Asian Journal of Chemistry Vol. 22, No. 7 (2010), 5619-5624

Synthesis, Spectral Characterization and Antimicrobial Studies of 2,3,4,5-Tetrahydroindeno-[1,2-d]-thiazolo-[3,2-a]-pyrimidine-10(H)semicarbazone Complexes of Co(II), Ni(II) and Cu(II)¶

B.K. RAI* and SATEYDEV SINGH
Department of Chemistry, L.N.T. College, Muzaffarpur-842 002, India
E-mail: binodkr_rai@yahoo.co.in

A new series of transition metal complexes of Co(II), Ni(II) and Cu(II) have been synthesized from the Schiff base derived from 2,3,4,5-tetrahydroindeno-[1,2-d]-thiazolo-[3,2-a]pyrimidine-10(H)-one. Structural features were obtained from their elemental analysis, molar conductance, Molar mass, IR, electronic spectral study and magnetic susceptibility data. Based on the stoichiometries and spectroscopic studies, the complexes have general formula $[M(TITPS)_2X_2]$; where M = Co(II), Ni(II) and Cu(II); TITPS = 2,3,4,5-tetrahydroindeno-[1,2-d]-thiazolo-[3,2-a]-pyrimidine-10(H)semicarbazone; X = Cl^-, Br^-, I^- and NO_3^-. The electronic spectral and magnetic susceptibility data of the complexes suggest an octahedral geometry around the central atom. The ligand and its complexes were tested for their antimicrobial study and antifungal screening gave good results in the presence of metal ion in the ligand system.

Key Words: Schiff base, TITPS, Co(II), Ni(II) and Cu(II), Antimicrobial study, Antifungal study.

INTRODUCTION

Metal complexes with Schiff base ligand have been subject of intense investigation for the last several years. Literature survey reveals that study of Schiff base ligand is linked with many of the key advances made in inorganic chemistry[1] and has played a vital role in the development of modern coordination chemistry[2] inorganic biochemistry[3], catalysis[4]. Schiff base ligand and their complexes are of current interest, not only due to their relevance to biological systems[5-7] but also because many of them exhibit unusual magnetic properties[8], noval structural features[9], antibacterial[10] and catalytic properties[11,12]. In continuation of our earlier publications[13] and keeping the above mentioned biological importance of Schiff base and their metal complexes in the present communication we report the synthesis and characterization of Co(II), Ni(II) and Cu(II) chelates with Schiff base ligand TITPS.

¶This work was presented in 28th Annual Conference of Indian Council of Chemists at North Gujarat University, Patan, India, 7-10 October, 2009.

EXPERIMENTAL

All the reagents were used in the present study of analytical grade. All the solvent were used without further purification. All the physico-chemical studies were performed as reported earlier[13].

Preparation of the ligand: Ethanolic solution of 2,3,4,5-tetrahydroindeno-[1,2-d]-thiazolo-[3,2-a]-pyrimidine-10(H)one in 1:1 molar ratio. The resulting reaction mixture were heated on water bath for 5-6 h, when polycrystalline colourless solid began to separate out after allowing the solution stand overnight. It was filtered washed with ethanol and dried in an air oven, yield 60 % m.p. 227 ± 1 ºC.

Preparation of the complexes: The complexes of Co(II), Ni(II) and Cu(II) have been formed by reacting an ethanolic solution of respective metal halide with the ethanolic solution of the ligand 2,3,4,5-tetrahydroindeno-[1,2-d]-thiazolo-[3,2-a]-pyrimidine-10(H)semicarbazone [TITPS] in the molar ratio 1:2. The procedure carried out in each case was of similar nature with a slight variation of timing of reflux. The coloured complexes obtained in each case were cooled, filtered and washed with ethanol several times to remove any excess of the ligand. Finally complexes were washed with anhydrous diethyl ether and dried in air oven. Yield 60-65 %.

The following general method was adopted for the preparation of nitrate and perchlorate complexes. By adding a ethanolic solution of respective metal nitrate or metal perchlorate (0.001 M) to a hot ethanolic solution of ligand, 2,3,4,5-tetrahydroindeno-[1,2-d]-thiazolo-[3,2-a]-pyrimidine semicarbazone [TITPS] (0.002 M) with vigorous stirring. The resulting solution was heated on a water bath for 3 h. The precipitated complexes were filtered, washed several times with ethanol and then dried in air oven. Yield 60-65 %. The analytical data of TITPS and its metal complexes are given in Table-1.

RESULTS AND DISCUSSION

The IR spectra of the ligands as well as complexes have been measured in the region 4000-200 cm^{-1} (Table-2). The IR spectra of the ligand shows strong band at 1480 cm^{-1} assignable[14,15] to the ν(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 420-400 cm^{-1} in the complexes assigned[16,17] to ν(M-N). The next IR spectra of the ligand shows a sharp and strong band at 1720 cm^{-1} assigned[18,19] to ν(C=O). In the spectra of the complexes this band also shows red shift appearing in the region at 1700 cm^{-1} indicating probable 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 520-500 cm^{-1} assigned[17,18] as ν(M-O). The coordination through metal halogen is indicated by the appearance of a band in the region 325-270 cm^{-1} assigned[19,20] to ν(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} cm^2 mol^{-1}.

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF THE COMPLEXES
OF TITPS AND ITS METAL COMPLEXES

Compounds (Colour)	m.w.	Yield (%)	Analysis found (calcd) (%)				μ_{eff}(B.M.)	Ω_m (ohm^{-1} cm^2 mol^{-1})	DT (ºC)	λ_{max} electronic (cm^{-1})
			M	C	H	N				
TITPS (Colourless)	299	60.3	–	56.01 (56.18)	3.98 (4.34)	23.33 (23.41)	–	–	–	–
[Co(TITPS)$_2$Cl$_2$] (Red)	727.54	62.2	7.94 (8.09)	45.92 (46.15)	3.51 (3.57)	19.11 (19.23)	5.14	8.7	262	9500, 13700, 19900
[Co(TITPS)$_2$Br$_2$] (Reddish brown)	816.17	63.7	7.13 (7.21)	40.94 (41.13)	3.10 (3.18)	17.04 (17.14)	5.10	8.3	271	9400, 13890, 19200
[Co(TITPS)$_2$I$_2$] (Reddish brown)	910.70	60.3	6.41 (6.47)	36.75 (36.89)	2.76 (2.83)	15.21 (15.27)	5.11	8.1	2.67	10100, 14200, 19960
[Co(TITPS)$_2$(NO$_3$)$_2$] (Red)	785.93	61.9	7.38 (7.49)	42.66 (42.75)	3.22 (3.30)	17.73 (17.81)	4.83	8.9	269	9600, 14100, 19300
[Ni(TITPS)$_2$Cl$_2$] (Green)	727.71	64.6	7.94 (8.09)	46.04 (46.17)	3.49 (3.57)	19.11 (19.23)	3.09	7.4	293	13300, 18220, 20240
[Ni(TITPS)$_2$Br$_2$] (Deep green)	816.52	65.3	7.10 (7.19)	40.93 (41.15)	3.11 (3.18)	17.10 (17.11)	3.12	7.9	291	13360, 18160, 20810
[Ni(TITPS)$_2$I$_2$] (Greenish brown)	910.53	62.4	4.38 (4.44)	36.81 (36.90)	2.83 (2.85)	15.22 (15.37)	3.10	7.1	289	13310, 18000, 20840
[Ni(TITPS)$_2$(NO$_3$)$_2$] (Greenish brown)	785.71	61.3	7.36 (7.47)	42.58 (42.71)	3.22 (3.30)	17.73 (17.81)	3.03	7.6	279	13380, 18260, 21260
[Cu(TITPS)$_2$Cl$_2$] (Blue)	732.54	62.1	6.58 (8.67)	45.77 (45.86)	3.45 (3.54)	19.03 (19.11)	1.93	10.3	301	12300, 17710
[Cu(TITPS)$_2$Br$_2$] (Blue)	821.35	61.3	7.64 (7.73)	40.69 (40.90)	3.10 (3.16)	16.90 (17.04)	1.89	10.9	301	12260, 17800
[Cu(TITPS)$_2$(NO$_3$)$_2$] (Blue)	785.54	60.4	7.94 (8.08)	42.60 (42.77)	3.23 (3.30)	17.70 (17.82)	1.92	10.7	304	12380, 12810

DT: Decomposition temperature.

On the basis of above IR spectral bands assignments, it is proposed that ligand TITPS behaves as neutral bidentate manner and coordination takes place through azomethine nitrogen and carbonyl oxygen atom of semicarbazone moiety. The remaining coordination positions of metal ions are occupied by anions such as Cl^-, Br^-, I^- and NO_3^-. The band at 1570 and 1451 cm^{-1} with a separation of 121 cm^{-1} indicates mono coordinated behaviour of nitrate group[21].

TABLE-2
KEY IR SPECTRAL BANDS OF LIGAND TITPS AND ITS METAL COMPLEXES

Compounds	ν(C=O)	ν(C=N)	ν(M-O)	ν(M-N)	ν(M-X)
TITPS	1720 m, b	1480 s, m	–	–	–
$[Co(TITPS)_2Cl_2]$	1700 m, b	1455 m, b	505 m	400 m	305 m
$[Co(TITPS)_2Br_2]$	1695 m, b	1460 m, b	510 m	420 m	280 m
$[Co(TITPS)_2I_2]$	1690 m, b	1455 m, b	515 m	410 m	270 m
$[Co(TITPS)_2(NO_3)_2]$	1695 m, b	1450 m, b	510 m	415 m	–
$[Ni(TITPS)_2Cl_2]$	1700 m, b	1460 m, b	400 m	400 m	325 m
$[Ni(TITPS)_2Br_2]$	1695 m, b	1455 m, b	395 m	395 m	295 m
$[Ni(TITPS)_2I_2]$	1690 m, b	1455 m, b	400 m	400 m	275 m
$[Ni(TITPS)_2(NO_3)_2]$	1695 m, b	1460 m, b	395 m	395 m	–
$[Cu(TITPS)_2Cl_2]$	1695 m, b	1455 m, b	495 m	410 m	315 m
$[Cu(TITPS)_2Br_2]$	1700 m, b	1450 m, b	500 m	420 m	285 m
$[Cu(TITPS)_2(NO_3)_2]$	1690 m, b	1455 m, b	495 m	415 m	–

m: medium, s: strong, b: broad.

Magnetic susceptibility and electronic spectral studies: The Co(II) complexes exhibit three absorption band in the region, 9400-10100, 13700-14700 and 19200-19960 cm^{-1} assignable to the transitions, $^4T_{2g}(F)\leftarrow{}^4T_{1g}(F)$, $^4A_{2g}(F)\leftarrow{}^4T_{1g}(F)$ and $^4T_{1g}(P)\leftarrow{}^4T_{1g}(F)$, respectively. The above mentioned spectral bands indicate octahedral[22,23] geometry for the Co(II) complexes. The octahedral geometry of Co(II) complexes is also supported[24-26] by magnetic susceptibility value in the range 4.83-5.11 BM. The Ni(II) complexes exhibit three absorption bands in the regions 13000-13390, 18000-18320 and 20240-21260 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 proposes octahedral geometry[22,27] for Ni(II) complexes which is also supported[25,26,28] by magnetic susceptibility values of the complexes in the range 3.03-3.12 B.M. The Cu(II) complexes exhibit two broad bands in the region 12260-12410 and 17710-17830 cm^{-1} assigned to transitions $^2T_{2g}\leftarrow{}^2E_g$ and charge transfer band, respectively which proposes octahedral[22,29] geometry for Cu(II) complexes. The magnetic moment values for Cu(II) complexes are found in the range 1.89-1.94 BM[25,26,30].

Conductivity measurement: 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 cohm^{-1} mol^{-1} cm^{-2} in DMF proposes their non electrolytic[31] nature. The molar conductance values also supported the structure assigned on the basis of physico-chemical and spectroscopic measurements.

Antimicrobial activity: The ligand TITPS and its complexes of Co(II), Ni(II) and Cu(II) complexes were screened for their antibacterial activity against bacteria, *Escherichia coli* and antifungal activity against *Aspergillus niger* by disc diffusion technique[32] using DMF as solvent at concentration of 50 μg[33]. The activity was compared with known standard drugs, tetracycline and diethane Z-78, respectively at same concentration 50 μg.

It was observed that on comparison with references to antibiotic and fungicides the complexes were found to be more effective than ligands. The data indicates antibacterial and antifungal activity of complexes were found to be in the order Cu(II) > Ni(II) > Co(II). It is established from the literature that the metal complexes shows 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 ligand[34]. The chelation increases lipophilic character in the complexes and results in the enhancement of fungicidal and antibacterial activity.

Conclusion

Thus on the basis of above observations it is concluded that the TITPS 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 NO_3^-. The geometry of the Co(II), Ni(II) and Cu(II) complexes are proposed to be octahedral in nature as shown in Fig. 1.

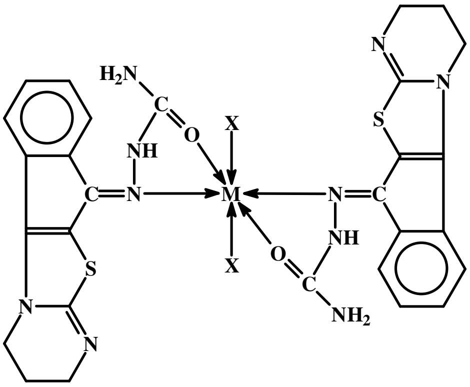

Fig. 1. $[M(TITPS)_2]X_2]$
M = Co(II), Ni(II) and Cu(II); X = Cl^-, Br^-, I^- and NO_3^-

ACKNOWLEDGEMENTS

The authors are grateful to the Principal, LNT College, Muzaffarpur for providing available laboratory facilities. The author [BKR] also grateful to University Grant Commission for financial supports [Grant No. PSB-001/08-09 dated 12 December 2008].

REFERENCES

1. D.A. Garnorski, L.A. Nivorozhkin and I.V. Minkin, *Coord. Chem. Rev.*, **126**, 1, (1993); S. Yamada, *Coord. Chem. Rev.*, **192**, 537 (1999).
2. R.H. Hol, *J. Am. Chem, Soc.*, **82**, 5632 (1960).
3. E.C. Niederhoffer, J.H. Timmons and A.E. Martell, *Chem. Rev.*, **84**, 137 (1984).
4. W. Zhang, J.L. Leobach, S.R. Wilson and E.N. Jacobsen, *J. Am. Chem. Soc.*, **112**, 2801 (1990).

5. W.L. Liu, Y. Zou, C.L. Ni, Z.P. Ni, Y.Z. Li, Z. Li, Y.G. Yao and Q.J. Meng, *Polyhedron*, **23**, 849 (2004).
6. J. Charo, J.A. Lindencrona, L.M. Carlson, J. Hinkula and R. Kiessling, *J. Virol.*, **78**, 11321 (2004).
7. M. Wang, L.F. Wang, Y.Z. Li, Q.X. Li, Z.D. Xu and D.Q. Qu, *Transition Met. Chem.*, **26**, 307 (2001).
8. H. Xu, C. He, Y. Sui, X.M. Pen, L.M. Guo, Y.G. Zhang, S. Nishihara and Y. Hosokoshi, *Polyhedron*, **26**, 4463 (2007).
9. I. Mauro, B. Federica, L. Vincenzo, M. Fabio, R. Andrea and B.G. Vcello, *Eur. J. Inorg. Chem.*, **9**, 1363 (2008).
10. N.N. Gulerman, S. Rollas, H. Erdeniz and M. Kiraj, *J. Pharm. Sci.*, **26**, 1 (2001).
11. M.R. Maurya and S. Sikarwar, *J. Mol. Catal.*, **263A**, 175 (2007).
12. Ana C.D. Midoes, P.E. Aranho, M.P. dos Santos, E. Tozzo, S. Romera, R.H. De, A. Santos and E.R. Dockal, *Polyhedron*, **27**, 59 (2008).
13. B.K. Rai and C. Kumar, *Asian J. Chem.*, **22**, 233 (2010) and references therein.
14. W. Kemp Organic Spectroscopy, Polgrave, Macmillan Press Ltd, New York; R.M. Silverstein and F.X. Webster, Spectrometric Identification of Organic Compounds, John Wiley & Sons, edn. 6, 109 (2008).
15. A. Rana, R. Dinda, P. Sengupta, S. Ghosh and Larry Falvello, *Polyhedron*, **21**, 1023 (2002).
16. M. Dolaz, M. Tumer and M. Digrak, *Transition Met. Chem.*, **29**, 528 (2004).
17. J.R. Ferraro, Low Frequency Vibration of Inorganic and Coordination Compound, Plenum Press, New York.
18. K. Nakanishi, Infrared Absorption Spectroscopy, Nankodo Company Ltd., Tokyo, p. 45 (1964).
19. B. Chatterjee, *Coord. Chem., Rev.*, **26**, 281 (1978).
20. 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).
21. B.J. Hathaway and A.E. Underhill, *J. Chem. Soc.*, 3091 (1961); C.C. Addison, N. Logan, S.C. Wallwork and C.D. Barner, *Quart Rev.*, **25**, 289 (1971).
22. A.B.P. Lever, Inorganic Electronics Spectroscopy, Elsevier Amsterdam 395 (1968); C.K. Jorgenson, *Acta Chem. Scand.*, **19**, 887 (1966); J.R. Allen, D.H. Brown, R.H. Nutal and D.W.A. Sharp, *J. Inorg. Nucl. Chem.*, **26**, 1895 (1964).
23. P.S. Mane, S.G. Shirodhar, B.R. Arbad and T.K. Chondekar, *Indian J. Chem.*, **40A**, 648 (2000).
24. C.J. Ballhauson and H.B. Gray, *Inorg. Chem.*, **1**, 111 (1962).
25. B.N. Figgis, Introduction to Ligand Field, Wiley Eastern Ltd., New Delhi, 279 (1976).
26. R.L. Carlin and A.J. Van Dryneveledt, Magnetic Properties of Transition Metal Compounds, Springer Verlag, New York (1997).
27. A.K. Tahir, H.S. Shivajni, J. Nafees and K. Shoukat, *Indian J. Chem. A*, **39**, 450 (2009).
28. V.K. Jetly, J. Singh, M. Sukla, Rehman and S.N. Rastogi, *J. Indian Chem. Soc.*, **67**, 987 (1990).
29. A.P. Mishra, M. Khare and S.K. Gautam, *Synth. React. Inorg. Met.-Org. Chem.*, **32**, 1485 (2002).
30. N.K. Singh and N.K. Agarwal, *Indian J. Chem. A*, **37**, 276 (1998).
31. 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).
32. P.K. Mukherjee, K. Saha, J. Das, S.N. Giri, M. Pal and B.P. Saha; *Indian J. Microbio.*, **35**, 327 (1995).
33. P.S. Mehta, D.M. Purohit and V.H. Shah, *Indian J. Heterocycl. Chem.*, **6**, 271 (1997).
34. N. Nishant, S. Ahmad and R.T. Ahmad, *J. Appl. Poly. Sci.*, **100**, 928 (2006).

(*Received*: 26 November 2009; *Accepted*: 31 March 2010) AJC-8599