Synthesis, Characterization and Biological Screening of 
Ti(III), Cr(III), Fe(III) and UO$_2$(VI) Mononuclear 
Complexes of Hydrazine Schiff Base Ligand Containing 
NON Moiety

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Abstract. New potentially tridentate hydrazine Schiff base ligand (H$_2$L) was prepared by the condensation of 2,4-
dihydroxybenzophenone with furoylhydrazide. Reaction of this ligand with titanium trichloride, chromium chloride 
hexahydrate, anhydrous ferric chloride, uranyl nitrate hexahydrate gave mononuclear metal complexes. The ligand and its 
complexes have been characterized by a variety of physico-chemical techniques. An octahedral geometry has been 
proposed for all the complexes. The ligand acts as a tridentate molecule coordinating through deprot onated 
phenolic/enolic oxygen atoms and azomethine nitrogen atom. Thermogravimetric analyses confirm coordination of 
water/methanol molecule in complexes. The antibacterial and antifungal activities of ligand (H$_2$L) and its complexes have 
been studied against various bacteria and fungi using the disc diffusion technique. All complexes exhibit good biological 
activity as compared to free ligand.

1. INTRODUCTION

In the past two decades, immense interest has been paid to design and synthesis of hydrazine ligands and their 
metal complexes due to presence of several coordination sites [1, 2]. The hydrazine ligands containing heterocyclic 
rings have valuable contribution in the coordination chemistry due to their diversity and structural variability. α-
dihydroxyacetophenone/benzophenone is a diverse building block because of its unique chemical structure, allowing 
for ring and phenolic group substitution as well as derivatization of the acetyl group. Coordination chemistry of 
hydrazine metal complexes has gained a special attraction due to their biological activity. Their anti-inflammatory, 
analgesic [3, 4], antibacterial [5, 6] and antitumor [7] activities are also reported in the literature. Moreover, 
deprotonation of the –NH group results in the formation of tautomeric anionic species having new coordination 
properties. In view of the above and the significant role played by the hydrazine metal complexes in biological 
systems and in various other fields, we have synthesized and characterized Ti(III), Cr(III), Fe(III) and UO$_2$(VI) 
complexes with 2,4-dihydroxybenzophenone-2-furoyl hydrazine (H$_2$L) and studied their antimicrobial properties.

2. EXPERIMENTAL WORK

2.1. Materials and Physical Measurements

All the chemicals were obtained from the commercial sources and used without further purification. Carbon, 
hydrogen and nitrogen contents were determined on a Carlo Erba 1108 elemental analyzer. The IR spectra were 
recorded as KBr pellets using a Shimadzu 8201 spectrophotometer in the range 400–4000 cm$^{-1}$. 1H–NMR spectrum
was recorded on Bruker Advance II, 400MHz, NMR spectrophotometer in d6-DMSO with TMS as an internal standard. Metal contents of the complexes were analyzed gravimetrically after decomposing the organic matter with a mixture of HClO4, H2SO4 and HNO3 (1:1.5:2.5) and then igniting to metal oxide. The magnetic susceptibility measurements of the metal complexes were carried out by Gouy’s method at room temperature using mercury(II)tetrathiocynatocobalt(II), Hg[Co(SCN)4] as the calibrant. Diamagnetic corrections were made using Pascal’s constants. The solid–state reflectance spectra of the metal complexes were recorded in the rage 200–1000 nm (as MgO) on a Beckman DK–2A spectrophotometer. Thermogravimetric analyses were performed on a Perkin Elmer, Diamond TG thermal analyzer in the temperature range 40–750 °C with a heating rate of 10 °C min⁻¹.

2.2. Synthesis of Ligand (H2L)

To a hot ethanolic solution (20 mL) of 2,4-dihydroxybenzophenone (15 mmol) a 10 mL ethanolic solution of furoylhydrazide (15 mmol) was added. The reaction mixture was refluxed for 4 h. On cooling to room temperature and the pale orange crystalline product was filtered off, washed with least amount of ethanol and diethyl ether, and then dried in vacuo. Yield: ~74%. m.p. (192–194 °C). The schematic representation of synthesis of H2L and its tautomeric forms are shown in Figure 1.

^1H–NMR: δ 15.82 (s, 1H, OH C2); δ 10.14 (s, 1H, OH C4); δ 9.17 (s, 1H, NH), δ 7.02–7.42 (m, 8H, Ar–H), δ 6.64–6.98 (C4H3O furoyl ring).

![FIGURE 1. Schematic representation of synthesis of H2L and its tautomeric forms](image)

2.3. Synthesis of Metal Complexes

Equimolar quantities (15 mmol) of H2L ligand and appropriate metal salt were dissolved separately in DMF (25 mL) and mixture of methanol & ethanol respectively. The solutions were filtered and mixed them in hot condition under continuous stirring. The resulting mixture was refluxed for 6–8 h on an oil bath. On cooling to room temperature, the colored complexes precipitated out was filtered, washed with DMF, methanol and petroleum ether and finally dried under vacuum at room temperature. Yield: 54–60 %.

3. RESULTS AND DISCUSSION

The complexes prepared from H2L ligand are coloured solids, air stable at room temperature, which decompose at high temperature. The elemental analysis of H2L ligand and its metal complexes are given in Table 1. The elemental analysis is in good agreement with that calculated for the proposed formula.
TABLE 1. Analytical data of H$_2$L and its metal complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular formula</th>
<th>Formula weight</th>
<th>Elemental analysis found (calcd.) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>H$_2$L</td>
<td>C$<em>{16}$H$</em>{14}$N$_2$O$_4$</td>
<td>322.32</td>
<td>67.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(67.68)</td>
</tr>
<tr>
<td>[TiL(Cl)(H$_2$O)$_2$]</td>
<td>C$<em>{18}$H$</em>{16}$ClN$_2$O$_6$Ti</td>
<td>439.64</td>
<td>49.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(50.06)</td>
</tr>
<tr>
<td>[CrL(Cl)(H$_2$O)$_2$]</td>
<td>C$<em>{18}$H$</em>{16}$ClN$_2$O$_6$Cr</td>
<td>443.78</td>
<td>48.72</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(48.96)</td>
</tr>
<tr>
<td>[FeL(Cl)(H$_2$O)$_2$]</td>
<td>C$<em>{18}$H$</em>{16}$ClN$_2$O$_6$Fe</td>
<td>447.62</td>
<td>48.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(48.42)</td>
</tr>
<tr>
<td>[UO$_2$L(CH$_3$OH)]</td>
<td>C$<em>{16}$H$</em>{16}$N$_2$O$_7$U</td>
<td>622.36</td>
<td>36.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(36.82)</td>
</tr>
</tbody>
</table>

3.1. IR Spectroscopy

The characteristic vibrational frequencies have been identified by comparing the spectra of the metal complexes with that of parent ligand and literature value of absorption of similar types of compounds. The IR spectrum of the ligand show band at 2940 cm$^{-1}$ due to free hydroxyl group which is absent in the spectra of all metal complexes and a higher shift of the phenolic ν(C–O) in the complexes, indicate that phenolic oxygen undergoes coordination with metal ion [8]. The strong band of azomethine of free ligand is observed at 1610 cm$^{-1}$. The shifting of ν(C=O) (azomethine) of the ligand to a lower wave number by 9–16 cm$^{-1}$ in the metal complexes indicates the coordination of azomethine nitrogen to the metal ion [9]. A ligand characteristic band at 995 cm$^{-1}$ due to ν(N–N) stretch undergoes a 10–17 cm$^{-1}$ shift to a higher wave number upon complexation due to diminished repulsion between the lone pairs of adjacent nitrogen atoms [10]. A remarkable difference between the IR spectra of the ligand and its metal complexes is that the bands due to ν(C=O) (1665 cm$^{-1}$) and ν(NH) (3410 cm$^{-1}$) disappear from the spectra of the metal complexes. The disappearance of both the bands confirms that the ligand coordinated with the metal ions is in the enol form [11]. This has been further confirmed by the appearance of new enolic band in the region 1228–1266 cm$^{-1}$ due to ν(C–O) in the spectra of all the metal complexes. The UO$_2$(VI) complex exhibits a strong band at 865 cm$^{-1}$ (ν$_1$) and medium intensity band at 804 cm$^{-1}$ (ν$_3$) assigned to ν$_{asy}$(O=U=O) and ν$_{sym}$(O=U=O) mode, respectively [12]. The ν(C–O) of CH$_3$OH occurs at 1014 cm$^{-1}$ and this band undergoes a negative shift in UO$_2$(VI) complex and is observed at ~999 cm$^{-1}$ indicating methanol is in coordination. The presence of coordinated water is indicated by the appearance of bands in the region 3360–3422, 1552–1583, and 817–868 cm$^{-1}$ due to stretching, rocking and deformation modes of water in the metal complexes [13]. In the far IR region, additional medium bands in the regions 505–537 and 470–492 cm$^{-1}$ are assigned to ν(M–O) and ν(M–N) modes, respectively [14]. In the present case the H$_2$L ligand bound to the metal ion as bi-negative ONO–tridentate through phenolate oxygen, azomethine nitrogen and deprotonated enolic oxygen [15].

3.2. Electronic Spectra and Magnetic Study

Magnetic moment, electronic bands and ligand field parameters of the metal complexes are shown in Table 2. The electronic spectrum of Cr(III) complex shows three broad band at 17412, 23654 and 38827 cm$^{-1}$ which may be assigned to the transitions, $^4$A$_{2g}$(F) → $^4$T$_{2g}$(F), $^4$A$_{2g}$(F) → $^4$T$_{1g}$(F) and $^4$A$_{2g}$(F) → $^4$T$_{1g}$(F) respectively, in octahedral environment of Cr(III) ion. Using the above values of Dq, B and β work out as 1741, 683 and 0.74 cm$^{-1}$ respectively. Also, the magnetic moment value 3.82 BM is consistent with those reported for octahedral geometry [16]. The electronic spectrum of Fe(III) complex displayed three bands at 16437, 24594 and 36610 cm$^{-1}$ corresponding to $^6$A$_{1g}$→ $^4$T$_{1g}$(G), $^6$A$_{1g}$→ $^4$T$_{2g}$(G) and $^6$A$_{1g}$→ $^4$E$_{g}$(D), transitions, respectively, characteristic of octahedral geometry [17]. The room temperature magnetic moment of Fe(III) complex is 4.89 B.M., corresponding
to five unpaired electrons. The electronic spectrum of the Ti(III) complex displays single band at 17763 cm\(^{-1}\). This band may be assigned to \(^2\)T\(_{2g}\) \(\rightarrow\) \(^2\)E\(_{g}\) transition. This suggests an octahedral environment around the Ti(III) ion [18]. The Ti(III) complex shows magnetic moment 1.50 B.M. corresponding to one unpaired electron. The diamagnetic UO\(_2\)(VI) complex shows two bands in its spectrum, the first at 28648 cm\(^{-1}\) is due to charge transfer, probably ligand to the uranyl ion, while the second band at 25014 cm\(^{-1}\) can be definitely assigned to electronic transitions from apical oxygen atom to the \(f\)-orbitals of the uranyl atom characteristic of the uranyl moiety [19].

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption band (cm(^{-1}))</th>
<th>Assignment</th>
<th>(\mu_{\text{eff}}) (B.M.)</th>
<th>B (cm(^{-1}))</th>
<th>(\beta)</th>
<th>Dq (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>[TiL(Cl)(H(_2)O)(_2)]</td>
<td>17763</td>
<td>(^2)T(<em>{2g}) (\rightarrow) (^2)E(</em>{g})</td>
<td>1.50</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>[CrL(Cl)(H(_2)O)(_2)]</td>
<td>17412 23654 38827</td>
<td>(^4)A(<em>{2g}) (\rightarrow) (^4)T(</em>{2g}) (F)</td>
<td>3.82</td>
<td>683</td>
<td>0.74</td>
<td>1741</td>
</tr>
<tr>
<td>[FeL(Cl)(H(_2)O)(_2)]</td>
<td>16437 24594 36610</td>
<td>(^6)A(<em>{1g}) (\rightarrow) (^4)T(</em>{1g}) (G)</td>
<td>4.89</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

3.3. Thermogravimetric Study

To examine the thermal stabilities of ligand (H\(_2\)L) and its metal complexes, thermogravimetric analysis (TG) of all compounds were done under dynamic air atmosphere at a heating rate of 10 °C min\(^{-1}\). The assignment of the different decomposition steps are given in Table 3. The thermogravimetric curves of ligand (H\(_2\)L) and one representative [FeL(Cl)(H\(_2\)O)\(_2\)] complex are shown in Figure 2 & 3. The thermogravimetric pattern of Ti(III), Cr(III), Fe(III) and UO\(_2\)(VI) is nearly same. In Ti(III), Cr(III) and Fe(III) complexes, the first mass loss of 8.28%, 8.20% and 8.80% (calc. 8.18%, 8.11% and 8.04%), respectively between 90 and 210 °C corresponds to the loss of two moles coordinated water molecules [20]. The UO\(_2\)(VI) complex is stable up to 135 °C temperature and loss of mass in the temperature 135–200 °C indicated the presence of one coordinated methanol molecule [% mass loss obs/calcd: UO\(_2\)(VI): 5.28/5.14] [21]. After the total loss of water/methanol molecules, the second stage occurs between 195–250 °C, mass loss corresponds to chlorine ion. A plateau obtained above 700 °C, corresponds to the stable metal oxides.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature range (°C)</th>
<th>% mass loss</th>
<th>Decomposition assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>[TiL(Cl)(H(_2)O)(_2)]</td>
<td>90–210 210–240 240–800</td>
<td>8.28 8.10  –</td>
<td>Loss of two moles of coordinated water molecules</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.18 8.07  –</td>
<td>Loss of one coordinated chloride ion</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Deligation</td>
</tr>
<tr>
<td>[CrL(Cl)(H(_2)O)(_2)]</td>
<td>95–195 195–230 230–750</td>
<td>8.20 8.24  –</td>
<td>Loss of two moles of coordinated water molecules</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.11 7.99  –</td>
<td>Loss of one coordinated chloride ion</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Deligation</td>
</tr>
<tr>
<td>[FeL(Cl)(H(_2)O)(_2)]</td>
<td>105–195 195–250 250–750</td>
<td>8.80 8.12  –</td>
<td>Loss of two moles of coordinated water molecules</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.04 7.93  –</td>
<td>Loss of one coordinated chloride ion</td>
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<td></td>
<td></td>
<td>Deligation</td>
</tr>
<tr>
<td>[UO(_2)L(CH(_3)OH)]</td>
<td>135–200 200–700</td>
<td>5.28 5.28  –</td>
<td>Loss of one mole of methanol molecule</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.14 5.14  –</td>
<td>Deligation</td>
</tr>
</tbody>
</table>
3.4. Antimicrobial Activity

The ligand (H$_2$L) and its metal complexes were screened against the bacteria *S. aureus*, *B. Subtilis* and *P. aeruginosa* and fungi *A. niger* and *C. albicans* by the disc diffusion method [22]. DMSO was taken as a control. In order to check the potency of the compounds, solutions were prepared with 500 ppm concentration in DMSO. Whatmann filter paper No.1 paper discs having a diameter of 10 mm were soaked in the solutions prepared. These discs were kept on the previously seeded petri plates for incubation at 37 °C for 24 h. The diameters of the zones of inhibition were measured in millimeter. It is clear that the Ti(III), Cr(III) and Fe(III) complexes exhibit significant activity against all bacteria and fungi as compare to UO$_2$(VI) complex. This may be due to the presence of chloride ion inside the structure playing an important role in the activity. It has been observed that the metal complexes show enhanced activity as compared to the free ligand against the same organism under identical experimental conditions. This is because of the chelation. According to Tweedy’s chelation theory [23], the chelation reduces the polarity of the metal atom mainly because of the partial sharing of its positive charge with donor groups and possible π electron
delocalization over the whole ring [24, 25]. This increases the lipophilic character of the metal chelate which favors its permeation through the lipid layer of bacterial membranes and results in activity enhancement.

REFERENCES