

## Synthesis, Spectral and Kinetic Study of Demi-macrocycle of $N_2O_2$ with Complex of Co (II) Ion

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**Abstract:** Macrocytic Co (II) complex was synthesized by the condensation reaction, with ligand donor  $N_2O_2$ . The complex was characterized with the aid of elemental analysis, spectral methods, and measurements of conductance and magnetic moment. The electronic spectral data suggested octahedral geometrics with coordination number six for the complex. The kinetic measurements was carried out under pseudo-first order condition in the pH range 4-0 to 5.2 and 5.0 to 6.6 for the Co (II) with the total ligand concentration at least 10 folds excess of the total concentration of Co (II) and its effect was successfully analysed in terms of different activities. The complex formation is found to be a one step first-order in both the metal ion and ligand. Thermodynamic parameters were evaluated and the kinetics of formation of complex was discussed.

**Keywords:** Macrocytic, condensation, analysis, activities, interference.

### 1. INTRODUCTION

Macrocytic complex are of great importance due to their resemblance to many naturally occurring macrocycles, such as porphyrins and cobalamins. During recent years, macrocytic chemistry has attracted much attention and has become a growing class of research. A number of nitrogen donor atoms macrocytic derivatives have long been used in analytical and medical application.<sup>1-3</sup> Macrocytic metal chelating agents are useful for detecting tumor lesions.<sup>4,5</sup> The chemistry of macrocytic complexes is also important due to their use in dyes and pigments as-well-as in study of NMR shift reagents etc.

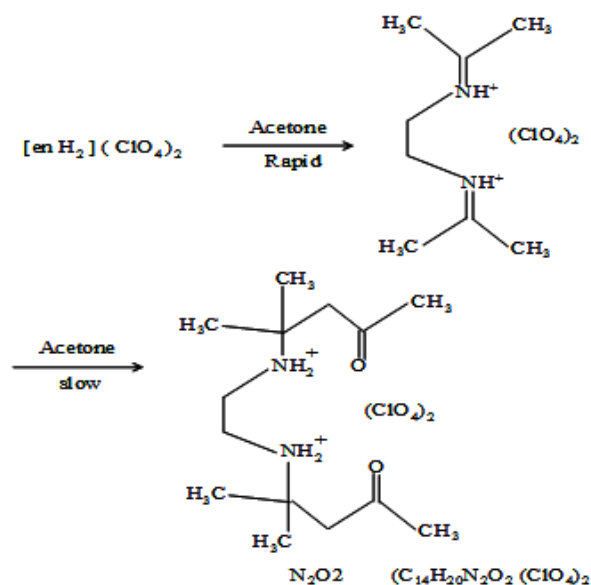
### 2. EXPERIMENTAL

All reagents and solvents used in the present investigation were of analytical grade. 1,2-diaminoethane, perchloric acid ( $HClO_4$ ), acetone ( $CH_3COCH_3$ ) etc. of Loba, Merck and Aldrich brand. The preparation of solutions, standardization, and procedures for demi-macrocytic complex formation and their spectral kinetic studies have been performed.

The carbon, hydrogen and nitrogen analysis of the samples were carried out microanalytically. Oxygen was determined by different methods. Metal and chloride were determined gravimetrically. The IR spectra ( $4000-400\text{ cm}^{-1}$ ) was recorded on a Jasco model 4100 FTIR spectrometer as KBr discs. UV-visible spectra was recorded on a Shimadzu 1700 pharmanalyzer. Conductivity measurements were made in DMSO or nitromethane ( $10^{-3}\text{ mho}$ ) at room temperature on systronics conductivitymeter. Magnetic susceptibility was measured at 8000 G in a Evans magnetic susceptibility balance using  $Co[(Hg(SCN)_4)]$  as calibrant and the experimental susceptibilities were corrected for diamagnetic correction with Pascal constants.

#### 2.1. Synthesis of ligand $N_2O_2$

4, 4, 9, 9-tetramethyl-5, 8-diazonium dodeca-2, 11-dione diperchlorate [ $make + H_2$ ] ( $ClO_4$ )<sub>2</sub>. Ethane-1, 2-diamine (20 ml) was added to acetone (300 ml) in a 500 ml flask and the solution cooled in an ice bath. Perchloric acid (72%) was added dropwise with constant stirring, below temperature  $20^\circ\text{C}$ . The flask was completely filled with acetone and left without agitation. After few hours, fine crystals of the product, which is very insoluble in acetone, commenced to separate and continued to form for a week. The bulk of the product being present after 10 days was filtered off, washed with acetone until the brown colour vanished and the product remained was colourless and was air dried. The yield was equal to 85% (Table 1).



Synthesis of Cobalt (II) complex (4, 4, 6, 6-tetramethyl-5, 18-diazadodeca-2,11-dione Cobalt(II) complex)

Procedure: Cobalt (II) perchlorate (20 ml) was dissolved in water followed by [amke + H<sub>2</sub>] (ClO<sub>4</sub>)<sub>2</sub> (24 gm, 0.052 mol). The mixture was refluxed until the colour of the solution changed from green to red. After sometime, the product was filtered, recrystallised from methanol and evaporated to dryness in vacuum (Table 2).

### 3. RESULTS AND DISCUSSION

#### 3.1. FTIR Spectra of N<sub>2</sub>O<sub>2</sub>

The IR spectra of the ligand shows characteristic strong absorption band at 2960 cm<sup>-1</sup> (Table 1) primarily due to asymmetric stretching mode in which two C–H bonds of the methyl group are extending while the third one is contracting and at 2904 cm<sup>-1</sup> due to symmetrical stretching ( $\nu_s CH_3$ ) in which all three of the C–H bond extend and contract in phase. The peaks at 2985 and 3007 are attributed to the asymmetrical stretching ( $\nu_{as} CH_2$ ) and symmetrical stretching ( $\nu_s CH_2$ ). The high energy shifting of these peaks reflect strain in the chain caused.<sup>6-8</sup> The symmetrical bending vibration ( $\delta_s CH_3$ ) causes peak at 1348cm<sup>-1</sup>, while the sharp peak at 1445 cm<sup>-1</sup> is attributed to asymmetrical bending ( $\delta_{as} CH_3$ ). Strong absorption band at 1473 is the scissoring band ( $\delta_s CH_2$ ) of methylene group. Absorption band between 1313 cm<sup>-1</sup> to 1156 cm<sup>-1</sup> is ascribed to the twisting and wagging vibrations of methylene group. Strong absorption peak at 1685 cm<sup>-1</sup> is due to ketonic stretching vibration. Overlapping band peaks at 3019, 3007, 3266 and 3370 are due to the N-H stretching vibration. Strong bands due to ionic perchlorate occur at 1105 cm<sup>-1</sup> and 655 cm<sup>-1</sup>.

The IR spectra of the complex exhibits a strong sharp to medium intensity band in 500-475 cm<sup>-1</sup> region, which may be assigned to metal-oxygen stretching vibration, the  $\nu(M-O)$  stretching frequencies upon complex formation. The intensities of some of the vibrations decrease which may be attributed to the hindered vibrations.

The characteristic  $\nu(C-O)$  absorption frequencies undergo a negative shift by about 50 cm<sup>-1</sup> in the complex which may be assigned to the relaxation effect caused due to the metal ion. The  $\nu(M-ClO_4)$  stretching frequency. Sharp band at 535-500 cm<sup>-1</sup> is assigned to metal nitrogen frequency, the non-appearance of  $\nu_s(N-H)$   $\nu_{as}(N-H)$  and  $\delta_s(N-H)$  vibrations in the complexes confirm the coordination of the metal ion by the deprotonation of the internal protons (Fig.1)

#### 3.2. UV- vis Spectra

The cobalt complex displays three absorption bands at 7940-7890, 15,620-15523 and 19260-19120 cm<sup>-1</sup>. These bands are assigned to  ${}^4T_2(F) \rightarrow {}^4T_2(F)$ ,  ${}^4T_1(F) \rightarrow {}^4A_2(F)$  and  ${}^4T_1(F) \rightarrow {}^4T_1(P)$  transitions respectively. The  ${}^4T_1(F) \rightarrow {}^4A_2(F)$  transition is assigned to the weak band present towards low energy side of the strongest band. The calculation of Dq and E(<sup>4</sup>P) values is based on the assumption that the most intense band at 7950 - 7871cm<sup>-1</sup> is due to  ${}^4T_1(F) \rightarrow {}^4T_1(P)$  transition. **The values of ligand field parameters are in good agreement with those reported for other Co (II)**

complexes, which indicated that the Dq values of the Co (II)<sup>9-13</sup> complex are always slightly higher than that for the Ni(II) complexes for the same ligand (Fig.2).

Cobalt complex has magnetic moment value 4.21 BM which is diagnostic of the high spin state of the metal ion in an octahedral field.<sup>14</sup>

### 3.3. Kinetic Study of Complex

The spectral kinetic study of 14-membered N<sub>2</sub>O<sub>2</sub> demi-macrocylic complex of Co(II) ion has been carried out by UV-Vis spectrophotometer in aqueous medium under pseudo-first order condition. The progress of the reaction was monitored spectrophotometrically. The wave length 240 nm for Co (II) shows peak of complex metal ions, that decrease in absorbance of complex with time. The Beer-Lambert law was verified one such exemplary of rate constant (k<sub>obs</sub>) determined from the slope of log (absorbance) vs. time of optical density in parcelled graph or versus time plot has been given as optical density for first-order rate constants Table 3 (Fig.3). The dielectric constant of the medium has shown insignificant effect. The double reciprocal plot for the demi-macrocylic complex of Co(II) ion with N<sub>2</sub>O<sub>2</sub> ligand has also been drawn between k<sub>obs</sub><sup>-1</sup> vs. 1/[Co(II)] which gives positive intercept on Y-axis.

The effect of pH on reaction rate was examined, and found that rate of formation of complex increases with increase in pH values Table 4 (Fig.4).

Various thermodynamic parameters were determined which support the kinetic of formation of Co (II) demi-macrocylic complex (Table 5).

**Table1.** Elemental Analysis of Ligand N<sub>2</sub>O<sub>2</sub>

Anal calculation %: C, 36.77; H, 6.61; N, 6.12; O, 34.98;

Cl, 15.50; found: C, 36.24; H, 6.59; N, 6.13; O, 34.92

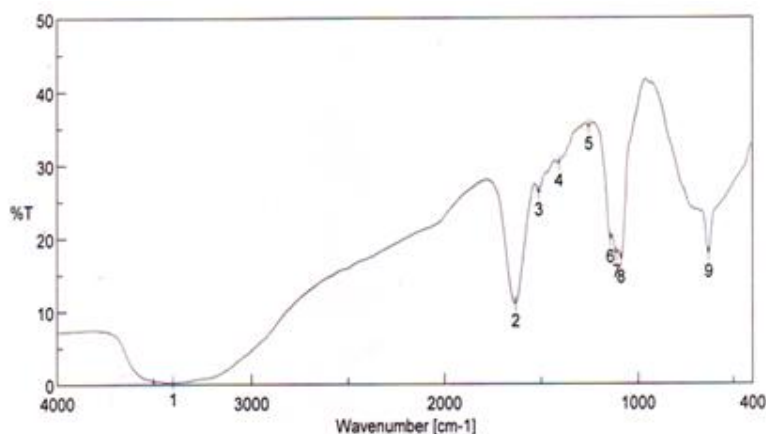
Cl, 15.49

IR (KBr) V<sub>a</sub> (C-H) 2960, V<sub>s</sub> (C-H) 2909 cm<sup>-1</sup>, V (-C-(CH<sub>3</sub>)<sub>2</sub>) 1385, 1565(s)

V (C=O) 1685 (s), V (N-H) 3370, 3266, 3007, V (N-C) 1260,

V<sub>as</sub> (CH<sub>2</sub>) 2985; V<sub>s</sub> (CH<sub>2</sub>) 3007; δ<sub>s</sub> (CH<sub>3</sub>) 1348 cm<sup>-1</sup>, δ<sub>as</sub> (CH<sub>3</sub>) 1445 cm<sup>-1</sup>

δ<sub>s</sub> (CH<sub>2</sub>) 1473 cm<sup>-1</sup> V(ClO<sub>4</sub>) 1105, 655 cm<sup>-1</sup>



[Comment]  
 Sample Name 21s Wave number (cm<sup>-1</sup>)  
 Comment instrumentation center ICSC  
 User dr bilal p mir  
 Division instrumentation, ICSC  
 Company Islamia college of science and commerce

[Measurement Information]  
 Model Name FT/IR-4100typeA  
 Serial Number B065061016  
 Light Source Standard  
 Detector TGS  
 Accumulation Auto (83)  
 Resolution 16 cm<sup>-1</sup>  
 Zero Filling On  
 Apodization Cosine  
 Gain Auto (8)  
 Aperture Auto (7.1 mm)  
 Scanning Speed Auto (2 mm/sec)  
 Filter Auto (30000 Hz)

**Table2.** Elemental Analysis and IR Spectra of Co (II) complex

C<sub>14</sub>H<sub>28</sub> N<sub>2</sub>O<sub>10</sub>Cl<sub>2</sub> Co (II), 519.94 Cal Mass (M)

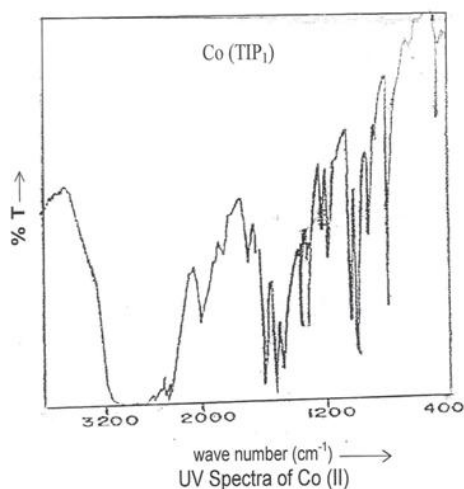
Anal calculation: C, 32.34; H, 5.42; N, 5.38; O, 30.77; Cl, 13.63; Co, 10.33

Found: C, 32.36; H, 5.43; 5.37; O, 30.73; Cl 13.63; Co-11.32

IR (KBr) cm<sup>-1</sup>

V (M-N) 530; V (M-O) 452 cm<sup>-1</sup>

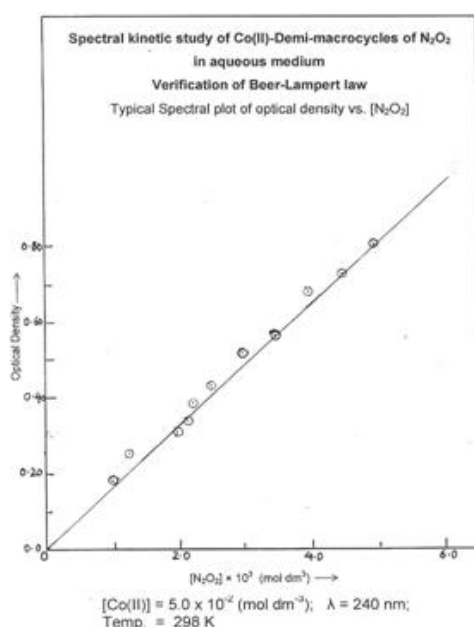
(d-d) spectra (DMSO) 7870 Tl (F) → <sup>+T</sup><sub>2g</sub> (F)



**Table3.** Effect of variation of concentration of N<sub>2</sub>O<sub>2</sub> (Donor ligand) on the rate of formation of demi-macrocylic complex of Co (II) ion with N<sub>2</sub>O<sub>2</sub> in aqueous medium

[Co (II) = 5.0 x 10<sup>-2</sup> (mol dm<sup>-3</sup>) ; λ<sub>max</sub> = 240 nm; Temperature = 298 K

Sr. No.	Time (min.)	Optical Density	[N <sub>2</sub> O <sub>2</sub> ] × 10 <sup>3</sup> (mol dm <sup>-3</sup> )
1.	0.0	0.801	5.00
2.	0.4	0.722	4.50
3.	0.8	0.673	4.00
4.	1.2	0.562	3.50
5.	1.6	0.511	3.00
6.	2.0	0.432	2.50
7.	2.4	0.383	2.25
8.	2.8	0.360	2.15
9.	3.2	0.306	2.00
10.	3.6	0.254	1.25
11.	4.0	0.182	1.00



**Table4.** Observed first-order rate constant  $k_{obs}$  (s<sup>-1</sup>) for the Co (II)-Demi-macrocylic complexes with N<sub>2</sub>O<sub>2</sub> under various pH conditions

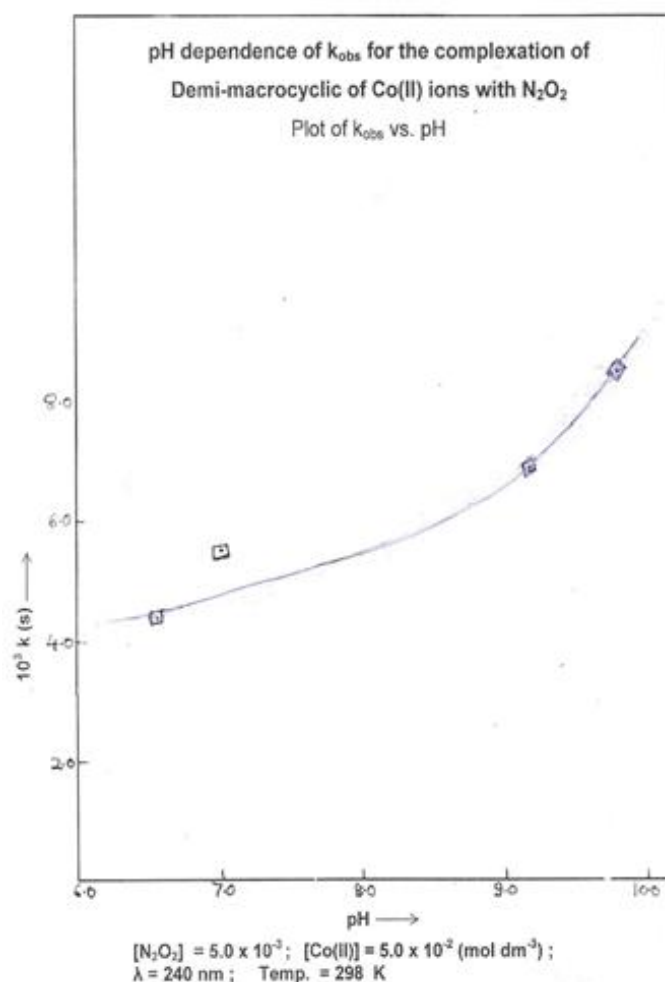
[Co (II) = 5.0 x 10<sup>-2</sup> (mol dm<sup>-3</sup>);

[Co (II) = 5.0 x 10<sup>-2</sup> (mol dm<sup>-3</sup>);

$\lambda_{max}$  = 240 nm

Temperature = 298 K

S. No.	pH	[Co L (ClO <sub>4</sub> ) <sub>2</sub> ] $k_{obs} \times 10^3$ (s <sup>-1</sup> )
1	6.55	4.38
2	7.00	5.41
3	9.20	6.78
4	9.80	8.52



**Table5.** Thermodynamic parameters for Co (II)-Demi-macrocylic of N<sub>2</sub>O<sub>2</sub> complex

S. No.	Demi-macrocylic complex	Ea kJ (mol <sup>-1</sup> )	$\Delta H^\ddagger$ kJ (mol <sup>-1</sup> )	$\Delta G^\ddagger$ kJ (mol <sup>-1</sup> )	$-\Delta S^\ddagger$ JK <sup>-1</sup> (mol <sup>-1</sup> )
1.	[Co L(ClO <sub>4</sub> ) <sub>2</sub> ]	19.28	15.74	79.59	212.48

#### 4. CONCLUSION

Demi-macrocylic complex of Co (II) was synthesized with donor ligand N<sub>2</sub>O<sub>2</sub>. Its kinetic study was also studied. The effect of pH was also discussed. The applications of [Co L (ClO)<sub>4</sub>] in the fields of dyes, pigment and in the study of NMR shift was also discussed.

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