Hydride-bridged Heterobimetallic Complexes of Gallium and Zinc: the First X-Ray Structural Determination of the GaH_4^- Moiety

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Reaction of 2 equivalents of $LiGaH_4$ or 1 equivalent of $NaGaH_4$ with $[ZnCl_2(pmdeta)]$ (pmdeta = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine) in diethyl ether at 0 °C gives the heterobimetallic species, $[Zn(\eta^1\text{-}GaH_4)Cl(pmdeta)]$ **1**, whereas reaction of $[M'GaH_4]$ with $[ZnCl_2(tmen)]$ (tmen = *N,N,N′,N′*-tetramethylenediamine) in 2 : 1 (M′ = Li) or 1 : 1 (M′ = Na) molar ratio, gives $[Zn(\eta^2\text{-}GaH_4)Cl(tmen)]$ **2**; the analogous $[Zn(\eta^2\text{-}BH_4)(Cl(tmen)]$ **3** is prepared from reaction with 2 molar equivalents of $LiBH_4$ or with 1 equivalent of $NaBH_4$; complexes **1** and **3** are structurally charactrerised, the former represents the first reported structure of the GaH_4 moiety.

There is a renewed interest in main-group chemistry[1] including that of compounds containing both transition and main-group elements.[2] As an extension of our research on the heavier Group 13 metal hydrides[3] we have investigated the reactions of hydridometalates of gallium with zinc halide complexes. A search of the Cambridge Structural Database revealed that the solid-state structure of GaH_4^- had not been reported unlike the congeneric AlH_4^- unit.[4] Given the thermal frailty of $LiGaH_4$ we attempted to attach GaH_4^- to a coordinatively unsaturated metal centre, previously successful in the structural characterisation of aluminohydrides.[5]

Reaction of 2 equivalents of $LiGaH_4$ with $[ZnCl_2(pmdeta)]$ (pmdeta = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine) in diethyl ether at 0 °C gave the heterobimetallic species, **1** (Scheme 1)† which is also accessible by use of 1 equivalent of $NaGaH_4$ in thf. Monodentate coordination of BH_4^- is rare and that of GaH_4^- found in **1** appears to have no precedent, while for the more extensively studied AlH_4^- there is but one structurally characterised example.[5] Reaction of $[M'GaH_4]$ with $[ZnCl_2(tmen)]$ (tmen = *N,N,N′,N′*-tetramethylenediamine) in 2 : 1 (M′ = Li) or 1 : 1 (M′ = Na) molar ratio (Scheme 1), results in complex **2** in which the GaH_4^- unit presumably adopts a bidentate hydride bridging mode. Compound **2** crystallised as very thin plates which were unsuitable for X-ray crystallography. Its structure was inferred from spectroscopic data and the crystal structure of a boron analogue, **3**. This was prepared from the analogous reaction with 2 molar equivalents of $LiBH_4$ or 1 equivalent of $NaBH_4$. Satisfactory microanalyses were obtained for **1** and **3** whereas **2** was too unstable at room temperature to obtain reliable elemental analysis.

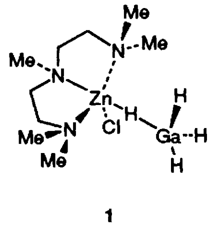
The bimetallic Zn/Ga hydrido species possess low thermal stabilities, decomposing to grey materials on prolonged standing at room temperature and appears to be a dependent on the number of N donor atoms at the metal centre. Thus, the pmdeta complex **1** is thermally stable at room temperature for hours, while the tmen analogue **2** decomposed within an hour. The boron analogue **3** is thermally more stable. Upon heating, **1**–**3** decomposed to grey materials, with melting and evolution of a gas, presumably hydrogen, upon further increase in temperature.

The IR spectrum of **3** suggests a covalent bidentate coordination mode for BH_4^-,[6] whilst compound **2** also showed two different M–H stretching modes.

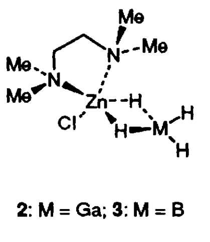
Solution ^1H NMR spectra exhibited the expected resonances for the N-donor ligands. A broad, featureless singlet at δ 4.80 in the ^1H NMR spectrum of **2** was unchanged in the temperature range −80 °C to 25 °C, suggesting rapid hydride exchange between terminal and bridging positions of the bidentate GaH_4^-. This behaviour was also shown by the analogous BH_4^- complex **3** which shows a broad quartet centred at δ 0.81 arising from coupling to ^{11}B, with J_{BH} 83.4 Hz.[6] In contrast the ^1H NMR spectrum of complex **1** showed a broad singlet at δ 4.38 which altered shape on cooling possibly due to hindered rotation about the Zn–H–Ga axis or more probably due to bidentate–monodentate fluxionality.

The solid-state structures of **1** and **3**‡ are shown in Figs. 1 and 2. Monodentate binding of tetrahydrogallate is unequivocally confirmed by the almost linear hydride bridge [Zn–H_b–Ga 177(3)°]; by contrast for the monodentate copper(I) compound $[Cu(BH_4)(triphos)]$ [triphos = 1,1,1-tris{[(diphenylphosphino)methyl]ethane}] this angle is bent [Cu–H_b–B 121(3)°].[7] The steric requirements of the Zn coordination sphere almost certainly imposes monodentate coordination for GaH_4^- in **1**. The zinc shows distorted trigonal bipyramidal geometry, with the bridging hydride H(1) and N(2) in apical positions.

The bidentate coordination mode of GaH_4 in **2** can be inferred from the solid-state structure of congeneric **3**. The geometry of the ligated BH_4 unit is unremarkable and common for transition metal tetrahydroborates.[6]



1



2: M = Ga; **3**: M = B

$$[Zn(\eta^2\text{-}GaH_4)Cl(tmen)] \xleftarrow{ii} M'[MH_4] \xrightarrow{i} [Zn(\eta^1\text{-}HGaH_3)Cl(pmdeta)]$$

Scheme 1 *Reagents and conditions*: i **1**, M′ = Li, M = Ga, 1/2 $[ZnCl_2(pmdeta)]$, Et_2O; M′ = Na, M = Ga, $[ZnCl_2(pmdeta)]$, thf; ii **2**, M′ = Li, M = Ga, 1/2$[ZnCl_2(tmen)]$, Et_2O; **3**, M′ = Li, M = B, 1/2$[ZnCl_2(pmdeta)]$, Et_2O; M′ = Na, M = B, $[ZnCl_2(pmdeta)]$, Et_2O

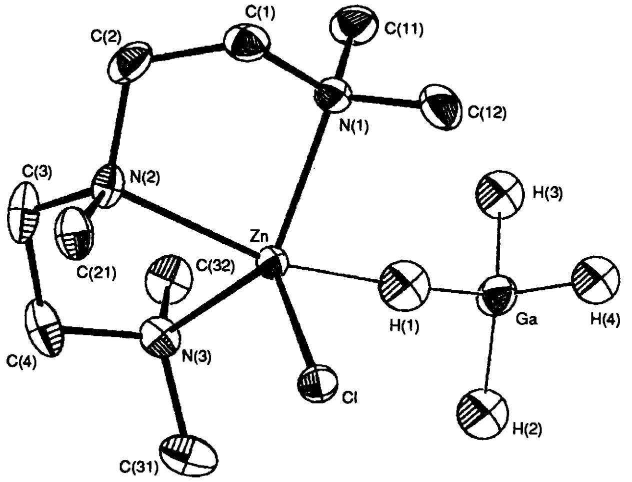


Fig. 1 ORTEP diagram of the structure of $[Zn(\eta^1\text{-}GaH_4Cl(pmdeta)]$. Selected bond lengths (Å) and angles (°); Zn–H(1) 2.01(5), Ga–H(1) 1.42(5), Ga–H(2), H(3), H(4) 1.61(5), 1.60(4), 1.54(4), Zn–H(1)–Ga 177(3).

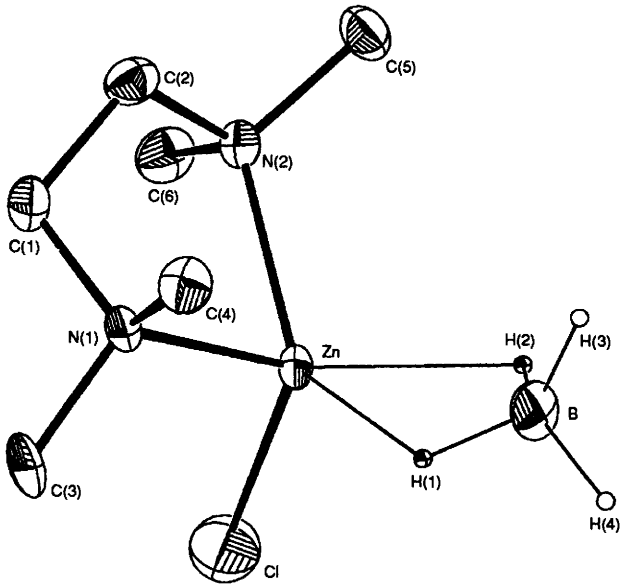


Fig. 2 ORTEP diagram of the structure of [Zn(η^2-BH_4)Cl(tmen)]. Selected bond lengths (Å) and angles (°); Zn–B 2.29(2), Zn–N(1) 2.09(1), Zn–N(2) 2.11(1), Zn–Cl 2.252(7), Zn–H(1) 1.983(2), Zn–H(2) 1.963(2), H(1)–Zn–H(2) 62.02(5), Zn–B–H(1) 60.1(8), Zn–B–H(2) 59.1(7), Zn–B–H(3) 116(2), Zn–B–H(4) 130(1), H(1)–B–H(2) 118(1), H(1)–B–H(3) 105.(2), H(1)–B–H(4) 108(2), H(2)–B–H(3) 112.(2), H(2)–B–H(4) 100(2).

In **1** the hydride atoms were located and refined isotropically. The geometry around the gallium atom is distorted tetrahedral with H–Ga–H angles in the range 107(2)–119(2)°. The Ga–H distances are not significantly different at *ca.* 1.5 Å with Zn–H_b 2.01(5); Zn–H distances for Zn–H–B moietes are in the range 1.78–1.90 Å.[8,9]

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Footnotes

† **1**: *Method* 1: To a stirred ethereal solution of $LiGaH_4$ (0.827 g, 3.23 mmol) at 0 °C [$ZnCl_2$(pmdeta)] (0.50 g, 1.615 mmol) was slowly added and the mixture stirred for 2 hours at room temp. Ether was decanted and the resulting white precipitate was recrystallised from thf (*ca.* 10 ml) to give colourless crystals of **1**, yield 0.30 g, 53%. *Method* 2: Solid [$ZnCl_2$(pmdeta)] (0.54 g, 1.739 nmol) was slowly added to a stirred solution (20 ml) of $NaGaH_4$ (0.17 g, 1.739 mmol) in thf at 0 °C. The resulting mixture was stirred for 2 hours at room temp. and filtered. The filtrate was concentrated to *ca.* 5 ml and cooled to −30 °C to give colourless crystals of **1**. Yield 0.30 g, 49%. Mp 94 °C (decomp.); IR [Nujol, ν/cm^{-1}]: 1766, 1708 (br, Ga–H); ^{1}H NMR (400 MHz, $C_6D_5CD_3$, 25 °C) δ 2.09 (br s, 15H, CH_3), 2.34, 2.43 (s, 2 × 4H, NCH_2), 4.38 (br s, 3H, GaH), 4.50 (s, 1H, ZnH); ^{13}C NMR (62.8 MHz, C_6D_6, 25 °C) δ 24.96 (NCH_2), 46.63 [$(NCH_3)_3$], 56.53 (NCH_3). **2**: Solid [$ZnCl_2$(tmen)] (0.50 g, 1.98 mmol) was slowly added to a stirred ethereal solution of $LiGaH_4$ (25 ml, 3.92 mmol) at 0 °C. The reaction mixture was stirred for 1 hour at 0 °C and then warmed to room temp. After a further hour the resulting white precipitate was removed by filtration and the filtrate was concentrated and cooled to −30 °C affording thin plates of **2**. Yield 0.44 g, 76%. Mp 88 °C (decomp); IR [Nujol, μ/cm^{-1}]: 1839 (br, Ga–H), 1955 (sh, Zn–H); ^{1}H NMR (250 MHz, C_6D_6, 25 °C) δ 1.87 (s, 12H, NCH_3), 2.59 (s, 4H, NCH_2), 4.84 (br, 4H, GaH); ^{13}C NMR (62.8 MHz, C_6D_6, 25 °C) δ 47.79 (NCH_3), 57.06 (NCH_2). **3**: *Method* 1: To a stirred slurry of $LiBH_4$ (0.15 g, 6.887 mmol) in diethyl ether (25 ml) at 0 °C solid [$ZnCl_2$(tmen)] (0.87 g, 3.446 mmol) was slowly added and warmed to room temperature. After 3 hours the reaction mixture was filtered and the filtrate concentrated and cooled to −30 °C to afford needle-like crystals of **3**. Yield 0.52 g, 65%. *Method* 2: To a stirred slurry of $NaBH_4$ (0.09 g, 2.379 mmol) in diethyl ether (25 ml) at 0 °C solid [$ZnCl_2$(tmen)] (0.60 g, 2.379 mmol) was slowly added. After stirring for 2 hours at room temp., diethyl ether was removed and the resultant white solid taken up in thf, filtered, concentrated and placed at −30 °C to afford crystals of **3**. Yield, 0.25 g, 45%. Mp 130–132 °C (decomp.); IR [Nujol, ν/cm^{-1}]: 2422, 2368 (br, B–H_t), 2207, 2120 (br, B–H_{br}); ^{1}H NMR (200 MHz, $C_6D_5CD_3$, 25 °C) δ 1.67 (s, 2H, NCH_2), 1.92 (s, 12H, NCH_3), 2.05 (2, 2H, NH_2), 0.81 (q, ^2J 83.4 Hz, 4H, BH_4); ^{13}C NMR (62.8 MHz, C_6D_6, 25 °C) δ 47.28, 51.99 (4 × NCH_3), 56.01, 59.24 (2 × NCH_2).

‡ *Crystal Structure Determinations* (Enraf-Nonius CAD4 diffractometer, crystal mounted in capillaries). **1**: single crystals from saturated thf solution, $C_9H_{27}ClGaN_3Zn$, monoclinic, $P2_1/n$, $Z = 4$, $a = 7.796(2)$, $b = 14.696(3)$, $c = 14.057(5)$ Å, $\beta = 96.73(1)°$, $V = 1599.5(7)$ Å^3, $D_c = 1.445$ g cm^{-1}, $\mu = 33.2$ cm^{-1} (absorption correction), CAD4 diffractometer, $T = 293$ K, $2\theta_{max} = 50°$, 2571 observed reflections [$I > 2.5\sigma(I)$], 244 refined parameters, $R = 0.029$, $R_w = 0.030$ (unit weights) structure solution with direct methods, XTAL3.2 (*Xtal3.2Reference Manual*, ed. S. R. Hall and J. M. Stewart, Lamb, Perth), all hydrogen atoms located and refined with U_{iso}, all non-hydrogen atoms refined with anisotropic temperature factors. **3**: single crystals from saturated diethyl ether solution, $C_6H_{20}BClN_2Zn$, monoclinic, $P2_1/n$, $Z = 4$, $a = 7.938(5)$, $b = 13.399(5)$, $c = 12.023(8)$'Å, $\beta = 108.06(3)°$, $V = 1216(1)$ Å^3, $D_c = 1.267$ g cm^{-1}, $\mu = 21.9$ cm^{-1} (absorption correction), CAD4 diffractometer, $T = 293$ K, $2\theta_{max} = 50°$, 1311 observed reflections [$I > 2.5\sigma(I)$], 100 refined parameters, $R = 0.077$, $R_w = 0.082$ (unit weights). Structure solution with direct methods as above; Atoms H(1), H(2) and H(3) were located and placed in fixed positions, all other hydrogen atoms were placed in calculated positions (C–H 0.95, B–H(4) 1.15 Å), all non-hydrogen atoms were refined with anisotropic temperature factors. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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