

## ***Microwave Assisted Synthesis, Spectral and Bio-Potential Characterization of Cr(III) and Hg(II) Metal Complexes of Ethyl-p-aminobenzoate and Oxalate ion***

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### **ABSTRACT**

*Binuclear Cr(III) and mononuclear Hg(II) complexes with ethyl-p-aminobenzoate have been synthesized using microwave irradiation and characterized by analytical, conductivity, magnetic, cyclic voltammetry, spectral and biological methods. Molecular formula, neutral nature and octahedral geometry of Cr(III), square planar geometry of Hg(II) complexes were confirmed by elemental analysis, metal estimation, molar conductance, redox properties, magnetic moment and UV-visible spectral studies. The complex formation, metal ligating ability, metal-metal bond, probable geometry and magnetic behavior also investigated by its IR, Far-IR and NMR spectral studies. The antifungal activities of ethyl-p-aminobenzoate and Hg(II) complex were screened against Aspergillus Niger by Agar Disc diffusion method using Fluconazole as standard and DMSO as control. The MIC values also find out and compared with the standard.*

**Key words:** Ethyl-p-aminobenzoate, Oxalate ion, Microwave irradiation, Binuclear,  
Aspergillus Niger,

### **INTRODUCTION**

Ethyl-p-aminobenzoate is an ethyl ester of para aminobenzoic acid. It was first synthesized by Edward Ritsert in 1890 by Fisher esterification using ethanol and para aminobenzoic acid. It has one hydrogen bond donor and three acceptor sites. [1] The formal charge is zero so it is used as a neutral ligand in coordination chemistry. This compound have variety of applications in pharmaceutical drug in the form of ear drops, dental sprays, skin gels and powders, it is poorly soluble in water but it has good inhibition character in growth so that they can be used as an antibacterial agent against gram-negative and gram positive bacteria.[2-5] with this huge level of applications ethyl-p-aminobenzoate used as the primary ligand and oxalate ion used as mixed anionic ligand in the present study. Microwave assisted reactions are reducing time and organic solvent and also minimize the production of hazardous substances [6-8]. This is safe, sustainable and the process is simple and easy in handling manner, with this the present study aims to microwave irradiated synthesis, spectral and biological characterization of metal complexes using organic and anionic mixed ligands.

### **MATERIALS AND METHODS**

#### **Experimental: Materials and methods**

All the chemicals viz., Vanadylsulphate, solvents and reagents were of AnalaR grade (99% pure) used as such without further purification. Ethyl-p-aminobenzoate was purchased from Alfa Aesar Company.

#### **Synthesis of metal complexes**

The binuclear Cr(III) complex were prepared by mixing ethyl-p-aminobenzoate 3.33 g (9.99 mmol) in ethanol, oxalate ion 2 g (7.49 mmol) in water to chromium nitrate g (2.49 mmol) in methanol. The mixture was irradiated on a microwave oven (CATA-R, model). The precipitated green color complex was filtered, washed, dried in a desicator and kept in an air-tight glass container. The complex is stable under ordinary conditions.

The mononuclear Hg(II) complex were prepared by mixing ethyl-p-aminobenzoate 1.22 g (7.36 mmol) in ethanol, oxalate ion 0.493 g (3.68 mmol) in water to mercury chloride 1g (3.68 mmol) in methanol. The mixture was irradiated on a microwave oven (CATA-R, model) for a few seconds. The precipitated colorless complex was filtered, washed, dried in a desicator and kept in an air-tight glass container. The complex is stable under ordinary conditions.

Elemental analysis was carried out using elemental Vario make EL-III model instrument at 950-1200°C temperature. The metal ions were estimated after decomposing a known weight of complex in acids by gravimetric/ colorimetric methods. Molar conductance of complex solution at 10<sup>-3</sup>M concentration was measured using Systronic Conductivity Bridge. The Cyclic voltammogram of the complexes was recorded in DMSO solution at room temperature on Versa Stat (Princeton Applied Research-Make) electrochemical analyzer. The magnetic moment of Cr(III) complex was measured using a Lake Shore 7410 Vibrating Sample Magnetometer (VSM) at room temperature. The solid state diffused reflectance spectral (DRS) methods of UV-Visible spectra of the complex were recorded by using Varian make, CARY-5000 model, UV-VIS-NIR Spectrophotometer. Using Shimadzu, FT-IR, 8400 S Model IR spectrometer, IR spectra of ligands and its metal complex were recorded. The Far IR spectra of the complex were recorded in a Bruker, Germany make, 3000 Hyperion Microscope with Vertex 80 FTIR system model instruments. The NMR spectra of Hg(II) complex was recorded in DMSO-d<sub>6</sub> using

#### Antimicrobial assay

Antibiogram of ligand and Hg(II) complex was done by Agar disc diffusion method at 50µl, 100µl and 150µl concentrations using *Aspergillus Niger* species. Each sample was tested in triplicate. The antimicrobial potential of test compounds was determined on the basis of mean diameter of zone of inhibition around the disc in millimeters. The zones of inhibition (MIC) of the tested microorganisms by the samples were measured using a millimeter scale.

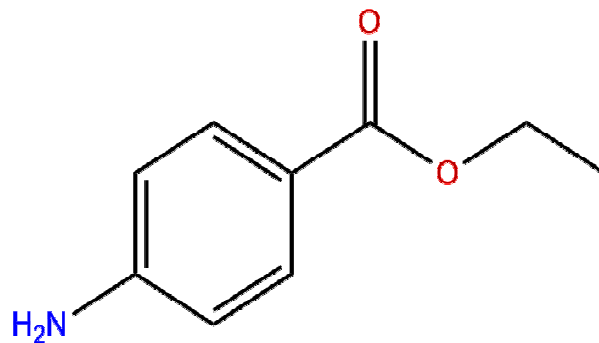


Figure-1

#### Structure of ethyl-p-aminobenzoate

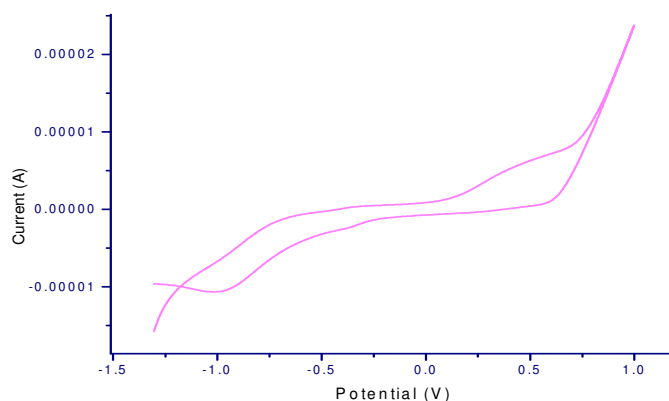
#### Results and Discussion

The complex Cr(III) is green and Hg(II) is colorless, they are stable under ordinary conditions. These are soluble in DMSO, CH<sub>3</sub>CN and ethanol but insoluble in water. Micro analytical data viz., elemental analysis of the ligand and the prepared complexes were carried out the found data is in good agreement with the calculated values which are confirmed by the stoichiometry of the ligand and metal in the complexes. The metal estimation was calculated using colorimetric and gravimetric after decomposing a known weight of metal complexes in acid solution. The result is good agreement with the found elemental analysis confirmed by the formulae of the complexes. The

complex is non-electrolyte was found by molar conductance of its  $10^{-3}$  M complex solution in  $\text{CH}_3\text{CN}$ . [9]

### Redox properties of Hg(II) complex

The redox properties of Hg(II) complex gives the well defined redox process to give  $E_{p_c}$  at -1.003V and  $E_{p_a}$  at -0.520 V. The peak to peak separation  $\Delta E_p$  is at 0.483 V and  $i_{p_a}/i_{p_c}$  is at 1.153 A indicating the quasi-reversible one electron transfer redox process with Hg(II)/Hg(I). The standard electrode potential  $E^0$  is at 0.242 V also confirming by the quasi reversibility [10].



**Figure-2**

### Cyclic voltammogram of Hg(II) complex

### Electronic spectra of the complexes (DRS method)

The electronic spectra of Cr(III) complex shows three transitions of  $4T_{2g} \leftarrow 4A_{2g}$  ( $\nu_1$ )  $10Dq$ ,  $4T_{1g}(F) \leftarrow 4A_{2g}$  ( $\nu_2$ )  $18Dq$ ,  $4T_{2g} \leftarrow 4A_{2g}$  ( $\nu_3$ ) ( $12Dq+15B$ ) at  $17513 \text{ cm}^{-1}$  (571 nm),  $17513 \text{ cm}^{-1}$  (411 nm),  $17513 \text{ cm}^{-1}$  (259 nm) with the Rache parameter B value at 743 indicates the octahedral geometry of Cr(III) complex. Due to the presence of three unpaired electrons in the complexes, the magnetic moment is at 3.80 BM and the hybridization is  $d^2sp^3$  is further confirmed by the octahedral geometry. [11]

In Hg(II) complex, the UV-spectra shows only one broad peak at  $26,667 \text{ cm}^{-1}$  (375nm) indicates the (C-T) charge transfer transition due to its completely filled 'd' orbital from this the tetrahedral/square planar geometry around the Hg(II) metal ion. [12]

### IR and Far-IR spectra of the complexes

The IR spectra of ethyl-p-aminobenzoate shows the symmetric and asymmetric  $\text{NH}_2$  frequencies at  $3423 \text{ cm}^{-1}$  and  $3342 \text{ cm}^{-1}$ , aromatic (C-C) at  $3047 \text{ cm}^{-1}$ , aromatic (C-H) at  $3223 \text{ cm}^{-1}$ , carboxylic ester (C=O) at  $1685 \text{ cm}^{-1}$  these frequencies are shifted to lower or higher frequencies in metal complexes in addition to that the asymmetric and symmetric O=C-O stretching frequencies of oxalate ion present in complexes due the mixed ligand is coordinate to the metal ion through the oxygen atom through bidentate mode. [13] (Table-1) the Far-IR spectra of metal complexes show the metal- linked atom stretching frequency at  $500-50 \text{ cm}^{-1}$ , in Cr(III) and Hg(II) complex the  $\nu$  (M-N) at  $502 \text{ cm}^{-1}$  &  $517 \text{ cm}^{-1}$ ,  $\nu$ (M-O) of oxalate ion at  $381 \text{ cm}^{-1}$  &  $375 \text{ cm}^{-1}$  respectively indicating the coordination of both ligand (4-EAB, and Oxalate ion) through the 'N' &

'O' donor atoms. In addition to that the low frequency region at  $134\text{ cm}^{-1}$  observed in Cr(III) complex due the M-M bond present in this complex, it is weaker due to its higher mass of the metal ion.[14]

**Table-1**

**IR spectral frequencies of 4-EAB and its metal complexes**

Ligand/ complex	Sy(NH <sub>2</sub> ) (cm <sup>-1</sup> )	Asy(NH <sub>2</sub> ) (cm <sup>-1</sup> )	Aromatic (C-C) (cm <sup>-1</sup> )	Aromatic (C-H) (cm <sup>-1</sup> )	Carboxylic ester (C=O) (cm <sup>-1</sup> )	Asy (O=C-O) (cm <sup>-1</sup> )	Sy (O=C-O)	O-C-O Plane deformation
<b>4-EAB</b>	3423	3342	3047	3223	1685	-	-	-
<b>Oxalate ion</b>	-	-	-	-	-	1407	1350- 1325	775
<b>Cr(III) complex</b>	3429	3348	3063	3226	1665	1442	1369	773
<b>Hg(II) complex</b>	3433	3345	3068	3225	1642	1443	1383	776

**<sup>1</sup>H & <sup>13</sup>C-NMR spectra of 4-EAB and Hg(II) complex**

The NMR spectra of 4-EAB and diamagnetic Hg(II) complex were carried out using DMSO-d<sub>6</sub>. The chemical shift values Hg(II) complex compared with 4-EAB. <sup>1</sup>H-NMR of 4-EAB shows the triplet at 1.27-1.26 ppm and quartet at 4.22-4.20 ppm indicating the aliphatic ethyl group in the ligand, one broad singlet at 5.93 ppm indicate the NH<sub>2</sub> group in the para position which is the coordinating site. The two different aromatic peaks observed at 6.60-6.57 ppm, doublet for ortho hydrogen and 7.66-7.65 ppm, doublet for Meta hydrogen of benzene ring. In Hg(II) complex the NH<sub>2</sub> peak shifted to downfield and deshielded high frequency region at 5.97ppm due the formation of complex and diamagnetic properties of the metal ion. All the other peaks are also shifted to down/up-field in the complex.[15]

The <sup>13</sup>C-NMR spectra shows the seven different peaks in various chemical shift values these are C=O at 166.36 ppm, O-CH<sub>2</sub> at 59.92 ppm, CH<sub>3</sub> at 14.78 ppm, C-NH<sub>2</sub> at 153.89 ppm and aromatic benzene ring at 131.50 ppm, 116.60 ppm & 113.11 ppm for three different carbon atoms (ortho, meta, para). These chemical shift values are shifted in the region of down field in Hg(II) complex which indicating the effective formation of metal complex and its diamagnetic properties.[16]

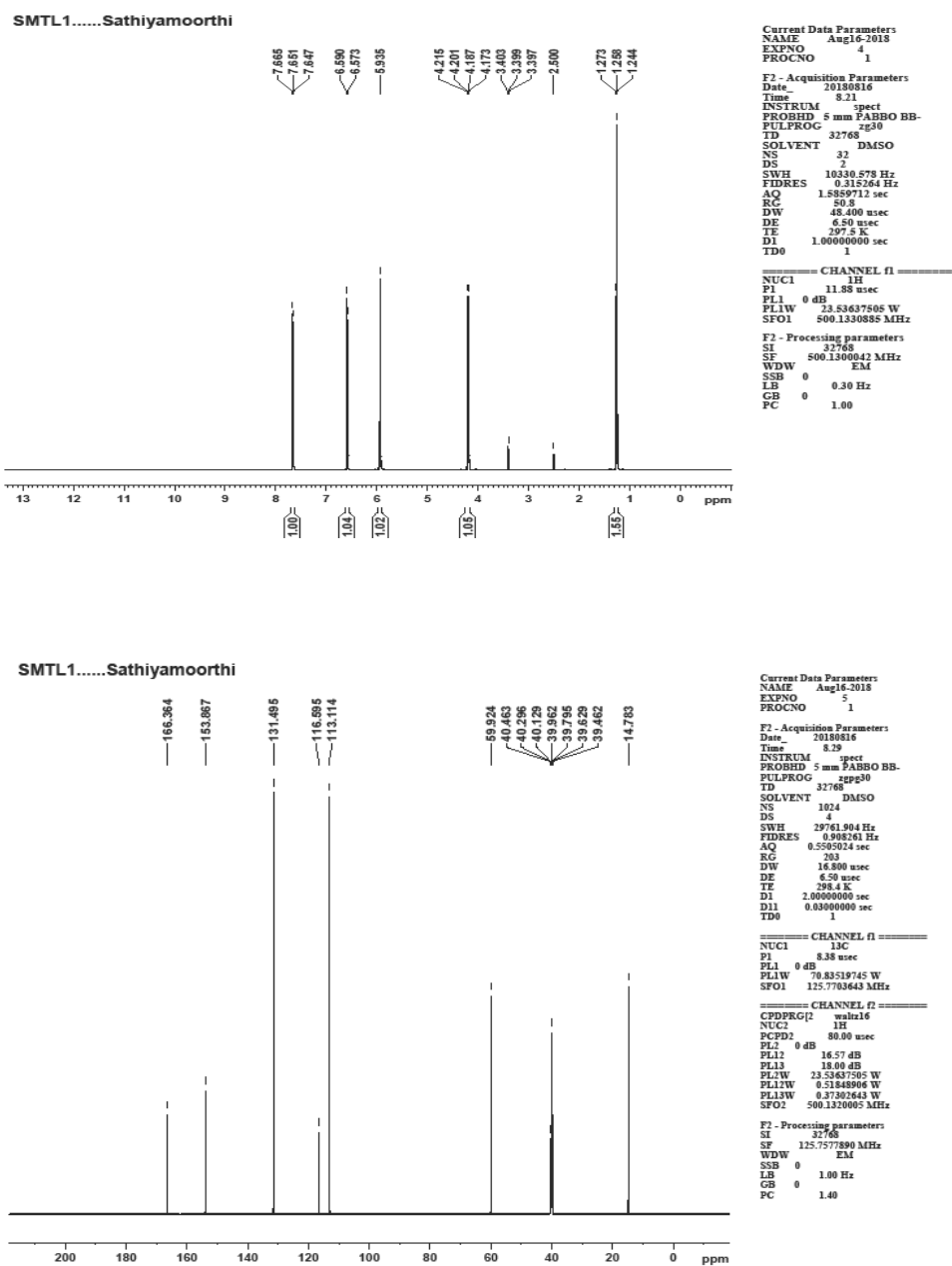


Figure-3

**$^1\text{H}$  &  $^{13}\text{C}$ -NMR spectra of 4-EAB**

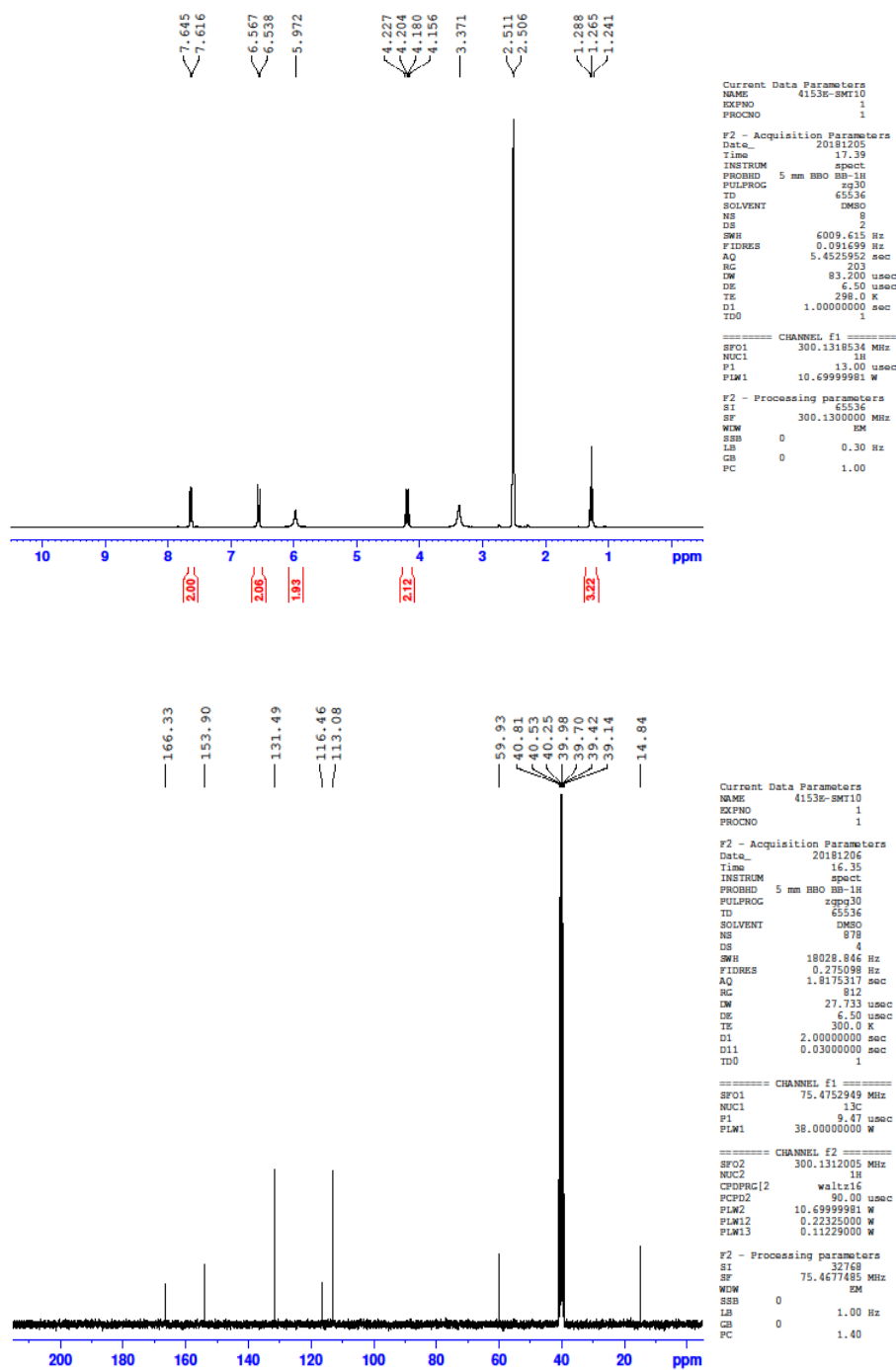


Figure-4

 $^1\text{H}$  &  $^{13}\text{C}$ -NMR spectra of Hg(II) complex

### Bio-potential activities of 4-EAB and Hg(II) complex

The antifungal activities of ligand and its Hg(II) complex was studies against the black mold fungus *Aspergillus Niger*. The results indicating that the complex is very good antifungal agent than the ligand but it is moderately active than the standard (Fluconazole). Because of ligand itself act as pharmaceutical drug, the poor solubility in water has good inhibition character and it is used as antibacterial agent against gram-negative and gram positive bacteria.[17]

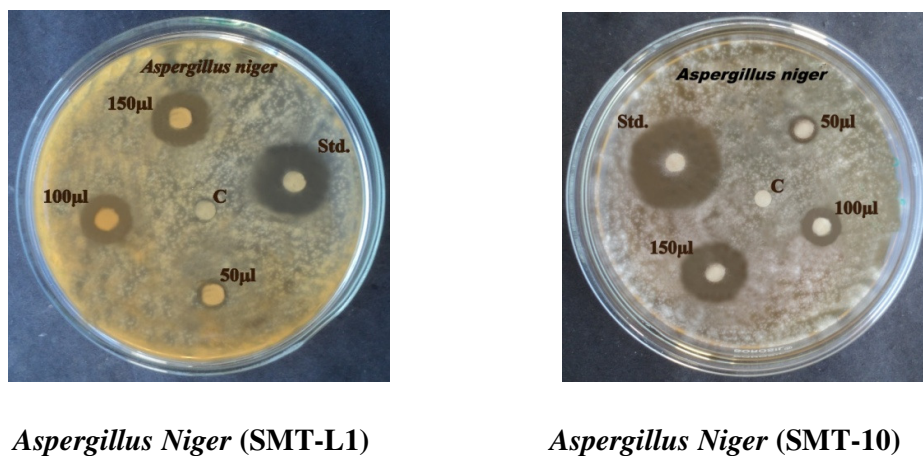


Figure-3

### Aspergillus Niger of ethyl-p-aminobenzoate and Hg(II) complex

Table-2

#### Antifungal activity of ethyl-p-aminobenzoate and Hg(II) complex

Microorganisms	Concentrations( $\mu\text{l/ml}$ )			Std. (30 $\mu\text{l/ml}$ )	Control (30 $\mu\text{l/ml}$ )
	50 $\mu\text{l}$	100 $\mu\text{l}$	150 $\mu\text{l}$		
<b>SMT-L1</b>					
<i>Aspergillus niger</i> (mm)	0.60 $\pm$ 0.04	2.50 $\pm$ 0.18	2.10 $\pm$ 0.36	9.60 $\pm$ 0.67	1.03 $\pm$ 0.07
<b>SMT-10</b>					
<i>Aspergillus niger</i> (mm)	0.50 $\pm$ 0.04	2.10 $\pm$ 0.15	4.50 $\pm$ 0.32	9.30 $\pm$ 0.65	0.68 $\pm$ 0.06

Values were expressed as Mean  $\pm$  SD

Fungi standard : Fluconazole

Control : DMSO

### Conclusion

The Cr(III) and Hg(II) complexes synthesized using ethyl-p-aminobenzoate and oxalate ion as ligands with microwave irradiation. The complexes are non-electrolyte, biologically active and the probable geometry of the complexes are octahedral binuclear for Cr(III) and square planar mononuclear for Hg(II). Effective coordination of both ligands through the 'N' atom of 4-EAB and 'O' atom of oxalate ion are also confirmed from its IR and Far-IR spectral studies. The para and dia magnetic properties of Cr(III) and Hg(II) respectively confirmed by its magnetic moment and NMR spectral studies.

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