



Synthesis and Characterization of Ni(II), Cu(II) and Co(II) Complexes with Bidentate Schiff Base Ligand Derived from 2,3,4,5-Tetrahydro indeno[1,2-d]thiazolo[3,2-a][1,3]pyrimidine-11(H)-one

B.K. RAI^{1,*} and BIMAL KUMAR²

¹Department of Chemistry, L.N.T. College, Muzaffarpur-842 002, India

²Department of Chemistry, R.S.S. College, Chochahan, Muzaffarpur-842 001, India

*Corresponding author: E-mail: binodkr_rai@yahoo.co.in

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The present work reports the synthesis of a series of Co(II), Ni(II) and Cu(II) complexes of neutral bidentate Schiff base prepared by the condensation of 2,3,4,5-tetrahydro indeno[1,2-d]thiazolo[3,2-a][1,3]pyrimidine-11(H)-one with semicarbazide hydrochloride. The ligand as well as metal complexes have been characterized by elemental analyses, molar mass, magnetic susceptibility, molecular conductivity, IR spectra, electronic spectra. On the basis of above observations, it is proposed that the ligand 2,3,4,5-tetrahydro indeno[1,2-d]thiazolo[3,2-a][1,3]pyrimidine-11(H)-semicarbazone behaves as neutral bidentate manner and coordination takes place through azomethine N and carbonyl oxygen of semicarbazone moiety. The remaining positions of the metal ion are satisfied by negative ions such as Cl⁻, Br⁻, I⁻ and NO₃⁻. The complexes were proposed octahedral geometry.

Key Words: Schiff base, Co(II), Ni(II), Cu(II), Complexes.

INTRODUCTION

Schiff bases and their metal complexes which exhibit wide applications¹⁻⁵ especially in biologically systems have been extensively studied by several workers⁶⁻¹¹. Because of wide ranging uses of Schiff base metal complexes and our earlier work¹²⁻¹⁸ on Schiff base complexes we herein report the synthesis and characterization of Co(II), Ni(II) and Cu(II) complexes with Schiff base ligand 2,3,4,5-tetrahydro indeno[1,2-d]thiazolo[3,2-a][1,3]pyrimidine-11(H)-semicarbazone [TITPS].

EXPERIMENTAL

All the chemicals used were of AR grade. The solvents were used without any purification. The metal contents were determined using standard method¹⁹. The analytical data of the complexes and their molar conductance values are given in Table-1. Conductivity measurements were made using Systronics conductivity meter model 303 in DMF. Electronic spectra of the complexes were recorded in DMF on Cary-2390 spectrophotometer. The IR spectra of ligands and its complexes were taken on Perkin-Elmer model 577 using KBr disc. Magnetic susceptibility were measured by Gouy method using Hg[Co(NCS)₄] as a calibrant.

Preparation of the ligand: The ligand 2,3,4,5-tetrahydro indeno[1,2-d]thiazolo[3,2-a][1,3]pyrimidine-11(H)-semicarbazone [TITPS] was prepared by condensation of ethanolic solution of 2,3,4,5-tetrahydro indeno[1,2-d]thiazolo[3,2-a][1,3]pyrimidine-11(H)-one [0.001 M] with semicarbazide hydrochloride [0.001 M] dissolved in 10 % ethanolic solution of sodium acetate. The resulting reaction mixture was refluxed on water bath for 4-5 h with occasional stirring. After cooling the refluxed solution, colourless solid was obtained which was separated by filtration, washed and finally dried and crystallized with tetrahydro furan to furnish 2,3,4,5-tetrahydro indeno[1,2-d]thiazolo[3,2-a][1,3]-pyrimidine-11(H)-semicarbazone [TITPS] as colourless silky prismatic needles m.p. 187 ± 1 °C (Yield 65 %).

Preparation of the complexes: The complexes of Co(II), Ni(II) and Cu(II) were prepared by the reaction between ethanolic solution of respective metal chloride/metal nitrate (0.01 M) with ethanolic solution of ligand 2,3,4,5-tetrahydro indeno[1,2-d]thiazolo[3,2-a][1,3]pyrimidine-11(H)-semicarbazone [TITPS] (0.02 M). The resulting reaction mixture was heating on water bath for 2-3 h with occasional stirring. The procedure carried out in each case was similar with slight variation in timing of reflux. On cooling solid coloured complexes separated out which were filtered, washed with ethanol, dried and recrystallized with tetrahydrofuran. Yield in cases 60-65 %.

TABLE-1
PHYSICO-CHEMICAL PROPERTIES OF LIGAND TITPS AND ITS Co(II), Ni(II) AND Cu(II) COMPLEXES

Compounds (Colour)	Molar mass	Yield (%)	Elemental analysis (%): Found (calcd.)				μ_{eff} (BM)	DT (°C)	Ω_m (ohm ⁻¹ cm ² mol ⁻¹)	λ_{max} electronic (cm ⁻¹)
			M	C	N	H				
TITPS (Colourless)	315.000	65	–	53.12 (53.33)	22.10 (22.22)	4.04 (4.12)	–	–	–	–
[Co(TITPS) ₂ Cl ₂] (Brown)	759.93	64	7.67 (7.75)	44.09 (44.21)	18.28 (18.42)	3.37 (3.42)	4.99	179	6.4	10760, 17460, 22300
[Co(TITPS) ₂ Br ₂] (Chocolate brown)	848.748	62	6.68 (6.94)	39.39 (39.58)	16.37 (16.49)	2.96 (3.06)	4.97	176	6.7	10770, 17380, 22360
[Co(TITPS) ₂ I ₂] (Brown)	942.738	65	6.16 (6.25)	35.52 (35.64)	14.69 (14.85)	2.68 (2.75)	4.93	184	5.8	10740, 17320, 22330
[Co(TITPS) ₂ (NO ₃) ₂] (Deep brown)	82.930	65	7.18 (7.24)	41.21 (41.33)	15.64 (15.76)	3.12 (3.19)	5.04	192	4.9	10730, 17430, 22380
[Ni(TITPS) ₂ Cl ₂] (Green)	759.710	63	7.66 (7.72)	44.10 (44.25)	18.34 (18.42)	3.77 (3.42)	3.1	184	4.3	12700, 16400, 23800
[Ni(TITPS) ₂ Br ₂] (Green)	848.028	63	6.83 (6.91)	39.43 (39.59)	16.38 (16.49)	2.94 (3.06)	3.7	179	4.1	12660, 16430, 23530
[Ni(TITPS) ₂ I ₂] (Green)	942.518	62	6.17 (6.22)	35.52 (35.64)	14.77 (14.85)	2.68 (2.75)	3.4	181	3.8	12780, 16480, 23870
[Ni(TITPS) ₂ (NO ₃) ₂] (Green)	812.710	61	7.16 (7.22)	41.25 (41.34)	17.10 (17.22)	3.08 (3.19)	3.7	183	3.9	12730, 16430, 24000
[Cu(TITPS) ₂ Cl ₂] (Blue)	764.540	65	8.22 (8.30)	43.70 (43.94)	18.20 (18.31)	3.33 (3.40)	1.96	203	3.2	13300, 15300
[Cu(TITPS) ₂ Br ₂] (Bluish green)	853.358	60	7.35 (7.44)	39.26 (39.37)	16.38 (16.49)	2.96 (3.04)	1.86	211	3.4	15100, 16200
[Cu(TITPS) ₂ (NO ₃) ₂] (Blue)	817.540	62	7.59 (7.77)	40.90 (41.09)	17.03 (17.12)	3.12 (3.18)	1.89	206	3.7	13310, 15430

DT = Decomposition temperature.

TABLE-2
IR SPECTRAL BANDS (cm⁻¹) OF LIGAND TITPS AND ITS COMPLEXES OF Co(II), Ni(II) AND Cu(II)

Compounds	$\nu(\text{N-H})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$	$\nu(\text{M-X})$
TITPS	3460 s,b	1700 s,b	1470 s,b	–	–	–
[Co(TITPS) ₂ Cl ₂]	3460 s,b	1680 m,b	1445 m,b	525 m	435 m	305 m
[Co(TITPS) ₂ Br ₂]	3460 s,b	1680 m,b	1450 m,b	515 m	435 m	325 m
[Co(TITPS) ₂ I ₂]	3460 s,b	1680 m,b	1450 m,b	520 m	435 m	315 m
[Co(TITPS) ₂ (NO ₃) ₂]	3460 s,b	1680 m,b	1455 m,b	525 m	435 m	–
[Ni(TITPS) ₂ Cl ₂]	3460 s,b	1675 m,b	1450 m,b	530 m	470 m	275 m
[Ni(TITPS) ₂ Br ₂]	3460 s,b	1680 m,b	1450 m,b	540 m	460 m	270 m
[Ni(TITPS) ₂ I ₂]	3460 s,b	1680 m,b	1455 m,b	535 m	465 m	295 m
[Ni(TITPS) ₂ (NO ₃) ₂]	3460 s,b	1680 m,b	1450 m,b	520 m	470 m	–
[Cu(TITPS) ₂ Cl ₂]	3460 s,b	1680 m,b	1445 m,b	540 m	455 m	305 m
[Cu(TITPS) ₂ Br ₂]	3460 s,b	1680 m,b	1445 m,b	540 m	455 m	290 m
[Cu(TITPS) ₂ (NO ₃) ₂]	3460 s,b	1680 m,b	1445 m,b	540 m	455 m	–

RESULTS AND DISCUSSION

A careful interpretation of infrared spectral bands of the ligand TITPS and its Co(II), Ni(II) and Cu(II) complexes reveal that there are certain bands of the ligand which are appreciably affected after the complex formation indicating the donor atoms of coordination centre of the ligand to form the linkage with metal ions. The ligand exhibits a sharp and strong band at 3460 cm⁻¹ assignable^{20,21} to $\nu(\text{N-H})$ vibration. In spectra of all the metal complexes this band was observed without change in position and intensity, clearly indicating non involvement of nitrogen atom of either amino or imino group in the coordination with metal ion. A broad and sharp band obtained at 1700 cm⁻¹ in ligand assignable^{20,22,23} to $\nu(\text{C=O})$ vibration. This band has been reduced by 20-30 cm⁻¹ in complexes suggesting coordination of carbonyl oxygen with metal ion. The next IR band of the ligand shows a broad and strong band at 1470 cm⁻¹ assignable^{20,23,24} to $\nu(\text{C=N})$ vibration. After

complexation this band shows red shift with slightly reduced intensity. The shift of the band and change in intensity indicate coordination of azomethine N with metal ion.

The conclusive evidence of bonding of ligand to metal through oxygen atom of nitrate group, carbonyl oxygen of semicarbazone moiety, nitrogen atom of azomethine group and sulphur atom of semicarbazone moiety are have indicated by the appearance of far ir region bands due to $\nu(\text{M-O})$ ^{25,26} at 540-515 cm⁻¹, $\nu(\text{M-N})$ ^{25,26} at 470-430 cm⁻¹ and $\nu(\text{M-S})$ ^{25,26} at 425-395 cm⁻¹, respectively. The evidence of metal halogen linkage is supported by the low molar conductance value of the complexes in the range 3.2-6.7 ohm⁻¹ cm² mol⁻¹ and appearance of a band in the far IR region at 325-270 cm⁻¹ assigned^{25,26} to $\nu(\text{M-X})$ (X = Cl⁻, Br⁻, I⁻).

The next IR bands at 1630 and 1500 cm⁻¹ with a separation of 120 cm⁻¹ suggest mono coordinated behaviour of nitrate group^{27,28}.

The magnetic susceptibility^{29,30} and electronic spectral measurements³¹ (Table-1) proposed octahedral geometry for the complexes of the type $[M(\text{TITPS})_2\text{X}_2]$.

Molar conductivity: Molar conductance data of the complexes were measured in the solvent DMF and the complexes were found to be non electrolytic³² in nature. The molar conductance value of the complexes are in the range 3.2-6.7 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$.

Conclusion

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

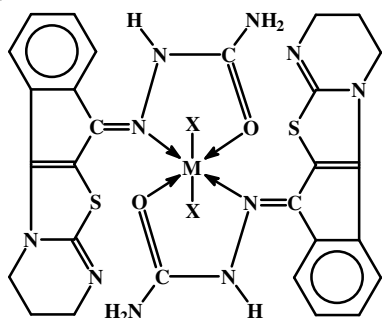


Fig. 1. $[M(\text{TITPS})_2\text{X}_2]$ [M = Co(II) and Ni(II); X = Cl^- , Br^- , I^- and NO_3^- ; M = Cu(II); X = Cl^- , Br^- and NO_3^-]

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