CHAPTER II

EXPERIMENTAL

This chapter includes the synthetic procedure of diphenylcarbazone (DPC) derivatives and their transition metal complexes. The methods of purification, instrumentation, analyses of metals and the determination of magnetic moments of the transition metal complexes are also presented in this chapter. The following diphenylcarbazone derivatives were prepared for the present investigation.

2.1) Di(3-chloro-4-methylphenyl)carbazone
2.2) Di(3,5-dichlorophenyl)carbazone
2.3) Di(2,6-dichlorophenyl)carbazone
2.4) Di(3,5-dimethylphenyl)carbazone
2.5) Di(4-fluorophenyl)carbazone
2.6) Di(4-ethylphenyl)carbazone
2.7) Di(4-methylphenyl)carbazone
2.8) Di(4-bromophenyl)carbazone

The preparation of these ligands was done in the manner described below. The ligands 2.1 to 2.6 listed above are synthesized for the first time.

2.1 Synthesis of di(3-chloro-4-methylphenyl)carbazone \[D3Cl4MPC]\n
The method of preparation of di(3-chloro-4-methylphenyl)carbazone involves the following three steps.

2.1 a. Preparation of 3-chloro-4-methylphenylhydrazine\[a\]

A mixture of 3-chloro-4-methylaniline (34.5 g., 0.25 mole) and \(\text{H}_2\text{O}\) (62.5 ml) was taken in a three-necked flask (1 litre) and cooled in an ice
bath. Concentrated HCl (62.5 ml) was added to the mixture with rapid stirring. The mixture was diazotised at \(-5 \, ^\circ\text{C}\) by drop wise addition of cold \text{NaNO}_2 solution (17.25 g. in 25 ml of \text{H}_2\text{O}) through a dropping funnel. The clear maroon coloured solution thus obtained after the completion of diazotization was filtered through a glass wool plug followed by rapid addition into a fresh solution of \text{Na}_2\text{SO}_3 (375 ml), which was prepared by passing \text{SO}_2 gas into a cold solution of \text{NaOH} (52 g. in 375 ml of \text{H}_2\text{O}) and then tested with phenolphthalein for the neutralization of \text{NaOH}. The resulting solution was kept on a water bath at 60 \, ^\circ\text{C} for 1 h. The solution was then acidified with HCl and heated on a hot water bath for 6 to 7 h. The hot solution was then treated with activated charcoal and filtered. To this filtrate concentrated HCl (250 ml) was added slowly with constant stirring, allowed to cool and filtered. The resulting white precipitate of hydrazinehydrochloride was washed with a little HCl (3 N) followed by \text{Et}_2\text{O} and dried over \text{P}_2\text{O}_5 under vacuum (Yield, 66.3 \%).

2.1 b. Preparation of di(3-chloro-4-methylphenyl)carbazide

The compound 3-chloro-4-methylphenylhydrazine (11.6 g.) was thoroughly mixed with \((\text{NH}_2)_2\text{CO}\) (2.3 g.), which was preheated for 3 h., at 100 \, ^\circ\text{C}. The mixture was taken in a R.B. Flask (100 ml), fitted with a water condenser and heated at 155 \, ^\circ\text{C} in an oil bath. After about 10 mins., \((\text{NH}_2)_2\text{CO}\) started to dissolve accompanied by evolution of ammonia. The heating was continued for 3 h. At 155 \, ^\circ\text{C} when a yellowish solid mass was obtained. It was cooled, refluxed with \text{EtOH} (70 ml) for 30 mins., filtered rapidly through a preheated buckner funnel and the filtrate was cooled when white crystal of carbazide were obtained, which were filtered, drained well washed with \text{H}_2\text{O} and \text{Et}_2\text{O} and then air dried. The carbazide obtained was recrystallised from \text{EtOH} (Yield, 62 \% ; m.p., 168 \, ^\circ\text{C}).
2.1 Preparation of di(3-chloro-4-methylphenyl)carbazone

Above synthesized di(3-chloro-4-methylphenyl)carbazide (4 g.) was dissolved in glacial acetic acid (240 ml) and diluted with 1 N H₂SO₄ (80 ml). A solution of 10 % of ferric alum (0.4 ml) was added to it. Then a solution of K₂S₂O₈ (3.8 g. in 80 ml of H₂O) was added drop wise with a vigorous stirring, allowed to stand for 30 mins., diluted with ice-cold H₂O and then extracted with Et₂O. The ethereal layer was repeatedly washed with H₂O till it was free from acetic acid. The solution was then dried over anhydrous Na₂SO₄. Et₂O was evaporated to get D₃Cl₄MPC (Yield, 61 %; m.p., 126 °C).

2.2 Synthesis of di(3,5-dichlorophenyl)carbazone [D₃,5DClIPC]

The second and third steps viz., preparation of carbazide and carbazone are similar to the method described under D₃Cl₄MPC (2.1) where as, the preparation of hydrazine was carried out by the method described below.³ 500 ml of concentrated hydrochloric acid was added with stirring into a solution of 25 g. of 3,5-dichloroaniline in 100 ml of glacial acetic acid at room temperature; the resulting solution was cooled to 0 °C and diazotised by adding a solution of 11 g. of sodium nitrite (NaNO₂) in 400 ml of water drop by drop. The resulting cold solution of the diazonium salt was filtered rapidly and a cold solution of 100 g. of stannous chloride dihydrate in 100 ml of concentrated hydrochloric acid was added to the filtrate drop wise. The resulting insoluble complex salt was collected by filtration, washed with saturated aqueous sodium chloride and treated with NaOH solution when 3,5-dichlorophenylhydrazine was obtained. The product was extracted with ether, washed with water, dried and concentrated until crystallization of 3,5-dichlorophenylhydrazine occurred. The product was purified by recrystallization using ether as a solvent. The last steps viz., preparation of carbazide and oxidation of carbazide to carbazone are similar to the method described under D₃Cl₄MPC (2.1). Carbazide: Yield, 62 %; m.p., 187 °C; Carbazone: Yield, 56 %; m.p., 112 °C
2.3 Synthesis of di(2,6-dichlorophenyl)carbazone [D2,6DC1PC]

2,6DC1PC was synthesized by the method described under D3,5DC1PC (2.2).

Carbazide: Yield, 60 %; m.p., 181 °C

Carbazone: Yield 56 %; m.p., 109 °C.

2.4 Synthesis of di(3,5-dimethylphenyl)carbazone [D3,5DMPC]

The first and last steps viz., preparation of hydrazine and oxidation of carbazide to carbazone are similar to the method described under D3Cl4MPC (2.1) where as, the preparation of carbazide was carried out by the method described below. The Et2O solution of 3,5-dimethylphenylhydrazine (10 g. in 100 ml of Et2O) in a conical flask (250 ml) was immersed in an ice bath and 20 % of COCl2 (6.3 ml) in toluene was added dropwise with vigorous stirring. The reaction mixture was allowed to stand for 30 mins. The solid separated out was filtered and boiled several times with HCl (0.1 M) to remove excess of hydrazine. It was filtered, washed with H2O and dried. The carbazide was recrystallised from benzene.

Carbazide: Yield, 70 %; m.p., 183 °C

Carbazone: Yield, 58 %; m.p., 113 °C

2.5 Synthesis of di(4-fluorophenyl)carbazone [D4FPC]

The second and third steps viz., preparation of carbazide and oxidation of carbazide to carbazone are similar to the method described under D3Cl4MPC (2.1) where as, the preparation of hydrazine was carried out by the method described below. A fine suspension of p-fluoroaniline hydrochloride (from 12.6 g. of p- fluoroaniline) in concentrated hydrochloric acid (140 ml) was diazotized at −10°C with 40 % sodium nitrite solution and reduced with stannous chloride (76.8 g.). The resulting creamy precipitate was collected after 1 h. Excess of acid was removed by washing with cold saturated sodium chloride solution and the pink solid was hew transferred a separate half
immersed in a freezing mixture. Addition of a saturated solution of ammonium or sodium acetate (30 – 50 ml) liberated the base, which was extracted with ether (2 x 30 ml). After drying (K₂CO₃) of the extract in the dark, the solvent was evaporated off and the residual oil twice distilled under reduced pressure. p-Fluorophenylhydrazine separated as nearly colourless needles, m.p. 37.5 °C, (67.5 %), from 1:1 ether-light petroleum (b.p. 60-80 °C).

Carbazide: Yield; 64 %; m.p., 180 °C

Carbazone: Yield; 61 %; m.p., 105 °C

2.6 Synthesis of di(4-ethylphenyl)carbazone [D4EPC]

D4EPC was synthesized by the method described under D3Cl4MPC (2.1).

Carbazide: Yield, 67 %; m.p., 157 °C

Carbazone: Yield, 61 %; m.p., 110 °C

2.7 Synthesis of di(4-methylphenyl)carbazone [D4MPC]

D4MPC was synthesized by the method described under D3Cl4MPC (2.1).

Carbazide: Yield, 69 %; m.p., 168 °C

Carbazone: Yield, 63 %; m.p., 125 °C

2.8 Synthesis of di(4-bromophenyl)carbazone [D4BrPC]

D4BrPC was synthesized by the method described under D3Cl4MPC (2.1).

Carbazide: Yield, 65 %; m.p., 204 °C

Carbazone: Yield, 60 %; m.p., 108 °C
2.9 General method for the synthesis of substituted diphenylcarbazones:

The substitutions $R_1$ and $R_2$ are as follows:

$R_1 = 3$-Cl, $R_2 = 4$-CH$_3$ for D3Cl4MPC;

$R_1 = 3$-Cl, $R_2 = 5$-Cl for D3,5DClPC;

$R_1 = 2$-Cl, $R_2 = 6$-Cl for D2,6DClPC;

$R_1 = 3$-CH$_3$, $R_2 = 5$-CH$_3$ for D3,5DMPC;

$R_1 = 4$-F, $R_2 = -H$ for D4FPC;

$R_1 = 4$-Br, $R_2 = -H$ for D4BrPC;

$R_1 = 4$-CH$_3$, $R_2 = -H$ for D4MPC and

$R_1 = 4$-C$_2$H$_5$, $R_2 = -H$ for D4EPC.
I. Synthesis of substituted phenylhydrazine

(a). Diazotization:

\[
\text{NH}_2 + \text{NaNO}_2 \xrightarrow{2 \text{HCl}} \text{N}_2^+ \xrightarrow{-5 \text{ to } -10 \degree \text{C}} \text{R}_2 \text{R}_1 \xrightarrow{\text{NaCl} + 2 \text{H}_2\text{O}} \]

(b). Reduction:

Method 1.

\[
\text{N} = \text{NSO}_3\text{Na} \xrightarrow{\text{NaHSO}_3} \text{R}_2 \text{R}_1 \xrightarrow{\text{HCl}} \text{NHNH}_2\text{HCl} \xrightarrow{\text{below } 15 \degree \text{C} + \text{NaOH}} \text{NHNH}_2
\]

Method 2.

\[
\text{N}_2^+ \xrightarrow{\text{Freshly prepared } \text{Na}_2\text{SO}_3} \xrightarrow{5 \degree \text{C}} \text{R}_2 \text{R}_1 \xrightarrow{\text{N} = \text{NSO}_3\text{Na}} \text{NHNHSO}_3\text{Na} \xrightarrow{\text{HCl}} \text{R}_2 \text{R}_1 \xrightarrow{\text{below } 15 \degree \text{C}} \text{NHNH}_2
\]

The reduction of the diazotised product of the ligands D3,5DC1PC and D2,6DC1PC were carried out by method 2 as mentioned above. The rest are followed by method 1.
II. Synthesis of substituted diphenylcarbazide:

(a) Method 1.

\[
\begin{align*}
\text{NHNH}_2 & \quad + \quad \text{R}_1 \quad \text{R}_2 \\
\text{NH}_2 & \quad \xrightarrow{\Delta} \quad 3 \text{ hrs}, 155 \, ^\circ\text{C} \\
\text{R}_1 \quad \text{R}_2 & \quad + \quad 2\text{NH}_3
\end{align*}
\]

(b) Method 2.

\[
\begin{align*}
\text{NHNH}_2 & \quad + \quad \text{COCl}_2 \\
\text{R}_1 \quad \text{R}_2 & \quad \xrightarrow{\text{ Partial oxid. K}_2\text{S}_2\text{O}_8 \text{ in AcOH media}} \\
\text{R}_1 \quad \text{R}_2 & \quad + \quad 2\text{HCl}
\end{align*}
\]

The method 2 is followed only for the preparation of the carbazide of the ligand D3,5DMPC

III. Synthesis of substituted diphenylcarbazone:

\[
\begin{align*}
\text{NHNH} - \text{C} - \text{NHNH} & \quad \xrightarrow{\text{ Partial oxid. K}_2\text{S}_2\text{O}_8 \text{ in AcOH media}} \\
\text{R}_1 \quad \text{R}_2 & \quad \text{R}_1 \quad \text{R}_2
\end{align*}
\]

2.10 Purification of the ligands

All the ligands (i.e. 2.1 - 2.8) were purified by column chromatography. The compound (0.5 g.) in CHCl₃ was passed through a column (1 feet long and 2 cm width) containing silica gel (60-120 mesh, 80 g.). The carbazone was eluted by the mixture of Me₂O:CHCl₃ as an eluent. The solvent mixture was slowly evaporated to obtain the crystals of carbazone.
The physical constants, elemental analyses, electronic, IR and NMR spectral data of all the DPC derivatives are given in the Chapter III.

2.11 Synthesis of metal complexes

All the metal chlorides used were of analytical reagent grade. A solution of metal chloride (1 g.) in a buffer was mixed with a 0.01 M EtOH solution of DPC derivative at room temperature. The mixture was stirred and the precipitate was collected by suction and washed several times with H₂O. The complex was dried over P₂O₅ in vacuo at room temperature.

The buffer solutions of various pH values used for the preparation of metal complexes of DPC derivatives are given below.

<table>
<thead>
<tr>
<th>Metal</th>
<th>pH of buffer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co, Ni, Zn, Cd</td>
<td>6.2</td>
</tr>
<tr>
<td>Cu</td>
<td>4.5</td>
</tr>
<tr>
<td>Pd</td>
<td>1.0</td>
</tr>
</tbody>
</table>

2.12 Purification of metal complexes

All the metal complexes were purified by Soxhlet method. The complex was taken into the Soxhlet tube fitted with a water condenser and R.B. Flask (100 ml) containing 1:1 mixture of Et₂O and petroleum ether. The mixture was heated gently, so that the solvent gets evaporated. The impurities were found to be dissolved in solvent mixture and the pure complex in the Soxhlet tube was obtained as a shining powder in each case.

2.13 C, H and N analyses

The C, H and N analyses of the DPC derivatives and their metal complexes were carried out on Perkin Elmer 240 CHN analyser.
2.14 Analyses of cobalt, nickel, copper, zinc and cadmium

A known weight (approx. 0.2 g.) of the complex was taken in a beaker (250 ml) and a mixture of 1:1 HClO₄ and HCl was added to it. The pasty mass was decomposed on a sand bath. The resultant clear solution was cooled and diluted with double distilled water to 100 ml, 20 ml of this solution was pipetted out into a clean conical flask (100 ml), neutralized with NaOH and diluted to 50 ml. A buffer of pH 10 (2 ml) was added followed by 2-3 drops of suitable indicator (given below) and titrated against standard EDTA (0.01 M) solution.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Indicator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co, Cd</td>
<td>1 – (2- pyridylazo) – 2 – naphthol [PAN]</td>
</tr>
<tr>
<td>Ni, Cu</td>
<td>Murexide</td>
</tr>
<tr>
<td>Zn</td>
<td>Eriochrom Black T</td>
</tr>
</tbody>
</table>

Amount of the metal in the complex was estimated from the volume of the EDTA solution required.

2.15 Analyses of palladium

The Pd(II) complex (approx. 0.1 g.) was dissolved in concentrated HCl and 2-5 ml solution of dimethylglyoxime (1 %) in 95 % EtOH was added to it at room temperature. The solution was allowed to stand for 1 h., and then filtered through a previously weighed sintered glass crucible. The filtrate was tested with a little of the reagent to make sure that the precipitation is complete. Washed the precipitate of palladium dimethylglyoxime thoroughly first with cold H₂O and dried at 110 °C to constant weight. The palladium was weighed as Pd(C₄H₇O₂N₂)₂.

2.16 Magnetic susceptibility measurements

Magnetic susceptibility measurements of the complexes were carried out at room temperature, by Gouy method. The previously weighed and calibrated Gouy tube was uniformly filled with finely powdered sample of the complex.
upto the mark. The tube was suspended vertically by means of an aluminium chain from the pan of a semi-micro single pan balance, at the center of the pole-gap between the poles of a strong electromagnet. The weight of the tube along with the complex was recorded without applying the magnetic field. When a strong magnetic field (~ 5000 gauss) was applied, the paramagnetic sample experienced magnetic gradient. This causes a change in the weight of the sample and thus the weight of the sample and thus the weight was recorded under the influence of magnetic field. The process of recording the weights with and without magnetic field was repeated thrice and the mean of the three observations was taken as apparent change in the weight. The compound Hg[Co(SCN)4] was employed as a calibrant.

Weight of the empty tube in the absence of field = m₁ g.
Weight of the empty tube in the presence of field = m₁′ g.
Diamagnetic correction for the tube (δ) = (m₁′ - m₁) g.
Weight of the tube with complex in the absence of the magnetic field = m₂ g.
Weight of the complex (w) = (m₂ - m₁) g.
Weight of the tube with complex in the presence of the magnetic field = m₃ g.
The apparent change in the weight with and without field can be expressed as

\[ \Delta m = (m₃ - m₂) \text{ g.} \]
\[ \Delta m' = \Delta m - \text{diamagnetic correction for the tube (δ)} \]

The gram magnetic susceptibility \( \chi_g \) of the sample is given by

\[ \chi_g \times 10^6 = (\alpha + \beta \Delta m') / w \]
where, \( \alpha \) and \( \beta \) are constants of Gouy tube
\[ \alpha = 0.029 \times \text{specimen volume} \text{ and } \beta \text{ is the tube calibration constant.} \]

The molar susceptibility \( \chi_M \) is given by

\[ \chi_M = \chi_g \times M \text{ where, } M \text{ is the molecular weight of the complex.} \]
\[ \chi_M^{(\text{corr})} = \chi_M - \text{diamagnetic correction of the ligand} \]

The magnetic moment, \( \mu_{\text{eff}} = 2.84 \left( \chi_M^{(\text{corr})} \times T \right)^{1/2} \)
where, T is the absolute temperature at which measurement is made.

2.17 Electronic spectral studies

The electronic spectra of the DPC derivatives and their metal complexes in CHCl₃ were recorded on Hitachi 150–20 uv–vis. spectrophotometer using optical cells of path length 10 mm at room temperature.

2.18 Infrared spectral studies

The IR spectra of the DPC derivatives and their metal complexes were recorded either on Nicolet 170 SX FT–IR or Perkin – Elmer 157 spectrometer either in KBr or nujol. The spectra were measured in the range 4000– 400 cm⁻¹.

2.19 Proton magnetic resonance spectral studies

The PMR (¹H-NMR) spectra of the DPC derivatives and diamagnetic complexes were recorded on VXR 300 S Varian spectrometer at 300 MHz. The spectra of a few samples were also scanned on Bruker NMR spectrometer at 400 MHz. The spectra were recorded in CDCl₃ using TMS as internal reference.

2.20 Electron spin resonance spectral studies

The ESR spectra of Cu(II) complexes were recorded both at room temperature (RT) and liquid nitrogen temperature (LNT) on an E – line x – band spectrometer using TCNE as the g – marker.

2.21 Fluorescence spectral studies

The fluorescence spectra were recorded on F-2000 Fluorescence spectrofluorimeter. The excitation wavelength chosen were the absorption maxima of the respective fluorophore.

2.22 Dielectric constant studies

The dielectric measurements were recorded with the help of Forbes Tinsley (FT) 6421 LCR Data Bridge at 10 kHz. frequency.

2.23 Thermogravimetric studies

Thermogravimetric measurements were carried out with a Rigaku TAS-100 Model thermal analyzer. About 2-6 mg of the pure sample was
subjected to dynamic T.G. scans at a heating rate of 10 °C min⁻¹ in an inert atmosphere, in the temperature range from ambient to 1000°C.

2.24 Cyclic voltammetric studies

The Cyclic Voltammetric (CV) studies were carried out using a potentiostat provided with the Data Acquisition PC interface card fabricated at Analytical Chemistry Division Bhabha Atomic Research Centre (BARC), Trombay, compatible with an IBM Personal Computer and coupled to a printer using tetrabutyl ammonium perchlorate as a supporting electrolyte.
Reference

1. A.I. Vogel, "Practical Organic Chemistry", 3rd edn., Longmans, 1964, (a) p. 636; (b) p. 954; (c) 153.


