Studies of some structural and transition metal complexes of Phenylazoacetoacetanilide

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ABSTRACT
Phenylazoacetoacetanilide complexes of the type M(PAAC)$_n$, where M is Zn(II), Hg(II), Mo(VI)$_2$, n is the valency of the metal, and HPAAC is Phenylazoacetoacetanilide (Butanamide 3-oxo-N-phenyl-2-(phenyl hydrazono), have been synthesized and characterized. Complexes were isolated in solid state and characterized from elemental analysis, magnetic studies, UV-visible, IR and NMR data. The elemental analysis confirms the assigned stoichiometries. The stereochemistries of the complexes were ascertained using magnetic studies, uv-visible diffusive reflectance, IR and $^1$H NMR. The present paper describes synthesis and characterization of these complexes. The complexes are found to have striking structural features. In these complexes, the phenylazo group $(C_6H_5N_2)$ exhibits bidentate character and coordinates with the metal through the phenylazo and methylketo groups. Metal: Ligand ratio is found to be 1:2. Mo (VI) complex shows the presence of O=M=O bond. Hence Zn (II), Hg (II) complex are tetrahedral and Mo (VI) complex is Octahedral in geometry.

Key words: - Phenylazoacetoacetanilide, transition metal complexes of hydrazone β-diketone ligands, Coordination compounds of Zn(II), Hg(II), Mo(VI).

INTRODUCTION
The chemistry of aryl diazenato complexes is of recent origin. Many researchers have been intrigued by the chemistry of aryl diazenato complexes of various transitional metals because of their striking structural features and applications in diverse areas, most notably in dyes and pigments. (Yagi and Yoshiharu 1963)
Azo compounds are also used as coordinating agents and the combination of azo compounds and β-diketones are good Ligands. β -diketones as well as hydrazones are well known chelating agents, capable of forming stable complexes with transition metal ions (Mohamed et al. 1990). β -diketones and their esters and anilides are found to be very good coordinating agents especially for transition and inner transition metal ions (Basheir et al. 1988).Their complexing ability is enhanced by introduction of active groups like oximes, hydrazones, thiosemicarbazones etc. The combination products of these two classes of chelating agents form new interesting compounds which act as very good bi- or tridentate ligands.

It is noticed that the preparation of metal complexes of various transition metals with different azo derivatives of β -ketoanilides compounds and their structural investigations have not been carried out much. It was therefore considered worthwhile to undertake this study systematically.

Literature studies reveal that hydrazone type of substitution has not been tried much to enhance the complexing ability.

It is of growing interest that the coordination compounds and metal chelates possessing nitrogen and oxygen donor atoms, show strong biological properties (Renu and Meena 2010, Harikumaran and Thankamani 2010). The present study investigates the physico-chemical properties of the complexes of chelating agents with transition and inner transition metals on both solution and solid states and will be characterized from elemental analysis, magnetic, uv-visible Diffusive reflectance, IR, NMR, etc.

MATERIALS AND METHODS
All reagents and chemical were used as AR grade.
Preparation of Ligand: The ligand phenylazoacetoacetanilide HPAAC (Structure 1) was prepared by standard method as described. β-diarobynyl compounds undergo diazo coupling at the reactive methylene group of acetoacetanilide. In this way phenylazo derivative of acetoacetanilide i.e phenylazoacetoacetanilide (Butanamide 3-oxo-N-phenyl-2-(phenyl hydrazono) were prepared (Parmeter 1959).
Preparation of metal complexes:
0.01 molar solution of the metal salt was prepared in 80:20 alcohol water medium. To this 0.02 molar solution of the reagent HPAAC in the same medium was added by constant stirring so that the reaction mixture contained metal to ligand molar ratio as 1:2. The 1:2 molar ratio of metal to ligand was confirmed by conductance measurements & by Job’s method. The pH of the reaction mixture was slowly raised by adding very dilute liq NH₃ solution. Complex was separated. It was dried in oven at 70 ° C (Desai and Sawant 1993, Desai and Sawant 1994).

Instrumentation:
Elemental analysis of the ligand and the complex was carried on Thermo Finnigan Flash 1112 series EA, CHNSO analyzer. Magnetic susceptibilities were recorded on Gouy’s balance at 303 K. The IR spectra of the complexes and ligand were recorded on Vertex 80 IR spectrophotometer in the range 4000-400 cm⁻¹. ¹H NMR spectra of the complexes and ligand were recorded on a Mercury Plus Varian 300 mega Hz NMR, using d⁶ DMSO as solvent.

RESULT AND DISCUSSION
Characterization of ligand: - The crystallized ligand showed the expected m.p, elemental composition, IR, NMR spectra. Melting point of Ligand is 110°C. Elemental analysis confirms the assigned stoichiometries of the ligand. (Desai and Sawant 1993, Desai and Sawant 1994).

<table>
<thead>
<tr>
<th>Sr. no</th>
<th>Component</th>
<th>%Element (Practical)</th>
<th>%Element (Theoretical)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Nitrogen</td>
<td>14.21</td>
<td>14.94</td>
</tr>
<tr>
<td>2</td>
<td>Carbon</td>
<td>68.88</td>
<td>68.32</td>
</tr>
<tr>
<td>3</td>
<td>Hydrogen</td>
<td>5.72</td>
<td>5.33</td>
</tr>
</tbody>
</table>

Characterization of metal complexes: Physical and analytical data of HPAAC complexes.

<table>
<thead>
<tr>
<th>Reagent / metal complex and color</th>
<th>Molecular weight</th>
<th>pH of formation</th>
<th>µeff /BM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reagent (HPAAC) C₁₆H₁₅O₂N₃</td>
<td>281</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zn(C₁₆H₁₄O₂N₃)₂</td>
<td>625</td>
<td>6.3</td>
<td>diamagnetic</td>
</tr>
<tr>
<td>Hg(II) (C₁₆H₁₄O₂N₃)₂</td>
<td>761</td>
<td>7.3</td>
<td>diamagnetic</td>
</tr>
<tr>
<td>MoO₂(C₁₆H₁₄O₂N₃)₂</td>
<td>655.9</td>
<td>6.7</td>
<td>diamagnetic</td>
</tr>
</tbody>
</table>
All the complexes were found to be non-electrolyte in nature. All the complexes were also found to be diamagnetic.

The stereochemistries of the complexes were ascertained using magnetic studies, diffuse reflectance, IR, $^1$H NMR (Desai and Sawant 1993, Desai and Sawant 1994).

**IR Spectral data of the HPAAC and metal complexes of HPAAC:**

The ligand HPAAC showed broad bands at 3028 cm$^{-1}$ & 3170 cm$^{-1}$ corresponding to ν (N-H) of hydrazone & ν (N-H) of anilide groups respectively. The spectra of all the metal complexes lacked the 3028cm$^{-1}$ band, indicating replacement of a proton from the hydrazone group, whereas the band at 3170 cm$^{-1}$ persisted suggesting noninvolvement of the anilide group in bonding. The band at 1664 cm$^{-1}$, due to the V$_{ar}$ (CH$_3$C=O) group in the ligand spectra, was found to be shifted to lower values of 1654 cm$^{-1}$ in all the complexes, suggesting coordination through the oxygen atom of the CH$_3$C=O group. These coordination sites were supported by the presence of bands at 580 cm$^{-1}$ & 430 cm$^{-1}$ attributed to M-N &M-O bonding respectively. Mo (VI) complex showed the presence of band at 970 cm$^{-1}$ assigned to O=Mo=O.

**NMR Spectral data of the HPAAC and metal complexes of HPAAC:**

$^1$H NMR spectra of the ligand in d$_{6}$-DMSO showed two prominent down field signals at δ-11.2(s) ppm and δ-13.6 (s) ppm, attributed to the anilide N-H and hydrazone N-H protons, respectively, whereas $^1$H NMR spectra of complexes in d$_{6}$-DMSO lacked the signal at δ-13.6 ppm, but the signal at δ-11.2 ppm was not affected. Also splitting of the CH$_2$=C=O signal (δ-2.45 ppm) was observed, proving that coordination was taking place through the N-H of hydrazone and oxygen atom of the CH$_2$=C=O. This coordination pattern of reagent HPAAC was analogous to that found for similar hydrazones reported by earlier workers (Krishnakutty and Umar 1988). The diffuse Reflectance spectra of the complexes exhibited bands at around 320, 430 nm which are ascribed to charge transfer bands.

**Conclusion:**

The coordination was taking place through the N-H of hydrazone and oxygen atom of the CH$_2$=C=O of the ligand with the metal atom. Also metal to ligand ratio was found to be 1:2. Mo (VI) complex shows the presence of O=M=O bond. All these experimental data suggest tetrahedral structures for the Zn (II), Hg (II), and octahedral structures for Mo (VI) complexes.

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**LITERATURE CITED**


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