



Research Article

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Synthesis and characterization of Hg complex with 1,4-bis([1,10]phenanthroline-[5,6-d]imidazol-2-yl)benzene

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ABSTRACT

A new Hg(II) complex of the type $[(\mu\text{-BPIB})\{\text{Hg}(\text{NO}_3)_2\}_2](\text{I})$ that BPIB = 1,4-bis([1,10] phenanthroline-[5,6-d]imidazol-2-yl)benzene has been synthesized and characterized using FT-IR, UV-vis and $^1\text{H-NMR}$ spectroscopies. Also electrochemical behavior of complex (I) was studied by Cyclic Voltammetric method. The FT-IR results showed that the ligand was coordinated to metal center. Electronic spectra of this complex was recorded in the DMSO solution. These spectra confirm the intraligand transition bands ($\pi\rightarrow\pi^*$), ($n\rightarrow\pi^*$) in UV region. The UV-vis spectrum of title complex don't show any $d\rightarrow d$ transition for central ion. Electrochemical data of this complex showed quasi-reversible waves attributed to redox BPIB ligand.

Keywords: Electrochemical; Cyclic Voltammetric; Metal Center; Intraligand Transition; Quasi-Reversible

INTRODUCTION

1,10-phenanthroline (phen) has a rigid framework and possesses a superb ability to coordinate to many metal ions[1]. This ligand is an attractive π -conjugated ligand and various metal complexes of phen and its derivatives have been synthesized [2].

1,4-bis([1,10] phenanthroline-[5,6-d]imidazol-2-yl)benzene (BPIB) is one of the phenanthroline derivatives that was synthesized for the first time in ethanol solvent by Mr Nobuaki Negishiy, in 2003, and many years later, in 2007. It was synthesized and detected, in acetic acid solvent by Chaofan Zhong and et al. [3].

BPIB contains two 1,10-phenanthroline groups and has two nitrogen donors on two sides that can chelate to two metal centers [4]. BPIB has a big π -conjugated structure, which results in maximum emission leading to red shift [5-7]. This ligand possesses empirical formula $\text{C}_{32}\text{H}_{18}\text{N}_8$ and its melting point is 120°C . It can be said that due to the benzene ring in the center of the ligand, it is considered as a flat ligand and especially the presence of imidazole double bonds reduces the possibility of rotation. Some applications of this ligand are catalytic role, special electrical and optical properties and also can be used as create polymeric complexes and molecular switches.

EXPERIMENTAL SECTION

Materials

All materials were obtained from Merck Co. and were used without any further purification. All solvents used in this work were analytical grade.

Instrument and measurements

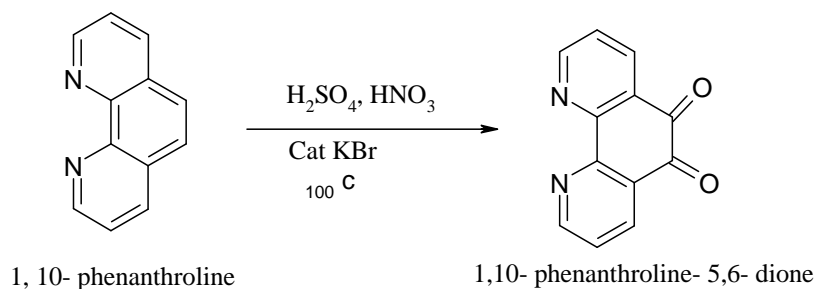
The FT-IR spectra were obtained on a Perkin-Elmer spectrum (KBr pellet). NMR spectra were recorded on a Bruker NMR400 spectrometer operating at 400 MHz at room temperature in DMSO solution. Ultraviolet visible (UV-vis) spectra were measured with JASCO V-570 spectrophotometer in DMSO solvents.

Cyclic voltammograms were recorded by using a Metrohm 694 apparatus. Three electrodes were utilized in this system, a platinum disk working electrode (RDE), a platinum wire auxiliary electrode and Ag/AgCl reference electrode. The platinum disk working electrode was manually cleaned with 1- μ m diamond polish prior to each scan. The supporting electrolyte, 0.1 M tetrabutylammoniumhexafluorophosphate (TBAH). DMF was distilled over alumina and degassed under vacuum prior to use in cyclic voltammetry. The solutions were deoxygenated by bubbling with Ar for 15 min.

Synthesis

Synthesis of 1,10-phenanthroline-5,6-dione (phen-dion)

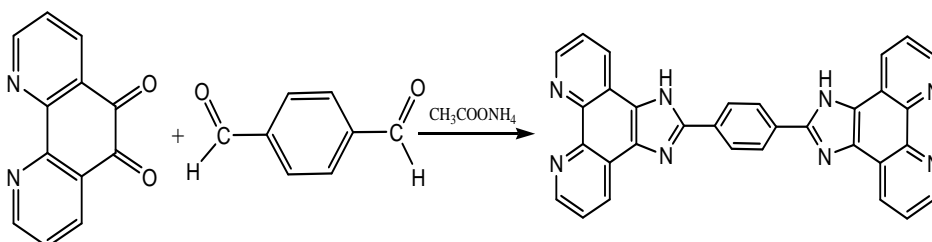
A mixture of 1,10-phenanthroline (4.0 g, 19 mmol) and KBr (4.0 g, 33 mmol) were added to a three-necked flask equipped with a dropping funnel. Then ice-cold mixture of concentrated H_2SO_4 (40 mL) and HNO_3 (20 mL) were added to this solution drop-wise. The mixture was heated to reflux for 4 h. The hot yellow solution was poured over 600 mL of ice and water and neutralized carefully with NaOH until neutral to slightly acidic pH was attained. Extraction with CHCl_3 was followed by drying with anhydrous Na_2SO_4 and removal of solvent and the precipitate was purified further by crystallization from absolute ethanol to give 5.6 g (96%) of 1,10-phenanthroline-5,6-dione [11]. Scheme 1 shows the synthesis of the 1,10-phenanthroline-5,6-dione (phen-dion) ligand from 1,10-phenanthroline (phen).



Scheme 1. Synthesis of the phen-dion ligand

Synthesis of 1,4-bis([1,10] phenanthroline-[5,6-d]imidazol-2-yl)benzene (BPIB)

The mixture of 0.335 g (0.25 mmol) of terephthalaldehyde, 0.105 g (0.5 mmol) of phenO₂ and 1.2 g of ammonium acetate in EtOH (100 mL) was refluxed for 7 h. During this time, the color gradually changed due to an orange precipitate is produced. The reaction mixture was cooled and EtOH was removed by rotary evaporation. After addition of water, the orange product was filtered off, washed with water and EtOH. Yield: 70%. Anal. Calc. C, 74.70; H, 3.52; N, 21.78. Found: C, 74.40; H, 3.43; N, 20.91. Scheme 2.

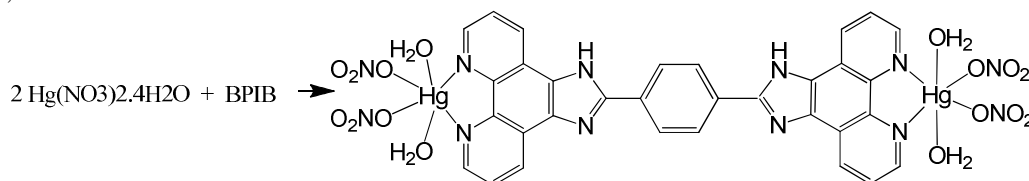


Scheme 2. Synthesis of the BPIB ligand

Synthesis of $[(\mu\text{-BPIB})\{\text{Hg}(\text{NO}_3)_2(\text{H}_2\text{O})_2\}_2](1)$

A DMSO solution (20 mL) of the ligand BPIB (0.257 g, 0.5 mmol) was added to a methanol solution (10 mL) of $\text{Hg}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.561 g, 1 mmol). The mixture was stirred for 48 h at 60°C. After removing the solvent, the precipitate was washed enough with absolute methanol until the filtrate was yellow, and then dried in vacuo at

appropriate temperature. Yield: 65%, Anal. Calc: C,31.66; H, 2.42; N, 13.43; O,20.45; Found: C, 31.69; H, 2.48; N, 13.50; O, 20.50. Scheme 3.



Scheme 3. Synthesis of $[(\mu\text{-BPIB})\{\text{Hg}(\text{NO}_3)_2(\text{H}_2\text{O})_2\}]_2(\mathbf{1})$

RESULTS AND DISCUSSION

The ligand and complex were fully characterized by FT-IR, UV-vis, $^1\text{H-NMR}$ and CV.

3.1. FT-IR spectra

Infrared spectral data of the free ligand and corresponding complex have been compared. The IR spectrum of the free BPIB contains a sharp band at 1620 cm^{-1} associated with the stretching frequency of the $\text{C}=\text{N}$ bond [12]. On complexation this frequency was observed to 1530 cm^{-1} that shift to a lower wavenumber [13]. The IR frequency shifts (relative to the free ligand) of the amide NH bands exhibited by the diamide complexes were used to establish whether coordination occurs through the amide nitrogen atoms and whether coordination involving nitrogen donors is accompanied by deprotonation [14]. The band around 1500 cm^{-1} assigned to NO_2 groups in complex. The IR spectrum of the complex (**1**) shows the band at 327 cm^{-1} associated with the stretching frequency of the Hg-N bond [15].

UV-vis spectra

Electronic spectrum of $[(\mu\text{-BPIB})\{\text{Hg}(\text{NO}_3)_2(\text{H}_2\text{O})_2\}]_2(\mathbf{1})$ in DMSO solution is shown in Fig. 1. UV-vis spectra shows two absorption bands in 255, 290 nm that attributed to the intra ligand transitions ($\pi \rightarrow \pi^*$) of phenanthroline and one absorption band at 370 nm related to ($\pi \rightarrow \pi^*$) of benzene which overlap with ($n \rightarrow \pi^*$) of phenanthroline [16-17]. Another bands at 380 nm and 395 nm are attributed to charge transfer (MLCT) from d-orbitals of Hg^{2+} to π^* phenanthroline ligand [18]. Also, UV-vis spectrum of title complex don't show any $d \rightarrow d$ transition of central ion.

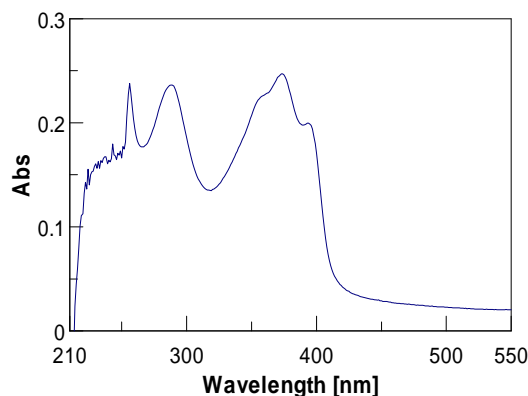


Fig 1. Absorption spectrum of $[(\mu\text{-BPIB})\{\text{Cd}(\text{NO}_3)_2\}]_2$ in DMSO solution

3.3. Electrochemical studies

Electrochemical behavior of the BPIB ligand and complex (**1**) with scan speed of 500 mvs^{-1} , in the DMF solvent were studied and show in Fig.2 and Fig.3. Voltammograms of the ligand and complex, shows cathodic and anodic steps which are corresponding to the oxidation and reduction of the ligand. Table.1. show electrochemical data of BPIB ligand and complex (**1**). [19-20]

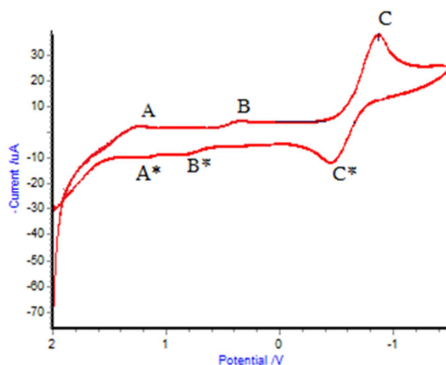


Fig 2. Cyclic voltammogram of BPIB ligand in DMF solution

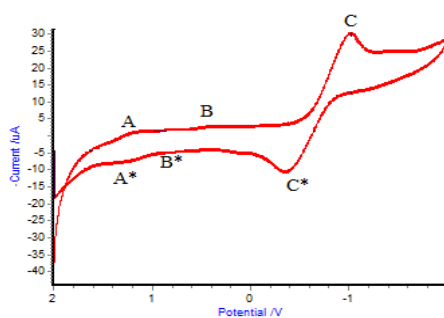


Fig 3. Cyclic voltammogram of [(μ-BPIB){Cd(NO₃)₂}₂] in DMF solution

Table 1. Electrochemical data for Ligand (BPIB) and complex(1) in DMF solution

BPIB	1.18/1.22 (AA*)	0.38/0.82 (BB*)	-0.89/-0.47 (CC*)
[(μ-BPIB){Cd(NO ₃) ₂ } ₂](1)	1.16/1.25 (AA*)	0.34/0.82(BB*)	-0.38/-0.10 (CC*)

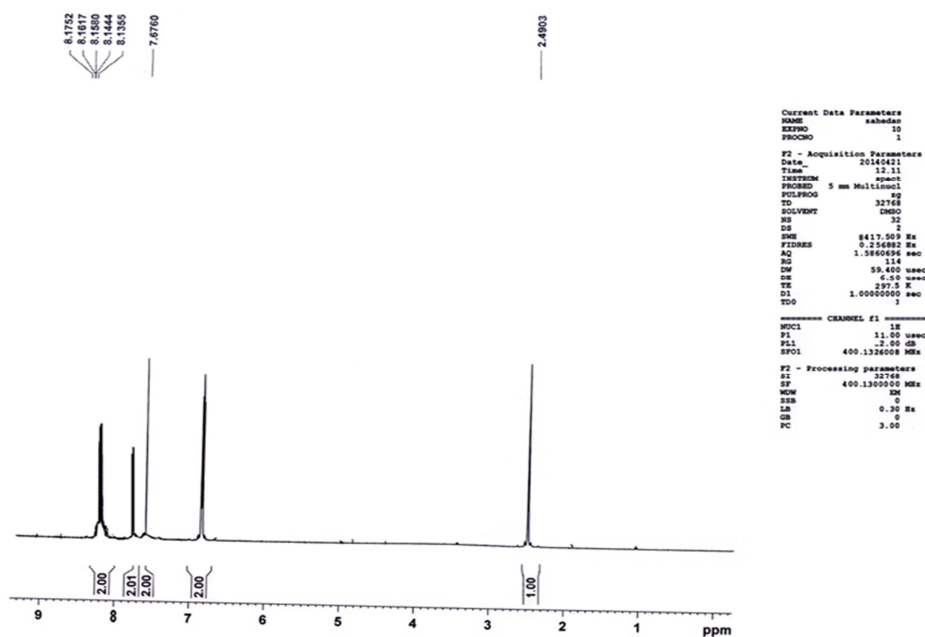


Fig4. ¹H-NMR spectrum of BPIB ligand

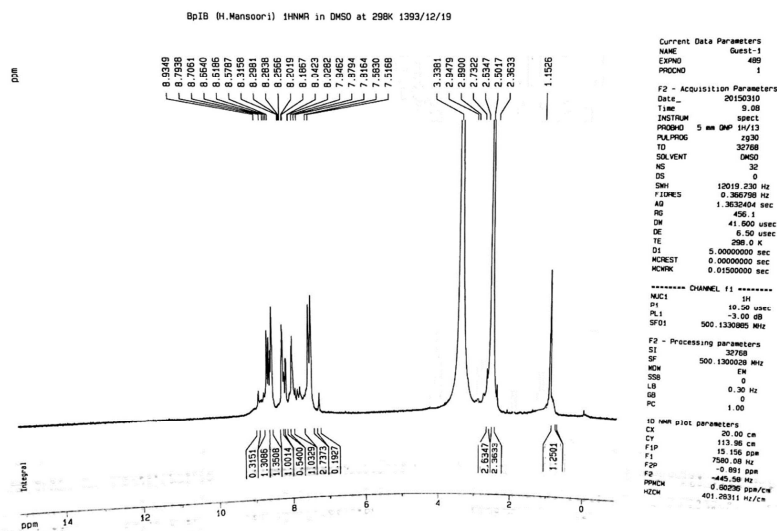


Fig 5. $^1\text{H-NMR}$ spectrum of $[(\mu\text{-BPIB})\{\text{Cd}(\text{NO}_3)_2\}_2]$

3.4. $^1\text{H-NMR}$ spectra

$^1\text{H-NMR}$ is a very powerful tool for characterization of compounds in solution. Figs.4 and 5 show the ^1H NMR spectra of free BPIB and complex(1) respectively in DMSO-d_6 solution at 25°C . Hydrogen atoms of imidazol groups are seen at 2.4 ppm in BPIB. These protons near to metal center accordingly appear in up field in complex (1) and are seen at 1.15 ppm in $[(\mu\text{-BPIB})\{\text{Cd}(\text{NO}_3)_2\}_2]$ (1). The signals observed in the region of 7-9 ppm in Figs. 4 and 5 are corresponding to phenanthroline groups.

CONCLUSION

In summary, we have successfully prepared complex of Hg with bridging ligand obtained from 1-10 phenanthroline. This compound has been characterized using FT-IR, UV-Vis, $^1\text{H-NMR}$ and Cyclic voltammetry (CV) techniques. The IR spectra suggest involvement of unsaturated nitrogen atoms of the $\text{C}=\text{N}$ moieties groups in bonding with the central metal ions. Cyclic voltammetry technique show complex(1) has good electrochemical behavior. Presence BPIB ligand in this compound causes catalytic and electron transfer properties in complex(1). Also this compound can be used to form an electrochemical polymer.

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