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Synthesis, magnetic and biological evaluation of 2-hydroxy-5-methyl-3-nitro acetophenone thiazole Schiff base complexes of Cr(III), Mn(III), Fe(III), VO(IV), Zr(IV) and UO_2(VI)

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ABSTRACT

The newly coordinating metal complexes of Cr(III), Mn(III), Fe(III), VO(IV), Zr(IV) and UO_2(VI) have been synthesized using 2-hydroxy-5-methyl-3-nitro acetophenone thiazole Schiff base ligand was derived from the condensation of 2-hydroxy-5-methyl-3-nitro acetophenone and thiazole. The Schiff bases behaved as charge bidentade ligand. The ligand was characterized by elemental analysis and spectral methods. Metal complexes characterized by elemental analysis, conductance measurements, molecular weight determinations and spectral studies. The Schiff base and their metal complexes have been evaluated for their antibacterial activities The synthesized products are coloured solids, soluble in DMF, DMSO and THF.

Keywords: Schiff base, Magnetic susceptibility, Antimicrobial

1. INTRODUCTION

In the development of coordination chemistry and biochemistry the compounds which contain pyridine and its derivatives or Schiff bases as ligands have occupied a central role. Schiff bases have often been used as chelating ligands in the field of coordination chemistry and their metal complexes are of great interest for many years. The chemical studies of metal complexes with heterocyclic Schiff base ligands containing nitrogen, sulfur, and oxygen has attracted increasing attention. It is well known that these heterocyclic compounds can exhibit bacterial, fungicidal, herbicidal and insecticidal activities in addition to their application as potential drugs. Such heterocyclic ligands, when complexed with metal ions, exhibit enhanced microbiological activities[1,2]. In the study of comparative reactivity of ambidendate ligand systems two or more potential donor centre of amino heterocycles plays an important role[3]. In the chemistry of organic and inorganic compound the number of Schiff base ligand and metal complexes are of substantial sake and attention because of their biological activity including anti-tumor, antibacterial, fungicidal and anti-carcinogenic properties[4,5]. Due to biological potency, pharmacological properties and synthetic flexibility of thiazole Schiff bases.

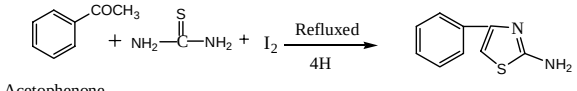
The aim of present investigation is to synthesize various transition metal complexes of Schiff base derived from 2-hydroxy-5-methyl-3-nitro acetophenone and 2-amino-4-phenylthiazole.

2. Experimental

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

2.1. Synthesis of 2-amino-4-phenylthiazole

The synthesis of 2-amino-4-phenylthiazole prepared by known method [7-9]. Yield: (75%); m.p: 148-150^{0}C



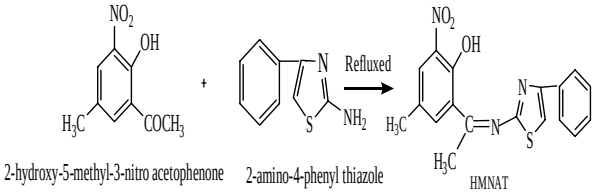
Acetophenone 2-amino-4-phenylthiazole

Scheme 1- Synthesis of 2-amino-4-phenylthiazole

2.2. Synthesis of 2-hydroxy-5-methyl-3-nitroacetophenone 4-phenyl-2 imino thiazole [HMNAT]

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-methyl-3-nitro acetophenone (0.02M) and the reaction mixture was refluxed on a water bath for 4-6h. 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:7o%; m.p. 310^{0}C



Scheme 2- Synthesis of HMNAT

2.3. Preparation of complexes

All the metal complexes were prepared in a similar way by following method. To a hot solution of ligand HMNAT (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 – 1: Analytical data of the Ligands.

Ligand	Molecular Formula	Formula Weight	Color and nature	Elemental Analysis		
				C% found (Cal.)	H% Found (Cal.)	S% Found (Cal.)
HMNAT	$C_{18}H_{15}N_3O_3S$	353.1	Yellow Crystalline	60.42 (61.17)	04.04 (04.24)	08.84 (09.06)

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%		
$[CrL_2(H_2O)Cl]\ H_2O$	827.7	Green	6.12 (6.28)	51.69 (52.19)	3.34 (3.86)	3.6	16.6
$[MnL_2(OAc)]\ H_2O$	854.1	Brown	6.28 (6.42)	53.18 (53.38)	4.15 (4.21)	4.2	17.4
$[FeL_2(H_2O)Cl]\ H_2O$	831.6	Black	6.40 (6.70)	51.05 (51.19)	4.03 (4.08)	5.6	20.2
$[VOL_2]$	771.2	Green	6.50 (6.60)	55.55 (56.01)	3.17 (3.89)	1.5	11.8
$[ZrL_2(OH)_2]\ 2H_2O$	865.4	Yellow	9.88 (10.53)	49.14 (49.91)	3.34 (3.92)	Dia	17.2
$[UO_2L_2]$	974.3	Orange	23.53 (24.43)	43.64 (44.33)	2.93 (3.07)	Dia	13.2

3. RESULT AND DISCUSSION

The Schiff base HMNAT 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 HMNAT shows signals at δ 12.24,(1H, *s* phenolic OH), δ 7.60, 7.74, 7.63 and 7.72 (4H, m, phenyl) δ 6.87, 6.88, and 6.72(3H, *s* Phenyl), 6.78 (1H *s* thiophene), and 2.66(3H, s, methyl) [11,13-15].

IR spectra of ligand and metal complexes shows ν(C=N) peaks at 1626 cm^{-1} and absence of C=O peak at around 1700 – 1740 cm^{-1} indicates the Schiff base formation[16-19].

3.1. Antimicrobial activity

Antimicrobial activity assay depends upon a comparison of the inhibition of growth of microorganism by measuring the concentration of the sample to be examined with the known concentration of standard antibiotic. For the antimicrobial analysis the agar diffusion method has been employed. In this study the ligand and their metal complexe were tested for their effect on certain human pathogenic bacteria such as Gram-positive.

The ligand HMNAT and its complexes[20-27] are found to show considerable bacteriocidal activity against *E. coli, A. aerogenes, S. aureus* and *B. subtilis* and are almost inactive against *B. megatherium, P. vulgaris* and *P. fluorescen*. The ligand inhibits the growth of *S. aureus* more than all its complexes. The results reveals that the sensitivity of ligand HMNAT and its complexes is shows in table 4.

Table – 3: IR spectra of ligand and metal complexes

Compound	ν(O–H) hydrogen bonded	ν(C=N) imine	ν(C–O) phenolic	ν(M–O)	ν(M–N)	ν(C–S)
HMNAT	3085	1626	1520	--	--	1128
$[CrL_2(H_2O)Cl]\ H_2O$	--	1596	1508	475	409	1116
$[MnL_2(OAc)]\ 2H_2O$	--	1566	1466	498	420	1091
$[FeL_2(H_2O)Cl]\ H_2O$	--	1606	1502	512	440	1082
$[VOL_2]$	--	1599	1502	514	445	1094
$[ZrL_2(OH)_2]\ 2H_2O$	--	1601	1488	445	412	1102
$[UO_2L_2]$	--	1588	1442	550	480	1084

Table – 4: Antimicrobial activity

Ligand and its complexes	*B. subtilis* (mm)	*P. vulgaris* (mm)	*S. aureus* (mm)	*E. coli* (mm)	*P. fluorescen* (mm)	*A. aerogenes* (mm)	*B. megatherium* (mm)
HMNAT	R	S_6	R	S_{12}	R	S_9	R
Cr- HMNAT	S_8	R	S_8	R	S_9	S_{11}	R
Mn- HMNAT	S_{12}	S_8	S_{12}	S_7	R	S_7	S_8
Fe- HMNAT	S_{11}	R	S_{11}	R	S_8	S_{23}	S_9
VO- HMNAT	R	R	S_{13}	S_{11}	R	S_{11}	S_9
Zr- HMNAT	S_{11}	S_{10}	S_{14}	R	R	S_{11}	R
UO_2-HMNAT	S_8	R	S_8	S_{13}	R	S_9	R

S-Sensitive, R-Resistant

4. CONCLUSION

In conclusion, we have synthesized new ligand 2-hydroxy-5-methyl-3-nitro acetophenone-2-imino thiazole and their metal complexes. The newly synthesized Metal complexes were confirmed by the spectral analysis and further evaluated for their antimicrobial activity. It is observed structural changes in metal complexes have marked effect on the sensitivity and sensitivity varies with organisms. The antibacterial activity revealed that most of the compounds showed moderate to good activity.

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