Original Article

Bulletin of Pure and Applied Sciences.
Vol.37 C (Chemistry), No.1, 2018: P.137-142
Print version ISSN 0970 4620
Online version ISSN 2320 320X
DOI 10.5958/2320-320X.2018.00019.5

Synthesis, characterization and biological studies of transition metal complexes of Mn(II), Cu(II) and Zn(II) with an azo dye (E)–4–((2,6–dihydroxyphenyl) diazenyl)benzoic acid

S. Mini[1]*, Aravind S.S. [1]

Author Affiliations
[1]University College, M G Road, Palayam, Thiruvananthapuram 695034 Kerala, India

Corresponding Author
***S. Mini,** University College, M G Road, Palayam, Thiruvananthapuram 695034 Kerala, India

E-mail: minissadasivan@yahoo.com

Received on 17th January 2018
Accepted on 31st January 2018

Abstract

The present work includes the synthesis and characterization of complexes of (E)–4–((2,6–dihydroxyphenyl)diazenyl)benzoic acid with metal ions Mn(II), Cu(II) and Zn(II) and characterized by elemental analysis, spectroscopic data including FT–IR, ^{1}H–NMR and electronic spectra. It has been found that the azodye behaves as a neutral bidentate N, O donor which chelates with the metal ions Cu(II) and Mn(II) in 1:2 and with Zn(II) in 1:1 stoichiometry. Magnetic moment and electrolytic conductance data confirms this. The azodyes and complexes were screened for antimicrobial activity. The ligand and the complexes show better antimicrobial activity.

Keywords: 4–aminobenzoic acid, resorcinol, antimicrobial activity, NMR spectra

1. INTRODUCTION

Many of the metal complexes are deeply colored and are used as dye and pigment before they were recognized as co-ordination compounds [1]. The structure and constitution of metal complexes of azo dyes are extensively studied by co-ordination chemists. It was Morgan and his students, who made significant contribution on the importance of co-ordination chemistry in dyeing technology. Variation in color or shade, resulting from changes in metal ion present in the bath, as on the fibre during dyeing supports the formation of co-ordination compounds [2–3].

The azo dyes having a donor group in the ortho position to the azo group are generally chelating agents. Stability and instability refers to the position of equilibrium, i.e., to the equilibrium constant. This constant is a measure of enthalpy and entropy changes and hence a thermodynamic property. The thermodynamic stability of metal chelates is influenced by the basicity of the ligand, chelate ring size, number of chelate rings per ligand and nature of metal. The stability of metal complexes increases with increase in basic strength [4]. It is found that the chelate ligands form stable complexes than those formed by their mono–dentate analogues. The chelate stability arises largely from favorable entropy changes [5]. In this work we have prepared an azo dye from resorcinol and 4–amino benzoic acid; (RABA). The complexes of Zn(II), Mn(II) and Cu(II) were prepared using RABA.

2. EXPERIMENTAL

2.1. Materials and Methods

All the chemicals used are of analytical grade and purchased from Merck. The complexes were analyzed for metal and halide content by standard methods [8]. The electrical conductance of the complexes in methanol and DMF (10^{-3} m solution) were measured at room temperature using a Systronics direct reading conductivity meter. The Infrared spectra of the ligands and complexes were recorded in the range of 4000–400 cm^{-1} on a Perkin Elmer spectrum 65 IR spectrophotometer. Electronic spectra of the ligands and the complexes in methanol were measured in the range 200–900 nm on Perkin Elmer Lamda 25 UV–Visible spectrophotometer. The Elemental analyses (C, H, N) were carried out on a Vario EL–III CHN Elemental analyzer at the SAIF, Cochin University of Science and Technology. The magnetic moments were measured at room temperature on a Sherwood Scientific magnetic susceptibility meter. The proton NMR spectrum of the ligand and zinc complex was recorded in Brucker, Ascend^{TM} 400 NMR spectrometer at 400MHz.

2.2. Preparation of ligand

The ligand used for the present study is resorcinol azo benzoic acid [RABA]. 3.425g of 4–aminobenzoic acid was dissolved in 14ml 1:1 HCl. Then it is cooled. This solution was diazotized by using a cooled solution of 1.725g of $NaNO_2$ in 10ml of water. This solution was filtered and cooled. Prepared another solution by dissolving 2.75g of resorcinol in 22.5ml 2%NaOH. Into this the diazotized mixture was added with constant stirring. The red precipitate obtained was allowed to attain room temperature. It was suction filtered and dried over anhydrous $CaCl_2$ in a desiccator.

2.3. Preparation of complexes

The complexes are synthesized by a general method. Methanolic solution of the metal salt (0.01mol) and ligand (0.01mol) are mixed. The ligand solution is added gradually in small portions with good stirring to the metal salt solution when sudden color change was occurred indicating the complex formation. Then it was kept under reflux for 2–3 hours, on a water bath for completion of reaction. Afterwards, the solid complexes formed were filtered, washed with ethanol to remove excess ligands. It was then dried in vacuum desiccator.

3. RESULTS AND DISCUSSIONS

The complexes reported here are stable, colored and non-hygroscopic amorphous solids. They are partially soluble in acetone and methanol, and completely soluble in DMSO, but insoluble in water, chloroform and ethanol. The microanalytical data are shown in the Table 1 given below. The experimental values are in good agreement with the theoretical values. Based on the elemental analysis , the empirical formulae of Zn(II), Mn(II) and Cu(II) complexes can be formulated as $[Zn(RABA)(H_2O)_2]CH_3COO^-$, $[Mn(RABA)_2(H_2O)_2]$ and $[Cu(RABA)_2]$ respectively.

Table 1: Microanalytical data of the complexes

Compound	C %		H%		N %		O %		Metal %	
	Cal	Obs	Cal	Obs	Cal	Obs	Cal	Obs	Cal	Obs
RABA	60.47	60.54	3.88	3.81	10.85	10.91	24.81	23.5	–	–
$[Zn(RABA)(H_2O)_2]$ CH_3COO^-	43.53	43.57	3.63	3.67	7.81	7.78	26.79	26.71	18.24	18.27
$[Mn(RABA)_2(H_2O)_2]$	51.58	51.52	3.64	3.61	9.26	9.30	26.45	26.47	9.08	10.01
$[Cu(RABA)_2]$	54.03	54.10	3.12	3.08	9.70	9.63	22.16	22.21	11.00	10.98

The magnetic moment value calculated for Mn(II) and Cu(II) complexes are 6.12 BM and 1.81 BM respectively. The magnetic moment value supports octahedral structure for Mn(II) complex and square planar structure for Cu(II) complex. The molar conductance of the complexes (10^{-3} molar concentration) were carried out in DMSO indicated that Mn and Cu complexes are non–electrolytes [6]. But Zn(II) complxes act as 1:1 electrolyte. The values are presented in the Table 2 below.

Table 2: Molar Conductance of the complexes in DMSO

Complex	**Molar Conductance in DMSO (ohm^{-1}cm^{2}mol^{-1})**	**Assignment**
$[Zn(RABA)(H_2O)_2]CH_3COO^-$	65	1:1electrolyte
$[Mn(RABA)_2(H_2O)_2]$	27	Non-electrolyte
$[Cu(RABA)_2]$	32	Non-electrolyte

3.1. UV-Vis Spectra

Table 3 given below shows the electronic spectral details of the synthesised compexes. The ligand is characterized by two absorption bands in the UV region. A high intensity band at 393nm is attributed to $n\rightarrow\pi^*$transition and low intensity band at 259 nm is attributed to $\pi\rightarrow\pi^*$ transition of azo group. The absorption bands in the complexes are shifted and new bands are appeared due to d→d transition. The band at 648 nm in Mn(II) complex suggests an octahedral geometry to the complex. The bands at 597 nm and 684 nm in Cu (II) complex suggests a square planar geometry to the complex.

Table 3: Absorptions of the ligand and complexes

Compound	**λ_{max} (nm)**	**Assignment**
RABA	393 259	$n\rightarrow\pi^*$ $\pi\rightarrow\pi^*$
$[Mn(RABA)_2(H_2O)_2]$	394 259 648	$n\rightarrow\pi^*$ $\pi\rightarrow\pi^*$ d→d transition
$[Cu(RABA)_2]$	390 259 597 684	$n\rightarrow\pi^*$ $\pi\rightarrow\pi^*$ $^2B_{1g}\rightarrow{}^2E_g$ $^2B_{1g}\rightarrow{}^2B_{2g}$

3.2. FT–IR Spectra

The IR spectral data (Table 4) of the ligand RABA and complexes with Zn(II), Mn(II) and Cu(II) are in agreement with an expected range.

Table 4: Infrared spectral data of the ligand and complexes

RABA ($\bar{\upsilon}$ cm^{-1})	**$Zn(RABA)(H_2O)_2]CH_3COO^-$ ($\bar{\upsilon}$ cm^{-1})**	**$[Mn(RABA)_2(H_2O)_2]$ ($\bar{\upsilon}$ cm^{-1})**	**$[Cu(RABA)_2]$ ($\bar{\upsilon}$ cm^{-1})**	**Assignment ($\bar{\upsilon}$ cm^{-1})**
1477	1417	1412	1420	$\bar{\upsilon}_{N=N}$
1242	1236	1241	1229	$\bar{\upsilon}_{C–O\ (chelated)}$
1602	1597	1596	1601	$\bar{\upsilon}_{C=O\ (free)}$
–	778	728	768	$\bar{\upsilon}_{M–N}$
–	690	667	653	$\bar{\upsilon}_{M–O}$

The band at 1477cm^{-1} in the ligand is attributed to azo group. This is shifted to 1417cm^{-1} in Zn complex, 1412cm^{-1} in manganese complex and 1420 cm^{-1} in copper complex suggesting a coordination of metal ion to nitrogen of azo group. The band at 1242cm^{-1} in the ligand is attributed to C–O stretching. This is shifted to 1236cm^{-1} in Zn complex, 1241cm^{-1} in manganese complex and 1229cm^{-1} in copper complex. The carbonyl absorption of ligand and complexes are given by the bands at 1602cm^{-1} (in ligand), 1597cm^{-1} (in Zn complex), 1596cm^{-1} (in Mn complex) and at 1601cm^{-1} (in Cu complex).

3.3. NMR Spectra

Proton NMR spectra (Figure 1) of the ligand RABA gives the following signals: Multiplet of aromatic proton of the benzoic acid part at 7.6–8.1 ppm. Multiplet of aromatic proton of the resorcinol part at 6.3–6.6 ppm. Singlet signal due to –OH of –COOH group at 12.39 ppm. Singlet signal due to –OH of resorcinol part at 10.89 ppm.

The proton NMR spectrum of the Zn(II) complex shows the following signals: Multiplet of aromatic proton of the benzoic acid part at 7.6–8.1 ppm. Aromatic proton of the resorcinol part shows a multiplet at 6.3–6.5 ppm. The singlet obtained due to –OH of –COOH group is seen at 12.57 ppm. Singlet signal of –OH (resorcinol part) is obtained at 10.79 ppm. From the spectra of the ligand and the complex we can confirm that one of the –OH group in the resorcinol is coordinated to the metal. The less intense peak at 10.78 ppm indicates the second –OH group of the resorcinol remain unchanged in its position. It is not coordinated to the metal.

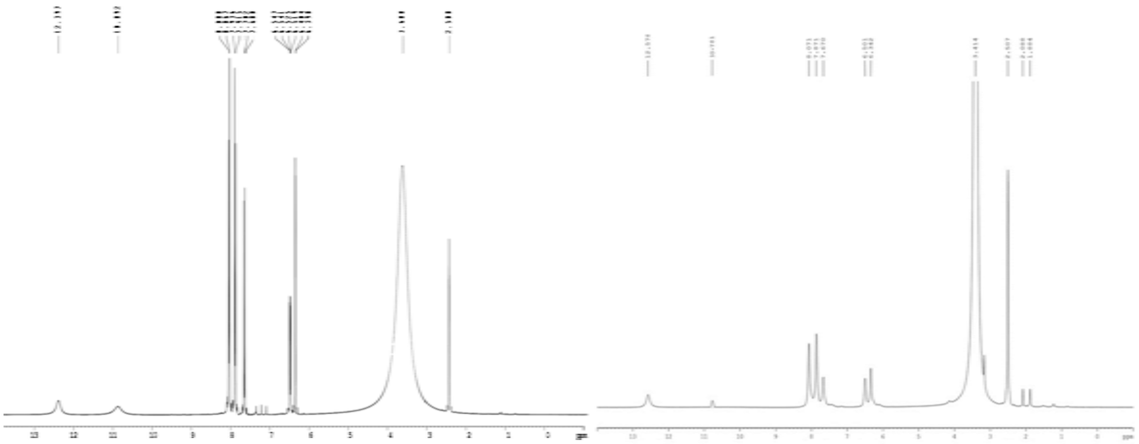
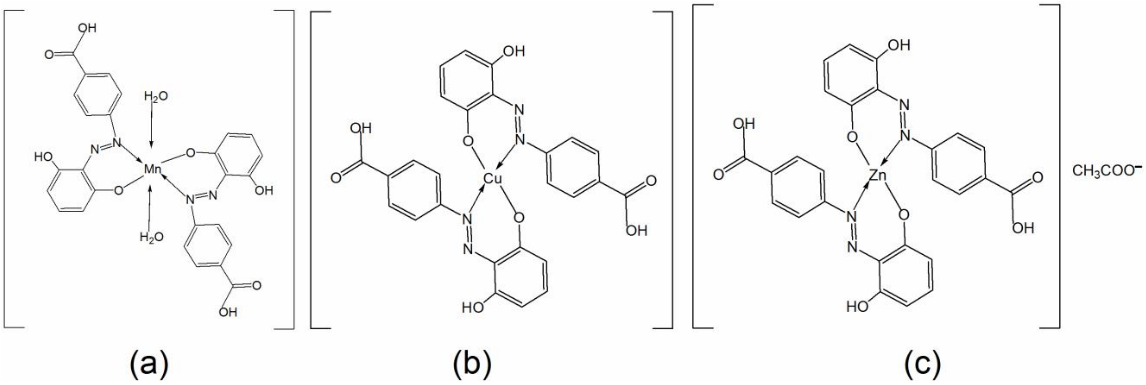


Fig. 1: NMR spectrum of RABA and $[Zn(RABA)(H_2O)_2]CH_3COO^-$



(a) (b) (c)

Fig. 2: Proposed structure for (a) $[Mn(RABA)_2(H_2O)_2]$, (b) $[Cu(RABA)_2]$ and (c) $[Zn(RABA)(H_2O)_2]CH_3COO^-$

On the basis of these observations and discussions it can be suggested that RABA is acting as a bidentate ligand. The Zn (II) and Cu(II) complexes have co-ordination number four and assumes tetrahedral and square planar geometry respectively and Mn(II) complex has co-ordination number six and assume octahedral geometry (Figure 2).

3.4. Antibacterial activity

The invitro biological screening effect of the investigated compounds were tested against the bacteria *Staphylococcus aureus* by using Agar-well diffusion method by taking DMSO as solvent for RABA and [Mn(RABA)$_2$(H$_2$O)$_2$].

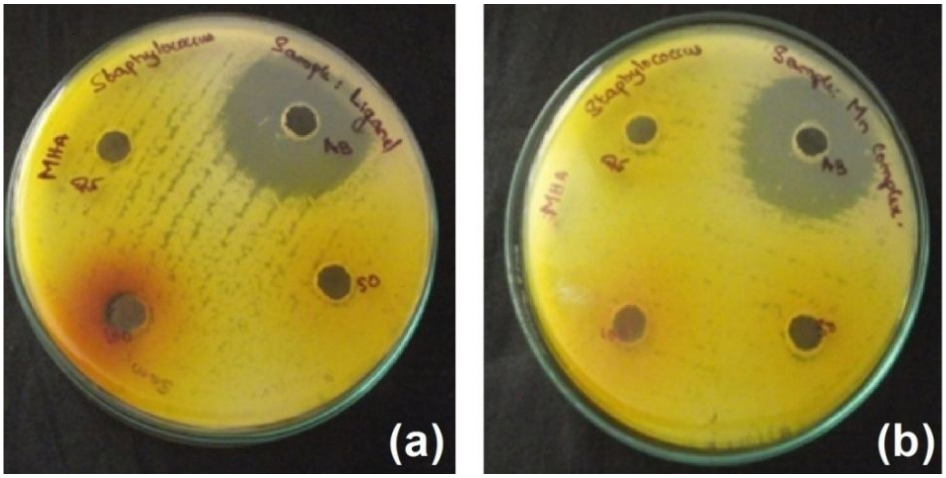


Fig. 3: Antibacterial activity of (a) RABA and (b) [Mn(RABA)$_2$(H$_2$O)$_2$]

The result indicates that the [Mn(RABA)$_2$(H$_2$O)$_2$] shows greater antibacterial activity (Figure 3) than RABA against *Staphylococcus aureus*. Stock concentration was taken as 10mg/ml. The details are given in Table 5.

Table 5: Antibacterial activity of the RABA and [Mn(RABA)$_2$(H$_2$O)$_2$]

Sample	**Concentration (µg/mL)**	**Zone of inhibition (cm)**
Ligand RABA	Streptomycin (10µg)	3.5
	250	Nil
	500	Nil
	1000	1.0
Mn complex [Mn(RABA)$_2$(H$_2$O)$_2$]	Streptomycin (10µg)	3.5
	250	Nil
	500	Nil
	1000	1.3

3.4. Antifungal activity

The antifungal activity was determined by Agar well diffusion method with concentration of stock as 10mg/ml against the organism *Candida albicans* (Figure 4) and the results are shown in Table 6. The results indicate that the [Mn(RABA)$_2$(H$_2$O)$_2$] shows greater antifungal activity than RABA against *Candida albicans*.

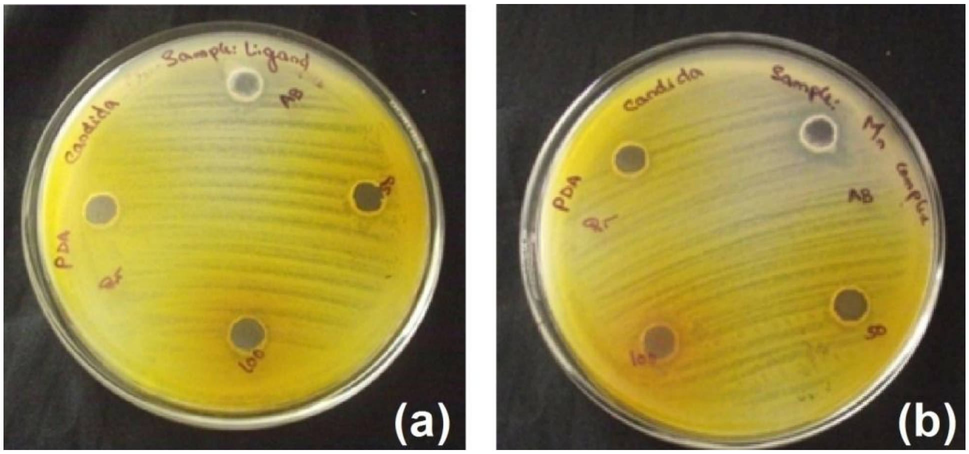


Fig. 4: Antibacterial activity of (a) RABA and (b) $[Mn(RABA)_2(H_2O)_2]$

Table 6: Antibacterial activity of the RABA and $[Mn(RABA)_2(H_2O)_2]$

Sample	Concentration (µg/mL)	Zone of inhibition (cm)
Ligand RABA	Clotrimazole	1.5
	250	Nil
	500	Nil
	1000	1.0
Mn complex $[Mn(RABA)_2(H_2O)_2]$	Clotrimazole	1.5
	250	Nil
	500	Nil
	1000	1.3

4. CONCLUSIONS

An azo dye is prepared from resorcinol and 4-amino benzoic acid (RABA). The complexes of Zn(II), Mn(II) and Cu(II) were prepared using RABA. Characterization of the ligand and complexes has been done on the basis of analytical and physico-chemical methods. From their spectral and magnetic data it is concluded that the manganese complex possess octahedral geometry having the formula $[Mn(RABA)_2(H_2O)_2]$ and copper complex possess square planar geometry having formula $[Cu(RABA)_2]$. Tetrahedral geometry is assigned for the zinc complex $[Zn (RABA) (H_2O)_2]$ on the basis of conductance measurements, IR and NMR spectral studies. The ligand and metal complexes were screened for their biological activities against *Staphylococcus aureus* and *Candida albicans*. The ligand and the complexes showed better antimicrobial activity.

REFERENCES

[1] Liehr A. D. and Balhausen C. J., Anna. Phy., **1958**, 304
[2] Stallmann O., J. Chem. Edn., 37, **1960**, 220
[3] Venkataraman K., The Chemistry of Synthetic Dyes, Academic Press, New York, **1952**,
[4] Khan O., Angero. Chem. Int. Engl., 24, **1985**, 834
[5] Engel A., Ger. Offen, Chem. Abstr., 120(16), 194131h
[6] Geary, W. J., Cood. Chem. Rev., 7, **1971**, 81-122
[7] Rajendra .K. Jain, Anand.P. Mishra, J.Seb.Chem. Soc., 77(8), **2012,** 1013-1029.