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Synthetic, Structural and Antifungal Studies of Some 3d - Metal Complexes of Salicylaldehyde - 2 - Benzo Furan Thiocarboxyhydrazone

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Abstract

The investigation on the metal complexes of salicylaldehyde–2–benzo furan thio carboxy hydrazone having the >N–C=S group. Salicylaldehyde–2–Benzofuran thiocarboxy hydrazone (H_2L) forms the adducts $Ni(H_2L)_2Cl_2$ and $Cu(H_2L)Cl_2$ and deprotonated complexes having a 1:1, 1:2 and/or 1:3 metal to ligand ratio. Infrared spectral studies show that H_2L behaves as a neutral bidentate in the adducts, as a uninegative bidentate in 1:2 and 1:3 deprotonated complexes and as a binegative tridentate in 1:1 deprotonated complexes. The ligand and its 1:2–deprotonated complexes of Mn(II), Co(III) and Cu(II) have been tested for their fungicidal action against Aspergillus niger and Rhizopus oryzae in which the Cu(II) complex displayed the maximum fungitoxicity.

Keywords: . Salicylaldehyde, Thiocarboxyhydrazone, Salicylaldehyde–2–Benzo Furan

1. Introduction

Thiosemicarbazones and their 3d–metal complexes have been found to exhibit fungicidal[(1)], bactericidal[(2)], antiviral and antitubercular[(3)] activities. The antifungal activity of these compounds is due to the presence of the toxophorically important >N–C–S moiety[(4)]. A survey of the literature shows that transition metal complexes of Schiff bases derived from the condensation of salicylaldehyde with thiosemicarbazide and S–methyl and benzyl dithiocarbazates[(5)] have been reported but no work seems to have been done on the metal complexes of salicylaldehyde 2–benzo furanthiocarboxy hydrazone having the >N–C=S group. The present chapter describes the results of our investigation on the title complexes.

2. Experimental

2.1 Materials and Methods

All the chemicals used were of analytical reagent grade or equivalent quality. Salicylaldehyde–2–benzo furan thiocarboxyhydrazone, $C_6H_4(OH)$ (CH:N.NH.C(S)$C_8H_5O(H_2L)$, was prepared by refluxing a mixture of 0.1 mol 2–benzo furan thiocarboxy hydrazide dissolved in 70 mL ethanol and 0.12 mol of salicylaldehyde for ~2 hr**.**

2.2 Preparation and Analysis of the Complexes

$Ni(H_2L)_2Cl_2$ and $Cu(H_2L)Cl_2$ were prepared by adding slowly with stirring 25 mL of an ethanolic solution of the respective hydrated metal(II) chloride (10mmol) containing a few drops of dil. HCl to 20 mmol solution of the ligand in 20mL ethanol. The complexes separated on cooling the reaction mixture in ice.

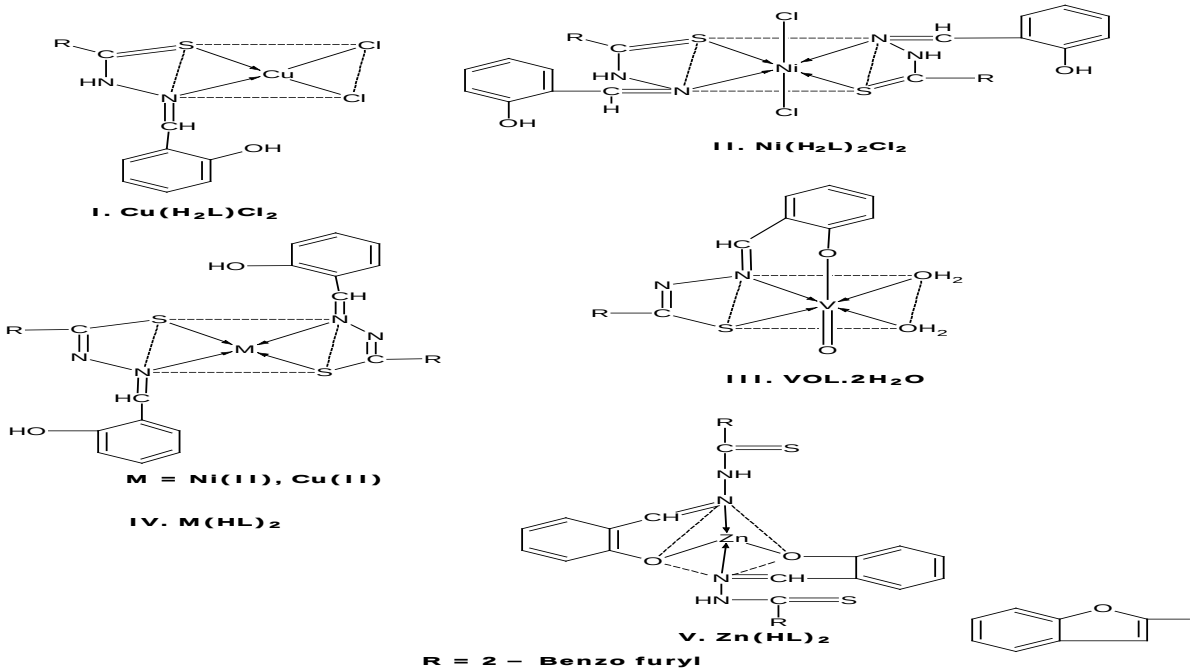

FIG. 1

$M(HL)_2$ [M= Mn(II), Ni(II) and Zn(II)] and Co(HL)(L) were prepared by adding 20 mL of an ethanolic solution of 20 mmol of the ligand to 20 mL of an aqueous solution of 10 mmol of the respective metal(II) acetate in the presence of 0.5 g sodium acetate and digesting the reaction mixture on a water bath for ~30 minutes**.**

3. Measurements and Observations:

Table-1. Analytical Data and General Behaviour of the Complexes

S.No.	Complex	Colour	Found (Calcd.) %				μ_{eff} (BM)	M.P.(°C)	Yield (%)
			Metal	Nitrogen	Chloride	Sulphur			
1.	$Ni(H_2L)_2Cl_2$	Violet	7.96 (8.13)	7.50 (7.75)	9.65 (9.83)	8.70 (8.86)	3.08	205	60
2.	$Cu(H_2L)Cl_2$	Light green	15.01 (14.75)	6.35 (6.50)	16.38 (16.49)	7.27 (7.43)	1.96	170	60
3.	$Mn(HL)_2$	Brown	8.45 (8.51)	8.56 (8.68)	–	9.77 (9.92)	6.02	210	70
4.	Co(HL)(L)	Maroon	8.89 (9.09)	8.50 (8.64)	–	9.70 (9.87)	Diamagnetic	>300	70
5.	$Ni(HL)_2$	Orange	8.91 (9.05)	8.48 (8.63)	–	9.71 (9.86)	Diamagnetic	260	65
6.	$Cu(HL)_2$	Green	9.56 (9.72)	8.40 (8.56)	–	9.63 (9.79)	1.67	260	70

% (water/ethanol) $H_2L=(C_{16}H_{12}N_2O_2S)$

4. Conclusions:

The results of the antifungal activity given in Table-2 and show that $Cu(HL)_2$ shows almost complete inhibition at all three concentrations. As compared to H_2L, $Mn(HL)_2$ and Co(HL)L exhibit greater fungitoxicity against R.oryzae but are less active against A.niger at all three concentration. The fungitoxicity of H_2L, $Mn(HL)_2$ and Co(HL)(L) decreases on lowering the concentration. The increased fungitoxicity of the complexes as compared to H_2L may be due to chelation which considerably reduces the polarity of the metal ion in the complexes, due mainly to partial sharing of its positive charge with the donor groups and possible π–electron delocalization over the whole chelate ring system.

Table-2: Fungicidal Activity of Salicylaldehyde–2–benzofuranthiocarboxyhydrazone (H_2L) and its complexes

Temp. 27 ± 1°C

S.No.	Compound	Average percentage inhibition after 96 hrs					
		Aspergillus niger (ppm)			Rhizopus oryzae (ppm)		
		10,000	5,000	1,000	10,000	5,000	1,000
1.	H_2L	75	60	40	41	30	15
2.	$Mn(HL)_2$	50	41	31	50	40	25
3.	Co(HL)(L)	64	50	36	69	56	38
4.	$Cu(HL)_2$	98	98	98	98	98	98

This is turn increases the hydrophobic character of the metal favouring its permeation through the lipoid layers of fungal membranes[(6)]. Dave et al. have also screened the antimicrobial activity of a number of Cu(II), Co(II) and Ni(II)[(7)] complexes of o–hydroxythiosemicarbazones together with the ligands against a variety of fungi and bacteria[(8)] and observed that Ni(II) complexes displayed better antimicrobial action than the free ligands. Co(II) and Cu(II) complexes also showed appreciable antifungal and antibacterial activities.

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