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Synthesis, Characterization and *in-vitro* Antimicrobial activity Studies of Co (II), Ni (II) and Cu (II) Complexes with ONSO Donor Coumarin Schiff Bases

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ABSTRACT

A series of Co(II), Ni(II) and Cu(II) complexes have been synthesized with Schiff bases derived from 3-substituted-4-amino-5-mercapto-1,2,4-triazole and 8-acetyl-7-hydroxy-4-methylcoumarin. The chelation of the complexes has been proposed in the light of analytical, spectral (IR, UV-Vis, ¹H NMR, ESR and FAB-mass), magnetic and thermal studies. The measured molar conductance values indicate that, the complexes are non-electrolytic in nature. The redox behavior of the complexes was investigated with electrochemical method by using cyclic voltammetry. The Schiff bases and their metal complexes have been screened for their *in vitro* antibacterial (*Escherichia coli*, *Staphylococcus aureus*, *Bacillus subtilis* and *Salmonella typhi*) and antifungal activities (*Candida albicans*, *Cladosporium* and *Aspergillus niger*) by MIC method.

Keywords: Coumarin; Antimicrobial; IR Spectra; Schiff bases; Spectroscopic studies; Transition metal complexes

INTRODUCTION

Chromenes, especially 2-oxo-2H-chromenes (coumarins), have been extensively studied due to their commercial applications in several fields. These compounds have outstanding optical properties, including an extended spectral range, high quantum yield, superior photostability and good solubility in common solvents. Typical feature of chromene derivatives is that photophysical and spectroscopic properties can be readily modified by introduction of substituents in the chromene ring, giving themselves more flexibility to fit to various applications [1-3]. Coumarins display a remarkable array of biochemical and pharmacological actions, some of which suggest that, certain members of this group of compounds may significantly affect the function of various mammalian cellular systems [4].

Schiff bases are important class of ligands in coordination chemistry and their complexing ability containing different donor atom is widely reported. The chemistry of transition metal complexes containing heterocyclic donor continues to be of interest on account of their biological importance. There is a growing interest in the studies on the metal complexes of Schiff bases derived from triazoles and its derivatives which are biologically important ligands [5]. Schiff base metal complexes have been widely studied because of their industrial and biological applications; several derivatives of these have been used as drugs. The triazole Schiff bases constitute one of the most important classes of O, N, and S donor atoms. Triazoles and their derivatives have been proved effective bacteriocides [6], pesticides [7], fungicides [8-9] and insecticides [10-11].

A survey of the literature reveals that, no work has been carried out on the synthesis of Co(II), Ni(II) and Cu(II) complexes with newly synthesized Schiff bases derived from 3-substituted-4-amino-5-mercapto-1,2,4-triazole and 8-acetyl-7-hydroxy-4-methylcoumarin. These Schiff bases have donor sites with the OONS sequence and varied coordination abilities. This nature of the Schiff bases (Figure-1) have attracted our attention and aroused our interest in elucidating the structure of metal complexes. The Schiff bases and their metal complexes were screened for their *in-vitro* antimicrobial activity.

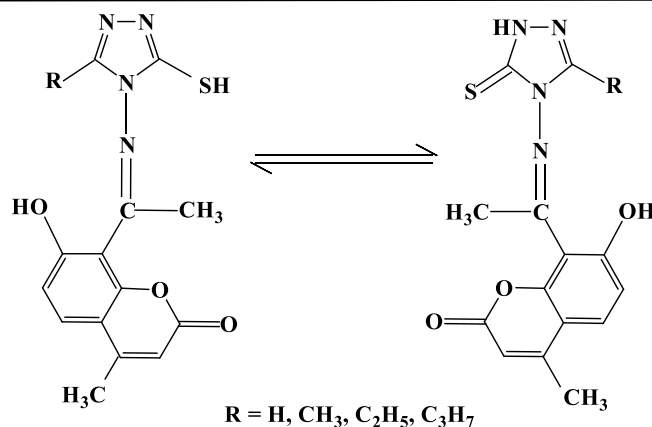


Figure 1: Structure of Schiff bases: Thiol–Thione tautomerism

EXPERIMENTAL

Analysis and Physical Measurements

Carbon, hydrogen and nitrogen were estimated by using Elemental Analyzer Truspec (Leco Corporation USA). The IR spectra of the Schiff bases and their Co(II), Ni(II) and Cu(II) complexes were recorded on a HITACHI-270 IR spectrophotometer in the 4000-250 cm^{-1} region in KBr disc. The electronic spectra of the complexes were recorded in HPLC grade DMF and DMSO solvent on a VARIAN CARY 50-BIO UV-spectrophotometer in the region of 200-1100 nm. The $^1\text{H-NMR}$ spectra of ligands were recorded in DMSO- d_6 on a BRUKER 300 MHz spectrometer at room temperature using TMS as an internal reference. The fluorescence studies of Schiff bases and their metal complexes were recorded on HITACHI F-7000 Fluorescence Spectrophotometer (Made in Japan). The solutions of 10^{-3} M concentration were prepared in HPLC grade DMF and DMSO solvents and the experiment was carried out at room temperature. The electrochemistry of the metal complexes was recorded on CHI1110A-electrochemical analyzer (Made in U.S.A) in dimethyl formamide (DMF) containing 0.05 M $n\text{-Bu}_4\text{NClO}_4$ as the supporting electrolyte. The ESR spectrum was recorded on Varian-E-4X-band EPR spectrometer and the field set is 3000 G at modulation frequency of 100 K Hz under liquid nitrogen temperature using TCNE as 'g' marker. FAB-Mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer/data system using Argon/Xenon (6KV, 10Am) as the FAB gas. The accelerating voltage was 10 KV and the spectra were recorded at room temperature and m-nitrobenzyl alcohol was used as the matrix. Thermogravimetric analyses data were measured from room temperature to 1000°C at a heating rate of 10°C/min. The data were obtained by using TA Instruments Water LLC, New castel, Delaware. USA. Model; DCS Q 20, 2009. Molar conductivity measurements were recorded on ELICO-CM-82 T Conductivity Bridge with a cell having cell constant 0.51 and magnetic moment of the complexes was carried out by using faraday balance.

Synthesis

All chemicals and solvents used were of AR grade. All metal (II) salts were used as their chlorides. 3-substituted-4-amino-5-mercapto-1,2,4-triazoles were synthesized by reported methods [12].

Synthesis of 7-Hydroxy-4-Methylcoumarin [13]

A mixture of dry resorcinol (0.2 mol) and ethylacetoacetate (0.2 mol) is cooled to 0-5°C and conc. sulphuric acid (25 mL) is added gradually with constant shaking. The reaction mixture is then kept in a refrigerator for 24 h. and poured into crushed ice with stirring. The separated solid is filtered washed with water and recrystallized from ethanol as cream colored needles. Yield: 80%; MP: 182°C.

Synthesis of 7-Acetoxy-4-Methyl Coumarin [14]

A mixture of 7-hydroxy-4-methyl coumarin (0.16 mol) and freshly distilled acetic anhydride (0.56 mol) was refluxed for 1.5 hr under anhydrous conditions. While the solution was hot, it was poured to crushed ice and the separated product was filtered and washed with water. It was crystallized from methanol as colorless needles. Purity of the compound was established by a single spot in TLC and the melting point was in agreement with the literature value (150°C); m.p 152-154°C.

Synthesis of 8-Acetyl-7-Hydroxy-4-Methyl Coumarin [14]

A mixture of 7-acetoxy-4-methyl coumarin (0.01 mol) and anhydrous AlCl_3 (0.03 mol) was heated under anhydrous conditions in an oil bath at 125°C and the temperature was raised during 2.5 hr period to 170°C. To the reaction mixture, crushed ice and dilute HCl were added with stirring and the mixture was left for 2-3 hr in order to decompose the complex. The separated product was filtered, washed with water and recrystallized from ethanol. A single spot in TLC indicated the purity of the compound. m.p. 159-160°C, yield 68%.

Synthesis of Schiff Bases [I-IV]

The Schiff bases were synthesized by the condensation of 3-substituted-4-amino-5-mercapto-1,2,4-triazole (0.01 mol) and 8-Acetyl-7-Hydroxy-4-Methylcoumarin (0.01 mol), dissolved in 30 ml alcoholic medium containing few drops of concentrated HCl. The resulting mixture was refluxed for 3-4 h. The solid product separated on evaporation of the solvent was filtered, washed with alcohol and then finely recrystallized from EtOH.

Synthesis of Co (II), Ni (II) and Cu (II) Complexes

An alcoholic solution (30ml) of Schiff bases (I-IV) 1 mmol was refluxed with 1 mmol of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ / $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ / $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in 30ml ethanol solution on steam bath for 1h. Then, to the reaction mixture 2 mmol of sodium acetate was added and refluxion was continued for 3h. The separated complex was filtered, washed thoroughly with water, Ethanol, Ether and finally dried in vacuum over fused CaCl_2 .

Pharmacology

In vitro antibacterial and antifungal assay

The biological activities of Synthesized Schiff bases and their Co (II), Ni (II) and Cu(II) complexes have been studied for their antibacterial and antifungal activities by agar and potato dextrose agar diffusion [15-16] method respectively. The antibacterial and antifungal activities were done at 25, 50 and 100 $\mu\text{g}/\text{mL}$ concentrations in DMSO solvent by using four bacteria (*Escherichia coli*, *Staphylococcus aureus*, *Bacillus subtilis* and *Salmonella typhi*) and three fungi (*Aspergillus niger*, *Candida albicans* and *cladosporium*) by the MIC method [32]. These bacterial strains were incubated for 24h at 37°C and fungal strains were incubated for 48h at 37°C. Standard antibacterial and antifungal drug (Gentamycine) and antifungal drug (Flucanazole) were used for comparison under similar conditions.

RESULT AND DISCUSSIONS

All the Co(II), Ni(II) and Cu(II) complexes were stable at room temperature, non-hygroscopic, insoluble in water and many common organic solvents but soluble in DMF and DMSO and infusible at high temperature. All the metal complexes are thought to be polymeric in nature. The elemental analysis results for the Co (II), Ni (II) and Cu (II) complexes agree with the calculated values showing that the complexes have 1:1 stoichiometry of the type $\text{ML} \cdot 2\text{H}_2\text{O}$, where 'L' stands for a deprotonated ligand. The observed molar conductances of the complexes in DMF for 10^{-3} M solutions at room temperature were consistent with the non-electrolytic nature (Table 1).

Table 1: Elemental Analyses of Co (II), Ni (II) and Cu (II) Complexes along with Molar Conductance and Magnetic Moment Data

Comp. No.	Empirical formula	M%		C%		N%		S%		Molar conductance $\text{Ohm}^{-1} \text{cm}^{-2} \text{mole}^{-1}$	Mag. Moments (μ_{eff} BM)
		Obsd	Calcd	Obsd.	Calcd	Obsd.	Calcd	Obsd.	Calcd		
1	$\text{Co}(\text{C}_{14}\text{H}_{10}\text{N}_4\text{O}_3\text{S}) \cdot 2\text{H}_2\text{O}$	14.36	14.42	41.05	41.07	13.60	13.69	7.80	7.82	19.22	4.61
2	$\text{Co}(\text{C}_{15}\text{H}_{12}\text{N}_4\text{O}_3\text{S}) \cdot 2\text{H}_2\text{O}$	13.90	13.94	42.51	42.55	13.16	13.23	7.50	7.56	22.06	4.76
3	$\text{Co}(\text{C}_{16}\text{H}_{14}\text{N}_4\text{O}_3\text{S}) \cdot 2\text{H}_2\text{O}$	13.48	13.50	43.90	43.93	12.77	12.81	7.28	7.32	24.52	4.90
4	$\text{Co}(\text{C}_{17}\text{H}_{16}\text{N}_4\text{O}_3\text{S}) \cdot 2\text{H}_2\text{O}$	13.00	13.08	45.21	45.23	12.33	12.41	7.03	7.09	17.28	4.96
5	$\text{Ni}(\text{C}_{14}\text{H}_{10}\text{N}_4\text{O}_3\text{S}) \cdot 2\text{H}_2\text{O}$	14.11	14.21	41.15	41.17	13.70	13.72	7.79	7.84	20.01	3.11
6	$\text{Ni}(\text{C}_{15}\text{H}_{12}\text{N}_4\text{O}_3\text{S}) \cdot 2\text{H}_2\text{O}$	13.71	13.74	42.62	42.65	13.22	13.27	7.52	7.58	23.07	3.20
7	$\text{Ni}(\text{C}_{16}\text{H}_{14}\text{N}_4\text{O}_3\text{S}) \cdot 2\text{H}_2\text{O}$	13.26	13.30	44.00	44.03	12.81	12.84	7.26	7.33	25.85	3.09
8	$\text{Ni}(\text{C}_{17}\text{H}_{16}\text{N}_4\text{O}_3\text{S}) \cdot 2\text{H}_2\text{O}$	12.82	12.88	45.31	45.33	12.40	12.44	7.10	7.11	18.03	3.29
9	$\text{Cu}(\text{C}_{14}\text{H}_{10}\text{N}_4\text{O}_3\text{S}) \cdot 2\text{H}_2\text{O}$	15.22	15.25	40.65	40.67	13.53	13.55	7.72	7.74	21.14	1.77
10	$\text{Cu}(\text{C}_{15}\text{H}_{12}\text{N}_4\text{O}_3\text{S}) \cdot 2\text{H}_2\text{O}$	14.70	14.45	42.13	42.15	13.10	13.11	7.45	7.49	23.43	1.76
11	$\text{Cu}(\text{C}_{16}\text{H}_{14}\text{N}_4\text{O}_3\text{S}) \cdot 2\text{H}_2\text{O}$	14.23	14.25	43.52	43.53	12.65	12.69	7.22	7.25	25.66	1.79
12	$\text{Cu}(\text{C}_{17}\text{H}_{16}\text{N}_4\text{O}_3\text{S}) \cdot 2\text{H}_2\text{O}$	13.82	13.84	44.80	44.83	12.01	12.03	7.01	7.03	18.46	1.73

IR Spectra

In order to study the binding mode of Schiff bases to metal ion in the complexes, IR spectrum of the Schiff bases were compared with the spectra of the metal complexes. The IR spectra of the Schiff bases (Table-2) display a broad band in the range $3109\text{-}3120 \text{ cm}^{-1}$, which is ascribed to the stretching vibration of -NH of the pyrrolic nitrogen atom. Although Schiff bases in solution exists in two tautomeric conformations exhibiting thiol \leftrightarrow thione isomerism involving $-\text{N}=\text{C}-\text{SH}$ and $-\text{NH}=\text{C}-\text{S}$ groups in a thiol-thione equilibrium [17-18], the IR spectrum of this ligands provides evidence of the thione form in the solid state along with little of the thiol structure, where, in addition to the weak band observed at $2440\text{-}2482 \text{ cm}^{-1}$, which is ascribed to the stretching vibration of SH [19-21]. The IR spectra of Schiff bases exhibited a broad band at $3251\text{-}3271 \text{ cm}^{-1}$, strong band at $1714\text{-}1720$, $1600\text{-}1610$ and $1271\text{-}1296 \text{ cm}^{-1}$ assigned to H-bonded -OH stretching, $\nu(\text{C}=\text{O})$ lactonic carbonyl, $\nu(\text{C}=\text{N})$ and phenolic $\nu(\text{C}-\text{O})$ vibrations respectively. A medium band around 1055 cm^{-1} is characterized for $\nu(\text{O}-\text{C}-\text{O})$.

Table 2: The Important Infrared Frequencies (in cm^{-1}) Schiff Bases (I-IV)

Schiff bases No.	Empirical Formula	H-bonded - OH Stretching	$\nu(\text{NH})$	Lactonil $\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{SH})$	$\nu(\text{C}=\text{S})$	Phenolic $\nu(\text{C}-\text{O})$
I	$\text{C}_{14}\text{H}_{12}\text{N}_4\text{O}_3\text{S}$	3251	3120	1720	1600	2458	1107	1269
II	$\text{C}_{15}\text{H}_{14}\text{N}_4\text{O}_3\text{S}$	3269	3118	1715	1608	2440	1040	1282

III	C ₁₆ H ₁₆ N ₄ O ₃ S	3271	3113	1714	1610	2480	1075	1289
IV	C ₁₇ H ₁₈ N ₄ O ₃ S	3258	3109	1719	1605	2482	1182	1296

In comparison with the spectra of the Schiff bases, all the metal complexes exhibit downward shift 8-20 cm⁻¹ of $\nu(\text{C}=\text{N})$ indicating the participation of azomethine nitrogen in the coordination to the metal ion (Table-3).

Table 3: Important Infrared Frequencies (in cm⁻¹) of Metal Complexes

Complex No.	$\nu(\text{OH})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	Phenolic $\nu(\text{C}-\text{O})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
1	3432	1705	1592	1325	468	489
2	3440	1700	1600	1333	473	467
3	3429	1704	1599	1342	463	471
4	3412	1708	1590	1346	468	484
5	3422	1706	1595	1344	474	487
6	3435	1699	1589	1358	465	481
7	3436	1695	1593	1346	463	484
8	3408	1702	1602	1348	484	456
9	3425	1706	1587	1352	470	487
10	3408	1703	1590	1345	481	459
11	3417	1700	1600	1349	446	486
12	3432	1709	1590	1358	443	467

The absorption bands associated with the $\nu(\text{OH})$ of the phenolic groups (observed at 3251-3271 cm⁻¹ in the free ligands) disappeared in the IR spectra of the metal complexes, indicating that, the loss of phenolic proton on complexation and formation of metal-oxygen bonds. The high intensity band due to phenolic $\nu(\text{C}-\text{O})$ appeared in the region at 1269-1296 cm⁻¹ in the Schiff bases appeared as a medium to high intensity band in the 1325-1358 cm⁻¹ region in the complexes and supports the suggestion that the ligands coordinate through their deprotonated form.

The most notable change in the Schiff bases spectral features when coordinated to metal ion is the lower frequencies about 10-20 cm⁻¹ in lactone $\nu(\text{C}=\text{O})$, suggesting that, the metal is coordinated to the lactone oxygen [22]. This further supported by downward shift in $\nu(\text{O}-\text{C}-\text{O})$ of the coumarin ring [23]. The presence of coordinated water was suggested by the very broad absorption band around 3408-3440 cm⁻¹ in the IR spectra of complexes. Bands at the region 760-800 and 705-720 cm⁻¹ may be attributed to rocking and wagging modes of coordinated water [24-26]. New bands at 500-400 cm⁻¹ are tentatively assigned to $\nu(\text{M}-\text{O})$, $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{S})$ (metal-ligand) stretching bands. On the basis of IR data, it is concluded that, all the metal ions are coordinated to the azomethine nitrogen, phenolic oxygen, sulphur atom and lactone oxygen.

Thus, the IR spectral data results provide strong evidences for the complexation of the tetradentate Schiff bases and also suggests that, the complexes are exist in the solid state as polymeric structure with bonding of metal likely to both the deprotonated phenolic oxygen and lactone carbonyl oxygen.

¹H NMR Spectral Studies of Schiff Bases

The spectral data of ¹H NMR of all the Schiff bases are given in Table-4. In the ¹H NMR spectra of Schiff bases **II** exhibit the singlet at 11.97 ppm (s, 1H) is ascribed to NH and a sharp signal at 10.09 ppm (s, 1H) is attributed to OH protons respectively. As multiplet, the aromatic ring protons are observed in the range 6.9-7.3 ppm (m, 4H). In addition to these signals, a sharp singlet at 3.45 ppm (s, 1H) is due to SH protons. The singlet observed at 2.48 ppm (s, 3H) and 2.85 ppm (s, 3H) are attributed to the coumarin methyl protons and the triplet observed at 2.70(t, 3H) are due to triazole methyl protons (Table-4).

Table 4: The Important ¹H NMR Data of Schiff Bases I-IV.

Schiff base	¹ H NMR (d ₆ -DMSO) (ppm)
I	12.09 (s, 1H, NH), 10.01 (s, 1H, OH), 6.7-7.2 (m, 4H, Ar-H), 3.42 (s, 1H, SH), 2.46 (s, 3H, CH ₃), 2.83 (s, 3H, CH ₃).
II	11.97 (s, 1H, NH), 10.09 (s, 1H, OH), 6.9-7.3 (m, 4H, Ar-H), 3.45 (s, 1H, SH), 2.48 (s, 3H, CH ₃), 2.85 (s, 3H, CH ₃), 2.70 (s, 3H, CH ₃ triazole).
III	12.02 (s, 1H, NH), 10.10 (s, 1H, OH), 6.5-7.1 (m, 4H, Ar-H), 3.43 (s, 1H, SH), 2.49 (s, 3H, CH ₃), 2.81 (s, 3H, CH ₃), 2.10 (q, 2H, CH ₂), 2.72 (s, 3H, CH ₃ triazole).
IV	12.96 (s, 1H, NH), 10.12 (s, 1H, OH), 6.6-7.0 (m, 4H, Ar-H), 3.41 (s, 1H, SH), 2.48 (s, 3H, CH ₃), 2.82 (s, 3H, CH ₃), 2.12 (t, 2H, CH ₂), 1.90 (m, 2H, CH ₂), 2.70 (t, 3H, CH ₃ triazole).

GC-Mass spectral studies of Schiff base

The GC-mass spectrum of the Schiff base **I** (Figure-2) shows a molecular ion (M^+) peak at m/z 316 which is equivalent to its molecular weight, which confirms the proposed formula.

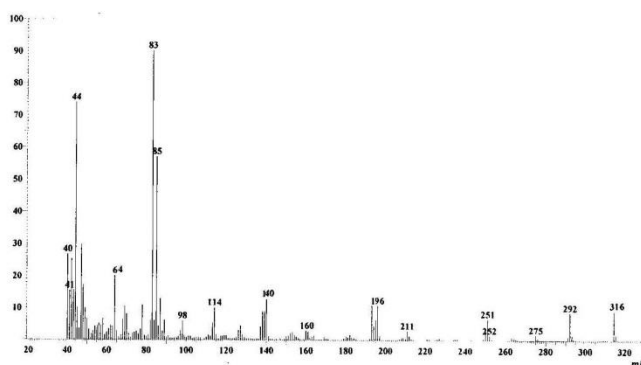


Figure 2: GC-Mass Spectrum of Schiff base-I

Electronic Absorption Spectral Studies

The electronic absorption spectra of the complexes in DMF were recorded at room. The cobalt(II) complexes exhibited two distinct absorption in the region $9880-9997\text{ cm}^{-1}$ and $17760-20660\text{ cm}^{-1}$ corresponding to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1) and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) transitions respectively which suggests an high spin octahedral geometry around the cobalt(II) ion [27]. The ν_2 band that involves a two-electron transition is not observed in spectra because of its proximity to strong ν_3 transition.

The Ni(II) complex (**6**), exhibited three bands at 10215 , 15620 and 26112 cm^{-1} attributed to the ${}^3A_{2g} \rightarrow {}^3T_{2g}$ (ν_1); ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2) and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3) transitions respectively, which indicate octahedral geometry around Ni(II) ion. The value of ν_2/ν_1 is found to be around 1.529 and the μ_{eff} value is around 3.179 which is within the range of 2.8-3.5 BM, suggesting the octahedral environment. The values of the nephelauxetic parameters, β , indicate low covalent character of the metal-ligand σ bonds [28]. Hence the ligand field parameters correlate the electronic spectral and magnetic properties. The ligand field parameters calculated for the Co (II) complexes are given in Table-5.

Table 5: Ligand Field Parameters of Ni (II) Complexes

Complex No.	Transitions (cm^{-1})			ν_2 Cald. cm^{-1}	Dq cm^{-1}	$B^1\text{ cm}^{-1}$	% Distortion	ν_1/ν_2	LSFE	μ_{eff} Cald. BM	β	$\beta^{\circ}\%$
	ν_1	ν_2	ν_3									
5	10239	15615	26108	16245.00	1023.9	775.76	3.881	1.525	35.105	3.178	0.735	26.537
6	10215	15620	26112	16225.78	1021.5	779.51	3.733	1.529	35.023	3.179	0.738	26.182
7	10231	15606	26123	16242.80	1023.1	778.18	3.921	1.525	35.078	3.179	0.737	26.308
8	10226	15631	26110	16234.79	1022.6	777.78	3.719	1.529	35.061	3.179	0.737	26.346

The electronic spectra of Cu (II) complexes showed low intensity broad band around $14380-14423\text{ cm}^{-1}$ is assignable to ${}^2T_{2g} \leftarrow {}^2E_g$ transition. Another high intensity band at $25477-25513\text{ cm}^{-1}$ is due to symmetry forbidden ligand \rightarrow metal charge transfer. On the basis of electronic spectra distorted octahedral geometry around Cu (II) ion is suggested [29]. On the basis of electronic spectra, distorted octahedral geometry around Cu(II) ion is suggested.

Magnetic Studies

The magnetic moments obtained at room temperature are listed in Table-1. The magnetic measurement for Co (II) complexes showed magnetic moment value 4.6-5.0 which is well within the range of 4.3-5.2 BM and Ni(II) complexes showed the magnetic moment value 3.0-3.3 within the range of 2.8-3.5 BM suggesting consistency with their octahedral environment [30, 31]. The Cu (II) complexes showed magnetic moment 1.74-1.79 BM, is slightly higher than the spin-only value 1.73 BM expected for one unpaired electron, which offers possibility of an octahedral geometry [32].

ESR Studies

The ESR spectral studies of Cu (II) complex provide information of the metal ion environment. The ESR spectrum of the Cu (II) complex was recorded in DMSO at room temperature (RT) and depicted in Figure-3. The Cu (II) complex (**10**) exhibits the g_{\parallel} value of 2.0513 and g_{\perp} value of 2.0248. These values $g_{\parallel} > g_{\perp}$ indicate that, the unpaired electron lies predominantly in the $d_{x^2-y^2}$ orbital [33]. The trend $g_{\parallel} > g_{\perp} > 2.0023$ observed for the complexes indicate that, the unpaired electron is localized in the $d_{x^2-y^2}$ orbital of the Cu(II) ion and are characteristic of the axial symmetry. Thus, the results suggested that, the Cu (II) complex (**10**) possess distorted octahedral geometry.

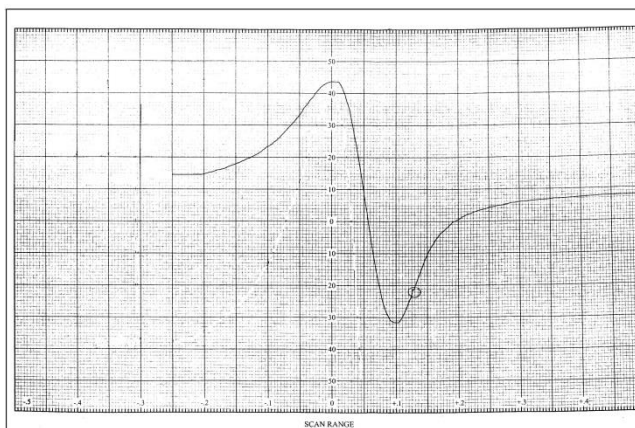


Figure 3: ESR Spectrum of Cu (II) Complex (10)

Thermal Studies

The thermal behavior of Co (II), Ni(II) and Cu(II) complexes has been studied as a function of temperature. The thermal behavior of all the complexes is almost same. Hence, only the representative TG/DTG of Co (II) (2), Ni (II) (6) and Cu (II) (10) complexes have been discussed here. Their stepwise thermal degradation data are given in Table-6.

Table 6: Thermogravimetric data of Co (II), Ni (II) and Cu (II) complexes

Empirical Formula	Decomposition temperature	%Weight loss		Metal Oxide %		Inference
	$^{\circ}\text{C}$	Obsd.	Calcd.	Obsd.	Calcd.	
$\text{Co}(\text{C}_{14}\text{H}_{10}\text{N}_4\text{O}_3\text{S})\cdot 2\text{H}_2\text{O}$	190-230	8.51	8.60	17.73	17.80	Loss of coordinated water molecules Loss of 1,2,4-triazole moieties Loss of acetyl coumarin moieties
	305-330	30.26	30.36			
	350-410	45.75	45.79			
$\text{Ni}(\text{C}_{14}\text{H}_{10}\text{N}_4\text{O}_3\text{S})\cdot 2\text{H}_2\text{O}$	195-236	8.53	8.72	17.53	17.59	Loss of coordinated water molecules Loss of 1,2,4-triazole moieties Loss of acetyl coumarin moieties
	325-335	30.08	30.19			
	400-430	47.86	47.95			
$\text{Cu}(\text{C}_{14}\text{H}_{10}\text{N}_4\text{O}_3\text{S})\cdot 2\text{H}_2\text{O}$	200-235	8.43	8.46	17.79	17.80	Loss of coordinated water molecules Loss of 1,2,4-triazole moieties Loss of acetyl coumarin moieties
	290-330	29.74	29.71			
	410-450	47.30	47.35			

The TG and DTG curves of Ni ($\text{C}_{14}\text{H}_{10}\text{N}_4\text{O}_3\text{S}$). $2\text{H}_2\text{O}$ are shown in Figure-4. The DTG curve of this complex shows three stages of decomposition within the temperature range (180-650 $^{\circ}\text{C}$). The first step of decomposition within the temperature range (180-250 $^{\circ}\text{C}$) corresponds to the loss of coordinated water molecule with mass loss of 8.53% (calcd. 8.72%). The second step (250-350 $^{\circ}\text{C}$) corresponds to the loss of 1,2,4-triazole moieties with mass loss of 30.08% (calcd. 30.19%). The third step (400-560 $^{\circ}\text{C}$) corresponds to the loss of acetylcoumarin (mass loss 47.86%; calcd. 47.95%). Finally the metal complexes decompose gradually with the formation of metal oxide above 560 $^{\circ}\text{C}$ (mass loss 17.53%).

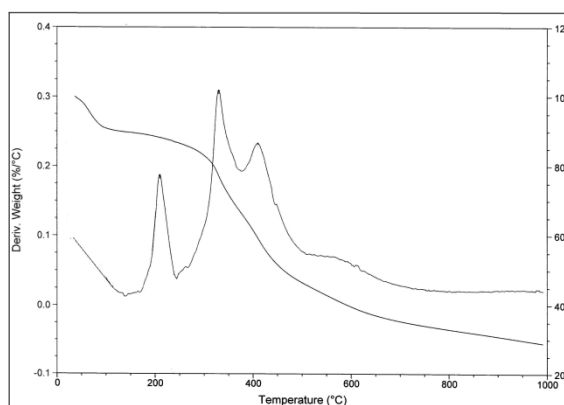


Figure 4: Thermogravimetric (TG/DTG) curves of $\text{Ni}(\text{C}_{14}\text{H}_{10}\text{N}_4\text{O}_3\text{S})\cdot 2\text{H}_2\text{O}$ complex

Thus, the TG and DTG provide the useful information about the coordination of water molecules to the metal ion and the stability of the complexes.

Electrochemistry

Electrochemical properties of the complexes were studied on a CHI1110A-Electrochemical analyzer in *N,N*-dimethyl formamide (DMF) containing 0.05 M $n\text{-Bu}_4\text{NClO}_4$ as the supporting electrolyte. A cyclic voltammogram of $\text{Cu}(\text{C}_{14}\text{H}_{10}\text{N}_4\text{O}_3\text{S})\cdot 2\text{H}_2\text{O}$ radical displays a reduction peak at $E_{pc} = 0.447\text{V}$ with a corresponding oxidation peak (Cu (I) radical) at $E_{pa} = 0.1$. The peak separation of this couple (ΔE_p) is 0.347V at 0.05V and increases with scan rate. The most significant feature of the Cu (II) complex is the Cu(II)/Cu(I) couple. The difference between forward and backward peak potentials can provide a rough evaluation of the degree of the reversibility of one electron transfer reaction. The analyses of cyclic voltametric responses with the scan rate varying 50 to 250 mV/s gives the evidence for quasi-reversible one electron oxidation state. The ratio of cathodic to anodic peak height was less than one. However, the peak current increases with the increase of the square root of the scan rates. This establishes the electrode process as diffusion controlled [33,34] (Figure 5,6).

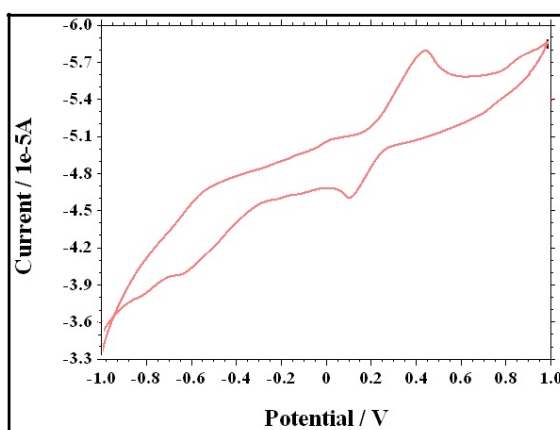


Figure 5: Cyclic voltammogram of $\text{Cu}(\text{C}_{14}\text{H}_{10}\text{N}_4\text{O}_3\text{S})\cdot 2\text{H}_2\text{O}$

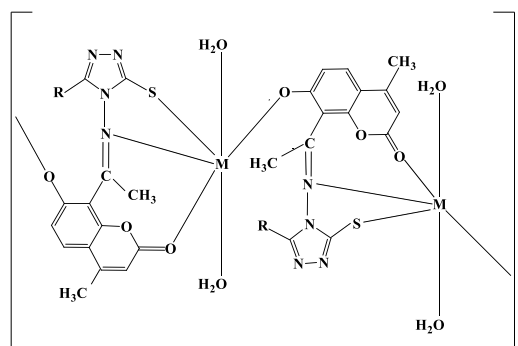


Figure 6: Structure of Metal complexes

Pharmacology Results

The Schiff bases and their metal complexes were evaluated for antimicrobial activity. The obtained results are systematized in Table 7 & 8. The antibacterial studies inferred that, Both the Schiff bases and their Co(II), Ni(II) and Cu(II) complexes showed high antibacterial and antifungal activity against all the bacterial strains. All the metal complexes possess higher antifungal activity than the Schiff bases. This higher activity of the metal complexes compared to Schiff bases is may be due to the change in structure due to coordination, which make the metal complexes act as

more powerful and potent bacteriostatic agents, thus inhibiting the growth of the microorganisms.

Table 7: Anti-bacterial and Anti-fungal results of Schiff bases

Compd.	Conc. ($\mu\text{g ml}^{-1}$)	Antibacterial activity (Zone of inhibition in %)				Antifungal activity (Zone of inhibition in %)		
		<i>E. coli</i>	<i>S. aureus</i>	<i>B. subtilis</i>	<i>S. typhi</i>	<i>C. albicans</i>	<i>Cladosporium</i>	<i>A Niger</i>
I	25	37	-	39	29	52	-	52
	50	47	20	41	49	58	33	67
	100	55	31	53	58	67	44	69
II	25	38	-	37	31	53	-	57
	50	52	24	47	47	58	31	62
	100	59	30	55	52	66	42	69
III	25	33	-	34	33	55	-	55
	50	58	23	57	46	65	39	66
	100	60	33	59	59	68	41	68
IV	25	37	-	33	31	53	-	66
	50	44	22	46	43	61	37	67
	100	58	31	57	58	63	47	67
Gentamycin e	25	81	62	77	73	-	-	-
	50	85	73	79	78	-	-	-
	100	86	75	81	80	-	-	-
Flucanazole	25	-	-	-	-	85	78	88
	50	-	-	-	-	93	83	89
	100	-	-	-	-	95	88	89

Table 8: Anti-bacterial results of Co(II) , Ni(II) and Cu(II) complexes (1-12)

Compd	Conc. ($\mu\text{g ml}^{-1}$)	Antibacterial activity (Zone of inhibition in %)				Antifungal activity (Zone of inhibition in %)		
		<i>E. coli</i>	<i>S. aureus</i>	<i>B. subtilis</i>	<i>S. typhi</i>	<i>C. albicans</i>	<i>Cladosporium</i>	<i>A Niger</i>
1	25	58	44	47	58	57	66	62
	50	67	63	50	66	61	66	64
	100	77	65	61	72	69	69	74
2	25	62	41	52	63	53	50	69
	50	69	62	57	67	66	52	71
	100	80	67	60	74	70	57	71
3	25	72	43	63	62	71	77	65
	50	77	66	69	68	78	78	67
	100	81	69	72	70	82	80	71
4	25	68	40	64	69	47	67	67
	50	78	62	67	72	62	71	69
	100	82	65	74	78	68	78	71
5	25	64	44	35	45	34	-	57
	50	71	64	46	56	45	35	69
	100	89	68	51	59	67	51	75
6	25	67	46	66	66	66	58	60
	50	71	61	68	69	71	60	73
	100	80	68	71	71	78	65	79
7	25	71	39	64	46	63	66	55
	50	80	68	71	52	71	71	69
	100	82	65	75	53	76	78	71
8	25	74	45	35	44	59	66	57
	50	70	62	44	52	66	62	68
	100	79	69	59	59	69	67	74
9	25	68	41	39	-	55	45	69
	50	77	63	48	36	67	55	73
	100	79	69	57	52	78	58	78
10	25	64	47	65	66	71	47	60
	50	66	60	69	71	77	59	69
	100	73	65	71	77	79	61	71
11	25	72	47	61	62	68	48	56
	50	77	63	65	66	69	58	69
	100	81	71	69	68	73	51	71
12	25	67	49	65	47	45	35	65
	50	71	65	68	52	56	41	76
	100	75	70	73	55	68	57	79

Gentamycine	25	81	62	77	73	-	-	-
	50	85	73	79	78	-	-	-
	100	86	75	81	80	-	-	-
Flucanazole	25	-	-	-	-	85	78	88
	50	-	-	-	-	93	83	89
	100	-	-	-	-	95	88	89

The minimum inhibitory concentration (MIC) of some selected compounds, which showed significant activity against selected bacterial and fungi strains were studied. The results indicated that these compounds were most active in inhibiting the growth of the tested organisms at 10 mgmL⁻¹ (Table 9).

Table 9: Results of Minimum inhibitory concentration (µg/ml)

Compound	<i>E. coli</i>	<i>S. aureus</i>	<i>B. subtilis</i>	<i>S. typhi</i>	<i>C. albicans</i>	<i>Cladosporiu m</i>	<i>A Niger</i>
I	15	-	10	25	10	10	-
II	25	10	10	-	-	25	25
III	10	-	10	-	25	-	-
IV	10	10	25	25	25	15	25
1	25	10	10	25	-	25	-
2	25	10	-	10	15	25	-
3	10	-	25	10	10	-	25
4	10	10	10	25	10	10	10
5	10	15	10	25	-	25	25
6	-	25	25	25	-	-	15
7	25	-	-	10	25	-	-
8	-	-	-	15	25	25	25
9	10	15	10	25	-	25	25
10	15	10	10	25	-	-	-
11	10	10	10	25	-	10	25
12	25	10	25	10	25	10	25

CONCLUSIONS

The Co(II), Ni(II) and Cu(II) complexes of Schiff bases with 3-substituted-4-amino-5-mercapto-1,2,4-triazole and 8-acetyl-7-hydroxy-4-methylcoumarin were prepared and characterized using different analytical techniques. The synthesized Schiff bases act as tetradentate Schiff bases. The metals are coordinated to azomethine nitrogen, lactonyl oxygen, Phenolic oxygen and sulphur atom. Suggest that, the complexes were polymeric in nature. The electronic spectral data and magnetic measurements suggest that Co (II) and Ni(II) complexes are Octahedral, while Cu(II) complex has distorted octahedral geometry. ESR spectrum of Cu (II) complex also reveals that it is distorted. TG/DTG analysis indicates the presence of coordinated water molecule in the complexes. The antimicrobial studies reveal that the complexes show higher activity than the Schiff bases.

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