



Synthesis, Spectral and Biocidal Screening of Schiff Base Complexes of Co(II), Ni(II) and Cu(II) Containing Nitrogen and Sulphur Donor atoms

B. K. RAI*, RANJANA¹, PREM PRAKASH² and PREM LATA³

*Department of Chemistry, L. N. T. College, Muzaffarpur, B.R.A. Bihar University, Muzaffarpur, India.

¹Research Scholar, B. R. A. Bihar University, Muzaffarpur, India.

²Assistant Manager, Quality and Product Division, A.C.C. Cement, Thane, Mumbai, India.

³Department of Chemistry, Central Hindu School, Gorakhpur, India.

*Corresponding author E-mail: binodkr_rai@yahoo.co.in

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ABSTRACT

The present paper is a report on the synthesis of some Co(II), Ni(II) and Cu(II) complexes by the condensation of 2 ethyl indole 3-carboxaldehyde with thiosemicarbazide hydrochloride using ethanol as reaction medium. The bonding pattern and structural studies of ligand and complexes have been carried out on the basis of elemental analyses, molar mass, IR spectra, electronic spectra, molar conductance and magnetic susceptibility measurements. The nonelectrolytic nature of the complexes has been proposed on the basis of their molar mass determination and conductance measurements. The ligand and their complexes have been screened in vitro for their antimicrobial activity. Some of the reported complexes were found to be quite active.

Key words : EICT, Schiff base, Co(II), Ni(II) and Cu(II), Complexes, Antimicrobial screening.

INTRODUCTION

Indole derivatives are the basic framework of biologically active compounds. The indole ring system is found to be present in a number of drug molecules and biologically active compounds¹⁻³. Indole derivative exhibits several biocidal activities such as chemotherapeutic importance. Indole derivatives possess various types of pharmacological properties⁴⁻⁶ such as antifungal, antibacterial, antitumour and antitubercular activities. It is established from the literatures survey

that biologically active compound when coordinated with suitable metal ion, its biological activity is enhanced⁷ many folds.

Schiff base complexes play a vital role in application in biocidal, clinical, analytical and pharmaceutical areas. Schiff bases are now attracting a new kind of chemotherapeutic activities by several workers⁸⁻⁹. Keeping the above considerations in mind and in continuation of our earlier work¹⁰⁻¹⁶ in this field, we herein report the synthesis, characterization and antifungal screening

of Schiff base, 2 ethyl indole 3-carboxaldehyde thiosemicarbazone (EICT) and its complexes with Co(II), Ni(II) and Cu(II).

EXPERIMENTAL

All the chemicals used were of AnalR grade and used without further purification. Metals salts were purchased from E-Merck and used as received.

Synthesis of ligand [EICT]

The hot ethanolic solution (20 ml) of 2 ethyl indole 3-carboxaldehyde (0.01 M) and thiosemicarbazide hydrochloride (0.01 M) dissolved in 10% ethanolic solution of sodium acetate were refluxed for 4 h. The resulting mixture was poured on crushed ice. The product obtained was filtered, washed with water, dried and recrystallized from ethanol. Yield-70%; m.p. $167 \pm 1^\circ\text{C}$.

Preparation of the Complexes

Preparation of halide complexes

The complexes were prepared by respective metal halides (0.001 M) in ethanol with ligand 2 ethyl indole 3-carboxaldehyde thiosemicarbazone (EICT) (0.002 M) in molar ratio 1:2. The resulting reaction mixture was refluxed on a water bath for 2-3 h. The precipitated complexes were filtered, washed with aqueous ethanol and dried in electric oven. Yield 65-70%.

Preparation of nitrate complexes

The following general method was adopted for the preparation of nitrate complexes. Ethanolic solution of respective metal nitrate (0.001 M) is treated with ligand 2 ethyl indole 3-carboxaldehyde thiosemicarbazone (0.002 M) dissolved in ethanol. The resulting reaction mixture was heated on a water bath for 2-3 h. The precipitated complexes were filtered, washed several times with ethanol and then dried in electric oven. Yield 70-75%.

Melting point was taken in open capillary tubes and is therefore uncorrected. Analytical data (C,H,N) were collected on Perkin Elmer-2400 CHNS/O elemental analyzer. Magnetic susceptibility of the samples were made on a Gouy balance using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as a calibrant. IR spectra of the ligand

and complexes were recorded on Perkin-Elmer-577 spectrophotometer in the range $4000\text{-}200\text{ cm}^{-1}$ using KBr disc. Molar conductance were recorded on Systronics conductivitymeter model 303 using DMF as a solvent. The electronic spectra were recorded on Cary 2390 spectrophotometer.

RESULTS AND DISCUSSION

The IR spectrum shows a sharp and strong band at 3400 cm^{-1} assignable^{17,19} to $\nu_{\text{N-H}}$ vibration. In spectra of all the complexes, this band without change in position and intensity, clearly indicates noninvolvement of nitrogen atom of either amino or imino group in coordination with metal ion. A broad and sharp band was obtained at 1470 cm^{-1} in the ligand assignable^{17,19,20} to $\nu_{\text{C=N}}$ vibration. This band has been reduced by $20\text{-}30\text{ cm}^{-1}$ in the complexes suggesting coordination of azomethine N with metal ion. The next IR band of the ligand shows a broad and strong band at 780 cm^{-1} assignable^{17,20,21} to $\nu_{\text{C=S}}$ vibration. After complexation this band shows red shift with slightly reduced intensity. The shift of the band and change in intensity indicate coordination of thione sulphur with metal ion.

The conclusive evidence of bonding of ligand to metal ion through oxygen atom of nitrate group, nitrogen atom of azomethine group and sulphur atom of thiosemicarbazone moiety is indicated by the appearance of far ir bands due to $\nu_{\text{M-O}}$ ^{22,23} at $540\text{-}510\text{ cm}^{-1}$, $\nu_{\text{M-N}}$ ^{22,23} at $475\text{-}455\text{ cm}^{-1}$ and $\nu_{\text{M-S}}$ ^{22,23} at $425\text{-}395\text{ cm}^{-1}$ respectively. The evidence of metal halogen linkage is supported by the low molar conductance value of the complexes in the range $12.1\text{-}17.9\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ and appearance of a band in the far ir region at $325\text{-}265\text{ cm}^{-1}$ assigned²²⁻²³ to $\nu_{\text{M-X}}$ (X=Cl,Br,I)

The next IR bands at 1635 and 1500 cm^{-1} with a separation of 135 cm^{-1} suggest monocoordinated behaviour of nitrate group²⁴⁻²⁶.

Electronic spectra and magnetic susceptibility of the complexes

The Co(II) complexes display three bands in the region, $10070\text{-}10160$, $16930\text{-}17110$ and $23540\text{-}23630\text{ cm}^{-1}$, assigned to the transitions, ${}^4\text{T}_{2g}(\text{F}) \leftarrow {}^4\text{T}_{1g}(\text{F})$, ${}^4\text{A}_{2g}(\text{F}) \leftarrow {}^4\text{T}_{1g}(\text{F})$ and ${}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{T}_{1g}(\text{F})$ respectively, which indicate octahedral^{27,28}

Table 1: Analytical, Molar mass, Electronic spectra, Magnetic susceptibility, Decomposition temperature, Molar conductance measurement of ligand EICT and its Metal Complexes

Compounds (Colour)	Molar mass	Yield %	% Analysis found (calculated)			N	°CH	λ_{max} electronic cm^{-1}	μ_{eff} B.M	DT	Ω_{in} $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$
			M	C	N						
EICT	263	70		54.63 (54.75)	21.18 (21.29)	5.62 (5.70)				167	
[Co(EICT) ₂ Cl ₂] (Colourless)	655.93	65	8.91 (8.98)	43.83 (43.90)	17.01 (17.07)	4.50 (4.57)	10090, 16980 , 23630	4.89	183	15.4	
[Co(EICT) ₂ Br ₂] (Chocolate brown)	744.94	68	7.87 (7.91)	38.60 (36 (67)	14.97 (15.03)	3.98 (4.02)	10070, 16960 , 26580	4.94	181	17.6	
[Co(EICT) ₂ I ₂] (Brown)	838.73	64	6.97 (7.02)	34.26 (34.33)	13.30 (13.35)	3.52 (3.57)	10110, 16930 , 23620	4.99	193	16.9	
[Co(EICT) ₂ (NO ₃) ₂] (Deep brown)	708.93	66	8.26 (8.31)	40.57 (40.62)	13.67 (13.71)	4.15 (4.23)	10100, 16930 , 23620	4.90	184	14.1	
[Ni(EICT) ₂ Cl ₂] (Green)	655.71	68	8.90 (8.95)	13.05 (13.12)	17.01 (17.08)	4.45 (4.57)	11530, 18300 , 13510	3.14	171	12.9	
[Ni(EICT) ₂ Br ₂] (Green)	744.52	63	7.80 (7.88)	38.60 (38.68)	14.94 (15.04)	3.93 (4.02)	11460, 18390 , 28310	3.2	189	11.7	
[Ni(EICT) ₂ I ₂] (Green)	838.71	61	6.90 (6.99)	34.25 (34.33)	13.29 (13.35)	3.26 (3.37)	11430, 18340 , 23220	3.6	183	12.1	
[Ni(EICT) ₂ (NO ₃) ₂] (Green)	708.71	67	8.21 (8.28)	40.57 (40.63)	15.73 (15.80)	4.15 (4.23)	11590, 18360 , 23170	3.9	176	13.2	
[Cu(EICT) ₂ Cl ₂] (Blue)	660.54	69	9.55 (9.61)	43.52 (43.60)	16.85 (16.95)	4.49 (4.54)	16220, 22100	1.89	217	14.3	
[Cu(EICT) ₂ Br ₂] (Bluish green)	749.35	63	8.41 (8.47)	38.35 (38.43)	14.07 (14.14)	3.92 (4.00)	16340, 22110	1.93	210	17.9	
[Cu(EICT) ₂ (NO ₃) ₂] (Blue)	713.54	69	8.83 (8.90)	40.30 (40.36)	15.61 (15.69)	4.11 (4.20)	16060 22060	1.96	207	13.8	

DT = Decomposition Temperature

geometry. The octahedral geometry of Co(II) complex is supported²⁹⁻³¹ by high m_{eff} value in the range 4.87-4.99 B.M. The Ni(II) complexes exhibit three bands in the region 11430-11540 cm^{-1} , 18300-18390 cm^{-1} and 23170-23400 cm^{-1} assigned to transitions ${}^3T_{2g}(\text{F}) \leftarrow {}^3A_{2g}(\text{F})$, ${}^3T_{1g}(\text{F}) \leftarrow {}^3A_{2g}(\text{F})$ and ${}^3T_{1g}(\text{P}) \leftarrow {}^3A_{2g}(\text{F})$ respectively, which indicate octahedral^{28,32} geometry for all the Ni(II) complexes, which is further supported^{29,30,33} by the m_{eff} value in the range 3.2-3.14 B.M. for all the Ni(II) complexes. The Cu(II) complexes display two ligand field bands in the region 16010-16220 cm^{-1} and 22100-22260 cm^{-1} assigned to the transitions ${}^2T_{2g} \leftarrow {}^2E_g$ and charge transfer band respectively. The electronic spectra of all the Cu(II) complexes suggest

octahedral^{28,34} geometry around central metal ion. The magnetic moment value of Cu(II) complexes lie in the range 1.87-1.96 B.M.^{29,30,35}

Molar conductivity

Molar conductance data of the complexes were measured in the solvent DMF and the complexes were found to be nonelectrolytic³⁶ in nature. The molar conductance value of the complexes is in the range 12.1-17.9 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$.

Antifungal activity

The ligand EICT and their complexes of Co(II), Ni(II) and Cu(II) have been screened for their

Table 2: IR spectral bands of ligand eict and its metal complexes of co(ii), ni(ii) and cu(ii)

Compounds	$\nu_{\text{N-H}}$	$\nu_{\text{C=N}}$	$\nu_{\text{C=S}}$	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-S}}$	$\nu_{\text{M-X}}$
EICT	3400 s,b	1470 s,b	780 s,b				
[Co(EICT) ₂ Cl ₂]	3400 s,b	1450 m,b	745 m,b		470 m		310 m
[Co(EICT) ₂ Br ₂]	3400 s,b	1445 m,b	750 m,b		470 m	425 m	315 m
[Co(EICT) ₂ I ₂]	3400 s,b	1440 m,b	755 m,b		470 m	435 m	315 m
[Co(EICT) ₂ (NO ₃) ₂]	3400 s,b	1445 m,b	755 m,b	535 m	470 m	420 m	
[Ni(EICT) ₂ Cl ₂]	3400 s,b	1445 m,b	755 m,b		475 m	425 m	280 m
[Ni(EICT) ₂ Br ₂]	3400 s,b	1440 m,b	750 m,b		475 m	415 m	275 m
[Ni(EICT) ₂ I ₂]	3400 s,b	1445 m,b	750 m		470 m	405 m	265 m
[Ni(EICT) ₂ (NO ₃) ₂]	3400 s,b	1445 m,b	750 m,b	520 m	470 m	410 m	
[Cu(EICT) ₂ Cl ₂]	3400 s,b	1445 m,b	750 m,b		460 m	400 m	280 m
[Cu(EICT) ₂ Br ₂]	3400 s,b	1450 m,b	750 m,b		465 m	395 m	315 m
[Cu(EICT) ₂ (NO ₃) ₂]	3400 s,b	1450 m,b	750 m,b	510 m	455 m	395 m	

m = medium, s = strong, b = broad

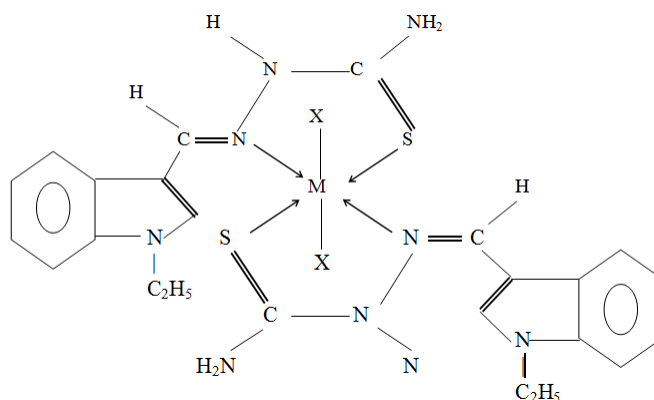


Fig.1: [M(EICT)₂X₂]; M = Co(II) and Ni(II); X = Cl⁻, Br⁻, I⁻ and NO₃⁻; M = Cu(II); X = Cl⁻, Br⁻ and NO₃⁻

antifungal activity against *Aspergillus flavus* and *Aspergillus niger* by disc plate method³⁷. On comparison with reference to fungicide, the complexes were found to move more effectively than free ligand due to chelation theory³⁸.

CONCLUSION

On the basis of above mentioned studies the complexes tentatively proposed an octahedral geometry as shown in Fig.1.

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