CHAPTER V

PHYSICO-CHEMICAL STUDIES AND CALCULATION OF I.P. AND LOG K VALUES OF OXOZIRCONIUM(IV) COMPLEXES WITH 2-FUROIN PHENOXY ACETYL HYDRAZIDE (FPAH) AND 2;4-DIMETHYL BENZALIDENE BENZOYL HYDRAZIDE (DBBH)

INTRODUCTION:

The configuration of divalent and trivalent zirconium ions given below indicate that 5s orbital is vacant.

\[ \text{Zr}^{2+} = 1s^2, 2s^2, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^2. \]

\[ \text{Zr}^{3+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^1. \]

This means that the d–d orbital is of lower energy than 5s orbital though the opposite is true for neutral metal atom. The outer electronic configuration of zirconium atom is thus \((n-1)\) d²ns², and shows a maximum covalency of four in their simple compounds such as tetrahalides, perchlorate and nitrate etc. In these derivatives one of the electron of ns level and both electrons of \((n-1)d\) orbital are promoted to the np orbital and the one–s and three–p orbitals are hybridized to give derivatives with tetrahedral structure. There is very little energy difference between \((n-1)\) d and ns orbitals and hence both energy levels can be used for bonding. The most stable oxidation state is +4, but the majority of compounds in this oxidation state are covalent. Because of the prohibitive energy requirements for the removal of four valency electrons, there is very little evidence for existence of \(\text{Zr}^{4+}\) cation. In aqueous solution, the tetravalent zirconium ions readily hydrolyse to give oxocation as given below:

\[ \text{Zr}^{4+} + \text{HOH} \rightarrow \text{ZrO}^{2+} + 2\text{H}^+ \]
The salts of this ion are well known viz., ZrO(NO$_3$)$_2$·2H$_2$O and ZrO (ClO$_4$)$_2$ etc. The high oxidation states of zirconium metal atom are brought about in combination with oxygen or fluorine atoms and low oxidation states are exhibited in complexes with π–bonding ligands. Because of the presence of vacant inner d–orbitals zirconium has tendency to expand its covalency with corresponding increase in coordination number. Coordination number greater than that of four is achieved by donation of electrons from ligands into the d–orbitals of zirconium ions. The coordination number of Zr$^{4+}$(IV) in oxozirconium(IV) complexes varies from 5 to 8, but the coordination number 5 and 7 are quite common$^{(1)}$.

Ramamurthy and Patel$^{(2)}$ were the first to synthesise pyridine N–Oxide complexes of oxozirconium(IV) perchlorate and found that the C.N. of Zr in this complex is 7 and has the face–centered octahedron or trigonal prismatic geometry. Agarwal and Rastogi$^{(3)}$ have also studied the ligational behaviour of 4–cyanopyridine N–oxide towards oxozirconium(IV) ions and found that the order of stability of the complexes is:

I  <  ClO$_4$  <  NCS  <  Br  <  Cl  <  NO$_3$.

Determination and separation of Zr(IV) was carried out by Singh and Coworkers$^{(4)}$ using 2$^1$–mercapto maleianilic acid as a gravimetric reagent. Complexes of oxozirconium(IV) and Th(IV) with Mannich bases [3–(p–dimethyl amino aniline)–methyl salicylic acid hydrazide (DAMSAH) and β–(α–naphthylamino)–2,3,4–trihydroxy propiophenone (NATPO)] with 1:2 (M:L) stoichiometry have been prepared and characterized$^{(5)}$. Some oxozirconium(IV) and dioxouranium(VI) Schiff base complexes have been studied by Shukla and Coworkers$^{(6)}$. Some macrocyclic complexes of oxozirconium(IV) have been prepared and investigated.$^{(7)}$ Spectrophotometric methods reported for
The determination of Zirconium(IV) have been reviewed by different authors.\(^{(8\text{--}10)}\) The methods proposed by Monica et.al\(^{(11)}\) Gunawardhana et.al\(^{(12)}\) and Chauhan et.al\(^{(12)}\) are not very sensitive. Yang and Wu\(^{(13)}\) reported a method which requires elevated temperatures. The methods reported by Ren et.al\(^{(14)}\) and Kanie et.al\(^{(15)}\) suffer from interference by a number of diverse ions.\(^{(16\text{--}19)}\)

A simple and sensitive spectrophotometric method has been developed for the determination of Zirconium(IV) in aqueous medium. The metal ion forms golden yellow coloured, soluble complex with 2:4–Dihydroxy benzaldehyde isonicotinoyl hydrazone at pH\(\approx 1.5\). The complex has a 1:2 stoichiometry.\(^{(20)}\)

A perusal survey of literature revealed that no work seems to have been done so far on the oxozirconium(IV) complexes of 2–furoin phenoxy acetyl hydrazide (FPAAH) and 2:4–Dimethyl benzalidene (DBBH) benzoyl hydrazide. Therefore it was decided to synthesise these complexes and to establish their structures on the basis of analytical, conductance and spectral studies. The ionization potential and log \(K\) (stability constant) values are also calculated.

**PREPARATION AND ISOLATION OF THE COMPLEXES:**

[Aquo (2–Furoin Phenoxy Acetyl Hydrazide)]–Oxozirconium(IV) Chloride,

[Aquo Nitrato (2–Furoin Phenoxy Acetyl Hydrazide)]–Oxozirconium(IV),

[Thiocyanato (2–Furoin Phenoxy Acetyl Hydrazide)]–Oxozirconium(IV),

[Aquo (2–Furoin Phenoxy Acetyl Hydrazide)]–Oxozirconium(IV)

Methanolic solution of oxozirconium salt (10 m mole) was gradually added to the ligand solution (10m mole) prepared in the same solvent in 1:1 ratio. The mixture was stirred vigorously using the magnetic stirrer. A dehydrating agent, 2,2–dimethoxypropane was added. After adjusting the pH of the mixture around 5.5 to 6.8 by adding acetate buffer, the contents were refluxed for 1–2 hour. In the
case of preparation of aquo(2–furoinphenoxy acetyl hydrazide)–oxozirconium(IV)
pH was adjusted at ~11 by the addition of a dilute solution of KOH. An excess of
the ligand solution was added in order to ensure complete precipitation of the
metal. Brown or grey precipitate gradually separated out. The precipitated
compounds were filtered off, washed with distilled water followed by dry ether.
The solid complexes were crystallized using petroleum ether, and dried in vacuo
over P₄O₁₀. Yield ~60–62%.

[Aquo Chloro (2:4–Dimethyl Benzalidene Hydrazide)]–Oxozirconium(IV),
[Dinitrato/Dithiocyanato (2:4–Dimethyl Benzalidene Benzoyl Hydrazide)]
Oxozirconium(IV) and [Bis (2:4–Dimethyl Benzalidene Benzoyl Hydrazide)]
Oxozirconium(IV) Perchlorate

A methanolic solution of oxozirconium(IV) salt (10 m mole) was refluxed
for ~5 hr at 70°C with an excess of solution (10 m mole) of 2:4–dimethyl
benzalidene benzoyl hydrazide in the same solvent. After removing the excess
solvent by distillation and the resulting mass was treated with excess of anhydrous
diethyl ether when the desired complexes separated out. They were filtered off and
washed properly with anhydrous diethyl ether and dried over P₄O₁₀ under vacuum
conditions. Yield ~50–55%.

RESULTS AND DISCUSSION:

The compounds are non–hygroscopic, stable and can be stored for a pretty
long time. They are insoluble in methanol, ethanol, acetone, chloroform and
benzene and considerably soluble in nitrobenzene, DMF and DMSO. Analytical
data reported in Table 5.1 correspond to 1:1 stoichiometric composition in all the
isolated complexes except the perchlorate complex with 2:4–Dimethyl
benzalidene benzoyl hydrazide which possesses 1:2 (M–L) stoichiometry. Molar
conductance values (Table 5.2) in nitrobenzene at the concentration $10^{-3}$M indicate the non–electrolytic behaviour of the complexes except 
\[(\text{ZrO}(\text{C}_{18}\text{H}_{15}\text{N}_{2}\text{O}_5)(\text{H}_2\text{O}))\text{Cl}\] and 
\[(\text{ZrO}(\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2))(\text{ClO}_4)_2\] which are 1:1 and 1:2 electrolytes\(^\text{(21)}\) respectively. The molecular weights of these compounds determined cryoscopically in nitrobenzene (Table 5.2) also support the same electrolytic/non–electrolytic behaviour. Colour and m.pt. of the complexes are recorded in Table 5.2.

**IR STUDIES:**

The bands appearing at 1665–1670, 1515–1510 and 1295–1288 cm\(^{-1}\) in the spectra of FPAH and DBBH are assigned to amide–I, amide–II and amide–III bands respectively. These bands are not traceable in the spectra of complexes 4 and 5 which shows the disappearance of $>$C=O group\(^\text{(22-23)}\) due to the amide imidol tautomerism of the ligands in these two complexes. On the other hand, in the spectra of complexes 1–3 and 6–8 amide–I, amide–II and amide–III bands get shifted from their original\(^\text{(24)}\) positions (in the ligands). In complexes 1–3 and 6–8, these are found to be present at 1635–1650, 1530–1535 and 1325–1330 cm\(^{-1}\) showing the coordination of carbonyl oxygen. The sharp band characteristic of vC=N existing at 1630–1635 cm\(^{-1}\) in the ligands shows a negative shift of \(~20\) cm\(^{-1}\) in the spectra of all the complexes which clearly sows that the azomethine nitrogen participates in complexation. In the spectra of complexes 4 and 5, two new bands are seen in 1560–1565 and 1350–1355 cm\(^{-1}\) region which are tentatively\(^\text{(25)}\) assigned to v(NCO\(^-\)). The appearance of these bands indicates the enolisation of keto group and its subsequent deprotonation during complex formation.
### TABLE 5.1

**ANALYTICAL DATA OF OXOZIRCONIUM(IV) COMPLEXES WITH 2–FUROIN PHENOXY ACETYL HYDRAZIDE AND 2:4–DIMETHYL BENZALIDENE BENZOYL HYDRAZIDE**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Complex</th>
<th>C% Calcd. (Found)</th>
<th>H% Calcd. (Found)</th>
<th>N% Calcd. (Found)</th>
<th>Metal% Calcd. (Found)</th>
<th>Cl/NCS/ClO$_4$% Calcd. (Found)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>[ZrO(C$<em>{18}$H$</em>{15}$N$_2$O$_5$)(H$_2$O)]Cl</td>
<td>43.10 (43.22)</td>
<td>3.18 (3.40)</td>
<td>5.50 (5.60)</td>
<td>18.15 (18.25)</td>
<td>7.02 (7.10)</td>
</tr>
<tr>
<td>2.</td>
<td>[ZrO(C$<em>{18}$H$</em>{15}$N$_2$O$_5$)NO$_3$(H$_2$O)]</td>
<td>40.93 (41.04)</td>
<td>3.17 (3.23)</td>
<td>7.86 (7.98)</td>
<td>7.24 (7.33)</td>
<td>–</td>
</tr>
<tr>
<td>3.</td>
<td>[ZrO(C$<em>{18}$H$</em>{15}$N$_2$O$_5$)NCS]</td>
<td>42.83</td>
<td>2.97</td>
<td>5.55</td>
<td>17.95 (18.09)</td>
<td>11.40 (11.50) a</td>
</tr>
<tr>
<td>4.</td>
<td>[ZrO(C$<em>{18}$H$</em>{14}$N$_2$O$_5$)(H$_2$O)]</td>
<td>46.43 (46.52)</td>
<td>3.37 (3.44)</td>
<td>5.95 (6.03)</td>
<td>19.58 (19.65)</td>
<td>–</td>
</tr>
<tr>
<td>5.</td>
<td>[ZrO(C$<em>{16}$H$</em>{15}$N$_2$O)Cl(H$_2$O)]</td>
<td>46.48 (46.63)</td>
<td>4.0 (4.12)</td>
<td>6.67 (6.80)</td>
<td>22.02 (22.15)</td>
<td>8.52 (8.62)</td>
</tr>
<tr>
<td>6.</td>
<td>[ZrO(C$<em>{16}$H$</em>{16}$N$_2$O)(NO$_3$)$_2$]</td>
<td>39.57 (39.73)</td>
<td>3.19 (3.31)</td>
<td>23.07 (23.17)</td>
<td>18.72 (18.87)</td>
<td>–</td>
</tr>
<tr>
<td>7.</td>
<td>[ZrO(C$<em>{16}$H$</em>{16}$N$_2$O)(NCS)$_2$]</td>
<td>40.24 (40.40)</td>
<td>3.20 (3.36)</td>
<td>5.73 (5.89)</td>
<td>19.03 (19.19)</td>
<td>24.30 (24.40)</td>
</tr>
<tr>
<td>8.</td>
<td>[ZrO(C$<em>{16}$H$</em>{16}$N$_2$O)$_2$(ClO$_4$)$_2$]</td>
<td>42.24 (47.39)</td>
<td>3.82 (3.94)</td>
<td>6.78 (6.91)</td>
<td>11.12 (11.25)</td>
<td>24.41 (24.56) a</td>
</tr>
</tbody>
</table>

*a* – NCS & ClO$_4$ estimated separately.
### TABLE 5.2

**PHYSICAL DATA OF OXOZIRCONIUM(IV) COMPLEXES WITH 2–FUROIN PHENOXY ACETYL HYDRAZIDE AND 2:4–DIMETHYL BENZALIDENE BENZOYL HYDRAZIDE**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Complex</th>
<th>$\Delta M$ (ohm$^{-1}$ cm$^2$ mol$^{-1}$)</th>
<th>Molecular Weight</th>
<th>Colour</th>
<th>M.Pt. (°C)</th>
<th>Electrolytic behaviour</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Found</td>
<td>Calcd.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>[ZrO(C$<em>{18}$H$</em>{15}$N$_2$O$_5$)(H$_2$O)]Cl</td>
<td>40.23</td>
<td>237</td>
<td>499.72</td>
<td>Brown</td>
<td>232±1</td>
</tr>
<tr>
<td>2.</td>
<td>[ZrO(C$<em>{18}$H$</em>{15}$N$_2$O$_5$)NO$_3$(H$_2$O)]</td>
<td>7.64</td>
<td>501</td>
<td>526.22</td>
<td>Dark brown</td>
<td>250±1</td>
</tr>
<tr>
<td>3.</td>
<td>[ZrO(C$<em>{18}$H$</em>{15}$N$_2$O$_5$)NCS]</td>
<td>2.21</td>
<td>493</td>
<td>504.22</td>
<td>Grey</td>
<td>208±1</td>
</tr>
<tr>
<td>4.</td>
<td>[ZrO(C$<em>{18}$H$</em>{14}$N$_2$O$_5$)(H$_2$O)]</td>
<td>6.50</td>
<td>448</td>
<td>463.22</td>
<td>Brown</td>
<td>270±1</td>
</tr>
<tr>
<td>5.</td>
<td>[ZrO(C$<em>{16}$H$</em>{15}$N$_2$O)Cl(H$_2$O)]</td>
<td>4.25</td>
<td>400</td>
<td>411.72</td>
<td>Black</td>
<td>265±1</td>
</tr>
<tr>
<td>6.</td>
<td>[ZrO(C$<em>{16}$H$</em>{16}$N$_2$O)(NO$_3$)$_2$]</td>
<td>3.72</td>
<td>473</td>
<td>483.22</td>
<td>Brown</td>
<td>280±1</td>
</tr>
<tr>
<td>7.</td>
<td>[ZrO(C$<em>{16}$H$</em>{16}$N$_2$O)(NCS)$_2$]</td>
<td>4.50</td>
<td>462</td>
<td>475.22</td>
<td>Grey</td>
<td>270±1</td>
</tr>
<tr>
<td>8.</td>
<td>[ZrO(C$<em>{16}$H$</em>{16}$N$_2$O)$_2$(ClO$_4$)$_2$]</td>
<td>60.23</td>
<td>253</td>
<td>810.22</td>
<td>Dark brown</td>
<td>87±1</td>
</tr>
</tbody>
</table>
A weak band existing at 970–985 cm\(^{-1}\) in the spectra of the ligands shows a positive shift of 30–40 cm\(^{-1}\) in all the complexes confirming the monodentate coordination of N–N moiety. \(v\)N–H band found at 3260–3245 cm\(^{-1}\) in the spectra of ligands remains unchanged in complexes 1–3 and 6–8 which shows its non–involvement in the formation of these complexes. The symmetric and asymmetric stretching bands characteristic of –CH\(_3\) group existing at 3425 and 3440 cm\(^{-1}\) in the spectrum of DBBH are found unaltered in the spectra of its complexes indicating their non–participation in complex formation.

Two strong bands observed at 610 and 590 cm\(^{-1}\) assigned to furan ring–deformation modes in FPAH are also seen in the spectra of its complexes occupying the same position showing the non–involvement of furan oxygen in coordination. The bands found at ~1410 and 1325 cm\(^{-1}\) characteristic of alcoholic O–H in plane bending mode are, however, missing in the spectra of its complexes with oxozirconium(IV) which suggested the participation of deprotonated alcoholic group. A negative shift of 10–15 cm\(^{-1}\) in the \(v\)(C–O) band noticed at 1215 cm\(^{-1}\) in the spectrum of FPAH confirms the involvement of alcoholic oxygen in complexation process. The FPAH & DBBH serve as tridentate and bidentate ligands respectively in the present complexes.\(^{(26–28)}\)

A band at 945–950 cm\(^{-1}\) in the complexes is assigned to \(v\)(Zr=O)\(^{(29,30)}\). The evidence of the bonding of oxygen and nitrogen atoms has been provided\(^{(31)}\) by the occurrence of \(v\)(M–O) and \(v\)(M–N) at ~450 and 360 cm\(^{-1}\) regions, respectively in the complexes. Further, the appearance of bands at 3495–3490, 1620–1615 and 730–725 cm\(^{-1}\) in the spectra of complexes 1,2,4 & 5 showed the presence of coordinated water in them.
The absence of the $v_3$ band of ionic nitrate ($D_{3h}$) around 1355 cm$^{-1}$ and the appearance of two strong bands at 1525 ($v_1$) and 1300 cm$^{-1}$ ($v_4$) in the spectra of complexes 2 & 6 suggested the coordination nature of nitrate.$^{32-35}$ Its bidentate behaviour is indicated by the presence of bands at $\sim$1030 ($v_2$), 800 ($v_6$) and $\sim$725 cm$^{-1}$ ($v_3/v_5$). In thiocyanato complexes, the bands noticed at $\sim$2050 cm$^{-1}$ ($v\text{C}≡\text{N}$), $\sim$845 cm$^{-1}$ ($v\text{C}−\text{S}$) and $\sim$485 cm$^{-1}$ ($δ\text{NCS}$) are due to the terminal N–bonded isothiocyanate ion. In the complex 5, a band observed at $\sim$200 cm$^{-1}$ is assigned to $v$(M–Cl). In the spectrum of perchlorate complex, the strong $v_3$ and $v_4$ bands appear at $\sim$1070 and 620 cm$^{-1}$, respectively for perchlorate ions, showing tetrahedral symmetry and non–bonding of perchlorate ions.$^{36-44}$

A stretching band seen at 3030–3015 cm$^{-1}$ characteristic of aromatic C–H occupy the same position in the spectra of all the complexes. Main IR spectral data are summarized in Table 5.3.

On the basis of the foregoing discussion coordination number (C.N.) five and seven are suggested for the present complexes and the tentative structures suggested for them are given on next pages.

**Relation Between Carbonyl Stretching Frequency and the Ionization Potential:**

Cook$^{45}$ derived a relation between the carbonyl stretching frequency and the ionization potential which is as follows:

$$\nu(C=O) = 29.20 \text{ (I.P.)} + 1409 \quad \text{(i)}$$

Stability constant ($\log K$) values are calculated by using the following equation:$^{(37)}$

$$\log K = 1.25 \text{ (I.P.)} − 4.2 \quad \text{(ii)}$$
TABLE 5.3
MAIN IR SPECTRAL BANDS (cm\(^{-1}\)) OF OXOZIRCONIUM(IV) COMPLEXES WITH 2-FUROIN PHENOXY
ACETYL HYDRAZIDE AND 2:4-DIMETHYL BENZALIDENE BENZOYL HYDRAZIDE

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Complex</th>
<th>(\nu)C=O</th>
<th>Amide–II</th>
<th>Amide–III</th>
<th>(\nu)C=N</th>
<th>(\nu)N–N</th>
<th>(\nu)ZrO</th>
<th>(\nu)M–O</th>
<th>(\nu)M–N</th>
<th>(\nu)OH(H(_2)O), (\delta)(H(_2)O) &amp; (\rho)(H(_2)O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[ZrO(C(<em>{18})H(</em>{15})N(_2)O(_5))(H(_2)O)]Cl</td>
<td>1630s</td>
<td>1530</td>
<td>1325</td>
<td>1620</td>
<td>1000w</td>
<td>945</td>
<td>455</td>
<td>365</td>
<td>3490, 1620, 725</td>
</tr>
<tr>
<td>2</td>
<td>[ZrO(C(<em>{18})H(</em>{15})N(_2)O(_5))NO(_3)(H(_2)O)]</td>
<td>1645s</td>
<td>1535</td>
<td>1320</td>
<td>1610s</td>
<td>1010w</td>
<td>950</td>
<td>450</td>
<td>360</td>
<td>3485, 1620, 730</td>
</tr>
<tr>
<td>3</td>
<td>[ZrO(C(<em>{18})H(</em>{15})N(_2)O(_5))NCS]</td>
<td>1635s</td>
<td>1525</td>
<td>1330</td>
<td>1615s</td>
<td>1000w</td>
<td>945</td>
<td>448</td>
<td>365</td>
<td>–</td>
</tr>
<tr>
<td>4</td>
<td>[ZrO(C(<em>{18})H(</em>{15})N(_2)O(_5))(H(_2)O)]</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1610s</td>
<td>1000w</td>
<td>945</td>
<td>450</td>
<td>360     3490, 1615, 730</td>
</tr>
<tr>
<td>5</td>
<td>[ZrO(C(<em>{16})H(</em>{15})N(_2)O)Cl(H(_2)O)]</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1615s</td>
<td>1025w</td>
<td>950</td>
<td>448</td>
<td>360     3495, 1615, 725</td>
</tr>
<tr>
<td>6</td>
<td>[ZrO(C(<em>{16})H(</em>{16})N(_2)O)(NO(_3))(_2)]</td>
<td>1640s</td>
<td>1535</td>
<td>1325</td>
<td>1615s</td>
<td>1020w</td>
<td>945</td>
<td>410</td>
<td>360</td>
<td>–</td>
</tr>
<tr>
<td>7</td>
<td>[ZrO(C(<em>{16})H(</em>{16})N(_2)O)(NCS)(_2)]</td>
<td>1635s</td>
<td>1535</td>
<td>1330</td>
<td>1610s</td>
<td>1015w</td>
<td>950</td>
<td>450</td>
<td>365</td>
<td>–</td>
</tr>
<tr>
<td>8</td>
<td><a href="ClO(_4)">ZrO(C(<em>{16})H(</em>{16})N(_2)O)(_2)</a>(_2)</td>
<td>1645s</td>
<td>1530</td>
<td>1330</td>
<td>1615s</td>
<td>1020w</td>
<td>950</td>
<td>450</td>
<td>360</td>
<td>–</td>
</tr>
</tbody>
</table>

s = sharp, w = weak
The calculated values of I.P. and log K have been reported in Table 5.4. By plotting a graph between \( \Delta v(C=O) \) and I.P. and log K, straight lines are obtained. From the stability constant (log K) values it is concluded that the stability of the complexes of oxozirconium(IV) with EPAAH follows the following sequence:

\[
[ZrO(C_{18}H_{15}N_2O_5)NO_3(H_2O)] > [ZrO(C_{18}H_{15}N_2O_5)(H_2O)]Cl > [ZrO(C_{18}H_{15}N_2O_5)NCS]
\]

and the stability of the complexes of oxozirconium(IV) with DBBH follows the sequence:

\[
[ZrO(C_{16}H_{16}N_2O)_2](ClO_4)_2 > [ZrO(C_{16}H_{16}N_2O)(NO_3)_2] > [ZrO(C_{16}H_{16}N_2O)(NCS)_2].
\]
### TABLE 5.4

VALUES OF (C=O) IONIZATION POTENTIAL AND LOG K FOR OXOZIRCONIUM(IV) COMPLEXES

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Ligand/Complex</th>
<th>ν(C=O) (cm⁻¹)</th>
<th>Δν(C=O) (cm⁻¹)</th>
<th>I.P. (e.V.)</th>
<th>Log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>(C₁₈H₁₆N₂O₅)</td>
<td>1665</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>2.</td>
<td>[ZrO(C₁₈H₁₅N₂O₅)(H₂O)]Cl</td>
<td>1640</td>
<td>25</td>
<td>7.9109</td>
<td>5.6886</td>
</tr>
<tr>
<td>3.</td>
<td>[ZrO(C₁₈H₁₅N₂O₅)NO₃(H₂O)]</td>
<td>1644</td>
<td>21</td>
<td>8.0479</td>
<td>5.8598</td>
</tr>
<tr>
<td>4.</td>
<td>[ZrO(C₁₈H₁₅N₂O₅)NCS]</td>
<td>1635</td>
<td>30</td>
<td>7.7397</td>
<td>5.4746</td>
</tr>
<tr>
<td>5.</td>
<td>[ZrO(C₁₈H₁₄N₂O₅)(H₂O)]</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>6.</td>
<td>(C₁₆H₁₆N₂O)</td>
<td>1670</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>7.</td>
<td>[ZrO(C₁₆H₁₅N₂O)Cl(H₂O)]</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>8.</td>
<td>[ZrO(C₁₆H₁₆N₂O)(NO₃)₂]</td>
<td>1645</td>
<td>25</td>
<td>8.0821</td>
<td>5.9026</td>
</tr>
<tr>
<td>9.</td>
<td>[ZrO(C₁₆H₁₆N₂O)(NCS)₂]</td>
<td>1640</td>
<td>30</td>
<td>7.9109</td>
<td>5.6886</td>
</tr>
<tr>
<td>10.</td>
<td><a href="ClO%E2%82%84">ZrO(C₁₆H₁₆N₂O)₂</a>₂</td>
<td>1650</td>
<td>20</td>
<td>8.2534</td>
<td>6.1167</td>
</tr>
</tbody>
</table>
1. Fig. 5.3: [Aquo (2–Furoin Phenoxy Acetyl Hydrazide)]–Oxozirconium(IV) Chloride

2. Fig. 5.4: [Aquo Nitrato (2–Furoin Phenoxy Acetyl Hydrazide)]–Oxozirconium(IV)

3. Fig. 4.5: [Thiocyanato (2–Furoin Phenoxy Acetyl Hydrazide)]–Oxozirconium(IV)
4. 

![Chemical Structure](image)

Fig. 5.6: [Aquo(2-Furoin Phenoxy Acetyl Hydrazide)]–Oxozirconium(IV)

5. 

![Chemical Structure](image)

Fig. 5.7: [Aquo Chloro (2:4-Dimethyl Benzalidene) Benzoyl Hydrazide]–Oxozirconium(IV)

6. 

![Chemical Structure](image)

Fig. 5.8: [Dinitrato (2:4-Dimethyl Benzalidene Benzoyl Hydrazide)]–Oxozirconium(IV)
Fig. 5.9: [Dithiocyanato (2:4–Dimethyl Benzalidene Benzoyl Hydrazide)]

Oxozirconium(IV)

Fig. 5.10: [Bis (2:4–Dimethyl Benzalidene Benzoyl Hydrazide)]–

Oxozirconium(IV) Perchlorate
CHAPTER-V

REFERENCES