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RESEARCH ARTICLE

SYNTHESIS, CHARACTERISATION AND ANTIMICROBIAL ACTIVITIES OF COPPER (II) MIXED LIGAND COMPLEXES

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ABSTRACT

A series of six mono nuclear Schiff-base complexes, namely [Cu(L1)(NO₃)]NO₃ (1), [Cu(L2)(NO₃)]NO₃ (2), [Cu(L1)phen](NO₃)₂ (3), [Cu(L1)bpy](NO₃)₂ (4), [Cu(L1)pybiH](NO₃)₂ (5) and [Cu(L1)dpk](NO₃)₂ (6) where L1 and L2 is a tridentate (N,N,N) Schiff-base ligand L1 = (N,N-dimethyl-N'-[phenyl(pyridin-2-yl)methylene]ethane-1,2-diamine), L2 = (N-[phenyl(pyridine-2-yl)methylene](pyridin-2-yl)methanamine), phen = 1, 10-phenanthroline, bpy = 2, 2'-bipyridinyl, pybim = 2-pyridin-2-yl-1H-benzoimidazole and dpk = di-pyridin-2-yl-methanone were synthesized and characterized by elemental analysis, UV-Vis, IR and EPR spectroscopy. In the complexes 3, 4, 5 and 6 the metal ion is coordinated by three nitrogen atoms from L1 or L2 ligand and two nitrogen atoms from the bidentate auxiliary ligand and approximately square pyramidal coordinate geometry. Complexes 1 and 2, the metal ion is coordinated by three nitrogen atoms from the Schiff base ligand and two oxygen atoms from nitrate anion. The in-vitro antimicrobial activity of the complexes were tested against the bacteria Escherichia coli, Staphylococcus aureus, Bacillus subtilis, fungi Candida albicans and Aspergillus flavus by disc diffusion method. All the copper (II) complexes show moderate antimicrobial activity.

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INTRODUCTION

Over the years, Schiff bases are well known organic compound that are widely used for the dyes, pigments, catalysts, intermediates in organic synthesis and polymer stabilizers (Gupta, 2008; Vigato, 2012 and Bartyzel, 2011). Schiff bases and their metal complexes are considered as promising class of compounds due to their bountiful physical and chemical properties. Interestingly Schiff base ligands are able to coordinate to different metal ions and stabilized in various oxidation states (Cozzi, 2004). Because of the relative easy synthesis and flexibility and the special property of azomethine group (-HC=N-), Schiff bases are considered as excellent chelating agents and are known to form potentially stable complexes with metal ions. Different types of Schiff base based metal complexes have been extensively studied due to their potential anti-cancer (Tang, 1985), antiviral (Silva, 2011) and catalytic properties⁷. Metal complexes of Schiff bases derived from heterocyclic compounds containing N, S and O as ligand atoms are of great interest for simple structural models of complicated biological systems (Mandal, 1997 and Dey, 2016). Metal complexes with mixed ligands is an area of current interest due to their structural diversity.

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Further, coordination chemistry is about tuning properties of metal ions using different ligands (Ahmed, 1988; Chikira, 2015 and Tsurugi, 2015). This includes stabilization of different oxidation states, modulation of the solubility and its photophysical properties. In the present work, the structures of synthesized bidentate ligands and its copper complexes have been characterized by various physicochemical techniques including elemental analysis, UV-Vis, IR and EPR spectral studies, and were also screened for antimicrobial activities against Gram-positive bacteria: Staphylococcus aureus (MTCC 96), Bacillus subtilis (MTCC 441), Gram-negative bacteria: Escherichia coli (MTCC 119) and Fungai as Candida albicans (MTCC 227), Aspergillus flavus (MTCC 230).

Experimental Section

MATERIALS AND METHODS

All the chemicals and reagents used were of analytical grade and were used as received without further purifications. Solvents were dried and distilled according to standard literature procedures (Armarego, 2003). Phenyl-pyridin-2-yl-methanone, 2-pyridin-2-yl-1H-benzoimidazole, di-pyridin-2-yl-methanone were obtained from Sigma Aldrich. N, N-dimethylethylenediamine, 2-aminomethyl pyridine, 1,10-

phenanthroline, 2,2'-bipyridine, copper nitrate trihydrate were purchased from Alfa Aesar. Elemental analyses were carried out with a Perkin-Elmer 2400 II elemental analyzer. The electronic spectra were measured on a Perkin-Elmer Lambda-40 (UV-Vis) spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer Spectrum RX FTIR instrument in the range of 4000-350 cm^{-1} as KBr pellets. Conductivity measurements were conducted using a Lab India, PICO conductivity meter. ESR spectra of the copper complexes in DMSO at liquid nitrogen temperature (77 K) were recorded on a JEOL JES-TE100 ESR spectrometer operating at X-band frequencies and having a 100 kHz field.

Synthesis of Ligand

(*N,N*-dimethyl-*N'*-[phenyl(2-pyridyl) methylene]ethane - 1,2-diamine (L1).

The ligand was synthesized following a reported procedure¹⁵. A solution of 2-benzoylpyridine (0.183 g, 1.0 mmol) in methanol (20ml) was added dropwise to a solution of *N,N*-dimethylethylenediamine (0.089 g, 1.0mmol) in methanol. After completion of addition the reaction mixture was refluxed for 3 hours and then allowed to cool. The solvent was removed in a rotary evaporator to give the compound as yellow oily liquid which was used without further purification.

(Phenyl-pyridin-2-yl-methylene)-pyridin-2-ylmethyl-amine (L2).

This ligand was prepared by adopting the procedure used for the isolation of L1 but using 2-aminomethyl pyridine instead of *N,N*-dimethylethylenediamine.

SYNTHESIS OF COMPLEXES

Synthesis of [Cu(L1)(NO₃)] NO₃ (1).

A methanolic solution (10 ml) of copper(II) nitrate trihydrate (0.241 g, 1 mmol) was added to a solution of L1 (0.253 g, 1 mmol) in methanol with constant stirring. The blue colored precipitate obtained was washed with cold methanol and diethyl ether and dried under vacuum. Yield: 70 %. Anal.calcd for $\text{CuC}_{16}\text{H}_{19}\text{N}_5\text{O}_6$: C, 43.59; H, 4.34; N, 15.88%. Found: C, 43.50; H, 4.40; N, 15.95 %. ESI-MS (m/z): = 378.89 $[\text{M}-\text{NO}_3]^+$.

Synthesis of [Cu(L2)(NO₃)] NO₃ (2).

The solution of copper nitrate trihydrate (0.241 g, 1.0 mmol) in methanol (20 ml) was mixed with the solution of ligand L2 (0.273g, 1.0 mmol) in ethanol (20 ml) and the mixtures were refluxed for 30 minutes and then cooled. The precipitate were filtered and washed with ethanol and then dried in a vacuum over anhydrous CaCl_2 . Yield: 68 %. Anal.calcd for $\text{CuC}_{18}\text{H}_{15}\text{N}_5\text{O}_6$: C, 46.91; H, 4.28; N, 15.20%. Found: C, 46.80; H, 4.30; N, 15.25 %. ESI-MS (m/z): = 398.10 $[\text{M}-\text{NO}_3]^+$.

Synthesis of [Cu(L1)(phen)](NO₃)₂ (3).

A methanolic solution (10 ml) of copper(II) nitrate trihydrate (0.370 g, 1 mmol) was added to a solution of L1 (0.253 g, 1 mmol) and phen (0.198 g, 1 mmol) in methanol with constant stirring. The blue colored precipitate obtained was washed

with cold methanol and then diethyl ether and dried under vacuum. Yield: 68 %. Anal.calcd for $\text{CuC}_{28}\text{H}_{27}\text{N}_7\text{O}_6$: C, 54.15; H, 4.38; N, 15.79%. Found: C, 54.10; H, 4.34; N, 15.75 %. ESI-MS (m/z): = 558.15 $[\text{M}-\text{NO}_3]^+$.

Synthesis of [Cu(L1)(bpy)](NO₃)₂ (4).

This complex was prepared by adopting the procedure used for the isolation of 3 but using 2,2'-bipyridine instead of 1,10-phenanthroline. Yield: 65%. Anal.calcd for $\text{CuC}_{26}\text{H}_{27}\text{N}_7\text{O}_6$: C, 52.30; H, 4.56; N, 16.42%. Found: C, 52.25; H, 4.40; N, 16.54%. ESI-MS (m/z): = 534.15 $[\text{M}-\text{NO}_3]^+$.

Synthesis of [Cu(L1)(pybim)](NO₃)₂ (5).

This complex was prepared by adopting the procedure used for the isolation of 3 but using 2,2'-bipyridyl benzimidazole instead of 1,10-phenanthroline. Yield: 67 %. Anal.calcd for $\text{CuC}_{28}\text{H}_{28}\text{N}_8\text{O}_6$: C, 52.87; H, 4.44; N, 17.62%. Found: C, 52.92; H, 4.50; N, 17.70%. ESI-MS (m/z): = 573.15 $[\text{M}-\text{NO}_3]^+$.

[Cu(L1)(dpk)](NO₃)₂ (6).

This complex was prepared by adopting the procedure used for the isolation of 3 but using di-pyridin-2-yl-methanone instead of 1, 10-phenanthroline. Yield: 77%. Anal.calcd for $\text{CuC}_{27}\text{H}_{27}\text{N}_7\text{O}_7$: C, 51.88; H, 4.35; N, 15.69%. Found: C, 51.70; H, 4.30; N, 15.75%. ESI-MS (m/z): = 562.15 $[\text{M}-\text{NO}_3]^+$.

Antimicrobial Screening

The standard microbial stains employed were Gram-positive bacteria: *Staphylococcus aureus* (MTCC 96), *Bacillus subtilis* (MTCC 441), Gram-negative bacteria: *Escherichia coli* (MTCC 119) and Fungai as *Candida albicans* (MTCC 227), *Aspergillus flavus* (MTCC 230) and were obtained from Microbial type culture collection (MTCC) at the institute of Microbial Technology (IMTECH), Chandigarh, India. The antibacterial activities of all the copper complexes were screened in vitro for the growth inhibitory against *Staphylococcus aureus*, *Bacillus subtilis* and *Escherichia coli* by disc diffusion method, at different concentrations compared with Chloramphenicol as appositive control. Then the antifungal activities of copper complexes (1-6) were investigated against *Candida albicans*, *Aspergillus flavus* by the same method as above mentioned but changed positive standard with Fluconazole.

RESULTS AND DISCUSSION

Synthesis and Characterisation

The ligands L1, L2 have been synthesized using the reported procedure with slight modifications, by condensing 2-benzoyl pyridine with *N,N*-dimethyl ethylenediamine and 2-amino methyl pyridine respectively. The Schiff base ligands readily formed complexes on treating of one equivalent each of copper(II) nitrate and corresponding co-ligands in methanol at room temperature. Mononuclear and mixed-ligand copper(II) complexes of the types $[\text{Cu}(\text{L})\text{NO}_3]\text{NO}_3$ and $[\text{Cu}(\text{L}) (\text{diimine}) (\text{ClO}_4)_2]$, where L is the tridentate ligand L = (*N,N*-dimethyl-*N'*-[phenyl(2-pyridyl) methylene]ethane - 1,2-diamine (L1), (Phenyl-pyridin-2-yl-methylene)-pyridin-2-ylmethyl-amine

Table 1. Electronic absorption and EPR spectral properties of copper(II) complexes (1-6)

EPR spectra in frozen dimethyl sulfoxide glass at 77k					
S.No.	Complex	UV-Vis	g_{\parallel}	g_{\perp}	A_{\parallel}
1	[Cu(L1)(NO ₃)] NO ₃	648, 315, 228	2.38	2.07	172
2	[Cu(L2)(NO ₃)] NO ₃	650, 319, 210	2.2	2.05	180
3	[Cu(L1)(phen)] (NO ₃) ₂	692, 272, 226	2.28	2.08	188
4	[Cu(L1)(bpy)] (NO ₃) ₂	634, 296, 216	2.26	2.06	180
5	[Cu(L1)(pbiH)] (NO ₃) ₂	645, 307, 214	2.29	2.06	193
6	[Cu(L1)(dpk)] (NO ₃) ₂	636, 272, 209	2.21	2.04	187

Table 2. IR spectral properties of copper(II) complexes (1-6)

S.No.	ν (C=N) ring	ν (C=N)	ν (Cu-N)	ν (C-H) ring	ν (C-H)	ν (NO ₃)
1	1597	1656	540	3061	2979	1364, 943
2	1486	1607	589	3014	2401	13,83,946
3	1587	1627	645	3056	2400	1365
4	1442	1599	651	3065	2808	1356
5	1447	1602	570	3063	2910	1300
6	1760	1609	621	3153	2411	1377

Table 3. Antibacterial activity of copper (II) complexes (1-6)

Compound	Zone of inhibition (in mm)														
	<i>Escherichia coli</i>			<i>Staphylococcus aureus</i>					<i>Bacillus subtilis</i>						
	Control	Standard	50	100	150	Control	Standard	50	100	150	Control	Standard	50	100	150
	30 ml	30 μ l	μ l	μ l	μ l	30 μ l	30 μ l	μ l	μ l	μ l	30 μ l	30 μ l	μ l	μ l	μ l
1	0	13.4	8.3	9.7	11.2	0	13.8	9.7	11.9	13.3	0	13.5	9.2	11.1	12.4
2	0.7	12.6	7.9	9.7	12.8	0.4	12.3	5.7	8.3	12.5	0.6	12.7	6.4	8.6	10.5
3	0	14.8	9.7	11.4	13.6	0	14.2	10.3	12.8	13.6	0	13.4	10.9	11.6	12.7
4	0	13.6	8.8	10.2	13.7	0	13.4	8.9	10.4	13.5	0	14.1	8.6	10.9	12.6
5	0	14.2	9.1	11.3	13.9	0	12.9	9.6	11.7	12.5	0	14.4	9.3	11.2	13.1
6	0	13.7	9.4	10.8	13.3	0	13.6	8.7	10.9	12.9	0	13.8	8.5	10.7	12.9

Table 4. Antifungal activity of copper (II) complexes (1-6)

Compound	Zone of inhibition (in mm)									
	<i>Candida albicans</i>					<i>Aspergillus flavus</i>				
	Control	Standard	50	100	150	Control	Standard	50	100	150
	30 ml	30 ml	μ l	μ l	ml	30 ml	30 ml	μ l	μ l	μ l
1	0	12.9	7.3	10.7	11.4	0	14	9.2	12.4	13.2
2	0.2	13.1	7.9	9.8	12.5	0.3	12.3	8.3	10.5	11.1
3	0	14.7	8.9	11.1	13.2	0	14.1	9.5	12.2	13.8
4	0	13.4	8.5	9.2	11.7	0	13.9	9.1	11.7	12.5
5	0	13.2	8.1	9.6	11.3	0	13.6	8.9	10.4	11.9
6	0	12.3	6.8	8.9	10.7	0	13.5	9.2	11.6	12.3

(L2) and diimine is 1,10-phenanthroline (phen), 2,2'-bipyridine (bpy), 2-pyridin-2-yl-1H-benzimidazole (pybim), di-pyridin-2-yl-methanone (dpk), have been isolated as their nitrate salts in good yields. All the complexes were obtained in good yield and characterized by using elemental analysis, UV-Vis, ESI-MS and EPR spectroscopic techniques.

The molar conductance ($90 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) of the complexes suggests that it behaves as 1:1 electrolyte in solution (Huheey, 2006).

Electronic spectral properties: The electronic spectral data of all the Cu(II) complexes are summarized in Table 1 and the typical electronic absorption spectrum of 3-6 are shown in

Figure 1. An intense band in the range 275-310 nm has been assigned to $N(\pi) \rightarrow Cu(II)$ ligand to metal charge transfer (LMCT) transition¹⁷ suggesting involvement in coordination of the diimine nitrogen atoms even in solution. Further, the complexes exhibit only one broad band in the visible region (635-690 nm), which is typical of a distorted square-based coordination geometry (Murali, 1996) around copper(II). The broadness associated with the d-d bands is generally taken as an indication of the geometrical distortion of the complex from perfect planar symmetry.

shown in Table 2. IR spectrum of complex 2 is shown in Figure 2. The IR spectra of all the compounds show $(=C-H)$ stretching vibration, due to the aromatic ring around 3040 cm^{-1} , while the $(-C-H)$ stretching vibration due to the CH_3 group appeared around 2865 cm^{-1} . The peak around $1590-1605\text{ cm}^{-1}$ in the complexes, indicate the presence of azomethine $C=N$ stretching frequency. In complex 5, the peaks observed at 1603 and 1624 cm^{-1} have been assigned to the $C=N$ stretching frequencies of benzimidazole group. The peaks corresponding to the ring stretching frequencies $\nu(C=C)$

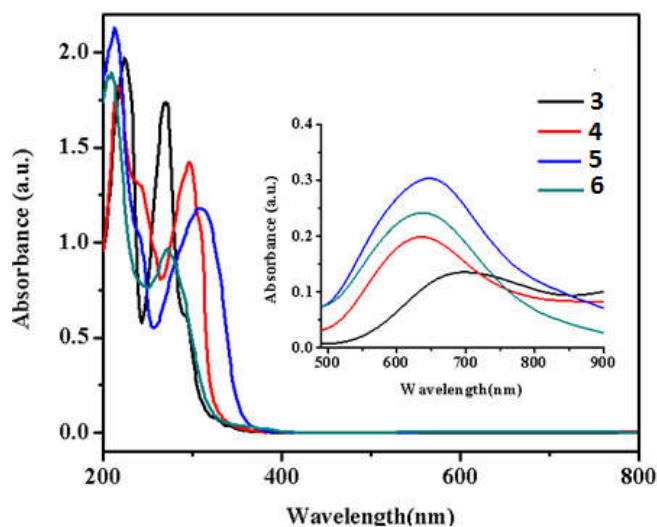
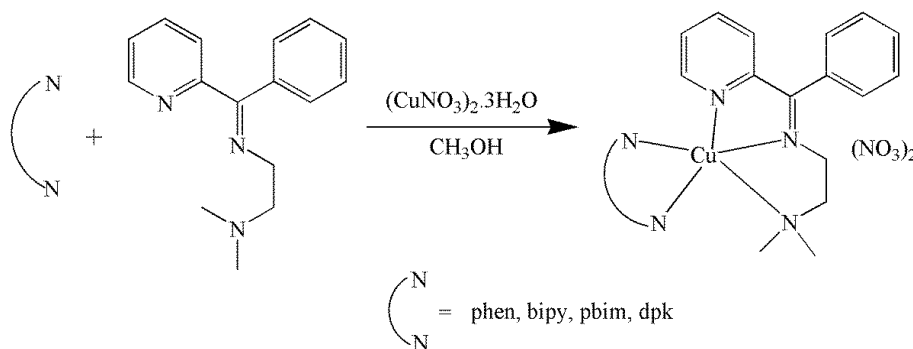
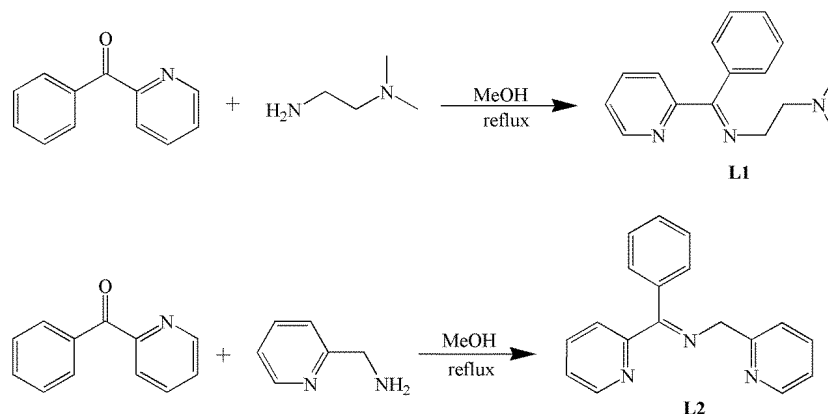


Fig. 1. IR spectrum of the complex 2.

IR Spectra

The important infrared spectral bands and their assignments for the synthesized complexes were recorded as KBr pellets are

and $\nu(C=N)$ at $1515-1520\text{ cm}^{-1}$ and $1445-1430\text{ cm}^{-1}$ indicating the coordination of the heterocyclic nitrogen atoms of phen and bipy with the metal ion (Abdelkarim, 2015).

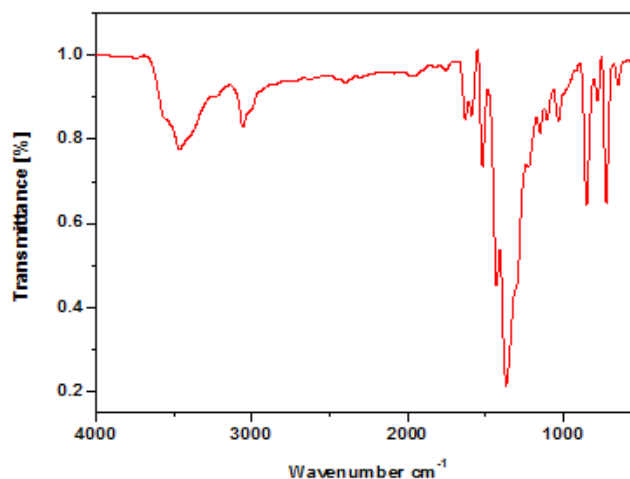


Fig. 2. IR spectrum of the complex 1

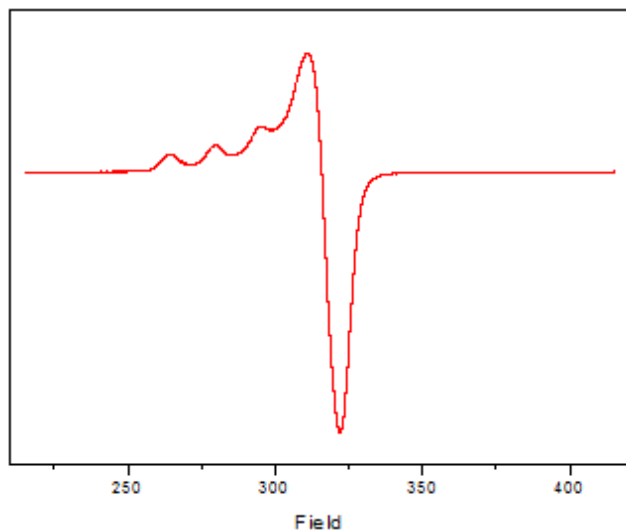


Fig. 3. X-band EPR spectrum of the complex 3

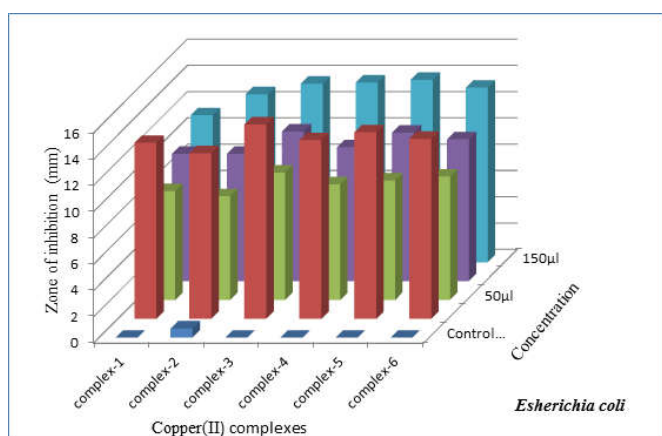


Fig. 4. Biological (bacterial) activity of copper complexes (1-6)

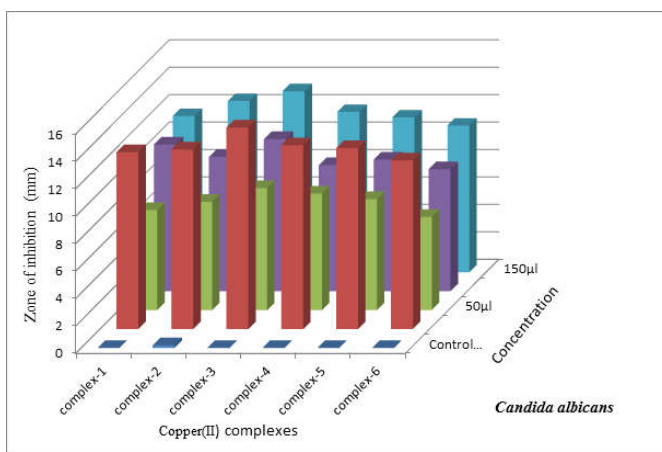


Fig. 5. Biological (fungal) activity of all copper complexes (1-6)

EPR Spectra

The EPR spectra of complexes 1-6 in DMSO at 70 K were found as anisotropic and their hyperfine features have been resolved into both parallel (g_{\parallel}) and perpendicular (g_{\perp}) regions (Figure 3, Table 1). The EPR spectra of all the complexes are axial with the range of g_{\parallel} (2.20 - 2.38) $>$ g_{\perp} (2.04 - 2.08) suggesting the presence of unpaired electron on $d_{x^2-y^2}$ orbital with $^1B_{2g}$ ground state (Kivelson, 1961 and Silver, 1974). Thus, highest-energy half-occupied d-orbital being $d_{x^2-y^2}$ because its lobes point directly at the ligands and thus it has

the largest repulsive or antibonding interaction with the ligand field (Hathaway, 1970 and Rapheal, 2007). All the complexes exhibit $g_{\parallel} > g_{\perp}$ with f-values of range 120-136 cm^{-1} , which are closer to the range of f-value observed for square-based geometries (105-135 cm^{-1}) (Hathaway, 1970). This is further supported by the large A_{\perp} values in the range of 163-186 $\times 10^{-4}$ cm^{-1} . The large hyperfine splitting in the g_{\parallel} region and A_{\parallel} , 172-193 $\times 10^{-4}$ cm^{-1} , suggesting the presence of square based geometry (Solomon, 2006). This hyperfine coupling A_{\parallel} of the unpaired electron to the nuclear spin of the copper (II) center is contributed from Fermi contact, spin dipolar and orbital dipolar²⁶. The observation of this larger g and lower A values suggests the coordination of an axial ligand and more delocalization of charge into the ligand orbitals due to the formation of a square pyramidal structure²⁷. Interestingly, the present complexes 1-6 exhibits very similar solution EPR parameter (g_{\parallel} , 2.20-2.38; A_{\parallel} , 172-193 $\times 10^{-4}$ cm^{-1}) to previous literature (Medda, 1997).

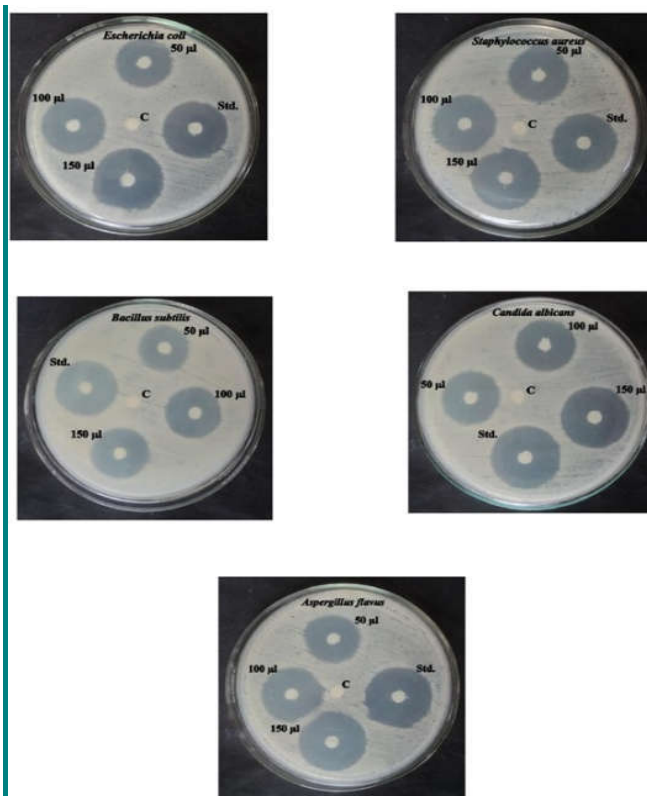


Fig. 6. Zone of inhibition against Gram-positive bacteria: *Staphylococcus aureus* (MTCC 96), *Bacillus subtilis* (MTCC 441), Gram-negative bacteria: *Escherichia coli* (MTCC 119) and Fungai as *Candida albicans* (MTCC 227), *Aspergillus flavus* (MTCC 230)

Antimicrobial Activity

In vitro antibacterial screening effects of the investigated copper (II) complexes (1-6) were tested against species *S. aureus*, *B. subtilis* and *E. coli* by disc diffusion producer (National Committee for Clinical Laboratory Standards, 1993 and Awoyinka, 2007). The observed activity values for copper (II) complexes are given in Table 3. These complexes showed more activity with 5-15 mm inhibition at different concentration. However, the complexes showed activity as closed to standard drug Chloramphenical. For antifungal activity of the all copper (II) complexes were tested against *C. albicans*, *A. flavus* are shown in Table 4. These complexes

indicated higher activity with 6-14 mm inhibition at different concentration. All complexes show a considerable biological activity at higher concentration 150 μ l against microorganisms and also the development of the complexes can be explained with the help of Tweedy's chelation theory (Dharamaraj, 2001), and Overtone's concept (Belaid, 2008). The result shows that the copper(II) complexes inhibit the development of microorganism by stopping the formation of protein and thus decelerating the respiration process. This inhibitory growth of bacteria and fungi may be explained on the basis of the structure due to the increase in liposolubility of the molecules across the cell membranes of the microorganisms. The antimicrobial activity of copper (II) complexes have promising and potential activity.

Conclusions

In summary, we have successfully synthesized six new mononuclear mixed ligand copper(II) complexes and characterised by physicochemical and spectroscopic methods. The analyses confirmed that the copper metal ion coordinated with three nitrogen atoms from the primary tridentate Schiff bases and two nitrogen atoms from the auxiliary ligands. The geometry of the complexes is assigned as square based pyramidal structure. All the complexes show moderate antimicrobial activity.

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