Crystal Structure of Dimethyl[4-*tert*-butyl-2,6-bis(1-naphthyliminomethylene)phenolato]gallium

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Crystals of dimethyl [4-*tert*-butyl-2,6-bis(1-naphthyliminomethylene)phenolato]gallium (**1**) are monoclinic, space group $P2_1/c$ with $a = 14.797(3)\text{\AA}$, $b = 10.651(2)\text{\AA}$, $c = 20.260(4)\text{\AA}$, $\beta = 93.55(1)^\circ$, $V = 3187.1(11)\text{\AA}^3$, $Z = 4$. The structure was solved by direct methods and refined to a final R value of 0.0412 of 4150 reflections ($I > 2\sigma(I)$). The gallium atom was bonded by one oxygen atom and coordinated by one imine nitrogen atom, forming one six-member ring.

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The chemistry of organoaluminum, gallium and indium compounds have received renewed interests in recent years due to their wide applications in material science¹ and organic reactions.² Among them, one of the major categories of the compounds is organometallic alkoxides or phenoxides. We recently synthesized the title compound **1** by using trimethylgallium reacting with 4-*tert*-butyl-2,6-bis(1-naphthyliminomethylene)phenol³ at room temperature. The hydroxyl in phenol reacts with trimethylgallium by removing one molecule of methane as a by-product, as shown in Fig. 1.

Fig. 1 Synthesis and chemical structure of the title compound **1**.

Fig. 2 Molecular structure of (**1**) showing 50% probability displacement ellipsoids along with the numbering scheme.

Single crystals for X-ray analysis were obtained by the slow evaporation of a benzene solution at room temperature. All of the non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were determined from a difference Fourier map, and riding models were applied on refinements. The crystal and experimental data are given in Table 1. The final fractional atomic coordinates and the equivalent isotropic thermal parameter for the non-hydrogen atoms are given in Table 2. Selected bond distances and bond

Table 1 Crystal and experimental data

Formula:	$C_{37}H_{36}GaN_2O$
Formula weight:	594.40
Crystal system:	monoclinic
Space group:	$P2_1/c$
Z :	4
a :	$14.797(3)\text{\AA}$
b :	$10.651(2)\text{\AA}$
c :	$20.260(4)\text{\AA}$
V :	$3187.1(11)\text{\AA}^3$
D_{calc} :	1.239 g/cm^3
$F(000)$:	1244
$\mu(\text{Mo } K\alpha)$:	8.94 mm^{-1}
T :	$293(2)\text{K}$
Color:	pale yellow
Crystal size:	$0.32 \times 0.25 \times 0.25\text{ mm}$
$\lambda(\text{Mo } K\alpha)$:	$0.71073\text{\AA}$
R :	0.0412/0.0687
R_w :	0.1023/0.1055
$(\Delta\rho)_{\text{max}}$:	0.00
$(\Delta\rho)_{\text{max}}$:	0.000
$(\Delta\rho)_{\text{min}}$:	-0.719
No. of reflections measured:	6934
No. of reflections used:	4150
Goodness-of-fit:	1.000
Measurement:	Bruker Smart Apex CCD diffractometer
Program system:	Bruker SMART
Structure determination:	direct method (SHELXTL-1997)
Refinement:	full-matrix least-squares

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Table 2 Final atomic coordinates and equivalent isotropic thermal parameters (U_{eq}) for non-hydrogen atoms

Atom	x	y	z	$U_{eq}(\text{\AA}^2)$
Ga(1)	0.131450(19)	0.11708(3)	0.444530(14)	0.05314(12)
N(1)	0.24255(14)	0.22996(19)	0.44244(10)	0.0533(5)
N(2)	0.23245(13)	-0.23016(19)	0.66121(10)	0.0497(5)
C(1)	0.24492(17)	0.3297(2)	0.39256(13)	0.0526(7)
C(2)	0.26969(18)	0.2997(3)	0.33170(13)	0.0593(7)
C(3)	0.27656(19)	0.3928(3)	0.28399(14)	0.0621(7)
C(4)	0.25441(18)	0.5158(3)	0.29841(13)	0.0576(7)
C(5)	0.22624(17)	0.5462(2)	0.36117(13)	0.0517(6)
C(6)	0.20336(18)	0.6689(3)	0.37756(15)	0.0618(7)
C(7)	0.1762(2)	0.6972(3)	0.43718(15)	0.0678(8)
C(8)	0.1712(2)	0.6084(3)	0.48560(14)	0.0666(8)
C(9)	0.19111(18)	0.4838(3)	0.47308(13)	0.0585(7)
C(10)	0.22171(17)	0.4504(3)	0.40882(13)	0.0555(7)
C(11)	0.15741(17)	-0.3095(2)	0.67336(12)	0.0512(6)
C(12)	0.07572(18)	-0.2618(3)	0.68849(13)	0.0579(7)
C(13)	0.00269(19)	-0.3417(3)	0.69638(14)	0.0642(8)
C(14)	0.01046(19)	-0.4652(3)	0.68947(13)	0.0629(8)
C(15)	0.09296(19)	-0.5186(2)	0.67501(12)	0.0562(7)
C(16)	0.1054(2)	-0.6511(3)	0.66550(14)	0.0656(8)
C(17)	0.1857(2)	-0.6995(3)	0.65272(14)	0.0690(8)
C(18)	0.2593(2)	-0.6235(3)	0.64905(14)	0.0666(8)
C(19)	0.25228(19)	-0.4969(3)	0.65594(13)	0.0567(7)
C(20)	0.16947(18)	-0.4422(2)	0.66878(12)	0.0499(6)
C(21)	0.26267(18)	0.0301(2)	0.54630(13)	0.0497(6)
C(22)	0.28651(17)	-0.0525(2)	0.60059(12)	0.0475(6)
C(23)	0.36855(17)	-0.0423(2)	0.63555(12)	0.0479(6)
C(24)	0.43284(17)	0.0484(2)	0.62335(12)	0.0482(6)
C(25)	0.40858(17)	0.1322(2)	0.57263(12)	0.0492(6)
C(26)	0.32643(17)	0.1252(2)	0.53438(12)	0.0494(6)
C(27)	0.31210(17)	0.2173(2)	0.48300(13)	0.0527(7)
C(28)	0.22002(17)	-0.1470(2)	0.61730(12)	0.0497(6)
C(29)	0.52457(17)	0.0600(2)	0.66279(13)	0.0501(6)
C(30)	0.53386(17)	0.1846(2)	0.69538(12)	0.0523(6)
C(31)	0.60084(17)	0.0551(2)	0.61527(12)	0.0533(7)
C(32)	0.53708(17)	-0.0429(2)	0.71281(12)	0.0526(7)
C(33)	0.12449(17)	0.0214(2)	0.36278(12)	0.0514(6)
C(34)	0.03354(16)	0.2079(2)	0.48224(12)	0.0518(6)
O(1)	0.18765(11)	0.01467(14)	0.51193(8)	0.0506(4)
C(36)	0.45023(17)	0.5385(2)	0.45670(13)	0.0498(6)
C(38)	0.5496(3)	0.3684(5)	0.4345(3)	0.0521(13)
C(37)	0.4824(3)	0.4576(5)	0.4150(3)	0.0521(13)
C(39)	0.5810(4)	0.3812(5)	0.5006(3)	0.0525(13)
C(35)	0.4837(4)	0.5474(5)	0.5224(3)	0.0526(13)

$$U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* (a_i a_j).$$

angles are listed in Table 3.

The results clearly show that the gallium atom is four-coordinate. The coordination sphere of the central gallium atoms can be described as a distorted tetrahedron. A benzene molecule is found on an inversion center, and is disordered into two sites with an occupancy of 0.5 each. The Ga1-O1 distance [1.8988(16)Å] is shorter than that of dimethyl[N-salicylidene 2-aminopyridine]gallium [1.917(2)Å] (**2**).⁴ The Ga1-N1 distances is 2.039(2)Å, which is shorter than that of **2** [2.059(2)Å].⁴ One

Table 3 Selected bond distances (Å), angles (°)

Bond distance			
Ga(1)-O(1)	1.8988(16)	Ga(1)-C(34)	1.938(2)
Ga(1)-C(33)	1.942(2)	Ga(1)-N(1)	2.039(2)
N(1)-C(27)	1.284(3)	N(1)-C(1)	1.468(3)
N(2)-C(28)	1.261(3)	C(21)-O(1)	1.284(3)
Bond angles			
O(1)-Ga(1)-C(34)	107.95(9)	O(1)-Ga(1)-C(33)	108.03(9)
C(34)-Ga(1)-C(33)	126.65(10)	O(1)-Ga(1)-N(1)	92.06(8)
C(34)-Ga(1)-N(1)	109.70(9)	C(33)-Ga(1)-N(1)	106.98(10)
C(27)-N(1)-C(1)	117.7(2)	C(27)-N(1)-Ga(1)	122.69(17)
C(1)-N(1)-Ga(1)	119.65(16)	C(28)-N(2)-C(11)	117.1(2)
C(10)-C(1)-N(1)	119.6(2)	C(12)-C(11)-N(2)	121.9(2)
N(2)-C(11)-C(20)	118.2(2)	O(1)-C(21)-C(26)	124.2(2)
O(1)-C(21)-C(22)	120.0(2)	C(21)-C(22)-C(28)	117.6(2)
N(1)-C(27)-C(26)	127.7(2)	C(21)-C(26)-C(27)	122.8(2)
N(2)-C(28)-C(22)	125.2(2)	C(21)-O(1)-Ga(1)	129.93(15)

Estimated standard deviations in the least-significant figure are given in parentheses.

nitrogen atom coordinates to the gallium atom, forming one irregular six-member ring (Ga1-N1-C27-C26-C21-O1). In the ring, the O1-Ga1-N1 angle is 92.06(8)°, which is larger than that of **2** (90.76(7)°).⁴

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