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Structural elucidation of Co(II), Ni(II) and Cu(II) complexes of Schiff base derived from 2, 3, 4, 5- tetrahydro indeno [1, 2-d] thiazolo [3, 2-a] [1,3] diazepine- 11 (H) one

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ABSTRACT

Some hexacoordinated Co(II), Ni(II) and Cu(II) Schiff base complexes have been prepared and characterized on the basis of analytical, magnetic susceptibility, molar mass, IR spectra, electronic spectra, molar conductance measurements. From the analytical and spectroscopic investigation the stoichiometry of the complexes has been found to be $[M(TITDT)_2X_2]$; where M = Co(II), Ni(II) and Cu(II); TITDT = 2, 3, 4, 5 tetrahydro indeno (1, 2-d) thiazolo [3,2-a] [1,3] diazepine- 11(H) thiosemicarbazone; X = Cl^-, Br^-, I^- and NO_3^-. IR spectra of the ligand and complexes proposes, TITDT acts as a neutral bidentate ligand and coordination proposed through azomethine nitrogen and thione sulphur atom of thiosemicarbazone moiety. The remaining coordination positions are satisfied by negative ions, such as Cl^-, Br^-, I^- and NO_3^-. On the basis of electronic spectra and magnetic susceptibility data the geometry of the complexes are monomeric octahedral in nature. The low value of molar conductance indicate complexes are non-electrolytic in nature.

Key words : Schiff base/ TITDT/ Co(II), Ni(II) and Cu(II)/ antifungal study.

INTRODUCTION

Thiosemicarbazone and its metal complexes have diverse applications in various fields including biology. They exhibit anticonvulsant[1], antiviral[2], antimicrobial[3], antifungicidal[4] and antiherbicidal activities[5]. The metal complex of thiosemicarbazone have various industrial applications[6-8]. In recent years S and N containing Schiff base derivatives have attracted more attention for their excellent corrosion inhibition activity. These compounds not only possesses very high values of inhibition efficiency but also bring down the permeation current to a considerable extent. Considering the above application of thisemicarbazone derivative and in continuation[10-16] of earlier publication on Schiff base metal chelates, we reported the synthesis and characterization of Co(II), Ni(II) and Cu(II) complexes with Schiff base ligand TITDT (2, 3, 4, 5-tetra hydro indeno [1,2-d] thiazolo [3,2-a] [1,3] diazepine 11(H) thiosemicarbazone.

EXPERIMENTAL

All reagents were analytical grade and used without further purification.

Synthesis of Ligand

This paper was presented in 46th Annual convention of Indian Chemical Society at Vellore on 02-06 Dec,2009.

The Schiff base was prepared by mixing equimolar quantities of 2, 3, 4, 5-tetra hydro indeno [1,2-d] thiazolo [3,2-a] [1,3] diazepine 11(H) one in ethanol and thiosemicarbazide hydrochloride dissolved in 10% solution of sodium acetate in ethanol. The resulting mixture was refluxed on water bath for 2 h with occasional stirring. The solvent was concentrated to half of its volume and then poured in ice cold water. A solid precipitated out immediately which was filtered, washed with distilled water and cold ethanol. Recrystallization of crude product from ethanol gave the Schiff base TITDT. Yield 60% m.p. 189±1°C.

Synthesis of the Co(II), Ni(II) and Cu(II) complexes

The Schiff base TITDT dissolved in ethanol (0.002 M) and respective metal halides dissolved in ethanol (0.001 M) were mixed together and stirred vigorously for 10 min. The resulting mixture were then refluxed on water bath for 2-3 h. The procedure carried out in each case of similar nature with slight variation of timing of reflux. The precipitated complexes were filtered, washed with aqueous ethanol and dried in electric oven. Yield 60-65%.

The following general method were adopted for the preparation of nitrate complexes. Ethanolic solution of respective metal nitrate (0.001 M) were condensed with ethanolic solution of ligand TITDT (0.002 M). The resulting mixtures were refluxed 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 60-65%.

The metal contents were analysed by standard procedure[17]. The electronic spectra of the complexes were recorded in DMF using Cary-2390 spectrophotometer. The IR spectra of the ligand and complexes were recorded using Perkin Elmer-577 spectrophotometer using KBr disc. Magnetic susceptibility measurements were performed using Gouy tube technique using $Hg[Co(NCS)_4]$ as a calibrant. Molar conductance were recorded on Systronics conductivity meter model-303 using DMF as a solvent.

RESULTS AND DISCUSSION

IR spectra

The characteristic observation peaks were observed for all the relevant groups. The IR spectrum of the ligand exhibit strong and broad band at 3200 cm^{-1} assigned[18,19] to ν_{N-H}. In the spectra of the complexes this band is unaffected which indicate non-participation of either primary amino or secondary amino group in the coordination. IR spectrum of the ligand exhibit a strong and broad band at 1500 cm^{-1} assignable[18,20] to $\nu_{C=N}$. In the spectra of the complexes this band shifted to lower (20-30 cm^{-1}) frequency region suggesting coordination with azomethine nitrogen atom. The next IR spectrum of the ligand exhibit a strong and broad band at 800 cm^{-1} assigned[18,21] to $\nu_{C=S}$. This band was also shifted to lower frequency region in the complexes suggesting linkage of metal ion through thione sulphur atom.

The conclusive evidence of bonding of ligand with metal ion through oxygen atom of nitrate group, nitrogen atom of azomethine group and sulphur atom of thiosemicarbazone moiety were supported by the presence of three far ir bands in the regions due to ν_{M-O}[22,23] at 525-500 cm^{-1}, ν_{M-N}[22,23] at 475-455 cm^{-1} and ν_{M-S}[22,23] at 420-390 cm^{-1} respectively. The linkage through metal-halogen is indicated by the appearance of a band in the far ir region at 325-270 cm^{1} assigned to ν_{M-X} (Cl^-, Br^- and I^-). The evidence of metal halogen linkage were supported by the low molar conductance value of the complexes in the range 6.3-11.6 ohm^{-1} cm^2 mol^{-1} for all metal complexes. The low conductance values indicate the non electrolytic nature of the complexes.

The occurrence of IR spectral bands at 1640 and 1525 cm^{-1} with a separation of 125 cm^{-1} indicate monocoordinated nature of nitrate group[24,25].

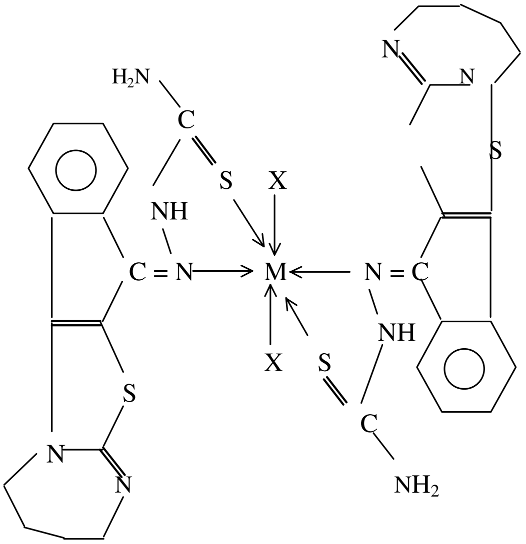

Fig. 1: M = Co(II) and Ni(II); X = Cl^-, Br^- , I^- and NO_3^- ; M = Cu(II); X = Cl^-, Br^- , I^- and NO_3^-M(TITDT)$_2$ X$_2$]

Table 1: Analytical and physical data of the complexes of the ligand TITDT

Compounds (Colour)	Mol. Wt.	Yield	% Analysis found (calculated)				μ_{eff} B.M.	λ_{max} electronic cm^{-1}	Ω_m ohm^{-1} cm^2 mol^{-1}	DT ^oC
		%	M	C	N	H				
TITDT	313.00	60		57.38	22.27	4.22				
(Colourless)				(57.50)	(22.36)	(4.79)				
[Co(TITDT)$_2$Cl$_2$]	755.93	64	7.68	47.43	18.38	3.90	4.87	8720, 17200,	6.3	219
(Brown)			(7.79)	(47.62)	(18.52)	(3.96)		20040		
[Co(TITDT)$_2$Br$_2$]	844.748	63	6.90	42.38	16.50	3.48	5.02	8700, 17000,	6.4	209
(Reddish brown)			(6.97)	(42.61)	(16.51)	(3.55)		20090		
[Co(TITDT)$_2$I$_2$]	938.75	61	6.18	38.23	14.80	3.10	5.11	8740, 17300,	6.9	214
(Dark brown)			(6.27)	(38.34)	(14.91)	(3.19)		20100		
[Co(TITDT)$_2$(NO$_3$)$_2$]	808.93	62	7.21	44.32	17.12	3.64	5.10	8760, 17000,	8.1	224
(Brown)			(7.28)	(44.50)	(17.30)	(3.70)		20200		
[Ni(TITDT)$_2$Cl$_2$]	755.71	62	7.70	47.48	13.92	3.91	3.02	10200, 14200,	11.3	202
(Yellowish green)			(7.76)	(47.63)	(13.96	(3.96)		25300		
[Ni(TITDT)$_2$Br$_2$]	844.52	63	6.89	42.47	16.49	3.46	3.6	10280, 14600,	11.6	206
(Yellowish brown)			(6.95)	(42.62)	(16.59)	(3.55)		25200		
[Ni(TITDT)$_2$I$_2$]	938.53	64	6.17	38.27	14.83	3.14	3.2	10300, 14400,	11.5	211
(Brown)			(6.25)	(38.35)	(14.90)	(3.19)		25320		
[Ni(TITDT)$_2$(NO$_3$)$_2$]	808.11	62	7.16	44.39	17.19	3.61	3.11	10340, 14640,	10.7	213
(Brown)			(7.25)	(44.52)	(17.31)	(3.70)		25310		
[Cu(TITDT)$_2$Cl$_2$]	760.54	62	8.29	47.20	18.29	39.37	1.84	13100, 24610,	9.4	207
(Green)			(8.35)	(47.33)	(18.40)	(39.48)		25340		
[Cu(TITDT)$_2$Br$_2$]	849.358	63	7.36	42.22	16.34	3.47	1.89	13130, 24640	9.7	228
(Green)			(7.48)	(42.38)	(16.48)	(3.53)				
[Cu(TITDT)$_2$(NO$_3$)$_2$]	813.54	63	7.74	44.72	17.12	3.61	1.90	13140, 24630	9.3	216
(Greenish red)			(7.81)	(44.25)	(17.20)	(3.68)				

DT = Decomposition Temperature

Table 2: Key ir spectral bands (cm^{-1}) of ligand TITDT and its metal complexes

Compounds	ν_{N-H}	$\nu_{C=N}$	$\nu_{C=S}$	ν_{M-O}	ν_{M-N}	ν_{M-S}	ν_{M-X}
TITDT	3200 s,b	1500 s,b	800 s,b				
[Co(TITDT)$_2$Cl$_2$]	3200 s,b	1470 m,b	780 m,b		460 m	395 m	315 m
[Co(TITDT)$_2$Br$_2$]	3200 s,b	1475 m,b	780 m,b		465 m	390 m	290 m
[Co(TITDT)$_2$I$_2$]	3200 s,b	1470 m,b	770 m,b		460 m	395 m	280 m
[Co(TITDT)$_2$(NO$_3$)$_2$]	3200 s,b	1475 m,b	775 m,b	520 m	470 m	410 m	
[Ni(TITDT)$_2$Cl$_2$]	3200 s,b	1470 m,b	775 m,b		470 m,b	420 m	325 m
[Ni(TITDT)$_2$Br$_2$]	3200 s,b	1470 m,b	770 m,b		475 m,b	415 m	300 m
[Ni(TITDT)$_2$I$_2$]	3200 s,b	1470 m,b	770 m,b		455 m	410 m	275 m
[Ni(TITDT)$_2$(NO$_3$)$_2$]	3200 s,b	1470 m,b	775 m,b	540 m	450 m	410 m	
[Cu(TITDT)$_2$Cl$_2$]	3200 s,b	1475 m,b	775 m,b	545 m	450 m	415 m	320 m
[Cu(TITDT)$_2$Br$_2$]	3200 s,b	1475 m,b	770 m,b		450 m	410 m	290 m
[Cu(TITDT)$_2$(NO$_3$)$_2$]	3200 s,b	1480 m,b	770 m,b	550 m	455 m	415 m	
[Cu(TITDT)$_2$(ClO$_4$)$_2$]	3200 s,b	1480 m,b	775 m,b	545 m	460 m	420 m	

m = medium, s = strong, b = broad

Magnetic susceptibility and electronic spectral studies of the complexes

The Co(II) complexes exhibit three electronic spectral bands at 8760-8720, 17300-17000, 20210-20040 cm^{-1} attributed to transitions $^4T_{2g}$ (F) ← $^4T_{1g}$ (F), $^4A_{2g}$ (F) ← $^4T_{1g}$ (F) and $^4T_{1g}$ (P) ←$^4T_{1g}$ (F) respectively which is compatible with these complexes having a octahedral[26,27] structure. The proposed configuration were further supported[28-30] by high μ_{eff} value in the range 4.87-5.11 B.M. for all the Co(II) complexes. The Ni(II) complexes exhibit absorption band in the region 10340-10200, 14700-14200 and 25340-25200 cm^{-1} attributable to transition, $^3T_{2g}$ (F) ← $^3A_{2g}$ (F), $^3T_{1g}$ (F) ← $^3A_{2g}$ (F) and $^3T_{1g}$ (P) ← $^3T_{2g}$ (F) respectively, suggesting an octahedral[27,31] geometry around Ni(II) complexes. The octahedral geometry of Ni(II) complexes were further supported[28,29,32] by μ_{eff} value in the range 3.02 to 3.11 B.M. Two broad band observed in the electronic spectra of the Cu(II) complexes first in the range 13160-13100 and 24640-24600 cm^{-1} assigned to transition $^2T_{2g}$ ← ^2E_g and charge transfer band which proposed distorted octahedral[27,33] geometry for all Cu(II) complexes. The magnetic susceptibility value of Cu(II) complexes were lie in the range 1.84 – 1.91 B.M.[28,29,34].

Molar Conductivity Value

Molar conductance measurements were taken on Systronics conductivity meter model 303 using DMF as a solvent. The molar conductance data of the complexes were found to be in the range of 6.3-11.6 ohm^{-1} cm^2 mol^{-1} suggesting the complexes are non electronic[35] in nature.

Antifungal Screening

Schiff base TITDT and their metal complexes of Co(II), Ni(II) and Cu(II) have been evaluated for their antifungal activity by disc plate diffusion method[36] on *Pencillum expansum* and *Aspergillus flavus*. On comparison with reference to fungicide, the complexes were found to be more effective than free ligand due to chelation theory[37].

CONCLUSION

Based on the physico chemical and spectroscopic studies it may be concluded that the complexes of Co(II), Ni(II) and Cu(II) were proposed to be octahedral in geometry as shown in Fig.1.

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