Polyhedron 28 (2009) 3055–3059

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Structural and photophysical studies on a linear trinuclear zinc complex of 2-[(2-hydroxyethylimino)methyl]quinolin-8-ol

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ARTICLE INFO

Article history:
Received 6 May 2009
Accepted 16 June 2009
Available online 24 June 2009

Keywords:
8-Hydroxyquinoline
Schiff base
Acetate bridge
Phenolate bridge
Trinuclear complex
Photophysical properties

ABSTRACT

A linear trinuclear zinc complex was obtained when after refluxing 8-hydroxyquinoline-2-carboxaldehyde and 2-aminoethanol (in a 1:1 molar ratio) until the formation of the H_2L ligand, a methanol solution of zinc acetate dihydrate was added. Reaction between $Zn(OAc)_2 \cdot 2H_2O$ and H_2L, both in 3:2 or 4:2 ratios, yielded $Zn_3(HL)_2(OAc)_4$. This latter could be crystallographically characterised, and rather surprisingly, the potentially tetradentate HL^- is only acting as an *O,N*-donor, while two phenolate and four acetate bridges hold together the three zinc ions. A study of the luminescence properties in methanol solution showed that the quantum yield of $Zn_3(HL)_2(OAc)_4$ ($\Phi_F = 0.07$) is slightly higher than that of 8-hydroxyquinoline-2-carboxaldehyde ($\Phi_F = 0.06$).

1. Introduction

During last years, 8-hydroxyquinoline and its derivatives have been the subject of a considerable number of papers, because they can be used as the emitting elements in electroluminescent devices [1,2]. Likewise, in supramolecular chemistry, 8-hydroxyquinoline derivatives [3–7] can be used for the formation of hydrogen-bonded networks, as well as of metal-supramolecular aggregates. To manipulate the self-assembly properties of the 8-hydroxyquinoline derivatives, some substituents that can act as additional hydrogen bond donor/acceptor units have been introduced [4,8].

The podant phenolate ligand H_2L (Scheme 1), which is derived from a 1:1 condensation of 8-hydroxyquinoline-2-carboxaldehyde and 2-aminoethanol, has been designed with the intention of adding a conjugated imine group to the chelating *O,N* binding site of the 8-hydroxyquinoline residue. In addition, the flexible 2-aminoethanol could add versatility for additional coordination, and facilitate the interconnection between molecules by means of hydrogen bonds.

Reaction between zinc acetate dihydrate and the free ligand have been assayed employing 3:2 and 4:2 molar ratios in order to study the influence of the stoichiometry on the formation of polynuclear complexes of the designed ligand. Assuming a monoanionic behaviour of H_2L, the use of 3:2 and 4:2 molar ratios provide the ideal amounts of metal ions for the obtaining of tri- and tetranuclear complexes of the types $M_3(HL)_2(OAc)_4$ and $M_4(HL)_2(OAc)_6$, respectively.

2. Experimental

2.1. Materials and methods

Zinc acetate dihydrate, 8-hydroxiquinoline-2-carboxaldehyde, and 2-aminoethanol of the highest commercial grades available were used as received, without further purification. Elemental analyses were performed on a Carlo Erba EA 1108 analyser. Positive ESI-TOF mass spectrum was recorded on a Bruker Microtof spectrometer, employing methanol as solvent. NMR spectra were recorded on Bruker spectrometers, using $[D_6]$-DMSO or $CDCl_3$ as solvents. Infrared spectra were recorded as KBr pellets on a Bio-Rad FTS 135 spectrophotometer in the range 4000–600 cm^{-1}. UV–Vis spectra in dilute MeOH solution (10^{-5} M) were recorded on a Kontron Instruments Uvikon 810 spectrophotometer. The emission and excitation spectra were measured in dilute MeOH solutions (10^{-4} M) at room temperature with a Jovin Yvon-Spex Fluoromax-2 spectrophotometer. Luminescence quantum yields were measured using a solution of pyrene in cyclohexane as a standard ($\Phi_F = 0.65$) and were corrected for the different refraction indices of the solvents [9].

2.2. Single crystal X-ray diffraction studies

Crystal data and some details of associated parameters are collected in Table 1. Diffraction data for $Zn_3(HL)_2(AcO)_4$ were

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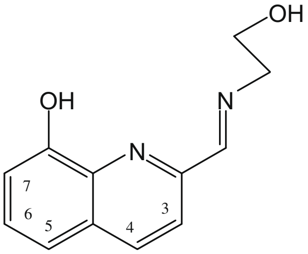
doi:10.1016/j.poly.2009.06.035



Scheme 1. Chemical structure of the 8-hydroxyquinoline derivative, 2-[(2-hydroxyethylimino)methyl]quinolin-8-ol (H_2L).

collected at 100 K on a Bruker CCD SMART1000 diffractometer, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) from a fine focus sealed tube. Data were processed and corrected for Lorentz, polarisation and absorption effects. The structure was solved by standard direct methods, and refined by full matrix least squares on F^2 using the SHELX-97 program package [10]. Non-hydrogen atoms were anisotropically refined, while H atoms of HL^- were found in the Fourier maps, and then isotropically treated. Methyl H atoms of the acetate groups were included in the structure factor calculation in geometrically idealised positions, with thermal parameters depending of the parent atom, although their orientations were also refined.

2.3. Ligand synthesis

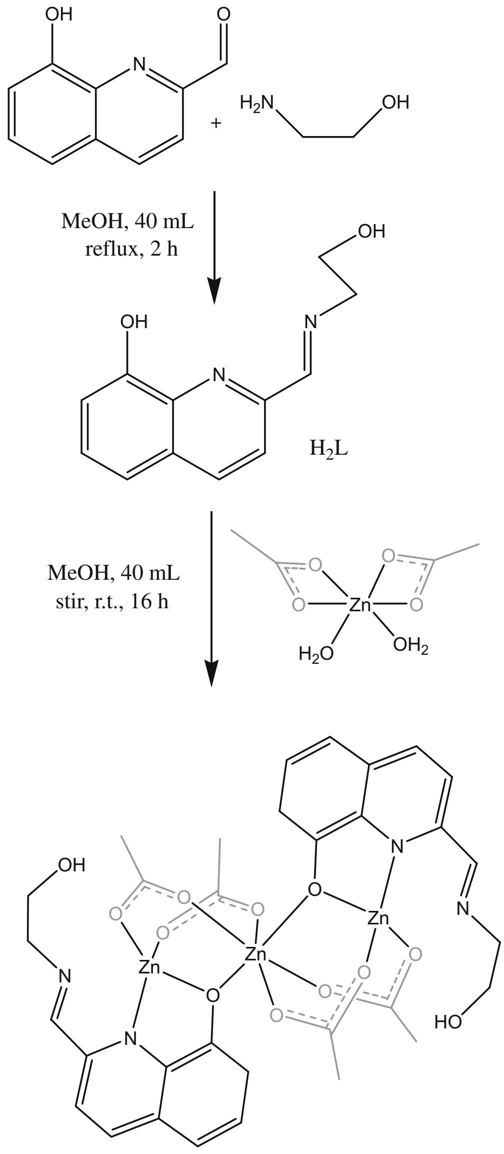
2-((2-Hydroxyethylimino)methyl)quinolin-8-ol (H_2L in Scheme 2) was obtained by refluxing a methanol solution (40 mL) containing 8-hydroxyquinoline-2-carboxaldehyde (0.352 g, 2 mmol) and 2-aminoethanol (0.12 mL, 2 mmol) for about 2 h. Vacuum concentration of the resulting yellow solution yielded a yellow solid that was filtered, washed with diethyl ether, and recrystallised in MeOH.

2.3.1. H_2L

Yellow powder (0.359 g, 83%). Anal. Calc. for $C_{12}H_{12}N_2O_2$ (M, 216.2 g.mol^{-1}) requires: C, 66.6; H, 5.6; N, 13.0. Found: C, 66.2; H, 5.4; N, 12.7%. m/z (ESI$^+$-TOF, methanol): 217.1 (100%) M$^+$; FTIR (KBr, cm^{-1}): $\nu(O_{phen}{-}H)$ 3379(b,s), ν(C=N) 1599(vs); ^{1}H NMR (300 MHz, $CDCl_3$, ppm) 8.57 (s, 1H, *H*CN), 8.55 (d, 1H, H3), 8.32 (d, 1H, H4), 8.16 (d, 1H, H5), 8.12 (t, 1H, H6), 8.07 (d, 1H, H7), 4.01 (t, 2H, H_2CO), 3.91 (t, 2H, H_2CN).

Table 1
Crystal and refinement data for $Zn_3(HL)_2(AcO)_4$.

	$Zn_3(HL)_2(AcO)_4$
Formula	$C_{32}H_{34}N_4O_{12}Zn_3$
M_r	862.74
Crystal system	monoclinic
Space group (No. 14)	$P2_1/n$
Unit cell	
a (Å)	7.680(1)
b (Å)	10.353(2)
c (Å)	20.773(4)
β (°)	90.973(3)
V (Å^3)	1651.6(5)
Z	2
D_c (Mg/m^3)	1.735
μ (mm^{-1})	2.233
F (0 0 0)	880
Intervalo de θ (%)	1.96 (Å) 27.10° (99.9)
Reflection collected/independent reflections	15389/3643
R_{int}	0.0515
Data/restraints/parameters	3643/0/278
R_1, wR_2 [$I > 2\sigma(I)$]	0.0267, 0.0676
R_1, wR_2 (all data)	0.0338, 0.0703
Residuals (e A^{-3})	0.448, −0.510



Scheme 2. Synthetic route used to obtain H_2L and $Zn_3(HL)_2(OAc)_4$.

2.4. Complex synthesis

$Zn_3(HL)_2(OAc)_4$ was obtained when 8-hydroxyquinoline-2-carboxaldehyde (0.176 g, 1 mmol) and 2-aminoethanol (0.06 mL, 1 mmol) were firstly refluxed in methanol (*ca.* 40 mL), and $Zn(OAc)_2{\cdot}2H_2O$ (0.329 g, 1.5 mmol) subsequently added to the resulting solution, which was stirred for about 16 h at room temperature. The same result was also obtained when using a 4:2 molar ratio. Vacuum concentration of the resulting solution yielded a solid that was filtered, washed with diethyl ether, and then dried in vacuum.

Single crystals suitable for X-ray diffraction studies were obtained from the mother liquor by simple evaporation at room temperature. Likewise, recrystallisation in acetone of the crude solid isolated from the mentioned reaction also resulted in the same. The same result was obtained by *r*.

2.4.1. $Zn_3(HL)_2(OAc)_4$

Orangish powder (0.240 g, 56%); Anal. Calc. for $C_{32}H_{34}N_4O_{12}Zn_3$ (M, 862, 8 g mol^{-1}) requires: C, 44.6; H, 4.0; N, 6.5. Found: C, 44.3; H, 4.0; N, 6.4%. FTIR (KBr, cm^{-1}): ν(C=N) 1620(vs), ν_a(COO)