

## SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL ACTIVITY OF COBALT (II), NICKEL (II), COPPER (II) AND MERCURY (II) COMPLEXES OF TETRADENTATE SCHIFF BASE DERIVED FROM 3,5- DIAMINO BENZOIC ACID AND THIOPHENE-2-CARBOXALDEHYDE

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Received: 02 December 2011, Revised and Accepted: 23 December 2011

### ABSTRACT

Co (II), Ni (II), Cu (II) and Hg (II) complexes of tetra dentate Schiff bases were synthesized by the reaction of 3, 5-Diaminobenzoic acid with Thiophene-2-carboxaldehyde (DABTCA). The Schiff base and its metal complexes were characterized using elemental analysis, infrared, electronic, mass, <sup>1</sup>H-NMR, VSM. Job's continuous variation method and Mole ratio method revealed 1:1 metal to ligand ratio.

**Keywords:** Tetra dentate Schiff base, 3, 5-Diaminobenzoic acid, Thiophene-2-carboxaldehyde acid, VSM, Biological activity.

### INTRODUCTION

Metal complexes of Schiff bases play a central role in the development of coordination chemistry. Schiff bases provide potential sites for chemical and biological activity of compounds<sup>1-4</sup>. From the survey of existing literature, it appears that Thiophene-2-carboxaldehyde and their complexes have a variety of applications in biological, clinical and analytical fields. More over these ligands form stable complexes with different metal cations<sup>5</sup>. Keeping the above facts in the mind and in continuation of our research work on transition metal (II) complexes with Schiff bases, we report the synthesis and characterization of Co (II), Ni (II), Cu (II) and Hg (II) metal complexes of Schiff bases derived from the condensation of 3,5-Diaminobenzoic acid and Thiophene-2-carboxaldehyde. Antifungal activity of Schiff base and its metal complexes have also been explored against different species of Fungi. Thus the aim of this study is to observe the impact of chelation on the therapeutic value of the organic compounds.

### MATERIALS AND METHODS

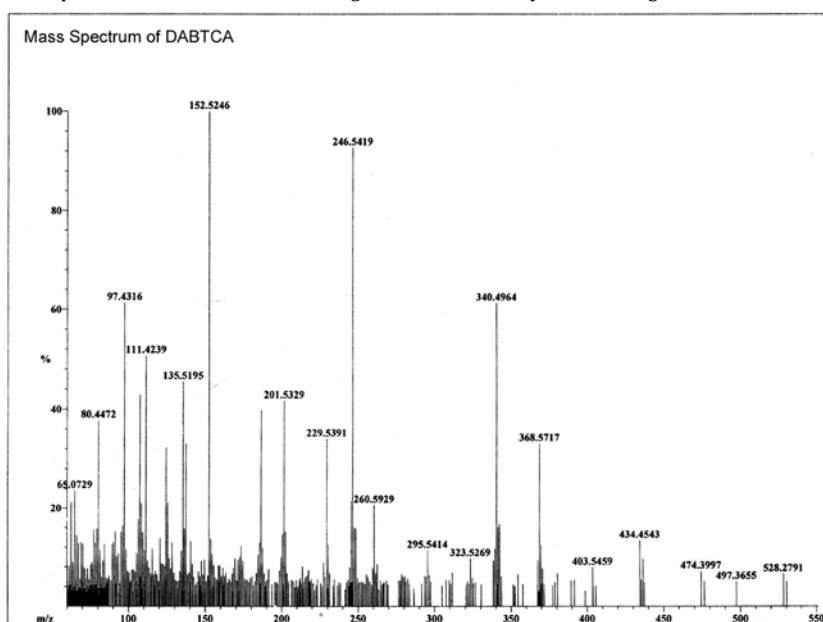
All the chemicals used were of AR grade and used without further purification. The elemental analyses were performed by the RSIC, CDRI, and Lucknow. The infrared spectra were recorded in the range

4000-180 cm<sup>-1</sup> with a Perkin Elmer 983 G spectrophotometer. The electronic spectra were recorded with Cary model 2390 spectrometer. The molar conductance of complexes in DMF ( ~ 10<sup>-3</sup> M ) were determined at 27± 2<sup>o</sup>C using a Systronic 303 direct reading conductivity bridge. The magnetic susceptibility measurements were made using a vibrating sample magnetometer ( VSM ) operating at a field strength of 5 KG. The <sup>1</sup>H NMR spectra was recorded on varian XL-300 MHz high resolution instrument in CDCl<sub>3</sub> solvent. The mass spectra were recorded using Fanning Mat 8230 Mass spectrometer.

### Synthesis of Ligand

The ligand DABTCA was prepared by the condensation of 1:2 molar quantities of 3, 5-Diaminobenzoic acid (1.63 g, 0.01069 mol) with Thiophene-2-carboxaldehyde (2 ml 0.02138 mol) in methanol. The reaction mixture was refluxed for 8-10 hours at 50<sup>o</sup> C. The yield, melting point and analytical data of Schiff base is given in Table-1.

The appearance of peak at m/e=340 confirms the proposed formula C<sub>17</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>. Other peaks 97.4316, 152.5, 246.5 may be due to different fragments. The intensity of these peaks gives an idea of the stability of these fragments.



Mass spectrum of DABTCA

### Synthesis of metal complexes

To a methanolic solution of the Schiff base, equal moles of metal salts dissolved in the methanol was added followed by 1 ml of 1M NaOAc was added. This reaction mixture was stirred constantly with magnetic stirrer for 20 minutes. Coloured products were formed after allowing to stand for one hour. The solids were collected and washed with n-Hexane and dried.

### RESULTS AND DISCUSSION

The analytical data for all the complexes are given in Table- 1. The molar conductivity data of the complexes are consistent with the non-electrolytic nature<sup>6, 7</sup> of the complexes. The ligand and complexes were characterized by elemental analysis to determine percentage of C, N, S and H. The observed and calculated percentages of the elements are in good agreement and support one ligand to a metal ion. The number of coordinated ligands to metal

determined by Job's continuous method and Mole ratio method established 1:1 metal to ligand ratio.

### IR- Spectra

The infrared spectra of DABTCA show bands at 1688.34  $\text{cm}^{-1}$  for VC=N; 710.90 for VC-S; 3352.94 for VC-COOH; indicating the Schiff base formation.

The lowering of VC=N of azomethine group to the extent of 30 -50  $\text{cm}^{-1}$  in all the complexes suggests the participation<sup>8-10</sup> of azomethine nitrogen in complexation. On coordination, this band is shifted to lower frequency suggests that the ligand is coordinated to metal ion via azomethine nitrogen in all complexes. This change in shift is due to the drift of the lone pair density of azomethine nitrogen towards metal atom<sup>11</sup>. In the far IR spectral region, additional medium to strong bands at 405-420 and 325-355  $\text{cm}^{-1}$  are assigned to VM-N and VM-S modes<sup>12,13</sup> respectively.

**Table 1: Analytical data of DABTCA and their metal complexes**

Compound/ complex (colour)	M.Pt. <sup>o</sup> C Yield %	Mol. Wt.	Elemental Analysis Found (calcd) C H N S M				
DABTCA (Brown)	178-180 80%	340	56.5 (60)	4.61 (4.65)	9.76 (8.23)	15.26 (18.82)	-
Cu-DABTCA (Black)	240 85%	403.5	50.23 (50.55)	2.12 (2.97)	6.45 (6.93)	14.43 (15.86)	14.97 (15.73)
Co-DABTCA (Greenish black)	220 85%	398.9	50.19 51.13	2.98 (3.02)	6.94 (7.01)	15.95 (16.04)	14.20 (14.77)
Ni-DABTCA (Black)	195 80%	398.69	50.15 (51.16)	2.93 (3.00)	6.80 (7.02)	15.16 (16.05)	14.22 (14.72)
Hg-DABTCA (Brown)	>300 (dc) 80%	540.6	37.52 (37.73)	2.02 (2.21)	4.97 (5.17)	10.85 (11.83)	35.5 (37.10)

**Table 2: Selected IR bands ( $\text{cm}^{-1}$ ) with tentative assignments**

compound	VC=N	VC-S	VC-COOH	VM-N	VM-S
DABTCA	1688	710	3352.9	-	-
Cu-DABTCA	1615	650	3416.6	420	355
Co-DABTCA	1608	708	3359.6	415	352
Ni-DABTCA	1610	709	3446.58	412	340
Hg-DABTCA	1623	712	3356	405	325

**Table 3: Molar conductance data of metal complexes of DABTCA**

Complex	Conductance ( $\text{Ohm}^{-1} \text{Cm}^2 \text{mol}^{-1}$ )
Cu-DABTCA	8.5
Co-DABTCA	8.6
Ni-DABTCA	9.5
Hg-DABTCA	8.5

**Table 4: Magnetic moment data of metal complexes of DABTCA**

Complex	Magnetic moment (B.M.)
Cu-DABTCA	2.11
Co-DABTCA	2.23
Ni-DABTCA	3.73

The magnetic moment value of Cu-DABTCA was 2.11 BM indicates one electron paramagnetism. This value is higher than the spin-only value of 1.73 BM for one unpaired electron. The higher value of the magnetic moment indicates that complexes are monomeric in nature and there is no metal-metal interaction along the axial position in the complex and have distorted octahedral environment<sup>14-16</sup>. The magnetic moment of Co-DABTCA was found to lie in 2.23 BM which is typically observed for low spin  $d^7$  system of the present type suggest its tetrahedral geometry. Monomeric cobalt complexes have lower magnetic moment values than would be expected for pure tetrahedral complexes suggesting flattening towards planar arrangement<sup>17-21</sup>.

The magnetic moments of Ni (II) complex was observed at 3.73 BM. This value is in the range reported earlier for octahedral complexes<sup>22</sup> but slightly higher than the spin only value of 2.83 BM probably due to slight distortion from the pure octahedral to  $D_{4h}$  symmetry<sup>23</sup>.

### Antifungal activity

Potential fungicidal activity of ligands and their metal complexes were screened against the four species of fungi, Fusarium oxysporum, Macrophomina phaseolina, Aspergillus flavus and Aspergillus niger by the agar growth food poison technique<sup>24</sup> at four

dilutions ( 25, 50, 100 and 200 ppm ). The percentage inhibition of growth by an inhibitor at different dilutions is determined as

$$100 \times \frac{C-T}{C}$$

Where C= diameter of fungus colony

C in control plate, T= diameter of fungus colony in test plate. The results presented in Table-5

The experimental results showed that there is an increase in the toxicity of the complexes as compared to the parent ligands. The

results recorded from the antifungal activity were also further compared with the standard fungicide Griseofulvin. The results are quite promising. It is clear from the antifungal screening data, that the metal complexes are more fungi toxic than the chelating agent itself<sup>25</sup>.

The enhanced activity of the metal complexes may be ascribed to the increased lipophilic nature of these complexes arising due to the chelation<sup>30</sup>. It was also noted that the toxicity of the metal chelates increases on increasing the concentration. The observed toxicity can be explained on the basis of the Tweedy's chelation theory.<sup>26</sup>

**Table 5: Fungal activity of DABTCA and its metal complexes**

Ligand/complex	concentration	F.Oxysporum	M.phaseolina	A.flavus	A.niger
DABTCA	25 ppm	75.55%	73.33%	73.33%	73.33%
	50 ppm	77.77%	76.66%	77.77%	78.88%
	100 ppm	80%	77.77%	82.22%	86.66%
	200 ppm	82.22%	77.77%	84.44%	88.88%
Cu-DABTCA	25 ppm	84.44%	90%	84.44%	84.44%
	50 ppm	86.66%	91.11%	86.66%	87.77%
	100 ppm	90%	92.22%	88.88%	90%
	200 ppm	92.22%	93.33%	92.22%	92.22%
Co-DABTCA	25 ppm	80%	80%	78.88%	80%
	50 ppm	82.22%	84.44%	82.22%	84.44%
	100 ppm	86.66%	84.44%	88.88%	86.66%
	200 ppm	88.88%	90%	90%	88.88%
Ni-DABTCA	25 ppm	78.88%	75.55%	74.44%	78.88%
	50 ppm	80%	76.66%	77.77%	80%
	100 ppm	82.22%	78.88%	82.22%	84.44%
	200 ppm	86.66%	84.44%	86.66%	86.66%
Hg-DABTCA	25 ppm	95.55%	96.66%	96.66%	97.77%
	50 ppm	96.66%	96.66%	97.77%	97.77%
	100 ppm	97.77%	97.77%	97.77%	97.77%
	200 ppm	98.88%	97.77%	98.88%	98.88%
Griseofulvin ( control)	25 ppm	77.77%	68.88%	88.88%	74.44%
	50 ppm	78.88%	75.55%	93.33%	77.77%
	100 ppm	88.88%	77.77%	94.44%	83.33%
	200 ppm	94.44%	80%	96.66%	94.44%

## CONCLUSION

A new Schiff base ligand is synthesized using 3,5-Diaminobenzoic acid and Thiophene-2-carboxaldehyde. It act as a tetra dentate ligand and forms stable complexes with transition metal (II) ions such as Cobalt (II), Nickel (II), Copper (II) and Mercury (II) in methanol. The ligand and its complexes were characterized by spectral and analytical data. From the spectral, VSM, stoichiometric analyses, a square-planar geometry were assigned for the monomeric metal complexes. A comparative study of the ligand and its complexes indicates that the complexes exhibit slightly higher antifungal activity than the free ligand.

## ACKNOWLEDGEMENT

The authors thank the CDRI, Lucknow and IIT-SAIF, Madras, Central University-Hyderabad for providing elemental analysis, spectral data and VSM data. The authors also thank Asst.Prof. Naga Lakshmi Devamma, Department of Botany, S.V.University, Tirupati for providing necessary facilities for studying antifungal activities of present compounds.

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