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 recrystallization 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 were carried out by the Central Drug Research Institute, Lucknow, India and Dr. Alfred Bernhardt's Microanalytical Laboratory, Germany. Elemental analyses of V, Cu, Ni, Pd, U, Mo, Zn, Cd were done in our Laboratory by the conventional procedures after decomposing the products in a mixture of conc. \( \text{H}_2\text{SO}_4 - \text{HNO}_3 \). Elemental analyses of N was done in our laboratory either by Dumas' method or Kjeldahl's method. Elemental analyses of S and halogens were also done in our laboratory by
the conventional procedures. Sodium was estimated in our Laboratory by Flame Photometry.

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 spectrometer or on a Beckmann DU-2 spectrophotometer.

Magnetic susceptibilities were measured in a Gouy balance at room temperature. The Gouy tubes were calibrated using $\text{Hg[Co(SCN)$_{4}$]}$ and the calculations of $\mu_{\text{eff}}$ were done according to Figgis and Lewis.

The conductance measurements were made with a 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 AND RELATED LIGANDS

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

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

The following Schiff bases were isolated (see abbreviations) and characterised.

(1) BSEN-Hg : Yield 80%; shining yellow crystals; m.p. 128°C
    Found: N, 10.20%; Calculated for C_{10}H_{16}O_{2}N_{2} : N, 10.45%
(ii) DCSEN-H₄ : Yield 70%; Yellow crystals; m.p. 302°C
(lit. ²⁹⁰°C)
Found: C, 60.80%; H, 4.63%; and N, 7.95%
Calculated for C₁₆H₁₆O₆N₂: C, 60.68%; H, 4.49%; and N, 7.87%.

(iii) BSTN-H₂ : Yield 80%; Yellow crystals; m.p. 53°C
Found: N, 10.00%; Calculated for C₁₇H₁₆O₂N₂: N, 9.96%

(iv) BCSTN-H₂ : Yield 80%; Yellow crystals; m.p. 272°C
Found: C, 61.96%; H, 5.02%; and N, 7.52%
Calculated for C₁₉H₁₈O₂N₂: C, 61.62%; H, 4.86%; and N, 7.59%

(v) BSDA-H₂ : Yield 75%; shining yellow crystals; m.p. 97-98°C
(lit. 432°C: 98-100°C)
Found: N, 9.35%; Calculated for C₁₇H₁₆O₂N₂: N, 9.40%

(vi) BCSDA-H₂ : Yield 70%; Yellow crystals; m.p. chars at around 265°C (lit. 432°C: chars at around 260°C)
Found: N, 7.10%; Calculated for C₁₉H₁₈O₂N₂: N, 7.25%

(vii) BSOP-H₂ : Yield 80%; Orange red crystals; m.p. 161-162°C
Found: N, 8.98%; Calculated for C₂₀H₁₆O₂N₂: N, 8.86%

(viii)BCSO₄-H₂ : Yield 70%; Orange yellow crystals; m.p. 203-205°C
(lit. 431°C: 200°C)
Found: C, 65.68%; H, 4.05%; and N, 6.84%
Calculated for C₂₀H₁₆O₂N₂: C, 65.34%; H, 3.96%; and N, 6.93%
(ix) **BAEN-H₂**: Yield 60%; Colorless crystals; m.p. 111°C
Found: C, 64.21%; H, 8.96% and N, 12.42%.
Calculated for $\text{C}_{18}\text{H}_{20}\text{O}_2\text{N}_2$: C, 64.30%; H, 8.93%; and N, 12.55%.

(x) **SOAP-H₂**: Yield 70%; Orange red crystals; m.p. 183-189°C
Found: N, 6.60%; Calculated for $\text{C}_{13}\text{H}_{11}\text{O}_2\text{N}_2$; N, 6.57%.

(xi) **SAA-H₂**: Yield 65%; Orange microcrystalline; m.p. 304°C;
Found: N, 7.93%; Calculated for $\text{C}_{14}\text{H}_{11}\text{O}_2\text{N}_2$; N, 7.81%.

(xii) **SAN-H**: Yield 60%; Yellow crystals; m.p. 49°C
Found: N, 6.96%; Calculated for $\text{C}_{13}\text{H}_{11}\text{ON}$; N, 7.10%.

(xiii) **AOAP-H₂**: Yield 70%; Light yellow crystals; m.p. 189°C
Found: N, 7.25%; Calculated for $\text{C}_{11}\text{H}_{15}\text{O}_2\text{N}_2$; N, 7.33%.

(xiv) **SETOL-H₂**: Yield 55%; Yellow viscous liquid; b.p. 170°-180°C (3.5 mm of Hg).
Found: N, 8.35%; Calculated for $\text{C}_{9}\text{H}_{11}\text{O}_2\text{N}_2$; N, 8.48%.

(xv) **SSA-INA**: Yield 60%; shining light yellow crystals;
Found: N, 4.51%; S, 10.75%; Na, 7.48%.
Calculated for $\text{C}_{13}\text{H}_{10}\text{O}_4\text{NSNa}$; N, 4.68%; S, 10.70%; Na, 7.69%.

(xvi) **SSAM-H**: Yield 70%; Yellow crystals; m.p. 208-210°C
Found: N, 9.98%; S, 11.72%.
Calculated for $\text{C}_{13}\text{H}_{12}\text{O}_3\text{N}_2$; N, 10.13%; S, 11.60%.
(xvii) HASA-HNa: Yield 65%; grayish-brown crystals; m.p. > 300°C
Found: N, 4.39%; S, 10.25%; Na, 7.21%
Calculated for C_{14}H_{12}O_{4}NSNa: N, 4.47%; S, 10.22%; Na, 7.35%

(xviii) HASAM-H: Yield 60%; White crystals; m.p. 141-142°C
Found: N, 9.42%; S, 10.92%
Calculated for C_{14}H_{12}O_{4}NS: N, 9.66%; S, 11.04%

(xix) CSSA-H_{2}Na: Yield 75%; Yellow crystals; m.p. > 300°C
Found: N, 3.92%; S, 9.21%; Na, 6.52%
Calculated for C_{14}H_{10}O_{6}NSNa: N, 4.08%; S, 9.33%; Na, 6.70%

(xx) CSSAM-H_{2}: Yield 70%; Orange-yellow crystals; m.p. 243-246°C
Found: N, 8.60%; S, 10.12%
Calculated for C_{14}H_{12}O_{4}NS: N, 8.75%; S, 10.00%

(xxi) ASA-HNa: Yield 55%; Light orange crystals; decomp. 300°C
Found: N, 5.12%; S, 11.62%; Na, 8.20%
Calculated for C_{11}H_{12}O_{4}NSNa: N, 5.05%; S, 11.55%; Na, 8.70%

(xxii) ACSAM-H: Yield 50%; White crystals; m.p. 140°C.
Found: N, 10.89%; S, 12.42%
Calculated for C_{11}H_{14}O_{3}NS: N, 11.03%; S, 12.60%

(xxiii) TCH-H:

It was prepared by a method described previously.\textsuperscript{434}
Yield 55%; light yellow crystals; m.p. 124°C (lit. 124°C)
Found: C, 11.05%; H, 3.61%; N, 25.98%; S, 59.12%
Calculated for CH_{4}N_{2}S_{2}: C, 11.11%; H, 3.70%; N, 25.93%;
S, 59.27%. 
(xxiv) CTCH : This ligand was prepared by a previously published method.\(^5\) Yield 60%; white powder, m.p. 193°C (lit. 192°-193°C)
Found: C, 15.98%; H, 4.82%; N, 46.29%; S, 21.23%
Calculated for C\(_{27}\)H\(_{49}\)O\(_2\)N\(_2\)S: C, 16.11%; H, 4.70%; N, 46.98%; S, 21.47%.

(xxv) TGTCH : It was prepared following literature method.\(^5\) Yield 30%; white powder; m.p. 203°C (lit. 203°C)
Found: C, 14.40%; H, 4.21%; N, 42.48%; S, 38.92%
Calculated for C\(_{27}\)H\(_{49}\)N\(_2\)S\(_2\): C, 14.57%; H, 4.24%; N, 42.48%; S, 38.79%.

(xxvi) AACD-NH\(_4\) : It was also prepared by a method described previously.\(^5\) Yield 80%; Yellow plates; m.p. 136°C (lit. 135°-137°C).
Found: C, 40.52%; H, 6.71%; N, 16.48%; S, 36.52%
Calculated for C\(_{12}\)H\(_{28}\)N\(_2\)S\(_2\): C, 40.91%; H, 6.82%; N, 15.92%; S, 36.37%.

(xxvii) Dm\(_2\)dte-Na : Pipdte-Na : Mordte-Na and Pyrdte-Na : The three ligands were prepared from carbon disulphide, sodium hydroxide and the appropriate amines, that is, N\(_2\)H\(_2\)-dibutylamine, piperidine, morpholine and pyrrolidine, respectively, essentially by the published methods.\(^5\)
PREPARATION OF SOME OXO-VANADIUM(IV), OXO-MOLYBDENUM(V), DIOXO-MOLYBDENUM(VI), DIOXO-URANIUM(VI), MOLYBDENUM(IV), NICKEL(II), COPPER(II), PALLADIUM(II), ZINC(II) AND CADMIUM(II) COMPLEXES (USED AS INTERMEDIATES)

Oxo-bis(acetylacetonato) aquovanadium(IV), $\text{VO(acac)}_2 \cdot \text{H}_2\text{O}$:

This compound was prepared following the published method. An ethanolic solution of vanadyl chloride dihydrate (1.74 g.; 0.01 M) was mixed with stoichiometric amount of acetylacetonato (2.0 g.; 0.02 M). The mixture was thoroughly stirred for a few minutes and then neutralised with an aqueous solution of sodium carbonate, during which greenish blue crystalline compound was separated out. This was filtered off, washed successively with water, ethanol and ether and finally dried in a vacuum desiccator over fused CaCl$_2$. Yield 70%.

Found: V, 17.82%; Calculated for $\text{C}_{10}\text{H}_{16}\text{O}_6\text{V} \cdot \text{V}$, 18.03%.

Oxo-bis(salicylaldehydeato) aquovanadium(IV), $\text{VO(sal)}_2 \cdot \text{H}_2\text{O}$:

This was prepared by the following method. Salicylaldehyde (2.44 g.; 0.02 M) in 50 ml ethanol was added to stoichiometric...
amount of vanadyl chloride dihydrate (1.74 g; 0.01 M) in 50% ethanol. The resulting solution was neutralised with an excess of sodium acetate and the solution set aside overnight in a refrigerator. The olive-green crystals separated out were filtered, washed successively with water, ethanol and finally dried in a vacuum desiccator over fused CaCl₂. Yield 60%.

Found: V, 15.33%; Calculated for C₁₄H₁₂O₅V: V, 15.60%

Bis(acetylacetonato) dioxo-molybdenum(VI), MoO₂(acac)₂

This compound was prepared following the published method. 10 g of reagent-grade MoO₃ was refluxed for 18 hours with 50 ml acetylacetone. The resulting mixture, containing several grams of unreacted Mo(VI) oxide, was filtered rapidly and the warm solution was poured into 150 ml of ligroin with stirring. The mixture was then chilled for one hour in an ice-bath. The orange-yellow powder was filtered, washed several times with rectified spirit and air-dried. Yield 50%.

Found: Mo, 29.29%; Calculated for C₁₀H₁₄O₅Mo: Mo, 29.45%

Ammonium oxo-pentachloromolybdate(V); (NH₄)₂(MoOCl₅)₂

This compound was prepared by a method described in literature.
5.5 g. of molybdenyl hydroxide, MoO(OH)₂, was dissolved in 70 ml concentrated HCl by gentle warming. To it was added 5 g. ammonium carbonate and then the solution was cooled in an ice-bath. A current of dry hydrogen chloride (conveniently generated by dropping concentrated hydrochloric acid into concentrated sulfuric acid) was passed into the cooled solution. Green crystals of the complex salt soon began to separate in quantity. The preparation was left overnight and then the solution was filtered through a large Gooch crucible with asbestos mat. The solid was washed with a small amount of concentrated hydrochloric acid and extracted it carefully from the crucible and dried in vacuo over sodium hydroxide. Yield 70%.

Found: Mo, 29.12%; N, 8.20%; Cl, 55.12%.

Calculated for H₅N₂OCl₅Mo: Mo, 29.45%; N, 8.59%; Cl, 54.45%.

N,N'-Ethylene bis(3-carboxyl-salicylideneiminato) oxo-vanadium(IV)

This compound was prepared by refluxing a mixture of the Schiff base BCSEN-H₄(3.56 g; 0.01 M) and NaOH (0.8 g; 0.02 M) in 10 ml water and vanadyl chloride dihydrate (1.74 g; 0.01 M) and sodium acetate trihydrate (2.72 g; 0.02 M) in 50 ml ethanol. The product was filtered, washed with water, then ethanol and finally dried in a desiccator over fused CaCl₂. Yield 60%; Color, Orange yellow; m.p. > 300°C; \( \mu_{\text{eff}} \) = 1.78 B.M. at 302°K.
Found: N, 6.34%; V, 11.95%  
Calculated for C_{16}H_{14}O_{7}N_{2}V: N, 6.63%; V, 12.12%

**N,N'-Propylenebis(3-carboxyl-salicylideneiminato) oxo-vanadium(IV)**

This compound was prepared in an exactly analogous manner using the Schiff base BCSTN-H$_2$. Yield 65%; Color: Yellowish - Grey; m.p. > 300°C; $\mu_{\text{eff}} = 1.71$ D.M. at 303 K

Found: N, 6.52%; V, 11.41%  
Calculated for C_{19}H_{16}O_{7}N_{2}V: N, 6.44%; V, 11.72%.

**N,N'-Phenylenebis(3-carboxyl-salicylideneiminato) oxo-vanadium(IV)**

Similarly this compound was prepared using the Schiff base BCSOP-H$_4$. Yield 70%; Color: Brown; m.p. > 300°C; $\mu_{\text{eff}} = 1.03$ D.M. at 302 K

Found: N, 5.79%; V, 11.12%  
Calculated for C_{22}H_{14}O_{7}N_{2}V: N, 5.97%; V, 10.87%

**Dioxo-N,N'-Ethylene bis(3-carboxyl-salicylideneiminato) aquo uranium(VI)**

Uranyl acetate (4.24 gm; 0.01M) was dissolved in minimum volume of water containing one drop of glacial acetic acid. This solution was added to an aqueous solution of equimolar amount of
Schoiff base BCSN-H₄ (3.36 g; 0.01 M) and NaOH (0.8 g; 0.02 M). The product was filtered, washed with water, then little ethanol and finally dried in vacuo. Yield 70%; Color: Yellowish orange; m.p. > 300°C; diamagnetic.

Found: C, 33.42%; H, 2.41%; N, 4.25%; U, 37.39%.
Calculated for C₁₈H₁₆O₉N₂U: C, 33.65%; H, 2.49%; N, 4.44%; U, 37.08%.

Dioxo-N,N'-propylenbis(3-carboxyl-salicylideneiminate) aquo uranium(VI): ⁴³¹

This compound was prepared in an exactly analogous method using the Schoiff base BCSN-H₄ and uranyl acetate. Yield 75%; Color: Orange yellow; m.p. > 300°C; \( \mu_{\text{eff}} = 1.20 \) B.M.

Found: C, 34.54%; H, 2.71%; N, 4.33%; U, 36.08%.
Calculated for C₁₉H₁₈O₉N₂U: C, 34.75%; H, 2.73%; N, 4.27%; U, 36.28%.

Dioxo-N,N'-o-phenylenbis(3-carboxyl-salicylideneiminate) aquo uranium(VI): ⁴³¹

This compound was also prepared by an analogous method using the Schoiff base BCSOP-H₄ and uranyl acetate. Yield 60%.
Color: Brownish orange; m.p. > 300°C; diamagnetic.

Found: C, 38.08%; H, 2.28%; N, 3.98%; U, 34.28%.
Calculated for C₂₂H₁₆O₉N₂U: C, 38.26%; H, 2.52%; N, 4.06%; U, 34.49%.
**Dioxo-N,N'-ethylenebis(3-carboxyl-salicylideneiminate)-
molybdenum(VI):**

Molybdic acid $\text{H}_2\text{MoO}_4$ (1.62 g; 0.01 M) was suspended in water (25 ml) and dilute HCl was added just to dissolve the solid. The pH was adjusted to $\sim 7$ by adding sodium acetate (solid). Finally, this solution was added to an aqueous solution of the Schiff base $\text{BCSNH}_2$ (3.56 g; 0.01 M) and NaOH (0.8 g; 0.02 M). The precipitated product was filtered, washed with water and ethanol, and finally dried in vacuo. Yield 70%.

**Color:** Yellow orange; m.p. 273°-277°C (decomp.); diamagnetic.

**Found:** C, 44.71%; H, 2.83%; N, 5.67%; Mo, 19.98%.

**Calculated for $\text{C}_{15}\text{H}_{14}\text{O}_6\text{N}_2\text{Mo}$:** C, 44.82%; H, 2.91%; N, 5.81%; Mo, 19.92%.

**Dioxo-N,N'-propylenebis(3-carboxyl-salicylideneiminate) molybdenum (VI):**

This compound was prepared in an exactly analogous method using the Schiff base $\text{BCSNH}_2$ and molybdic acid. Yield 80%.

**Color:** Orange; m.p. 258-260°C; diamagnetic.

**Found:** C, 45.81%; H, 3.19%; N, 5.75%; Mo, 19.22%.

**Calculated for $\text{C}_{19}\text{H}_{16}\text{O}_8\text{N}_2\text{Mo}$:** C, 45.96%; H, 3.23%; N, 5.64%; Mo, 19.36%.
Dioxo-N,N'-o-phenylenebis(3-carboxyl-salicylideneiminate)
molybdenum(VI)

Analogously this compound was prepared from BCSOP-H₄ and
molybdic acid. Yield 65%.
Color: Brown; m.p. 265°C-266°C (decomp.); diamagnetic
Found: C, 49.68%; H, 2.61%; N, 3.39%; Mo, 17.95%.
Calculated for C₂₂H₁₄O₈N₂Mo: C, 49.80%; H, 2.64%; N, 3.28%; Mo, 18.11%.

N,N'-Ethylenebis(3-carboxyl-salicylideneiminate) copper(II)

Same method was used to prepare this complex from BCSOP-H₄
and copper acetate hydrate. Yield 80%.
Color: Violet; m.p. > 300°C; \( \mu_{\text{eff}} = 1.66 \) B.M. at 302°C
Found: N, 6.52%; Cu, 13.15%
Calculated for C₁₈H₁₄O₆N₂Cu: N, 6.71%; Cu, 15.22%

N,N'-o-Phenylenebis(3-carboxyl-salicylideneiminate) copper(II)

This compound was prepared similarly using the Schiff base
BCSOP-H₄. Yield 80%.
Color: greyish-brown; m.p. > 300°C; \( \mu_{\text{eff}} = 1.84 \) B.M. at 302°C
Found: N, 6.12%; Cu, 13.52%
Calculated for C₂₂H₁₄O₆N₂Cu: N, 6.01%; Cu, 13.64%
Following a similar method described above this Ni(II) complex was prepared from the Schiff base BCSN-H₂ and Nickel acetate dihydrate. Yield 70%.

Color: Orange-Yellow, m.p. > 300°C; \( \mu_{\text{eff}} = 1.27 \) B.M. at 302°K

Found: N, 6.13%; Ni, 13.21%

Calculated for C₁₈H₁₈₂0₂N₂Ni : N, 6.24%; Ni, 13.08%

N,N'-Propylenebis(3-carboxyl-salicylideneiminato) diaquo nickel(II)

This compound was prepared analogously using the Schiff base BCSN-H₂ and nickel acetate dihydrate. Yield 70%.

Color: green; m.p. > 300°C; \( \mu_{\text{eff}} = 2.41 \) B.M. at 302°K

Found: N, 6.12%; Ni, 12.45%

Calculated for C₁₉H₂₀₂₈₂N₂Ni : N, 6.05%; Ni, 12.69%

N,N'-a-Phenylenebis(3-carboxyl-salicylideneiminato) diaquo nickel(II)

Same method was used to prepare this compound. Yield 80%.

Color: grey; m.p. > 300°C; \( \mu_{\text{eff}} = 3.69 \) B.M. at 302°K

Found: N, 5.52%; Ni, 11.95%.
N,N'-Ethylenebis(3-carboxyl-salicylideneiminato) palladium(II)

This compound was prepared by the following method:

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 3-formyl salicylic acid (2.0 g; 0.012 mole) in 30 ml of 95% ethanol was added with stirring. The yellowish green precipitate separated out, filtered off, washed with water, alcohol and ether and dried in a desiccator over fused CaCl₂. Yield 60%.

Found: Pd, 24.29%; Calculated for C₁₁₂H₁₀₀₈₆N₂Pd: Pd, 24.38%.

To a suspension of this compound, viz., bis(3-carboxylsalicylaldehydeato) palladium(II) (2.19 g; 0.005 mole) in 50 ml absolute ethanol, was added ethylenediamine (0.3 g; 0.005 mole) in 10 ml ethanol and the mixture was refluxed on a steam-bath for 30 minutes. The solution was then cooled to get green crystals. It was filtered, washed with ethanol and ether and dried in a desiccator over fused CaCl₂. Yield 90%.

Found: C, 46.72%; H, 3.00%; N, 5.97%; Pd, 23.22%.

Calculated for C₁₈₂H₁₄₂₆N₂Pd: C, 46.91%; H, 3.04%; N, 6.08%; Pd, 23.11%.
This compound was prepared by a method similar to that used for the preparation of analogous oxo-vanadium(IV) complex using BCSEn-H4 and zinc acetate. Yield 80%.

Color: Yellow; m.p. > 300°C; diamagnetic

Found: N, 6.51%; Zn, 15.85%

Calculated for \(\text{C}_{18}\text{H}_{14}\text{O}_{6}\text{N}_{2}\text{Zn}\) : N, 6.68%; Zn, 15.60%

**N,N'-propylenesbis(3-carboxyl-salicylideneiminate) zinc(II)**

Same method (as described above for Zn complex) was used to prepare this complex. Yield 70%.

Color: Light yellow; m.p. > 300°C diamagnetic

Found: N, 6.58%; Zn, 14.96%

Calculated for \(\text{C}_{19}\text{H}_{16}\text{O}_{6}\text{N}_{2}\text{Zn}\) : N, 6.46%; Zn, 15.10%

**N,N'-o-Phenylenesbis(3-carboxyl-salicylideneiminate) zinc(II)**

This compound was also prepared by the above mentioned method.

Yield 75%.

Color: Grey; m.p. > 300°C; diamagnetic

Found: N, 5.83%; Zn, 13.95%

Calculated for \(\text{C}_{22}\text{H}_{14}\text{O}_{6}\text{N}_{2}\text{Zn}\) : N, 5.99%; Zn, 13.87%.
N,N'-Ethylenebis(3-carboxyl-salicylideneiminato) cadmium(II)

Analogous reaction between BCSEN-II₄ & cadmium acetate gave this compound in ~ 60% yield.
Color: Yellow; m.p. > 300°C; \( \mu_{\text{eff}} \) = diamagnetic.
Found: N, 5.89%; Cd, 24.23%
Calculated for \( \text{C}_{18}\text{H}_{14}\text{O}_{4}\text{N}_{2}\text{Cd} \): N, 6.00%; Cd, 24.10%.

N,N'-Propylenebis(3-carboxyl-salicylideneiminato) cadmium(II)

This compound was prepared in ~ 50% yield from BCSEN-II₄ and cadmium acetate as described above.
Color: Yellow; m.p. > 300°C; diamagnetic.
Found: N, 5.82%; Cd, 23.12%
Calculated for \( \text{C}_{19}\text{H}_{16}\text{O}_{6}\text{N}_{2}\text{Cd} \): N, 5.83%; Cd, 23.40%.

N,N'-o-Phenylenebis(3-carboxyl-salicylideneiminato) cadmium(II)

This compound was also prepared similarly in ~ 60% yield.
Color: Brownish grey; m.p. 250°C (decomp); diamagnetic.
Found: N, 5.31%; Cd, 21.71%
Calculated for \( \text{C}_{22}\text{H}_{14}\text{O}_{6}\text{N}_{2}\text{Cd} \): N, 5.44%; Cd, 21.85%
Pyridinium hexathiocyanato-molybdate(IV), (PyH₂₅)₂ Mo(NCS)₆ :  

This compound was prepared by a method described previously.  

7.5 g (0.05 mole) of molybdenum trioxide was dissolved in 75 ml of 8(N) hydrochloric acid by heating. The solution was cooled to room temperature, set aside 25 ml and the remaining 50 ml was reduced electrolytically to the tervalent stage. Reduction was complete when the blood-red color associated with Mo(IV) had given place to the pinkish-red color of Mo(III) salts in the presence of excess of acid and hydrogen was being freely released at the cathode.  

The 25 ml of Mo(VI) solution previously reserved was placed in a tap funnel, the funnel filled with carbon dioxide by displacement and then the reduced solution was discharged into it directly from the electrolytic cell. On mixing, the deep color of Mo(IV) compounds appeared:  

\[ 2\text{Mo}^{3+} + \text{Mo}^{6+} = 3\text{Mo}^{4+} \]

This indirect method of obtaining a Mo(IV) preparation was necessitated by the absence of a sharp break at the quadrivalent stage in the direct reduction.  

32 g (about 0.4 mol) of ammonium thiocyanate was dissolved in 30 ml water, and the solution was placed in a stout-walled filter flask. After running off any mercury discharged into the
tap funnel from the electrolytic cell, the Mo(IV) solution was run into the thiocyanate. After mixing well, 20 ml freshly distilled pyridine was added and then an equi-volume mixture of conc. NH₃ solution and water until the separation of a very dark colored 'oil' was complete. During the foregoing operations an atmosphere of CO₂ was, as far as possible, maintained over the solution, but once the insoluble complex thiocyanate was separated, such precautions might be discontinued. The flask with the dark viscid mass was immersed in an ice-bath and left it overnight to solidify. The mass was filtered, washed with little ethanol and air dried.

Found: Mo, 15.52%; N, 18.21%; S, 32.20%
Calculated for C₁₆H₁₂N₈S₆Mo: Mo, 15.91%; N, 18.57%; S, 31.79%

Bis(cyclopentadienyl) vanadium(IV) chloride:

Bis(cyclopentadienyl) vanadium(IV) dichloride, C₈VCl₂, was prepared from VCl₄ and sodium cyclopentadienide in benzene by a method described earlier.⁴⁴¹

Found: C, 47.25%; H, 3.88%; V, 20.09%; Cl, 28.45%.
Calculated for C₁₀H₁₀VCl₂: C, 47.62%; H, 3.97%; V, 20.24%; Cl, 28.28%