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# Analytical Behaviour of Biacetyl Monoxime Thiosemicarbazone towards Ni(II), Cu(II) and Pd(II) Metals

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Complexes of Ni(II), Cu(II) and Pd(II) have been synthesized with biacetyl monoxime thiosemicarbazone and structures of the complexes have been determined and found to be $ML_2$. This new reagent can be used over a large concentration range for gravimetric analysis. The reagent is sensitive and detective in the sense that they can be used to precipitate Pd in the stray acid medium. The reagent can be used for the estimation of Ni(II) in the presence of Pd(II) and Co(II) but not Cu(II).

**Key Words: Ni(II), Cu(II), Pd(II) Gravimetric, Biacetyl monoxime thiosemicarbazone.**

## INTRODUCTION

Schiff bases derived from condensation of semicarbazide and thiosemicarbazide with carbonyl compounds have been reported as complexing agents for various transition metal ions. In the present study we studied the biacetyl monoxime, thiosemicarbazone as a gravimetric reagent for Ni(II), Cu(II) and Pd(II).

**Synthesis of Biacetyl monoxime thiosemicarbazone:** About 1 g of biactyl monoxime was dissolved in 20 mL of alcohol and it was boiled for 2 h with a solution of 1 g thiosemicarbazide in 20 mL of water. It was then concentrated in vacuum and recrystallized from alcohol when pale yellow crystals of biacetyl monoxime thiosemicarbazone were obtained[1].

**Preparation of Monoammine biacetyl monoxime thiosemicarbazone Ni(II):** Nickel(II) sulphate was dissolved in minimum quantity of water and then treated with concentrated ammonium hydroxide to form the ammine complex. After filtration for any suspended impurity it was treated with an alcoholic solution of the ligand, stirred well and digested on a steam bath for 1/2 h, when a red precipitate separated out. The precipitate was filtered, washed with water and dried in air.

**Gravimetric estimation of Ni(II):** 4.784 g of $NiSO_4·7H_2O$ (BDH, AnalaR) was taken in a 1 L measuring flask and dissolved in distilled water. 1–2 mL of concentrated $H_2SO_4$ was added. The volume was made up to the mark with occasional shaking and left to stand for about 1 h to ensure that the solution has become homogeneous. From this solution 10 mL, 15 mL, 20 mL, . . . were taken out by means of pipette and added in a beaker. After that each set was diluted with distilled water to make the volume 100 mL.

The solution was heated with 6 N $NH_3$ so that a deep blue colouration was

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obtained and then 25% alcoholic solution of the ligand was added slowly with constant stirring. In practice 3 to 5 mL of ligand solution is needed for every 10 mg of Ni(II) ion present. Red precipitation formed immediately after the addition of the ligand solution. The whole mass was digested on a steam bath for 1 h. The complete precipitation was tested. Use of large excess of ligand is not preferred as the ligand itself is insoluble in water. Finally the complex was filtered through a previously washed, dried and weighed sintered glass crucible ($G_3$). The precipitate was washed several times with cold water. The precipitate was dried to constant weight in a hot air oven at 110°C and weighed as $[Ni(C_5H_8N_4OS)NH_3]$.

Similar experiment was performed for each solution and for higher accuracy triplicate experiments for each set were done. The amount of precipitate is recorded in Table-1.

TABLE-1

| Amount of metal (mg) | Wt. of nickel complex (mg) | Expected wt. of complex (mg) | Error (mg) | Wt. of copper complex (mg) | Expected wt. of complex (mg) | Error (mg) |
|---|---|---|---|---|---|---|
| 10 | 41.9 | 42.2 | 0.3 | 39.6 | 39.6 | 0.2 |
| 15 | 63.1 | 63.2 | 0.1 | 59.4 | 59.6 | 0.2 |
| 20 | 84.3 | 84.4 | 0.3 | 79.4 | 79.5 | 0.1 |
| 25 | 105.2 | 126.6 | 0.3 | 99.1 | 99.4 | 0.3 |
| 30 | 126.6 | 126.6 | 0.3 | 119.1 | 119.3 | 0.2 |
| 35 | 147.4 | 147.7 | 0.3 | 130.8 | 130.2 | 0.4 |
| 40 | 168.3 | 168.8 | 0.5 | 158.8 | 159.0 | 0.2 |
| 45 | 189.7 | 189.9 | 0.2 | 178.7 | 178.9 | 0.2 |
| 50 | 210.8 | 211.0 | 0.2 | 198.6 | 198.8 | 0.2 |
| 55 | 252.9 | 253.2 | 0.3 | 218.4 | 218.7 | 0.3 |
| 60 | 252.9 | 253.2 | 0.3 | 238.4 | 238.6 | 0.2 |
| 65 | 274.2 | 274.3 | 0.1 | 253.6 | 253.7 | 0.1 |
| 70 | 295.2 | 295.4 | 0.2 | 278.0 | 278.3 | 0.3 |
| 75 | 316.3 | 316.5 | 0.2 | 297.9 | 298.2 | 0.3 |
| 80 | 337.3 | 337.7 | 0.4 | 302.5 | 302.7 | 0.2 |
| 85 | 358.3 | 358.8 | 0.1 | 337.8 | 338.0 | 0.2 |
| 90 | 379.6 | 379.8 | 0.1 | 357.6 | 357.8 | 0.3 |
| 95 | 400.5 | 400.9 | 0.4 | 377.5 | 377.8 | 0.3 |
| 100 | 421.8 | 422.0 | 0.2 | 397.4 | 397.6 | 0.2 |

**Monoammine biactyl monoxime thiosemicarbazone Cu(II):** This compound was prepared by dissolving Cu(II) chloride in minimum quantity of water and alcohol (1 : 1) and then treated with 6 N ammonia solution so that a deep blue colouration of $[Cu(NH_3)_4]$ was obtained. It was then treated with an alcoholic solution of ligand and digested on a steam bath for some time and filtered. The filtrate on cooling deposited green crystals. It was washed with water and dried in an air oven and analyzed chemically.

The compound is insoluble in water but dissolves in methanol and ethanol.

**Gravimetric estimation of Cu(II) with bi-acetyl monoxime thiosemicarbazone:** 3.929 g of $CuSO_4 \cdot 5H_2O$ was taken in a 1000 mL measuring flask and dissolved in distilled water. 1–2 mL of concentrated $H_2SO_4$ was added. The volume was made up to the mark with occasional shaking and left to stand for about 1 h to ensure that the solution has become homogeneous. To this solution (6 N) ammonia was added till deep blue colour was obtained and it was treated with 2% alcoholic solution of ligand; in practice 3–5 mL of ligand solution is needed for every 10 mg of Cu(II) present. Precipitation started immediately. The mass was digested on a steam bath for about 1.5 h. The complete precipitation was tested. Use of large excess of ligand was avoided as the ligand itself is insoluble in water. Finally the complex was filtered through previously washed, dried and weighed sintered glass crucibles ($G_3$). The precipitate was washed several times with cold water. The precipitate $[Cu(C_5H_8N_4O_5)NH_3]$ was dried to constant weight. The amount of precipitate obtained in each set was recorded (Table-1). For accuracy triplicate experiments for each set were done.

**Monoaquobiacetyl monoxime thiosemicarbazone Pd(II):** Palladium chloride was dissolved in hydrochloric acid and the pH was adjusted to 4–5 with sodium acetate. The ligand was dissolved in alcohol and was added to the palladium solution with stirring when a yellow precipitate separated. out. The precipitate was filtered, washed with water, dried in air and analyzed.

The complex is insoluble in water but slightly soluble in organic solvents such as methanol, ethanol, chloroform.

**Gravimetric estimation of Pd(II) with Biacetyl monoxime thiosemicarbazone:** 1.666 g of $PdCl_2$ AR (Arror Methey Ltd.) was weighed accurately and transferred to a 1 L measuring flask. It was dissolved in minimum volume of 1 : 1 HCl. The solution contains 1 g of Pd(II) in 1 L, *i.e.*, each mL of solution contains 1 mg of the metal ion. 10 mL, 15 mL, . . . 100 mL of solution were taken in 500 mL beakers and the volume of each was made 100 mL. To 100 mL of this solution (each set) 2% solution of ligand was added slowly with constant stirring. About 3–5 mL of the ligand solution is nceded for every 10 mg of the metal present. After that 10% sodium acetate solution was added till the pH of the solution became 4–5. A yellow precipitate separated out. It was left overnight in the cold and then filtered through a previously washed, dried and weighed sintered glass crucible. The complex was dried in a hot air oven at 100°C and weighed as $[Pd(C_5H_9ON_4S) \cdot H_2O]Cl$ to constant weight. For accuracy triplicate experiments were done for each set. The amount of complex obtained was tabulated.

## RESULTS AND DISCUSSION

The analytical and conductivity data of the ligand and its metal complexes are given in Table-2

In case of the complex monoamine biacetyl monoxime thiosemicarbazone Ni(II), two bands have been observed at 15550 and 19970 $cm^{-1}$ which may be assigned to a $A_{1g} \longrightarrow A_{2g}$ and $A_{1g} \longrightarrow B_{1g}$ transition respectively, suggesting the square-planar nature for the complex. The compound is found to be diamagnetic in nature[2, 3].

In the electronic absorption spectra of the copper complex a single broad band is observed at about 16250 $cm^{-1}$ which may be assigned to be due to a combination of transitions $B_{1g} \longrightarrow A_{2g}$ and $B_{1g}$. The magnetic moment value is found to be 1.87 B.M. which suggests the square-planar geometry of the copper complex[2, 3].

TABLE-2
ANALYTICAL AND CONDUCTIVITY MEASUREMENT OF THE COMPLEXES

| Composition (Colour) | % Analysis: found (calculated) | | | | Conductivity ($ohm^{-1}$ $cm^{-2}$ mol) |
|---|---|---|---|---|---|
| | C | H | N | M | |
| $C_5H_{10}N_4OS$<br>(Yellow) | 34.40<br>(34.42) | 5.74<br>(5.72) | 32.18<br>(32.16) | — | — |
| $Ni(C_5H_8N_4OS)NH_3$<br>(Red) | 24.10<br>(24.22) | 4.56<br>(4.44) | 28.22<br>(28.26) | 23.58<br>(23.69) | 8.7 |
| $Cu(C_5H_8N_4OS)NH_3$<br>(Green) | 23.52<br>(23.76) | 4.48<br>(4.35) | 27.61<br>(27.72) | 25.09<br>(25.14) | 12.9 |
| $Pd(C_5H_9N_4OS)H_2O$<br>(Yellow) | 18.85<br>(19.25) | 2.98<br>(2.89) | 17.62<br>(17.78) | 33.51<br>(33.79) | 0.0 |

IR spectra H-bonded stretching frequency of free ligand is lowered by 30–35 $cm^{-1}$ on complexation, which indicates the involvement of O—H (phendic or oxalic) in the co-ordination.

Another band observed at 1200 $cm^{-1}$ in the ligand assigned to C—O stretching (phenolic) increased by about 15–20 $cm^{-1}$ in the complex; so the coordination might have taken place through the phenolic —O atom by deprotonation.

A sharp band observed in the ligand at 1640 $cm^{-1}$ assigned to C—N stretching band in free ligand shifted to lower frequency by about 20–10 $cm^{-1}$ confirming the coordination occurs through N-atom. A band observed at 980 $cm^{-1}$ in the ligand did not change on complexation which indicates that oxalic H-atom was not liberated on complexation. A band in the IR spectra of ligand at 1250 $cm^{-1}$ assigned to Ph-$OCH_3$ stretching vibration remained unchanged on complexation, suggesting the non-participation of methoxy oxygen atom in coordination. Two new bands appeared in IR spectra of complex at 535 and 480 $cm^{-1}$ respectively, which were due to ν(M—N) and ν(M—O) respectively[4, 5].

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