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Synthesis, Physico-chemical and Antimicrobial Studies of Bidentate Schiff Base Complexes of Co(II), Ni(II) and Cu(II)⁺

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ABSTRACT

Neutral bidentate Schiff base ligand 3, 4-diethyl isoquinoline semicarbazone [DIES] and its complexes of Co(II), Ni(II) and Cu(II) complexes have been prepared. The ligand as well as metal complexes were characterized by analytical and physicochemical methods such as elemental analyses, molar mass, IR, U.V., magnetic susceptibility, molar conductance measurements. On the basis of these studies, it is proposed that DIES acts as neutral bidentate ligand and coordination proposed through azomethine nitrogen and carbonyl oxygen of semicarbazone moiety. On the basis of electronic spectra and magnetic susceptibility measurements, it is proposed that complexes have monomeric octahedral geometry. The ligand as well as metal complexes were also screened for their antimicrobial study.

Key words: Schiff base/ Co(II), Ni(II) and Cu(II)/ Semicarbazone/ Antimicrobial/ Antifungal studies.

INTRODUCTION

Isoquinolone derivatives are important heterocyclic compounds of biologically active compounds¹⁻⁵. They possess useful biological activities such as antimalarial⁶, antibacterial^{7,8}, antimicrobial⁹ activities. Keeping the above consideration and our earlier work¹⁰⁻¹⁷ on Schiff base metal complexes with first row transition metal complexes we herein report, synthesis, characterization and antimicrobial screening of Co(II), Ni(II) and Cu(II) metal complexes with Schiff base ligand 3, 4-diethyl isoquinolone semicarbazone [DIES].

EXPERIMENTAL

Preparation of ligand [DIES]

The ligand 3, 4-diethyl isoquinoline semicarbazone [DIES] was prepared by condensing quimolar quantities of 0.01 M of each 3, 4-diethyl isoquinolone (2.59 g) in 20 ml ethanol with aqueous ethanolic solution of semicarbazide hydrochloride (1.2 g). The reaction mixture was refluxed on water bath for 3 h. The solid which separated at the end of the refluxing period, was filtered, dissolved in boiling water and purified (charcol). Neutralisation with sodium carbonate solution gave colourless solid. m.p $-221 \pm 1^\circ\text{C}$; yield (60%).

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Preparation of the complexes

The Co(II), Ni(II) and Cu(II) complexes were synthesized by refluxation-precipitation method. The ethanolic solution of the ligand [0.002 M] was mixed with ethanolic solution of corresponding salts (metal halide/ metal nitrate/ 0.001 M) with occasional stirring. The resulting mixture refluxed for 3-4 h on water bath. On cooling, coloured complexes were precipitated out. It was filtered washed with cold ethanol and dried in electric oven. Yield 60-65%.

The percentage of C, H, N metal ions, IR, U.V. spectra were recorded at CDRI, Lucknow. Magnetic susceptibility were measured by Gouy method using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as a calibrant. Molar conductance were recorded on Systronics conductivity meter model 303 in DMF.

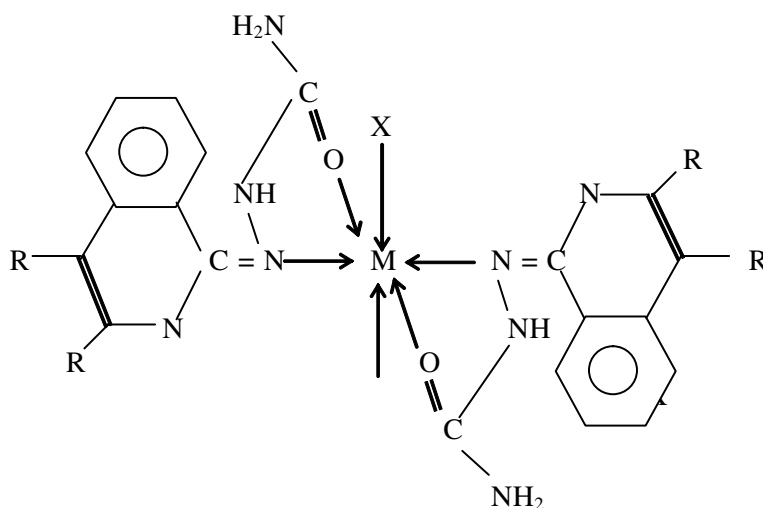
RESULTS AND DISCUSSION

The IR spectrum of the ligand DIES shows a broad band of medium intensity at 3460 cm^{-1}

assigned^{18,19} to $\nu_{\text{N-H}}$. The band without change in intensity indicating non-participation of N atom of either amino or imino group in the coordination with metal ion. The spectrum of the ligand shows a sharp and strong band at 1720 cm^{-1} assigned^{18,20,21} to $\nu_{\text{C=O}}$ group. In the complexes this band suffered a downward shift by $20\text{-}30\text{ cm}^{-1}$ in the complexes indicating the coordination of the carbonyl oxygen to the metal ion

The spectrum of the ligand shows a strong and broad band at 1480 cm^{-1} assigned^{18,21,22} to $\nu_{\text{C=N}}$. On complexation this band also suffered a downward shift in the spectra of the complexes indicating coordination of the metal ion through azomethine nitrogen atom of semicarbazone moiety.

The coordination through azomethine nitrogen and carbonyl oxygen atom of semicarbazone moiety as well as oxygen atom of NO_3^- are further supported by the appearance of bands in the far IR region at $570\text{-}540$ and $470\text{-}420$ assigned²³⁻²⁵ to $\nu_{\text{M-O}}$ and $\nu_{\text{M-N}}$. The linkage through metal-halogen is confirmed by the appearance of a band in the region $320\text{-}275\text{ cm}^{-1}$ assigned²³⁻²⁶ to $\nu_{\text{M-X}}$ (X = Cl⁻, Br⁻ and I⁻). These assignments are confirmed by the low molar conductance of the



$[\text{M}(\text{DIES})_2 \text{X}_2]$

M = Co(II), Ni(II); X = Cl⁻, Br⁻, I⁻ and NO_3^-

M = Cu(II); X = Cl⁻, Br⁻ and NO_3^-

R = Ethyl

Fig.1.

Table 1: Analytical and physicochemical measurements of ligand DIES and its metal complexes

Compounds electronic (Colour)	Mol. mass	Yield %	% Analysis found (calculated)				μ_{eff} B.M.	Ω_m ohm ⁻¹	DT °C	λ_{max} cm ⁻¹
			Metals	C	N	H				
DIES (Colourless)	259	60		64.74 (64.86)	21.49 (21.62)	7.26 (7.33)				
[Co(DIES) ₂ Cl ₂] (Brown)	647.93	62	8.93 (9.09)	52.01 (52.17)	17.28 (17.39)	5.82 (5.90)	4.84	3.2	169	9470, 17430, 24130
[Co(DIES) ₂ Br ₂] (Brown)	736.748	64	7.91 (7.99)	45.48 (45.60)	15.11 (15.20)	5.10 (5.15)	4.86	2.8	161	9430, 17470, 24100
[Co(DIES) ₂ I ₂] (Brownish red)	830.73	63	6.95 (7.09)	40.31 (40.44)	13.37 (13.48)	4.48 (4.57)	4.89	8.4	164	9490, 16990, 24170
[Co(DIES) ₂ (NO ₃) ₂] (Brownish red)	700.93	61	8.31 (8.40)	47.84 (47.93)	15.88 (15.97)	5.06 (5.13)	4.99	2.9	173	10110, 16930, 24140
[Ni(DIES) ₂ Cl ₂] (Green)	647.71	60	8.96 (9.06)	51.74 (51.87)	17.18 (17.29)	5.80 (5.86)	3.04	4.3	183	1330, 19360, 25340
[Ni(DIES) ₂ Br ₂] (Green)	736.528	62	7.90 (7.97)	45.50 (45.61)	15.09 (15.20)	4.79 (5.86)	3.08	5.2	180	13390, 19330, 25210
[Ni(DIES) ₂ I ₂] (Green)	830.52	61	6.93 (7.06)	40.33 (40.45)	13.39 (13.48)	5.79 (5.86)	3.1	6.4	179	13110, 19700, 25140
[Ni(DIES) ₂ (NO ₃) ₂] (Green)	700.71	62	8.29 (8.37)	47.80 (47.95)	15.89 (15.98)	5.09 (5.13)	3.06	5.7	177	13060, 19480, 25170
[Cu(DIES) ₂ Cl ₂] (Blue)	652.54	61	9.64 (9.73)	51.33 (51.49)	17.08 (17.16)	5.74 (5.82)	1.88	5.7	189	11470, 22340
[Cu(DIES) ₂ Br ₂] (Blue)	741.348	60	8.48 (8.57)	45.26 (45.38)	15.02 (15.10)	5.04 (5.12)	1.92	4.7	171	11320, 22280
[Cu(DIES) ₂ (NO ₃) ₂] (Deep blue)	705.54	60	8.91 (9.00)	47.53 (47.64)	15.78 (15.87)	5.30 (5.38)	1.94	4.5	163	11290, 22240

DT = Decomposition Temperature

Table 2: IR spectral data of ligand DIES and Co(II), Ni(II) and Cu(II) metal complexes

Compounds	$\nu_{\text{N-H}}$	$\nu_{\text{C=O}}$	$\nu_{\text{C=N}}$	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-X}}$
DIES	3260 s,b	1700 s,b	1480 s,b			
[Co(DIES) ₂ Cl ₂]	3260 s,b	1675 m,b	1455 m,b	540 m	445 m	300 m
[Co(DIES) ₂ Br ₂]	3260 s,b	1675 s,b	1455 m,b	525 m	445 m	320 m
[Co(DIES) ₂ I ₂]	3260 s,b	1670 s,b	1450 s,b	520 m	440 m	310 m
[Co(DIES) ₂ (NO ₃) ₂]	3260 s,b	1695 s,b	1455 s,b	515 m	445 m	
[Ni(DIES) ₂ Cl ₂]	3260 s,b	1670 s,b	1450 m,b	540 m	420 m	280 m
[Ni(DIES) ₂ Br ₂]	3260 s,b	1670 s,b	1455 m,b	540 m	430 m	275 m
[Ni(DIES) ₂ I ₂]	3260 s,b	1675 s,b	1450 m,b	535 m	435 m	
[Ni(DIES) ₂ (NO ₃) ₂]	3260 s,b	1670 s,b	1455 s,b	520 m	440 m	
[Cu(DIES) ₂ Cl ₂]	3260 s,b	1670 s,b	1455 s,b	535 m	445 m	280 m
[Cu(DIES) ₂ Br ₂]	3260 s,b	1670 s,b	1460 m,b	535 m	440 m	305 m
[Cu(DIES) ₂ (NO ₃) ₂]	3260 s,b	1670 s,b	1460 m,b	530 m	470 m	

m = medium, s = strong, b = broad

complexes in the range 2.8-6.4 ohm⁻¹ cm² mol. The significant band at 1520 cm⁻¹ and 1420 cm⁻¹ with a separation of 120 cm⁻¹ indicates monocoordinate nature of nitrate group²⁷.

The electronic spectral²⁸ and magnetic susceptibility measurements²⁹⁻³⁰ suggest octahedral geometry for the complexes which is justified by other physico-chemical as well as IR spectral data.

Conductivity measurement

Molar conductance values of the complexes of Co(II), Ni(II) and Cu(II) were found to be in the range 2.8-6.4 cohm⁻¹ mol⁻¹ cm² in DMF which proposes their non electrolytic³¹ nature. The molar conductance values also supported the structure assigned on the basis of physicochemical and spectroscopic measurements.

Antifungal activity

Fungicidal activity of the ligand DIES and their metal complexes of Co(II), Ni(II) and Cu(II) were done by disc plate method³² on *Penicillium expansum* and *Aspergillus flavus*. On comparison

with reference to fungicide, the complexes were found to be more effective than free ligand due to chelation theory³³.

CONCLUSION

Thus on the basis of above studies it is concluded that the ligand DIES acts in a bidentate manner and coordination is proposed through azomethine N and thione S of thiosemicarbazone moiety. The remaining center of metal ions are satisfied by negative ions such as Cl⁻, Br⁻, I⁻ or NO₃⁻. On the basis of physicochemical and spectroscopic observations it is proposed that the geometry of the complexes of the type [M(DIES)₂X₂] are monomeric octahedral in geometry as shown in Fig.1.

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REFERENCES

1. Elguero J., Comprehensive heterocyclic chemistry (ed.) A Mckillop (Oxford-Pergaman Press) **5**: 167 (1984).
2. Penning T. D., Talley J. J., Bertenshaw S. R., Carter J. S., Colins P. W., Graneton J. M., Lee L.F. and Malecha J. W., *J. Med. Chem.*, **40**: 1347 (1997).
3. Menozzi G., Mosti L., Fossa P., Maltoli F. and Ghia M., *J. Heterocycl. Chem.*, **34**: 963 (1997).
4. Verma M., Nath S., Singh K.N. and James P. S., *Acta Pharmaceutica*, **54**: 49 (2004).
5. Kidwai M. and Negi N., *Monatsh; Chem.*, **128**: 85 (1997).
6. Joshi A. A., Narkhede S. S. and Viswanathan C. L., *Bioorg. Med. Chem. Lett.*, **15**: 73 (2005).
7. Suresh T., Nandha R. Kumar, Magesh S. and Mohan P. S., *Indian J. Chem.*, **42B**: 688 (2003).
8. Suresh T., Nandha R. Kumar, Magesh S. and Mohan P. S. Mohan, *Indian J. Chem.*, **42B**: 2133 (2003).
9. Selvi S. T., Nadaraj V., Mohan S., Sasi R. and Hema M., *Biorg. Ed. Chem.*, **14**: 3896 (2006).
10. a) Rai B. K. and Sharma K., *Asian J. Chem*, **20**: 137 (2008).
b) Rai B. K., Rai R, Sahi P. and Rana Swaty, *Asian J. Chem*, **20**: 143, 149 (2008).
11. Rai B. K., Kumar Arbind, *Ultra J. Chem*, **4**: 179 (2008).
12. a) Rai B. K. and Vinayak, *J. Ultra Chem*, **5**: 67 (2009)
b) Rai B. K., Kumar Arvind and Ravishankar, *Ultra J. Chem*, **5**: 73 (2009).
c) Rai B. K., Kumari Sapna, Singh R. K., Prasad Anukul, Sinha M. P. and Mishra P. M., *Ultra J. Chem*, **5**: 83 (2009)
d) Prasad Anukul and Rai B. K., *Orient J. Chem*, **25**: 175 (2005).
13. a) Rai B. K., Baluni A., Prasad Anukul, Thakur R. and Prakash Prem, *Asian J. chem.*, **21**: 3708, 3713 (2009)
b) Rai B. K., Ravishankar and Pandey S., *Asian J. Chem*, **21**: 5409, 5994 (2009).
14. a) Rai B. K., Prasad Anukul, Vinayak, Kumar Arbind and Jha Shaktidhar 'Sunit', *Asian J. Phys.*, **18**: 63 (2009).
b) Rai B. K., Singh Vineeta, Vinayak, Singh Shiv Pujan and Jha Shaktidhar 'Sunit', *Asian J. Phys.*, **18**: 63 (2009)
c) Rai B. K., *J. Ind. Council Chem*, **26**: 121 (2009).
d) Rai B. K., *Asian J. Chem.*, **22**: 2761 (2010).
15. a) Rai B. K. and Kumar Chandan, *Asian J. Chem.*, **22**: 5613 (2010).
b) Rai B. K. and Singh Sateydeo, *Asian J. Chem.*, **22**: 5619.
c) Rai B. K. and Sharma K. K., *Asian J. Chem.*, **22**: 5625 (2010).
16. Rai B. K., Kumar H., Sharma M. and Rastogi V. K., *J. Indian Chem Soc.*, **87**: 1241 (2010).
17. a) Kishore R. K. and Rai B. K., *Asian J. Chem.*, **22**: 8055 (2010).
b) Rai B. K.I and Kumar Bimal, *Asian J. Chem.*, **22**: 8073 (2010).
c) Rai B. K. and Singh S., *Orient J. Chem.*, **26**: 989 (2010).
d) Rai B. K. and Kumar Chandan, *Orient J. Chem.*, **26**: 1019 (2010).
18. Kemp William, Organic Spectroscopy, Polgrave, Macmillan Press Ltd, New York, R. M. Silverstein and F. X. Webster, Spectrometric Identification of Organic Compounds 6th edn, John Wiley and Sons, 109 (2008).
19. Patil M. S. and Shah J. R., *J. Indian Chem; Soc*, **58**: 944 (1981).
20. Chaterjee B., *Coord. Chem., Revs.*, **26**: 281 (1978).
21. Rao C.N., Chemical Application of IR Spectroscopy, Academic Press, New York, 260 (1963).
22. Maurya R.C., Patel P. and Rajput S., *Synth. React. Inorg. Metal-Org. Chem.*, **33**: 817 (2003).
23. Ferraro J. R., "Low Frequency Vibration of Inorganic and Co-ordination Compound", Plenum Press, New York.
24. Goldstein M. and Unswarth D., *Inorg. Chim, Acta*, **4**: 342 (1970).

25. Bellamy L.J., *The Infrared Spectra of Complex Molecules*, Vols 1 and 2, Chapman and Hall, London, (1975).
26. Nyquist R.A., Putzig C.L., Leugers M.A., *Infrared and Raman Spectral Atlas of Inorganic Compounds and Organic Salts*, Academic Press, New York, (1995).
27. Addison C.C., Logan N., Wallwork S.C. and Barner D.C., *Quart. Rev.*, (1971).
28. a) Lever, A.B.P., *Inorganic Electronics Spectroscopy*, Elsevier Amsterdam, 395 (1968);
b) Jorgenson, C. K., *Acta Chem.; Scand*, **19**: 887 (1966).
c) Allen J. R., Brown D.H., Nutal R. H. and Sharp D. W. A, *J. Inorg Nucl. Chem*, **26**: 1895 (1964).
29. Figgis B. N., *Introduction to Ligand Field*, Wiley Eastern Ltd., New Delhi, 279 (1976).
30. Carlin R.L. and Van A.J. Drynevedt, *Magnetic Properties of Transition Metal Compounds*, Springer Verlag, New York, (1997).
31. a) Wolmsley J. A. and Tyree S. V., *Inorg. Chem.*, **2**: 312 (1963).
b) Sathyanarayan D.N. and Patel C.C., *Indian J. Chem.*, **5**: 360 (1967).
32. Mukherjee P. K., Saha K., Giri S.N., Pal M. and Saha B. P.; *Indian J. Microbiology*, 35 (1995).
33. Nishant N., Ahmad S. and Ahmad R. T., *J. Appl. Polym. Sci.*, **100**: 928 (2006).