

# SYNTHESIS AND CHARACTERIZATION OF TRANSITION METAL COMPLEXES WITH A TETRAAZA MACROCYCLIC LIGAND: INHIBITORY ACTIVITY AGAINST SOME FUNGI

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## ABSTRACT

Co(II), Ni(II) and Cu(II) complexes were synthesized with a tetraaza macrocyclic ligand i.e. 1,5-dioxo-9,10-diaza-3,ol-tribenzo-(7,6,10,11,14,15) heptadecane. The ligand was characterized on the basis of elemental analysis, IR, <sup>1</sup>H NMR, ESI Mass studies while the complexes were characterized by elemental analysis, molar conductance measurements, magnetic susceptibility measurements, IR, electronic and EPR spectral studies. The molar conductance values of the complexes indicate the non-electrolyte nature and the complexes may be formulated as [M(L)X<sub>2</sub>], where M = Co(II), Ni(II), Cu(II) and X = Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup>. On the basis of spectral studies, an octahedral geometry has been assigned for the Co(II) and Ni(II) complexes, whereas tetragonal geometry was found for Cu(II) complexes. In vitro antifungal activity was evaluated for the ligand and its complexes against some pathogenic fungi to assess their growth inhibiting potential.

**Keywords:** IR and NMR spectra, Co Ni Cu Antifungal screening.

## INTRODUCTION

The field of macrocyclic chemistry is developing very rapidly because of its applications and importance in the area of coordination chemistry [1,2]. The stability of macrocyclic metal complexes depends upon a number of factors, including the number and types of donor atoms present in the ligand and their relative positions with in the macrocyclic skeleton, as well as the number and size of the chelate rings formed on complexation [3]. Macrocyclic complexes are thermodynamically more stable and more selective metal ion chelates than open chain analogue so the study of macrocyclic complexes is a growing class of research [4-6]. In living systems, metal ions play an important role as catalyst for many biological reactions. Macrocyclic complexes of transition metal ions have received great attention due to their biological activities, including antiviral, anticarcinogenic, antifertile, antibacterial and antifungal [7-13].

Therefore, it is worthwhile to carry out the synthesis and study the spectral properties of the macrocyclic ligand derived from salicylaldehyde, 1,3-dichloro-2-propanol and *o*-phenylenediamine. The goal of the study presented here is to synthesize the Co(II), Ni(II) and Cu(II) metal complexes of synthesized macrocyclic ligand and to provide a baseline of structural data using various spectroscopic techniques and antifungal activity.

## MATERIALS AND METHOD

All the chemicals were used of Anala R grade and received from Sigma-Aldrich and Fluka. Metal salts were purchased from E. Merck and used as received.

### *Synthesis of Ligand*

#### *Synthesis of 2-[3-(*o*-formyl phenoxy)-2-hydroxypropoxy] benzaldehyde (I)*

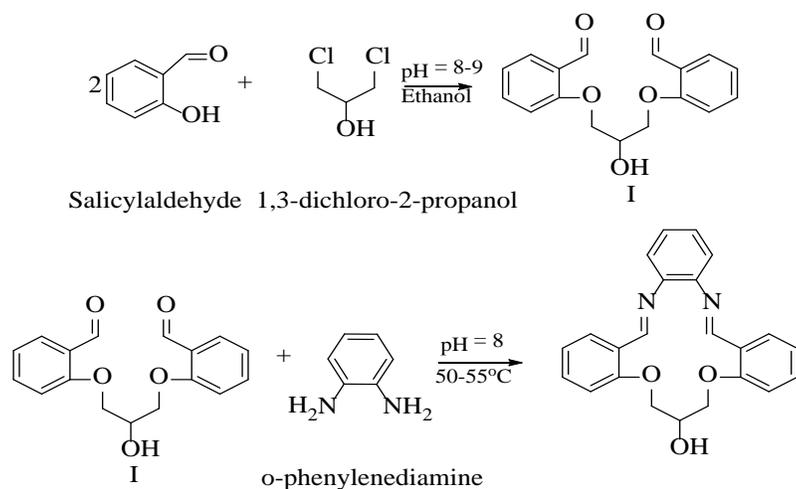
The compound I was prepared by the method reported in the literature [14]. A solution of NaOH (8.0 g, 0.2 mol) in water (400 mL) was added to a ethanolic solution of salicylaldehyde (20.98 mL, 0.2 mol). The resulting solution was heated up to 55–60

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**Scheme 1 Synthesis of macrocyclic ligand (L)**

$^\circ\text{C}$  for 1 h and then 1,3-dichloro-2-propane (9.54 mL, 0.1 mol) was added. The solution was made homogenous by addition of sufficient amount of ethanol. The resulting solution was refluxed for 72 h ( $\text{pH} \cong 8-9$ ) at  $78^\circ\text{C}$  and then cooled at  $0^\circ\text{C}$ . The cream colored solid product was recrystallized in ethanol–water (2:1). The resulting product was collected by filtration and dried in a vacuum over  $\text{P}_4\text{O}_{10}$ .

#### Synthesis of macrocyclic ligand (L)

To a hot ethanolic solution (20 mL) of 2-[3-(2-formyl phenoxy)-2-hydroxypropoxy] benzaldehyde (I) (6 g, 0.02 mol), a hot solution of o-phenylenediamine (2.162 g, 0.02 mol) was added with constant stirring. The solution was heated at  $50-55^\circ\text{C}$  ( $\text{pH} \cong 8$ ) for 8 h. On cooling at  $0^\circ\text{C}$ , an solid product was precipitated out. It was filtered, washed several times with cold ethanol and dried over  $\text{P}_4\text{O}_{10}$  (Scheme 1).

#### Synthesis of metal complexes

Hot ethanolic solution (20 mL) of metal salts (1 mmol) was added drop wise to a magnetically stirred solution of macrocyclic ligand L (1 mmol) in ethanol (30 mL). The resultant mixture was refluxed for 36 h and the clear solution was allowed to cool at  $0^\circ\text{C}$ .

The solid product precipitated out which was filtered, washed with ethanol, diethyl ether and dried under vacuum over  $\text{P}_4\text{O}_{10}$ . The same method was used for the preparation of metal complexes 2–6 in metal : ligand (1:1). Physical, analytical and spectral data of ligands and metal complexes are given in Table 1.

#### Analysis

The carbon and hydrogen were analyzed on Carlo-Erba 1106 elemental analyzer. The nitrogen content of the complexes was determined using Kjeldahl's method. Molar conductance was measured on the ELICO (CM82T) conductivity bridge. ESI-MS spectra were obtained using a VG Biotech Quattro mass spectrometer equipped with an electrospray ionisation source in the mass range of  $m/z$  100 to  $m/z$  1000. IR spectra (CsI) were recorded on FTIR spectrum BX-II spectrophotometer. NMR spectrum was recorded with a model Bruker Avance DPX-300 spectrometer operating at 400 MHz using  $\text{DMSO-d}_6$  as a solvent and TMS as internal standard. The electronic spectra were recorded in DMSO on Shimadzu UV mini-1240 spectrophotometer. EPR spectra was recorded on E4-EPR spectrometer at room temperature using DPPH as standard.

### Antifungal activity

The preliminary fungitoxicity activity of macrocyclic ligand and its complexes were examined by Poison Food Technique [15]. *Fusarium oxysporum*, *Rhizoctonia solani* and *Botrytis cinerea* were used for test fungi. The stock solution of the compound was directly mixed into the PDA (Potato Dextrose Agar) medium at the tested concentration.

Chlorothalonil used as commercial fungicide and DMSO served as control. Potato dextrose agar medium was prepared by using potato, dextrose, agar-agar and distilled water. Appropriate quantities of the compounds in DMSO was added to potato dextrose agar medium in order to get a concentrations of 100, 200 and 300 ppm of compound in the medium. The medium was poured into a set of two petriplates under aseptic conditions in a laminar flow hood. When the medium in the plates was solidified, a mycelial discs of 0.5 cm in diameter cut from the periphery of the 7 day old culture and it was aseptically inoculated upside down in the centre of the petriplates. These treated petriplates were incubated at  $28 \pm 1$  °C until fungal growth in the control

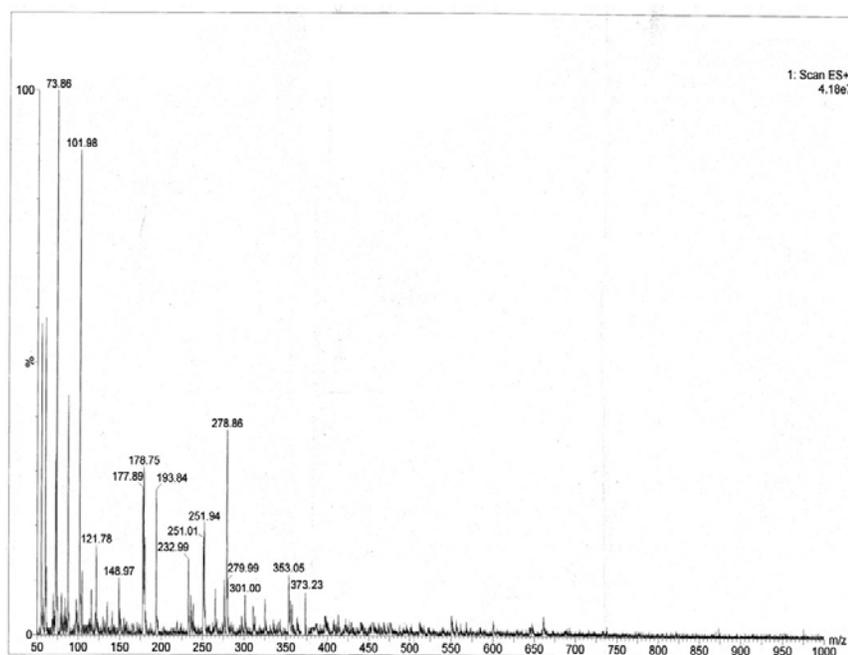


Fig. 1. Mass spectrum of the macrocyclic ligand L

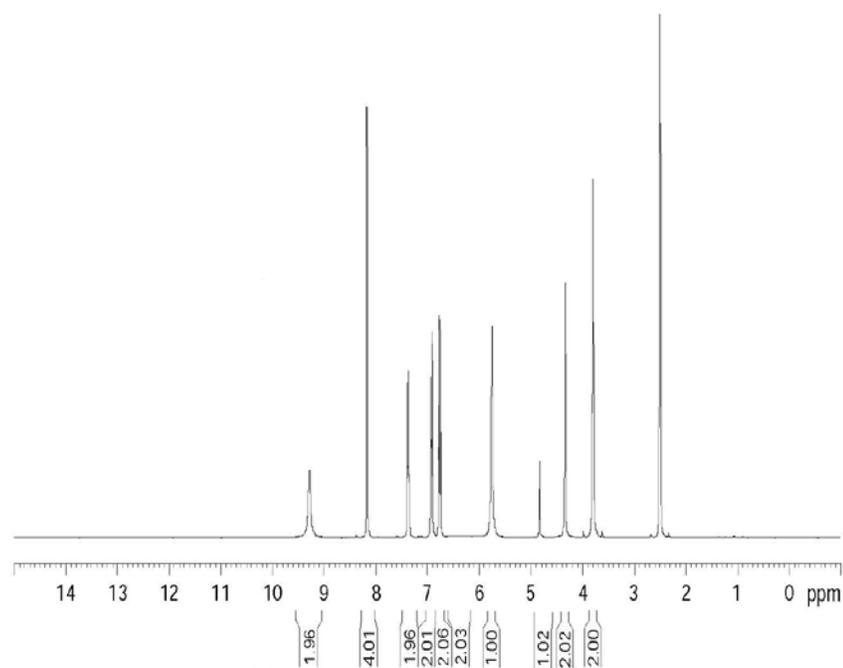


Fig. 2.  $^1\text{H}$  NMR of ligand L

petriplates was almost complete. The inhibition of the fungal growth expressed in percentage terms was determined from the growth in the test plate relative to the respective control plate as given

below:

$$\text{Inhibition (\%)} = (C-T) \times 100 / C$$

where C = diameter of fungal growth in the control plate and T = diameter of fungal growth in the test

**Table 1: Physical and Analytical data of Ligand L and metal complexes 1–6**

No	Molecular Formula	Color	Yield	M. Pt (°C)	Elemental Analysis (%) found (calc.)			
					C	H	N	M
L	C <sub>23</sub> H <sub>20</sub> N <sub>2</sub> O <sub>3</sub>	Orange	68	212	74.12 (74.18)	5.45 (5.41)	7.48 (7.52)	-
1	Ni(L)Cl <sub>2</sub> C <sub>23</sub> H <sub>20</sub> Cl <sub>2</sub> N <sub>2</sub> NiO <sub>3</sub>	Green	54	<280	55.12 (55.03)	4.11 (4.02)	5.51 (5.58)	11.65 (11.69)
2	Ni(L)(NO <sub>3</sub> ) <sub>2</sub> (C <sub>23</sub> H <sub>20</sub> N <sub>4</sub> NiO <sub>9</sub> )	Light Green	62	<280	49.84 (49.76)	3.65 (3.63)	10.15 (10.09)	10.51 (10.57)
3	Co(L)Cl <sub>2</sub> C <sub>23</sub> H <sub>20</sub> Cl <sub>2</sub> CoN <sub>2</sub> O <sub>3</sub>	Pink	65	<280	55.04 (55.00)	4.03 (4.01)	5.63 (5.58)	11.78 (11.73)
4	Co(L)(NO <sub>3</sub> ) <sub>2</sub> (C <sub>23</sub> H <sub>20</sub> CoN <sub>4</sub> O <sub>9</sub> )	Pink	67	<280	49.75 (49.75)	3.59 (3.63)	10.15 (10.09)	10.65 (10.61)
5	Cu(L)Cl <sub>2</sub> C <sub>23</sub> H <sub>20</sub> Cl <sub>2</sub> CuN <sub>2</sub> O <sub>3</sub>	Blue	57	<280	54.55 (54.50)	3.92 (3.98)	5.51 (5.53)	12.50 (12.54)
6	Cu(L)(NO <sub>3</sub> ) <sub>2</sub> (C <sub>23</sub> H <sub>20</sub> CuN <sub>4</sub> O <sub>9</sub> )	Blue	68	<280	49.37 (49.33)	3.55 (3.60)	10.06 (10.01)	11.29 (11.35)

**Table 2 : Magnetic Moment (BM) and Electronic Spectral data (cm<sup>-1</sup>) and Ligand Field parameter of the complexes**

Complex	$\mu_{\text{eff}}$ (BM)	Electronic data (cm <sup>-1</sup> )			Ligand Field Parameter			
		$\nu_1$	$\nu_2$	$\nu_3$	Dq (cm <sup>-1</sup> )	B (cm <sup>-1</sup> )	B	LFSE (kJmol <sup>-1</sup> )
1	4.89	10470	16702	21188	1177.1	532	0.70	112.50
2	4.99	10383	16325	18621	984.2	784	0.48	94.07
3	2.86	11248	18621	21412	1124.8	419	0.40	161.26
4	2.92	11185	18688	27322	1118.5	830	0.79	160.36
5	1.98	12380	18268	24645	-	-	-	-
6	1.95	15250	19467	26345	-	-	-	-

**Table 3 . EPR spectral data of the Co(II) and Cu(II) complexes**

Complex	Temp.	Data as polycrystalline sample			G
		$g_{  }$	$g_{\perp}$	$g_{iso}$	
1	LNT	-	-	2.1430	-
2	LNT	-	-	2.1004	-
5	RT	2.0853	2.0597	-	1.4288
6	RT	2.1182	2.0669	-	1.7668

plate.

## RESULTS AND DISCUSSION

The macrocyclic ligand L (Scheme 1) was prepared by mixing hot ethanolic solution (20 mL) of 2-[3-(formyl phenoxy)-2-hydroxypropoxy] benzaldehyde (I) (6 g, 0.02 mol), a hot solution of o-phenyldiamine (2.162 g, 0.02 mol) was added with constant stirring. The solution was heated at 50–55 °C (pH  $\cong$  8) for 8 h. On cooling at 0 °C, a solid product was precipitated out. It was filtered, washed several times with cold ethanol and dried over P<sub>4</sub>O<sub>10</sub> (Scheme 1). The structure of ligand thus formed was established by IR, <sup>1</sup>H NMR, Mass spectrophotometry and Analytical data (Table 1). The molar conductance value of complexes 1–6 lie in the range of 8.4–11.3 ( $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ), which indicates their non electrolytic nature.

### Mass Spectrum

The ESI mass spectrum of ligand L showed a molecular ion peak at  $m/z = 373.23$  amu corresponding to  $[M + H]^+$ , which confirms the proposed formula (Figure 1). It also shows a series of peaks at 353.05, 301.0, 278.86, 251.94, 232.99, 178.75, 121.78, 101.98 and 73.86 corresponding to various fragments. The intensities of these peaks give the idea of the stability of the fragments.

### <sup>1</sup>H NMR Spectrum

The <sup>1</sup>H NMR spectrum was recorded for ligand L (Figure 2). The characteristic signals, due to azomethine protons appear as singlet 9.28 ppm. The

aromatic region is a set of doublets and multiplets in the range 6.74–8.16 ppm, while the aliphatic proton appear in the range of 3.79 – 4.88 ppm. The D<sub>2</sub>O exchangeable –OH proton shows a singlet at 5.78 ppm. All the proton peaks were found to be in their expected regions.

### IR Spectra

The IR spectrum of the ligand was compared with those of the metal complexes in order to confirm the binding mode of the ligand to the corresponding metal ion. A very broad band at 3414  $\text{cm}^{-1}$  in ligand L corresponds to –OH vibration, while the band for the –CH=N- group appear at 1593  $\text{cm}^{-1}$ . However, in metal complexes 1–6, this band shifts to lower wave number in range of 1570–1577  $\text{cm}^{-1}$ , which indicates the coordination of azomethine nitrogen to metal ion [16]. This is also supported by the appearance of new band corresponds to M-N bond in the region of 492 – 503  $\text{cm}^{-1}$ . Similarly, appearance of new band in the region of 570–592  $\text{cm}^{-1}$  corresponds to M–O bond [17].

The presence of bands at 1450-1410 ( $\nu_5$ ), 1348 -1320 ( $\nu_1$ ) and 1058-1025( $\nu_2$ )  $\text{cm}^{-1}$ , in the IR spectra of the metal complex 2, 4 and 6 suggests that both the nitrate groups are coordinated to the central metal ion in a unidentate fashion [18]. The chloro complexes show the IR bands in the region 340-385  $\text{cm}^{-1}$  due to  $\nu(\text{M-Cl bond})$  [19]. The IR spectral data indicates that the ligand L coordinates to metal ion in tetradentate fashion. Based on above interpretation following structure can be proposed for metal complexes (Figure 3).

**Table 4. Antifungal activities data of the macrocyclic ligand and its complexes**

Compounds	Fungus species (tested )	Fungal inhibition (%) Concentrations( $\mu\text{g ml}^{-1}$ )		
		100	200	300
<b>L</b>	<i>F. oxysporum</i>	40 $\pm$ 4	51 $\pm$ 4	58 $\pm$ 6
	<i>R. solani</i>	49 $\pm$ 2	63 $\pm$ 6	71 $\pm$ 3
	<i>B. cinerea</i>	47 $\pm$ 6	57 $\pm$ 2	67 $\pm$ 4
	<i>F. oxysporum</i>	50 $\pm$ 3	65 $\pm$ 2	73 $\pm$ 4
<b>1</b>	<i>R. solani</i>	52 $\pm$ 6	60 $\pm$ 4	75 $\pm$ 2
	<i>B. cinerea</i>	61 $\pm$ 6	69 $\pm$ 5	80 $\pm$ 3
	<i>F. oxysporum</i>	49 $\pm$ 3	56 $\pm$ 3	72 $\pm$ 4
<b>2</b>	<i>R. solani</i>	54 $\pm$ 4	65 $\pm$ 5	77 $\pm$ 2
	<i>B. cinerea</i>	56 $\pm$ 4	61 $\pm$ 5	78 $\pm$ 5
	<i>F. oxysporum</i>	59 $\pm$ 2	72 $\pm$ 6	81 $\pm$ 3
<b>3</b>	<i>R. solani</i>	75 $\pm$ 6	81 $\pm$ 4	89 $\pm$ 2
	<i>B. cinerea</i>	65 $\pm$ 2	76 $\pm$ 4	85 $\pm$ 3
	<i>F. oxysporum</i>	63 $\pm$ 3	77 $\pm$ 3	89 $\pm$ 6
<b>4</b>	<i>R. solani</i>	71 $\pm$ 4	78 $\pm$ 2	88 $\pm$ 6
	<i>B. cinerea</i>	60 $\pm$ 3	71 $\pm$ 5	89 $\pm$ 5
	<i>F. oxysporum</i>	68 $\pm$ 6	77 $\pm$ 5	98 $\pm$ 3
<b>5</b>	<i>R. solani</i>	75 $\pm$ 6	89 $\pm$ 3	92 $\pm$ 4
	<i>B. cinerea</i>	68 $\pm$ 2	85 $\pm$ 2	95 $\pm$ 6
	<i>F. oxysporum</i>	71 $\pm$ 5	82 $\pm$ 2	99 $\pm$ 4
<b>6</b>	<i>R. solani</i>	75 $\pm$ 5	89 $\pm$ 6	95 $\pm$ 3
	<i>B. cinerea</i>	64 $\pm$ 3	86 $\pm$ 4	99 $\pm$ 3
	<i>F. oxysporum</i>	69 $\pm$ 0	79 $\pm$ 2	97 $\pm$ 1
<b>Chlorothalonil</b>	<i>R. solani</i>	72 $\pm$ 1	85 $\pm$ 2	96 $\pm$ 0
	<i>B. cinerea</i>	65 $\pm$ 2	82 $\pm$ 0	100 $\pm$ 1

<sup>a</sup>The results are expressed as the percentage of fungal inhibition with respect to control and are presented as mean  $\pm$  SD

### Magnetic moments

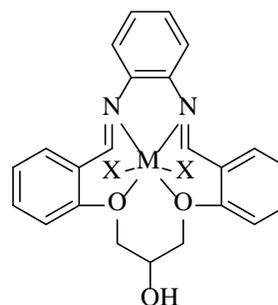
At room temperature the magnetic moment of cobalt(II) complexes lie in the range 4.89– 4.99 BM which correspond to three unpaired electrons. Ni(II) complexes show magnetic moment in the range 2.86-2.92 BM corresponding to two unpaired electron. At room temperature Cu(II) complexes show magnetic moment in the range 1.95-1.98 BM corresponding to one unpaired electron [20].

### Electronic spectra

The electronic spectra of the complexes were recorded in DMSO solutions. The electronic spectral data of the complexes are given in Table 4. The

electronic spectra of cobalt(II) complexes display the d–d transition bands in the region 10,383-10,471, 16,325-16,702 and 18,621-21,188  $\text{cm}^{-1}$ . These transitions may be assigned to the  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F) \nu_1$ ,  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F) \nu_2$  and  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P) \nu_3$ , respectively. These transitions correspond to the octahedral geometry around the Co(II) metal ion [21].

The absorption spectra of nickel(II) complexes display three d-d transition bands in the range 11,185– 11,248, 18,621– 18,688 and 21,412–27,322  $\text{cm}^{-1}$ . These transitions correspond to the  ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F) \nu_1$ ,  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F) \nu_2$  and  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P) \nu_3$ , respectively [22]. These transitions reveal that the nickel complexes possess an octahedral geometry.



M = Ni, Co, and Cu; X =  $\text{Cl}^{-1}$ ,  $\text{NO}_3^{-1}$

**Figure 3: Proposed structured of metal complexes**

Electronic spectra of Cu(II) complexes show the d-d transition bands in the range 12,380–15,250, 18,268–19,467 and 24,645–26,345  $\text{cm}^{-1}$ . These bands correspond to  ${}^2B_{1g} \rightarrow {}^2A_{1g}$  ( $d_{x^2-y^2} \rightarrow d_{z^2}$ ),  ${}^2B_{1g} \rightarrow {}^2B_{2g}$  ( $d_{x^2-y^2} \rightarrow d_{xy}$ ) and  ${}^2B_{1g} \rightarrow {}^2E_g$  ( $d_{x^2-y^2} \rightarrow d_{xz}, d_{yz}$ ) transitions, respectively [23]. On the basis of electronic transitions, a tetragonal geometry is suggested for Cu(II) complexes.

The ligand field parameters like Racah inter-electronic repulsion parameter B, ligand field splitting stabilization energy 10 Dq, covalency factor  $\beta$  and ligand field stabilization energy (LFSE) have been calculated for the Co(II) and Ni(II) complexes. The values of B and Dq of Co(II) complexes were calculated from the transition energy ratio diagram using  $\nu_3/\nu_1$  ratio. The value of  $\beta$  for the complexes under study accounts for the covalent nature of the complexes [24]. The evaluated parameters are listed in Table 2.

#### EPR Spectrum

The X-band EPR spectra of the Co(II) complexes were recorded at liquid nitrogen temperature in polycrystalline form. The line shaped EPR spectra of Co(II) complexes show the value of  $g_{\text{iso}} = 2.1004\text{--}2.1430$  (Table 3) around the Co(II) atoms.. The large deviation in the g values from the free electron value ( $g = 2.0023$ ) is due to large angular momentum contribution.

EPR spectra of the Cu(II) complexes were recorded, at room temperature as polycrystalline samples, on the X-band at 9.1 GHz under the magnetic field range 3000 G. The trend  $g_{\parallel} > g_{\perp} > 2.0023$ , observed for the complexes, under study, indicate that the unpaired electron is localized in the  $d_{x^2-y^2}$  orbital of the Cu(II) ion and the spectral features are characteristic for the axial symmetry. Tetragonally elongated geometry is thus confirmed for the aforesaid complexes.  $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$ , which measure the exchange interaction between the metal centers in a polycrystalline solid has been calculated. The complexes show the G values smaller than 4 which indicate exchange interaction in the solid complexes [25].

#### Antifungal Screening

Results of anti-fungal screening as shown in Table 4 indicate that the metal complexes inhibit higher anti-fungal activity than controlled one. Among all of the screened samples, complex 5 and 6 were observed to have a significant anti-fungal activity at quite a low concentration and could be considered to be a broad spectrum anti-fungal compound. The increased activity of the metal chelates can be explained on the basis of chelation theory [26]. Chelation reduces the polarity of metal ion, mainly by the partial sharing of its positive charge with the chelate rings. It increases the lipophilic character of the metal, which subsequently favours its permeation through the lipid layer of microorganism membrane, thereby impairing the normal cell processes [27]. It has also been proposed that concentration plays a vital role in increasing the degree of inhibition; as the concentration increases, the activity increases [28].

#### CONCLUSION

Co(II), Ni(II) and Cu(II) complexes with a tetradentate macrocyclic ligand have been prepared and characterized by using various spectroscopic techniques. On the basis of above spectral studies an octahedral geometry has been assigned for Co(II) and Ni(II) complexes while tetragonal geometry for Cu(II) complexes. Various ligand field parameters have been calculated and discussed. Metal complexes show potentially activity towards microbial strains in comparison to free ligand.

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