

## Mn(II), Co(II), Ni(II) and Cu(II) Complexes of a Tetraaza Macrocyclic Ligand: Synthesis, Characterization and Biological Screening

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Manganese(II), cobalt(II), nickel(II) and copper(II) complexes with 1,5,11,15-tetraaza-21,22-dioxo-tricyclo [19,3,1,<sup>6,10</sup>]-5,10,15-20-dicosatetraene (L), as a new macrocyclic ligand, have been synthesized with and characterized by elemental analysis, molar conductance measurements, magnetic susceptibility measurements, mass, IR, electronic and EPR spectral studies. The molar conductance measurements of the complexes in DMF correspond to non-electrolytic nature of Mn(II), Co(II) and Cu(II) complexes, while showing a 1:2 electrolyte for the Ni(II) complex. Thus, these complexes may be formulated as  $[M(L)X_2]$  and  $[Ni(L)]X_2$  (where M = Mn(II), Co(II) and Cu(II) and X = Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup>). On the basis of IR, electronic and EPR spectral studies, an octahedral geometry has been assigned for Mn(II) and Co(II), a square planar for Ni(II) and tetragonal for Cu(II) complexes. *In vitro* ligand and its metal complexes were also screened against the growth of some fungal and bacterial species in order to assess their antimicrobial properties.

**Keywords:** Macrocyclic ligand, Metal complexes, Spectral characterization, Biological screening

### INTRODUCTION

The field of macrocyclic chemistry of metals is developing very rapidly because of its applications and importance in the area of coordination chemistry [1,2]. Structural factors such as ligand rigidity, the types of donor atoms and their disposition have shown to play significant roles in determining the binding features of macrocyclic ligands toward metal cations [3,4]. The development of the field of bioinorganic chemistry has been another important factor in spurring the growth of macrocyclic compounds [5]. The chemical properties of macrocyclic complexes can be tuned to force metal ions to adopt unusual coordination geometry. Transition metal macrocyclic complexes have received much attention as an

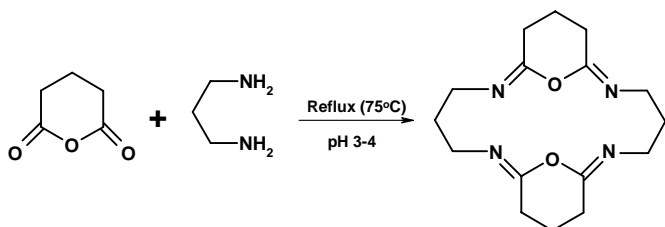
active part of metalloenzymes [6] and as biomimic model compounds [7]. It is due to their resemblance with natural proteins like hemerythrin and enzymes. The chemistry of macrocyclic compounds in particular is also important due to their catalytic [8] and biological applications [9].

In view of above applications in this paper we report the synthesis, characterization and biological studies of Mn(II), Co(II), Ni(II) and Cu(II) with a nitrogen donor [N<sub>4</sub>] macrocyclic ligand (L) (Fig. 1).

### EXPERIMENTAL

All the chemicals used were of Anala R grade and were procured from Aldrich. Metal salts were purchased from Merck and used as received. All solvents used were of standard/spectroscopic grade.

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**Fig. 1.** Preparation and structure of the ligand (L).

### Synthesis of Ligand

A hot ethanolic solution of glutaric anhydride (2.28 g, 0.02 mol) was added to an EtOH solution of 1,3-diaminopropane (1.48 g, 0.02 mol). This mixture was refluxed at  $\sim 75^\circ\text{C}$  for 8 h in the presence of few drops of concentrated HCl (pH  $\sim 3-4$ ). On cooling a solid white precipitate was formed. It was filtered, washed with cold EtOH and dried *in vacuo*.

### Synthesis of Complexes

A hot EtOH solution of ligand (0.60 g, 0.002 mol) was mixed with an EtOH solution of the corresponding metal salt (0.001 mol) with constant stirring and boiled under reflux for 7-12 h at  $75-90^\circ\text{C}$  ( $\pm 5$ ). On cooling a colored complex precipitated. It was filtered, washed with cold EtOH and dried under *in vacuo*.

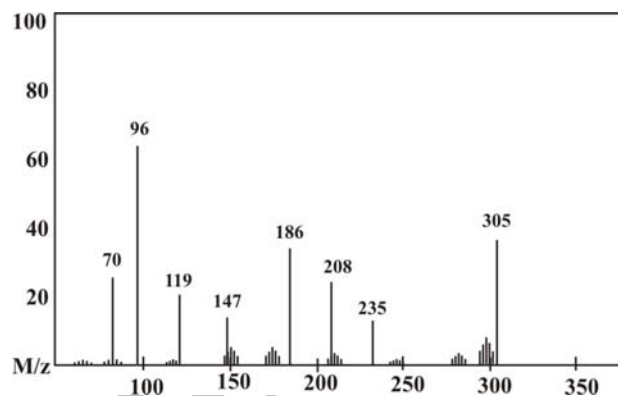
### Physical Measurements

The C, H and N were analysed on a Carlo-Erba 1106 elemental analyzer. Molar conductance was measured on a ELICO (CM82T) conductivity bridge. Magnetic susceptibility was measured at room temperature on a Gouy-balance using  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  as a calibrant. Electron-impact mass spectra were recorded on a JEOL, JMS, DX-303 mass spectrometer. IR spectra (CsI) were recorded on a Perkin Elmer FTIR Spectrum BX-II spectrophotometer. The electronic spectra were recorded in DMSO on a Shimadzu mini-1240 spectrophotometer. The EPR spectra of the complexes were recorded as polycrystalline samples and in DMSO solution, at liquid nitrogen temperature for Co(II) and at room temperature for Mn(II) and Cu(II) complexes, on a  $E_4$ -EPR spectrometer using DPPH as the g-marker.

## RESULTS AND DISCUSSION

### Ligand

The El-mass spectrum of the ligand (L) (Fig. 2) shows a



**Fig. 2.** Electron impact mass spectrum of the ligand (L).

final peak at 305 amu corresponding to the macrocyclic moiety  $[\text{C}_{16}\text{H}_{24}\text{N}_4\text{O}_2]^+$  (atomic mass 304 amu). Other peaks like 70, 96, 119, 147, 186, 209 and 235 amu correspond to various fragments. The intensity of these peaks gives the idea of the stability of fragments. The IR spectrum of the ligand does not exhibit any band corresponding to free diamine or keto group. It suggests complete condensation of the amino group with the keto group. A new band due to  $\nu(\text{C}=\text{N})$  group appeared at  $1598\text{ cm}^{-1}$  appeared in the ligand.

### Complexes

On the basis of elemental analysis, the complexes were found to have the composition as shown in Table 1. The molar conductance data of the Mn(II), Co(II) and Cu(II) complexes in DMSO correspond to their non-electrolytic nature [10] while the Ni(II) complex was found to be 1:2 electrolytic in solution. Thus, these complexes may be formulated as  $[\text{M}(\text{L})\text{X}_2]$  and  $[\text{Ni}(\text{L})]\text{X}_2$ , respectively [ $\text{M} = \text{Mn}(\text{II}), \text{Co}(\text{II})$  and  $\text{Cu}(\text{II})$  and  $\text{X} = \text{Cl}^-$  and  $\text{NO}_3^-$ ]. On complexation, the position of band corresponding to  $\nu(\text{C}=\text{N})$  group is shifted towards lower wavenumbers (*Ca.*,  $20-30\text{ cm}^{-1}$ ). This suggests that ligand acts in a tetradentate manner, which coordinates through the nitrogen atoms of the  $\nu(\text{C}=\text{N})$  group [11]. This is also confirmed by the appearance of bands in the range  $452-480\text{ cm}^{-1}$ . These are due to formation of the  $\nu(\text{M}-\text{N})$ . In the IR spectra of chloro complexes bands corresponding to  $\nu(\text{M}-\text{Cl})$  are observed at  $297-318\text{ cm}^{-1}$  indicating the presence of M-Cl bond. The IR spectra of nitrate complexes display three (N-O) stretching bands at  $1420-1428\text{ cm}^{-1}$  ( $\nu_3$ ),  $1308-1325\text{ cm}^{-1}$  ( $\nu_1$ )

**Table 1.** Physical Properties and Analytical Data of L and its Metal Complexes

Compound	Molar conductance ( $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ )	Color	M.P. ( $^{\circ}\text{C}$ )	Yield (%)	Elemental analysis found (calcd.) %			
					M	C	H	N
L	-	White	265	68	-	63.20 (63.16)	7.91 (7.89)	18.38 (18.42)
[Mn(L)Cl <sub>2</sub> ] MnC <sub>16</sub> H <sub>24</sub> N <sub>4</sub> O <sub>2</sub> Cl <sub>2</sub>	08	Cream	285	65	12.84 (12.79)	44.60 (44.65)	6.01 (5.58)	13.00 (13.02)
[Mn(L)(NO <sub>3</sub> ) <sub>2</sub> ] MnC <sub>16</sub> H <sub>24</sub> N <sub>6</sub> O <sub>8</sub>	03	Cream	290	67	11.36 (11.39)	39.78 (39.75)		11.64 (11.59)
[Co(L)Cl <sub>2</sub> ] CoC <sub>16</sub> H <sub>24</sub> N <sub>4</sub> O <sub>2</sub> Cl <sub>2</sub>	11	Pink	>300	70	13.52 (13.57)	44.29 (44.24)	5.48 (5.53)	12.86 (12.90)
[Co(L)(NO <sub>3</sub> ) <sub>2</sub> ] CoC <sub>16</sub> H <sub>24</sub> N <sub>6</sub> O <sub>8</sub>	14	Shiny Pink	>300	67	13.04 (12.08)	39.48 (39.43)	4.90 (4.93)	11.42 (11.50)
[Ni(L)Cl <sub>2</sub> ] NiC <sub>16</sub> H <sub>24</sub> N <sub>4</sub> O <sub>2</sub> Cl <sub>2</sub>	128	Brick Red	298	74	14.00 (13.53)	44.22 (44.24)	5.50 (5.53)	12.94 (12.90)
[Ni(L)(NO <sub>3</sub> ) <sub>2</sub> ] NiC <sub>16</sub> H <sub>24</sub> N <sub>6</sub> O <sub>8</sub>	130	Orange Red	292	72	12.09 (12.05)	39.46 (39.43)	4.97 (4.93)	11.45 (11.50)
[Cu(L)Cl <sub>2</sub> ] CuC <sub>16</sub> H <sub>24</sub> N <sub>4</sub> O <sub>2</sub> Cl <sub>2</sub>	07	Green	279	82	15.05 (14.58)	43.68 (43.74)	5.41 (5.47)	12.70 (12.76)
[Cu(L)(NO <sub>3</sub> ) <sub>2</sub> ] CuC <sub>16</sub> H <sub>24</sub> N <sub>6</sub> O <sub>8</sub>	05	Green		78	12.96 (13.01)	38.97 (39.02)	4.93 (4.88)	11.42 (11.38)

**Table 2.** Magnetic moment and Electronic Spectral Data of the Complexes

Complex	$\mu_{\text{eff}}$ (B.M.)	$\lambda_{\text{max}}$ ( $\text{cm}^{-1}$ )	$\epsilon$ ( $\text{l mol}^{-1} \text{cm}^{-1}$ )
[Mn(L)Cl <sub>2</sub> ]	5.82	18506, 22552, 26525, 35425	29, 37, 65, 129
[Mn(L)(NO <sub>3</sub> ) <sub>2</sub> ]	5.89	17794, 21978, 25974, 37575	27, 35, 62, 133
[Co(L)Cl <sub>2</sub> ]	4.87	9524, 14388, 18656, 37736	55, 66, 82, 155
[Co(L)(NO <sub>3</sub> ) <sub>2</sub> ]	4.92	9784, 14684, 18974, 38462	56, 68, 84, 158
[Ni(L)Cl <sub>2</sub> ]	Diamagnetic	15822, 20920, 28571	51, 95, 129
[Ni(L)(NO <sub>3</sub> ) <sub>2</sub> ]	Diamagnetic	16528, 22085, 29540	52, 83, 132
[Cu(L)Cl <sub>2</sub> ]	1.98	10449, 15948	50, 58, 149
[Cu(L)(NO <sub>3</sub> ) <sub>2</sub> ]	1.95	10526, 16181	51, 59, 151

and 1020-1045  $\text{cm}^{-1}$  ( $\nu_2$ ). The position of these bands suggested that both nitrate groups are coordinated to the central metal ion as a unidentate fashion. However, nitrate complex of Ni(II) shows a sharp strong band at 1387  $\text{cm}^{-1}$ , corresponding to uncoordinated nitrate group [12-14].

**Manganese(II) complexes.** The manganese(II) complexes

show magnetic moments in the range 5.82-5.89 B.M. at room temperature corresponding to five unpaired electrons. The electronic spectra of the Mn(II) complexes exhibit four weak intensity absorption bands in the range 17794-18506 ( $\epsilon = 27$ -29  $\text{l mol}^{-1} \text{cm}^{-1}$ ), 21978-22552 ( $\epsilon = 35$ -37  $\text{l mol}^{-1} \text{cm}^{-1}$ ), 25974-26525 ( $\epsilon = 62$ -65  $\text{l mol}^{-1} \text{cm}^{-1}$ ) and 35425-37575  $\text{cm}^{-1}$  ( $\epsilon =$

129-133 l mol<sup>-1</sup> cm<sup>-1</sup>). These bands may be assigned to the [15] transitions: <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>T<sub>1g</sub>(<sup>4</sup>G), <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>E<sub>g</sub>, <sup>4</sup>A<sub>1g</sub>(<sup>4</sup>G) (10B+5C), <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>E<sub>g</sub>(<sup>4</sup>D) (17B+5C) and <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>T<sub>1g</sub>(<sup>4</sup>P) (7B+7C), respectively.

The EPR spectra were recorded at room temperature, as a polycrystalline sample, and in DMSO solution. The polycrystalline spectra were isotropic and exhibit the 'g' value in the range 2.06-2.18. However, in DMSO solution it gives well-resolved six line spectra which may be due to the hyperfine interaction between the unpaired electron with the <sup>55</sup>Mn nuclear (I = 5/2).

**Cobalt(II) complexes.** At room temperature, the Co(II) complexes show magnetic moments in the range 4.87-4.92 B.M. corresponding to three unpaired electrons. The electronic spectra of Co(II) complex, recorded in DMSO solution, exhibit absorption in the region, 9524-9784 (ε = 55-56 l mol<sup>-1</sup> cm<sup>-1</sup>), 14388-14684 (ε = 66-68 l mol<sup>-1</sup> cm<sup>-1</sup>), 18656-18974 (ε = 82-84 l mol<sup>-1</sup> cm<sup>-1</sup>) and 3736-38462 cm<sup>-1</sup> (ε = 155-158 l mol<sup>-1</sup> cm<sup>-1</sup>). These bands may be assigned to <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>T<sub>2g</sub>(F), <sup>4</sup>T<sub>1g</sub> → <sup>4</sup>A<sub>2g</sub> and <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>T<sub>1g</sub>(P) transitions, respectively. The fourth band may be due to charge transfer. The position of these bands suggest an octahedral environment around the Co(II) ion [16,17].

The EPR spectra of Co(II) complexes were recorded as polycrystalline sample and in DMSO solutions at liquid nitrogen temperature. The 'g' values were found to be almost same in both cases. This indicates that the complexes have same geometry in solid form as well as in the solution.

**Nickel(II) complexes.** At room temperature these complexes show a diamagnetic behavior, indicating the square planar environment around the Ni(II) ion. The electronic spectra of Ni(II) complexes display three absorption bands in the range 15822-16528 (ε = 51-52 l mol<sup>-1</sup> cm<sup>-1</sup>), 20920-22085 (ε = 155-158 l mol<sup>-1</sup> cm<sup>-1</sup>) and 28571-29540 cm<sup>-1</sup> (ε = 129-132 l mol<sup>-1</sup> cm<sup>-1</sup>). These bands may be assigned [18,19] to three spin allowed transitions <sup>1</sup>A<sub>1g</sub>(D) → <sup>1</sup>A<sub>2g</sub>(G) (ν<sub>1</sub>), <sup>1</sup>A<sub>1g</sub>(D) → <sup>1</sup>B<sub>2g</sub>(G) (ν<sub>2</sub>) and <sup>1</sup>A<sub>1g</sub>(D) → <sup>1</sup>E<sub>g</sub>(G) (ν<sub>3</sub>), respectively.

**Copper(II) complexes.** The magnetic moments of Cu(II) complexes were recorded at room temperature. The complexes show magnetic moments in the range 1.95-1.98 B.M. corresponding to one unpaired electron. The electronic spectra of Cu(II) complexes exhibit bands in the range 10449-10526 and 15948-16181 cm<sup>-1</sup>. These bands correspond to the

transitions <sup>2</sup>B<sub>1g</sub> → <sup>2</sup>A<sub>1g</sub>(d<sub>x<sup>2</sup>-y<sup>2</sup> → d<sub>z<sup>2</sup></sub>) ν<sub>1</sub> and <sup>2</sup>B<sub>1g</sub> → <sup>2</sup>B<sub>2g</sub>(d<sub>x<sup>2</sup>-y<sup>2</sup> → d<sub>zy</sub>) ν<sub>2</sub>, respectively.</sub></sub>

EPR spectra of Cu(II) complexes were recorded as polycrystalline sample and in DMSO solution, on X-band at frequency 9.3 GHz under the magnetic field strength 3400 G. Polycrystalline spectra exhibit a well resolved anisotropic broad signal. The analysis of spectra gives the values for g<sub>||</sub> 2.22-2.27 and g<sub>⊥</sub> = 2.09-2.10 (Table 3). The observed g values for the complexes are less than 2.3 in agreement with the covalent character of the metal ligand bond. The trend g<sub>||</sub> > g<sub>⊥</sub> > 2.0023 observed for the complexes indicates that the unpaired electron is localized in d<sub>x<sup>2</sup>-y<sup>2</sup></sub> orbital of the Cu(II) ion and spectral features are characteristic of axial symmetry. Tetragonal elongated structure is confirmed for the aforesaid complexes [22,23].

### Ligand Field Parameters

Various ligand field parameters were calculated for the complexes and are listed in Table 4. The values of D<sub>q</sub> in Co(II) complexes were calculated from transition energy ratio diagram using the ν<sub>3</sub>/ν<sub>2</sub> ratio [15]. Our results are in agreement with the complexes reported earlier [24,25]. The Nephelauxetic parameter β was readily obtained by using the relation: β = B (Complex)/B (free ion), where B (free ion) for Mn(II) is 786 cm<sup>-1</sup>, for Co(II) is 1120 cm<sup>-1</sup> [26,27]. The values of β lie in the range of 0.58-0.78. These values for β and h<sub>x</sub> indicate the appreciable covalent character of metal-ligand 'σ' bond. In the Mn(II) the values B and C were calculated from the second and third transitions because these transitions are free from the crystal field splitting and depend on B and C parameters [28]. Slater Condon-shortly parameter F<sub>2</sub> and F<sub>4</sub> are related to the Racah parameter B and C as: B = F<sub>2</sub> - 5F<sub>4</sub> and C = 35F<sub>4</sub>. On the basis of above spectral studies following structures may be suggested for the complexes (Fig. 3).

### Biological Screening

The ligand (L), ligand free metal ions and its metal complexes were evaluated against different species of fungi and bacteria. The antimicrobial data reveals that ligand free metal ions in solution show inhibition capacity slightly more than the ligand but much less than the corresponding complexes against all the species under study.

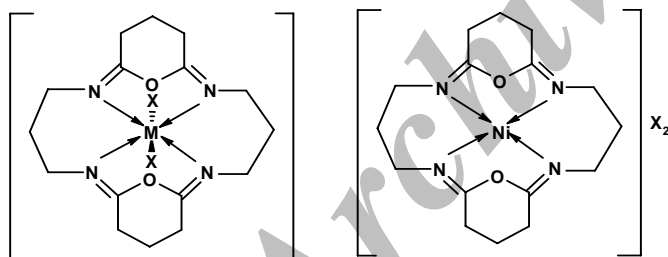
**Antifungal activities.** The preliminary fungitoxicity

**Table 3.** Ligand Field Parameters and g Values of the Complexes

Complex	Dq (cm <sup>-1</sup> )	B (cm <sup>-1</sup> )	β	C (cm <sup>-1</sup> )	v <sub>2</sub> /v <sub>1</sub>	F <sub>4</sub>	F <sub>2</sub>	h <sub>x</sub>	LFSE (Kj mol <sup>-1</sup> )
[Mn(L)Cl <sub>2</sub> ]	1850	568	0.72	3374	1.2	96.4	1.48	4.00	-
[Mn(L)(NO <sub>3</sub> ) <sub>2</sub> ]	1779	571	0.73	3254	1.2	93.0	1.36	3.86	-
[Co(L)Cl <sub>2</sub> ]	1191	644	0.58	-	1.5	-	-	-	113.9
[Co(L)(NO <sub>3</sub> ) <sub>2</sub> ]	1223	661	0.59	-	1.5	-	-	-	117.0
[Ni(L)Cl <sub>2</sub> ]	1582	779	0.75	-	1.3	-	-	-	227.0
[Ni(L)(NO <sub>3</sub> ) <sub>2</sub> ]	1652	814	0.78	-	1.3	-	-	-	237.0

**Table 4.** EPR Spectral Data of the Complexes

Complex	Temp.	Data as polycrystalline sample				Data as DMSO solution			
		g <sub>  </sub>	g <sub>⊥</sub>	g <sub>iso</sub>	G	g <sub>  </sub>	g <sub>⊥</sub>	A°/g <sub>iso</sub>	G
[Mn(L)Cl <sub>2</sub> ]	RT	-	-	2.18	-	-	-	166.6	-
[Mn(L)(NO <sub>3</sub> ) <sub>2</sub> ]	RT	-	-	2.06	-	-	-	121.3	-
[Co(L)Cl <sub>2</sub> ]	LNT	3.62	3.45	3.50	-	3.76	3.49	3.58	-
[Co(L)(NO <sub>3</sub> ) <sub>2</sub> ]	LNT	3.50	3.27	3.35	-	3.62	3.40	3.47	-
[Cu(L)Cl <sub>2</sub> ]	RT	2.22	2.08	2.12	2.75	2.24	2.09	2.14	2.66
[Cu(L)(NO <sub>3</sub> ) <sub>2</sub> ]	RT	2.27	2.10	2.15	2.70	2.26	2.10	2.15	2.60

[M = Mn(II), Co(II) and Cu(II) and X = Cl<sup>-1</sup> and NO<sub>3</sub><sup>-</sup>]**Fig. 3.** Suggested structure of the complexes.

screening of the compounds were performed against the photopathogenic fungi *R. bataticola*, *A. alterata* and *F. odum* *in vitro* by the Food poison technique [29,30]. The appropriate quantities of the compounds in DMSO were directly mixed to the potato agar dextrose (PDA) medium in different concentrations. When the medium in the plates were solidified, a mycelial disc of 0.5 cm in diameter cut from the periphery of the 7 days old culture and it was aseptically

inoculated upside down in the centre of the petriplates. These treated petri plates were incubated at 25 ± 1 °C until fungal growth in the control petriplates were almost complete. The inhibition of fungal growths expressed in percentage terms was determined on the growth in test plates compared to the respective control plates as given inhibition %.

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

(where C, diameter of the fungal growth on the control, T; diameter of the fungal growth on the test plate). All the compounds show fungal growth inhibition in follow the order Cu(II) > Ni(II) > Co(II) ≈ Mn(II) > ligand (Graph 1a).

**Antibacterial activities.** The antibacterial action of the ligand and its Mn(II), Co(II), Ni(II) and Cu(II) complexes was checked by disc diffusion method [31,32]. This was done by the bacterial species *Staphylococcus aureus*, *Pseudomonas striata* and *Escherchia coli*. 0.25 ml of sterilized nutrient agar media (NA) was poured in each petriplates and, after solidification, 0.1 ml of test bacteria spreads over the medium

using a spreader. The discs of Whatman No. 1 filter paper with the diameter 6 mm, were soaked in the solutions in the compounds in DMSO ( $1.0 \text{ mg/cm}^{-1}$ ). All the compounds were placed at 4 equidistant places at a distance of 2 cm from the center in the inoculated Petriplates. DMSO served as control and *Streptomycin* used as standard drug. All determinations were made in duplicate for each of the compounds. Average of two independent readings for each compound was recorded. These Petriplates were kept in refrigerator for 24 h for Pre-diffusion. Finally petriplates were incubated at  $30^\circ\text{C}$  for 24 h.

The bacterial growth inhibitory capacity of the ligand and its complexes follow the order  $\text{Cu(II)} > \text{Ni(II)} > \text{Co(II)} > \text{Mn(II)}$  ligand, given in the (Graph 1b).

## CONCLUSIONS

The present study revealed an octahedral geometry around the Mn(II) and Co(II) complexes, a square planar for Ni(II), and a tetragonal for Cu(II) complexes, in which the ligand acts as tetradentate manner coordination through the nitrogen atoms of  $\nu(\text{C}=\text{N})$  group. The results of antimicrobial activity indicates that metal chelates show more inhibitory effects than the parent ligand. It has also been proposed that concentration plays a vital role in increasing the degree of inhibition; as the concentration increases, the activity increases.

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