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Formation and Characterization of the Cationic Gallane Derivatives $[(RH_2N)_2GaH_2]Cl$ (R = Me or *i*Pr) and $[\{(iPrH_2N)GaH_2NHiPr\}_2GaH_2]Cl$

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The reaction of $LiGaH_4$ with an excess of the hydrochloride of a primary amine RNH_2 in ether solution yields in $[(RH_2N)_2GaH_2]Cl$ (R = Me, **1**, or *i*Pr, **2**) additional examples of cationic gallane derivatives. The cation $[(iPrH_2N)_2GaH_2]^+$ reacts further with $LiGaH_4$, also in ether solution, with H_2 elimination and formation of the trigallium cationic derivative $[\{(iPrH_2N)GaH_2NHiPr\}_2GaH_2]Cl$, **3**. Prolonged standing of $[(iPrH_2N)_2GaH_2]Cl$ in the presence of LiCl results in partial exchange of Ga–H by Ga–Cl bonds, with the isolation in low yield of crystals, **4**, of $[(iPrH_2N)_2GaH_2]Cl$ in which about 7 % of the H atoms attached to Ga were replaced by Cl. All of the compounds **1**–**4** having been characterized crystallographically, the results are discussed in relation to the different reaction pathways open to $[RNH_3]Cl$ and $LiMH_4$ (M = Al or Ga).

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Introduction

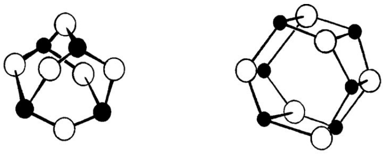
The reaction between an amine hydrochloride salt, $[R_xNH_{4-x}]Cl$ (x = 1–3), and a lithium tetrahydridometalate, $LiMH_4$ (M = B, Al or Ga), in ether solution has been commonly used as a route to the neutral amine complex $R_xH_{3-x}N{\cdot}MH_3$ [Equation (1)],[1–7] HCl being effectively displaced as the acid by MH_3. However, it has long been appreciated that, depending on the relative proportions of the reagents and the precise conditions under which they are held, other reactions may intervene. Thus, we have reported recently[8] the preparation of complexes of monochlorogallane, GaH_2Cl, by the reaction of an excess of the hydrochloride of the base (or the base + HCl) with $LiGaH_4$ in ether solution, thereby circumventing the difficulties of preparing, purifying and manipulating monochlorogallane itself.[9,10] With the primary amines sBuNH$_2$ and tBuNH$_2$, one reaction proceeds in accordance with Equation (2), with the elimination of H_2 and the formation of the first clearly authenticated examples of 2:1 cationic monochlorogallane complexes of the type $[(RH_2N)_2GaH_2]Cl$ (R = *s*Bu or *t*Bu).[8]

$$[R_xNH_{4-x}]Cl + LiMH_4 \rightarrow R_xH_{3-x}N{\cdot}MH_3 + LiCl + H_2 \quad (1)$$

$$2\,[RNH_3]Cl + LiGaH_4 \rightarrow [(RH_2N)_2GaH_2]^+Cl^- + LiCl + 2\,H_2 \quad (2)$$

Similar alane derivatives of the type $[H_2AlL]^+[AlH_4]^-$ had been prepared previously by treatment of $Me_3N{\cdot}AlH_3$ with a tridentate or macrocyclic base L.[11]

Such compounds are of interest in their own right, as well as being potential intermediates in the formation of cyclic amido or cagelike imido derivatives of the group 13 hydrides MH_3.[4,5,12,13] By contrast with the corresponding reactions of $LiGaH_4$, the reaction of $LiAlH_4$ with an excess of the amine hydrochloride $[RNH_3]Cl$ (R = Me or *t*Bu) in an ether solution proceeds mainly with H_2 elimination and formation of the imidoalane anion $[(RN)_4(AlH_2)_6]^{2-}$ possessing the adamantoid Al_6N_4 skeleton **I**.[13] On the other hand, the main product of the reaction between $LiAlH_4$ and $[iPrNH_3]Cl$ under similar conditions is the neutral, hexameric imidoalane $[iPrNAlH]_6$ (**II**).[13]



I **II**

Here we report the isolation, in $[(MeH_2N)_2GaH_2]Cl$ (**1**) and $[(iPrH_2N)_2GaH_2]Cl$ (**2**), of two further examples of cationic gallane complexes, the structures of which have been authenticated by X-ray analysis. A noteworthy reaction involving 2 mol of **2** is that with 1 mol of $LiGaH_4$, leading to the elimination of LiCl and H_2 and the formation of the trigallium cationic derivative $[\{(iPrH_2N)GaH_2NHiPr\}_2GaH_2]Cl$ (**3**) [Equation (3)].

$$2\,[(iPrH_2N)_2GaH_2]Cl + LiGaH_4 \rightarrow LiCl + 2\,H_2 + [\{(iPrH_2N)GaH_2NHiPr\}_2GaH_2]Cl \quad (3)$$

Prolonged standing of $[(iPrH_2N)_2GaH_2]Cl$ in the presence of LiCl results in the isolation in low yield of crystals, **4**, initially mistaken for $[(iPrH_2N)_2GaHLi]Cl$ containing a

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Ga–Li bond. However, closer scrutiny suggests that partial H/Cl and not H/Li exchange has actually occurred to give crystals of $[(i\text{PrH}_2\text{N})_2\text{GaH}_2]\text{Cl}$ in which about 7% of the sites occupied by H atoms bound to Ga have been replaced by Cl atoms. As with the case of supposed "bond-stretch isomerism" involving the compound *cis*-*mer*-$\text{MoOCl}_2(\text{PMe}_3)_3$,[14] this provides another warning of the potential for deception inherent in undue reliance on the results of single-crystal X-ray diffraction.

Previous research carried out in our laboratories has shown that gallanes formally of the type GaH_2X (X = GaH_4, BH_4, or halogen)[1,4,5–8,15,16] resemble analogous boranes[1,17,18] in many ways in adding to amine and other donor molecules L to form (*i*) molecular 1:1 complexes L·GaH_2X and (*ii*) 1:2 complexes with either a molecular (L_2GaH_2X) or an ionic formulation ($[\text{H}_2\text{GaL}_2]^+X^-$). The corresponding alanes likewise form 1:1 complexes L·AlH_2X that are molecular in nature, but 1:2 complexes are typically also molecular with a pentacoordinate metal atom.[1,4,5] Moreover, where there is a protonic hydrogen attached to nitrogen in the amine molecule L, the alane complexes are much quicker than their borane or gallane counterparts to suffer H_2 elimination, with the formation of amido- or imidoalanes.[12,13] Various factors affect the nature of the complex formed and whether the polar M–X bond (M = B, Al, or Ga) is retained or undergoes heterolytic cleavage with the addition of a second L molecule, namely the inherent acidity and coordinating ability of M, the bulk and donor strength of L, and also the size and other properties of the prospective anion X^-. For example, the partiality of aluminum for coordination numbers greater than 4 is plainly in evidence with the finding that the H_2Al^+ fragment requires for its isolation as a stable salt base coordination at the metal at more than two sites.[11] MH_2X complexes are of interest as convenient sources of the parent hydride MH_2X, e.g. as a reductant in organic chemistry, and also as a potential means of vapor transport in the chemical vapor deposition of films of III–V compounds such as GaN.[4,5] The amine complexes of borane, $\text{Me}_x\text{H}_{3-x}\text{N·BH}_3$ (x = 0–2), have lately come to prominence as possible agents for hydrogen storage.[19]

As first reported in 1988,[20] monochlorogallane, GaH_2Cl, can be successfully prepared by the reaction of GaCl_3 with an excess of Me_3SiH. It has found some applications, primarily through metathesis, as a source of not only gallane itself,[15] but also other monosubstituted derivatives of gallane, e.g. H_2GaBH_4,[16] $\text{H}_2\text{GaB}_3\text{H}_8$,[21] and H_2GaN_3.[22] With bases such as NMe_3 it has been shown to form 1:1 molcular complexes, although the 1:2 complex with NH_3 is believed on the evidence of its IR spectrum to be more aptly formulated as $[\text{H}_2\text{Ga}(\text{NH}_3)_2]^+\text{Cl}^-$.[10] However, the difficulty of handling the parent compound, which decomposes slowly at ambient temperatures,[10,13] makes it a less than ideal synthon. Alternative routes to the complexes, which are appreciably more robust, have involved redistribution reactions such as that represented by Equation (4),[23,24] or the action of HCl on the corresponding GaH_3 complex;[23] these have afforded, for example, molecular 1:1 or 1:2 GaH_2Cl complexes with the bases PCy_3[23] and quinuclidine.[24]

$$2\ \text{Cy}_3\text{P·GaH}_3 + \text{Cy}_3\text{P·GaCl}_3 \rightleftharpoons 3\ \text{Cy}_3\text{P·GaH}_2\text{Cl} \qquad (4)$$

A still simpler procedure we have adopted[13] depends on the reaction of the hydrochloride of the base (or the base + HCl) with LiGaH_4 in appropriate proportions. This has led to the successful synthesis of the molecular 1:1 complex $\text{Me}_3\text{P·GaH}_2\text{Cl}$, as well as ionic 1:2 complexes $[\text{H}_2\text{Ga}(\text{NH}_2\text{R})_2]^+\text{Cl}^-$ with R = *t*Bu and *s*Bu, albeit in not always high yield.

Results and Discussion

By taking LiGaH_4 and the amine hydrochloride in the proportions 1:1.5 and careful control of the temperature, we have succeeded in optimizing the conditions for formation of the 1:2 complexes $\text{H}_2\text{GaCl·2NH}_2\text{R}$ for R = Me, **1**, and *i*Pr, **2**. Both of these are white solids lastingly stable at ambient temperatures and prepared in accordance with Equation (2) in yields of 45–65% based on the amount of LiGaH_4 taken. Neither dissolves readily in organic solvents with which it does not react, thereby precluding useful NMR measurements. The Raman spectra of the solids show numerous features attributable to internal vibrations of the coordinated amine molecule but, in addition, significant scattering at 1935 and 722 cm^{-1} (**1**) and 1938/1908 and 739 cm^{-1} (**2**). The intense bands at 1908–1938 cm^{-1} patently correspond to ν(Ga–H) vibrations, the relatively high wavenumber contrasting with those registered by the corresponding vibrations of the molecular complexes $\text{Me}_3\text{P·GaH}_2\text{Cl}$ (1889.5 cm^{-1})[8] and quin·GaH_2Cl (1892 cm^{-1}).[24] Instead, the wavenumbers are comparable with those found for the ν(Ga–H) modes in the 1:2 complexes of monochlorogallane with NH_3 (1915 cm^{-1}),[10] $t\text{BuNH}_2$ (1927/1910 cm^{-1}),[13] and $s\text{BuNH}_2$ (1923 cm^{-1}),[13] and established more or less certainly as containing cationic $[(\text{RH}_2\text{N})_2\text{GaH}_2]^+$ units (R = H, *t*Bu, and *s*Bu).

The presence of similar base-supported GaH_2^+ cations well-separated from Cl^- anions in **1** and **2** has now been authenticated by X-ray structure analysis of single crystals of each of the compounds. Thermal ellipsoid plots of the cations are given in Figure 1, salient dimensions being listed in Table 1. The shortest interionic contacts are those between Cl^- and the four N–H protons [ranging from 2.39(4) to 2.47(4) Å for **1** and from 2.40(3) to 2.50(3) Å for **2**, as against 2.95 Å for the sum of the relevant van der Waals radii[25]]. These hydrogen bonds result in the formation of infinite sheets running parallel to the crystallographic *bc* plane in **1** and *ab* plane in **2** (see Figure 2, for example). In both cases, the shortest Ga···Cl distance (3.881 Å for **1** and 4.008 Å for **2**) is well in excess of the normal range for covalent Ga^{III}···Cl interactions [cf. 2.237(2) Å in $\text{Me}_3\text{P·GaH}_2\text{Cl}$][13].

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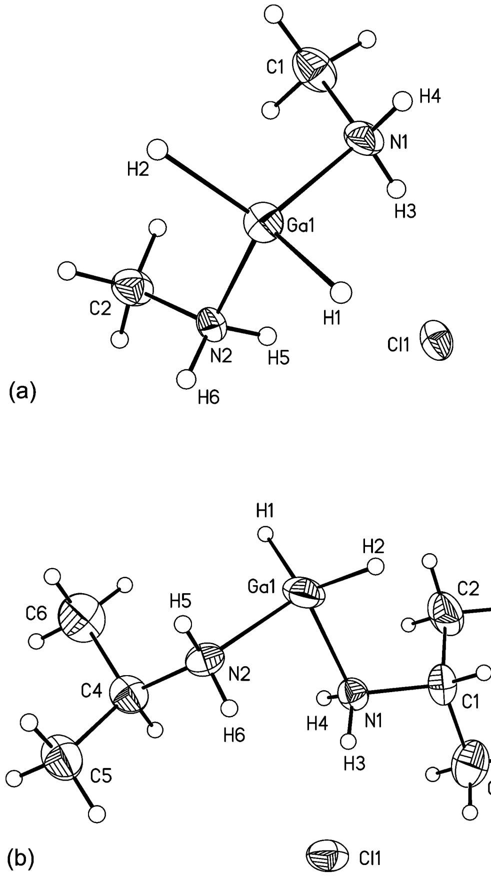

Figure 1. Thermal ellipsoid plots at 40% probability showing the cations $[(\mathrm{MeH_2N})_2\mathrm{GaH_2}]^+$ and $[(i\mathrm{PrH_2N})_2\mathrm{GaH_2}]^+$ in the compounds (a) **1** and (b) **2**.

The cations are characterized by dimensions averaging as follows: **1** Ga–N 1.998 Å, Ga–H 1.55 Å, N–Ga–N 100.2°, H–Ga–H 120°; **2** Ga–N 1.997 Å, Ga–H 1.52 Å, N–Ga–N 97.8°, H–Ga–H 127°. Apart from small differences reflecting, at least in part, the bulk of the alkyl group, there is thus an obvious resemblance to the cation $[(t\mathrm{BuH_2N})_2\mathrm{GaH_2}]^+$ (Ga–N 2.017 Å, Ga–H 1.58 Å, N–Ga–N 97.55°, H–Ga–H 124.5°) in its chloride salt.[13] In all three cases, the two alkyl groups are bent away from the metal, giving Ga–N–C angles averaging 117.5° (**1**), 117.2° (**2**), and 121.2° ($[(t\mathrm{BuH_2N})_2\mathrm{GaH_2}]^+$); the more bulky *i*Pr and *t*Bu groups are arranged mutually *trans* to each other, but the Me groups in **1** take on a more nearly *gauche* orientation. The coordinated alkylamine molecules are unremarkable in their dimensions. Perhaps the closest analogy is provided by the bromide salt of the cation $[(t\mathrm{BuH_2N})_2\mathrm{GaMe_2}]^+$[26] featuring a structure closely akin to those of the $[(\mathrm{RH_2N})_2\mathrm{GaH_2}]^+$ cations.

Table 1. Selected distances [Å] and interbond angles [°] in the $[(\mathrm{MeH_2N})_2\mathrm{GaH_2}]^+$ cation of **1** and the $[(i\mathrm{PrH_2N})_2\mathrm{GaH_2}]^+$ cation of **2**.

1	Distances[a]			
	Ga(1)–N(1)	1.993(5)	N(1)–H(3)	0.831(19)
	Ga(1)–N(2)	2.003(4)	N(1)–H(4)	0.835(19)
	Ga(1)–H(1)	1.542(18)	N(2)–C(2)	1.480(8)
	Ga(1)–H(2)	1.567(19)	N(2)–H(5)	0.838(19)
	N(1)–C(1)	1.484(7)	N(2)–H(6)	0.843(19)
	Angles[a]			
	N(1)–Ga(1)–N(2)	100.20(17)	Ga(1)–N(1)–H(4)	103(4)
	N(1)–Ga(1)–H(1)	106(2)	C(1)–N(1)–H(4)	109(4)
	N(2)–Ga(1)–H(1)	107.5(16)	H(3)–N(1)–H(4)	112(5)
	N(1)–Ga(1)–H(2)	112.7(18)	Ga(1)–N(2)–C(2)	117.9(3)
	N(2)–Ga(1)–H(2)	107.9(18)	Ga(1)–N(2)–H(5)	100(4)
	H(1)–Ga(1)–H(2)	120(3)	C(2)–N(2)–H(5)	114(4)
	Ga(1)–N(1)–C(1)	117.1(3)	Ga(1)–N(2)–H(6)	105(4)
	Ga(1)–N(1)–H(3)	98(4)	C(2)–N(2)–H(6)	107(4)
	C(1)–N(1)–H(3)	117(4)	H(5)–N(2)–H(6)	113(5)
2	Distances[a]			
	Ga(1)–N(1)	1.999(2)	C(1)–C(3)	1.515(5)
	Ga(1)–N(2)	1.994(2)	C(4)–N(2)	1.499(4)
	Ga(1)–H(1)	1.57(3)	C(4)–C(5)	1.520(4)
	Ga(1)–H(2)	1.47(4)	C(4)–C(6)	1.508(5)
	N(1)–C(1)	1.494(3)	C(4)–H(41)	1.000(3)
	N(1)–H(3)	0.87(4)	N(2)–H(5)	0.88(3)
	N(1)–H(4)	0.83(3)	N(2)–H(6)	0.85(3)
	C(1)–C(2)	1.507(5)		
	Angles[a]			
	N(1)–Ga(1)–N(2)	97.78(10)	C(2)–C(1)–C(3)	112.6(3)
	N(1)–Ga(1)–H(1)	106.2(11)	N(2)–C(4)–C(5)	110.0(2)
	N(2)–Ga(1)–H(1)	112.1(11)	N(2)–C(4)–C(6)	109.8(2)
	N(1)–Ga(1)–H(2)	104.3(16)	C(5)–C(4)–C(6)	112.0(3)
	N(2)–Ga(1)–H(2)	105.8(16)	N(2)–C(4)–H(41)	109.8(2)
	H(1)–Ga(1)–H(2)	126.6(20)	C(5)–C(4)–H(41)	107.5(3)
	Ga(1)–N(1)–C(1)	115.56(19)	C(6)–C(4)–H(41)	107.7(3)
	Ga(1)–N(1)–H(3)	107(2)	Ga(1)–N(2)–C(4)	118.90(18)
	C(1)–N(1)–H(3)	109(2)	Ga(1)–N(2)–H(5)	108(2)
	Ga(1)–N(1)–H(4)	107(2)	C(4)–N(2)–H(5)	111(2)
	C(1)–N(1)–H(4)	108(2)	Ga(1)–N(2)–H(6)	107.4(19)
	H(3)–N(1)–H(4)	110(3)	C(4)–N(2)–H(6)	105.8(20)
	N(1)–C(1)–C(2)	109.4(2)	H(5)–N(2)–H(6)	105(3)
	N(1)–C(1)–C(3)	110.2(3)		

[a] See Figure 1 for atom labeling. Geometrically positioned H atoms have been excluded.

Compound **3** displayed a Raman spectrum that included all the features characteristic of *i*Pr, $\mathrm{NH_2}$, and Ga–H functions, but with an altogether more complicated pattern of bands in the ν(Ga–H) region than for **2**, with wavenumbers ranging from 1912 to 1857 $\mathrm{cm^{-1}}$. While the higher wavenumbers are consistent with the presence of one or more $\mathrm{GaH_2}^+$ cationic functions, the lower ones are more characteristic of covalently bound, neutral $\mathrm{GaH_2}$ functions [cf. amidogallanes of the type $(\mathrm{RHNGaH_2})_n$ (n = 2 or 3)[7]]. X-ray analysis of a single crystal revealed the compound to be the chloride of the unusual trigallium cation $[\{(i\mathrm{PrH_2N})\mathrm{GaH_2NH}i\mathrm{Pr}\}_2\mathrm{GaH_2}]^+$ having the structure depicted in Figure 3. The asymmetric unit contains a cation located on a crystallographic mirror plane and a $\mathrm{Cl^-}$ anion located on the same plane. The shortest Ga···Cl distance, that involving the central Ga atom, is 4.025 Å.

The cation can be regarded as a central $\mathrm{GaH_2}^+$ unit coordinated not by two $i\mathrm{PrNH_2}$ molcules as in **2**, but via the amido nitrogen of each of two neutral $i\mathrm{PrNHGaH_2{\cdot}NH_2}i\mathrm{Pr}$ fragments. The more significant dimensions are given in Table 2. All of the NH groups from the $i\mathrm{PrNH_2}$ and *i*PrNH components of the cation engage in hydrogen bonding to $\mathrm{Cl^-}$ ions. From each cation, four hydrogen bonds are estab-

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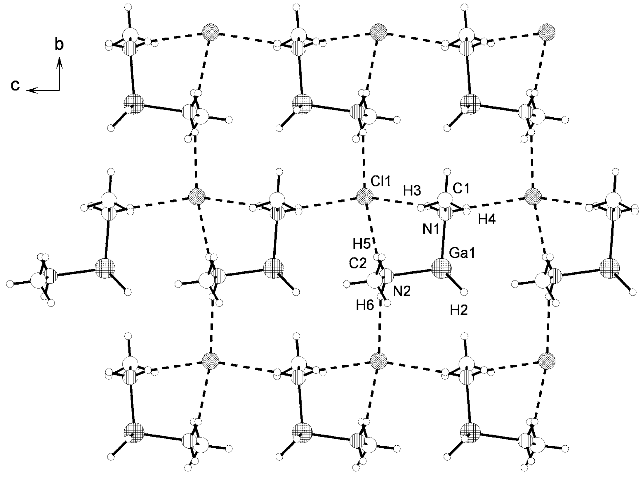

Figure 2. Formation of infinite sheets via N–H···Cl$^–$ interactions along the *bc* plane in crystals of **1**.

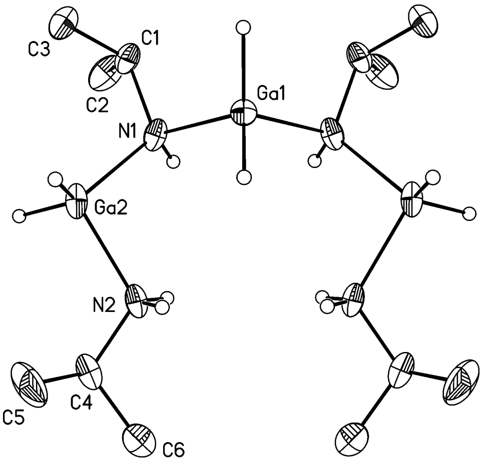

Figure 3. Thermal ellipsoid plot at 40% probability showing one of the two orientations of the disordered isopropyl groups C(1)–C(3) and C(11)–C(13) of the cation $[\{(i\text{PrH}_2\text{N})\text{GaH}_2\text{NH}i\text{Pr}\}_2\text{GaH}_2]^+$ in the compound **3**.

Table 2. Selected distances [Å] and interbond angles [°] in the $[\{(i\text{PrH}_2\text{N})\text{GaH}_2\text{NH}i\text{Pr}\}_2\text{GaH}_2]^+$ cation of **3**.

Distances[a]			
Ga(1)–N(1)	2.0068(14)	Ga(2)–H(3)	1.44(3)
Ga(1)–H(1)	1.47(3)	Ga(2)–H(4)	1.48(3)
Ga(1)–H(2)	1.47(4)	N(1)–H(5)	0.80(3)
Ga(2)–N(1)	1.9884(14)	N(2)–H(6)	0.82(2)
Ga(2)–N(2)	2.0269(15)	N(2)–H(7)	0.80(2)
Angles[a]			
N(1)–Ga(1)–N(1)[b]	105.14(8)	N(2)–Ga(2)–H(4)	103.5(9)
N(1)–Ga(1)–H(1)	104.7(7)	H(3)–Ga(2)–H(4)	122.2(14)
N(1)–Ga(1)–H(2)	109.8(9)	Ga(1)–N(1)–Ga(2)	111.19(6)
H(1)–Ga(1)–H(2)	121(2)	Ga(1)–N(1)–H(5)	103.1(16)
N(1)–Ga(2)–N(2)	99.87(5)	Ga(2)–N(1)–H(5)	102.4(16)
N(1)–Ga(2)–H(3)	111.7(10)	Ga(2)–N(2)–H(6)	108.5(16)
N(2)–Ga(2)–H(3)	106.4(10)	Ga(2)–N(2)–H(7)	111.8(17)
N(1)–Ga(2)–H(4)	110.3(10)	H(6)–N(2)–H(7)	105(2)

[a] See Figure 3 for atom labeling. Dimensions of the disordered *i*Pr groups have been excluded. [b] Related by crystallographic reflection, symmetry operator *x*, 3/2 – *y*, *z*.

lished from the two NH_2 groups to one anion [H···Cl 2.56(2), 2.65(2) Å], and two more are established from the two NH groups to a second anion [H···Cl 2.61(2) Å] (see Figure 4). These bonds form infinite chains of alternating cations and anions running parallel to the crystallographic *a* axis. Despite the presence of both protic and hydridic H atoms within the crystal of **3**, as in those of **1** and **2**, there is no suggestion of Ga–H···H–N "non-classical" hydrogen bonding[27] analogous to that found, for example, in trigallazane, $[H_2NGaH_2]_3$.[28]

The cation in **3** displays two features of interest. Firstly, the Ga–N bonds between the central Ga atom, Ga(1), and the NH*i*Pr bridging groups measure 2.0068(14) Å, while the corresponding bonds between each of the terminal Ga atoms, Ga(2), and the NH*i*Pr bridges and coordinated NH_2iPr ligands measure 1.9884(14) and 2.0269(15) Å, respectively. There is thus surprisingly little difference between what may be regarded as Ga–N covalent bonds and Ga←N coordinate links, and none of the bonds differs significantly in length from those found in cyclic amidogallanes of the type $[RR'NGaH_2]_n$ (R, R′ = H or an organic group; n = 2 or 3) which fall in the range 1.96–2.10 Å.[6,7,28–30] Secondly, it is noteworthy that the N–Ga(1)–N and Ga(1)–N–Ga(2) angles of 105.14(8) and 111.19(6)° are also close to those found in the skew-boat Ga_3N_3 ring of the neutral amidogallane $[MeHNGaH_2]_3$ (101.4 and 113.2°).[7] In other words, the horseshoe shape of the new cation, supported by hydrogen bonding to a Cl$^–$ anion, prefigures closely the structures adopted by neutral amidogallanes of the type $[RR'NGaH_2]_3$.[6,7,28,29] Such compounds are, in turn, normally accessed through elimination reactions of amine complexes of gallanes.[1,4–7] This suggests that the cation $[\{(i\text{PrH}_2\text{N})\text{GaH}_2\text{NH}i\text{Pr}\}_2\text{GaH}_2]^+$ may well exemplify a key intermediate in the formation of amidogallanes. Although no analogous aluminum species has yet been identified, we have suggested elsewhere[13] that such an analogue may well play an essential part in the formation of the adamantoid anion $[(RN)_4(AlH_2)_6]^{2-}$ (**I**) in the reaction of $LiAlH_4$ with $[RNH_3]Cl$ (R = Me or *t*Bu).

Evidence in support of these notions is afforded by experiments aimed at preparing a [D$_8$]toluene solution of compound **3**. The ^{1}H NMR spectrum then revealed a solute species characterized at room temperature by resonances at δ_H 4.98, 2.9, 0.82, and 0.73 ppm with relative intensities of 2:1:6:1, respectively. The first is a broad signal plainly associated with one or more GaH_2 fragments; the second, two overlapping septets, must be due to the unique CH protons of two kinds of *i*Pr group; the third, a pair of doublets, is then due to the CH_3 protons of these groups; and the fourth, a doublet, suggests the protons of an NH function. Lowering the temperature of the solution to –80 °C revealed additional detail. For example, the GaH_2 resonance now appeared as a singlet overlaid by an AB doublet of doublets of similar overall intensity, while the supposed NH signal developed into a pair of doublets. This behavior resembles very closely that of the amidogallane [*t*BuHN-

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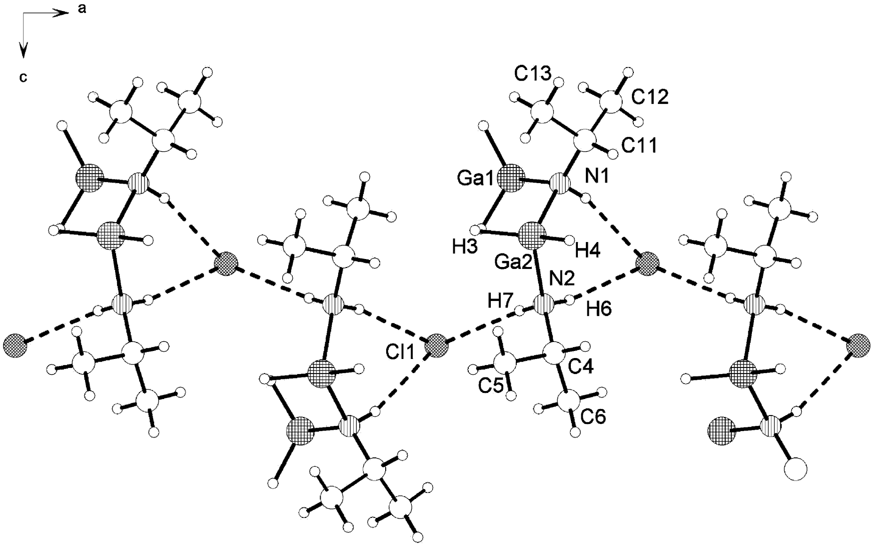

Figure 4. Chain formation via N–H···Cl⁻ interactions in crystals of **3**.

$GaH_2]_2$ with a cyclic Ga_2N_2 skeleton,[6] and there can be little doubt that the solute in this case is the corresponding *i*Pr derivative [*i*PrHNGaH$_2$]$_2$, a compound first isolated and characterized, *e. g.* by its ^{1}H NMR spectrum, by Storr and Penland.[31] The finer details of the spectrum indicate that this, like the *t*Bu compound, exists in both *cis* and *trans* forms. Hence, the attempted dissolution of **3** has actually resulted, at least formally, in elimination of [(*i*PrH$_2$N)$_2$GaH$_2$]Cl and formation of the neutral amidogallane [Equation (5)]. Alternatively, protonation of an *i*PrNH$_2$ ligand and elimination of [*i*PrNH$_3$]Cl may be accompanied by reorganization of what would otherwise be the trimer [*i*PrHNGaH$_2$]$_3$ to the corresponding dimer [see Equation (6)] so as better to accommodate the bulk of the *i*Pr groups.[6]

$$[\{(i\text{PrH}_2\text{N})\text{GaH}_2\text{NH}i\text{Pr}\}_2\text{GaH}_2]\text{Cl} \rightarrow [i\text{PrHNGaH}_2]_2 + [(i\text{PrH}_2\text{N})_2\text{GaH}_2]\text{Cl} \quad (5)$$

$$2\ [\{(i\text{PrH}_2\text{N})\text{GaH}_2\text{NH}i\text{Pr}\}_2\text{GaH}_2]\text{Cl} \rightarrow 3\ [i\text{PrHNGaH}_2]_2 + 2\ [i\text{PrNH}_3]\text{Cl} \quad (6)$$

Compound **4**, isolated as crystals in low yield in a solid mixture after prolonged standing at –10 °C, represents a case of potentially mistaken identity, serving as a further warning against undue reliance on X-ray diffraction as a means of identifying an unknown compound. Elemental analysis and X-ray diffraction of a single crystal clearly point to a product closely related to **2**, [(*i*PrH$_2$N)$_2$GaH$_2$]Cl, although there are small but significant discrepancies, and the Raman spectrum of the solid also finds appreciable differences from that of **2**. The crystal structure of **4** could be solved quite successfully on the basis of its being [(*i*PrH$_2$N)$_2$GaHLi]Cl, but the unexpectedness of this result, combined with the inconsistencies described in the Experimental section, led to the conclusion that it must actually be a case of compositional disorder within crystals of **2** involving cocrystallization with about 7 % of the compound [(*i*PrH$_2$N)$_2$GaHCl]Cl. The incorporation of chloride into a fraction of the hydridic sites has then resulted in an artificial increase of the relevant bond length, as well as creating the impression of an atom with an atomic number greater than that of H. Indirect evidence of a similar hydride/halide exchange involving the indane InH$_3$(quinuclidine) and LiBr has been reported previously.[32] A similar problem of compositional disorder with what purported to be *cis-mer*-MoOCl$_2$(PMe$_3$)$_3$ led to the mistaken impression of two different isomers differing only in the lengths of what were taken to be their "Mo=O" bonds.[14]

Conclusions

By optimizing the conditions, it has been possible to isolate in fair yield the cationic gallane derivative [(RH$_2$N)$_2$GaH$_2$]$^+$Cl$^-$ for R = Me and *i*Pr from the reaction of LiGaH$_4$ with a 50 % mol excess of the amine hydrochloride [RNH$_3$]Cl in ether solution. A significant secondary product of the reaction with [*i*PrNH$_3$]Cl is the trigallium compound [{(*i*PrH$_2$N)GaH$_2$NH*i*Pr}$_2$GaH$_2$]$^+$Cl$^-$. Crystallographic characterization of the compounds reveals cationic units containing tetra-coordinated gallium centers and having skeletal dimensions similar to those in neutral amidogallanes of the type [RR′NGaH$_2$]$_3$ (R, R′ = H or an organic group). The N–H bonds engage in interionic N–H···Cl hydrogen bonding to produce infinite sheets in the crystals of the monogallium compounds [(RH$_2$N)$_2$GaH$_2$]Cl and infinite chains of alternating cations and anions in the crystal of [{(*i*PrH$_2$N)GaH$_2$NH*i*Pr}$_2$GaH$_2$]Cl. The crystallographic and other properties suggest that the gallane cations may be key intermediates in the formation of neutral oligomeric amidogallanes. Prolonged interaction of [(*i*PrH$_2$N)$_2$GaH$_2$]Cl with LiCl results in limited replacement of Ga–H by Ga–Cl bonds. This leads to cocrystallization of [(*i*PrH$_2$N)$_2$GaH$_2$]Cl with about 7 % of [(*i*PrH$_2$N)$_2$GaHCl]Cl to afford another example of compositional disorder.

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Experimental Section

The vacuum-line methods used for the preparation of the cationic gallane compounds **1**–**3** have been described elsewhere.[15] Diethyl ether and other solvents were dried by standard methods and distilled before use. All the source materials (LiH, $GaCl_3$, $[MeNH_3]Cl$, and $[i\text{Pr}NH_3]Cl$) were from Aldrich Chemicals. LiH and $GaCl_3$ were used without purification; the amine hydrochlorides were recrystallized before use. $LiGaH_4$ was freshly prepared from the reaction between LiH and $GaCl_3$ in an Et_2O solution.[3]

Raman spectra, excited at λ = 514.5 nm with an Ar^+ laser, were recorded with a Dilor Labram 300 spectrometer having a CCD detector. ^1H NMR spectra were measured for $[D_8]$toluene solutions at 500 MHz using a Varian UNITY-plus spectrometer. C, H, and N analyses were carried out, where possible, by the Elemental Analysis Service at London Metropolitan University or by the analytical service in the Inorganic Chemistry Laboratory at Oxford.

The bis(methylamine) and bis(isopropylamine) adducts of monochlorogallane, $(RH_2N)_2GaH_2Cl$ (R = Me, **1**, and *i*Pr, **2**), were each prepared by a method similar to that used for methylamine–gallane, $MeH_2N{\cdot}GaH_3$.[7] In an optimum experiment, dry Et_2O was used to dissolve a mixture of freshly recrystallized $LiGaH_4$ (0.81 g, 10 mmol) and $[MeNH_3]Cl$ (1.02 g, 15 mmol). The solution, initially at –78 °C, was warmed to 0 °C to initiate the reaction, and then slowly warmed further to room temperature over a period of 3 h. To ensure completion of the reaction, the resulting mixture was stirred at room temperature for another 2 h before filtering the solution into a pre-conditioned Schlenk tube. The solvent was evaporated in vacuo from the filtrate, and the concentrated liquor kept at 0 °C, whereupon white crystals of **1** (0.77 g, 4.5 mmol) were observed to separate. The yield of **1** was thus 45% based on Equation (2) and the mass of $LiGaH_4$ taken.

In a similar experiment with $LiGaH_4$ (0.81 g, 10 mmol) and $[i\text{Pr}NH_3]Cl$ (1.43 g, 15 mmol), the reaction was initiated at room temperature and the mixture stirred for 5 h under these conditions. Filtering and concentration of the filtrate then led to the separation of white crystals of **2** (1.47 g, 6.5 mmol) at 0 °C in a yield of 65% based on the amount of $LiGaH_4$ taken.

Standing of the concentrated solution that delivered **2** at 0 °C for 6 weeks produced a small crop of crystals (ca. 90 mg) distinctly different from those of **2**. No satisfactory elemental analysis was possible, but X-ray structure determination proved these to be the trigallium compound $[\{(i\text{Pr}H_2N)GaH_2NH i\text{Pr}\}_2GaH_2]Cl$ (**3**). The yield amounted to 5–6% with respect to the $LiGaH_4$ precursor and Equation (7).

$$3\ LiGaH_4 + 4\ [i\text{Pr}NH_3]Cl \rightarrow [\{(i\text{Pr}H_2N)GaH_2NH i\text{Pr}\}_2GaH_2]Cl + 3\ LiCl + 6\ H_2 \quad (7)$$

In one experiment designed to give **2**, the white solid (containing LiCl among other products) removed on filtration of the ether solution was stored for a long time (1–2 years) under vacuum at about –10 °C. This led to the growth of crystals of a product **4** (ca. 50 mg) which resembled **2** in some ways but showed distinct differences in others. The nature of **4**, which was initially mistaken for the unusual compound $[(i\text{Pr}H_2N)_2GaHLi]Cl$, is discussed below.

$[(MeH_2N)_2GaH_2]Cl$ (1): $C_2H_{12}ClGaN_2$ (169.30): calcd. C 14.19, H 7.15, N 16.55; found C 14.12, H 6.93, N 16.35. Raman spectrum: $\tilde{\nu}$ = 3177 mw, 3094 mw, 3008/2993 mw, 2953 m, 2897 w, 2821 w, 1935 vs, 1458 wbr, 1079 w, 1002 m, 722 mw, 636 w, 559 mw, 507 w, 419 mw, 199 vw cm^{-1}.

$[(i\text{Pr}H_2N)_2GaH_2]Cl$ (2): $C_6H_{20}ClGaN_2$ (225.41): calcd. C 31.97, H 8.94, N 12.43; found C 31.83, H 8.83, N 12.36. Raman spectrum: $\tilde{\nu}$ = 3163 wsh, 3071 ms, 2976/2962 ms, 2932 s, 2908 s, 2872 s, 2728 mw, 1992 w, 1938/1908 s, 1462/1445 mw, 1396 w, 1345 w, 1252 w, 1164 w, 1109 w, 1083 w, 945 m, 819 m, 739 ms, 676 w, 525 w, 469 mw, 390 w, 293 w cm^{-1}.

$[\{(i\text{Pr}H_2N)GaH_2NH i\text{Pr}\}_2GaH_2]Cl$ (3): Raman spectrum: $\tilde{\nu}$ = 3195 mw, 3171 sh, 2973 s, 2935 s, 2910 ms, 2886 m, 2871 ms, 2734 w, 1912/1897 s, 1857 ms, 1466 mw, 1458 sh, 1401 w, 1345 w, 1259 w, 1247 w, 1234 w, 1148 vw, 1133 w, 1115 vw, 1105 vw, 944 mw, 823 m, 745 mw, 721/705 w, 621 vw, 601 vw, 572 vw, 524 w, 450 w, 394 w, 285 mw, 200 w, 176 w, 151 vw cm^{-1}.

Compound 4: $C_6H_{20}ClGaN_2$ (225.41): calcd. C 31.97, H 8.94, N 12.43, Ga 30.93, Cl 15.73. $C_6H_{19}ClGaLiN_2$ (231.34): calcd. C 31.15, H 8.28, N 12.11, Ga 30.14, Cl 15.32; found C 30.66, H 8.01, N 11.77, Ga 31.92, Cl 16.15. Raman spectrum: $\tilde{\nu}$ = 3217 mbr, 3112 wbr, 2976 s, 2932 s, 2787 vw, 2736 w, 1965 mvbr, 1576 w, 1461/1452 m, 1394 w, 1371 w, 1344 w, 1223 wbr, 1160 w, 1096 wbr, 1071 vw, 940 mw, 813 m, 544 mw, 388 w, 335 w, 290 vw, 229 w cm^{-1}.

X-ray Crystallography: Table 3 gives crystal data and other information relating to the structure determination and refinement for single crystals of **1**, **2**, **3**, and **4**. Each set of measurements was made on a crystal mounted under perfluoropolyether oil on a glass fiber and held at 150 K. X-ray diffraction data [λ(Mo-K_α) = 0.71073 Å] were collected on an Enraf–Nonius Kappa CCD diffractometer. Semiempirical absorption corrections were made from equivalent reflections.[33] The intensity data were processed using the DENZO-SMN package.[33]

Examination of the diffraction pattern of the crystal of **1** showed it to be a twin with two components related by a 180° rotation about the reciprocal *c* axis. No such problem was encountered with the crystals of **2**, **3**, and **4**. Examination of the systematic absences of the intensity data showed the space group of **1** to be either $P2_1$ or $P2_1/m$; the structure was successfully solved in the former space group. Similar examination showed the space group of the crystal of **2** to be $P2_1/c$ and that of the orthorhombic crystal of **3** to be either *Pnma* or *Pn2a*, of which the former afforded a satisfactory structure solution. The structures of **1**–**3** were all solved with the aid of the direct methods program SIR92,[34] which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite.[35] The coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. The *i*Pr groups centered on C(1) and C(3) in **3** (see Figure 3) were modelled as disordered over two orientations related by a displacement and rotation about the N–C bond. The coordinates, anisotropic thermal parameters and site occupancies of the disordered C atoms were refined subject to restraint of the N–C and C–C bond lengths to their common means (with a standard uncertainty of 0.02 Å) and of the N–C–C and C–C–C angles likewise (standard uncertainty 2°). The H atoms attached to the N and Ga centers were located in Fourier difference maps and their coordinates and isotropic thermal parameters subsequently refined. The remaining H atoms in all three structures were positioned geometrically after each cycle of refinement. A 3-term Chebychev polynomial weighting scheme was applied in each case. Refinement converged satisfactorily to give R = 0.0294, 0.0309, and 0.0238 and R_w = 0.0290, 0.0310, and 0.0313 for **1**, **2**, and **3**, respectively.

A single crystal of **4** proved to resemble that of **2** in being monoclinic and having only slightly but significantly different lattice dimensions. Systematic absences in the intensity data suggested at first the space group $P2_1/c$. Attempts to solve the structure with SIR92[34] on this basis located all the non-hydrogen atoms but im-

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Table 3. Crystallographic data for compounds **1**, **2**, **3**, and **4**.

	1	**2**	**3**	**4**
Empirical formula	$C_2H_{12}ClGaN_2$	$C_6H_{20}ClGaN_2$	$C_{12}H_{40}ClGa_3N_4$	$C_6H_{19.93}Cl_{1.07}GaN_2$
Formula mass	169.30	225.41	485.09	227.99
Crystal dimensions [mm]	0.06 × 0.06 × 0.34	0.10 × 0.12 × 0.24	0.12 × 0.24 × 0.32	0.18 × 0.12 × 0.06
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	$P2_1$	$P2_1/c$	$Pnma$	$P2_1/n$
Unit cell dimensions				
a [Å]	5.4901(3)	5.5477(2)	10.5461(2)	5.5433(2)
b [Å]	11.6180(8)	10.6101(4)	19.1794(2)	10.6272(3)
c [Å]	6.0266(4)	20.3063(7)	11.2613(2)	20.3706(8)
α [°]	90	90	90	90
β [°]	98.940(3)	95.0621(17)	90	94.6340(10)
γ [°]	90	90	90	90
V [Å^3]	379.73(4)	1190.60(7)	2277.80(6)	1196.10(7)
Z	2	4	4	4
$d_{calcd.}$ [Mg m^{-3}]	1.481	1.257	1.414	1.266
Absorption coeff. [mm^{-1}]	3.870	2.486	3.638	2.491
θ_{max} [°]	27.5	27.5	27.5	27.5
Reflections measured	4278	8792	35 241	4901
Unique reflections (R_{int})	1486 (0.040)	2698 (0.039)	2925 (0.026)	2702 (0.024)
Number of parameters	80	115	142	101
Conventional R [$R > n\sigma(F)$]	0.0294[a]	0.0309[a]	0.0238[a]	0.0416[b]
Weighted R (F^2 and all data)	0.0290	0.0310	0.0313	0.0464
GOF on F^2 (S)	1.1203	1.1137	0.9891	1.1002
Largest difference peak/hole [e Å^{-3}]	+0.53/–0.64	+0.36/–0.67	+0.61/–0.59	+0.74/–0.93

[a] $n = 3$. [b] $n = 4$.

plied on refinement that one of the H atoms attached to Ga in **2** had been replaced by an atom of slightly higher atomic number (but <6). Li being the only obvious candidate, the structure could then be solved and refined satisfactorily with CRYSTALS[35] for the unusual compound [(iPrH$_2$N)$_2$GaHLi]Cl in which H$^-$ had been formally replaced by Li$^-$ ($R = 0.0413$, $R_w = 0.0501$ for 2028 data). However, apart from the unexpectedness of this conclusion, the structure showed some disturbing features. Firstly, the Ga–Li distance came out to be 1.758(9) Å, only slightly longer than the Ga–H distance of 1.60(4) Å. Although there are no established precedents for what approximates to a covalent Ga–Li bond, this is much shorter than might be anticipated. For example, DFT calculations on the [(iPrH$_2$N)$_2$GaHLi]$^+$ cation give a Ga–Li distance of 2.568 Å.[36] Secondly, the thermal amplitudes for the supposed Li site appeared unusually large. Closer scrutiny showed in fact that this site could be refined slightly better in the space group $P2_1/n$ as a mixture of Cl and H to give $R = 0.0416$, $R_w = 0.0464$ for 2039 data. Hence it appeared that the crystal is made up of [(iPrH$_2$N)$_2$GaH$_2$]Cl doped with [(iPrH$_2$N)$_2$GaHCl]Cl so that 7% of one of the H sites at Ga are occupied by Cl. It was impossible to separate out these Cl and H sites but with a distance of only about 0.5 Å between them and such a small proportion of Cl, this was not altogether surprising. Hence we were bound eventually to conclude that exchange had taken place not totally between one H$^-$ and Li$^-$, but partially between one H$^-$ and Cl$^-$.

CCDC-662741 (for **1**), -662742 (for **2**), -662743 (for **3**) and -662744 (for **4**) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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