

# Synthesis and Characterization of Novel Quadri-dentate Demi-macrocylic Ligand Having $N_2O_2$ as its Donors

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**Abstract:** A novel quadric-dentate demi-macrocycle of the type  $[C_{14}H_{30}N_2O_2] (ClO_4)_2^-$  was synthesized by 1:2 condensation reaction at high dilution process. The desired demi-macrocycle was characterized by spectral methods such as UV-visible, IR, <sup>1</sup>HNMR and elemental analysis. The results obtained were in close conformity with properties and proposed structure.

**Keywords:** Quadri-dentate, Novel, Exploration, Versatile, Chromophores

## 1. INTRODUCTION

Demi-macrocylic ligands or macrocylic ligands are polydentate containing their donor atoms incorporated in or less commonly attached to a cyclic back bone consisting of a minimum of nine atoms including all heteroatoms.<sup>[1]</sup> and at least having three or more donors. Macrocylic ligands have undergone lot of growth since they were first synthesized by Curtis and House.<sup>[2]</sup> The synthesis and exploration of macrocycles have undergone tremendous growth and their complexation chemistry with a wide variety of metal ions has been extensively studied.<sup>[3]</sup> Macrocylics are able to form stable, selective complexes with a variety of inorganic and organic cations by reaction with some anionic and neutral organic and biological substrates with specific properties and applications.<sup>[4]</sup> Macrocylic ligand systems for example are important to the mechanism of photosynthesis of plants and bacteria or for transportation of oxygen in mammalian and other respiratory systems.<sup>[5]</sup> Macrocylic ligands have been employed as selective extractants/ionophores for transition and post-transition metal ions in a range of solvent extraction and bulk membrane transport studies.<sup>[6]</sup> Macrocylic ligands find extensive bio-medical applications as contrast enhancing agents in magnetic resonance imaging (MRI)<sup>[7,8]</sup> as NMR shift reagents for biological systems<sup>[9]</sup> and as catalysts for the cleavage of RNA.<sup>[10,11]</sup> Macrocylic ligands have received special attention and attracted several national and international laboratories because of their mixed soft-hard donor character, versatile coordination behavior,<sup>[12]</sup> and of their pharmacological properties, i.e. toxicity against bacterial/fungal growth<sup>[13,14]</sup> as well as anticancerous,<sup>[15]</sup> antitumor<sup>[16,17]</sup> and anti-inflammatory<sup>[18]</sup> agents.

## 2. MATERIALS AND METHODS

All reagents and chemicals were of analytical grade and were used without further purification. Ethylene diamine, acetone and perchloric acid was of Fischer Scientific, Sisco Research Laboratories and Rankem brand respectively.

The proposed demi-macrocycle i.e. 4,4,9,9-tetramethyl-5,8-diazoniumdodeca-2,11-dione, diperchlorate was synthesized by 1: 2 condensation reactions via two different routes i.e. indirect protonation and direct protonation of ethylene diamine by perchloric acid in acetone medium at high dilution.

Ethylene diamine was added to acetone in a 250 ml flask and the solution was cooled in an ice bath. Perchloric acid (71%-73%) was added drop-wise with stirring. The addition of acid activates the amine group by protonation. Keeping the temperature below 20°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 24 hours while transferring the reaction contents contained in the flask to a deep freezer. The bulk of the product being present after 2 days was filtered off, washed with acetone until the brown color appeared due to the excess side products faded completely and the resultant white colored crystals were air dried and kept in amber colored bottles due to the photosensitivity of the desired ligand. The yield was ~ 85%.

The same protocol was applied in direct protonation of ethylene di-amine. The difference was there only in crystal growth and yield. The direct protonation gave a better yield in the ratio of 1:1.25 in comparison to indirect protonation.

The resultant ligand is a 14 memberd demi-macro-cyclic backbone (excluding its four donors i.e.  $N_2O_2$ ). The cyclization of the ligand occurs at high dilution while low dilution does not yield the desired product and that is the beauty of this reaction.

The desired quadri-dentate demi-macrocylic ligand is colorless solid soluble in aqueous medium insoluble in most of the organic solvents. The desired ligand is photosensitive and explosive in nature because of two nitrogen functionalities.

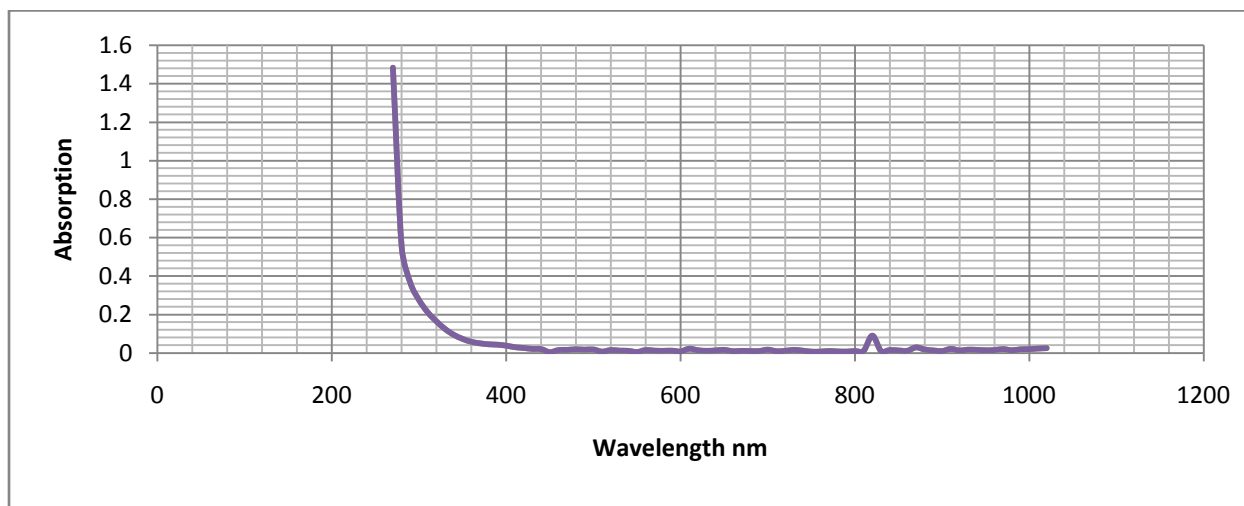
The melting point of the ligand was recorded on high precision digital auto melting point (Model No.  $\mu$  Processor 115 from Labtronics) apparatus. The ligand remains stable up to a temperature of 150°C after which it starts decomposing with appearance

of slight reddish color until the temp reaches 164° C a wine red coloration appears. As the temperature increases up to 180° C the compound decomposes completely while wine red color shows upward movement.

### 3. RESULT AND DISCUSSION

#### UV-visible Spectra

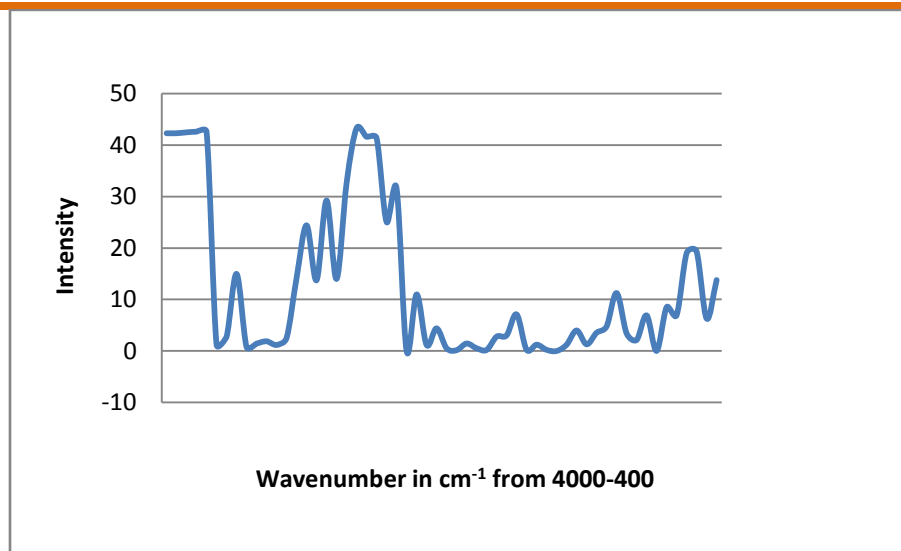
The UV-visible spectrum of the desired quadri-dentate ligand was recorded in an entire range from near IR to extreme ultraviolet region i.e. 1020-190 nm. The visible spectrum of the ligand does not show much absorption in visible region due to the absence of most of the chromophores while it does show characteristic absorption in the ultraviolet region from 270-300 nm particulars of ketonic group due to the  $\pi - \pi^*$  and  $n - \pi^*$  transitions of the ketonic group. The ligand does not show absorption for saturated secondary amine (Fig.1).



**Fig. 1** UV-visible spectrum of quadri-dentate demi-macrocylic N<sub>2</sub>O<sub>2</sub> ligand recorded on UV-vis Single Beam Spectrophotometer-LI-285

#### IR Spectra

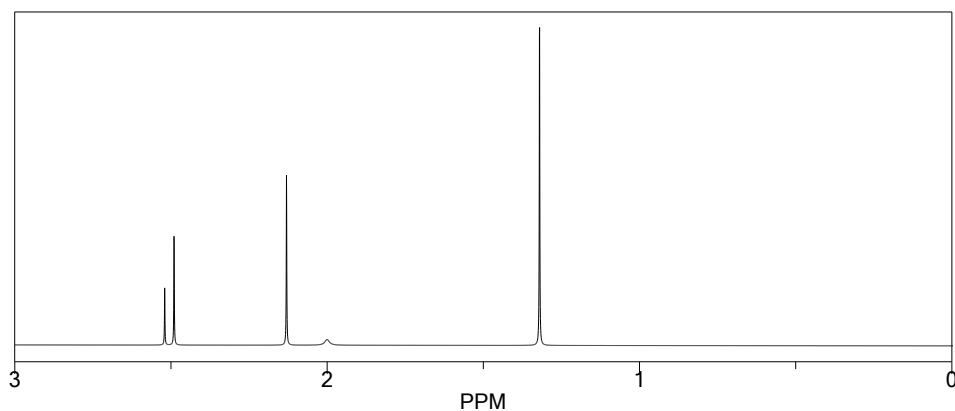
The IR spectrum of ligand shows characteristic absorption band at 2960cm<sup>-1</sup> primarily due to asymmetric stretching mode in which two C-H bonds of the methyl group are extending while the third one is contracting at 2904cm<sup>-1</sup> due to symmetrical stretching ( $\nu_s$ CH<sub>3</sub>) in which all the three C-H bonds extend and contract in phase. The peak at 2985 and 3007 are attributed to the asymmetrical stretching ( $\nu_{as}$ CH<sub>2</sub>) and symmetrical stretching ( $\nu_s$ CH<sub>2</sub>). The high energy shifting of these peaks reflect strain in the chain caused. The symmetrical bending vibration ( $\delta_s$ CH<sub>3</sub>) 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<sub>3</sub>). Strong absorption band at 1473cm<sup>-1</sup> band of ( $\delta_s$ CH<sub>2</sub>) of methylene group. Absorption band between 1313cm<sup>-1</sup> to 1156cm<sup>-1</sup> is ascribed to the twisting and wagging vibrations of methylene group. Strong absorption peak at 1685cm<sup>-1</sup> is due to ketonic stretching vibration. The slight shift in ketonic stretching vibration towards higher energy end is due the shielding of ketonic group. Overlapping band peaks at 3019, 3007, 3266 cm<sup>-1</sup> and 3370 cm<sup>-1</sup> are due to the N-H stretching vibration. Strong bands due to ionic perchlorate occur at 1105cm<sup>-1</sup> and 655cm<sup>-1</sup>. (Fig. 2.)



**Fig.2** IR Spectrum of novel quadri-dentate demi-macrocylic ligand having  $N_2O_2$  as its donors recorded from  $4000-400\text{ cm}^{-1}$  on Jasco model FT/IR-4100 Spectrophotometer

### $^1\text{H}$ NMR Spectra

The  $^1\text{H}$  NMR spectrum for the ligand shows a broad signal between 1-1.32 ppm for the protons of four methyl groups attached to the main cyclic backbone depicting same environment for the all methyl protons. The signal at 2-2.13 ppm is for protons of two methyl group having an electronegative group of per chlorate in the close vicinity. The medium signals at 2.49 ppm to 2.52 ppm are for the four methylene group protons attached to an ketonic carbon and amine carbon respectively. The ligand also shows a very rough peak for the two amine group protons. (**Fig.3**).



**Fig.3**  $^1\text{H}$  NMR spectrum of the novel quadri-dentate demi-macrocylic ligand having  $N_2O_2$  as its donors.

### Elemental Analysis

The elemental analysis for Carbon, Hydrogen, Nitrogen and Oxygen was performed on Elementar (Vario EL-III) model elemental analyzer. The results obtained after calculating by established methods and recording were almost in close conformity with the properties of the ligand (**Table 1**).

**Table 1** A comparison of the calculated and recorded percentage of the constituent elements of the novel quadri-dentate  $N_2O_2$  demi-macrocylic ligand.

Calculated	Observed/Found
Carbon = 36.73	Carbon = 34.56
Hydrogen = 6.61	Hydrogen = 5.90
Nitrogen = 6.12	Nitrogen = 5.84
Oxygen = 34.96	Oxygen = 32.55

#### 4. CONCLUSION

The desired quadric-dentate demi-macrocyclic ligand having  $N_2O_2$  as its donors is a 14 membered flexible ligand system (excluding its four donor atoms). The motive for selecting the particular ligand is its extreme stability as compared to its lower membered analogues. The resultant demi-macrocyclic was characterized by different spectral methods such as UV-visible, IR,  $^1H$ NMR and foremost by elemental analysis. The results obtained were in close conformity for the proposed ones.

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