Synthesis, Characterization and Antimicrobial Studies of Novel Binuclear Transition Metal Complexes of Schiff Base Derived from 1-Amino-5-methyl-2,6-pyrimidine-dione and 2,3-Butanedione

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A series of binuclear transition metal complexes of the type $[M_2(L)_2X_4]\cdot nH_2O$ (where, M = Cu(II), Ni(II), Co(II) or Zn(II), X= Cl$^-$/ CH_3COO^- and L = ligand) of a Schiff base ligand derived from 1-amino-5-methyl-2,6-pyrimidine-dione and 2,3-butanedione have been synthesized and characterized by elemental analysis, molar conductance measurements, magnetic moment measurements, IR, UV-visible, ^{1}H NMR, EPR and mass spectral studies. Electronic spectral data and magnetic moment values indicate octahedral geometry for all the metal complexes. *In vitro* antimicrobial activity of ligand and its metal complexes were also studied against bacteria (*Bacillus subtilis* and *Escherichia coli*) and fungi (*Aspergillus niger* and *Aspergillus flavus*) which show antimicrobial activity of ligand and binuclear metal complexes.

Key Words: Octahedral metal complexes, Amino-pyrimidine, Antimicrobial activity, Schiff base.

INTRODUCTION

Pyrimidines, being an integral part of DNA and RNA, play an essential role in several biological processes and have considerable chemical and pharmacological importance. Most of the transition metal complexes containing nucleobase ligands or analogs have been used to understand various biological phenomena as well as to get new biologically active metallodrugs[1,2]. Due to multifunctional coordinating ability of pyrimidines and its derivatives, they have been used for synthesis of mononuclear and binuclear transition metal complexes[3,4]. The enormous interest in the field of coordination chemistry of transition metal ions with Schiff bases is due to variety of applications of these compounds in biological, clinical, analytical and pharmacological areas[5,6]. Recently, some of the Schiff base complexes possessing potent antibacterial activities have been reported[7]. Some other transition metal complexes have also been synthesized recently which show good biological activities *viz.* antimicrobial, DNA interaction and antitumor[8,9]. In view of these importance of metal complexes, we report herein preparation, characterization and *in vitro* antimicrobial activity of binuclear transition metal complexes of a novel Schiff base ligand derived from 1-amino-5-methyl-2,6-pyrimidine-dione and 2,3-butanedione.

EXPERIMENTAL

All the chemicals used were of analytical reagent grade and used as received. 2,3-Butanedione (Sigma-Aldrich), hydrated metal salts, methanol, ethanol and diethyl ether (Qualigens). 1-Amino-5-methyl-2,6-pyrimidine-dione was synthesized according to the method reported in literature[10]. Elemental analysis (C, H, N) were performed using a VarioEL elementar analysensysteme. Metals and chlorides were determined volumetrically[11] and gravimetrically[12]. IR spectra were recorded using KBr discs (4000-400 cm^{-1}) on a Shimadzu 8300 IR spectrophotometer. Electronic absorption spectra in the 200-900 nm range were obtained in DMF on a Systronic UV-visible spectrophotometer. ^{1}H NMR spectra (at room temperature) (in DMSO-d_6) was recorded on a Bruker Avance II 400 NMR spectrometer with reference to TMS (0.0 ppm). The FAB mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer/data system using argon/xenon (6 kV, 10 ma) as the FAB gas. Molar conductance measurements were determined in DMSO (*ca.* 10^{-3} M) at room temperature using a Jenway Model 4070 conductivity meter. Magnetic moment measurement were carried out by the Gouy method using Hg[Co(SCN)$_4$] as calibrant. EPR spectra of Cu(II) and Co(II) complexes were recorded as polycrystalline sample on a Varian

E-112 spectrometer at the X-band region with frequency of 9.1 GHz under the magnetic field strength 3200 G using TCNE (tetracynaoethylene) as field marker (g = 2.0027).

Synthesis of the Schiff base ligand (L): To an aqueous ethanolic solution (20 mL) of 1-amino-5-methyl-2,6-pyrimidine-dione (1.41 g, 10 mmol), 2,3-butanedione (0.87 mL, 10 mmol) was added drop wise. The resulting solution was stirred for 0.5 h and then refluxed at 65 ºC for 1.5 h. The creamish solid product (L) obtained was filtered off, washed with water, methanol, ethanol and diethyl ether and dried in vacuum desiccator over anhydrous calcium chloride (**Scheme-I**). Yield 72 %; m.p.: 214 ºC; creamish solid. Anal. calcd. for $C_9H_{11}N_3O_3$ (209.12): C 51.69, H 5.35, N 20.09 %. Found: C 51.62, H 5.26, N 20.01 %.

Synthesis of binuclear metal complexes (1-4): To a hot aqueous ethanolic solution (25 mL) of ligand (L) (2 mmol, 0.42 g), methanolic solution of 2 mmol of hydrated metal salt [$CuCl_2 \cdot 2H_2O$ (0.34 g), $NiCl_2 \cdot 6H_2O$ (0.47 g), $CoCl_2 \cdot 6H_2O$ (0.48 g) and $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.44 g)] was added drop wise with constant stirring. The resulting solution mixture was stirred for 1.5 h and then refluxed for 10-12 h. On cooling this reaction mixture in refrigerator for overnight, solid coloured products were obtained which were filtered off, washed with hot water, methanol, ethanol and diethyl-ether and dried in vacuum desiccator over anhydrous calcium chloride (**Scheme-II**).

Complex (1) [$Cu_2(L)_2Cl_4$]·4H$_2$O: Yield 64%; m.p.: 242 ºC (dec.); dark brown solid. Anal. calcd. for $C_{18}H_{30}N_6O_{10}Cu_2Cl_4$ (759.54): C 28.46, H 4.26, N 11.06, Cu 16.73, Cl 18.69 %. Found: C 28.35, H 4.14, N 10.94, Cu 16.53, Cl 18.57 %. Molar conductance Λ_M: 8.5 Ω^{-1} cm^2 mol^{-1}. μ_{eff}: 1.56 μ_B. UV-VIS (DMF), λ_{max}: 354, 580, 734 nm.

Complex (2) [$Ni_2(L)_2Cl_4$]·4H$_2$O: Yield 68 %; m.p.: 236 ºC (dec.); brown solid. Anal. calcd. for $C_{18}H_{30}N_6O_{10}Ni_2Cl_4$ (749.90): C 28.82, H 4.03, N 11.21, Ni 15.66, Cl 18.93 %. Found: C 28.79, H 4.00, N 11.17, Ni 15.61, Cl 18.89 %. Molar conductance Λ_M: 7.6 Ω^{-1} cm^2 mol^{-1}. μ_{eff}: 1.80 μ_B UV-VIS (DMF), λ_{max}: 378, 502, 690 nm.

Complex (3) [$Co_2(L)_2Cl_4$]·H$_2$O: Yield 61 %; m.p.: 254 ºC (dec.); reddish brown solid. Anal. calcd. for $C_{18}H_{24}N_6O_7Co_2Cl_4$ (696.30): C 31.05, H 3.47, N 12.07, Co 16.93, Cl 20.40 %. Found: C 30.98, H 3.36, N 12.01, Co 16.88, Cl 20.23 %. Molar conductance Λ_M: 5.2 Ω^{-1} cm^2 mol^{-1}. μ_{eff}: 2.62 μ_B UV-VIS (DMF), ;λ_{max}: 382, 456, 598, 780 nm.

Complex (4) [$Zn_2(L)_2(CH_3CO_2)_4$]·4H$_2$O: Yield 67 %; m.p.: 232 ºC (dec.); colourless. Anal. calcd. for $C_{26}H_{42}N_6O_{18}Zn_2$ (857.38): C 36.42, H 4.94, N 9.80, Zn 16.18 %. Found: C 36.31, H 4.82, N 9.70, Zn 16.06 %. Molar conductance Λ_M: 3.4 Ω^{-1} cm^2 mol^{-1}. UV-VIS (DMF), λ_{max}: 372 nm.

***In vitro* antibacterial and antifungal activity:** Synthesized compounds were evaluated for their *in vitro* antibacterial activity against *B. subtilis* and *E. coli* and antifungal activity against *A. niger* and *A. flavus* by the agar-well diffusion method[13] at the concentration of 500 and 100 µg mL^{-1} of each chemical compound. Bacteria were inoculated into Nutrient Broth (Difco) and incubated for 30 h and the fungi studied incubated in Malt Extract Broth (Difco) for 54 h. The dilution plate method was used to enumerate microorganism (10^5 bacteria per mL and 10^3-10^4 fungi per mL) for 24 h. By using a sterilize cork borer (6 mm diameter), wells were dug in the culture plates. Compounds dissolved in DMSO were added (0.2 µL) to these wells. The Petri dishes were left at 4 ºC for 2 h and then the plates were incubated at 30 ºC for bacteria (24 h) and 25 ºC for fungi (72 h). At the end of the period, inhibition
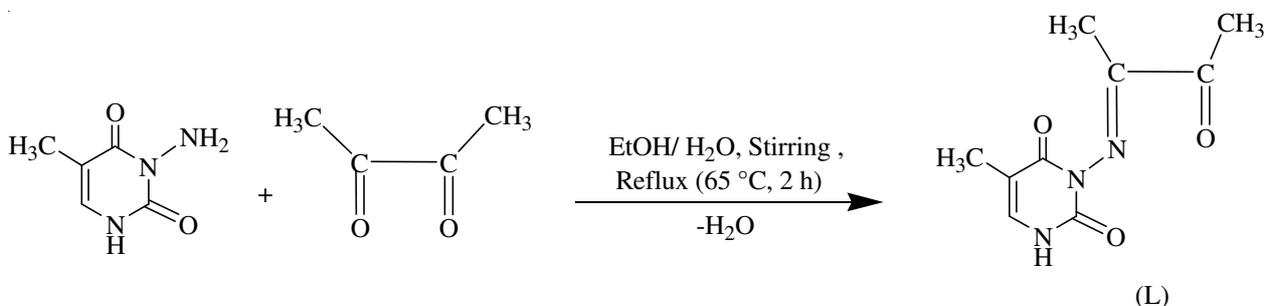
Scheme-I: Synthesis of ligand (L)
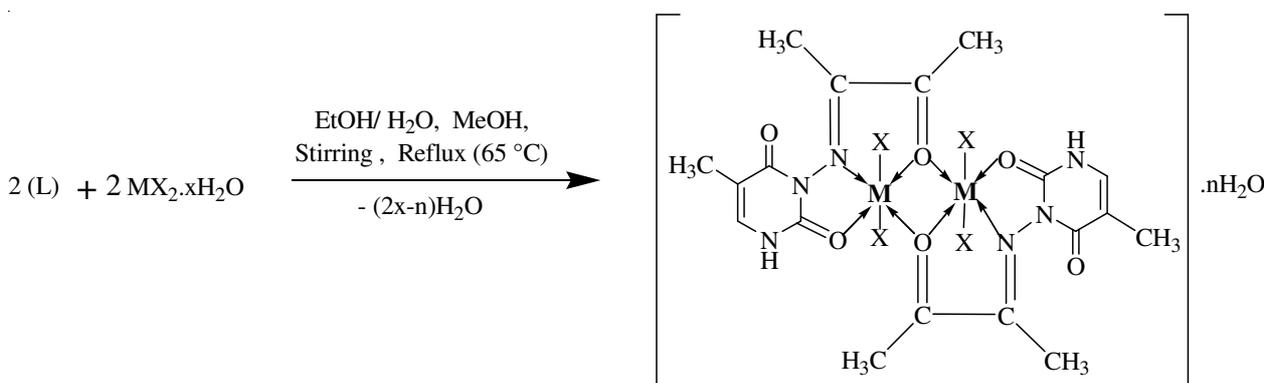
Scheme-II: Synthesis of binuclear metal complexes

			TABLE-1			
		IR SPECTRAL BAND (ν, cm^{-1}) OF THE SCHIFF BASE LIGAND AND ITS METAL COMPLEXES				
Compound	(-OH)/H$_2$O	(C=N)azo.	(C=O)	(N-C=O)pym.	(M-N)	(M-O)
(L)	–	1612	1768	1692	–	–
[Cu$_2$(L)$_2$Cl$_4$]·4H$_2$O	3428	1626	1592	1670	478	523
[Ni$_2$(L)$_2$Cl$_4$]·4H$_2$O	3432	1620	1588	1678	462	506
[Co$_2$(L)$_2$Cl$_4$]·4H$_2$O	3420	1624	1592	1672	475	518
[Zn$_2$(L)$_2$(CH$_3$CO$_2$)$_4$]·4H$_2$O	3438	1632	1588	1668	488	512

	TABLE-2
	^{1}H NMR SPECTRAL DATA OF THE LIGAND (L) AND ITS Zn(II) COMPLEX (IN DMSO-d_6)
Compound	^{1}H NMR (δ/ppm)
(L)	1.02 [O=C-CH$_3$ (s, 3H)], 1.60 [N=C-CH$_3$ (s, 3H)], 1.74 [-CH$_3$ (s, 3H)], 7.36 [-CH (pym.) (s, 1H)], 11.28 [-NH (pym.) (br, s, 1H)].
[Zn$_2$(L)$_2$(CH$_3$CO$_2$)$_4$]·4H$_2$O	0.90 [O=C-CH$_3$ (s, 6H)], 1.12 [N=C-CH$_3$ (s, 6H)], 1.73 [-CH$_3$ (s, 6H)], 2.17 [-CH$_3$COO (br, s, 12H)], 3.34 [H$_2$O (br, m, 8H)], 7.34 [-CH (pym.) (s, 2H)], 10.98 [-NH (pym.) (br, s, 2H)].

zones formed on the medium were evaluated as millimeters (mm) diameter. Biological activity data of all compounds were expressed as percent inhibition over control calculated from the size of inhibition zone. The per cent inhibition was calculated using the formula:

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

where C is the diameter of the microbial colony in the control plate and T is the diameter of the microbial colony in the tested plate after same incubation period.

RESULTS AND DISCUSSION

The newly synthesized ligand and binuclear metal complexes are quite stable at room temperature in solid state. Analytical and spectral data are consistent with the proposed molecular formula and structure of the ligand and metal complexes. Molar conductance values (3.4-8.5 Ω^{-1} cm^2 mol) in DMSO show that all the complexes are non-electrolyte in nature[14]. An octahedral geometry was assigned for all binuclear metal complexes. The ligand is soluble in common organic solvents but metal complexes are soluble in DMF and DMSO.

IR spectra: The most relevant IR absorption bands from the spectra of the Schiff base ligand (L) and binuclear complexes are given in Table-1. The IR spectrum of ligand (L) shows a band at 1612 cm^{-1} indicating the presence of azomethine group vibration ν(-C=N)[15]. There is no peak of unreacted -NH$_2$ group in the IR spectra of ligand which indicate the synthesis of proposed ligand. The band in the IR spectra of ligand at 1692 cm^{-1} is assigned for (N-C=O) group of pyrimidine ring[16]. The band at 1768 cm^{-1} indicate the presence of free ketonic (-C=O) group of ligand[17]. A band at 3065 cm^{-1} may be due to stretching vibration of heterocyclic -NH group of characteristics of pyrimidine ring[16]. The IR spectra of metal complexes show significant changes compared to the free ligand. In the IR spectra of all the complexes bands in the range 3438-3420 cm^{-1} due to the stretching vibration of ν(OH) of water molecule[18]. In the IR spectra of all metal complexes, bands of azomethine group (-C=N) shifted by 1632-1620 cm^{-1}, suggesting coordination through nitrogen atom of azomethine group[19]. This is further supported by the presence of new bands in the range of 490-475 cm^{-1} which is assignable to ν(M-N) vibration[20]. In the IR spectra of binuclear metal complexes, there is no band in the range of 1768 cm^{-1}, so it is clear that the oxygen atom of ketonic carbonyl group has been participated

in coordination. The appearance of band in the range 1592-1588 cm^{-1} indicates the presence of bridging ketonic oxygen atom. The band observed at 1692 cm^{-1} in free ligand, shifted by 1678-1657 cm^{-1} in the spectra of metal complexes which are assigned to coordinated (N-C=O) group of pyrimidine ring[21]. Coordination through oxygen atom of carbonyl group is further proved by the appearance of new band in the region of 536-506 cm^{-1} which may be assigned for ν(M-O) vibration[22]. In the IR spectrum of [Zn$_2$(L)$_2$(CH$_3$CO$_2$)$_4$]·4H$_2$O complex two characteristic bands appeared in the range 1560 cm^{-1} and 1352 cm^{-1} may be assigned to ν(COO$^-$) asymmetric and ν(COO$^-$) symmetric stretching vibration of acetate ion. A difference between (ν$_{as}$-ν$_s$) is 308 cm^{-1} which is greater than 144 cm^{-1} indicates the coordination of the acetate ion in unidentate fashion with central metal ion[18].

^{1}H NMR spectra: The ^{1}H NMR spectral data of ligand and its Zn(II) metal complex were recorded in solvent DMSO-d_6 and given in Table-2. In the ^{1}H NMR spectrum of ligand, no signal observed corresponding to primary amine proton which suggest that formation of ligand. In the ^{1}H NMR spectrum of Zn(II) complex, the signal of (CH$_3$-C=N) protons, (CH$_3$-C=O) protons and (-NH) proton of pyrimidine ring shifted compared to the free ligand, suggesting coordination through azomethine nitrogen atom, oxygen atoms of (CH$_3$-C=O) and (NH-C=O) group[23].

Mass spectra: The FAB mass spectra of ligand and binuclear complexes have been recorded. The proposed molecular formula of these compounds was confirmed by comparing their molecular formula weight with m/e values. The molecular ion peaks obtained from various compounds are as follows: (1) m/e = 210.01 [ligand], (2) m/e = 760.55 [Cu(II) complex], (3) m/e = 750.91 [Ni(II) complex], (4) m/e = 697.31 [Co(II) complex], (5) m/e = 858.24 [Zn(II) complex]. These data are in good agreement with the proposed molecular formula for these compounds. In addition to the peaks due to the molecular ion, the spectra exhibit peaks assignable to various fragments arising from the thermal cleavage of the complexes. Electronic absorption spectra and magnetic moment measurements

The electronic absorption spectra of binuclear metal complexes were recorded in DMF solution. The electronic absorption spectrum of [Cu$_2$(L)$_2$Cl$_4$]·4H$_2$O exhibits bands at 734 nm and 580 nm attributed to $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$

TABLE-3
ANTIBACTERIAL AND ANTIFUNGAL ACTIVITY OF LIGAND AND METAL COMPLEXES (% INHIBITION)

Compound	Conc. (µg/mL)	*B. subtilis*	*E. coli*	*A. niger*	*A. flavus*
(L)	100	38	52	58	66
	500	46	60	68	76
$[Cu_2(L)_2(Cl)_4]\cdot 4H_2O$	100	54	73	80	81
	500	62	84	88	87
$[Ni_2(L)_2(Cl)_4]\cdot 4H_2O$	100	49	57	77	73
	500	54	64	82	84
$[Co_2(L)_2(Cl)_4]\cdot H_2O$	100	45	53	66	70
	500	51	59	69	72
$[Zn_2(L)_2(CH_3CO_2)_4]\cdot 4H_2O$	100	53	70	74	80
	500	60	82	87	85

transitions, respectively. These transitions are consistent with a distorted octahedral geometry of Cu(II) complex[24]. The spectra of Cu(II) complex further display a shoulder at 354 nm assigned to charge transfer transition from the ligand to metal ion (LMCT)[24]. The obtained magnetic moment value (μ_{eff}) for Cu(II) complex is 1.56 µB indicates that magnetic exchange occurs between the two copper sites and also support distorted octahedral geometry of binuclear Cu(II) complex. The electronic absorption spectrum of $[Ni_2(L)_2Cl_4]\cdot 4H_2O$ complex show broad band at of 690 nm and 502 nm, which are assigned to $^3A_{2(g)} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2(g)} \rightarrow {}^3T_{1g}(P)$ transitions, respectively. The absorption spectra of complex also display a band at 378 nm assigned to charge transfer transition from the ligand to metal ion (LMCT)[24]. These transitions are consistent with an octahedral geometry of Ni(II) complex[25]. The magnetic moment value (μ_{eff}) of Ni(II) complex is 1.80 μ_B which indicates the presence of two unpaired electron per Ni(II) ion and also confirming octahedral geometry of binuclear Ni(II) complex. At room temperature, low μ_{eff} value for Ni(II) complex may be due to a strong Ni-Ni interaction. The electronic absorption spectrum of $[Co_2(L)_2Cl_4]\cdot H_2O$ complex exhibits absorption bands in the region 780, 598 and 456 nm, which may be assigned to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions, respectively, indicating octahedral geometry of Co(II) complex[26]. In addition, a band observed at 382 nm attributed to charge transfer transition from the ligand to metal ion (LMCT)[24]. Furthermore, octahedral geometry for Co(II) complex is also supported by its magnetic moment value (μ_{eff}) at room temperature which is 2.62 μ_B per Co atom. The electronic spectrum of $[Zn_2(L)_2(CH_3CO_2)_4]\cdot 4H_2O$ exhibits a band at 372 nm which may be assigned to transition of charge transfer from the low energy π^* orbital of the ligand to the *d*-orbitals of Zn(II) ion (LMCT)[24]. Zn(II) belongs to d^{10} system. So the Zn(II) complex is diamagnetic because of unavailability of unpaired electrons in this system.

EPR spectra: The X-band spectrum of $[Cu_2(L)_2Cl_4]\cdot 4H_2O$ and $[Co_2(L)_2Cl_4]\cdot H_2O$ complexes were recorded. The X-band EPR spectrum of Cu(II) complex was recorded at frequency of 9.1 GHz under the magnetic field strength 3200 G at room temperature (298 K) and Co(II) complex at liquid nitrogen temperature (77 K) as polycrystalline sample. As a consequence of the fast spin relaxation time of high spin Co(II) ion, the signals are observed only at low temperature. The $g_\parallel$, $g_\perp$ and g_{av} values of both complexes have been calculated by using formula $g^2_{av} = (g^2_\parallel + 2\ g^2_\perp)/3$. The values of EPR parameters $g_\parallel$, $g_\perp$ and g_{av} for Cu(II) complex are 2.148, 2.046 and 2.080,

respectively. The EPR spectrum of Cu(II) complex shows a single absorption band. The absence of hyperfine lines in the spectrum of complexes may be due to strong dipolar and exchange interaction between Cu(II) ions in the unit cell. The trend $g_\parallel > g_\perp > 2.002$ observed for the complex under study indicates that the unpaired electron is localized in the $d_{x^2-y^2}$ orbital of Cu(II) ion[27]. Thus, EPR spectral data are in accordance with distorted octahedral geometry around Cu(II) ion[28]. The analysis of the EPR spectrum of $[Co_2(L)_2Cl_4]\cdot H_2O$ gives $g_\parallel$ 2.328, $g_\perp$ 2.016 and g_{av} 2.2215. The trend $g_\parallel > g_\perp > 2.002$ observed for the Co(II) complex under study is due to a large angular momentum contribution. The $g_\parallel > 2.3$ is characteristic of an ionic environment and $g_\parallel < 2.3$ indicate a covalent environment in metal ligand bonding. The $g_\parallel$ values for both complexes are less than 2.3 ($g_\parallel < 2.3$), indicates an appreciable metal ligand covalent character[29]. Thus, EPR values also support octahedral geometry of Co(II) complex[28].

***In vitro* antibacterial and antifungal activity:** *In vitro* antibacterial and antifungal activity of newly synthesized ligand and its binuclear metal complexes have been tested against the bacteria *B. subtilis* and *E. coli* and fungi *A. niger* and *A. flavus*. Antimicrobial activity data (Table-3) show that the binuclear metal complexes were more toxic than free ligand. Of the tested compounds, $[Cu_2(L)_2Cl_4]\cdot 4H_2O$ complex shows highest biological activity and $[Co_2(L)_2Cl_4]\cdot H_2O$ complex exhibits lowest activity against studied microbes. Such increased activity of the metal complexes can be explained on the basis of chelation theory. On chelation, the polarity of the metal ion will be reduced to a greater extent due to overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further, it increases the delocalization of π-electrons over the whole chelate ring and enhances the penetration of the complexes into lipid membranes and blocking of the metal binding sites in enzymes of microorganism. These complexes also disturb the respiration process of the cell and thus block the synthesis of proteins, which restricts further growth of microorganism[30].

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