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Synthesis, Characterization and Antimicrobial Activity of N-(N,N-Diethylaminobenzyl)thiosemicarbazone and Its Transition Metal Complexes

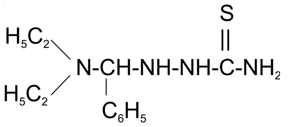
A.N. MOHAMED KASIM* and R.SRINIVASAN†
Department of Chemistry, Jamal Mohamed College, Tiruchirappalli-620 020, India

The new Mannich base N-(N,N-diethylaminobenzyl)thiosemicarbazone is synthesized by condensing N,N-diethylamine, benzaldehyde and thiosemicarbazide and characterized by elemental analysis, FT IR and PMR spectral data. Solid complexes of N-(N,N-diethylaminobenzyl)-thiosemicarbazone with bivalent Mn, Co, Ni, Cu and Cd metal salts have been synthesized and characterized by elemental analysis, conductance, UV, IR and PMR spectral and DTA studies. The ligand acts as the bidentate coordinating through the N of diethylamine and S of thiosemicarbazide moieties. The ligand and the complexes have also been screened for *in vitro* disc diffusion studies for antimicrobial activities.

Key Words: Metal complexes, N-(N,N-Diethylaminobenzyl)-thiosemicarbazone.

INTRODUCTION

Several amino methylated as well as amino benzylated mannich bases using formaldehyde and benzaldehyde have been reported to have good biological activities and complexation characteristics with transition metal ions. Some of the mannich bases of semicarbazide and benzaldehyde have been reported[1-8]. But the literature survey does not reveal the synthesis and characterization of N-(N,N-diethylaminobenzyl)thiosemicarbazone by the condensation of diethylamine, benzaldehyde and thiosemicarbazide.



$$(H_5C_2)_2N-\underset{C_6H_5}{CH}-NH-NH-\overset{\overset{S}{\|}}{C}-NH_2$$

Structure of N-(N,N-diethylaminobenzyl)thiosemicarbazone

EXPERIMENTAL

All the chemicals used in the present study were from BDH or E. Merck quality. Metal salts and solvents were of reagent grade. The metal salts were used as such without dehydrating them. The purity of ligand was checked by melting point, TLC

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†Department of Chemistry, Governments Arts College, Karur-639 005, India.

and CHN analysis. The ligand being insoluble in water, all the complexes were prepared in non-aqueous media. FTIR spectra in KBr medium were recorded on Perkin-Elmer 983 spectrometer. PMR spectral data were taken on Brucker SF 300 MHZ using deuterated DMSO at CARSIM-SASTRA University, Thanjavur.

Metal ions and anions in the complexes were determined by standard method. CHN contents of the complexes were analyzed by Carlo Erbo 1106 and Thomas Micro analyzers. The sulphur content was determined gravimetrically[9] by precipitating into $BaSO_4$. Magnetic susceptibilities were measured by Gouy's method at room temperature.

Preparation of N-(N,N-diethylaminobenzyl)thiosemicarbazone (DBT): Diethylamine, thiosemicarbzide and benzaldehyde in (1:1:1) mole ratio were stirred well along with CCl_4 (5mL) and 5 drops of 10 % aqueous NaOH and then cooled in ice bath. The appeared solid was purified by several washings with water and aqueous solutions of $NaHCO_3$ and $NaHSO_3$ to remove the unreacted components. The purity of the compound was checked by TLC. The melting point of the sample was found to be 148-152 ºC. The elemental analysis data is reported in Table-1.

TABLE-1
PHYSICAL AND ANALYTICAL DATA OF LIGAND AND ITS COMPLEXES

	Complex (colour)	Elemental analysis (%)				μ_{eff} (BM)	Molar cond. (Ω^{-1} cm^2 mol^{-1})
		C	N	S	M		
1	DBT (Colourless)	57.14	22.22	12.70	–	–	–
2	$[CuL(H_2O)_2SO_4]$ (Yellow)	32.26	12.71	14.50	14.37	1.90	23.10
3	$[CuL_2(NO_3)_2]$ (Brown)	41.70	26.31	9.29	9.35	1.83	30.00
4	$[NiL_2Cl_2]$ (Yellow)	45.71	17.90	10.21	9.40	2.85	20.20
5	$[NiL_2Br_2]$ (Yellow)	35.08	13.50	7.60	7.33	2.56	30.15
6	$[NiL_2(NO_3)_2]$ (Greenish yellow)	41.95	20.41	9.60	8.61	2.80	27.20
7	$[CoLCl_2]$ (Blue)	37.90	14.80	8.45	15.60	3.85	15.30
8	$[CoL_2(NO_3)_2]$ (Brown)	41.95	20.71	9.50	8.70	3.65	17.30
9	$[MnL_2Cl_2]$ (Faint pink)	41.98	16.35	9.50	8.80	5.20	40.15
10	$[CdL_2Cl_2]$ (White)	41.98	16.35	9.50	16.41	Diamag.	25.15
11	$[CdL_2(NO_3)_2]$ (White)	38.90	18.95	8.81	15.30	Diamag.	37.25

Preparation of metal complexes of DBT (2-11): The metal complexes were prepared by mixing the solutions of ligand and the corresponding metal salts in methanol in 2:1 mole ratio and refluxed on the water bath for 1 h. The resultant solid was washed with acetone and dried over anhydrous $CaCl_2$.

RESULTS AND DISCUSSION

All the complexes are stable in air and non hygroscopic. They are soluble in DMF and DMSO. The analytical results indicate 1:2 (M:L) stoichiometry for all the complexes except $CuSO_4$ and $CoCl_2$ complexes. All the complexes in DMF at 10^{-3} M show lower molar conductivity values in the range of 15.3 to 40.5 Ω^{-1} cm^2 mol^{-1} (Table-1) indicating their non-electrolytic nature.

Infrared spectra of DBT and complexes: The ligand DBT shows aromatic phenyl ν(C-H) band at 3155 cm^{-1} and bending modes at 763 cm^{-1}. The ν(C-N) frequency of diethyl amino group is shown at 1374 cm^{-1}. A sharp intense band at 1546 cm^{-1} is due to ν(C=S) mode frequency. The strong band obtained at 1296 cm^{-1} is assigned to tertiary ν(C-N-C) and the band at 3546 cm^{-1} is due to ν(N-H) mode of $-NH_2$ group.

The ligand DBT also exhibits bands at 3419 of $\nu_{asym.}$(NH) and 3255 cm^{-1} of ν_{sym}(NH). The persistence of these bands in the complexes indicate the non-involvement of the nitrogens of thiosemicarbazide moiety of DBT for coordination. The ligand absorption bands at 1546 of ν(C=S) and 1296 cm^{-1} of ν_{tert}(CNC) undergo downward shifts in all the complexes by about 30-40 cm^{-1} suggesting the bidentate nature of DBT bonding through thiocarbonyl sulphur and tertiary N of diethyl amino group.

The copper complex (**2**) also exhibits bands at 1220, 1149 (ν_3), 1030, 1002 (ν_1) and 941 cm^{-1} (ν_4) indicating the bidentate nature of sulphate group. The observed additional bands at 1615, 864 and 630 cm^{-1} are due to the presence of coordinated water in the complex. An endothermic curve in DTA also supports the presence of two coordinated water molecules in the complex. The loss of mass equivalent to two water molecules of the copper complex in the range 120-170 ºC upon isothermal heating is also observed.

The complexes (**3, 6, 8, 11**) also show additional bands in the ranges 1415-1385 (ν_5) and 1360-1340 cm^{-1} (ν_1) assignable to ν(N-O) modes of the coordinated nitro group. Since the (ν_5) and (ν_1) bands are separated to the extent of 50-70 cm^{-1}, the unidentate behaviour of nitrato groups in these compounds is suggested. IR absorption bands at about 650-600 cm^{-1} assignable to coordinated water are absent in the spectra of complexes except complex (**2**).

PMR spectra: The spectrum of ligand DBT exhibits multiplets at δ 7.8-7.31 ppm due to phenyl group and the triplet at δ 6.8 ppm assigned to the -NH group. The intense signal at δ 2.5 ppm corresponds to the N-CH part of diethyl amino group and at δ 3.5 ppm is assigned to the $-CH_2$ of the ethyl groups. Thus the PMR data confirm the presence of diethyl amino, substituted benzyl and thioamide moieties.

The secondary thioamide (N-H) triplet signal in all the complexes (**2-11**) appear at about which are slightly down field to that of the free ligand denoting the coordination of (C=S) group to metal ion. The intense signal at δ 2.5 ppm due to N-CH of diethyl amino group of the ligand is also drifted slightly upwards in PMR spectra of metal complexes indicating the coordination of tertiary N- of diethyl amino group. Thus PMR spectra confirms the bidentate nature of DBT upon complexation.

Magnetic susceptibility and electronic spectra: The room temperature magnetic moments of the complexes (**2-9**) reveal the paramagnetic behaviour and they are all coloured. The Cd(II) complexes are diamagnetic and colourless (**10,11**). The electronic spectra of the six coordinated Cu(II) sulphato (**2**) and nitrato (**3**) complexes exhibit broad bands at 15361 and 15737 cm^{-1} assignable to $^2E_g \rightarrow ^2T_g$ transition. The Ni(II) complexes (**4-6**) exhibits ν_1, ν_2 and ν_3 absorption bands around 14500, 16000 and 32000 cm^{-1} due to allowed transition states of $^3A_{2g}(F)\rightarrow{}^3T_{2g}(F)$, $^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$ and $^3A_{2g}(F)\rightarrow{}^3T_{1g}(P)$, respectively when are assignable to octahedral geometry. The four coordination and the blue colour of the Co(II) high spin (**7**) exhibits bands at 14860 (ν_3) and 7080 cm^{-1} (ν_2) corresponding to $^4A_{2g}(F)\rightarrow{}^4T_1(P)$ and $^4A_{2g}(F)\rightarrow{}^4T_{1g}(F)$ transition of the complex indicating tetrahedral geometry. The Co(II) spin complex (**8**) exhibits three transition bands at 8700 (ν_1), 14300 (ν_2) and 20400 cm^{-1} (ν_3) in its electronic spectra which suggests distorted octahedral geometry for this complex. The six coordinated Cd(II) high spin complexes (**10,11**) showed absorption peaks around 11100 and 29940 cm^{-1} due to $^4A_{2g}(F)\rightarrow{}^4T_{2g}(F)$ and $^4A_{2g}(F)\rightarrow{}^4T_{2g}(P)$ transitions.

Antimicrobial screening: The ligand and its complexes were tested *in vitro* for their antimicrobial activity against *Escherichia coli, Pseudomonas aeruginosa* and *Staphylococcus aureus* by filter paper disc method[10]. All the test chemicals were dissolved in DMSO. Filter paper disc of 0.6 mm diameter containing 100 µg of the test compound per disc was prepared, dried and placed on the surface of bacteria seeded agar plates. It was incubated at 37 ºC for 24 h.

Compound	*E. coli*	*P. aeruginosa*	*S. aureus*
N-(N,N-Diethylaminobenzyl)thiosemicarbazone	60	69	45
$[CuL_2(NO_3)_2]$	65	73	50
$[NiL_2(NO_3)_2]$	72	80	54
$[CoL_2(NO_3)_2]$	64	71	46
$[NiL_2Cl_2]$	78	82	58
$[CoLCl_2]]$	70	73	47
Ciprofloxacin	100	100	100

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