



Coordination Modes of a Schiff Base Derived from Substituted 2-Aminothiazole with Chromium(III), Manganese(II), Iron(II), Cobalt(II), Nickel(II) and Copper(II) Metal Ions: Synthesis, Spectroscopic and Antimicrobial Studies

AMBIT THAKAR*, KRISHNAKANT JOSHI[§],
KISHOR PANDYA and ARVIND PANCHOLI[§]

*Zydus Research Centre, Ahmedabad-382 210, India

[§]Department of Chemistry
Navjivan Science College, Dahod-389 151, India
Sir P.T. Science College, Modasa-383 315, India
krishnakant_joshi@yahoo.co.in

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Abstract: Transition metal complexes of Cr(III), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) metal ions with general stoichiometry $[ML_2 \cdot 2H_2O]$ and $[ML_3]$, where M= Mn(II), Cr(III), Fe(II), Co(II), Ni(II) and Cu(II), L= Schiff base derived from the condensation of 2-amino-4(4'-phenyl/methylphenyl)-5-methyl-thiazole with 4-acetyl-1(3-chloro phenyl)-3-methyl-2-pyrazoline-5-ones, have been synthesized and structurally characterized by elemental analysis, molar conductance measurements, magnetic susceptibility measurements and spectral techniques like IR, UV, ¹H NMR, ¹³C NMR and Mass Spectra. All the complexes were found to be octahedral geometry. The ligand and its complexes have been screened for their antifungal and antibacterial activities against three fungi, i.e. *Alternaria brassicae*, *Aspergillus niger* and *Fesarium oxysporum* and two bacteria, i.e. *Xanthomonas compestris* and *Pseudomonas aeruginosa*.

Keywords: 2-Aminothiazole, Schiff base, Transition metals, Biological activities

Introduction

The thiazole ring is important in nature. It occurs, for example, in thiamine, a coenzyme required for the oxidative decarboxylation of α -keto acids. A tetrahydrothiazole also appears

in the skeleton of penicillin which is one of the first and still most important of the broad-spectrum antibiotics. Thiazolamine are key intermediates for synthesizing many pharmaceuticals¹. Some thiazolidone are valuable medicines². It is obvious that compounds with the thiazole ring have potential biological activity. It is also known that some Schiff bases are effective antitumor drugs and antibacterials. Aminothiazoles are known to be ligands of the estrogen receptor and as a novel class of adenosine receptor antagonists³. We were interested in examining the biological activities of NO-donor schiff's bases and their transition metal complexes, thus, in this article, we report the anti fungal and antibacterial activities of the Schiff base ligands 1-(3-chlorophenyl)-3-methyl-4-(1-((5-methyl-4-phenylthiazol-2-yl)imino)ethyl)-1*H*-pyrazol-5-ol (**L**), 1-(3-chlorophenyl)-3-methyl-4-(1-((5-methyl-4-(*p*-tolyl)thiazol-2-yl)imino)ethyl)-1*H*-pyrazol-5-ol (**L₁**) and Its complexes with Cr(III), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) metal ions. The ligand and its complexes were characterized by physiochemical and spectral studies.

Experimental

All the chemicals used in the present study were of A.R. grade. 1,4-Dioxane and methanol (SD's fine chemical Ltd., Mumbai and Merck chemicals., Mumbai) were used without further purification. Absolute ethanol from alembic chemical works Co. Ltd., Baroda was used after distillation. Cr(III), 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.

Melting points were taken in one side open capillaries on a melting point apparatus having model number VMP-D of a make VEEGO. The Mass spectra of all ligands were recorded on the instrument named LCMS-2010A 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 the Schiff base ligands

*1-(3-Chlorophenyl)-3-methyl-4-(1-((5-methyl-4-phenylthiazol-2-yl)imino)ethyl)-1*H*-pyrazol-5-ol (L)*

A hot solution of 4-acetyl-3-methyl-1-(3'-chlorophenyl)-2-pyrazolin-5-one (0.1 mol, 25 g) in methanol (50 mL) was slowly added drop wise to a hot solution of 2-amino-4-phenyl-5-methyl thiazole (0.1 mol, 19 g) in methanol (38 mL). The resulting solution was refluxed for 7 h at 64°C. The Solid compound precipitated out is filtered, washed with cold methanol and dried under vacuum oven at 50°C. Yield: 28.6 g (68%). m.p.= 191 °C. Anal. Calcd. For C₂₂H₁₉ClN₄O₂: C, 62.48; H, 4.53; N, 13.25; S, 7.58. Found: C, 61.80; H, 4.44; N, 13.04; S, 7.82.

*1-(3-Chlorophenyl)-3-methyl-4-(1-((5-methyl-4-(*p*-tolyl)thiazol-2-yl)imino)ethyl)-1*H*-pyrazol-5-ol (L₁)*

A hot solution of 4-acetyl-3-methyl-1-(3'-chlorophenyl)-2-pyrazolin-5-one (0.1 mol, 25 g)

in methanol (50 mL) was slowly added drop wise to a hot solution of 2-amino-4-(4'-methylphenyl)-5-methyl thiazole (0.1 mol, 20.4 g) in methanol (40 mL). The resulting solution was refluxed for 7 h at 64 °C. The Solid compound precipitated out is filtered, washed with cold methanol and dried under vacuum oven at 50°C. Yield: 30.48 g (70%). M.P. = 178 °C. Anal. Calcd. For C₂₂H₁₉ClN₄OS: C, 63.22; H, 4.84; N, 12.82; S, 7.34. Found: C, 61.53; H, 4.69; N, 12.37; S, 7.47.

Synthesis of the metal complexes

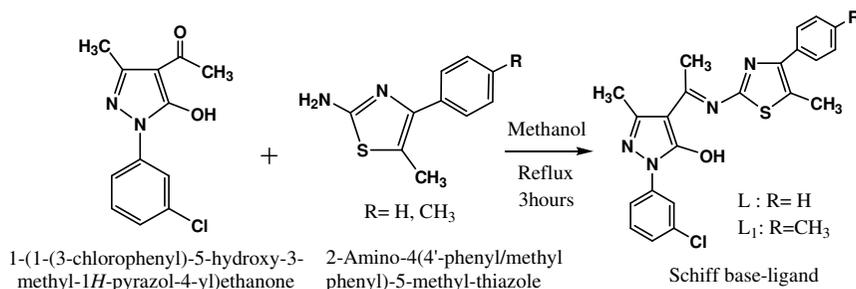
To hot solution of Schiff base ligands (1 mmol) in dioxane (15 mL), a hot solution of corresponding metal salt like nitrate, chloride, acetate or sulphate (1 mmol) in dioxane (10 mL) was added slowly with constant stirring. The resulting mixture was refluxed for 8 to 10 h at 85 to 90 °C. On cooling the mixture overnight at 0 °C, the colored product which separated out was filtered, washed with dioxane and dried under vacuum oven at 60 °C.

Results and Discussion

The synthesized novel Schiff base ligands, 1-(3-chlorophenyl)-3-methyl-4-(1-((5-methyl-4-phenylthiazol-2-yl)imino)ethyl)-1*H*-pyrazol-5-ol (**L**) and 1-(3-chlorophenyl)-3-methyl-4-(1-((5-methyl-4-(*p*-tolyl)thiazol-2-yl)imino)ethyl)-1*H*-pyrazol-5-ol (**L**₁) (Scheme 1) forms stable complexes with Cr(III), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) metal ions. The analytical data of complexes, together with physical properties are given in Table 1. The analytical data of the complexes correspond to the general stoichiometry [ML₂.2H₂O] and [ML₃], where M= Cr(III), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II), Ligand L=Schiff base L and L₁. The value of molar conductance (λ_M) of the complexes in DMSO indicates that the [ML₂.2H₂O] and [ML₃] are non-electrolytes⁴. Magnetic moments lie in the range 1.81-1.89 B.M., 5.72-5.76 B.M., 4.96-5.02 B.M., 4.42-4.48 B.M., 2.89-2.95 B.M and 1.90-1.94 B.M., for Cr(III), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) complexes respectively.

Mass spectra

Mass spectra provide a vital clue for elucidation of compounds. The ESI mass spectrum of ligand L and L₁ are given below. The spectrum in Figure 1 shows the molecular ion peak at $m/z = 423.14$ and the isotopic peak at $m/z = 424.99$ due to ³⁵Cl and ³⁷Cl isotopes of ligand L. The spectrum in Figure 2 shows the molecular ion peak at $m/z = 437.13$ and the isotopic peak at $m/z = 439.18$ due to ³⁵Cl and ³⁷Cl isotopes. In both the spectra the molecular ion peak is base peak and the intensity of these peaks reflects the stability and abundance of the ions⁵.



Scheme 1. Synthesis of ligand

Table 1. Analytical data and physical properties of complexes

Complex	M W	Color	M P, °C	$\lambda_M,$ $\Omega^{-1}\text{cm}^{-1}$ mol^{-1}	Yield, %	Elemental analysis data (%)					
						Found (Calculated)					
						C	H	N	S	M	Cl
Ligand-L C ₂₂ H ₁₉ ClN ₄ OS	422.93	Brown	191	-	68	61.80 (62.48)	4.44 (4.53)	13.04 (13.25)	7.82 (7.58)	-	8.11 (8.38)
Cr (L) ₃ C ₆₅ H ₅₂ Cl ₃ CrN ₁₂ O ₃ S ₃	1303.7	Brown	256*	11.94	65	59.82 (59.88)	3.97 (4.02)	12.87 (12.89)	7.36 (7.38)	3.94 (3.99)	8.13 (8.16)
Mn (L) ₂ .2H ₂ O C ₄₄ H ₄₀ Cl ₂ MnN ₈ O ₄ S ₂	934.81	Creamy	239	12.12	70	56.55 (56.53)	4.34 (4.31)	12.01 (11.99)	6.84 (6.86)	5.90 (5.88)	7.61 (7.59)
Fe (L) ₂ .2H ₂ O C ₄₄ H ₄₀ Cl ₂ FeN ₈ O ₄ S ₂	935.72	Brown	224*	10.25	65	56.50 (56.48)	4.33 (4.31)	11.94 (11.98)	6.87 (6.85)	5.99 (5.97)	7.59 (7.58)
Co (L) ₂ .2H ₂ O C ₄₄ H ₄₀ Cl ₂ CoN ₈ O ₄ S ₂	938.81	Dark Brown	263*	12.21	62	56.32 (56.29)	4.28 (4.29)	11.97 (11.94)	6.85 (6.83)	6.29 (6.28)	7.45 (7.55)
Ni (L) ₂ .2H ₂ O C ₄₄ H ₄₀ Cl ₂ NiN ₈ O ₄ S ₂	938.57	Green	281*	9.32	60	56.34 (56.31)	4.32 (4.30)	11.92 (11.94)	6.87 (6.83)	6.24 (6.25)	7.59 (7.55)
Cu (L) ₂ .2H ₂ O C ₄₄ H ₄₀ Cl ₂ CuN ₈ O ₄ S ₂	943.42	Brown	210	11.32	64	56.06 (56.02)	4.24 (4.27)	11.86 (11.88)	6.85 (6.80)	6.76 (6.74)	7.49 (7.52)
Ligand-L ₁ C ₂₃ H ₂₁ ClN ₄ OS	436.96	Brown	178	-	70	61.53 (63.22)	4.69 (4.84)	12.37 (12.82)	7.47 (7.34)	-	8.08 (8.11)
Cr (L) ₃ C ₆₈ H ₅₈ Cl ₃ CrN ₁₂ O ₃ S ₃	1345.8	Brown	266*	8.88	70	60.72 (60.69)	4.36 (4.34)	12.47 (12.49)	7.12 (7.15)	3.85 (3.86)	8.01 (7.90)
Mn (L) ₁ .2H ₂ O C ₄₆ H ₄₄ Cl ₂ MnN ₈ O ₄ S ₂	962.67	Creamy	222	10.34	65	57.40 (57.38)	4.62 (4.61)	11.67 (11.64)	6.67 (6.66)	5.70 (5.71)	7.41 (7.36)
Fe (L) ₁ .2H ₂ O C ₄₆ H ₄₄ Cl ₂ FeN ₈ O ₄ S ₂	963.77	Brown	231	9.32	60	57.36 (57.33)	4.62 (4.60)	11.60 (11.63)	6.67 (6.64)	5.77 (5.79)	7.32 (7.36)
Co (L) ₁ .2H ₂ O C ₄₆ H ₄₄ Cl ₂ CoN ₈ O ₄ S ₂	966.86	Dark Brown	252	10.24	67	57.17 (57.14)	4.57 (4.59)	11.62 (11.59)	6.66 (6.62)	6.14 (6.10)	7.11 (7.33)
Ni (L) ₁ .2H ₂ O C ₄₆ H ₄₄ Cl ₂ NiN ₈ O ₄ S ₂	966.62	Green	276*	10.35	65	57.19 (57.16)	4.62 (4.59)	11.57 (11.59)	6.66 (6.63)	6.04 (6.07)	7.29 (7.34)
Cu (L) ₁ .2H ₂ O C ₄₆ H ₄₄ Cl ₂ CuN ₈ O ₄ S ₂	971.47	Brown	229	12.45	62	56.88 (56.87)	4.59 (4.57)	11.50 (11.53)	6.59 (6.60)	6.56 (6.54)	7.22 (7.30)

* decomposition temperature

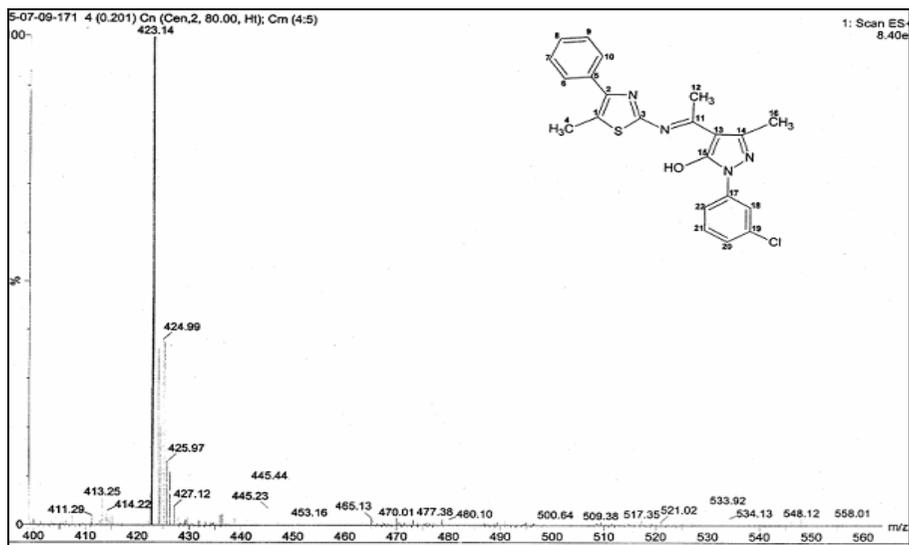


Figure 1. Mass spectrum of the ligand L

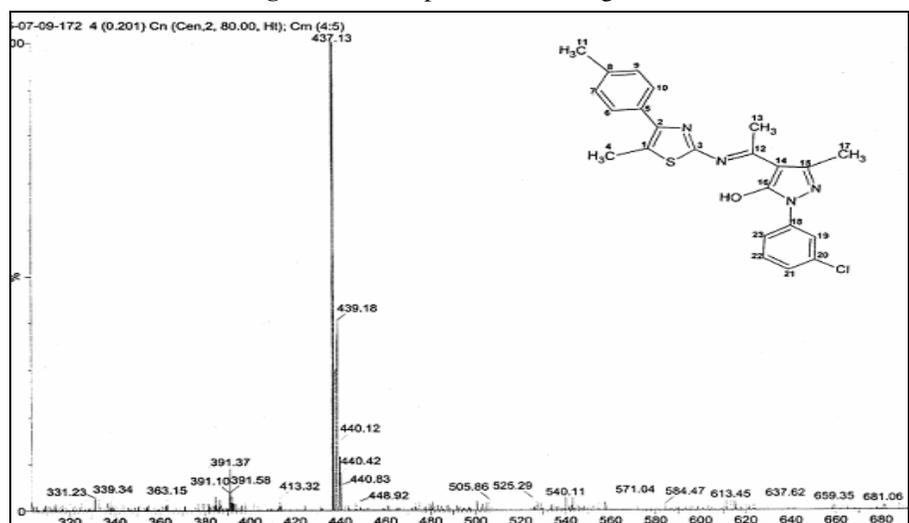


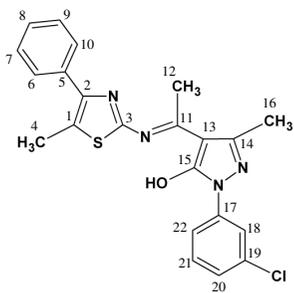
Figure 2. Mass spectrum of the ligand L₁

NMR spectra

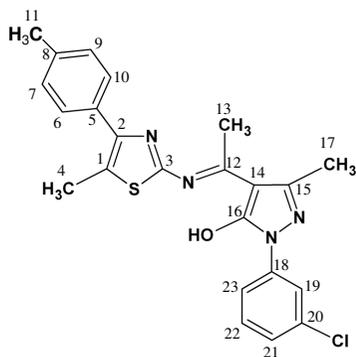
NMR data of ligand L are given in Table 2. Its ¹H NMR spectrum (Figure 3) displays three singlets at ca. δ 2.43 -2.86 ppm (s, 9H, 3H₃C-C) due to the nine protons of three methyl groups, at ca. δ 7.12-8.08 ppm (m, 9H, aromatic) due to the protons of two phenyl rings and a singlet at ca. δ 13.75 ppm (s, 1H, -OH) due to the alcohol and NMR data of ligand L₁ are given in Table 3. Its ¹H NMR spectrum (Figure 4) displays four singlets at ca. δ 2.36 -2.86 ppm (s, 12H, 4H₃C-C) due to the twelve protons of four methyl groups, at ca. δ 7.12-8.08 ppm (m, 9H, aromatic) due to the protons of two phenyl rings and a singlet at ca. δ 13.73 ppm (s, 1H, -OH) due to the alcohol⁶.

Table 2. The NMR data of Schiff base ligand L

¹ H NMR		¹³ C NMR	
δ, ppm	Assignment	δ, ppm	Assignment
2.43-2.86	s, 9H, 3H ₃ C-C	12.72	Primary Carbon C(4)
7.12-8.08	m, 9H, Ar	17.87	Primary Carbon C(16)
13.75	s, 1H, -OH	18.31	Primary Carbon C(12)
		102.96	C=C of Pyrazolone C(13)
		116.94-128.55	Tertiary Aromatic Carbon
		129.91-134.63	Quaternary Aromatic Carbon C(5), C(19), C(17)
		139.79	C=C of thiazole ring C(1)
		148.48	C=N of Pyrazolone C(14)
		148.51	C=C of thiazole ring C(2)
		154.94	C-OH of Pyrazolone C(15)
		161.49	C=N of Azomethine C(11)
		165.51	C=N of thiazole ring C(3)

**Table 3.** The NMR data of Schiff base ligand L₁

¹ H NMR		¹³ C NMR	
δ, ppm	Assignment	δ, ppm	Assignment
2.36-2.86	s, 12H, 3H ₃ C-C	12.73	Primary Carbon C(4)
7.12-8.08	m, 8H, Ar	17.88	Primary Carbon C(17)
13.73	s, 1H, -OH	18.31	Primary Carbon C(13)
		21.40	Primary Carbon C(11)
		102.91	C=C of Pyrazolone C(14)
		116.97-129.26	Tertiary Aromatic Carbon
		129.91-137.86	Quaternary Aromatic Carbon C(5), C(8), C(20), C(18)
		139.83	C=C of thiazole ring C(1)
		148.29	C=N of Pyrazolone C(15)
		148.60	C=C of thiazole ring C(2)
		154.79	C-OH of Pyrazolone C(16)
		161.54	C=N of Azomethine C(12)
		165.53	C=N of thiazole ring C(3)



The ¹³C NMR spectrum of ligand L (Figure 5) displays the signals corresponding to the different non-equivalent carbon atoms at different values of δ as follows: at ca. δ 12.72 ppm, δ 17.87 ppm and δ 18.31 ppm (H₃C-C) corresponding to carbon atoms of methyl groups; at ca. δ 102.96 ppm (C=C) due to carbon atom of pyrazolone ring; at ca. δ 116.97-134.36 ppm due to aromatic carbon atoms; at ca. δ 139.79 (C=C) due to carbon atom of thiazole ring; at ca. δ 148.48 (C=N) due to carbon atom of pyrazolone ring; at ca. δ 148.51 (C=C) due to carbon atom of thiazole ring; at ca. δ 154.94 (C-OH) due to carbon atom of pyrazolone ring; at ca. δ 161.49 (C=N) due to carbon atom of azomethine and at ca. δ 165.51 (C=N) due to carbon atom of thiazole ring. In the same manner ¹³C-NMR spectrum of ligand L₁ (Figure 6) describe in Table 3.

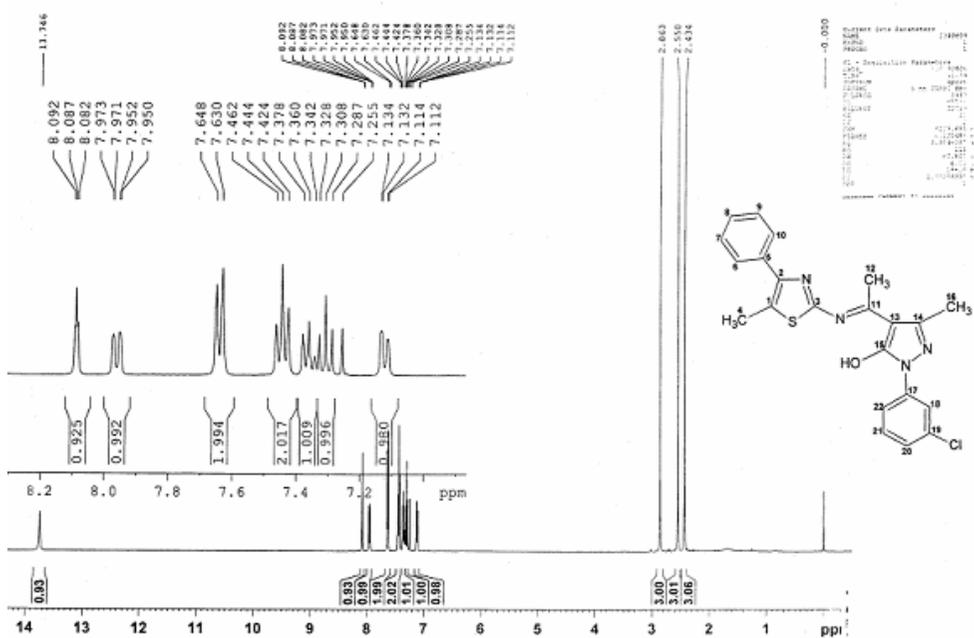


Figure 3. ¹H NMR spectrum of the ligand L

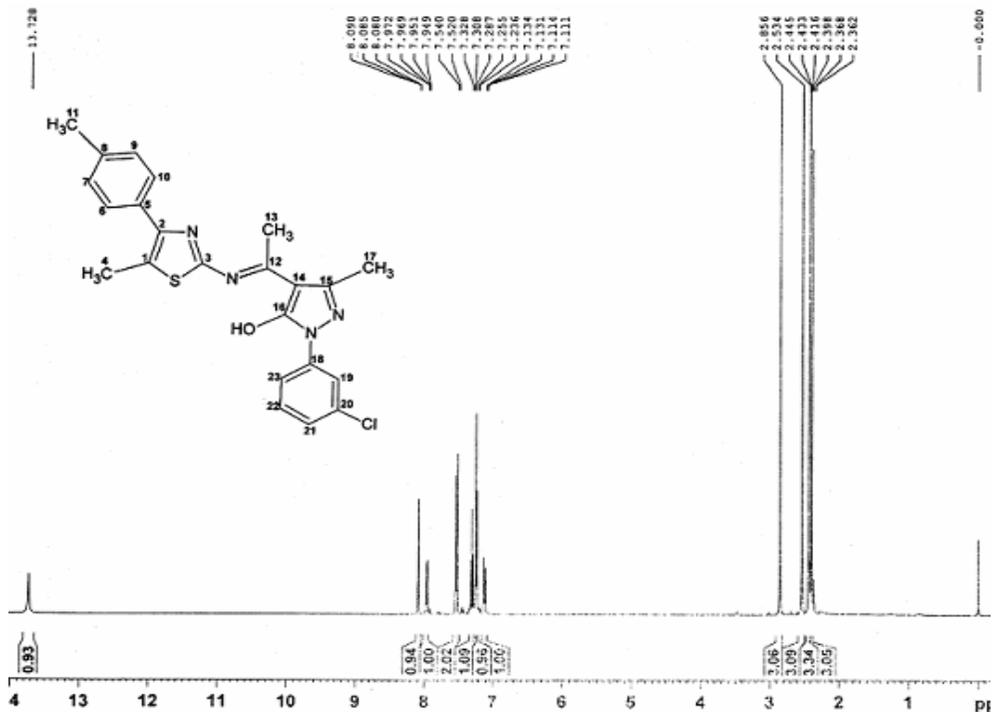


Figure 4. ¹H NMR spectrum of the ligand L₁

IR spectra

Selected IR bands of the ligand and its complexes are listed in Table 4. The infrared spectra of the both ligands L and L₁ show $\nu_{\text{O-H}}$ (weakly H-bonded) at 3345 cm^{-1} and 3320 cm^{-1} respectively⁷. 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 $\sim 1315 \text{ cm}^{-1}$ (in ligand) to the higher frequency 1330-1400 cm^{-1} (in complexes)⁸. The sharp intense band at 1626 cm^{-1} and 1627 cm^{-1} respectively in the ligands can be assigned to $\nu_{\text{C=N}}$ (azomethine). A downward shift ($\Delta\nu = 15\text{-}35 \text{ cm}^{-1}$) 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 3250 cm^{-1} to 3500 cm^{-1} which may be assigned to $\nu_{\text{O-H}}$ of coordinated water⁹. To account for the octahedral stereochemistry of the metal complexes, the coordination of two water molecules is expected.

Table 4. Selected IR bands of Schiff base ligand L, ligand L₁ and its complexes

Ligand	Metal complexes of						Assignment
	Cr(III)	Mn(II)	Fe(II)	Co(II)	Ni(II)	Cu(II)	
Ligand L							
3345 (w,br)	-	-	-	-	-	-	$\nu_{\text{O-H}}$ (Enolic)
-	-	3431	3371	3423	3404	3358	$\nu_{\text{O-H}}$ (Coordinated water)
1626 (s,s)	1604	1613	1614	1600	1604	1591	$\nu_{\text{C=N}}$ (Azomethine)
1587 (s,s)	1582	1589	1591	1583	1590	1586	$\nu_{\text{C=N}}$ (Pyrazolin)
1516 (s,s)	1535	1520	1533	1535	1520	1520	$\nu_{\text{C=C}}$ (Phenyl ring)
1477 (s,s)	1487	1485	1492	1473	1490	1495	Thiazole ring stretching
1452 (s,s)	1442	1431	1444	1411	1454	1467	Pyrazolin ring stretching
1315 (s,s)	1383	1381	1383	1354	1346	1330	$\nu_{\text{C-O}}$ (Enol)
1265 (m,s)	-	-	-	-	-	-	$\delta_{\text{O-H}}$ (Enol)
1120 (m,br)	1120	1124	1128	1190	1120	1120	Pyrazolin ring breathing
-	-	883	819	871	801	846	$\nu_{\text{O-H}}$ (coordinated water)
767 (m,br)	758	731	756	756	729	709	C-Cl Stretch
-	657	657	653	623	682	640	$\nu_{\text{M-O}}$
-	520	582	510	518	530	590	$\nu_{\text{M-N}}$
Ligand L ₁							
3320 (w,br)	-	-	-	-	-	-	$\nu_{\text{O-H}}$ (Enolic)
-	-	3396	3346	3423	3443	3246	$\nu_{\text{O-H}}$ (Coordinated water)
1627 (s,s)	1600	1622	1609	1602	1606	1610	$\nu_{\text{C=N}}$ (Azomethine)
1589 (s,s)	1583	1582	1585	1586	1585	1588	$\nu_{\text{C=N}}$ (Pyrazolin)
1527 (s,s)	1533	1520	1532	1521	1520	1530	$\nu_{\text{C=C}}$ (Phenyl ring)
1498 (s,s)	1494	1504	1501	1496	1483	1502	Thiazole ring stretching
1479 (s,s)	1475	1477	1479	1465	1442	1425	Pyrazolin ring stretching
1310 (s,s)	1323	1357	1332	1327	1354	1355	$\nu_{\text{C-O}}$ (Enol)
1209 (m,s)	-	-	-	-	-	-	$\delta_{\text{O-H}}$ (Enol)
1178 (m,br)	1187	1141	1101	1111	1176	1141	Pyrazolin ring breathing
-	-	829	833	829	821	806	$\nu_{\text{O-H}}$ (coordinated water)
759 (m,br)	717	727	735	780	775	738	C-Cl Stretching
-	673	605	690	667	682	623	$\nu_{\text{M-O}}$
-	590	509	565	516	468	484	$\nu_{\text{M-N}}$

The bands in the range between 450 cm^{-1} to 590 cm^{-1} may be due to metal-nitrogen stretching vibration¹⁰ of Cr(III), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) complexes. The bands in the range between 600 cm^{-1} to 690 cm^{-1} may be due to metal-oxygen stretching vibration¹¹ of Cr(III), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) complexes. A less intense band between 1610 cm^{-1} - 1560 cm^{-1} in the spectrum of ligand may be assigned to $\nu_{\text{C=N}}$ (pyrazolin ring)¹². 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 ring has not participated in the chelation. However, in water containing chelates, this band is observed as a broad. This may be due to coupling of the bending mode of coordinated water molecules with $\nu_{\text{C=N}}$ ¹³.

Electronic spectra

The electronic spectra of the complexes were recorded in DMSO solution. Both the ligands show two absorption bands (Figure 7) at 37313 cm^{-1} , 26385 cm^{-1} and (Figure 8) 37453 cm^{-1} , 26246 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 $\pi \rightarrow \pi^*$ transitions.

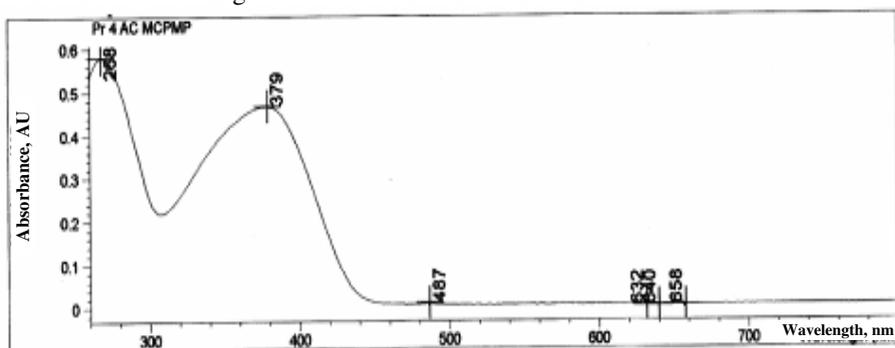


Figure 7. UV spectra of the ligand L

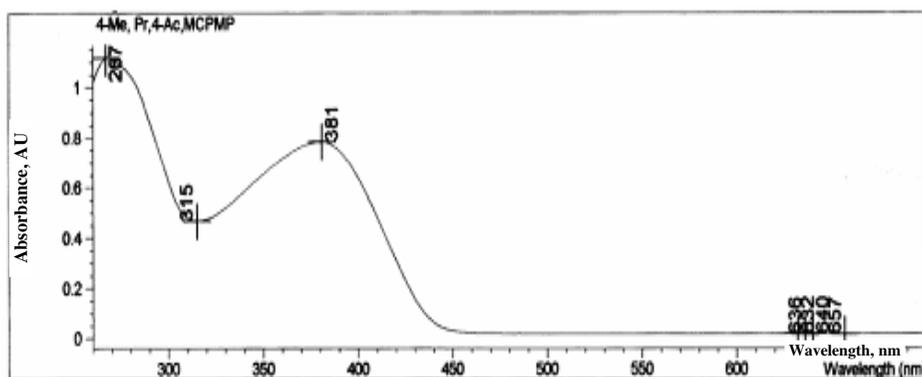


Figure 8. UV spectra of the ligand L₁

The electronic spectra of chromium(III) complexes display the d-d transition bands in the region $23,000$ - $15,900\text{ cm}^{-1}$ and $29,100$ - $24,500\text{ cm}^{-1}$. This transitions may be assigned to the ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g} (\nu_1)$ and ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g} (F) (\nu_2)$ and respectively. The transitions correspond to the typical octahedral geometry of the complexes.

The electronic spectra of Manganese (II) complexes display the d-d transition bands in the region 17,000-14,800 cm⁻¹, 19,200-17,900 cm⁻¹ and 26,300-25,300 cm⁻¹. This transitions may be assigned to the ⁶A_{1g} → ⁴T_{1g}(G), ⁶A_{1g} → ⁴T_{2g}(G) and ⁶A_{1g} → ⁴A_{1g}, ⁴E_g(G) respectively. The transitions correspond to the octahedral geometry of the complexes¹⁴.

The electronic spectra of iron(II) complexes display the d-d transition broad bands in the region 14,700-12,300 cm⁻¹ and 27,300-25,100 cm⁻¹. The latter high energy band might be charge transfer in nature and low energy band may be assigned to the spin-allow transition ⁵T_{2g} → ⁵E_g which correspond to the typical octahedral geometry of the complexes.

The electronic spectra of cobalt(II) complexes display the d-d transition bands in the region 9,350-8,400 cm⁻¹, 20,000-18,600 cm⁻¹ and 28,100-26,500 cm⁻¹. The first two bands may be correspond to ⁴T_{1g}(F) → ⁴T_{2g}(F) v₁ and ⁴T_{1g}(F) → ⁴T_{1g}(P) v₃ transitions respectively. These bands are the characteristics of high spin octahedral Co(II) complexes. However v₂ band is not observed because of its proximity to strong v₃ transitions.

The electronic spectra of nickel(II) complexes display the d-d transition bands in the region 11,900-8,500 cm⁻¹, 20,700-13,200 cm⁻¹ and 26,200-19,500 cm⁻¹. This transitions may be assigned to the ³A_{2g} → ³T_{2g}(F) v₁, ³A_{2g} → ³T_{1g}(F) v₂ and ³A_{2g} → ³T_{1g}(p) v₃ respectively. These transitions reveal that the nickel complexes possess an octahedral geometry and D_{4h} symmetry.

For the Cu(II) complexes with D_{4h} symmetry, three spin allowed transitions ²B_{1g} → ²A_{1g} (v₁), ²B_{1g} → ²B_{2g} (v₂) and ²B_{1g} → ²E_g (v₃) are possible but the electronic spectra of Cu(II) complexes display two bands at 14,367 cm⁻¹, 21,448 cm⁻¹ and 14,198 cm⁻¹, 21,290 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 rule out the possibility for tetrahedral structure of the present complexes are also suggestive for distorted octahedral geometry of the complexes.

Thermogravimetric analysis

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

The thermograms of this group of metal complexes show three stages decomposition (Table 5). All the metal complexes do not show weight loss below 120 °C, it indicates the absence of lattice water in the metal complexes.

Table 5. Thermo analytical results of metal complexes of Schiff base ligand L and ligand L₁

Compounds	Stage-I [140-210 °C]	Stage-II [210-400 °C]	Stage-III [400-900 °C]
	Mass lose Obs. (Calc.)	Mass lose Obs. (Calc.)	Mass lose Obs. (Calc.)
[Mn(L) ₂ .2H ₂ O]	3.81 (3.85)	87.67 (87.92)	8.12 (8.20)
[Fe(L) ₂ .2H ₂ O]	3.82 (3.85)	87.58 (87.83)	8.47 (8.53)
[Co(L) ₂ .2H ₂ O]	3.80 (3.84)	88.41 (88.49)	7.84 (7.99)
[Ni(L) ₂ .2H ₂ O]	3.81 (3.83)	90.19 (90.12)	6.20 (6.25)
[Cu(L) ₂ .2H ₂ O]	3.86 (3.81)	88.04 (87.96)	8.37 (8.43)
[Mn(L ₁) ₂ .2H ₂ O]	3.69 (3.74)	88.16 (88.27)	8.41 (8.54)
[Fe(L ₁) ₂ .2H ₂ O]	3.78 (3.74)	88.14 (88.19)	8.22 (8.28)
[Co(L ₁) ₂ .2H ₂ O]	3.70 (3.72)	88.64 (88.73)	7.65 (7.75)
[Ni(L ₁) ₂ .2H ₂ O]	3.64 (3.72)	90.32 (90.41)	6.12 (6.07)
[Cu(L ₁) ₂ .2H ₂ O]	3.66 (3.70)	90.79 (90.94)	8.09 (8.19)
Assignment	Loss of two coordinated water molecules	Loss of two Schiff base ligand molecules	Metal oxide

The first stage decomposition is obtained in the temperature range 140-210 °C. The % weight loss in this range is corresponds the loss of two coordinated water molecules¹⁵⁻¹⁷. The second stage decomposition is obtained in the temperature range 210-400 °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 400-900 °C. The % weight loss in this range is corresponds % weight loss of metal oxide residue.

Thermogravimetric analysis of Cr(III) complexes

The thermograms of all Cr(III) metal complexes show two stage decompositions are listed in Table 6. All the metal complexes do not show % weight loss below 205 °C suggest the absence of coordinated and/or lattice water molecule/molecules.

Table 6. Thermo analytical results of Cr(III) complexes of Schiff base ligand L and ligand L₁

Compounds	<205 °C]	Stage-I [205-400 °C]	Stage-II [400-900 °C]
	Mass Lose Obs. (Calc.)	Mass Lose Obs. (Calc.)	Mass Lose Obs. (Calc.)
[Cr(L) ₃]	Not Observed	95.36 (95.48)	5.79 (5.83)
[Cr(L ₁) ₃]	Not Observed	95.49 (95.62)	5.59 (5.65)
Assignment	Absence of coordinated water molecules	Loss of three Schiff base ligand molecules	Metal Oxide

The first and second stage decomposition in the thermogram curves shows the removal of three Schiff base ligands.

The decomposition temperatures (>250 °C) of the metal complexes indicate that they are thermally quite stable, suggesting strong metal-ligand bonding¹⁸. All the metal complexes show further weight loss beyond 250 °C, which may be due to the weight loss of organic matter (ligand), leaving metal(II) or metal(III) oxide as the final product of the thermal decomposition¹⁹.

Antibacterial activity

In recent years, nitrogen heterocyclic compounds have gained importance on account of their varied types of biological activities²⁰⁻²² pyrazole derivatives have been reported to possess antidiuretic²³, antihelminthic²⁴, hypoglycaemic, fungicidal, antituberculous²⁵, antineoplastic²⁶ and antifertility²⁷ activities.

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 against Bacterial [*Escherichia coli*, *Bacillus subtilis* and *S. aureus*] and fungal [*A.niger*] and yeast [*S. cerevisiae*] cultures with both ligands and their metal complexes using Agar cup assay method.

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 7.

Table 7. Antimicrobial activity of Schiff base ligand L, ligand L₁ and their metal complexes

Compounds	<i>E. coli</i>	<i>B. subtilis</i>	<i>S. aureus</i>	<i>S. cerevisiae</i>	<i>A. niger</i>
[L]	+	+	+	+	+
[Cr(L) ₃]	++	++	+	++	+
[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]	+	++	++	++	+
[L ₁]	+	+	+	+	+
[Cr(L ₁) ₃]	++	+	++	+	++
[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]	+	++	++	+	++

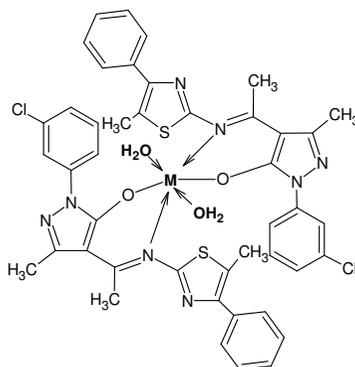
The Schiff base ligand L without metal is slightly effective against all strains of microorganisms.

- The Cr(III) metal complex is slightly effective against *S. aureus* & *A. niger* and moderately effective against *E. coli*, *B. subtilis* and *S. cerevisiae*.
 - The Mn(II) metal complexes are slightly effective against *B. subtilis* & *S. cerevisiae* and moderately effective against *E. coli*, *S. aureus* and *A. niger*.
 - The Fe(II) metal complex is slightly effective against *A. niger* and moderately effective against *E. coli*, *B. subtilis*, *S. aureus* and *S. cerevisiae*.
 - The Co(II) metal complex is slightly effective against *S. aureus* and moderately effective against *E. coli*, *B. subtilis*, *S. cerevisiae* and *A. niger*.
 - All the 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 *E. coli* & *A. niger* and moderately effective against *B. subtilis*, *S. aureus* and *S. cerevisiae*.
- The Schiff base ligand L₁ without metal is slightly effective against all strains of microorganisms.
- The Cr(III) metal complex is slightly effective against *B. subtilis* & *S. cerevisiae* and moderately effective against *E. coli*, *S. aureus* and *A. niger*.
 - The Mn(II) metal complexes are slightly effective against *S. aureus* & *S. cerevisiae* and moderately effective against *E. coli*, *B. subtilis* and *A. niger*.

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

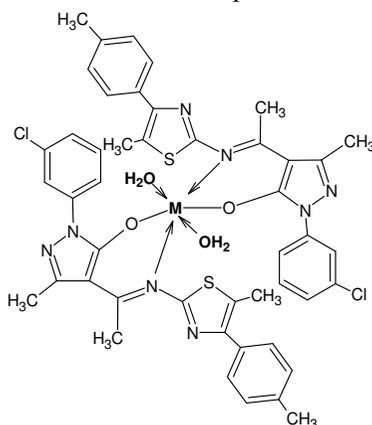
Conclusion

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



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

Figure 9. Structure of Complexes of the ligand



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

Figure 10. Structure of Complexes of the ligand L

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

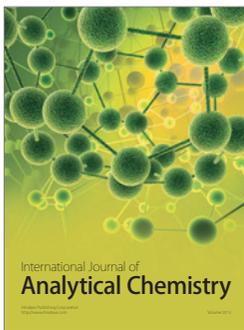
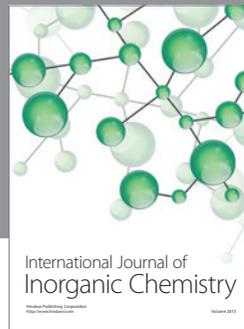
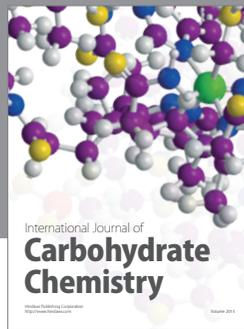
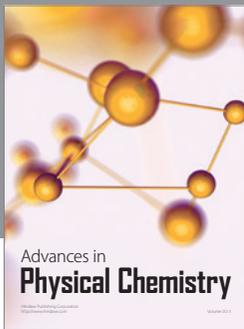
complexes became more pronounced when coordinated with metal ions. The biological activity of the complexes follow the order Co(II)=Ni(II)> Mn(II), Fe(III), Cu(II).

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