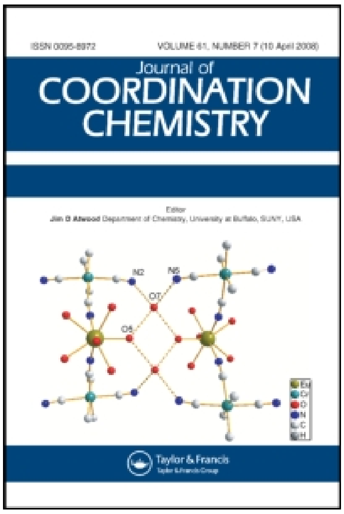

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Synthesis, characterization, electrochemical and *in-vitro* antimicrobial studies of Co(II), Ni(II), and Cu(II) complexes with Schiff bases of formyl coumarin derivatives

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Synthesis, characterization, electrochemical and *in-vitro* antimicrobial studies of Co(II), Ni(II), and Cu(II) complexes with Schiff bases of formyl coumarin derivatives

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A series of Co(II), Ni(II), and Cu(II) complexes have been synthesized with Schiff bases (H_2L^I and H_2L^{II}) derived from 8-formyl-7-hydroxy-4-methylcoumarin or 5-formyl-6-hydroxycoumarin and *o*-aminophenol. Structures have been proposed from elemental analyses, spectral (IR, UV-Vis, FAB-mass, and Fluorescence), magnetic, and thermal studies. The measured low molar conductance values in DMF indicate that the complexes are non-electrolytes. Elemental analyses indicate $ML \cdot 3H_2O$ [M = Co(II), Ni(II), and Cu(II)] stoichiometry. Spectroscopic studies suggest coordination through azomethine nitrogen, phenolic oxygen of *o*-aminophenol, and the coumarin *via* deprotonation. The Schiff bases and their complexes have been screened for antibacterial (*Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, and *Salmonella typhi*) and antifungal (*Aspergillus niger*, *Aspergillus flavus*, and *Cladosporium*) activities by minimum inhibitory concentration (MIC) method. The redox behavior of the complexes was investigated using cyclic voltammetry (CV).

Keywords: Antibacterial; Antifungal; Coumarin; Electrochemical; Spectral

1. Introduction

Coumarins are members of the benzopyrone class, which display significant biological [1–5] and pharmacological [6, 7] properties. Many of these compounds possess antibacterial [6], antifungal [7] and antiallergic [4] activities. The addition of 4- and 7-hydroxy substituents in the coumarin ring improved potency of the compounds. The antitumor effects of coumarin and its major metabolite, 7-hydroxycoumarin, were tested in several human tumor cell lines by Weber *et al.* [8]. Coumarin and derivatives have been studied extensively for complexation with metal ions [9]. Recently, it has been reported that 4-methyl-7-hydroxycoumarin complexes with several metals might be applicable as anticoagulants and spasmolytic agents [10]. We have reported

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a number of metal complexes with various Schiff bases and studied their biological applications [11–15].

In this study we have synthesized Co(II), Ni(II), and Cu(II) complexes with ONO donor Schiff bases derived from 8-formyl-7-hydroxy-4-methylcoumarin or 5-formyl-6-hydroxycoumarin and *o*-aminophenol and characterized them by spectral (IR, UV-Vis, FAB-mass, ESR, and Fluorescence), thermal, magnetic, and molar conductivities. The Schiff bases and their metal complexes have been studied for biological activity against various pathogenic bacterial strains using minimum inhibitory concentration (MIC); their redox behavior is established electrochemically.

2. Experimental

2.1. *Analysis and physical measurements*

Carbon, hydrogen, and nitrogen were estimated by an Elemental Analyzer Carlo Erba EA1108. The IR spectra of the Schiff bases and their complexes were recorded on a HITACHI-270 IR spectrophotometer in the region of 4000–250 cm^{-1} in KBr disc. Electronic spectra of the complexes were recorded in HPLC grade DMF and DMSO on a VARIAN CARY 50-BIO UV-spectrophotometer in the region 200–1100 nm. The ^{1}H-NMR spectra of ligands were recorded in D_6-DMSO on a BRUKER 300 MHz spectrometer at room temperature using TMS as an internal reference. Fluorescence studies were recorded on a HITACHI F-7000 Fluorescence Spectrophotometer (made in Japan) with 10^{-3} M solutions in HPLC grade DMF and DMSO at room temperature. FAB-mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer/data system using Argon/Xenon (6 kV, 10 A) as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded at room temperature with *m*-nitrobenzyl alcohol as the matrix. The mass spectrometer was operated in the positive ion mode. Electrochemistry of all the complexes was recorded on a CHI1110A-electrochemical analyzer (made in USA) in DMF containing 0.05 M n-Bu_4NClO_4 as the supporting electrolyte. ESR spectra were recorded on a Varian-E-4X-band EPR spectrometer at 3000 G with modulation frequency of 100 kHz at liquid nitrogen temperature using TCNE as *g*-marker. Thermogravimetric analyses were measured from room temperature to 1000°C at a heating rate of 10°C min^{-1} on a Perkin-Elmer Diamond TG/DTA instrument. Molar conductivity measurements were recorded on an ELICO-CM-82 T Conductivity Bridge with a cell having a cell constant of 0.51 using a Faraday balance.

2.2. *Synthesis*

All chemicals used were of reagent grade. 7-Hydroxy-4-methylcoumarin and 6-hydroxy coumarin were synthesized according to the procedure given in [16].

2.2.1. Synthesis of 8-formyl-7-hydroxy-4-methylcoumarin. 8-Formyl-7-hydroxy-4-methylcoumarin is prepared as described in [17]. 7-Hydroxy-4-methylcoumarin (5.28 g, 0.03 mol) and hexamine (9.8 g, 0.07 mol) in glacial acetic acid (50 mL) was heated for 4–5 h. Then, 20% HCl (75 mL) was added and further heated for 20 min, cooled and extracted with ether. Pale yellow 8-formyl-7-hydroxy-4-methylcoumarin, obtained after extraction, was recrystallized from ethanol, m.p. 176–177°C, yield 2.5 g; 16.36%.

2.2.2. Synthesis of 5-formyl-6-hydroxycoumarin. 5-Formyl-6-hydroxycoumarin is prepared as described in [18]. 6-Hydroxycoumarin (4.86 g, 0.03 mol), hexamine (9.8 g, 0.07 mol), and glacial acetic acid (100 mL) were heated on a steam bath for 8 h. A hot mixture of 75 cc each of concentrated hydrochloric acid and hot water were added and further heated for 2 h, cooled and extracted with ether. A deep yellow product, obtained after extraction, was crystallized from alcohol in clusters of yellow needles, m.p. 189°C, yield 2.2 g; 14.80%.

2.2.3. Synthesis of H_2L^I. H_2L^I is synthesized by refluxing the reaction mixture of hot ethanol solution (30 mL) of *o*-aminophenol (1.09 g, 0.01 mol) and hot ethanol solution (30 mL) of 8-formyl-7-hydroxy-4-methylcoumarin (2.04 g, 0.01 mol) for 4–5 h with the addition of 2–3 drops of hydrochloric acid. The precipitate formed during reflux was filtered, washed with cold EtOH, and recrystallized from hot EtOH, m.p. 272°C, yield 2.63 g; 84%.

2.2.4. Synthesis of H_2L^{II}. H_2L^{II} is synthesized by refluxing hot ethanol solution (30 mL) of *o*-aminophenol (1.09 g, 0.01 mol) and hot ethanol solution (30 mL) of 5-formyl-6-hydroxycoumarin (1.90 g, 0.01 mol) for 4–5 h with addition of 2–3 drops of hydrochloric acid. The precipitate formed during reflux was filtered, washed with cold EtOH, and recrystallized from hot EtOH, m.p. 253°C, yield 2.45 g; 82%.

2.2.5. Synthesis of Co(II), Ni(II), and Cu(II) complexes [1–6]. Alcoholic solutions of Schiff bases (H_2L^I 2.95 g; H_2L^{II} 2.81 g; 0.01 mol) (30 mL) were refluxed with $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, or $CuCl_2 \cdot 2H_2O$ (2.37g/2.36g/1.70g) in ethanol (30 mL) on a water bath for 1 h. Then, 1 mmol of sodium acetate was added and reflux was continued for 3 h. The separated complex was filtered, washed thoroughly with water, ethanol, ether and finally dried in vacuum over fused $CaCl_2$.

2.3. In-vitro *antibacterial and antifungal assay*

The biological activities of metal salts, 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 method, respectively. The antibacterial and antifungal activities were done at 25, 50 and 100 $\mu g\,mL^{-1}$ concentrations in DMF by using four bacteria (*Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, and *Salmonella typhi*) and three fungi (*Aspergillus niger*, *Aspergillus flavus*, and *Cladosporium*) by the MIC method [19]. These bacterial strains were incubated for 24 h at 37°C and fungal strains for 48 h at 37°C. Standard antibacterial (Gentamycine) and antifungal (Flucanazole) drugs were used for comparison under similar conditions.

3. Results and discussion

The Co(II), Ni(II), and Cu(II) complexes are colored (table 1), stable non-hygroscopic and soluble in DMF and DMSO. Elemental analyses show that the Co(II), Ni(II), and Cu(II) complexes have 1 : 1 stoichiometry, $ML \cdot 3H_2O$, where L is a doubly-deprotonated ligand (figure 1). The molar conductance values in DMF indicate non-electrolytes (table 1). Several attempts to develop single crystals failed due to poor solubility of the complexes in common organic solvents.

In order to establish whether the water molecules present in the complexes are coordinated, the weighed complex was heated for 2 h at 105°C, cooled in a desiccator and weighed again; no loss in weight of the complex was observed [15]. These observations suggest that water present in the complexes is coordinated to the metal ion.

3.1. *Infrared spectral studies*

The IR spectra (table 2) of the Schiff bases show a characteristic high intensity band at 1633–1630 cm^{-1}, attributed to ν(C=N) [20]. The broad band at 3051–3055 cm^{-1}, strong bands at 1720–1722 and 1282–1280 cm^{-1}, in the IR spectra of the Schiff bases are assigned to H-bonded –OH stretching, ν(C=O) lactonyl carbon [7] and phenolic ν(C–O), respectively.

In comparison with the spectra of the Schiff bases, the complexes exhibited a downward shift of ν(C=N) to 1576 cm^{-1}, indicating that the azomethine nitrogen coordinates to the metal [21]. The band due to H-bonded –OH stretching in the Schiff bases disappeared in the spectra of complexes. The high intensity band due to phenolic ν(C–O) at 1282 cm^{-1} in the Schiff bases is a medium to high intensity band in the region 1305–1328 cm^{-1} in the complexes. This shift of ν(C–O) in the metal complexes is due to the expected high mesomeric interaction in the complex activated by the presence of the metal [22]. Rupini *et al.* [21] and El-Sharief *et al.* [22] reported similar features of ν(C=N) and phenolic OH of Schiff bases of formyl coumarin derivatives. The presence of coordinated water in the complexes is confirmed by a broad band around 3445–3425 cm^{-1} and two weak bands in the region 750–800 and 700–720 cm^{-1} due to ν(–OH) rocking and wagging vibrations, respectively [21, 23]. New bands in the region 381–372 and 469–445 cm^{-1} in the complexes are assigned to stretching frequencies of (M–O) and (M–N) bonds, respectively [24, 25]. The unaltered position of bands assigned to ν(C=O) (lactonyl carbon) confirms its non-involvement in coordination.

Thus, the IR spectral results provide strong evidence for the complexation of the potentially tridentate Schiff bases.

3.2. *^{1}H-NMR spectral study of H_2L^I and H_2L^{II}*

In the ^{1}H-NMR spectrum of H_2L^I, the phenolic –OH is at 10.42 ppm (s, 2H) [26] and a characteristic proton signal at 9.31 ppm (s, 1H) is assigned to –CH=N. In addition, signals in the region 6.3–7.6 ppm (m, 7H) and a sharp signal at 2.4 ppm (s, 3H) are due to aromatic and methyl protons. For H_2L^{II}, the signal at 10.21 ppm (s, 2H) is attributed to the phenolic –OH, a signal at 9.21 ppm (s, 1H) is ascribed to –CH=N and signals in the region 6.1–7.7 ppm (m, 8H) are due to aromatic protons.

Table 1. Elemental analyses of Schiff bases and their Co(II), Ni(II), and Cu(II) complexes along with molar conductance and magnetic moment data.

Empirical formula	Color/Yield %	M%		C%		H%		N%		Molar conductance (Ohm^{-1} cm^{-2} mol^{-1})	μ_{eff} (BM)
		Obs.	Calcd	Obs.	Calcd	Obs.	Calcd	Obs.	Calcd		
H_2L^I, $C_{17}H_{13}NO_4$	84%	–	–	69.13	69.15	4.39	4.41	4.73	4.75	–	–
H_2L^{II}, $C_{16}H_{11}NO_4$	82%	–	–	68.35	68.33	3.93	3.91	4.98	4.98	–	–
$Co(C_{17}H_{11}NO_4) \cdot 3H_2O$	Brown/68%	14.536	14.532	50.25	50.25	4.18	4.19	3.44	3.45	29.8	4.6
$Co(C_{16}H_9NO_4) \cdot 3H_2O$	Brown/67%	15.049	15.051	48.96	48.98	3.83	3.83	3.59	3.57	30.22	4.8
$Ni(C_{17}H_{11}NO_4) \cdot 3H_2O$	Yellowish green/71%	14.322	14.320	50.36	50.37	4.17	4.19	3.45	3.46	22.25	3.1
$Ni(C_{16}H_9NO_4) \cdot 3H_2O$	Yellowish green/73%	14.836	14.833	49.11	49.10	3.85	3.84	3.56	3.58	23.67	2.9
$Cu(C_{17}H_{11}NO_4) \cdot 3H_2O$	Dark green/69%	15.366	15.365	49.75	49.76	2.66	2.68	3.41	3.42	32.4	1.76
$Cu(C_{16}H_9NO_4) \cdot 3H_2O$	Dark green/68%	15.907	15.909	48.46	48.48	3.78	3.79	3.53	3.54	31.3	1.77

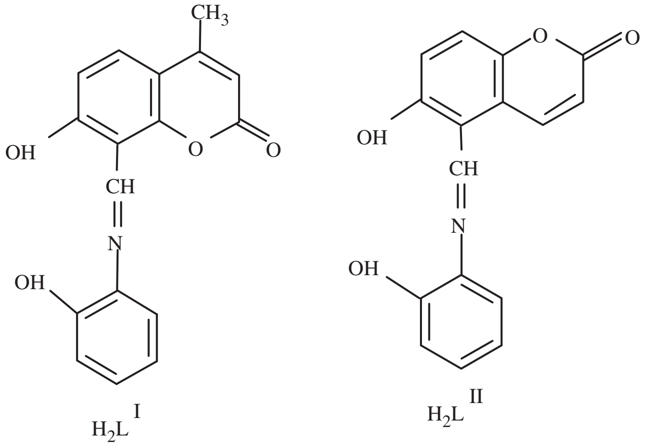


Figure 1. Structure of Schiff base.

Table 2. Important infrared frequencies (in cm^{-1}) of Schiff bases derived from 8-formyl-7-hydroxy-4-methylcoumarin or 5-formyl-6-hydroxycoumarin and *o*-aminophenol and their metal complexes.

Compound	Coordinated water ν(OH)	Lactonyl ν(C=O)	ν(C=N)	H-bonded –OH stretching	Phenolic ν(C–O)	ν(M–N)	ν(M–O)
$C_{17}H_{13}NO_4$	–	1720	1633	3051	1282	–	–
$C_{16}H_{11}NO_4$	–	1722	1630	3055	1280	–	–
$Co(C_{17}H_{11}NO_4) \cdot 3H_2O$	3431	1721	1576	–	1307	445	376
$Co(C_{16}H_9NO_4) \cdot 3H_2O$	3425	1722	1582	–	1305	447	372
$Ni(C_{17}H_{11}NO_4) \cdot 3H_2O$	3435	1721	1579	–	1310	458	378
$Ni(C_{16}H_9NO_4) \cdot 3H_2O$	3430	1720	1580	–	1312	454	380
$Cu(C_{17}H_{11}NO_4) \cdot 3H_2O$	3445	1720	1582	–	1328	467	380
$Cu(C_{16}H_9NO_4) \cdot 3H_2O$	3430	1721	1578	–	1322	469	381

3.3. *Electronic spectral studies*

Electronic spectra of Co(II) complexes exhibit absorption bands in the region 8000–10,000 and 18,000–20,000 cm^{-1} corresponding to ν_1 and ν_3 transitions, respectively, attributed to $^4T_{1g}$ (F) → $^4T_{2g}$ (F) (ν_1) and $^4T_{1g}$ (F) → $^4T_{1g}$ (P) (ν_3) for octahedral complexes. The brown Co(II) complexes in our experiment show absorptions at 9784–9754 and 19,920–19,944 cm^{-1}, characteristic of high spin octahedral Co(II) [23, 27]. The ν_2 band is not observed because of its proximity to the strong ν_3 transition. The ligand field parameters are given in table 3. The β-values (0.779 and 0.783) indicate considerable covalence in metal ligand bonding [28].

The yellowish-green $Ni(C_{17}H_{11}NO_4) \cdot 3H_2O$ (table 3) exhibits three bands at 10,582, 16,393, and 26,178 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, for octahedral Ni(II). The value of ν_2/ν_1 is 1.549 and the μ_{eff} value is around 3.167, also consistent with octahedral environment. Values of the nephelauxetic parameters, β, indicate little covalent character of the metal–ligand bonds [29].

Table 3. Ligand field parameters of Co(II) and Ni(II) complexes.

Complex	Transitions (cm^{-1})			ν_2 Calcd (cm^{-1})	D_q (cm^{-1})	B^1 (cm^{-1})	ν_2/ν_1	LSFE	μ_{eff} Calcd (BM)	β	β (%)
	ν_1	ν_2	ν_3								
$Co(C_{17}H_{11}NO_4) \cdot 3H_2O$	9784	–	19,920	20,743	1095	754	2.1	25	–	0.779	22
$Co(C_{16}H_9NO_4) \cdot 3H_2O$	9754	–	19,944	20,684	1093	757	2.1	24	–	0.783	21
$Ni(C_{17}H_{11}NO_4) \cdot 3H_2O$	10,582	16,393	26,178	16,534	1058	731	1.5	36	3.167	0.692	30
$Ni(C_{16}H_9NO_4) \cdot 3H_2O$	10,446	16,386	26,848	16,632	1044	809	1.5	35	3.17	0.767	23

Electronic spectra of Cu(II) complexes display a low intensity broad band at 14,492 cm^{-1} assignable to $^2T_{2g} \leftarrow {}^2E_g$ transition and a high intensity band at 25,523 cm^{-1} due to symmetry forbidden ligand → metal charge transfer. Electronic spectra indicate distorted octahedral geometry around Cu(II) [30].

3.4. *Magnetic studies*

The magnetic moments obtained at room temperature (table 1) are consistent with octahedral Co(II), Ni(II), and Cu(II) complexes [28, 31, 32].

3.5. *ESR spectra of Cu($C_{17}H_{11}NO_4$)$\cdot$3H_2O complex*

The ESR spectrum of Cu(II) complex at liquid nitrogen temperature using TCNE as *g*-marker (2.00277) showed $g_\parallel$ and $g_\perp$ values to be 2.034 and 2.1522, respectively. The g_{av} was calculated to be 2.1128. The $g_\perp > g_\parallel$ suggests Cu(II) complex would have an essentially d_z^2 ground state in either a compressed tetragonal, *cis*-octahedral, or a distorted octahedral structure [33, 34]. Thus, the ESR spectral results provide further evidence to the magnetic and electronic spectral results.

3.6. *FAB-mass spectral studies of Schiff bases and their complexes*

The FAB-mass spectrum of H_2L^I showed a molecular ion peak at *m/z* 295 equivalent to its molecular weight. In addition to this, the fragment peaks observed at *m/z* 278, 188, 175, 158, and 143 are due to the cleavage of –OH, C_6H_4N, CH, OH, and CH_3, respectively. For H_2L^{II} the molecular ion peak at *m/z* 281 is ascribed to $C_{16}H_{11}NO_4$.

The FAB-mass spectra of $Co(C_{17}H_{11}NO_4) \cdot 3H_2O$, $Ni(C_{17}H_{11}NO_4) \cdot 3H_2O$, and $Cu(C_{17}H_{11}NO_4) \cdot 3H_2O$ complexes of Schiff base H_2L^I showed molecular ion peaks M^+ at *m/z* 406, 405, and 410, which is equivalent of their molecular weight. All $[MH_2L^I \cdot 3H_2O]^+$ undergoes demetallation to form $[L+2H]^+$ at *m/z* 295. For $Co(C_{16}H_9NO_4) \cdot 3H_2O$, $Ni(C_{16}H_9NO_4) \cdot 3H_2O$, and $Cu(C_{16}H_9NO_4) \cdot 3H_2O$, the FAB-mass spectra showed molecular ion peaks at *m/z* 392, 391 and 396 equivalent to their molecular weights and also undergo demetallation to form $[L+2H]^+$ at *m/z* 281.

3.7. *Thermal studies*

The thermal behavior of Co(II), Ni(II), and Cu(II) complexes are all the same. The TG/DTG analysis of $Co(C_{17}H_{11}NO_4) \cdot 3H_2O$ (Supplementary material) is used as a representative example. The thermal decomposition takes place in three steps as indicated by DTG peaks around 205–255°C, 325–370°C, and 505–545°C, corresponding to the mass loss of coordinated water molecules, aminophenol, and formyl coumarin moieties, respectively. The TGA studies confirm coordination of water with weight loss up to 255°C of 13.33–13.18% (Calcd 13.30–13.17%) for three coordinated water molecules. The metal complexes decompose gradually with formation of metal oxide above 545°C. The proposed chemical changes with temperature range and percent of metal oxide obtained are given in table 4.

Table 4. Thermogravimetric data of Co(II), Ni(II), and Cu(II) complexes.

Compound	Decomposition temperature (°C)	% Weight loss		Metal oxide %		Inference
		Obs.	Calcd	Obs.	Calcd	
$Co(C_{17}H_{11}NO_4)\cdot 3H_2O$	205–255	13.33	13.30	18.44	18.47	Loss of coordinated water molecules
	325–370	26.13	26.11			Loss of aminophenol
	505–545	46.04	46.06			Loss of coumarin moieties
$Ni(C_{17}H_{11}NO_4)\cdot 3H_2O$	210–225	13.31	13.33	18.25	18.27	Loss of coordinated water molecules
	330–367	26.14	26.17			Loss of aminophenol
	510–525	46.19	46.17			Loss of coumarin moieties
$Cu(C_{17}H_{11}NO_4)\cdot 3H_2O$	205–245	13.18	13.17	19.28	19.27	Loss of coordinated water molecules
	325–365	25.84	25.85			Loss of aminophenol
	520–545	45.62	45.61			Loss of coumarin moieties

3.8. *Electrochemistry*

The Co(II) and Ni(II) complexes do not show a redox couple, but Cu(II) complexes have similar quasi reversible one electron transfer. A cyclic voltammogram of $Cu(C_{17}H_{11}NO_4)\cdot 3H_2O$ (Supplementary material) displays a reduction peak at $E_{pc} = -0.0062$ V with a corresponding oxidation peak at $E_{pa} = 0.5524$ V. The peak separation of this couple (ΔE_p) is 0.5462 V at 0.1 V and increases with scan rate. For $Cu(C_{16}H_9NO_4)\cdot 3H_2O$, a reduction peak at $E_{pc} = -0.0056$ V with a corresponding oxidation peak at $E_{pa} = 0.4634$ V was observed and the peak separation, ΔE_p, was 0.4578 at 0.1 V. The difference between forward and backward peak potentials provides a rough evaluation of the degree of reversibility of the one electron transfer reaction. The cyclic voltammetric responses with the scan rate varying from 100 to 400 $mV\,s^{-1}$ indicate quasi-reversible one electron oxidation. The ratio of cathodic to anodic peak height was <1, but the peak current increases with increase of the square root of the scan rates, establishing the electrode process as diffusion controlled [35].

The separation in peak potentials increasing at higher scan rates is consistent with quasi-reversibility of the Cu(II)/Cu(I) couple.

3.9. *Fluorescence studies*

H_2L^I is characterized by an emission band at 543 nm in DMF and 544 nm in DMSO. Upon addition of 2–3 drops of aqueous alkali (2% NaOH) to H_2L^I solution, the λ_{max} values shift to 514 nm in DMF and 521 nm in DMSO due to the formation of phenoxide. For H_2L^{II} the emission band (522 nm in DMF and 524 nm in DMSO) shifts (496 nm in DMF and 498 nm in DMSO) on addition of 2–3 drops of aqueous alkali (2% NaOH).

The Co(II), Ni(II), and Cu(II) complexes of H_2L^I and H_2L^{II} (table 5) are characterized by blue shift of the λ_{max} value compared with the Schiff bases due to deprotonation of the hydroxyl (Supplementary material).

Table 5. Stokes shift of Schiff bases and their metal complexes.

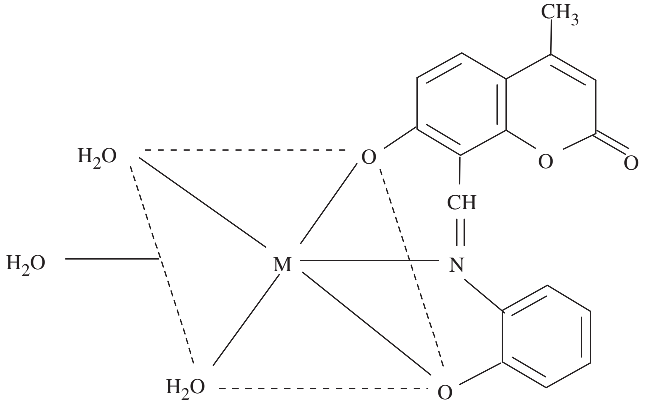
	Excitation (in nm)		Emission (in nm)	
Compound	DMF	DMSO	DMF	DMSO
$C_{17}H_{13}NO_4$	436	438	543	544
$C_{16}H_{11}NO_4$	421	425	522	524
$Co(C_{17}H_{11}NO_4) \cdot 3H_2O$	400	402	531	521
$Co(C_{16}H_9NO_4) \cdot 3H_2O$	389	394	511	513
$Ni(C_{17}H_{11}NO_4) \cdot 3H_2O$	396	399	527	526
$Ni(C_{16}H_9NO_4) \cdot 3H_2O$	392	394	504	502
$Cu(C_{17}H_{11}NO_4) \cdot 3H_2O$	401	399	517	515
$Cu(C_{16}H_9NO_4) \cdot 3H_2O$	386	388	496	491

Table 6. Antimicrobial results of Schiff bases and their metal complexes.

		% Inhibition against bacteria				% Inhibition against fungi		
Compound	Conc. ($\mu g\,mL^{-1}$)	*E. coli*	*S. aureus*	*P. aeruginosa*	*S. typhi*	*A. flavus*	*Cladosporium*	*A. niger*
$C_{17}H_{13}NO_4$	25	25	–	28	0	16	35	13
	50	62	–	31	47	26	53	43
	100	69	3	89	69	61	74	50
$C_{16}H_{11}NO_4$	25	24	–	26	–	18	33	15
	50	61	–	32	44	30	53	41
	100	68	5	86	70	62	71	52
$CoCl_2 \cdot 6H_2O$	100	21	23	22	20	26	24	27
$NiCl_2 \cdot 6H_2O$	100	24	21	19	14	23	19	22
$CuCl_2 \cdot 2H_2O$	100	16	14	12	20	18	12	21
$Co(C_{17}H_{11}NO_4) \cdot 3H_2O$	25	46	–	46	40	58	59	49
	50	72	5	69	65	75	81	74
	100	82	5	83	76	87	92	82
$Co(C_{16}H_9NO_4) \cdot 3H_2O$	25	44	–	43	35	55	55	48
	50	70	6	67	64	75	80	72
	100	81	7	80	72	85	91	81
$Ni(C_{17}H_{11}NO_4) \cdot 3H_2O$	25	39	–	42	46	59	65	50
	50	66	3	72	69	69	78	66
	100	76	5	82	78	78	85	75
$Ni(C_{16}H_9NO_4) \cdot 3H_2O$	25	33	–	44	44	54	61	48
	50	67	5	72	68	68	72	64
	100	74	6	81	76	76	81	71
$Cu(C_{17}H_{11}NO_4) \cdot 3H_2O$	25	20	–	18	9	16	35	13
	50	30	–	31	21	45	38	31
	100	62	4	44	28	57	53	54
$Cu(C_{16}H_9NO_4) \cdot 3H_2O$	25	22	–	22	8	14	33	12
	50	31	–	30	22	45	42	30
	100	61	9	42	28	56	51	53
Gentamycin	25	86	6	81	61	–	–	–
	50	88	7	86	71			
	100	88	14	89	80			
Flucanozole	25	–	–	–	–	88	92	84
	50					92	94	94
	100					97	97	96

Table 7. Minimum inhibitory concentration ($\mu g\,mL^{-1}$) of selected compounds against selected bacteria.

Compound	*E. coli*	*P. aeruginosa*	*S. typhi*	*A. flavus*	*Cladosporium*	*A. niger*
$C_{17}H_{13}NO_4$	25	10	25	25	10	>100
$C_{16}H_{11}NO_4$	25	10	25	25	25	>100
$Co(C_{17}H_{11}NO_4)\cdot 3H_2O$	10	10	10	10	10	10
$Co(C_{16}H_9NO_4)\cdot 3H_2O$	10	10	25	10	10	10
$Ni(C_{17}H_{11}NO_4)\cdot 3H_2O$	10	10	10	10	10	10
$Ni(C_{16}H_9NO_4)\cdot 3H_2O$	10	10	10	10	10	25
$Cu(C_{17}H_{11}NO_4)\cdot 3H_2O$	25	>100	–	25	>100	>100
$Cu(C_{16}H_9NO_4)\ 3H_2O$	25	>100	–	>100	>100	>100



M = Co(II), Ni(II), and Cu(II)

Figure 2. Structure of metal complexes $Co(C_{17}H_{11}NO_4)\cdot 3H_2O$ (**1**), #$Ni(C_{17}H_{11}NO_4)\cdot 3H_2O$ (**3**) and $Cu(C_{17}H_{11}NO_4)\cdot 3H_2O$ (**5**).

4. Biological studies

The antimicrobial results are presented in table 6. The Schiff bases showed some activity against *P. aeruginosa* and good activity against *E. coli* and *S. typhi*. The Co(II) and Ni(II) complexes show high activity against *E. coli*, *P. aeruginosa*, and *S. typhi*. The Schiff bases show high antifungal activity against *Cladosporium* and promising results against *A. flavus*. The metal complexes showed good antifungal activity against *A. niger*, *A. flavus*, and *Cladosporium*. Metal salts exhibited negligible activity towards all bacterial and fungi. The MIC of compounds that showed significant activity against selected bacterial and fungi species was determined (table 7).

It is evident from the results that biological activities of metal complexes are higher than ligands [36]. Metal complexes with Schiff bases of formyl coumarin derivatives have been reported to have high antimicrobial activity [7, 37–39].

5. Conclusion

The new Schiff bases are tridentate ligands, coordinated through the azomethine nitrogen, phenolic oxygen of *o*-aminophenol, and coumarin. The nature of the complexes was confirmed by analytical, spectral, magnetic, thermal, and fluorescence studies. The Cu(II) complexes show one electron transfer process corresponding to Cu(II)/Cu(I). The Schiff bases and some metal complexes were highly active against *E. coli* and *P. aeruginosa* and the Co(II) complexes were highly active against *Cladosporium* and *A. niger*.

These observations indicate the structure represented for L^I in figure 2 for $ML \cdot 3H_2O$ [M = Co(II), Ni(II), and Cu(II)].

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