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Amidoalane, amidogallane and amidoindane, H_2MNH_2 (M = Al, Ga or In): a matrix study of three prototypal molecules with the potential for M–N multiple bonding

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Photolysis of Al, Ga or In atoms (M) isolated in NH_3-doped Ar matrices gives first the divalent amido derivative $HMNH_2$ (λ = 436 nm) and then the univalent and trivalent amido derivatives MNH_2 and H_2MNH_2 (λ = 200–800 nm); the measured and calculated properties of H_2MNH_2 are outlined.

Amido derivatives of group 13 metals are potentially relevant to the fabrication and properties of the III–V semiconductor materials AlN, GaN and InN.[1] Such compounds are normally oligomeric or polymeric, with a coordination number of four or greater at M; only with the introduction of bulky substituents at M and N can monomeric compounds with tri-coordinated M atoms be sustained under normal conditions.[2] The properties of these monomeric amido derivatives have attracted considerable theoretical attention, mainly in relation to the potential for M–N multiple bonding.[2,3]

Matrix isolation offers a highly instructive method of reconnaissance and characterisation for simple, previously unknown hydride derivatives of the main group metals.[4–6] Hence, for example, photoexcitation of metal atoms contained in solid Ar matrices doped with NH_3 has been shown previously to result in insertion of the metal into an N–H bond of NH_3 with the formation of the species $HMNH_2$ (M = Al[7]) and MNH_2 (M = Li[8] or Al[7]). Here we report specifically on the formation of the simple monomeric compounds H_2MNH_2 (M = Al, Ga or In) as products of the reactions set in train by photolysis of NH_3-doped Ar matrices containing the relevant M atoms.[9] The molecules have been identified by their IR spectra, with the conclusions being underpinned (i) by the observed effects of exchanging $^{14}NH_3$ for $^{14}ND_3$ or $^{15}NH_3$, and of the isotopes ^{69}Ga and ^{71}Ga present in natural Ga; (ii) by parallels with the spectra of related hydrido and amido derivatives, *e.g.* MH_3,[4] H_2MCl,[5,10] and $AlNH_2$[7] (M = Al, Ga or In); and (iii) by comparisons with the IR spectra forecast by density functional theory (DFT) calculations.[11] In the following account we will concentrate on the formation and characterisation of H_2GaNH_2; the aluminium and indium analogues follow a very similar pattern, with the results summarized in Table 1.

An Ar matrix containing *ca.* 0.2% Ga atoms and up to 2% NH_3 gave an IR spectrum including, in addition to the absorptions characteristic of NH_3 and $[NH_3]_n$,[12] a new absorption at 1104.2 cm^{-1} attributable to an adduct $Ga{\cdot}NH_3$ **1**. There was also associated with this product a visible absorption centered at 440 nm. Irradiation of the matrix with radiation having λ = 436 nm for 5 min resulted in the decay of the spectroscopic features due to **1** and the appearance of new IR bands at 1721.8, 1528.7, 746.2, 668.5/667.4 494.1 and 210.9 cm^{-1} attributable on the strength of their constant relative intensities to a second product **2**. All the criteria (i)–(iii) indicate that **2** is the gallium(II) amide $HGaNH_2$, showing clear spectroscopic analogies with GaH_2[4] and CH_3GaH.[6]

Photolysis for a further 30 min, but with broad-band UV–VIS light (200 < λ < 800 nm) led to the decay of the bands due to

Table 1 Structures (distances in Å, angles in degrees), rotational barriers ΔE (kJ mol^{-1}), wavenumbers [cm^{-1}, intensities (km mol^{-1}) are given in parentheses] and M–N force constants f(MN) (N m^{-1}) for H_2MNH_2 molecules (M = Al, Ga and In)

Parameter		H_2AlNH_2		H_2GaNH_2		H_2InNH_2	
M–N		1.7790		1.8211		1.9703	
M–H		1.5811		1.5621		1.7252	
N–H		1.0100		1.0086		1.0169	
H–M–H		124.4		126.7		126.9	
H–N–H		110.0		111.7		110.3	
ΔE		50.6		65.7		51.5	
Description of vibrational mode	Assignment	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
ν_{sym}(N–H)	ν_1 (a_1)	3499.7	3572.0 (11)	3413.4	3581.9 (9)	—[a]	3517.1 (10)
ν_{sym}(M–H)	ν_2 (a_1)	1891.0	1959.3 (81)	1970.8—[c]	1995.9 (64)	—[a]	1770.2 (68)
δ(NH_2)	ν_3 (a_1)	1541.6	1631.2 (49)	1530.4	1621.6 (30)	1506.6	1579.4 (23)
ν(M–N)	ν_4 (a_1)	818.7	830.1 (192)	706.2/704.1	689.0 (124)	616.3	575.8 (153)
δ(MH_2)	ν_5 (a_1)	755.0	754.6 (86)	779.6	740.3 (40)	—[a]	634.2 (84)
Twist	ν_6 (a_2)	—[b]	499.9 (0)	—[b]	545.8 (0)	—[b]	480.8 (0)
$\rho_{out-of-plane}$(MH_2)	ν_7 (b_1)	608.7	608.4 (150)	567.7	607.9 (43)	—[a]	535.2 (95)
$\rho_{out-of-plane}$(NH_2)	ν_8 (b_1)	518.3	483.0 (309)	304.9	337.3 (280)	—[a]	177.6 (237)
ν_{asym}(N–H)	ν_9 (b_2)	—[a]	3655.8 (11)	3510.7	3681.7 (13)	—[a]	3621.9 (18)
ν_{asym}(M–H)	ν_{10} (b_2)	1899.3	1964.2 (288)	1970.8—[c]	1998.6 (245)	1805.9	1756.9 (272)
$\delta_{in-plane}$(NH_2)	ν_{11} (b_2)	769.8	767.6 (151)	782.8	789.8 (110)	733.3	696.3 (126)
$\delta_{in-plane}$(MH_2)	ν_{12} (b_2)	—[a]	433.5 (22)	—[a]	441.8 (26)	—[a]	368.5 (33)
f(MN)		407.5		384.9		315.3	

[a] Not observed. [b] IR silent. [c] Both modes contained within a single broad absorption.

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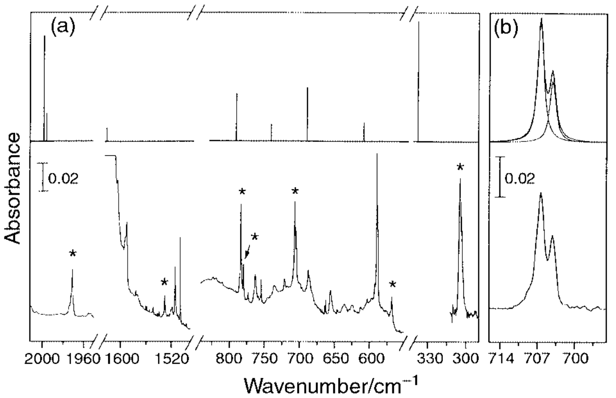

Fig. 1 (a) Bottom: IR spectrum of an Ar matrix containing Ga and NH_3 following photolysis first at λ = 436 nm and then at λ = 200–800 nm; top: calculated IR absorptions for H_2GaNH_2. (b) Bottom: IR spectrum of H_2GaNH_2 in the region around 700 cm^{-1}; top: curve fit with two Lorentzian-type functions with an intensity ratio reflecting the proportions $^{69}Ga/^{71}Ga$ = 60.1 : 39.9 in naturally occurring Ga.

2 with the simultaneous appearance and growth of a new family of bands having a common origin in a third product **3**. Occurring at 3471.6, 1505.9, 589.3/587.9 and 314.5 cm^{-1}, these could be identified with the gallium(I) amide $GaNH_2$, a conclusion supported by the criteria (i)–(iii) and by analogy with the IR spectrum reported for $AlNH_2$.[7] Extending the period of photolysis resulted in the continued accumulation of **3** at the expense of **2**. Additionally, another group of bands, also with constant relative intensities and therefore associated with a fourth distinct product **4**, was observed to develop (see Fig. 1). The members of this group were located at 3510.7, 3413.4, 1970.8, 1530.4, 782.8, 779.6, 706.2/704.1, 567.7 and 304.9 cm^{-1}, those at 1970.8, 782.8, 706.2/704.1 and 304.9 cm^{-1} being the most prominent. Diagnostic aspects are (i) the strong absorption at 1970.8 cm^{-1} occurring in the region characteristic of ν(Ga–H) vibrations of terminal Ga(III)–H bonds (*cf.* GaH_3 1923.2 cm^{-1} [4] and H_2GaCl 1964.6–1978.1 cm^{-1} [9]); (ii) the absorptions at 3510.7, 3413.4 and 1530.4 cm^{-1} implying the presence of an NH_2 group; and (iii) the doublet pattern at 706.2/704.1 cm^{-1} attributable to $^{69}Ga/^{71}Ga$ splitting arising from the motion of a single Ga atom (see Fig. 1). The criteria (i)–(iii) leave little doubt that **4** is monomeric amidogallane, H_2GaNH_2, more familiar as a trimer which is stable at temperatures up to nearly 150 °C.[13] Out of the 11 IR-active modes ($5a_1 + 2b_1 + 4b_2$) expected for planar H_2GaNH_2 with C_{2v} symmetry, all but one have been satisfactorily located in the spectrum measured for **4**, the only absentee being ν_{12} (b_2) which is expected to lie near 420 cm^{-1} but is probably obscured by extraneous absorptions. In other respects the calculations anticipate remarkably closely the observed wavenumbers, relative intensities, and isotopic shifts to provide a convincing basis for the assignments entered in Table 1. For example, the observed $^{69}Ga/^{71}Ga$ splitting of 2.1 cm^{-1} displayed by the absorption near 705 cm^{-1} matches admirably the calculated value of 1.9 cm^{-1} for the ν(Ga–N) mode, ν_5 (a_1).

The amides H_2AlNH_2 and H_2InNH_2 have each been formed and characterised in analogous experiments involving Al and In atoms, respectively. With the indium compound, formed only in low concentrations, no more than four weak IR absorptions could be clearly associated, although the wavenumbers and isotopic shifts, allied to the circumstances, vouch for its identity. Nine of the IR-active fundamentals of H_2AlNH_2 were located with confidence. Two of the most prominent bands, at 1899.3 and 1891.0 cm^{-1}, tally with features reported in earlier matrix studies[7] of the reactions between laser-ablated Al atoms and NH_3 and assigned somewhat tentatively not to H_2AlNH_2 but to the quasi-linear, high-energy HAlNH molecule. Experiments with all three metals and involving different concentrations of NH_3 or mixtures of NH_3 and H_2 make it clear that H_2MNH_2 is formed from $HMNH_2$ or MNH_2 by the addition of H atoms generated by the photodecomposition of $HMNH_2$ (or MH_2 when H_2 is present[4]).

Calculated and observed properties of H_2AlNH_2, H_2GaNH_2 and H_2InNH_2 are listed in Table 1. In each case, the global minimum is calculated to correspond to a planar ethene-like geometry, although, as noted elsewhere,[2] a planar M–NH_2 geometry is not necessarily a sign of strong π bonding. The calculated M–N distances are indeed short, near or below the lower limits for the observed distances in tri-coordinated amido derivatives of these elements (1.78, 1.818 and 2.049 Å for M = Al, Ga and In, respectively);[2] with respect to related species the order is $M{\cdot}NH_3 > H_3M{\cdot}NH_3 > MNH_2 > MN > HMNH_2 \geqslant H_2MNH_2 > HMNH'$. The M–N stretching force constants, based where possible on the measured spectra, vary in the orders (i) $H_2MNH_2 \geqslant HMNH_2 \geqslant MNH_2 \gg H_3M{\cdot}NH_3 \gg M{\cdot}NH_3$, and (ii) $M = B \gg Al \geqslant Ga > In$ for H_2MNH_2. Calculation of the energy of the transition state in which the H_2M and NH_2 planes are orthogonal gives an estimate of the barrier to rotation about the M–N bond, ΔE, in H_2MNH_2. The results included in Table 1 are consistent with those reported elsewhere,[2] with ΔE = 161.9, 50.6, 65.7 and 51.5 kJ mol^{-1} for M = B, Al, Ga and In, respectively. Gallium may then be seen once again to be out of line with its neighbours and to show a modest return to the behaviour of boron,[1] but the barriers support the general view that, with the exception of M = B, the primary influence on the M–N bonding is not the π interaction but the polarity of the unit.

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