



Spectroscopic Study of Co(II), Ni(II) and Cu(II) Complexes with Nitrogen and Sulphur Containing Schiff Base Ligands

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A series of Co(II), Ni(II) and Cu(II) Schiff base complexes of the general composition $[M(\text{TITPT})_2\text{X}_2]$ where M = Co(II), Ni(II) and Cu(II); TITPT= 2,3,4,5-tetrahydroindeno(1,2-d)thiazolo(3,2-a)[1,3]pyrimidine-(10H) thiosemicarbazone; X=Cl⁻, Br⁻, I⁻ and NO₃⁻ were synthesized and characterized. The ligand and its Co(II), Ni(II) and Cu(II) complexes were formulated by elemental analyses, molar mass, infrared spectra, electronic spectra, magnetic susceptibility and molar conductance data. In the light of above studies it is proposed that the TITPT behaves as bidentate ligand and coordination takes place through azomethine nitrogen and thione sulphur atom of thiosemicarbazone moiety. The remaining positions of metal ions are satisfied by negative ions such as Cl⁻, Br⁻, I⁻ and NO₃⁻. The complexes were proposed to be octahedral in geometry.

Key Words: Metal complexes, Schiff base, 2,3,4,5-tetrahydroindeno(1,2-d)thiazolo(3,2-a)[1,3]pyrimidine-(10H) thiosemicarbazone.

INTRODUCTION

Thiosemicarbazone and its metal complexes are important ligand because of their antibacterial and antifungal¹, antiviral, antitumor², antimalarial activities. They have been used for the analytical determination of metals. A number of metal complexes of thiosemicarbazones, because of their properties and a wide variation in the modes of bonding and stereochemistry are reported³⁻⁵. Schiff base complexes have undergone a phenomenal growth during the recent years because of the versatility offered by these complexes in the field of industries, catalysis and in biological systems⁶⁻¹⁴. Keeping in view of interesting structural diversity of Schiff base and their wide applications of metal complexes and as a part of our continuing¹⁵⁻²¹ investigation in the coordination chemistry of multidentate ligand containing Schiff base we undertake this work.

EXPERIMENTAL

Preparation of ligand [TITPT]: The ligand 2,3,4,5-tetrahydroindeno(1,2-d)thiazolo(3,2-a)[1,3]pyrimidine-(10H) thiosemicarbazone (TITPT) were prepared by condensing equimolar quantities (0.01 mol of each) of 2,3,4,5-tetrahydroindeno(1,2-d)thiazolo(3,2-a)[1,3a]pyrimidine-(10H) one (1.46 g) in 20 mL of ethanol with aqueous ethanolic solution of thiosemicarbazide hydrochloride. The reaction mixture was refluxed on water bath for 6 h. The solid which separated at

the end of the refluxing period was filtered, dissolved in boiling water and purified (charcoal). Neutralization with sodium carbonate solution gave yellow coloured solid m.p. 221 ± 1 °C; (yield 63 %) (Table-1).

Preparation of the metal 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) was mixed together with constant stirring. The mixture refluxed for 2-3 h on water bath. On cooling, coloured complexes were precipitated out. It was filtered washed with cold ethanol and dried in electric oven (Table-2).

The complexes were analyzed using standard procedure²². IR spectra of the ligand as well as metal complexes were recorded on Perkin-Elmer-577 spectrometer in the range 4000-200 cm⁻¹ using KBr disc. The electronic spectra were recorded on Cary-2390 spectrophotometer. Molar conductance of the complexes was measured on Systronics conductivity meter model 303 using DMF as a solvent. Magnetic susceptibility of the complexes was measured on Gouy balance using Hg[Co(NCS)₄] as a calibrant.

RESULTS AND DISCUSSION

The IR spectrum of the ligand TITPT shows a broad band of medium intensity at 3100 cm⁻¹ assigned^{23,24} to $\nu(\text{N-H})$.

TABLE-1
ANALYTICAL, COLOUR, MOLECULAR WEIGHT, MAGNETIC SUSCEPTIBILITY, ELECTRONIC SPECTRA, MOLAR CONDUCTIVITY AND DECOMPOSITION TEMPERATURE OF LIGAND TITPT AND ITS METAL COMPLEXES

Compounds (Colour)	m.w.	Elemental analysis (%): Found (calcd.)				μ_{eff} (BM)	λ_{max} electronic (cm^{-1})	DT ($^{\circ}\text{C}$)	Ω_m (ohm^{-1} $\text{cm}^2 \text{mol}^{-1}$)
		M	C	N	H				
TITPT (Yellow)	316	–	52.82 (53.16)	22.03 (22.15)	4.37 (4.43)	–	–	–	–
[Co(TITPT) ₂ Cl ₂] (Brown)	761.93	7.64 (7.73)	43.78 (44.09)	18.24 (18.37)	3.59 (3.67)	4.93	10400 17300 22100	212	10.1
[Co(TITPT) ₂ Br ₂] (Reddish brown)	850.75	6.73 (6.92)	39.28 (39.40)	16.29 (16.45)	3.20 (3.29)	4.89	10800 17400 22600	202	10.4
[Co(TITPT) ₂ I ₂] (Deep brown)	944.73	6.17 (6.23)	35.38 (35.56)	14.69 (14.81)	2.90 (2.96)	5.30	10200 17600 22300	189	11.3
[Co(TITPT) ₂ (NO ₃) ₂] (Deep brown)	814.93	7.14 (7.23)	41.10 (41.23)	17.01 (17.17)	3.36 (3.43)	5.70	10500 17800 22400	192	11.0
[Ni(TITPT) ₂ Cl ₂] (Green)	761.71	7.57 (7.70)	43.83 (44.11)	18.19 (18.37)	3.58 (3.67)	3.16	11400 16200 24600	194	9.2
[Ni(TITPT) ₂ Br ₂] (Green)	850.58	6.81 (6.90)	39.33 (39.50)	16.37 (16.46)	3.20 (3.29)	3.11	11500 15700 24200	207	9.7
[Ni(TITPT) ₂ I ₂] (Greenish brown)	944.518	6.01 (6.21)	35.29 (35.56)	4.71 (4.82)	2.90 (2.96)	3.17	11100 15600 24500	201	9.9
[Ni(TITPT) ₂ (NO ₃) ₂] (Deep green)	814.71	7.04 (7.20)	40.88 (41.24)	17.04 (17.18)	3.29 (3.43)	3.14	11300 15700 24800	220	8.4
[Cu(TITPT) ₂ Cl ₂] (Blue)	766.54	8.19 (8.28)	43.71 (43.83)	8.20 (8.26)	3.55 (3.65)	1.92	12400 15500	196	7.7
[Cu(TITPT) ₂ Br ₂] (Blue)	855.36	7.36 (7.42)	39.26 (39.28)	16.28 (16.36)	3.21 (3.27)	1.89	12300 15400	199	7.4
[Cu(TITPT) ₂ (NO ₃) ₂] (Bluish red)	819.54	7.67 (7.75)	40.78 (40.99)	16.91 (17.08)	3.33 (3.41)	1.94	12000 15100	207	7.3

DT = Decomposition Temperature

TABLE-2
KEY IR SPECTRAL BANDS (cm^{-1}) OF LIGAND TITPT AND ITS METAL COMPLEXES

Compounds	$\nu(\text{N-H})$	$\nu(\text{C=N})$	$\nu(\text{C=S})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$	$\nu(\text{M-S})$	$\nu(\text{M-X})$
TITPT	3100 m,b	1620 s, s	800 s,b	–	–	–	–
[Co(TITPT) ₂ Cl ₂]	3100 m,b	1590 m,b	780 m,b	–	450 m	400 m	305 m
[Co(TITPT) ₂ Br ₂]	3100 m,b	1590 m,b	780 m,b	–	455 m	405 m	280 m
[Co(TITPT) ₂ I ₂]	3100 m,b	1595 m,b	775 m,b	–	450 m	410 m	270 m
[Co(TITPT) ₂ (NO ₃) ₂]	3100 m,b	1600 m,b	775 m,b	495 m	445 m	410 m	–
[Ni(TITPT) ₂ Cl ₂]	3100 m,b	1590 m,b	770 m,b	–	450 m	415 m	325 m
[Ni(TITPT) ₂ Br ₂]	3100 m,b	1590 m,b	770 m,b	–	455 m	415 m	295 m
[Ni(TITPT) ₂ I ₂]	3100 m,b	1595 m,b	775 m,b	–	450 m	395 m	275 m
[Ni(TITPT) ₂ (NO ₃) ₂]	3100 m,b	1595 m,b	780 m,b	515 m	455 m	400 m	–
[Cu(TITPT) ₂ Cl ₂]	3100 m,b	1595 m,b	775 m,b	–	460 m	425 m	315 m
[Cu(TITPT) ₂ Br ₂]	3100 m,b	1595 m,b	780 m,b	–	455 m	420 m	285 m
[Cu(TITPT) ₂ (NO ₃) ₂]	3100 m,b	1590 m,b	770 m,b	515 m	450 m	415 m	–

After complexation this band shows without any 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 1620 cm^{-1} assigned^{23,25} to $\nu(\text{C=N})$ group. In the complexes this band suffered a downward shift by 20-30 cm^{-1} indicating the coordination of the azomethine nitrogen to the metal ion.

The spectrum of the ligand shows a strong and broad band at 800 cm^{-1} assigned^{22,26} to $\nu(\text{C=S})$. On complexation this band also suffered a downward shift in the spectra of the complexes indicating coordination of the metal ion through thione sulphur atom of thiosemicarbazone moiety.

The coordination through azomethine nitrogen and thione sulphur atom of thiosemicarbazone and oxygen atom of NO_3^- is further supported by the appearance of bands in the far IR region at 520-495, 460-440 and 425-395 cm^{-1} assigned^{27,28} to

$\nu(\text{M-O})$, $\nu(\text{M-N})$ and $\nu(\text{M-S})$, respectively. The linkage through metal-halogen is confirmed by the appearance of a band in the region 320-260 cm^{-1} assigned^{27,28} to $\nu(\text{M-X})$. (X = Cl⁻, Br⁻ and I⁻). These assignments are confirmed by the low molar conductance of the complexes in the range 7.3-11.3 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$. The significant band at 1520 and 1420 cm^{-1} with a separation of 120 cm^{-1} indicates monocoordinate nature of nitrate group^{29,30}.

The electronic spectra of all the Co(II) complexes exhibit three bands in the region 10200-10800, 17300-17960 and 22600-22100 cm^{-1} assignable to the transitions ${}^4\text{T}_{2g}(\text{F}) \leftarrow {}^4\text{T}_{1g}(\text{F})$, ${}^4\text{A}_{2g}(\text{F}) \leftarrow {}^4\text{T}_{1g}(\text{F})$ and ${}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{T}_{1g}(\text{F})$ respectively. The above mentioned spectral bands indicate octahedral^{31,32} geometry for the Co(II) complexes. The octahedral geometry of Co(II) complexes is also supported^{33,34} by magnetic susceptibility value in the range 4.89-5.10 BM. The Ni(II) complexes

exhibit three absorption bands in the region 11500-11100, 16200-15300 and 24900-24200 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 propose octahedral^{32,35} geometry for Ni(II) complexes, which is also supported^{33,34} by magnetic susceptibility values of the complexes in the range 3.11-3.18 BM. The Cu(II) complexes exhibit two broad bands in the regions, 12600-12000 and 15600-15100 cm^{-1} assigned to transitions ${}^2T_{2g}(F) \leftarrow {}^2E_g$ and charge transfer band respectively, which proposes octahedral geometry^{32,36} for Cu(II) complexes. The magnetic moment values for Cu(II) complexes are found in the range 1.89-1.94 BM^{33,34}.

Conductivity measurement: Molar conductance values of the complexes of Co(II), Ni(II) and Cu(II) were found to be in the range 7.3-11.3 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ in DMF which proposes their non electrolytic³⁷ nature. The molar conductance values also supported the structure assigned on the basis of physico-chemical and spectroscopic measurements.

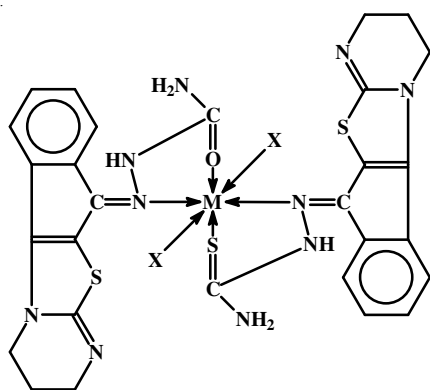


Fig. 1. $[M(\text{TITPT})_2] X_2$; M = Co(II) and Ni(II); X = Cl⁻, Br⁻, I⁻ and NO₃⁻; M = Cu(II); X = Cl⁻, Br⁻ and NO₃⁻

Conclusion

Thus on the basis of above studies it is concluded that the ligand TITPT acts in a bidentate manner and coordination is proposed through azomethine N and thione S of thiosemicarbazone moiety. The remaining positions of metal ions are satisfied by negative ions such as Cl⁻, Br⁻, I⁻ or NO₃⁻. The geometry of the Co(II), Ni(II) and Cu(II) complexes are proposed to be octahedral in nature as shown in Fig.1.

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