

## Synthesis and Structure of a Five-coordinate Triarylgallium Complex

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The neutral gallium(III) compounds L<sub>3</sub>Ga, L<sub>2</sub>GaCl and [L<sub>2</sub>GaOH]<sub>2</sub> (L = -C<sub>6</sub>H<sub>4</sub>-*o*-CH<sub>2</sub>NMe<sub>2</sub>) are synthesized and shown by X-ray crystallographic analysis to adopt trigonal bipyramidal coordination geometries; L<sub>3</sub>Ga is the first example of a five-coordinate triorganogallium(III) complex.

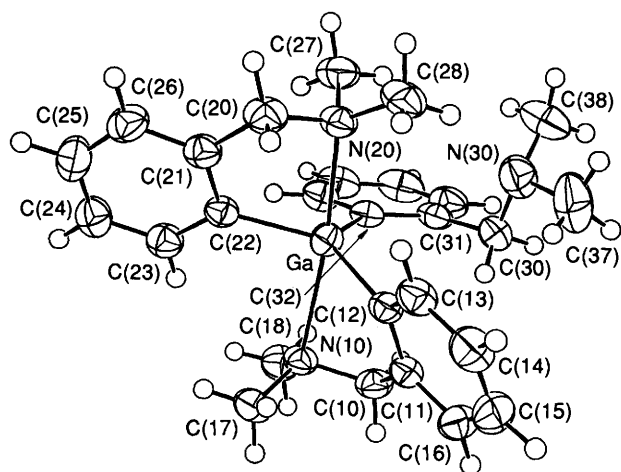
Organogallium coordination chemistry has recently attracted considerable interest in the search for new semiconductor precursors.<sup>1</sup> Gallium chemistry also finds application in the practice of nuclear medicine, where radioisotopes such as <sup>66</sup>Ga, <sup>67</sup>Ga and <sup>68</sup>Ga serve as labels for radiopharmaceuticals used in diagnostic imaging.<sup>2</sup> The present work is part of an on-going investigation undertaken to determine whether the aqueous stability of the covalent gallium-carbon bond<sup>3</sup> can be exploited in radiopharmaceutical design and development. Herein, we report the synthesis and structures of three pentacoordinate organogallium compounds, L<sub>3</sub>Ga **1**, L<sub>2</sub>GaCl **2** and [L<sub>2</sub>GaOH]<sub>2</sub> **3**, containing the potentially bidentate ligand -C<sub>6</sub>H<sub>4</sub>-*o*-CH<sub>2</sub>NMe<sub>2</sub> (L).

Compounds **1** and **2** were prepared by a halogen-aryl exchange reaction between GaCl<sub>3</sub> and [2-((dimethylamino)methyl)phenyl]lithium<sup>4</sup> in diethyl ether.† Solid-state samples

† [2-((Dimethylamino)methyl)phenyl]lithium (LLi) was prepared by literature methods.<sup>4</sup> Using inert atmosphere techniques, a suspension of LLi (2.45 g, 17.4 mmol) in diethyl ether was treated with a solution of GaCl<sub>3</sub>·OEt<sub>2</sub> (7.2 ml, 5.2 mmol). After refluxing for 61 h the white suspension was filtered and the filtrate reduced to dryness *in vacuo*. Hexanes were used to separate the mixture of compounds, **2** is insoluble in hexanes whereas **1** is moderately soluble. Compounds **1** and **2** can also be obtained when the reaction is carried out at room temp.

of **1** and **2** appear to be stable in dry air. ‡ Crystals suitable for X-ray structure analyses were grown from mixtures of  $\text{CHCl}_3$ , diethyl ether and hexanes. §

The crystal structures of **1** and **2** are shown in Figs. 1 and 2, respectively. The gallium(III) atoms of both compounds have distorted trigonal bipyramidal coordination geometries, in which the N donors occupy the axial coordination sites. Compound **1** appears to be structurally unique. Triorganogallium complexes are mild Lewis acids that generally react with non-protic bases, X, to form four-coordinate tetrahedral  $\text{R}_3\text{GaX}$  adducts.<sup>5</sup> The exceptional five-coordinate  $\text{C}_3\text{N}_2$  coordination sphere in **1** ( $\text{R}_3\text{GaX}_2$ ) apparently results from the imminent proximity of nitrogen lone pairs imposed by the three potentially chelating [2-((dimethylamino)methyl)-phenyl] ligands. Note, however, that the gallium(III) centre of **1** does not become octahedral by coordination of the third N



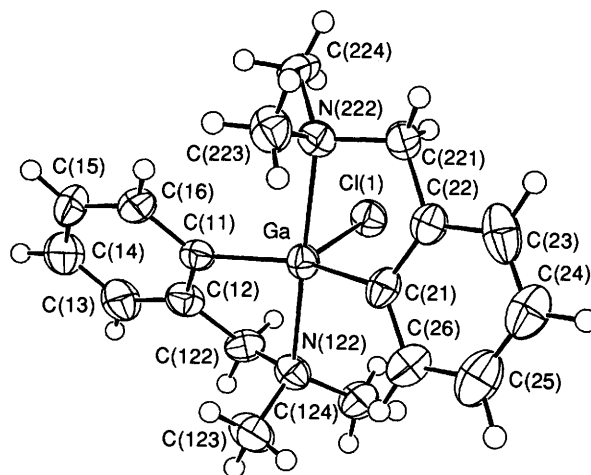
**Fig. 1** ORTEP representation of  $\text{L}_3\text{Ga}$  **1** showing 50% thermal ellipsoids and the atom-labelling scheme. Selected distances (Å) and angles (°): Ga–N(10), 2.551(2); Ga–N(20), 2.399(2); Ga–C(12), 1.988(3); Ga–C(22), 1.991(3); Ga–C(32), 2.001(3); C(12)–Ga–C(22), 126.5(1); C(12)–Ga–C(32), 118.3(1); C(22)–Ga–C(32), 114.1(1); N(10)–Ga–N(20), 170.68(7); N(10)–Ga–C(12), 76.02(9); N(20)–Ga–C(22), 79.03(9).

‡ *Physical data* for **1**: colourless crystals (1.61 g, 66%) m.p. 110–115 °C;  $\delta_{\text{H}}$  (500 MHz; solvent  $\text{CDCl}_3$ ; standard  $\text{SiMe}_4$ ) 2.07 (6H, s,  $\text{CH}_3$ ), 3.52 (2H, s,  $\text{CH}_2$ ), 7.12–7.20 (3H, m,  $\text{C}_6\text{H}_4$ ), 7.70 (1H, m,  $\text{C}_6\text{H}_4$ ). For **2**: colourless crystals (0.36 g, 18%), m.p. 175–178 °C;  $\delta_{\text{H}}$  (500 MHz; solvent  $\text{CDCl}_3$ ; standard  $\text{SiMe}_4$ ) 2.55 (6H, s,  $\text{CH}_3$ ), 3.81 (2H, v br,  $\text{CH}_2$ ), 7.15 (1H, m,  $\text{C}_6\text{H}_4$ ), 7.19–7.27 (2H, m,  $\text{C}_6\text{H}_4$ ), 7.68 (1H, m,  $\text{C}_6\text{H}_4$ ). For **3**: colourless crystals, m.p. 143–147 °C,  $\delta_{\text{H}}$  (500 MHz; solvent  $\text{CDCl}_3$ ; standard ( $\text{SiMe}_4$ ) 2.42 (6H, br s,  $\text{CH}_3$ ), 3.68 (2H, br,  $\text{CH}_2$ ), 7.11 (1H, m,  $\text{C}_6\text{H}_4$ ), 7.15–7.22 (2H, m,  $\text{C}_6\text{H}_4$ ), 7.66 (1H, m,  $\text{C}_6\text{H}_4$ ).

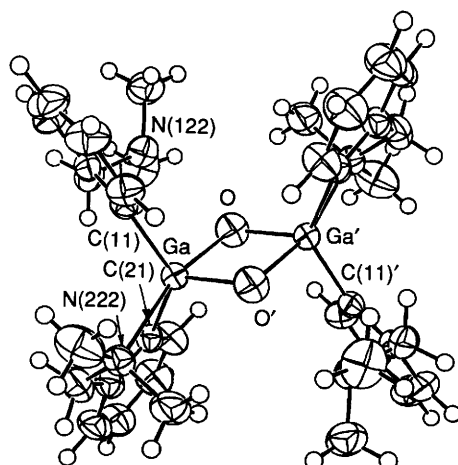
§ *Crystal data* for **1**:  $\text{C}_{27}\text{H}_{36}\text{N}_3\text{Ga}$ ,  $M = 472.33$ , triclinic,  $a = 9.2302(9)$ ,  $b = 9.4267(9)$ ,  $c = 14.619(2)$  Å,  $\alpha = 93.63(1)$ ,  $\beta = 97.08(1)$ ,  $\gamma = 97.049(8)^\circ$ ,  $U = 1248.8(5)$  Å<sup>3</sup>, Mo–K $\alpha$  ( $\lambda = 0.71073$  Å), space group  $\text{P}\bar{1}$ ,  $Z = 2$ ,  $D_c = 1.256$  g cm<sup>-3</sup>,  $F(000) = 500.0$ , colourless chunk,  $\mu(\text{Mo-K}\alpha) = 11.14$  cm<sup>-1</sup>,  $R(R_w) = 0.032$  (0.042) for 2920 unique reflections with  $I > 3.0\sigma(I)$ . For **2**:  $\text{C}_{18}\text{H}_{24}\text{N}_2\text{GaCl}$ ,  $M = 373.58$ , orthorhombic,  $a = 9.4038(6)$ ,  $b = 10.1549(5)$ ,  $c = 18.743(1)$  Å,  $U = 1789.9(3)$  Å<sup>3</sup>, Cu–K $\alpha$  ( $\lambda = 1.54184$  Å), space group  $\text{P}2_12_12_1$ ,  $Z = 4$ ,  $D_c = 1.386$  g cm<sup>-3</sup>,  $F(000) = 776.0$ , colourless prism,  $\mu(\text{Cu-K}\alpha) = 34.60$  cm<sup>-1</sup>,  $R(R_w) = 0.036$  (0.059) for 1471 unique reflections with  $I > 3.0\sigma(I)$ . For **3**:  $\text{C}_{36}\text{H}_{49.68}\text{N}_4\text{O}_{1.68}\text{Ga}_2\text{Cl}_{0.32}$ ,  $M = 716.19$ , triclinic,  $a = 9.318(1)$ ,  $b = 10.280(1)$ ,  $c = 10.416(1)$  Å,  $\alpha = 77.798(9)$ ,  $\beta = 73.92(1)$ ,  $\gamma = 73.92(1)^\circ$ ,  $U = 911.3(2)$  Å<sup>3</sup>, Mo–K $\alpha$  ( $\lambda = 0.71073$  Å), space group  $\text{P}\bar{1}$ ,  $Z = 1$ ,  $D_c = 1.305$  g cm<sup>-3</sup>,  $F(000) = 389.0$ , colourless plate,  $\mu(\text{Mo-K}\alpha) = 15.18$  cm<sup>-1</sup>,  $R(R_w) = 0.036$  (0.047) for 2073 unique reflections with  $I > 3.0\sigma(I)$ . Atomic coordinates, bond lengths and angles, and thermal parameters for compounds **1**, **2** and **3** have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

lone pair, somewhat in contrast with the six-coordinate structure observed in the trimethylindium adduct of  $N,N',N''$ -triisopropyl-1,3,5-triazacyclohexane.<sup>6</sup> The three Ga–C distances in **1** are virtually identical; they are similar to the Ga–C distances in **2** and lie within the range [1.924(4)–2.080(4) Å] reported for other five-coordinate organogallium compounds.<sup>7,8</sup> In contrast, the two Ga–N distances in **1** differ significantly, with the longer distance [2.551(2) Å] exceeding the range of previously reported Ga–N bond lengths [2.024(5)–2.471(4) Å].<sup>7,8</sup>

The structure of **2** is similar to the analogous diaryl indium(III) compound,  $\text{L}_2\text{InCl}$  **4**.<sup>9</sup> The  $\text{N}_2\text{MCl}$  ( $M = \text{Ga}, \text{In}$ ) portion of both **2** and **4** approaches an ideal trigonal bipyramidal geometry with N–M–N bond angles of 178.6(2) and 178.4(1)° for Ga and In, respectively; the Cl–M–N angles average 90.2(2)° for Ga and 89.6(1)° for In. Angular distortions of the trigonal bipyramids arise from the geometric constraints associated with the bite of the bidentate ligands [N–M–C angles of 80.3(2) and 77.8(2)° for Ga, 77.0(1) and 76.1(1)° for In] in the presence of the nearly linear N–M–N bond angle.



**Fig. 2** ORTEP representation of  $\text{L}_2\text{GaCl}$  **2** showing 50% thermal ellipsoids and the atom-labelling scheme. Selected distances (Å) and angles (°): Ga–Cl(1), 2.269(2); Ga–N(122), 2.304(6); Ga–N(222), 2.385(6); Ga–C(11), 1.975(6); Ga–C(21), 1.977(7); Cl(1)–Ga–C(11), 105.3(2); Cl(1)–Ga–C(21), 105.2(2); C(11)–Ga–C(21), 149.4(3); N(122)–Ga–N(222), 178.6(2); N(122)–Ga–C(11), 80.3(2); N(222)–Ga–C(21), 77.8(2).



**Fig. 3** ORTEP representation of  $[\text{L}_2\text{GaOH}]_2$  **3** showing 50% thermal ellipsoids and the atom-labelling scheme. Selected distances (Å) and angles (°): Ga...Ga', 2.9787(8); Ga–O', 1.8929(4); Ga–O, 2.0216(4); Ga–N(222), 2.576(3); Ga–C(21), 1.973(4); Ga–C(11), 1.979(4); Ga–O–Ga', 99.04(2); O–Ga–O', 80.96(2); C(11)–Ga–O', 107.4(1); O'–Ga–C(21), 121.3(1); C(11)–Ga–C(21), 129.8(2); N(222)–Ga–O, 165.19(8); N(222)–Ga–C(21), 76.2(1).

Trialkyl and triaryl complexes of gallium(III) are normally hydrolysed rapidly by water to tetrahedral  $R_2Ga(H_2O)_{2-n}(OH)_n$  ( $n = 0, 1$  or  $2$ ) Lewis base adducts of the corresponding diorgano  $[R_2Ga]^{1+}$  fragment.<sup>5</sup> The susceptibility of **1** towards hydrolysis has been investigated by  $^1H$  NMR spectroscopy. In wet  $CDCl_3$  **1** reacts with water to form free ligand (HL) and, presumably, the  $L_2GaOH$  or  $[L_2GaOH_2]^+$  analogues of **2**. 15 min and 26 h after mixing, compound **1** accounts for 88 and 8% of the gallium-containing species in solution, respectively. The  $^1H$  NMR of the new gallium-containing species [ $\delta$ : 2.44(br), 3.71(br), 7.12(m), 7.16–7.23(m) and 7.66(m)] exhibits somewhat broadened peaks but is otherwise identical to that of compound **3**, which is a dimer in the solid state (see below).

Crystals of **3** were obtained while recrystallizing a crude mixture of **1** and **2** in  $CHCl_3-Et_2O$  over a period of several days. X-Ray structural analysis of **3** reveals the presence of a single centrosymmetric dimer (Fig. 3). Like compounds **1** and **2**, the gallium atoms in **3** have distorted trigonal bipyramidal geometries. The bridging hydroxide oxygen atom, O,¶ occupies an axial position on Ga and an equatorial site on Ga'. The other axial position on Ga is taken by N(222), while aryl carbons C(11) and C(21) occupy the remaining equatorial sites to complete the  $C_2NO_2$  gallium coordination sphere. As in compound **1**, it appears that the pentacoordination of the gallium atoms in **3** is due to the close proximity of the nitrogen lone pairs provided by the [2-((dimethylamino)methyl)phenyl] ligands. The length of the Ga–N(222) bond [2.576(3) Å] slightly exceeds (0.025 Å) the long Ga–N distance reported for **1**.

The four-membered  $Ga_2O_2$  ring in **3** differs significantly from those in other five-coordinate organogallium dimers.<sup>8</sup> The bridging O atoms in all of the previous reports were provided by chelating bidentate ligands, thus, creating an extended system of fused rings. In contrast, the present dimer does not have any fused rings. In these previous reports,<sup>8</sup> the O–Ga–O' bond angles ranged from 71.3(1)–75.5(1)° and the Ga–O–Ga' bond angles ranged from 104.5(1)–108.7(1)°. The corresponding bond angles in **3** are 80.96(2) and 99.04(2)°, respectively. In addition, both Ga–O bonds in **3** are shorter

than the Ga–O distances found in these other gallium dimers [ $Ga-O_{(eq)}$  1.913(3)–1.937(3) Å,  $Ga-O_{(ax)}$  2.073(3)–2.462(3) Å].<sup>8</sup>

The preparation of  $L_3Ga$  **1**,  $L_2GaCl$  **2** and  $[L_2GaOH]_2$  **3** provides new examples of five-coordinate organogallium compounds, with **1** being a structurally novel pentacoordinate triorganogallium complex. These and related compounds remain under investigation as potential gallium-labelled radiopharmaceuticals.

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¶ The bridging ligands in **3** are actually disordered, hydroxide O atoms occupy 84% of the available sites while Cl atoms occupy the remaining 16%.