Synthesis and X-ray crystallographic structure of $Ga_4(OH)_6(3\text{-}Bu^tpzH)_{10}I_6\cdot 2MeCN$: a quasi double heterocubane

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The reaction of $K[HB(3\text{-}Bu^tpz)_3]$ with GaI_3 resulted in breakdown of the ligand and formation of a novel Ga/O cluster. This compound can be described as four edge-sharing Ga/O,N octahedra or as two face sharing partial Ga/O heterocubanes, *i.e.* a quasi double heterocubane.

In a previous publication we reported the reaction of $Na[MeGa(pz)_3]$ with $GaCl_3$ to give $Ga_8(pz)_{12}O_4Cl_4\cdot 2THF$, which is based on a Ga_4O_4 core.[1] However, this core contains edge bridging groups and we therefore refer to this and analogous structures as 'non-discrete'. 'Discrete' Ga_4N_4, Ga_4S_4, Ga_4Se_4 and Ga_4Te_4 cubanes are known,[2,3] but to date no 'discrete' Ga_4O_4 cubane has been reported. A similar situation existed in indium chemistry with 'discrete' In_4N_4, In_4S_4, In_4Se_4 and In_4Te_4 cubanes[2,4] and a 'non-discrete' In_4O_4 cubane[5] being known. However, very recently, a 'discrete' In_4O_4 cubane, $In_4O_4(C(SiMe_3))_4$ has been reported.[6]

As an extension of our work on Ga/O cubanes we attempted to synthesise a 'discrete' Ga_4O_4 cubane by replacing $Na[MeGa(pz)_3]$ with $K[HB(3\text{-}Bu^tpz)_3]$, thus eliminating the possibility of Ga–pz bridging, and $GaCl_3$ with GaI_3, since I^- is a better leaving group than Cl^-. $HB(3\text{-}Bu^tpz)^-$ was chosen in preference to less hindered trispyrazolylborates because of the stabilisation that would be conferred on the cubane by the bulky $(3\text{-}Bu^tpzH)$ groups, a known breakdown product of $HB(3\text{-}Bu^tpz)_3^-$.[7] We therefore reacted $K[HB(3\text{-}Bu^tpz)_3]$ with GaI_3 in THF. The clear diamond shaped plate crystals, **1**, isolated from the reaction mixture were subjected to elemental analysis, IR, ^1H and ^{13}C NMR, and mass spectral analysis.† It was not possible to deduce the structure of **1** from this data and so an X-ray crystallographic study was undertaken.‡ The results are shown in Fig. 1 from which the six I^- ions, all the hydrogen atoms and the two molecules of MeCN have been omitted for clarity. From Fig. 1 it is evident that the target compound has not been synthesised but instead $Ga_4(OH)_6(3\text{-}Bu^tpzH)_{10}I_6\cdot 2MeCN$, **1**. The structure of **1** can be described in terms of four, edge sharing, Ga/O,N octahedra. However, given the main thrust of this work we describe it as two face sharing heterocubanes each of which is missing a Ga ion on the long diagonal through the centre of the shared face, an inversion centre. This particular structure is unprecedented in Ga chemistry although $[(CpAl)_6P_4]$[8] and $Al_{10}(OH)_{16}(OSiEt_3)_{14}$[9]

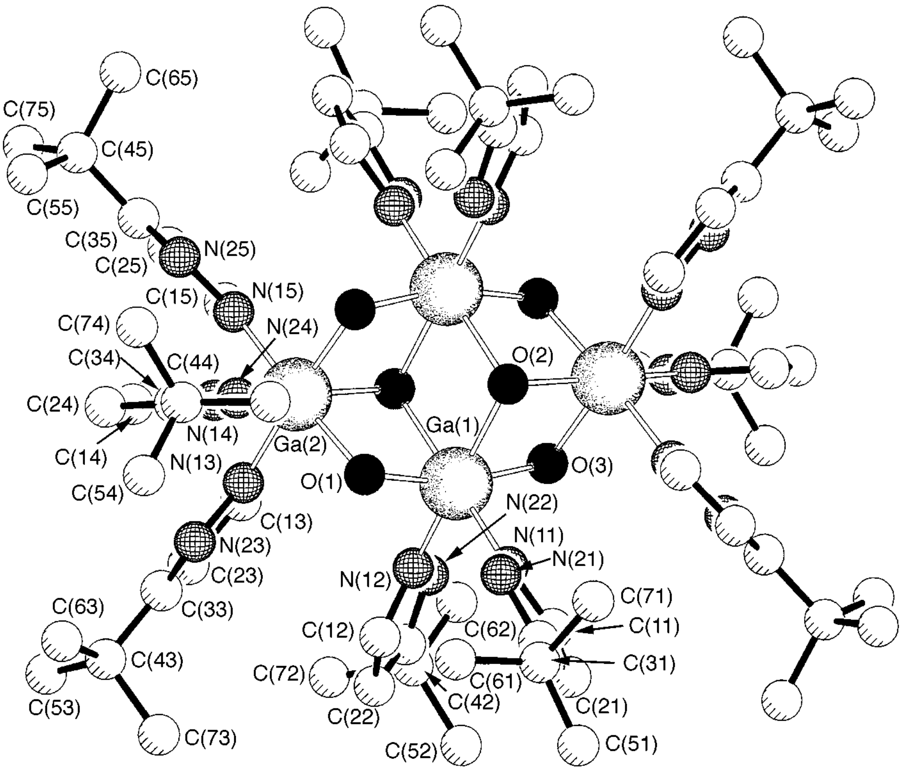

Fig. 1 Structure of **1** with the I^-, H and MeCN removed. Selected bond lengths (Å) and angles (°): Ga(1)–O(1) 1.896(5), Ga(1)–O(2) 2.090(6), Ga(1)–O(3) 1.912(5), Ga(1)–O(2′) 2.106(5), Ga(2)–O(1) 1.963(6), Ga(2)–O(2) 2.021(5), Ga(2)–O(3′) 1.951(5); Ga(1)–O(1)–Ga(2) 106.3(2), Ga(1)–O(2)–Ga(2) 97.4(2), Ga(1)–O(2)–Ga(1′) 101.8(2), Ga(1)–O(3)–Ga(2′) 106.4(2), Ga(2)–O(2)–Ga(1′) 97.1(2), O(1)–Ga(1)–O(2) 77.7(2), O(3)–Ga(1)–O(2) 91.0(2), O(1)–Ga(1)–O(2′) 90.5(2), O(3)–Ga(1)–O(2′) 77.4(2), O(2)–Ga(1)–O(2′) 78.2(2), O(1)–Ga(2)–O(3′) 89.7(2), O(2)–Ga(2)–O(3′) 78.6(2), O(1)–Ga(2)–O(2) 77.0(2). Symmetry transformation used to generate primed atoms: ′ $-x, -y, -z + 1$.

can be claimed to be structurally analogous. Each Ga in **1** attains six coordination by bonding to either two or three 3-Bu^{t}pzH groups and it is thought that the presence of these bulky groups help stabilise the complex. The Ga/O bond lengths and angles that define **1** are given in Fig. 1, from which it can be seen that the corresponding parameters in $Ga_8(pz)_{12}O_4Cl_4\cdot 2THF$ *viz.* Ga_c–O–Ga_c 98.26(6)°, O–Ga_c–O 81.08(6)° and Ga_c–O 2.003(1) Å are within comparable range.[1] Given the reducing properties of $HB(3\text{-}Bu^tpz)_3^-$,[7] the Ga–Ga distances were examined for evidence of metal–metal bonding. However, since these distances fall within the range 3.089–3.256 Å, whereas the Ga–Ga distances in a series of Ga^I dimers range from 2.34 to 2.54 Å,[8] such bonding is precluded. However, the Ga–Ga distances in **1** are less than the sum of the van der Waals radii of Ga (3.80 Å).[10] Similarly the O–O distances, which are in the range 2.50–2.76 Å, are less than the sum of the van der Waals radii of O (3.00 Å).[10] These observations indicate some degree of strain within the cluster. The corresponding distances in $Ga_8(pz)_{12}O_4Cl_4\cdot 2THF$ are Ga–Ga 3.022 Å and O–O 2.61 Å.[1]

A number of important questions are raised by the structure of **1** with, perhaps, the most important being the origin of the hydroxyl groups. This question was raised in our previous publication with reference to the formation of $Ga_8(pz)_{12}O_4Cl_4\cdot 2THF$, where it was suggested that the source of the oxygen was either air or moisture entering the system on prolonged standing at low temperature.[1] Although dried solvents and Schlenk techniques were used in the synthesis of **1** the conditions for air/moisture exclusion were not the most stringent possible. This was part of the synthetic strategy. However, it is now proposed to repeat this experiment under the most strictly controlled conditions to investigate the method of oxygen inclusion through ^{17}O studies.

Given that, at present, examples of quasi double heterocubanes are extremely rare it would seem that this structural type is an oddity with little relevance to cubane chemistry. However, we do not subscribe to this view and are confident that other examples will be identified thus establishing quasi double heterocubanes as a significant structural type with implications for the synthesis of compounds of higher nuclearity. The reason for this confidence is that we believe the difference between a quasi double cubane and a cubane, in this case $[Ga_4(OH)_6(3\text{-}Bu^tpzH)_{10}]^{6+}$ and $[Ga(OH)_4(3\text{-}Bu^tpzH)_{12}]^{8+}$, is finely balanced sterically and by judicious choice of ligand and control of stoichiometry interconversion can be achieved.

Notes and References

† *Synthesis*: all manipulations were performed under argon using standard Schlenk techniques and all solvents dried prior to use. To a Schlenk tube charged with GaI_3 (1.05 g, 2.33 mmol) was added $K[HB(3\text{-}Bu^tpz)_3]$ (0.98 g, 2.33 mmol) and 60 cm^3 of THF. The pale yellow slurry was stirred for 18 h after which the solvent was removed *in vacuo*. Dichloromethane (60 cm^3) was added to the off-white residue, stirred, and the suspension filtered to remove KI. CH_2Cl_2 was removed *in vacuo* and 60 cm^3 of MeCN was added to the off-white residue. The pale yellow solution was reduced to one third of its original volume and placed in a freezer. After one week clear diamond shaped plates formed which were filtered off and used in the X-ray analysis. Yield: 1.04 g, 75% (Found: C, 33.73; H, 5.35; N, 11.15; Ga, 11.49; I, 34.26. Calc. for $C_{78}H_{132}N_{24}O_6Ga_4I_6$: C, 36.85; H, 5.23; N, 13.22; Ga, 10.97; I, 29.25%). We attribute the poor analysis to solvent dependency. NMR (250 MHz): δ_H 10.42 (br s, NH + OH), 7.70 (br s, H^3), 6.27 (br s, H^4), 5.23 (s, MeCN), 1.38 (s, CMe_3); D_2O addition, δ 7.50 (d, H^3), 6.18 (d, H^4), 4.20 (br s, NH + OH), 1.50 (s, CMe_3); δ_C 156.6 (C^5), 134.9 (C^3), 102.6 (C^4), 30.2 (CMe_3). IR 3197 [ν(NH)], 3100 [ν(CH)], 2966 [ν(CH)], 1495 (ring breathing).

‡ *Crystal data* for **1**: $C_{78}H_{132}N_{24}O_6Ga_4I_6$, M = 2536.31, orthorhombic, space group *Pbca*, a = 16.00(3), b = 25.051(5), c = 26.424(5) Å, U = 10591(4) $Å^3$, Z = 2, D_c = 1.591 Mg m^{-3}, $F(000)$ = 5008, λ = 0.71069 Å, T = 150 K, μ(Mo-Kα) = 2.811 mm^{-1}. Data were collected on a Delft Instruments FAST TV area detector diffractometer. Of a total of 38 055 collected reflections 8332 were unique. The structure was solved by direct methods. Refinement was by full matrix least squares on F^2. Non hydrogen atoms were refined anisotropically and all hydrogen atoms except those on the hydroxyl groups were included in fixed positions and refined with the riding model. Final R indices [$I > 2\sigma(I)$] $R1$ = 0.0538, $wR2$ = 0.1188. One of the two solvent molecules, MeCN, showed slight disorder but this was not modelled. CCDC 182/951.

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