

PHYSICO CHEMICAL STUDIES OF MANGANESE (II), COBALT (II), ZINC (II) AND COPPER (ii) COMPLEXES DERIVED FROM 2-SUBSTITUTED BENZALDEHYDE THIOSEMICARBAZONES

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ABSTRACT

The metal complexes of manganese (II), Cobalt (II), Zinc (II) and Copper (II) with 2-chlorobenzaldehyde thiosemicarbazone (cbtsc) and 2-ethoxybenzaldehyde (ebtsc) have been synthesized and characterized by means of various physico-chemical techniques viz. elemental analysis, magnetic susceptibility measurements, Infrared and electronic spectral studies. IR spectral data showed monoegative bidentate chelating behaviour of ligand coordinating through deprotonated thiol sulphur and azomethine nitrogen atoms. Magnetic moment of these complexes indicates high spin configuration. The probable structure for all the metal complexes is proposed here.

KEYWORDS: Metal complex, ligand, magnetic moments, thiosemicarbazones

The study of thiosemicarbazone compounds has received great impetus in recent years due to perhaps to their remarkable potential in inhibiting ribonucleotide reductase, an obligatory enzyme in DNA synthesis (Mullier and Fontecave, 1999). As a consequence compounds containing these pharmacophores have been evaluated for their antiproliferative properties against a variety of tumors (Li et al., 2001). Thiosemicarbazones have been a subject of interest in the recent decades due to their variable applications in industries and analytical chemistry. Several activities have been tested in dithiocarbamate derivatives potent herbicides, insecticides and pesticides have been reported. Dithiocarbamate complexes of transitional and non transitional metal ions have been reported by various workers. The present paper reports synthesis of some complexes of cbtsc and ebtsc with Mn(II), Co(II) Zn(II) and Cu (II) and characterized them 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 Perkin-Elmer

1600 FTIR automatic recording spectrophotometer in potassium bromide. Electronic spectra were recorded in ethanol on shimadzu UV and visible spectrophotometer 1601 C.P. The magnetic susceptibility measurements of the complexes were determined by Guoy's method using Hg[Co(CNS)₄] as a calibrant. Metal contents were estimated by following the literature method (Vogel, 1962). The analysis of C, H and N were done by microanalytical techniques.

Synthesis of Ligands

The ligands 2-Chlorobenzaldehyde/2-ethoxybenzaldehyde thiosemicarbazones were synthesized according to the literature procedure (Vogel, 1973) by refluxing thiosemicarbazide with respective aldehydes and confirmed by elemental analysis and IR spectral studies.

General Method for the Preparation of Metal Complexes

The ammonical solution (20 ml) of metal salt (0.05 mol) was mixed with a hot ethanolic solution (20 ml) of the respective ligands (0.10 mol) in molar ratio 1:2. The contents were refluxed for about 4-5 hours. On cooling the contents coloured complexes separated out. The same was filtered, washed with 50% ethanol, dried in electric oven, analysed and the data is represented in table-1.

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RESULTS AND DISCUSSION

Synthesized metal complexes are insoluble in water but are appreciably soluble in DMF, DMSO and

pyridine. The analytical data of all the complexes confirm to 1:2 (M:L) stoichiometric ratio corresponding to general formula ML₂. (MMn(II), Co(II), Zn(II), and Cu(II), Lcbtsc and ebtsc).

Table 1:Elemental analysis data of Complexes

Complexes	Colour	% found (Calculated)			
		M	C	H	N
Mn (C ₈ H ₈ N ₃ SCl) ₂	Greenish	11.50	39.80	3.40	17.35
	Yellow	(11.58)	(39.76)	(3.31)	(17.39)
Co (C ₈ H ₈ N ₃ SCl) ₂	Greenish Black	12.15	39.59	3.25	17.21
		(12.13)	(39.51)	(3.29)	(17.29)
Cu (C ₈ H ₈ N ₃ SCl) ₂	Dull Red	13.00	39.04	3.18	17.14
		(12.95)	(39.14)	(3.26)	(17.12)
Zn (C ₈ H ₈ N ₃ SCl) ₂	Light Yellow	13.40	39.00	3.36	17.00
		(13.33)	(38.97)	(3.25)	(17.05)
Mn (C ₁₀ H ₁₃ N ₃ OS) ₂	Redish Brown	11.08	47.89	5.20	16.80
		(11.14)	(47.81)	(5.18)	(16.74)
Co (C ₁₀ H ₁₃ N ₃ OS) ₂	Dull Green	11.70	47.45	5.18	16.70
		(11.67)	(47.53)	(5.15)	(16.64)
Cu (C ₁₀ H ₁₃ N ₃ OS) ₂	Black	12.49	47.19	5.17	16.42
		(12.47)	(47.10)	(5.10)	(16.49)
Zn (C ₁₀ H ₁₃ N ₃ OS) ₂	White	12.92	46.97	5.20	16.33
		(12.84)	(46.90)	(5.08)	(16.42)

Infrared Evidences

A comparative scrutiny of the IR spectral data of complexes with those of free ligand gave clues regarding the dono sites of the ligand molecules. The stretching frequencies appearing at ~3015~3030 cm⁻¹ and ~1610 cm⁻¹ are assigned to ν(C-H) and ν(C=C) vibrations respectively and are suggestive of the aromatic character (Bellamy, 1985) of the ligands and their complexes. The bands boriginated at ~745~760 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 NH₂ groups. The intensity of these bands is considerably lowered in metal complexes. These changes suggest a system -C=N-NH-CS-NH₂ participate in the chelate formation. The strong band at ~1532 cm⁻¹ is due

to ν(C=N) stretching vibration while the medium intensity bands at ~995~1000 cm⁻¹ assigned to ν(N-N) vibrations. The presence of bands in the region 2485-2550 cm⁻¹ which would be due to ν(S-H) vibrations indicates the ligands in the thiol form. The bands appearing about at 815 cm⁻¹ in the ligands may be assigned to (C=S) stretching vibrations. However this band suffers a large lowering by 80105 cm⁻¹ in the complexes through the deprotonation of S-H group to yield the mono valent ligand anion and the band at ~1532 cm⁻¹ ν(C=N) vibrations shift to lower wave number side by about 35-70 cm⁻¹ in the metal complexes. This suggests that both thiosemicarbazones behave as monoegative bidentate ligands coordinating via the deprotonated thiol sulphur (C-S) and azomethine nitrogen (C=N) atoms.

Magnetic Moment and Electronic Spectral Studies

The magnetic moments for manganese complexes lie in the range 5.90-5.96 B.M. at room temperature very close to spin only value corresponding to five unpaired electrons, which is obtained for high spin six coordinated

octahedral configuration (Eamshaw, 1962). The electronic spectral bands for Mn(II) complexes of cbtsc and ebtsc lie in the region 18700, 18780 cm^{-1} , 23845, 28675 cm^{-1} and 31800, 31740 cm^{-1} respectively. These spectral bands are assigned as six tetquartet ${}^6A_{1g} \rightarrow {}^4T_{1g} ({}^4G)$, ${}^6A_{1g} \rightarrow {}^4E_g ({}^4G)$, ${}^6A_{1g} \rightarrow {}^4E_g ({}^4D)$

Table 2: Electronic spectral data and Magnetic moment of thiosemicarbazone Complexes

Complexes	Spectral Bands	Assignments	μ_{eff} (B.M.)
Mn(cbtsc-H) ₂	18700	${}^6A_{1g} \rightarrow {}^4A_{1g} ({}^4G)$	5.96
	23845	${}^6A_{1g} \rightarrow {}^4E_{1g} ({}^4G)$	
	28708	${}^6A_{1g} \rightarrow {}^4E_{1g} ({}^4D)$	
	31800	${}^6A_{1g} \rightarrow {}^4T_{1g} ({}^4P)$	
Co(cbtsc-H) ₂	8990	${}^4T_{1g} \rightarrow {}^4T_{2g}$	4.94
	16040	${}^4T_{1g} \rightarrow {}^4A_{2g}$	
	20085	${}^4T_{1g} \rightarrow {}^4T_{1g} (P)$	
Cu(cbtsc-H) ₂	16200	${}^2B_{1g} \rightarrow {}^2A_{1g}$	1.84
	21985	${}^2B_{1g} \rightarrow {}^2E_g$	
Zn(cbtsc-H) ₂	—	—	—
Mn(ebtsc-H) ₂	18780	${}^6A_{1g} \rightarrow {}^4A_{1g} ({}^4G)$	5.90
	23800	${}^6A_{1g} \rightarrow {}^4E_{1g} ({}^4G)$	
	28675	${}^6A_{1g} \rightarrow {}^4E_{1g} ({}^4D)$	
	31740	${}^6A_{1g} \rightarrow {}^4T_{1g} ({}^4P)$	
Co(ebtsc-H) ₂	9000	${}^4T_{1g} \rightarrow {}^4T_{2g}$	4.86
	14765	${}^4T_{1g} \rightarrow {}^4A_{2g}$	
	19850	${}^4T_{1g} \rightarrow {}^4T_{1g} (P)$	
Cu(ebtsc-H) ₂	15470	${}^2B_{1g} \rightarrow {}^2A_{1g}$	1.80
	21600	${}^2B_{1g} \rightarrow {}^2E_g$	
Zn(ebtsc-H) ₂	—	—	—

and ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (4P) transitions respectively and are characteristic for six coordinate octahedral stereochemistry (Liver, 1968). The magnetic moment values for cobalt (II) complexes lie in the range 4.864.94 B.M. close to distorted octahedral geometry (Selwood, 1956). The slightly lower moment values may be attributed to spin exchange interaction arising due to sulphur bridges. An equilibrium between the high spin and low spin states may be also possible reason. The electronic spectral data of the Co (II) complexes of cbtsc and ebtsc show to sharp absorption bands at 89900 & 9000 cm^{-1} and 20085 & 19850 cm^{-1} with a shoulder at 16040 & 14765 cm^{-1} respectively. Electronic spectrum is consistent with high spin distorted octahedral cobalt (II) which gives rise to the three transitions although ν_2 is not always observed. These spectral bands are attributable to ${}^4T_{1g} \rightarrow {}^4T_{2g}$ (ν_1), ${}^4T_{1g} \rightarrow {}^4A_{2g}$ (ν_2) and ${}^4T_{1g} \rightarrow {}^4T_{1g}$ (ν_3) transitions respectively. The value of ν_2/ν_1 also confirm distorted octahedral geometry. The zinc (II) complexes were found to be diamagnetic as expected for d^{10} system. Four coordinated tetrahedral geometry may be proposed for these complexes. The copper(II) complexes exhibit magnetic moment of 1.84 & 1.80 B.M. corresponding to the spin only value irrespective of the stereochemistry indicating that the orbital contribution is almost quenched by the crystalline ligand field. The electronic spectral bands corresponding to the transitions ${}^2B_{1g} \rightarrow {}^2A_{1g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ are observed at 16200 & 15470 cm^{-1} and 21985 & 21600 cm^{-1} for copper (II) complexes of cbtsc and ebtsc respectively. These are suggestive for square planar geometry for these complexes (Table 2).

Based on elemental analysis, magnetic moment, Infrared and electronic spectral studies polymeric six coordinated octahedral geometry may be proposed for manganese (II) and Cobalt (II) complexes, four coordinated tetrahedral geometry for Zinc (II) and square planar geometry for Copper (II) complexes.

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