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Agricultural Application Of Cr(Iii), Mn(Iii) And Fe(Iii) Complexes Derived From 4-Phenyl-2 Imino Thiazole Thiazoleschiff Base

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Abstract:
The newly synthesized thiazole Schiff base ligand was derived from the condensation of thiazole and 2-hydroxy-5-chloro-3-nitro acetophenone. The Schiff bases behaved as charge bidentade ligand. The ligand was characterized by elemental analysis and spectral methods. The coordinating ability of the ligand is investigated by preparing its metal complexes with Cr(III), Mn(III) and Fe(III),) have been prepared and characterized by elemental analysis, conductance measurements, molecular weight determinations, spectral and agriculture studies. The synthesized products are coloured solids, soluble in DMF, DMSO and THF.

Keywords: Schiff base, Magnetic susceptibility, Agriculture

Introduction:

Synthesis, characterization and antifungal activity of manganese (II) complex with Schiff Base derived from acetylacetone and leucine[1] synthesis, characterisation and various methods of Schiff base derived from sulphanilic acid and salicylaldehyde and Comparative study of Schiff base using various synthesis methods and their theoretical prediction of activities[2] The newly synthesized Schiff bases, 2-acetylthiophene thiosemicarbazone and thiophene-2-aldehyde thiosemicarbazone and their metal complexes with Co(II), Cu(II), Zn(II) and Ni(II) complexes and Their Schiff bases metal complexes were tested for antibacterial activity[3] There is the combination of the azo group, the imidazole unit and the Schiff base fragment to studies the synthesis, characterization, and optical properties of four different Schiff bases ligands. They are reported the possible use of such systems in biological applications for their antifungal properties and antioxidant activities[4]. Synthesis and structural diversity transition metal coordination complexes with diverse Schiff base ligands and macrocyclic systems[5] The aim of present investigation is to synthesize various transition metal complexes of Schiff base derived from 2-hydroxy-5-chloro-3-nitro acetophenone and 2-amino-4-phenylthiazole

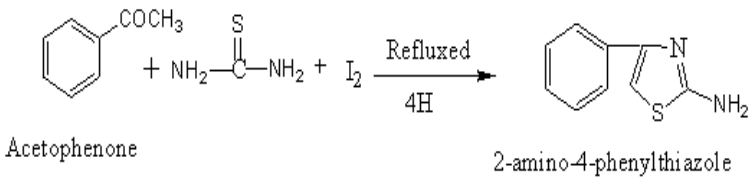
Experimental:

All the chemicals were of A.R. grade and used as received. 2-hydroxy-5-chloro-3-nitro acetophenone (HCNA) and 2-amino-4-phenylthiazole was prepared by known methods[6-9]. The solvents were purified by standard methods[10].

Synthesis of 2-amino-4-phenylthiazole;

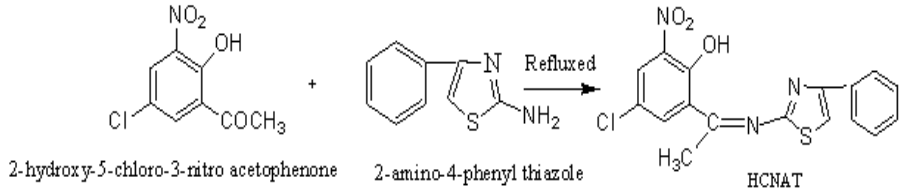
The synthesis of 2-amino-4-phenylthiazole prepared by known method[7-9]. The product was filtered and crystallized from 70% ethanol, after several minutes the

golden coloured product of 2-amino-4-phenylthiazole was separated out. Yield: 9g (75%); m.p.: 148-150^{0}C



Acetophenone 2-amino-4-phenylthiazole

Synthesis of 2-hydroxy-5-chloro-3-nitroacetophenone 4-phenyl-2 imino thiazole [HCNAT]: A solution of 4-phenyl-2 imino thiazole (0.02M) in 25ml of ethanol was added to an ethanolic solution(25ml) of 2-hydroxy-5-chloro-3-nitro acetophenone (0.02M) and the reaction mixture was refluxed on a water bath for 4h. After cooling a pale yellow coloured crystalline solid was separated out. It was filtered and washed with ethanol, crystallized from DMF and dried under reduced pressure at ambient temperature. The purity of ligand was checked by elemental analysis and m.p. It was also characterized by IR and ^{1}H NMR spectral studies. Yield:75%; m.p. 305^{0}C



2-hydroxy-5-chloro-3-nitro acetophenone 2-amino-4-phenyl thiazole HCNAT

Table1. Analytical data of the Ligands.

Ligand	Molecular Formula	Formula Weight	Color and nature	Elemental Analysis			
				C% found (Cal.)	H% Found (Cal.)	Cl% Found (Cal.)	S% Found (Cal.)
HCNAT	$C_{17}H_{12}N_3O_3SCl$	373.06	Yellow Crystalline	52.35 (52.20)	03.20 (03.34)	9.22 (9.38)	08.34 (08.46)

Preparation of complexes:

All the metal complexes were prepared in a similar way by following method. To a hot solution of ligand HCNAT (0.02M) in 25ml of ethanol a suspension of respective metal salts was added drop wise with constant stirring. The reaction mixture was refluxed on a water bath for 3-5 h. The precipitated complexes were filtered, washed with ethanol followed by ether and dried over fused calcium chloride. Yield : 55-60%. The complexes are soluble in DMSO and DMF but insoluble in water and common organic solvents. The metal chloride content of complexes were analyzed by standard methods[11,12] The ^{1}H NMR spectra of ligand was recorded and obtained from RSIC Chandigarh. IR spectra of the compounds were recorded on Perkin Elmer 842 spectrophotometer in the region 400-4000cm^{-1}, Carbon, Hydrogen and Nitrogen analysis were carried out at RSIC, Punjab University, Chandigarh. The molar conductance of the complexes at 10^{-3} M dilution in DMF were determined using equiptronic digital conductivity meter EQ-

660 with a cell constant 1.00 cm^{-1} at room temperature. The magnetic moment measurement were made on a Gouy balance at room temperature using $[HgCo(SCN)_4]$ as the calibrant. The thermogravimetric analysis were performed on laboratory set up apparatus in air atmosphere at 10^0 C min^{-1} heating rate. The molecular weights of the complexes were determined by Rast method.

Table 2. Analytical data and molar conductance of the compounds.

Ligand	Formula weight g $mole^{-1}$	Colour	Elemental Analysis Found (Calcd.)				μ_{eff} B. M	M (Ω^{-1} cm^2 mol^{-1})
			M%	C%	H%	Cl%		
$[CrL_2(H_2O)Cl]$ H_2O	868.7	Green	5.42	44.98	2.56	11.18	3.6	17.6
			(5.96)	(45.29)	(2.98)	(11.19)		
$[MnL_2(OAc)]$ H_2O	895.1	Brown	5.46	46.35	3.23	7.41	4.8	17.4
			(5.80)	(46.59)	(3.42)	(7.53)		
$[FeL_2(H_2O)Cl]$ H_2O	872.6	Black	6.12	44.85	3.22	11.46	5.4	21.2
			(6.19)	(45.10)	(3.28)	(11.72)		

Result and Discussion:

The Schiff base HCNAT and its complexes have been characterized on the basis of ^1H NMR, IR spectral data, elemental analysis, molar conductance, magnetic succeptibility measurements and thermogravimetric analysis data. All these values and analytical data is consistent with proposed molecular formula of ligand. All the compounds are coloured solid and stable in air. They are insoluble in water but soluble in coordinating solvents like DMF and DMSO. The molar conductance values in DMF(10^{-3} M) solution at room temperature (Table2) shows all the complexes are non electrolytes.

The ^1H NMR spectra of ligand shows signals at δ 12.14,(1H, s phenolic OH), δ 7.56, 7.54, 7.53 and 7.52 (4H, m, phenyl) δ 6.81,6.80, and 6.78 (3H, s, Phenyl), 6.68 (1H,s, thiophene), and 2.56 (3H, s, methyl) [11,13-15].

IR spectra of ligand and metal complexes shows (C=N) peaks at 1622 cm^{-1} and absence of C=O peak at around 1700 – 1750 cm^{-1} indicates the Schiff base formation[16-17].

Table 3. IR spectra of ligand and metal complexes

Compound	□(O□H) hydrogen bonded	□(C=N) imine	□(C□O) phenolic	□(M□O)	□(M□N)	□(C□S)
HCNAT (LH)	3119	1622	1514	--	--	1126
$[CrL_2(H_2O)Cl]$ H_2O	--	1595	1500	478	406	1118
$[MnL_2(OAc)]$ $2H_2O$	--	1567	1462	498	418	1095
$[FeL_2(H_2O)Cl]$ H_2O	--	1605	1505	513	436	1085

Agricultural application of metal complexes: Chromium and manganese metal complexes used in agriculture to increase the production of crops. They are used prior to the seedling stage to loosen up the soil. Essential observed that iron complexes with schiff base plays a beneficial role in plant growth and development. Synthetic Action on Insecticides: Schiff base ligand was derived from the condensation of thiazole and 2-hydroxy-5-chloro-3-nitro acetophenone. Their metal complexes show high activity against insects[18]. 2-amino-4-phenylthiazole acts as intermediate in synthesis of photostable pyrthriod insecticides[19]. Flourination on aldehyde part of Schiff base increases insecto acracicidal activity[20]. Schiff bases and their metal complexes with metal commplexes show insecticidal activities against bollworm [21].

Conclusions:

In conclusion, Schiff base metal complexes plays a beneficial role in plant growth and development. We have synthesized new ligand 2-hydroxy-5-chloro-3-nitro acetophenone 4-phenyl-2 imino thiazole and their metal complexes.

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