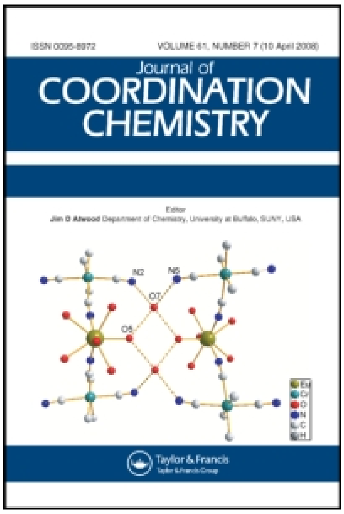

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, spectral, electrochemical and biological studies of Co(II), Ni(II) and Cu(II) complexes with Schiff bases of 8-formyl-7-hydroxy-4-methyl coumarin

Ajaykumar Kulkarni[a]; Prakash Gouda Avaji[a]; Gangadhar B. Bagihalli[a]; Sangamesh A. Patil[a]; Prema S. Badami[b]
[a] P.G. Department of Chemistry, Karnatak University, Dharwad-580 003, Karnataka, India [b] Department of Chemistry, Shri Sharanabasaveswar College of Science, Gulbarga-585102, Karnataka, India

To cite this Article Kulkarni, Ajaykumar , Avaji, Prakash Gouda , Bagihalli, Gangadhar B. , Patil, Sangamesh A. and Badami, Prema S.(2009) 'Synthesis, spectral, electrochemical and biological studies of Co(II), Ni(II) and Cu(II) complexes with Schiff bases of 8-formyl-7-hydroxy-4-methyl coumarin', Journal of Coordination Chemistry, 62: 3, 481 — 492, First published on: 10 December 2009 (iFirst)

To link to this Article: DOI: 10.1080/00958970802226387

URL: http://dx.doi.org/10.1080/00958970802226387

Journal of Coordination Chemistry
Vol. 62, No. 3, 10 February 2009, 481–492

Taylor & Francis
Taylor & Francis Group

Synthesis, spectral, electrochemical and biological studies of Co(II), Ni(II) and Cu(II) complexes with Schiff bases of 8-formyl-7-hydroxy-4-methyl coumarin

AJAYKUMAR KULKARNI†, PRAKASH GOUDA AVAJI†,
GANGADHAR B. BAGIHALLI†, SANGAMESH A. PATIL*†
and PREMA S. BADAMI‡

†P.G. Department of Chemistry, Karnatak University, Dharwad – 580 003, Karnataka, India
‡Department of Chemistry, Shri Sharanabasaveswar College of Science, Gulbarga – 585102, Karnataka, India

(*Received 22 January 2008; in final form 27 March 2008*)

A series of Co(II), Ni(II) and Cu(II) complexes have been synthesized with Schiff bases derived from 8-formyl-7-hydroxy-4-methyl coumarin and o-chloroaniline/o-toluidine. The structures of the complexes have been proposed from analytical, spectral (IR, UV-Vis, ESR and FAB-mass), magnetic, thermal and fluorescence studies. The complexes are soluble in DMF and DMSO and molar conductance values indicate the complexes are non-electrolytes. Elemental analyses indicate $ML_2 \cdot 2H_2O$ [M = Co(II), Ni(II) and Cu(II)] stoichiometry. Spectroscopic studies (IR, UV-Vis, ESR and fluorescence) indicate octahedral geometry, in which ligand coordinates through azomethine nitrogen and phenolic oxygen via deprotonation. Thermal studies suggest coordination of water to the metal ion. Redox behavior of the complexes was investigated by cyclic voltammetry. The Schiff bases and their complexes were screened for their antibacterial (*E. coli*, *S. aureus*, *P. aeruginosa* and *S. typhi*) and antifungal activities (*A. niger*, *A. flavus* and *Cladosporium*) by MIC method.

Keywords: Synthesis; Electrochemical; Coumarin; Spectral; Biological; Complexes

1. Introduction

The coumarins and their derivatives possess antiallergic [1], insecticidal, antifungal [2], antiviral and antibacterial [3] activities. Hydroxycoumarins are typical phenolic compounds, and therefore act as potent metal chelators and free radical scavengers. Coumarin and 7-hydroxycoumarin have been reported to inhibit the proliferation of a number of human malignant cell lines *in vitro* [4–7] and have demonstrated activity against several types of animal tumors [8–11]. Complexes of 4-methyl-7-hydroxycoumarin with several metals are reported as anticoagulants and spasmolytic agents [12]. Metal complexes with coumarin derivatives have been reported from our laboratory [13].

---

*Corresponding author. Email: patil1956@rediffmail.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970802226387

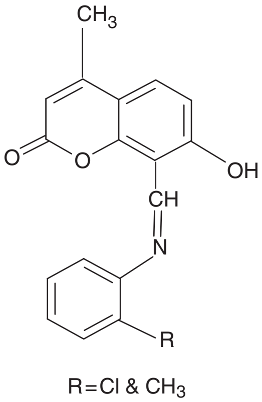

Figure 1. Structure of Schiff base.

Such a variety of interesting biological properties of coumarin derivatives prompted us to synthesize Co(II), Ni(II) and Cu(II) complexes with new Schiff bases (figure 1) derived from 8-formyl-7-hydroxy-4-methylcoumarin and o-toluidine/o-chloroaniline possessing phenolic oxygen and azomethine nitrogen donor sites. The complexes are characterized by spectral (IR, UV-Vis, FAB-mass, ESR, fluorescence), electrochemical, thermal and magnetic properties and molar conductivities and investigated for their antibacterial and antifungal properties against various pathogenic bacterial strains using the minimum inhibitory concentration method.

2. Experimental

2.1. *Physical measurements*

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. The electronic spectra of the complexes were recorded in 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. 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, the spectra were recorded at room temperature and m-nitrobenzyl alcohol was used as the matrix. The mass spectrometer was operated in the positive ion mode. The electrochemistry of Cu(II) complexes was recorded on a CHI1110A-electrochemical (HCH Instruments) analyzer (made in U.S.A). ESR spectra were recorded on a Varian-E-4X-band EPR spectrometer with field set to 3000 G at modulation frequency of 100 K Hz 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} using a PERKIN-ELMER DIAMOND TG/DTA instrument. Molar conductivity measurements were recorded on a ELICO-CM-82 T conductivity bridge with a cell having cell constant 0.51; magnetic moment was carried out by using a Faraday balance.

2.2. *Synthesis*

All chemicals were of reagent grade; 7-hydroxy-4-methyl coumarin was synthesized by literature procedure [14].

2.2.1. Synthesis of 8-formyl-7-hydroxy-4-methylcoumarin. 7-hydroxy-4-methyl coumarin (0.03 mol) and hexamine (0.07 mol) in glacial acetic acid (50 mL) were heated for 4–5 h and then 20% HCl (75 mL) was added with further heating for 20 min, cooled and extracted with ether. Pale yellow solid of 8-formyl-7-hydroxy-4-methyl coumarin, which was obtained after extraction, was recrystallized from ethanol.

2.2.2. Synthesis of Schiff bases [I and II]. The Schiff bases were synthesized by refluxing hot ethanolic solution (30 mL) of o-chloroaniline/o-toluidine (0.01 mol) and hot ethanolic solution (30 mL) of 8-formyl-7-hydroxy-4-methylcoumarin (0.01 mol) for 4–5 h with addition of a few drops of hydrochloric acid. The precipitate that formed during reflux was filtered, washed with cold EtOH, and recrystallized from EtOH.

2.2.3. Synthesis of Co(II), Ni(II) and Cu(II) complexes [1–6]. An alcoholic solution of Schiff base (2 mmol) was refluxed with 1 mmol of $CoCl_2 \cdot 6H_2O$/$NiCl_2 \cdot 6H_2O$/ $CuCl_2 \cdot 2H_2O$ on a water bath for 1 h. Then, 2 mmol of sodium acetate was added and reflux 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. *Analyses*

The metal contents were estimated gravimetrically by the standard method [15]. Carbon, hydrogen and nitrogen were estimated by using a C, H, N analyzer. Elemental analyses and molar conductance values are listed in table 1.

3. Results and discussion

The Co(II), Ni(II) and Cu(II) complexes are colored non-hygroscopic solids, stable in air and soluble in DMF and DMSO. The analytical data indicate 1 : 2 stoichiometry $ML_2 \cdot 2H_2O$, where L stands for a singly deprotonated ligand. The molar conductance values are too low for dissociation of the complexes in DMF, indicating the non-electrolytic nature of the complexes (table 1).

In order to establish whether the water molecules are present in the complexes coordinated to the metal ion, the weighed complex was heated for about 2 h at 105°C and then cooled in a desiccator and weighed again with no loss in weight of the complex, suggesting that water present in the complexes is coordinated to the metal ion.

3.1. *Infrared spectra*

Prominent infrared spectral data of the Schiff bases and their complexes are presented in table 2.

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

Complex	Molecular formula	Color	M%		C%		H%		N%		Molar conductance ($Ohm^{-1} cm^{-2} mol^{-1}$)	μ_{eff} (BM)
			Obsd.	Calcd	Obsd.	Calcd	Obsd.	Calcd	Obsd.	Calcd		
I	$C_{17}H_{12}NO_3Cl$		–	–	65.15	65.17	3.81	3.83	4.45	4.47	–	–
II	$C_{18}H_{15}NO_3$		–	–	73.69	73.72	5.09	5.11	4.76	4.77	–	–
1	$[Co(C_{17}H_{11}NO_3Cl)_2 \cdot 2H_2O]$	Brown	8.19	8.20	56.72	56.74	3.59	3.61	3.87	3.89	27.8	4.72
2	$[Ni(C_{17}H_{11}NO_3Cl)_2 \cdot 2H_2O]$	Yellowish green	8.05	8.07	56.81	56.82	3.60	3.62	3.88	3.90	20.6	3.12
3	$[Cu(C_{17}H_{11}NO_3Cl)_2 \cdot 2H_2O]$	Green	8.69	8.71	56.40	56.43	3.58	3.59	3.85	3.87	33.25	1.78
4	$[Co(C_{18}H_{14}NO_3)_2 \cdot 2H_2O]$	Brown	8.67	8.68	63.60	63.62	4.69	4.71	4.10	4.12	28.9	4.86
5	$[Ni\ (C_{18}H_{14}NO_3)_2 \cdot 2H_2O]$	Yellowish green	8.53	8.55	63.69	63.71	4.71	4.72	4.11	4.13	21.6	3.24
6	$[Cu(C_{18}H_{14}NO_3)_2 \cdot 2H_2O]$	Green	9.21	9.22	63.23	63.25	4.66	4.68	4.07	4.09	34.0	1.81

Table 2. The important infrared frequencies (in cm^{-1}) of Schiff bases derived from 8-formyl-7-hydroxy-4-methylcoumarin and o-chloroaniline/o-toluidine and their metal complexes.

Compound	Coordinated water ν(OH)	Lactonyl ν(C=O)	ν(C=N)	H-bonded –OH stretching	ν(C=C)	Phenolic ν(C–O)	ν(M–N)	ν(M–O)
$C_{17}H_{12}NO_3Cl$	–	1724	1613	3078	1567	1313	–	–
$C_{18}H_{15}NO_3$	–	1723	1620	3060	1590	1314	–	–
$[Co(C_{17}H_{11}NO_3Cl)_2 \cdot 2H_2O]$	3446	1720	1584	–	–	1336	447	376
$[Ni(C_{17}H_{11}NO_3Cl)_2 \cdot 2H_2O]$	3450	1728	1582	–	–	1339	456	378
$[Cu(C_{17}H_{11}NO_3Cl)_2 \cdot 2H_2O]$	3443	1728	1580	–	–	1336	463	375
$[Co(C_{18}H_{14}NO_3)_2 \cdot 2H_2O]$	3445	1715	1582	–	–	1342	448	379
$[Ni\ (C_{18}H_{14}NO_3)_2 \cdot 2H_2O]$	3454	1723	1594	–	–	1341	450	380
$[Cu(C_{18}H_{14}NO_3)_2 \cdot 2H_2O]$	3445	1720	1587	–	–	1338	458	381

The IR spectra of the Schiff bases have a characteristic high intensity band at 1613 cm^{-1} attributed to ν(C=N) [16], rendering proof for the presence of 8-formyl-7-hydroxy-4-methylcoumarin. The broad band at 3078 cm^{-1} and strong bands at 1724 and 1313 cm^{-1} are assigned to phenolic H-bonded –OH stretching, ν(C=O) of lactonyl carbonyl and phenolic ν(C–O), respectively.

In comparison with spectra of the Schiff bases, all complexes exhibit ν(C=N) around 1585 cm^{-1}; the downward shift indicates azomethine nitrogen coordinates to the metal. The high intensity band due to phenolic C–O at 1313 cm^{-1} in the Schiff bases is a medium to high intensity band in the 1336–1342 cm^{-1} region in the complexes. These observations support the formation of M–O bonds via deprotonation.

The presence of coordinated water in the complexes is confirmed by a broad band around 3443 cm^{-1} and two weak bands in the region 750–800 and 700–720 cm^{-1} due to ν(–OH), rocking and wagging modes of vibrations, respectively [17]. The unaltered position of ν(C=O) (lactonyl carbon) confirms its non involvement in coordination.

New bands in the region 375–381 and 447–463 cm^{-1} in all the complexes are assigned to stretching frequencies of (M–O) and (M–N) bonds, respectively. Thus, the IR spectral data provide strong evidence for complexation of the bidentate Schiff bases.

3.2. *^{1}H NMR spectra*

A singlet at 9.42 ppm is attributed to the phenolic –OH of the Schiff bases. The characteristic singlet at 8.62 ppm is due to the azomethine proton (–CH=N) and multiplets around 7.0–7.6 ppm are assigned to aromatic protons. In addition to these signals, the sharp signal at 2.84 ppm is ascribed to methyl.

3.3. *Electronic spectra*

Electronic spectra of high-spin octahedral Co(II) complexes [17] exhibit absorption bands in the region 8000–10000 cm^{-1} and 18000–20000 cm^{-1} corresponding to ν_1 and ν_3 transitions $^4T_{1g}$ (F) $\rightarrow$ $^4T_{2g}$ (F) (ν_1); $^4T_{1g}$ (F) $\rightarrow$ $^4T_{1g}$ (P) (ν_3), respectively; ν_2 is not observed because of its proximity to strong ν_3 transition. In the present study, Co(II) complex shows bands at 9661 and 19417 cm^{-1} corresponding to ν_1 and ν_3.

The Ni(II) complex exhibits bands at 10471, 16393 and 26856 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, in octahedral geometry. The ligand field parameters are listed in table 3. The value of ν_2/ν_1 is found to be around 1.58 and the μ_{eff} value is 3.17 within the range of 2.8–3.5 BM for octahedral complexes. The values of the nephelauxetic parameters, β, indicate low covalent character of the metal-ligand σ bonds [18].

Electronic spectra of Cu(II) complexes display two prominent bands. One a low intensity broad band at 14492 cm^{-1} is assigned to $^2T_{2g} \leftarrow {}^2E_g$ transition, suggesting distorted octahedral geometry around Cu(II). A high intensity band at 25523 cm^{-1} is due to symmetry forbidden ligand → metal charge transfer [19].

3.4. *Magnetic studies*

The magnetic moments obtained at room temperature are listed in table 1. The magnetic measurement for Co(II) complexes exhibit magnetic moment values of

Table 3. Ligand field parameters of Ni(II) complexes with Schiff bases derived from 8-formyl-7-hydroxy-4-methylcoumarin and o-chloroaniline/o-toluidine.

Complex	Transitions (cm^{-1}) ν_1	ν_2	ν_3	ν_2 Calcd (cm^{-1})	D_q (cm^{-1})	B^1 (cm^{-1})	% Distortion	ν_2/ν_1	LSFE	μ_{eff} Calcd BM	β	β°%
2	10471	16393	26856	16657	1047.100	806.681	1.586	1.566	35.901	3.171	0.764	23.610
5	10446	16386	26848	16632	1044.6	809.512	1.483	1.569	35.815	3.17	0.767	23.342

4.72–4.86, consistent with the octahedral range of 4.3–5.2 BM; Ni(II) complexes showed magnetic moment values of 3.12–3.24 within the range of 2.8–3.5 BM [20] suggesting octahedral environment. The Cu(II) complexes show magnetic moments 1.78–1.81 BM, slightly higher than the spin-only value 1.73 BM expected for one unpaired electron, consistent with an octahedral geometry [21].

3.5. *ESR spectra of copper(II) complex 3*

A representative ESR spectrum of Cu(II) complex **3** (Supplementary Material) at liquid nitrogen temperature in solid state using TCNE as g marker showed a single g value (2.00277). The spectrum was isotropic in nature.

3.6. *FAB-mass spectrum of Schiff base (I) and its Ni(II) complex 2*

The FAB-mass spectrum of Schiff base I, available in Supplementary Material, shows a molecular ion peak at *m*/*z* 313, equivalent to its molecular weight.

The FAB-mass spectrum of **2** (Supplementary Material) shows a molecular ion peak M^+ at *m*/*z* 718, equivalent to its molecular weight $[ML_2 \cdot 2H_2O]^+$. The molecular ion by the loss of two water molecules gave a fragment ion peak at *m*/*z* 682 for $[ML_2]^+$ which undergoes demetallation to form $[L+H]^+$ at *m*/*z* 313.

3.7. *Thermal studies*

The thermal behavior of all the complexes is almost the same. Hence, only representative Co(II) (**1**), Ni(II) (**2**) and Cu(II) (**3**) complexes will be discussed. These complexes decomposed in two steps as indicated by DTG peaks around 110–125 and 470–510°C (Supplementary Material) corresponding to the mass loss of two coordinated water molecules [17, 22–24] and organic moiety, respectively; the metal oxide formed above 510°C. The nature of the proposed chemical change with the temperature range and the percentage of metal oxide obtained are given in table 4.

3.8. *Electrochemistry*

A cyclic voltammogram of **3** (Supplementary Material) displays a reduction peak at $E_{pc} = 0.3241$ V with a corresponding oxidation peak at $E_{pa} = 0.4582$ V. The peak

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

Empirical formula	Decomposition temperature (°C)	% Weight loss Obsd.	% Weight loss Calcd	Metal oxide % Obsd.	Metal oxide % Calcd	Inference
$[Co(C_{17}H_{11}NO_3Cl)_2 \cdot 2H_2O]$	115–125	4.95	4.99	10.38	10.40	Loss of coordinated water molecules
	470–490	86.79	86.82			Loss of organic moieties
$[Ni(C_{17}H_{11}NO_3Cl)_2 \cdot 2H_2O]$	110–120	4.98	5.01	10.25	10.28	Loss of coordinated water molecules
	475–495	86.92	86.94			Loss of organic moieties
$[Cu(C_{17}H_{11}NO_3Cl)_2 \cdot 2H_2O]$	110–125	8.70	8.71	19.20	19.23	Loss of coordinated water molecules
	480–510	30.68	30.71			Loss of organic moieties

separation of this couple (ΔE_p) is 0.134 V at 100 mV s^{-1} and increases with scan rate. The difference between forward and backward peak potentials provides a rough evaluation of the degree of reversibility of electron transfer. Cyclic voltammetric responses with scan rate varying 50 to 400 mV s^{-1} gives evidence for a quasi-reversible one-electron oxidation. The ratio of cathodic to anodic peak height was less than one. However, the peak current increases with increase of the square root of the scan rates, establishing the electrode process as diffusion controlled [25].

The separation in peak potentials increases at higher scan rates, consistent with quasi-reversibility of a Cu(II)/Cu(I) couple.

3.9. *Fluorescence studies*

The Schiff bases were characterized by an emission band around 466 nm in DMF and 447 nm in DMSO due to formation of phenolate and cleavage of the imine bond. Addition of aqueous alkali (2% NaOH) to all the above solutions enhanced intensity, indicating proton-transferred (H-bonded ion pair) species exist in equilibrium [26]. The λ_{max} of the Schiff bases undergoes red shift in DMF and DMSO solutions due to hydrogen bond formation [27].

The Co(II), Ni(II) and Cu(II) complexes were characterized by emission bands around 462 nm, 464 nm and 459 nm, respectively; the emission band of Schiff bases around 447 nm disappeared because of interaction of the phenolic oxygen with the metal (figure 2). There was decrease in intensity of fluorescence of Co(II), Ni(II) and Cu(II) complexes in both DMF and DMSO solutions. Previous studies reported that transition metal ions decrease the fluorescence quite effectively [27, 28]. Magnetic perturbation, redox activity, etc., have been invoked [27] to rationalize fluorescence quenching by transition metal ions.

4. Biological studies

The biological activities of the Schiff bases and their complexes have been studied for antibacterial and antifungal activities by agar and potato dextrose agar diffusion

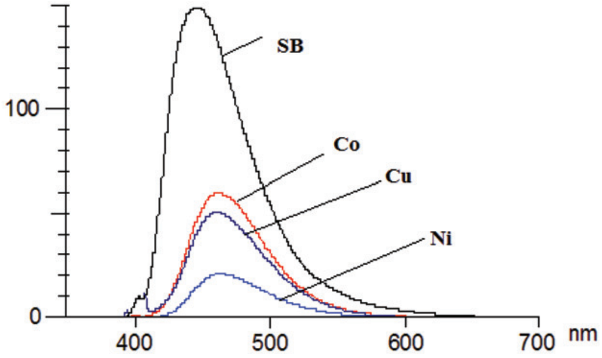

Figure 2. Emission spectrum of Schiff base (**I**) and its Co(II), Ni(II) and Cu(II) complexes in DMSO.

methods, respectively. The antibacterial and antifungal activities were done at 25, 50 and 100 μg mL^{-1} concentrations in DMF solvent by using four bacteria (*E. coli*, *S. aureus*, *P. aeruginosa* and *Salmonella typhi*) and three fungi (*A. niger*, *A. flavus* and *Cladosporium*) by the MIC method [29]. These bacterial strains were incubated for 24 h at 37°C and fungal strains were incubated for 48 h at 37°C. Standard antibacterial (Gentamycine) and antifungal drugs (Flucanazole) were used for comparison under similar conditions.

4.1. *Minimum inhibitory concentration (MIC)*

The microbial results presented in table 5 and figures 3 and 4 suggest that the Schiff bases were biologically active and their metal complexes showed enhanced antibacterial and antifungal activity. Chelating tends to make the Schiff bases more potent bactereostatic agents [30, 31], thus inhibiting the growth of bacteria and fungi more than parent Schiff bases. Factors such as solubility, conductivity, dipole moment and cell permeability mechanism (influenced by the presence of metal ions) may be possible reasons for the increase in activity.

Both Schiff bases were active against *E. coli* and *P. aeruginosa* and moderately active against *Salmonella typhi*. All the Co(II), Ni(II) and Cu(II) complexes show promising results against *E. coli* and *P. aeruginosa* and moderate activity against *Salmonella typhi*; all the Co(II), Ni(II) and Cu(II) complexes show higher activity than the standard drug against *S. aureus*.

For antifungal activity, the Schiff bases and their Co(II), Ni(II) and Cu(II) complexes show promising results against *A. niger* and *Cladosporium*.

5. Conclusion

The Schiff bases are bidentate, coordinated through the azomethine nitrogen and phenolic oxygen, confirmed by analytical, spectral, magnetic, thermal and fluorescence studies.

Table 5. Biological results of Schiff bases and their 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*
$C_{17}H_{12}NO_3Cl$	25	41.86	2.94	52.63	–	56.66	69.23	69.04
	50	51.16	4.41	68.42	16.66	70.58	74.35	83.33
	100	60.46	7.35	86.84	54.76	78.43	79.48	88.09
$C_{18}H_{15}NO_3$	25	45.65	4.4	55.32	–	42.67	57.89	62.90
	50	59.03	9.52	63.29	21.03	57.33	74.38	76.54
	100	68.23	17.25	72.03	52.36	68.12	79.87	82.98
$[Co(C_{17}H_{11}NO_3Cl)_2 \cdot 2H_2O]$	25	55.81	2.94	52.63	26.19	72.54	76.92	57.14
	50	67.44	4.41	55.26	42.85	78.43	82.05	73.8
	100	86.04	4.41	65.78	76.19	82.35	92.3	85.71
$[Ni(C_{17}H_{11}NO_3Cl)_2 \cdot 2H_2O]$	25	62.79	–	57.89	23.8	50.98	71.71	50
	50	88.37	2.94	63.15	47.61	66.66	79.48	71.42
	100	65.34	5.88	78.94	57.14	74.5	84.61	78.57
$[Cu(C_{17}H_{11}NO_3Cl)_2 \cdot 2H_2O]$	25	46.51	35.44	52.63	35.71	47.05	58.97	47.61
	50	46.51	47.35	68.42	38.09	62.74	71.79	69.04
	100	87.34	55.11	78.94	50.0	78.43	87.17	90.47
$[Co(C_{18}H_{14}NO_3)_2 \cdot 2H_2O]$	25	58.12	6.23	61.23	29.36	58.44	68.98	59.89
	50	75.33	23.15	72.36	56.36	69.87	79.98	76.98
	100	86.02	36.26	82.15	78.23	79.65	90.87	80.97
$[Ni(C_{18}H_{14}NO_3)_2 \cdot 2H_2O]$	25	59.12	–	63.25	22.36	54.12	70.09	59.89
	50	83.25	25.12	75.32	52.38	60.23	81.67	77.67
	100	74.26	45.63	83.12	72.35	69.09	88.92	81.68
$[Cu(C_{18}H_{14}NO_3)_2 \cdot 2H_2O]$	25	79.06	19.11	55.26	16.66	37.25	74.35	42.85
	50	90.69	20.58	60.52	30.95	39.21	84.61	54.76
	100	93.02	22.05	63.15	69.04	60.78	94.87	73.8
Gentamycin	25	86.04	5.88	81.57	61.9	–	–	–
	50	88.37	7.35	86.84	71.4			
	100	88.37	14.7	89.47	80.95			
Flucanozole	25	–	–	–	–	84.31	92.3	88.09
	50					94.1	94.87	92.85
	100					96.08	97.43	97.61
Control	25	100	100	100	100	100	100	100
	50	100	100	100	100	100	100	100
	100	100	100	100	100	100	100	100

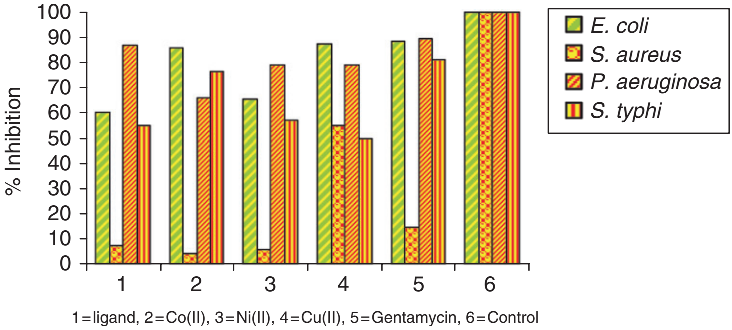

Figure 3. Antibacterial studies of Schiff bases and their Co(II), Ni(II) and Cu(II) complexes.

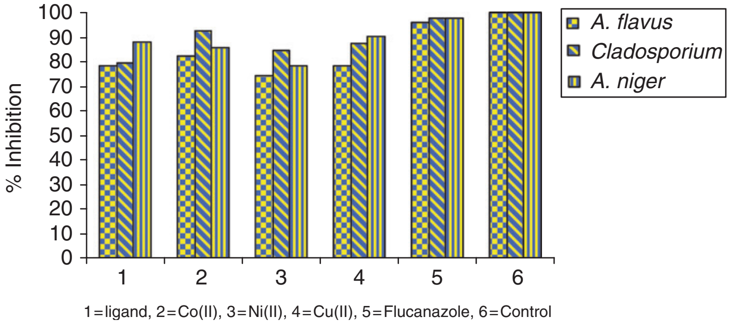

Figure 4. Antifungal studies of Schiff base and its Co(II), Ni(II) and Cu(II) complexes.

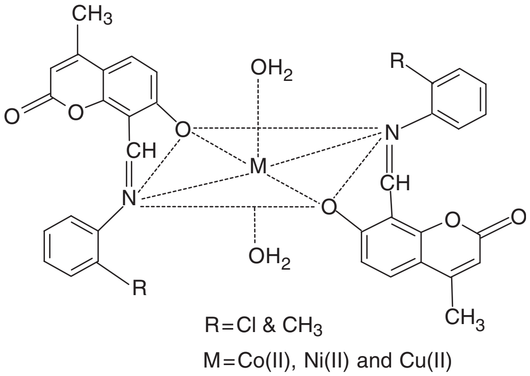

Figure 5. Octahedral structure of Co(II), Ni(II) and Cu(II) complexes.

Electrochemical properties of the metal complexes investigated in DMF show the Cu(II)/Cu(I) couple. Biological study reveals that Schiff bases and some metal complexes were active against *E. coli* and *P. aeruginosa* and Co(II) complexes are highly active against *Cladosporium*.

We propose the structure shown in figure 5 for $ML_2 \cdot 2H_2O$ [M=Co(II), Ni(II) and Cu(II)].

References

[1] D.T. Connor. U.S. Patent, **126**, 287 (1981).

[2] S.U. Rehman, Z.H. Chohan, F. Gulnazl, C.T. Supuran. *J. Enz. Inhib. Med. Chem.*, **20**, 333 (2005).

[3] P. Laurin, D. Ferroud, M. Klich, C. Dupuis-Hamelin, P. Mauvais, P. Lassaigne, A. Bonnefoy, B. Musicki. *Bioorg. Med. Chem. Lett.*, **9**, 2079 (1999).

[4] M.E. Marshall, J.L. Mohler, K. Edmonds, B. Williams, K. Butler, M. Ryles, L. Weiss, D. Urban, A. Bueschen, M. Markiewicz, G. Cloud. *J. Cancer Res. Clin. Oncol.*, **120**, S39 (1994).

[5] E. Moran, E. Prosser, R. O'Kennedy, R.D. Thornes. *J. Irish Colleges of Physicians & Surgeons*, **22**, 41 (1993).

[6] C.P. Siegers, H.C. Bostelmann. *J. Irish Colleges of Physicians & Surgeons*, **22**, 47 (1993).

[7] R.B. Myers, M. Parker, W.E. Grizzle. *J. Cancer Res. Clin. Oncol.*, **120**, S11 (1994).

[8] D. Thrones, L. Daly, G. Lynch, H. Browne, A. Tanner, F. Keane, S. O'Loughlin, T. Corrigan, P. Daly, G. Edwards. *Eur. J. Surg. Oncol.*, **15**, 431 (1989).

[9] B. Omarbasha, W.R. Fair, W.D. Heston. *Cancer Res.*, **49**, 3045 (1989).

[10] L.D. Raev, E. Voinova, I.C. Ivanov, D. Popov. *Die Pharmazie*, **45**, 696 (1990).

[11] A. Maucher, E. Von Angerer. *J. Cancer Res. Clin. Oncol.*, **120**, 502 (1994).

[12] I.P. Kostova, I. Manolov, I. Nicolova, N. Danchev. *Farmaco*, **56**, 707 (2001).

[13] G.B. Bagihalli, P. G. Avaji, P.S. Badami, S.A. Patil. *J. Coord. Chem.*, 2007 (In press).

[14] V.K. Ahluwalia, P. Bhagat, R. Aggarwal, R. Chandra. *Intermediates for Organic Synthesis*, I.K. International Pvt. Ltd (2005).

[15] A.I. Vogel. *A Text Book of Quantitative Inorganic Analyses*, 3rd Edn, ELBS Longman's Green and Co. Ltd., London (1962).

[16] S.A. Patil, V.H. Kulkarni. *Polyhedron*, **3**, 21 (1984).

[17] K. Singh, M. Singh Barwa, P. Tyagi. *Eur. J. Med. Chem.*, **41**, 147 (2006).

[18] A.K. El-Sawaf, D.X. West, F.A. El-Saied, R.M. El-Bahnasawy. *Transition Met. Chem.*, **23**, 649 (1998).

[19] H. Liu, H. Wang, F. Gao, D. Niu, Z. Lu. *J. Coord. Chem.*, **60**, 2671 (2007).

[20] C.J. Balhausen. *An Introduction to Schiff Bases Field*, McGraw Hill, New York (1962).

[21] B.K. Patel, M.M. Patel. *Ind. J. Chem.*, **29**, 90 (1990).

[22] P.G. Avaji, S.A. Patil, P.S. Badami. *J. Coord. Chem.*, 2007 (in press).

[23] A.A.A. Emara, O.M.I. Adly. *Transition Met. Chem.*, **32**, 889 (2007).

[24] W.-K. Dong, J.-H. Feng, L. Wang, L. Xu, L. Zhao, X.-Q. Yang. *Transition Met. Chem.*, **32**, 1101 (2007).

[25] A.J. Bard, L.-R. Izatt (Eds.), *Electrochemical Methods*: *Fundamentals and Applications*, 2nd Edn, Wiley, New York (2001).

[26] S. Mukherjee. *Indian J. Chem.*, **26**, 1002 (1987).

[27] P.G. Avaji, B. Nagaraja Reddy, S.A. Patil. *Trans. Met. Chem.*, **31**, 842 (2006).

[28] A.W. Czarnik. *Chem. Biol.*, **2**, 423 (1995).

[29] A.K. Sadana, Y. Miraza, K.R. Aneja, O. Prakash. *Eur. J. Med. Chem.*, **38**, 533 (2003).

[30] Z.H. Chohan, C.T. Supuran, A. Scozzafava. *J. Enz. Inhib. Med. Chem.*, **19**, 79 (2004).

[31] Z.H. Chohan, M. Praveen. *Appl. Organomet. Chem.*, **15**, 617 (2001).