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Bis(2-methylquinolin-8-olato-κ^2N,O)(6-phenyl-2-naphtholato-κO)aluminium(III)

Manju Rajeswaran,* David W. Place, Vincent W. Bakos, Joseph C. Deaton, Christopher T. Brown and William C. Lenhart

Eastman Kodak Company, Research Laboratories, Rochester, NY 14650-2106, USA

Correspondence e-mail:
manju.rajeswaran@kodak.com

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Key indicators

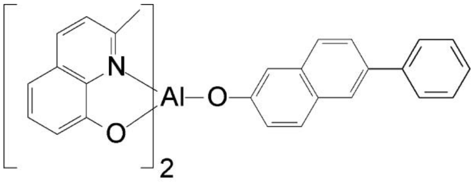
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.053
wR factor = 0.150
Data-to-parameter ratio = 17.2

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

The five-coordinate geometry of the Al atom in the title compound, $[Al(C_{10}H_8NO)_2(C_{16}H_{11}O)]$, is trigonal–bipyramidal, in which the O-donor atoms of the naphtholate and the two quinolinolate ligands are in the trigonal equatorial plane and the N atoms in the axial positions.

Comment

The group of compounds known as the blue aluminium chelates are useful in organic electroluminescent devices (Bryan *et al.*, 1992) because of their wider HOMO–LUMO (highest occupied molecular orbital–lowest unoccupied molecular orbital) gap and blue-shifted emission relative to that of the well known compound tris(8-quinolinolato)aluminium(III) (Tang & VanSlyke, 1987). These compounds are five-coordinate heteroleptic complexes (Rajeswaran *et al.,* 2006) containing two 8-quinolinolate ligands and one anionic ancillary ligand, typically a phenolate. The blue shift in the emission properties is affected not only by the coordination geometry but also by substitution of the 8-quinolinolate at the 2- and/or 4-positions by electron-donating groups such as methyl groups. In this paper, we report the synthesis and crystal structure determination of the title compound, (I) (Fig. 1).



(I)

The geometry of (I) may be described as approximately trigonal–bipyramidal, with the O-donor atoms of the three ligands forming the trigonal equatorial base. The ancillary ligand is less sterically demanding in (I) than in the corresponding ligand in bis(2-methylquinolin-8-olato)(2,6-diphenylphenolato)aluminium(III), (II), which was structurally characterized in a previous report (Rajeswaran *et al.*, 2006). Selected bond lengths and angles for (I) and (II) are compared in Table 1. The Al—O3 bond to the ancillary ligand in (I) is slightly shorter than in (II). The Al—N bonds are also slightly shorter in (I) than in (II). The N1—Al—N2 bond angle deviates from linearity in (I) just slightly less than in (II), and the O3—Al—N1 and O3—Al—N2 bonds are slightly smaller in (I) compared with those in (II). Interestingly, the O3—Al—O2 and O3—Al—O1 bond angles are 124.00 (8) and

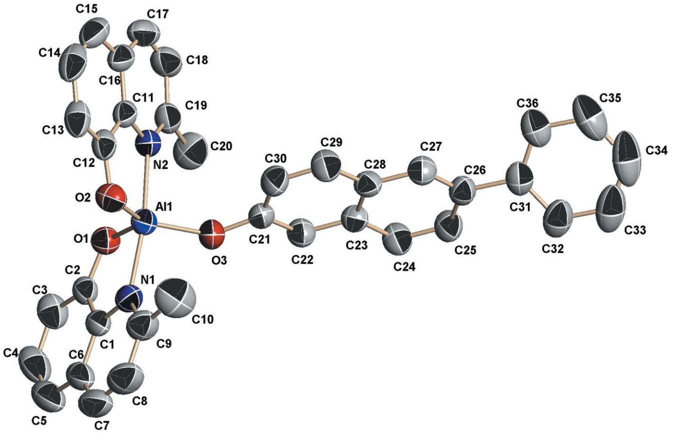


Figure 1
The molecular structure of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted.

116.14 (8)°, respectively, in (I), but are nearly equal in (II), with an average of 118.47°. Thus, the *ortho*-phenyl groups in (II) do not appear to distort significantly the core geometry of (II) relative to (I) by steric crowding of the 2-methylquinolin-8-olate ligands. On the contrary, the phenyl groups in (II) are oriented in a manner that may indicate a π-stacking interaction with the 2-methylquinolin-8-olate ligands.

Experimental

For the synthesis of 6-phenyl-2-naphthol, a round-bottomed flask was charged with potassium phosphate (500 g, 2.36 mol) and water (750 ml). To this solution, *N*-methylpyrrolidinone (875 ml), 6-bromo-2-naphthol (131.5 g, 0.590 mol) and phenylboronic acid (75.5 g, 0.619 mol) were added. This slurry was degassed with a nitrogen sparge for 1 h. Under a nitrogen atmosphere, Pd^{II} acetate (4 g, 18 mmol) and tricyclohexylphosphine (7.5 g, 27 mmol) were added and this mixture was then warmed to 373 K. After 3.5 h, the reaction mixture was cooled to room temperature and allowed to stand overnight. The resulting cooled slurry was poured into 10% (*v*/*v*) H_2SO_4 (875 ml) with mechanical stirring. The resulting suspension was filtered and the product cake was washed with water. This solid was filtered through a glass-fritted funnel. The filtrate was washed with water and brine, and dried over $MgSO_4$. The solvent was removed on a rotary evaporator to yield 133 g of crude product. This was dissolved in boiling dichloromethane (6.5 l). Most of the solvent (6 l) was distilled off to leave a slurry. After cooling to room temperature, the slurry was filtered to collect the solid, which was washed with dichloromethane and then dried under vacuum to yield 114.3 g of 6-phenyl-2-naphthol (88% yield).

For the synthesis of bis(2-methylquinolin-8-olato)(6-phenylnaphth-2-olato) aluminium(III), a round-bottomed flask was charged with toluene (6 l) (HPLC grade, dried over molecular sieves) under nitrogen. Some of the toluene (1 l) was removed by distillation. The vessel was then cooled to room temperature and 8-hydroxyquinaldine (217.9 g, 1.37 mol) and aluminium isopropoxide (127.1 g, 0.622 mol) were added. The reaction was heated at reflux for 2 h and then cooled to room temperature. 6-Phenyl-2-naphthol (137.1 g, 0.622 mol) was added and the reaction slurry was heated at reflux for 15.5 h. More of the toluene (1 l) was removed from the reaction mixture by distillation. After cooling the reaction mixture in an ice–water bath, the resulting precipitate was collected by filtration, followed by a wash with cold toluene (500 ml) and a final wash with heptane (100 ml). This material was dried under vacuum to provide 352 g of a crude product. This crude material was dissolved in toluene (6 l), and the solution was filtered through a coarse glass frit and concentrated by distilling off some (2 l) of the toluene. The concentrated solution was cooled in an ice–water bath for 1 h. Crystals were collected by filtration and washed with toluene and then heptane, and finally dried under vacuum to yield 336 g (88%) of a light-green product. Crystals of (I) suitable for single-crystal X-ray diffraction were obtained by sublimation at 512 K in a tube furnace (Lindberg/Blue) with N_2 entrainment gas.

The NMR spectrum for compound (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 ^1H chemical shifts is shown in Table 2.

Crystal data

$[Al(C_{10}H_8NO)_2(C_{16}H_{11}O)]$
$M_r = 562.58$
Monoclinic, $P2_1/n$
$a = 11.7002$ (3) Å
$b = 16.9926$ (4) Å
$c = 14.5778$ (4) Å
$\beta = 93.5190$ (10)°
$V = 2892.91$ (13) Å^3
$Z = 4$
$D_x = 1.292$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.11$ mm^{-1}
$T = 293$ (2) K
Block, green
0.47 × 0.45 × 0.25 mm

Data collection

Noniu KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan *SORTAV* (Blessing, 1995)]
$T_{min} = 0.786$, $T_{max} = 0.986$
29300 measured reflections
6568 independent reflections
3383 reflections with $I > 2\sigma(I)$
$R_{int} = 0.095$
$\theta_{max} = 27.4°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.150$
$S = 0.99$
6568 reflections
381 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0723P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.17$ e Å^{-3}
$\Delta\rho_{min} = -0.23$ e Å^{-3}

Table 1
Selected bond lengths (Å) and angles (°) in (I) and (II).

	(I)[a]	(II)[b]
Al—O3	1.7284 (16)	1.7387 (12)
Al—O2	1.7860 (15)	1.7921 (12)
Al—O1	1.7868 (16)	1.7886 (12)
Al—N2	2.0405 (18)	2.0686 (14)
Al—N1	2.0466 (18)	2.0605 (13)
N1—Al—N2	171.72 (7)	169.50 (6)
O3—Al—N2	96.45 (8)	92.20 (5)
O3—Al—N1	91.62 (7)	98.29 (5)
O3—Al—O2	124.00 (8)	118.77 (6)
O3—Al—O1	116.14 (8)	118.16 (6)

References: (*a*) this work; (*b*) Rajeswaran *et al.* (2006).

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Table 2
Chemical shift assignments.

Proton on atom No.	Chemical shift (p.p.m.)
C7 and C17	8.27 (*d*, *J* = 8.3 Hz, 2H)
C27	7.77 (*d*, *J* = 1.9 Hz, 1H)
C31 and C36	7.62 (*d*, *J* = 8.3 and 1.2 Hz, 2H)
C4 and C14	7.51 (*t*, *J* = 8.1 Hz, 2H)
C25	7.47 (*dd*, *J* = 8.6 and 1.9 Hz, 1H)
C29	7.43 (*d*, *J* = 8.8 Hz, 1H)
C33 and C35	7.42 (*t*, *J* = 8.3 Hz, 2H)
C8 and C18	7.38 (*d*, *J* = 8.3 Hz, 2H)
C34	7.3 (*m*, 1H)
C24	7.27 (*d*, *J* = 8.6 Hz, 1H)
C5 and C15	7.26 (*dd*, *J* = 8.1 and 1.0 Hz, 2H)
C3 and C13	7.1 (*dd*, *J* = 8.1 and 1.0 Hz, 2H)
C30	6.73 (*dd*, *J* = 8.8 and 2.4 Hz, 1H)
C22	6.61 (*d*, *J* = 2.4 Hz, 1H)
C10 and C20	3.02 (*s*, 6H)

There is slight disorder in some C atoms of the phenyl ring. However, this disorder was left untreated, and all non-H atoms were refined with anisotropic displacement parameters. All H atoms bound to carbon were refined using a riding model, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic H, and with C—H = 0.96 Å and $U_{iso} = 1.5U_{eq}(C)$ for methyl atoms.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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