SYNTHESIS, CHARACTERISATION AND BIOLOGICAL ACTIVITIES OF MULTIDENTATE Schiff BASES AND THEIR METAL COMPLEXES

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ABSTRACT

Few complexes of 2-hydroxy napthaldehyde 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 napthaldehyde isonicotinic acid hydrazone, 5-bromosalicylaldehyde and biological studies.

INTRODUCTION

The Schiff bases have pronounced biological activities1-2 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 moieties3.

Derivatives of isonicotinic acid (isonicanin) and its hydrazide (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-craig4. Some complexes of transition metals with Schiff bases derived from this hydrazide have been mentioned in literature5-7. The present note deals with the synthesis and characterization of the title compounds.

EXPERIMENTAL

The chemicals and reagent used were of high spirty, A R or equivalent. The aldehydes used were 2-hydroxy napthaldehyde (Ranbaxy) and 5-bromo salicylaldehyde (sigma) whereas the amino compound were isonicotinic acid hydrazide 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 recrystallise 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
napthaldehyde isonicotinic acid hydrazone and 5-
bromo salicylaldehyde sulfisoxazole. Ti(III) chloride
was prepared by standard method given in chemical
literature whereas V(III) (BDH) and oxavanadium
sulphate (Ranbaxy) were used as such.

**Preparation of the complexes**

The complexes of TiCl₃ 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
decicater. 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 (Guoy’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 stitiometry.
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
10⁻⁶M dilution at room temperature in three solvent,
methanol, DMF and DMSO indicated 1:1 electrolytic
nature of the complexes except in case of
oxavanadium complexes which were non
electrolytes.

The magnetic susuptibility 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 d¹ system in case of Ti⁺³ and Vo⁻² and d²
system in case of V⁺³ complexes. The magnetic
property indicated octahedral geometry for all these
complexes⁸⁻¹¹.

**Electronic spectra**

Electronic spectra of the titanium (III)
chloride complexes exhibit only one band in the
range of 15000-15600 which were assigned to ³t₂g-
²Eg transition. The spectra helped to find our the
presence of unpaired electron in the metal ion and
also octahedral geometry of complexes¹².

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 ³t₁g – ³t₂g and ³t₁g – ³t₂g(p) transitions
respectively. The electronic spectra suggested
octahedral geometry for all V(III) complexes¹³.

Electronic spectra of oxavanadium (IV)
sulphate complexes exhibit, three bands at 10800
cm⁻¹, 15000 cm⁻¹ and 21000 cm⁻¹. These band may
assigned to ²B₂ – ²E, ²B₂ – ²B₁, and ²B₂ – ²A₁ transition
respectively. It suggested octahedral geometry for
the complexes¹⁴.

**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 n o-H and wagging and
rocking mode of co-ordinated water molecules. This
is also supported by thermogravimetric analyses.
The thermogram show 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±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 respectively¹⁵,¹⁶. In the case of all these
coplexes of 2-hydroxyl napthaldehyde isonicotinic
acid hydrazone. The coordination has occurred
Table 1:

<table>
<thead>
<tr>
<th>S. N.</th>
<th>Name of Complex</th>
<th>Molecular Formula</th>
<th>M.P. (°C)</th>
<th>Elemental Analysis</th>
<th>Magnetic Moments</th>
<th>Molar Conductance</th>
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<tr>
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<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>% OF C</td>
<td>% OF H</td>
<td>% OF H</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>42.47 (42.23)</td>
<td>2.94% (2.94)</td>
<td>8.25% (8.11)</td>
</tr>
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<td>1</td>
<td>Sulfexazole-5 bromo Salicyladehyde</td>
<td>[Ti(C(<em>{18}H</em>{15}N_3O_4)]</td>
<td>Redish</td>
<td>yellow</td>
<td></td>
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<tr>
<td></td>
<td>titanium III chloride</td>
<td>S. Br(_2) 2H(_2)O  Cl</td>
<td>225°C</td>
<td></td>
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</tr>
<tr>
<td>2</td>
<td>Sulfisoxazole-5 Bromo Salicyladehyde</td>
<td>[V(^{3+})(C(<em>{18}H</em>{15}N_3O)]</td>
<td>Redish</td>
<td>yellow</td>
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</tr>
<tr>
<td></td>
<td>vanadium (III) chloride</td>
<td>S. Br(_2) 2H(_2)O  Cl</td>
<td>230°C</td>
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</tr>
<tr>
<td>3</td>
<td>Sulfisoxazole-5 Bromo Salicyladehyde</td>
<td>[VO(C(<em>{18}H</em>{15}N_3O)]</td>
<td>Yellow</td>
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<tr>
<td></td>
<td>oxovanadium (IV) chloride</td>
<td>S. Br(_2) H(_2)O]</td>
<td>228°C</td>
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<td>4</td>
<td>2-hydroxy napthaldehyde isonicotinic acid hydrazone titanium (III) chloride</td>
<td>[Ti(^{2+})(C(<em>{18}H</em>{12}N_3)] O(_2)(_2)]Cl</td>
<td>Dull</td>
<td>yellow</td>
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<td></td>
<td>260°C</td>
<td>62.88% (62.81)</td>
<td>3.49%</td>
<td>(3.41)</td>
<td>12.22%</td>
<td>(12.20)</td>
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<td>5</td>
<td>2-hydroxy napthaldehyde isonicotinic acid hydrazone vanadium (III) chloride</td>
<td>[V(^{3+})(C(<em>{18}H</em>{12}N_3)] O(_2)(_2)]Cl</td>
<td>Greenish</td>
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<tr>
<td></td>
<td>265°C</td>
<td>62.60% (62.58)</td>
<td>3.47%</td>
<td>(3.41)</td>
<td>12.17%</td>
<td>(12.13)</td>
</tr>
<tr>
<td>6</td>
<td>2-hydroxy napthaldehyde isonicotinic acid hydrazone oxo vanadium (IV) sulphate</td>
<td>[Vo(C(<em>{18}H</em>{12}N_3)] O(_2)(_2)]</td>
<td>Lite</td>
<td>yellow</td>
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<tr>
<td></td>
<td>263°C</td>
<td>64.38% (64.19)</td>
<td>3.57%</td>
<td>(3.31)</td>
<td>12.51%</td>
<td>(12.43)</td>
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<tr>
<td>6</td>
<td>90</td>
<td>55</td>
<td>120</td>
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</table>
Scheme 1: Sulfisoxazole 5-bromo salicylaldehyde metal (III) chloride \([M=Ti \text{ or } V]\)

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

Scheme 3: 2-Hydroxy Napthalaldehyde isonicotinic acid hydrazone metal (III) chloride \([M=Ti \text{ or } V]\)

Scheme 3: 2-Hydroxy Napthalaldehyde isonicotinic acid hydrazone oxovanadium (IV) sulphate
through azomethine nitrogen and carbonyl oxygen\textsuperscript{17,18}. 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\textsuperscript{27}. 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 ambition weans calculated as 100 (C-T)/C where C and T are the diameter of the fungus colony in the couoprol 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.

**REFERENCES**