Synthesis, structural, thermal and biological studies of Cr(III), Mn(III), Fe(III), VO(IV), Zr(IV) and UO$_2$(VI) Schiff base complexes

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Complexes of Cr(III), Mn(III), Fe(III), VO(IV), Zr(IV) and UO$_2$(VI) with Schiff base derived from 2-hydroxy-5-chloroacetophenone and isonicotinoyl hydrazide (HCAIH) have been prepared and characterized by elemental analysis, IR, molar conductance, electronic spectra, magnetic susceptibility measurements and thermogravimetric (TG) analysis. The HCAIH acts as monobasic bidentate ON donor towards Cr(III), Fe(III), and Zr(IV) monobasic tridentate ONO donor towards UO$_2$(VI) and dicationic tridentate ONO donor towards Mn(III) and VO(IV). The Mn(III) complex has been assigned square pyramidal and the VO(IV) complex has been assigned dimeric square pyramidal structure while all other complexes are octahedral. TG data shows that first order kinetics in all complexes and thermal activation energies have also been calculated by using Broido method. The antimicrobial activities of the ligand and its metal complexes have been studied by screening the compounds against various microorganisms and the results have been compared.

Schiff bases derived from heteroaroyl hydrazides have an additional donor site in C = O as compared to simple hydrazide Schiff bases$^{1}$, which may lead to varied bonding and stereochemical behaviours in complexes with different metal ions. Literature survey reveals that some complexes of transition metals with Schiff bases derived from aroylhydrazides have been reported$^{2-8}$. Although the transition metal complexes of heteroaroyl hydrazones have been reported in literature, studies on Schiff base complexes with substituted acetophenones are scanty. Hence, it was thought of interest to carry out systematic investigation on Cr(III), Mn(III), Fe(III), VO(IV), Zr(IV) and UO$_2$(VI) complexes of 2-hydroxy-5-chloroacetophenoneisonicotinoylhydrazone (HCAIH).

Experimental

All the chemicals and solvents were of reagent grade and used without further purification. Hydrazide was obtained from E. Merck (India). 2-Hydroxy-5-chloroacetophenone was prepared by known method$^9$. Manganese(III) acetatedihydrate was prepared by Christensen's method$^{10}$.

Preparation of HCAIH

A solution of isonicotinoyl hydrazide (0.005mol) in ethanol (25 ml) was added to an ethanolic solution (25 ml) of 2-hydroxy-5-chloroacetophenone (0.005 mol) and the reaction mixture was refluxed on a water bath for 4 h. On cooling at room temperature a pale yellow coloured solid was obtained which was filtered, washed with ethanol, recrystallized from DMF and dried in vacuo at ambient temperature. The purity of ligand was checked by elemental analysis, m. p. and TLC. It was also characterized by IR and $^1$H NMR spectral studies. Yield: 80%, m. p. 218°C. [Found : C, 58.43; H, 4.28; N, 14.82; Cl, 12.53; Calc: for C$_{19}$H$_{12}$N$_2$O$_2$Cl, C, 58.03, H, 4.15, N, 14.51, Cl, 12.26%].

Preparation of Cr(III) and Fe(III) Complexes

To a hot solution of HCAIH (0.002 mol) in DMF-ethanol (50 ml, 1:4 v/v) a suspension of respective metal chloride in ethanol (0.001 mol) was added dropwise with constant stirring. The reaction mixture was refluxed on a water bath, for about 4-5 h. The complexes precipitated out on cooling and were filtered, washed with methanol, followed by ether and dried over fused calcium chloride, yield: 65-70%.

Preparation of Mn(III), VO(IV), UO$_2$(VI) complexes

To a hot solution of HCAIH (0.002 mol) dissolved in DMF-ethanol (25 cm$^3$; 1:4 v/v), a suspension of metal salt (acetates of Mn(III), UO$_2$ (VI) and vanadyl sulphate) in ethanol (0.002 mol) was added dropwise with constant stirring and the mixture was refluxed on a water bath for 5-6 h. The precipitated complexes were suction-filtered, washed with hot water, ethanol, followed by ether and dried over fused calcium chloride. Yield 60-70%.

Preparation of Zr(IV) complex

A methanolic solution of sodium acetate (15 ml, 0.004 mol) was added to the methanolic solution of zirconyloxychloride (15 ml, 0.002 mol) with constant stirring, separated NaCl was filtered off. The solution of HCAIH (0.002 mol) in DMF-methanol (40 cm$^3$, 1:4 v/v) was added and refluxed for 4 h. The product
obtained was filtered, washed with hot water followed by methanol and finally dried over fused calcium chloride. Yield 70%.

The metal and chloride contents of the complexes were analyzed using standard methods\(^{11}\). The \(^1\)H NMR spectra of ligand was recorded on a EM-360 spectrophotometer. IR spectra of the compounds were recorded on Perkin Elmer-842 spectrophotometer in the region 400-4000 cm\(^{-1}\), C, H and N analyses were carried out at RSIC, Chandigarh. The diffuse reflectance spectra were recorded on a Cary-2390 in 300-2000 nm region at RSIC, Chennai. The molar conductance of the complexes at 10\(^{-3}\) M dilution in DMF was determined using equi-tronic digital conductivity meter EQ-660 with a cell constant of 1.00 cm\(^{-1}\) at room temperature. The magnetic measurements were made on a Gouy balance at room temperature using Hg [Co(SCN)]\(_4\) as the calibrant. The molecular weight of the complexes was determined by Rast method. Thermogravimetric analyses were performed on laboratory set-up apparatus in air atmosphere at a 10°C min\(^{-1}\) heating rate.

**Results and discussion**

The analytical data of HCAIH is consistent with its proposed molecular formula. Its \(^1\)H NMR spectrum shows signals at \(\delta 12.9\) (phenolic OH, br, 1 H), \(\delta 11.40\) (imino H, s, 1H), \(\delta 9.1\) and \(\delta 8.15\) (isonicotine H, m, 4 H) \(\delta 7.76, 7.45\) and \(\delta 7.2\) (phenyl H, m, 3 H) and \(\delta 3.43\) (methyl H, s, 3H)

All the complexes are coloured solids and air stable for extended period of time. The complexes 1-5 are insoluble in water and common organic solvents but soluble in coordinating solvents like DMF and DMSO. While complex 6 is soluble in MeOH, EtOH, DMF and DMSO. The organic solution of the complexes appear to be unchanged at room temperature for several days and the original material can be re-isolated. The analytical results (Table 1) suggest that Cr(III), Fe(III) and Zr(IV) form 1:2 complexes, Mn(III) and UO\(_2\)(VI) form 1:1, mononeric complexes while VO(VI) form 1:1 (m:l) dimeric complex. The molar conductance value in DMF (10\(^{-3}\) mol) at room temperature was found in the range 15 to 24 ohm\(^{-1}\)cm\(^2\) mol\(^{-1}\), suggesting their nonelectrolyte nature.

**Infrared spectra**

A Schiff base exhibits a broad band at around 2945 cm\(^{-1}\) attributable to hydrogen bonded phenolic O-H. The other bands at 3220, 1669 and 1607 cm\(^{-1}\) are assignable to \(\nu(N-H), \nu(C=O), \nu(C=N)\) vibrations respectively. The absence of \(\nu(O-H)\) and the shifting of \(\nu(C=N)\) to lower frequencies in the spectra of all complexes suggest the deprotonation of phenolic group and subsequent coordination of phenolic oxygen and azomethine nitrogen to the metal\(^{13}\), which is supported by increase in phenolic C-O stretching frequencies in the spectra of complexes. The spectra of Cr(III), Fe(III) and Zr(IV) complexes display \(\nu(N-H)\) and \(\nu(C=O)\) vibrations almost at the same frequencies as in the spectra of ligand indicating the coordinated ligand is in keto form and noninvolvement of amide oxygen in the coordination\(^{2}\). It is, therefore, inferred that the ligand in 1, 3 and 4 complexes coordinates in a monobasic bidentate fashion. The spectra of Mn(III) and VO(VI) complexes do not show the band due to \(\nu(N-H)\) and \(\nu(C=O)\) frequencies, indicating the destruction of the carbonyl moiety as a result of enolization and subsequent coordination of the enolic oxygen after proton replacement. It is supported by the presence of new bands in the 1575-1590 cm\(^{-1}\) and 1229-1233 cm\(^{-1}\) due to azine (C=N-N=C) and \(\nu(C-O)\) (enolic modes) in the spectra of these complexes indicating the dibasic tridentate nature of the ligand\(^{14}\). The UO\(_2\)(VI) complex shows the \(\nu(C=O)\) band at lower frequency by 20 cm\(^{-1}\) suggesting the coordination of amide oxygen to metal ion as well as coordination of ligand in ketoform\(^{14}\), indicating monobasic tridentate nature of the ligand. A medium weak band appearing at 995 cm\(^{-1}\) in free ligand due to pyridine ring breathing vibration remains unshifted in position indicating noninvolvement of pyridyl ring nitrogen atom in coordination\(^{2}\). The spectra of complexes 2 and 6 show two bands near 1605-1612 and 1400-1410 cm\(^{-1}\) attributed to \(\nu_{asym} COO\) and \(\nu_{sym} COO\) respectively. This indicates that acetate group coordinates as a monodentate ligand\(^{15}\). The presence of O-H group of water molecules in the spectra of 1, 2 and 3 has been observed in the region 3300-3500 cm\(^{-1}\). The bands in 830-780 cm\(^{-1}\) range attributed to rocking and wagging modes of coordinated water in these complexes\(^{16}\). In UO\(_2\)(VI) complex, the bands at 554 and 506 cm\(^{-1}\) have been assigned to \(\nu(U-O)\) and \(\nu(U-N)\) vibrations respectively\(^{17}\), while in other complexes the bands in the range 471-490 and 415-435 cm\(^{-1}\) have been assigned to \(\nu(M-O)\) and \(\nu(M-N)\) vibrations respectively\(^{18}\). The strong bands at 965 cm\(^{-1}\) in VO(VI) and at 915 cm\(^{-1}\) in UO\(_2\)(VI)
complexes are assigned to $\nu$(V=O) and trans $\nu$(O=U=O) vibrations\(^{19}\) respectively. The absence of a new band in the region 850-950 cm\(^{-1}\) due to $\nu$(Zr=O) and the presence of a new band at 1154 cm\(^{-1}\) due to $\delta$(Zr-OH) favour the formation of [Zr (OH)\(_2\)]\(_2\)(LH)\(_2\). 3H\(_2\)O and not [ZrO(LH)\(_2\)]\(_2\) 4H\(_2\)O complex\(^{20}\).

The magnetic moment values of Cr(III), Mn(III) and Fe(III) complexes are in good agreement with the presence of three, four and five unpaired electrons respectively. The diffused reflectance spectra of Cr(III) complex exhibits three bands at 18950, 20130 and 25510 cm\(^{-1}\). The lowest energy spin allowed transition at 18950, 17920 cm\(^{-1}\) respectively, can be assigned to the transitions $^5$B\(_1\) → $^4$A\(_2\), $^5$B\(_1\) → $^5$B\(_2\), $^5$B\(_1\) → $^2$E and LMCT\(^{23-25}\). The Fe(III) complex exhibits 3 bands at 13850, 17920 and 22990 cm\(^{-1}\) respectively, can be assigned to the transitions, $^6$A\(_{1g}\) (S) → $^4$T\(_{1g}\) (F), $^6$A\(_{1g}\) (S) → $^4$T\(_{2g}\)(F) and $^6$A\(_{1g}\) (S) → $^6$E (D)\(^{21}\). The VO(IV) complex displays band at 13750, 16810, 22090 and 29255 cm\(^{-1}\), respectively which may be assigned to the $^3$B\(_2\) → $^3$E, $^3$B\(_2\) → $^3$B\(_1\), $^3$B\(_2\) → $^3$A\(_1\) and LMCT\(^{26}\) transitions. The Zr(IV) and UO\(_2\)(VI) complexes show a band at 41600 and 40000 cm\(^{-1}\), respectively corresponding to CT transitions only and are diamagnetic as expected. The band assignment and the magnetic moment values to Cr(III), Mn(III), Fe(III) and diamagnetic nature of Zr(IV) and UO\(_2\)(VI) complexes are consistent with octahedral geometry while for Mn(III) and VO(IV) the values are consistent with square pyramidal geometry. The same position of the absorption maxima were found in the UV spectra of the sample in DMF, indicated that no ligand dissociation occurs in DMF solution\(^{27}\).

Thermogravimetry study indicates that complexes are stable up to 70°. Elimination of one water molecule each in Cr(III), Mn(III) and Fe(III) and three water molecules in Zr(IV) complexes has been observed in raising the temperature upto 150°C (% wt loss obs/calc.: Cr(III): 2.63/2.57; Mn(III): 4.26/4.11; Fe(III): 2.67/2.55; Zr(IV): 7.56/7.14). In Cr(III), Mn(III) and Fe(III) complexes further lose in weights up to 250°C. Indicating the presence of one coordinated water molecule in each complex\(^{28}\) (% wt loss obs/calc.: Cr(III): 2.60/2.57; Mn(III): 4.31/4.11; Fe(III): 2.65/2.55). There is no weight-loss up to 260° indicating the absence of lattice or coordinated water in the VO(IV) and UO\(_2\)(VI) complexes. The thermal degradation of the metal chelates occurs mainly in two steps except in VO(IV), UO\(_2\)(VI) complexes. The decomposition steps for the compounds are shown in Table 2. The activation energy for each

<table>
<thead>
<tr>
<th>Complexes (Colours)</th>
<th>Mol.Wt. Found (Calc.)</th>
<th>Analysis % Found (Calc.)</th>
<th>$\mu_{\text{eff}}$ B.M</th>
<th>$\Lambda_{\text{M}}$ $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$</th>
<th>Half Dec. Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cr(LH)(_2)H(_2)O(_2)]Cl(_2)(_2)H(_2)O (1)</td>
<td>704.5 (700.9)</td>
<td>C 48.08 (47.98) H 3.76 (3.74) N 12.07 (11.99) Cl 15.22 (15.17) M 7.53 (7.42)</td>
<td>4.06</td>
<td>19.7</td>
<td>457.5</td>
</tr>
<tr>
<td>[Mn (L)(_2).H(_2)O(_2)Ac(_2).H(_2)O (2)]</td>
<td>442.2 (437.7)</td>
<td>C 43.94 (43.90) H 3.99 (3.91) N 9.73 (9.60) Cl 8.17 (8.09) M 12.68 (12.55)</td>
<td>4.88</td>
<td>15.8</td>
<td>492.5</td>
</tr>
<tr>
<td>[Fe (LH)(_2).H(_2)O(_2)]Cl(_2)H(_2)O (3) (Brown)</td>
<td>706.8 (704.8)</td>
<td>C 47.83 (47.72) H 3.78 (3.72) N 11.98 (11.92) Cl 15.13 (15.09) M 7.96 (7.92)</td>
<td>5.94</td>
<td>18.4</td>
<td>405</td>
</tr>
<tr>
<td>[VO(_2) (LH)(_2)] (4) (Orange red)</td>
<td>715.4 (709.3)</td>
<td>C 23.75 (23.71) H 2.94 (2.84) N 11.95 (11.84) Cl 10.05 (9.99) M 14.48 (14.36)</td>
<td>1.52</td>
<td>12.3</td>
<td>445</td>
</tr>
<tr>
<td>[Zr(LH)(_2)(OH)(_2)].3H(_2)O (5) (Yellow)</td>
<td>760.3 (756.7)</td>
<td>C 44.61 (44.44) H 4.13 (4.00) N 11.13 (11.10) Cl 9.43 (9.37) M 12.13 (12.05)</td>
<td>0</td>
<td>23.8</td>
<td>525</td>
</tr>
<tr>
<td>[UO(_2)(LH)(_2)OAc] (6) (Orange red)</td>
<td>622.9 (617.8)</td>
<td>C 31.23 (31.11) H 2.32 (2.28) N 6.89 (6.80) Cl 5.79 (5.73) M 38.65 (38.53)</td>
<td>0</td>
<td>21.4</td>
<td>485</td>
</tr>
</tbody>
</table>

Table 1—Analytical and physical data of complexes
Table 2—Thermal decomposition data of the Schiff base complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Step</th>
<th>Decomposition range °C</th>
<th>Activation energy (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cr(LH)₂H₂O₂Cl]H₂O</td>
<td>I</td>
<td>80-220</td>
<td>25.2</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>260-400</td>
<td>27.86</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>400-600</td>
<td>57.39</td>
</tr>
<tr>
<td>[Mn(LH)₂H₂O₂Cl]H₂O</td>
<td>I</td>
<td>80-220</td>
<td>18.40</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>260-500</td>
<td>37.66</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>500-680</td>
<td>19.88</td>
</tr>
<tr>
<td>[Fe(LH)₂H₂O₂Cl]H₂O</td>
<td>I</td>
<td>80-220</td>
<td>17.50</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>260-420</td>
<td>49.10</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>420-600</td>
<td>27.19</td>
</tr>
<tr>
<td>[VO₂Cl₂]</td>
<td>I</td>
<td>360-440</td>
<td>50.90</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>440-600</td>
<td>65.12</td>
</tr>
<tr>
<td>[Zr(LH)₂(OH)₂]₃H₂O</td>
<td>I</td>
<td>80-160</td>
<td>50.17</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>260-500</td>
<td>22.96</td>
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<tr>
<td></td>
<td>III</td>
<td>500-700</td>
<td>40.66</td>
</tr>
<tr>
<td>[UO₂(LH)₃OAc]</td>
<td>I</td>
<td>340-440</td>
<td>94.60</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>440-600</td>
<td>27.73</td>
</tr>
</tbody>
</table>

Decomposition steps were calculated using Broido method. The half-decomposition temperature decreases in the order Zr(IV) > Mn(III) > UO₂(VI) > Cr(III) > VO(IV) > Fe(III). The thermograms of complexes depict that the final decomposition products correspond to Cr₂O₃, MnO₄, Fe₂O₃, V₂O₅, ZrO₂ and U₃O₈, respectively.

**Biological activities**

The ligand and its complexes were screened for their antibacterial activities by agar cup plate method. The antibacterial activity of the compounds were tested against *E. coli*, *S. typhii* and *Rhizobium*. The concentrations used were 1 mg cm⁻³ in DMF. It is evident from the results that the Mn(III) complex is highly active against *E. coli* bacteria. The Fe(III) and VO(IV) complexes have shown good activity against *S. typhii* organism. The complexes of Cr(III) and Zr(IV) show moderate to weak activity against the all microorganisms. The complex UO₂(VI) shows poor activity against *E. coli* but good activity against *S. typhii* and *Rhizobium* organisms.

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**References**