Asian Journal of Chemistry Vol. 22, No. 10 (2010), 8073-8078

Synthesis, Characterization and Antimicrobial Screening of Some 3*d*-Metal Complexes of N and O Containing Schiff Bases

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Complexes of Co(II), Ni(II) and Cu(II) with 8,8-dimethyl-2,3,4, 5,7,8-hexahydro diazepino[2,1-b]benzothiazol-10(9*H*) semicarbazone [DHDBS] have been prepared and their characterization have been done by microanalytical data, IR, UV, molar conductance and magnetic measurements. On the basis of above physicochemical and spectroscopic measurements, it is proposed that the compound DHDBS behaves as a neutral bidentate ligand and coordination proposes through azomethine N and carbonyl oxygen atom of semicarbazone moiety. The remaining positions of metal ions are satisfied by negative ions, such as, Cl^-, Br^-, I^- and NO_3^-. Electronic spectral data and magnetic susceptibility measurement proposes octahedral geometry for the complexes. The complexes are also screened for their antimicrobial potential against selected bacteria and fungi.

Key Words: DHDBS, Schiff base, Co(II), Ni(II), Cu(II) complexes, Antimicrobial studies.

INTRODUCTION

The use of antibiotic in medicine has resulted in an increasing number of resistant strains of microorganism, through mutation and Gene transfer. This alarming situation and accelerating rate of resistance is creating life threatening effect for society. Increasing of drug resistant microorganism and new emerging diseases coupled with the toxicity and unavailability of alternative non toxic medicine, which may be Schiff base compound with improved properties and extended antibacterial spectrum towards the future resistant strains[1-5]. The study of these new Schiff bases provide the basis for developing functional models as antiviral, antifungal, antimalarial, anticancer and antibacterial properties. Literature survey indicate the biocidal activity of Schiff base is increased[6] many fold on coordination with suitable metal ion. Keeping the above facts in mind and in continuation of earlier work[7-15] in this field, the synthesis and characterization of Co(II), Ni(II) and Cu(II) complexes with Schiff base, 8,8-dimethyl-2,3,4,5,7,8-hexahydro diazepino[2,1-b]benzothiazol-10(9*H*)-semicarbazone [DHDBS] are reported in this paper.

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EXPERIMENTAL

All the chemicals used were of Analytical grade and were used without further purification.

The metal contents were determined using standard method[16]. IR spectra of the ligand DHDBS and its complexes were measured on Perkin-Elmer model-577 using KBr disc. Electronic spectra were measured on Carry-2390 spectrophotometer. Magnetic susceptibility were measured by Gouy method using $Hg[Co(NCS)_4]$ as a calibrant. Molar conductivity of the complexes were measured by Systronics conductivity meter model 303 in DMF.

Preparation of Schiff base [DHDBS]: The ligand 8,8-dimethyl-2,3,4,5,7,8-hexahydro diazepino[2,1-b]benzothiazol-10(9*H*)semicarbazone was prepared by condensing equimolar quantity of dissolving minimum volume of ethanol with ethanolic solution of semicarbazide hydrochloride (0.001 M) dissolving in 10 % solution of sodium acetate in THF with ethanolic solution of 8,8-dimethyl-2,3,4,5,7,8-hexahydro diazepino[2,1-b]benzothiazol-10(9*H*)one (0.001 M). The resulting mixture were refluxed on water bath for 4 h. The solid which separated at the end of refluxing period was filtered and cooled with ethanol several times to remove any unreacted ligand. Finally the compound was recrystallized with THF and dried as yellow coloured solid (yield 65 %, m.p.176 ± 1 ºC).

Preparation of the complexes: The complexes of Co(II), Ni(II) and Cu(II) were prepared by refluxation and precipitation method. The ethanolic solution of the ligand (0.002 M) was mixed with ethanolic solution of corresponding metal (metal halide/metal nitrate) (0.001 M) was mixed occasional stirring. The resulting mixture was refluxed on water bath for 3-4 h. On cooling, coloured complexes were obtained which were filtered, washed with cold ethanol. The procedure carried out in each case were similar nature with slight variation of timing of reflux (yield in all cases 60-65 %). The analytical data of the metal complexes are given in Table-1.

RESULTS AND DISCUSSION

The IR spectra of the ligand shows a broad band of medium intensity at 3200 cm^{-1}, assigned[17,18] to ν(N-H). The spectra of all the complexes show this band without change in position and intensity, clearly indicating non involvement of nitrogen atom of either primary or secondary amino group with metal ion. The next spectrum of the ligand shows a sharp and strong band at 1720 cm^{-1} assigned[17,19] to ν(C=O). In the spectra of the complexes this band has shifted to lower wave number with slightly reduced intensity. The shift of the band and change in intensity suggest coordination of >C=O group of semicarbazone to the metal ion. The other IR band of structural significance in the spectra of the ligand appears at 1500 cm^{-1} assigned[17,20] to ν(C=N) group. This band also suffered a downward shift by 20-30 cm^{-1} in the complexes indicating the coordination of the nitrogen to the metal ion.

TABLE-1
ANALYTICAL, COLOUR MOLAR MASS, MAGNETIC SUSCEPTIBILITY, ELECTRONIC SPECTRA, MOLAR CONDUCTANCE DATA AND DECOMPOSITION TEMPERATURE OF LIGAND DHDBS AND ITS METAL COMPLEXES

Compound (Colour)	Mol. Mass (Yield, %)	Elemental analysis (%): Found (Calcd.)				μ_{eff} (BM)	λ_{max} electronic (cm^{-1})	Ω_m (ohm^{-1} cm^2 mol^{-1})	DT (ºC)
		M	C	N	H				
DHDBS (Yellow)	307 (65)	–	54.65 (54.72)	22.70 (22.80)	6.75 (6.84)	–	–	–	–
$[Co(DHDBS)_2Cl_2]$ (Red)	743.93 (65)	7.83 (7.92)	45.04 (45.16)	18.73 (18.81)	4.25 (4.30)	4.96	10360, 17470, 22300	3.6	183
$[Co(DHDBS)_2Br_2]$ (Red)	832.74 (64)	6.95 (7.07)	40.22 (40.34	16.73 (16.81)	3.77 (3.84)	4.83	10140, 17430, 22320	3.1	192
$[Co(DHDBS)_2I_2]$ (Rose red)	926.73 (62)	6.26 (6.35)	36.14 (36.25)	15.01 (15.10)	3.38 (3.45)	4.99	10220, 17490, 22430	4.3	197
$[Co(DHDBS)_2(NO_3)_2]$ (Deep Red)	796.93 (63)	7.31 (7.39)	42.04 (42.16)	17.46 (17.56)	3.94 (4.01)	4.88	102691, 17520, 22470	4.7	187
$[Ni(DHDBS)_2Cl_2]$ (Green)	743.71 (63)	7.80 (7.85)	45.03 (45.17)	18.74 (18.82)	4.23 (4.30)	3.16	12730, 18300, 24300	4.7	196
$[Ni(DHDBS)_2Br_2]$ (Green)	832.52 (62)	6.93 (7.05)	40.22 (40.35)	16.70 (16.81)	3.78 (3.84)	3.16	12770, 18240, 24210	5.4	201
$[Ni(DHDBS)_2I_2]$ (Greenish brown)	726.51 (60)	6.24 (6.33)	36.14 (36.26)	15.02 (15.11)	3.39 (3.45)	3.11	12710, 15300, 24370	6.1	207
$[Ni(DHDBS)_2(NO_3)_2]$ (Deep brown)	796.71 (63)	7.28 (7.36)	42.04 (42.17)	17.48 (17.57)	3.95 (4.01)	3.12	12670, 16280, 24280	5.8	209
$[Cu(DHDBS)_2Cl_2]$ (Blue)	748.54 (62)	8.32 (8.48)	44.78 (44.88)	18.61 (18.70)	4.20 (4.27)	1.96	11400, 26340	4.9	217
$[Cu(DHDBS)_2Br_2]$ (Blue)	837.35 (64)	7.50 (7.58)	40.01 (40.12)	16.62 (16.71)	3.76 (3.82)	1.89	11470, 26430	5.6	202
$[Cu(DHDBS)_2(NO_3)_2]$ (Blue)	801.54 (65)	7.84 (7.92)	41.80 (41.91)	17.33 (17.46)	3.92 (3.99)	1.94	11450, 26360	5.9	201

DT = Decomposition temperature.

The coordination through azomethine nitrogen and oxygen atom are further supported by the appearance of bands in the far infrared regions at 500-530, 475-425 assigned to ν(M-O)[21-25] and ν(M-N)[21-25], respectively (Table-2).

IR bands at 1660 and 1530 cm^{-1} with a separation of 120 cm^{-1} suggest mono coordinated[26] behaviour of NO_3^- ion. The evidence of metal halogen is confirmed by the appearance of a band in the region 325-265 cm^{-1} assigned[21-25] to ν(M-X) (X = Cl^-, Br^- and I^-). These assignments are supported by low value of molar conductance of the complexes lie in the range 3.1-6.7 ohm^{-1} cm^2 mol^{-1} indicating non electrolytic[27] nature of the complexes (Table-1).

The electronic spectral and magnetic moment data (Table-1) propose octahedral geometry of the complexes. On the basis of studies, the probable structure of the complexes are given in Fig. 1.

TABLE-2
SALIENT FEATURES OF INFRARED SPECTRAL BANDS OF
LIGAND DHDBS AND ITS METAL COMPLEXES

Compounds	ν(N–H)	ν(C=O)	ν(C=N)	ν(M–O)	ν(M–N)	ν(M–X)
DHDBS	3420 s,b	1740 s,b	1475 s,b	–	–	–
$[Co(DHDBS)_2Cl_2]$	3420 s,b	1720 m,b	1450 m,b	535 m	450 m	305 m
$[Co(DHDBS)_2Br_2]$	3420 s,b	1715 m,b	1455 m,b	535 m	455 m	320 m
$[Co(DHDBS)_2I_2]$	3420 s,b	1715 m,b	1450 m,b	530 m	475 m	315 m
$[Co(DHDBS)_2(NO_3)_2]$	3420 s,b	1715 m,b	1455 m,b	530 m	470 m	–
$[Ni(DHDBS)_2Cl_2]$	3420 s,b	1720 m,b	1450 m,b	535 m	470 m	285 m
$[Ni(DHDBS)_2Br_2]$	3420 s,b	1715 m,b	1455 m,b	530 m	465 m	280 m
$[Ni(DHDBS)_2I_2]$	3420 s,b	1720 m,b	1455 m,b	520 m	465 m	–
$[Ni(DHDBS)_2(NO_3)_2]$	3420 s,b	1720 m,b	1455 m,b	530 m	450 m	–
$[Cu(DHDBS)_2Cl_2]$	3420 s,b	1720 m,b	1455 m,b	520 m	475 m	285 m
$[Cu(DHDBS)_2Br_2]$	3420 s,b	1720 m,b	1455 m,b	520 m	470 m	310 m
$[Cu(DHDBS)_2(NO_3)_2]$	3420 s,b	1720 m,b	1450 m,b	525 m	470 m	–

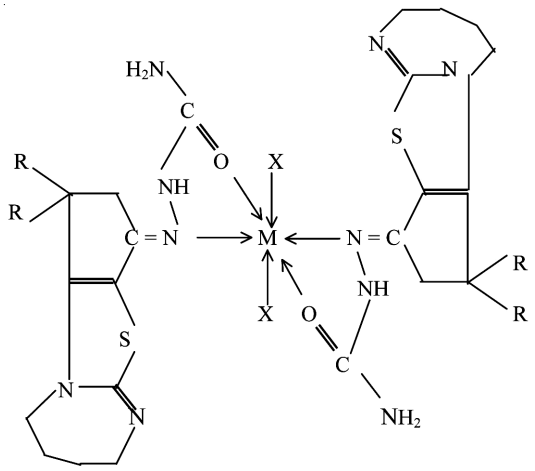

Fig. 1. $[M(DHDBS)_2X_2]$; M = Co(II) and Ni(II); X = Cl^-, Br^-, I^- and NO_3^-; M = Cu(II); X = Cl^-, Br^- and NO_3^-

Antimicrobial screening: Biocidal screening effects of the prepared ligand and complexes were tested against bacteria such as *Escherichia coli* by the disc plate diffusion method[28] using agar nutrient as the medium and streptomycin as the standard. The antifungal activities of the ligand and complexes were evaluated by the disc diffusion method[28] against the fungi *viz. Aspergillus niger* cultured on potato dextrose agar as a standard. The stock solution (10^{-2} M) was prepared by dissolving the prepared compounds in ethanol and the solutions were serially diluted in order to find out the minimum inhibitory concentration values. Filter paper disc after incubating for a period of 72 h at room temperature were recorded in Table-3. It is observed that the complexes were found to be more effective than free ligand which is also supported by the literature[29-31] (Table-3).

TABLE-3
ANTIBACTERIAL AND ANTIFUNGAL DATA OF THE LIGAND DHDBS AND ITS COMPLEXES [MIC CONCENTRATION × 10^{-2} M]

Compounds	Antibacterial screening *E. coli*	Antifungal screening *A. niger*
$[Co(DHDBS)_2Cl_2]$	3.4	4.2
$[Co(DHDBS)_2(NO_3)_2]$	3.6	4.3
$[Ni(DHDBS)_2Cl_2]$	4.7	5.1
$[Ni(DHDBS)_2(NO_3)_2]$	4.9	5.4
$[Cu(DHDBS)_2Cl_2]$	6.3	6.7
$[Cu(DHDBS)_2(NO_3)_2]$	6.9	7.2

Conclusion

On the basis of above mentioned observations, the complexes tentatively propose the octahedral geometry as shown in Fig. 1.

ACKNOWLEDGEMENT

One of the authors (B.K.R.) is grateful to University Grant Commission, for financial assistance Fellowship [Grant No.PSB-001/08-09 dated 12 Dec-2008].

REFERENCES

1. E.M. Hidnot and W.J. Dunn, *J. Med. Chem.*, **15**, 339 (1972).
2. H. Sigel and A. Sigel, Metals Ions in Biological Systems, Mercel Decker, New York, Vol. 1-40 (1973).
3. A.P. Mishra, M. Khare and S.K. Gautam, *Synth. React. Inorg. Metal Org. Chem.*, **32**, 1485 (2002).
4. S. Sanabhore, S. Padhye, D. Billington, D. Rathbore, S. Franzblau, C.E. Anson and A.K. Powell, *J. Inorg. Biochem.*, **90**, 127 (2002).
5. K.H. Thomson, J.H. Moneil and C. Orvig, *Chem. Rev.*, **99**, 2561 (1999).
6. D.C. Crans, J.J. Srmee, E. Gaidamaskas and L. Yang, *Chem. Rev.*, **104**, 849 (2004).
7. B.K. Rai and K. Sharma, *Orient. J. Chem.*, **22**, 645 (2006).
8. B.K. Rai, P. Choudhary, U.P. Singh, P. Sahi, Z. Hussain and S. Rana, *Orient. J. Chem.*, **23**, 271, 291 (2007).
9. B.K. Rai, I. Kostova, S.P. Ojha, R. Tomar and V.K. Rastogi, *Asian J. Phys.*, **16**, 29 (2007); B.K. Rai, *Asian J. Phys.*, **16**, 71 (2007); B.K. Rai, H.C. Rai, S.P. Singh, R. Tomar and O. Prakash, *Asian J. Phys.*, **16**, 76 (2007).
10. B.K. Rai and K. Sharma, *Asian J. Chem.*, **20**, 137 (2008); B.K. Rai, R. Rai, P. Sahi and S. Rana, *Asian J. Chem.*, **20**, 143, 149 (2008).
11. B.K. Rai, Z. Hussain, U.P. Singh, S.N. Prasad, A. Prasad and P.M. Mishra, *Ultra J. Chem.*, **4**, 53 (2008); B.K. Rai and S.N. Prasad, *J. Ultra Chem.*, **4**, 71 (2008); B.K. Rai and A. Kumar, *Ultra J. Chem.*, **4**, 179 (2008); B.K. Rai, *J. Indian Coun. Chem.*, **25**, 137 (2008).
12. B.K. Rai and Vinayak, *Ultra J. Chem.*, **5**, 67 (2009); B.K. Rai, A. Kumar and Ravishankar, *Ultra J. Chem.*, **5**, 73 (2009); B.K. Rai, S. Kumari, R.K. Singh, A. Prasad, M.P. Sinha and P.M. Mishra, *Ultra J. Chem.*, **5**, 83 (2009).
13. B.K. Rai, A. Baluni, A. Prasad, R. Thakur and P. Prakash, *Asian J. Chem.*, **21**, 3708, 3713 (2009); B.K. Rai, Ravishankar and S.N. Pandey, *Asian J. Chem.*, **21**, 5409, 5994 (2009).
14. A. Prasad and B.K. Rai, *Orient. J. Chem.*, **25**, 175 (2009); B.K. Rai, *J. Indian Coun. Chem.*, **26**, 121 (2009); B.K. Rai, *Asian J. Chem.*, **23**, 2761 (2010).

15. B.K. Rai, A. Prasad, Vinayak, S.P. Singh and S.J. Sunit, *Asian J. Phys.*, **18**, 63 (2009); B.K Rai, V. Singh, Vinayak, S.P. Singh and S.J. Sunit, *Asian J. Phys.*, **18**, 67 (2009).
16. A.I. Vogel, in eds.: J. Mendham, R.C. Denny, J.D. Barnes and M. Thomas, A Textbook of Quantitative Chemical Analysis, Pearson Education (2008).
17. W. Kemp, in eds.: R.M. Silverstein and F. X. Webster, Organic Spectroscopy, Polgrave, MacMillan Press Ltd., New York, Spectrometric Identification of Organic Compounds, John Wiley & Sons, edn. 6, p. 109 (2008).
18. M.S. Patil and J.R. Shah, *J. Indian Chem. Soc.*, **58**, 944 (1981).
19. B. Chatterjee, *Coord. Chem. Rev.*, **26**, 281 (1978).
20. A. Rana, R. Dinda, P. Sengupta, S. Ghosh and L. Falvello, *Polyhedron*, **21**, 1023 (2002).
21. J.R. Ferraro, Low Frequency Vibration of Inorganic and Co-ordination Compound, Plenum Press, New York.
22. K. Nakanishi, Infrared Absorption Spectroscopy, Nankodo Company Ltd., Tokyo, p. 45 (1964).
23. K. Nakamoto, Spectroscopy and Structure of Metal Chelate Compounds, John Wiley, New York (1968); M. Goldstein and D. Unsworth, *Inorg. Chim. Acta*, **4**, 370 (1970).
24. M. Dolaz, M. Tumer and M. Digrak, *Transition Met. Chem.*, **29**, 528 (2004).
25. L.J. Bellamy, The Infrared Spectra of Complex Molecules, Chapman and Hall, London, Vol. 1 and 2 (1975).
26. R.A. Nyquist, C.L. Putzig and M.A. Leugers, Infrared and Raman Spectral Atlas of Inorganic Compounds and Organic Salts, Academic Press, New York (1995).
27. J.A. Wolmsley and S.V. Tyree, *Inorg. Chem.*, **2**, 312 (1963); D.N. Sathyanarayan and C.C. Patel, *Indian J. Chem.*, **5**, 360 (1967).
28. P.K. Mukherjee, K. Saha, J. Das, S.N. Giri, M. Pal and B.P. Saha, *Indian J. Microbiol.*, **35**, 327 (1995).
29. K.D. Rainsford and M.W. Whitehouse, *J. Pharmacol.*, **28**, 83 (1976).
30. R.K. Parasher and R.C. Sharma, *J. Inorg. Biochem.*, **28**, 225 (1987).
31. N. Nishant, S. Ahmad and R.T. Ahmad, *J. Appl. Polym. Sci.*, **100**, 928 (2006).

(*Received*: 25 March 2010; *Accepted*: 2 August 2010) AJC-8939