



Synthesis, crystal structure and luminescence properties of acenaphthene benzohydrazide based ligand and its zinc(II) complex



Mukesh Kumar ^a, Soumyabrata Roy ^b, Md. Serajul Haque Faizi ^c, Santosh Kumar ^a, Mantu Kumar Singh ^a, Shyam Kishor ^d, Sebastian C. Peter ^b, Rohith P. John ^{a,*}

^a Department of Applied Chemistry Indian School of Mines, Dhandad 826004, Jharkhand, India

^b New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560064, India

^c Department of Chemistry, Indian Institute of Technology Kanpur 208016, Uttar Pradesh, India

^d Department of Chemistry, J. V. College, Baraut, Uttar Pradesh 250611, India

ARTICLE INFO

Article history:

Received 2 March 2016

Received in revised form

3 August 2016

Accepted 5 August 2016

Available online 6 August 2016

Keywords:

Zinc complexes

Benzohydrazide

Crystal structure

Photoluminescence

DFT studies

ABSTRACT

The complex compound of zinc(II) supported by (Z)-2-hydroxy-N'-(1-oxoacenaphthylen-2(1H)ylidene) benzohydrazide ligand (H_2L^1) has been reported and discussed. The reaction of zinc acetate with H_2L^1 ligand leads to the formation of a mononuclear zinc(ii) complex, $[Zn(HL^1)_2H_2O]$. The ligand, H_2L^1 has been characterized by elemental analysis, 1H , ^{13}C and 1H -COSY-NMR, IR and ESI-MS, while the complex was characterized by elemental analysis, IR, and ESI-MS. The crystal structures of the free ligand H_2L^1 and the complex have also been determined by single crystal X-ray diffraction. The ligand chelates with metal centre with a nitrogen atom of imino moiety and an oxygen atom of enolic group. The complex shows distorted trigonal bipyramidal geometry around the metal centre with oxygen atoms lying in the equatorial plane and imino nitrogen atoms along the axial direction. The DFT/TD-DFT calculations were performed on both the ligand and its zinc complex to get insight into the structural, electronic and optical properties. The photoluminescence, fluorescence properties of the complex have been investigated.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

A large number of Schiff base derived ligands and their complexes of transition, inner transition and main group elements have been studied extensively over the past few decades [1–5]. Zinc(II) complexes of Schiff base compounds which are thermally stable, structurally diverse and easily modifiable have attracted great interest due to their potential applications in photoluminescence materials, bio sensors and as therapeutic drugs. Besides, ligands possessing N and O donors also have great interest in inorganic, organic biomimetic and medicinal chemistry. Transition metal complexes of hydrazones and their derivatives are reported to have been used as selective chemo sensors [6,7], anti-bacterial and anti-fungal agents [8–22], and as potential anti-cancer agents [23–25]. Some of the complexes exhibit their inhibitory activity by means of their ability to bind specific DNA targets in the cell by intercalation [26–28]. In a few instances, the complexes of hydrazones also show

improved anti-oxidant activity compared to their ligands [29,30]. A recent clinical study finds two salicylaldehyde benzoylhydrazone zinc(II) complexes as having potent anti-inflammatory activity [31,32]. The chelating ability of hydrazone type ligands with transition metals and lanthanide ions make them attractive as analytical reagents for spectrometric determinations [33,34] and are therefore used for sensitive spectrofluorimetric determination of trace amounts of these cations [35–42]. Some of the bis-hydrazide compounds have been used for detection of zinc in cancerous cells owing to fluorescent emission properties of their complexes [43]. The fluorescence emission behavior of acenaphthaquinone derived compounds and their complexes have been widely employed to study photophysical properties [44,45] and in bio-imaging applications [46–48]. Acenaphthenequinone based zinc(II) complexes exhibit comparable cytotoxicity with respect to *cis*-platin in the MCF-7 cell line and exhibited fluorescence emission property as well [49]. In the above context, considering the immense opportunities in bio-imaging applications, we have designed and synthesized a ligand, H_2L^1 , obtained by condensation of 2-hydroxybenzohydrazide and acenaphthaquinone [(Z)-2-hydroxy-

* Corresponding author.

E-mail address: rohithjohn@gmail.com (R.P. John).

N'-(1-oxoacenaphthyl-2(1H)ylidene) benzohydrazide] (Scheme 1) as a target system with potential photo luminescent properties. Herein we report, the synthesis, structural characterization of the new acenaphthene derived ligand and its mononuclear zinc(II) complex. The work also involves correlation of structural and electronic properties using DFT/TD-DFT and investigation of their photoluminescence behavior.

2. Experimental

2.1. Materials and methods

All the reagents were purchased from commercially available sources such as Sigma-Aldrich (USA), Merck (India) or Spectrochem (India). All solvents were purified by standard methods before use, while the fine chemicals obtained from Sigma-Aldrich was used without further purification. NMR spectra were recorded on a Jeol NM-ECS 400 MHz and Bruker Avance II 400 MHz spectrometer in DMSO-*d*₆ solvent. FT-IR spectra were recorded on a Perkin Elmer RXI FTIR spectrometer as KBr discs in the range of 4000–400 cm⁻¹ with 4 cm⁻¹ resolution and 20 scans. Elemental analyses were performed on a Vario Micro cube analyser by Elemental analyser system GMBH. UV–Vis measurements were recorded on a Shimadzu – UV-2450 spectrophotometer in DMF solution using quartz cells. The ESI-Mass spectra was recorded on a VARIAN 410 Prostar Binary LC with 500 MS IT PDA in positive mode. The photoluminescence spectra were measured in powder samples at room temperature by using a HITACHI F 2500 Fluorescence Spectrophotometer of 150 V Xenon lamp. The fluorescence measurements were carried out on a Perkin Elmer LS 55 Fluorescence spectrometer in DMF solvent. Both excitation and emission slit widths in the solid state were 10 nm and that for solution were 12 nm.

2.2. Synthesis of ligand (H₂L¹)

Acenaphthenequinone (100 mg, 0.55 mmol) was taken in an R.B flask, mixed with glacial acetic acid (10 mL) and heated to 60 °C for 15 min. After that a solution of 2-hydroxybenzohydrazide (295 mg, 1.93 mmol) in glacial acetic acid (5 mL) was added drop wise to this solution [50]. Then reaction mixture was refluxed for 1.5 h along with stirring, cooled to room temperature. Then the reaction mixture was poured into ice followed by neutralization with an aqueous solution of K₂CO₃ which resulted in a yellow precipitate. It was then collected by vacuum filtration and dried under vacuum in the presence of P₂O₅ (yield: 96.0%). (m.p.>250 °C), Anal. data Calc. for C₁₉H₁₂N₂O₃: Calc. C, 72.15; H, 3.86; N, 8.86. Found C, 71.95; H, 3.67; N, 8.69%. Exact Mass: 316.08 Selected IR data (KBr, ν cm⁻¹): 3463 ν(OH), 3210(sh), 3147(broad) ν(N–H), 1701(s), 1642 ν(C=O), 1606(m) ν(C=N), 1516(w), 1487(w) 1354(s), 1283(s), 1144(s), 954(m), 774(m), 689(m). ¹H NMR spectrum, (DMSO-*d*₆, 400 MHz, δ): 14.65 (s, 1H), 11.81 (s, 1H), 8.36 (d, 1H, *J* = 8.12 Hz), 8.13 (d, 1H, *J* = 8.32 Hz), 8.08 (d, 1H, *J* = 3.24 Hz), 8.07 (d, 1H, *J* = 7.88 Hz), 7.99 (d, 1H, *J* = 6.92 Hz), 7.88 (t, 1H, *J* = 7.6 Hz), 7.82 (t, 1H, *J* = 7.6 Hz), 7.45

(t, 1H, *J* = 7.68 Hz), 7.08 (d, 1H, *J* = 7.86 Hz), 7.00 (t, 1H, *J* = 15.12 Hz), ¹³C NMR spectrum, (DMSO-*d*₆, 100 MHz, δ): 187.4, 162.9, 156.5, 142.2, 139.1, 134.3, 132.6, 131.5, 130.6, 130.4, 129.9, 129.5, 128.5, 127.1, 121.9, 119.7, 118.1, 117.4, 116.8; ESI mass (*m/z*) M+1, 317.09.

2.3. Preparation of zinc complex [Zn(HL¹)₂(H₂O)]

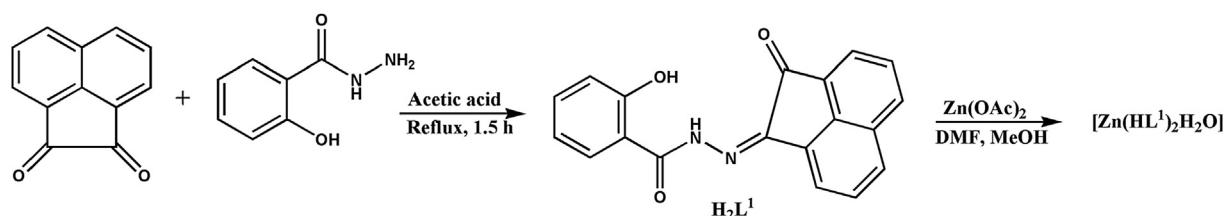
The ligand H₂L¹ (63 mg, 0.2 mmol) was dissolved in 6 mL DMF and layered with Zn(OAc)₂·2H₂O (21 mg, 0.1 mmol) in methanol (10 mL), microcrystals of [Zn(HL¹)₂H₂O], were obtained when set aside overnight (Yield: 130 mg, 90%). X-ray quality single crystals were obtained when a solution of the zinc(ii) complex in DMF was layered with methanol as red coloured crystals in 6–7 days. Anal. Calc. for C₃₈H₂₄N₄O₇Zn: Calc. C, 64.10; H, 3.65; N, 7.72. Found, C, 64.28; H, 3.78; N, 7.84. IR (KBr pellet, cm⁻¹): 3391(b), 3258(b), 3058(m), 1702(m), 1658(m), 1609(m), 1580(m), 1503(w), 1363(w), 1176(s), 1009(w), 962(w), 765(w).

2.4. Single crystal X-ray diffraction (SCXRD)

SCXRD data for ligand H₂L¹ and zinc complex were collected on a Bruker Smart X2 APEX II CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source with graphite monochromatic Mo-Kα radiation (λ = 0.71073 Å) operating at 50 kV and 30 mA, with ω scan mode. Bruker SAINT [51] was used for integration of diffraction profiles and absorption corrections were made with Bruker SADABS [52]. Structures were solved by direct method and followed by successive Fourier and difference Fourier Syntheses using SHELXL 97 [53] and SHELXS-97 programs [54], all non-hydrogen atoms were refined anisotropically and hydrogen atoms were allowed to ride on their respective parent atoms with isotropic displacement parameter 1.5eq for methyl, 1.2eq for CH₂ and OH respectively. WinGX system 1.80.05 [55,56] was used for preparation of publication data. Crystallographic data and details of refinements are reported in Table 1.

2.5. Computational methodology

Geometric and frequency optimization of the zinc(ii) complex was performed using Gaussian 9.0 supported by GaussView 5.0 [57]. The starting geometries for the calculations were taken from the structure obtained from SCXRD data. First principles calculations were carried out within the framework of density functional theory (DFT) using the Becke Three-parameter Hybrid Functional using the Lee-Yang-Parr (LYP) Correlation Functional [58] and the 6-31G basis sets as implemented in the Gaussian 09 software package. The structure of the ligand and the complex were optimized in dimethyl formamide (DMF) solvent via direct inversion in iterative subspace (DIIS), until the largest component of the ionic forces attained a value 0.00045a.u. Absence of imaginary vibration during harmonic vibration frequency calculations confirmed that the optimized structures are at the local minima. The polarisable continuum model (CPCM) was employed to investigate the effect of



Scheme 1. Synthetic route of H₂L¹ and [Zn(HL¹)₂H₂O] complex.

Download English Version:

<https://daneshyari.com/en/article/1408685>

Download Persian Version:

<https://daneshyari.com/article/1408685>

[Daneshyari.com](https://daneshyari.com)