SYNTHESIS AND CHARACTERIZATION
Of 4-ACYLTHIOSEMICARBAZONE-3-
METHYL-1-[4'-METHYLPHENYL]-2-
PYRAZOLIN-5-ONES AND
THEIR METAL COMPLEXES.
2. A. **Present Work:**

This chapter describes the experimental methods used to synthesize the following ligands.

(a) 4-Acetylthiosemicarbazone-3-methyl-1-[4'-methylphenyl]-2-pyrazolin-5-one [HActhPz].

\[
\text{Molecular Formula : } \quad \text{C}_{14}\text{H}_{17}\text{N}_{5}\text{OS}
\]

\[
\text{Molecular Weight : } \quad 303.38
\]

\[
\text{Structural Formula : }
\]
(b) 4-Propionylthiosemicarbazone-3-methyl-1-[4'-methylphenyl]-2-pyrazolin-5-one [HPrthPz].

Molecular Formula : C_{15}H_{19}N_{5}O_{5}
Molecular Weight : 317.40
Structural Formula :

(c) 4-Butyrylthiosemicarbazone-3-methyl-1-[4'-methylphenyl]-2-pyrazolin-5-one [HButhPz].

Molecular Formula : C_{16}H_{21}N_{5}O_{5}
Molecular Weight : 331.41
Structural Formula :
(d) 4-Benzoylthiosemicarbazone-3-methyl-1-[4'-methylphenyl]-2-pyrazolin-5-one [HBzthPz].

Molecular Formula : $C_{19}H_{19}N_{5}O_S$
Molecular Weight : 365.45
Structural Formula :

2. B. Materials:

The A. R. grade solvents and chemicals were used in the present study. 3-methyl-1-[4-methylphenyl]-2-pyrazolin-5-one was purchased from Prima Chemicals [Ahmedabad, India] and was used after crystallizing in water. Calcium hydroxide, benzoyl chloride, acetyl chloride, propionyl chloride, butyryl chloride, hydrochloric acid, thiosemicarbazide, 1,4-Dioxane and N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), methanol and acetic acid [S.D fine chemicals Ltd., Ahmedabad] and absolute alcohol [Alembic Chemical Works Co. Ltd., Baroda] were also used. The solvents used in the present study were purified by standard method and were dried if necessary. Cr(III) and Mn(II) metal acetates, potassium permanganate, [S.D fine
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chemicals Ltd., Ahmedabad] were also used. Sodium iodide, sodium azide, sodium acetate, ammonium acetate, ammonium thiocyanate and sodium nitrate [S.D fine chemicals Ltd., Ahmedabad] were also used.

2. C. **Experimental:**

All ligands prepared in the present study are characterized by colour, differential scanning calorimetry (DSC), melting point, elemental analyses, IR, $^1$H-NMR, $^{13}$C-NMR and MASS spectral studies. Melting points were taken in open capillaries and are uncorrected. The IR spectra were recorded on a Perkin-Elmer infrared spectrophotometer Model 783 and 597 in the range of 4000-200 cm$^{-1}$ (IIT, Mumbai, India and RSIC, Chennai, India). Elemental analysis (C, H, N and S) was performed on a "Perkin Elmer, Series II, 2400" C-H-N-S analyzer at Central Salt and Marine Chemical Research Institute, Bhavnagar, India. Nuclear magnetic resonance spectra ($^1$H-NMR and $^{13}$C-NMR) were recorded on a Bruker -400 MHz, spectrometer using TMS, [(CH$_3$)$_4$ Si] as internal standard and DMSO-d$_6$ as a solvent (Central Salt and Marine Chemical Research Institute (CSMCR), Bhavnagar, India). The DSC was determined on Mettler Star SW 8.10 at (Alembic Lab, Gujarat, India). The mass spectra of all ligands were recorded on a Jeol SX-102 FAB mass spectrometer (Alembic Laboratory Ltd, Baroda, India).

2. D. **Synthesis of thiosemicarbazone Schiff-base ligands:**

The 4-Acylthiosemicarbazone-3-methyl-1-[4'-methyl phenyl]-2-pyrazolin-5-one ligands used in the present study were prepared using literature method in following three steps [5-12]:

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(a) 3-methyl-1-[4-methylphenyl]-2-pyrazolin-5-one (purchased from Prima Chemicals, Ahmedabad, India)

(b) Synthesis of 4-Acyl-3-methyl-1-[4'-methylphenyl]-2-pyrazol in-5-one.

(c) Synthesis of 4-Acylthiosemicarbazone -3-methyl-1-[4'-methylphenyl]-2-pyrazolin-5-one.

2. D.1. 3-Methyl-1-[4-methylphenyl]-2-pyrazolin-5-one

3-Methyl-1-[4-methylphenyl]-2-pyrazolin-5-one was purchased from Prima Chemicals (Ahmedabad, India) and was used after crystallization in ethanol-water.

Analysis for C_{11}H_{12}N_{2}O,

Elemental analysis Calculated: C, 70.19; H, 6.43; N, 14.88%.
Found: C, 69.87; H, 6.51; N, 15.18 (%).

DSC : 134.46°C and 139.86°C.

^1H NMR (400MHz, DMSO-d_6, TMS ), δ ppm: 2.097, s (3H, Pz-CH_3), 2.50, s (3H, Ph-CH_3), 3.36, s (2H, Pz-CH_2), 7.20, m (2H,Ph), 7.55-7.57, m (2H,Ph).

Mass spectral data m/z Calculated: 188.22. Molar mass found 189.12(M\(^+\)).

2. D.2. Preparation of 4-Acyl-3-methyl-1-[4'-methylphenyl]-2-pyrazolin-5-one

The 4-Acyl-3-methyl-1-[4'-methylphenyl]-2-pyrazolin-5-one were synthesized by using modified Jensen method [10-12].

3-methyl-1-[4-methylphenyl]-2-pyrazolin -5-one (25.0 g, 0.1 mol) was placed in a three neck flask equipped with stirrer, addition funnel and reflux condenser. It was then dissolved in dioxane (250 mL)
by applying heat. To the reaction mixture, calcium hydroxide (13.97g, 0.2 mol) was added, followed by the drop wise addition of the acetyl chloride (10.64 g, 0.1 mol) or propionyl chloride (12.28 g, 0.1mol.) or butyryl chloride (14.17 g, 0.1mol) or benzoyl chloride (18.74 g, 0.1 mol). At this stage, mixture becomes thick paste and its temperature increases as this being a exothermic reaction. The reaction mixture was then refluxed on oil bath for an hour. The resulting calcium complex was then decomposed by pouring it into 2N hydrochloride acid (40 mL HCl in 600 mL water). The resulting colour compounds were collected by filtration, washed several times with water and finally dried in air try dryer. The products were then recrystallized in hot ethanol.

(a) 4-Acetyl-3-methyl-1-[4'-methylphenyl]-2-pyrazolin-5-one: light yellow; m. p. found: 98-100°C; Yield 89 %,

Analysis for C_{13}H_{14}N_{2}O_{2},

Elemental analysis Calculated: C, 67.81; H, 6.13, N, 12.17%.

Found : C, 67.67; H, 6.151; N,12.15 %;

\[ ^1H \text{ NMR (400MHz, DMSO-d6, TMS ) } \delta \text{ ppm: } 2.33, s(3H, CH}_3, 2.45, s(3H, Pz-CH}_3), 2.51, s(3H, Ph-CH}_3), 4.16, s(1H, Pz-H), 7.28-7.58, m(4H,Ph),. \]

IR(KBr Pellet) \( v_{\text{max}} \) in cm\(^{-1}\): 1785(s,s) (\( \nu\text{C=O} \)), 1635(s,s) (\( \nu\text{C=N} \)), 1361(w,sh) (Pz ring stretch), 1552(s,s) (Ph ring \( \nu\text{C=C} \), Stretch), 1127(s,s) (Pz ring Breathing ), 827(s,s) (C- CH3 Stretch) cm\(^{-1}\)

DSC: 103.14°C..

Mass spectral data m/z Calculated : 230.2. Molar mass found 230.86 (M\(^+\)).
(b) 4-Propionyl-3-methyl-1-[4'-methylphenyl]-2-pyrazolin-5-one: light yellow; m. p. found: 108-110°C; Yield 85%.

Analysis for C_{14}H_{16}N_{2}O_{2},

Elemental analysis Calculated: C, 68.83; H, 6.60; N, 11.47%.

Found: C, 68.71; H, 6.65; N, 11.48%.

^{1}H NMR (400MHz, DMSO-d_{6}, TMS ) \delta ppm : 1.031-1.049, t (3H, -CH_{3}), 2.33-2.41, s (3H, PZ-CH_{3}), 2.49-2.50, s (3H, PhCH_{3}), 2.80, q (2H, -CH_{2}-), 4.03, s (1H, Pz-H), 7.28-7.30, m (2H, Ph), 7.53-7.55, m (2H, Ph).

IR(KBr Pellet,) \nu_{\text{max}} \text{ in cm}^{-1} : 1774(s,s) (\nu_{\text{C-o}}), 1621(s,s)( \nu_{\text{C=N}}), 1364(w,sh)( Pz ring stretch), 1553(s,s) (Ph ring \nu_{\text{C=C}}, Stretch), 1140(s,s)( Pz ring Breathing ), 857(s,s)( C- CH_{3} Stretch) cm^{-1}

DSC: 101.19°C.

Mass spectral data m/z Calculated : 244.9. Molar mass found 245 (M^+).

(c) 4-Butyryl-3- methyl-1-[4'-methylphenyl]-2-pyrazolin-5-one: light yellow; m. p. found: 95-96°C; Yield 79%.

Analysis for C_{15}H_{18}N_{2}O_{2},

Elemental analysis Calculated: C, 69.74; H, 7.02; N, 10.84%.

Found: C, 69.56; H, 7.12; N, 10.85%.

^{1}H NMR (400MHz, DMSO-d_{6}, TMS ) \delta ppm : 1.00-1.08, t (3H, -CH_{3}), 1.59-1.63, tq (2H, -CH_{2}-), 2.30-2.33, s (3H, Pz-CH_{3}), 2.50, s (3H, PhCH_{3}), 2.62, t (2H, -CH_{2}-), 4.03, s (1H, Pz-H), 7.19-7.21, m (1H, Ph), 7.83-7.98, m (1H, Ph), 8.00-8.25 m (2H, Ph).

IR(KBr Pellet) \nu_{\text{max}} \text{ in cm}^{-1} : 1764(s,s) (\nu_{\text{C-o}}), 1624(s,s)( \nu_{\text{C=N}}), 1382(w,sh)( Pz ring stretch), 1555(s,s) (Phenyl ring \nu_{\text{C=C}}, Stretch), 1147(s,s)( Pz ring Breathing ), 835(s,s)( C- CH_{3} Stretch) cm^{-1}
DSC: 84.43°C..

Mass spectral data m/z Calculated : 258.31. Molar mass found 259 (M+).

(d) 4-Benzoyl-3-methyl-1-[4'-methylphenyl]-2-pyrazolin-5-one: light yellow; m. p. found: 116-118°C; Yield 81 %,
Analysis calculated for C_{18}H_{16}N_{2}O_{2},
Elemental analysis Calculated: C, 73.95; H, 5.52; N, 9.58%.
Found: C, 73.3; H, 5.52; N, 9.55 %.

{\textsuperscript{1}}H NMR (400MHz, DMSO-d6, TMS ) δ ppm : 1.93, s (3H, Pz-CH\textsubscript{3}), 2.51, s(3H, PhCH\textsubscript{3}), 4.02, s (1H, Pz-H), 7.21-7.31, m (4H, Ph), 7.47-7.58, td (1H, Ph), 7.73-7.89, m (4H, Ph).

IR(KBr Pellet,) ν\textsubscript{max} in cm\textsuperscript{-1}: 1714(s,s) (\nu\textsubscript{C=O}), 1601(s,s) (\nu\textsubscript{C-N}), 1387(w,sh)(Pz ring stretch), 1542(s,s) (Phenyl ring \nu\textsubscript{C=C}, Stretch), 1125(s,s)(Pz ring Breathing ), 820(s,s)( C- CH\textsubscript{3} Stretch) cm\textsuperscript{-1}

DSC : 107.15°C..

Mass spectral data m/z Calculated : 292.33. Molar mass found 293 (M+).

2. D. 3. **Preparation of 4-Acylthiosemicarbazone-3-methyl-1-[4'-methylphenyl]-2-pyrazolin-5-one**

Following general literature procedure was adopted to prepare all 4-Acylthiosemicarbazone-3-methyl-1-[4'-methylphenyl]-2-pyrazolin-5-ones [5, 6, 10, 11,14-17].
Equimolar quantities of 4-Acyl-3-methyl-1-[4'-methylphenyl]-2-pyrazolin-5-one [0.01 mol] and thiosemicarbazide hydrochloride [0.01 mol] were dissolved in 75mL of methanol separately and these solutions were mixed with constant stirring. The reaction mixture was then heated on a water bath for 2hrs. The reaction mixture was then allowed to stand overnight. The solid product obtained was collected by filtration, and washed with water-methanol mixture and dried in an air try drier. The acylthiosemicarbazones were then recrystallized from methanol-water mixture till desired purity confirmation was checked by TLC method.

The physical properties and analytical data of the ligands are presented in Table 2.1.
### TABLE 2.1

**PHYSICAL PROPERTIES AND ANALYTICAL DATA OF LIGAND**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting Point °C</th>
<th>Colour</th>
<th>Elemental analysis Found (calculate) percentage</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Carbon</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>HActhPz</td>
<td>200-202</td>
<td>Yellow</td>
<td>55.42</td>
<td>5.65</td>
</tr>
<tr>
<td></td>
<td>(55.43)</td>
<td></td>
<td>(5.63)</td>
<td>(23.04)</td>
</tr>
<tr>
<td>HPrthPz</td>
<td>170-173</td>
<td>Yellow</td>
<td>56.76</td>
<td>6.03</td>
</tr>
<tr>
<td></td>
<td>(56.33)</td>
<td></td>
<td>(6.04)</td>
<td>(22.65)</td>
</tr>
<tr>
<td>HButhPz</td>
<td>152-155</td>
<td>Pale yellow</td>
<td>57.98</td>
<td>6.39</td>
</tr>
<tr>
<td></td>
<td>(58.03)</td>
<td></td>
<td>(6.06)</td>
<td>(20.91)</td>
</tr>
<tr>
<td>HBzthPz</td>
<td>210-212</td>
<td>Off-white to yellow</td>
<td>62.44</td>
<td>5.24</td>
</tr>
<tr>
<td></td>
<td>(63.01)</td>
<td></td>
<td>(5.59)</td>
<td>(18.89)</td>
</tr>
</tbody>
</table>
2. E. **Characterization of 4-Acylthiosemicarbazone-3-methyl-1-[4'-methylphenyl]-2-pyrazolin-5-one**

The identity of 4-Acylthiosemicarbazone-3-methyl-1-[4'-methylphenyl]-2-pyrazolin-5-one were confirmed by the melting point, colour, elemental analysis (Table 2.1), $^1$H NMR, $^{13}$C NMR, IR, DSC and by mass spectral studies. The $^1$H NMR, $^{13}$C NMR, IR, DSC and mass spectra of all ligands are shown in Fig. : 2.1 – 2.9

The detailed assignments of infrared bands of all ligands used in the present study are given in chapter IV. The present chapter describes only important infrared bands [14-17] of all thiosemicarbazone schiff-base ligands used. The $^1$H and $^{13}$C chemical shifts have been made using reported values for the 2-pyrazolin-5-one derivatives [18-22]. The following 4-Acylthiosemicarbazone-3-methyl-1-[4'-methylphenyl]-2-pyrazolin-5-one ligands [I-IV] were used in present investigation to prepare the metal complexes.
(I) 4-Acetylthiosemicarbazone-3-methyl-1-[4'-methylphenyl]-2-pyrazolin-5-one [HActhPz].

Molecular Formula : $C_{14}H_{17}N_5OS$

Molecular Weight : 303.0

Structural Formula :

Yellow colour; m.p. found: 200-202°C; yield 64%.

Analysis calculated for $C_{14}H_{17}N_5OS$,

Elemental analysis Calculated: C, 55.42; H, 5.65; N, 23.08; S, 10.57%.
Found: C, 55.43; H, 5.63; N, 23.04; S, 10.98%.

$^1$H NMR (400MHz, DMSO-d$_6$, TMS ) $\delta$ ppm : 2.16, s (3H, CH$_3$), 2.21-2.22, s (3H, Pz-CH$_3$) , 2.33-2.55, s (3H, Ph-CH$_3$), 4.32, s (1H, PzH), 7.11-7.22, m (2H,Ph), 7.82-7.87, m (2H,Ph),  8.02-8.04, s (2H, -NH$_2$), 11.87, s (1H, -NH).

$^{13}$C NMR (400MHz, DMSO-d$_6$, TMS ) $\delta$ ppm : 14.82 (C-1, CH$_3$), 17.31(C-2, Pz-CH$_3$), 20.93 (C-3, Ph-CH$_3$), 118.51-137.05 (C-4, C-5, C-6, C-7, C-8, C-9 Ph), 55.07 (C-10, Ph-CH), 147.73(C-11, -N=C-), 150.31(C-12, -N=C-), 164.82(C-13, Ph-C=O), 187.82 (C-14, C=S).
IR(KBr Pellet,) $v_{\text{max}}$ in cm$^{-1}$: 1720(s,s) ($\nu_{\text{C} = \text{O}}$), 3220(s,s) ($\nu_{\text{NH}_2 \text{ sym}}$), -3390(s,s) ($\nu_{\text{NH}_2 \text{ asym}}$), 3295(w,s) ($\nu_{\text{N-H}}$), 1610(s,s) ($\nu_{\text{C} = \text{N}}$), 1591(s,br) ($\nu_{\text{C} = \text{N}}$ Pz-ring), 1362(w,sh) ($\nu_{\text{Pz ring}}$, stretch), 1053(s,s) ($\nu_{\text{N-N}}$, Stretch), 830(s,s) ($\nu_{\text{C} = \text{S}}$, Stretch). and

DSC : 205.28°C..

Mass spectral data m/z Calculated: 303. Molar mass found 304 (M$^+$).303, 304, 276, 184, 147, 130, 102, 121, 91, 60, 57 and 41.03
Fig: 2.1$^1$HNMR SPECTRA OF HActhPz
Fig: 2.3 IR SPECTRA OF HActhPz
Fig: 2.4 DSC SPECTRA OF HActhPz

Integral: 295.01 mJ
normalized: 200.14 Jg\(^{-1}\)
Onset: 203.23 °C
Peak: 205.28 °C

![Chemical Structure]
The possible fragmentation for the HActhPz ligand may be as follow.
(II) 4-Propionylthiosemicarbazone-3-methyl-1-[4'-methylphenyl]-2-pyrazolin-5-one [HPrthPz].

Molecular Formula : \( \text{C}_{15}\text{H}_{19}\text{N}_{5}\text{O}_{5} \)
Molecular Weight : 317.40
Structural Formula :

Yellow; m.p. found: 170-173°C; yield 70%.

Analysis calculated for \( \text{C}_{15}\text{H}_{19}\text{N}_{5}\text{O}_{5} \),

Elemental analysis Calculated: C, 56.76; H, 6.03; N, 22.06; S, 10.10%.
Found: C, 56.13; H, 6.04; N, 22.65; S, 10.24%.

\(^1\text{H} \text{NMR (400MHz, DMSO-d}_6, \text{TMS ) \delta ppm : 1.0-1.23, s (3H, CH}_3, 2.13-2.33, s (6H, Pz-CH}_3 \text{ and Ph-CH}_3), 2.51-2.92, q (2H, -CH}_2, -), 4.49, s (1H, PzH), 7.19-7.67, m (2H,Ph), 7.82-7.98, m (2H,Ph), 8.66, s (2H, -NH}_{2}, 12.10, s (1H, -NH).;\)

\(^{13}\text{C} \text{NMR (400MHz, DMSO-d}_6, \text{TMS ) \delta ppm : 14.16 (C-1, CH}_3), 16.30 (C-2, -CH}_2, -), 18.45 (C-3, Pz-CH}_3), 29.2 (C-4, Ph-CH}_3), 117.94-136.42 (C-5, C-6, C-7, C-8, C-9, C-10, Ph), 53.2 (C-1^1, Pz-CH), 146.54 (C-12, -)
N=C-, 149.3 (C-13, -N=C-), 164.66 (C-14, Ph-C=O), 184.68 (C-15, C=S);

IR(KBr Pellet,) \( \nu_{\text{max}} \) in cm\(^{-1} \): 1718(s,s) (\( \nu_{\text{C=O}} \)), 3310(s,s) (\( \nu_{\text{NH}_2 \text{ sym}} \)), 3430(s,s) (\( \nu_{\text{NH}_2 \text{ asym}} \)), 3270 (w,s) (\( \nu_{\text{N-H}} \)), 1619 (s,s) (\( \nu_{\text{C=N}} \)), 1586(s,br)(\( \nu_{\text{C=N \ Pz-ring}} \)), 1390 (w,sh)(\( \nu_{\text{Pz ring, stretch}} \)), 1049 (s,s) (\( \nu_{\text{N-N, Stretch}} \)), 825(s,s) (\( \nu_{\text{C=S, Stretch}} \)).

DSC : 135.48°C and 178.88°C..

Mass spectral data m/z Calculated : 317.4 Molar mass found 318 (M\(^+\)).317, 318, 290, 199, 147,144, 121, 102, 90, 60, 57 and 41.03.
Fig. 2.6: H NMR SPECTRA OF HPthPz
Fig: 2.7 $^{13}$C NMR SPECTRA OF HPrthPz
Fig. 2.8 IR SPECTRA OF HPrthPz.

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Fig: 2.9 DSC SPECTRA OF HPrthPz

Integral: -16.85 mJ
Normalized: -10.60 Jg^-1
Onset: 116.52 °C
Peak: 135.48 °C

Integral: -231.02 mJ
Normalized: -145.30 Jg^-1
Onset: 173.82 °C
Peak: 178.88 °C
Fig: 2.10 MASS SPECTRA OF HPrthPz
The possible fragmentation for the HPrthPz ligand may be as follow.

The diagram illustrates the fragmentation process with mass-to-charge ratios (m/z) indicated for each step.
(III) 4-Butyrylthiosemicarbazone-3-methyl-1-[4'-methylphenyl]-2-pyrazolin-5-one [HButhPz].

Molecular Formula : \( C_{16}H_{21}N_{5}OS \)

Molecular Weight : 331.41

Structural Formula :

![Structural Formula](image)

Pale-Yellow colour; m.p. found: 152-155°C; yield 73%.

Analysis calculated for \( C_{16}H_{21}N_{5}OS \),

Elemental analysis Calculated: C, 57.98; H, 6.39; N, 21.13; S, 9.67%.
Found: C, 58.03; H, 6.06; N, 20.91; S, 9.28%.

\(^1\)H NMR (400MHz, DMSO-d6, TMS ) \( \delta \) ppm : 1.0-1.08, s (3H, CH\(_3\)), 1.59, m (2H, -CH\(_2\)-), 2.30-2.33, s (3H, Pz-CH\(_3\)), 2.50-2.51, s (3H, Ph-CH\(_3\)), 2.51-2.92, t (2H, -CH\(_2\)-), 4.03, s (1H, PzH), 7.19-7.21, m (2H,Ph), 7.83-7.98, m (2H,Ph), 8.25, s (2H, -NH\(_2\)), 12.15, s (1H, -NH).;
$^{13}$C NMR (400MHz, DMSO-d$_6$, TMS) δ ppm: 12.32 (C-1, -CH$_2$-), 14.70 (C-2, CH$_3$), 16.29 (C-3, -CH$_2$-), 20.44-20.92 (C-4, Pz-CH$_3$), 26.42 (C-5, Ph-CH$_3$), 118.02-136.48 (C-6, C-7, C-8, C-9, C-10, C-11, C-12, Ph), 54.01 (C-13, Pz-CH), 146.57 (C-14, -N=C-), 149.08 (C-15, -N=C-), 164.02 (C-16, Pz-C=O), 178.89 (C-17, C=S);

IR (KBr Pellet,) $\nu_{\text{max}}$ in cm$^{-1}$: 1722(s,s) ($\nu_{\text{C=O}}$), 3290 (s,s) ($\nu_{\text{NH}_2 \text{ sym}}$), 3400 (s,s) ($\nu_{\text{NH}_2 \text{ asym}}$), 3248 (w,s) ($\nu_{\text{N-H}}$), 1625 (s,s) ($\nu_{\text{C=N}}$), 1585(s,br) ($\nu_{\text{C=N Pz-ring}}$), 1400 (w,sh) ($\nu_{\text{Pz-ring stretch}}$), 1051 (s,s) ($\nu_{\text{N-N Stretch}}$), 832(s,s) ($\nu_{\text{C=S Stretch}}$).

DSC: 159.7°C.

Mass spectral data m/z Calculated: 331.41 Molar mass found 332 (M$^+)$, 331, 332, 304, 212, 147, 144, 121, 102, 90, 60, 57 and 41.03
Fig. 2.1 NMR SPECTRA OF HButPz
Fig: 2.12 $^{13}$C NMR SPECTRA OF HButhPz
Fig. 2.13 IR SPECTRA OF HButhPz
Fig: 2.14 DSC SPECTRA OF HButHpz

Integral normalized:
-200.29 mJ
-143.37 Jg⁻¹

Onset: 156.41 °C
Peak: 169.79 °C

Method: 25-300°C/10°C/Min
25.0-300.0°C/10.0°C/Min

mW
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30

0 120 240°C
260
Fig: 2.15 MASS SPECTRA OF HButhPz
The possible fragmentation for the HButhPz ligand may be as follow.

\[
\begin{align*}
\text{m/z 41.03} & \quad \text{CH}_3 \\
\text{m/z 91.05} & \quad \text{CH}_3
\end{align*}
\]
(IV) 4-Benzoylthiosemicarbazone-3-methyl-1-[4'-methylphenyl]-2-pyrazol in -5-one [HBzthPz].

Molecular Formula : \(C_{19}H_{19}N_{5}OS\)

Molecular Weight : 365.45

Structural Formula :

Off-white to Yellow colour; m.p. found: 210-212°C; yield 82%.

Analysis calculated for \(C_{19}H_{19}N_{5}OS\),

Elemental analysis Calculated: C, 62.44; H, 5.24; N, 19.16; S, 8.77%. Found: C, 63.01; H, 5.59; N, 18.89; S, 9.02%.

\(^1\text{H} \text{NMR } (400\text{MHz, DMSO-d6, TMS }) \delta \text{ ppm : 2.21-2.34, s (3H, Pz-CH}_3\text{), 2.51, s (3H, Ph-CH}_3\text{), 4.32, s (1H, PzH), 7.82-7.89, m (3H,Ph), 7.21-7.31, m (2H,Ph), 7.41-7.47, m (2H,Ph), 7.58-7.82, m (2H,Ph), 8.24, s (2H, -NH}_2\text{), 11.89, s (1H, -NH).}
\(^{13}\)C NMR (400MHz, DMSO-d\(_6\), TMS) \(\delta\) ppm: 20.47 (C-1, Pz-CH\(_3\)), 29.30 (C-2, Ph-CH\(_3\)), 118.03-136.96 (C-3, C-4, C-5, C-6, C-7, C-8, C-9, C-10, C-11, C-12, C-13, C-14 Ph), 56.01 (C-15, Pz-CH), 146.08 (C-16, -N=C-), 148.98 (C-17, -N=C-), 165.48 (C-87, Pz-C=O), 181.17 (C-19, C=S);

IR (KBr Pellet,) \(\nu_{\text{max}}\) in cm\(^{-1}\): 1718(s, s) (\(\nu_{\text{c=0}}\)), 3330(s, s) (\(\nu_{\text{NH2 sym}}\)), 3450 (s, s) (\(\nu_{\text{NH2 asym}}\)), 3256 (w, s) (\(\nu_{\text{N-H}}\)), 1623 (s, s) (\(\nu_{\text{C=N}}\)), 1583(s, br) (\(\nu_{\text{C=N Pz-ring}}\)), 1392 (w, sh) (Pz ring stretch), 1051 (s, s) (\(\nu_{\text{N-N\ Stretch}}\)), 828(s, s) (\(\nu_{\text{C=S\ Stretch}}\)) and

DSC : 212.12°C.

Mass spectral data m/z Calculated: 365.45 Molar mass found 366 (M\(^+\)). 366, 338, 246, 192, 178, 147, 144, 121, 102, 90, 60, 57 and 41.03
Fig. 2.16: 1H NMR SPECTRA OF HBzthPz
Fig: 2.17 $^{13}$C NMR PECTRA OF HBzthPz
Fig: 2.18 IR SPECTRA OF HBzthPz
Fig: 2.19 DSC SPECTRA OF HBzthPz

Integral: -224.68 mJ
Normalized: -113.25 Jg^-1
Onset: 208.38 °C
Peak: 212.12 °C
Fig: 2.20 MASS SPECTRA OF HBzthPz
The possible fragmentation for the HBzthPz ligand may be as follow.
2. F. **Synthesis of the Metal Complexes** :

The following general procedure was used in the synthesis of all metal complexes.

The preformed 0.02 mole of 4-Acylthiosemicarbazone-3-methyl-1-[4'-methylphenyl]-2-pyrazolin-5-ones (6.06g for HActhPz, 6.34 g for HPrthPz, 6.64 g for HButhPz and 7.38 g for HBzthPz) was dissolve in minimum hot Methanol. To this solution 0.01mol of powdered Mn(III)acetate (2.68g) (Freshly prepared) or Cr(III)acetate (2.29g) was added with constant stirring over a period of 30 minutes, followed by the addition of excess of the inorganic salts containing desired anions [NH$_4$SCN, NaN$_3$, NH$_4$NO$_3$, NaI] dissolved in minimum hot water. The reaction mixture was refluxed for 3-4 hrs. on water bath. The resulting mixture thus obtained was distilled to half volume and 100ml of water was added to the reaction mass and mixture was cooled to room temperature. The product obtained is collected by filtration, and washed several time with hot de-ionized water and finally with hot methanol. The product was recrystallized in mixture of Methanol-water, dried under vacuum at 50-60°C. in vacuum oven.
REFERENCES


