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Synthesis, structure and luminescence study of a binuclear aluminium complex: A novel structure containing six coordinated aluminium atoms in two distinct coordination geometries

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Abstract

Novel binuclear complexes of aluminium alkoxides were prepared by the reaction of 8-hydroxyquinoline with aluminium 2-methoxyethoxide and aluminium 2-ethoxyethoxide in refluxing benzene. Both compounds, $[Al(C_9H_6NO)_2(\mu\text{-}OCH_2CH_2OR)]_2$ [where $R = CH_3$ (**1**) and C_2H_5 (**2**)], have been characterized by elemental analysis and spectral studies. The molecular structure determination of compound **2** by single crystal X-ray analysis revealed a discrete unsymmetrical dimer (C_2 symmetry) containing aluminium atoms in two distinct coordination geometries that are linked to each other by two bridging alkoxy groups. ^{27}Al NMR spectra of compounds **1** and **2** shows that the solid state structure of the complexes is not retained in solution, and four-coordinate aluminium atoms form in solution. Both compounds display luminescence upon illumination by UV light. Specific rotation measurements show that for both complexes extra enantiomers (**ee**) exist in solution. The hydroxyquinoline derivatives of both aluminium alkoxides have good solubility in common organic solvents and have suitable thermal stability.

Keywords: Aluminium complex; Aluminium alkoxide; 8-Hydroxyquinoline; Luminescence; ^{27}Al NMR

1. Introduction

Among the metal 8-hydroxyquinoline chelates, tris(8-quinolinolate) aluminium (AlQ_3) has widely been used as a light emitting layer in organic light-emitting devices (OLED) [1–4]. Interest in AlQ_3 complexes with extended conjugated chromophores [5] and other metal 8-hydroxyquinoline chelates for improving and understanding the correlation between the electronic structure and photonic properties continues to thrive [6]. To this end several 8-hydroxyquinoline derivatives of main and transition metal ions have been synthesized, including, beryllium [7] and magnesium [8] from group IA, boron [9], gallium [10,11] and indium [12] from group IIIB, zinc [13] from group IIIB, antimony from group VB [14] and gold from group IB [15]. Interestingly, their electroluminescent light frequency depends on the type of metal ions in addition to the substituents on the 8-hydroxyquinoline ligand [8]. However, AlQ_3 still continuous to be the key compound among the low molecular weight materials for the use in electroluminescent devices [16–19].

AlQ_3 is a stable metal chelate with low solubility in various solvents and is widely used as a precursor for the fabrication of organic electroluminescent diodes in form of amorphous thin films by vacuum deposition techniques [20]. However, the current trend and interest have shifted to the fabrication of OLEDs by solution-processing due to the low cost of manufacturing [20]. In one approach, incorporation of AlQ_3 as a pendant group into a polymer structure has been suggested [21]. These polymers can easily be used in the solution processing method including low

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cost ink-jet printing techniques [22,23]. However, because of the complicated and multi-step synthetic strategy for the preparation of polymer-supported AlQ_3, commercialization by this route is doubtful. Alternatively, reactive AlQ_3 derivatives such as $Al(Et)_2Q$ [24], $Al(Et)Q_2$ [25] and $Al(Q)_2(OH)$ [26] can be incorporated into polymers containing OH side groups by condensation reactions. High reactivity of the former and low solubility of the latter mentioned compounds can be overcome by replacing the ethyl or hydroxide group with long alkoxy groups. Furthermore, it has recently been proposed that the aluminium–nitrogen bond strength can be used as a parameter for tuning the complex emission wavelength [27], alternatively it may be possible to alter the emission wavelength to some extent using various alkoxy groups. As a contribution to the latest development of this interesting field, we would like to report the synthesis and characterization of the first examples of two highly soluble and stable alkoxy derivatives of AlQ_3, $[Al(Q_2)(OCH_2CH_2OR)]_2$ [R = CH_3 (**1**) and C_2H_5 (**2**)]. In addition, their photoluminescence behaviour was investigated and the molecular structure of complex **2** was determined by X-ray analysis.

2. Experimental

All manipulations were carried out under nitrogen, using standard Schlenk techniques. All chemicals were purchased from Merck and were used as received, except solvents which were dried and distilled under nitrogen prior to use. Both $Al(OCH_2CH_2OCH_3)_3$ and $Al(OCH_2CH_2OCH_2CH_3)_3$ were prepared by the alcohol exchange method from $Al(OCH(CH_3)CH_2CH_3)$ according to a previous report [28].

Infrared spectra were recorded on a Shimadzu 470 instrument, using KBr pellets. ^1H and ^{13}CNMR spectra were recorded in C_6D_6 on a Bruker AVANCE 300-MHz instrument using TMS as an internal reference. ^{27}Al NMR spectra were obtained on a Bruker AVANCE 500-MHz spectrophotometer in C_6D_6 using aluminium nitrate as an external reference in aqueous solution. The mass spectroscopy was performed on a Varian Matt 44 instrument (electron impact, 20 eV). Absorption spectra of solutions (10^{-6} M) were obtained in CH_2Cl_2 on a Shimadzu 2100 UV–Vis spectrophotometer. Emission spectra were recorded at room temperature on a Perkin–Elmer MPF-43A spectrofluorimeter from 440 to 550 nm by excitation with UV light using 30 μM solutions of **1** and **2** in dichloromethane.

2.1. Synthesis of *1*

Compound **1** was prepared by the reaction of 8-hydroxyquinoline (0.73 g, 5 mmol) with $Al(OCH_2CH_2OCH_3)_3$ (1.26 g, 5 mmol) in benzene (30 ml). The mixture was refluxed for 3 h and the solvent was removed under reduced pressure to leave a yellow solid. The solid was crystallized from dichloromethane–hexane; single crystals of the complex were isolated from the solution after several days at −5° C, m.p. decomposes at 280 °C. *Anal*. Calc. for $C_{21}H_{19}N_2O_4Al$: C, 64.62; H, 4.87; N, 7.18. Found: C, 64.22; H, 4.80; N, 6.62%. UV (CH_2Cl_2, nm): 318 (MLCT), 335 (π–π*) and 382 (n–π*). IR (cm^{-1}): 3035 (C–H, aromatic), 2968 (C–H, aliphatic), 1605 (C═N), 1575 (C═C), 1078 (C–O), 639 (Al–O), 752 (Al–O–Al). ^1H NMR (C_6D_6, ppm): 2.5 (3H, s, –OC*H*$_3$), 2.9–3.8 (4H, m, AlOC*H*$_2$C*H*$_2$–). C_9H_6NO ligand protons: 6.4 (1H, q), 6.9 (1H, d), 7.0 (1H, d), 7.1 (1H, d), 7.3 (2H, m), 7.4 (1H, t), 7.5 (1H, d) 7.6 (1H, t), 7.9 (1H, d), 8.6 (1H, d), 9.5 (1H, d). ^{13}C NMR (ppm): 57.15, 61.11, 73.63, 110.48, 110.79, 111.59, 120.67, 121.04, 129.25, 129.68, 130.44, 130.77, 138.33, 138.42, 140.31, 140.49, 144.21, 144.85, 147.25, 160.72, 160.87. ^{27}Al NMR (ppm): 26.8, 71.4. Mass spectral data, aluminium-bearing fragments (*m*/*e*): 390 $[Al(OCH_2CH_2OCH_3)(C_9H_6NO)_2]^{+\cdot}$, 315 $[Al(C_9H_6NO)_2]^+$, 246 $[Al(OCH_2CH_2OCH_3)(C_9H_6NO)]^{+\cdot}$, 201 $[Al(OCH_2)(C_9H_6NO)]^+$, 188 $[Al(C_9H_6NO)(OH)]^{+\cdot}$, 171 $[Al(C_9H_6NO)]^+$. Mass numbers are based upon ^1H, ^{12}C, ^{14}N, ^{16}O and ^{27}Al.

2.2. Synthesis of *2*

Compound **2** was prepared by the reaction of 8-hydroxyquinoline (0.73 g, 5 mmol) with $Al(OCH_2CH_2OCH_2CH_3)_3$ (1.47 g, 5 mmol) in benzene (30 ml). The mixture was refluxed for 3 h and the solvent was removed under reduced pressure to leave a yellow solid. The solid was crystallized from dichloromethane–hexane at −5 °C, m.p., decomposes at 240 °C. *Anal*. Calc. for $C_{22}H_{21}N_2O_4Al$: C, 65.34; H, 5.20; N, 6.93. Found: C, 64.75; H, 5.12; N, 7.1%. UV (CH_2Cl_2, nm): 317 (LMCT), 334 (π–π*), 382 (n–π*). IR (cm^{-1}): 3035 (C–H, aromatic), 2967 (C–H, aliphatic), 1603 (C═N), 1578 (C═C), 1081 (C–O), 644 (Al–O), 750 (Al–O–Al). ^1H NMR (C_6D_6, ppm): 0.6 (3H, t, –OCH$_2$C*H*$_3$), 2.7–3.7 (4H, m, –C*H*$_2$OC*H*$_2$CH$_3$), 3.8–4.0 (2H, m, AlOC*H*$_2$). C_9H_6NO ligand protons: 6.4 (1H, q), 6.9 (1H, d), 7.0 (1H, d), 7.0 (1H, d), 7.3 (2H, m), 7.4 (1H, t), 7.5 (1H, d) 7.6 (1H, t), 7.9 (1H, d), 8.6 (1H, d), 9.5 (1H, d). ^{13}C NMR (C_6D_6, ppm): 14.48, 61.60, 65.14, 71.93, 110.46, 110.89, 110.98, 111.52, 120.57, 121.8, 129.25, 129.89, 130.44, 130.79, 138.25, 138.44, 140.82, 141.15, 144.25, 147.19, 160.67, 160.90. ^{27}Al NMR (C_6D_6, ppm): 26.9 and 69.5. Mass spectral data, aluminium-bearing fragments (*m*/*e*): 404 $[Al(OCH_2CH_2OCH_2CH_3)(C_9H_6NO)_2]^{+\cdot}$, 315 $[Al(C_9H_6NO)_2]^+$, 260 $[Al(OCH_2CH_2OCH_2CH_3)(C_9H_6NO)]^{+\cdot}$, 201 $[Al(OCH_2)(C_9H_6NO)]^+$, 188 $[Al(C_9H_6NO)(OH)]^{+\cdot}$, 171 $[Al(C_9H_6NO)]^+$. Mass numbers are based upon ^1H, ^{12}C, ^{14}N, ^{16}O and ^{27}Al.

3. X-ray crystallography

A yellow prism-shaped crystal of **2**, air stable at room temperature, was used for the crystallographic measurements. The data were collected at 193 K on a Siemens P3 four-circle diffractometer. Crystal data and details of structure determination for compound **2** are presented in