PART I

METAL-CHELATE COMPLEXES OF SCHIFF'S BASES DERIVED FROM 5-FORMYL-8-HYDROXY QUINOLINE AND DIAMINES.
INTRODUCTION TO THE PRESENT WORK.
Introduction to the present work

The demand in some industry for new materials with high thermal and chemical stability has recently stimulated researches in various fields of polymer chemistry. As a result, Schiff's bases and related azomethines along with other organic compounds as chelating ligands attracted the attention of the chemists for the preparation of coordination polymers containing metal atoms. Bis-Schiff's bases as catenating chelates were first reported by Pfeiffer and Pfitzner and since then attempts have been made to prepare metal-chelate polymers of bis-Schiff's bases. The present investigation was undertaken with a view to explore the possibility of synthesizing bis-Schiff's bases containing suitable chelate-forming groupings at the two ends of the molecule of the ligand which could be polymerised through coordination with a metal ion.

Since the chelate forming capacity of 8-hydroxy quinoline is well-known, bis-(8-hydroxy quinolines) were suggested as precipitants in analytical chemistry long ago and Judd, Korshak and others studied the metal chelate polymers of bis-(8-hydroxy quinolines) and their derivatives.

The present investigation describes the syntheses of bis-Schiff's bases obtained from the condensation of 5-formyl-8-hydroxy quinoline and suitable aliphatic and aromatic diamines and also the isolation of metal-chelate polymers of these ligands.
The bis-Schiff's bases have been prepared through the condensation of 5-formyl-8-hydroxy quinoline with hydrazine, ortho-phenylenediamine, para-phenylenediamine and oxal-hydrazimidine, by refluxing the requisite amounts of the aldehyde and the corresponding diamine in alcoholic media. These Schiff's bases are all yellow in colour, mostly amorphous in nature having definite but high melting points; only the bis-Schiff's base of 5-formyl-8-hydroxy quinoline and hydrazine decomposes at 280°C without melting. From the elemental analyses, these Schiff's bases may be assigned the following general structure:

\[
\begin{array}{c}
\text{HO} \\
\text{N} \\
\text{CH==N R} \\
\text{N==HC OH} \\
\text{N} \\
\end{array}
\]

where \( R = \text{nil, ortho-C}_6\text{H}_4 \), \( \text{para-C}_6\text{H}_4 \) and \( \text{H} \)

\[
\begin{array}{c}
\text{HN} \\
\text{C} \\
\text{C} \\
\text{NH} \\
\end{array}
\]

According to the solubility of these Schiff's bases in organic solvents, proper choice was made for the solvent for the preparation of the metal-chelate polymers. Thus the bis-Schiff's base derived from 5-formyl-8-hydroxy quinoline and ortho-phenylenediamine being soluble in
absolute alcohol, the metal-chelate polymers of this Schiff's base were prepared by refluxing the Schiff's base and the corresponding metal-acetate in absolute alcohol. The bis-Schiff's bases derived from the condensation of 5-formyl-8-hydroxy quinoline with hydrazine, para-phenylene-diamine and oxal-hydrazimidine, on the other hand, were all sparingly soluble in alcohol, but completely soluble in hot dimethyl-formamide. Metal-chelate polymers of these Schiff's bases were prepared by refluxing in each case the corresponding Schiff's base and the appropriate metal acetate in dimethyl-formamide for several hours. In most of the cases, the metal-chelate polymers were precipitated during the reflux as highly coloured (deep brown, red, orange-red, yellow etc.) amorphous powders which were often purified by repeated digestion with alcohol to remove the alcohol-soluble impurities; in the cases of cobalt(II)-5-formyl-8-hydroxy quinoline-p-phenylene-diamine, however, the metal-complexes were obtained by the addition of water and in the case of uranyl-5-formyl-8-hydroxy quinoline-oxal-hydrazimidine, the compound was isolated by the addition of alcohol to the refluxates. The elemental analyses of the metal-chelate polymers of the bis-Schiff's bases derived from 5-formyl-8-hydroxy quinoline and hydrazine, ortho-phenylene-diamine and para-phenylene-diamine point out to the formation of compounds with metal:ligand ratio as 1:1 i.e. they correspond to the general composition $[ML]_n$ or in some cases to the composition $M_nL_{n+1}$ where $LH_2$ = a molecule of the
bis-Schiff's base. For some of the metal-chelate polymers of these Schiff's bases, agreement between calculated and observed values of elemental analyses can be greatly improved if two water molecules are taken to be associated per unit of the polymer, thus conforming to the composition $[ML\cdot 2H_2O]_n$. This assumption is reasonable since metal atoms are present in the polymer chain and water of crystallisation is possible; moreover, the maximum coordination number of the metals concerned is six which need be satisfied. Thermal stability studies on the basis of weight loss percentage at definite temperature also support this. From the geometry of the ligand molecule and from elemental analyses of the metal-chelates, the following tentative polymeric structure may be suggested for the compounds of the composition $[ML]_n$

$$\begin{align*}
&\text{[Diagram of polymer structure]} \\
\text{where } R = \text{nil, ortho-C}_6\text{H}_4\text{ and para-C}_6\text{H}_4\text{ and } M = \text{Cu(II), Ni(II), Co(II), Mn(II), Zn(II), Cd(II) and UO}_2^{+2}. A
\end{align*}$$

A number of metallic chelates of these Schiff's bases having the general composition $M_nL_{n+1}$ may be assigned the following polymeric structure probably with hydroxy-quinoline end-groups:
Thus, manganese(II)-5-formyl-8-hydroxy quinoline-hydrazine corresponds to metal:ligand ratio as 3:4; uranyl-5-formyl-8-hydroxy quinoline-hydrazine were isolated in two different varieties, the black compound conforming to the metal:ligand ratio as 2:3, while the deep red compound conformed to the metal:ligand ratio as 6:7. It is quite probable that the black uranyl compound which precipitated out during the preparation just at the beginning of the reflux will have less degree of polymerisation. Again, the uranyl compound of 5-formyl-8-hydroxy quinoline-o-phenylenediamine corresponds to the metal:ligand ratio as 7:8, while the cadmium(II)-5-formyl-8-hydroxy quinoline-para-phenylenediamine corresponds to the metal:ligand ratio as 3:4.

The compositions of the various metallic complexes of the Schiff's bases just mentioned are given in a tabular form below:
<table>
<thead>
<tr>
<th>Ligand</th>
<th>Copper</th>
<th>Nickel</th>
<th>Cobalt</th>
<th>Manganese</th>
<th>Zinc</th>
<th>Cadmium</th>
<th>Uranyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. 5-Formyl-8-hydroxy</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>3:4</td>
<td>1:1</td>
<td>1:1</td>
<td>2:3</td>
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<tr>
<td>quinoline-hydrazine.</td>
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<tr>
<td>II. 5-Formyl-8-hydroxy</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>7:8</td>
</tr>
<tr>
<td>quinoline-o-phenylene-</td>
<td></td>
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<tr>
<td>diamine.</td>
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</tr>
<tr>
<td>III. 5-Formyl-8-hydroxy</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>3:4</td>
<td>3:4</td>
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<tr>
<td>quinoline-p-phenylene-</td>
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<td>diamine.</td>
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</tbody>
</table>
From the elemental analyses of the metal-chelates of the bis-Schiff's base obtained from the condensation of 5-formyl-8-hydroxy quinoline and oxal-hydrazimidine, three general formulations seem probable viz. $\left[ M_{2}L \right]_{n}$ where $M = \text{Cu(II)}$, $M_{n}(LH_{2})_{n}$ where $M = \text{UO}_{2}^{2+}$ and $\left[ M_{2}L.4H_{2}O \right]_{n}$ where $M = \text{Ni(II)}, \text{Co(II)}, \text{Mn(II)}, \text{Zn(II)}$ and $\text{Cd(II)}$ and $LH_{4}$ = a molecule of the bis-Schiff's base containing two moles of 5-formyl-8-hydroxy quinoline and one mole of oxal-hydrazimidine. As all these metal-chelates except the uranyl compound have metal-ligand ratio as 2:1, metallation in the polymer chain by the oxal-hydrazimidine part is highly probable as has been shown by Sacconi$^{13}$ in the structure of Ni(II) complex of the condensation product of oxal-hydrazimidine and salicylaldehyde. Thus, the following polymeric structure may be assigned for the metal-chelates of the bis-Schiff's base obtained from 5-formyl-8-hydroxy quinoline and oxal-hydrazimidine:

$$\text{CH=N-NH-C-C-NH-N=CH}$$

$$\text{M--R N--M}$$

$n$

where $M = \text{Cu(II)}, \text{Ni(II)}, \text{Co(II)}, \text{Mn(II)}, \text{Zn(II)}$ and $\text{Cd(II)}$. The uranyl compound may be represented by a similar structure except metallation taking part from the hydrazimidine part. For the metal-chelate polymers of the composition $\left[ M_{2}L.4H_{2}O \right]_{n}$, two molecules of water have been assumed to be associated per metal atom in the polymer chain and this assumption has been
The bis-Schiff's base of 5-formyl-8-hydroxy quinoline and ethylenediamine could not be isolated in the pure state, so attempts were made to prepare the metal-chelates of this Schiff's base by refluxing appropriate proportions of a mixture of the aldehyde, ethylenediamine and the metal acetate in dimethyl-formamide for several hours. In each case, a product was isolated which has been characterised from elemental analyses. The metal-complexes correspond to the general composition \([\text{ML}_2\cdot 2\text{H}_2\text{O}]_n\), except the uranyl-chelate which agrees closely to the composition \((\text{UO}_2)_6\text{L}_7\), where \(\text{LH}_2\) = a molecule of the bis-Schiff's base containing two molecules of 5-formyl-8-hydroxy quinoline and one molecule of ethylenediamine, and \(\text{M} = \text{Cu(II)}, \text{Ni(II)}, \text{Co(II)}, \text{Zn(II)}\) and \(\text{Cd(II)}\). The copper(II) compound of this Schiff's base was instantaneously precipitated during the reflux in dimethyl-formamide; all the other metal-chelates except the uranyl compound, were isolated by the addition of water to the dark-coloured concentrated refluxates; the uranyl compound was isolated by adding acetone to the deep-red refluxate. That these compounds were of the bis-Schiff's base of 5-formyl-8-hydroxy quinoline and ethylenediamine was shown by their infrared spectral data taken in Nujol mull. The spectra show a band at 1510 cm\(^{-1}\) which may be assigned to the absorption originating from the stretching
vibration of the azo-methine grouping C=N of the bis-Schiff's base associated with the conjugated ring system (Keihei Ueno and Arthur. E. Martell, J.Phys.Chem. 60, 1270, 1956). The band at about 1115 cm\(^{-1}\) due to the vibrations of M-O-C\(^{=}\) bond of the metallic chelates of 8-hydroxy quinoline (cf. Charles et al, Spectrochim.Acta, 8, 1959) has been observed at about 1150 cm\(^{-1}\); it may be mentioned that this band was observed by Berg and Alam (Anal.chim.Acta, 1962, 454) at about 1125 cm\(^{-1}\) for the coordination polymers of 8,8'-dihydroxy-5,5'-biquinolyl. The band at 1565 cm\(^{-1}\) may be attributed to the -C=N- vibration of the quinoline ring. The band due to this grouping which generally comes at 1580-1600 cm\(^{-1}\) is shifted in these cases due to chelation. Thus the following structure may be given to the metal-chelate of the bis-Schiff's base of 5-formyl-8-hydroxy quinoline and ethylenediamine:

\[
\begin{align*}
\text{M} & \left[ \begin{array}{c}
\text{O} \\
\text{N} \\
\text{CH}=\text{N}-(\text{CH}_2)_2-\text{N}=&\text{HC} \\
\text{O} \\
\text{N}
\end{array}\right]_{\text{M}} \\
\text{OH}_2 & \uparrow \\
\text{OH}_2 & \downarrow \\
\text{M} & \end{align*}
\]

where M = Cu(II), Ni(II), Co(II), Mn(II), Zn(II) and Cd(II).

The uranyl-compound of the composition \((\text{UO}_2)_6\text{L}_7\) will have the same type of structure, the polymeric chain being terminated by hydroxy-quinoline end-groups.
The condensation product of 5-formyl-8-hydroxy quinoline and benzidine can be isolated in the form of the bis-Schiff's base as a yellow powder, but due to its sparing solubility even in hot dimethyl-formamide, the metal-chelates of this Schiff's base were prepared by refluxing a mixture of the aldehyde, benzidine and the metal acetate in dimethylformamide. Compounds which have been obtained as highly coloured amorphous powders by the addition of water to the concentrated refluxates, correspond to the general composition \([\text{ML}_2\text{H}_2\text{O}]_n\) where \(M = \text{Cu(II)}, \text{Ni(II)}, \text{Co(II)}, \text{Mn(II)}, \text{Zn(II)}\) and to \([\text{ML}]_n\) where \(M = \text{Cd(II)}, \text{UO}_2^2+\) and \(\text{LH}_2\) = a molecule of the bis-Schiff's base containing two moles of 5-formyl-8-hydroxy quinoline and one mole of benzidine. The following polymeric structure is proposed for these metal-chelates:

![Polymeric Structure]

The above structure is supported by infrared data of the metal-chelates of 5-formyl-8-hydroxy quinoline-benzidine on Nujol mull. The presence of the Schiff's base in these compounds is shown by a band at 1510 cm\(^{-1}\) which has been assigned to the absorption originating from C=N stretching vibration of the conjugated ring system. The band at 1080 cm\(^{-1}\) is assigned to
the vibrations of the M-O-C< bond (E. Horowitz and T. P. Perros, J. Inorg. Nucl. Chem. 1964, 26, 139) and the sharp band at 1570 cm⁻¹ may be attributed to -C=N- vibration of the quinoline ring after chelation.

All the above metal-chelates are either slightly soluble or insoluble in common solvents like alcohol, acetone, chloroform, benzene etc. and often in hot dimethylformamide. This insolubility of the metal-chelates is probably due to their polymeric structures proposed.

To study the effect of heat on these compounds, they were subjected to increasing temperatures in an oven starting from 100°C. The temperature was increased by 25°C gaps and the compounds were kept at any particular temperature for a period of two hours and then weighed to determine the loss in weight of the sample. Heating was continued in this manner till the sample showed signs of decomposition which was evident from an abrupt large loss in the weight. The weight loss percentages against temperatures were plotted in each case. It has been observed that the temperature at which the compounds start decomposition range from 325°C to 400°C. Below this temperature, the weight loss percentages are different for different compounds, usually ranging from 7 to 25%. This fact that the complexes are comparatively much more stable thermally than the simpler compounds of the Schiff's bases and 8-hydroxy quinoline, seems to suggest their polymeric structures.
It has been found from the weight-loss percentage data at different temperatures of the compounds that the zinc(II)-chelates in all the series are thermally most stable i.e. the weight-loss percentage before the onset of decomposition is minimum. This is probably due to the completely filled 3d orbitals in zinc(II) which is known to be the most stable energy-state in first transition series.

An examination of the thermal stability curves drawn on the basis of weight-loss percentages against temperatures reveals that the initial slopes in the curves represent the volatilisation of water and low molecular-weight moieties. For example, loss in weight of the compounds of the general composition \([ML\cdot2H_2O]_n\) corresponds approximately to two moles of water per unit prior to the sharp break in the respective curves; the initial weight-loss (at 120°C) of the polymers of the composition \([M_2L\cdot4H_2O]_n\) also agree closely with the water-content as shown in the formula. After the initial weight-loss, a rather sharp break occurred in each of the curves signifying the onset of a decomposition process accompanied by a rapid loss of volatile fragments. The high thermal stability of the metal-chelates evidently points to their polymeric structures proposed.

The actual molecular weights and the degree of polymerisation of the metal-chelates could not be ascertained by usual cryoscopic methods for lack of their solubility in
common organic solvents. But it seems obvious that when the compounds were immediately precipitated during their preparations, the degree of polymerisation was low. On the other hands, those compounds which were isolated by prolonged refluxes in a high-boiling solvent like dimethyl-formamide and the solid materials were then isolated by concentrating the refluxates or by adding other solvents to them are expected to have a high degree of polymerisation. However, although the exact degree of polymerisation and the molecular weights of the metal-chelates could not be determined, their extreme insolubility and high thermal stability evidently point to their polymeric nature.
EXPERIMENTAL.
EXPERIMENTAL

1. Metal chelate-complexes of the Schiff's base derived from 5-formyl-8-hydroxy quinoline and hydrazine:

Preparation of 5-formyl-8-hydroxy quinoline:

5-Formyl-8-hydroxy quinoline was prepared following the method of Clemo and Howe (J.C.S. 1955, 3552).

8-Hydroxy quinoline (20 g), ethanol (80 ml.) and aqueous sodium hydroxide (40 g in 50 ml. of water) were refluxed on a waterbath for one hour during which chloroform (27 g) was added dropwise. The refluxing was then continued for 12 hours, after which ethanol and excess chloroform were distilled off. The residue was dissolved in water (600 ml.) and the solution acidified with hydrochloric acid. The solid which separated was filtered and dried and then extracted in a Soxhlet apparatus with light petroleum ether (b.p. 80-100°C). The extract on evaporation yielded 5-formyl-8-hydroxy quinoline as straw coloured needles (2 g), m.p. 172°C (recrystallised from ethanol).

Preparation of the Schiff's base:

To an alcoholic solution of 5-formyl-8-hydroxy quinoline (6.9 g) was added hydrazine hydrate (80% solution, 1.3 g); the resulting solution was refluxed on the waterbath for about two hours. The pale-yellow solution obtained after the reflux was concentrated on waterbath to a very small volume
and then kept at room temperature. Gradually, a shining yellow mass separated which was taken up with a few ml. of absolute alcohol, filtered and dried in a desiccator over fused CaCl₂.

The Schiff's base is insoluble in water, sparingly soluble in alcohol, but completely soluble in boiling dimethyl-formamide.

The melting point of the base is very high. At 280°C the substance starts slight decomposition without melting.

Analysis:

Nitrogen was estimated by Dumas' method. 0.01020 g of the Schiff's base gave 1.5 ml. of nitrogen at 29.5°C and 747.4 mm. pressure of mercury.

Nitrogen = 16.32%

Calculated for C₂₀H₁₄O₂N₄

Nitrogen = 16.37%

Copper(II)-5-formyl-8-hydroxy quinoline-hydrazine:

1.0 g of copper acetate monohydrate dissolved in 50 ml. of hot dimethyl-formamide and 1.71 g of the Schiff's base dissolved in 30 ml. of hot dimethyl-formamide were mixed together when a brownish-red compound separated out. The mixture was refluxed for about four hours and then filtered.
hot; the precipitated gummy compound was first washed with dimethyl-formamide and then with absolute alcohol and dried in a desiccator over fused CaCl$_2$ when an amorphous powder was obtained. 

The deep-brown compound is insoluble in cold and hot water, alcohol, and other organic solvents like acetone, chloroform, benzene, etc. It is insoluble in cold dimethyl-formamide, but very slightly soluble in boiling dimethyl-formamide. The compound is stable in dilute alkali even on boiling, but is slightly decomposed by hot dilute hydrochloric acid.

**Analysis:**

Copper was estimated iodometrically after decomposing the complex with concentrated H$_2$SO$_4$ and HNO$_3$. Nitrogen was estimated by Dumas method.

0.01445 g of the substance required 1.5 ml. of 0.02438(N) sodium thiosulphate solution.

Copper = 16.09%

0.02350 g of the substance gave 2.7 ml. of nitrogen at 29°C and 751.2 mm. pressure of mercury.

Nitrogen = 12.83%

Calculated for $[\text{CuL}]_n$, $L = \text{C}_{20}\text{H}_{12}\text{O}_2\text{N}_4$

Copper = 15.59%

Nitrogen = 13.74%
Nickel(II)-5-formyl-8-hydroxy quinoline-hydrazine:

Solutions of nickel acetate tetrahydrate (1.3 g) and the Schiff's base (1.7 g) in hot dimethyl-formamide were mixed together when a reddish-brown product separated out. The mixture was then refluxed for four hours and the precipitated compound was filtered hot, washed first with dimethyl-formamide and then with absolute alcohol and dried in a desiccator over fused CaCl₂.

The deep-brown crystalline compound is insoluble in water, alcohol, chloroform, acetone, benzene and dimethyl-formamide. It is quite stable in dilute alkali, but is slightly decomposed with hot dilute hydrochloric acid.

Analysis:

Nickel was estimated gravimetrically as nickel dimethyl-glyoxime after decomposing the complex with concentrated nitric acid and hydrochloric acid.

0.01620 g of the substance gave 0.01115 g of nickel dimethyl-glyoxime.

Nickel = 13.98%

0.01225 g of the substance gave 1.4 ml. of nitrogen at 31°C and 747.4 mm. pressure of mercury.

Nitrogen = 12.62%
Calculated for $[\text{NiL}_2\text{H}_2\text{O}]_n$, $L = \text{C}_{20}\text{H}_{12}\text{O}_2\text{N}_4$

- Nickel = 13.50%
- Nitrogen = 12.88%

**Cobalt(II)-5-formyl-8-hydroxy quinoline-hydrazine**:

To a hot dimethyl-formamide solution of the Schiff's base (1.7 g) was added a solution of cobalt acetate tetrahydrate (1.3 g) also in dimethyl-formamide. There was a change in the colour of the solution accompanied by separation of a reddish-brown product. The mixture was refluxed for four hours and the compound that separated, was collected on a filter, washed first with dimethyl-formamide, then with absolute alcohol and finally dried in a desiccator in vacuum.

The reddish-brown compound is insoluble in water, alcohol, acetone, chloroform and benzene, and very slightly soluble in boiling dimethyl-formamide. It is quite stable in dilute alkali, but is slightly decomposed with hot dilute hydrochloric acid.

**Analysis**:

Cobalt was estimated gravimetrically as anhydrous cobalt sulphate.

0.03110 g of the substance gave 0.01220 g of anhydrous cobalt sulphate.

Cobalt = 14.94%
0.01730 g of the substance gave 2.16 ml. of nitrogen at 29.5°C and 748 mm. pressure of mercury.

Nitrogen = 13.88%

Calculated for \([\text{CoL}]_n, \text{~L = C}_{20}\text{H}_{12}\text{O}_2\text{N}_4\)

Cobalt = 14.79%
Nitrogen = 14.04%

**Manganese(II)-5-formyl-8-hydroxy quinoline-hydrazine**:

Manganous acetate tetrahydrate (1.2 g) and the Schiff's base (1.7 g) were separately dissolved in hot dimethyl-formamide. The two solutions were mixed together when a dirty yellow product separated out. The mixture was then refluxed for four hours. The precipitated compound was filtered hot, washed first with dimethyl-formamide and then with alcohol to remove alcohol-soluble impurities and finally dried in a desiccator over concentrated \(\text{H}_2\text{SO}_4\).

The yellowish-brown compound is insoluble in water, alcohol, acetone, chloroform, benzene and even in hot dimethyl-formamide. It is stable in dilute alkali, but is slightly decomposed by hot dilute hydrochloric acid.

**Analysis**:

Manganese was estimated gravimetrically as anhydrous manganous sulphate.
0.03690 g of the substance gave 0.01030 g of anhydrous manganous sulphate.

Manganese = 10.16%

0.01225 g of the substance gave 1.5 ml of nitrogen at 31°C and 751.3 mm pressure of mercury.

Nitrogen = 13.59%

Calculated for \([\text{L}_4\text{Mn}_3\text{H}_2\text{O}_3]\cdot 3\text{H}_2\text{O}\), \(L = \text{C}_{20}\text{H}_{12}\text{O}_{2}\text{N}_4\)

Manganese = 10.10%

Nitrogen = 13.72%

Zinc(II)-5-formyl-8-hydroxy quinoline-hydrazine:

To a hot dimethyl-formamide solution of the Schiff's base (1.7 g) was added a hot dimethyl-formamide solution of zinc acetate dihydrate (1.1 g) when the colour of the solution changed to bright-red accompanied by the separation of a very fine precipitate. The mixture was refluxed and after about 30 minutes, a bright brick-red compound resulted. The reaction mixture was refluxed for additional 3 hours and the product was collected on a filter, washed with dimethyl-formamide and alcohol and finally dried in a desiccator over fused calcium chloride.

The brick-red compound is insoluble in water, alcohol, acetone, chloroform, benzene and even in dimethyl-formamide, both cold and hot. It is slightly decomposed by
dilute alkali, but is completely decomposed by hot dilute mineral acids.

Analysis:

Zinc was estimated gravimetrically as zinc-ammonium phosphate.

0.03220 g of the substance gave 0.01440 g of zinc-ammonium phosphate.

Zinc = 16.40%

0.0110 g of the substance gave 1.34 ml. of nitrogen at 29°C and 752.3 mm. pressure of mercury.

Nitrogen = 13.63%

Calculated for \( \text{ZnL} \), \( L = \text{C}_{20}\text{H}_{12}\text{O}_{2}\text{N}_{4} \)

Zinc = 16.14%

Nitrogen = 13.81%

Cadmium(II)-5-formyl-8-hydroxy quinoline-hydrazine:

To a hot dimethyl-formamide solution of the Schiff's base (1.7 g) was added a hot dimethyl-formamide solution of cadmium acetate dihydrate (1.3 g), when an immediate precipitation of an orange-yellow product occurred. The reaction mixture was refluxed for 4 hours; the separated compound was filtered hot, washed with dimethyl-formamide and absolute alcohol and finally dried in a desiccator over fused calcium chloride.
The orange-yellow compound is insoluble in water, alcohol, acetone and chloroform, but very slightly soluble in boiling benzene and in boiling dimethyl-formamide. It is slightly decomposed by hot dilute alkali and dilute hydrochloric acid.

Analysis:

Cadmium was estimated gravimetrically as cadmium oxinate.

0.03330 g of the substance gave 0.02870 g of cadmium oxinate.

Cadmium = 24.19%

0.01320 g of the substance gave 1.44 ml. of nitrogen at 29°C and 755.3 mm. pressure of mercury.

Nitrogen = 12.26%

Calculated for $\text{[CdL]}_n$, L = $\text{C}_{20}\text{H}_{12}\text{O}_2\text{N}_4$

Cadmium = 24.85%

Nitrogen = 12.38%

Uranyl-5-formyl-8-hydroxy quinoline-hydrazine:

Uranyl acetate (1.0 g) and the Schiff's base (0.9 g) were separately dissolved in hot dimethyl-formamide. The two solutions were mixed together, when a deep-red solution resulted. This was refluxed for 4 hours. During the reflux, a black amorphous mass separated out which was collected on a filter, washed with alcohol and dried in
a desiccator over fused calcium chloride (Compound I). The deep-red filtrate, from the above, was concentrated on the waterbath nearly to dryness and recrystallised from absolute alcohol when a deep-red compound (Compound II) separated out. This was collected on a filter, washed with alcohol and finally dried in a desiccator over fused calcium chloride.

The black compound (I) is completely insoluble in water, alcohol, acetone, benzene, chloroform, both in the cold and hot, but was slightly soluble in boiling dimethylformamide. It is decomposed by hot dilute alkali and mineral acids.

The deep-red compound (II) is insoluble in water, alcohol, acetone, benzene and chloroform, but highly soluble in hot dimethyl-formamide giving a bright red solution.

Analysis:

**Compound I (black):**

Uranium was estimated gravimetrically as \( \text{U}_3\text{O}_8 \).

0.02375 g of the substance gave 0.0085 g of \( \text{U}_3\text{O}_8 \).

\[
\text{Uranium} = 30.35\% \\
0.01020 \text{ g of the substance gave 0.96 ml. of nitrogen at 28^\circ C and 755.2 mm. pressure of mercury.} \\
\text{Nitrogen} = 10.60\%
\]
Calculated for \((\text{UO}_2)_2\) \((\text{L})_3\), \(\text{L} = \text{C}_{20}\text{H}_{12}\text{O}_2\text{N}_4\)

Uranium = 30.47%
Nitrogen = 10.75%

Compound II (deep-red)

0.03320 g of the substance gave 0.01410 g of \(\text{U}_3\text{O}_8\).

Uranium = 36.01%

0.01260 g of the substance gave 1.14 ml. of nitrogen at 28°C and 754.2 mm. pressure of mercury.

Nitrogen = 10.18%

Calculated for \((\text{UO}_2)_6\) \((\text{L})_7\), \(\text{L} = \text{C}_{20}\text{H}_{12}\text{O}_2\text{N}_4\)

Uranium = 35.69%
Nitrogen = 9.79%
II. Metal chelate-complexes of the Schiff's base derived from 5-formyl-8-hydroxy quinoline and ortho-phenylenediamine:

Preparation of the Schiff's base:

5-Formyl-8-hydroxy quinoline (3.5 g) and ortho-phenylenediamine (1.1 g) were refluxed with 80 ml. alcohol for about two hours on waterbath. The deep-red solution obtained after the reflux was allowed to stand under vacuum for several hours when gradually fine needle-shaped orange-yellow crystals of the Schiff's base separated out. These were filtered, washed with cold alcohol and dried in a desiccator over fused calcium chloride.

The substance melts at 143-144°C. It is insoluble in water, but soluble in hot alcohol and other organic solvents like acetone, benzene etc. It is decomposed by mineral acids on heating.

Analysis:

0.0090 g of the Schiff's base gave 1.1 ml. of nitrogen at 31°C and 743.6 mm. pressure of mercury.

Nitrogen = 13.44%

Calculated for $C_{26}H_{18}O_{2}N_4$,

Nitrogen = 13.40%
Copper(II)-5-formyl-8-hydroxy quinoline-o-phenylenediamine:

0.5 g of copper acetate monohydrate dissolved in 20 ml. of alcohol and 1.0 g of the Schiff's base dissolved in 30 ml. of hot alcohol were mixed together when immediately a bright red product formed, which remained dispersed throughout the liquid. The mixture was refluxed on waterbath for about three hours. The precipitated red compound was filtered hot, washed with alcohol and finally dried in a desiccator over fused calcium chloride.

The bright red amorphous compound is insoluble in water and alcohol, very slightly soluble in hot organic solvents like acetone, benzene and chloroform, but appreciably soluble in boiling dimethyl-formamide. It is stable in hot dilute alkali, but is decomposed by hot dilute mineral acids.

Analysis:

0.03980 g of the substance required 1.9 ml. of 0.04465(N) sodium thiosulphate solution.

Copper = 13.55%

0.01425 g of the substance gave 1.5 ml. of nitrogen at 31°C and 735.4 mm. pressure of mercury.

Nitrogen = 11.44%

Calculated for $[CuL_n, L = C_{26}H_{16}O_2N_4$:

Copper = 13.24%

Nitrogen = 11.68%
Nickel(II)-5-formyl-8-hydroxy quinoline-o-phenylenediamine:

On mixing hot alcoholic solutions of nickel acetate tetrahydrate (0.6 g) and the Schiff's base (1.0 g), a red precipitate came down immediately. The mixture was refluxed on waterbath for about three hours and during the reflux the initial red product gradually changed to yellow. This was collected on a filter, washed with alcohol and dried in a desiccator over fused calcium chloride.

The compound forms yellow powder which is insoluble in water, and alcohol, very slightly soluble in boiling benzene, acetone and chloroform, but is highly soluble in boiling dimethyl-formamide giving a bright orange-yellow solution. It is stable in hot dilute alkali, but is decomposed by hot dilute hydrochloric acid.

Analysis:

0.03065 g of the substance gave 0.01710 g of nickel dimethyl-glyoxime.

Nickel = 11.33%

0.01840 g of the substance gave 1.82 ml. of nitrogen at 30°C and 745.4 mm. pressure of mercury.

Nitrogen = 10.93%

Calculated for \( \frac{[\text{Ni}\text{L}\cdot2\text{H}_{2}\text{O}]}{\text{L} = C_{26}H_{16}O_{2}N_{4}} \)

Nickel = 11.49%

Nitrogen = 10.96%
Cobalt(II)-5-formyl-8-hydroxy quinoline-o-phenylenediamine:

To an alcoholic solution of cobalt acetate tetrahydrate (0.6 g) was added a solution of the Schiff's base (1.0 g) in hot alcohol when a yellow product separated out. The mixture was refluxed on waterbath for about three hours and during the reflux, the precipitated compound turned yellowish-brown in colour. This was then filtered hot and the solid product was washed with alcohol and dried in a desiccator over fused calcium chloride.

The substance forms yellowish-brown powder which is insoluble in water and alcohol, very slightly soluble in boiling benzene, chloroform and acetone, but is appreciably soluble in boiling dimethyl-formamide giving a deep brownish-red solution. It is stable in dilute hot alkali, but is slightly decomposed by dilute mineral acids on heating.

Analysis:

0.02320 g of the substance gave 0.00770 g of anhydrous cobalt sulphate.

Cobalt = 12.64%

0.01610 g of the substance gave 1.68 ml. of nitrogen at 31°C and 746 mm. pressure of mercury.

Nitrogen = 11.50%

Calculated for \([\text{CoL}]_n\), \(L = C_{26}H_{14}O_2N_4\)

Cobalt = 12.43%

Nitrogen = 11.79%
Manganese(II)-5-formyl-8-hydroxy quinoline-o-phenylenediamine :

Alcoholic solutions of the Schiff's base (1.0 g) and manganese acetate tetrahydrate (0.6 g) were mixed together and the mixture was refluxed on waterbath for about three hours. The precipitated light yellowish-green product was collected on a filter while hot, washed with alcohol and finally dried in a desiccator over fused calcium chloride.

The compound forms light yellowish-green powder which is insoluble in water, alcohol, benzene and chloroform, very slightly soluble in boiling acetone, but appreciably soluble in boiling dimethyl-formamide giving a brownish-red solution. It is stable in hot dilute alkali, but is decomposed by mineral acids on heating.

Analysis :

0.01810 g of the substance gave 0.00550 g of anhydrous manganous sulphate.

\[
\text{Manganese} = 11.07\% 
\]

0.01415 g of the substance gave 1.38 ml. of nitrogen at 30°C and 743.4 mm. pressure of mercury.

\[
\text{Nitrogen} = 10.75\% 
\]

Calculated for \([\text{MnL}.2\text{H}_2\text{O}]_n\), \(L = \text{C}_{26}\text{H}_{16}\text{O}_2\text{N}_4\)

\[
\text{Manganese} = 10.85\% 
\]

\[
\text{Nitrogen} = 11.05\% 
\]
Zinc(II)-5-formyl-8-hydroxy quinoline-o-phenylenediamine

On mixing hot alcoholic solutions of the Schiff's base (1.0 g) and zinc acetate dihydrate (0.5 g), there was an immediate precipitation of an orange-yellow product which remained dispersed throughout the solution. The mixture was refluxed on waterbath for about three hours. At the end of the reflux, the precipitated compound was collected on a filter, washed several times with alcohol and then dried in a desiccator over fused calcium chloride.

The substance forms orange-yellow powder which is completely insoluble in solvents like water, alcohol, acetone, benzene and chloroform, both hot and cold, but is slightly soluble in boiling dimethyl-formamide. It is stable in dilute alkali, but is decomposed by dilute mineral acids on heating.

Analysis:

0.04170 g of the substance gave 0.01510 g of zinc-ammonium phosphate.

Zinc = 13.27%

0.01985 g of the substance gave 1.86 ml. of nitrogen at 30°C and 743.2 mm. pressure of mercury.

Nitrogen = 10.32%

Calculated for \( \text{ZnL}_2\cdot 2\text{H}_2\text{O} \), \( \text{L} = \text{C}_{26}\text{H}_{16}\text{O}_2\text{N}_4 \)

Zinc = 12.64%

Nitrogen = 10.82%
Cadmium(II)-5-formyl-8-hydroxy quinoline-o-phenylenediamine:

To a hot alcoholic solution of the Schiff's base (1.0 g) was added a solution of cadmium acetate dihydrate (0.6 g) in alcohol when there was an immediate precipitation of a voluminous orange-red product. The mixture was refluxed on waterbath for three hours and during this time, the precipitated compound became granular and changed its colour to orange-yellow. This was then filtered hot, washed with alcohol and dried in a desiccator over fused calcium chloride.

The product forms orange-yellow powder which is insoluble in water, alcohol, acetone, benzene and chloroform, but is slightly soluble in boiling dimethyl-formamide. It is stable in dilute alkali, but is decomposed by mineral acids on heating.

**Analysis:**

0.03080 g of the substance gave 0.02095 g of cadmium oxinate.

Cadmium = 19.09%

0.01780 g of the substance gave 1.54 ml. of nitrogen at 31°C and 743.4 mm. pressure of mercury.

Nitrogen = 9.50%

Calculated for \( \text{[CdL}_2\text{H}_2\text{O]}_n \), \( L = C_{26}H_{16}O_2N_4 \)

Cadmium = 19.92%

Nitrogen = 9.92%
Uranyl-5-formyl-8-hydroxy quinoline-o-phenylenediamine:

On mixing hot alcoholic solutions of the Schiff's base (0.5 g) and uranyl acetate tetrahydrate (0.5 g), a deep red voluminous precipitate came down. The mixture was refluxed on waterbath for three hours and during the reflux, the precipitated compound became gradually dull red in colour. At the end of the reflux, the compound was collected on a filter while hot, washed with alcohol and finally dried in a desiccator over fused calcium chloride.

The dull red compound is insoluble in solvents like water, alcohol, acetone, benzene and chloroform, but is completely soluble in boiling dimethyl-formamide giving a deep red solution. It is decomposed by hot dilute alkali and dilute mineral acids on heating.

Analysis:

0.03190 g of the substance gave 0.01225 g of $\text{U}_3\text{O}_8$.

$\text{Uranium} = 32.57\%$

0.01455 g of the substance gave 1.16 ml. of nitrogen at 31°C and 741.4 mm. pressure of mercury.

$\text{Nitrogen} = 8.73\%$

Calculated for $(\text{UO}_2)_7(L)_8$, \hspace{1cm} L = C_{26}H_{16}O_2N_4

$\text{Uranium} = 31.92\%$

$\text{Nitrogen} = 8.58\%$
III. Metal chelate-complexes of the Schiff's base derived from 5-formyl-8-hydroxy quinoline and para-phenylene-diamine:

Preparation of the Schiff's base:

To a hot alcoholic solution of 5-formyl-8-hydroxy quinoline (3.5 g) was added a solution of para-phenylenediamine (1.1 g) in alcohol and the resultant solution was refluxed on waterbath. After about 30 minutes, a bright yellow solid formed. The reaction mixture was heated for an additional one and a half hour and then allowed to cool to room temperature. The solid product was collected on a filter, washed with alcohol and dried in a desiccator over fused calcium chloride.

The Schiff's base forms yellow powder which melts at 266-267°C. It is insoluble in water, sparingly soluble in boiling alcohol, acetone and methanol, but completely soluble in hot dimethyl-formamide.

Analysis:

0.01390 g of the substance gave 1.66 ml. of nitrogen at 32°C and 743 mm. pressure of mercury.

Nitrogen = 13.07%

Calculated for $C_{26}H_{18}O_2N_4$,

Nitrogen = 13.40%
Copper(II)-5-formyl-8-hydroxy quinoline-p-phenylenediamine :

1.0 g of the Schiff's base dissolved in about 40 ml. of hot dimethyl-formamide and 0.5 g of copper acetate monohydrate dissolved in 20 ml. of hot dimethyl-formamide were mixed together when there was an immediate precipitation of a voluminous reddish-brown product. The mixture was refluxed for two hours and filtered hot. The deep brown solid on the filter was washed first with dimethyl-formamide and then with alcohol in order to remove the alcohol-soluble impurities and finally dried in a desiccator over fused calcium chloride.

The compound forms deep brown crystals which is insoluble in water, alcohol, acetone, benzene, chloroform and even in hot dimethyl-formamide. It is quite stable in hot dilute alkali, but is only slowly decomposed by mineral acids on heating.

Analysis :

0.02235 g of the substance required 1.95 ml. of 0.02324(N) sodium thiosulphate solution.

Copper = 12.87%

0.01925 g of the substance gave 1.84 ml. of nitrogen at 30°C and 739.4 mm. pressure of mercury.

Nitrogen = 10.48%

Calculated for \( \left[\text{CuL}_2\text{H}_2\text{O}\right]_n \), \( \text{L} = \text{C}_{26}\text{H}_{16}\text{O}_2\text{N}_4 \)

Copper = 12.32%

Nitrogen = 10.86%
Nickel(II)-5-formyl-8-hydroxy quinoline-p-phenylenediamine:

To a hot dimethyl-formamide solution of the Schiff's base (1.0 g) was added a hot solution of nickel acetate tetrahydrate (0.6 g) also in dimethyl-formamide, a bright red precipitate appeared. The reaction mixture was refluxed for two hours and during this time, the precipitated product became brownish-red in colour. This was then filtered hot and the solid compound was washed with dimethyl-formamide and alcohol and finally dried in a desiccator in vacuum.

The product forms brownish-red powder which is insoluble in water, acetone, benzene and chloroform, but very slightly soluble in hot alcohol and dimethyl-formamide leaving a deep brown residue. It is slightly decomposed by hot dilute alkali, but is decomposed by mineral acids on heating.

Analysis:

0.02115 g of the substance gave 0.01250 g of nickel dimethyl-glyoxime.

Nickel = 12.00%

0.01680 g of the substance gave 1.86 ml. of nitrogen at 32°C and 745 mm. pressure of mercury.

Nitrogen = 12.15%

Calculated for \([\text{NiL}]_n\), \(L = C_{26}H_{16}O_2N_4\)

Nickel = 12.37%

Nitrogen = 11.80%
Cobalt(II)-5-formyl-8-hydroxy quinoline-p-phenylenediamine:

On mixing hot dimethyl-formamide solutions of the Schiffs base (1.0 g) and cobalt acetate tetrahydrate (0.6 g), a brown solution resulted. The reaction mixture was refluxed for two hours and during this time, the solution became dark-brown in colour. After the reflux, the solution was poured into a beaker and concentrated to one-third of its original volume on waterbath. Then the solution was cooled to room temperature and cold water was added to it with stirring when a granular brown compound separated out. This was then refrigerated overnight and the precipitated compound was filtered, washed with water and alcohol and finally dried in a desiccator over concentrated sulphuric acid.

The substance forms deep brown powder which is slightly soluble in hot alcohol and benzene, sparingly soluble in hot acetone and chloroform, but completely soluble in dimethylformamide. It is not decomposed by dilute alkali and dilute hydrochloric acid.

Analysis:

0.02365 g of the substance gave 0.00670 g of anhydrous cobalt sulphate.

Cobalt = 10.78%

0.02060 g of the substance gave 1.9 ml. of nitrogen at 29°C and 752.4 mm. pressure of mercury.

Nitrogen = 10.32%
Calculated for \([\text{CoL}_2\text{H}_2\text{O}_2]_n\), \(\text{L} = \text{C}_{26}\text{H}_{16}\text{O}_{2}\text{N}_4\)

Cobalt = 11.54%
Nitrogen = 10.96%

\text{Manganese(II)-5-formyl-8-hydroxy quinoline-p-phenylenediamine:}

Hot dimethyl-formamide solutions of the Schiff's base (1.0 g) and manganese acetate tetrahydrate (0.6 g) were mixed together when a brown solution resulted. The reaction mixture was refluxed for two hours and the dark-brown solution, thus obtained, was poured into a beaker, concentrated to half its original volume. It was then cooled to room temperature and cold water was added to it with stirring when granular brown compound separated out. After refrigerating for several hours, the precipitated brown compound was collected on a filter, washed with water and alcohol and finally dried in a desiccator in vacuum.

The brown compound is insoluble in water, acetone, benzene and chloroform, slightly soluble in hot alcohol, but appreciably soluble in hot dimethyl-formamide giving a reddish-brown solution. It is slightly decomposed by hot dilute alkali, but is completely decomposed by hot dilute hydrochloric acid.

\text{Analysis:}

0.03080 g of the substance gave 0.00890 g of anhydrous manganous sulphate.

\text{Manganese 10.52%}
0.01800 g of the substance gave 1.84 ml. of nitrogen at 30°C and 748.4 mm. pressure of mercury.

\[ \text{Nitrogen} = 11.34\% \]

Calculated for \( [\text{MnL}.2\text{H}_2\text{O}]_n \), \( L = \text{C}_{26}\text{H}_{16}\text{O}_2\text{N}_4 \)

Manganese = 10.85%
Nitrogen = 11.05%

\text{Zinc(II)-5-formyl-8-hydroxy quinoline-p-phenylenediamine :}

On adding a hot dimethyl-formamide solution of zinc acetate dihydrate (0.5 g) to a hot dimethyl-formamide solution of the Schiff's base (1.0 g), a reddish-orange product separated out. The reaction mixture was refluxed for two hours and during this time, the colour of the precipitated product changed to dull red. At the end of the reflux, the solid compound was collected on a filter, washed with dimethyl-formamide and then with alcohol and finally dried in a desiccator in vacuum.

The substance forms brick-red powder which is insoluble in solvents like water, acetone, benzene and chloroform, very slightly soluble in hot alcohol and dimethyl-formamide. It is quite stable in hot dilute alkali, but is decomposed by dilute mineral acids on heating.

\text{Analysis :}

0.04410 g of the substance gave 0.01625 g of zinc-ammonium phosphate.

\[ \text{Zinc} = 13.53\% \]
0.01720 g of the substance gave 1.7 ml. of nitrogen at 27°C and 756 mm. pressure of mercury.

Nitrogen = 11.19%

Calculated for \( [\text{ZnL}]_n \), \( L = \text{C}_2\text{H}_16\text{O}_2\text{N}_4 \)

Zinc = 13.58%

Nitrogen = 11.63%

Cadmium(II)-5-formyl-8-hydroxy quinoline-p-phenylenediamine:

To a hot dimethyl-formamide solution of the Schiff's base (1.0 g) was added a solution of cadmium acetate dihydrate (0.6 g) in dimethyl-formamide when there was an immediate precipitation of a pale yellow product. The mixture was refluxed for two hours and then filtered hot; the pale yellow solid product was washed with dimethyl-formamide and then with alcohol and finally dried in a desiccator in vacuum. After drying, the solid product became yellowish-brown in colour.

The compound is insoluble in solvents like water, alcohol, acetone, benzene, chloroform and even in hot dimethyl-formamide. It is slightly decomposed by hot dilute alkali, but completely decomposed by mineral acids on heating.

Analysis:

0.04815 g of the substance gave 0.02910 g of cadmium oxinate.

Cadmium = 16.97%
0.02035 g of the substance gave 1.7 ml. of nitrogen at 25°C and 753.6 mm. pressure of mercury.

Nitrogen = 9.49%

Calculated for $\text{Cd}_3\text{L}_4$, $\text{L} = \text{C}_{26}\text{H}_{16}\text{O}_2\text{N}_4$

Cadmium = 16.85%
Nitrogen = 9.59%

Urananyl-5-formyl-8-hydroxy quinoline-p-phenylene diamine:

Hot dimethyl-formamide solutions of the Schiff's base (0.5 g) and uranyl acetate tetrahydrate (0.5 g) were mixed together when a deep red solution resulted. The reaction mixture was refluxed for two hours and the resultant deep red solution was poured into a beaker, concentrated to half of its volume on waterbath. It was then cooled to room temperature and cold water was added to the solution with stirring when a granular reddish-brown solid separated out. It was then refrigerated for several hours and the precipitated solid product was collected on a filter, washed with water and alcohol and finally dried in a desiccator in vacuum. On drying, the compound became deep brown in colour.

The compound is insoluble in water, acetone, alcohol, benzene and chloroform, but sparingly soluble in boiling dimethyl-formamide. It is quite stable in dilute alkali, but is decomposed by hot dilute hydrochloric acid.
Analysis:

0.03290 g of the substance gave 0.01110 g of U₃O₈.

Uranium = 28.61%

0.04175 g of the substance gave 2.82 ml. of nitrogen at 24°C and 754 mm. pressure of mercury.

Nitrogen = 7.70%

Calculated for (UO₂)₃L₄, L = C₂₆H₁₆O₂N₄

Uranium = 28.86%
Nitrogen = 7.76%
IV. Metal chelate-complexes of the Schiff's base derived from 5-formyl-8-hydroxy quinoline and oxal-hydrazimidine:

Preparation of oxal-hydrazimidine:

Oxal-hydrazimidine was prepared by the method described by Dedichen (J. Prakt. Chem. (2), 50, 254, (1894)).

A slurry of 20 g of dithiooxamide in 400 ml of 20% ethanol was placed in a beaker. Hydrazine hydrate was added to it dropwise with stirring until all the dithiooxamide had reacted. At this point, the suspension had changed in colour from orange to tan with no orange specks of solid dithiooxamide. The solid reaction product, oxal-hydrazimidine, was collected by filtration, washed with 20% alcohol and then dried in a desiccator over fused calcium chloride.

Preparation of the Schiff's base:

5-Formyl-8-hydroxy quinoline (3.46 g, 0.02 mole) and oxal-hydrazimidine (1.16 g, 0.01 mole) were refluxed in absolute alcohol. After about 30 minutes, a bright yellow solid appeared. The reaction mixture was heated under reflux for an additional one hour and then allowed to cool to room temperature. The product was collected on a filter, washed with alcohol and dried in a desiccator over fused calcium chloride.
The Schiff's base forms bright yellow amorphous powder which is insoluble in water, very slightly soluble in hot organic solvents like alcohol, acetone and benzene, but is completely soluble in hot dimethyl-formamide. It is decomposed on heating by strong mineral acids. The substance melts at 256-257°C.

Analysis:

0.00645 g of the substance gave 1.54 ml. of nitrogen at 33°C and 746 mm pressure of mercury.

Nitrogen = 26.14%

Calculated for \( \text{C}_{22}\text{H}_{18}\text{O}_2\text{N}_8 \):

Nitrogen = 26.29%

Copper(II)-5-formyl-8-hydroxy quinoline-oxal-hydrazimidine:

To a hot dimethyl-formamide solution of the Schiff's base (1.1 g, 0.0025 mole) was added a solution of copper acetate monohydrate (1.0 g, 0.005 mole) in dimethyl-formamide when a brownish-red compound separated out. The reaction mixture was refluxed for four hours and during the reflux, the solid reaction product became reddish-brown in colour. The precipitated compound was collected by filtration while hot, washed with dimethyl-formamide and then digested with absolute alcohol for one hour in order to remove the alcohol-soluble impurities. It was filtered hot, washed with hot alcohol and...
dried in a desiccator over concentrated sulphuric acid.

The product forms reddish-brown powder which is insoluble in water, alcohol, acetone, benzene and chloroform and even in hot dimethyl-formamide. It is quite stable in dilute alkali, and is only slightly decomposed by heating with strong mineral acids.

Analysis:

0.00930 g of the substance required 3.0 ml. of 0.01109(N) sodium thiosulphate solution.

Copper = 22.74%

0.00970 g of the substance gave 1.74 ml. of nitrogen at 32°C and 745 mm. pressure of mercury.

Nitrogen = 19.68%

Calculated for \([\text{Cu}_2\text{L}]_n\), \(\text{L} = \text{C}_{22}\text{H}_{14}\text{O}_2\text{N}_8\)

Copper = 23.13%

Nitrogen = 20.40%

Nickel(II)-5-formyl-8-hydroxy quinoline-oxal-hydrazimidine:

1.1 g (0.0025 mole) of the Schiff's base dissolved in hot dimethyl-formamide was mixed with a solution of 1.2 g (0.005 mole) nickel acetate tetrahydrate in hot dimethyl-formamide when a bright red precipitate formed. The reaction mixture was refluxed for four hours during which the colour of the solid reaction product changed to deep brown. The
precipitated compound was filtered hot, washed with dimethylformamide and alcohol and then dried in a desiccator over fused calcium chloride.

The compound forms deep brown amorphous powder which is insoluble in solvents like water, alcohol, acetone, benzene, chloroform and even in hot dimethyl-formamide. It is quite stable in hot dilute alkali, but is decomposed on heating with mineral acids.

Analysis:

0.01090 g of the substance gave 0.01045 g of nickel dimethyl-glyoxime.

Nickel = 19.47%

0.01020 g of the substance gave 1.74 ml. of nitrogen at 33°C and 740 mm. pressure of mercury.

Nitrogen = 18.53%

0.02150 g of the substance lost 0.00260 g in its weight at 120-125°C.

Water = 12.10%

Calculated for \([\text{Ni}_2\text{L}.4\text{H}_2\text{O}]_n\), \(\text{L} = \text{C}_{22}\text{H}_{14}\text{O}_2\text{N}_6\)

Nickel = 19.21%

Nitrogen = 18.32%

Water = 11.78%
Cobalt(II)-5-formyl-8-hydroxy quinoline-oxal-hydrazimidine:

On adding hot dimethyl-formamide solution of cobalt acetate tetrahydrate (1.2 g, 0.005 mole) to a solution of the Schiff’s base (1.1 g, 0.0025 mole) in hot dimethyl-formamide, a voluminous brownish-red precipitate formed. The reaction mixture was refluxed for four hours and during this time, the solid reaction product changed its colour to reddish-brown. The precipitated compound was then collected on a filter, washed with dimethyl-formamide and was digested with alcohol for two hours to remove any alcohol-soluble impurities. It was then filtered hot, washed with hot alcohol and dried in a desiccator over fused calcium chloride.

The substance forms reddish-brown amorphous powder which is insoluble in water, alcohol, acetone, benzene, chloroform and dimethyl-formamide in the hot. It is not decomposed by hot dilute alkali, but decomposes on heating with dilute mineral acids.

Analysis:

0.01420 g of the substance gave 0.0074 g of anhydrous cobalt sulphate.

Cobalt = 19.84%

0.0090 g of the substance gave 1.42 ml. of nitrogen at 34°C and 740.6 mm. pressure of mercury.

Nitrogen = 17.10%
0.01605 g of the substance lost 0.00180 g in its weight at 120°C.

Water = 11.21%

Calculated for \(\text{Co}_2\text{L}\cdot 4\text{H}_2\text{O}\)

- Cobalt = 19.28%
- Nitrogen = 18.30%
- Water = 11.76%

Manganese(II)-5-formyl-8-hydroxy quinoline-oxal-hydrazimidine:

To a hot dimethyl-formamide solution of the Schiff's base (1.1 g, 0.0025 mole) was added a hot solution of manganous acetate tetrahydrate (1.2 g, 0.005 mole) also in dimethyl-formamide, when a pale brownish-yellow precipitate formed. The reaction mixture was heated under reflux for four hours when the solid reaction product changed its colour to yellowish-brown. The separated compound was collected on a filter, washed with dimethyl-formamide and alcohol and finally dried in a desiccator over fused calcium chloride.

The product forms yellowish-brown powder which is insoluble in water and organic solvents like alcohol, acetone, benzene, chloroform and dimethyl-formamide even in the hot. It is only slightly decomposed by heating with dilute alkali and dilute mineral acids.
Analysis:

0.01600 g of the substance gave 0.00820 g of anhydrous manganous sulphate.

Manganese = 18.66%

0.00880 g of the substance gave 1.46 ml. of nitrogen at 33°C and 740.6 mm. pressure of mercury.

Nitrogen = 18.04%

0.01570 g of the substance lost 0.00180 g in its weight at 120°C.

Water = 11.47%

Calculated for \([\text{Mn}_2\text{L} \cdot 4\text{H}_2\text{O}]_n\), \(\text{L} = \text{C}_{22}\text{H}_{14}\text{O}_2\text{N}_8\)

Manganese = 18.22%
Nitrogen = 18.55%
Water = 11.94%

Zinc(II)-5-formyl-8-hydroxy quinoline-oxal-hydrazimidine:

On mixing hot dimethyl-formamide solutions of the Schiff's base (1.1 g, 0.0025 mole) and zinc acetate dihydrate (1.1 g, 0.005 mole), an orange compound precipitated out. The reaction mixture was refluxed for four hours and then the separated compound was collected on a filter, washed with dimethyl-formamide and alcohol repeatedly in order to remove the soluble impurities and finally dried in a desiccator over fused calcium chloride.
The substance forms bright orange amorphous powder which is insoluble in water and organic solvents like alcohol, acetone, benzene and chloroform and dimethyl-formamide. It is only slightly decomposed on heating with dilute alkali and dilute mineral acids.

**Analysis**:

0.02680 g of the substance gave 0.01570 g of zinc-ammonium phosphate.

\[
\text{Zinc} = 21.48\%
\]

0.00905 g of the substance gave 1.42 ml. of nitrogen at 29.5°C and 741.6 mm. pressure of mercury.

\[
\text{Nitrogen} = 17.38\%
\]

0.01720 g of the substance lost 0.00205 g in its weight at 120°C.

\[
\text{Water} = 11.92\%
\]

Calculated for \( [\text{Zn}_2\text{L}.4\text{H}_2\text{O}]_n \), \( \text{L} = \text{C}_{22}\text{H}_{14}\text{O}_2\text{N}_8 \)

\[
\text{Zinc} = 20.92\%
\]

\[
\text{Nitrogen} = 17.93\%
\]

\[
\text{Water} = 11.52\%
\]

**Cadmium(II)-5-formyl-8-hydroxy quinoline-oxal-hydrazimidine**:

On adding a hot dimethyl-formamide solution of cadmium acetate dihydrate (1.3 g, 0.005 mole) to a hot
dimethyl-formamide solution of the Schiff's base (1.1 g, 0.0025 mole), a bright orange-red product precipitated out. The reaction mixture was heated under reflux for four hours and during this time, the colour of the reaction product gradually faded out leaving only a pale reddish-orange compound. This was collected on a filter, washed repeatedly with dimethyl-formamide and alcohol to remove the soluble impurities and finally dried in a desiccator over fused calcium chloride.

The metal-chelate forms pale reddish-orange powder which is insoluble in water, alcohol, acetone, benzene and chloroform and even in hot dimethyl-formamide. It is quite stable in hot dilute alkali, but is slightly decomposed on heating with mineral acids.

Analysis:

0.01450 g of the substance gave 0.01580 g of cadmium oxinate.

Cadmium = 30.59%

0.00840 g of the substance gave 1.18 ml. of nitrogen at 31°C and 742.4 mm. pressure of mercury.

Nitrogen = 15.41%

0.00815 g of the substance lost 0.00080 g in its weight at 120°C.

Water = 9.81%
Calculated for \[ \text{Cd}_2\text{L}.4\text{H}_2\text{O} \] _n_ , \hspace{1cm} \text{L} = \text{C}_{22}\text{H}_{14}\text{O}_2\text{N}_8 \\
\text{Cadmium} = 31.27\% \\
\text{Nitrogen} = 15.58\% \\
\text{Water} = 10.02\% \\

_Uranyl-5-formyl-8-hydroxy quinoline-oxal-hydrazimidine:_

Hot dimethyl-formamide solutions of the Schiff's base (1.1 g, 0.0025 mole) and uranyl acetate dihydrate (2.1 g, 0.005 mole) were mixed together. The resultant deep red solution was heated under reflux for four hours and during this time, the colour of the solution gradually deepened. At the end of the reflux, the deep red solution was concentrated to a small volume on waterbath, cooled to room temperature and alcohol was added to it when a reddish-brown compound separated out. This was allowed to settle in the cold for an hour and then collected on a filter, washed with alcohol and finally dried in a desiccator over fused calcium chloride.

The substance forms reddish-brown powder which is insoluble in water, alcohol, benzene, acetone and chloroform, but is sparingly soluble in hot dimethyl-formamide giving a deep red solution. It is slightly decomposed on heating with dilute alkali and dilute mineral acids.
Analysis:

0.02040 g of the substance gave 0.00790 g of $U_3O_8$.

$U_3O_8$:

Uranium = 33.24%

0.02100 g of the substance gave 2.9 ml. of nitrogen at 31°C and 743 mm. pressure of mercury.

Nitrogen = 15.17%

Calculated for $[\text{UO}_2L]_n$, $L = C_{22}H_{16}O_2N_8$

Uranium = 34.30%

Nitrogen = 16.14%
V. Metal chelate-complexes of the Schiff's base derived from 5-formyl-8-hydroxy quinoline and ethylenediamine:

Copper(II)-5-formyl-8-hydroxy quinoline-ethylenediamine:

To a hot dimethyl-formamide solution of 5-formyl-8-hydroxy quinoline (0.8 g) was added with stirring a solution of copper acetate monohydrate (0.5 g) in dimethyl-formamide, followed by the dropwise addition of ethylenediamine (0.2 g). Immediately, a yellowish-green precipitate separated out. The reaction mixture was gently refluxed for eight hours to ensure completion of the reaction. The hot reaction mixture was then filtered, the residue was repeatedly washed with dimethyl-formamide and then with alcohol and finally dried in a desiccator over fused calcium chloride.

The yellowish-green amorphous compound is insoluble in water and in organic solvents like alcohol, benzene, acetone and dimethyl-formamide. It is slightly decomposed by hot dilute alkali and dilute hydrochloric acid.

Analysis:

0.03570 g of the substance required 1.8 ml. of 0.04465(N) sodium thiosulphate solution.

Copper = 14.31%

0.02450 g of the substance gave 2.72 ml. of nitrogen at 31°C and 745.6 mm. pressure of mercury.

Nitrogen = 12.24%
Calculated for $[\text{CuL}]_n$, 
$L = C_{22}H_{16}O_{2}N_4$

Copper = 14.73%
Nitrogen = 12.97% 

Nickel(II)-5-formyl-8-hydroxy quinoline-ethylenediamine:

A mixture of 5-formyl-8-hydroxy quinoline (0.8 g), nickel acetate tetrahydrate (0.6 g) and ethylenediamine (0.2 g) was refluxed with 100 ml. of dimethyl-formamide. After about 30 minutes, the colour of the solution turned dark brown. The reaction mixture was refluxed for a total of eight hours and then the resultant dark solution was concentrated on the water-bath to remove most of the dimethyl-formamide, when a dark coloured sticky mass was obtained. Ice-cold water was added to this mass with vigorous stirring when a granular brown compound separated out. This was refrigerated overnight and then filtered, washed with water and dried in a desiccator over fused calcium chloride.

The dark brown crystalline compound is insoluble in water, benzene and acetone, slightly soluble in hot alcohol, but completely soluble in hot dimethyl-formamide. It is quite stable in dilute alkali, but is slightly decomposed by hot dilute hydrochloric acid.
Analysis:

0.10700 g of the substance gave 0.06800 g of nickel dimethyl-glyoxime.

\[ \text{Nickel} = 12.90\% \]

0.01835 g of the substance gave 1.9 ml of nitrogen at 31°C and 748.6 mm. pressure of mercury.

\[ \text{Nitrogen} = 11.46\% \]

Calculated for \( \left[ \text{NiL}_2\text{H}_2\text{O} \right]_n \), \( L = C_{22}H_{16}O_2N_4 \)

\[ \text{Nickel} = 12.69\% \]
\[ \text{Nitrogen} = 12.11\% \]

Cobalt(II)-5-formyl-8-hydroxy quinoline-ethylenediamine:

On mixing hot dimethyl-formamide solutions of 5-formyl-8-hydroxy quinoline (0.8 g), cobalt acetate tetrahydrate (0.6 g) and ethylenediamine (0.2 g), a brownish-red solution resulted. The reaction mixture was refluxed for eight hours during which the solution became dark brown in colour. At the end of the reflux, the hot reaction mixture was filtered to remove the slight precipitated product and the filtrate was evaporated on the waterbath almost to dryness. A dark coloured sticky mass was obtained. On adding ice-cold water to this mass with vigorous stirring, a deep brown solid separated out. This was refrigerated overnight and then filtered, washed with water and then dried in a desiccator over fused calcium chloride.
The deep brown compound is insoluble in water and acetone, slightly soluble in hot alcohol and benzene, but completely soluble in boiling dimethyl-formamide. It is quite stable in dilute alkali, but is slightly decomposed by heating with dilute mineral acids.

Analysis:

0.02640 g of the substance gave 0.0090 g of anhydrous cobalt sulphate.

Cobalt = 12.98%

0.01495 g of the substance gave 1.6 ml. of nitrogen at 33°C and 743.8 mm. pressure of mercury.

Nitrogen = 11.69%

Calculated for \[\text{CoL}_2\text{H}_2\text{O}_2\text{N}_4\], \(\text{L} = \text{C}_{22}\text{H}_{16}\text{O}_2\text{N}_4\)

Cobalt = 12.75%

Nitrogen = 12.10%

**Manganese(II)-5-formyl-8-hydroxy quinoline-ethylenediamine**

Solutions of 5-formyl-8-hydroxy quinoline (0.8 g), manganese acetate tetrahydrate (0.6 g) and ethylenediamine (0.2 g) in hot dimethyl-formamide were mixed together, when a brown solution was obtained. The reaction mixture was refluxed gently for eight hours and during this time, the solution became dark brown in colour. After the reflux, the hot reaction mixture was filtered and the filtrate was evaporated almost to dryness. Ice-cold water was then added.
to the brown sticky mass and stirred well, when an yellowish-brown compound separated out. This was refrigerated overnight and then collected on a filter, washed with water and dried in a vacuum desiccator over fused calcium chloride. The compound became dark brown on drying.

The substance is insoluble in water and acetone, slightly soluble in hot alcohol and benzene, but completely soluble in boiling dimethyl-formamide. It is slightly decomposed by hot dilute alkali, but is completely decomposed by heating with dilute mineral acids.

Analysis:

0.01890 g of the substance gave 0.00650 g of anhydrous manganous sulphate.

Manganese = 12.52%

0.01700 g of the substance gave 1.78 ml. of nitrogen at 30°C and 742.6 mm. pressure of mercury.

Nitrogen = 11.53%

Calculated for \( \left[ \text{MnL}_2\text{H_2O} \right]_n \), \( \text{L} = \text{C}_{22}\text{H}_{16}\text{O}_2\text{N}_4 \)

Manganese = 11.99%
Nitrogen = 12.20%

**Zinc(II)-5-formyl-8-hydroxy-quinoline-ethylenediamine:**

The yellow solution obtained by mixing hot dimethyl-formamide solutions of 5-formyl-8-hydroxy quinoline
(0.8 g), zinc acetate dihydrate (0.5 g) and ethylenediamine (0.2 g) was refluxed gently for eight hours. At the end of the reflux, the reaction mixture was concentrated to a very small volume, cooled to room temperature and ice-cold water was added to it with vigorous stirring. A yellow compound gradually separated out. This was refrigerated overnight and then collected on a filter, washed with water and then dried in a desiccator over fused calcium chloride. The compound became brown in colour on drying.

The compound is insoluble in water, benzene and acetone, slightly soluble in hot alcohol, but completely soluble in hot dimethyl-formamide. It is appreciably decomposed on heating with dilute alkali and dilute mineral acids.

**Analysis:**

Zinc was estimated gravimetrically as zinc-oxinate.

0.07025 g of the substance gave 0.05050 g of zinc-oxinate.

\[
\text{Zinc} = 13.29\%
\]

0.01900 g of the substance gave 2.00 ml. of nitrogen at 33°C and 741.2 mm. pressure of mercury.

\[
\text{Nitrogen} = 11.45\%
\]

Calculated for \([\text{ZnL} \cdot 2\text{H}_2\text{O}]_n\), \(\text{L} = \text{C}_{22}\text{H}_{16}\text{O}_{2}\text{N}_4\)

\[
\text{Zinc} = 13.93\%
\]

\[
\text{Nitrogen} = 11.93\%
\]
Cadmium(II)-5-formyl-8-hydroxy quinoline-ethylenediamine:

Hot-dimethyl-formamide solutions of 5-formyl-8-hydroxy quinoline (0.8 g), cadmium acetate dihydrate (0.6 g) and ethylenediamine (0.2 g) were mixed together, when an yellow solution resulted. The reaction mixture was refluxed gently for eight hours and then filtered hot to remove the trace amount of solid which separated out. The filtrate was concentrated to a very small volume, cooled to room temperature and ice-cold water was added to it with stirring when a yellowish-brown compound precipitated out. This was refrigerated overnight and then collected on a filter, washed with water and then dried in a desiccator over fused calcium chloride. The compound became deep brown on drying.

The compound is insoluble in water, acetone and benzene, slightly soluble in hot alcohol, but completely soluble in hot dimethyl-formamide. It is slightly decomposed by dilute alkali, but a deep red solution is obtained with dilute hydrochloric acid.

Analysis:

0.04880 g of the substance gave 0.03680 g of cadmium oxinate.

Cadmium = 21.16%
0.02425 g of the substance gave 2.2 ml. of nitrogen at 30°C and 748.6 mm pressure of mercury.

Nitrogen = 10.07%

Calculated for \([\text{CdL}_2\text{H}_2\text{O}]_n\),
\[
\text{L} = \text{C}_{22}\text{H}_{16}\text{O}_2\text{N}_4
\]

Cadmium = 21.77%
Nitrogen = 10.85%

**Uranyl-5-formyl-8-hydroxy quinoline-ethylenediamine**:  

A bright red solution resulted on mixing hot dimethyl-formamide solutions of 5-formyl-8-hydroxy quinoline (0.8 g), uranyl acetate dihydrate (1.0 g) and ethylenediamine (0.2 g). The reaction mixture was refluxed gently for eight hours. The resultant deep red solution was concentrated to a small volume on waterbath and then cooled to room temperature. Acetone was added to it with stirring, when a brick-red compound precipitated out. This was allowed to stand for several hours and then collected on a filter, washed with alcohol and dried in a desiccator over fused calcium chloride.

The substance forms brick-red powder which is insoluble in water, alcohol, acetone and benzene, but is completely soluble in hot dimethyl-formamide. It is slightly decomposed by dilute alkali, but is completely decomposed by hot dilute hydrochloric acid.
Analysis:

0.02365 g of the substance gave 0.00935 g of $\text{U}_3\text{O}_8$.

Uranium = 33.53%

0.02010 g of the substance gave 1.54 ml. of nitrogen at 28° C and 747.8 mm. pressure of mercury.

Nitrogen = 8.55%

Calculated for $(\text{UO}_2)_6\text{L}_7$ , \( \text{L} = \text{C}_{22}\text{H}_{16}\text{O}_2\text{N}_4 \)

Uranium = 34.04%
Nitrogen = 9.34%
VI. Metal chelate-complexes of the Schiff's base derived from 5-formyl-8-hydroxy quinoline and benzidine:

**Copper(II)-5-formyl-8-hydroxy quinoline-benzidine**: 

0.8 g of 5-formyl-8-hydroxy quinoline dissolved in about 25 ml. of hot dimethyl-formamide, 0.5 g of copper acetate monohydrate dissolved in 15 ml of dimethyl-formamide and 0.4 g of benzidine dissolved in 15 ml of dimethyl-formamide were mixed together, when a brown solution resulted and some brown precipitate was formed. The reaction mixture was refluxed for two hours and then poured into a beaker, concentrated to a small volume on the waterbath. It was then cooled to room temperature and cold water was added to it with stirring, when the quantity of the original brown precipitate increased. After refrigeration for several hours, the brown precipitate was collected on a filter, washed with water and alcohol and finally dried in a vacuum desiccator over fused calcium chloride.

The deep brown crystalline compound is insoluble in water, alcohol, acetone, benzene and chloroform even in the hot, but is sparingly soluble in boiling dimethyl-formamide. It is quite stable in hot dilute alkali, but is slightly decomposed by mineral acids on heating.
Analysis:

0.01640 g of the substance required 1.2 ml. of 0.02324(N) sodium thiosulphate solution.

Copper = 10.81%

0.02690 g of the substance gave 2.14 ml. of nitrogen at 31°C and 746 mm. pressure of mercury.

Nitrogen = 8.77%

Calculated for \(\left[\text{CuL}_2\text{H}_2\text{O}\right]_n\), \(\text{L} = \text{C}_3\text{H}_2\text{O}_2\text{N}_4\)

Copper = 10.74%

Nitrogen = 9.46%

Nickel(II)-5-formyl-8-hydroxy quinoline-benzidine:

Hot dimethyl-formamide solutions of 5-formyl-8-hydroxy quinoline (0.8 g), nickel acetate tetrahydrate (0.6 g) and benzidine (0.4 g) were mixed together when a clear yellowish-green solution was obtained. The reaction mixture was refluxed for two hours and the resultant solution was then poured into a beaker, concentrated on waterbath to a small volume, cooled to room temperature and cold water was added to this solution, when granular yellowish-brown compound separated out. After refrigeration for several hours, the precipitated product was filtered, washed with water and alcohol and finally dried in a desiccator over fused calcium chloride.
The substance forms yellowish-brown powder which is insoluble in water, very slightly soluble in hot alcohol, acetone, benzene and chloroform, but is completely soluble in hot dimethyl-formamide giving a deep brown solution. It is quite stable in dilute alkali and only slightly decomposed by mineral acids on heating.

Analysis:

0.02980 g of the substance gave 0.01440 g of nickel dimethyl-glyoxime.

Nickel = 9.81%

0.02285 g of the substance gave 1.92 ml. of nitrogen at 25°C and 756 mm. pressure of mercury.

Nitrogen = 9.57%

Calculated for $\left[\text{NiL}_2\text{H}_2\text{O}\right]_n$, $L = \text{C}_{32}\text{H}_{20}\text{O}_2\text{N}_4$

Nickel = 10.00%
Nitrogen = 9.54%

Cobalt(II)-5-formyl-8-hydroxy quinoline-benzidine:

On mixing hot dimethyl-formamide solutions of 5-formyl-8-hydroxy quinoline (0.8 g), cobalt acetate tetrahydrate (0.6 g), and benzidine (0.4 g), a deep red solution resulted. The reaction mixture was refluxed for two hours and during this time, the solution became reddish-brown in colour. At the end of the reflux, the resultant solution was
concentrated to a small volume on waterbath, cooled to room temperature and then cold water was added to the solution, when a voluminous reddish-brown compound separated out. This was refrigerated for several hours and then the precipitated compound was collected on a filter, washed with water and alcohol and finally dried in a desiccator over fused calcium chloride.

The compound forms reddish-brown powder which is insoluble in water, slightly soluble in boiling alcohol, acetone, benzene and chloroform, but is completely soluble in boiling dimethyl-formamide producing a brownish-red solution. It is not decomposed by dilute alkali, and is only slightly decomposed by dilute hydrochloric acid on heating.

**Analysis:**

0.03120 g of the substance gave 0.00780 g of anhydrous cobalt sulphate.

\[
\text{Cobalt} = 9.51\%
\]

0.02060 g of the substance gave 1.74 ml. of nitrogen at 25°C and 755.6 mm. pressure of mercury.

\[
\text{Nitrogen} = 9.62\%
\]

Calculated for \(\text{[CoL}_2\text{H}_2\text{O]}_n\), \(L = \text{C}_3\text{H}_2\text{O}_2\text{N}_4\)

\[
\text{Cobalt} = 10.06\%
\]

\[
\text{Nitrogen} = 9.54\%
\]
Manganese(II)-5-formyl-8-hydroxy quinoline-benzidine:

A light brown solution resulted when solutions of 5-formyl-8-hydroxy quinoline (0.8g), manganese acetate tetrahydrate (0.6 g) and benzidine (0.4 g) in hot dimethyl-formamide were mixed together. The reaction mixture was refluxed for two hours and during the reflux, the solution became dark brown in colour. The solution was then concentrated to a small volume, cooled to room temperature and on adding cold water to this solution, a granular reddish-brown compound separated out. After refrigeration for several hours, the precipitated compound was collected on a filter, washed with water and alcohol and then dried in a desiccator over fused calcium chloride.

The substance forms reddish-brown powder which is insoluble in water, slightly soluble in hot alcohol, acetone, benzene and chloroform, but is completely soluble in hot dimethyl-formamide producing a deep brownish-red solution. It is quite stable in dilute alkali, but is appreciably decomposed by dilute hydrochloric acid on heating.

Analysis:

0.03230 g of the substance gave 0.00820 g of anhydrous manganous sulphate.

Manganese = 9.25%
0.01550 g of the substance gave 1.2 ml. of nitrogen at 25°C and 754.6 mm pressure of mercury.

Nitrogen = 8.81%

Calculated for \([\text{MnL}.2\text{H}_2\text{O}]_n\), \(L = \text{C}_{32}\text{H}_{20}\text{O}_{4}\text{N}_4\)

Manganese = 9.43%
Nitrogen = 9.60%

Zinc(II)-5-formyl-8-hydroxy quinoline-benzidine:

The greenish-yellow solution obtained by mixing hot dimethyl-formamide solutions of 5-formyl-8-hydroxy quinoline (0.8 g), zinc acetate dihydrate (0.5 g) and benzidine (0.4 g) was refluxed for two hours. The clear solution gradually became turbid during the reflux. At the end of the reflux, the reaction mixture was concentrated to a small volume on waterbath and filtered hot to remove the trace amount of solid which separated out. The filtrate was cooled to room temperature and cold water was added to it, when a granular orange compound precipitated out. This was allowed to settle for several hours and then collected on a filter, washed with water and alcohol and finally dried in a desiccator over fused calcium chloride.

The substance forms yellowish-orange powder which is insoluble in water, alcohol, acetone, benzene and chloroform, but is appreciably soluble in hot dimethyl-formamide. It is
stable in dilute alkali and is only slightly decomposed by mineral acids on heating.

**Analysis:**

0.04535 g of the substance gave 0.01250 g of zinc-ammonium phosphate.

\[ \text{Zinc} = 10.10\% \]

0.0200 g of the substance gave 1.54 ml. of nitrogen at 24°C and 757.6 mm. pressure of mercury.

\[ \text{Nitrogen} = 8.82\% \]

Calculated for \( \left[ \text{ZnL}_2\text{H}_2\text{O} \right]_n \), \( \text{L} = \text{C}_3\text{H}_2\text{O}_2\text{N}_4 \)

\[ \text{Zinc} = 11.03\% \]

\[ \text{Nitrogen} = 9.43\% \]

**Cadmium(II)-5-formyl-8-hydroxy quinoline-benzidine:**

Hot dimethyl-formamide solutions of 5-formyl-8-hydroxy quinoline (0.8 g), cadmium acetate dihydrate (0.6 g) and benzidine (0.4 g) were mixed together, when an orange-yellow solution resulted. The reaction mixture was refluxed for two hours and then concentrated to a small volume on waterbath. It was cooled to room temperature and cold water was finally added to it with stirring, when an orange-yellow compound separated out. After refrigeration for several hours, the precipitated compound was collected on a filter, washed with water and alcohol and finally dried in a desiccator over fused calcium chloride.
The compound forms orange-yellow powder which is insoluble in water, benzene and chloroform in the cold, but is very slightly soluble in hot alcohol and acetone. It is completely soluble in hot dimethyl-formamide giving an orange-yellow solution. It is stable in alkali, but is appreciably decomposed by dilute mineral acids on heating.

Analysis:

0.03340 g of the substance gave 0.02240 g of cadmium oxinate.

\[
\text{Cadmium} = 18.82\% 
\]

0.01615 g of the substance gave 1.28 ml. of nitrogen at 24°C and 756.6 mm. pressure of mercury.

\[
\text{Nitrogen} = 9.06\% 
\]

Calculated for \([\text{Cdl}_{\text{L}}]_n\), \(L = \text{C}_{32}\text{H}_{20}\text{O}_{2}\text{N}_4\)

\[
\text{Cadmium} = 18.60\% 
\]

\[
\text{Nitrogen} = 9.26\% 
\]

Uranyl-5-formyl-8-hydroxy quinoline-benzidine:

A deep red solution resulted on mixing hot dimethyl-formamide solutions of 5-formyl-8-hydroxy quinoline (0.8 g), uranyl acetate dihydrate (1.0 g) and benzidine (0.4 g). The reaction mixture was refluxed for two hours and the resultant dark red solution was concentrated to a small volume.
on waterbath. It was cooled to room temperature and cold water was added to it with stirring when a deep red compound separated out. After refrigeration for several hours, the precipitated deep red compound was collected on a filter, washed with water and alcohol and finally dried in a desiccator over fused calcium chloride.

The substance forms deep red powder which is insoluble in water, benzene and chloroform, very slightly soluble in hot alcohol and acetone, but is appreciably soluble in hot dimethyl-formamide producing a bright red solution. It is stable in dilute hot alkali, and is only slightly decomposed by mineral acids on heating.

Analysis:

0.02420 g of the substance gave 0.0086 g of $\text{U}_3\text{O}_8$.

Uranium = 30.14%

0.02425 g of the substance gave 1.4 ml. of nitrogen at 24°C and 759.4 mm. pressure of mercury.

Nitrogen = 6.63%

Calculated for $\left[\text{UO}_2\cdot\text{L}\right]_n$, $\text{L} = \text{C}_{32}\text{H}_{20}\text{O}_2\text{N}_4$

Uranium = 31.23%

Nitrogen = 7.35%