

## Synthesis, and Spectral Studies of Demi-macrocycles of Ligand N<sub>2</sub>O<sub>2</sub> with Ni (II) and Cu (II) Ions

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**Abstract:** The new series of demi-macrocycles of the type  $[C_{14}H_{30}N_2O_2(Cl_2O_4)_2]$  having N<sub>2</sub>O<sub>2</sub> as donors ligand were synthesized by the equimolar condensation reaction of ethane-1,2-diamine in acetone in presence of perchloric acid. The head unit of demi-macrocyclic complex formed was proposed by the two acetone molecules  $[M(C_{14}H_{30}N_2O_2)(ClO_4)_2]$  where, M = Ni(II) and Cu(II) were formed by the reaction of proposed demi-macrocyclic complex with respective metal salts. The complexes formed were characterized by the elemental analysis, conductance and magnetic susceptibilities measurements, and also by spectral methods.

**Keywords:** Attributed, implications incur, quest, relaxation.

### 1. INTRODUCTION

Macrocyclic ligands are considerably attractive in the quest for new chemistry, because they offer a wide variety of donor atoms, ionic charges, coordination numbers and geometry of the resultant complexes.<sup>[1-5]</sup> During recent years macrocyclic chemistry has attracted much more attention, so it has become a growing class of research. The structure of mono-nucleating aza-macrocyclic ligand is a organic framework which holds a transition metal ion via a nitrogen atoms, with varying substituents on the carbon atoms. Macrocyclic or demi-macrocyclic ligands are polydentate ligand containing their donor atoms either incorporated in or less commonly attached to a cyclic backbone.

The understanding of the metal ion chemistry of macrocyclic ligands has important implications for a range of chemical and biochemical applications.<sup>[6,7]</sup> Macrocyclic ligand complexes are of great importance in enhancing various industrial applications and in a number of biological processes such as photosynthesis and di-oxygen transport.<sup>[8]</sup> Cu(II) is the most studied metal ions<sup>[9,10]</sup> playing significant role either in naturally occurring biological systems or as pharmacological agents.<sup>[11,12,13]</sup> Here we report the synthesis of demi-macrocyclic complexes of ethylene diamine and acetone with Ni(II) and Cu(II).

### 2. MATERIALS AND METHODS

All reagents and solvents used in the present investigation were of standard grade. 1,2 diaminoethane, perchloric acid (HClO<sub>4</sub>), acetone (CH<sub>3</sub>COCH<sub>3</sub>) of Loba, Merck and Aldrich brands. The preparation of solutions, standardization, and procedures for demi-macrocyclic 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 cm<sup>-1</sup>) were recorded on a Jasco model 4100 FTIR spectrometer as KBr discs. UV-visible spectra were recorded on a Shimadzu 1700 pharmanalyzer. Conductivity measurements were made in DMSO or nitromethane (10<sup>-3</sup> mho) at room temperature on systronics conductivitymeter. Magnetic susceptibility was measured at 8000 G in a Evans magnetic susceptibility balance using Co[(Hg(SCN)<sub>4</sub>)] as calibrant and the experimental susceptibilities were corrected for diamagnetic correction with Pascal constants.<sup>[14-16]</sup>

## 2.1. Synthesis of Ligand

4,4,9,9-tetramethyl-5,8-diazoniumdiodeca-2,11-dione diperchlorate

Ethane-1,2-diamine (33.83) ml was added to acetone(36.80) ml in 5000 ml flask and solution was cooled in a icebath, perchloric acid was added drop wise with stirring and keeping the temperature below 5° C, the flask was completely filled with acetone and left without agitation under freezing conditions. After two days fine crystals of the product, which is insoluble in acetone, commenced to separate. The bulk of the product being present after two days was filtered off, washed with acetone until brown color vanished and the product remained was colorless and was air dried. The yield was equal to 85% (Table 1).

**Table1.**  $C_{14}H_{30}N_2O_{10}Cl_2$  457.30 Calcd. Mass (M)

| % Calculated Mass | % Observed Mass |
|-------------------|-----------------|
| C = 36.77         | C = 36.24       |
| H = 6.61          | H = 6.59        |
| N = 6.12          | N = 6.15        |
| O = 34.98         | O = 34.92       |
| Cl = 15.50        | Cl = 15.49      |

### IR Spectral data of Ligand

IR (KBr)  $\nu_{as}$  (C-H) 2960 (M),  $\nu_s$  (C-H) 2909  $cm^{-1}$ ,  $\nu$  (-C -(CH<sub>3</sub>)<sub>2</sub>) 1385, 1565 (s)

$\nu$  (C=O) 1685 (s),  $\nu$  (N-H) 3370,  $\nu$  (N-C) 1260,

$\nu_{as}$  (CH<sub>2</sub>) 2985,  $\nu_s$  (CH<sub>2</sub>) 3007,  $\delta_s$  (CH<sub>3</sub>) 1348  $cm^{-1}$ ,  $\delta_{as}$  (CH<sub>3</sub>) 1445  $cm^{-1}$

$\delta_s$  (CH<sub>2</sub>) 1473  $cm^{-1}$   $\nu$  (ClO<sub>4</sub><sup>-</sup>) 1105, 655  $cm^{-1}$

## 2.2. Syntheses of Demi-Macrocyclus Complexes

### a) Synthesis of Ni(II) Complex

4,4,9,9-Tetramethyl-5,8- diazadodeca-2,11-dione Nickel (II) complex

Nickel (II) sulphate hexahydrate (1.31gms) was dissolved in water (18ml) followed by respective ligand (4.57gms). The mixture was stirred until the liquid dissolved, the colour of the solution gradually changed from blue to red and the orange product crystallized. After several hours the solution was cooled in ice and the product was filtered off and washed with ice cold water yield (3gms, 80%) recrystallised from hot 1:1 water methanol or from hot acetonitrile /propanol-2, the compound was also formed by reacting respective ligand with nickel acetate tetrahydratpin methanol (Table 2).

**Table2.**  $C_{14}H_{28}N_2O_{10}ClNi$  513.994 Calcd. Mass (M)

| % Calculated Mass | % Observed Mass |
|-------------------|-----------------|
| C = 32.71         | C = 32.72       |
| H = 5.49          | H = 5.47        |
| N = 5.45          | N = 5.43        |
| O = 31.12         | O = 31.11       |
| Cl = 13.79        | Cl = 13.78      |
| Ni = 11.42        | Ni = 11.4       |

### IR (KBr)

$\nu$  (ClO<sub>4</sub><sup>-</sup>) 1100 s, 620 s

$\nu$  (Ni-O) 470  $cm^{-1}$ ,  $\nu$  (Ni-N) 405  $cm^{-1}$

(d-d) Spectra (methanol)  $cm^{-1}$  8140 <sup>3</sup>A<sub>2</sub> (F) → <sup>3</sup>T<sub>2</sub> (F)

13477 <sup>3</sup>A<sub>2</sub> (F) → <sup>3</sup>T<sub>1</sub> (F)

24000 <sup>3</sup>A<sub>2</sub> (F) → <sup>3</sup>T<sub>2</sub> (F)

35350 → CT

Dq= 820, B = 873, β= 839

$\mu_{eH}$  = 3.51 BM

## b) Synthesis of Demi-Macro-Cyclic Complex of Cu(II)

4,4, 9, 9-Tetramethyl - 5, 8-diazadodeca-2,11-dione copper (II) complex

Copper (II) sulphate (1.29 gms) was dissolved in water (36 ml) followed by the ligand (4.57 gms). The mixture was refluxed until the ligand dissolved. The color of the solution changed gradually from fast blue to light blue and black colored product crystallized. After several hours the solution was cooled in ice bath and the product was filtered off and washed with ice cold water, yield (3 gms, 76%) recrystallised from 1:1 hot water methanol or from hot acetonitrile propanol-2. The compound was also formed by reacting the respective ligand with copper acetate tetrahydrate in methanol (Table 3).

**Table 3.** C<sub>14</sub>H<sub>28</sub>N<sub>2</sub>O<sub>10</sub>Cl<sub>2</sub>Cu, 524.55 Calcd. Mass (M)

| % Calculated Mass | % Observed Mass |
|-------------------|-----------------|
| C = 32.33         | C = 32.34       |
| H = 5.33          | H = 5.29        |
| N = 5.27          | N = 5.30        |
| O = 31.05         | O = 31.10       |
| Cl = 13.50        | Cl = 13.54      |
| Cu = 11.19        | Cu = 11.24      |

### IR (KBr)

$\nu$  (Cu-N) 522 cm<sup>-1</sup>,  $\nu$  (Cu-O) 495 cm<sup>-1</sup>

d-d spectra (DMSO) 10810 E<sup>2</sup> → <sup>2</sup>T<sub>2</sub> Dq= 1081

35010 → CT

= 2.08 BM

Conductivity ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> = 13.0

## 3. RESULTS AND DISCUSSION

### 3.1. Characterization of the Ligand

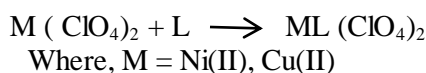
The 14-membered N<sub>2</sub>O<sub>2</sub> demi-macrocycle has been synthesized by mixed condensation of ethane-1,2-diamine with acetone as per the standard method. The addition of acids activates the amine group by protonation. The analytical results of the ligand and complexes are in conformity with their proposed compositions.

### 3.2. IR 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> primarily due to the asymmetric stretching mode in which the 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 (ν<sub>s</sub>GHb) in which all three of the C–H bond extend and contract in phase. The peak at 2985 cm<sup>-1</sup> and 3007 are attributed to the asymmetrical stretching (ν<sub>as</sub>CH<sub>2</sub>) and symmetrical stretching (ν<sub>s</sub>CH<sub>2</sub>). The high energy shifting of these peaks reflect strain in the chain. The symmetrical bending vibration (5<sub>s</sub>CH<sub>3</sub>) causes peak at 1348 cm<sup>-1</sup>, while the sharp peak at 1445 cm<sup>-1</sup> is attributed to asymmetrical bending (5<sub>as</sub>CH<sub>3</sub>). Strong absorption band at 1473 cm<sup>-1</sup> is the scissoring band (5<sub>s</sub>CH<sub>2</sub>) of methylene group. Absorption band between 1313 cm<sup>-1</sup> to 1156 cm<sup>-1</sup> is ascribed to twisting and wagging vibrations of methylene group. Strong absorption peak at 1685 cm<sup>-1</sup> is due to ketonic stretching vibration. Overlapping band peak at 3019, 3007, 3266 and 33701 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> (Fig. 1).

### 3.3. Characterization of Complexes

The metal complexes have been synthesized by the reaction of the respective metal perchlorates with the demi-macrocylic ligand according to the following reaction.



The molar conductance values ( $\lambda_m = 5\text{--}15 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ) of the complexes in DMSO (10<sup>-3</sup>M) indicate their non-electrolytic nature.

### 3.4. IR Spectra

The IR spectra of the complexes exhibit a strong sharp to medium intensity band at 500-457 cm<sup>-1</sup> region which may be assigned to metal oxygen stretching vibration. The  $\nu(\text{M-O})$  stretching frequency are in order of Cu > Ni. Upon complex formation the intensities of some the vibrations are decreased which may be attributed to the hindered vibrations.

The characteristic  $\nu(\text{C-O})$  absorption frequencies undergo a negative shift by about 50 cm<sup>-1</sup> in the complexes which may be ascribed to the relaxation effect caused to the lone pair donation by the oxygen atom to the metal ion. The  $\nu(\text{M-C1O}_4)$  stretching frequency sharp band at 535-500 cm<sup>-1</sup> is assigned to the metal-nitrogen stretching frequency. The order of  $\nu(\text{M-N})$  stretching frequencies is Cu > Ni. The non-appearance of  $\nu_s(\text{N-H})$ ,  $\nu_{as}(\text{N-H})$  and  $\delta(\text{N-H})$  vibrations in the complexes confirm the co-ordination of the metal ion by the deprotonation of the internal protons.

### 3.5. UV-Visible Spectra

The electronic spectra of the complexes was recorded in various solvents. The electronic spectral data of the complexes indicate an octahedral geometry around tire metal ion.

The electronic spectra of the copper complex shows a band at 10,869-10,752 cm<sup>-1</sup> corresponding to <sup>2</sup>E → <sup>2</sup>T<sub>2</sub> transition, which is characteristic of the octahedral Cu (II) complex.

The Ni(II) complex exhibits three absorption bands at 8, 200-8,140, 13,531-13,477 and 24,096-24,000 cm<sup>-1</sup> which can be attributed to the three allowed d-d transitions arising from <sup>2</sup>A<sub>2</sub> (F) ground state to <sup>3</sup>T<sub>2</sub>(F) ( $\nu_1$ ), <sup>3</sup>T<sub>2</sub> (F) ( $\nu_2$ ), and <sup>3</sup>T<sub>2</sub> (F) ( $\nu_3$ ) excited states respectively indicating an octahedral environment around Ni(II). These assignments are further supported by a close agreement between the observed and calculated values of A<sub>max</sub> for the  $\nu_2$  transition and also by the constant value of the intensity ratio of <sup>3</sup>A<sub>2</sub> (F) <sup>3</sup>T<sub>1</sub> (P) to <sup>3</sup>A<sub>2</sub> (F) <sup>3</sup>T<sub>2</sub> (F) transitions.

The observed magnetic moment of 2.08 BM of copper complex are higher than the expected values, probably due to octahedral geometry around Cu(II) ion.

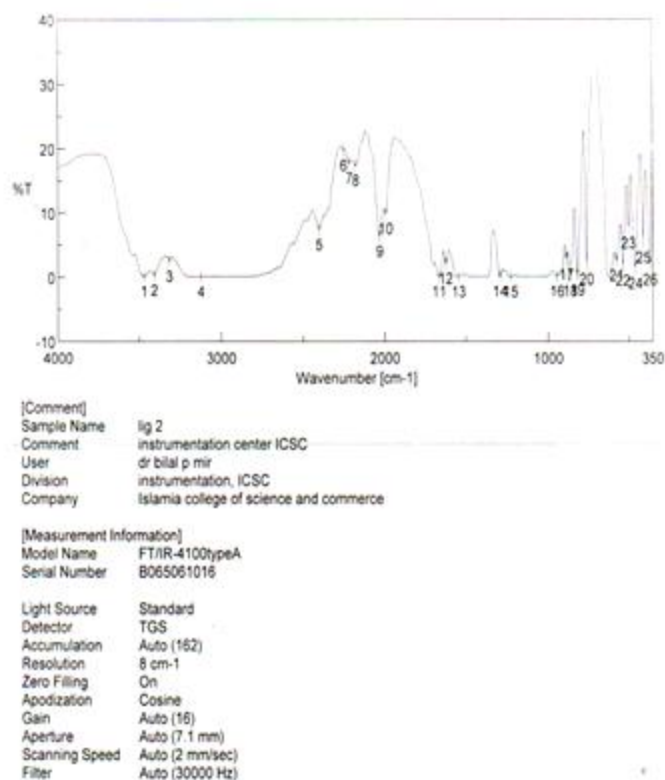


Fig1. IR Spectra of N<sub>2</sub>O<sub>2</sub>

## 4. CONCLUSION

Synthesis and spectral studies of demi-macrocycles of ligand N<sub>2</sub>O<sub>2</sub> with Ni(II) and Cu(II) ions are characterized by the elemental analysis. Conductance measurements and IR spectral methods show important implications for a range of chemical and bio-chemical applications as well as in biological processes.

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