



COORDINATION BEHAVIOR OF 4-((3-CHLORO-2-METHYLPHENYL)AMINO)BENZOIC ACID TOWARDS CR(III) AND CU(II) IONS: SYNTHESIS, CHARACTERIZATION AND ANTIBACTERIAL ACTIVITY

Monika Chaudhary, Mradula Mittal*

Department of Chemistry, DAV PG College, Muzaffarnagar, Uttar Pradesh, India

ABSTRACT

Cr(III) and Cu(II) complexes (1–6) of general composition $M(L1)_X2$ and $M(L1)_2$ ($M=Cr(III)$, $Cu(II)$, $X=Cl-1$, $NO3-1$) with ligand 4-((3-chloro-2-methylphenyl)amino)benzoic acid (HL1) were synthesized. The characterization of newly synthesized ligand and complexes was done by 1H NMR, UV–VIS, IR, Mass spectrophotometry and molar conductivity studies. On the basis of the spectral study, octahedral geometry was assigned to Cr(III) metal complexes. Cu(II) complexes in metal:ligand (1:1) show square planar geometry and distorted octahedral geometry in metal:ligand (1:2) complexes. All the synthesized compounds were screened for antibacterial activity against the bacterial strains i.e. Escherichia coli and Pseudomonas striata. The antibacterial results reveal that metal complexes show enhance activity as compared to the free ligand.

Key words: Chromium(III), Copper(II), spectral studies, antibacterial screening

the last few years so many studies has been done on the structure and chemical behavior of several metal complexes to find out a substitute against the drugs. [1-3]. Many biologically active compounds used as drugs possess modified pharmacological and toxicological potentials when superintend in the form of metal based compounds [4-6]. Research has shown momentous growth in employment of transition metal complexes as drugs to treat several human diseases. Transition metals exhibit different oxidation states and can interact with a number of negatively charged molecules. This activity of transition metals has started the development of metal based drugs with promising pharmacological application and may offer unique therapeutic opportunities. In the last few years so many studies has been done on the structure and chemical behavior of several metal complexes to find out an alternative against the drugs. It has been reported that metal complexes show enhanced biological activity as compared to free ligands due to reduction in polarity of metal after complexation. Though many structure-activity correlation studies of transition metals have been reported [7-10].

Therefore, it is worthwhile to carry out the synthesis and study the spectral properties of the ligand derived from the condensation of p-chlorobenzoic acid and 3-chloro-2-methylaniline. The goal of the study presented here is to synthesize the Cr(III) and Cu(II) metal complexes of 4-((3-chloro-2-methylphenyl)amino)benzoic acid produced from condensation of p-chlorobenzoic acid and 3-chloro-2-methylaniline and to provide a baseline of structural data using various spectroscopic

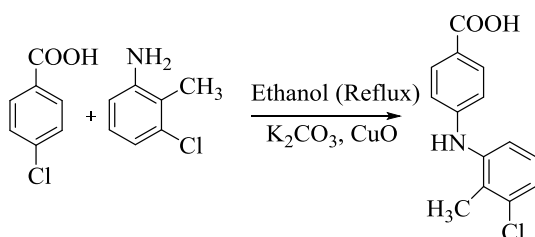
INTRODUCTION

Inorganic compounds particularly transition metals have played a significant role in the development of new metal based drugs. During the past decades, much attention has been given to the synthesis of new metal complexes and the evaluation of these agents for antibacterial activity. This interest was generated by the discovery of the antimicrobial activity of several metal complexes. In

***Corresponding author:**

Email: mridula.dav@gmail.com

techniques, and antibacterial activity.



Scheme 1: Synthesis of ligand HL¹

MATERIALS AND METHODS

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

The Schiff base HL¹ (Scheme 1) was prepared by mixing equimolar amount of p-chlorobenzoic acid (1 mmol) and 3-chloro-2-methylaniline (1 mmol) in absolute ethanol. To this anhydrous potassium carbonate and copper oxide was added. The resulting solution was refluxed for 3–4 hours. The mixture tends to foam during the earlier part of heating due to evolution of carbon dioxide. The product separated out which was filtered off, washed, recrystallized with cold ethanol and dried under vacuum over P₄O₁₀.

Synthesis of metal complexes

Hot methanolic solution (15 mL) of CrCl₃ (1

mmol) was added drop wise to a magnetically stirred solution of 4-(phenylamino)benzoic acid HL¹ (1 mmol) in ethanol (20 mL) (scheme 1). The resultant mixture was refluxed for 12 h and the clear solution was allowed to cool at room temperature. The solid product precipitated out which was filtered, washed with ethanol, diethyl ether and dried under vacuum over P₄O₁₀. The same method was used for the preparation of metal complexes 2–4 in metal : ligand (1:1). The metal complexes 5–6 were synthesized by using the above mentioned same procedure by taking metal : ligand in a 1:2 molar ratio. 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 (CsBr) were recorded on FTIR spectrum BX-II spectrophotometer. NMR spectra were recorded with a model Bruker Advance DPX-300 spectrometer operating at 400 MHz using DMSO-d₆ 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

Table 1: Physical and Analytical data of ligand HL¹ and metal complexes 1–6

Comp. No.	Color	Molecular Formula	Yield (%)	Elemental Analysis (%) found				Molar Conductance (Ω ⁻¹ cm ² mol ⁻¹)	Melting Pt. (°C)
				(calc.)					
				C	H	N	M ^a		
HL ¹	Pale Yellow	C ₁₄ H ₁₂ ClNO ₂	66	64.30 (64.25)	4.65 (4.62)	531 (5.35)	-	-	198
1	Green	[Cr(L ¹)(Cl) ₂ (H ₂ O) ₂]	58	40.12 (40.07)	3.52 (3.60)	3.35 (3.34)	12.43 (12.39)	6.2	>280
2	Light Green	[Cr(L ¹)(NO ₃) ₂ (H ₂ O) ₂]	54	35.62 (35.57)	3.27 (3.20)	8.85 (8.89)	10.98 (11.00)	5	>280
3	Blue	[Cu(L ¹)(Cl)(H ₂ O)]	61	44.56 (44.52)	3.52 (3.47)	3.73 (3.71)	16.85 (16.82)	8.9	>280
4	Light Blue	[Cu(L ¹)(NO ₃)(H ₂ O)]	63	41.55 (41.60)	3.27 (3.24)	6.95 (6.93)	15.71 (15.72)	11.6	>280
5	Green	[Cu(L ¹) ₂ (H ₂ O) ₂]	57	54.23 (54.16)	4.34 (4.22)	4.55 (4.51)	10.26 (10.23)	7.4	>280
6	Green	[Cu(L ¹) ₂ (H ₂ O) ₂]	53	54.19 (54.16)	4.17 (4.22)	4.51 (4.51)	10.22 (10.23)	10.2	>280

E4-EPR spectrometer at room temperature using DPPH as standard.

5.00 mm each containing (1.5 mg cm⁻¹) of compounds were placed at 4 equidistant places at a

Table 2 : Magnetic Moment (B.M) and Electronic Spectral data (cm⁻¹) and Ligand Field Parameter of the complexes

Complex	μ eff B.M.	Electronic data (cm ⁻¹)			Ligand Field Parameter			
		ν_1	ν_2	ν_3	Dq (cm ⁻¹)	B (cm ⁻¹)	B	LFSE (kJmol ⁻¹)
1	3.78	16240	21120	26840	1624	559	0.61	246
2	3.73	17740	20533	27300	1774	495	0.54	236
3	1.72	-	-	18122	-	-	-	-
4	1.77	-	-	20267	-	-	-	-
5	1.91	14723	19672	26545	-	-	-	-
6	1.95	12912	18478	23456	-	-	-	-

Antibacterial activity

The antibacterial activity of the ligands(HL¹-HL⁷) and their metal complexes were tested by using Disc Diffusion Method [11] against *Escherichia coli* and *Pseudomonas striata*. The test compounds in measured quantities were dissolved in DMF to get a

distance of 2 cm from the center in the inoculated petriplates. Filter paper disc treated with DMF served as control and Streptomycin used as a standard drug. All determinations were made in triplicate for each of the compounds. Average of three independent readings for each compound was

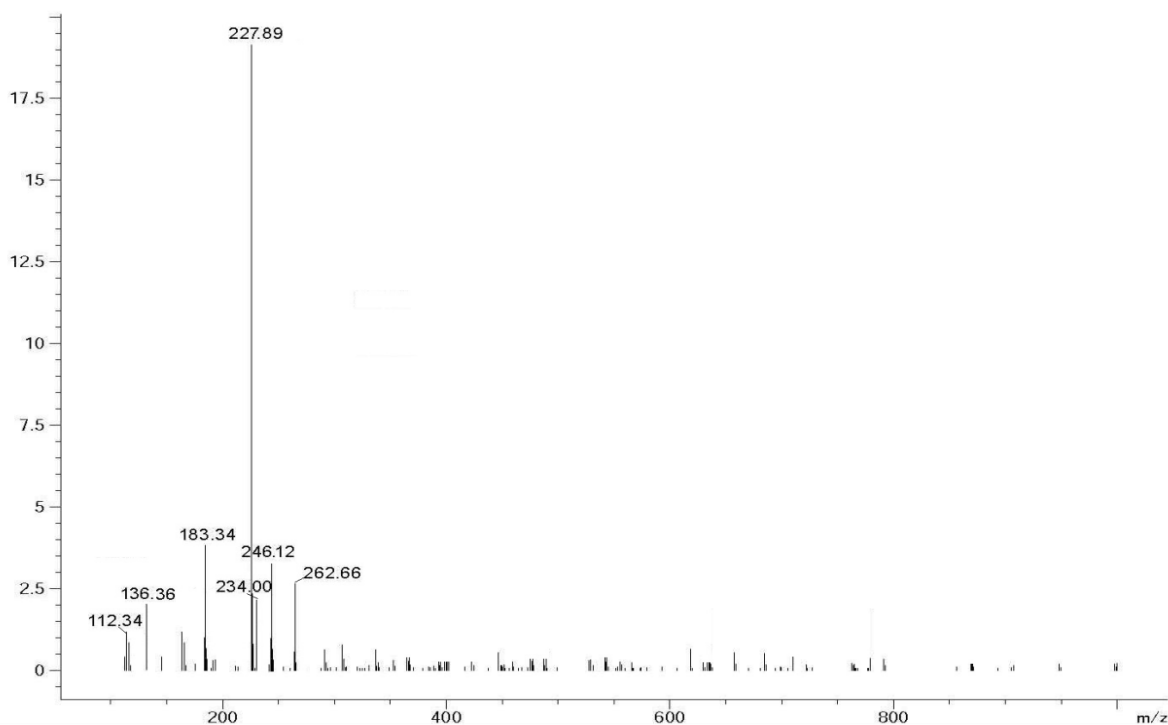


Figure 1 : Mass spectra of ligand HL¹

concentrations of 500 and 1000 ppm of compounds. 25 mL nutrient agar media (NA) was poured in each petriplate. After solidification 0.1 mL of test bacteria spreads over the medium using a spreader. The disc of Whatmann no 1 filter paper having the diameter

recorded. These petriplates were kept in refrigerator for 24 hrs for Pre-diffusion. Finally petriplates were incubated for 26-30 hours 28±2°C. The zone of inhibition was calculated in mm carefully.

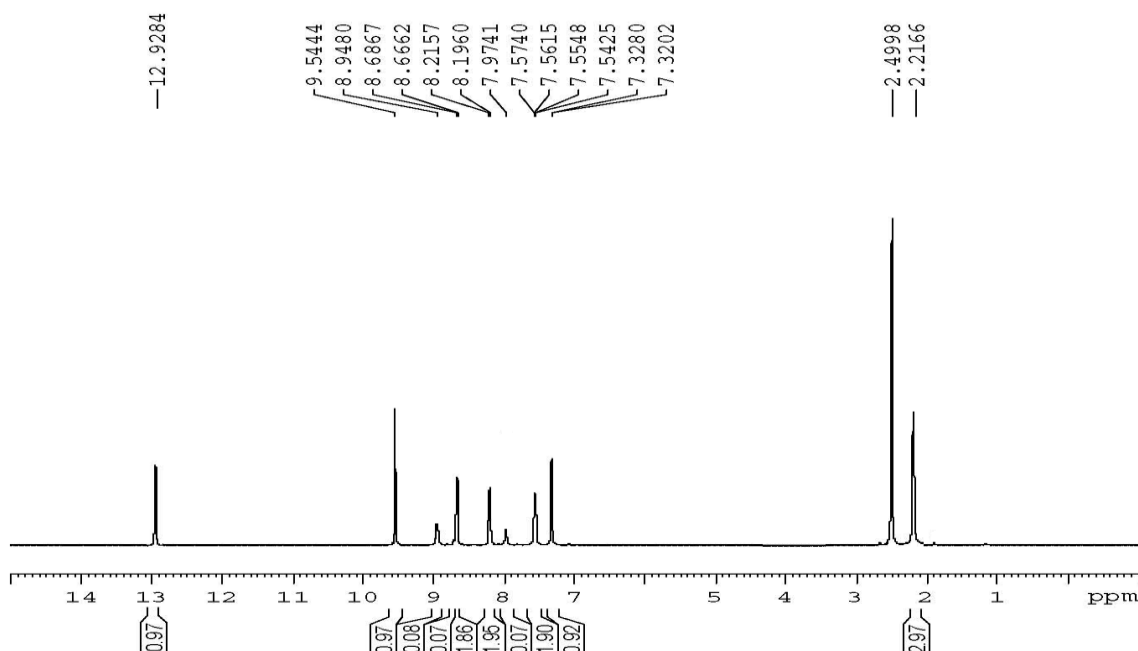


Figure 2: ^1H NMR spectra of ligand HL^1

RESULTS AND DISCUSSION

The ligand HL^1 (Scheme 1) was prepared reaction of p-chlorobenzoic acid (1 mmol) and 3-chloro-2-methylaniline (1 mmol) in absolute ethanol in presence of potassium carbonate and copper oxide. The separated product was filtered off, washed, recrystallized with cold ethanol and dried under vacuum over P_4O_{10} . The structure of ligand thus formed was established by IR, ^1H NMR and Mass spectrophotometry.

Table 3 . EPR spectral data of the Cr(III) and Cu(II) complexes

Complex	Data as polycrystalline sample			G
	g_{\parallel}	g_{\perp}	g_{iso}	
1	--	--	1.7620	----
2	----	---	1.9750	---
3	2.2343	2.0706	2.1251	3.3186
4	2.1892	2.1156	2.1401	1.6366
5	2.2343	2.1220	2.1594	1.9204
6	2.0773	2.0318	2.0469	2.4308

The synthesized ligand was further used for the complexation with Cr(II) and Cu(II) metal ions, using the following metal salt: CrCl_3 for complex 1,

$\text{Cr}(\text{NO}_3)_3$ for complex 2, CuCl_2 for complexes 3 & 5 and $\text{Cu}(\text{NO}_3)_2$ for complexes 4 & 6. The obtained complexes are microcrystalline solids which are stable in air and decompose above 280°C (Table 1). They are insoluble in common organic solvents such as acetone & chloroform, sparingly soluble in ethanol & methanol and completely soluble in DMF & DMSO. The molar conductance of the soluble complexes in DMF showed values indicating that complexes 1–6 ($5\text{--}11.6\ \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$) [12] are non-electrolytes in nature. The elemental analysis data of the ligand are in agreement with the structure of the ligand. The physical and analytical data of the ligand (HL^1) and metal complexes (1–6) are given in Table 1.

Mass Spectra

The ESI mass spectrum of ligand showed a molecular ion peak at $m/z = 262.66$ amu corresponding to $[\text{M} + \text{H}]^+$, which confirms the proposed formula (Figure 1). It also shows a series of peaks at 246.12, 234.00, 227.89, 183.34, 136.36 and 112.34 corresponding to various fragments. The intensities of these peaks give the idea of the stability of the fragments.

^1H NMR Spectra

The ^1H NMR spectra have been recorded for ligand HL^1 (Figure 2). The characteristic signals, due

to –NH and –COOH protons appear at 9.54 and 12.92 ppm, respectively. The aromatic region is a set of doublets and multiplets in the range 7.32–8.94 ppm for the ligand. All the proton peaks were found to be in the expected regions.

of the metal complexes 2, 4 and 6 suggest that both the nitrate groups are coordinated to the central metal ion in a unidentate fashion [15]. Furthermore, the presence of coordinated water molecules is evidenced by broad bands corresponding to O-H

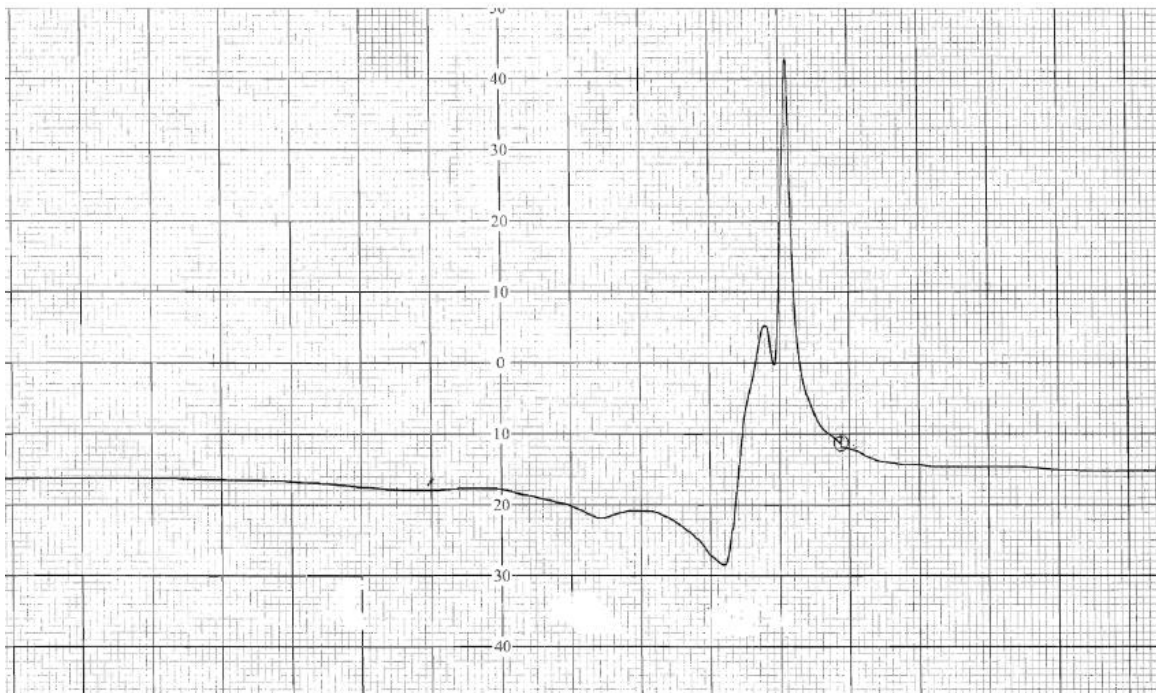


Figure 3. EPR spectrum of Copper complex 3

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 3144 cm^{-1} corresponds to –COOH group in ligand HL¹. However, in metal complexes 1–6 this band disappears, which indicates that the –COOH group deprotonate and coordinates to metal ion. In metal complex 1, The stretching bands corresponding to $\nu_{\text{asym}}(\text{COO}^-)$ appeared at 1537 cm^{-1} , while the band corresponding to $\nu_{\text{sym}}(\text{COO}^-)$ appeared at 1445 cm^{-1} . The separation value ($\Delta\nu$) of 92 cm^{-1} indicates bidentate binding of the carboxylato group [13]. Similarly, for metal complexes 2-6 the band for $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$ appeared in the range of $1532\text{--}1557$ and $1435\text{--}1455\text{ cm}^{-1}$, respectively. This is also supported by the appearance of band in range of $522\text{--}537\text{ cm}^{-1}$, which corresponds to $\nu(\text{M-O})$ bond [14].

The presence of bands at $1444\text{--}1423$ (ν_5), $1345\text{--}1331$ (ν_1) and $1052\text{--}1028$ (ν_2) cm^{-1} , in the IR spectra

stretching vibration [16] at $3370\text{--}3440\text{ cm}^{-1}$ in complexes 1–6. The chloro complexes show the IR bands in the region $322\text{--}367\text{ cm}^{-1}$ due to $\nu(\text{M-Cl})$ [17]. The IR spectral data indicates that the ligand HL¹ behaves uninegative bidentately.

Magnetic moments

Generally the magnetic moment of chromium(III) complexes at room temperature lies near 3.87 B.M. i.e. equal to spin-only value. For the Cr(III) compounds the magnetic moment is reduced below the spin-only value because of the ($1-4\lambda/10Dq$) effect. The spin-orbit coupling constant for Cr(III) is rather small. The magnetic moment of complexes under study at room temperature lies in range of 3.73-3.78 B.M. (Table 2) [18] corresponding to three unpaired electrons. At room temperature Cu(II) complexes show magnetic moment in the range 1.72-1.95 B.M. corresponding to one unpaired electron [19].

Electronic spectra

For Cr(III) (d^3 , the spin quantum number $S=3/2$), the strong field ground configuration is $t_{2g}^3 e_g^0$. The excited configuration $t_{2g}^2 e_g^1$ is six fold orbitally degenerate and the second excited configuration $t_{2g}^1 e_g^2$ is three fold orbitally degenerate. The ground state can be written by considering a spin of $3/2$ as it is an orbital singlet. The free ion split quartet term 4F and 4P . These terms in octahedral field split into $^4A_{2g}$, $^4T_{1g}$, $^4T_{2g}$ and $^4T_{1g}$ (P), respectively. The electronic spectra of the Cr(III) complexes 1–2 recorded in DMSO, display three bands in the range of 16240–17170, 20320–21120 and 26660–26840 cm^{-1} (Table2). These spin allowed bands shown by six coordinated complexes having Oh symmetry could be assigned to the transitions: $^4A_{2g}(F) \rightarrow ^4T_{2g}(F)$, ν_1 ; $^4A_{2g}(F) \rightarrow ^4T_{1g}(F)$, ν_2 ; $^4A_{2g}(F) \rightarrow ^4T_{1g}(P)$, ν_3 [20].

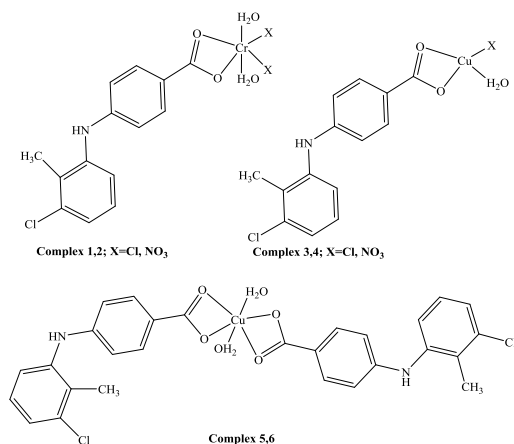


Figure 4. Proposed structures of metal complexes 1–6

Electronic absorption spectra of the copper complexes 3 and 5 display a transition in the region 18122–20267 cm^{-1} , which can be assigned as the $^2B_{1g} \rightarrow ^2A_{1g}$ transition, revealing that the Cu(II) complexes exist in the square planar geometry [21]. Electronic spectra of Cu(II) complexes 4 and 6 show the d–d transition bands in the range 12,912–14,723, 18,478–19,672 and 23,456–26,545 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 [22]. On the basis of electronic transitions, a distorted octahedral geometry is suggested for complexes 4 and 6.

Various ligand field parameters are calculated for the complexes. The energy of the first spin allowed transition i.e. $^4A_{2g}(F) \rightarrow ^4T_{2g}$, directly gives the value of $10 Dq$ ($\nu_1=10Dq$). The Nephelauxetic parameter β is calculated by the relation $\beta = B_{\text{complex}} / B_{\text{free}}$

ion. For Cr(III) the value of B free ion is 918 [20]. The value of β calculated for Cr(III) complexes lie in the range of 0.54–0.61 given in table. These values indicate that the complexes have appreciable covalent character.

EPR spectra

The X-band EPR spectra of all the Cr(III) complexes in solid state show a broad signal (Fig.) in the vicinity of $g_{iso} \approx 2.0$. Due to large line widths and dominance of $g_{iso} \approx 2.0$ peaks, no hyperfine splitting is observed and the estimation of parameters D and E is not possible. The EPR results of Cr(III) complexes in the present study are consistent with the presence of hexacoordinated Cr(III) centers.

EPR spectra (Figure 3) 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 $g_{||} > g_{\perp} > 2.0023$, 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 figures are characteristic for the axial symmetry. Tetragonally elongated geometry is thus confirmed for the afore-said complexes. $G = (g_{||} - 2)/(g_{\perp} - 2)$, which measure the exchange interaction between the metal centers in a polycrystalline solid has been calculated. According to Hathaway and Billing [20] if $G > 4$ the exchange interaction is negligible, but $G < 4$ indicates considerable exchange interaction in the solid complexes. The complexes show the G values smaller than 4 which indicate exchange interaction in the solid complexes.

Based on above observations following structures are proposed for metal complexes 1–6 (Figure 4).

Antibacterial Activity

The antibacterial screening data shows that the compounds exhibit antibacterial properties and it is important to note that the metal chelates exhibit more inhibitory effects than the parents ligand (Figure 5). The increased activity of the metal chelates can be explained on the basis of chelation theory [23]. It is known that chelation tends to make the ligand act as more powerful and potent bactericidal agents, thus killing more of the bacteria than the ligand. It is observed that in complexes the positive charge of the metal is partially shared with the donor atoms present in the ligands and there may be π -electron delocalization over the whole

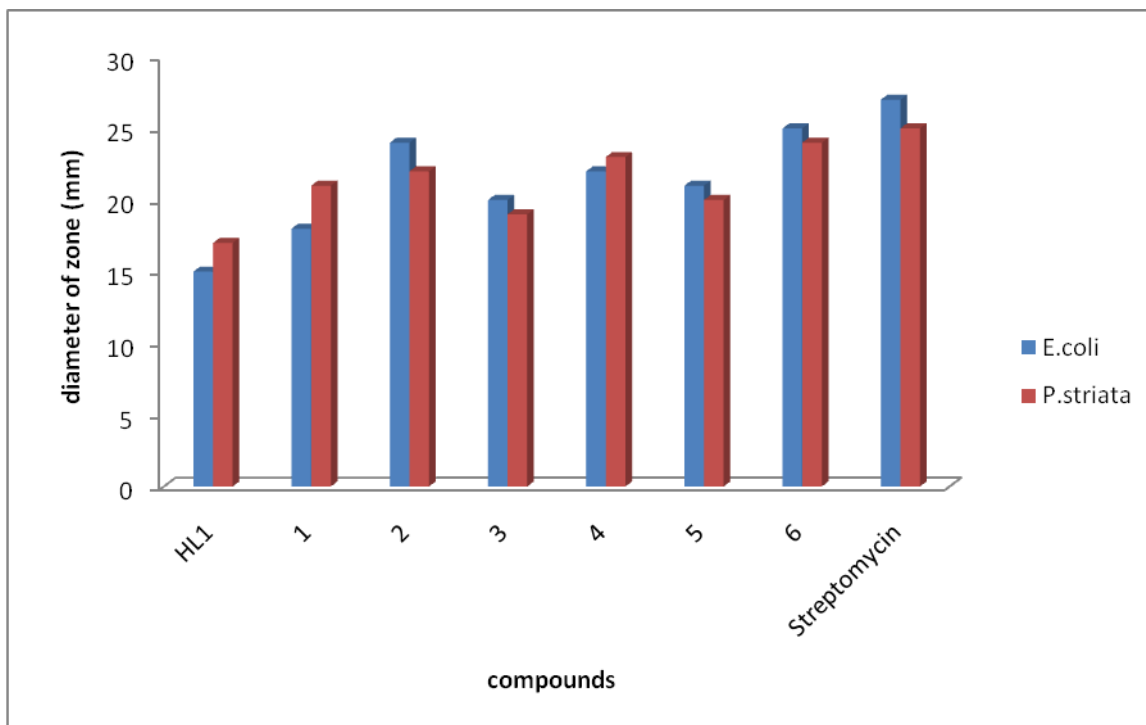


Figure 5: Antibacterial activity of ligand HL¹ and metal complexes 1–6

chelate [24]. This increases the lipophilic character of the metal chelate and favors its permeation through the lipid layer of the bacterial membranes. There are other factors which also increased the activity these are solubility, conductivity and bond length between the metal and ligand.

The mode of action may involve the formation of a hydrogen bond through the azomethine nitrogen atom with the active centers of the cell constituents, resulting in interference with the normal cell process. The variation in the effectiveness of different compounds against different organisms depend either on the impermeability of the cells of the microbes or difference in ribosomes of microbial cells [25].

CONCLUSION

The analytical and physico-chemical analyses confirmed the composition and the structure of the newly obtained ligand and metal complexes. On the basis of the spectral studies Cr(III) complexes were found to have a octahedral geometry whereas Cu(II) complexes has a square planar geometry in 1:1 (metal:ligand) complexes and distorted octahedral in 1:2 complexes. In all complexes the ligand HL¹ acts as uninegative bidentate around the metallic ion. Results of the antibacterial activity revealed that

metal complexes show enhanced activity in comparison to free ligand. The increase in activity after metal complexation can be explained on the basis of overtone concept.

REFERENCES

1. West DX, Bain GA, Butcher *et al.* (1996). Synthesis, Characterization, and Biological Activity of Some Transition Metal Complexes of N-Benzoyl-N'-2-thiophenethiocarbohydrazide. *Polyhedron*, 15, 665.
2. Pegfei X, Ximping Y, Shaozn W, Ziyl Z. (1998). Synthesis of 5-Benzimidazolylbenzofuran derivatives. *Indian J Chem*, 127, 3713.
3. Puratchikody A, Sivagothi V. (2001). Synthesis of benzimidazole derivatives of biological interest. *Indian J Heterocycl Chem*, 241.
4. Kiran M, Singh RV, Tandon JP. 1H-Indole-3-carbaldehyde thiosemicarbazone. (1986). *Inorg Met Org Chem*, 16,1341.
5. Agarwal RK, Singh L. (2006). Synthesis, Spectral, and Biological Properties of Copper (II) Complexes of Thiosemicarbazones of Schiff Bases Derived from 4-Aminoantipyrine and Aromatic Aldehydes. *Bioinorg Chem Appl*, 2006, 1.

6. Ibrahim G, Khan MA, Bouet GM. (2002). Complexes of 2-furaldehyde 4-phenylsemicarbazone. *Trans Met Chem*, 27, 34.
7. Ibrahim G, Khan MA, Bouet GM, Chebli E. (1999). Metallic complexes from 2-furaldehyde semicarbazone and 5-methyl-(2- furaldehyde) semicarbazone. *Trans Met Chem*, 24, 294.
8. Trinagaraju K, Prasad AVGS, Rao PV, Prasad PSS. (2015). Synthesis, Characterization and Biological activity of 3- Indole Acetic acid. *International Journal of International Journal of Novel Trends in Pharmaceutical Sciences*, 5, 21.
9. Trinagaraju K, Prasad AVGS, Rao PV, Prasad PSS. (2015). Synthesis, physicochemical and biological properties of 3,4,5-trimethoxybenzoates of Mn(II), Co(II), Ni(II) and Zn(II). *International Journal of Medicinal Chemistry and Analysis*, 5, 65.
10. Trinagaraju K, Prasad AVGS, Rao PV, Prasad PSS. (2015). Synthesis, characterization and biological properties of metal 1-(4-carboxy3-hydroxy phenyl aminomethyl)benzimidazole complexes. *International Journal of Pharmacy*, 5, 33.
11. Singh DP, Kumar K, Chopra RM . (2011). Spectroscopic studies and antibacterial activities of some new 16-membered octaazamacrocyclic complexes derived from thiocarbonylhydrazide and pentane-2,4-dione. *Spectrochim Acta A*, 78, 629.
12. Chandra S, Vandana, Kumar S. (2015). Synthesis, spectroscopic, anticancer, antibacterial and antifungal studies of Ni(II) and Cu(II) complexes with hydrazine carboxamide, 2-[3-methyl-2-thienyl methylene]. *Spectrochim Acta A*, 135, 356.
13. Swamy SJ, Pola S. (2008). Spectroscopic Studies on Co(II), Ni(II) Cu(II) and Zn(II) Complexes with N4-Macrocyclic Ligands. *Spectrochim Acta A*, 70, 929.
14. Swamy SJ, Veerapratap B, Nagaraju D, Suresh K, Someshwar P. (2003). Non-template Synthesis of 'N4' Di- and Tetra-amide Macrocyclic Ligands with Variable Ring Sizes. *Tetrahedron*, 59, 10093.
15. Goeta AE, Howard JAK, Maffeo D, Puschmann H, Williams JAG, Yufit DS. (2000). Copper(II) complexes of the Isomeric tetraazamacrocyclic ligands 1,11- and 1,8-Bis-(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane and of the 1,4,8,11-tetraazacyclotetradecane-5-12-dione analogue at neutral and basic pH. *J Chem Soc Dalton Trans*, 1873.
16. Chandra S, Sharma AK.(2009). Applications of several spectral techniques to characterize coordination compounds derived from 2,6-diacetylpyridine derivative. *Spectrochim Acta A*, 74, 271.
17. Chandra S, Ruchi, Qanungo K, Sharma SK. (2011). Synthesis, molecular modeling and spectroscopic characterization of nickel(II), copper(II), complexes of new 16-membered mixed-donor macrocyclic schiff base ligand incorporating a pendant alcohol function. 79,1326.
18. Lever, ABP. Inorganic Electronic Spectroscopy, 1st ed. (Elsevier, Amsterdam) 1968.
19. Greenwood NN, Earnshaw A. Chemistry of the Elements, 1st edition. (Pergamon Press, UK) 1983, 1379.
20. Tyagi M, Chandra S, Tyagi P. (2014). Mn(II) and Cu(II) complexes of a bidentate Schiff's base ligand: Spectral, thermal, molecular modelling and mycological studies. *Spectrochim Acta A*, 117, 1.
21. Bhaskar R, Salunkhe N, Yaul A, Aswar A.(2015). Bivalent transition metal complexes of ONO donor hydrazone ligand: Synthesis, structural characterization and antimicrobial activity. *Spectrochim Acta A*, 151, 621.
22. Sastry BA, Asadullah SMD, Ponticelli G, Massacesi M, Pinna R. (1981). Electron paramagnetic resonance studies on Cu(enEt₂)(NCS)₂. *J Mol Struct*, 73, 257.
23. Shankarwar SG, Nagolkar BB, Shelke VA, Chondhekar TK. (2015). Synthesis, spectral, thermal and antimicrobial studies of transition metal complexes of 14-membered tetraaza[N₄] macrocyclic ligand. *Spectrochim Acta A*, 145, 188.
24. Osowole AA, Balogun SA. (2012). Spectral, magnetic, thermal and antibacterial properties of some metal(II) complexes of Aminoindanyl Schiff Base. *European Journal of Applied Sciences*, 4 (1),6.
25. Kumar N, Prasad AVGS, Sharma P. (2013). Synthesis and antibacterial Evaluation of some New Schiff Bases. *Int J Pharm Sci Rev Res*, 23(2), 231.