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Preliminary communication

The synthesis of mono- and di-methyl gallium tetraaza macrocycles [$MeGa(C_{22}H_{22}N_4)$] and [$Me_2Ga(C_{22}H_{23}N_4)$] and the molecular structure of the dimethyl gallium derivative

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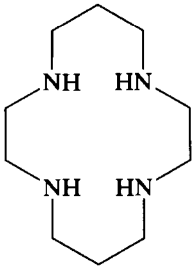
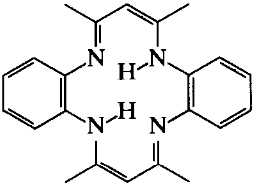
Abstract

The reaction of gallium trimethyl with the dibenzo-tetra-aza macrocycle, $C_{22}H_{24}N_4$, results in the formation of the dimethyl gallium-macrocycle, [$Me_2Ga(C_{22}H_{23}N_4)$]. A single crystal X-ray diffraction study of the complex shows the gallium to be in a near tetrahedral environment and bonded to two of the four nitrogen atoms, with two nearly equal Ga-N distances. The other two nitrogen atoms form an internal hydrogen bond (N · · · N 2.675(8) Å). The compound loses an additional mole of methane above 200 °C and is converted quantitatively into the monomethyl derivative [$MeGa(C_{22}H_{22}N_4)$].

The study of the interactions between organo-group 13 compounds and multidentate ligands is of current interest [1]. This is due in part to the diverse uses of such compounds, ranging from their ability to act as photocatalysts in polymerisation reactions, to their use as intermediates in the production of semi-conductors containing metals from groups 13 and 15. However, tetra-aza macrocyclic ligands have been largely studied in reaction with organo-aluminium derivatives [2–5], and relatively little attention has been paid to the heavier group 13 elements. Thus apart from some alkylgallium porphyrin compounds [1a,6,7], and some methylgallium derivatives of cyclam I [1b,8], no tetra-aza species have been reported. We have now prepared compounds containing the $GaMe_2$ and GaMe fragments inserted in the dibenzo macrocycle II, and to the best of our knowledge this is the first example of a tetra-aza macrocycle bonded to a single gallium atom as a $GaMe_2$ unit.



$C_{10}H_{24}N_4$ (I)



$C_{22}H_{24}N_4$ (II)

Reaction of II with trimethylgallium in hexane at room temperature proceeds with rapid evolution of one mole of methane and precipitation of a lemon yellow solid. Recrystallisation from toluene-hexane solution yields brick-shaped yellow, slightly air-sensitive crystals of $[Me_2Ga(C_{22}H_{23}N_4)]$ (III). It is noteworthy that although only one of the two macrocycle N–H groups has reacted in this case, no further reaction occurs on addition of an excess of trimethylgallium. Indeed the surplus $GaMe_3$ does not even co-ordinate with any of the basic nitrogen centres. This is in contrast to I, where two moles of $GaMe_3$ are co-ordinated by pairs of N–H groups without the elimination of methane, giving $[(GaMe_3)_2(C_{10}H_{24}N_4)]$ [8], while at higher temperature all the N–H groups react with $GaMe_3$ to release methane, and a further two moles of $GaMe_3$ then co-ordinate to yield $[(GaMe)_2(C_{10}H_{20}N_4)(GaMe_3)_2]$ [1b].

The spectroscopic properties of III indicate the presence of a $GaMe_2$ group, and one remaining N–H bond on the macrocycle. Thus the ^1H NMR spectrum ($CDCl_3$) shows a resonance (relative intensity 1) at 12.43 ppm (rel. $SiMe_4 = 0$) from the N–H group (cf. 12.57 ppm in II) and two singlets (rel. int. 3 each) at -0.38 and -1.15 ppm from the two inequivalent methyl groups attached to gallium. Other resonances, slightly shifted from those in II, occur at 7.13–6.98 (Ph, rel. int. 8), 4.94 and 4.79 (doublet, methine CH, rel. int. 1 : 1), and 2.09 and 1.64 ppm (doublet C–Me, rel. int. 6 : 6). We have not been able to detect the N–H bond in the IR spectrum of III, probably because it is H-bonded to the other nitrogen atom. A weak molecular ion (M^+) at $m/e = 442$ (based on ^{69}Ga) is observed in the EI mass spectrum. A single crystal X-ray diffraction study of III * (Fig. 1a, b) shows a structure with one $GaMe_2$ unit bound to two nitrogen atoms at almost equal distances [1.965(4) and 1.985(5) Å]. The macrocycle is strongly folded into butterfly form, bridged at one side by the $GaMe_2$ unit and at the other by a N–H $\cdots$ N hydrogen bond (N $\cdot\cdot$ N 2.675(8) Å. The conformation of the macrocycle is similar to that in the $[MeAlC_{22}H_{22}N_4]$ complex [3].

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* *Crystallographic data for III*: $C_{24}H_{29}N_4Ga$. $M = 443$, monoclinic space group $C2/c$. $a = 30.672(13)$, $b = 9.494(4)$, $c = 15.657(5)$ Å, $\beta = 100.24(3)°$, $U = 4486$ Å^3, $Z = 8$, $D_c = 1.32$ g cm^3, Mo-K_α radiation, $\lambda = 0.71073$ Å, μ(Mo-K_α) = 12.4 cm^{-1}, $T = 290$ K, $R = 0.054$ for 2465 unique observed ($I/\sigma(I) \geqslant 2.0$) reflections. $R_w = 0.054$ (modified statistical weights)

Data taken to $2\theta = 50°$ (Siemens $P2_1$ diffractometer $\omega/2\theta$ scan), graphite monochromatised Mo-K_α radiation, structure solved by Patterson methods. Anisotropic thermal parameters for non-hydrogen atoms: hydrogen atoms at calculated positions, with that attached to N(1) refined; 284 parameters refined.

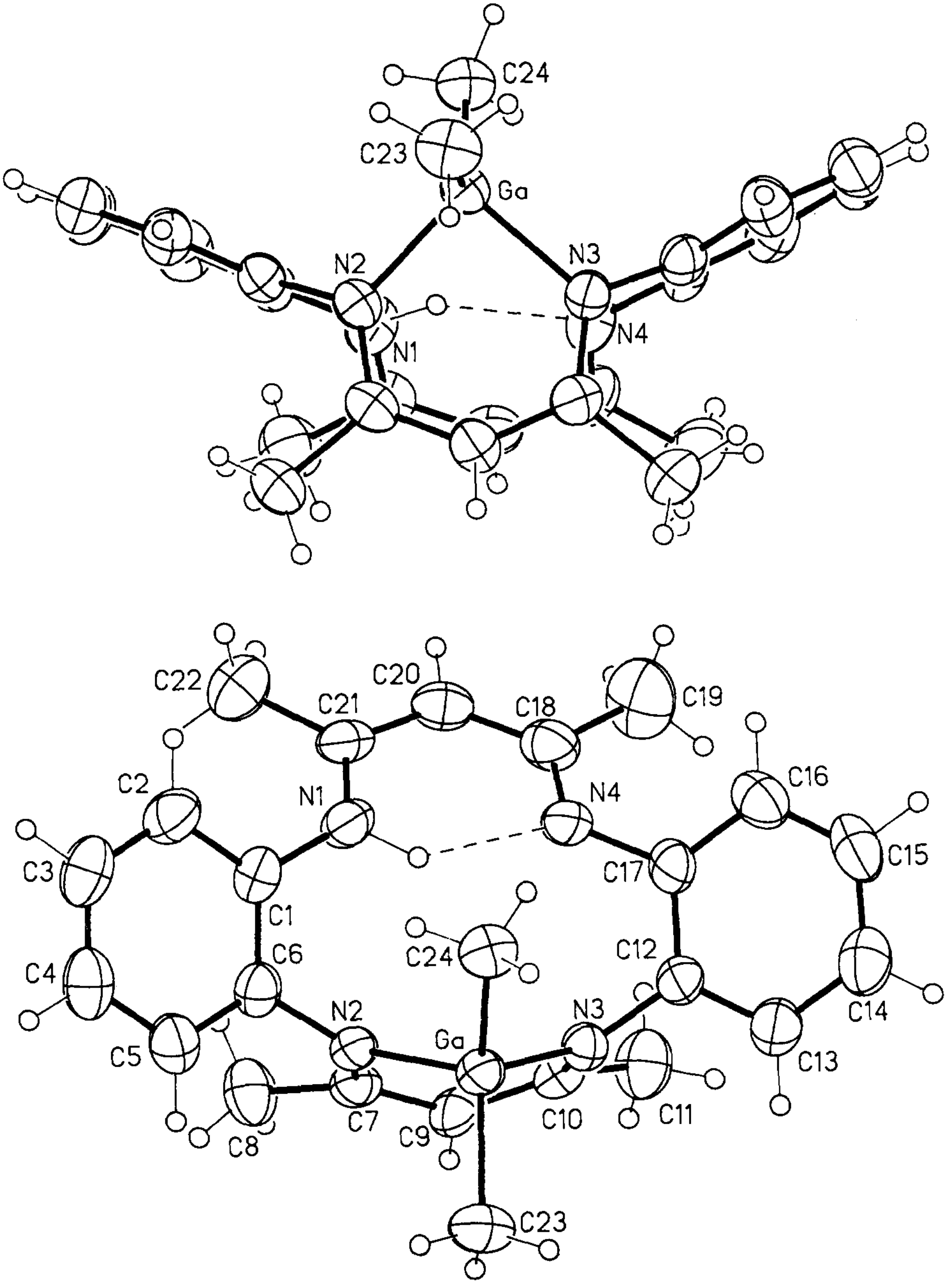

Fig. 1. Two views of the crystal structure of III. The internal hydrogen bond is dashed. Principal dimensions: Ga–C(23) 1.961(6), Ga–C(24) 1.953(6), Ga–N(2) 1.965(4), Ga–N(3) 1.985(5) Å; C–Ga–C 124.3(3), N–Ga–N 90.7(2)°.

When a sample of III is heated as the solid above 200 °C evolution of a further mole of methane occurs. The resulting orange crystalline solid is the mono-methylgallium compound, $[MeGa(C_{22}H_{22}N_4)]$ (IV). The ^1H NMR spectrum of IV ($CDCl_3$)

shows no resonance from any N–H group, and only a singlet at -0.93 ppm (rel. int. 3) from the Ga–Me entity, other resonances occurring at 7.07–6.97 (Ph, 8), 4.80 (methine CH, 2) and 2.21 (C–Me, 12). A molecular ion, $m/e = 426$ (from ^{69}Ga), is observed in the EI mass spectrum of IV, and elemental analysis is consistent with the above formulation. The most plausible structure for (IV) is one in which the GaMe moiety is bonded symmetrically to the four nitrogen atoms, but the metal atom may not be in the N_4 plane since the structure of the related aluminium derivative, $[MeAl(C_{22}H_{22}N_4)]$, shows that the metal atom is slightly displaced from the N_4 plane [3]. IV shows remarkably high thermal stability for a metal alkyl compound, decomposing slowly above 300 °C, and also shows only slight sensitivity in air. Studies are being pursued on related systems to investigate these properties in more detail.

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