



Synthesis, Characterization and Antibacterial Activity of Novel Schiff Bases Derived from 4-Phenyl-2-aminothiazole and their Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) Metal complexes

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Abstract: Novel Schiff bases and their metal complexes were derived from some hetero cyclic β -diketones with 4-phenyl-2-aminothiazole. All the synthesized compounds were confirmed their structure by Elemental analysis, FT-IR, ^1H NMR, ^{13}C NMR, Mass spectra, TGA analysis and UV spectra. All the compounds were tested for their antibacterial activity. Spectroscopic measurements suggest that all Schiff base metal complexes are of type $\text{ML}_2(\text{H}_2\text{O})_2$ ($\text{M}=\text{Mn}$, Fe , Co , Ni , and Cu) and all the metal complexes shows moderate antibacterial activity in the agar cup assay method.

Keywords: Thiazole, Pyrazolin-5-one, Schiff base, Metal complex

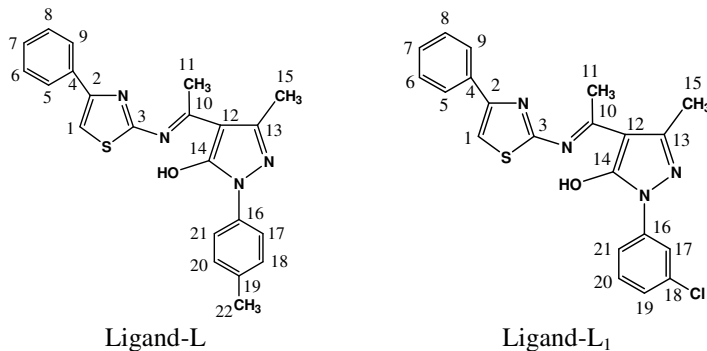
Introduction

The thiazole ring is very important in nature. It occurs for example, in thiamine, a coenzyme is required for the oxidative decarboxylation of α -keto acids. A tetra hydrothiazole also appears in the skeleton of penicillin, which is one of the first and still most important broad-spectrum antibiotics. Thiazole, thiazolamines are valuable medicines¹⁻³. It is obvious that compounds with the thiazole ring have a potential biological activity. Similarly 2-aminothiazoles are known as biologically active compounds with a broad range of activity and they are also used as intermediate products in the synthesis of antibiotics and dyes⁴.

2-Aminothiazole derivatives are widely used in pharmacology⁴. Aminothiazole exhibits antimicrobial and antioxidant⁵ activity. Some substituted aminothiazole derivatives are used as antioxidant additives to hydrocarbon fuels, minerals and synthetic lubricating oils, solid paraffin,

polyolefins and vegetable fats. Sym triazine derivatives containing substituents with 2-amino-thiazole fragments are effective anticorrosive, antiwear and antiscuff additives to lubricating oils⁶.

In continuation of our work⁷⁻¹⁴ on the metal complexes of Schiff bases, we report here the study of Schiff base metal complexes of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) derived from 2-amino-4-phenylthiazole and substituted 4-acetyl-1-phenyl-3-methyl-2-pyrazolin-5-one. Preparation, characterization and antibacterial activity of above metal complexes with Schiff bases Ligand-L and Ligand-L₁ are also reported here.



Where, Ligand-L is a Schiff base of 2-amino-4-phenyl-thiazole with 4-acetyl-1-(4'-methylphenyl)-3-methyl-2-pyrazolin-5-one and Ligand-L₁ is a Schiff base of 2-amino-4-phenyl-thiazole with 4-acetyl-1-(3'-chlorophenyl)-3-methyl-2-pyrazolin-5-one.

Experimental

All the chemicals used in the present study were of A.R. grade. Acetophenone, 4-methyl acetophenone, propiophenone, 4-methylpropiophenone, iodine, hydrochloric acid, sulfuric acid, thiourea, ethylacetoacetate, sodium acetate, calcium hydroxide, benzoyl chloride, acetyl chloride, 1,4-dioxane and methanol (SD's fine chemical Ltd and Merck chemicals., Mumbai) were used without further purification. Absolute ethanol from alembic Chemical Works Co. Ltd., Baroda was used after distillation. The Mn(II), Co(II), Ni(II), Cu(II) metal acetate and Fe(II) sulphate (SD's fine chemical Ltd, Qualigens-Glaxo, Mumbai and Merck chemicals., Mumbai) were used for the preparation of Schiff base metal complexes.

Melting points were taken in one side open capillaries on a Melting point apparatus having model number VMP-D of a make VEEGO. Electronic Spectra were recorded in DMF solution on LAMBDA 19, UV/VIS/NIR ("SICART-CVN" at Vallabh Vidyanagar, Gujarat, India). The Mass spectra of all ligands were recorded on the instrument named LCMS-2010 A of make Shimadzu. Carbon, hydrogen and nitrogen were estimated on a thermo fisher (Thermo electron corporation Limited), flash elemental analyzer-1112. The ¹H NMR and ¹³C NMR spectra of all the ligands [in Deuterated Chloroform(CDCl₃)] were recorded on a AVANCE-II 400 of make BRUKER spectro-photometer using TMS [(CH₃)₄Si] as internal standard. The Infrared spectra of the ligands studied in the present work were recorded on the model FT-IR-8300 of Shimadzu in KBr (Zydus Research Center, Ahmedabad, India).

Synthesis of Schiff base ligands

5-Methyl-4-[1-(4-phenyl-thiazole-2-yl-imino)-ethyl]-2-p-tolyl-2H-pyrazol-3-ol (L)

A hot solution of 4-acetyl-1-(4'-methylphenyl)-3-methyl-2-pyrazolin-5-one (0.1 mol, 23 g) in methanol (50 mL) was slowly added drop wise to a hot solution of 2-amino-4-phenyl-

thiazole¹⁵ (0.1 mol, 17.6 g) in methanol (35 mL). The resulting solution was refluxed for 3 h at 64 °C. Solid compound precipitate out is desire Schiff base. Filtered and washed with cold methanol and dried under vacuum oven at 50 °C. Yield: 29 g (75%). M.P. = 216 °C. Anal. Calcd. For C₂₂H₂₀N₄OS: C, 68.02; H, 5.19; N, 14.42; S, 8.25. Found: C, 67.94; H, 5.12; N, 14.32; S, 8.26. ¹H NMR: (400 MHz, CDCl₃ δ=14.10 (s, 1H, OH), 7.33 (s, 1H, Thiazole ring), 7.22-7.85 (m, 9H, 2Ar), 2.96 (s, 3H, CH₃), 2.47 (s, 3H, CH₃), 2.31 (s, 3H, CH₃). ¹³C NMR: (400 MHz, CDCl₃ δ=165.18 (C=N, 3C), 161.02 (C=N, 10C), 159.56 (C-OH, 14C), 153.08 (C=C, 2C), 147.71 (C=N, 13C), 136.20, 134.65, 133.96, 129.49, 128.94, 128.73, 128.62, 127.89, 126.27, 126.14, 120.87, 119.54, (12C, 2Ar), 108.51 (C=C, 1C), 103.60 (C=C, 12C), 21.12 (CH₃, 15C), 18.47(CH₃, 22C), 17.94 (CH₃, 11C).

2-(3-Chloro-phenyl)-5-methyl-4-[1-(4-phenyl-thiazol-2-ylimino)-ethyl]-2H-pyrazol-3-ol (L₁)

A hot solution of 4-acetyl-1-(3'-chlorophenyl)-3-methyl-2-pyrazolin-5-one¹⁶ (0.1 mol, 25 g) in methanol (50 mL) was slowly added drop wise to a hot solution of 2-amino-4-phenyl-thiazole (0.1 mol, 17.6 g) in methanol (35 mL). The resulting solution was refluxed for 3 h at 64 °C. Solid compound precipitate out is desire Schiff base. Filtered and washed with cold methanol and dried under vacuum oven at 50 °C. Yield: 32.6 g (80%). M.P. = 174 °C. Anal. Calcd. For C₂₁H₁₇ClN₄OS: C, 61.68; H, 4.19; N, 13.70; S, 7.84. Found: C, 57.59; H, 3.97; N, 12.77; S, 8.79. ¹H NMR: 400 MHz, CDCl₃ δ=13.93 (s, 1H, OH), 7.22 (s, 1H, Thiazole ring), 7.13-8.09 (m, 9H, 2Ar), 2.93 (s, 3H, CH₃), 2.45 (s, 3H, CH₃). ¹³C NMR: (400 MHz, CDCl₃ δ=165.55 (C=N, 3C), 161.42 (C=N, 10C), 159.26 (C-OH, 14C), 153.18 (C=C, 2C), 148.35 (C=N, 13C), 139.79, 137.48, 134.70, 133.87, 128.94, 128.69, 126.28, 124.79, 119.17, 117.03 (12C, 2Ar), 108.76 (C=C, 1C), 103.40 (C=C, 12C), 18.49(CH₃, 11C), 17.94 (CH₃, 15C).

Synthesis and characterization of metal complexes

For the preparation of complexes, an aqueous solution of metal acetate (0.05 M) and 1:4 dioxane solution of ligand (0.05 M) were mixed in presence of acetate buffer (pH=6.5) and the mixture was digested on sand bath for 30 minutes, cooled and filtered the precipitate and then washed with water and then methanol to remove excess metal ions and unreacted Schiff bases respectively.

All the complexes are colored, non-hygroscopic and stable solids. They are insoluble in water, sparingly soluble in all the common organic solvents but fairly soluble in DMF. Physical properties of the complexes are given in Table 1. The molar conductance of the complexes is in the range of 7.68 to 15.32 ohm⁻¹cm²mol⁻¹ indicates their non-electrolytic nature.

The metal contents in all the complexes were determined gravimetrically as MoO₃ by the method reported by Mohanti *et al*¹⁷. Carbon, hydrogen and nitrogen were determined micro analytically. Molar conductivities in 10⁻³ M DMF were measured using "Equiptronics EQ-660 digital conductivity meter" and a calibrated conductivity cell at room temperature. Magnetic susceptibilities of the complexes were measured at room temperature (30 °C) using Gouy balance (Sartorius, semi-micro, Sardar Patel University, Vallabh Vidyanagar, India).

Results and Discussion

Mass spectra

Mass spectra provide a vital clue for elucidation of compounds. The mass spectrum of ligand L shows the molecular ion peak at $m/z = 389.18$ (M⁺), confirms the theoretical molecular weight *i.e.* 388.49 of ligand L and spectrum of ligand L₁ shows the molecular ion peak at $m/z = 409.15$ (M⁺) and the isotopic peak at $m/z = 411.16$ due to ³⁵Cl and ³⁷Cl isotopes of ligand L₁. In both the spectra the molecular ion peak is base peak and the intensity of these peaks reflects the stability and abundance of the ions.

Infrared spectral analysis of ligands and their metal complexes

The infrared spectra of the both ligands show $\nu_{\text{O-H}}$ (weakly H-bonded) band at 3086 cm^{-1} and 3134 cm^{-1} respectively¹⁸. The absence of this band in all the metal complexes indicates the removal of proton of hydroxyl group of pyrazolin ring during the chelation. This is further supported by the shift of C-O frequency from 1350 cm^{-1} (in ligand-L) to $1381\text{--}1356\text{ cm}^{-1}$ (in complexes) and from 1321 cm^{-1} (in Ligand-L₁) to $1325\text{--}1379\text{ cm}^{-1}$ (in complexes) at the higher frequency respectively¹⁹. The sharp intense band at 1626.05 cm^{-1} and 1624.12 cm^{-1} respectively in the ligands can be assigned to $\nu_{\text{C=N}}$ (azomethine). A downward shift ($\Delta\nu = 10\text{--}35\text{ cm}^{-1}$) in $\nu_{\text{C=N}}$ (azomethine) is observed upon coordination indicating that the nitrogen of azomethine group is involved in coordination. All the complexes show broad band in the region 3300 cm^{-1} to 3550 cm^{-1} which may be assigned to $\nu_{\text{O-H}}$ of coordinated water²⁰. To account for the octahedral stereochemistry of the metal complexes, the coordination of two water molecules is expected.

The bands present at $\sim 500\text{ cm}^{-1}$ in Mn(II) complexes, $\sim 560\text{ cm}^{-1}$ in Fe(II) complexes, $\sim 590\text{ cm}^{-1}$ in Co(II) complexes, $\sim 490\text{ cm}^{-1}$ in Ni(II) complexes and $\sim 590\text{ cm}^{-1}$ in Cu(II) complexes respectively may be due to metal-nitrogen stretching vibration^{21,22}. A less intense band at $\sim 1610\text{ cm}^{-1}$ in the spectrum of ligands may be assigned to $\nu_{\text{C=N}}$ (ring)²³. All the metal complexes do not show shifting in $\nu_{\text{C=N}}$ compared to its respective ligands. This suggests that the nitrogen atom of the thiazole ring has not participated in the coordination. However, in water containing metal complexes, this band is observed as a broad band with some fine structures this may be due to coupling of the bending mode of coordinated²⁴ water molecules with $\nu_{\text{C=N}}$.

Electronic spectra and magnetic studies of both ligands and their metal complexes

Both the ligands show two absorption bands at 38314 cm^{-1} , 27472 cm^{-1} and 36900 cm^{-1} , 26247 cm^{-1} respectively. No absorption was observed in the visible region for any of the ligands. In the absence of quantum mechanical calculation, it is not possible to assign the absorption bands to definite electronic transitions with complete certainty. However, it appears reasonable to assign the bands to $\pi \rightarrow \pi^*$ transitions²⁵. The electronic spectra of Mn(II) complexes exhibit three very low intense bands, one at 16995 cm^{-1} , 17012 cm^{-1} respectively which may rise due to ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$ (G) transition, another band at 18790 cm^{-1} , 18305 cm^{-1} respectively assigned to ${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{1g}$ (G) transition and the third band at 26049 cm^{-1} , 25580 cm^{-1} respectively may be assigned to ${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{1g}$, ${}^4\text{E}_g$ (G) transition for Mn(II) ion in octahedral environment. The μ_{eff} (*c.f.* Table 1) value of the complexes suggests the spin $3d^5$ configuration²⁶. The electronic spectra of all Fe(II) complexes shows a broad band at 14700 cm^{-1} , 15700 cm^{-1} respectively which may be assigned to the ${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$ transition. The magnetic moment value 4.99 and 5.09 B M respectively which indicates that the complexes are spin-free and it has octahedral geometry²⁷. The electronic spectra of Co(II) complexes exhibited absorption bands in the region 8400 cm^{-1} to 9350 cm^{-1} and 18600 cm^{-1} to 19700 cm^{-1} corresponding to ν_1 and ν_3 transitions ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})(\nu_1)$; ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})(\nu_3)$. In the present investigation, Co(II) complexes show the absorption bands at 9350 cm^{-1} , 6670 cm^{-1} and 18600 cm^{-1} , 19100 cm^{-1} corresponding to ν_1 and ν_3 transitions respectively. These bands are the characteristics of high spin octahedral Co(II) complexes. However, ν_2 band is not observed because of its proximity to strong ν_3 transition. The magnetic measurement of Co(II) complexes display magnetic moment value of 4.41 and 4.55 B.M. which is in the octahedral range 4.40 to 4.53 B.M.²³. The Ni(II) complexes exhibited three bands at 11047 cm^{-1} , 15265 cm^{-1} and 26400 cm^{-1} as well as three bands at 10255 cm^{-1} , 17501 cm^{-1} and 26299 cm^{-1} which are attributed to the ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{F})(\nu_1)$; ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})(\nu_2)$

and ${}^3A_{2g} \rightarrow {}^3T_{1g}(p)$ (ν_3) transitions respectively indicating octahedral geometry around Ni(II) ion. Ni(II) complexes showed the magnetic moment value of 2.93 and 2.86 which is in the range of 2.90 to 3.02 B.M suggesting consistency with their octahedral environment²⁸. For the Cu(II) complexes with D_4h symmetry, three spin allowed transitions ${}^2B_{1g} \rightarrow {}^2A_{1g}$ (ν_1), ${}^2B_{1g} \rightarrow {}^2B_{2g}$ (ν_2) and ${}^2B_{1g} \rightarrow {}^2E_g$ (ν_3) are possible but the electronic spectra of Cu(II) complexes display two bands at 14295 cm^{-1} , 21548 cm^{-1} and 14156 cm^{-1} , 21380 cm^{-1} respectively. There should be third transition but we could not observe the same which may be due to very close energy values of different states. Absence of any spectral band below 10000 cm^{-1} rules out the possibility for tetrahedral structure of the present complexes are also suggestive for distorted octahedral geometry of the complexes²⁹. The low molar conductance values in DMF solution for all metal complexes (Table 1) are indicating that the complexes are nonelectrolytes.

Magnetic properties

The room temperature magnetic moments of all the metal complexes are listed in Table 1. The magnetic moment of Mn(II), Fe(II), Co(II) and Ni(II) metal complexes are in the range required for high-spin octahedral metal complexes³⁰⁻³⁵ and Cu(II) metal complexes correspond to one-unpaired electron^{36,37}.

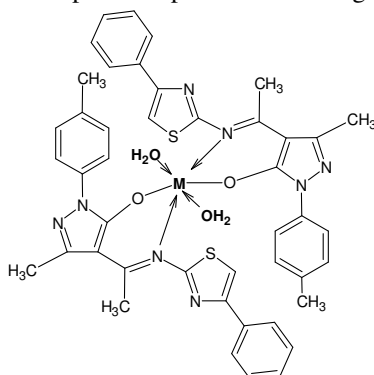
TGA analysis of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) metal complexes

The thermograms of this group of metal complexes show three stage decomposition (*c.f.* Table 2). All the metal complexes do not show weight loss below $120\text{ }^\circ\text{C}$, it indicates the absence of lattice water in the metal complexes.

The first stage decomposition is obtained in the temperature range $140\text{--}210\text{ }^\circ\text{C}$. The % weight loss in this range is corresponds the loss of two coordinated water molecules^{38,41}. The second stage decomposition is obtained in the temperature range $210\text{--}400\text{ }^\circ\text{C}$. The % weight loss in this range is corresponds % weight loss of two Schiff base ligands.

The third stage decomposition range is obtained in the temperature range $400\text{--}900\text{ }^\circ\text{C}$. The % weight loss in this range is corresponds % weight loss of metal oxide residue. The decomposition pattern for the metal complexes of this category may be as follow: On the basis of TGA and analytical data of all Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) complexes studied in the present work correspond to $[\text{ML}_2(\text{H}_2\text{O})_2]$ group.

On the basis of these results obtained from elemental analysis, infrared spectra, electronic spectra, TGA analysis and magnetic susceptibility measurements the following structures are proposed for the complex compounds of both ligands (Figure 1 & 2).



Where $M = \text{Mn(II), Fe(II), Co(II), Ni(II) and Cu(II)}$

Figure 1. Metal complexes of ligand-L

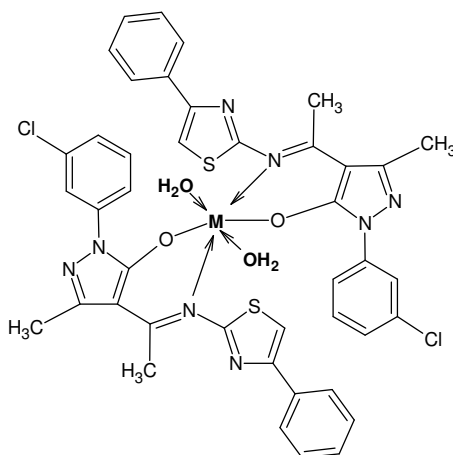
Table 1. Analytical and physical data of Schiff base ligands and their metal complexes

Ligand/Complexes	Colour	M. F.	M. W.	Yield %	Elemental analysis, % Found (Calculated)						μ_{eff} B.M.	λ_{M} Ohm^{-1} $\text{cm}^2 \text{mol}^{-1}$
					C	H	N	S	Cl	M		
Ligand-L	Yellow	$\text{C}_{22}\text{H}_{20}\text{N}_4\text{OS}$	388.49	75	67.94 (68.02)	5.12 (5.19)	14.32 (14.42)	8.26 (8.25)	-	-	-	-
$\text{Mn}(\text{L})_2 \cdot 2\text{H}_2\text{O}$	Creamy	$\text{C}_{44}\text{H}_{42}\text{MnN}_8\text{O}_4\text{S}_2$	865.9	68	60.95 (61.03)	4.86 (4.89)	12.98 (12.94)	7.45 (7.41)	-	6.37 (6.34)	5.81	9.15
$\text{Fe}(\text{L})_2 \cdot 2\text{H}_2\text{O}$	Brown	$\text{C}_{44}\text{H}_{42}\text{FeN}_8\text{O}_4\text{S}_2$	866.8	68	60.99 (60.97)	4.92 (4.88)	12.90 (12.93)	7.38 (7.40)	-	6.43 (6.44)	4.99	13.62
$\text{Co}(\text{L})_2 \cdot 2\text{H}_2\text{O}$	Dark brown	$\text{C}_{44}\text{H}_{42}\text{CoN}_8\text{O}_4\text{S}_2$	869.9	61	60.74 (60.75)	4.82 (4.87)	12.85 (12.88)	7.42 (7.37)	-	6.74 (6.77)	4.55	15.32
$\text{Ni}(\text{L})_2 \cdot 2\text{H}_2\text{O}$	Green	$\text{C}_{44}\text{H}_{42}\text{NiN}_8\text{O}_4\text{S}_2$	869.6	65	60.79 (60.77)	4.92 (4.87)	12.92 (12.88)	7.39 (7.37)	-	6.70 (6.75)	2.93	11.25
$\text{Cu}(\text{L})_2 \cdot 2\text{H}_2\text{O}$	Brown	$\text{C}_{44}\text{H}_{42}\text{CuN}_8\text{O}_4\text{S}_2$	874.5	60	60.46 (60.43)	4.81 (4.84)	12.84 (12.81)	7.36 (7.33)	-	7.29 (7.27)	1.92	7.68
Ligand-L ₁	Yellow	$\text{C}_{21}\text{H}_{17}\text{ClN}_4\text{OS}$	408.90	80	61.59 (61.68)	4.20 (4.19)	13.77 (13.70)	7.89 (7.84)	8.72 (8.67)	-	-	-
$\text{Mn}(\text{L}_1)_2 \cdot 2\text{H}_2\text{O}$	Creamy	$\text{C}_{42}\text{H}_{36}\text{Cl}_2\text{MnN}_8\text{O}_4\text{S}_2$	906.76	60	55.23 (55.63)	3.98 (4.00)	112.41 (12.36)	7.01 (7.07)	7.73 (7.82)	6.07 (6.06)	5.78	10.87
$\text{Fe}(\text{L}_1)_2 \cdot 2\text{H}_2\text{O}$	Brown	$\text{C}_{42}\text{H}_{36}\text{Cl}_2\text{FeN}_8\text{O}_4\text{S}_2$	907.66	61	55.61 (55.58)	3.99 (4.00)	12.41 (12.35)	7.19 (7.07)	6.97 (7.01)	6.11 (6.15)	5.09	12.85
$\text{Co}(\text{L}_1)_2 \cdot 2\text{H}_2\text{O}$	Dark brown	$\text{C}_{42}\text{H}_{36}\text{Cl}_2\text{CoN}_8\text{O}_4\text{S}_2$	910.75	55	55.60 (55.39)	4.12 (3.98)	12.27 (12.30)	7.14 (7.04)	7.71 (7.79)	6.65 (6.47)	4.41	15.14
$\text{Ni}(\text{L}_1)_2 \cdot 2\text{H}_2\text{O}$	Green	$\text{C}_{42}\text{H}_{36}\text{Cl}_2\text{NiN}_8\text{O}_4\text{S}_2$	910.51	56	54.89 (55.40)	3.67 (3.99)	12.41 (12.31)	7.01 (7.04)	7.73 (7.79)	6.61 (6.45)	2.86	9.56
$\text{Cu}(\text{L}_1)_2 \cdot 2\text{H}_2\text{O}$	Brown	$\text{C}_{42}\text{H}_{36}\text{Cl}_2\text{CuN}_8\text{O}_4\text{S}_2$	915.37	65	55.17 (55.11)	4.01 (3.96)	12.34 (12.24)	7.03 (7.01)	7.81 (7.75)	6.69 (6.94)	1.87	12.51

Spectroscopic analysis of the Schiff bases Ligand-L and Ligand-L₁ are given below

Table 2. Thermo analytical results of ligands and its metal complexes (control-DMF)

Compounds	Mass lose observed (Calculated)		
	Stage-I [140-210 °C]	Stage-II [210-400 °C]	Stage-III [400-900 °C]
[Mn(Ligand-L) ₂ .2H ₂ O]	4.12 (4.16)	86.85 (86.96)	9.07 (9.11)
[Fe(Ligand-L) ₂ .2H ₂ O]	4.11 (4.15)	86.79 (86.87)	9.25 (9.21)
[Co(Ligand-L) ₂ .2H ₂ O]	4.20 (4.14)	88.45 (88.49)	8.49 (8.61)
[Ni(Ligand-L) ₂ .2H ₂ O]	4.07 (4.14)	89.28 (89.35)	6.66 (6.75)
[Cu(Ligand-L) ₂ .2H ₂ O]	4.09 (4.12)	86.85 (87.02)	8.97 (9.10)
[Mn(Ligand-L ₁) ₂ .2H ₂ O]	3.93 (3.97)	87.34 (87.54)	8.77 (8.70)
[Fe(Ligand-L ₁) ₂ .2H ₂ O]	3.87 (3.96)	87.35 (87.45)	8.76 (8.79)
[Co(Ligand-L ₁) ₂ .2H ₂ O]	3.99 (3.95)	88.09 (88.04)	8.12 (8.22)
[Ni(Ligand-L ₁) ₂ .2H ₂ O]	3.97 (3.95)	89.77 (89.82)	6.39 (6.44)
[Cu(Ligand-L ₁) ₂ .2H ₂ O]	3.89 (3.93)	87.55 (87.59)	8.66 (8.69)
Assignment	Loss of two coordinated water molecules	Loss of two Schiff base ligand molecules	Metal Oxide



Where M = Mn(II), Fe(II), Co(II), Ni(II) and Cu(II)

Figure-2. Metal complexes of ligand-L₁

Antibacterial activity

The effect of the ligands and their metal complexes in the growth media were investigated by standard microbiological parameters. Concentration of the test compounds were kept constant (500 ppm) during all the experiments. The bacterial, fungal and yeast cultures were maintained on Nutrient-agar, Potato dextrose-agar and YEDP culture-tubes (slants) respectively and were sub cultured every fortnight and stored at 0-5 °C temperature.

The compounds were tested in vitro for the antibacterial activity (Table 3) against bacterial [*Escherichia coli*, *Bacillus subtilis* and *S. aureus*] and fungal [*A.niger*] and yeast [*S. cerevisiae*] cultures were tested with both ligands and their metal complexes using Agar cup assay method.

Table 3. Antibacterial activity of ligands and its metal complexes (control-DMF)

Compounds	<i>E. coli</i>	<i>B. subtilis</i>	<i>S. aureus</i>	<i>S. cerevisiae</i>	<i>A. niger</i>
[Ligand-L]	+	+	+	+	+
[Mn(L) ₂ (H ₂ O) ₂]	++	+	+	++	+
[Fe(L) ₂ (H ₂ O) ₂]	++	++	++	+	+
[Co(L) ₂ (H ₂ O) ₂]	++	++	++	++	++
[Ni(L) ₂ (H ₂ O) ₂]	++	++	++	++	++
[Cu(L) ₂ (H ₂ O) ₂]	++	+	++	++	+
[Ligand-L ₁]	+	+	+	+	+
[Mn(L ₁) ₂ (H ₂ O) ₂]	++	+	+	+	+
[Fe(L ₁) ₂ (H ₂ O) ₂]	++	++	+	++	+
[Co(L ₁) ₂ (H ₂ O) ₂]	+++	++	++	++	++
[Ni(L ₁) ₂ (H ₂ O) ₂]	+++	++	++	+++	++
[Cu(L ₁) ₂ (H ₂ O) ₂]	++	+	++	+	+

The degree of effectiveness was measured by determining the diameters of the zone of inhibition caused by the compounds. Effectiveness was classified into three zones on the bases of their diameter of zone of inhibition.

- +++ : Most effective
- ++ : Moderate effective
- + : Slightly effective
- : Non effective

Most of the compounds were active against both gram (-) negative and gram (+) positive bacteria. The results are presented in table given below.

The Schiff base Ligand-L without metal is slightly effective against all strains of microorganisms.

- The Mn(II) metal complexes are slightly effective against *B. subtilis*, *S. aureus* & *A. niger* when moderately effective against *E. coli* and *S. cerevisiae*.
- The Fe(II) metal complexes are slightly effective against *S. cerevisiae* & *A. niger* when moderately effective against *E. coli*, *B. subtilis* and *S. aureus*.
- All the Co(II) and Ni(II) metal complexes are moderately effective against *E. coli*, *B. subtilis*, *S. aureus*, *S. cerevisiae* and *A. niger*.
- The Cu(II) metal complexes are slightly effective against *B. subtilis* & *A. niger* when moderately effective against *E. coli*, *S. aureus* and *S. cerevisiae*.

The Schiff base Ligand-L₁ without metal is slightly effective against all strains of microorganisms.

- The Mn(II) metal complexes are slightly effective against *B. subtilis*, *S. aureus*, *S. cerevisiae* and *A. niger* when moderately effective against *E. coli*.
- The Fe(II) metal complexes are slightly effective against *A. niger* and *S. aureus* when moderately effective against *E. coli*, *B. subtilis* and *S. cerevisiae*.
- The Co(II) metal complexes are moderately effective against *S. aureus*, *B. subtilis*, *S. cerevisiae* and *A. niger* when most effective against *E. coli*.
- The Ni(II) metal complexes are moderately effective against *S. aureus*, *B. subtilis* and *A. niger* when most effective against *E. coli* and *S. cerevisiae*.
- The Cu(II) metal complexes are slightly effective against *A. niger*, *B. subtilis* and *S. cerevisiae* when moderately effective against *S. aureus* and *E. coli*.

Conclusion

Spectroscopic measurements suggest that all Schiff base metal complexes are of type $ML_2(H_2O)_2$ (M=Mn, Fe, Co, Ni and Cu). The synthesized metal complexes in comparison to the uncomplexed Schiff base ligand were screened for their antibacterial activity against pathogenic bacteria species (*Escherichia coli*, *Bacillus subtilis*, *S. aureus*, *A. niger* and *S. cerevisiae*). The activity of the Schiff base complexes became more pronounced when coordinated with metal ions. The biological activity of the complexes follow the order $Co(II)=Ni(II) > Mn(II), Fe(III), Cu(II)$.

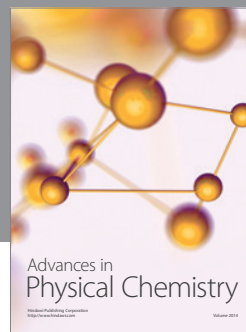
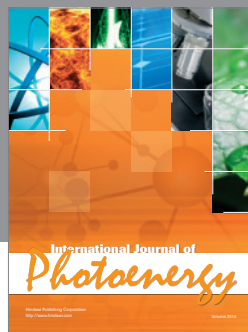
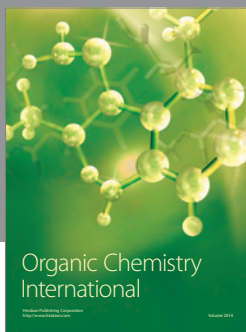
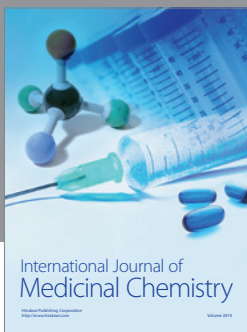
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