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### RESEARCH ARTICLE

#### SYNTHESIS AND CHARACTERIZATION OF Ni(II) AND Zn(II) COMPLEXES OF AN AZODYE DERIVED FROM 2-AMINO-5-CHLORO BENZOPHENONE.

S. Mini.

Department of Chemistry, University College, Thiruvananthapuram 695034 Kerala, India.

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#### Abstract

Ni(II) and Zn(II) complexes were synthesized using the azodye derived from 2-amino-5-chloro benzophenone and 1,3-benzene diol. The complexes were characterized by elemental analysis, metal estimation, electrolytic conductance, and magnetic susceptibility measurements. Their characterization were further confirmed by spectral techniques like FTIR, FTNMR, Electronic and Mass spectra. Nickel and the zinc complexes were subjected to antimicrobial study. The results indicate the metal and the azodye coordinated in the ratio 1:2. The complexes exhibit non-electrolytic behavior.

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#### Introduction:-

2-amino-5-chlorobenzophenone derivatives have been used as a starting material for the synthesis of 1,4-benzodiazepines (Sternbach, L.H., *et al.*, 1962) proquazone and amfenac as anti-inflammatory agents (Coombs, R.V., *et al.*, 1973; Welstead, W.J., *et al.*, 1979). These derivatives are important compounds in organic chemistry because of their application in heterocyclic synthesis and medicines (Walsh, D.A., 1980). All drugs synthesized from 2-amino-5-chloro benzophenone possess CNS activity (Rajesh K. Singh, *et al.*, 2011).

The present work deals with the preparation of an azodye by diazotizing 2-amino-5-chlorobenzophenone and coupling with 1,3-benzene diol, followed by the synthesis and characterization of two new complexes of the metal ions Ni(II) and Zn(II).

#### Experimental:-

##### Materials and methods:-

BDH-AR, Merck grade samples of the reagents 2-amino-5-chlorobenzophenone, 1,3-benzene diol were purchased and used as such for the synthesis of ligand. Acetone, ethanol, methanol, DMF, DMSO etc are the solvents used. Commercial grade ethanol and acetone were purified by standard procedure (Weissberger, A., *et al.*, 1956). E-Merck AR grade samples of methanol were used for conductivity measurements.

Estimation of the metal and anions present in the complexes were done by standard methods (Vogel, A.I., 1989). Elemental analyses were determined by CHNS analysis at SAIF, Cochin. The molar conductivity measurements were made using Systronics direct reading conductivity meter. Infrared spectra were recorded on a Perkin-Elmer Spectrum 65 infrared spectrophotometer using KBr pellets. The magnetic moments were measured at room temperature on a Sherwood Scientific Magnetic Susceptibility balance. Electronic absorption spectral measurements of the ligand and the complexes in methanol were recorded on a Perkin-Elmer Lambda 25 UV-Visible spectrophotometer. <sup>1</sup>H NMR

**Corresponding Author:- S Mini.**

Address:- Department of Chemistry, University College, Thiruvananthapuram 695034 Kerala, India

spectra were recorded on a 400 MHz FTNMR instrument using TMS as reference. The mass spectra of the ligand and Zn(II) complex was recorded on ESI-FTMS instrument at NIIST, Thiruvananthapuram.

### Synthesis of [2-chloro-5-(2,4-dihydroxy phenylazo)phenyl]phenylmethanone [RABP]:-

The ligand RABP is prepared by diazotizing 2-amino-5-chlorobenzophenone and coupling with resorcinol (Mini S., *et al.*, 2013). The resulting product was recrystallised from DMF.

### Synthesis of complexes:-

The complexes of [2-chloro-5-(2,4-dihydroxyphenylazo)phenyl]-phenyl methanone [RABP] with Ni(II), and Zn(II), were prepared by refluxing a methanolic solution of the corresponding metal salt [NiCl<sub>2</sub>.6H<sub>2</sub>O, Zn(SO<sub>4</sub>).7H<sub>2</sub>O] with a solution of RABP in acetone for about 4-5 hours.. The metal salt to ligand molar ratio was kept 1:2. The resulting solution was concentrated to get the solid complex. It was filtered, washed with methanol-acetone mixture, dried and kept in a desiccator over anhydrous CaCl<sub>2</sub>.

### Results and Discussion:-

The ligand RABP and its complexes are non hygroscopic solids, stable in air, and soluble in DMSO, DMF and Chloroform. The purity of the azodye was confirmed by elemental analysis as well as by IR spectral studies. The microanalytical data obtained: C 64.6% H 3.8% N 8.0% agree well with the calculated data: C 64.6% H 3.9% N 7.9%, corresponds to the molecular formula C<sub>19</sub>H<sub>13</sub>N<sub>2</sub>O<sub>3</sub>Cl. The elemental analysis data obtained for the complexes are in good agreement with the theoretical values calculated which suggest that the metal ions and the ligand are coordinated in the ratio 1:2. The electrolytic conductance value supports nonelectrolyte behavior of the complexes (Geary W. J., 1971). Analytical data along with magnetic moment and conductance values are presented in table 1.

**Table 1:-** Analytical data of the complexes.

Complex	Metal%	Anion%	C%	N%	H%	$\mu_{\text{eff}}$	Conductivity	
							Methanol	DMF
[Ni(RABP) <sub>2</sub> ]	7.6 (7.8)	7.9 (7.8)	59.7 (60.1)	7.3 (7.8)	3.4 (3.3)	3.3	17.6	5.6
[Zn(RABP) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	8.1 (8.1)	-	56.6 (56.5)	6.9 (6.8)	3.2 (3.3)	diamagnetic	38.4	14.1

### IR spectral data:-

The strong absorption band shown by the ligand RABP at 1460 cm<sup>-1</sup> corresponds to  $\nu_{\text{N=N}}$  stretching frequency shifted to 1473 and 1475 cm<sup>-1</sup> in Ni(II) and Zn(II) complexes indicates the coordination of azo nitrogen with the metal ions (Gaber, M., *et al.*, 2008). This is supported by the appearance of new bands at 450 and 434 cm<sup>-1</sup> assignable to  $\nu_{\text{M-N}}$  (Beecroft, B., *et al.*, 1974) in Ni(II) and Zn(II) complexes. The strong  $\nu_{\text{C=O}}$  band at 1619 cm<sup>-1</sup> of RABP get shifted to 1610 in Ni(II) complex indicates the coordination of >C=O group to the metal, which is supported by the appearance of new band in 512 cm<sup>-1</sup> assignable to  $\nu_{\text{M-O}}$ . In the Zn(II) complex the band due to  $\nu_{\text{C=O}}$  remains unaltered indicates its non coordination.

The two hydroxyl groups in the 1,3- benzene diol part of the ligand exhibit a broad band at 3418 cm<sup>-1</sup>. In the IR spectra of Zn(II) a broad band appears at 3428 cm<sup>-1</sup>, may be due to the uncoordinated phenolic OH and  $\nu_{\text{OH}}$  of coordinated water. It is supported by the unianionic behavior of RABP and the bands corresponding to  $\nu_{\text{HOH}}$  (def) at 1667 cm<sup>-1</sup> and  $\nu_{\text{HOH}}$  (rock) at 949 cm<sup>-1</sup>. This is supported by the NMR and mass spectra. As in the case of the IR band shown by Ni(II) complex at 3352 cm<sup>-1</sup> may due to the presence of one uncoordinated hydroxyl group in the 1,3-benzene diol part of the ligand. IR spectral data of the ligand and the complexes are given in table 2.

**Table 2:-** IR Spectral bands of the ligand and complexes.

RABP	[Ni(RABP) <sub>2</sub> ]	[Zn(RABP) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	Assignments
3418	3352	----	$\nu_{\text{OH}}$ phenolic
		3428	$\nu_{\text{OH}}$ phenolic & water
2873	2873	2870	$\nu_{\text{C-H}}$ (aromatic stretching)
1619	1614	1621	$\nu_{\text{C=O}}$
1460	1473	1475	$\nu_{\text{N=N}}$
832	832	829	$\nu_{\text{C-H}}$ aromatic bond
-	450	434	$\nu_{\text{M-N}}$ bond
-	512	523	$\nu_{\text{M-O}}$ bond

**Electronic spectra:-**

Ni(II) complex of RABP display two absorptions at 499 nm and 608 nm which corresponds to  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$  and  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ . The band corresponds to the transition  ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$  is 770 nm. This suggests an octahedral geometry to the Ni(II) complex (Lever, A. B. P., 1968). The electronic spectral data of RABP and the nickel complex are shown in table 3.

**Table 3:-** Electronic spectral bands of RABP and its Ni(II) complex.

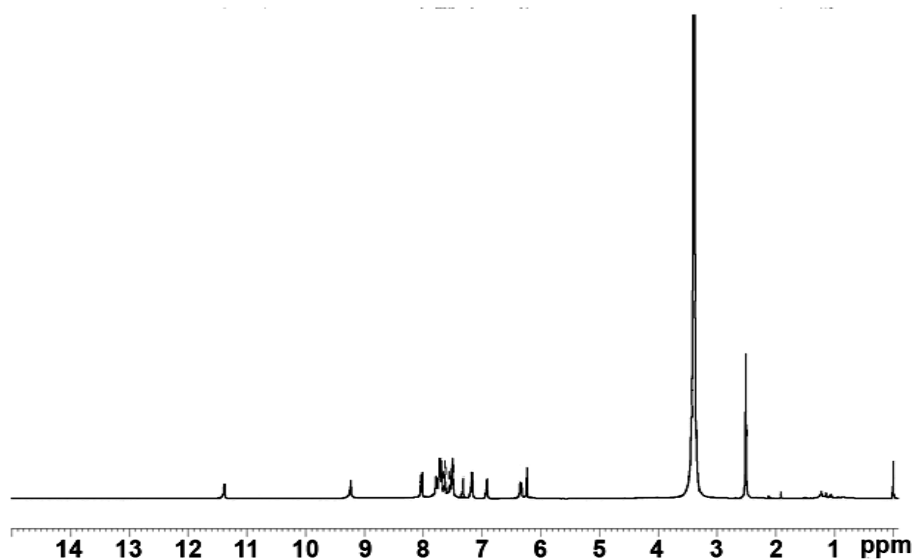
Compound	$\lambda_{\max}$ nm	Assignments
RABP	426	$n \rightarrow \pi^*$
	262	$\pi \rightarrow \pi^*$
[Ni(RABP) <sub>2</sub> ]	429	$n \rightarrow \pi^*$
	499	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$
	608	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$
	770	${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$

**Table 4:-** NMR spectral data of RABP and its Zn(II) complex.

RABP	[Zn(RABP) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	Assignments
11.38 ppm (s)	11.38ppm (s)	Phenolic OH (hydrogen bonded)
9.21 ppm (s)	----	Phenolic OH (hydrogen bonded)
8.04 ppm (s) 8.01 ppm (s)	8.03 ppm (s) 8.01 ppm (s)	Aryl protons
7.43-7.68 ppm (m)	7.60-7.75 ppm (m)	Aryl protons
6.12-6.90 ppm (m)	6.23-7.11 ppm (m)	Aryl protons

**<sup>1</sup>H NMR Spectra:-**

The <sup>1</sup>H NMR spectra of the ligand and its Zn(II) complex are recorded in DMSO-d<sub>6</sub> solution on a 400MHz FTNMR Spectrometer using TMS as the reference material. The <sup>1</sup>H NMR data of RABP and its Zn(II) complex are presented in table 4. Two singlets are observed at  $\delta$  9.21 ppm and 11.38 ppm in the ligand NMR spectrum corresponds to phenolic OH group of the resorcinol part. Among this one peak at  $\delta$  9.21 ppm is found to be absent in the Zn(II) complex, which indicate that one of the OH groups of the ligand get deprotonated and coordinated to the metal. A multiplet observed at  $\delta$  7.43-7.68 ppm in the ligand due to aromatic protons get shifted to  $\delta$  7.60-7.75 ppm in the complex. The nmr spectra of the ligand and complex are shown in figure 1 and 2.

**Fig 1:-** <sup>1</sup>H NMR spectrum of RABP.

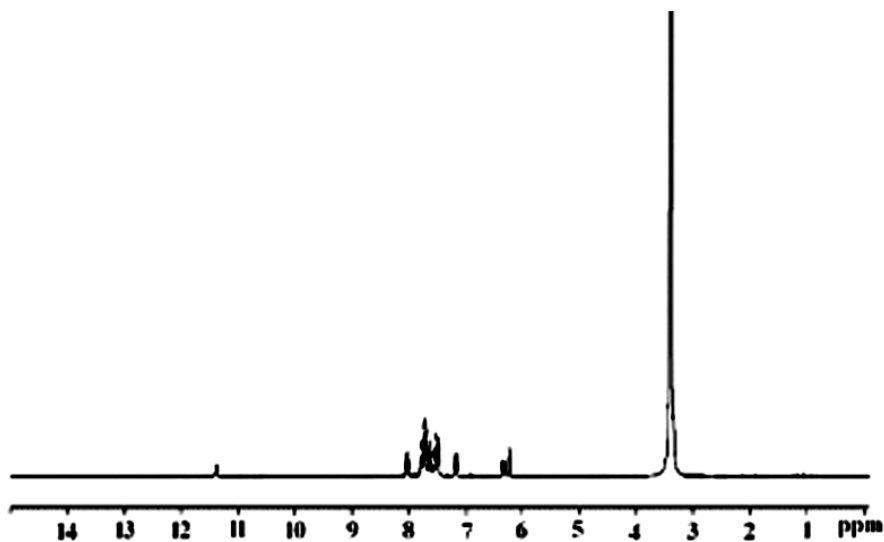


Fig 2:- <sup>1</sup>H NMR spectrum of [Zn(RABP)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]

**Mass spectrum:-**

Mass spectra of the Zn(II) complex shows the molecular ion peak at m/z 805 which is due to [Zn(RABP)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>+</sup>, and the peak observed at m/z 381 is due to [Zn(C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>+</sup>. The peak at m/z 353 is due to free ligand. From the mass spectra of the complex, it is confirmed that two ligand molecules are coordinated to the Zn(II) metal ion. The mass spectra of the ligand and complex are shown in figures 3 and 4.

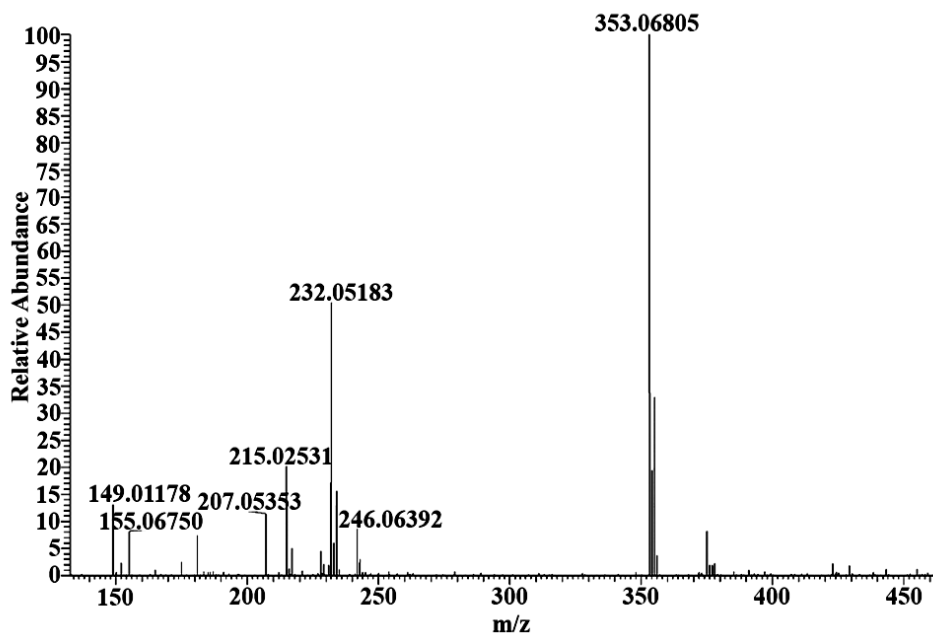


Fig 3:- Mass spectrum of RABP

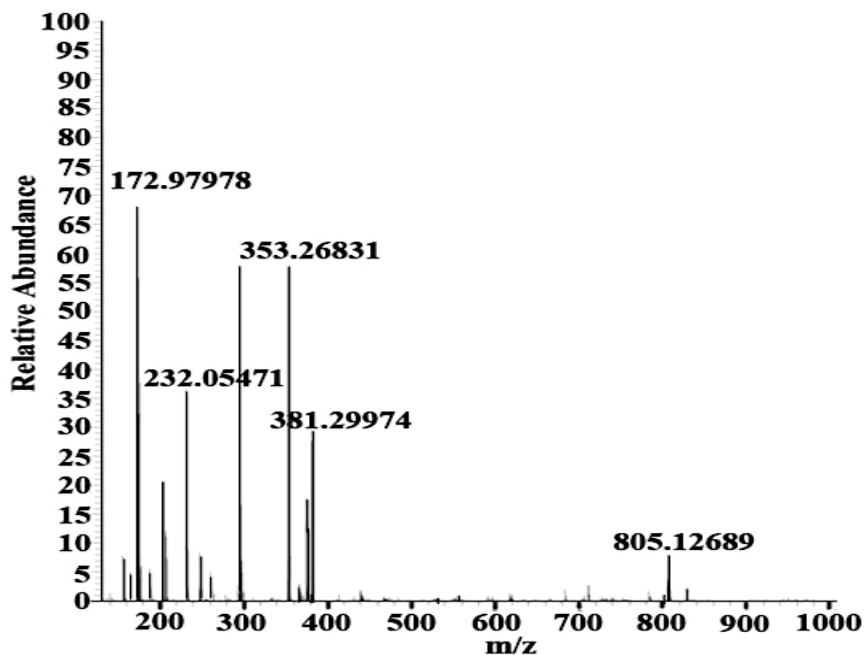
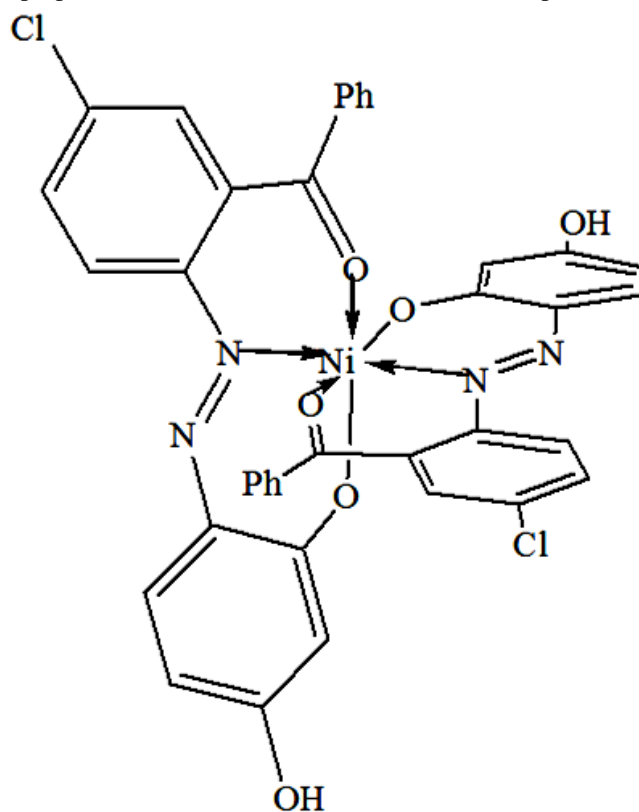


Fig 4:- Mass spectrum of  $[\text{Zn}(\text{RABP})_2(\text{H}_2\text{O})_2]$

Based on the analytical data and spectral studies the RABP complexes can be formulated as  $[\text{Ni}(\text{RABP})_2]$  and  $[\text{Zn}(\text{RABP})_2(\text{H}_2\text{O})_2]$ . The proposed two dimensional structures for the complexes are shown in figures 5 and 6.



Ph = phenyl ring

Fig 5:- Proposed structure of  $[\text{Ni}(\text{RABP})_2]$

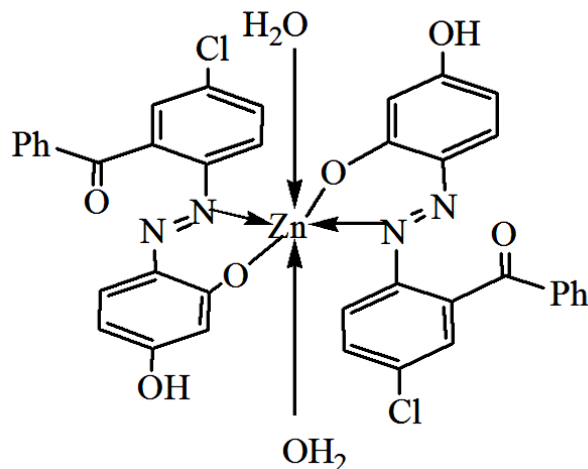


Fig: 6 Proposed structure of  $[Zn(RABP)_2(H_2O)_2]$

### Conclusion:-

Analytical data shows that the metal to ligand ratio in Ni(II) and Zn(II) complexes were found to be 1:2. The infrared spectrum of RABP complex of Ni(II) shows that it is acting as univalent tridentate ligand, but in Zn(II) complex, RABP acting as univalent bidentate ligand. The ligand exhibits univalent nature in both the complexes. Infrared spectra indicates the presence of coordinated water in Zn(II) complex. Electrolytic conductance values indicate the non electrolytic nature of the complexes. On the basis of spectral and physicochemical analyses octahedral geometries have been proposed for the complexes.

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