PART II.

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INTRODUCTION TO THE PRESENT WORK.
Introduction to the present work

Section A: Metal chelate-complexes of Schiff's bases obtained from dicarboxylic acid dihydrazides and diacetyl.

The metallic chelates of the condensation products of aliphatic dicarboxy-dihydrazides with aldehydes and ketones have not been studied in details. Sacconi reported the nickel(II) chelates of the condensation products of aliphatic dicarboxy-dihydrazides with salicylaldehyde, ortho-hydroxy-naphthaldehyde, ortho-amino benzaldehyde etc. But no such study appears to have been made about the polymeric ligands obtained by the condensation of dicarboxy-dihydrazides with aldehydes and ketones. The present study was undertaken with a view to explore the possibility of synthesizing polymeric ligands through the condensation of aliphatic dicarboxy-dihydrazides with \( \alpha \)-diketones, such as diacetyl and also of incorporating metallic ions into the pre-formed polymeric organic ligands.

Oxalylldihydrazide was condensed with diacetyl by refluxing the two components in aqueous alcoholic medium to give a product of the Schiff's base-type which from elemental analyses has been found to be a pentamer with acetyl end-groups. The Schiff's base so produced may have the tautomeric formula (A):
The presence of acetyl end-groups has been qualitatively shown by reaction of (A) with a primary amine such as methylamine whereby the corresponding imine has been formed and the structure (B) has been suggested for this product.

The insolubility of the Schiff's base (A) in common organic solvents like acetone, chloroform, benzene etc. did not permit the determination of its molecular weight by usual cryoscopic methods. The substance was completely soluble in aqueous ammonia-alcohol mixture and hence for the purpose of metallizing the polymeric Schiff's base, this mixed solvent was chosen. Highly coloured metal-chelates of the polymeric
Schiff's base (A) have been prepared by refluxing on the waterbath, a mixture of the Schiff's base and acetate salt of bivalent metals like Cu(II), Ni(II), Zn(II) and Cd(II) in aqueous ammoniacal alcohol media. All the metal-chelates were precipitated in highly dispersed state during the reflux and a considerable time was required for their coagulation which was facilitated by refrigerating overnight. From elemental analyses, the metal-chelates closely agree with the general formulation: 

$$H_2C.OC\left[LM.2H_2O\right]_5CO.CH_3$$

where $M = Cu(II), Ni(II), Zn(II)$ and Cd(II) and $LH_2$ represents a unit condensation product of one mole of oxalylidihydrazide and one mole of diacetyl. Agreement between the calculated and the observed values of elemental analyses have been greatly improved by assuming two water molecules to be associated per metal atom. 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. Evaluation of the water content of these compounds supports this assumption. The compounds may be considered as the metal-chelates of the preformed polymeric Schiff's base and the following structure (C) appears highly probable for them, taking for granted that the Schiff's base reacts in its enolic form:
where M = Cu(II), Ni(II), Zn(II) and Cd(II).

The extreme insolubility of all the metal-chelates in common organic solvents like alcohol, acetone, chloroform and benzene points to their polymeric structures proposed.

Thermal stability studies of the polymeric metal-chelates up to the onset of decomposition point indicate that they are thermally quite stable and the temperatures at which the compounds start decomposition range from 300-325°C. The weight-loss percentages at different temperatures for the metal-chelates reveal the following facts:

(a) The weight-loss percentage at temperature between 120-125°C corresponds closely to the water content of the metal-chelates.
(b) Zinc(II) compound is thermally the most stable one as shown by the minimum weight-loss percentage viz. 15% (at 300°C) before decomposition, while the copper(II) compound is thermally the least stable, the percentage weight-loss being 57.5% (at 300°C) with decomposition. The latter observation can be accounted for by the fact that Zn(II) with completely filled 3d orbitals is known to be in a more stable energy state than Cu(II).

In the thermal decomposition curves drawn by plotting the weight-loss percentages against temperatures, the initial slopes probably represent the volatilisation of water molecules associated with the metal atom in the polymer; thus the Zn(II) polymer lost approximately 12% of its weight prior to the sharp break in the curve and this value agrees closely with the calculated 12.6% water content in the polymeric molecule, CH₃CO.[ZnL₂H₂O]₅CO.CH₃. After this initial weight-loss, a rather sharp break occurred in each of the curves, signifying the onset of a decomposition process.

Although the exact molecular weights of these metal-chelate polymers could not be determined for lack of their solubility in common organic solvents, the geometry of the ligand molecule, the extreme insolubility of the compounds, their characteristic colours and great thermal stability seem to suggest in almost all probability that they are the metal-chelates of the preformed polymeric Schiff's base.
Section B: Metal chelate-complexes of the Schiff's base obtained from salicylhydrazide and diacetyl.

A report on the preparations and properties of the metal-chelates of the condensation product of salicylhydrazide and diacetyl has been given in this section of the thesis.

Salicylhydrazide has been condensed with diacetyl by refluxing the components in alcoholic medium to give a product of the Schiff's base-type which, as evident from its elemental analyses, conforms to the composition corresponding to the compound formed by the condensation of one molecule of diacetyl with two molecules of salicylhydrazide through elimination of two molecules of water. As in the case of the condensation product of diacetyl and carboxylic acid hydrazide, this compound may also be represented by the structure (D) which is capable of existing in the tautomeric form (E) as well:

![Chemical Structures]

(D)

(E)
The study of the metallic chelates of this ligand reveals that in forming the complexes, it reacts in the tautomeric 'enol' form.

The metallic complexes were obtained by heating on waterbath a mixture of alcoholic solutions of the metal acetate and a solution of the ligand in aqueous ammonia till the smell of ammonia subsided. The metallic chelates were precipitated as highly coloured amorphous products, insoluble in water, slightly soluble in hot alcohol and benzene, but easily soluble in chloroform. They are also soluble in dilute alkali solution on warming when ammonia is evolved. Complex salts of bivalent metallic ions like Cu(II), Ni(II), Zn(II) and Cd(II) of this ligand have been prepared, but those of cobaltous, manganous and uranyl ions could not be isolated in the pure state. This is probably due to the very condition of preparation viz. the ammoniacal medium, which prevented their formations. All the metallic complexes isolated correspond to the empirical formula $ML_22NH_3$ where $LH_2$ represents a molecule of the ligand and $M = Cu(II), Ni(II), Zn(II)$ and $Cd(II)$; but the determination of the molecular weights of the metallic chelates by elevation of boiling points of the chloroform solutions point to their dimeric formula. These are, therefore, represented by the following structure (F), the ligand exhibiting bidentate function:
where \( M = \text{Cu}(\text{II}), \text{Ni}(\text{II}), \text{Zn}(\text{II}) \) and \( \text{Cd}(\text{II}) \).

The deep brown copper(II) compound with a magnetic moment 1.84 B.M. is most probably a true penetration complex with \( \text{dsp}^2 \) hybrid bonds. The orange-red nickel(II) complex is diamagnetic and is probably planar with \( \text{dsp}^2 \) hybrid bonds. Zinc(II) and cadmium(II) form deep yellow diamagnetic complexes as expected.
Section C: **Metal chelate-complexes of thiosemicarbazone of pyruvic acid.**

Gringras et al.\(^{16}\) studied in detail the chelate-forming capacity of the thiosemicarbazones of some diketones. The present study was undertaken with a view to explore the possibility of preparing metallic chelates with the thiosemicarbazone of an α-keto acid viz. pyruvic acid.

The thiosemicarbazone of pyruvic acid was obtained in the form of yellow needle-shaped crystals (m.p. 176°C) by refluxing the two components in aqueous alcohol. This Schiff’s base-type product is insoluble in water, but soluble in alcohol and other organic solvents. The thiosemicarbazone may exist in the following two tautomeric forms (G):

\[
\begin{align*}
 & \text{H}_3\text{C} - \overset{\equiv}{\text{C}} - \overset{\equiv}{\text{N}} - \overset{\equiv}{\text{N}} - \overset{\equiv}{\text{C}} - \overset{\equiv}{\text{NH}_2} \\
 & \text{COOH} \quad \text{S} \quad \text{SH}
\end{align*}
\]

\[(G)\]

The ligand reacts in its tautomeric 'thiol form' with the chloride, sulphate or acetate salts of Cu(II), Ni(II), Co(II), Mn(II), Fe(II), Fe(III), Zn(II) and Cd(II) in aqueous alcoholic
medium, yielding metal-chelates with characteristic colours. From elemental analyses, the metal-chelates agree to the general composition $ML_2$, where LH represents a molecule of thiosemicarbazone of pyruvic acid and $M = \text{Cu(II), Ni(II), Co(II), Mn(II), Zn(II) and Cd(II)}$; the ferrous complex, however, corresponds to the composition $[\text{FeL}_2(\text{H}_2\text{O})_2]$ and the ferric complex to the composition $[\text{FeL}_2(\text{H}_2\text{O})(\text{OH})]$. These metal chelates are all insoluble in water. They are soluble in dilute alkali which probably seems to suggest that $-\text{COOH}$ group in the ligand molecule is unattached and the thiosemicarbazone exhibits bidentate function in forming these metal-chelates. Thus the metal-chelates of the composition $ML_2$ may be structurally represented by (H):

\[
\begin{align*}
\text{H}_3\text{C} & - \text{C} = \text{N} - \text{N} = \text{C} - \text{NH}_2 \\
\text{H}_3\text{C} & - \text{C} = \text{N} - \text{N} = \text{C} - \text{NH}_2 \\
\text{COOH} &
\end{align*}
\]

The ferrous complex and the ferric complex may be structurally represented by (I) and (J) respectively:
The cobaltous complex can be oxidised by passing air for several hours through its ammoniacal solution to yield a brownish-red crystalline compound which corresponds to the composition \( \text{NH}_4\left[\text{CoL}_2\right] \). This compound is highly soluble in water and the equivalent conductivity value agrees closely with that of 1:1 electrolyte, thus supporting the ionic nature of the complex species. The compound liberates ammonia on heating with dilute alkali. Based on these facts, it seems that
the ligand exhibits here tridentate function and structurally the cobalt(III) complex may be represented as (K):

\[
\begin{align*}
&\text{H}_3\text{C} - \text{C} = \text{N} - \text{N} = \text{C} - \text{NH}_2 \\
&\text{COO} \quad \text{Co} \quad \text{S} \\
&\text{COO} \quad \text{S} \\
&\text{H}_3\text{C} - \text{C} = \text{N} - \text{N} = \text{C} - \text{NH}_2
\end{align*}
\]

(K)

The magnetic moment values of the metal-chelates correspond more or less to those of the free metal ions except the cobalt(III) complex which is diamagnetic. Thus the cobaltic complex is obviously an inner metallic one with $d^{2}sp^{3}$ hybrid bonds and the others are outer-level or associated type of complexes, resonating with ionic ones.
EXPERIMENTAL

Section A: Metal chelate-complexes of the Schiff's base derived from dicarboxylic acid dihydrazides and diacetyl.

Preparation of oxalylhydrazide:

Diethyl oxalate (0.1 mole, 14.6 g) and hydrazine hydrate (0.2 mole, 12.5 g, 80% solution) were mixed together in 25 ml. of alcohol. The reaction mixture was heated on waterbath for ten minutes and then cooled to room temperature. It was finally refrigerated for an hour when shining white solid separated out. The solid product was collected on a filter, washed with aqueous alcohol and then dried in air.

Preparation of the Schiff's base:

Oxalylhydrazide (0.1 mole, 11.8 g) and diacetyl (a slight excess over 0.1 mole, 9.0 g) were refluxed in aqueous alcohol on a waterbath. After about 30 minutes, a light yellow solid formed. The reaction mixture was heated for an additional one hour and then allowed to cool to room temperature. The product was collected on a filter, washed with aqueous alcohol and dried in a desiccator over fused calcium chloride.
The substance forms light yellow amorphous powder which is insoluble in common solvents like water, acetone, benzene and chloroform, very slightly soluble in hot alcohol and dimethyl-formamide, but completely soluble in hot dilute ammonia.

Analysis:

0.00775 g of the substance gave 2.14 ml. of nitrogen at 31.5°C and 744.2 mm. pressure of mercury.

Nitrogen = 30.32%

Calculated for $\text{CH}_3\text{CO} \left[\text{C}_6\text{H}_5\text{O}_2\text{N}_4\right]_5 \text{CO} \cdot \text{CH}_3$

Nitrogen = 30.24%

Qualitative detection of the acetyl end-groups of the polymeric Schiff's base:

To a suspension of the Schiff's base in alcohol, an aqueous solution of methylamine was added dropwise until a clear yellow solution was obtained. The resultant solution was refluxed on the waterbath for an hour and then concentrated to a small volume on waterbath. It was then left at room temperature for some time when a yellow solid separated out. This was collected on a filter, washed repeatedly with water and finally dried in a desiccator over fused calcium chloride.
The substance forms yellow powder which is insoluble in water, but sparingly soluble in hot benzene, and completely soluble in hot alcohol and chloroform.

**Analysis:**

0.00810 g of the substance gave 2.36 ml. of nitrogen at 31.5°C and 748.4 mm. pressure of mercury.

Nitrogen = 32.17%

Calculated for \( CH_3.C=NH_3 \left[ C_6H_8O_2N_4 \right] 5 H_2O.N=C.CH_3 \)

Nitrogen = 32.36%

**Preparation of the metal-chelates of the polymeric Schiff's base:**

**Copper(II)-oxalyldihydrazide-diacetyl:**

To a suspension of the Schiff's base (0.001 mole, 0.9 g) in alcohol, aqueous ammonia was added dropwise while heating on waterbath until a clear yellow solution was obtained. To this hot yellow solution of the reagent was added an aqueous alcoholic solution of copper acetate monohydrate (0.005 mole, 1.0 g) when a deep brown solution accompanied by the formation of a precipitate of the same colour was obtained. The reaction mixture was refluxed for 3 hours on the waterbath and during the reflux, the quantity
of the precipitation of the deep brown compound increased gradually, but it remained dispersed throughout the solution. After the reflux, the reaction mixture was concentrated to a small volume on the waterbath and then refrigerated overnight. The solid product, thus settled, was collected by filtration, washed with water and alcohol and then dried in a desiccator over fused calcium chloride.

The substance forms deep brown powder which is insoluble in water, alcohol, acetone, benzene and chloroform, very slightly soluble in hot dimethyl-formamide. It is decomposed by hot dilute alkali and mineral acids.

**Analysis:**

0.02225 g of the substance required 1.6 ml. of 0.0477(N) sodium thiosulphate solution.

**Copper = 21.80%**

0.00910 g of the substance gave 1.7 ml. of nitrogen at 31°C and 743 mm. pressure of mercury.

**Nitrogen = 20.51%**

0.02310 g of the substance lost 0.0030 g in its weight at 120°C.

**Water = 12.99%**
Nickel(II)-oxalylldihydrazide-diacetyl:

To a hot solution of the Schiff's base (0.001 mole, 0.9 g) in aqueous alcoholic ammonia (made as above) was added an alcoholic solution of nickel acetate tetrahydrate (0.005 mole, 1.2 g). The resultant bright-red solution was refluxed on the waterbath for 3 hours and during the reflux, a bright red solid separated out. This remained dispersed throughout the solution. After the reflux, the reaction mixture was concentrated to a small volume on the waterbath and then refrigerated overnight. The bright-red compound, thus settled, was collected by filtration, washed with water and alcohol and then dried in a desiccator over fused calcium chloride.

The compound forms bright-red powder which is insoluble in cold and hot water, alcohol, acetone, benzene, chloroform and dimethyl-formamide. With hot dilute alkali, the compound gives a deep red solution, but on heating with dilute mineral acids, it decomposes.
Analysis:

0.01525 g of the substance gave 0.01600 g of nickel dimethyl-glyoxime.

Nickel = 21.31%

0.00875 g of the substance gave 1.58 ml. of nitrogen at 32°C and 741.2 mm. pressure of mercury.

Nitrogen = 19.72%

0.02650 g of the substance lost 0.00335 g in its weight at 120°C.

Water = 12.59%

Calculated for $\text{CH}_3.00 \left[\text{C}_6\text{H}_6\text{O}_2\text{N}_4\text{Ni.}2\text{H}_2\text{O}\right]_5 \text{CO.CH}_3$

Nickel = 21.13%
Nitrogen = 20.16%
Water = 12.95%

Zinc(II)-oxalylidihydrazide-diacetyl:

To a hot solution of the Schiff's base (0.001 mole, 0.9 g) in aqueous alcoholic ammonia was added an alcoholic solution of zinc acetate dihydrate (0.005 mole, 1.1 g). The resultant orange-yellow solution was refluxed for 3 hours and during the reflux, a light orange-yellow solid product separated out, which remained dispersed throughout the solution. After the reflux, the reaction mixture was concentrated to a small volume on the waterbath and then refrigerated.
overnight. The orange-yellow compound, thus settled, was collected on a filter, washed with water and alcohol and finally dried in a desiccator over fused calcium chloride.

The substance forms orange-yellow amorphous powder which is insoluble in water, acetone, benzene, chloroform and hot dimethyl-formamide, but very slightly soluble in hot alcohol. It is decomposed by heating with alkali and mineral acids.

Analysis:

0.01985 g of the substance gave 0.01230 g of zinc-ammonium phosphate.

Zinc = 22.72%

0.00825 g of the substance gave 1.44 ml. of nitrogen at 31°C and 740.6 mm. pressure of mercury.

Nitrogen = 19.10%

0.02200 g of the substance lost 0.00265 g in its weight at 120°C.

Water = 12.04%

Calculated for \( \text{CH}_3\text{CO}[\text{C}_6\text{H}_6\text{O}_2\text{N}_2\text{Zn}.2\text{H}_2\text{O}] \cdot 5\text{CO.CH}_3 \)

Zinc = 22.98%

Nitrogen = 19.67%

Water = 12.65%
Cadmium(II)-oxalyldihydrazide-diacetyl :

To a hot solution of the Schiff's base (0.001 mole, 0.9 g) in aqueous alcoholic ammonia was added an alcoholic solution of cadmium acetate dihydrate (0.005 mole, 1.3 g), when an immediate precipitation of a light yellow compound occurred. The solid product remained dispersed throughout the solution. The reaction mixture was refluxed for 3 hours and then concentrated to a small volume on the waterbath and finally refrigerated overnight. The light yellow compound, thus settled, was collected by filtration, washed with water and alcohol and then dried in a desiccator over fused calcium chloride.

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

Analysis :

0.04730 g of the substance gave 0.05695 g of cadmium oxinate.

Cadmium = 33.81%
0.02380 g of the substance gave 3.5 ml. of nitrogen at 30.5°C and 740.6 mm. pressure of mercury.

Nitrogen = 16.13%

0.02810 g of the substance lost 0.0030 g in its weight at 120°C.

Water = 10.68%

Calculated for $\text{CH}_3\text{CO}\left[\text{C}_6\text{H}_6\text{O}_2\text{N}_4\text{Cd}\cdot\text{H}_2\text{O}\right]_5\text{CO.CH}_3$

Cadmium = 33.89%
Nitrogen = 16.89%
Water = 10.85%
Section B: Metal chelate-complexes of the Schiff's base derived from salicylhydrazide and diacetyl:

Preparation of salicylhydrazide:

Methyl salicylate (15.2 g) and hydrazine hydrate (6.2 g, 80% solution) were mixed together in alcohol and the resultant solution was refluxed on the waterbath for an hour. After the reflux, the solution was cooled to room temperature and then refrigerated for several hours. The white crystalline solid which separated out was filtered, washed with aqueous alcohol and then dried in air. The crude sample of salicylhydrazide was recrystallised from alcohol.

Preparation of the Schiff's base:

To a hot alcoholic solution of salicylhydrazide (0.1 mole, 15.2 g) was added diacetyl (0.05 mole, 4.3 g) and the reaction mixture was refluxed on the waterbath. After about 30 minutes, a white solid with a yellowish-tinge was formed. The reflux was continued for an additional one hour and then the reaction mixture was allowed to cool to room temperature. The product was collected on a filter, washed with alcohol, and then dried in a desiccator over fused calcium chloride.
The base forms white powder with a yellowish-tinge which chars above 195°C. It is insoluble in water, slightly soluble in hot alcohol, sparingly soluble in benzene, but is completely soluble in aqueous ammonia giving an yellow solution.

Analysis:

0.01140 g of the substance gave 1.64 ml. of nitrogen at 33°C and 740.6 mm. pressure of mercury.

\[
\text{Nitrogen} = 15.64\% 
\]

Calculated for \( \text{C}_{16}\text{H}_{18}\text{O}_4\text{N}_4 \)

\[
\text{Nitrogen} = 15.82\% 
\]

Copper(II)-salicylhydrazide-diacetyl:

To a suspension of the Schiff's base (1.7 g) in alcohol, aqueous ammonia was added dropwise with stirring until a clear yellow solution was obtained. To this yellow solution was added a solution of copper acetate monohydrate (1.0 g) in aqueous ammonia. The resultant brown solution on heating on the waterbath became deep brown in colour from which a deep brown compound separated out, when the excess ammonia was boiled off from the solution. The reaction mixture was cooled to room temperature and the precipitated compound was filtered, washed with water and alcohol and then dried in a desiccator.
The substance forms deep brown powder which is insoluble in water, slightly soluble in hot alcohol and benzene, but is appreciably soluble in chloroform. It is soluble in dilute alkali and the resultant solution on heating liberates ammonia.

The substance is paramagnetic ($\mu_b = 1.34$).

**Analysis:**

0.02040 g of the substance required 2.1 ml. of 0.0228(N) sodium thiosulphate solution.

Copper = 14.92%

0.01155 g of the substance gave 1.86 ml. of nitrogen at 20°C and 755 mm. pressure of mercury.

Nitrogen = 18.14%

Calculated for $[\text{C}_{18}\text{H}_{16}\text{O}_{4}\text{N}_{4}\text{Cu}.2\text{NH}_3]$:

Copper = 14.13%

Nitrogen = 18.69%

**Nickel(II)-salicylhydrazide-diacetyl**:

To a solution of the Schiff's base (1.7 g) in aqueous alcoholic ammonia (prepared as before), was added a solution of nickel acetate tetrahydrate (1.2 g) in aqueous ammonia. The resultant deep red solution was heated on the
waterbath for about half an hour when a bright orange-red compound separated out. The reaction mixture was then cooled to room temperature and the orange-red product was collected on a filter, washed with aqueous alcohol and dried in a desiccator over fused calcium chloride.

The substance forms orange-red powder which is insoluble in water, slightly soluble in hot alcohol and benzene, moderately soluble in chloroform, but is completely soluble in hot dimethyl-formamide giving a red solution. It liberates ammonia on heating with dilute alkali. It is decomposed by mineral acids.

The substance is diamagnetic.

Analysis:

0.01710 g of the substance gave 0.01055 g of nickel dimethyl-glyoxime.

Nickel = 12.53%

0.01065 g of the substance gave 1.8 ml. of nitrogen at 27.5°C and 756.7 mm. pressure of mercury.

Nitrogen = 19.12%

Calculated for \[ \text{Ni} \cdot \text{C}_{18} \text{H}_{16} \text{O}_{4} \text{N}_{4} \text{Ni}.2\text{NH}_{3} \]

Nickel = 12.90%
Nitrogen = 18.89%
Zinc(II)-salicylhydrazide-diacetyl:

An alcoholic ammoniacal solution of the Schiff's base (1.7 g) and aqueous ammonia solution of zinc acetate dihydrate (1.1 g) were mixed together, when a bright yellow solution accompanied by a precipitation of the same colour was obtained. The reaction mixture was heated on the waterbath for about half an hour in order to remove the excess of ammonia, when a bright yellow solid product settled down. This was cooled to room temperature and the solid was collected by filtration, washed with water and alcohol and then dried in a desiccator over fused calcium chloride.

The substance forms bright yellow powder which is insoluble in water, slightly soluble in hot alcohol and benzene, but moderately soluble in hot chloroform. The solution of the compound in dilute alkali liberates ammonia on heating. It is decomposed by hot dilute mineral acids.

The substance is diamagnetic.

Analysis:

0.02175 g of the substance gave 0.00845 g of zinc-ammonium phosphate.

\[
\text{Zinc} = 14.24\%
\]

0.01155 g of the substance gave 1.96 ml. of nitrogen at 30.5°C and 740.4 mm. pressure of mercury.

\[
\text{Nitrogen} = 18.31\%
\]
Calculated for $\left[ C_{18}H_{16}O_4N_4Zn\cdot 2NH_3 \right]$

Zinc = 14.49%
Nitrogen = 18.61%

**Cadmium(II)-salicylhydrozide-diacetyl**

To a solution of the Schiff's base (1.7 g) in alcoholic ammonia was added a solution of cadmium acetate dihydrate (1.3 g) in aqueous ammonia. A deep yellow solution accompanied by a precipitation of the same colour was obtained. The reaction mixture, after heating on the waterbath for about half an hour, was allowed to cool to room temperature. The deep yellow compound which settled down was collected on a filter, washed with water and alcohol and then dried in a desiccator over fused calcium chloride.

The substance forms deep yellow powder which is insoluble in water, slightly soluble in hot alcohol and benzene, but is completely soluble in hot chloroform producing an yellow solution. It is also soluble in dilute alkali and the solution liberates ammonia on heating. The compound is decomposed by heating with mineral acids.

The substance is diamagnetic.
Analysis:

-0.02645 g of the substance gave 0.02155 g of cadmium oxinate.

Cadmium = 22.88%

0.01680 g of the substance gave 2.54 ml. of nitrogen at 31.5°C and 744.4 mm. pressure of mercury.

Nitrogen = 16.61%

Calculated for $\left[\text{C}_{18}\text{H}_{16}\text{O}_4\text{N}_4\text{Cd}.2\text{NH}_3\right]$:

Cadmium = 22.55%

Nitrogen = 16.86%
Section C: Metal chelate-complexes of thiosemicarbazone of pyruvic acid.

Preparation of thiosemicarbazone of pyruvic acid:

To a suspension of thiosemicarbazide (0.1 mole, 9.1 g) in water, dilute acetic acid was added dropwise while heating on the waterbath until a clear solution was obtained. To this solution of thiosemicarbazide was added pyruvic acid (0.1 mole, 8.8 g) followed by the addition of a few ml. of alcohol. The resultant pale yellow solution was refluxed for 2 hours on the waterbath and the colour of the solution became intense yellow during the reflux. After the reflux, the yellow solution was concentrated to a small volume on the waterbath, cooled to room temperature and then refrigerated for several hours. The yellow needle-shaped crystals which separated out, were collected on a filter, washed with aqueous alcohol and then dried in air.

The base forms yellow needle-shaped crystals which melts at 176-177°C. It is insoluble in water, benzene and chloroform, but is completely soluble in hot alcohol. It is decomposed on heating with strong mineral acids.

Analysis:

0.00960 g of the substance gave 2.24 ml. of nitrogen at 31°C and 750 mm. pressure of mercury.

Nitrogen = 25.86%
Copper(II) complex of thiosemicarbazone of pyruvic acid:

To a hot alcoholic solution of the Schiff's base (1.6 g) was added an aqueous solution of cupric chloride dihydrate (0.8 g) when a bluish-green solution was obtained. The resultant solution was warmed on the waterbath with stirring for 10 minutes and then left at room temperature when a pale blue compound separated out. This was filtered, washed with water and finally dried in a desiccator over fused calcium chloride.

The substance forms pale blue amorphous powder which is insoluble in water, benzene and chloroform, slightly soluble in hot alcohol, but is completely soluble in dilute alkali producing a bluish-green solution. It is decomposed on heating with mineral acids.

The substance is paramagnetic ($\mu = 1.96$)

Analysis:

0.01415 g of the substance required 1.6 ml. of 0.02365(N) sodium thiosulphate solution.

Copper = 17.00%
0.00720 g of the substance gave 1.44 ml. of nitrogen at 31.5°C and 749 mm pressure of mercury.

Nitrogen = 22.11%

Calculated for Cu(ClO₂N₃S)₂

Copper = 16.58%
Nitrogen = 21.90%

Nickel(II) complex of thiosemicarbazone of pyruvic acid:

Alcoholic solution of the Schiff's base (1.6 g) and aqueous alcoholic solution of nickel chloride hexahydrate (1.2 g) were mixed together when a light green product was formed which remained dispersed throughout the solution. The reaction mixture was heated on the waterbath for 10-15 minutes and then left at room temperature when a light green compound settled down. The product was collected on a filter, washed with water and alcohol and then dried in a desiccator over fused calcium chloride.

The substance forms light green amorphous powder which is insoluble in water, alcohol, benzene and chloroform, but is completely soluble in dilute alkali giving a greenish-yellow solution. It is appreciably decomposed on heating with mineral acids.

The substance is paramagnetic (μ₈ = 2.72).
Analysis:

0.02805 g of the substance gave 0.02110 g of nickel dimethyl-glyoxime.

Nickel = 15.28%

0.00840 g of the substance gave 1.7 ml. of nitrogen at 31°C and 750.2 mm. pressure of mercury.

Nitrogen = 22.44%

Calculated for $\text{Ni(C}_4\text{H}_6\text{O}_2\text{N}_3\text{S)}_2$

Nickel = 15.50%
Nitrogen = 22.18%

Cobalt(II) complex of thiosemicarbazone of pyruvic acid:

To a hot alcoholic solution of the Schiff's base (1.6 g) was added an aqueous solution of cobalt chloride hexahydrate (1.2 g) when there was an immediate precipitation of a pink-red compound. The reaction mixture was warmed on the waterbath for 5-10 minutes and then allowed to stand at room temperature. The pink-red compound, thus settled, was collected on a filter, washed with water and alcohol and then dried in a desiccator in vacuum over fused calcium chloride.

The substance forms pink-red powder which is insoluble in water and chloroform, very slightly soluble in hot alcohol and benzene, but is completely soluble in dilute alkali producing a brownish-red solution. It is decomposed by heating with mineral acids.
The substance is paramagnetic ($\mu_B = 4.55$).

**Analysis:**

0.03735 g of the substance gave 0.01505 g of anhydrous cobalt sulphate.

Cobalt = 15.34%

0.00945 g of the substance gave 1.86 ml. of nitrogen at 30.5°C and 749.6 mm. pressure of mercury.

Nitrogen = 21.85%

Calculated for $\text{Co(C}_4\text{H}_6\text{O}_2\text{N}_3\text{S)}_2$

Cobalt = 15.57%

Nitrogen = 22.17%

**Ammonium bis-(thiosemicarbazone of pyruvic acid) cobalt(III):**

To a suspension of the above mentioned cobalt(II) complex in distilled water, excess liquor ammonia was added when a clear red solution was obtained. Air was passed through the mixture for about 4 hours. The resultant deep red solution was first concentrated to half its original volume on steambath and then further concentrated in a vacuum desiccator over fused calcium chloride. A brownish-red crystalline compound separated out. This was filtered, washed with a little aqueous alcohol and dried in a desiccator over fused calcium chloride.
The compound is highly soluble in water, appreciably soluble in alcohol, but is insoluble in benzene and chloroform. On heating with dilute caustic soda solution, it liberates ammonia. The compound is decomposed by hot dilute mineral acids.

The substance is diamagnetic.

Analysis:

0.02115 g of the substance gave 0.0082 g of anhydrous cobalt sulphate.

Cobalt = 14.76%

0.01160 g of the substance gave 2.56 ml. of nitrogen at 29.5°C and 752.2 mm. pressure of mercury.

Nitrogen = 24.65%

Calculated for $\text{NH}_4\left[\text{Co(C}_4\text{H}_5\text{O}_2\text{N}_3\text{S})_2\right]$

Cobalt = 14.94% 
Nitrogen = 24.80%

Equivalent conductivity measurement:

A weighed amount of the substance was dissolved in water in a 25 ml. volumetric flask. The solution was taken in a conductivity cell whose cell constant was previously determined and the conductance measured. Equivalent conductivity was calculated using the formula:
\[ v = \frac{c \times 1000 \times \text{cell constant}}{\text{concentration in g equivalent/litre}} \]

\[ t = 29^\circ \text{C} \quad \text{Cell constant} = 1.95 \]

Concentration in g equivalent/litre = \(21.98 \times 10^{-4}\)

Conductance in water solution (c) = \(1.3 \times 10^{-4}\) mhos.

Equivalent conductivity = 115.3

The conductance measurement shows the presence of 1:1 electrolyte in water solution.

**Manganese(II) complex of thiosemicarbazone of pyruvic acid:**

Alcoholic solution of the Schiff's base (1.6 g) and aqueous solution of manganous chloride tetrahydrate (1.0 g) were mixed together when a light yellow solution accompanied by a precipitation of the same colour was obtained. The reaction mixture was heated on the waterbath for 5-10 minutes with stirring and then allowed to stand at room temperature. A light yellow granular precipitate settled down. This was collected on a filter, washed with water and alcohol and then dried in a desiccator over fused calcium chloride.

The substance forms light yellow powder which is insoluble in water, alcohol, methanol, benzene and chloroform, but is soluble in very dilute alkali giving a light yellow solution. It is decomposed by hot dilute mineral acids.

The substance is paramagnetic (\(\mu_\parallel = 5.4\)).
Analysis:

0.02465 g of the substance gave 0.01005 g of anhydrous manganous sulphate.

Manganese = 14.85%

0.01405 g of the substance gave 2.88 ml. of nitrogen at 31°C and 750.4 mm. pressure of mercury.

Nitrogen = 22.74%

Calculated for Mn(C_4H_6O_2N_3S)_2

Manganese = 14.67%
Nitrogen = 22.41%

Ferrous complex of thiosemicarbazone of pyruvic acid:

To a hot alcoholic solution of the Schiff's base (1.6 g) was added an aqueous solution of ferrous ammonium sulphate (1.9 g). The resultant deep brown solution was heated on the waterbath for 10 minutes with stirring and then left at room temperature, when gradually a shining deep brown compound separated out. This was filtered, washed with water and alcohol and then dried in a desiccator over fused calcium chloride.

The deep brown compound is insoluble in benzene and chloroform, slightly soluble in hot water and alcohol, but is highly soluble in very dilute caustic soda solution.
giving a reddish-brown solution. With excess of alkali, the compound decomposes with the precipitation of the metal-hydroxide. It is also decomposed on heating with mineral acids.

The substance is paramagnetic ($\mu_b = 4.9$).

**Analysis:**

Iron was estimated gravimetrically as $\text{Fe}_2\text{O}_3$ after decomposing the substance with a mixture of concentrated hydrochloric acid and nitric acid.

0.01980 g of the substance gave 0.0038 g of $\text{Fe}_2\text{O}_3$.

Iron = 13.44\%

0.00975 g of the substance gave 1.78 ml. of nitrogen at 30.5°C and 748.8 mm. pressure of mercury.

Nitrogen = 20.24\%

Calculated for $\text{Fe}((\text{C}_4\text{H}_6\text{O}_2\text{N}_3\text{S})_2(\text{H}_2\text{O})_2$:

Iron = 13.59\%
Nitrogen = 20.39\%

**Ferric complex of thiosemicarbazone of pyruvic acid:**

Hot alcoholic solution of the Schiff's base (1.6 g) and aqueous solution (pH = 3) of ferric chloride hexahydrate (1.3 g) were mixed together. The resultant deep red solution was heated on the waterbath for 15 minutes with
stirring and then left at room temperature when a shining pink-red compound separated out. This was collected on a filter, washed with water and alcohol and dried in a desiccator over fused calcium chloride.

The substance forms shining pinkish-red powder which is insoluble in water, benzene and chloroform, but is slightly soluble in hot alcohol. The compound is soluble in very dilute alkali producing a reddish solution, but with a slight excess of alkali, it is decomposed accompanied by the precipitation of ferric hydroxide. It is also decomposed by heating with mineral acids.

The substance is paramagnetic ($\mu_0 = 5.93$).

**Analysis:**

0.01555 g of the substance gave 0.00305 g of Fe$_2$O$_3$.

Iron = 13.73%

0.00675 g of the substance gave 1.26 ml. of nitrogen at 29°C and 752 mm. pressure of mercury.

Nitrogen = 20.88%

Calculated for $[\text{Fe}(\text{C}_4\text{H}_6\text{O}_2\text{N}_3\text{S})_2(\text{OH})(\text{H}_2\text{O})]$

Iron = 13.62%

Nitrogen = 20.44%
Zinc(II) complex of thiosemicarbazone of pyruvic acid:

On mixing a hot alcoholic solution of the Schiff's base (1.6 g) and an aqueous solution of zinc acetate dihydrate (1.1 g), a light yellow product dispersed throughout the solution was obtained. The reaction mixture was heated on the waterbath for 10 minutes and then allowed to stand at room temperature when the light yellow precipitate settled down. This was collected on a filter, washed with water and alcohol and then dried in a desiccator over fused calcium chloride.

The compound forms light yellow amorphous powder which is insoluble in water, alcohol, benzene and chloroform, but is soluble in very dilute caustic soda solution giving a light yellow solution. It is decomposed by heating with mineral acids.

The substance is diamagnetic.

Analysis:

Zinc was estimated gravimetrically as zinc oxinate.

0.04005 g of the substance gave 0.03800 g of zinc oxinate.

Zinc = 17.56%

0.01345 g of the substance gave 2.62 ml. of nitrogen at 25°C and 754.4 mm. pressure of mercury.

Nitrogen = 22.16%
Calculated for $\text{Zn(C}_4\text{H}_6\text{O}_2\text{N}_3\text{S)}_2$

Zinc = 16.96%

Nitrogen = 21.79%

Cadmium(II) complex of thiosemicarbazone of pyruvic acid:

A hot alcoholic solution of the Schiff's base (1.6 g) and an aqueous alcoholic solution of cadmium acetate dihydrate (1.3 g) were mixed together. A light yellow precipitate was formed. The reaction mixture was heated on the waterbath for 10-15 minutes and then cooled to room temperature when the solid product settled down. This was filtered, washed with water and alcohol and then dried in a desiccator over fused calcium chloride.

The substance forms light yellow amorphous powder which is insoluble in water, alcohol, benzene and chloroform, but is soluble in dilute caustic soda solution giving a light yellow solution. It is decomposed by hot dilute mineral acids.

The substance is diamagnetic.

Analysis:

0.02650 g of the substance gave 0.02390 g of cadmium oxinate.

Cadmium = 25.32%
0.01670 g of the substance gave 2.78 ml. of nitrogen at 24\(^{\circ}\)C and 756.6 mm. pressure of mercury.

Nitrogen = 19.05%

Calculated for \(\text{Cd(C}_4\text{H}_6\text{O}_2\text{N}_3\text{S})_2\)

Cadmium = 25.99%
Nitrogen = 19.43%