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Synthesis and Characterization of Co(II), Ni(II) and Cu(II) Complexes with Some Schiff Bases

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Metal chelates of Co(II), Ni(II) and Cu(II) with Schiff bases have been synthesized by the condensation of 1-oxo-1,2,3,4-tetrahydrocarbazoles with semicarbazide/thiosemicarbazide hydrochloride and characterised by using physico-chemical and spectroscopic methods. The ligands OTCS and OTCTS were suggested to behave as neutral tridentate (N,N,O/S) ligand and have octahedral geometry. The complexes have general composition $[M(OTCS)_3]$ and $[M(OTCTS)_2]$, M = Co(II), Ni(II) and Cu(II). The complexes were found to be non-electrolytic in nature due to low value of electrical conductivity.

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

INTRODUCTION

Carbazole derivatives possess interesting biological activities[1–4] such as anticancer, antihistamine, antibiotic, antiflammatory and antimicrobial properties. The antimicrobial activity of a ligand increased manifolds on coordinating with a suitable metal ion. Keeping the above facts in mind and in continuation of our research work[5–8] on transition metal complexes with semicarbazone and thiosemicarbazone ligands, in the present paper, synthesis and characterisation of Co(II), Ni(II) and Cu(II) complexes with ligands OTCS and OTCTS are reported.

EXPERIMENTAL

All the chemicals used were of AnalaR grade. The ligand as well as metal complexes were analysed by standard methods. Conductivity measurements were carried out on Toshniwal conductivity bridge using 10^{-3} M DMF solution. The IR spectra were recorded on Beckmann IR-20 spectrophotometer using KBr pellets. Electronic spectra were recorded on Carry-2390 spectrophotometer. Magnetic susceptibility was measured at 300 ± 1 K on a Gouy balance using mercury tetraisothiocynato cobaltate as a calibrant. The analytical data, colour, electronic spectra, magnetic moment and conductivity data are recorded in Table-1.

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Preparation of the ligands OTCS and OTCTS

Alcoholic solutions of 1-oxo-1,2,3,4-tetrahydro carbazoles were reacted with semicarbazide/thiosemicarbazide hydrochloride dissolved in 10% alcoholic solution of sodium acetate. The resulting reaction mixtures were heated on a water bath for 5–6 h, when a crystalline colourless solid began to separate out after allowing the solution to stand for 24 h. It was filtered, washed with ethanol and dried in an electric oven at *ca.* 60°C; yield 65–70%, OTCS, m.p. = 136 ± 1°C and OTCTS, m.p. = 142 ± 1°C.

Preparation of the complexes

A mixture of ethanolic solutions of the ligands OTCS and OTCTS in 20 mL ethanol and corresponding metal salts of Co, Ni and Cu were refluxed for 3–4 h in the molar ratio 2 : 1. The complexes were cooled, filtered and washed with ethanol several times to remove any excess of the metal chloride and/or ligand. Finally it was washed with anhydrous diethyl ether and dried in an electrical oven.

RESULTS AND DISCUSSION

The analytical data of compounds are given in Table-1. The characteristic infrared bands (4000–200 cm^{-1}) for the free ligands OTCS/OTCTS when compared with those of its Co(II), Ni(II) and Cu(II) complexes provide meaningful information regarding the bonding sites of the ligands (Table-2).

TABLE-1
ANALYTICAL, MAGNETIC MOMENT, ELECTRONIC SPECTRA AND CONDUCTIVITY DATA FOR OTCS, OTCTS AND THEIR COMPLEXES

Compound (Colour)	% Analysis: Found (Calculated)				μ_{eff} (B.M.)	λ_{max} electronic (cm^{-1})	Ω_{max} (ohm^{-1} cm^{-1} mol^{-1})
	M	C	N	H			
OTCS (Colourless)		64.41 (64.73)	23.02 (23.23)	5.32 (5.39)	—	—	—
OTCTS (Colourless)		60.53 (60.70)	21.69 (21.78)	4.97 (5.05)	—	—	—
$[Co(OTCS)_2]$ (Brown)	9.01 (9.19)	57.49 (57.67)	20.58 (20.70)	4.73 (4.80)	4.90	10700 21000	10.31
$[Co(OTCTS)_2]$ (Deep brown)	10.13 (10.28)	54.31 (54.45)	19.43 (19.54)	4.41 (4.53)	5.20	10200 20600	12.34
$[Ni(OTCS)_2]$ (Green)	10.72 (10.85)	57.93 (57.70)	20.53 (20.71)	4.71 (4.80)	3.02	11300 18900 27000	14.31
$[Ni(OTCTS)_2]$ (Violet)	10.31 (10.25)	54.29 (54.47)	19.38 (19.55)	4.41 (4.53)	3.14	11700 18300 27600	15.36
$[Cu(OTCS)_2]$ (Grey)	11.76 (11.64)	57.32 (57.19)	20.39 (20.53)	4.84 (4.76)	1.87	13000 18100	17.34
$[Cu(OTCTS)_2]$ (Brown)	10.89 (11.00)	54.26 (54.02)	19.27 (19.39)	4.63 (4.50)	1.93	13700 18600	19.26

TABLE-2
KEY IR SPECTRAL BANDS (cm^{-1}) OF LIGANDS OTCS AND OTCTS AND THEIR METAL COMPLEXES

Compounds	ν(N—H)	ν(C=O)	ν(C=N)	ν(C=S)	ν(M—O)	ν(M—N)	ν(M—S)
OTCS	3300 s, b	1740 s, b	1600 s, b	—	—	—	—
OTCTS	3370 s, b	—	1640 s, b	820 s, b	—	—	—
$[Co(OTCS)_2]$	3270 s, b	1705 s, b	1560 s, b	—	400 m	530 m	—
$[Co(OTCTS)_2]$	3340 s, b	—	1605 s, b	790 s, b	—	520 m	430 m
$[Ni(OTCS)_2]$	3275 s, b	1710 s, b	1555 s, b	—	380 m	535 m	—
$[Ni(OTCTS)_2]$	3335 s, b	—	1600 s, b	780 s, b	—	540 m	460 m
$[Cu(OTCS)_2]$	3260 s, b	1705 s, b	1565 s, b	—	410 m	535 m	—
$[Cu(OTCTS)_2]$	3330 s, b	—	1595 s, b	785 s, b	—	550 m	440 m

It is well known that the semicarbazone and thiosemicarbazone ligands can coordinate as bidentate ligands[9], in most cases, *via* the azomethine nitrogen and oxygen/sulfur atoms[10]. The IR spectra of the ligands OTCS/OTCTS exhibit strong and broad bands in the region 3370–3300 cm^{-1} due to asymmetric and symmetric modes of terminal secondary amine[11]. In the spectra of the complexes this band shows red shift indicating that coordination takes place through N atom of secondary amino group of pyrazole ring.

A red shift in ν(C=N)[12] band (1640–1600 cm^{-1}) in the spectra of free ligand to lower value (1590–1540 cm^{-1}) in their complexes is consistent with coordination of the azomethine nitrogen to the central metal ion; the infrared bands at 550–520 cm^{-1} in the complexes are then assignable to ν(M—N). The infrared spectrum of the ligand OTCS shows strong broad bond at 1740 cm^{-1} which may be assignable to ν(C=O).[13] In the spectra of the complexes this band also shows red shift at 1700 cm^{-1} and appearance of a band at 410–380 cm^{-1} in the complexes indicating that ν(M—O) confirms the coordinating of carbonyl oxygen atom to the metal ion. A strong and broad band at 820 cm^{-1} in the free ligand (OTCTS) spectrum is due to ν(C=S)[14] which has been found to shift to lower frequency region (790–780 cm^{-1}) in the complexes pointing to the coordination of the thione sulfur atom of thiosemicarbazone moiety, which is further confirmed by the occurrence of a new band at 460–430 cm^{-1} which may be assigned to ν(M—S).

The Co(II) complexes recorded two bands one in the region 16300–15900 cm^{-1} and the other in the 21000–19800 cm^{-1} region which indicate octahedral geometry[15] of the Co(II) complexes which are further supported[16] by high μ_{eff} value in the range 4.90–5.20 B.M. for all the Co(II) complexes. The Ni(II) complexes recorded three bands in the ranges 12600–9400 cm^{-1}, 18300–15200 cm^{-1} and 27000–25000 cm^{-1} indicating octahedral[15] geometry, which are further confirmed[16] by the μ_{eff} value in the range 3.02–3.14 B.M. for all the Ni(II) complexes. The electronic spectra of all the complexes of Cu(II) exhibit two ligand field bands, one in the region 13700–13000 cm^{-1} and another in the region 18600–18100 cm^{-1} which explain the octahedral geometry[15] of the Cu(II) com-

plexes, and which are further confirmed[16] by the μ_{eff} value in the range 1.87–1.93 B.M. for all the complexes.

Conductivity of the complexes was measured in the solvent dimethyl formamide and all the complexes were found to be non-electrolytic in nature giving conductivity values in the range 10–20 cm^{-1} ohm^{-1} cm^2 mol^{-1} (Table-2). The conductivity value also supports the assigned structure on the basis of elemental analysis, IR/electronic spectra and magnetic moment data. From the above observations, Co(II), Ni(II) and Cu(II) complexes of the types $[M(OTCS)_2]$ and $[M(OTCTS)_2]$ can be presumed to have octahedral geometry as shown in Fig. 1.

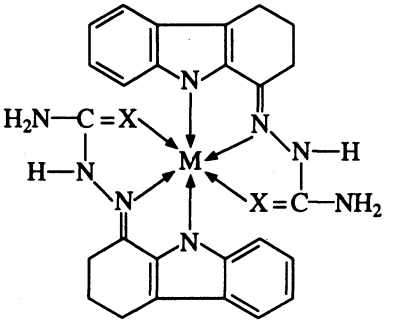

Fig. 1. $[M(OTCS)_2]$ and $[M(OTCTS)_2]$ X = O or S, M = Co(II), Ni(II) and Cu(II)

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