

## Dehydroacetic Acid Oxime as a New Ligand for Spectrophotometric Determination of Cobalt

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**Summary:** Dehydroacetic acid oxime (DAO) has been used as a ligand for spectrophotometric determination of cobalt. The reaction took place in a slightly acidic medium at pH 5.8 and Co-DAO complex showed  $\lambda_{max}$  at 645 nm and the absorption was observed to be free from any spectral interferences.

### Introduction

Azide ion [1], acetylacetone [2, 3], dithiocarbamates [4], dithizone [5], EDTA [6], ethylenediamine [7], nitroso-R-salt [8], xylenol orange [9], 8-hydroxyquinoline [10], thiocyanate [11] and dimethyl glyoxime are well known ligands. Other ligands such as aliphatic hydroxyoxime (II) are well known for the extraction of copper (II), nickel (II), cobalt (II) and iron (II) but the methods are tedious and lengthy in procedures.

There are some other simple organic reagents, such as dehydroacetic acid oxime (DAO), which have not been explored to a great extent for their metalcobaltic properties. The purpose of this work was to synthesize and evaluate the metal complexation reactions of this new reagent, which has oxygen as donor atom and shows its colored complex stability toward  $Co^{2+}$  ion. Thus, it seems better suited for spectrophotometric determination of different metal ions.

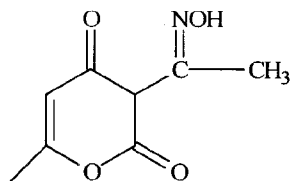


Fig. 1: Dehydroacetic acid oxime

### Results and Discussion

#### *Dehydroacetic Acid Oxime and Its Infra-Red Spectrum*

Infra-red spectrum [12] of DAO is usually simple with few peaks; O – H stretching mode occurs around  $3764\text{ cm}^{-1}$  due to free oxime. C – H stretching mode occurs around  $3144\text{ cm}^{-1}$ , which shows olefinic unsaturation. C = N or (C = O) stretching mode around  $1644\text{ cm}^{-1}$  may be due to oxime, ester or ketone. O – H deformation occurs around  $1416\text{ cm}^{-1}$ , which is a characteristic absorption of the oxime. C = O stretching mode, appearing around  $1262\text{ cm}^{-1}$ , is most probably due to the cyclic skeleton. H – C – H bending mode around  $1166\text{ cm}^{-1}$  occurs due to the methyl group. C – C vibration appears around  $1030\text{ cm}^{-1}$ . N – O stretching mode occurs around  $932\text{ cm}^{-1}$ , showing the presence of oxime. Finally =NOH group has a characteristic absorption appearing at  $682\text{ cm}^{-1}$ . This IR spectral information established that the compound was an oxime having structure as shown in Fig. 1. This further needed confirmation by elemental analysis, which was not conducted in this study.

#### *Absorption Spectra*

The complexing reagent, dehydroacetic acid oxime underwent reaction with cobalt chloride in a solution, preferably in acetonitrile solvent system. The complex formed was yellowish green in color and showed  $\lambda_{max}$  at 645 nm. The absorption spectra as

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shown in Fig. 2, showed a wavelength of maximum absorption for [Co(II)-DAO] complex. It also showed the wavelength of maximum absorption for DAO and cobalt chloride solutions separately at 265 nm, and 290 nm respectively. This clearly shows that all these species absorb at different wavelengths. The determination of cobalt is thus free from any spectral interference as far as the complexing reagent is concerned.

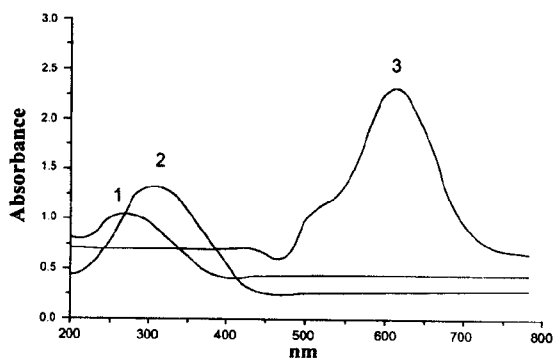


Fig. 2: Absorption spectra;  
1 - Dehydroacetic acid oxime (DAO)  
2 - Cobalt chloride, 3 - Co-DAO complex

#### Determination of Mole Ratio

Various mole concentrations of oxime were taken by taking 1 to 8 ml of  $2 \times 10^{-3}$  M oxime solution for each 2 ml of  $2 \times 10^{-3}$  M solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  separately in different 10 ml measuring flasks. The procedure was the same as described in the

experimental part. The absorbance was measured and plotted against the varying amounts of oxime used in the reaction and it was observed that the absorbance reached its maximum for the quantity of oxime when it was exactly double that of the metal (Co) content, see Fig. 3. This indicates that the reaction between the metal and the reagent was in 1: 2 mole ratio.

#### Effect of pH and Temperature on the Complex

The experiment showed that the reaction in a medium at pH 5.8 at more reliable, although the reaction in buffer of pH below 5.8 was equally good. The reaction was also found to greatly depend on temperature. A temperature of  $70^\circ\text{C}$  (by heating in a water bath) gave maximum absorbance and this temperature was maintained throughout experiments. The reaction was very fast and completed within few minutes with results being reproducible.

#### Stability of the Metal-Oxime Complex

The metal oxime complex is very stable. In order to establish that the complex formed is suitable and can be safely considered as analytically important for the estimation of cobalt, the absorbance of the complexes produced for varying concentrations of cobalt was measured at regular intervals of time. These absorbances remained unchanged even on long standing experiments.

Fig. 4 clearly showed that complexes irrespective of cobalt being at high or low concentration were independent of time and showed

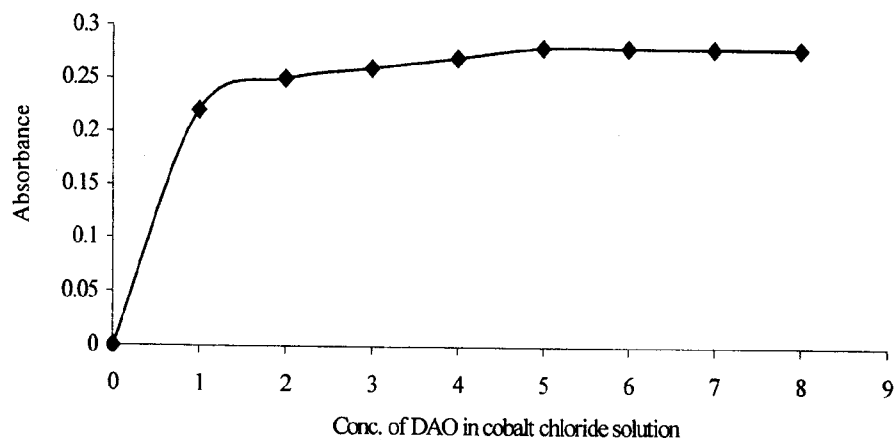


Fig.3: Determination of mole ratio in metal-ligand complexation reaction.

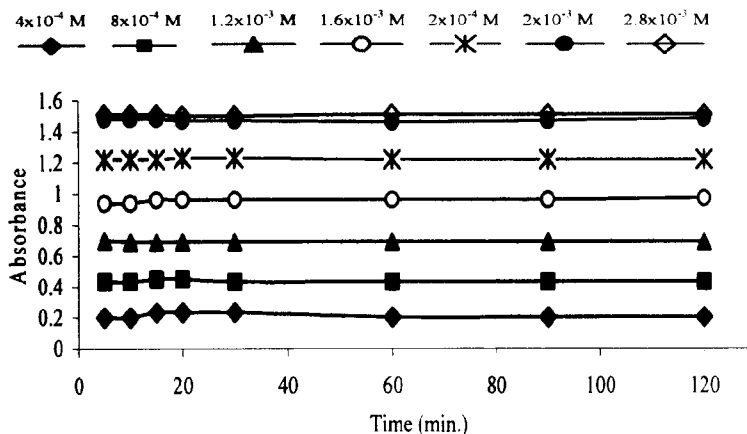


Fig. 4: Study of the stability of the metal ligand.

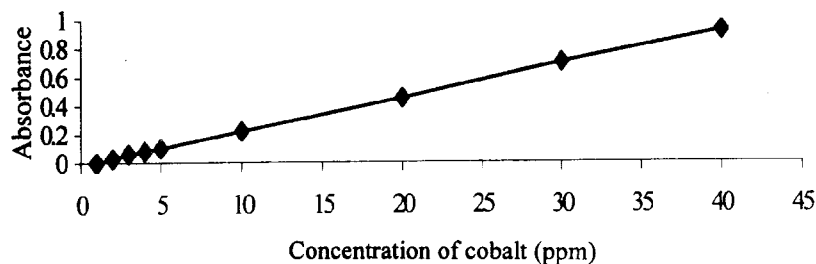


Fig.5: Calibration curve for cobalt

very little change in the absorbance. A concentration of cobalt varying from  $2 \times 10^{-3}$  M to  $4 \times 10^{-3}$  M gave complexes with oxime, which were stable for over a period of two hours with very minimal degradation.

#### Absorbance Versus Concentration Relationship

The reaction is quantitative. It was observed that the metal ion concentration in the range of 5 ppm to 100 ppm was suitable to give a linear relationship for complexation reaction with oxime, Fig. 5.

### Experimental

#### Instrumentation

The melting point was determined on melting point apparatus using capillary method. IR spectra were recorded by Hitachi 260-50. The mull for the IR spectra was prepared by grinding about 1 mg of the sample with a drop of Nujol and was pressed between NaCl plates. The spectrum was calibrated with a standard polystyrene film. A solution spectrum of the complex was obtained on Hitachi U-2000 double beam spectrophotometer.

#### General

Dehydroacetic acid, hydroxylamine hydrochloride and sodium acetate were purchased from BDH. Acetonitrile, dimethyl sulphoxide and dimethyl formamide were purchased from E. Merck, Germany, and were used without further purification. Reagent grade ethanol was purified further by distillation process using sodium wires as dehydrating agent. All other chemicals used were of analytical reagent grade.

#### Cobalt Chloride Solution

Standard cobalt (II) chloride solution ( $1 \times 10^{-2}$  M) was obtained by dissolving 1.64 g of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  in acetonitrile and volume was made up to one liter. This was diluted five times to obtain its  $2 \times 10^{-3}$  M solution.

#### Oxime Solution

Standard oxime solution ( $1 \times 10^{-2}$  M) was obtained by dissolving 1.89 g of DAO in acetonitrile, making the volume up to one liter in the same solvent [13, 14].

### Hydrochloric Acid Solution

Hydrochloric Acid (HCl) solution (9 M, 6 M, and 4 M) was obtained by diluting 776 ml, 517 ml, and 666.5 ml of analytical grade HCL (11.6 M) to one liter distilled water in a measuring flask.

### Synthesis of DAO

1.0g (6.0 mmol) dehydroacetic acid, 0.42 g (6.0 mmol) hydroxylamine hydrochloride, 0.78 g (9.86 mmol) pyridine and 25ml ethanol were taken in a 100ml round bottom flask fitted with a reflux condenser. The solution was stirred under reflux for 2-3 hours in an inert environment of water bath. The pale yellow reaction solution turned brown and then reddish brown at the end of the reaction. The solution was cooled at room temperature and then was added with 2ml ice cooled water. The reaction mixture was again stirred for 5 minutes and the reaction contents were placed in an ice bath for crystallization. The crude product amounted to about 70 % of solid. Recrystallization from ethanol gave golden crystals. The m.p. recorded was  $162 \pm 2$  °C [15, 16].

### General Experimental Procedure

5 ml of  $2 \times 10^{-3}$  M cobalt chloride solution was pipetted out into a 25ml beaker and 10 ml of  $1 \times 10^{-2}$  M dehydroacetic acid oxime solution was mixed in it and the pH was checked and maintained to remain between 5 and 5.8. The solution was warmed on water bath at up to 70 °C. Then, it was cooled down and transferred to a 25 ml measuring flask. The volume was increased up to the mark with acetonitrile solvent. The absorbance was measured at 645 nm ( $\lambda_{\max}$ ) against a blank reagent, using a quartz cell of 1 cm path length. The  $\lambda_{\max}$  at 645 was experimentally determined [13, 14].

### Conclusion

The reagent is inexpensive and readily available, in keeping with quantitative estimation of cobalt in an acidic medium, preferably at pH 5.8. It

can also be used for figuring out other metal ions by maintaining a suitable pH other than 5.8.

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