

Short Communication

Synthesis and reactivity of $\text{Al}(\text{Et})\text{q}'_2$ ($\text{q}' = 2\text{-methyl-8-quinolinolato}$) and crystal structures of $[\text{Al}(\text{Et})_2\text{q}]_2$ and $\text{Alq}'_2\text{q}$ ($\text{q} = 8\text{-quinolinolato}$)

Isao Yamaguchi, Takayuki Iijima, Takakazu Yamamoto*

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

Received 12 March 2002; accepted 15 March 2002

Abstract

A crystal structure of a dimeric aluminum complex ($[\text{Al}(\text{Et})_2(\text{q})]_2$, $\text{q} = 8\text{-quinolinolato}$) (**1**) obtained by reaction of AlEt_3 with 8-quinolinol has been determined by X-ray crystallography. Reaction of AlEt_3 with 2-methyl-8-quinolinol gave a new reactive complex ($[\text{Al}(\text{Et})\text{q}'_2]$ ($\text{q}' = 2\text{-methyl-8-quinolinolato}$) (**2**)) in good yield. Reaction of **2** with 8-quinolinol provided $\text{Alq}'_2\text{q}$ (**3**) and the crystal structure of **3** was determined. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Aluminum; 8-Quinolinol; 2-Methyl-8-quinolinol; Crystal structures

1. Introduction

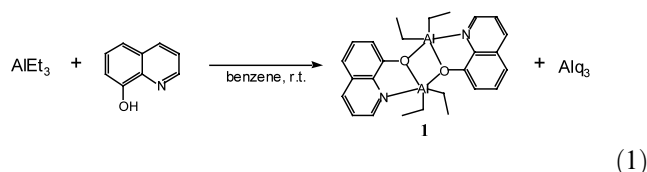
Tri(8-quinolinolato)aluminum (Alq_3) is one of the most widely used complexes for organic light emitting devices (OLED), because Alq_3 is not only a good green emitter but also a highly efficient electron transporting material [1,2]. Various modifications of 8-quinolinolato ligand to improve the performance of Alq_3 have been carried out [3,4]. Recently, an aluminum complex having a reactive OH group ($\text{Alq}_2(\text{OH})$) has also been reported [5]. Such a reactive complex would be a good starting material for high performance aluminum complexes in OLED.

$\text{Al}(\text{R})\text{q}_2$ -type complex having a reactive M–R ($\text{R} = \text{alkyl group}$) bond is also expected as a promising starting material for the high performance aluminum complexes, if it can be isolated. Reaction of AlR_3 with 8-quinolinol has been reported [6]. However, the reaction did not give the expected $\text{Al}(\text{R})\text{q}_2$ -type complex but afforded a mixture of an Alq_3 -type complex and a dimeric aluminum complex ($[\text{Al}(\text{R})_2\text{q}]_2$) [6]. The crystal structure of the $[\text{Al}(\text{R})_2\text{q}]_2$ -type complex has not been determined. We thought that 1:2 reaction of AlR_3 with 2-methyl-8-quinolinol ($\text{q}'\text{H}$) would give an $\text{Al}(\text{R})\text{q}'_2$

complex selectively, because a steric hindrance of the methyl group will prevent formation of Alq'_3 . In this work, we report preparation of a new reactive aluminum complex, $\text{Al}(\text{Et})\text{q}'_2$ and a crystal structure of the $[\text{Al}(\text{R})_2\text{q}]_2$ -type dinuclear aluminum complex obtained by reaction of AlEt_3 with 8-quinolinol. Reaction of $\text{Al}(\text{Et})\text{q}'_2$ with 8-quinolinol and a crystal structure of the reaction product ($\text{Alq}'_2\text{q}$) are also reported.

2. Results and discussion

We first followed the previously reported reaction between AlEt_3 and 8-quinolinol [6]. The reaction of AlEt_3 with 8-quinolinol in a 1:2 molar ratio gave a mixture of Alq_3 and $[\text{Al}(\text{Et})_2\text{q}]_2$ (**1**) in 36 and 18% yields, respectively Eq. (1). Complex **1** is sensitive to air and changed slowly to Alq_3 in solutions, which makes isolation of **1** difficult. We now report isolation of **1** and characterization of **1**.



¹H-NMR spectrum of **1** shows peaks in the range δ

* Corresponding author. Tel.: +81-45-9245220; fax: +81-45-9245276.

E-mail address: tyamamot@res.titech.ac.jp (T. Yamamoto).

7.39–8.73 and at 0.81 and 0.08 due to aromatic hydrogens and Et groups, respectively.

The structure of **1** was confirmed by a single-crystal X-ray crystallography, as shown in Fig. 1. Complex **1** has a dimeric structure with a lozenge plane occupying Al(1), Al(2), O(1), and O(2) atoms. Each ethyl group bonded to Al is on the opposite side from the lozenge plane. The Al(1)–O(1) and Al(2)–O(1) bond lengths are essentially same to those of Al(2)–O(2) and Al(1)–O(2), respectively. The O(1)–Al(1)–O(2) and Al(1)–O(1)–Al(2) bond angles are 72.8 and 107.7°, respectively. The Al–N bond distances of **1** are comparable to those of Alq₃ [7].

Reaction of AlEt₃ with 2-methyl-8-quinolinol (q'H) in a 1:2 molar ratio selectively gave Al(Et)q'₂ (**2**) in 97% yield Eq. (2).

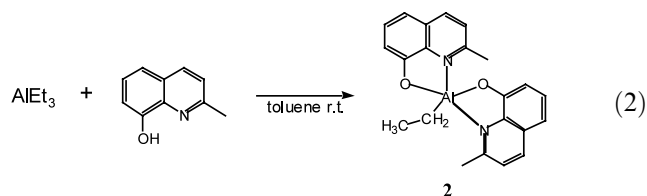


Fig. 2 depicts ¹H-NMR spectrum of **2**. The ¹H-NMR spectrum of **2** shows peaks due to aromatic hydrogens in the range δ 6.91–8.23 and assignment of the peaks is shown in Fig. 2. The CH₃ peak is observed at a lower magnetic field (δ 3.07) than that of 2-methyl-8-quinolinol (δ 2.70) presumably due to a magnetically anisotropic effect in the aluminum complex. Methyl hydrogens of the Et group give a triplet signal at δ 0.59. The methylene hydrogens bonded to Al afford two multiplets centered at δ –0.06 and 0.13, revealing that the Al center has a chirality and the CH₂ hydrogens become diastereotropic due to the chirality. Integral

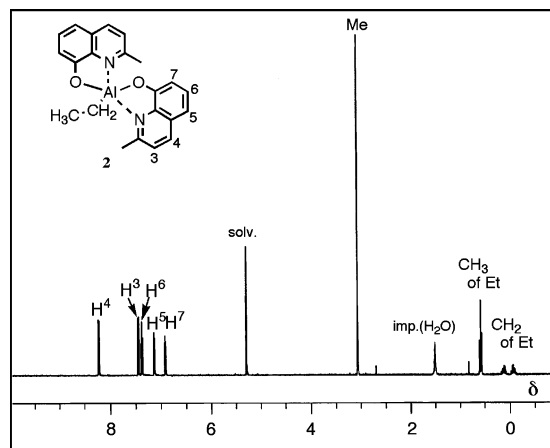
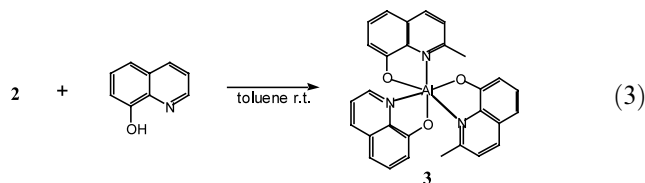


Fig. 2. ¹H-NMR spectrum of **2** in CD₂Cl₂.

ratio of the ¹H-NMR peaks and analytical data support the structure of **2** (See Section 3).

In order to reveal chemical reactivity of **2**, reaction of **2** with 8-quinolinol was carried out to obtain Alq'₂q (**3**) in 27% isolation yield Eq. (3). Reaction of **2** with 2-methyl-8-quinolinol resulted in recovery of the starting materials, suggesting that formation of Alq'₃ was difficult due to steric reasons.



Complex **3** is stable to air in solid state, while a THF solution of **3** decomposed gradually under air.

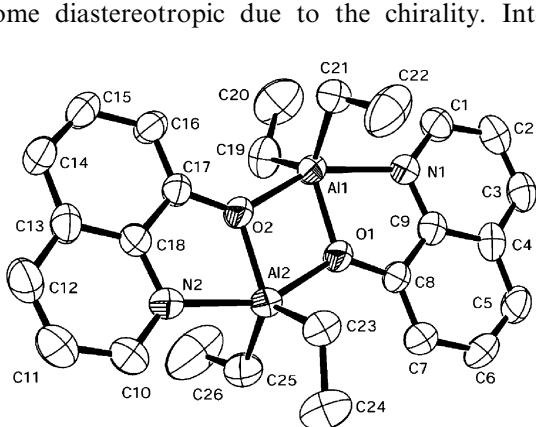


Fig. 1. Crystal structure of **1** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Al(1)–O(1), 1.868(3); Al(1)–N(1), 2.132(5); Al(1)–O(2), 2.009(4); Al(1)–C(19), 1.971(5); Al(1)–C(21), 1.979(5); Al(2)–O(2), 1.882(3); Al(2)–N(2), 2.132(5); Al(2)–O(1), 2.003(4); Al(2)–C(23), 1.977(5); Al(2)–C(25), 1.982(5); O(1)–Al(1)–O(2), 72.8(1); O(1)–Al(2)–O(2), 72.7(2); O(1)–Al(1)–N(1), 79.3(2); O(2)–Al(2)–N(2), 78.9(2); Al(1)–O(1)–Al(2), 107.7(2); Al(1)–O(2)–Al(2), 106.8(2).

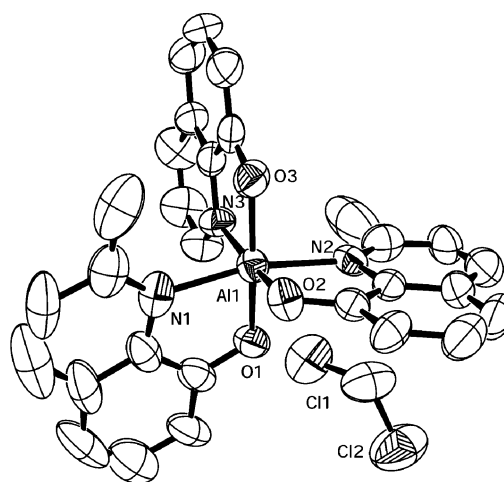


Fig. 3. Crystal structure of **3** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Al(1)–O(1), 1.837(6); Al(1)–O(2), 1.830(6); Al(1)–O(3), 1.852(6); Al(1)–N(1), 2.090(8); Al(1)–N(2), 2.087(7); Al(1)–N(3), 2.101(8); O(1)–Al(1)–N(1), 83.1(3); O(2)–Al(1)–N(2), 83.4(3); O(3)–Al(1)–N(3), 81.0(3).

Fig. 3 shows an ORTEP diagram of **3** as determined by X-ray crystallography. Complex **3** contains a solvated CH_2Cl_2 molecule used as the recrystallization solvent and has a six-coordinate octahedron structure similar to Alq_3 . The Al–N bond distances of **3** are similar to those of Alq_3 , whereas the Al–O bond lengths of **3** are somewhat shorter than those of Alq_3 [7]. As described above, a new reactive complex of a type of $\text{Al(R)}\text{q}_2$ has been isolated, and this complex is expected to serve as a starting material of aluminum complexes.

3. Experimental

All reactions and manipulations were carried out under inert gas using standard Schlenk techniques. All solvents were dried and distilled prior to use. IR and NMR spectra were recorded on a JASCO-IR 810 spectrophotometer and JEOL EX-400 spectrometer, respectively. Elemental analyses were carried out with a Yanagimoto Type MT-2 CHN autocorder.

3.1. Synthesis of **1**

To a benzene solution (25 ml) of AlEt_3 (1.52 ml, 10.0 mmol) was added dropwise a benzene solution (20 ml) of 8-quinolinol (2.90 g, 20.0 mmol) for 1 h. The reaction mixture was stirred at room temperature (r.t.) for 3 h. The resulting yellow precipitate was washed with benzene and dried in vacuo to give **1** as a yellow solid (0.83 g, 18%). Evaporation of the benzene filtrate afforded Alq_3 (1.65 g, 36%). Crystals for microanalysis and the X-ray crystallographic analysis were obtained by recrystallization from a CHCl_3 solution at r.t. Anal. Found: C, 68.27; H, 7.23; N, 6.14. Calc. for $\text{C}_{26}\text{H}_{32}\text{Al}_2\text{N}_2\text{O}_2$: C, 68.11; H, 7.03; N, 6.11%. ^1H -NMR (400 MHz, CD_2Cl_2): δ 8.73 (dd, 2H), 8.40 (dd, 2H), 7.64 (dd, 2H), 7.59 (t, 2H), 7.42 (dd, 2H), 7.39 (dd, 2H), 0.81 (t, 12H), 0.08 (m, 8H).

3.2. Synthesis of **2**

To a toluene solution (50 ml) of AlEt_3 (4.60 ml, 30.0 mmol) was added dropwise a toluene solution (80 ml) of 2-methyl-8-quinolinol (9.55 g, 60.0 mmol) for 1 h. After stirring for 12 h, the resulting precipitate was washed with toluene and dried under vacuum to give **2** as a yellow solid (10.9 g, 97%). Anal. Found: C, 70.81; H, 5.39; N, 7.49. Calc. for $\text{C}_{22}\text{H}_{21}\text{AlN}_2\text{O}_2$: C, 70.76; H, 5.68; N, 7.52%. ^1H -NMR (400 MHz, CD_2Cl_2): δ 8.23 (d, 2H), 7.45 (d, 2H), 7.13 (dd, 2H), 6.91 (dd, 2H), 3.07 (s, 12H), 0.70 (t, 3H), 0.13 (m, 1H), -0.06 (m, 1H).

3.3. Synthesis of **3**

To a toluene solution (20 ml) of **2** (1.01 g, 2.71 mmol) was added dropwise a toluene solution (10 ml) of 8-quinolinol (0.42 g, 2.89 mmol) for 1 h. The reaction mixture was stirred at r.t. for 6 h. The resulting precipitate was washed with toluene, dried under vacuum, and recrystallized from a CH_2Cl_2 solution at r.t. to give **3** as yellow needles (0.36 g, 27%). Anal. Found: C, 62.84; H, 4.14; N, 7.59; Cl, 12.14. Calc. for $\text{C}_{29}\text{H}_{22}\text{AlN}_3\text{O}_3 \cdot \text{CH}_2\text{Cl}_2$: C, 62.95; H, 4.23; N, 7.34; Cl, 12.39%.

3.4. Crystal data for **1** and **3**

1: $\text{C}_{26}\text{H}_{32}\text{Al}_2\text{N}_2\text{O}_2$, $M = 458.51$, monoclinic, space group $P2_1/a$ (No. 14), $a = 15.18(2)$ Å, $b = 9.77(2)$ Å, $c = 18.081(5)$ Å, $\beta = 111.84(5)^\circ$, $V = 2487.8(5)$ Å³, $Z = 4$, $D_c = 1.224$ Mg m^{−3}, $F(000) = 976.00$. **3**: $\text{C}_{28}\text{H}_{22}\text{AlN}_3\text{O}_3 \cdot \text{CH}_2\text{Cl}_2$, $M = 572.43$, monoclinic, space group $P2_1/n$ (No. 14), $a = 11.386(4)$ Å, $b = 13.571(2)$ Å, $c = 17.064(3)$ Å, $\beta = 95.09(2)^\circ$, $V = 2026.4(1)$ Å³, $Z = 4$, $D_c = 1.448$ Mg m^{−3}, $F(000) = 1184.00$. The diffraction data were collected with a Rigaku AFC5R diffractometer at ambient temperature (23 °C) using the ω scan mode ($2\theta \leq 55^\circ$). Correction for Lorentz and polarization effects and an empirical absorption correction (Ψ scan) were applied. The structure was solved by a common combination of direct methods (SAP1-91 and SIR-92 for **2** and **3**, respectively) and subsequent Fourier techniques. The positional and thermal parameters of non-hydrogen atoms were refined anisotropically, while hydrogen atoms were located by assuming the ideal geometry.

Acknowledgements

We gratefully acknowledge the help of Dr. Y. Nishihara in our institute for the X-ray crystallographic analysis of molecular structures of the complexes.

References

- [1] (a) C.W. Tang, S.A. VanSlyke, Appl. Phys. Lett. 51 (1987) 913; (b) C.W. Tang, S.A. VanSlyke, C.H. Chen, J. Appl. Phys. 65 (1989) 3611; (c) Y. Hamada, T. Sano, M. Fujita, T. Fujii, Y. Nishio, K. Shibata, Jpn. J. Appl. Phys. 32 (1993) L514; (d) V. Bulovic, G. Gu, P.E. Burrows, S.R. Forrest, Nature 380 (1996) 29.
- [2] (a) C. Adachi, S. Tokio, T. Tsutsui, S. Saito, Jpn. J. Appl. Phys. 27 (1988) L713; (b) Z. Shen, P.E. Burrows, V. Bulovic, S.R. Forrest, M.E. Thompson, Science 276 (1997) 2009; (c) H. Aziz, Z.D. Popovic, N.-X. Hu, A.-M. Hor, S. Xu, Science 283 (1999) 1900;

- (d) Q. Wu, M. Esteghamatian, N.H. Hu, Z. Popovic, G. Enright, Y. Tao, M. D'Iorio, S. Wang, *Chem. Mater.* 12 (2000) 79.
- [3] (a) W. Liu, A. Hassan, S. Wang, *Organometallics* 16 (1997) 4527;
(b) A. Hassan, S. Wang, *J. Chem. Soc. Chem. Commun.* (1998) 211;
(c) J. Ashenhurst, L. Brancalion, A. Hassan, W. Liu, H. Schmider, S. Wang, Q. Wu, *Organometallics* 17 (1998) 3186;
(d) J. Ashenhurst, L. Brancalion, S. Gao, W. Liu, H. Schmider, S. Wang, G. Wu, Q.G. Wu, *Organometallics* 17 (1998) 5334;
(e) S.F. Liu, C. Seward, H. Aziz, N.-X. Hu, Z. Popovic, S. Wang, *Organometallics* 19 (2000) 5709;
(f) J. Ashenhurst, G. Wu, S. Wang, *J. Am. Chem. Soc.* 122 (2000) 2541.
- [4] J. Yu, Z. Chen, S. Miyata, *Synth. Methods* 123 (2001) 239.
- [5] L.M. Leung, W.Y. Lo, S.K. So, K.M. Lee, W.K. Choi, *J. Am. Chem. Soc.* 122 (2000) 5640.
- [6] T.J. Hurley, M.A. Robinson, J.A. Scruggs, S.I. Troz, *Inorg. Chem.* 6 (1967) 1311.
- [7] M. Brinkmann, G. Gadret, M. Muccint, C. Taliani, N. Masciocchi, A. Sironi, *J. Am. Chem. Soc.* 122 (2000) 5147.