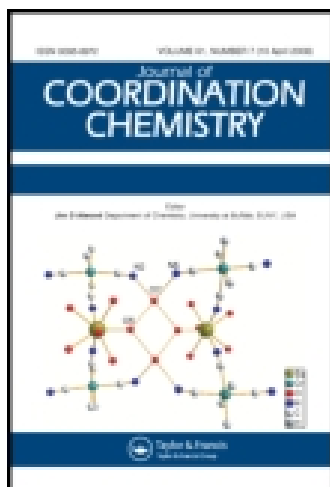


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Srinivasa Budagumpi^a, Ullas N. Shetti^b, Naveen V. Kulkarni^a & Vidyanand K. Revankar^a

^a Department of Studies in Chemistry, Karnatak University, Pavate Nagar, Dharwad, 580 003, Karnataka, India

^b Department of Chemistry, Government Arts and Science College, Karwar, 581 301, Karnataka, India

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Ligational behavior of a bidentate coumarin derivative towards Co^{II} , Ni^{II} , and Cu^{II} : synthesis, characterization, electrochemistry, and antimicrobial studies

SRINIVASA BUDAGUMPI[†], ULLAS N. SHETTI[‡],
NAVEEN V. KULKARNI[†] and VIDYANAND K. REVANKAR^{*†}

[†]Department of Studies in Chemistry, Karnatak University,
Pavate Nagar, Dharwad 580 003, Karnataka, India

[‡]Department of Chemistry, Government Arts and Science College,
Karwar 581 301, Karnataka, India

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A series of new $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$, and $\text{Cu}(\text{II})$ complexes of Schiff base derived from coumarin have been prepared and characterized by analytical and spectral methods. The Schiff base is synthesized by the condensation of 2,6-diaminopyridine and 3-acetylcoumarin in 1:1 stoichiometric ratio. All complexes have 1:1 metal:ligand ratio except the nickel complex, where it was found to be 1:2. UV-Vis spectra and magnetic moment studies confirm the existence of tetrahedral and octahedral geometries around cobalt(II) and nickel(II) metal ions, respectively, but copper(II) chloride/nitrate/sulfate complexes have square-planar geometry and copper(II) acetate complex is distorted octahedral. ESR spectra of copper complexes at room temperature and liquid nitrogen temperature were tetragonal. All the complexes were found to be more active against bacteria except $\text{Ni}(\text{II})$ complex; only CuLSO_4 and $\text{CuL}(\text{CH}_3\text{COO})_2$ have shown the enhanced activity against fungi.

Keywords: 2,6-Diaminopyridine; 3-Acetylcoumarin; Tetragonal; Bacteria; Fungi

1. Introduction

Interaction of coordination compounds with pathogenic microorganisms gives preliminary ideas about applications of coordination compounds toward medicinal chemistry. A prominent place is held by metal complexes of Schiff bases in coordination chemistry for their extensive applications as therapeutic agents and biological models [1, 2]. Schiff bases possess fungicidal, bactericidal [3], and antiviral [4] activities. Azomethine >C=N aided by additional groups like phenolic $-\text{OH}$ and other donor groups was used in the preparation of complexes [5–10]. Schiff bases having N_2O donating sites are of more interest because of the structural and functional relevance with many metallo enzymes.

Coumarin derivatives serve as active pharmaceutical ingredients [11]. The behavior of unsaturated lactones, or more particularly, coumarins with substitution at the third position, toward transition metal ions produce biologically active metal complexes.

*Corresponding author. Email: vkrevankar@rediffmail.com

Ester or acid-substituted coumarin derivatives are potent antibacterial and antifungal agents [12] and coordination compounds derived from coumarin possess antibacterial and antifungal activities [13]. Complexes of *bis*-(3-acetylcoumarin)thiocarbohydrazone show enhanced antitumor activity compared to the activity of ligand [14]. Pyridine containing compounds exhibit a wide range of biological applications and show promising antimicrobial activity. Therefore, we consider it pharmacologically promising to obtain compounds containing coumarin at the 2-position of pyridine and complexes of Co(II), Ni(II), and Cu(II) to study their structures and antimicrobial activities.

2. Experimental

All chemicals were of reagent grade, and solvents were dried and distilled before use according to the standard procedures. 3-Acetylcoumarin was prepared according to earlier reports [15] and 2,6-diaminopyridine was procured. The metal chlorides used were in the hydrated form. Estimation of cobalt, copper, and nickel were carried out according to standard methods. Molar conductivity measurements were made on an ELICO-CM-82 conductivity bridge with cell constant 0.51. Magnetic susceptibility measurements were made on a Gouy balance at room temperature using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant. IR absorption spectra were recorded in a KBr matrix using a Perkin-Elmer IR spectrometer model 983 in the range 4000 to 400 cm^{-1} . Far IR spectra (600 – 200 cm^{-1}) were recorded using the polyethylene pellet method. UV-Vis near IR (300 – 1800 nm) spectra of Co(II) and Ni(II) complexes in nujol and DMF were scanned on a Carry 2390 instrument. For copper(II) complexes, electronic spectra in nujol and DMF were scanned on a Spectronic 2000 spectrophotometer from 200 to 850 nm . Cyclic voltammetric studies were performed at room temperature in DMF in the absence of air using CH instruments Electrochemical analyzer, CHI-1110A. The ESR spectra of the copper complexes as powder and in DMF solution at room temperature and liquid nitrogen temperature were scanned on a Varian E-4 X-band EPR spectrometer using DPPH or TCNE as the *g*-marker.

2.1. Synthesis of the ligand

3-Acetylcoumarin (3.76 g, 0.02 mol) and 2,6-diaminopyridine (2.18 g, 0.02 mol) were dissolved in dry ethanol or benzene and stirred continuously for 15 min, and then the homogeneous reaction mixture was refluxed on a water bath for 3 h. The solid ligand was obtained by removing the excess solvent under reduced pressure. The Schiff base was purified by recrystallization from ethanol–benzene mixture (m.p.: 258°C , yield: 73%) (figure 1).

2.2. Synthesis of metal(II) chloride/nitrate/sulfate complexes

Metal(II) chloride/nitrate/sulfate (0.004 mol), namely, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.95 g), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.887 g), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.684 g), $\text{Cu}(\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$ (1.254 g), and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.998 g), in the same solvent was added to an ethanolic solution of

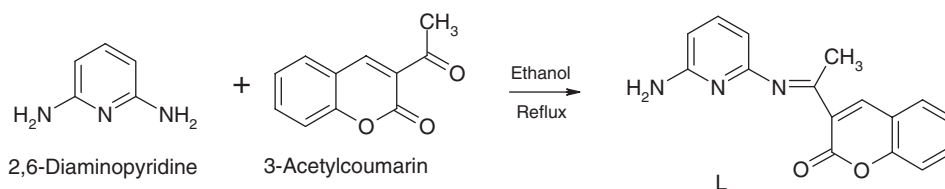


Figure 1. Synthesis of Schiff-base ligand.

Table 1. Analytical, magnetic moment, and conductance data of Co(II), Ni(II), and Cu(II) complexes^a.

Complex	Yield (%)	Metal	Nitrogen	Cl ⁻ /SO ₄ ²⁻ (%)	μ_{eff} (BM)	Molar conductance
CoLCl ₂	98.2	15.21 (14.40)	10.82 (10.27)	16.82 (17.36)	4.32	10.2
NiL ₂ Cl ₂	49.6	9.12 (8.34)	11.74 (12.21)	9.68 (10.32)	2.91	11.2
CuLCl ₂	99.2	14.82 (15.35)	10.51 (10.16)	17.96 (17.17)	2.06	9.5
CuL(NO ₃) ₂	94.8	13.22 (13.61)	14.29 (15.01)	—	1.96	13.2
CuLSO ₄	96.0	13.16 (13.79)	9.92 (9.58)	21.25 (21.89)	1.82	14.1
CuL(CH ₃ COO) ₂	99.7	13.16 (13.79)	9.76 (9.12)	—	1.92	9.8

^aCalculated values are given in parentheses.

Schiff base (1.116 g, 0.004 mol) and stirred continuously for 15–20 min. The resultant reaction mixture was refluxed on a water bath for about 2 h and then cooled. The separated solid complexes were filtered under suction and washed with ethanol and dried in vacuum over fused calcium chloride (yields are given in table 1).

2.3. Synthesis of copper(II) acetate complex

Copper(II) acetate (0.87 g, 0.004 mol) in water was added to an ethanolic solution of Schiff base (1.116 g, 0.004 mol). The resulting precipitate was refluxed with constant stirring. The complex was filtered under suction and washed first with hot water and then with aqueous ethanol and dried in vacuum over phosphorus pentoxide.

2.4. Microbiological studies

Antibacterial activities were tested against *Escherichia coli*, *Staphylococcus aureus*, and *Bacillus aureus* by the cup-plate method at 1 mg mL⁻¹ and the antifungal activity of the compounds was tested against *Aspergillus niger* and *Candida albicans* by the turbidity method at 1 mg mL⁻¹ according to standard methods [16].

3. Results and discussion

The analytical data and physical properties of the complexes are summarized in table 1. These complexes are soluble in DMF, DMSO, and acetonitrile.

3.1. Infrared spectral studies

Infrared frequencies along with their assignments for the ligand and complexes are presented in table 2. The ligand exhibits three characteristic bands of medium intensity due to N–H stretching [17] at 3470, 3352, and 3244 cm⁻¹. Bands at 1735 and 1655 cm⁻¹ were attributed to lactonic carbonyl (>C=O) and azomethine (>C=N) fragments, respectively. The pyridine ring vibration is observed at 1593 cm⁻¹. Spectra of complexes show two broad bands at 3350 to 3200 cm⁻¹ observed with lower intensity; this lowering in multiplicity and frequency compared to ligand indicates the coordination of NH₂ to metal. The lactone carbonyl frequency of the complexes, remained unchanged in the position and intensity, indicating the non-coordination of lactonic oxygen. The azomethine stretching frequency experiences a negative shift of 5–35 cm⁻¹, indicating the participation of azomethine nitrogen in coordination. Vibrations due to pyridine remained unchanged, which shows the non-involvement of pyridine in coordination. The IR spectra of the nitrate complex exhibit bands in the region 1495 and 1380 cm⁻¹, due to the symmetric (ν₁) and antisymmetric (ν₄) stretch of NO₂ group. The difference ν₁ – ν₄ of 115 cm⁻¹ supports monodentate coordination of nitrate [18]. The IR spectrum of the copper(II) sulfate complex shows bands at 1272, 1115, 1040, and 948 cm⁻¹ for the bidentate chelating coordination of sulfate [18]. The acetate complex exhibits bands at 1430 and 1515 cm⁻¹, characteristic of the bidentate chelate coordination of acetate [19]. Coordination of nitrogen, oxygen, and chloride is supported by new bands at 440–490, 340–350, and 295–320 cm⁻¹, respectively.

3.2. Molar conductivity measurements

The molar conductance values of the complexes in DMF at 10⁻³ M were in the range of 10–15 mho cm² mole⁻¹ (table 1), much less than that expected for 1 : 1 electrolytes [20], hence all complexes are considered as non-electrolytes. The values indicate solvation resulting from the displacement of anion from the coordination sphere by strong donor DMF.

Table 2. Infrared spectral data of ligand and its complexes.

Compound	ν(NH)	ν(C=O) lactone	ν(C=N)	Pyridine ring vibrations	ν(M–O)	ν(M–N)	ν(M–Cl)
Ligand	3470 3352 3244	1735	1655	1593	–	–	–
CoLCl ₂	3270 3350	1740	1620	1590	–	480	295
NiL ₂ Cl ₂	3250 3320	1735	1650	1590	–	490	300
CuLCl ₂	3300	1735	1625	1590	–	440	320
CuL(NO ₃) ₂	3280 3350	1735	1620	1595	350	440	–
CuLSO ₄	3250 3340	1735	1620	1590	–	480	–
CuL(CH ₃ COO) ₂	3250 3330	1730	1620	1593	–	490	–

3.3. Electronic spectral studies

The electronic spectrum of cobalt complex consists of ν_3 and ν_2 bands assignable to tetrahedral geometry [21]. The intense band at $15,060\text{ cm}^{-1}$ is assigned as ν_3 arising from ${}^4\text{T}_1(\text{P}) \leftarrow {}^4\text{A}_2(\text{F})$ and the band at 7663 cm^{-1} is attributed to $\nu_2[{}^4\text{T}_1(\text{F}) \leftarrow {}^4\text{A}_2(\text{F})]$. The absorption at $\sim 27,000\text{ cm}^{-1}$ is from ligand to metal charge transfer. The nickel complex exhibits three bands at 9091, 15,385, and $26,316\text{ cm}^{-1}$ attributable to ${}^3\text{T}_{2g}(\text{F}) \leftarrow {}^3\text{A}_{2g}(\text{F})$ (ν_1), ${}^3\text{T}_{1g}(\text{F}) \leftarrow {}^3\text{A}_{2g}(\text{F})$ (ν_2), and ${}^3\text{T}_{1g}(\text{P}) \leftarrow {}^3\text{A}_{2g}(\text{F})$ (ν_3), respectively, from octahedral metal [22]. The electronic spectra of copper(II) complexes display three prominent bands, a low-intensity broad band at $15,750\text{--}16,350\text{ cm}^{-1}$ assigned as 10Dq corresponding to ${}^2\text{T}_{2g} \leftarrow {}^2\text{E}_g$, a high-intensity band in the region $24,200\text{--}24,700\text{ cm}^{-1}$ assigned to ligand to metal charge transfer, and an intra ligand band above $29,000\text{ cm}^{-1}$. The electronic spectra of the complexes in nujol show similar features as in DMF solution. On the basis of electronic spectra, square-planar geometry is assigned to copper complexes (C3–C5) except copper(II) acetate, which is distorted octahedral.

3.4. Magnetic susceptibility measurements

The magnetic moments measured at room temperature are listed in table 1. The observed magnetic moment for the cobalt(II) complex is 4.32 BM, indicating tetrahedral environment around cobalt(II) [23]. Nickel(II) complex shows 2.91 BM magnetic moment, near the spin-only value (2.83 BM), with slight orbital contribution consistent with octahedral geometry [23]. The magnetic moment values of copper(II) complexes are in the range 1.82–2.06 BM, slightly higher than the spin-only value (1.73 BM) corresponding to one unpaired electron. This accounts for a small orbital contribution to the spin-only value and supports the absence of spin–spin interaction between copper(II) centers in the complexes [23].

3.5. ESR spectral studies

ESR spectra recorded for polycrystalline copper(II) complexes at room temperature and liquid nitrogen temperature were tetragonal characteristic. The spin-Hamiltonian parameters are summarized in table 3. The complexes possess a characteristic spectrum having asymmetric bands with two “ g ” values, $g_{\perp}$ and $g_{\parallel}$. It is evident from the ESR spectral data that considerable covalent character exists between metal and ligand in the complexes [24], further supported by the residence time (α^2) of unpaired electron

Table 3. ESR spectral data of copper(II) complexes.

Complex	Room temperature (liquid nitrogen temperature)					
	$g_{\parallel}$	$g_{\perp}$	g_{av}	$A_{\parallel} \times 10^4\text{ (cm}^{-1}\text{)}$	α^2	G
CuLCl_2	2.25 (2.27)	2.05 (2.06)	2.12 (2.13)	126.2 (130.9)	0.662 (0.699)	5.0 (4.5)
$\text{CuL}(\text{NO}_3)_2$	2.22 (2.24)	2.05 (2.06)	2.11 (2.12)	158.9 (168.3)	0.723 (0.773)	4.4 (4.0)
CuLSO_4	2.22 (2.24)	2.05 (2.06)	2.11 (2.12)	154.2 (158.9)	0.709 (0.747)	4.4 (4.0)
$\text{CuL}(\text{CH}_3\text{COO})_2$	2.27 (2.28)	2.06 (2.07)	2.13 (2.14)	140.2 (149.6)	0.725 (0.764)	4.5 (4.0)

Table 4. Antimicrobial activity of ligand and its complexes.

Compound	Zone of inhibition (mm)			Inhibition in % transmission	
	<i>E. coli</i>	<i>S. aureus</i>	<i>B. aureus</i>	<i>A. niger</i>	<i>C. albicans</i>
Ligand	18	14	12	62	68
CoLCl ₂	20	12	12	69	76
NiL ₂ Cl ₂	18	14	12	55	63
CuLCl ₂	22	16	18	44	32
CuL(NO ₃) ₂	22	18	16	61	57
CuLSO ₄	20	16	15	74	85
CuL(CH ₃ COO) ₂	22	16	12	71	72
Gentamycine (bacteria)	23	20	23	–	–
Flucanazole (fungi)	–	–	–	100	100
Control	9	12	9	31	53

on copper(II). The trend $g_{\parallel} > g_{\perp} > g_e$ (2.0023) observed for these complexes shows that the unpaired electron is localized in $d_{x^2-y^2}$ orbital of copper(II). The axial symmetry parameter G is more than 4 for all the complexes showing no exchange coupling between copper centers in solid state. The $A_{\parallel} \times 10^4$ values for the complexes in polycrystalline state both at room temperature and liquid nitrogen temperature are indicative of monomeric complexes.

3.6. Cyclic voltammetric studies

Typical cyclic voltammograms of copper(II) chloride/sulfate are shown in “Supplementary material”. The cyclic voltammograms were scanned in the potential range of +1.0 to –1.0 V with scan rates 0.05, 0.1, and 0.15 V s^{–1} in DMF under oxygen-free conditions. Ligand is electrochemically inactive in the working potential range. Only two copper(II) complexes are electroactive. The cyclic voltammogram of copper(II) chloride/sulfate complexes show a single electron transfer process, a cathodic peak was observed at 0.3 and 0.35 V, respectively, assigned to the reduction of Cu^{II} → Cu^I. In the reverse scan, the anodic peak is observed at 0.5 and 0.52 V, in both cases it is attributed to the oxidation of Cu^I → Cu^{II}. The separation between anodic and cathodic peak potentials (ΔE_p) is 217 and 153 mV, respectively. I_{pc}/I_{pa} for both complexes is constant and less than 1, indicating a quasireversible redox process for both electroactive copper complexes.

3.7. Antimicrobial analysis

The ligand and its complexes were screened for antibacterial and antifungal activities, and the results are tabulated in table 4. Antibacterial activity of the compounds was tested against *E. coli*, *S. aureus*, and *B. aureus* by the cup-plate method at 1 mg mL^{–1}. The nickel(II) complex exhibits antibacterial activity approximately equal to the ligand. All copper(II) complexes show remarkable activity, especially against *E. coli*. Cobalt(II) complex shows moderate activity against the bacteria tested.

Antifungal activities of the compounds were tested against *A. niger* and *C. albicans* by the turbidity method at 1 mg mL^{–1}. CuLSO₄ and CuL(CH₃COO)₂ show good activity

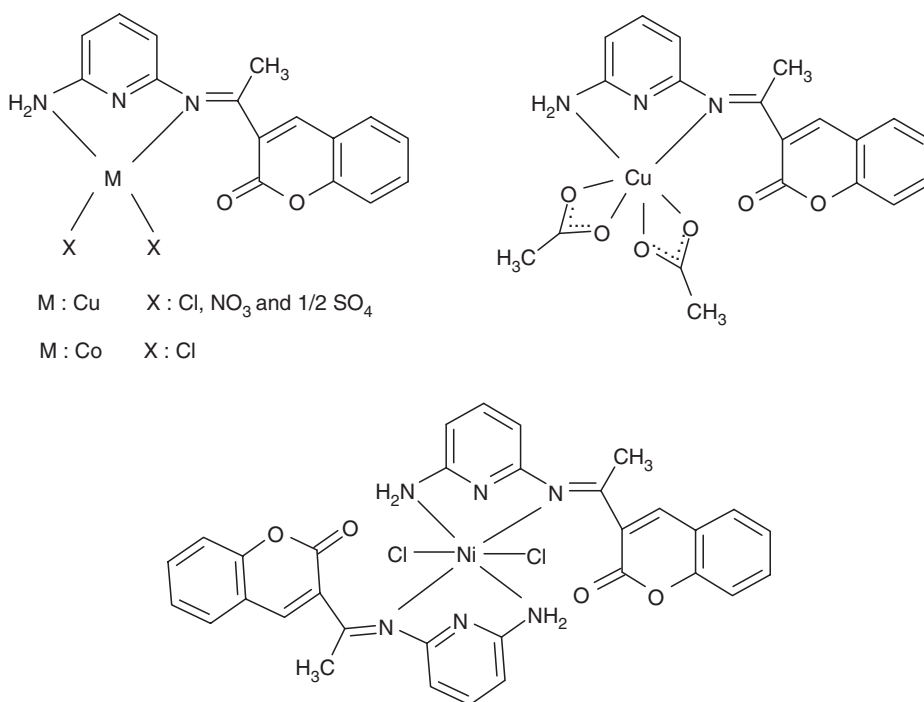


Figure 2. Proposed structures of the complexes.

against both fungi; the remaining copper(II) complexes were less active than the ligand. Ligand, cobalt, and nickel complexes were equally active against the fungi tested. Proposed structures of the complexes are shown in figure 2.

4. Conclusion

This article has thus shown that the ligand is neutral bidentate with coordination through nitrogens of free amine and azomethine. Lactonic carbonyl of coumarin is not involved in coordination. Only in the nickel complex the metal-to-ligand ratio is 1 : 2, unlike others where it is 1 : 1. Magnetic moment and UV-Vis studies reveal the presence of tetrahedral cobalt(II) and square planar copper(II) complexes (C1, C3–C5), and nickel(II) and copper(II) acetate complexes are distorted octahedral. Cyclic voltammograms of copper(II) complexes show quasireversible redox properties. All complexes were found to be more active than ligand against bacteria except Ni(II) complex, and only CuLSO₄ and CuL(CH₃COO)₂ show enhanced activity against fungi.

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