STUDY OF NEW COMPLEX FORMATION OF DITHIOCARBAMTE WITH Co2+,IN NON-AQUEOUS SOLVENT USING SPECTROPHOTOMETRY

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Abstract:

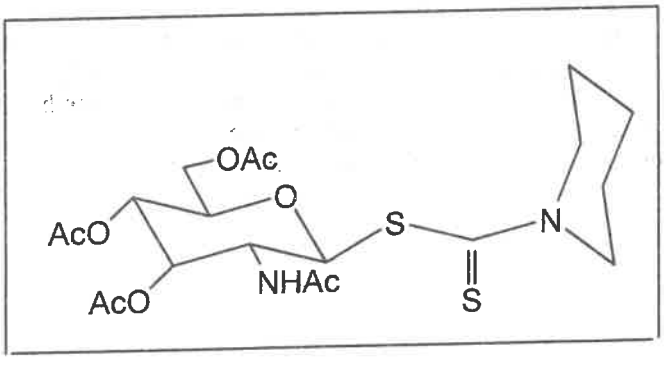
The formation complex between 2-acetamido-3,4,6-tri-o-acetyl-2-deoxy-β-o-glucopyranosyl,1-piperidyldithiocarbamate ligand and Co^{2+} has been studied in acetone .The spectrophotometric method was used for the determination of formation constants and the stoichiometries. The stoichiometry of the complexes is established 1:1 by Job's method,the stability constant and free energy $\Delta G^0$of cobalt-ligand is (logK=3.92) and (-5.470Kcal/mol) respectively at room temperature 30°C and pH=4.5 .

INTRODUCTION

The study of the cobalt halides in organic solvent has been pioneered by Katzin, he was one of the first researchers who used optical spectroscopic data to analyze cobalt salts structures[1]. Fine and Trutia revealed the presence of several types of complexes in some of these systems[2,3].The complexation ability of some quinolines with different cations such as Sn(IV), Cu(II), Co(II), and Nb(V) have been investigated using different spectrophotometric techniques [4-8]

Transition metal complexes have been recently investigated in view of their potent biological activity involving metal ions like Cu(II), Co(III), Pt(II), and Pd(II) [9–13].The spectrophotometric method for the study of Co^{2+}, Zn^{2+}, Mn^{2+}, Pb^{2+} and Cd^{2+} complexes with iodoquinol , 2-benzoylpyridine 4-phenyl-3-thiosemicarbazone has been studied[14,15]

In this paper the spectrophotometric method used to investigate the Co^{2+} complex with the following ligand in acetone .



Chemical structure of 2-acetamido-3,4,6-tri-o-acetyl-2-deoxy-β-o-glucopyranosyl,1-piperidyldithiocarbamate

2. EXPERIMENTAL

2.1. Apparatus

Spectrophotometric measurements were performed on analytic Jena AG 07745-Jena, using matched 10 mm quartz cells. The scanning speed was 50 nm/s.pH meter, calibrated with standard buffer solutions, were used for pH measurements.

2.2. Reagents

Anhydrous cobalt(II) chloride was prepared by drying $CoCl_2 \cdot 6H_20$, (E.Merck) at about I50°C for about 30 hours[16]. The completion of the dehydration was confirmed by weighing the material.

2-acetamido-3,4,6-tri-o-acetyl-2-deoxy-β-o-glucopyranosyl,1-piperidyldithiocarbamate ligand was synthesized and purified according to the procedure reported by Atta I. Atta [17]

2.3. Preparation of stock Solutions

2.3.1. 1.0×10^{-2} M cobalt chloride solution

0.13 g (1 mmole) of $CoCl_2$. (M. Wt.: 129.84 g /mol) was dissolved in acetone and was diluted to 100 mL in a volumetric flask.

2.3.2. 1.0×10^{-2} M dithiocarbamte ligand

0.245 g (0.5 mmole) of 2-acetamido-3,4,6-tri-o-acetyl-2-deoxy-β-o-glucopyranosyl,1-piperidyldithiocarbamate (M. Wt.: 490.60 g /mol) was dissolved in acetone in a beaker and was diluted to 50 mL in a volumetric flask.

2.3.3. Continuous variation method

1.0×10^{-2} M cobalt(II) chloride solution (0, 2, 4, 6,8 and 10 mL) was pippeted into sex 25mL volumetric flasks and an aliquot (10,8,6,4,2 and 0 mL) of 1.0×10^{-2} M dithiocarbamte was added in a way that the mole fraction of the solution remained constant. The color of the solution changed. The wavelength of absorbance was noted against the reagent blank at room temperature (30 °C)

3. RESULTS AND DISCUSSION

Figuers.1 and 2 show the absorption spectrum and first derivative spectroscopy of cobalt chloride in acetone at pH=4.5, the absorption spectra were recorded over the wavelength range of 400–800 nm, this solution has a tetrahedral-type co-complex with two chloride and two acetones and the spectrum of this $CoCl_2$/acetone solution is assigned to the $[CoCl_2Ac_2]$-complex[16].

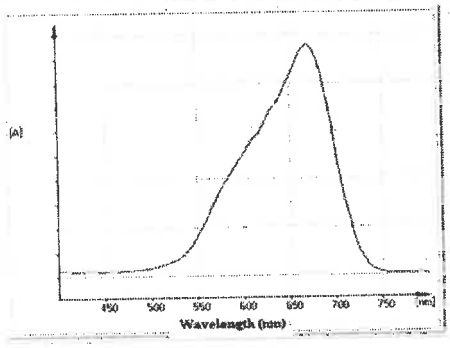


Figure 1 . Absorption spectra of cobalt(II) chloride 1×10^{-2} M in acetone

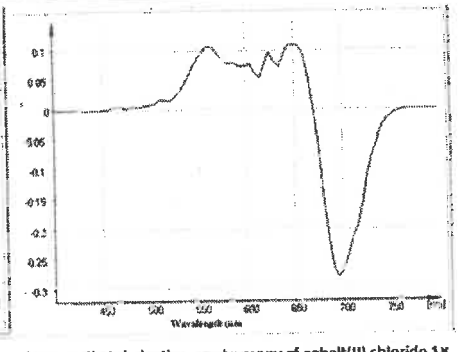


Figure 2 .First derivative spectroscopy of cobalt(II) chloride 1×10^{-2} M in acetone

The first derivative method was used to reveal the elemental absorption band positions of these tetrahedral and tetrahedral-like Co(II)complexes[16]. Figures 3 and 4 show the absorption spectrum and first derivative spectroscopy of cobalt chloride and ligand in acetone at stiochemitry(1:1) ,when the ligand is added the colure of solution changes from blue to pale green and the spectrum changes to other specie of the Co(II) complex and that is identified by the peak at 590nm, corresponding to this type of Co-complexes

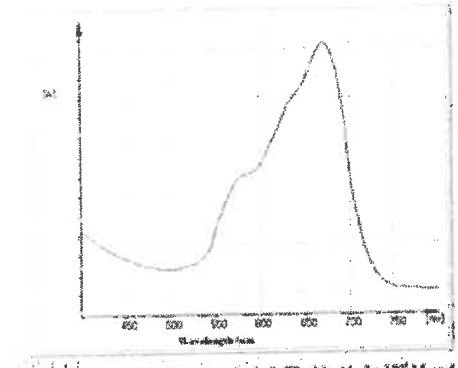


Figure 3. Absorption spectra of cobalt(II) chloride 5×10^{-4} M and ligand 5×10^{-3} M in acetone

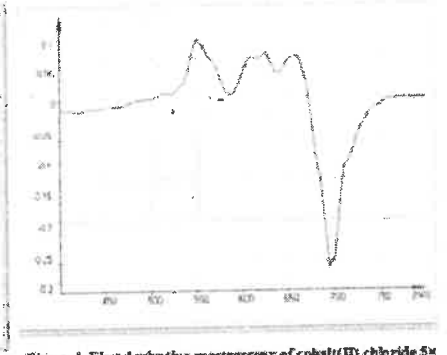


Figure 4. First derivative spectroscopy of cobalt(II) chloride 5×10^{-4} M and ligand 5×10^{-3} M in acetone

The resulted complex takes the form of tetrahedral, because the bond between acetone and the central metal ion is a weak while the bond between chloride ions and the central metal ion is a strong, the emergence of acetone is the preferred process and to replace the ligand ,the evidence for the emergence of the 590 nm band in the region of the visible spectrum, which were not present in spectrume of the parent compound, observed existence coordination between the sulfur and nitrogen atom with the central metal ion [18].

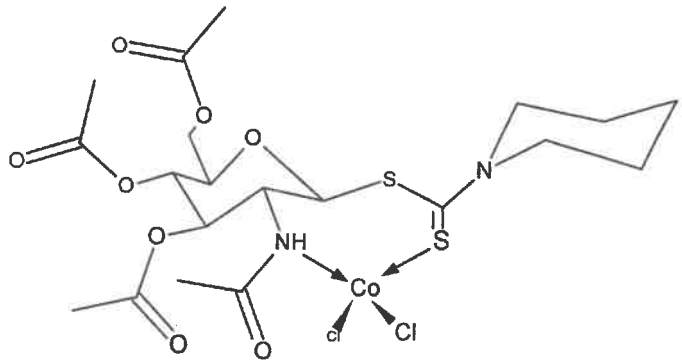


Figure.5: Molecular structure proposal for dithiocarbamte ligand complex

The stability of the resulted complex has been studied in acetone solution by the follow-up of the time effect on absorption of cobalt(II)-ligand complex at pH=4.5 and 590 nm has been studied at room temperature (30 °C) , Figure.(6) shows the stability of complex through 30 minutes

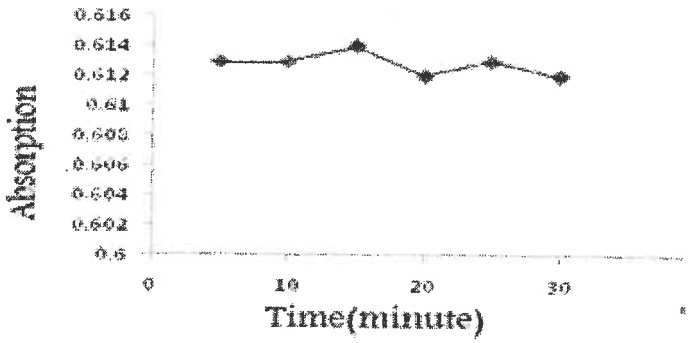


Figure 6 The time effect on absorption of Co(II)-ligand complex

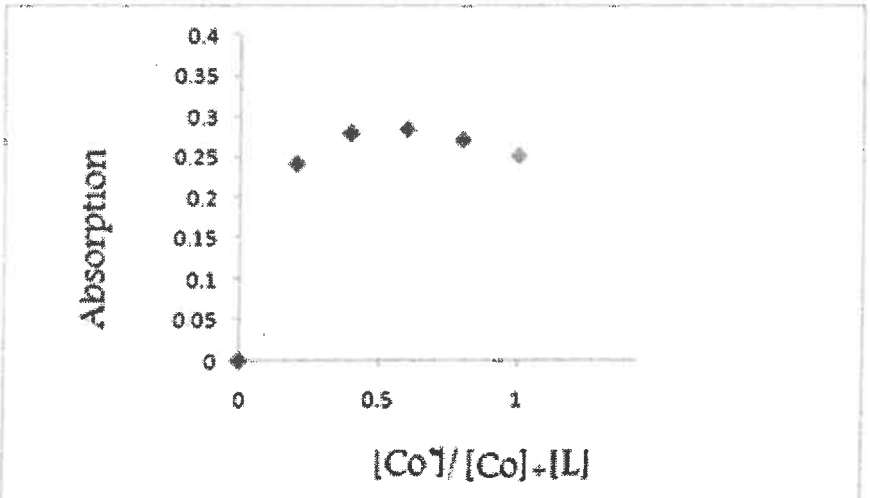
The stochiometric ratio of Co(II) to ligand was determined by Job's method of equimolar solutions [19,20]. The curve displayed maximum absorbance at mole fraction X_{metal} = 0.46, which indicates the formation of complex with metal ion to ligand ratio 1:1. (Figure.7). Experimental data of Co(II)–ligand by continuous variation method is given in Table 1. The corresponding equation used in this study for Job's method is as follows:

$$K = \frac{[A_2/A_1]}{[1-A_2/A_1]\times[C_L-C_M\times A_2/A_1]}$$

where, A_1 = maximum absorbance obtained from the horizontal portion of the curve, or at the intersect of extrapolated lines, A_2 = absorbance at the stoichiometry molar ratio of the metal to reagent in complex, C_M = concentration of Co(II), and C_L = concentration of ligand

Table 1. Experimental data of cobalt(II)-ligand by continuous variation method at pH=4.5 and 30°C

Sr. No.	Cobalt solution taken mL	Reagent solution taken mL	Absorbance at 590 nm and 30 °C	logK
1	0	10	0.001	
2	2	8	0.243	3.92
3	4	6	0.279	
4	6	4	0.285	
5	8	2	0.271	
6	10	0	0.251	



Figuer.7.Job's curve of equimolar solution at pH=4.5 and 30°C

The standard free energy change ΔG^0 for the formation reaction of complex has been calculated from stability constant using the following formula

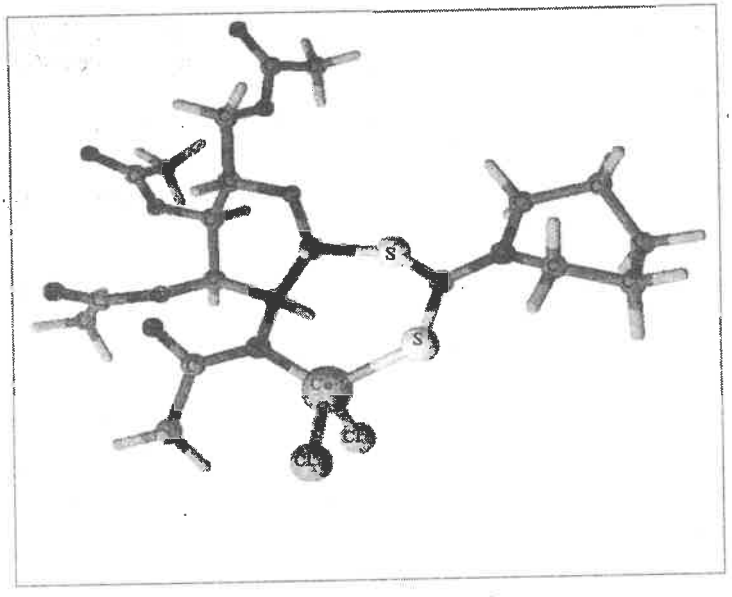
$$\Delta G^0 = -RT\ln K$$

Table 2. Stability constant and free energy of complex at pH=4.5 and 30°C

Method Job's	λ	A_1	A_2	logK	ΔG^0
Co(II) complex	590	0.330	0.280	3.92	-5.470Kcal/mol

The data in Table 2 shows that spontaneity of these metal-ligand reaction however ΔG^0 value is negative and the stability constant of complex (logK=3.92).

Geometry optimization of the complex by theoretical calculation were made by the molecular mechanics MM+ and MM2 methods using the hyperchem and chemoffice molecular modeling program package therefore [21]. Theoretical calculations have paid a considerable attention to the characterization and inferences of geometrical optimization of the prepared complex. Chem3D provides computational tools based on molecular mechanics for optimizing models, conformational searching, molecular dynamics, and calculating single point energy? for molecules. Therefore, we could obtain the optimized geometry for complex by computing the minimum steric energy for complex using MM+ and MM2 methods to emphasize data. The calculations of steric energy for the complex indicate that there is a tetrahedral configuration around the cobalt ion [22-24] (see Figure.8., several MM+ calculation were stopped when the RMS – gradient was < 0.1 [Kcal/mol] [25-27]



Figure(8): proposed optimum molecular geometry of complex from MM+ and MM2 calculation

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