Refinement of the crystal structure of the δ -modification of tris(8-hydroxyquinoline)aluminum(III), δ -Al(C₉H₆NO)₃, the blue luminescent Alq₃

M. Rajeswaran*, T. N. Blanton and K. P. Klubek

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

Received June 11, 2003, accepted in revised form and available on-line October 29, 2003; CCDC-No. 1267/1106

Abstract

C₂₇H₁₈AlN₃O₃, triclinic, $P\bar{1}$ (No. 2), $a = 6.181(1)$ Å, $b = 13.268(3)$ Å, $c = 14.430(3)$ Å, $\alpha = 66.06(3)^\circ$, $\beta = 88.56(3)^\circ$, $\gamma = 84.03(3)^\circ$, $V = 1075.5$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.108$, $wR_{\text{ref}}(F^2) = 0.437$, $T = 293$ K.

Source of material

Sublimed bright-yellow tris(8-hydroxyquinoline)aluminum(III) (Alq₃, Eastman Kodak Company) was placed into a glass ampoule (cylindrical shaped bulb 3 cm $\times$ 2.5 cm with a neck 7 cm long and 0.5 cm inside diameter). The ampoule was evacuated (10^{-5} – 10^{-6} Torr) and the end of the neck sealed. The ampoule was placed into a tube furnace and heated to 663 K over a period of 4 h at a rate of 100 K/h, and held at 663 K for 3.5 h. The heating source for the furnace was turned off and the ampoule (still in the furnace) was allowed to slowly cool to room temperature overnight. The ampoule was removed and the resulting Alq₃ specimen was observed to be a dull yellow color and displayed blue luminescence when irradiated by 365 nm UV light. The neck of the ampoule was removed; an aliquot of the thermally processed Alq₃ was analyzed by powder XRD, and the conversion to δ -Alq₃ was found to be complete. Upon careful examination of the thermally processed sample, thin, plate-shaped δ -Alq₃ crystals were observed to be present. Although thin, these crystals were found to be of acceptable quality for single-crystal data collection. To our knowledge, this is the first report of the generation of single-crystals of δ -Alq₃.

Experimental details

The single-crystal structure is of tremendous value, even though structure from powder data is available [1], because the data-to-parameter ratio is very high for single crystal data, i.e., 2830 reflections (560 with $I_{\text{obs}} > 2\sigma(I_{\text{obs}})$) versus 357 reflections for powder data. Thus, the high data-to-parameter ratio leads to a more accurate structure. Also for structure determination using powder data, an idealized model is the starting point, which is then refined under constraints to closely match the powder pattern. This approach is in contrast to actually locating atomic positions in electron density maps for single-crystal data. Otherwise, the atomic positions were not refined anisotropically because of the relatively low quality data.

Discussion

The original report describing organic light-emitting diodes (OLEDs) began with the observation of efficient green electroluminescence from tris(8-hydroxyquinoline)aluminum (α -, β -Alq₃) [2]. Braun et al. [3] reported a new crystalline phase of Alq₃ (δ -Alq₃) exhibiting strongly blue shifted fluorescence. Based upon vibrational analysis, a facial isomer for δ -Alq₃ was proposed [4,5], which was later supported by structure analysis from powder X-ray diffraction data [1]. The unit cell dimensions for δ -Alq₃ are similar to those observed for α -Alq₃ ($a = 6.246$ Å, $b = 12.871$ Å, $c = 14.739$ Å, $\alpha = 69.89^\circ$, $\beta = 89.46^\circ$, $\gamma = 82.52^\circ$ [6]). The α and δ Alq₃ powder XRD patterns are unique and provide unequivocal identification of the Alq₃ phase present in a sample. In this current study, we are able to confirm the facial structure for δ -Alq₃ using single-crystal X-ray crystallography.

A structural diagram of δ -Alq₃, showing the atomic numbering scheme and its facial isomeric nature, is depicted in the figure. Conformation of the Alq₃ molecule and lattice packing from single-crystal structure elucidation were found to be similar to that obtained using powder XRD data [1]. The molecular structure of Alq₃ is comprised of a six coordinate aluminum compound. The aluminum atom is coordinated to the bidentate 8-hydroxyquinoline ligands in a distorted octahedral configuration. The angles around the aluminum atom range from $82.7(6)^\circ$ ($\angle \text{O2-Al1-N2}$) to $97.3(5)^\circ$ ($\angle \text{O2-Al1-O3}$). As expected, the structural data show that the bond distances Al–N (2.07(1) Å, 2.04(1) Å, 2.06(1) Å) and Al–O (1.86(1) Å, 1.83(1) Å, 1.85(1) Å) are very similar to those for the other Alq₃ structures reported in the literature [6–11]. Triclinic space group $P\bar{1}$ indicates that three 8-hydroxyquinoline ligands are crystallographically independent. Though the intermolecular ligands in δ -Alq₃ are at a stacking distance of about 3.326 Å, there is no stacking of ligands. Hence, there is significantly reduced π -orbital overlap in δ -Alq₃ as compared to that in the α -Alq₃[6] and β -Alq₃ structures[7]. In the final difference Fourier map, the highest peak is at $0.25 \text{ e}/\text{\AA}^3$ and the deepest hole is at $-0.33 \text{ e}/\text{\AA}^3$, thus confirming the absence of any solvent in the lattice.

* Correspondence author (e-mail: manju.rajeswaran@kodak.com)

Table 1. Data collection and handling.

Crystal:	green yellow fragment, size 0.02 × 0.02 × 0.07 mm
Wavelength:	Mo K_{α} radiation (0.71073 Å)
μ :	1.31 cm ⁻¹
Diffractometer, scan mode:	Nonius Kappa CCD, ω/ϕ
$2\theta_{\max}$:	50.46°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	4506, 2830
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 560
$N(\text{param})_{\text{refined}}$:	137
Program:	SHELXTL [12]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
Al(1)	2i	0.2714(8)	0.3120(5)	0.3143(4)	0.062(2)
O(1)	2i	0.395(2)	0.4441(9)	0.2794(8)	0.065(3)
O(2)	2i	0.440(2)	0.2639(9)	0.2314(8)	0.064(3)
O(3)	2i	0.438(2)	0.2372(9)	0.4311(9)	0.070(4)
N(1)	2i	0.051(2)	0.410(1)	0.199(1)	0.060(4)
N(2)	2i	0.104(2)	0.182(1)	0.329(1)	0.057(4)
N(3)	2i	0.055(2)	0.349(1)	0.410(1)	0.063(4)
C(1)	2i	-0.126(2)	0.389(2)	0.162(1)	0.071(5)
H(1)	2i	-0.1668	0.3175	0.1881	0.086
C(2)	2i	-0.253(2)	0.473(2)	0.086(1)	0.072(5)
H(2)	2i	-0.3730	0.4555	0.0599	0.086
C(3)	2i	-0.206(3)	0.579(2)	0.047(1)	0.079(6)
H(3)	2i	-0.2949	0.6342	-0.0027	0.095
C(4)	2i	-0.022(3)	0.605(2)	0.084(1)	0.069(5)
C(5)	2i	0.106(2)	0.519(2)	0.162(1)	0.055(5)
C(6)	2i	0.293(3)	0.531(2)	0.210(1)	0.070(5)
C(7)	2i	0.354(2)	0.638(1)	0.174(1)	0.056(5)
H(7)	2i	0.4757	0.6516	0.2017	0.067

Table 2. Continued.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
C(8)	2i	0.231(3)	0.727(2)	0.095(1)	0.080(6)
H(8)	2i	0.2779	0.7972	0.0690	0.096
C(9)	2i	0.049(3)	0.710(2)	0.057(1)	0.086(6)
H(9)	2i	-0.0342	0.7711	0.0099	0.103
C(10)	2i	-0.074(2)	0.138(2)	0.385(1)	0.071(5)
H(10)	2i	-0.1349	0.1694	0.4278	0.085
C(11)	2i	-0.169(3)	0.048(2)	0.381(1)	0.078(6)
H(11)	2i	-0.2859	0.0203	0.4215	0.094
C(12)	2i	-0.087(3)	0.002(2)	0.316(1)	0.078(6)
H(12)	2i	-0.1500	-0.0562	0.3111	0.093
C(13)	2i	0.097(3)	0.046(2)	0.254(1)	0.066(5)
C(14)	2i	0.186(3)	0.131(2)	0.268(1)	0.066(5)
C(15)	2i	0.370(3)	0.180(2)	0.215(1)	0.070(5)
C(16)	2i	0.458(3)	0.135(2)	0.149(1)	0.071(5)
H(16)	2i	0.5817	0.1631	0.1131	0.085
C(17)	2i	0.369(3)	0.050(2)	0.133(2)	0.091(7)
H(17)	2i	0.4301	0.0247	0.0856	0.110
C(18)	2i	0.200(3)	0.007(2)	0.185(1)	0.092(6)
H(18)	2i	0.1463	-0.0512	0.1755	0.111
C(19)	2i	-0.141(2)	0.404(1)	0.398(1)	0.071(5)
H(19)	2i	-0.2108	0.4319	0.3352	0.085
C(20)	2i	-0.245(3)	0.423(2)	0.476(1)	0.075(6)
H(20)	2i	-0.3820	0.4625	0.4636	0.090
C(21)	2i	-0.156(3)	0.385(2)	0.568(2)	0.078(6)
H(21)	2i	-0.2301	0.3993	0.6187	0.094
C(22)	2i	0.057(2)	0.322(1)	0.590(1)	0.066(5)
C(23)	2i	0.149(2)	0.308(1)	0.505(1)	0.050(4)
C(24)	2i	0.359(2)	0.249(1)	0.511(1)	0.060(5)
C(25)	2i	0.466(2)	0.206(1)	0.605(1)	0.065(5)
H(25)	2i	0.6034	0.1600	0.6132	0.078
C(26)	2i	0.365(3)	0.220(2)	0.688(2)	0.086(6)
H(26)	2i	0.4386	0.1865	0.7498	0.103
C(27)	2i	0.174(3)	0.277(2)	0.685(2)	0.086(6)
H(27)	2i	0.1183	0.2864	0.7416	0.103

References

- Cölle, M.; Dinnebier, R. E.; Brütting, W.: The structure of the blue luminescent δ -phase of tris(8-hydroxyquinoline)aluminum(III) (Alq₃). ChemComm (2002) 2908-2909.
- Tang, C. W.; Van Slyke, S. A.: Organic electroluminescent diodes. Appl. Phys. Lett. **51** (1987) 913-915.
- Braun, M.; Gmeiner, J.; Tzolov, M.; Coelle, M.; Meyer, F. D.; Milius, W.; Hillebrecht, H.; Wendland, O.; von Schütz, J. U.; Brütting, W.: A new crystalline phase of the electroluminescent material tris(8-hydroxyquinoline)aluminum exhibiting blueshifted fluorescence. J. Chem. Phys. **114** (2001) 9625-9632.
- Cölle, M.; Gmeiner, J.; Milius, W.; Hillebrecht, H.; Brütting, W.: Thermal and structural properties of the organic electroluminescent material tris(8-hydroxyquinoline)aluminum (Alq₃). Proc. of the EL2002, Ghent 2002, p. 133-136.
- Cölle, M.; Gmeiner, J.; Milius, W.; Hillebrecht, H.; Brütting, W.: Preparation and characterization of blue-luminescent tris(8-hydroxyquinoline)aluminum (Alq₃). Adv. Funct. Mater. **13** (2003) 108-112.
- Rajeswaran, M.; Blanton, T. N.: Single-crystal structure determination of the elusive facial isomer of Alq₃, tris(8-hydroxyquinoline)aluminum. Unpublished results (2003).
- Brinkmann, M.; Gadret, G.; Muccini, M.; Taliani, C.; Masciocchi, N.; Sironi, A.: Correlation between Molecular packing and Optical Properties in Different Crystalline Polymorphs and Amorphous Thin Films of mer-Tris(8-hydroxyquinoline)aluminum(III). J. Am. Chem. Soc. **122** (2000) 5147-5157.
- Muccini, M.; Brinkmann, M.; Gadret, G.; Taliani, C.; Masciocchi, N.; Sironi, A.: Optical spectroscopy of unsolvated and solvated crystalline Alq₃. Synthetic Met. **122** (2001) 31-35.
- Ul-Haque, M.; Horne, W.; Lyle, S. J.: Crystal and molecular structure of tris-(8-quinolinolato)aluminium (III) containing occluded acetylacetone. J. Crystallogr. Spectrosc. Res. **21** (1991) 411-417.
- Schmidbaur, H.; Lettenbauer, J.; Wilkinson, D. L.; Muller, G.; Kumberger, O.: Modellsysteme für die Gallium-Extraktion, I Struktur und Molekuldynamik von Aluminium- und Galliumtris(oxinat). Z. Naturforsch. B **46** (1991) 901-911.
- Fujii, I.; Hirayama, N.; Ohtani, J.; Kodama, K.: Crystal Structure of Tris(8-quinolinolato)aluminum(III)-Ethyl Acetate (1/0.5). Anal. Sci. **12** (1996) 153-154.
- Sheldrick, G.-M.: SHELXTL, Structure Analysis Program, version 6.10. Bruker Analytical X-ray systems. Madison, WI, USA 2000.