Iranian Journal of Organic Chemistry Vol. 3, No. 2 (2011) 611-614

Synthesis and characterization of new four-coordinated Zinc(II) complex containing phenanthroline derivatives

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Received: February 2011; Revised: February 2011; Accepted: April 2011

Abstract: The tetrahedral Zinc(II) complex [Zn(biq)Br_2] where biq = biquinoline was synthesized and characterized by IR, UV– vis, ^{1}H- NMR spectroscopies, CV and elemental analysis. The cyclic voltammetry study in DMF gave all the expected waves for the redox processes of the ligands.

Keywords: Cyclic voltammetry; Redox processes; Tetrahedral; Biquinoline**.**

Introduction

The role of zinc in a wide range of cellular processes, including cell proliferation, reproduction, immune function and defense against free radicals, has been well established [1].

2,2'-Biquinoline (abbreviated as biq) and its derivatives owing to their strong photoluminescence and electroluminescence properties [2] are widely used in various thin film application devices system to mimic photosynthetic light harvesting [3]. When biquinoline derivatives are attached to certain other suitable liquid crystal, electro-optical display is observed [4]. Moreover these compounds could find applications as the parent compound to make drugs especially anti-malarial medicines, fungicides, biocides, alkaloids [5], rubber chemicals and flavoring agents. Previous studies show that, the bidentate nitrogen donor ligands such as pyridine, di- and polypyridine and their derivatives are also of great interest due to their ability to modify chemical, catalytic, photochemical properties and facile electrochemical process. Furthermore, their ability to absorb visible light to act as electron reservoirs are promising factors in their applications as photosensitives [6-14]. The complexes of zinc chelates with bidentate heterocyclic nitrogenous bases, such as biquinoline not only have nitrogenous important biological properties [15], but also have bases, such as biquinoline not only have important biological properties [15], but also have gained importance of their versatile roles as building blocks for the synthesis of metallo-dendrimers and as molecular scaffolding for supramolecular assemblies, and in analytical chemistry, catalysis, electrochemistry, ring-opening metathesis polymerization and biochemistry [16-30]. Hence, several of the first-row transition metals play major roles in a diverse range of enzymatic and electon-transfer processes in biological systems. In this present paper we report the synthesis of new zinc(II) addition compound under the formula [Zn(biq)Br_2]. The resultant tetrahedral compound was characterized by physico-chemical methods and spectroscopic studies (IR, UV–Vis). The cyclic voltammetry (CV) study was employed to investigate its electrochemical behavior. Correlation between theoretical results and electronic excitation data was under taken and the results are presented and discussed.

Results and discussion

The reaction of $ZnBr_2$ with 2,2'-biquinoline led to the formation of the crystalline colorless product. This compound is insoluble in water and common organic solvents such as acetonitrile, chloroform and soluble in dimethylformamid (DMF), dimethylsulfoxide (DMSO) and leading to deep blue solution. This complex is

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stable in air at room temperature. Single crystal structure of [Zn(biq)Br_2] has been characterized [31]. The coordination mode of the ligand in the compound was studied using spectroscopic methods.

Infrared spectral data of the free ligand and corresponding compound are presented in Table **1** and were assigned according to literature [33]. The IR frequency shifts (relative to the free ligands) of the amide NH bands exhibited by the diamide complexes were used to establish whether coordination occurs through the amide nitrogen atoms [34] and whether coordination involving nitrogen donors is accompanied by deprotonation. Vibrational spectra were run in the IR region to determine the disposition (tetrahedral or octahedral) of the bromide ligands in the Zn(II) complexes. Although the two Zn-Br bands characteristic of tetrahedral geometry about the metal centre (at *ca.* 180 and 200 cm^{-1}) [35] were not present in the IR spectra of the [Zn(biq)Br_2], but we assigned a band at 184 cm^{-1}. Due to the presence of a single band is attributed to accidental degeneracy of the symmetric and asymmetric Zn–Br stretches, and is considered to indicate distorted tetrahedral zinc geometry [36, 37].

Table 1: Selected IR frequencies of 2,2'-biquinolin and complex [Zn(biq)Cl_2].

Compound	ν(C=C), ν(C=N)	ν(Zn-N)	ν(Zn-Br)
2,2'-Biquinoline	1423, 1508, 1550, 1614	-	-
[Zn(biq)Br_2]	1333, 1430, 1505, 1586	318	184

The IR spectrum of the free biquinoline has a sharp band at 1614 cm^{-1} associated to the stretching frequency of the C=N band [33, 34]. It was observed that this band did not shift considerably in the corresponding complexes, which is reasonable since the C=N moieties are far from the site of coordination of this ligand with the metal ion [32,38]. The IR spectrum of the complex [Zn(biq)Br_2] shows a band around 1586 cm^{-1} assigned to the ν(C=N) band of the biquinoline ligand. The band at 318 cm^{-1} was assigned to Zn-N stretching. In addition the Zn-Br frequencies appear at 180 cm^{-1} which is characteristic of distorted tetrahedral zinc geometry [36-40].

Electronic spectrum of the [Zn(biq)Br_2] was taken in DMF solution and exhibits several absorption bands in the UV region. The intense bands in the UV region, present at around 242 nm (logε = 5.3), 264 nm (logε =5.7), 314 nm (logε = 5.3), 326.0 nm (logε = 5.4), 338 nm (logε = 5.3) in complex were assigned to intra ligand π → π* transition, evidence arising from the position and intensity, as well as from the comparison with the spectra of the free ligand, [41], Figure **1**.

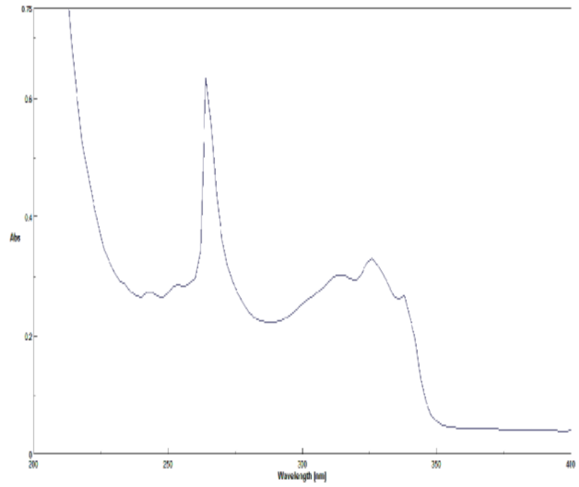

Fig. 1. UV-vis absorption spectra of [Zn(biq)Br_2]in DMF (1.35×10^{-6} M).

Cyclic voltammetry was used as a powerfull technique in electrochemical investigation of this complex in nonaqueous solution. The electrochemical data for 2,2'-biquinoline ligand has been previously reported but is reproduced here for comparison[42]. The free ligand 2,2'-biquinoline exhibits one reversible reduction step at -1.62 V, which is assigned to a one-electron addition to the lowest unoccupied molecular orbital (LUMO) to give $(\pi^*)^1$ electronic configuration [43]. A further irreversible reduction step can be assumed at approximately -2.12 V. Due to the electrochemically innocent behavior of the Zn(II) ion in comparison to other biquinoline transition metal complexes, there is not any reduction couple associated to metal center [44-46].

For this complex one quasi reversible wave related to free ligand in negative potential (E_{pc}≈-1.6 ; E_{pa}≈-1.2) and one quasi reversible peak in positive potential (E_{pc}≈+0.2 ; E_{pa}≈+0.4) and one irreversible wave at +1.8 V attributed to DMF solvent .

The ^1H NMR spectra for the free biquinoline and [Zn(biq)Br_2] show six signals at 7.5–8.9 ppm. The relative intensities of these signals are in accord with the proposed structure. Due to high lebility of Zn(II) complex to exchange of ligand, the ^1H-NMR signals are broad and difficult to see the splitting of each peak (Figure **2**)[48].

Conclusion

In this article, we have synthesized a tetrahedral complex of Zn(II), [Zn(biq)Br_2] and characterized it by

IR, UV-vis, CV and single crystal X-ray diffraction methods.

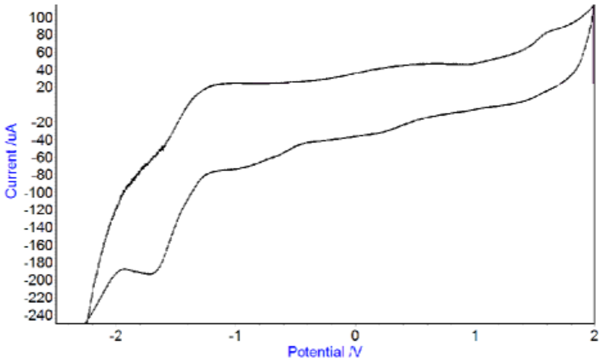

Fig. 2. Cyclic voltammogram of [Zn(biq)Br_2] in DMF at scan rates of 100mVs^{-1}; 0.1 M TBAH as a supporting electrolyte.

Experimental

Instrumentation/analytical procedures

All chemicals and solvents were reagent grade or better, obtained from either Merck or Aldrich and used without further purification. Infrared spectra (4000-250 cm^{-1}) of solid samples were taken as 1% dispersion in KBr pellets using a Shimadzu-470 spectrometer. Electronic absorption spectra in DMF solution at room temperature were taken on a Cary Bio 300 spectrometer. All the voltammetric analysis was performed using an SAMA500, potentiostat/galvanostat (Iran) connected to a three-electrode cell, linked with a computer (Pentium IV) and with SAMA software. A platinum wire was used as the auxiliary electrode. Glassy carbon electrode and Ag wire were used as the working and reference electrodes, respectively. The glassy carbon working electrode was manually cleaned with 1-µm diamond polish prior to each scan. The supporting electrolyte, 0.1 M tetrabutylammonium hexafluorophosphate (TBAH), was recrystallized twice from ethanol-water (1/1) and vacuum-dried at 110°C overnight. Scan rates 100-500 mV s^{-1} were used for electrochemical investigation.

Ferrocene was used as an internal standard to compensate the junction potential variability among experiments.Elemental analysis was performed using a Heraeus CHN–O Rapid analyzer.

Preparation of [Zn(biq)Br_2]

To a methanolic solution (20 ml) of $ZnBr_2$ (0.225 g, 1 mmol) was added 2,2'-biquinoline (0.253g, 1 mmol) dissolved in 20 ml mixture of 1:1 methanol/chloroform. The resulting solution was stirred at 55-60 ºC for 2h. The solid (desired product) was collected by suction filtration, washed with acetone then air dried. (yield 0.57g, 74%, decomposed > 300°C). IR (KBr, cm^{-1}): 1586m, 1505s, 1430s, 1361m, 1333w, 1212s, 1142s, 953w, 870s, 829s, 782s, 747s, 484s, 318s υ(Zn-N), and 180s υ(Zn-Br). *Anal. Calc:* C, 44.90; H, 2.51; N, 5.82; Found: C, 45.07; H, 2.74; N, 5.71.

Acknowledgements

The authors are grateful to University of Sistan and Baluchestan for partial financial support.

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