Synthesis and characterization of cobalt (II), nickel (II), copper (II) and mercury (II) complexes of hetero donor ligand

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ABSTRACT

Copper (II), Cobalt (II), Nickel(II) and Mercury(II) Complexes of Rhodanine-3-acetic acid-2-imino thiophenol (RDABT) have been synthesized and characterized by elemental analysis, conductivity, magnetic susceptibility measurements, IR, ESR and electronic spectral data. The molar conductivity data showed as slight ionic nature of the complexes. The tri dentate nature and electronic spectral data suggest that all the metal complexes are square planar geometry. The antimicrobial activities of the ligand and its complexes have been screened and showed in Table-7 &8. Based on the experimental results metal complexes showed more toxic effects than free ligand (RDABT). It has been reported that the metal complexes of ligand containing sulphur as a donor atom and electron with drawing group exhibit improved biological activity[1]. It led us to synthesize and characterize the new Schiff base (RDABT) and its complexes.

Key words: Rhodanine-3-acetic acid, 2-Aminothiophenol, VSM, ESR, Antimicrobial activity.

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INTRODUCTION

Rhodanine derivatives are attractive compounds owing to their outstanding biological activities such as anticonvulsant, antibacterial, antiviral and antidiabetic[2]. These derivatives also act as hepatitis C virus (HCV) protease inhibitor[3]. It is known that Rhodanine metal complexes plays an important role in biological reactions due to their unusual magnetic properties. Due to various possibilities of chemical derivatization of the rhodanine ring, rhodanine-based compounds will probably remain a privileged scaffold in drug discovery[4].

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It is, therefore interesting and convenient to isolate and study some new Co(II), Ni(II), Cu(II) and Hg(II) Schiff base complexes of Rhodanine-3-aceticacid derivatives. The goal at the outset of this research was to develop more effective antimicrobial analogue of Rhodanine-3-aceticacid.

EXPERIMENTAL SECTION

All the chemicals used were of AR grade and used without further purification. The elemental analysis was performed at RSIC, CDRI, and Luck now. The infrared spectra were recorded in the range 4000-200 cm^{-1} with a Perkin-Elmer 783 spectrophotometer. The electronic spectra were recorded on a Shimadzu UV-1601 spectrophotometer using DMF as solvent. The molar conductance of complex in DMF ($\sim 10^{-3}$N) were determined at 27 ± 2^0C using a systronic 303 direct reading conductivity bridge. The magnetic susceptibility measurements were made using a vibrating sample magnetometer (VSM) operating at field strength of 5 KG. The ^{1}H NMR spectra were recorded on various XL-300 MHz high resolution instrument is CDCl$_3$ solvent. The mass spectra were recorded using FANNING MAT 8230 mass spectrometer. ESR spectra are obtained on varion E-112 X-band spectrophotometer at room temperature and LNT.

Synthesis of Schiff Base

The Schiff base Rhodonine-3-acetic acid-2-iminothiophenol was prepared by the condensation of Rhodanine-3-acetic acid with 2-aminothiophenol in methanol. To the hot methanol solution (25 ml) of Rhodonine-3-acetic acid (1.4 gm, 0.00732 mol) was added 2-aminothiophenol (1.08 gm, 0.0079 mol) is 25 ml methanol and the reaction mixture was refluxed for 18 hrs at 50^0 C. The light yellow solution changed to light brown color. After reducing the solvent the solution was allowed to stand for overnight. The separated yellowish brown solid was recrystallized from methanol. The yield, melting point and analytical data of this Schiff base are given in Table-1.
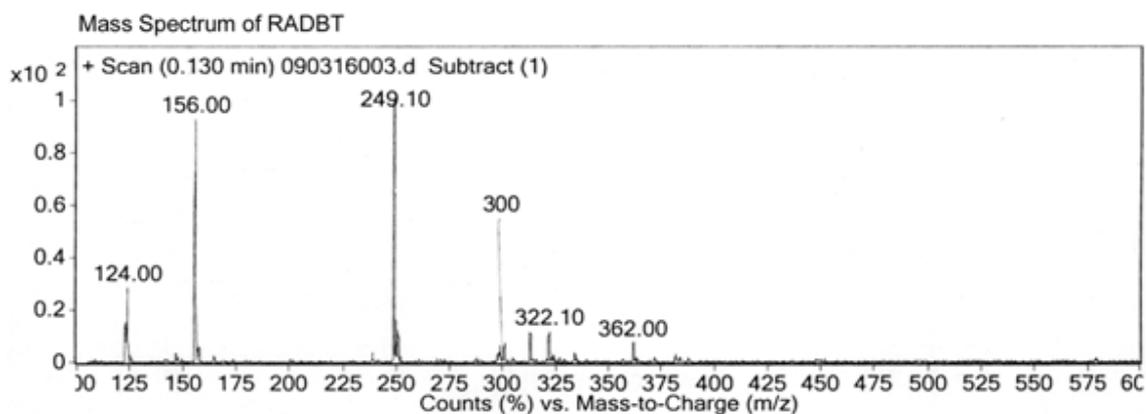
Table – 1: Analytical data of RDABT and its metal complexes

Compound	Color	M.P(^{0}c) Yield(%)	Molecular Weight	Elemental analysis, Found (calcd)				
				C	H	N	S	M
RDABT	Yellow	44-46^{0}c	282	45.35 (46.8)	3.71 (3.55)	9.31 (9.9)	22.59 (22.69)	-
Cu-RDABT	Black	150^{0}c	344.5	38.21 (38.31)	2.59 (2.61)	8.05 (8.12)	18.29 (18.57)	18.15 (18.43)
Co-RDABT	Dark brown	205^{0}c(dc)	339.9	38.42 (38.83)	2.88 (2.65)	8.17 (8.23)	18.62 (18.82)	17.18 (17.33)
Ni-RDABT	Black	120^{0}c(dc)	339.69	38.75 (38.86)	2.40 (2.65)	8.18 (8.24)	18.72 (18.84)	17.20 (17.28)
Hg-RDABT	Wheat colour	170^{0}c(dc)	481.6	27.25 (27.40)	1.75 (1.86)	5.75 (5.81)	13.25 (13.28)	41.54 (41.65)

Synthesis of Complexes

To a methanolic solution (25 ml) of the Schiff base (0.5 g, 0.001 mol), a solution of appropriate Cu(II) solution (0.43 g, 0.001 mol) in hot methanol (25 ml) was added followed by 1 ml of 1 M NaOAC was added. A black complex is formed is separated out, washed with n-hexane and dried in air. The same procedure was adopted for the preparation of Co (II), Ni (II), and Hg (II) complexes. The resultant solids were filtered and washed with n-Hexane and dried in air.

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Fig-1: The mass spectra of RDABT show molecular ion peaks at 298 ±2, 124, 152, 249 (m/z) respectively corresponding to their molecular weights m, 298± 2; M-$C_5H_5NO_2S_2$; M-C_4H_4NOS; M- S, OH.

Mass Spectrum of RADBT

+ Scan (0.130 min) 090316003.d Subtract (1)

x10 2

156.00   249.10

300

124.00

322.10   362.00

00 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 6C
Counts (%) vs. Mass-to-Charge (m/z)

RESULTS AND DISCUSSION

Infrared spectra of RDABT recorded in KBr medium and Bands at 1614 cm⁻¹ for ∨ C=N; 2593 cm⁻¹ for ϑS-H; 1721 cm⁻¹ for ϑC=0 are observed in the IR spectra of RDABT. Strong and broad absorption band at 2593 cm⁻¹ in the IR spectra of RDABT assignable for ϑO-H stretching band. Thus infrared spectral data of present ligand indicate the Schiff base formation. Infrared spectra of RDABT ligand is compared with its metal complexes. Important IR spectral bands and their assignments are presented in the Table-2. The weak S-H stretching frequency which appears around 2593 cm⁻¹ in the infrared spectra of RDABT ligand does not appear in the spectra of their complexes indicates the deprotonating of Thiolic protons on complex formation [5, 6, 7]. A strong band exhibited at 1614 cm⁻¹ the IR spectrum of the ligand has been assigned to the (C=N) stretching vibration of the azomethine group. On complexation, this band is shifted to 1594 cm⁻¹, 1600 cm⁻¹, 1599 cm⁻¹, 1578 cm⁻¹ for Cu (II), Co (II), Ni (II), Zn (II) complexes respectively. This shift to lower wave numbers supports the participation of the azomethine group of this ligand in binding to the metal ion [8, 9]. The coordination of azomethine nitrogen to the metal atom would be expected to reduce the electron density in azomethine group and thus cause for a reduction in C=N stretching frequency. The participation of Thiolic sulphur in bonding to the metal ion is supported by a upward shift in ϑC-S by 19-21 cm⁻¹. This shift is due to the presence of aromatic ϑC-S [10]. In the far IR spectral region, additional bands at 400-390 and 340-295 are assigned to ϑM-N [11,12] and ∨ϑM-S modes [13,14] respectively.

Table-2: Selected IR bands (cm⁻¹) with tentative assignments

Compound	ϑ(C=N)	ϑ (C-OH)	ϑ (C-S)	ϑ (S-H)	ϑ (C=S)	ϑ (M-N)	ϑ (M-S)
RDABT	1615	3502	647	2593	1192	-	-
Cu-RDABT	1594	3416	668	-	1161	400	340
Co-RDABT	1600	3363	668	-	1187	390	305
Ni-RDABT	1599	3403	666	-	1184	395	295

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Table-3: Molar Conductance data of metal complexes

Complex	Conductance(ohm^{-1} cm^2 mol^{-1})
Cu-RDABT	6.0
Co-RDABT	8.0
Ni-RDABT	8.0
Hg-RDABT	0.0

^{1}H-NMR Spectra
^{1}H-NMR spectra of RDABT is recorded in CDCl3. In ^{1}H-NMR spectra of RDABT, the signals due to Thiolic proton appeared at 4.2. Multiplets in the regions 6.5, 6.8, 7.1 are due to the presence of aromatic protons. A singlet appeared in the region of 4.7 is due to methylene protons.

Table-4: Electronic spectral data and ligand field parameters of a nickel complex

complex	Method of evaluation	$\vartheta 1$	$\vartheta 2$	$\vartheta 3$	B	β_{35}	10Dq	$\vartheta 2$- $\vartheta 1$	$\vartheta 2$/ $\vartheta 1$
Ni-RDABT	Observed values	8701	16077	25641	742.2	0.7187	8701	7376	1.85
	10Dq	15282	25512				8701	6581	1.76

Table-5: Magnetic moment data of metal complex of RDABT

Complex	Magnetic moment(B.M)
Co-RDABT	3.038
Ni-RDABT	2.372
Cu-RDABT	2.28

The observed magnetic moments of Co-RDABT, Ni-RDABT and Cu-RDABT complexes were found to be 3.038, 2.372 and 2.28 B.M respectively, which are subnormal to the range (2.9 – 3.4 B.M) which suggest their tetrahedral geometry. Low spin square planar complexes of Co (II) exhibit a narrow band near 8460 cm^{-1} and second stronger and broader band near 20,703 cm^{-1}.

Bands observed at 8701 cm^{-1} (ϑ_1), 15282-16077 cm^{-1} (ϑ_2)   and 25512-25641 cm^{-1} (ϑ_3)   in the electronic spectra of Ni-RDABT.   These bands suggest the presence of square planar geometry. Spectral data have been utilized to compute important ligand field parameter 10 Dq and Rocha inter electronic repulsion parameters (B) are employed to calculate ϑ_2 and ϑ_3 (Table-4). Comparison of 10 Dq and B values for the nickel complex indicates that the ligand give reasonably strong covalent bonds. The electronic spectral data together with reported magnetic moment value suggest a square planar geometry for nickel complex [15].

In ESR studies, the spin Hamiltonian, orbital reduction and bonding parameters of Cu-RDABT complex is presented in table-5. The g$_{II}$ and g$_{I}$ are computed from the spectrum using DPPH free radical as g marker, Kivelson and Neiman [16] have reported that g$_{II}$ value is less than 2.3 for covalent character metal ligand bond and is greater than 2.3 for ionic character. Applying this criterion, the covalent character of the metal ligand bond in complexes under study can be predicted. The trend g$_{II}$ > g$_{I}$ > g$_e$ (2.0023) observed for the complexes suggests that the unpaired electron is localized in d$_{x^2-y^2}$

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orbital [15] of the Copper (II) ion. The α^2 value for present chelate lie in the range 0.0185, supporting slight ionic nature of the complex.

Table-6

complex	g_{II}	g_I	g_{av}	G	A_{II}	α^2
Cu-RDABT	2.4183	2.1675	2.2511	2.5258	0.01053	0.8185

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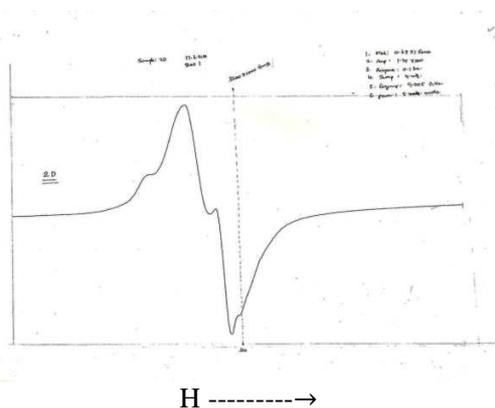
Fig.2: X-band ESR spectra of Cu-RDABT at Room temperature
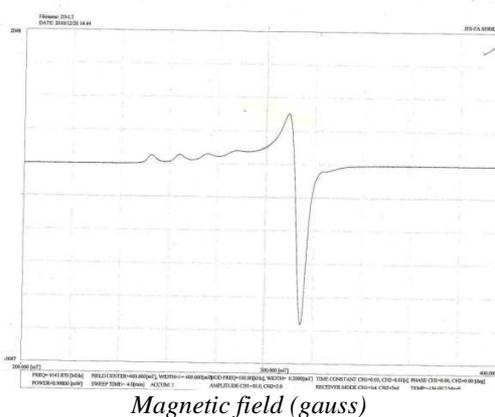

Magnetic field (gauss)

Fig.3: X-band ESR spectra of Cu-RDABT at liquid nitrogen temperature in DMF

Antimicrobial activity

Schiff base RDABT and its Co (II), Ni (II), Cu (II) and Hg (II) Metal chelates were evaluated for their antibacterial and antifungal activity against bacterial species like Bacillus, E.coli, Pseudomonas, Staphylococcus and fungal species like Fusarium oxysporum, Macrophomina phaseolina, Aspergillus flavus and Aspergillus Niger. The compounds were tested at a four different concentrations i.e., 25 ppm, 50 ppm, 100 ppm and 200 ppm. The result was compared with the free ligand and its metal complexes.

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Table-7: Fungal activity of RDABT and its metal complexes

Compound	concentration	F.oxysporum	M.phaseolina	A.flavus	A.niger
RDABT	25 ppm	72.22%	1.1%	86.66%	62.22%
	50 ppm	77.77%	1.1%	90%	72.22%
	100 ppm	83.33%	1.1%	92.22%	77.77%
	200 ppm	88.88%	1.1%	95.55%	93.33%
Cu-RDABT	25 ppm	87.77%	1.1%	88.88%	66.66%
	50 ppm	88.88%	1.1%	92.22%	74.44%
	100 ppm	90%	1.1%	95.55%	78.88%
	200 ppm	93.33%	1.1%	96.66%	88.88%
Co-RDABT	25 ppm	80%	1.1%	72.22%	62.22%
	50 ppm	86.66%	1.1%	74.44%	72.22%
	100 ppm	88.88%	1.1%	92.22%	78.88%
	200 ppm	90%	1.1%	94.44%	80%
Ni-RDABT	25 ppm	80%	1.1%	50%	70%
	50 ppm	84.44%	1.1%	66.66%	73.33%
	100 ppm	86.66%	1.1%	86.66%	75.55%
	200 ppm	90%	1.1%	94.44%	80%
Hg-RDABT	25 ppm	81.11%	1.1%	72.22%	72.22%
	50 ppm	88.88%	2.2%	86.66%	73.33%
	100 ppm	90%	4.4%	94.44%	77.77%
	200 ppm	94.44%	8.8%	95.55%	82.22%
Grisifluvin (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%

Table-8: Bacterial activity of RDABT and its metal complexes

compound	Name of the bacteria	Zone of Inhibition(cm)/concentration (ppm)			
		25	50	100	200
RDABT	*Bacillus*	0.7	0.9	1.2	1.7
	E.coli	0.8	1.1	1.3	1.8
	Pseudomonas	0.7	1.1	1.2	1.8
	Staphylococcus	0.8	0.9	1.0	1.8
Cu-RDABT	*Bacillus*	0.9	1.4	1.6	1.8
	E.coli	0.9	1.4	1.8	2.2
	Pseudomonas	0.9	1.6	2.0	2.0
	Staphylococcus	1.0	1.4	2.0	2.2
Co-RDABT	*Bacillus*	0.7	0.9	1.2	1.4
	E.coli	0.9	1.2	1.4	1.6
	Pseudomonas	0.9	1.2	1.6	1.4
	Staphylococcus	0.8	1.4	1.8	1.2
Ni-RDABT	*Bacillus*	-	0.8	0.9	1.2
	E.coli	-	1.0	1.0	1.4
	Pseudomonas	0.8	1.0	1.2	1.2
	Staphylococcus	0.9	0.9	1.4	1.3
Hg-RDABT	*Bacillus*	1.2	2.1	2.2	2.8
	E.coli	1.0	1.5	2.2	2.7
	Pseudomonas	1.7	2.4	2.6	3.2
	Staphylococcus	1.8	1.6	2.4	2.8

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Metal complexes have more biological activity than ligand. Such increased activity of the metal chelates can be explained based on Tweedy's chelation theory [17,18]. On chelation , the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups [19,20]. Further it increases the delocalization of π electrons over the whole chelate ring and enhances the penetration of the complexes into lipid membranes and blocking of the metal binding sites in the enzymes of microorganisms [21]. These complexes also disturb the respiration process of the cell and thus block the synthesis of proteins, which restricts further growth of the organisms [22].

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