

SYNTHESIS, SPECTROSCOPIC CHARACTERIZATION AND BIOLOGICAL EVALUATION OF MACROCYCLIC SCHIFF'S BASE BENZIL BIS(5-AMINO-1,3,4-THIADIAZOLE-2-THIOL) WITH NI(II), AND CO(II) METAL COMPLEXESA. Rajput^{*1,2}, S. Gautam², S. Chandra² and S. P. Sati¹¹Hemvati Nandan Bahuguna Garhwal University, Shri Nagar (Garhwal) Uttarakhand-246174.²Department of Chemistry Zakir Husain Delhi College University of Delhi, J.L.N. Marg New Delhi-110002, India.***Corresponding Author: A. Rajput**

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ABSTRACT

Co (II) and Ni (II) complexes of general composition $[ML_2]X_2$ (M = Co(II), Ni(II); X = Cl⁻, NO₃) were synthesized by the condensation of metal salts with semicarbazone / thiosemicarbazone derived from pdimethylaminobenzaldehyde. The metal complexes were characterized by elemental analysis, molar conductance, magnetic susceptibility measurements, IR and atomic absorption spectral studies. On the basis of electronic and infrared spectral studies, the metal complexes were found to have tetrahedral geometry. The Schiff bases and their metal complexes were tested for their antibacterial and antioxidant activities.

KEYWORD: Co (II) and Ni (II) complexes pdimethylaminobenzaldehyde.**INTRODUCTION**

Schiff bases are regarded as "privileged ligands" due to their capability to form complexes with a wide range of transition metal ions yielding stable and intensely colored metal complexes. Some of them have been shown to exhibit interesting physical and chemical properties and potential biological activities (Chandra et. al; 2009). Thiosemicarbazones are very versatile ligands. They can coordinate to metal as neutral molecules or after deprotonation as anionic ligands and can adopt

- 1: They have better co-ordination tendency.
- 2: They form more stable complexes.
- 3: They have better selectivity.
- 4: They may form macrocyclic ligands.
- 5: They have the ability to produce some new and unique complexes with enhanced biological and analytical properties. Thiosemicarbazones usually act as chelating ligands with transition metal ion bonding through the sulphur and hydrazine nitrogen atom. Thiosemicarbazones and their complexes have received considerable attention because of their pharmacological activities (Kothari and Sharma, 2011). Thiosemicarbazones and their complexes have received considerable attention because of their antifungal (Prasad and Agarwal, 2007), antitumor (Ainscough et.al., 1998) antibacterial (Chandra et.al, 2009), antiamoebic, antimalarial, antiviral (Kolocouris et.al, 2002) radio protective and anti-inflammatory activities. Certain thiosemicarbazones are relatively specific inhibitors of ribonucleotide reductase, which is an important metabolic target for the development of

chemotherapeutic agents against cancer (Sandercock et.al, 2007).

RESULTS AND DISCUSSION

The hydrazone based Schiff's base ligand L was obtained in good yield by reacting benzil and carbohydrazide in 1:2 ratio (Supplementary material). The complexes with Ni(II) and Co(II) metal ions were also obtained in the satisfactory yield on reaction of the ligand with metal salts.

Physical properties

The complexes are insoluble in the nonpolar solvents but soluble in the polar solvents like DMSO. The elemental, molar conductivities studies of the complexes suggest the $[M(L)]X_2$ and $[Co(L)X_2]$ compositions, where M = Ni(II) and CO(II), and $X^{1/4}NO$ and Cl.^[6] The analytical data of ligand and its complexes with their physical properties are given in Table 1 in supporting information, which indicates 1:1:2 metal:ligand:anion stoichiometry for all the complexes. Measured values of magnetic moments indicate that the nickel (II) complexes are diamagnetic whereas the copper(II) and cobalt(II) complexes are paramagnetic having the magnetic moments 1.86–1.93 and 4.80–4.92 BM respectively.

Electronic spectra

The UV/Visible spectra of complexes were recorded in DMSO solvent. The data of electronic spectra are summarized in Table 1.

Table 1
Microanalytical data of complexes with their physical properties.

S. no.	Complex	Color	m.p. (°C)	Molar conductance ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$)	Yield (%)	Microanalytical data (%) calcd. (found)			
						M	C	H	N
1	[Cu(L)]Cl ₂ CuC ₁₆ H ₁₈ N ₈ O ₂ Cl ₂	Green	220	127	73	11.34 (12.08)	38.30 (38.38)	3.54 (3.62)	21.82 (21.92)
2	[Cu(L)](NO ₃) ₂ CuC ₁₆ H ₁₈ N ₁₀ O ₈	Brown	160	122	63	11.22 (11.32)	35.26 (35.62)	3.42 (3.56)	24.62 (24.76)
3	[Ni(L)]Cl ₂ NiC ₁₆ H ₁₈ N ₈ O ₂ Cl ₂	Orange	225	130	68	12.86 (12.92)	38.68 (38.75)	3.82 (3.88)	22.88 (22.94)
4	[Ni(L)](NO ₃) ₂ NiC ₁₆ H ₁₈ N ₁₀ O ₈	Brown	300	142	72	10.36 (10.56)	34.78 (34.84)	3.32 (3.40)	25.82 (25.88)
5	[Co(L)]Cl ₂ CoC ₁₆ H ₁₈ N ₈ O ₂ Cl ₂	Brown	190	13	65	12.27 (12.36)	38.52 (38.68)	3.72 (3.78)	24.18 (24.26)
6	[Co(L)](NO ₃) ₂ CoC ₁₆ H ₁₈ N ₁₀ O ₈	Brown	230	12	67	10.82 (10.93)	36.52 (36.68)	3.36 (3.42)	26.12 (26.18)

3.1. Molar conductance

The molar conductance (ΔM) values of the complexes (Table 1) have been carried out using DMF as the solvent at the concentration of 10⁻³ M are in the range of 12–181 cm² mol⁻¹ for all the complexes. The low values indicate the non-electrolytic nature of the complexes. Thus, the complexes may be formulated as [CoL₂X₂].

3.2. Magnetic susceptibility measurements

The complexes show room temperature magnetic moments in the range 4.67–4.92 BM (Table 1) corresponding to three unpaired spins of high spin cobalt(II), but these values are noticeably higher than the spin-only value, i.e. 3.87 BM for d⁷ case. The deviation from the spin-only value is due to mixing of angular momentum from excited states vis spin-orbit coupling^[10] (Fig. 1).

Fig. Structure of the ligand.

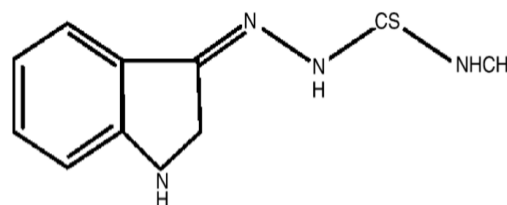


Fig. 1. Structure of the ligand

IR spectra

The main assignments of IR absorption bands of the ligand and its metal complexes are given in Table 2. The IR spectrum of free ligand shows m(C@N) azomethine band at 1606cm⁻¹^[14] and band at 786cm⁻¹ due to m(C@S)^[15] (Fig. 1). On complexation, the position of these bands is shifted towards lower frequency.

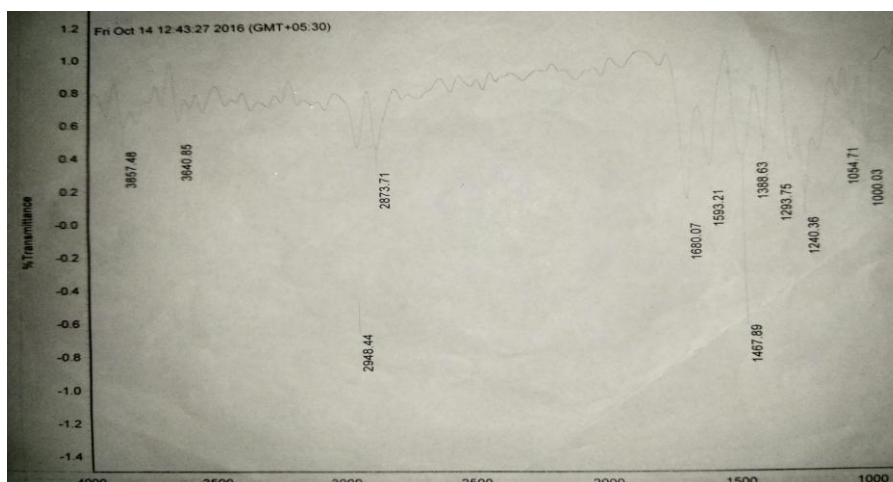


Fig.2: IR spectrum of macrocyclic schiff's base Ligand.

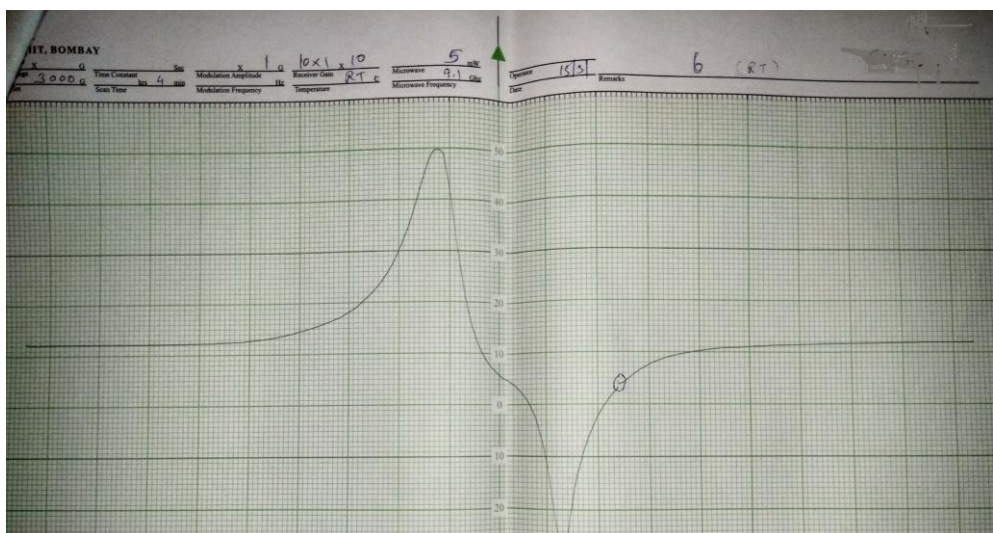
EPR spectrum

EPR studies of Copper(II) complexes were carried out on the X-band at 9.1 GHz under the magnetic field strength 3000 G. polycrystalline samples in DMSO were used to record X-band EPR spectra of the Cu(II) complexes and

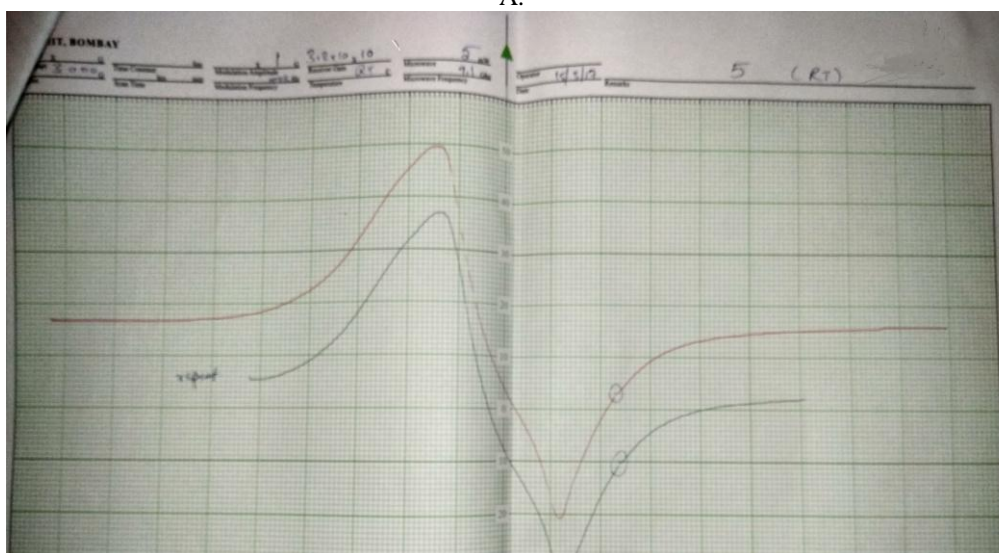
the spectra were recorded in DMSO at room temperature (Table 4). The trend $g_{\parallel} > g_{\perp} > 2.0024$ indicated that the copper the unpaired electron is localized in the $x^2 - y^2$ orbital of the Cu(II) ion and the spectral figures are characteristic for the axial symmetry tetragonal geometry. The parameter

G, determined as $G = (g_{\parallel} - 2) / (g_{\perp} - 2)$, which measures the exchange interaction between the metal centers in a polycrystalline solid, has been calculated. According to Hathaway [27] if $G > 4$, the exchange interaction is negligible, but $G < 4$ indicates considerable exchange

interaction in the solid complexes. The Cu(II) complexes reported in this paper gave the “G” values which are greater than 4 indicating the exchange interaction is absent in solid complexes.



A.



B.

Fig.3: electronic spectra of the complexes (a) Co(L)Cl_2 and (b) Ni(L)Cl_2 .

Table 2: Magnetic movement and electric spectral bands of Ni(II) and Cu(II) complexes with MSB ligands.

Complexes	electronic spectral bands (cm^{-1})				$\mu_{\text{eff}}(\text{B.M.})$
	$\nu_1(\text{cm}^{-1})$	$\nu_2(\text{cm}^{-1})$	$\nu_3(\text{cm}^{-1})$	$\nu_4(\text{cm}^{-1})$	
$[\text{Ni(L)Cl}_2]$	9542,	10799,	21930,	37453	2.96
$[\text{Ni(L)(OAc)}_2]$	9479,	12642,	27322,	35714	2.98
$[\text{Ni(L)Cl}_2]$	10695	19066	27919	38023	1.97
$[\text{Co(L)(OAc)}_2]$	10373	18622	24496	36364	1.94

Table 3: Epr data of Ni(II) and Co(II) complexes with MSB ligands.

S.no	Complexes	g_{\parallel}	g_{\perp}
1	$[\text{Co(L)Cl}_2]$	2.226	2.182
2	$[\text{Co(L)(OAc)}_2]$	2.214	2.524
3	$[\text{Ni(L)Cl}_2]$	2.113	2.017
4	$[\text{Ni(L)(OAc)}_2]$	2.138	2.242

Ligand field parameters

Various ligand field parameters were calculated and listed in Table 3. The values of Dq have been calculated

from transition energy ratio diagram.^[39] Our results are in agreement with the same type of complexes reported earlier.^[40] The Nephelauxe.

Table 4: ligands field parameter of Co(II) and Ni(II) complexes with MSB ligands.

Complexes	Dq (cm^{-1})	B (cm^{-1})	C	β	F_2	F_4
[Ni(L)Cl ₂]	959.2	266.86	1618.08	.339	498.01	46.23
[Ni(L)(OAc) ₂]	952.9	730.46	1049.4	.929	880.36	29.98
[Co(L)Cl ₂]	1069.5	926.6	1960.0	.827	1206	56.0
Co(L)(OAc) ₂]	985.4	454.33	2319.4	.405	785.63	66.26

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CONCLUSION

The size of cavity and different donor atoms in the macrocyclic ligands affected the stability of complexes, which can be easily explained by comparing between the values of crystal field splitting energy. The redox properties and stability of the complexes towards oxidation wave explored by cyclic voltammetry are related to the electron withdrawing or releasing ability of the substituents of macrocyclic ligands moiety. Proposed structures of the ligands and their nickel (II) complexes have been given. It is found out that the geometry of the complexes is depended on the number of coordination sites of the ligands and different anion. All the complexes are showing diamagnetic character comparatively other anions in L1 and L2. Magnetic moment data are supported by the infrared information about the diamagnetic nickel (II) complexes which show uncoordinated behaviour of nitrate group. The detailed information about the geometrical arrangements of atoms in a cyclic environment has been discussed on the basis of ¹H NMR and ¹³C NMR data. The cyclic voltammetry of the complexes showed that the nickel (II) complexes undergo one-electron reduction and oxidation to form the corresponding nickel (I) and nickel (III). These kinds of different oxidizing compounds may be found being used as one electron redox reagent since the former is a strong reducing agent and the latter is strong oxidizing agent. All the complexes in present study show kinetic property due to the chemical reaction coupled between two charges transfer processes in which irreversible first order chemical reaction is interposed between two successive one-electron transfers. The EF values of the complexes are strongly anion dependent. Ligands.

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