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Research Articles

SYNTHESIS AND SPECTRAL KINETIC STUDY OF DEMI-MACROCYCLES OF N_2O_2 WITH COMPLEX OF Cr(II) ION

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ABSTRACT

The demi-macrocyclic complex of Cr(II) ion involving donor ligand N_2O_2 has been synthesized and characterized spectrometrically by IR and UV techniques to establish their identify. Tthe magnetic susceptibility of the complex was measured. The spectral kinetic of [Cr $L(ClO_4)_2$] complex formation was spectrophotometrically studied and Beer-Lamert law was verified at required wavelength 240nm. Various thermodynamic activation parameters were determined in consistent with the proposed mechanism.

Key Words : Magnetic susceptivity, Vacuum, Characterization, Excellent, conformity,

INTRODUCTION

A demi-macrocyclic[1] ligand or complexes may be defined as a cyclic molecule which is open at one end and whose size and shape may be varied according to reaction. Templates used changing its macrocyclic back bone as well as hetero atoms, relative to their open analogues. Demi-macrocycles have additional stereochemical constrains resulting from their cyclic nature, which depend upon

several factors such as macrocyclic ring size, number, and nature of chelate rings, formed on co-ordination[2] influence positions of donor and central metal ion. Macrocyclic ligand may also promote the formation of less common coordination geometries for particular metal ion, because of increased ring-strain on co-ordination. The synthesis, spectral characterization enhanced kinetic and thermodynamic stabilities[3] of macrocyclic complex formation found commendable position in the field of demi-macrocylic complexes which attracted a large number of national and international laboratories in resent era.

The synthesis, and spectral kinetic study of Fe(II) and Co(II) ions of 14-membered N_2O_2 demi-macrocylic complexes have already been acclaimed by various authors,[4-14] spectrophotometrically. However, available literature pertaining to the demi-macrocyclic complex of Cr(II) ion has not been studied spectrophotometrically. Hence, authors have considered probe to bring out the hither to unreported results of above investigation.

EXPERIMENTAL

The chemicals and solvents used in the present study were of Analar R grade. The synthesis of N_2O_2 (4,4,9,9-tetramethyl-5, 8-diazoniumdodec-2, 11-dione diperchlorate) abbreviated as [amke + H_2O] $(ClO_4)_2$ was carried out. Ethane 1, 2-diamine (20 ml) was added to acetone and finally treated with $HClO_4$ (72%) below 20^0 C. The fine crystals obtained after few hours. The colourless, product was air dried, with an yield 85%. The elemental analysis C, H, and N of the sample were carried out microanalytically, Oxygen was determined by different methods. Cr(II) and chloride were determined gravimetrically[15].

The synthesis of ligand N_2O_2 and its complex of Cr(II) was identified by the IR Jasco model spectrometer as Ubr discs. UV-Visible spectra was recorded on a Shimedzu 1700 pharmaspectrometer. The magnetic susceptibility[16] was measured at 8000 G in a balance using as Co [Hg $(SCN)_4$] as calibrant. The spectral kinetic study of Cr(II)-demi-macrocyclic complex of with N_2O_2 has been carried by UV-Vis spectrophotometer under pseud first-order the condition [Cr(II)] << [N_2O_2] in aqueous medium at 25^0C. The progress of reaction was monitored spectro-photometrically at wave length 240nm that shows peaks of complexes of metal ion with decreases in

absorption of complex with time for nearly 80% of the completion of the reaction. Integration ($k = 2.303/t \log D_o\text{-}D_e / D_t\text{–}D_e$) and graphical methods were used. The rate constant was determined from the slope of linear plots of log a / (a-x) and log (a-x) versus time. The observation indicated that rate constant was reproducible within an error of $\pm$ 5%.

RESULTS AND DISCUSSION

Characterization of ligand N_2O_2

The IR spectra of the ligand shows characteristic strong absorption band at 2960 cm^{-1} primarily due to asymmetric stretching mole in which two C-H bonds of the methyl group are extending while the third one is contracting at 2904 cm^{-1} due to symmetrical stretching (V_sCH_3) in which all the three of the C-H bonds extend and contract in phase. The peaks at 2985cm^{-1} and 3007cm^{-1} are attributed to the asymmetrical stretching (V_{as} CH_2) and symmetrical stretching (V_sCH_2). The high energy shifting of there peaks reflect strain ion the chain caused. The symmetrical bending vibrations (V_s CH_3) causes peak at 1348 cm^{-1} while the sharp peak at 1445 cm^{-1} is attributed to asymmetrical bending (δ as CH_3). Strong absorption and at 1473 is the scissoring and (δ_s CH_2) of methylene group. Absorption and between 1313cm^{-1} to 1156cm^{-1} is descried to the twisting and wagging vibrations of methylene group strong absorption peak at 1685cm^{-1} is due to ketonic stretching vibration. Overlapping band peaks at 3019, 3007, 3266 and 3370 cm^{-1} are due to the N-H stretching vibration. Strong bands due to ionic perchlorate occur at 1105cm^{-1} and 655cm^{-1} Table:1 (Fig.1).

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Electronic Journal of Advanced Research

An International Peer review E-Journal of Advanced Research

Table: 1

Elemental Analysis of Ligand N_2O_2

Anal calculation %: C, 36.77; H, 6.61: N, 6.12; 0.34.98;

Cl, 1550; found: C, 36.24; H, 6.59; N, 6.13; O, 34.92

Cl, 15.49

IR (KBr) Va (C-H) 2960, V_S (C-H) 2909 cm^{-1}, V (-C-$(CH_3)_2$) 13.85.1565(s)

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

Vas (CH_2) 2985; V_S (CH_2) 3007; δs (CH_3) 1348 cm^{-1}, δas (CH_3) 1445 cm^{-1}

δs (CH_2) 1473 cm^{-1} V(ClO_4) 1105, 655 cm^{-1}

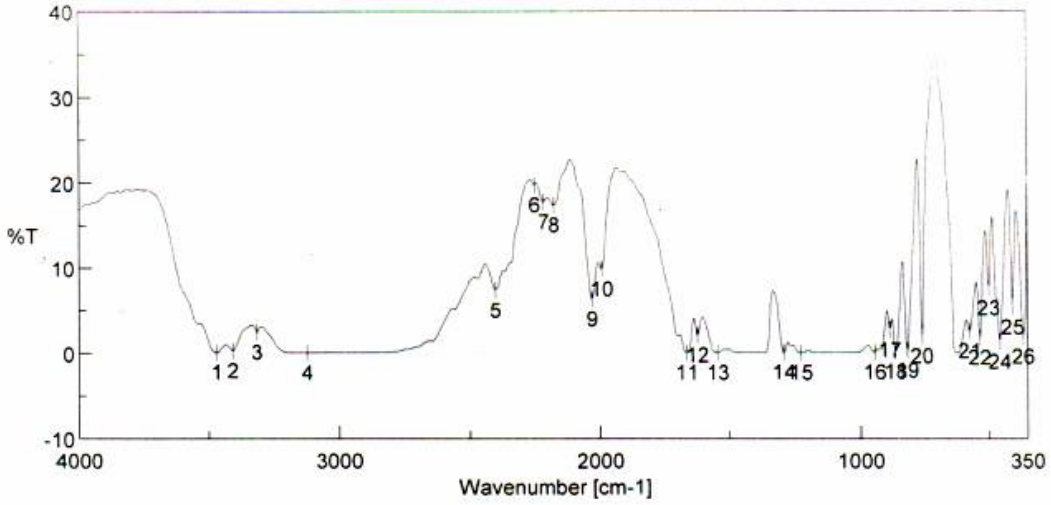

Fig.1

[Comment]

Sample Name	lig 2
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 (162)
Resolution	8 cm-1
Zero Filling	On
Apodization	Cosine
Gain	Auto (16)
Aperture	Auto (7.1 mm)
Scanning Speed	Auto (2 mm/sec)
Filter	Auto (30000 Hz)

Oct 2017 - Dec 2017 ,Vol 3, No. 2, 102-112 ISSN 2394-9449

Electronic Journal of Advanced Research

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Characterization of [Cr L(ClO_4)$_2$] Complex

The Cr(II) complex (4,4,9,9-tetramethyl-5, 8-diazadodec-2, 11-dione Cr(II) perchlorate) was synthesized by initiating Cr(II) perchlorate 10 ml was dissolved in methanol followed by (make + H_2) $(ClO_4)_2$ (24gm, 0.052 ml), the mixture was refluxed until colour of solution changed from purple violet to blood red. After some times, the product was filtered, recrystallized from methanol and evaporated to dryness in vacuum (Table:2).

Table: 2

Elemental analysis and IR Spectra of Cr(II) complex

$C_{14}H_{28}$ $N_2O_{10}Cl_2$ Cr (II)

Anal calculation : C, 32. 62; H, 5.48; N, 5.45; O 30.97

Cl, 13.81; Cr, 10, 82

Found; C 32, 63, H, 5.41; N, 5.40; O, 30.91

Cr = 10.81

IR (KBr) cm^{-1}

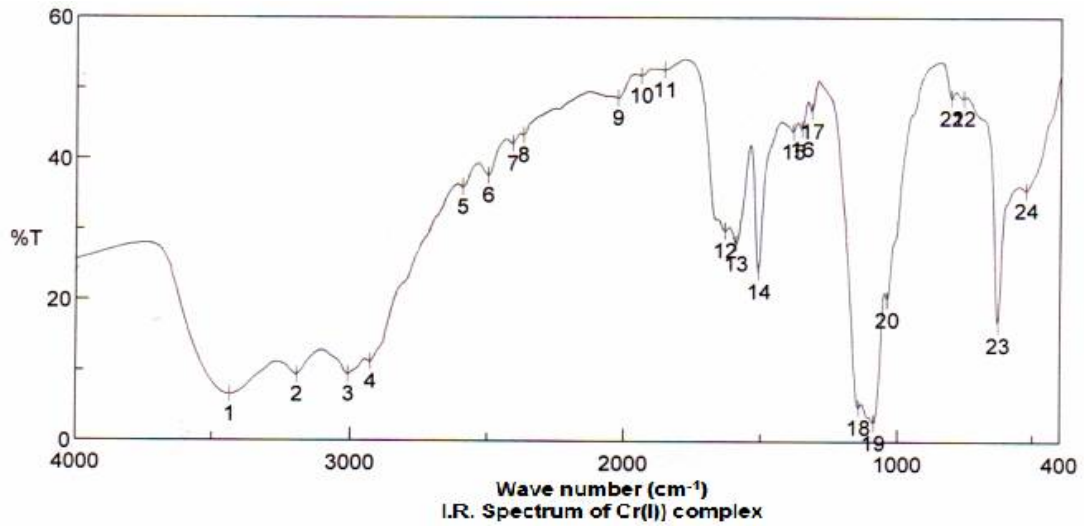

Fig.2

Oct 2017 - Dec 2017 ,Vol 3, No. 2, 102-112 ISSN 2394-9449
Electronic Journal of Advanced Research
An International Peer review E-Journal of Advanced Research

[Comment]	
Sample Name	1.1p
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 (42)
Resolution	16 cm-1
Zero Filling	On
Apodization	Cosine
Gain	Auto (4)
Aperture	Auto (7.1 mm)
Scanning Speed	Auto (2 mm/sec)
Filter	Auto (30000 Hz)

The Cr(II) complex has been synthesized by the reaction of Cr(II) perchlorate with demi-macrocylic of ligand donor N_2O_2 according to the following reaction :

$$Cr\ (ClO_4)_2\ +\ L = [Cr\ L\ (ClO_4)_2]$$

where, L = Ligand, N_2O_2

The IR spectra of complex exhibits a strong sharp to medium intensity band in 500-457 cm^{-1} region which may be assigned to Cr-oxygen stretching vibration. The frequency (Cr-O) stretching frequencies is lowest and intensity of the vibration is decreased which may be attributed to the hindered vibrations.

The electronic spectra of the Cr(II) complex exhibits a single allowed absorption and at 13000 cm^{-1} – 17000 cm^{-1} assignable to ^5Eg- ^5T_2g. The observed bands in the visible and near UV region were due to d-d transition. The intense CT bands at 10200 cm^{-1} is assigned to ligand to metal CT (Figs. 2 and 3).

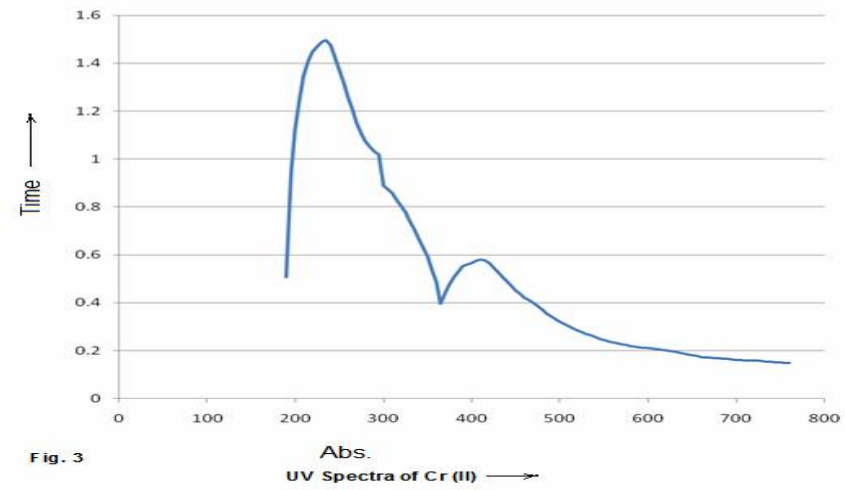

Fig. 3

Oct 2017 - Dec 2017 ,Vol 3, No. 2, 102-112 ISSN 2394-9449

Electronic Journal of Advanced Research

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The spectral kinetic study of Cr(II) demi-macrocyclic complex with N_2O_2 has been explored spectrophotometrically at wave length 240 nm whoes peaks of complex Cr(II) metal ion that decreases in absorbance of complex with time the Beer-Lambert law was verified from the slope of log (absorbance) or optical Vs. time for first-order rate constant (Tables:3 and Fig. 4).

Table: 3

Dependence of rate on varying concentration Cr(II) in the formation of demi-macrocycles complexes with ligand donor N_2O_2

$[N_2O_2]$ = 5.0×10^{-3} (mol dm^{-3}); λ = 240 nm ;

Temperature = 298 K

Sr. No.	[Cr(II)] × 10^2 (mol dm^3)	10^3 k (s^{-1}) For [Cr L $(ClO_4)_2$]
1	1.00	1.37
2	2.50	2.03
3	5.00	2.85
4	7.00	3.31
5	10.00	3.72

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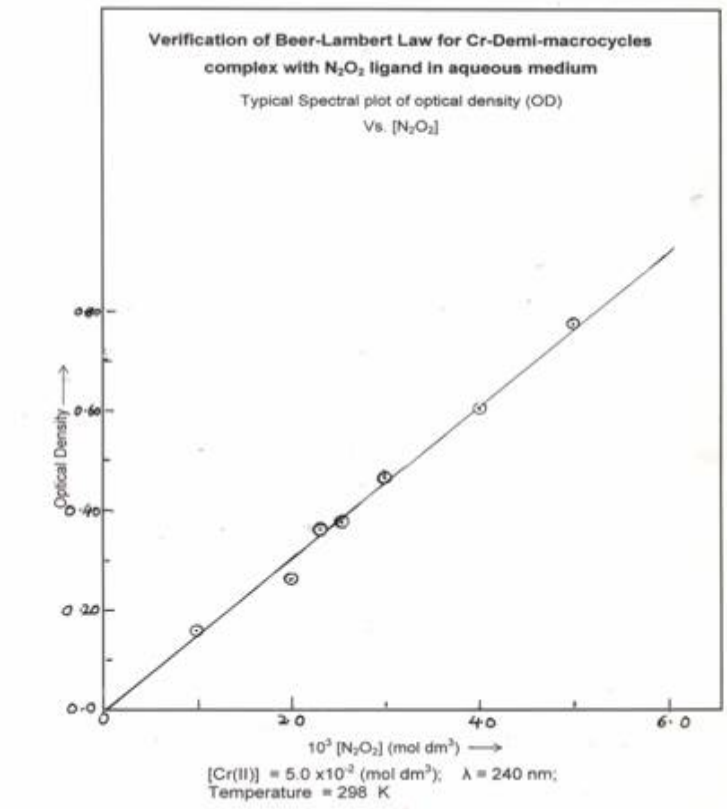

Fig. 4

The molar conductance values (λ max= 5- 15 Ω^2 cm^2 mol^{-1}) of the complex in DMSO (10^3M) indicates the non-electrolyte nature. The magnetic moment (μ) value of Cr(II) complex is an octahedral field is due to high spin approximately 3.95 B.M.

The rate of formation of complex increases with rise of pH (4.97) at constant ionic strength of the medium but shows a neutral nature of complex. One kinetic process was observed which was attributed to reverse reaction :

$$Cr^{2+} + 2\,L \underset{k_d}{\overset{k_f}{\rightleftharpoons}} [Cr\ L^{+2}] \qquad \ldots\ldots\ldots (1)$$

The final rate law was derived as:

$$k_{obs} = k_f\,[Cr^{2+}] + k_d \qquad \ldots\ldots\ldots (2)$$

Various thermodynamic activation parameters were determined (Table: 4).

Table: 4

Oct 2017 - Dec 2017 ,Vol 3, No. 2, 102-112 ISSN 2394-9449
Electronic Journal of Advanced Research
An International Peer review E-Journal of Advanced Research

Thermodynamic parameters

S. No.	Demi-macrocyclic complex	Ea kJ (mol^{-1})	$\Delta H^{\#}$ kJ (mol^{-1})	$\Delta G^{\#}$ kJ (mol^{-1})	$-\Delta S^{\#}$ JK^{-1} (mol^{-1})
1.	[Cr L$(ClO_4)_2$]	2.38	16.41	69.30	176.0

The analytical and spectral kinetic results of Cr(II) demi-macrocycles with N_2O_2 complex are in an excellent conformity with its proposed composition. Similar mechanism has also been earlier reported for the said complex by a couple of authors.[17]

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