

Synthesis, Characterization and Antifungal Screening of Ni(II), Cu(II) and Co(II) Complexes with Nitrogen and Oxygen Containing Schiff Base

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[M(L)₂X₂], where M = Co(II), Ni(II) and Cu(II); L = 2-ethylindole-3-carboxaldehydesemicarbazone [EICS], X = Cl⁻, Br⁻, I⁻ and NO₃⁻ have been synthesized. The ligand and its metal complexes have been characterized by elemental analyses, molar mass, IR, UV, molar conductance and magnetic susceptibility measurements. Octahedral structure has been proposed on the basis of above physicochemical and spectroscopic measurements. These complexes have been screened for their antifungal effect on *Aspergillus flavus* and *Salmonella typhi*. All the complexes of Co(II), Ni(II) and Cu(II) have been shown good activity as antifungal agents on some selected fungal strains.

Key Words: Schiff base, Co(II), Ni(II) and Cu(II), Semicarbazone, Antifungal.

INTRODUCTION

The indole derivatives have wide applications in numerous natural or synthetic alkaloids¹, in medicinal chemistry², as well as their biological and pharmaceutical relevance that have motivated research aimed in the development of new economical, efficient and selective synthetic strategies, particularly for the substituted indole rings^{3,4}. Substituted indoles have been referred to as privileged structures since they are capable of binding to many receptors with high affinity⁵. Keeping the synthesis and selective functionalization of indoles derivative⁶⁻⁸ and in continuation of our earlier work⁹⁻¹⁶ on Schiff base metal complexes, in this paper synthesis and characterization of Co(II), Ni(II) and Cu(II) complexes with Schiff base ligand, 2-ethylindole-3-carboxaldehyde semicarbazone (EICS) are reported herein.

EXPERIMENTAL

All the reagents used were of analytical grade and were used without further purification. The metal contents were determined using standard procedure¹⁷. Electronic spectra were measured on Cary-2390 spectrophotometer. IR spectra of ligand as well as metal complexes were taken on Perkin-Elmer model-577 using KBr disc. Magnetic susceptibility was measured by Gouy method using Hg[Co(NCS)₄] as a calibrant. Molar conductance of the complexes were measured by Systronics conductivity meter model 303 in DMF.

Preparation of ligand (EICS): The ligand was synthesized by condensing 2-ethylindole-3-carboxaldehyde (0.001 M) dissolving in ethanol with ethanolic solution of semicarbazide hydrochloride (0.001 M) in presence of 10 % sodium acetate solution in THF. The reaction mixture was refluxed in water bath for 5 h and resulting mixture was poured in crushed ice when colourless precipitate was obtained. It was filtered, washed several times with water, recrystallized from ethanol and finally dried in electric oven, m.p. 147 ± 1 °C, yield 65 % (Table-1).

Preparation of the complexes: The complexes of the type [M(EICS)₂X₂] (where M = Co(II), Ni(II) or Cu(II); EICS = 2-ethylindole-3-carboxaldehyde semicarbazone; X = Cl⁻, Br⁻, I⁻ or NO₃⁻) were prepared by refluxation precipitation procedure. The hot ethanolic solution of the ligand 2-ethylindole-3-carboxaldehyde semicarbazone [EICS] (0.002 M) was mixed with ethanolic solution of respective metal salt (metal halide/ metal nitrate) (0.001 M). The resulting mixture was heated on water bath for 3-4 h with occasional stirring. On cooling, coloured complexes were obtained which was filtered and washed with cold ethanol. The procedure carried out in each case was of similar nature with slight variation of timing of reflux. Yield in all cases 70-75 % (Table-1).

RESULTS AND DISCUSSION

The IR spectra of the ligand as well as complexes have been measured in the region 4000-200 cm⁻¹. The IR spectra of

TABLE-1
ANALYTICAL, MOLAR MASS, MAGNETIC SUSCEPTIBILITY, MOLAR CONDUCTIVITY, DECOMPOSITION TEMPERATURE AND ELECTRONIC SPECTRAL DATA OF THE LIGAND EICS AND ITS METAL COMPLEXES

Compounds (Colour)	Mol. mass	Yield (%)	Elemental analysis (%): Found (calcd.)				μ_{eff} (BM)	Ω_m (ohm ⁻¹ cm ² mol ⁻¹)	DT (°C)	μ_{max} electronic (cm ⁻¹)
			M	C	N	H				
EICS (Colourless)	247	65	–	58.10 (58.20)	22.50 (22.67)	6.02 (6.07)	–	–	–	–
[Co(EICS) ₂ Cl ₂] (Brown)	623.93	72	9.35 (9.44)	46.03 (46.15)	17.87 (17.95)	4.71 (4.80)	4.93	7.1	193	9760, 17340, 23410
[Co(EICS) ₂ Br ₂] (Brown)	712.74	71	8.16 (8.26)	3.94 (4.04)	15.60 (15.71)	4.12 (4.20)	4.87	8.1	186	9748, 17290, 23440
[Co(EICS) ₂ I ₂] (Brownish red)	806.73	74	7.19 (7.30)	35.56 (35.69)	13.76 (13.88)	3.66 (3.71)	4.96	10.3	201	9768, 17280, 23530
[Co(EICS) ₂ (NO ₃) ₂] (Brownish red)	676.93	70	8.61 (8.70)	42.45 (42.54)	16.45 (16.54)	4.30 (4.43)	5.1	10.7	189	9730, 17200, 23436
[Ni(EICS) ₂ Cl ₂] (Green)	623.71	72	9.32 (9.41)	46.09 (46.17)	17.86 (17.95)	4.71 (4.80)	2.97	10.9	178	11200, 18300, 25300
[Ni(EICS) ₂ Br ₂] (Green)	712.52	71	5.17 (5.25)	40.29 (40.41)	15.62 (15.71)	4.15 (4.21)	3.1	10.4	183	11180, 15240, 25270
[Ni(EICS) ₂ I ₂] (Green)	805.51	70	7.23 (7.30)	35.62 (35.70)	13.77 (13.85)	3.64 (3.71)	3.4	10.2	188	11130, 15210, 25340
[Ni(EICS) ₂ (NO ₃) ₂] (Green)	767.71	74	8.58 (8.70)	42.42 (42.55)	16.45 (16.55)	4.37 (4.43)	3.12	10.1	173	11320, 18170, 25310
[Cu(EICS) ₂ Cl ₂] (Blue)	628.54	70	10.02 (10.10)	45.75 (45.82)	17.72 (17.81)	14.65 (14.77)	1.94	7.1	207	16430, 21400
[Cu(EICS) ₂ Br ₂] (Blue)	717.35	71	8.76 (8.85)	40.3 (40.14)	15.55 (15.61)	4.11 (4.18)	1.91	8.3	211	16420, 21460
[Cu(EICS) ₂ (NO ₃) ₂] (Deep blue)	681.54	72	9.22 (9.32)	41.91 (42.01)	16.35 (16.43)	4.31 (4.40)	1.86	8.3	211	16380, 21330

DT= Decomposition temperature.

TABLE-2
IR SPECTRAL DATA OF LIGAND EICS AND Co(II), Ni(II) AND Cu(II) METAL COMPLEXES

Compounds	$\nu(\text{N-H})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$	$\nu(\text{M-X})$
EICS	3370 s,b	1760 s,b	1480 m,b	–	–	–
[Co(EICS) ₂ Cl ₂]	3370 s,b	1740 m,b	1455 m,b	510 m	450 m	310 m
[Co(EICS) ₂ Br ₂]	3370 s,b	1740 m,b	1455 m,b	515 m	460 m	325 m
[Co(EICS) ₂ I ₂]	3370 s,b	1740 m,b	1455 m,b	515 m	465 m	315 m
[Co(EICS) ₂ (NO ₃) ₂]	3370 s,b	1740 m,b	1455 m,b	515 m	460 m	–
[Co(EICS) ₂ (ClO ₄) ₂]	3370 s,b	1740 m,b	1450 m,b	515 m	460 m	–
[Ni(EICS) ₂ Cl ₂]	3370 s,b	1730 m,b	1460 m,b	540 m	450 m	260 m
[Ni(EICS) ₂ Br ₂]	3370 s,b	1730 m,b	1460 m,b	540 m	455 m	275 m
[Ni(EICS) ₂ I ₂]	3370 s,b	1730 m,b	1460 m,b	535 m	460 m	–
[Ni(EICS) ₂ (NO ₃) ₂]	3370 s,b	1730 m,b	1460 m,b	535 m	465 m	–
[Cu(EICS) ₂ Cl ₂]	3370 s,b	1735 m,b	1455 m,b	550 m	470 m	280 m
[Cu(EICS) ₂ Br ₂]	3370 s,b	1735 m,b	1450 m,b	540 m	475 m	310 m
[Cu(EICS) ₂ (NO ₃) ₂]	3370 s,b	1735 m,b	1450 m,b	540 m	475 m	–

the ligand shows strong band at 1480 cm⁻¹ assignable^{18,19} to the $\nu(\text{C=N})$. In the spectra of the complexes this band shows red shift with slightly reduced intensity. The shift of the band and change in intensity suggest coordination of the azomethine nitrogen with metal ion. The linkage with azomethine N is further supported by the appearance of a far IR band in the region 475-450 cm⁻¹ in the complexes assigned²⁰⁻²² to $\nu(\text{M-N})$. The next IR spectra of the ligand shows a sharp and strong band at 1760 cm⁻¹ assigned^{18,22,23} to $\nu(\text{C=O})$. In the spectra of the complexes of this band also show red shift appearing in the region at 1740 cm⁻¹ proposing coordination through carbonyl oxygen of semicarbazone moiety. The coordination with carbonyl oxygen atom is further supported by the appearance of a band in the far ir region at 550-510 cm⁻¹ assigned^{21,22,24} as $\nu(\text{M-O})$. The coordination through metal halogen is indicated by the appearance of a band in the region 325-260 cm⁻¹

assigned^{21,22} to $\nu(\text{M-X})$ (Cl⁻, Br⁻ or I⁻). The evidence of metal halogen is further supported by the low value of molar conductance of the complexes in the range 7.1-10.9 ohm⁻¹ cm² mol⁻¹.

On the basis of above IR spectral bands assignments, it is proposed that ligand EICS behaves as neutral bidentate manner and coordination may take place through azomethine nitrogen and carbonyl oxygen atoms of semicarbazone moiety. The remaining coordination positions of metal ions are occupied by anions such as, Cl⁻, Br⁻, I⁻ and NO₃⁻. The bands at 1550 and 1430 cm⁻¹ with a separation of 120 cm⁻¹ indicates mono coordinated behaviour of nitrate group^{25,26}.

The Co(II) complexes exhibit three absorption bands in the region, 9730-9768, 17200-17340, 23410-23530 cm⁻¹ assignable 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. The above mentioned spectral bands indicate octahedral^{27,28} geometry for the Co(II) complexes.

The octahedral geometry of Co(II) complexes is also supported²⁹⁻³¹ by magnetic susceptibility value in the range 4.87-5.1 B.M. The Ni(II) complexes exhibit three absorption bands in the region 11130-11320, 18170-18300 and 25270-25340 cm⁻¹ respectively assignable to ${}^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$, ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$ and ${}^3T_{1g}(P) \leftarrow {}^3T_{2g}(F)$ transitions respectively. The above mentioned spectral bands propose octahedral geometry^{27,32} for Ni(II) complexes which is also supported^{30,31,33} by magnetic susceptibility values of the complexes in the range 2.97-3.12 B.M. The Cu(II) complexes exhibit two broad bands in the region 16380-16430 cm⁻¹ and 21330-21460 cm⁻¹ assigned to transitions ${}^2T_{2g} \leftarrow {}^2E_g$ and charge transfer band respectively which proposes octahedral^{27,34} geometry for Cu(II) complexes. The magnetic moment values for Cu(II) complexes are found in the range 1.86-1.94 BM^{30,31,35}.

The molar conductance values of the complexes of Co(II), Ni(II) and Cu(II) were found to be in the range 7.1-10.9 ohm⁻¹ cm² mol⁻¹ in DMF proposes their nonelectrolytic³⁶ nature. The molar conductance values also supported the structure assigned on the basis of physicochemical and spectroscopic measurements.

Antimicrobial activity: The ligand EICS and its complexes of Co(II), Ni(II) and Cu(II) complexes were screened for their antifungal activity against *Aspergillus niger* by disc diffusion technique³⁷ using DMF as solvent at concentration of 50 mg mL⁻¹. The activity was compared with known standard drug, diethane Z-78, respectively at same concentration 50 µg mL⁻¹.

It was observed that on comparison with references to fungicides the complexes were found to be more effective than ligands. The data indicates antifungal activity of complexes were found to be in the order Cu(II) > Ni(II) > Co(II). It is established from the literature³⁸ that the metal complexes show enhanced antimicrobial activity than free ligand. This is due to chelation, which reduces the polarity of metal ion due to partial sharing of its positive charge with ligand³⁹. The chelation increases lipophilic character in the complexes and results in the enhancement of fungicidal activity.

Conclusion

Thus on the basis of above observations it is concluded that the EICS acts as a neutral bidentate ligand and coordination is proposed through azomethine N and carbonyl oxygen of semicarbazone moiety. The remaining positions of metal ion is satisfied by negative ions such as Cl⁻, Br⁻, I⁻ and NO₃⁻. The geometry of the Co(II), Ni(II) and Cu(II) complexes are proposed to be octahedral in nature as shown in Fig. 1.

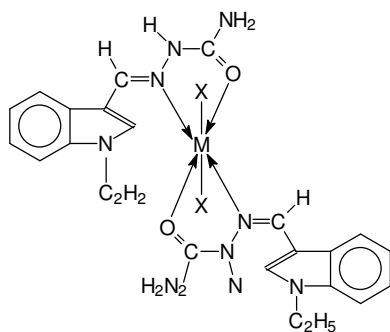


Fig. 1. $[M(EICS)_2]X_2$; M = Co(II), Ni(II); X = Cl⁻, Br⁻, I⁻ and NO₃⁻; M = Cu(II); X = Cl⁻, Br⁻ and NO₃⁻; EICS = 2-ethylindole-3-carboxaldehyde semicarbazone

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