Synthesis and characterization of niobium(V) complexes with terdentate ONO donor hydrazones

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The metal complexes of niobium(V) with 2-benzimidazolyl mercaptoacetohydrazones have been synthesized in dry alcohol under nitrogen atmosphere and characterized by elemental analyses, molar conductance measurements, infrared, electronic and $^1$H NMR spectral studies. The spectral studies show that the hydrazones react in enol form and act as dibasic terdentate ONO donor nature. The thermal stabilities have been studied and the kinetics of these complexes are calculated using Coats-Redfern and MKN methods. From the results, a coordination number seven for niobium ion in the complexes of the type Nb(L)$_2$Cl is proposed. All the ligands and their niobium(V) complexes have been screened for their antimicrobial activity.

The complexes of niobium(V) with a wide range of Schiff bases containing a variety of donor sites have been reported in the literature$^{1-4}$. A number of workers have prepared and characterized metal complexes of hydrazones and studied their biological significance in different fields$^{5-8}$. The tautomeric nature of the hydrazones, biological importance and stereochemistry of niobium(V) complexes initiated us for the present investigation and the interest is focused on the synthesis of niobium(V) complexes of hydrazones derived from 2-benzimidazolyl mercaptoacetohydrazide with o-hydroxy aromatic aldehydes (Structure I).

Experimental
The chemicals used for the synthesis of ligands and complexes were of AR reagent grade, the solvents were dried and distilled before use according to standard procedures. 2-Mercapto benzimidazole was prepared using the standard method$^9$. Niobium pentachloride was of Fluka grade.

Niobium was determined gravimetrically as niobium pentoxide$^{10}$ and chloride as silver chloride using standard procedures. The elemental analysis of complexes was recorded on Elemental analyzers Heraeus Carlo-Erba-1108. Conductance measurements were made using $10^{-3}$ M solutions of complexes in DMF using Elico conductivity bridge type CM-82 provided with a cell having cell constant 0.51 cm$^{-1}$. The electronic spectra of complexes in DMF were recorded on Hitachi 150-20 spectrophotometer. The IR spectra were recorded in the range 4000-200 cm$^{-1}$ on a Perkin Elmer-783 model in KBr pellets. $^1$H NMR spectra were recorded in DMSO-$d_6$ on a Bruker AC 300F (300 MHz) spectrometer using TMS as an internal standard. TG and DTG were carried out for representative complexes in the range of room temperature to about 800°C in nitrogen atmosphere maintaining a heating rate of 10°C/min. Kinetic parameters were computed from the thermal decomposition data.

Preparation of 2-benzimidazolyl mercaptoacetohydrazide (ref.11)
To an absolute ethanolic solution (100 ml) containing sodium metal (2.8 g) was added with stirring, 2-mercapto benzimidazole (18.7 g) and the resulting mercaptide was slowly treated with ethyl chloroacetate (35-40 ml). The solution turned turbid and in a few min, separation of sodium chloride was observed. The mixture was refluxed on a steam bath for about
Table 1—Characterization data of niobium(V) complexes with hydrazones

<table>
<thead>
<tr>
<th>Complex Code</th>
<th>Complex (Abbrev.)</th>
<th>Found (Calcd.) %</th>
<th>Molar conductance (cm²/m²)</th>
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<tr>
<td>C₁</td>
<td>[NbC₆H₄(N₃O₂S)₂Cl]</td>
<td>12.11</td>
<td>10.10</td>
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<tr>
<td></td>
<td>(Nb(L¹)₂Cl)</td>
<td>11.95</td>
<td></td>
</tr>
<tr>
<td>C₂</td>
<td>[NbC₆H₄(N₃O₂SBr)₂Cl]</td>
<td>10.39</td>
<td>13.09</td>
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<tr>
<td></td>
<td>(Nb(L²)₂Cl)</td>
<td>10.98</td>
<td></td>
</tr>
<tr>
<td>C₃</td>
<td>[NbC₆H₄(N₃O₂SBr)₂Cl]</td>
<td>11.01</td>
<td>15.14</td>
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<tr>
<td></td>
<td>(Nb(L²)₂Cl)</td>
<td>9.93</td>
<td></td>
</tr>
<tr>
<td>C₄</td>
<td>[NbC₆H₄(N₃O₂SBr)₂Cl]</td>
<td>11.33</td>
<td>8.76</td>
</tr>
<tr>
<td></td>
<td>(Nb(L²)₂Cl)</td>
<td>11.54</td>
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<tr>
<td>C₅</td>
<td>[NbC₆H₄(N₃O₂SBr)₂Cl]</td>
<td>10.92</td>
<td>12.00</td>
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<tr>
<td></td>
<td>(Nb(L²)₂Cl)</td>
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<tr>
<td>C₆</td>
<td>[NbC₆H₄(N₃O₂SBr)₂Cl]</td>
<td>10.64</td>
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<tr>
<td></td>
<td>(Nb(L²)₂Cl)</td>
<td>10.59</td>
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</table>

Preparation of 2-benzimidazolyl mercaptoaceto hydrazone (L₅H₅)

To an ethanolic solution of 2-benzimidazolyl mercaptoaceto hydrazone (0.1 mol) was added salicylaldehyde / substituted salicylaldehyde (0.1 mol) and the mixture was refluxed on a steam bath for 3 h. The solution was filtered hot from the suspended impurities, concentrated and cooled. The separated solid was filtered, washed with water and recrystallized from alcohol.

Preparation of niobium(V) complexes

Niobium pentachloride (0.001 mol) in dry chloroform was treated with various 2-benzimidazolyl mercaptoaceto hydrazones (0.002 mol) in the same solvent and the reaction mixture was stirred under nitrogen atmosphere for 4 h. The precipitated complex was filtered at suction and washed with dry chloroform. The complexes were then dried and stored in vacuo over fused calcium chloride.

Results and discussion

All the complexes of niobium(V) are insoluble in common organic solvents such as methanol, ethanol, benzene, chloroform but soluble in DMF and DMSO. The elemental analysis (Table 1) show that all the complexes are of 1:2 stoichiometry. The molar conductivity of niobium(V) complexes measured in DMF at 10⁻³ M concentration fall in the range 8.76 to 15.14 ohm⁻¹ cm² mol⁻¹. These values are much less than those expected for 1:1 electrolytes and hence all complexes are treated as non-electrolytes. All the complexes are diamagnetic as expected for d⁵ niobium(V) states.
and the band is usually sharp and stronger than $\nu$(Nb-N). These observations are in accordance with the structure of niobium(V) complexes with the hydrzone ligands in which the central metal ion acquires a coordination number seven.

The proton magnetic resonance spectrum of the ligand shows a multiplet between 7.06 to 7.88 ppm due to aromatic protons. It shows the signal at 3.7 ppm assigned to the protons of -CH$_2$ group. The singlet observed at 8.56 ppm is due to resonance of azomethine proton. The three singlets corresponding to one proton each at 11.96, 10.89 and 12.79 ppm are assigned to -OH (phenolic), -NH (hydrazine) and -NH (imidazole) respectively. In the complex, the multiplet observed between 7.18-7.92 ppm is due to aromatic protons. The proton signal at 11.96 ppm due to -OH (phenolic) in the ligand disappeared suggesting that the -OH group is deprotonated on complexation. In the spectrum of niobium(V) complex, shifting of azomethine proton to the downfield ($\delta$ 8.78) confirms involvement of azomethine nitrogen in coordination to the metal ion. The -NH (hydrazine) peak disappears in the complex, suggesting that the ligand is in enol form followed by coordination of carbonyl oxygen to the metal ion via deprotonation.

The thermal behaviour of niobium(V) complexes, including stability ranges, peak temperatures, percentage of weight loss and percentage of residue obtained after decomposition process has been studied. The niobium(V) complexes undergo decomposition in two stages. The TG curves of niobium(V) complexes do not show the presence of water molecules either in or out of the coordination sphere. In the complexes (C$_1$)
and \((C_6)\), the first step of decomposition occurs between 45-205 and 65-215°C with weight loss of 4.67 and 3.97% (Calcd. 4.56 and 4.04%) respectively. The values correspond to the loss of one chloride. The second step of decomposition occurs between 205-645°C and 215-665°C with weight loss of 77.42 and 80.29% (Calcd. 78.92 and 81.32%) respectively, accounts for the loss of two molecules of ligands. Beyond 665°C a plateau is obtained, which indicates the formation of stable \(\text{Nb}_2\text{O}_5\). The weight of residue \(\text{Nb}_2\text{O}_5\) agrees well with the calculated value. The parameters such as energy of activation, entropy of activation and pre-exponential factor calculated using Coats-Redfern and MKN equations are presented in Table 2.

The thermal decomposition reactions of these complexes were studied using non-isothermal method. In the present complexes, the kinetic parameters for the decomposition stages of each complex have been calculated using Coats-Redfern and MKN equations by graphical as well as least square method (Fig. 1). The energy of activation values for the second stage decomposition of the complexes were found to be higher than those for the first stage decomposition. The higher value of energy of activation indicates the decreased rate at this stage.

The negative entropy of activation values for all degradation stages show that complexes are more ordered in the activated state through the chemisorption of oxygen and other decomposition products. The negative entropy of activation values are compensated by the values of the energies of activation. The entropy of activation value increases from first step to second step indicating that the rate of decomposition decreases in stepwise reactions.

The compounds were tested for their in vitro antibacterial activity against \(\text{Escherichia coli}\) and \(\text{Bacillus cirroflagellus}\) and antifungal activity against \(\text{Aspergillus niger}\) and \(\text{Candida albicans}\) by the cup plate method.

The complexes were found to be relatively more active than the corresponding ligands. Overall, the ligands and complexes are less active as compared to the standards Cotrimoxazole and Fluconazole used in the present study.

From the foregoing discussion, it is concluded that the ligands react in an enol form based upon analytical and spectral studies. The coordination number seven for niobium ion in the complexes of the type \(\text{Nb}(L)_7\text{Cl}\) has been proposed as shown in Structure II.

**Acknowledgement**

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**References**

17. Sacco H, S J, \(\text{Ac/om Rev}, 74 (1952) 4503\).

**NOTES**

Proposed structures of Nb(V) complexes