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Pd(II) Complex with 4-Bromo-Bis-Hydroxymethyl Phenol and Nicotinamide: Synthesis and Spectral Analysis

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***Abstract*—**In the present study, the reactions involving 4-bromo-2,6-bis-hydroxymethyl-phenol (BBHMP) and nicotinamide (NA) in the presence of Pd(II) ions were investigated. Optimum conditions for the reactions were established as pH = 7 and λ = 450 nm. According to absorbance measurements, the molar ratio of BBHMP: NA: Pd^{2+} was found to be 1: 2: 2. As a result of physicochemical, spectrophotometric and thermal analyses, the reactions of BBHMP and NA with Pd(II) are complexation reactions and one molecule of BBHMP and two molecules of NA react with two molecules of the Pd(II) ion.

***Keywords*—**Nicotinamide, 4-bromo-2,6-bis-hydroxymethyl-phenol, Pd(II), spectral analysis, synthesis.

I. Introduction

BBHMP ($C_8H_9BrO_3$, 233.06 g/mol^{-1}) is a halogenated phenol derivative for proteomics research and is prepared from 4-bromophenol and formaldehyde in the presence of sodium hydroxide [1], 82]. A literature survey suggests that many studies about BBHMP can be seen from previous years [3]-[9]. For example, a multidentate ligand was synthesized using BBHMP and diehylenetriamine which used copper(II) precursors to form copper(II) complexes [2]. In another work [10], the colorimetric method is described for naked-eye detection of F in the presence of BBHMP. BBHMP was found to show a selective and sensitive fluorescence quenching response toward fluoride compared to Cl, Br, I and AcO.

In this study, we synthesized Pd(II) complex in the presence of BBHMP with NA and determined optimum conditions and the molar ratio for the reactions using spectral measurements.

II. Experimental

A. Material and Measurements

All chemical reagents were purchased and used as supplied. Elemental analysis for C, H, O and N was measured using dried samples with a Perkin Elmer 2400 elemental analyzer. Conductivity measurements were calculated in $CHCl_3$ with an Inolab Thermal 740P. The magnetic moment measurements were obtained with a MK-1 Sherwood scientific magnetic susceptibility balance. pH measurements were made with a calibrated Metrohm 654 digital pH meter with a Sensorex combination pH glass electrode assembly. UV/Vis spectra were determined at 25 °C with a Shimadzu UV-1700 Pharma spectrophotometer in the 200-800 nm range. Mass spectra were obtained on an AB-SCIEX Triple TOF 4600 System. IR spectra were measured in transmission mode using a Shimadzu IR-470 spectrometer in the wavenumber range 4000-400 cm^{-1}. KBr was used as matrix material for pellets. Thermal analysis curves were created with a Seiko Exstar TG/DTA 6200 thermal analyzer in static atmosphere of dry air with a heating rate of 10 °C min^{-1} with a sample size of 5-10 mg in platinum crucibles.

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B. Synthesis of Pd(II) Complex

0.116 g (1x10^{-3} mmol) BBHMP, 0.06 g (3x10^{-3} mmol) NaOH and 0.121 g (2x10^{-3} mmol) NA were dissolved in 25 ml ethanol. An equivalent amount of solution with 0.355 g (2x10^{-3} mmol) $PdCl_2$ was added and the system was heated to reflux for 3 h at 75-80 °C. A brown, solid precipitate was obtained, washed with water and dried. The product was soluble in organic solvents such as DMSO, DMF and THF.

For $[Pd_2(BBHMP)(NA)_2$, the yield was 75%, with brown crystalline solid and M.P. 207 °C. Elemental analysis in percentages was C 28.97, H 2.41, O 9.66, N 6.76 calculated and C 28.93, H 2.38, O 9.62, N 6.72 found. UV-Vis values were 242, 450 nm with diamagnetic moment. Conductivity was 18.34 $\Omega^{-1}cm^2mol^{-1}$. MS (m/z, ESI) calcd. for complex: 722.34, found: 722.5.

C. Determination of the Wavelength for the Reaction

In order to determine the wavelength for the reactions, various solutions of mixed ligand (BBHMP + NA) in the presence of Pd(II) between pH 1-10 were prepared in the proportion of 2: 1: 2 (Pd^{2+}: BBHMP: NA) and the spectra were measured after waiting for 10 min at room temperature. In various pH ranges, the product showed absorption peaks at λ = 245, and 492 nm, respectively, and the absorbance was fixed after pH > 7 (Fig. 1). As a working medium, the absorbance value λ = 492 nm and a pH value of 7 was chosen [11], [12].

III. Results and Discussion

A. Spectral Analysis Results of Complex

Elemental analysis of C, H, N, O, S and metal determination are in good agreement with the general formula given for the complex. The molar conductance value obtained for this complex at the concentration of 10^{-3} M is in the range

of 10-25 $ohm^{-1}mol^{-1}cm^2$. This value is too low to account for any dissociation of the complex in DMSO. Hence, the obtained complex can be regarded as non-electrolyte [13]. The magnetic moment of the Pd(II) complex was 0.00 BM indicating that the gold complex is typically a low spin complex with square-planar structure. The value of μ_{eff} for the Pd^{2+} complex is diamagnetic. In the mass (LC-MS) spectrum of the complex (Fig. 2), there is one peak and this is in agreement with the molecular weight of the complex. According to these results, obtained product is a complex.

The FT-IR spectra of the free ligands and complex are presented in Table I. In the FT-IR spectrum of NA [14], the band at 3210 cm^{-1} is assigned to the ν(NH) stretching vibration in free NA and this band is also observed at 3446 cm^{-1} in the Pd (II) complex. The vibrations at 1680, 1612, 1542 and 1255 cm^{-1} due to ν(C=O), ν(C=N), ν(C=C) and ν(CN) stretching move to higher wave numbers of 1695, 1621, 1526 and 1278 cm^{-1} compared to free NA, respectively. The coordination through the nitrogen atom in the ν(C-N) group is further supported by the occurrence of new bands at 585 cm^{-1} in the spectra of the complex which may be assigned to ν(M-N) [15].

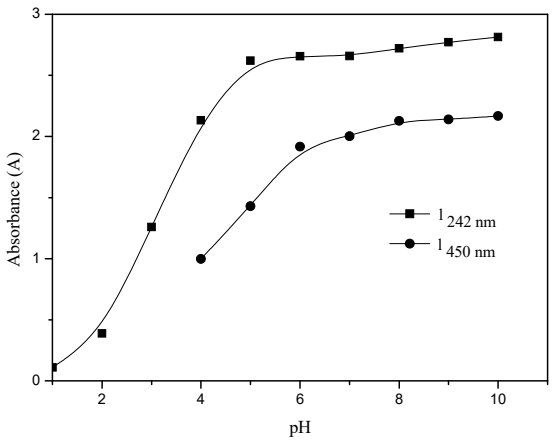

Fig. 1 The effect of pH

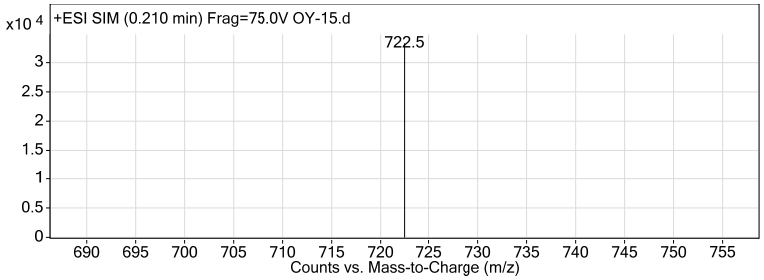

Fig. 2 The LC-MS spectrum of complex

TABLE I
CHARACTERISTIC IR BANDS (CM^{-1}) OF LIGANDS AND PD(II) COMPLEX

Comp.	NH	C=O	C=N	C=C	CN	CH_2	MN	MO
BBHM	-	-	-	1618	-	2926	-	-
NA	3210	1680	1612	1542	1255	-	-	-
Pd (II) Comp.	3446	1695	1621	1526	1278	-	585	680

TABLE II
UV-VIS SPECTRA OF LIGANDS AND PD(II) COMPLEX

Compound	λ_{max}(nm)	ABS	Assignment
BBHMP	246	2.533	π-π*
	353	0.645	n-π*
NA	254	2.515	π-π*
	360	1.272	n-π*
Pd (II) complex	242	2.581	n→π*, π→π* $^1A_{1g}(D) \rightarrow {}^1E_u(D)$
	450	3.215	n→π*, π→π* $^1A_{1g}(D) \rightarrow {}^1A_{2g}(D)$

The UV-Visible spectra of the ligands and gold complex in DMSO showed absorption bands between 290-850 nm (Fig. 3, Table II). In the electronic spectra of the ligands and complex, the presence of a wide range of bands is due to both π-π* and n-π* and also due to a charge transfer transition arising from π electron interactions between the metal and ligand that involves either a metal-to-ligand or ligand-to-metal electron transfer. The absorption spectra of the Pd(II) complex shows an absorption band at 245 nm, which is attributed to the electronic transition of $^1A_{1g}$ (D) → ^1E_u (D), while the band at 492 nm is caused by the electronic transition of $^1A_{1g}$ (D) → $^1A_{2g}$ (D). These transitions and assignments indicate that the complex has a square-planar geometry.

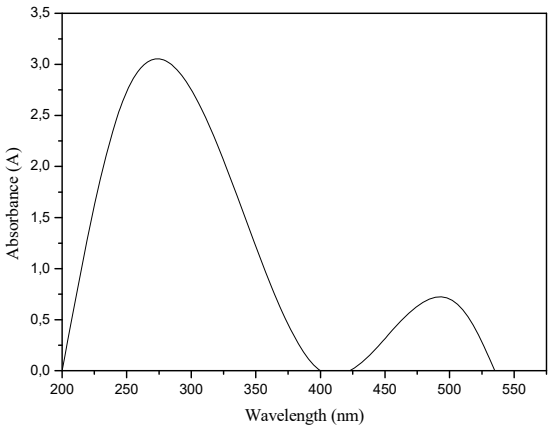

Fig. 3 UV-Vis spectrum of the complex

^{1}H data of the BBHMP, NA and their Pd (II) complex are summarized in Table III.

TG-DTA analysis (Fig. 4) was completed in the temperature range of 25 °C and 1200 °C in static atmosphere of dry air to examine thermal stability of the complex. In the thermal behavior of the Pd(II) complex, the first stage decomposition is endothermic in the range of 200-600 °C which is the decomposition of the organic component (63.2%). The compound remaining above 600 °C is determined as PdO (36.8%). These results are in good agreement with the suggested structures of the complex. It is confirmed that most of the complex contains water in the structure. As a result of the thermal study, qualitative conclusions can be made about the stability of the complex.

TABLE III
^{1}H NMR SHIFTS (Δ,PPM) OF LIGANDS AND PD(II) COMPLEX

Compound	BBHMP	NA	Pd (II) Complex
C_2-H	7.41, s	7.46, s	7.62, s 8.95, s
C_3-H	-	-	-
C_4-H	-	8.48, d	8.68, d
C_5-H	-	7.55, t	7.49, t
C_6-H	7.41, s	8.36, d	7.62, s 8.22, d
C_7-H	4.62, s	-	4.36, s
C_8-H	4.62, s	-	4.36, s
NH_2	-	5.14, s	6.72, s
H_2O	-	-	-
OH	5.81, s	-	-

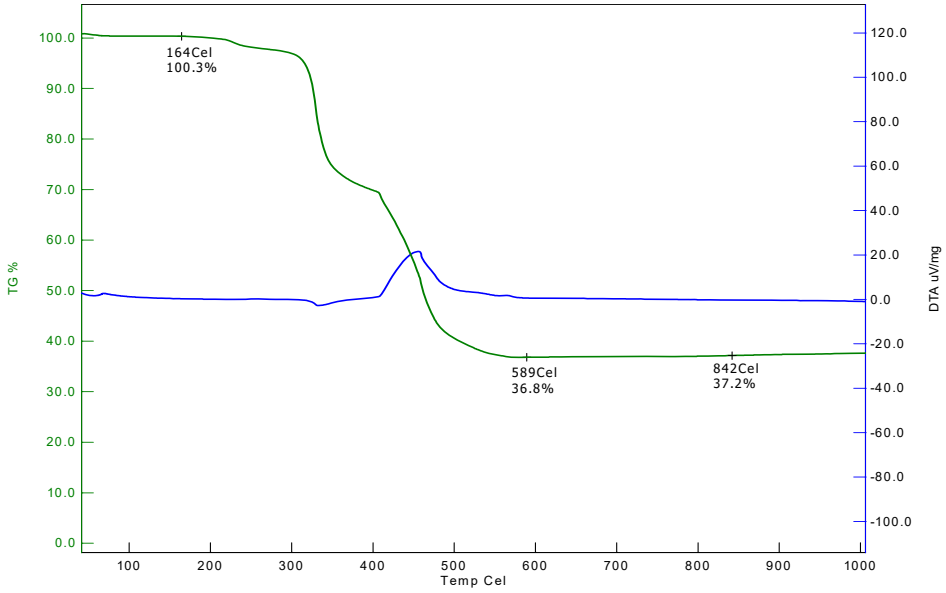

Fig. 4 TG-DTA graph of Pd (II) complex

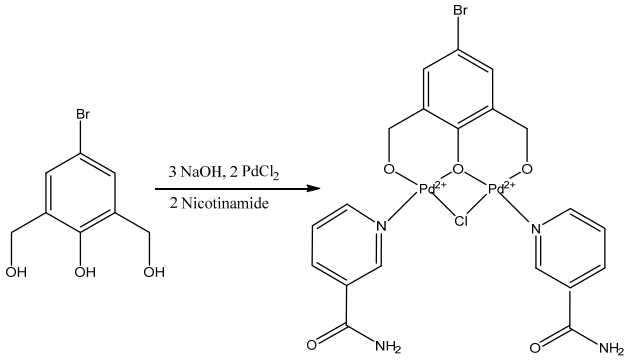

Fig. 5 Proposed reaction mechanism

IV. Conclusion

In this work, we studied synthesis and spectral analysis of Pd(II) complex with BBHMP and NA. According to physicochemical, spectrophotometric and thermal analysis results, small changes in the spectral analyses are observed in Pd(II) complex and the reaction of BBHMP and NA in the presence of Pd(II) is a complex reaction. One molecule of BBHMP and two molecules of NA react with two molecules of Pd^{2+} ions.

Accordingly, reaction mechanism in Fig. 5 is proposed.

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