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Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.035
 wR factor = 0.096
Data-to-parameter ratio = 17.2

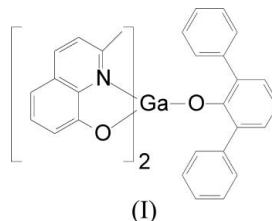
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

(2,6-Diphenylphenolato- κO)bis(2-methylquinolin-8-olato- $\kappa^2\text{N},\text{O}$)gallium(III)

The title compound, $[\text{Ga}(\text{C}_{10}\text{H}_8\text{NO})_2(\text{C}_{18}\text{H}_{13}\text{O})]$, is a mononuclear five-coordinate Ga complex having a trigonal-bipyramidal geometry in which the O-donor atoms of the phenolate and of the two quinolinolate ligands form the trigonal equatorial plane, and the N atoms are in axial positions.

Comment

Aluminium and gallium chelate compounds have found applications in organic electroluminescent devices (Tang & Van Slyke, 1987). Among these are heteroleptic complexes having two 8-quinolinolate ligands substituted at the 2- and/or 4- positions with electron-donating groups, often methyl groups, and one anionic ancillary ligand, usually a phenolate (Bryan *et al.*, 1992). We have recently published the crystal structures of two such aluminium complexes (Rajeswaran *et al.*, 2006, 2007). We report here the synthesis and structure of a gallium analogue, (I).



The title compound, (I) (Fig. 1), and the previously reported aluminium analogue (II) (Rajeswaran *et al.*, 2006) are isomorphous and isostructural. The Ga—O bond to the phenolate ligand in (I) is longer by 0.0947 Å compared to the phenolate Al—O bond reported (Rajeswaran *et al.*, 2007) for analogue (II). The Ga—O bonds to the quinolinolate ligand are longer than the corresponding Al—O bonds by an average of 0.082 Å, while the Ga—N bonds are longer than the Al—N bonds by an average of 0.037 Å. Similar differences in respective bond lengths are found in a comparison of *mer*-tris(quinolin-8-olate) complexes of Al^{III} (Rajeswaran & Blanton, 2005; Brinkmann *et al.*, 2000; Schmidbaur *et al.*, 1991) and Ga^{III} (Rajeswaran & Jarikov, 2004; Schmidbaur *et al.*, 1991). Thus, it appears that Ga^{III} compared to Al^{III} has a greater affinity for the *N*-donor ligands relative to the anionic *O*-donor ligands.

The structure of *mer*-tris(2-methylquinolin-8-olato)gallium(III) Ga(2Meq)₃ has also been reported (Sapochak *et al.*, 1996). In (I), the average of the Ga—N bonds is 0.112 (3) Å shorter than in Ga(2Meq)₃ but only 0.011 (2) Å longer than that of Ga(q)₃ (Rajeswaran & Jarikov, 2004). The average

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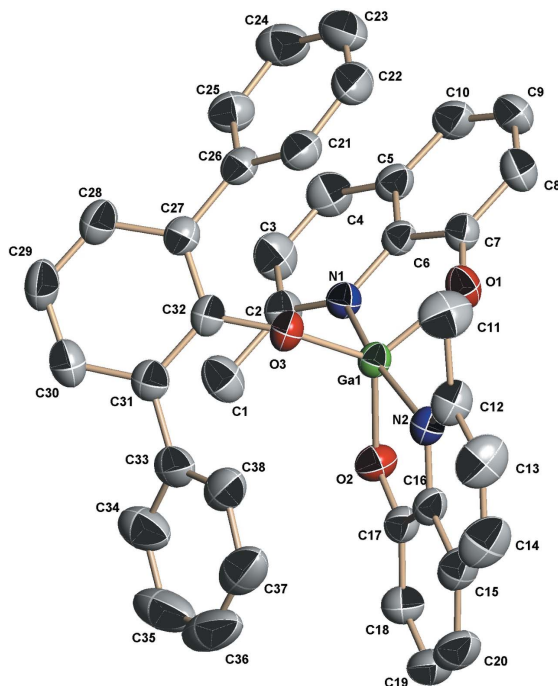


Figure 1
The molecular structure of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms and H atoms have been omitted for clarity.

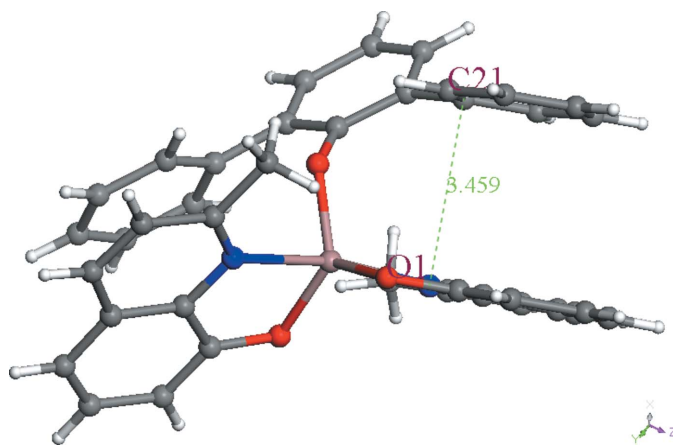


Figure 2
A edge-on view of (I), showing the orientation of the *o*-phenyl group containing C21, which is nearly parallel to the N1/O1 quinolinolate ligand.

quinolinolate Ga—O bond in (I) is shorter than that in $\text{Ga}(\text{2Meq})_3$ by 0.032 (3) Å and that in Gaq_3 by 0.059 (2) Å. While steric effects cannot be separated from other differences in the coordination geometry, it seems most reasonable that the shortening of the Ga—N bonds in (I), relative to those in $\text{Ga}(\text{2Meq})_3$, mainly results from alleviation of the steric crowding of the 2-methyl group.

Another interesting structural feature found in both (I) and (II) is the orientation of the *o*-phenyl substituents of the phenolate ligand, shown in Fig. 2. It is seen that the *o*-phenyl group containing C21 is nearly parallel to the N1/O1 quino-

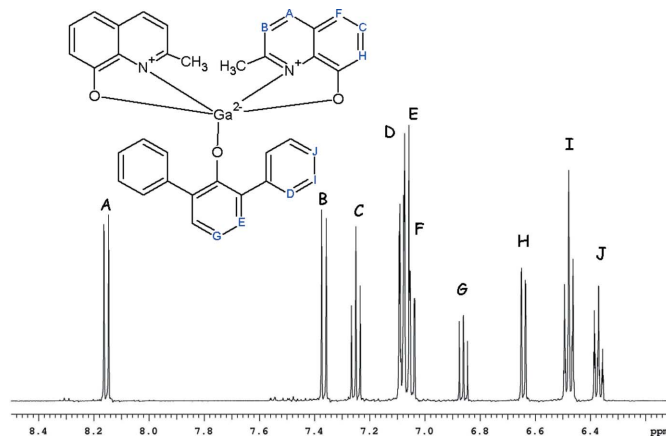


Figure 3
Aromatic expansion of ^1H NMR spectrum of (I), methyl resonance at 2.71 p.p.m.

linolate ligand. The distance from C21 to N1 is 3.459 (2) Å, suggesting a weak π – π interaction. The other *o*-phenyl group is also roughly aligned with the N2/O2 ligand, but at a somewhat longer distance and not nearly as parallel.

Experimental

A one-litre three-necked flask was purged with N_2 using two pump-purge cycles. To the flask were added 8-hydroxyquinoline (35.3 g, 0.222 mol) and tris(acetylacetonato)gallium(III) (36.7 g, 0.1 mol). Anhydrous toluene (400 ml) was then added, forming a yellow solution. The mixture was heated at reflux for 2 h and cooled to room temperature, at which time 2,6-diphenylphenol (24.6 g, 0.1 mol) was added. The reaction was returned to reflux and held there overnight. 275 ml of toluene was removed by distillation and then 400 ml of xylene was added to the flask. Another 325 ml of solvent was removed from the reaction mixture by distillation. The reaction was cooled to room temperature and followed by an ice–water bath. The resulting solids were collected on a glass frit and washed with 50 ml of ice-cooled toluene and 200 ml of heptane to yield 56.07 g (89%) of crude material after drying in high vacuum. These solids were triturated from 500 ml of toluene. 300 ml of toluene was removed by distillation and cooled in an ice bath. The solids were collected, and crystals suitable for single-crystal X-ray diffraction were obtained by sublimation at 503 K in a tube furnace (Lindberg/Blue) with N_2 entrainment gas.

The NMR spectrum for (I) was acquired in dichloromethane- d_2 on a Varian INOVA spectrometer operating at a proton Larmor frequency of 500 MHz, utilizing a 5 mm PFG probe at 296 K, and was referenced with respect to TMS (0.00 p.p.m.). Subsequent assignment of the ^1H spectrum is shown in Fig. 3.

Crystal data

$[\text{Ga}(\text{C}_{10}\text{H}_8\text{NO})_2(\text{C}_{18}\text{H}_{13}\text{O})]$
 $M_r = 631.35$
 Monoclinic, $P2_1/n$
 $a = 15.4090$ (2) Å
 $b = 13.0970$ (2) Å
 $c = 15.7150$ (2) Å
 $\beta = 107.7830$ (7)°
 $V = 3019.94$ (7) Å³

$Z = 4$
 $D_x = 1.389$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 0.95$ mm⁻¹
 $T = 293$ (2) K
 Block, green
 $0.47 \times 0.42 \times 0.37$ mm

Data collection

Nonius KappaCCD diffractometer	34545 measured reflections
φ and ω scans	6868 independent reflections
Absorption correction: multi-scan (<i>SORTAV</i> ; Blessing, 1995)	5361 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.538$, $T_{\max} = 0.703$	$R_{\text{int}} = 0.062$ $\theta_{\max} = 27.5^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0496P)^2 + 0.7063P]$
$R[F^2 > 2\sigma(F^2)] = 0.035$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.096$	$(\Delta/\sigma)_{\max} = 0.002$
$S = 1.03$	$\Delta\rho_{\max} = 0.32 \text{ e } \text{\AA}^{-3}$
6868 reflections	$\Delta\rho_{\min} = -0.51 \text{ e } \text{\AA}^{-3}$
399 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (\AA , $^\circ$).

Ga1—O3	1.8334 (13)	Ga1—N1	2.0968 (15)
Ga1—O1	1.8710 (13)	Ga1—N2	2.1067 (15)
Ga1—O2	1.8736 (13)		
O3—Ga1—O1	116.19 (6)	O2—Ga1—N1	92.05 (6)
O3—Ga1—O2	119.72 (6)	O3—Ga1—N2	90.93 (6)
O1—Ga1—O2	123.75 (6)	O1—Ga1—N2	90.59 (6)
O3—Ga1—N1	100.53 (6)	O2—Ga1—N2	82.96 (6)
O1—Ga1—N1	83.56 (6)	N1—Ga1—N2	168.51 (6)

All H atoms were refined using a riding model, with C—H = 0.93 \AA and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic, and C—H = 0.96 \AA and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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