Structural and Electronic Study of Palladium(II) Complexes by a Theoretical Approach

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Abstract. The established method of synthesising tetraaza macrocyclic ligand by introducing a transition metal ion as a templating agent has demonstrated difficulties in the decomplexation process. Therefore, this study examined the potential of forming the ligand before converting them into transition metal complex and further explored the characteristic of Pd²⁺ tetraaza macrocyclic complex through density functional theory (DFT) calculation. The results show that the cation successfully fits in the macrocyclic ligand as a result of the electron transfer process.

1. Introduction
Macrocyclic compound has garnered wide attention from researchers since its discovery due to its wide range of application. The tetraaza macrocyclic ligand containing four nitrogen atoms is the most widely known type of macrocyclic compound [1]. It is utilised in many areas including in catalysis, biomedicine, and waste treatment technologies. Ligand with nitrogen donor atoms has a high tendency to form a coordination bond with a transition metal ion [2]. Recent experimental studies have reported the successful template-free synthesis of tetraaza macrocyclic ligand and its metal complex in electrolyte nature [3-4]. However, until today, there are limited theoretical studies that specifically reported on metal-ligand interaction. This present work was carried out to investigate the role of tetraaza macrocyclic ligand in the complexation process with Pd²⁺ cation by adopting DFT simulation, as shown in Figure 1. Furthermore, it aims to understand the structural and electronic behaviour of Pd(II) complex as a cation compound for future implementation in technology development.

2. Method
This study performed the geometry optimisation and frequency calculation of tetraaza macrocyclic ligands using the hybrid functional RB3LYP combined with 6-311G(d,p,++) basis set. Meanwhile, the Pd²⁺ complex was predicted by using the LANL2DZ basis set containing electron core potential. The optimised structures were confirmed by the absence of imaginary frequencies [5]. All DFT calculations were operated using the Gaussian09 package.
3. Results and discussion

3.1. Molecular geometries

The optimised structures of tetraaza macrocyclic ligand and Pd$^{2+}$ complex are shown in Figure 2. The cyclisation process of tetraaza macrocyclic ligand occurs in the presence of secondary amine hydrogen atoms to reduce lone-pair repulsion. As shown in the DFT calculation, the bond length of Pd-N13 and Pd-N40 are similar to each other while Pd-N31 and Pd-N10 are longer than other bonds in the metal complex. The selected bond angles are summarised in Table 1. Sum all the four angles around the central Pd$^{2+}$ ion is 361°. This indicates Pd$^{2+}$ ion best fits the centre of tetraaza macrocyclic ligand as exhibited square planar geometry consequences from coordination bond formation [6]. The configuration of Pd(II) complex is comparable to Bohari's finding where macrocyclic tetraaza ligand behaves as a bidentate chelating, which binds with the metal ion through azomethine and imine nitrogen [3].

![Figure 1. Synthetic route of palladium(II) complex.](image)

![Figure 2. Optimised structure of tetraaza macrocyclic ligand and its complex.](image)

| Bond   | Length (Å) | Angle (°) |
|--------|------------|-----------|
| Pd-N13 | 2.03       | 83.13     |
| Pd-N31 | 2.09       | 97.87     |
| Pd-N40 | 2.03       | 82.13     |
| Pd-N10 | 2.09       | 97.87     |
| C-N    | 1.55       | 124.63    |
| C=N    | 1.30       | 119.72    |

Table 1. Selected bond length and bond angle of the Pd(II) complex.
3.2. Atomic charge analysis

The atomic polar tensor (APT) was obtained from the sum of charge and the charge flux tensors leading to a charge-charge flux model [7]. It requires calculating the second-order derivatives of wave function hence providing reliable results that correlate with experimental data [8]. Based on Table 2, the APT charge on N40 and N13 of free ligand has the highest negative charge, indicating a more electronegative region. This is due to the existence of lone pairs of nitrogen that act as donor atoms. When Pd\(^{2+}\) binds to the ligand, the APT charges are almost equally distributed to the four nitrogen atoms. This subsequently provides the initial indication that the bond formed between nitrogen and palladium in tetraaza will form a single bond structure. However, the types of bond formed needs to be confirmed through the electron density distribution using contour analysis, as discussed in the proceeding section.

| Atoms | Ligand | Complex |
|-------|--------|---------|
| N10   | -0.491 | -0.429  |
| N13   | -0.721 | -0.443  |
| N31   | -0.491 | -0.429  |
| N40   | -0.721 | -0.443  |
| Pd\(^{2+}\) | -     | 0.598   |

3.3. Molecular Electrostatic Potential Surface

The ligand's reactivity and its complex can be predicted through electron density illustrated by molecular electrostatic potential surface (MEPS). The total density surface mapped with electrostatic potential corresponds to partial charges, electronegativity and chemical reactivity of the molecule [9]. The MEPS visualises colour scheme is as follows; the blue region represents the partial positive charge (electron-deficient), light blue (slightly electron-deficient), the red region as partial negative (electron-rich), yellow (slightly electron-rich) and green region for neutral. Figure 3 shows that the light blue region on ligand structure could be seen clearly at C=N bond due to minimum positivity compared to other regions, indicating the reactivity sites with approaching ionic species [10]. Since N atoms at the light blue region possess lower isosurface (0.23), the electron density shows a withdrawal to Pd\(^{2+}\) during the electrophilic attack. After the complexation, the same contribution of electron density among atoms in the macrocyclic cavity could be observed.

![Figure 3. Molecular electrostatic potential surface of macrocyclic tetraaza ligand (left) and Pd(II) complex (right) on 0.02 isosurface value](image-url)
3.4. Contour maps of electron density
The two dimensional (2D) contour maps drawn in the molecular plane best describe the distribution of electron charge density in the title compound. It shows the amount of electronic charge at every point in the space, and all points with the same value for the electron density in the plane, are joined by the contour line. The total density of the contour map is projected in Figure 4. The isodensity of the ligand decreases from the outermost line towards the centre. In contrast, the contour maps of Pd(II) complex shows a decrease from the central metal towards the outermost line. This occurs due to the higher electron density in the almost spherical region surrounding each nucleus and much lower density in the bonding region [11]. From the contour plot analysis, we can infer that the bond formed in tetraaza between Pd$^{2+}$ falls under the ionic bond properties. This can be confirmed when we look at the electron density contour located between Pd ion and nitrogen, where the higher Laplacian indicates a nearly zero value. An interpretation of the topology of the total density at the critical bond point is proposed. It is characterised as ionic, and charge-shift bonding from the density point of view.

3.5. Frontier Molecular Orbital
The energy change in molecular orbitals was determined by the frontier molecular orbital analysis involving the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The orbitals scheme of free ligand and its complex are elucidated in Figure 5. HOMO indicates the $\pi$ bonding character, while LUMO indicates $\pi^*$ anti-bonding character. In the ligand structure, most electron clouds (red colour) found on the nitrogen atoms are attributed to the lone pairs. Meanwhile, at the LUMO state, the electron cloud concentrated at the centre of macrocyclic ligand, welcoming cation to form a dative bond. This signifies that Pd$^{2+}$ acts as an acceptor in the Lewis acid-base interaction. Therefore, the active sites for reaction mostly can be seen in the region of Pd and N atoms as visualised by complex orbitals [12]. The energy difference between the two orbitals, known as the energy gap, $E_{\text{gap}}$ was calculated using equation (1).

$$E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}}$$

It was found that the value of the energy gap for an electron to transfer from $\pi \rightarrow \pi^*$ orbital in the complex structure is smaller than the free ligand. The smaller energy gap determines the high electron transition to a higher energy state. Hence, the metal complex’s high reactivity and polarisability can be applied as future frontiers in optoelectronics.

4. Conclusion
The tetraaza macrocyclic ligand and its complex structural and electronic properties were examined using a theoretical approach. The DFT calculation indicates that the tetraaza macrocyclic ligand plays
an essential role in complexation by donating electron pairs to cation to form a stable complex. The HOMO-LUMO gap observation shows high electron mobility in Pd (II) complex system since only little energy is required for the electron transfer process. Based on the result of this pioneering work, in-depth investigations will be conducted on hybrid orbital to determine the ligand's optical properties and its complexity.

![Figure 5](image)

**Figure 5.** Frontier Molecular Orbital analysis of ligand (left) and Pd^{2+} complex (right).

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6. References
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