig 2. (a) View (ORTEP) of 2 showing the atom numbering scheme. Hydrogen atoms on carbon omitted for clarity (b) End on view of 2.

Adducts **2** and **3** are also stable in solution. Thus it is only after prolonged reflux in toluene that decomposition is detectable. The resulting white insoluble solids are tentatively formulated as alkyl metal-imido polymers.

Crystals of **2** and **3** suitable for X-ray structural studies were obtained by cooling concentrated hexane solutions to −30°C for several days. ORTEP views of **2** and **3** are shown in Figs. 2 and 3 respectively, and pertinent crystallographic data are presented in Table 1. Key bond lengths and angles are listed in Table 4 and positional parameters are assembled in Table 5. The geometry around the nitrogen and gallium atoms in **2** is approximately tetrahedral. The Ga–N bond distance for **2** is 2.12(1) Å, this compares to 2.246(9) Å for the more sterically hindered, $^{t}Bu_3GaNH_2Ph$. A mirror plane is present in **2** and bisects the atoms C(5), Ga, N, C(1) and C(3). Atoms C(2) and C(4) are reflected through the plane. Although the indium adduct **3** has no internal symmetry, the arrangement of the methyl groups

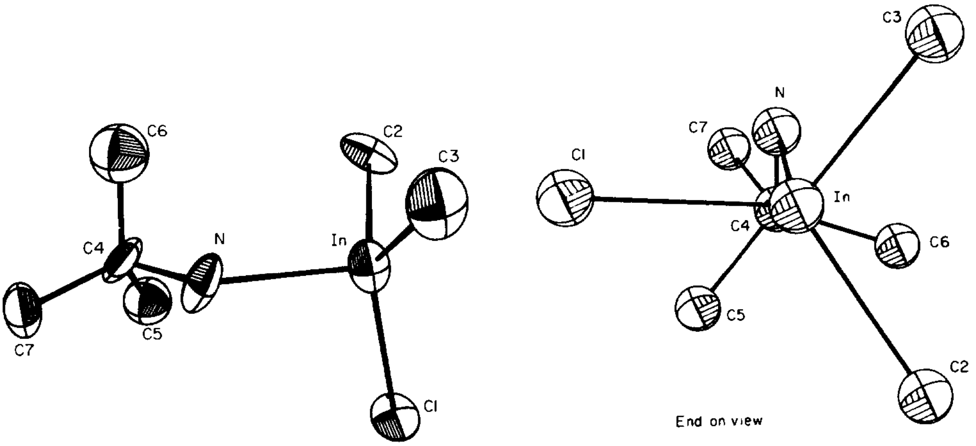

Fig. 3. View (ORTEP) of 3 showing the atom numbering scheme. Hydrogen atoms on carbon omitted for clarity. (b) End on view of 3.

Table 4

Selected bond lengths (Å) and angles (°) for adducts **2** and **3**

Atoms	Distance	Atoms	Angle
Adduct 2			
Ga–N	2.12(1)	Ga–N–C(1)	129.2(8)
Ga–C(4)	2.01(1)	C(4)–Ga–C(4)′	111.8(4)
Ga–C(5)	1.95(1)	C(4)–Ga–C(5)	117.1(4)
N–C(1)	1.47(2)	N–Ga–C(4)	98.5(4)
		N–Ga–C(5)	110.4(5)
Adduct 3			
In–N	2.363(8)	In–N–C(4)	124.7(4)
In–C(1)	2.24(2)	C(1)–In–C(2)	125.2(7)
In–C(2)	2.27(2)	C(1)–In–C(3)	117.7(9)
In–C(3)	2.17(3)	N–In–C(1)	97.2(7)
N–C(4)	1.53(2)	N–In–C(2)	106.7(4)

is staggered as in **2**. However, the geometry of the methyl groups around indium is closer to trigonal planar. (Al C–In–C angles are within 120 ± 7°.) For both adducts the obtuse M–N–C angles (129.2(8)° for **2** and 124.7(9)° for **3**) can be attributed to steric repulsions between the nitrogen t-butyl methyls and the metal methyls. In **3** the M–N–C angle is slightly smaller than that for **2** due to the longer M–N bond length. Finally, we note that the Ga ··· H separation in **2** (2.52 Å) is close to the average of the two Ga ··· H distances in the somewhat distorted adduct $^{t}Bu_3Ga \cdot NH_2Ph$ (2.42 and 2.63 Å [4]).

Table 5

Atomic coordinates for adducts **2** and **3**

Atom	*x*	*y*	*z*
Adduct 2			
Ga	0.1577(2)	0.2500	0.4031(2)
N	0.435(2)	0.2500	0.631(1)
C(1)	0.440(2)	0.2500	0.807(2)
C(2)	0.315(2)	0.136(1)	0.832(2)
C(3)	0.678(3)	0.2500	0.917(2)
C(4)	0.230(2)	0.095(1)	0.299(1)
C(5)	−0.119(2)	0.2500	0.452(2)
Adduct 3			
In	0.1388(2)	0.000	0.3877(1)
N	0.442(2)	0.020(2)	0.641(1)
C(1)	0.234(4)	−0.181(2)	0.308(2)
C(2)	−0.0162(2)	0.033(2)	0.450(2)
C(3)	0.197(3)	0.166(3)	0.269(2)
C(4)	0.441(2)	−0.011(3)	0.815(1)
C(5)	0.335(3)	−0.136(2)	0.814(2)
C(6)	0.313(4)	0.094(3)	0.854(3)
C(7)	0.678(3)	−0.030(2)	0.946(2)

Experimental

All reactions were carried out under a dry nitrogen atmosphere using high vacuum line or Schlenk-type techniques. The crystals for the X-ray diffraction studies were sealed in Lindemann capillaries and mounted in an argon-filled dry box. Methyllithium was prepared by the reaction of MeI with Li metal in diethyl ether. n-Butyl lithium (Aldrich) was filtered prior to use. Both alkyllithiums were titrated immediately prior to use. Trimethyl gallium was prepared by the literature method [10]. Trimethyl indium was used as received from Alfa. Chlorodimethyl gallium was prepared by the reaction of methyllithium with gallium trichloride in a 2:1 molar ratio at −78°C in Et_2O. t-Butyl amine was dried over CaH_2 and distilled under nitrogen. All NMR solvents were dried over 4 Å molecular sieves prior to use.

Infrared spectra were obtained on a Digilab FT spectrometer. NMR spectra were recorded on a GE QE 300 spectrometer operating at a frequency of 300 MHz. Proton chemical shifts are quoted relative to tetramethylsilane with the signals due to incomplete solvent deuteration used as internal standards. Mass spectra, EI and CI, were run on a Bell and Howell 21-491 instrument. Only the peaks of major intensity are reported. Elemental analyses (Perkin–Elmer 2400, C, H, N) for **1–3** fell within acceptable limits.

Bis(μ-tert-butylamido)tetramethyldigallium (III)

Methyllithium (62.6 ml of 0.74 *M* solution, 46 mmol) in diethyl ether was added dropwise to a stirred solution of $GaCl_3$ (4.08 g, 23.17 mmol) in 50 ml of Et_2O solution at −78°C. The reaction mixture was allowed to warm to 25°C and then stirred for a further 6 h prior to filtration. To the filtrate was added (at −78°C) 1 equiv. of LiNH(^{t}Bu) which had been prepared by the action of ^{t}BuLi (27.92 ml of 0.83 *M* hexane solution, 23.17 mmol) with $^tBuNH_2$ (2.43 ml, 23.17 mmol) in 20 ml of Et_2O. The resulting reaction mixture was allowed to warm to 25°C and then stirred for 12 h. The solvents and volatiles were removed *in vacuo* and the residue was extracted with 50 ml of hexane then filtered. Colorless crystals of **1** (m.p. 72–76°C, dec.) formed after prolonged storage of the filtrate at −30°C. ^1H NMR (300 MHz, C_6D_6): −0.08 (12H, s, Me–Ga); 0.98 (18H, s, ^{t}BuN) ppm; N–H resonances not observed. MS (70 eV, 25°C): *m/z* 329 (100%, dimer-Me); IR: 1290w, 1100w, 1022m, 960s, 950m, 875s, 800w cm^{-1}, ν(N–H) (not observed).

Trimethylgallium-tert-butyl amine (2)

A slight excess of $^tBuNH_2$ was added to a stirred solution of Me_3Ga at −78°C. The reaction mixture was allowed to warm to 25°C and the solvent and excess amine were removed *in vacuo*. The residue was redissolved in 20 ml of hexane then filtered. Clear, cubic crystals of **2** (m.p. 65–67°C) formed after storage of the filtrate at −30°C. ^1H NMR (300 MHz, toluene-d_8, C_6D_6): −0.09 (9H, s, Me–Ga), 0.63 (9H, s, ^{t}BuN) ppm; N–H resonances not observed. MS (70 eV, 25°C): *m/z*, 129 (100%) $GaMe_3$, no parent peak observed; IR: 3308s, 3259s, 1580m, 1340m, 1212w, 885w, 796m cm^{-1}.

Trimethylindium-tert-butyl amine (3)

A slight excess of $^tBuNH_2$ was added to a stirred toluene solution of Me_3In at −78°C. The reaction mixture was allowed to warm to 25°C and then stirred for 12 h at this temperature before the solvents and excess amino were removed *in vacuo*. The residue was redissolved in 20 ml of hexane and then filtered. Large rectangular crystals of **3** (m.p. 80–81°C sub.) formed after storage of the filtrate at -30°C. ^{1}H NMR (300 MHz, toluene-d_8): -0.12 (9H, s, Me–In); 0.57 (9H, s, ^{t}BuN); 1.29 (2H, br, N–H$_2$) ppm. MS (70 eV, 25°C): m/z 218 (100% monomer). IR: 3282m, 3216m, 1540m, 1318m, 1160w, 920w, 900w, 790s cm^{-1}.

X-Ray crystallography

For each of the three compounds studied, a single crystal was sealed in a Lindemann capillary. Final lattice parameters were determined from 25 reflections ($2\theta > 30°$) accurately centered on an Enraf–Nonius CAD-4 diffractometer utilizing Mo-K_α radiation (0.71069 Å). Intensity data were recorded in the usual manner [11]. The position of the heavy atom in each compound was determined from a Patterson map. Subsequent difference Fourier maps permitted the location of all non-hydrogen atoms. All hydrogen atoms were placed in calculated positions and allowed to "ride" upon the appropriate carbon or nitrogen atoms. The largest parameter shifts in the final cycles of refinement were less than 0.01 of their estimated standard deviations. Neutral atom scattering factors were taken from the usual sources [12]. All computer programs were taken from the SHELX suite [13].

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