CHAPTER II

EXPERIMENTAL

GENERAL DESCRIPTIONS

Purification of the products:

Solvents were generally removed by distillation at atmospheric pressure, and the liquid products were purified by fractional distillation at reduced pressure.

Boiling points (uncorrected) were those of middle fractions. Solid products were purified either by recrystallisation from suitable solvents (wherever possible), or by washing with more than one solvents. Melting points recorded were uncorrected.

Purity of the compounds were checked by elemental analyses. Microanalyses of C, H and N of the compounds were carried out by the Central Drug Research Institute, Lucknow, India and Dr. Alfred Bernhardt's Microanalytical Laboratory, Germany. Elemental analyses of Co, Cu, Ni, Pd, and halogens were done in our Laboratory by the conventional procedures after decomposing the products in a mixture of conc. H₂SO₄-HNO₃. Elemental analyses of N was also done in our Laboratory either by Dumas' method or Kjeldahs method.

Molecular weights were determined ebullioscopically.

Infrared spectra were recorded in KBr phase by the Central Drug Research Institute, Lucknow, India.

Electronic spectra were recorded either on a Spectromom or on a Beckmann Du-2 spectrophotometer.
Magnetic susceptibilities were measured in a Gouy balance at room temperature. The Gouy tubes were calibrated using Hg $\left[\text{Co(SCN)}_4\right]$, and the calculations of $\mu_{\text{eff}}$ were done according to Figgis and Lewis.

The conductance measurements were made with an Electrolytic conductivity Bridge of Leeds and Northrup Co. Cat. No. 4959.

Chemicals, solvents and reagents used were all A.R. grade and they were purified and dried (wherever necessary) by usual procedures.
SECTION - A

PREPARATION OF THE SCHIFF BASES.

The following general method was used for the preparation of the Schiff bases:

To an ethanolic solution of aldehyde (salicylaldehyde or substituted salicylaldehyde) or ketone (acetylacetone) (1 mole), was added an ethanolic solution of diamine (0.5 mole) or monoamine (amino-alcohol, -acid, etc.) (1 mole) and the mixture was refluxed for about 1-3 hours. The resulting coloured solution was filtered and the filtrate on cooling yielded solid Schiff bases. The crude products were recrystallised from suitable solvents (e.g. ethanol, methanol, water etc.). The liquid Schiff base was purified by fractionation at reduced pressure.

The following Schiff bases had been isolated (see abbreviations).

(i) BSEN-H<sub>2</sub> : Yield 80%; shining yellow crystals; m.p. 128°C
    Found: N, 10.20%; Calculated for \( \text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_2 \) : N, 10.45%.

(ii) BCSEN-H<sub>4</sub> : Yield 70%; yellow crystals; m.p. 302°C (lit. 211-290°C)
    Found: C, 60.80; H, 4.65; and N, 7.95%.
    Calculated for \( \text{C}_{18}\text{H}_{16}\text{O}_6\text{N}_2 \) : C, 60.68; H, 4.49; and N, 7.87%.

(iii) BSTN-H<sub>2</sub> : Yield 80%; yellow crystals; m.p. 53°C.
    Found: N, 10.00%; Calculated for \( \text{C}_{17}\text{H}_{18}\text{O}_8\text{N}_2 \) : N, 9.96%.
(iv) BCSIH-H$_4$ : Yield 80%; yellow crystals; m.p. 272°C.
Found : C, 61.96; H, 5.02; and N, 7.52%.
Calculated for C$_{19}$H$_{18}$O$_6$N$_2$ : C, 61.62; H, 4.86; and N, 7.59%.

(v) BSDA-H$_2$ : Yield 75%; shining yellow crystals; m.p. 97-98°C (lit. 98-100°C).
Found : N, 9.35%; Calculated for C$_{17}$H$_{18}$O$_3$N$_2$ : N, 9.40%.

(vi) BCSDA-H$_4$ : Yield 70%; yellow crystals; m.p. chars at around 265°C (lit. chars at around 260°C).
Found : N, 7.10%; Calculated for C$_{19}$H$_{18}$O$_7$N$_2$ : N, 7.25%.

(vii) BSOP-H$_2$ : Yield 80%; orange red crystals; m.p. 161-162°C
Found : N, 8.98%; Calculated for C$_{20}$H$_{16}$O$_2$N$_2$ : N, 8.86%.

(viii) BCSOP-H$_4$ : Yield 70%; orange yellow crystals; m.p. 203-205°C (lit. 200°C).
Found : C, 65.68; H, 4.05; and N, 6.84%.
Calculated for C$_{22}$H$_{16}$O$_6$N$_2$ : C, 65.34; H, 3.96; and N, 6.93%.

(ix) BHAE-H$_2$ : Yield 60%; yellow crystalline; m.p. 190-191°C (lit. 188-189°C).
Found : N, 9.57%; Calculated for C$_{16}$H$_{20}$O$_2$N$_2$ : N, 9.46%.

(x) BADA-H$_2$ : Yield 50%; yellowish pink; m.p. 102-103°C (lit. 101-102°C)
Found : N, 11.32%; Calculated for C$_{13}$H$_{22}$O$_3$N$_2$ : N, 11.02%.

(xi) SOAP-H$_2$ : Yield 70%; orange red crystals; m.p. 183-185°C.
Found : N, 6.60%; Calculated for C$_{13}$H$_{11}$O$_2$N : N, 6.57%. 
(xii) SAA-H₂ : Yield 65%; orange microcrystalline; m.p. 204°C.
    Found : N, 5.93%; Calculated for C₁₄H₁₁O₆N : N, 5.81%.

(xiii) CSA-H : Yield 80%; yellow crystals; m.p. 190°C
    (lit. 191-192°C).
    Found : N, 5.98%; Calculated for C₁₄H₁₁O₆N : N, 5.81%.

(xiv) SA-H : Yield 60%; yellow crystals; m.p. 49°C.
    Found : N, 6.96%; Calculated for C₁₃H₁₀ON : N, 7.10%.

(xv) BAPE : Yield 60%; shining white needles; m.p. 108-109°C.
    Found : N, 10.43%; Calculated for C₁₈H₂₀N₂ : N, 10.60%.
SECTION-B

PREPARATION OF SOME COBALT(II), COBALT(III) AND PALLADIUM(II)
COMPLEXES (USED AS INTERMEDIATES).

Bis(salicylaldehydato) cobalt(II) dihydrate, Co(sal)$_2$$\cdot$2H$_2$O :

This compound was prepared following the published method.$^{215}$
A saturated solution of cobalt(II) acetate tetrahydrate in 50% alcohol was mixed with stoichiometric amount of salicylaldehyde. The mixture was thoroughly stirred for 2 hours at room temperature, during which orange yellow crystalline compound was separated out. This was filtered off, washed successively with water, ethanol and ether and finally dried in a vacuum desiccator over conc. H$_2$SO$_4$. Yield 70%.

Found : Co, 17.89%; Calculated for C$_7$H$_8$O$_4$Co : Co, 17.51%.

Bis(acetylacetonato) cobalt(II) dihydrate, Co(acac)$_2$$\cdot$2H$_2$O :

This was prepared by the following method described in literature.$^{216}$

5 Weight percent solution of cobalt nitrate hexahydrate (1 mole) was buffered by adding 5 gm of sodium acetate for every 100 ml. of solution. This buffered metal ion solution was shakened with alcoholic solution of acetylacetone (2 mole). Pink coloured crystalline precipitate gradually appeared and ultimately the amount was increased sufficiently. After complete precipitation, the complex was collected by filtration, washed with water, aqueous-ethanol
(1:1, v/v) and finally dried in a desiccator over fused CaCl₂.
Yield 50\%, sublimed above 118°C (lit. sublimed above 120°C).
Found: Co, 19.79\%; Calculated for C₁₀H₁₈O₆Co: Co, 20.14\%.

**Bis-N,N'-disalicylaldehydato ethylenediamine - \(\mu\) - aquo-cobalt(II),**
\[\text{Co}(C_{16}H_{14}N₂O₂)\text{H₂O}.\]

This compound was prepared by the method of Diehl and Hach.²¹⁷

**BSEN-H₂** (26.80g., 0.1 mole), sodium hydroxide (8.0g., 0.2 mole) and sodium acetate trihydrate (1.0g., 0.0075 mole) were dissolved in 300 ml of boiling water. To this solution was added cobaltous chloride hexahydrate (23.80g., 0.1 mole) in 50 ml of hot water and stirred thoroughly until the mixture set up to reddish brown paste. The mixture was covered by half inch water and was allowed to stand for 15 minutes. It was then filtered and the deep brown hard cake obtained was washed with water several times and dried in a vacuum desiccator over fused CaCl₂. Yield 80\%.

Found: N, 7.42; Co, 16.10\%.
Calculated for C₃₂H₃₀N₄O₅Co: N, 7.69; Co, 16.21\%.

**N,N'-Ethylenebis(salicylidineiminato) cobalt(II), \(\text{Co(BSEN)}\)\]**

A literature method²¹⁷,²¹⁸ was used for the preparation of this well-known Schiff base complex of cobalt(II).

The Schiff base **BSEN-H₂** (2.68g., 0.01 mole) was dissolved in 25 ml of absolute ethanol and was added to the boiling solution of cobalt acetate tetrahydrate, (2.40g., 0.01 mole) in aqueous ethanol.
The mixture was refluxed for nearly two hours and the brown crystals separated during the reflux was filtered while hot through a sunction, washed with ethanol, dried in a vacuum desiccator. Yield 60%.

Found: N, 8.06; Co, 17.95%.

Calculated for $\text{Co} \cdot (\text{BSEN})_2$: $\text{N}, 8.61$; Co, 18.15%.

$\text{N, N'-trimethylenebis(salicylidineiminato) cobalt(II)}, \text{Co} \cdot (\text{BSEN})_2$.

This brown crystalline compound was prepared by the method analogous to $\text{Co} \cdot (\text{BSEN})_2$.

Found: N, 8.01; Co, 16.95%.

Calculated for $\text{Co} \cdot (\text{BSEN})_2$: $\text{N}, 8.26$; Co, 17.40%.

$\text{Hexammine Cobaltic Chloride, Co} \cdot (\text{NH}_3)_6 \cdot \text{Cl}_3$.

This complex was also prepared by a previously published method.

Air was bubbled through a mixture of cobaltous chloride hexahydrate (24.0g., 0.1 mole), ammonium chloride (16.0g., 0.1 mole), liquor ammonia (50 ml), water (20 ml), and activated charcoal (catalytic amount) till the red solution attained yellow brown colour. The precipitated complex and charcoal was filtered off, and the cobalt complex was dissolved in hydrochloric acid (2%). The solution was filtered while hot, and the pure complex was precipitated by the addition of concentrated hydrochloric acid (40 ml) and chilling to 0°C. The orange yellow crystals thus obtained, was collected on a filter and washed with ethanol and dried at 80-100°C. Yield 75%.
Hydroxopentammine Cobaltic Chloride monohydrate, \( \text{Co(} \text{NH}_3)_5 \text{OHCl}_2 \cdot \text{H}_2\text{O} \).

This compound was prepared by the method of Morgan and Smith.\(^{220}\)

An ice cold solution of cobaltous chloride hexahydrate (23.8g., 0.1 mole) in 15 ml. of water together with 8.5 ml. of 12(N) \( \text{H}_2\text{O}_2 \) was added slowly to 57 ml. of 18(N) ammonia maintained at 0°C. On evaporating almost to dryness in a vacuum desiccator over fused \( \text{CaCl}_2 \), the intensely dark brown solution yielded flattened reddish purple needles. Washed with aqueous-ethanol and dried in a desiccator over \( \text{CaCl}_2 \). Yield 80%.

Found : N, 27.14; Cl, 27.75; Co, 23.45%.

Calculated for \( \text{N}_5\text{H}_{18}\text{O}_2\text{Cl}_2\text{Co} \): N, 28.00; Cl, 28.41; Co, 23.60%.

Sodium cobaltinitrite, \( \text{Na}_3 \text{Co(NO}_2\text{)}_6 \).

This complex was also prepared by a previously published method.\(^{221}\)

To sodium nitrite (15g., 0.22 mole) dissolved in 15 ml of water at 50-60°C, was added cobalt nitrate hexahydrate (5.0g., 0.017 mole), followed by the addition of 5 ml 50% acetic acid in small portions with constant stirring. Thereafter, air was drawn through the solution for one hour and allowed to stand for an hour. The brown ppt. appeared at this stage was filtered off. The filtrate
was kept for subsequent treatment. The brown precipitate was treated with ~10 ml of water at 70-80°C and filtered. The filtrate was mixed with the first filtrate. The clear solution thus obtained on treatment with about 30 ml of ethanol, yielded orange crystalline compound. This was collected on a filter and washed with ethanol and finally with ether, dried in air. Yield 70%.

Found: N, 21.15; Co, 15.10%.

Calculated for \( \text{HgO}_2 \text{Na}_2 \text{Co} \): N, 20.79; Co, 14.61%.

Bis(salicylaldoxime) palladium(II), \( \text{Pd(sal)}_2 \)

Previously published method\(^\text{222}\) was used for the preparation of this compound.

A cold solution containing palladium(II) chloride (1.10 g., 0.006 mole) in 0.5 ml concentrated HCl and 30 ml of water was adjusted to pH 5-6 by the addition of 2% sodium acetate trihydrate. A solution of salicylaldehyde (1.46 g., 0.012 mole) in 20 ml of 95% ethanol was added with stirring. Yellowish orange precipitate separated out, which was filtered off, washed with water, alcohol and ether and dried in a desiccator over fused CaCl\(_2\). Yield 60%.

Found: Pd, 30.62%. Calculated for \( \text{C}_{14} \text{H}_{10} \text{O}_4 \text{Pd} \): Pd, 30.47%.