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Synthesis of a GaN Cage Compound with a Hydrazinetetraide Fragment, $[N{-}N]^{4-}$, Stabilised by Six Gallium Atoms

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Abstract: Thermolysis of the bicyclic gallium hydrazide $[(GaMe_2)_4(NH{-}NMe)(NH{-}NHMe)_2]$ (**1**) yielded the unique cage compound $[(GaMe)_4(GaMe_2)_4(N_2)(NH{-}NMe)_4]$ (**2**). Compound **2** contains a remarkable hydrazinetetraide moiety, $[N{-}N]^{4-}$, as the central structural motif which is stabilised by coordination to six gallium atoms.

Keywords: cage compounds · gallium · hydrazides · nitrogen · pernitride

Introduction

There has recently been a great interest in the synthesis of new metal nitrides and pernitrides as a result of their theoretically predicted, and in many cases experimentally verified, interesting materials properties, such as hardness, superconductivity and various forms of magnetism.[1–6] Group 13 nitrides in contrast have industrial importance in semiconductors and optical devices. In our group we have a long standing research interest in Group 13 hydrazides[7] that are of some relevance as single source precursors in Metal–organic chemical vapor deposition (MOCVD) synthesis and related procedures for the preparation of Group 13 nitrides.[8] Further, they exhibit a fascinating coordination behaviour similar to that of hydroxyl amides or peroxides.[9] As a result of our work we now present the first molecular main-group-metal pernitride with an isolated $[N{-}N]^{4-}$ ion coordinated to six Ga atoms. It was obtained by thermolysis of a Group 13 hydrazide precursor. Such compounds are conveniently synthesised from 1) trialkylelement compounds or dialkylelement hydrides and hydrazines via the intermediate formation of adducts, 2) dialkylelement halides or their hydrazine adducts upon treatment with lithium hydrazides or butyllithium, 3) aminoalanes and hydrazines, and 4) the reactions of compounds with suitable Al–H and C=N functionalities (hydroalumination).[7,10,11] The processes during the thermal decomposition of these hydrazides to form AlN or GaN are poorly understood, and we are currently trying to establish a better understanding of the underlying chemistry by investigating the controlled and, where possible, stepwise thermolysis of well-defined precursors and the isolation and characterisation of the resulting intermediates. Initial progress has revealed that controlled heating of the reagents has led in several cases to cage compounds with interesting structural motifs. This may be exemplified by compounds such as $[Al\{[NHN(Me)]_2AlMe_2\}_3]$[12] and $[(GaMe)_4(NHNPh)_4]$[10,13] bearing dianonic hydrazindiido ligands with intact N–N bonds or by the imido cages $[(Al\mathit{t}Bu)_6(NMe)_6]$ and $[(Al\mathit{t}Bu)_7(NH)_6(NMe)]$ resulting from a cleavage of all N–N bonds.[14] A related reaction, that is, the thermolysis of bicyclic gallium hydrazide $[(GaMe_2)_4(NH{-}NMe)(NH{-}NHMe)_2]$ (**1**), has now led to the isolation of the unprecedented compound $[(GaMe)_4(GaMe_2)_4(NH{-}NMe)_4(N_2)]$ (**2**).

Results and Discussion

We have recently reported on the synthesis of the bicyclic gallium hydrazide $[(GaMe_2)_4(NH\text{-}NMe)(NH\text{-}NHMe)_2]$ (**1**; and similarly the corresponding indium analogue) from the thermal decomposition of the adduct $[GaMe_3(NH_2NHMe)]$ in toluene under reflux conditions.[12] Compound **1** has a

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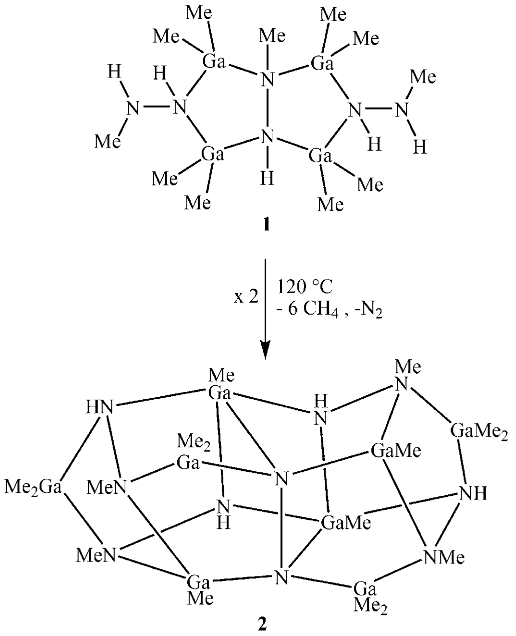
bridging hydrazindiido group coordinated by four gallium atoms. When neat **1** was further heated in an argon atmosphere for 2 h at 120 °C the melting of the solid starting material was accompanied by a visible gas evolution (Scheme 1). Extraction of the solid product with toluene and crystallisation yielded $[(GaMe)_4(GaMe_2)_4(NH{-}NMe)_4(N_2)]$ (**2**) in a moderate yield of 42 %. The balanced stoichiometric equation for the conversion of **1** to **2** (Scheme 1) requires the loss of six equivalents of CH_4 and one equivalent of N_2. This was confirmed by thermogravimetric analysis that displayed at 122 °C a mass loss of 11.6 % (123.6 $g\,mol^{-1}$; 6 CH_4 and 1 N_2 adds up to 124.3 $g\,mol^{-1}$) and peaks in the corresponding mass spectrometric trace that are consistent with the formation of methane ($m/z = 16$) and dinitrogen ($m/z = 28$) as major fragments. The NMR spectra of **2** showed a complicated pattern of two NH, two NMe and six GaMe resonances in the expected intensity ratio (^1H) that is consistent with **2** having C_2 symmetry in solution. A set of very low intensity signals close to the major peaks may indicate the presence of a second isomer of yet unknown constitution.



Scheme 1.

The molecular structure of **2** (Figure 1) obtained by X-ray diffraction shows a Ga_8N_{10} core that is composed of ten five-membered Ga_2N_3 heterocycles in an approximate envelope conformation that share one or two common sides and one puckered (angle between GaN_2 planes 57°) four-membered Ga_2N_2 heterocycle (Ga1-N11-Ga3-N31). The eight Ga atoms of the GaMe or $GaMe_2$ groups are bridged by four hydrazindiide ligands, $[H\text{-}N\text{-}N\text{-}Me]^{2-}$, and a hydrazintetraide group, $[N\text{-}N]^{4-}$. There is an approximate C_2-rotation axis passing through the centres of the central N51–N52 bond and the four-membered Ga_2N_2 heterocycle, which is in agreement with the observed NMR spectra. The Ga and N atoms are, with the exception of Ga1 and Ga3, four-coordinate with an approximately tetrahedral coordination sphere. Ga1 and Ga3 are both five-coordinate with a distorted trigonal bipyramidal coordination sphere. The Ga–C distances are unexceptional and range from 194.3(5) to 198.1(5) pm. The Ga–N distances in contrast differ considerably with the axial distances of the five-coordinate Ga atoms (Ga1–N11, Ga1–N21, Ga3–N31, Ga3–N41) being significantly longer (216.2(4)–223.8(4) pm) than the equatorial or tetrahedral Ga–N contacts (194.7(4)–203.7(4) pm). The most exciting feature of the structure is the unique $Ga_3N{-}NGa_3$ fragment (Figure 2) representing a fully deprotonated hydrazine or a pernitride. The six Ga atoms are in a staggered arrange-

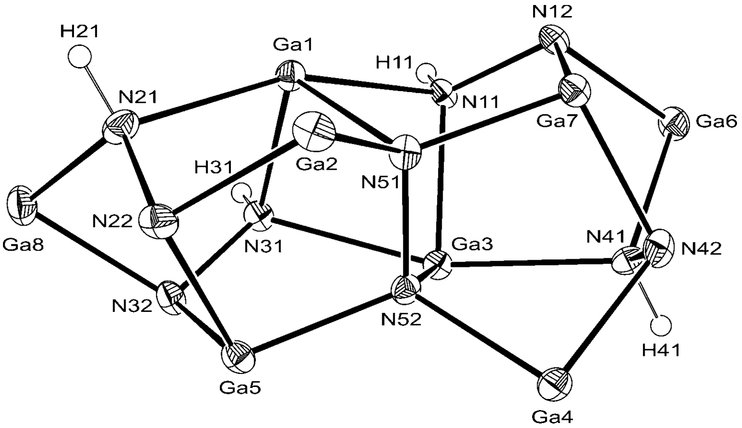


Figure 1. Molecular structure and numbering scheme of **2**; displacement ellipsoids are drawn at the 40 % level. Methyl groups have been omitted for clarity. Important bond lengths [pm] and angles [°]: N51–N52 154.9(6), N–N of the N(H)–N(Me) groups 145.9(5) to 150.8(5) (148.4(av), N51–Ga and N52–Ga 194.7(4) to 203.6(4) (199.0(av)), Ga-N51-Ga and Ga-N52-Ga 104.5(2) to 119.6(2), Ga-N51-N52 and Ga-N52-N51 102.1(2) to 111.2(2).

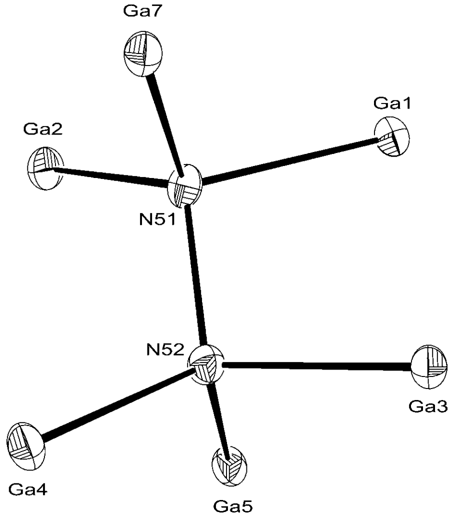


Figure 2. Coordination geometry around the central $[N{-}N]^{4-}$ fragment of **2**. Displacement ellipsoids are drawn at the 40 % level.

ment. The N–N distance is with 154.9(6) pm and in accordance with the increased electron density on the nitrogen atoms significantly longer than in neutral hydrazine (145 pm)[15] or the remaining hydrazide substituents in **2** (145.9(5)–150.8(5) pm). In the IR and Raman spectra of **2** the N–N stretching vibration of the central hydrazintetraide was detected at 891 and 892 cm^{-1}, respectively, which is in the range characteristic of hydrazine derivatives.[6,16] It was assigned on the base of quantum-chemical simulations,[17] which gave an excellent agreement of experimental and calculated spectra (see below). The only other structurally authenticated example of a molecular six-coordinate pernitride is the dication $[\{(Ph_2iPrP)_3Au\}_3N\text{-}N\{Au(PPh_2iPr)_3\}_3]^{2+}$,[18] which has a much shorter N–N distance of only 147.5(14) pm. This may be compared to a value of 152 pm as estimated by quantum mechanical calculations for $[(PH_3Au)_6N_2]^{2+}$.[19] The two lanthanide dinitrogen clusters $[(\{p\text{-But-calix[4]-}(OMe)_2O_2Sm\}_4(thf)N_2\{Na(thf)\}_2]$[20] and $[\{(CH_2)_5C(C_4H_3N)_2\}Sm]_4N_2(THF)_2$[21] are reported to incorporate four-coordinate dinitrogen tetraanions with N–N bond lengths of 161.1(16) and 141.2(17) pm, respectively. Very recently there have been reports of inorganic materials such as OsN_2,[2] IrN_2[3,4] and PtN_2[3,5] that were synthesised under high pressure and drastic temperature conditions and found to have $[N{-}N]^{4-}$ ions in octahedral interstices of the metal sub-lattice with N–N bond lengths in the region of 141 pm. The presence of $[N{-}N]^{4-}$ ions in these materials was confirmed by high-level quantum chemical calculations.[6] A theoretical investigation of the chemical bonding in Group 13 nitrides obtained in contrast a much shorter bond length of 134 pm for a N_2 fragment in an octahedral interstice of a hypothetical Ga_6N_2 cluster despite the fact that the Ga–Ga distances in the region of 320–340 pm are in good agreement with the experimental values found in **2**.[22]

Quantum chemical calculations have been performed using the Gaussian 09 suite of programs[17] on the C_2-symmetric structure. The B3LYP functional with the 6-311+G(d,p) basis set was used to compute the geometry and the 6-31G(d) basis set for the normal mode vibrational frequencies of the 6-31G(d) structure. Unfortunately, due to the high CPU demand we were not able to complete high-level frequency calculations. The calculated $Ga_3N{-}NGa_3$ distance is 154 pm, which is in excellent agreement with the experimental value (154.9(6) pm). The N–N stretching vibration was found at 889 cm^{-1} as a relatively low intensity signal in full agreement with the experiment (892 cm^{-1}). NBO analysis revealed charges of −1.28 and −0.8 to −0.9 for the nitrogen atoms of the $[N{-}N]^{4-}$ unit and the hydrazindiide ligands, respectively. The Ga atoms had charges of +1.5 and +1.6 (Me_2GaN_2), +1.7 ($MeGaN_4$) and +1.8 ($MeGaN_3$).

The characterisation of **2** shows that the thermolysis of Group 13 hydrazides may be carried out in a controlled fashion that leads to extremely interesting products. The observed scission of the generally inert aliphatic N–C bond is notable in view of the very few reported examples of transition metal mediated N–C bond cleavage reactions.[23]

Experimental Section

General: All procedures were carried out under an atmosphere of purified argon in dried solvents (*n*-pentane over $LiAlH_4$, toluene over Na/benzophenone). The bicyclic compound **1** was obtained according to a literature procedure.[12a]

Synthesis of 2: Compound **1** (0.80 g, 1.50 mmol) was heated slowly to 120 °C in the absence of a solvent . The solid melted and gas evolution took place. The reaction mixture was stirred for 2 h at the same temperature until the gas evolution had ceased. The initially yellow melt had by then turned into a glassy solid which was washed with a small quantity of *n*-pentane (10 mL) and dissolved in toluene (4 mL). The solution was kept for several days at −15 °C to give colourless crystals of compound **2** (0.30 g, 42 %). M.p. 128 °C; ^1H NMR (400 MHz, [D$_8$]toluene, 27 °C): δ = 2.34 and 2.30 (each s, 3H, NMe), 1,97 and 1.78 (each s, 1H, NH), −0.12, −0.19, −0.239, −0.243, −0.41, −0.47 ppm (each s, 3H, GaMe); ^{13}C NMR (100 MHz, [D$_8$]toluene, 27 °C) δ = 43.1 and 41.7 (s, NMe), 2.3, −4.7, −4.9, −8.9, −10.3, −12.8 ppm (all GaMe); IR (nujol): $\tilde{\nu}$ = 3472 (s, br, νN–H), 2920 (vs), 2851 (vs, nujol), 1609 (m, δN–H), 1456 (vs), 1377 (vs, nujol), 1204 (m), 1155 (w), 1134 (w), 1045 (s), 914 (w, δCH_3, νCH, νCN, νNN), 891 (m, νNN of N_2^{4-}), 833 (w), 797 (w), 721 (s, nujol), 598 (m), 565 (m), 527 (w), 494 (w), 463 cm^{-1} (w, νGaN); Raman (single crystal, excitation line 632.8 nm): $\tilde{\nu}$ = 1470 (w), 1445 (w), 1410 (w), 1209 (m), 1192 (s, δCH_3), 1138 (vw), 1050 (vw), 917 (vw), 892 (w, νN–N), 790 (w, δCH_3), 581.3 (s), 566 (vs), 543 (vs), 537 (vs, breathing modes of the cage), 496 (m), 441 cm^{-1} (m); MS (EI, 20 eV, 70 °C): *m/z* (%) (experimental intensities agree with expected isotopic distribution; only the most intense peak of each fragment is given): 942 (14) [M^+], 927 (9) [M^+−Me], 828 (100) [$M^+{-}Me_2GaNH$], 784 (18) [$M^+{-}Me_2GaN(H)NMe_2$]; elemental analysis calc (%) for $C_{16}H_{52}Ga_8N_{10}$ (942.4): C 20.4, H 5.6, N 14.9; found: C 20.5, H 5.4, N 14.4.

Crystal structure determination: Intensity data were collected on a Bruker APEX II diffractometer with monochromated $Mo_{K\alpha}$ radiation. The collection method involved ω scans. Data reduction was carried out using the program SAINT+.[24] The crystal structure was solved by direct methods using SHELXTL.[25] Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix least-squares calculation based on F^2 using SHELXTL. Hydrogen atoms were positioned geometrically and allowed to ride on their respective parent atoms. Crystal size = 0.17 × 0.09 × 0.05 mm, min/max θ = 1.69/27.99°, index ranges: $-16 \leq h \leq 16$, $-20 \leq k \leq 20$, $-24 \leq l \leq 24$, independent reflns: 8097 (R_{int} = 0.1568); completeness to θ = 27.99°: 99.2 %, max/min transmission: 0.74/0.41; parameters: 319; R_1 [$I > 2\sigma(I)$] = 0.0419, w$R2$ (all data) = 0.0932; largest diff. peak/hole 0.98/−1.13 e Å^{-3}. CCDC-778222 contains the supplementary crystallographic data for this paper. 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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