metal-organic papers

Bis(2,6-diphenylphenolato)(2-methylquinolin-8-olato)aluminium(III)

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The title compound, [Al(C$_{10}$H$_8$NO)$_2$(C$_{18}$H$_{13}$O)], is representative of the class of compounds commonly known as the blue aluminium chelates (BAlq) that are useful in organic electroluminescent devices. The geometry of this compound is approximately trigonal–bipyramidal, with the trigonal base formed by the O donor atoms of the phenolate and two quinolinolate ligands.

Comment

Aluminium chelate complexes such as tris(8-quinolinolato)-aluminium(III) (Alq$_3$) are now well known for their electroluminescence properties (Tang & VanSlyke,1987). In the search for blue luminophores, substitutions on the quinolinol ring were examined, including 2-methyl- and 2,3-dimethyl-8-quinolinol. The tris complexes with these ligands seem to be less stable due to steric limitations of the 2-methyl groups and can be made only under limited conditions (Kushi & Fernando, 1970; Yu *et al.*, 1999). As an alternative to the homoleptic tris complexes, heteroleptic complexes having ancillary phenolate ligands were synthesized and successfully employed in organic electroluminescent devices (Bryan *et al.*, 1992). Here we report a modified synthesis and the crystal structure determination of one of these heteroleptic complexes, (I) (Fig. 1). The molecular unit is monomeric with fivefold coordination. The geometry is approximately trigonal–bipyramidal, with the trigonal base formed by the O donor atoms of the phenolate and two quinolinolate ligands. The N atoms are *trans*, occupying the axial positions of the trigonal bipyramidal coordination environment [Al1—N1 = 2.0605 (13) Å and Al1—N2 = 2.0686 (14) Å]. The Al—O3 bond to the phenolate ligand is relatively short, 1.7387 (12) Å compared with the Al—O bonds to the quinilinolate ligands [Al1—O1 = 1.7886 (12) Å and Al2—O2 =1.7921 (12) Å]. The O—Al—O angles are distorted from 120° for a trigonal base [O3—Al1—O1 = 118.16 (6)°, O3—Al1—O2 = 118.77 (6)° and O1—Al1—O2 = 122.91 (6)°.

(I)
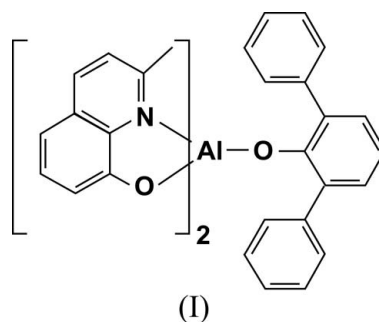
Experimental

A three-necked 1 l round-bottomed flask equipped with a Dean–Stark trap was charged with 700 ml of toluene and heated at vigorous reflux/distillation under nitrogen for 30 min; 50 ml of distillate were removed and the contents were allowed to cool to room temperature (298 K). To the flask were added 8-hydroxyquinaldine (32 g, 0.2 mol) and aluminium isopropoxide (19.5 g, 0.096 mol). The resulting yellow solution (temperature dropped to 292 K) was then heated at vigorous reflux/distillation. After 30 min, the reaction mixture temperature was 377 K. At this time 25 ml of distillate were removed, resulting in a reaction temperature increase to 380 K. Finally, another 25 ml of distillate were removed, resulting in a reaction temperature increase to 382.5 K. The reaction was held at this temperature for 1.5 h and then cooled to room temperature, resulting in a yellow slurry. To this mixture was added 2,6-diphenyl phenol (23.5 g, 0.095 mol) and the resulting yellow slurry was heated at a vigorous reflux/distillation. Another 50 ml of distillate were removed and the reaction was held at 383 K for 1.5 h and then allowed to cool to room temperature overnight. This mixture was finally cooled in an ice–water bath and the resulting solids were collected by filtration through a glass-fritted funnel. The yellow solids were washed with 75 ml of toluene and 2 × 125 ml of heptane and dried in a vacuum oven at 368 K for 2 h. Crystals of (I) suitable for single-crystal X-ray diffraction were obtained by sublimation at 513 K in a tube furnace (Lindberg/Blue) with N_2 entrainment gas. ^{1}H NMR (500 MHz, tetrachloroethane-d_2): 2.77 (s, 6H), 6.45 (m, 2H), 6.53 (m, 4H), 6.71 (dd, J = 7.7, 1 Hz, 2H), 6.89 (t, J = 7.4 Hz, 1H), 7.04 (m, 4H), 7.11 (d, J = 7.4 Hz, 2H), 7.12 (dd, J = 8.1, 1 Hz, 2H), 7.32 (dd, J = 7.7, 8.1 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 8.19 (d, J = 8.4 Hz, 2H).

Crystal data

$[Al(C_{10}H_8NO)_2(C_{18}H_{13}O)]$	$Z = 4$
$M_r = 588.61$	$D_x = 1.298$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 15.4526$ (3) Å	$\mu = 0.11$ mm^{-1}
$b = 13.0266$ (4) Å	$T = 295$ (2) K
$c = 15.7570$ (3) Å	Block, green
$\beta = 108.205$ (2)°	$0.32 \times 0.30 \times 0.20$ mm
$V = 3013.04$ (12) Å^3	

Data collection

Nonius KappaCCD diffractometer	22312 measured reflections
φ and ω scans	5684 independent reflections
Absorption correction: multi-scan	4167 reflections with $I > 2\sigma(I)$
(SORTAV; Blessing, 1995)	$R_{int} = 0.045$
$T_{min} = 0.695$, $T_{max} = 0.760$	$\theta_{max} = 25.7°$
(expected range = 0.895–0.978)	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0622P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.042$	$+ 0.3029P]$
$wR(F^2) = 0.119$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
5684 reflections	$\Delta\rho_{max} = 0.23$ e Å^{-3}
399 parameters	$\Delta\rho_{min} = -0.24$ e Å^{-3}
H-atom parameters constrained	
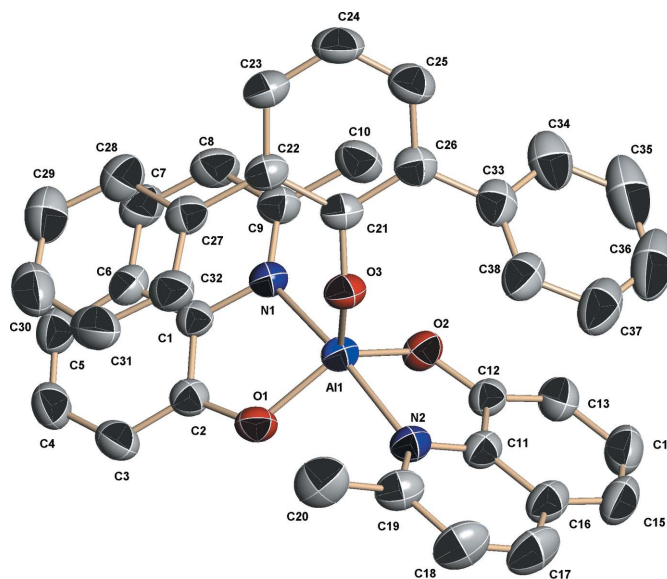
Figure 1
The structure of (I) showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms; H atoms have been omitted for clarity.

There is slight disorder in some of the outer ring C atoms; however, disorder was left untreated and all non-H atoms were refined with anisotropic displacement parameters. All H atoms were refined using a riding model with C—H = 0.93 Å, $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic and C—H = 0.96 Å, $U_{iso}(H) = 1.5U_{eq}(C)$ for CH$_3$ atoms.

Data collection: COLLECT (Nonius, 2000); cell refinement: HKL SCALEPACK (Otwinowski & Minor, 1997); data reduction: HKL DENZO (Otwinowski & Minor, 1997) and SCALEPACK; 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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