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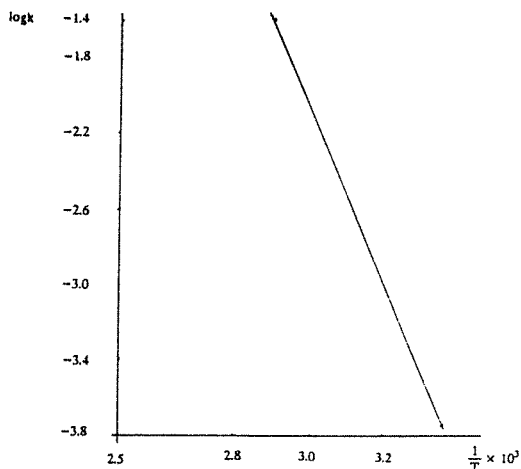


Fig. 3: The plot of  $\log k$  versus  $1/T$  (the reciprocal of the absolute temperature) for  $[\text{Co}(\text{NH}_3)_5\text{ONO}](\text{IO}_3)_2$

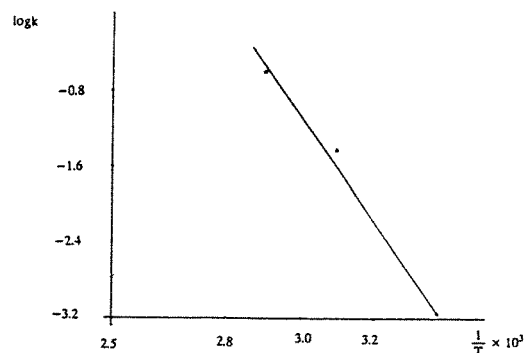


Fig. 4: The plot of  $\log k$  versus  $1/T$  (the reciprocal of the absolute temperature) for  $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{SO}_4$

Table 1: Thermodynamic quantities of activation for isomerization of  $[\text{Co}(\text{NH}_3)_5\text{ONO}](\text{IO}_3)_2$  in the solid state in KBr pellet (At 298K).

$\Delta H^\ddagger$ (kcal.mol <sup>-1</sup> )	$\Delta S^\ddagger$ (cal.deg <sup>-1</sup> .mol <sup>-1</sup> )	$\Delta G^\ddagger$ (kcal.mol <sup>-1</sup> )
21.42	-3.99	22.61

Table 2: Thermodynamic quantities of activation for isomerization of  $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{SO}_4$  in the solid state in KBr pellet (At 298K).

$\Delta H^\ddagger$ (kcal.mol <sup>-1</sup> )	$\Delta S^\ddagger$ (cal.deg <sup>-1</sup> .mol <sup>-1</sup> )	$\Delta G^\ddagger$ (kcal.mol <sup>-1</sup> )
25.89	13.94	21.74

#### FOOTNOTE :

1- Corresponding author.

2- Data for sulfate complex are given in parenthesis.

3- The absorbances were calculated by base line method.

4- All slopes of the plots were calculated by least squares

method.

5- On the basis of equation (1)  $k = k_1 + k_2$ .

6-  $\Lambda = k'T/h e^{\Delta S^\ddagger/R}$

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constant ( $K = k_1/k_2$ ) from equation (2),  $k_1$  and  $k_2$  can be determined.

$$K = \frac{k_1}{k_2} = \frac{A_o(ONO) - A_e(\dot{ONO})}{A_e(ONO)} \quad (2)$$

$A_o(ONO)$  in equation (2) is the absorbance of nitrito complex at  $1049\text{cm}^{-1}$  ( $1048\text{cm}^{-1}$ ) region at the beginning of the reaction ( $t = 0$ ). The measurements were carried out at 298, 325, and 345K.

On the basis of the following equation [12], the plot of  $\log k$

$$\log k^5 = -\frac{E_a}{2.303 R} \frac{1}{T} + \log \Lambda^6 \quad (3)$$

versus  $1/T$  gave a straight line (Figures 3 and 4) with a slope of  $-E_a/2.303R$  and an intercept of  $\log \Lambda$ , where  $\Lambda$  is frequency factor. By using the slope and intercept values,  $\Delta S^\ddagger$  and  $\Delta G^\ddagger$  of isomerization were obtained (Tables 1 and 2).

The electronic spectra of the complexes like  $[\text{Co}(\text{en})_3]^{3+}$  and  $[\text{Co}(\text{en})_2(\text{NH}_3)_2]^{3+}$  are very similar to octahedral ammonia complex [13, 14] i.e.,  $[\text{Co}(\text{NH}_3)_6]^{3+}$ . In effect, the intensities and apparent splitting patterns from the absorption spectra reflect the essentially octahedral  $[\text{M}(\text{NH}_3)_6]^{3+}$  chromophore.

Similar spectra could be expected for  $[\text{Co}(\text{NH}_3)_5\text{NO}_2](\text{IO}_3)_2$  and  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{SO}_4$  complexes. The electronic spectrum of each complex has four bands. The first band could be assigned to the following spin allowed d - d transition :

${}^1A_{1g} \longrightarrow {}^1T_{1g}$   $21832\text{cm}^{-1}$  ( $\epsilon_{max} = 93\text{cm}^{-1}\text{M}^{-1}$ );  
 $21832\text{cm}^{-1}$  ( $\epsilon_{max} = 76\text{cm}^{-1}\text{M}^{-1}$ ) which is similar to the first band of  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $21200\text{cm}^{-1}$  ( $\epsilon_{max} \cong 56\text{cm}^{-1}\text{M}^{-1}$ ), the second band could be assigned to the following spin allowed d - d transition :

${}^1A_{1g} \longrightarrow {}^1T_{2g}$   $30864\text{cm}^{-1}$  ( $\epsilon_{max} = 1592\text{cm}^{-1}\text{M}^{-1}$ );  
 $30769\text{cm}^{-1}$  ( $\epsilon_{max} = 1206\text{cm}^{-1}\text{M}^{-1}$ )

Which is similar to the second band of  $[\text{Co}(\text{NH}_3)_6]^{3+}$   $29550\text{cm}^{-1}$  ( $\epsilon_{max} = 46\text{cm}^{-1}\text{M}^{-1}$ ) region, thus, could be obscured, by the first charge transfer ( ${}^1A_1 \longrightarrow {}^1B_1$ ). The third band is assigned to the second charge transfer:

${}^1A_1 \longrightarrow {}^1B_2$   $43668\text{cm}^{-1}$  ( $\epsilon_{max} = 13283\text{cm}^{-1}\text{M}^{-1}$ );  
 $42194\text{cm}^{-1}$  ( $\epsilon_{max} = 10222\text{cm}^{-1}\text{M}^{-1}$ )

Finally, the fourth band probably could be assigned to Metal- to - Ligand charge transfer.

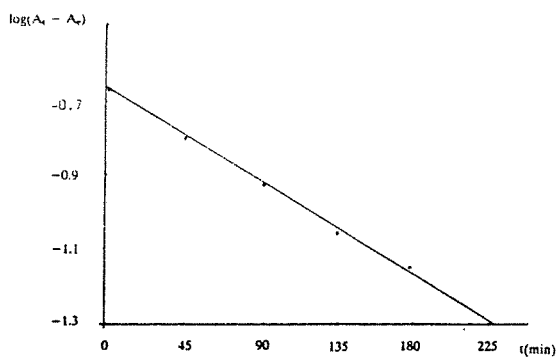


Fig. 1: The plot of  $\log(A_t - A_e)$  versus time ( $t$ ) at 325K that indicates the first order relationship for isomerization of  $[\text{Co}(\text{NH}_3)_5\text{ONO}](\text{IO}_3)_2$

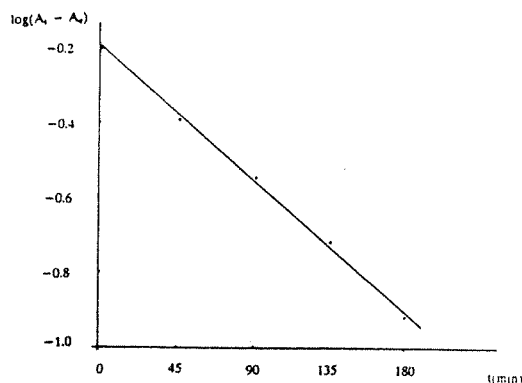


Fig. 2: The plot of  $\log(A_t - A_e)$  versus time ( $t$ ) at 325K that indicates the first order relationship for isomerization of  $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{SO}_4$

### A- preparation

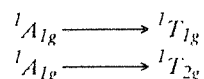
All complexes as well as  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  and nitro and nitropentaammine cobalt (III) chloride have been prepared by the methods reported in the literatures [4-7]. Measurement of  $\text{SO}_4^{2-}$  and  $\text{IO}_3^-$  Ions were performed according to usual methods [8, 9].

### B- Infrared spectra of nitro and nitrito complexes<sup>2</sup>

The stretching vibration and degenerate deformation of  $\text{NH}_3$  group appear at  $3256$  ( $3266$ ) and  $1310\text{cm}^{-1}$  ( $1310\text{cm}^{-1}$ ) respectively. Presence of a band at  $1427\text{cm}^{-1}$  ( $1428\text{cm}^{-1}$ ) could be assigned to asymmetric stretching of nitro group [in nitrito form, instead of this band, there are two bands at  $1049$  ( $1048$ ) and  $1459\text{cm}^{-1}$  ( $1459\text{cm}^{-1}$ ) that belong to symmetric and asymmetric stretching of nitrito group respectively] [10].

### C- Electronic spectra of nitro complexes<sup>2</sup>

In the electronic spectra four bands are observed. The first and the second bands [ $21832$ ,  $\epsilon_{\text{max}} = 93$  ( $21832$ ,  $\epsilon_{\text{max}} = 76$ ) and  $30864\text{cm}^{-1}$ ,  $\epsilon_{\text{max}} = 1592\text{cm}^{-1}\text{M}^{-1}$  ( $30769\text{cm}^{-1}$ ,  $\epsilon_{\text{max}} = 1206\text{cm}^{-1}\text{M}^{-1}$ )] could be assigned to the following spin- allowed d - d transitions :



but the second transition could be obscured by charge transfer because of high intensity. The next two electronic transitions [ $43668$ ,  $\epsilon_{\text{max}} = 13283$  ( $42194$ ,  $\epsilon_{\text{max}} = 10222$ ) and  $48780\text{cm}^{-1}$ ,  $\epsilon_{\text{max}} = 15920\text{cm}^{-1}\text{M}^{-1}$  ( $47619\text{cm}^{-1}$ ,  $\epsilon_{\text{max}} = 8794\text{cm}^{-1}\text{M}^{-1}$ )] could be assigned to charge transfer.

### D- Kinetic study

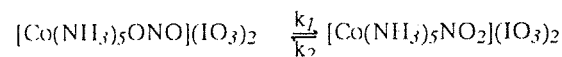
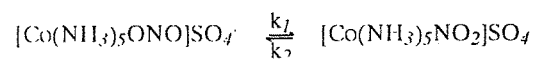
Kinetic study of the isomerization of nitrito  $\rightleftharpoons$  nitro was carried out by measuring the change in absorbance<sup>3</sup> of nitrito peak at  $1049\text{cm}^{-1}$  ( $1048\text{cm}^{-1}$ ) against time<sup>4</sup>. Therefore, after preparation of KBr pellet of each complex, it was irradiated by a  $366\text{ nm}$  UV lamp from a distance of  $80\text{ mm}$  for  $2$  and  $4.5$  hours {for  $[\text{Co}(\text{NH}_3)_5\text{NO}_2](\text{IO}_3)_2$  and  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{SO}_4$  respectively} to ensure a complete conversion of the

nitro isomer into the nitrito isomer. Then at  $298\text{ K}$  the IR spectrum of each sample was taken and during the isomerization (for several times) and finally at the equilibrium, spectrum taking was repeated.

Kinetic measurements were repeated at  $325$  and  $345\text{ K}$  to calculate the  $\Delta S^\ddagger$  and  $\Delta G^\ddagger$  of isomerization. During the isomerization the KBr disc was placed in a thermostated aluminum box with some calcium chloride powder in the bottom. The isomerization during the time of taking the IR spectra, is negligible.

## RESULTS AND DISCUSSION

The complexes of  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{NO}_2](\text{IO}_3)_2$  were changed to  $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{ONO}](\text{IO}_3)_2$  respectively by UV irradiation with a  $366\text{ nm}$  wavelength and after a period of time the nitrito complexes were reached an equilibrium with nitro complexes. The reactions are as follow:



The kinetic study of these isomerizations were carried out in solid state by measuring the change in infrared absorption peak at  $1049\text{cm}^{-1}$  ( $1048\text{cm}^{-1}$ ) which is due to the symmetric stretching vibration of nitrito group. Starting with  $100\%$  nitrito isomer, the following equation can be used [11] :

$$2.3 \log \frac{\Lambda_t - \Lambda_e}{\Lambda_t - \Lambda_0} = kt = (k_1 + k_2)t \quad (1)$$

where  $\Lambda_t$ ,  $\Lambda_e$  and  $\Lambda_0$  are the absorbance of the nitrito complex at  $1049\text{cm}^{-1}$  ( $1048\text{cm}^{-1}$ ) at time  $t$ , equilibrium (infinite time) and  $t = 0$  respectively.  $100\%$  nitrito isomer was obtained by irradiation of nitro isomer by using UV ( $366\text{ nm}$ ) for  $2$  and  $4.5$  hours.

A plot of  $\log(\Lambda_t - \Lambda_e)$  versus time ( $t$ ) gave a straight line (that was expected for a first order reaction) with a slope of  $-(k_1 + k_2)/2.3$ . For example this plot at  $325\text{ K}$  is shown in Figures (1) and (2). By using the slope of this plot  $-(k_1 + k_2)/2.3$  and calculating the equilibrium

# The Kinetic Study of The Linkage Isomerism In $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{SO}_4$ & $[\text{Co}(\text{NH}_3)_5\text{NO}_2](\text{IO}_3)_2$ Complexes

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## ABSTRACT

*In this article the nitrito  $\rightleftharpoons$  nitro isomerization of  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{NO}_2](\text{IO}_3)_2$  complexes have been studied. Isomerization of these two complexes in the solid state follow a first order kinetics. The rates of isomerization at different temperatures (298, 325, and 345K) were determined by infrared spectrophotometer.  $\Delta S^\ddagger$  and  $\Delta G^\ddagger$  are calculated at 298K. The infrared, visible, and ultraviolet spectra of both complexes are reported.*

**KEY WORDS :** *Co(III) complexes, Linkage isomerism, Vibrational spectra, Electronic spectra.*

## INTRODUCTION

An extensive investigation of the nitrito  $\longrightarrow$  nitro isomerization was made by Adell [1]. The rates of rearrangement were determined spectrophotometrically. Measurements were made on the solid state and aqueous solution, in all cases the data were found to give a first-order plot.

Heravi and Abedini have studied the effect of the size of the counter ions (non coordinated groups) on the rate of isomerization in nitrito pentaammine cobalt (III) halides ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ )[2].

The kinetic study of linkage isomerism in  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{F}_2$  is reported recently [3].

In this article the kinetic study of the linkage isomerism in  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{NO}_2](\text{IO}_3)_2$  are reported.

In infrared region, the nitrito group in these two complexes has a strong absorption band at  $\cong 1048\text{cm}^{-1}$ . Whereas the pure nitro complexes do not show any band at this region. The change of the intensity of this absorption band was used to study the isomerization of  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{NO}_2](\text{IO}_3)_2$  complexes in the solid state in KBr pellet.

## EXPERIMENTAL

Elemental analyses were performed with a Elemental Analyzer CHN-O-RAPID, Heraeus and a Atomic Absorption, 2830, Perkin- Elmer. Infrared spectra were obtained on a spectrophotometer, 843, Perkin- Elmer. UV/visible spectra were recorded on a Chimadzu 2100 UV/visible spectrophotometer.