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Physico-chemical Studies of Cobalt(II) Complexes Derived from 2-Substituted Benzaldehyde Semicarbazones and Thiosemicarbazones

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Cobalt(II) complexes with 2-chlorobenzaldehyde/2-ethoxybenzaldehyde semicarbazone and thiosemicarbazone (cbsc, cbtsc, ebsc and ebtsc) have been synthesized and characterized by means of various physico-chemical techniques *viz.*, elemental analysis, magnetic moment, infrared spectral and electronic spectral studies. IR spectral studies showed bidentate chelating behaviour of the ligands coordinating through azomethine nitrogen and carbonyl oxygen/thioketo sulphur atoms. Magnetic moment of these complexes indicates high spin configuration. The probable structure for all the metal complexes is also proposed here.

Key Words: Cobalt(II) complexes, Semicarbazones, Thiosemicarbazones.

INTRODUCTION

The study of semicarbazone and thiosemicarbazone compounds has received great impetus in recent years due perhaps to their remarkable potential in inhibiting ribonucleotide reductase, an obligatory enzyme in DNA synthesis[1, 2]. As a consequence, compounds containing these pharmacaphores have been evaluated for their antiproliferative properties against a variety of tumours[3, 4]. Besides antitumour properties, these compounds have also been shown to possess antitubercular[5] and antimalarial[6] activities. Thiosemicarbazones have been a subject of interest in the recent decades due to their variable applications in industries and analytical chemistry[7]. Some derivatives of thiosemicarbazones have shown antiparasitic, antimicrobial, antineoplastic and biological activity[8].

Naturally occurring cobalt compounds involve the corrin ring system, as it is a unique trace element, as it is the only metal present in vitamin B_{12}. It was the first metallic complex in living systems to be studied in great depth[9, 10]. Cobalt(II) attains a variety of stereochemical configurations into its complexes; the best known are four-coordinated tetrahedral, five-coordinated trigonal bipyramidal and six-coordinated octahedral[11]. The present paper reports the synthesis of some complexes of 2-chlorobenzaldehyde semicarbazone (cbsc), 2-ethoxybenzaldehyde semicarbazone (ebsc), 2-chlorobenzaldehyde thiosemicarbazone (cbtsc) and 2-ethoxybenzaldehyde thiosemicarbazone (ebtsc) with cobalt(II) ion and their characterization by means of various physico-chemical techniques.

EXPERIMENTAL

All the chemicals and solvents used were of analytical reagent grade. The infrared spectra of the ligands and their metal complexes were scanned on a

Perkin-Elmer 1600 FTIR automatic recording spectrophotometer in potassium bromide. Electronic spectra were recorded in ethanol on Shimadzu UV-Vis spectrophotometer 1601 CP, while magnetic susceptibility measurements of the complexes were determined by Gouy's method using $Hg[Co(CNS)_4]$ as a calibrant. The analyses of C, H and N were done by microanalytical techniques. Cobalt contents were estimated by titrating with EDTA using xylenol orange as indicator[12].

Synthesis of ligands: The ligands 2-chlorobenzaldehyde/2-ethoxybenzaldehyde semicarbazone and thiosemicarbazone were synthesized according to literature procedure[13] by refluxing semicarbazide hydrochloride and thiosemicarbazide with 2-chlorobenzaldehyde and 2-ethoxybenzaldehyde respectively and confirmed by elemental analysis and IR spectral studies.

General Method for the preparation of metal complexes : A hot aqua ethanolic solution (20 ml) of cobalt salt (0.05 mol) was mixed with a hot ethanolic solution (20 ml) of the respective ligand (0.10 mol) in molar ratio 1 : 2. The contents were refluxed for about 4–5 h. On cooling the contents, the coloured complexes separated out. The product obtained were filtered, washed with 50% ethanol and dried in the electric oven.

RESULTS AND DISCUSSION

The analytical data (Table-1) of all the complexes confirm the 1 : 2 (M : L) stoichiometric ratio corresponding to the general formula ML_2X_2 (M = Co, L = cbsc, cbtsc, ebsc and ebtsc, X = Cl^-, NO_3^-, CH_3COO^-). Synthesized metal complexes are insoluble in water but are appreciably soluble in DMF, DMSO and pyridine.

The main vibrational bands (cm^{-1}) of the ligands and complexes are reported. A comparative scrutiny of the IR spectral data of complexes with those of free ligand gave clues regarding the donor sites of the ligand molecules. The stretching frequencies appearing at *ca.* 3030–3015 cm^{-1} and *ca.* 1610 cm^{-1} are assigned to ν(C—H) and ν(C═C) vibrations respectively and are suggestive of the aromatic character[14] of the ligands and their complexes. The bands originating at *ca.* 760–745 cm^{-1} may be assigned due to *ortho* substitution. The IR spectra of the free ligands show bands in the region 3370–3125 cm^{-1} assigned to the stretching vibration of the NH and NH_2 groups[15] and remain practically unchanged or shift to higher side indicating no coordination.

The strong band at *ca.* 1660 cm^{-1} is attributed to ν(C═O) stretching vibration[16] while the band at *ca.* 1532 cm^{-1} is due to ν(C═N) stretching vibration[16]. The medium intensity bands at *ca.* 1000–995 cm^{-1} are assigned to ν(N—N) vibration while that at *ca.* 815 cm^{-1} is attributed to ν(C═S) vibrations[16, 17]. The IR data of all the complexes reveal that the bands assigned to the donor molecules ν(C═S) have shifted to the lower region, suggesting that sulphur is involved in the coordination with the metal ion. The absence of bands above 3400 cm^{-1} or in the region 2600–2500 cm^{-1}, which would be due to ν(OH) and ν(SH) vibrations respectively, indicates the ligands existing in the keto/thione form[18].

The characteristic absorption bands of the free ligands are shifted on complexation, showing that both the ligands behave in a bidentate manner in all cobalt (II) complexes. The strong bands observed at *ca.* 1660 cm^{-1} due to ν(C═O) vibrations[16] shift to lower wave number side by about 50–25 cm^{-1} in all the metal complexes. This suggests the coordination of oxygen atom with metal ion. The band at *ca.* 1532 cm^{-1} due to $\nu(C{=}N)$[16] vibrations shifts to lower wavenumber side by about 50–30 cm^{-1} in the metal complexes indicating the coordination of azomethine nitrogen atom with metal ion.

TABLE-1
ELEMENTAL ANALYSIS DATA OF COBALT(II) COMPLEXES

Complexes	Colour	% Found (Calcd.)			
		Co	C	H	N
$Co(C_8H_8N_3OCl)_2Cl_2$	Yellow	11.29 (11.22)	36.53 (36.58)	3,14 (3.05)	16.06 (16.00)
$Co(C_8H_8N_3OCl)_2(NO_3)_2$	Pale yellow	10.30 (10.20)	33.31 (33.22)	2.88 (2.77)	19.31 (19.38)
$Co(C_8H_8N_3OCl)_2(CH_3COO)_2$	Pale yellow	10.25 (10.30)	42.00 (41.96)	3.98 (3.85)	14.75 (14.69)
$Co(C_8H_8N_3SCl)_2Cl_2$	Blackish Green	10.00 (10.04)	34.59 (34.47)	3.00 (2.87)	15.00 (15.08)
$Co(C_8H_8N_3SCl)_2(NO_3)_2$	Blackish yellow	9.74 (9.66)	31.41 (31.48)	2.56 (2.62)	18.40 (18.36)
$Co(C_8H_8N_3SCl)_2(CH_3COO)_2$	Yellowish black	10.14 (10.02)	41.00 (40.82)	3.89 (3.74)	14.42 (14.29)
$Co(C_{10}H_{13}N_3O_2)_2Cl_2$	Pink	10.87 (10.83)	44.03 (44.12)	4.71 (4.78)	15.50 (15.44)
$Co(C_{10}H_{13}N_3O_2)_2(NO_3)_2$	Dark brown	9.80 (9.87)	40.30 (40.21)	4.24 (4.36)	18.68 (18.76)
$Co(C_{10}H_{13}N_3O_2)_2(CH_3COO)_2$	Dark brown	10.08 (9.97)	48.35 (48.44)	4.47 (4.40)	14.10 (14.21)
$Co(C_{10}H_{13}N_3OS)_2Cl_2$	Dark green	10.10 (10.23)	41.78 (41.67)	4.43 (4.51)	14.67 (14.59)
$Co\ (C_{10}H_{13}N_3OS)_2(NO_3)_2$	Dull green	9.30 (9.37)	38.04 (38.16)	4.16 (4.13)	17.91 (17.80)
$Co(C_{10}H_{13}N_3OS)_2(CH_3COO)_2$	Dark red	9.52 (9.46)	46.37 (46.23)	5.28 (5.14)	13.40 (13.48)

In acetate complexes IR frequency bands corresponding to $\nu_{asym}(COO^-)$ and $\nu_{sym}(COO^-)$ at *ca.* 1605 and 1372 cm^{-1} indicate that the acetate groups are unidentate. The IR spectra of nitrate complexes show absorption bands corresponding to both coordinated and uncoordinated nitrate group. The semicarbazone ligand complexes show bands at *ca.* 1435, 1380, 1276, 1015 and 842 cm^{-1}. The separation (*ca.* 160 cm^{-1}) indicates the monodentate nature of the nitrate group[19, 20]. The thiosemicarbazone complexes of cabalt(II) show IR spectral band $\nu(NO_2)$ asymmetric stretching[21] of ionic nitrate at *ca.* 1393 cm^{-1} but do not show bands which could be attributed to the coordinated[19, 20] nitrate group in the regions 1535–1516, 1309–1270 and 1075–950 cm^{-1}. Thus two bidentate ligand molecules around cobalt (II) should give rise to four-coordinated tetrahedral geometry.

The magnetic mement[22] values for all complexes under study lie in the range 4.46–5.20 B.M. at room temperature indicating high spin configuration which is obtained for four-coordinated tetrahedral, five-coordinated square pyramidal or trigonal bipyramidal or six coordinated octahedral cobalt (II). The electronic spectra of all semicarbazone cobalt (II) complexes under study originate spectral bands (Table-2) in the range 9205–8500 cm^{-1} (ν_1), 16408–15800 cm^{-1} (ν_2) and 21050–20580 cm^{-1} (ν_3).

TABLE-2
ELECTRONIC SPECTRAL DATA AND MAGNETIC MOMENT OF SEMICARBAZONE Co(II) COMPLEXES

Complexes	$\nu_1(cm^{-1})$ $^4T_{1g}\rightarrow{}^4T_{2g}$	$\nu_2(cm^{-1})$ $^4T_{1g}\rightarrow{}^4A_{2g}$	$\nu_1(cm^{-1})$ $^4T_{1g}\rightarrow{}^4T_{1g}(P)$	μ_{eff} (B.M.)
$Co(cbsc)_2Cl_2$	8615	16408	21050	4.46
$Co(cbsc)_2(NO_3)_2$	9205	15004	20670	4.53
$Co(cbsc)_2(CH_3COO)_2$	8708	16000	20580	4.94
$Co(ebsc)_2Cl_2$	8500	15800	20575	4.63
$Co(ebsc)_2(NO_3)_2$	8698	16100	21025	4.92
$Co(ebsc)_2(CH_3COO)_2$	8525	15980	20910	4.53

These spectral bands are attributable to $^4T_{1g} \rightarrow {}^4T_{2g}$ (ν_1), $^4T_{1g} \rightarrow {}^4A_{2g}$ (ν_2) and $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ (ν_3) transitions respectively. These spectral bands are characteristic for six-coordinated octahedral geometry[23] for the complexes. The electronic spectra of the thiosemicarbazone cobalt (II) complexes are virtually identical and display well defined bands (Table-3) at 5208–5850, 6300–6500, 13400–14000 and 16845–17320 cm^{-1}. Similar spectral bands have been reported[24, 25] for high spin, five-coordinated cobalt(II) complexes.

TABLE-3
ELECTRONIC SPECTRAL BANDS AND MAGNETIC MOMENT OF THIOSEMICARBAZONE Co(II) COMPLEXES

Complexes	Spectral bands (cm^{-1})				μ_{eff} (b.m.)
$Co(cbtsc)_2Cl_2$	5208	6300	13410	16845	5.20
$Co(cbtsc)_2(NO_3)_2$	6015	16580			4.48
$Co(cbtsc)_2(CH_3COO)_2$	5605	6503	13898	17318	5.05
$Co(ebtsc)_2Cl_2$	5847	6375	9263	13706	4.53
$Co(ebtsc)_2(NO_3)_2$	6100	16522			4.92
$Co(ebtsc)_2(CH_3COO)_2$	5778	8198	8775		4.72

Based on the above observations of elemental analysis, magnetic moment, Infrared and electronic spectral studies six-coordinated octahedral structures are suggested for semicarbazone complexes whereas five-coordinated trigonal bipyramidal structure for thiosemicarbazone complexes except nitrate complexes for which tetrahedral geometry is proposed.

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