



Research Article

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Synthesis, Characterization and Antimicrobial activity Cr(III), Mn(III), Fe(III), VO(IV), Zr(IV) and UO₂(VI) Metal Complexes derived from Bidentate thiazole Schiff base.

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ABSTRACT

A new series of 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 bidentate 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), Fe(III), VO(IV), Zr(IV) and UO₂(VI) have been prepared and characterized by elemental analysis, conductance measurements, molecular weight determinations and spectral studies. The synthesized products are coloured solids, soluble in DMF, DMSO and THF. The Schiff base and their metal complexes have been evaluated for their antibacterial activities

Keywords: Schiff base, Magnetic susceptibility, Antimicrobial activity

INTRODUCTION

Schiff's bases, widely used as analytical reactants and have been studied for chemistry.^{1,2} Schiff bases metal complexes have many applications in different fields. The Schiff bases derived from thiazole and substituted acetophenone have been widely used as ligand for the synthesis of transition metal complexes. Thiazole Schiff base ligands and their metal complexes are biologically active³ and are known for their biological application⁴ i.e. one of the drug in cytotoxicity of anticancer⁵. Due to biological potency, pharmacological properties and synthetic flexibility of thiazole Schiff bases. 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-phenylthiazol

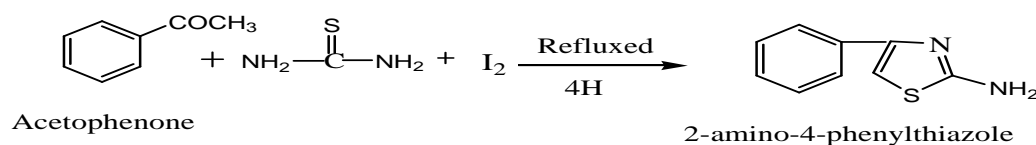
EXPERIMENTAL SECTION

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 methods⁶⁻⁹. The solvents were purified by standard methods¹⁰.

Synthesis of 2-amino-4-phenylthiazole;

The synthesis of 2-amino-4-phenylthiazole prepared by known method⁷⁻⁹. 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.: 148-150⁰C



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 ¹H NMR spectral studies.

Yield:75%; m.p. 305⁰C

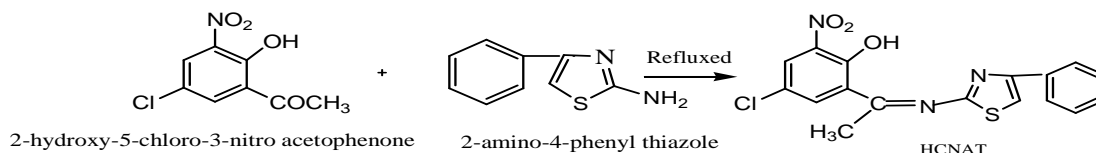


Table1. Analytical data of the Ligands.

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 ₃ O ₃ SCl	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 ¹H 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 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	Λ _M (Ω ⁻¹ cm ² mol ⁻¹)
			M%	C%	H%	Cl%		
[CrL ₂ (H ₂ O)Cl] H ₂ O	868.7	Green	5.42 (5.96)	44.98 (45.29)	2.56 (2.98)	11.18 (11.19)	3.6	17.6
[MnL ₂ (OAc)] H ₂ O	895.1	Brown	5.46 (5.80)	46.35 (46.59)	3.23 (3.42)	7.41 (7.53)	4.8	17.4
[FeL ₂ (H ₂ O)Cl] H ₂ O	872.6	Black	6.12 (6.19)	44.85 (45.10)	3.22 (3.28)	11.46 (11.72)	5.4	21.2
[VOL ₂]	812.2	Green	5.65 (6.09)	48.23 (48.29)	2.35 (2.86)	8.42 (8.69)	1.5	12.1
[ZrL ₂ (OH) ₂] 2H ₂ O	906.4	Yellow	9.42 (9.61)	43.23 (43.68)	3.26 (3.39)	7.46 (7.64)	Dia	16.8
[UO ₂ L ₂]	1015.3	Orange	22.34 (22.62)	38.58 (38.63)	2.12 (2.22)	6.52 (6.86)	Dia	14.7

RESULTS 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 susceptibility 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 (Table 2) 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 $\nu(\text{C}=\text{N})$ peaks at 1622 cm^{-1} and absence of $\text{C}=\text{O}$ peak at around $1700 - 1750\text{ cm}^{-1}$ indicates the Schiff base formation¹⁶⁻¹⁹.

Table 3. IR spectra of ligand and metal complexes

Compound	$\nu(\text{O}-\text{H})$ hydrogen bonded	$\nu(\text{C}=\text{N})$ imine	$\nu(\text{C}-\text{O})$ phenolic	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$	$\nu(\text{C}-\text{S})$
HCNAT (LH)	3119	1622	1514	--	--	1126
$[\text{CrL}_2(\text{H}_2\text{O})\text{Cl}] \cdot \text{H}_2\text{O}$	--	1595	1500	478	406	1118
$[\text{MnL}_2(\text{OAc})] \cdot 2\text{H}_2\text{O}$	--	1567	1462	498	418	1095
$[\text{FeL}_2(\text{H}_2\text{O})\text{Cl}] \cdot \text{H}_2\text{O}$	--	1605	1505	513	436	1085
$[\text{VOL}_2]$	--	1595	1508	515	438	1092
$[\text{ZrL}_2(\text{OH})_2] \cdot 2\text{H}_2\text{O}$	--	1605	1499	448	418	1102
$[\text{UO}_2\text{L}_2]$	--	1590	1448	542	485	1074

Antimicrobial activity

The inhibition effect of the ligand and its metal complexes on the growth of various bacteria is summarized in table 4. The compounds are found to show low bacteriocidal behavior against most of the bacterial culture and are resistance towards the other. In general the results reveal that the activity of the ligand was found to enhance on complexation with metal.

Table 4. Antimicrobial activity²⁰⁻³²

Ligand and its Complexes	Zone of inhibition (in mm)						
	<i>B.subtilis</i> (mm)	<i>P.vulgaris</i> (mm)	<i>S.aureus</i> (mm)	<i>E.coli</i> (mm)	<i>P.fluorescen</i> (mm)	<i>A.aerogenes</i> (mm)	<i>B.megatherium</i> (mm)
HCNAT	R	R	R	S ₁₂	R	S ₈	R
Cr- HCNAT	S ₁₁	R	R	S ₁₁	S ₁₄	R	R
Mn- HCNAT	R	R	R	S ₁₃	R	S ₁₁	S ₁₁
Fe- HCNAT	S ₁₂	S ₁₁	S ₁₂	S ₁₃	S ₁₂	R	S ₁₂
VO- HCNAT	S ₈	R	S ₁₃	S ₁₀	S ₁₁	S ₈	R
Zr- HCNAT	S ₁₁	S ₁₃	S ₁₄	S ₈	S ₁₁	S ₁₁	S ₁₁
UO ₂ - HCNAT	S ₈	S ₁₀	S ₁₂	S ₉	S ₁₂	S ₁₀	S ₁₂

S-Sensitive (Bacteriocidal)

R-Resistant (Bacteriostatic)

CONCLUSION

In conclusion, we have synthesized new ligand 2-hydroxy-5-chloro-3-nitro acetophenone 4-phenyl-2 imino thiazole and their metal complexes. Ligand was found to bind the metal ion monobasic (ON) bidentate manner. The Schiff bases ligand and their metal complexes shows more activity towards *E.coli* and least activity towards *P.vulgaris*. The structural changes have marked effect on the sensitivity and sensitivity varies with organisms

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