Oxovanadium(IV) and dioxouranium(VI) complexes of some acyclic monoterpenic constituents of essential oil

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A series of complexes of acyclic monoterpenoids, viz. 2-cis-3,7-dimethyl 2,6-octadien-1-al (CDOA); 3,7-dimethyl 6-octen-1-ol (DOO) and 3,7-dimethyl 7-hydroxy octane-1-al (DHOA) with vanadyl sulphate and uranyl nitrate have been prepared and characterized by conductometric, pH-metric, spectrophotometric studies, elemental analysis, infrared spectra and magnetic susceptibility. The geometry of complexes is found to be octahedral and square pyramidal. CDOA shows pharmacological activity on central nervous system and cardiovascular system. These terpenoids and their vanadyl and uranyl complexes show activity against fungal strains at 37°C.

The chemistry of oxocations has been very interesting because the metal-oxygen multiple bond in them could be used as an internal molecular probe to understand more about the nature of the metal ligand bonds as the M-L bonds perturb the more sensitive (M=O) double bonds. Further, the information is useful to know about the chemical environment around the metal ion. One of the coordination sites around vanadium ion is occupied by oxygen atom and complexes of this species VO(IV) are interesting, because it may utilize five coordination positions resulting in squre pyramidal complexes. The complex of Fe(III) with CDOA has been reported and thermodynamic studies have been carried out by conductometric, pH-metric, spectrophotometric studies, elemental analysis, infrared spectra and magnetic susceptibility measurements. The complexes of Fe(III), Co(II) and Ni(II) with DHOA also have been reported. The complexes of transition metal ions with oxygen donor ligands show significant antifungal and antimicrobial activities.

Preparation of oxovanadium (IV) and dioxouranium (VI) complexes

Each of the ligands (viz CDOA, DOO and DHOA, I), 0.02 mol was dissolved in 15 ml of ethanol. The pH of the solution was adjusted to 6.0 by adding ethanolic solution of NaOH and appropriate metal salt (0.01 mol vanadyl sulphate and uranyl nitrate) dissolved in 5 ml of ethanol was added slowly with constant stirring and then refluxed for 5 h at 70°C. The microcrystalline complexes formed were suction filtered and washed with hot ethanol several times. The products were dried in vacuo over anhydrous calcium chloride. The analytical data of the prepared complexes are presented in Table I.

A Bausch and Lomb's spectronic-20 spectrophotometer equipped with 10 cm quartz cell was used for all the spectral measurements. A phillip pH-meter, model pH-9404 was used for pH adjustments.

Physicochemical studies have been carried out in order to show composition and stability of the complexes. Reverse conductometric titration by Job's molar ratio method was carried out by taking 40 ml of solution of ligand (ten times diluted than metal salt solution) in the cell and by addition of metal salt solution. Simultaneously, by plotting a graph between conductance and volume of metal ion added an inflection in the curve is obtained at point of complexation. Molar conductance was calculated by measuring the conductance at complexation point. The pH-metric titrations were carried out at two different temperatures with 10°C difference. The method of Calvin and Bjerrum modified by Irving and Rossotti was used to obtain logk value. Kinetics of the complexes i.e. free energy change of the reaction (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were carried at 10°C temperature difference by Gibb's Halmholtz equation. Frequency of monochromatic radiation have been calculated. Elemental analysis and infrared spectra of the ligand and isolated complexes have been recorded separately by KBr technique.

Experimental

All the chemicals used were of AR grade. The purity of these ligands was checked by TLC. Vanadium and uranium content in the complexes was determined by spectrophotometric method.

Results and discussion

The complexes are non-hygroscopic and stable at room temperature. They are soluble in DMF and DMSO, slightly soluble in acetonitrile and chloroform.
Table 1—Characterization data of the synthesized complexes

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Colour</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>S (%)</th>
<th>M (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. [VO(CDOA)₂]SO₄</td>
<td>Greenish blue</td>
<td>51.39</td>
<td>6.90</td>
<td>6.86</td>
<td>10.90</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(51.73)</td>
<td>(7.15)</td>
<td>(7.21)</td>
<td>(10.55)</td>
<td></td>
</tr>
<tr>
<td>2. [UO₂(CDOA)₂][NO₃]₂</td>
<td>Orange</td>
<td>34.39</td>
<td>4.62</td>
<td>4.01</td>
<td>34.08</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(34.65)</td>
<td>(4.36)</td>
<td>(4.06)</td>
<td>(33.94)</td>
<td></td>
</tr>
<tr>
<td>3. [VO(DOO)₂]SO₄</td>
<td>Dark green</td>
<td>50.74</td>
<td>8.09</td>
<td>6.77</td>
<td>10.76</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(51.90)</td>
<td>(8.04)</td>
<td>(7.48)</td>
<td>(10.52)</td>
<td></td>
</tr>
<tr>
<td>4. [VO(DHOA)₂]SO₄</td>
<td>Greenish blue</td>
<td>49.63</td>
<td>7.92</td>
<td>6.00</td>
<td>9.53</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(50.42)</td>
<td>(8.10)</td>
<td>(6.49)</td>
<td>(9.69)</td>
<td></td>
</tr>
<tr>
<td>5. [UO₂(DHOA)₂][NO₃]₂</td>
<td>Orange</td>
<td>34.66</td>
<td>5.53</td>
<td>3.66</td>
<td>31.09</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(34.78)</td>
<td>(5.49)</td>
<td>(3.76)</td>
<td>(31.13)</td>
<td></td>
</tr>
</tbody>
</table>

Structure of binary complexes

and insoluble in water and other common organic solvents. The titrations were performed using buffer of pH 4 and 9.2 respectively. The lowering in the value of pH was due to complex formation reaction.

Electromagnetic radiation of monochromatic light have been studied in the visible range between 4000 to 7500 Å. The maxima for the complexes of VO (IV) with DOO and DHOA in nm were found to be 580.

Aldehydes and ketones add on to many metal ion forming covalent molecules. Order of stability for the complexes of these ligands were found to be for CDOA UO₂⁵⁺ > VO²⁺ while for DOO and DHOA VO²⁺ > UO₂²⁺.

Thermodynamic parameters i.e. free energy changes ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$) were calculated by usual relations at 10°C temperatures difference and showed that reactions are spontaneous. The negative values of free energy were found in the range. For CDOA ligand $-1.486$ k.cal./mol. to $-8.765$ k.cal./mol; DOO ligand $-5.356$ k.cal./mol to $20.295$ k.cal./mol; DHOA ligand $-8.295$ k.cal./mol to $19.908$ k.cal./mol; The enthalpy change of the reactions show negative values in the range for CDOA ligand $7.171$ k.cal./mol to $116.18$ k.cal./mol; DOO ligand $-12.600$ k.cal./mol to $-308.75$ k.cal./mol; DHOA ligand $-16.380$ k.cal./mol to $-117.60$ k.cal./mol; The entropy values were found positive in the range for CDOA ligand $2.181$ cal./mol. to $-344.45$ cal./mol. For DOO ligand $4.362$ cal./mol to $201.70$ cal./mol; DHOA ligand $5.859$ cal./mole to $344.45$ cal./mol.

The excitation of molecular vibrations and rotations give rise to absorption bands in the infrared regions of the spectrum. In the spectrum of CDOA, sharp band at 1760 cm⁻¹ is due to aldehyde group, weak band at 1655 cm⁻¹ is due to p-allylic bond and medium sharp peaks at 1460 cm⁻¹ is due to methyl group. In the spectrum of DOO weak band at 3600 cm⁻¹ is due to free hydroxy group and broad band at 1655 cm⁻¹ is due to p-allylic bond. In DHOA spectrum medium band at 3600 cm⁻¹ is due to hydroxy group and sharp band at 1760 cm⁻¹ is due to
aldehyde group. The shift of these frequencies at lower or higher frequency region and disappearance of π-allylic bond indicate ligand acting as a bidentate. Most of the oxovanadium (IV) complexes exhibit a strong band near 1000 cm⁻¹, which has been assigned to ν(V=O)¹¹. All oxovanadium complexes have been reported in which this stretching mode appears at quite lower wavenumbers around 900 cm⁻¹ (ref. 12). In dioxouranium complexes, the band appears at 930 cm⁻¹ corresponding to symmetrical stretching confirming the linear nature of the UO₂ group¹³,¹⁴.

The elemental analysis of complexes showed that found values are in good agreement with the calculated values. Measurements of magnetic susceptibilities and magnetic moments derived therefrom, provided useful information regarding the bonding in various types of complexes.

Biocidal assay

These acyclic monoterpenic constituents of essential oils and their metal complexes have been screened in vitro for their antimicrobial activity using disc diffusion method¹⁵ against bacterial species viz. Escherichia coli (gram negative) and Staphylococcus aureus (gram positive) and fungal strains viz. Aspergillus niger and Candida albicans. The result of the activities show that the complexes have been found to possess greater biological effect as compared to the ligand fragments and the metal salts. The "MIC" value for the compound i.e. the minimum concentration which is able to prevent any detectable growth of the microorganism is enhanced due to complexes. More lipophilicity of the metal complexes and more rapid penetration of the complexes as a whole through the cell walls of the microorganism causes damage to the synthesis of protein and nucleic acids of the microbe.

References