

# Synthesis, characterisation and biological activities of multidentate schiff bases and their metal complexes

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## ABSTRACT

Few complexes of 2-hydroxy naphthaldehyde isonicotinic acid hydrazone, 5-bromosalicylaldehyde sulfisoxazole were prepared with the metal Ti(III), V(III) and oxovanadium (IV). These were characterized by elemental analyses, molar conductance, magnetic susceptibility, IR and electronic spectra and thermogravimetric studies. The ligand and their respective complexes were also screened for their biological studies.

**Key words:** 2-hydroxy naphthaldehyde isonicotinic acid hydrazone, 5-bromo salicylaldehyde and biological studies.

## INTRODUCTION

The Schiff bases have pronounced biological activities<sup>1-2</sup> and form a class of important compounds in medicine and pharmaceutical field. Most of the common biological active compounds have structure quite suitable for chelation with metal ions and studies on the chelation tendency of various organic compounds have supported the hypothesis that formation of strain free chelate rings enhance the biological activity. In recent years immense interest has been developed in metal with ligand containing N-S-O and N-O-O moieties<sup>3</sup>.

Derivatives of isonicotinic acid (isonicanin) and its hydrazone (isoniazid) are well known for their high specific antitubercular activity, but their metal complexes have not attracted much attention. The co-ordination chemistry of isoniazid has been reported by cymerman-craig<sup>4</sup>. Some complexes of

transition metals with Schiff bases derived from this hydrazide have been mentioned in literature<sup>(5-7)</sup>. The present note deals with the synthesis and characterization of the title compounds.

## EXPERIMENTAL

The chemicals and reagent used were of high purity, A R or equivalent. The aldehydes used were 2-hydroxy naphthaldehyde (Ranbaxy) and 5-bromo salicylaldehyde (sigma) whereas the amino compound were isonicotinic acid hydrazone and sulfisoxazole (sigma).

### Preparation of the ligands

The ligands were synthesized by refluxing the respective carbonyl and amino compounds, the solid obtained from the reaction mixture washed and recrystallised from menthol. The purity of Schiff bases was tested by TLC. The melting points of Schiff bases were determined and IR spectra were

recorded. The prepared Schiff bases were 2-hydroxy naphthaldehyde isonicotinic acid hydrazone and 5-bromo salicylaldehyde suffisoxazole. Ti(III) chloride was prepared by standard method given in chemical literature whereas V(III) (BDH) and oxavanidium sulphate (Ranbaxy) were used as such.

#### Preparation of the complexes

The complexes of  $TiCl_3$  were prepared in a glove bag under the atmosphere of nitrogen by adding the solution of ligand. The precipitate so obtained was washed filtered and dried in a vacuum desiccator. Similar methods were used for the preparation of V(III) and oxavanadium complexes.

#### Characterisation of complexes

The melting points of the complex were determined in the lab. The molar conductance, magnetic susceptibility (Gouy's method) and gravimetric estimation was carried out at Chemistry Department of Bareilly College, Bareilly. The elemental analyses and IR spectra were carried out at CDRI Lucknow. The antimicrobial activity was tested at IVRI Izatnagar, Bareilly. The analytical data is given in Table 1.

### RESULTS AND DISCUSSION

The elemental analyses for all the reported complexes has indicated 1:2 metal ligand stoichiometry. The vast difference in the melting points of the ligand and their corresponding complexes indicate the formation of these adducts.

The molar conductance measurement at  $10^{-3}M$  dilution at room temperature in three solvent, methanol, DMF and DMSO indicated 1:1 electrolytic nature of the complexes except in case of oxavanidium complexes which were non electrolytes.

The magnetic susceptibility of these complexes were measured by Gouy's balance. The values of magnetic moment were calculated for all the complexes and were very close to the calculated values of  $d^1$  system in case of  $Ti^{+3}$  and  $Vo^{+2}$  and  $d^2$  system in case of  $V^{+3}$  complexes. The magnetic property indicated octahedral geometry for all these complexes<sup>8-11</sup>.

#### Electronic spectra

Electronic spectra of the titanium (III) chloride complexes exhibit only one band in the range of 15000-15600 which were assigned to  ${}^2t_{2g} - {}^2E_g$  transition. The spectra helped to find out the presence of unpaired electron in the metal ion and also octahedral geometry of complexes<sup>12</sup>.

Electronic spectra of these vanadium (III) chloride complexes were observed in pyridine solution. Two bands in the range of 15800-16000 and 19000-19990 were observed which were assigned to  ${}^3t_{1g} - {}^3t_{2g}$  and  ${}^3t_{1g} - {}^3t_{2g}(p)$  transitions respectively. The electronic spectra suggested octahedral geometry for all V(III) complexes<sup>13</sup>.

Electronic spectra of oxavanidium (IV) sulphate complexes exhibit, three bands at 10800  $cm^{-1}$ , 15000  $cm^{-1}$  and 21000  $cm^{-1}$ . These bands may be assigned to  ${}^2B_2 - {}^2E$ ,  ${}^2B_2 - {}^2B_1$  and  ${}^2B_2 - {}^2A_1$  transition respectively. It suggested octahedral geometry for the complexes<sup>14</sup>.

#### IR spectra

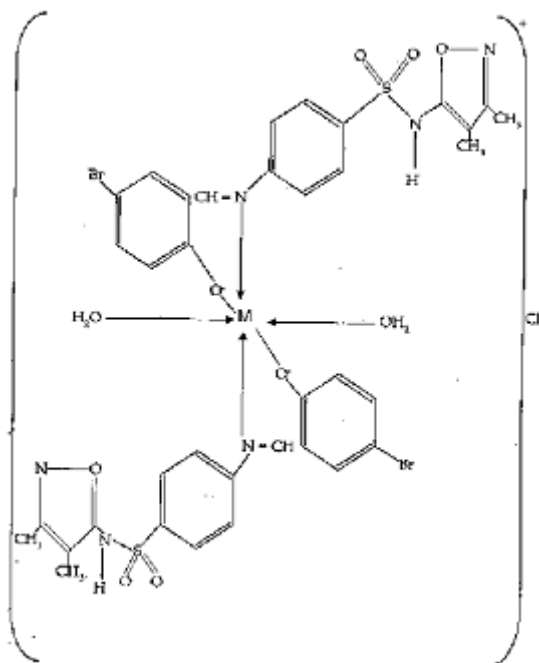
The infrared spectra of all the complexes were recorded in KBr phase. All these complexes of 5-bromo salicylaldehydesulfisoxazole exhibit bands around 3310  $cm^{-1}$  to 3331  $cm^{-1}$  and 870 to 900  $cm^{-1}$  assignable to  $\nu$  O-H and wagging and rocking mode of co-ordinated water molecules. This is also supported by thermogravimetric analyses. The thermogram shows loss of two molar molecules in the range of 150-170°C.

The IR spectrum of these complexes indicate that the coordination occurred through 'O' atom of phenolic group and 'N' atom of azomethine group. This is indicated by the downward shift of the band by  $20 \pm 5$   $cm^{-1}$  of this band whereas the band due to OH group has disappeared in the IR spectra of the complexes indicating deprotonation and subsequent co-ordination through phenolic oxygen.

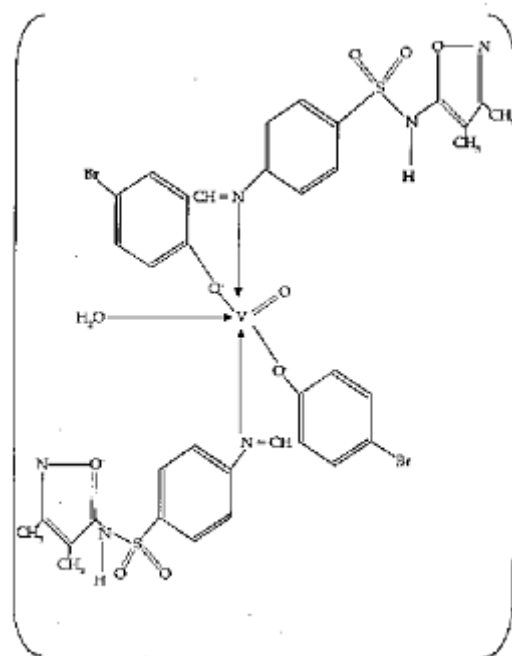
The IR spectra of all these complexes shows some additional band, at 630  $cm^{-1}$  and 560  $cm^{-1}$  which may be assigned to M-O and M-N linkages respectively<sup>15,16</sup>. In the case of all these complexes of 2-hydroxyl naphthaldehyde isonicotinic acid hydrazone. The coordination has occurred

Table 1:

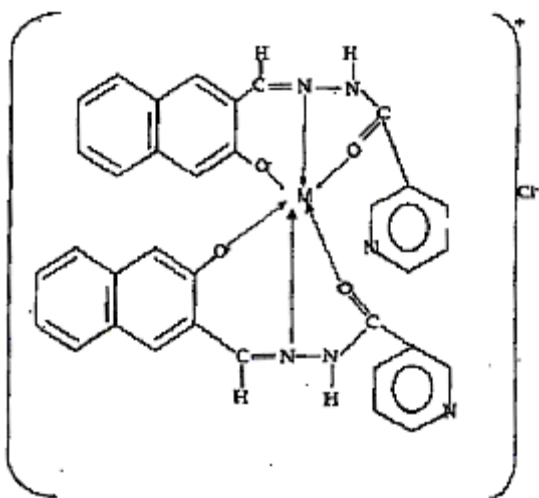
S. N.	Name of Complex	Molecular Formula	M.P. (°C)	Elemental Analysis					Magnetic			Molar Conductance	
				% OF C	% OF H	% OF H	% OF S	% OF N	5	OF S	OF N	DMF	DMSO
1.	Sulfexazole-5 bromo Salicylaldehyde titanium III chloride	$[\text{Ti}(\text{C}_{18}\text{H}_{15}\text{N}_3\text{O}_4)_2 \cdot 2\text{H}_2\text{O}] \text{Cl}$	225°C	42.47 (42.23)	2.94% (2.94)	8.25% (8.11)	6.29% (6.20)	4.71% (4.67)	1.70 B.M.	80	50	-	
2.	Sulfisoxazole-5 Bromo Salicylaldehyde vanadium (III) chloride	$[\text{V}^{+3}(\text{C}_{18}\text{H}_{15}\text{N}_3\text{O}_4)_2 \cdot 2\text{H}_2\text{O}] \text{Cl}$	230°C	42.35% (42.29)	2.94% (2.88)	8.23% (8.10)	6.27% (6.25)	5.09% (4.95)	2.76 B.M.	85	70	-	
3.	Sulfisoxazole-5 Bromo Salicylaldehyde oxovanadium (IV) chloride	$[\text{VO}(\text{C}_{18}\text{H}_{15}\text{N}_3\text{O}_4)_2 \cdot \text{H}_2\text{O}] \text{Cl}$	228°C	43.94% (43.76)	3.05% (3.00)	8.54% (8.22)	6.51% (6.42)	10.27% (9.98)	1.78 B.M.	70	44	115	
4.	2-hydroxy naphthaldehyde isonicotinic acid hydrazone titanium (III) chloride	$[\text{Ti}^{+3}(\text{C}_{18}\text{H}_{12}\text{N}_3\text{O}_2)_2] \text{Cl}$	260°C	62.88% (62.81)	3.49% (3.41)	12.22% (12.20)	-	6.98% (6.92)	1.70 B.M.	80	45	110	
5.	2-hydroxy naphthaldehyde isonicotinic acid hydrazone vanadium (III) chloride	$[\text{V}^{+3}(\text{C}_{18}\text{H}_{12}\text{N}_3\text{O}_2)_2] \text{Cl}$	265°C	62.60% (62.58)	3.47% (3.41)	12.17% (12.13)	-	7.39% (7.21)	2.72 B.M.	75	60	-	
6.	2-hydroxy naphthaldehyde isonicotinic acid hydrazone oxo vanadium (IV) sulphate	$[\text{VO}(\text{C}_{18}\text{H}_{12}\text{N}_3\text{O}_2)_2]$	263°C	64.38% (64.19)	3.57% (3.31)	12.51% (12.43)	-	9.98% (9.84)	1.78 B.M.	90	55	120	



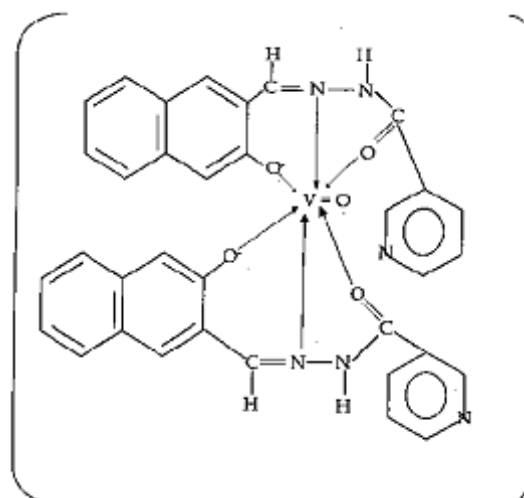
Scheme 1: Sulfisoxazole 5-bromo salicylaldehyde metal (III) chloride [M=Ti or V]



Scheme 2: Sulfisoxazole 5-bromo salicylaldehyde oxovanadium (IV) sulphate



Scheme 3: 2-Hydroxy Naphthalaldehyde isonicotinic acid hydrazone metal (III) chloride [M=Ti or V]



Scheme 3: 2-Hydroxy Naphthalaldehyde isonicotinic acid hydrazone oxovanadium (IV) sulphate

through azomethine nitrogen and carbonyl oxygen<sup>17,18</sup>. The ligand is, therefore, behaving in a dibasic bidentate manner.

#### Antimicrobial activity

The ligands and the complexes were screened for this antimicrobial activities using agar plate technique<sup>27</sup>. The compounds were dissolved in MeOH and solutions of different concentration were used. The solutions were then mixed with the

medium the liner growth of the fungus was obtained by measuring the diameter of the colony in petrel plate after 75 hours and the percentage inhibition was calculated as  $100(C-T)/C$  where C and T are the diameter of the fungus colony in the control and test plates respectively. The ligands and their corresponding metal complexes were found to be active against fungi but the complexes exhibits higher anti fungal activity than their respective ligands.

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