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

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Abstract: The metal complex of 1,4-bis([1,10] phenanthroline-[5,6-d] imidazol-2-yl)benzene (BPIB) with Cadmium(II) ion has been synthesized and characterized using FT-IR, UV-vis, elemental analysis, ^{1}H-NMR also electrochemical behavior was studied by Cyclic Voltammetric method. The FT-IR results showed that the ligand is coordinated to metal center. Electronic spectra of this complex was recorded in DMSO solution (1×10^{-5} M). These spectra confirm the intraligand transition ($\pi\rightarrow\pi^*$), ($n\rightarrow\pi^*$) bands in UV region. UV-vis spectrum of title complex doesn't show any d→d transition of central ion. Electrochemical data of this complex show quasi-reversible weaves attributed to redox BPIB ligand.

Keywords: Metal complex, Phenanthroline, Electrochemical behavior, Intraligand transition.

Introduction

1,10-Phenanthroline(phen) has a rigid framework and possesses a superb ability to coordinate many to metal ions[1]. This ligand is π-conjugated and various metal complexes have been synthesized with its derivatives [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 Nobuaki Negishiy, in 2003, and many years later, in 2007, it was synthesized and detected, in acetic acid solvent by Chaofan Zhong et. al. [1, 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 redshif [5-7]**.** This ligand possesses empirical formula $C_{32}H_{18}N_8$ with melting point 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 bands reduces the possibility of rotation.

Application of this ligand may be made to:

- ➢Catalyst role
- ➢Create polymeric complexes
- ➢Magnetic and superconducting properties
- ➢Molecular switches and simulate biological systems
- ➢Special electrical and optical properties [1, 4, 6-10]

Results and discussion

The following scheme (Scheme **1**) shows the synthesis of the 1,10-phenanthroline- 5,6-dion (phendion) ligand from 1,10 phenanthroline (phen).

Scheme **2** shows overview of the synthesis of BPIB ligand from phendion [11], terephthaladehyde and ammonium acetate.

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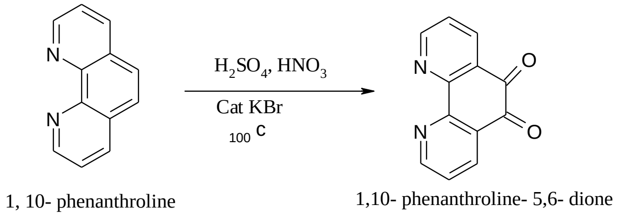
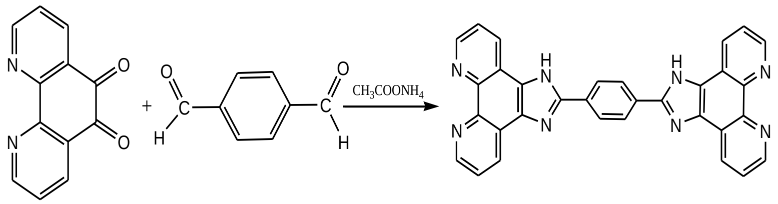
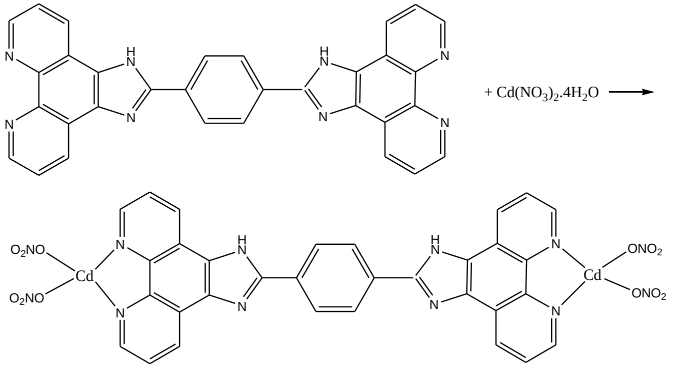


Scheme 1: Synthesis of the phen-dion ligand [11].



Scheme 2: Synthesis of the BPIB ligand.

As can be seen, ammonium acetate is as a source of ammonia for imidazole ring closure. Also, the following Scheme (Scheme **3**) shows the connection of Cd $(NO_3)_2.4H_2O$ to the BPIB ligand.



Scheme 3: Synthesis of the complex$[(\mu\text{-BPIB})\{Cd(NO_3)_2\}_2]$.

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

FT-IR spectra:

The FT-IR spectra of ligand and complex are shown in Figures **1** and **2**.

Comparison of the ligand and complex spectrum show that the H-N band in complex shifts from 3415.47 cm^{-1} to 3414.51 cm^{-1} and C=N, C=C bands in complex shifts from 1566.64cm^{-1}, 1451cm^{-1} to 1618.83 cm^{-1} , 1452.59 cm $^{-1}$. Strong and branch absorption bands at 1384.49 cm^{-1} are related to cadmium nitrate groups. The bands at 400-550 cm^{-1}is corresponding to binding of ligand to metal [1, 12- 16].

Changes in the vibrational frequencies of complex show that ligand was coordinated to the metal ions [12, 13].

UV-vis spectra:

Figures **3** and **4** show the UV-vis spectra of the ligand in EtOH solution and complex in DMSO solution respectively.

UV-vis spectra of ligand show two absorption bands in 203, 217nm that attributed to the intraligand transitions (π→π*) of phenanthroline[17] and one absorption band at274nm related to (π→π*) of benzene which overlap with (n→π*) of phenanthroline [1, 18]. Another bonds at 368nm and 388nm assigned to intraligand transition (π→π*), (n→π*) of imidazol rings [17].

Three absorption bands at 224, 243nm and 256 nm in Figure **4** attributed to the intraligand transition[15, 18]. Also the absorption bands in the UV region(288,374 nm) assigned to intraligand π→π* transition of benzene and imidazol, respectively too[1, 17]

Electrochemical:

Electrochemical behavior of the BPIB ligand and complex, with scan speed of 500 mVs $^{-1}$, in the DMF solvent were studied. Voltamograms of the ligand and complex, shows cathodic and anodic steps which are corresponding to the oxidation and reduction of the ligand [19].

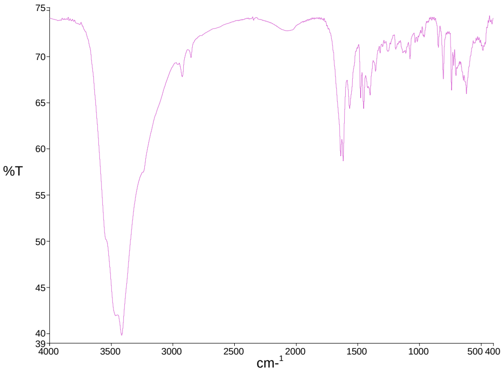


Figure 1: FT-IR spectrum (KBr) of BPIB ligand.

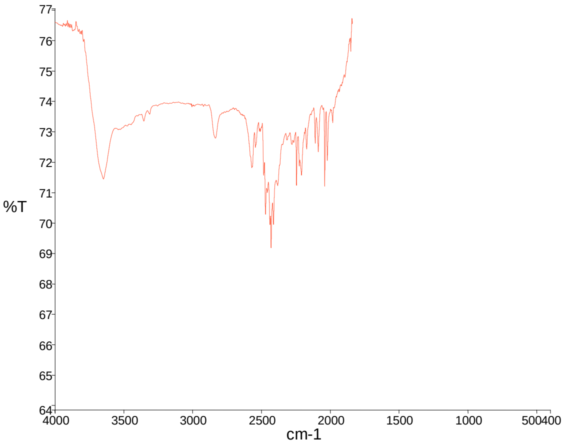


Figure 2: FT-IR spectrum(KBr) of [(μ-BPIB){$Cd(NO_3)_2$}$_2$].

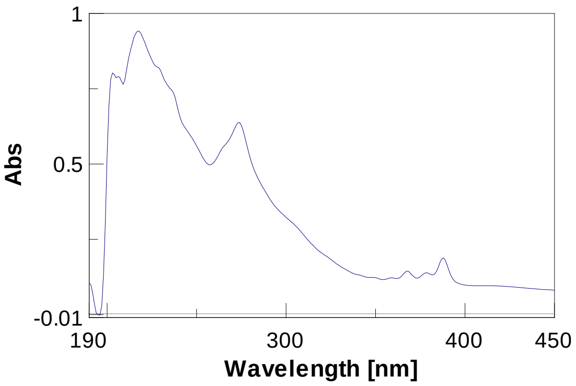


Figure 3: Absorption spectrum of BPIB ligand in ethanol solvent (1×10^{-5} M).

^{1}H-NMR spectra:

The ^{1}H NMR spectrum of the free BPIB in DMSO solution has shown proton chemical shifts at 2.4, 6.8, 7.8 and 8.1 ppm corresponding to imidazole, - 3,8 – 4,7- 2,9 phenanthroline. The ^{1}H NMR spectrum of the complex in DMSO solution has shown proton chemical shifts at 2.4, 7.8, 9.1, 9.5 ppm corresponding to imidazol- 3.8 – 4.7- 2.9 phenanthroline.

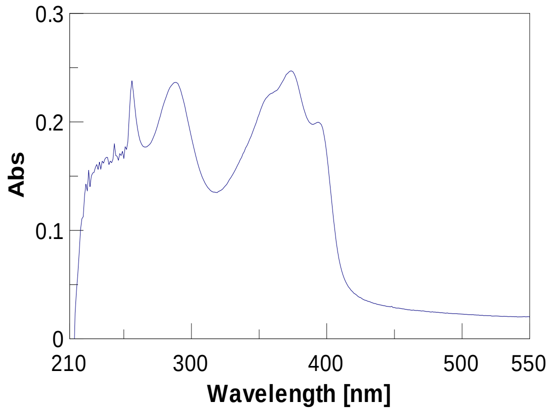


Figure 4: Absorption spectrum of [(μ-BPIB){$Cd(NO_3)_2$}$_2$] in DMSO solvent(1×10^{-5} M).

1.181v, 1.22v (AA*)
0.821v, 0.377v (BB*)
-0.469v, -0.891v (CC*)

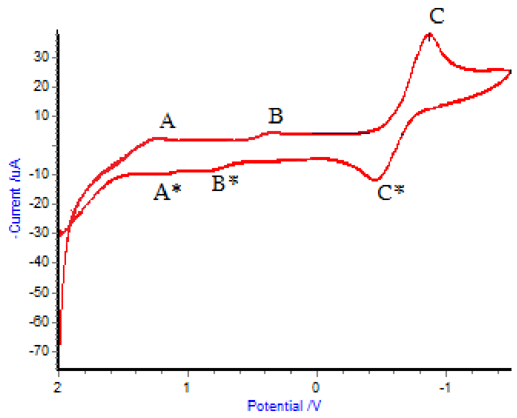


Figure 5: Cyclic voltammogram of BPIB ligand in DMF at scan rates of 500mVs^{-1}; 0.1 M TBAH as a supporting electrolyte.

Conclusion

In this study, structure of the synthesized complex confirmed useing methods such as FT-IR, UV-vis and ^{1}H-NMR spectroscopy. Electrochemical behavior investigated by cyclic voltammetry technique. This method shows the presence of activated ligand.

Experimental

Materials:

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

1.217v, 1.145v(AA*)
0.842v, 0.337v (BB*)
-0.381v, -0.995v(CC*)

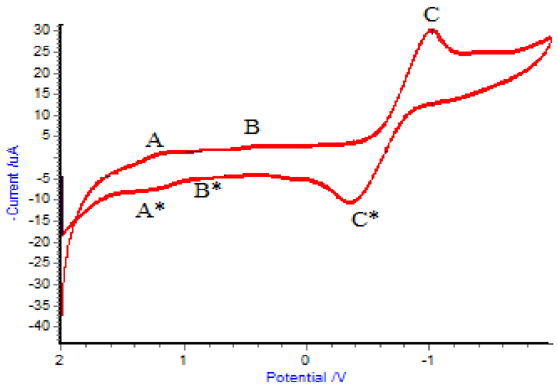
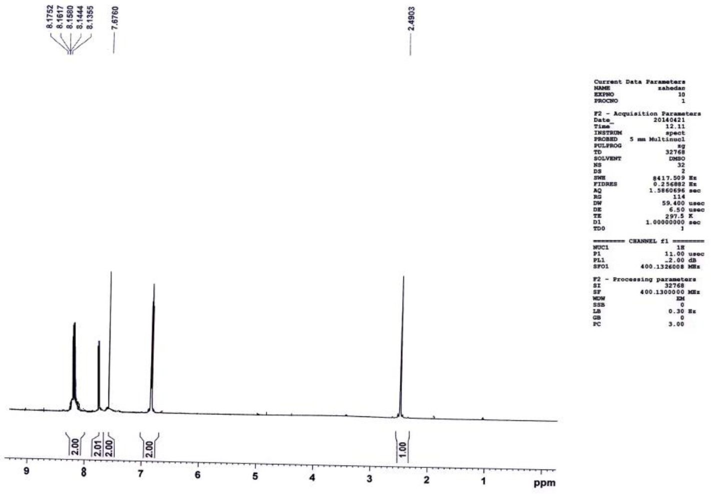


Figure 6: Cyclic voltammogram of $[(\mu\text{-BPIB})\{Cd(NO_3)_2\}_2]$ in DMF at scan rates of $500 mVs^{-1}$; 0.1 M TBAH as a supporting electrolyte.

Instrument and measurements:

The FT-IR spectra were obtained on a Perkine-Elmer spectrum One Fourier transform infrared spectrometer (KBr pellet). NMR spectra were recorded on a Bruker NMR400 spectrometer operating at 400 MHz at room temperature in DMSO solution. Elemental analysis for C, H, O, and N elements was carried out using a Heraeus CHNO rapid analysis instrument. Ultraviolete 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-lm diamond polish prior to each scan. The supporting electrolyte, 0.1 M tetrabutylammonium hexafluorophosphate (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.



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PULPROG                zg
TD                  32768
SOLVENT              DMSO
NS                     32
DS                      2
SWH              8417.509 Hz
FIDRES           0.256882 Hz
AQ              1.5860696 sec
RG                    114
DW                 59.400 usec
DE                   6.50 usec
TE                  297.5 K
D1             1.00000000 sec
TD0                     1

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P1                  11.00 usec
PL1                 -2.00 dB
SFO1          400.1326008 MHz

F2 - Processing parameters
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SF            400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   3.00
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Figure 7: ^{1}H-NMR spectrum of BPIB ligand in DMSO-d_6 at room temperature.

Synthesis:

Synthesis of 1,10-phenanthroline- 5,6-dion:

A mixture of 1,10 phenanthroline (4.0 g, 19mmol) 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 droppwise. The mixture was heated to reflux for4 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].

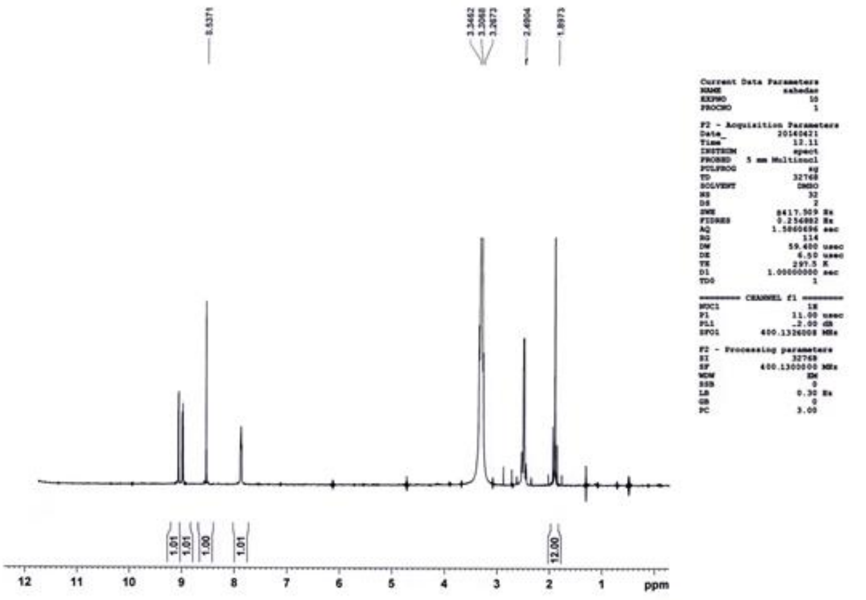

Figure 8: ^{1}H-NMR spectrum of $[(\mu\text{-BPIB})\{Cd(NO_3)_2\}_2]$ in DMSO-d_6 at room temperature.

Synthesis of BPIB:

The mixture of 0.335 g (0.25 mmol) ofter ephthalaldehyde, 0.105 g (0.5 mmol) of phenO_2 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 precipitateis produced. The reaction mixture was cooled and EtOHwas removed by rotary evaporation. After addition of water, the orange product was filtered off, washed with water and EtOH. Yield: 70% [3]. Anal. Calc. C, 74.70; H, 3.52; N, 21.78. Found: C, 74.40; H, 3.43; N, 20.91.

Synthesis of $[(\mu\text{-BPIB})\{Cd(NO_3)_2\}_2]$:

A DMSO solution (20 mL) of the ligand BPIB (0.257 g, 0.5 mmol)was added to a methanol solution (10 mL) of $Cd(NO_3)_2.4H_2O$ (0.308 g, 1 mmol). The reaction 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 colorless, and then dried in vacuo at appropriate temperature. Yield: 73%, Anal. Calc: C, 39.50; H, 2.21; N, 16.75; O, 19.13; Found: C, 39.59; H, 2.29; N, 16.81; O, 19.18.

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