X-Ray crystallographic structure of $Ga_8(pz)_{12}O_4Cl_4\cdot 2thf$: a novel gallium pyrazololate complex with a Ga_4O_4 core

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The reaction of Na[MeGa$(pz)_3$] with $GaCl_3$ leads to the formation of the novel cubane $Ga_8(pz)_{12}O_4Cl_4\cdot 2thf$ 1, and not the expected product [{MeGa$(pz)_3$}$_2$Ga][$GaCl_4$]; the ease with which 1 forms is illustrated by its formation in a subsequent reaction of Na[MeGa$(pz)_3$] with $GaCl_3$.

There has been a resurgence of interest in compounds of main-group metals with a heterocubane core.[1–6] The recent work on gallium–group 16 cubanes describes the synthesis and structure of compounds with Ga_4S_4, Ga_4Se_4 and Ga_4Te_4 cores.[7]

However, prior to this communication there are no reported examples of compounds with a Ga_4O_4 cubane core. We herein describe the synthesis (albeit serendipitous) and X-ray crystallographic structure of such a compound, namely $Ga_8(pz)_{12}O_4Cl_4\cdot 2thf$.

In previous publications we drew attention to two significant features of some trispyrazolyl derivatives of group 13 [specifically HB(3-Bu^{t}Pz)$_3^-$ and HB(3-PhPz)$_3^-$], namely their stabilisation of low oxidation states and their redox properties with main-group metals.[8,9] We now identify a third significant feature of a member of this class of ligand [specifically MeGa(pz)$_3^-$], *viz.* heterocubane formation.

In an attempt to synthesise a gallium analogue of [{MeGa$(pz)_3$}$_2$In][InI_4],[10] *i.e.* [{MeGa$(pz)_3$}$_2$Ga][$GaCl_4$] **2**, we reacted Na[MeGa$(pz)_3$] with $GaCl_3$ in dry thf under an atmosphere of argon, filtered the precipitated NaCl and left the filtrate to crystallise at −10 °C. After several months crystals of **1** formed which were subjected to elemental, mass spectral, ^{71}Ga, ^{1}H and ^{13}C NMR analysis.† An X-ray crystal structure determination of **1** was also undertaken. The results are shown in Fig. 1(*a*) and (*b*) with selected bond lengths and angles given in Table 1.‡ The structure is based on a distorted Ga_4O_4 cube. Coordinated to and above each cube oxygen is a Ga atom, the centres of which define a tetrahedron. In addition, each of these Ga atoms is coordinated to three pyrazole rings and a chloride such that the five-coordinate Ga, [OGa$(pz)_3$Cl], is trigonal bipyramidal *TBPY*. The three pyrazole rings of each *TBPY* Ga coordinate

Table 1 Mean values[a] of selected bond lengths (Å) and angles (°)

Ga(e)–Cl	2.278(1)*		
Ga(e)–O	1.931(2)*	Ga(c)–O	2.003(1)
Ga(e)–N	1.976(2)	Ga(c)–N	2.017(2)
Coordination about Ga(e) (*TBPY*)		Coordination about Ga(c) (*octahedral*)	
Cl–Ca(e)–O	179.35(6)*	*trans*-O–Ga(c)–N	162.39(6)
N–Ga(e)–N	119.63(9)	*cis*-O–Ga(c)–N	83.44(6)[b]
Cl–Ga(e)–N	93.53(6)	*cis*-O–Ga(c)–N	104.78(6)[b]
O–Ga(e)–N	86.49(6)	O–Ca(c)–O	81.08(6)
		N–Ga(c)–N	92.52(8)
Coordination about O (*tetrahedral*)			
Ga(c)–O–Ga(c)	98.26(6)		
Ga(c)–O–Ga(e)	119.16(6)		

[a] Bond lengths and angles are weighted averages, $x = \Sigma\ \sigma_i^{-2}x_i/\Sigma\sigma_i^{-2}$, where σ_i are the e.s.ds from least-squares refinement; errors (within parentheses) are $s = (\Sigma\ \sigma_i^{-2})^{-1/2}$. Values marked with an asterisk are averages of four values; all other values are averages of 12 values. [b] There are two different types of *cis*-O–Ga(c)–N angles, depending if the O and N atoms belong to the same (83.44°) or to different (104.78°) five-membered chelate rings O–Ga(e)–N–N–Ga(c).

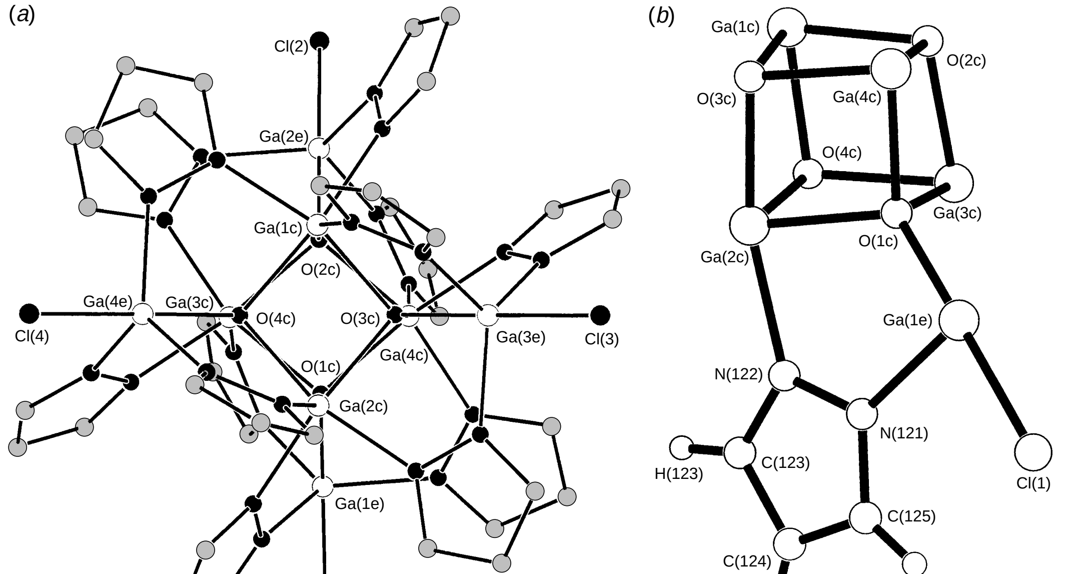

Fig. 1 (*a*) Structure of compound **1** and (*b*) with some of the 'outer atoms' omitted to show the Ga_4O_4 core

through their second nitrogen to the three Ga atoms of the cube that are edge connected to the same oxygen, thus making each cube Ga six-coordinate (3N,3O).

The formation of this compound raises problems, *e.g*. what is the source of the oxygen atoms? A possible solution is that on prolonged standing at low temperature traces of air or water, or both, entered the system resulting in oxygen incorporation. Therefore, to investigate this problem, a second attempt was made to synthesise **2** (the assumption being that this, or a similar gallium complex, is the precursor of **1**) in order to study its controlled hydrolysis. Elemental, mass spectral, ^{71}Ga, ^{1}H and ^{13}C NMR analyses of the small block-like single crystals that formed,† are very similar to those of **1**. These results indicated that this sample and **1** are very probably identical. This was confirmed by an X-ray crystallographic structure determination.

Footnotes

† *Synthesis*: all manipulations were performed under argon using standard Schlenk techniques and all solvents dried prior to use.

1 *method A*: to a Schlenk tube charged with $GaCl_3$ (0.04 g 2.27 mmol) in 20 cm^3 of thf was added a solution of Na[MeGa(pz)$_3$] (0.52 g 1.68 mmol) in 15 cm^3 of thf. An immediate turbidity occurred and the resulting solution stirred for 3 days. The solution was filtered and stored at −30 °C for one week. Attempts were made to filter the large crystals that formed but these redissolved on slight warming. A further 20 cm^3 of thf was added to the solution which was then stored at −30 °C for about six months. After this time the small block-like clear crystals that had formed were filtered. These crystals, although twinned, were used for the X-ray crystallographic structure determination. Yield 0.14 g (17%).

Method B: Na[MeGa(pz)$_3$] (2.28 g, 7.38 mmol) in 60 cm^3 thf was added to a Schlenk tube charged with freshly distilled $GaCl_3$ (1.30 g, 7.38 mmol). The resulting white slurry was stirred for three days after which time the thf was removed under vacuum. 60 cm^3 of dichloromethane was added to the resulting white mass, the slurry stirred and then filtered. The filtrate was evaporated to dryness. Dissolution of this in 60 cm^3 of MeCN, evaporation under vacuum to about 30 cm^3 and storing for one week at −30 °C produced small block-like single crystals of X-ray quality. Yield 1.92 g (61%). ^{1}H NMR [250 MHz, $(CD_3)_2SO$] δ 8.29 (d, 12 H, Ar H), 6.21 (t, 12 H, Ar H), 5.72 (d, 12 H, Ar H), 3.40 (8 H, thf), 1.28 (8 H, thf). ^{71}Ga NMR [250 MHz, $(CD_3)_2SO$] (dissolution only achieved with warming and sonication) δ 250.5 (ω 46 Hz), 10.7 (ω 912 Hz). IR (KBr) ν/cm^{-1} 2094, 2871, 1499, 1425, 1381, 1295, 1186, 1163, 1059, 973, 769, 620, 535, 342, 308. MS (FAB) 1570 (M + H)$^+$ < 1%.

‡ *Crystal data* for **1**: $C_{44}H_{52}Cl_4Ga_8N_{24}O_6$, M = 1712.62, triclinic, space group $P\bar{1}$ (no. 2), a = 12.494(4), b = 21.415(4), c = 12.349(4) Å, α = 91.90(2), β = 108.74(3), γ = 90.21(2)°, U = 3126(1) Å^3, Z = 2, D_c = 1.819 Mg m^{-3}, F(000) = 1696, λ = 0.710 69 Å, T = 296 K, μ(Mo-Kα) = 36.23 cm^{-1}. Absorption correction with DIFABS. Data were collected on a Rigaku AF7TS diffractometer. Of a total of 6162 collected reflections 5802 were unique. The structure was solved by direct methods. After refining all atoms in the molecule, a difference Fourier synthesis showed a large number of peaks of residual electron density located in empty regions of the unit cell, out of the range of bonding distances of the molecule, which were attributed to disordered solvent (thf) molecules. Two C_5 rings could be modelled, each one disordered over two positions, with total occupancies of 0.87 and 0.82. These C atoms were assigned fixed occupancies, fixed coordinates and refined isotropic displacement parameters. In the final difference Fourier synthesis the ten largest peaks (0.34–0.96 e Å^{-3}) were located in the vicinity of the C_5 ring atoms. Refinement was by full-matrix least squares on F, final R indices [$I > 2\sigma(I)$] R = 0.0309, R_w = 0.0381. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/423.

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