Albert Ofori

Inter- and intramolecular interactions in the stabilization and coordination of palladium and silver complexes: DFT and QTAIM studies

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Albert Ofori

Department of Chemistry,
University of Eastern Finland,
Finland.

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ABSTRACT

The utilization of inter- and intramolecular interactions in the area of solid state chemistry, especially in crystal engineering, calls for more understanding in the field. In this study, the interactions involved in the stabilization and coordination of palladium and silver complexes were fully studied. A Density Functional Theory (DFT) level of quantum chemical methods was used to investigate the relative stability of the complexes. The interactions were further analyzed with the Quantum Theory of Atoms In Molecules (QTAIM) method. Eight new paddlewheel palladium complexes and six distinctive silver compounds were synthesized and characterized, and their properties were computationally investigated.

Evidence provided from the results show the possibility of substituting a hard O atom with a softer S atom as a donor in a ligand coordinated to Pd(II) or Pd(III) dimers. When O is substituted with S, the S atom forms an intermolecular interaction with the phenyl group nearby (S···H-Ph), thereby stabilizing the structure. Moreover, in an attempt to explain the initial oxidative addition step in 2-phenylation of 1-methylindole and indole with palladium(II) compounds as a pre-catalyst using the newly synthesized palladium benzoato and thiobenzoato compounds (compound 1), the computational results revealed that the antibonding d-orbital in the HOMO of compound 1 was changed to bonding orbitals causing the axial phenyl to coordinate to the Pd metal. Therefore, fairly strong Pd···C(Ph) interactions existed making compound 1 a favorable structure for a pre-catalyst.

In addition, compounds formed from pyrazole and pyrazolato ligands were shown to stabilize themselves via additional weak intramolecular interactions, as observed in the Br···H-Npz interaction. Enhanced stability was also detected in compound 5 with mixed metal-metal interactions. The results showed that oxidized palladium(II) compounds always form the most stable compounds when compared to the starting compounds.

Furthermore, weak intramolecular interactions were found to play the main role in determining the favorable structures in the silver imidazolecarbaldehyde oximes. Slight changes in the imidazole ligand modify the entire solid state structures. Counter ions were found to influence the packing of the molecular structures in the solid state via intermolecular interaction, such as hydrogen bonding, but have no major role in controlling the molecular structure.

This study provides the basis for the main factors that control the inter- and intramolecular interactions, which will help in the design of new palladium and silver materials.
LIST OF ORIGINAL PUBLICATIONS

This dissertation is a summary of the following original publications I - III.


The joint publications were done in collaboration with experimental groups, but the author was solely responsible for the computational part of all publications I, II and III. The topic, the intra- and intermolecular interactions, is very challenging to be studied experimentally, and computational chemistry methods had an essential role in explaining the details of the experimental findings. The author has been active in planning the computational studies, testing the computational methods, performing the calculations and interpreting the results. Moreover, the author has written the computational part of the publications together with the main supervisor.
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ABBREVIATIONS

AIM  Atoms in molecule
BPW91  Becke’s exchange functional and Perdew and Wang’s gradient-corrected correlation functional
BCPs  Bond critical points
CPCM  Conductor-like polarized continuum model
DFT  Density functional theory
DCM  Dichloromethane
ECP  Effective core potential
PBE1PBE (PBE0)  Exchange correlation functional created by Perdew, Burke and Ernzerhof.
FMO  Frontier molecular orbital
HOMO  Highest occupied molecular orbital
LUMO  Lowest unoccupied molecular orbital
M-L  Metal – ligand
M-M  Metal – metal
NMR  Nuclear magnetic resonance
QTAIM  Quantum theory of atoms in molecules
SDD  Stuttgart-Dresden effective core potential basis set
R and R1  Substituents
TD-DFT  Time-dependent density functional theory
UV-vis  Ultraviolet visible
1 INTRODUCTION

Progress is being made in the effective application of intra- and intermolecular interactions, for example, in the field of active drugs  and in new materials and technologies . Understanding the nature of both inter- and intramolecular interactions is crucial for a chemist, because these interactions serve as a tool in building up new materials to produce desired properties, such as catalytic, optical, electronic and magnetic properties. Therefore, molecular interactions are one of the most promising and developing research areas for chemists today and will continue to be used in the future.

Interactions can span between covalent and non-covalent interactions. The latter has recently been the most discussed topic because of developments in the field of supramolecular chemistry. For instance, hydrogen bonding, halogen bonding, \( \pi-\pi \) interactions, and metallophilic interaction are forms of non-covalent interactions that exist in a molecular structure.

The structure of transition metal complexes in their solid states depends on the different kinds of intra- and intermolecular interactions that exist in the compound. Figure 1 shows an example of a simple schematic presentation of how these interactions in a molecular structure link the individual atoms and extend the structure in the solid state. Basically, intermolecular interactions occur between separate molecular structures. On the other hand, when the interactions occur within the same molecular structure, the intramolecular interaction is said to have taken place. Generally, a bond involves a strong interaction between atoms which can account for the short interatomic bond distances and strong binding energies. Therefore, interactions are forms of bonding. In this work, the term “interactions” is used to mean all kinds of interactions, especially focusing on non-covalent intra- and intermolecular interactions. The most paramount concern is to understand and explain the structures formed in experiments and to be able to predict future results using the knowledge obtained from the molecular interactions.

In the next sections, the general view on how interactions influence molecular structures and affect their stabilities will be elaborated upon. Moreover, the interactions involved when ligands are coordinated to metals and the effect of substituents on the ligand coordination are also discussed in this work.
Figure 1. A simple representation of bonding, inter- and intramolecular interactions in the solid state structure of molecular compounds. Red balls represent the individual atoms involved in the interactions.

1.1 Structure and stability

The crystal structure of a molecular compound is related to stability which is influenced by numerous factors. One of these factors is a result of inter- and intramolecular interactions which aid in stabilizing the crystal structure. Interactions influence the ability for each molecule to assemble with each other according to their reactivities. Another factor that influences the stability of a crystal structure is the reaction conditions. The crystals structure depend on the surroundings of the molecule, for example on the counter ions or solvent used in the reaction. Additionally, the geometry (structural composition) can affect the stabilization of the complex. The amount of stabilization can be observed in the relative energies of the compounds formed.

This work addresses molecular structures and their stabilities with the aid of experimental and computational studies. A reasonable distinction can be made between covalent and non-covalent interactions using the interatomic distances, and the interaction (binding) energies when these two studies are combined. However, since the stability of every crystal structure depends on the nature of inter- and intramolecular interactions, care must be taken during the analysis. This is due to the fact that the final self-assembly of the complex moieties is made possible due to these interactions, so every detail must be considered.
1.1.1 Energetics in structural stabilization

The ability of individual atoms in a molecular structure to stay close together is a result of each contributing to the lower state energies to form more stable compounds. The energetics involved in every structure stabilization is well understood by use of the computational approach. For example, how the structures are formed and why they are formed can be attended to by using theoretical methods.\cite{8} The calculated energies can mostly be correlated with experimental results.\cite{9} However, obtaining a proposed crystal structure experimentally might pose a great challenge. Because of this challenge, all other conditions which may or may not favor structures must be considered and optimized during calculations in order to obtain a minimal energy structure. The minimal energy structure is what gives an indication of whether or not a structure is favorable. Generally, isomeric complexes will have somewhat closely related energies because of the similar structural composition but can be differentiated by their geometries. For instance, Figure 2 shows two barbituric acid isomers A and B which have close relative electronic energies but are different in structural geometries.\cite{10} The more favorable structure is A, as observed in their energetics.

![Figure 2. Isomeric structures with similar energies but different geometries of barbituric acids.\cite{10}
Color code: red = oxygen, blue = nitrogen, gray = carbon, white = hydrogen.](image)
1.1.2 Geometries in structural stabilization

The structural composition and the structural diversities in terms of the coordination mode give guidelines as to where interactions can occur in a complex. The lowest energy geometry can therefore be calculated, leading to information on the structural stability of a compound. Calculations and analysis of the stability of a structure always begin with the geometry. If the right geometry (model) is chosen, the right results for the calculation can be obtained.

Studies on solid state structures have reported how crystal structures are stabilized in their solid states. For example, the solid state structures involve various interactions, including the weak intermolecular interactions between the adjacent molecule. The interactions have different roles in different molecular structures. Previous studies revealed, we cannot just give special names to the interactions until we know the special roles they play and how they contribute towards stabilizing the crystal structure.

A detailed study of the interactions involved in solid state structures can lead to the prediction of a crystal structure when the right model and correct conditions are selected. The geometrical environment of the crystal structure in terms of interactions can alter the final predicted structure and hence the molecule’s environment should be modelled as well in order to reduce errors in the proposed structure. In addition, the geometry of the ligand can pose a great challenge when predicting a crystal structure, hence the full properties of the free ligands must be studied.

1.2 Coordination in metal complexes

In transition metal complexes, ligands play an important role because of their coordination behavior toward transition metals. With different coordinations it is possible to affect the final solid state structure and enhance the number of applications, for example, by optimizing their optical properties and predicting their connectivity. Interactions in metal complexes affect the structural environment as well, in the sense that their availability induces and controls the coordinations in the crystal structure. For example, the self-assembly process of a molecule (crystal formation) is made possible when the individual parts; the metal, the counter ions and the ligands are well coordinated using different inter- and intramolecular interactions. It can then lead to the variety of coordinations involving metal-metal (M-M) and metal-ligand (M-L) bonding systems.
Such versatile coordinations are the most observed and are well understood in the chemistry of crystal structures.

**1.2.1 Metal-metal interactions in complexes**

Metal-metal (M-M) interactions, also known as metallophilic interactions, have been found to further stabilize and order the arrangement of complexes.\(^{19}\) They play the primary role in the aggregation of metal clusters in the crystal structures.\(^{19,\,20}\) Metallophilic interaction is said to exist when the M-M interatomic distance is shorter than the sum of the van der Waals radii of the individual atoms.\(^{21}\) They help in stabilizing metal complexes through extra intramolecular interactions. Theoretically, any factor that affects the metal center, such as electron density, can affect the extent of the metallophilic interactions.\(^{22}\) It is therefore imperative to consider the metal surrounding when describing metallophilic interactions. M-M interactions can be described by using the Frontier Molecular Orbital (FMO) approach.\(^{23}\) One challenge of M-M interactions is that electron delocalization can occur at the metal centers. For example, using the M-M bond distance only according to the sum of van der Waals radii to show metallophilic interactions may not be enough, and should be verified by computational methods.\(^{24}\)

**1.2.2 Metal-ligand interactions in complexes**

The steric and electronic flexibility of any ligand moiety will lead to many possible coordination modes.\(^{25}\) The ligands have donor sites (a negatively charged site) which react directly with metals (a positively charged site). The variable oxidation states that exist for transition metals also make it possible for a variety of coordination modes.\(^{26}\) Figure 3 shows a simple presentation of the common coordination modes of metal complexes observed in the Cambridge Crystallographic Database. Complexes involved in these bonding modes exhibit various inter- and intramolecular interactions as they coordinate with the different ligands.
Figure 3. Common coordination modes that exist in metal-ligand complexes reported in the Cambridge Crystallographic Database; (a) terminal – (b) chelating – (c) bridging bonding modes. Color code: blue = donor sites of ligands, cyan = transition metal ion.

The functional groups of the ligands that react with the metal salts must also be examined because many of their functions and properties are directly related to their bonding efficiency, which affects the final structure. The functional groups and their environment are often able to stabilize the solid state material using interactions such as π-π stacking and hydrogen bonding. It should be noted that all of the target sites of a ligand may or may not be directly involved in the reaction. When they are, the positions of the reactive sites will bring about the different coordination modes when coordinated. The metal-ligand interactions can be informative when dealing with the stability of complexes.

1.2.3 Effect of substituents on metal-ligand interactions

Substituents on ligands can be used to create changes in the electronic and the steric properties of a complex, because it is possible for the substituent to reprogram the ligand to coordinate with the metals involved. Substituents, to some extent, are “facilitators”. The nature and position of the substituent on the ligand can be used to determine whether or not a ligand is suitable for reacting with a metal salt to form a complex when all experimental conditions are favorable. Substituent
groups on a ligand can be either classified as electron withdrawing or electron donating depending on their composition and the effect they have on the ligand.

By virtue of analysis using the most promising tools, such as the atoms in molecule (AIM) method, their effect can be explained with the properties of electron density. Although not in all cases, it has been found that substituents influence intramolecular bond distances via hydrogen bonding. Influencing the bond distance basically means influencing the stability of a structure. Conventionally, the bond distance can be used to evaluate the substituent effect on a complex, whether it causes bond strengthening or bond weakening. Typically, M−M interactions are affected by the electronic contributions from the substituents of the ligand.

1.3 Aims of this study

Basically, once the type of interactions involved in the complexes is known, lots of questions can be answered. Theoretically, the region between the nuclei of atoms where electrons are concentrated and depleted is where most of the answers to interactions can be found.

The aim of this study is to describe the structural and electronic properties of transition metal coordination compounds to in order establish basic knowledge regarding the interactions and to use this knowledge to explain trends in the relative stability of the experimentally obtained compounds. The overall objectives of the study are:

1. To examine, by means of computational chemistry, the metal-metal and metal-ligand interactions in transition metal (Pd(II), Pd(III), Ag) complexes to discover the effect of the structural modifications on the stability, activity and selectivity of the compounds.
2. To examine the computational properties, such as the charge density in transition metal complexes, in order to study the nature of the interactions in detail.
3. To examine the effects of the interactions in the electronic absorption properties (UV-vis) in the transition metal complexes.
4. To examine the plausibility of re-engineering similar complexes when all properties are fully studied.
2 COMPUTATIONAL DETAILS

2.1 Density functional theory (DFT) method

By approaching this study of intra- and intermolecular interactions in transition metal complexes by using a computational method, this work is focused on the confirmation and explanation of experimental results. The computational work was conducted by modern quantum chemical methods. In general, modelling transition metal complexes can be more challenging than modelling the properties of purely organic molecules, because of the large number of electrons present, especially in the late transition metals. Hence, the method should be able to account for the electron correlation and the computational time. Moreover, the relativistic effects can cause very severe errors in the structures of the complexes, particularly those containing heavier transition metals.\textsuperscript{30} These errors might lead to inconsistent results for different metals. Therefore, the choice of the method in this work was conducted very carefully in order to maintain the required accuracy and reliability. Density functional theory (DFT) is a good compromise when large or medium-sized systems are to be studied. The implementation and application of the Kohn-Sham’s density functional theory (DFT)\textsuperscript{31} gives better results than the Hartree-Fock (HF) calculations on transition metal complexes. For this reason, a DFT level was chosen as a method to study the interactions in the transition metal complexes obtained from experiments. The accuracy of the DFT was verified by comparing the results with experimental findings.

Various hybrid functionals were tested together with different basis sets before usage. Hybrid functionals, such as B3PW91 and PBE1PBE (PBE0)\textsuperscript{32, 33}, were adopted throughout the study. Basis sets, such as a Stuttgart-Dresden effective core potential with an additional p-polarization function (SDD (p))\textsuperscript{34}, were used for Pd atoms. Moreover, a def2-TZVPPD\textsuperscript{35} effective core potential with triple-zeta-valence basis set with two sets of polarization and diffuse basis functions was used for Ag atoms. A standard all-electron basis set, 6-31G(d) or 6-31G(d, p), for all the other atoms was found to give reliable results in the study. The quantum chemical calculations were conducted with the Gaussian09 program package\textsuperscript{36} at the DFT level of theory.
2.2 Quantum theory of atoms in molecules (QTAIM) method

There are some properties of an atom which can only be characterized at the atomic level. However, some of these properties are transferable into a molecule and from one molecule to another on the electronic basis. This is where Bader and his co-workers' quantum theory of atoms in molecules (QTAIM) is of assistance.\textsuperscript{37, 38} With QTAIM, one can give a clear-cut definition of nature bonding in molecules, since QTAIM provides different levels of chemical concepts, where even weak bonding between closed shell systems can be defined.\textsuperscript{39}

The development of QTAIM has led to various applications. For example, the correlation between computational and experimental results are made possible with QTAIM, when all the boundaries of atoms in molecules are defined.\textsuperscript{40, 41} QTAIM allows open and closed systems to be examined.\textsuperscript{42} Also, atomic and bond properties obtained from QTAIM analysis can be good statistical data in establishing a structure-activity relationship.\textsuperscript{43} Other applications include drug development\textsuperscript{44} and accounting for the relativistic effects in transition metal complexes.\textsuperscript{45}

Calculations of electronic properties from QTAIM have been shown to have correlation with various experimental properties.\textsuperscript{37, 46} In this study, topological charge density analysis was performed, which allowed us to access the nature of the bonding by calculating different properties of the electron density at the bond critical points (BCPs). Typically, each atom in a molecule tends to attract or repel each other depending on the electronic distribution. The influence of attraction or repulsion is perceived at a point between the atoms called the critical point. Theoretically, the critical point is the point in space at which the first derivative of the density disappears (\textit{i.e.} $\rho$ assumes almost constant value).\textsuperscript{38} BCPs are where the all the information about the electron density can be obtained in order to explain the properties of the interactions in the solid state structure. Figure 4 shows a graphical representation of the Laplacian maps, including the BCPs for all the bond paths on a simple free organic ligand.
At each BCP, some properties of the electron density were selected to specifically describe the interactions involved in this work. The properties include $\rho$ (eÅ$^{-3}$), which describes the local electron density at the BCP and Laplacian of the electron density ($\nabla^2 \rho$ (eÅ$^{-5}$)), which is the second derivative of $\rho$, and also shows whether electrons are concentrated or depleted with respect to the environment in question. For example, when the calculated value of $\rho$ is more than 1.6 eÅ$^{-3}$, it indicates a shared shell bonding (covalent). Also, when $\rho$ is lower than 0.8 eÅ$^{-3}$ then a closed shell interaction, such as ionic, van der Waals, halogen or hydrogen bonding, is expected. According to the Laplacian property, the bond can be classified as closed shell interaction (when electron density is depleted i.e $\nabla^2 \rho > 0$) or shared shell interaction (when electron density is concentrated i.e $\nabla^2 \rho < 0$).

The interaction energy ($E_{\text{INT}} = \frac{1}{2} \times V_{\text{BCP}}$) between two interacting atoms tells whether interactions are strong or weak. $|V|/G$ is the ratio of potential energy density and kinetic energy density, and shows if the interactions are pure shared shell interactions (when $|V|/G>2$) or pure closed shell interaction (when $|V|/G <1$); when $1 \leq |V|/G \leq 2$, the interaction is electrostatic with some covalent nature.\textsuperscript{46,48}
In addition, the absolute values of the total atomic charge \( q(M) \) of the coordinating atoms was also calculated, even if different computational methods give different values and the charge cannot be practically measured. However, previous studies by Matta and Bader have shown that such an indirect property from QTAIM tends to support the experimental findings.\(^{49}\) The atomic charge helps when not much information is obtained from the molecular orbitals of the compound or the electrostatic potential maps, because of the similarity of the compounds.

The number of shared electrons outside the boundaries of an atom with another is called the delocalization index \( \Omega(M, X) \), where \( M = \) metal and \( X = \) ligand donor atom or another metal. The delocalization index is a quantitative property for measuring the extent of electron sharing and hence the pair of the atoms involved can be observed as bonded or not. Therefore, the degree of covalency can be expressed using the delocalization index property. In ionic systems, \( \Omega(M, X) \) assumes zero and close to one in mononuclear covalently bonded systems.\(^{50}\) In this study, the delocalization index \( \Omega(M, X) \) between \( M-X \) (bonding) atoms was considered to describe the nature of bonding. All QTAIM analyses were done with the AIMall program\(^{51}\) by using the wave functions obtained from the DFT calculations on the selected models.

### 2.3 Time-dependent density functional theory (TD-DFT)

The time dependent density functional theory (TD-DFT) utilizes time-dependent perturbing potentials formatted from the Kohn-Sham potentials, as shown in equation 1.\(^{52, 53}\)

\[
V_{KS}(r, t) = V_{ext}(r, t) + \int dr' \frac{n(r', t)}{|r-r'|} + V_{xc}[n(r, t)]
\]  

(1)

Where \( V_{ext} (r, t) \) is the external potential (time dependent) and \( V_{xc} (r, t) \) the exchange correlation potential (for density functional theory). The introduction and development of TD-DFT is currently ongoing, with different applications after several decades.\(^{54}\) Mostly the applications of TD-DFT nowadays can be compared to experimental findings, for example, in the area of organic light-emitting diode (OLED) emitters.\(^{55-59}\) In addition, photochemical and photophysical systems have been widely studied by using the TD-DFT method.\(^{60-62}\) In this work, the TD-DFT was used to calculate the absorption properties. The simulated spectra obtained from the calculations were then correlated to the experimental spectra. The solvent effects in the absorption properties were further...
described by using the conductor-like polarized continuum model (CPCM). The solvent mainly used was dichloromethane (DCM), because it was often used in the experimental measurement of the UV-vis spectra in the study. The chosen functionals and basis sets remained the same as in the energy calculations for the TD-DFT calculations.

2.4 Models

The obtained crystal structure as well as characterization results from the experimental studies was the starting point in the computational calculations. The models of the solid state structures were directly cut from the corresponding experimental crystal structures and analyzed with or without geometry optimization, depending on the question. The geometry of the Pd compounds was fully optimized. Frequency calculations with no scaling were conducted to ensure optimizations are true minima. None of the optimized structures gave imaginary frequencies. The models for the Ag complexes were taken from the crystal structure without optimization. Extended models were used for further interpretation of the intermolecular interactions, especially when the effects of hydrogen bonding, counter ions and the solvent were studied (Figure 5).

Figure 5. An extended model of a silver imidazolecarbaldehyde oxime complex involving counter ions. Color codes: light blue = Ag, white = hydrogen, red = oxygen, blue = nitrogen, gray = carbon, green = Cl, small green = BCPs.
2.5 Summary

The intermolecular and intramolecular interactions of solid state structures pertaining to their stabilities were studied. The procedure describing this work is summarized in scheme 1. The study started from a solved crystal structure of the synthesized compounds. The chosen model from the geometry was put through a full optimization or analyzed in experimental geometry and the selected properties were calculated.

Scheme 1. Schematic summary of the quantum chemical calculations and procedures involved in this study.
3 RESULTS AND DISCUSSIONS

3.1 Dinuclear palladium compounds

The chemistry of palladium compounds has been widely developed in recent decades, making the field an interesting topic for further studies. This study is seeking to expand the chemistry of palladium compounds both experimentally and computationally. The palladium complexes involve bidentate ligands, such as benzoato (O, O), thiobenzoato (O, S), and pyrazole or pyrazolato (N, N) ligands. The coordination of palladium to these organic ligands forms a rich chemistry and is explained using interactions that existed within the molecular structures. The dinuclear palladium compounds considered in the study were: \([\text{Pd}_2 \{(\text{C}_6\text{H}_4)\text{PPh}_2\}_2\{\text{OXC}(\text{C}_6\text{H}_5)\}_2\} (X = \text{O}, 1\text{a}; X = \text{S}, 1\text{b})\) and \([\text{Pd}_2\{\mu-(\text{C}_6\text{H}_4)\text{PPh}_2\}_2\{\mu-(\text{R,R'}_2\text{pz})\}_2\} \text{ for } 2, [\text{Pd}_4\{\mu-(\text{C}_6\text{H}_4)\text{PPh}_2\}_4(\mu-\text{pz})_2(\mu-\text{OH})_2] \text{ for } 3, [\text{Pd}_2\{\mu-(\text{C}_6\text{H}_4)\text{PPh}_2\}_2\text{Br}_2(\text{R,R'}_2\text{pzH})_2] \text{ for } 4, [\text{Pd}_2\{\mu-(\text{C}_6\text{H}_4)\text{PPh}_2\}_2\{\mu-(\text{R,R'}_2\text{pz-Ag-R,R'}_2\text{pz})\}_2\} \text{ for } 5, [\text{Pd}_2\{\mu-(\text{C}_6\text{H}_4)\text{PPh}_2\}_2\{\mu-(\text{R,R'}_2\text{pz})\}_2\text{Cl}_2\} \text{ for } 6\) (where \(\text{Pz} = \text{pyrazole or pyrazolate, R = R'} = \text{H, a; R = Br, R'} = \text{H, b; R = CH}_3, \text{R'} = \text{H, c; R = H, R'} = \text{CH}_3, \text{d; R = Br, R'} = \text{CH}_3, \text{e})

3.1.1 Properties of electron density

In this study, topological charge density analysis was performed on the various optimized dinuclear Pd(II) and Pd(III) complexes obtained. The results are grouped into two parts for the electron density analysis.

A. Palladium benzoate and thiobenzoate compounds

Two synthesized compounds were structurally characterized, palladium(II) complex containing a benzoate ligand (1a) and palladium(II) complex with thiobenzoato ligand (1b), (Figure 6). The two compounds form a complete square-planar coordination mode around palladium and hence can be called paddlewheel ortho-metalated palladium(II) compounds. The Pd-Pd bond distances were 2.6865(10) Å and 2.7395(4) Å for 1a and 1b, respectively, which are shorter compared to the sum of van der Waals radii (3.26 Å). The bond distance, when compared to the literature, showed that 1a was the second shortest Pd-Pd distance for paddlewheel palladium (II or III) compounds with two ortho-metalated phosphine ligands. However, when the ligand was slightly modified in the case of 1b, a longer bond distance was observed, when compared with other paddlewheel ortho-metalated palladium supported phosphine compounds with N,S ligands. The Pd-Pd, Pd-O and Pd-S bonding
was then monitored to study the interactions and the changes involved. The palladium benzoato and palladium thiobenzoato complexes were fully optimized. It should be noted that the two structures 1a and 1b are symmetric isomers with head-to-tail configuration of the phosphines.

Figure 6. Optimized structures of the Pd(II) benzoato (1a) and Pd(II) thiobenzoato (1b) complexes. For clarity, hydrogens and free phenyl groups of the phosphines have been omitted. Coloring scheme: Pd = blue, O = red, S = yellow, P = orange, C = gray. Blue dashed lines = the axial Pd-Pd interactions.1

The only difference in the structure of the two complexes can be seen in the S and O atoms which are trans to the P atoms and was observed in the change of the 31P-NMR chemical shift, which moved to lower frequencies when oxygen was replaced with sulfur. Therefore, the phosphorus atoms will obviously have an influence on O and S via its trans effect. Another isomer of 1b, where the S atom is trans to the C atom was calculated, to ascertain the preference of the symmetry of 1b. The DFT calculations revealed that 1b had a lower relative energy of c.a 32 kJ/mol than the other isomer 1b’, affirming the stabilities of the compounds. According to the optimized structures 1a and 1b, it was detected that the trans effect shortens the Pd-O bond, whereas it increases the Pd-S bond, thereby yielding a stronger interaction energy (E_{INT}) of -144 kJ/mol for Pd-O than the Pd-S bond, -128 kJ/mol, according to the QTAIM analysis. There was an increase in the electron density at the
Pd-S BCP, compared to that at the Pd-O BCP which lowered the interaction energy due to electronic effect. The weakened interactions affected to some extent, the stability of the 1b compound, thus its stability was lowered. However, the difference in stability was not too large to allow both 1a and 1b to be experimentally obtained.

Previous studies on the N, S-bridging ligand with dinuclear palladium (II) phosphines revealed that contribution of the p-orbital of the S atom in the highest occupied molecular orbital (HOMO) led to greater stability of Pd metal complexes. A detailed analysis was also performed here on frontier molecular orbitals (FMO) and by using Laplacian to distinguish the Pd-O and Pd-S bonding nature in compounds 1a and 1b (Figure 7). The results showed that Pd-S is more covalent because of the larger amount of electron sharing. The fragment analysis of the FMO shows a larger contribution of electron density from the S atom compared with the O atom. The ratio between potential and kinetic energy density (|V|/G = 1.32) and the delocalization index (Ω = 0.74) which estimates the bond index indicates the more covalent nature of the Pd-S bond. Replacing the O atom in 1a with the S atom in 1b, the S atom forms intermolecular interactions with the nearby hydrogen of the phenyl group (S−H-Ph) of the phosphines. 1b therefore stabilizes itself with the weak interactions. However, the substituent effect on the ligands cannot be overlooked. The strong electron withdrawing substituents were found to weaken the Pd(II)⋯Pd(II) interactions in both 1a and 1b, however the electron donating groups to strengthened the Pd(II)⋯Pd(II) interactions. Similar observations were made on the Pd-Pd interactions by M. A. Ubeda and co-workers in previous studies on dinuclear palladium (II) complexes.
**Figure 7.** (a) The frontier molecular orbital analysis and (b) the Laplacian of the electron density at the Pd1-Pd2-X (X = O, S) plane for Pd(II) compounds 1a and 1b (optimized structure of 1b showing interactions, extra phenyl group in the phosphine ligand omitted for clarity).

---

**1a:**
\[
\begin{align*}
\rho(\text{Pd-Pd}) &= 0.301 \text{ eÅ}^{-3} \\
\rho(\text{Pd-O1}) &= 0.521 \text{ eÅ}^{-3} \\
\rho(\text{Pd-O2}) &= 0.466 \text{ eÅ}^{-3}
\end{align*}
\]

**1b:**
\[
\begin{align*}
\rho(\text{Pd-Pd}) &= 0.277 \text{ eÅ}^{-3} \\
\rho(\text{Pd-S1}) &= 0.547 \text{ eÅ}^{-3} \\
\rho(\text{Pd-O2}) &= 0.427 \text{ eÅ}^{-3}
\end{align*}
\]
B. Palladium pyrazole and pyrazolate compounds

Pyrazolato ligands are well known for their stability and versatility in coordinating with the transition metals, especially with those with the oxidation state of II.\textsuperscript{71-76} In this part of the studies, a series of the first stable paddlewheel dinuclear palladium (II) and (III) pyrazolato compounds were synthesized and characterized (Figure 8). The stability of these compounds was studied by using the DFT method and their topological charge density analysis was performed by the QTAIM method in order to evaluate the nature of the interactions.

![Optimized structures of the Pd(II) and Pd(III) pyrazole or pyrazolato complexes 2-6 including their derivatives.](image)

For clarity, free phenyl groups of the phosphines are omitted. Coloring scheme: Pd = green, Ag = light blue, O = red, Br = deep red, P = orange, Cl = light green, H = white and C = gray.

The goal was to discover how the different pyrazolato derivatives aid in stabilizing complexes 2 - 6. The emphasis was on the effect of the ligands on the Pd\textsuperscript{2+}-Pd interaction, which was experimentally observed to be shorter than the usual bond length for Pd\textsuperscript{2+}-Pd interatomic interactions, and clearly shorter than the sum of the van der Waals radii. The usual metallophilic interactions reported to be favorable for metal complexes with bridging pyrazolato ligands fall within the range of 2.4 - 4.6
Å.\textsuperscript{71,77,78} Pd-Pd interactions were compared to ascertain the stability of the complexes formed. The selected, detailed results of the Pd-Pd analysis at BCPs can be seen in Table 1.

Table 1. Properties of the electron density at the \(M-M^1\) (where \(M, M^1 = \text{Pd or Ag}\)) bond critical points (BCPs) according to the Quantum Theory of Atoms in Molecules (QTAIM) analysis for selected palladium pyrazolato structures. The selected properties are: \(\rho = \) local electron density at the BCP; \(\nabla^2 \rho = \) second derivative of \(\rho\); \(|V|/G = \) ratio of potential energy density and kinetic energy density; \(E_{\text{INT}} = \) interaction energy between two interacting atoms; \(\Omega(M,M^1) = \) delocalization index between \(M-M^1\) (bonding) atoms; \(\text{gap} = \)HOMO-LUMO gap; \(\text{BD} = \) bond distance.

| Complex | Type | BD / Å | \(\rho / e\text{Å}^{-3}\) | \(\nabla^2 \rho / e\text{Å}^{-5}\) | \(|V|/G\) | \(\Omega(M,M^1)\) | \(E_{\text{INT}} / \text{kJmol}^{-1}\) | \(\text{gap} / \text{eV}\) |
|---------|------|--------|----------------|-----------------|-------------|----------------|-----------------|--------------|
| 2 a Pd····Pd | 2.67 | 0.309  | 3.071         | 1.23            | 0.32        | –67.4          | 3.86           |
| 3 a Pd····Pd | 3.12 | 0.135  | 1.17          | 1.12            | 0.19        | –19.5          | 3.85           |
| 4 a Pd····Pd | 3.07 | 0.162  | 1.296         | 1.17            | 0.23        | –25.1          | 4.08           |
| a Pd····Pd | 3.57 | 0.071  | 0.533         | 0.99            | 0.09        | –7.0           | 4.69           |
| 5 a Pd····Ag | 3.30 | 0.089  | 0.944         | 0.98            | 0.09        | –12.4          |                |
| a Ag····Ag | 3.43 | 0.071  | 0.695         | 0.90            | 0.07        | –7.8           |                |
| 6 a Pd····Pd | 2.51 | 0.457  | 2.338         | 1.44            | 0.64        | –81.7          | 2.97           |
The compounds 2a – e form stable structures which have a shorter Pd-Pd bond distance in the range of 2.6724(7) Å to 2.684(12) Å. The strong Pd···Pd interactions were observed in the experimental UV-vis spectra and were supported by the simulated spectra from calculations (see section 3.1.3 for details). The structure of 3 is a tetranuclear complex, thus there are two symmetric Pd···Pd interactions. The Pd-Pd bond distance in 3 increased when compared with compound 2. The increase in bond distance reduces the strength of the Pd-Pd interaction with the interaction energy of -19 kJ/mol in 3 compared to the -67 kJ/mol of 2. The HOMO-LUMO gaps for both revealed similar stability. The hydroxo bridging groups were not symmetrical in the coordination with Pd metal, thereby influencing the Pd-Pd interatomic distance.

According to the QTAIM analysis for 4, smaller interaction energies and electron densities at the Pd-Pd BCPs were observed. This can be attributed to the different bonding mode of the N, N-donor ligand (Figure 8). The ligand is mono-coordinated and has a neighboring bromido ligand on the same Pd metal. This accounted for the reduction in the covalency and the strength of the Pd-Pd interaction of structure 4. However, the pyrazolato ligand and bromido ligand form intramolecular hydrogen bonding interactions with each other in the form of Br···H-Npyrazolato (Figure 9a), which stabilize the structure. The interaction energy and the delocalization index at the Br···HNpz BCP were -24 kJ/mol and 0.123, respectively, which are larger than the typical Br···H interactions. It was observed by the 1H-NMR that the intramolecular hydrogen bonding affected the signals, which caused the NH signal to change from a broad signal as in the pyrazolato ligand to a sharp signal in the complex with similar chemical shift values. Evidence of more stability was observed in the HOMO-LUMO gaps, which increased compared to those in 2 or 3.

Compound [Pd2{µ-(C6H4)PPh2}2{µ-(R,R′2pz-Ag-R,R′2pz)}2] (5) comprises of a mixed metal tetrahedron system, thus it contains a Pd2Ag2 metal core. According to the DFT calculations, compound 5 maintained its geometry after optimization, since the overall tetrahedron of the metals were maintained (Figure 9b). Different weak M···M interactions were observed from the QTAIM analysis. For example, interaction energies at Pd···Pd, Pd···Ag and Ag···Ag BCPs were -7.0, -12.4 and -7.8 kJ/mol, respectively. These weak interactions had an effect in stabilizing compound 5. On the other hand, with the exception of the 5a and 5b derivatives that were obtained experimentally, the remaining derivatives could not be structurally solved. Other reasons, such as the bulky substituents on the pyrazolato ligand causing steric hindrance, also accounted for the stability of the crystal structures of 5.
Compound 6 was obtained from the oxidation of compound 2. It forms the most stable complex of all the palladium compounds formed and will be discussed in detail in section 3.1.2

**Figure 9.** (a) The optimized structure of 4 showing Br····HNpz interaction; the phosphine ligands were omitted for clarity (b) optimized structure of 5; the phosphine and pyrazolato ligands were omitted for clarity, and only the metal core of the Pd₂Ag₂ tetrahedron is shown. The compounds stabilize their selves using extra intramolecular interactions.

### 3.1.2 Chemical oxidation of dinuclear palladium (II) compounds

After the first synthesis and characterization of a dinuclear Pd(III) complex, increasing effort has been directed towards characterizing the oxidized Pd(II) compounds. The chemical oxidation of Pd(II) to Pd(III) by the addition of axial chlorido ligands has been shown to be plausible, and has been confirmed by DFT calculations. The model reaction of Cl₂ with compound \([\text{Pd}_2\{\text{C}_6\text{H}_4\text{PPh}_2\}_2\{\text{OXC}(\text{C}_6\text{H}_5)\}_2\], 1, or \([\text{Pd}_2\{\mu-(\text{C}_6\text{H}_4)\text{PPh}_2\}_2\{\mu-(\text{R,R’pz})\}_2\], 2, is shown in equation 2. Such oxidized complexes have already been found to be the most stable ones for palladium(II) and –(III) compounds with O,O-chelating and N,S-donor ligands in previous studies. In this study, attention was given to the oxidation of Pd(II) to Pd(III), since similar stable compounds 6 and 7 were obtained and characterized experimentally (Figure 10). Compounds 1a and 1b were oxidized to 7a and 7b, respectively, and 2 was oxidized to 6 (Figure 8).
Figure 10. Optimized structures of 7. For clarity, hydrogens and free phenyl groups of the phosphines are omitted. Coloring scheme: Pd = blue, O = red, S = yellow, Cl = light green, P = orange, C = gray. Blue dashed lines = the axial interactions.¹

\[
[Pd_2\{\text{(C}_6\text{H}_4)\text{PPh}_2\}_2\text{L}_2\} + \text{Cl}_2 \rightarrow \ Pd_2\{\text{(C}_6\text{H}_4)\text{PPh}_2\}_2\text{L}_2\text{Cl}_2
\]  

(Where L is \[\{\text{OXC(C}_6\text{H}_5)\}_2\], X = O or S for 1a or 1b and \[\{\text{µ-(R,R'}\text{pz)}\}_2\], for 2)

The favorability of the oxidation process was studied by calculating the reaction energies in order to classify the stability of the oxidized product. In compound 7, the oxidation leads to similar reaction energies for 7a and 7b of -146 and -140 kJ/mol, respectively, according to the DFT calculations. Also, the reactions for 6a and 6b gave higher values of – 197 kJ/mol and – 182 kJ/mol, respectively. These favorable energies again confirmed that the oxidation led to more stable complexes. To study the oxidized complexes further, the nature of interactions at the Pd-Pd, Pd-O, Pd-S, Pd-N and Pd-Cl BCPs were monitored using the QTAIM tool. Consequently, the nature of Pd-Pd interactions changed after the attachment of the axial chloride in comparison to the initial compounds 1 or 2. The addition of the axial chloride introduced more electron density around the Pd metal, thereby affecting the Pd-Pd interaction. The Pd-Pd interaction became stronger with increasing covalency for both 7a and 7b, therefore a short Pd(III)-Pd(III) bond distance was
recorded. Very high interaction energies (c.a – 82 kJ/mol) were obtained for compounds 6. The high stability was a result of the nature of the pyrazolato ligand, which is less bulky and does not interfere with the addition of the axial chlorido ligands. The obtained Pd(III)-Pd(III) bond distance (2.5212(10) Å) was among the shortest bond distances characterized for paddlewheel ortho-metalated palladium(III) complexes.\textsuperscript{70, 79-81, 84, 85} Moreover, not only did the oxidation affect the Pd-Pd interactions, it also affected the M-L (either O, S or N) interactions as well. In 7a and 7b, the Pd-O bonds showed increasing strength while the Pd-S bonds showed weakened interactions with reference to their starting compounds 1a and 1b. Therefore, the axial chloride tends to weaken the Pd-S interaction as a result of the concentration of electrons. However, the S atom was found to form an additional stabilizing interaction with the nearby phenyl hydrogens (S$^\text{•••}$H(Ph) interaction, as shown in Figure 7), which affected the strength of the Pd-S interaction as well, and also stabilized the structure of 7b.

It has been previously suggested that oxidized dinuclear Pd(III) complexes are potential intermediates for the 2-phenylation in the cross-coupling catalytic reactions.\textsuperscript{70, 86} In this intermediate, the axial chlorides of the oxidized complex are replaced by phenyl groups from Ph$_2$I$^+$PF$_6^-$ in the initial oxidative stage of the reaction (scheme 2). A similar chemical oxidation procedure was used to establish the initial step in the 2-phenylation of 1-methylindole and indole with 1a and 1b.

\begin{center}
\begin{align*}
\text{Ph} & \quad \text{Ph}\text{$_2$I$^+$PF$_6^-$} \\
\text{AcOH, 298K} & \quad \text{1a or 1b} \\
\text{R = CH$_3$ (MI), H(IN)} & \quad \text{R = CH$_3$ (MI), H(IN)} \\
\end{align*}
\end{center}

\textbf{Scheme 2.} 2-phenylation of the 1-methylindole (MI) or indole (IN) in the cross-coupling catalysis using compound 1a and 1b as a pre-catalyst.\textsuperscript{1}

It must be noted that the steric properties of 1a and 1b are different from the previously studied Pd triazenido as a pre-catalyst\textsuperscript{70}, hence, the attachment of the phenyl groups was found to be favorable in the case of 1a and 1b (equation 3).
[Pd₂{(C₆H₄)PPh₂}₂{OXC(C₆H₅)}₂] + 2Ph → [Pd₂{(C₆H₄)PPh₂}₂{OXC(C₆H₅)}₂{Ph}₂]  (3)

(Where X = O or S for 1a or 1b)

Here, the oxidation, according to calculations, revealed that the reaction of 1a and 1b had the energies of -40 and -68 kJ/mol, respectively. The Frontier Molecular Orbital approach was also used to examine the effect of the axial phenyl groups on the Pd-Pd interaction. The results revealed that the antibonding metal d-orbital in the HOMO of both 1a and 1b changed to a bonding orbital when the phenyl group strongly interacted with the Pd metal, forming a strong Pd···C(Ph) interaction. Moreover, there were no major differences between the stability of the oxidized chlorido complex and the complexes with axial phenyl groups, since their HOMO-LUMO gaps were in the same range. Therefore, using 1a and 1b as an intermediate compound would be a suitable and efficient structure for a pre-catalyst.

3.1.3 UV-vis simulation

The charge density analysis supported the existence of a Pd(II)···Pd(II) interaction, which was confirmed via the experimental UV-vis spectra. To explain the UV-vis spectra obtained experimentally, time-dependent density functional theory (TD-DFT) calculations were performed to examine the Pd···Pd interactions. The simulated spectra showed a very similar lowest energy signal that was also observed in the experimental spectra (Figure 11). The different transitions were further supported in the frontier molecular orbital analysis. The major contributions arose from Pd d-orbitals in both the HOMO and LUMO+1, which shows that the lowest energy signal was mainly constituted of d−d excitations.
Figure 11. (a) Comparison of the simulated spectra obtained from TD-DFT calculations (Calculated) and the experimental UV-vis spectra (Experimental) (b) comparison of frontier molecular orbitals involved in the lowest energy excitation, HOMO (left) and LUMO+1 (right), of the palladium(II) compound 2. Notation Lp = phosphine ligand and Pz = pyrazolate ligand. Hydrogen atoms were omitted for clarity.
3.2 Silver imidazolecarbaldehyde oxime compounds

Oxime ligands are well known for their flexibility in forming different coordination modes with metals. However, only few investigations have systematically examined the coordination of imidazole oxime complexes. This work considers the effect of changes on the imidazole oxime ligand on their bonding modes, especially the factors that affect the versatile coordination modes when the ligand coordinates with silver.

3.2.1 The nature of free neutral imidazolecarbaldehyde oxime ligands

To understand the various coordination modes of the silver imidazolecarbaldehyde oxime complexes, the free neutral ligands were first fully studied. Figure 12 shows the Laplacian of free neutral imidazolecarbaldehyde oxime ligands selected for this study, namely 1-methyl-1H-imidazole-2-carbaldehyde oxime (L1), 1H-imidazole-2-carbaldehyde oxime (L2), N-hydroxy-1-methyl-1H-imidazole-2-carboximidamide (L3) and 1H-4(5)-methyleneimidazole-5(4)-carbaldehyde oxime (L4) (the ligand L4 is a mixture of tautomers 1H-5-methyleneimidazole-4-carbaldehyde oxime (L4A) and 1H-4-methyleneimidazole-5-carbaldehyde oxime (L4B)). These ligands were selected because of the prospect of the two donor sites of the ligand being able to form various coordinations modes.
The results showed that there were torsional differences in the oxime group (tail) of the selected ligands and a larger negative charge at the imidazole ring (head) than at the tail. In order to reveal the differences, a limited conformational analysis was performed to explain the structures adopted in the solid state coordinated complexes. Three different conformers were used in the analysis, one having a straight oxime tail, the other bent with an oxime OH pointing to the imidazole nitrogen and the third conformer was the one adopted in the silver imidazole oxime complexes obtained from the experiments (Figure 13). In all the calculations, the conformer with the straight oxime tail does not form any additional intramolecular interactions, therefore it formed the less favorable structure as compared with the bent conformer with strong OH···N(imidazole) intramolecular interaction. Moreover, the electronic properties favor the two N(imidazole)-donor sites of the ligands because of the large negative charge observed from the QTAIM. Substituents, on the other hand, create steric collisions with the ligand atoms, thereby affecting their electronic properties.
properties and form additional stabilizing intermolecular interactions, which may alter the preference of the coordination sites to bind to the silver ion.

Figure 13. Relative energies (kJmol\(^{-1}\)) for three different conformers of free ligands L1-L4. The energies are referenced to the structure with a bent oxime tail conformer, which exhibits a strong OH…N(imidazole) interaction.

3.2.2 Coordination modes of silver imidazolecarbaldehyde oxime complexes

The versatile coordination modes of imidazole oxime ligands when reacted with silver salts were studied, as represented in scheme 3. In this study, six structures were experimentally formed with different bonding modes of the imidazole oxime ligands represented as chelating, bridging (dimeric and polymeric) and terminal bonding modes in Figure 14.
Scheme 3. (a-b) Reactions of the imidazolecarbaldehyde oxime ligands with silver salts to form complexes 8 – 13.

Figure 14. Experimental structures of 8-13. For clarity, counter ions and solvents are omitted. Coloring scheme: Ag = light blue, O = red, H = white, N = blue, C = gray. Structure 9 has been omitted due to its similarity with 8.
A mononuclear [Ag(L1)]⁺ motif was obtained for complexes 8 and 9 (Figure 14). They are structurally similar, the only difference is their corresponding counter ions, NO₃⁻ for 8 and ClO₃⁻ for 9. Therefore, the results obtained for both were similar. The silver ion coordinated to the ligand at both the imidazole N-donor (head) and the oxime group N-donor (tail) sites. According to the QTAIM calculations in 8, the calculated interaction energy (E_int) revealed a stronger interaction at the head than at the tail (-172 and -15 kJ/mol respectively), giving rise to the asymmetric chelating coordination. These calculated energies correspond with the calculated larger negative charge at the head than at the tail (Figure 12). Electron sharing observed from the results revealed a partial covalent nature with a larger contribution from the head, which is also in agreement with the observed structure.

According to the conformation analysis, the straight conformer in L4A was a more favorable structure as compared with the straight conformer in L1 and it yielded 10, a dimeric bridging mode. The difference in L1 and L4A is in the location of the methyl substituent. The electronic effects led to additional H—H interaction which stabilizes the straight conformation. Also, the strong argentophilic interaction may have facilitated the bridging coordination of L4A more than would result from L1. Therefore, slight changes in the ligand structure control the coordination of the solid state structure. The results from the QTAIM analysis were found to support the strong Ag—Ag interaction with -47 kJ/mol for 10 at the BCP, which is expected for M-M interaction. The strong argentophilic interaction as well as the covalent bonding nature between the Ag and the ligand lead to the formation of the dimeric structure in 10, and allow further axial coordination, for instance with counter ions.

Ligands L2 and the other tautomeric form of L4 (i.e. L4B) were involved in a polymeric bridging coordination mode to form complexes 11 and 12, respectively. The only difference is the arrangements of the ligands (Figure 14). The L4B compared with L4A has its N-donor site in the opposite direction, which is far from the oxime tail. Following the Ag-N(ligand) interactions for both nitrogens at the head and at the tail, the topological electron density properties were studied in reference to what was obtained from the experimental findings. The interaction energies of -165 and -133 kJ/mol for the head and the tail, respectively, revealed that the head binds more strongly than the tail in the case of 12. In 12, the ligands are in alternating orientation around the silver ions, either head-head or tail-tail. In 11, the more symmetric coordination around the silver ions (head-tail-head-tail) leads to similar interactions. Thus, both head and tail have similar coordination almost with the same strength (-140.9 and -140.8 respectively), leading to the formation of structure.
Therefore, when the imidazole oxime ligand is tuned with respect to slight changes in the geometry of the coordination sphere, different coordination modes are formed.

Ligand $L_3$ resulted in a special case of coordination mode, having a combination of bridging and terminal modes. The ligand adjusts to overcome its bulky nature, thereby bringing the coordinated silver metal closer to form an argentophilic interaction with -24 kJ/mol, which supports the Ag...Ag interactions. $L_3$ terminally coordinates to fill additional coordination sites and complete the structure of $13$. In the terminal ligand, the preferred coordination site is again the imidazole nitrogen, as expected.

### 3.2.3 Hydrogen bonding interactions: the role of counter ions in controlling structures

It has been frequently suggested that counter ions control crystal structures of complexes. In this study, we showed that in the case of imidazole oximes they are not a major factor controlling the crystal structure (geometry) but rather aid in crystal packing. The counter ions highlighted in this work were $\text{NO}_3^-$, $\text{ClO}_3^-$ and $\text{CF}_3\text{SO}_3^-$. Extended models including the counter ions were cut from the packed crystal structures. The models were then analyzed via the QTAIM method and the interactions between the counter ions and the cationic motifs of the complexes were compared with other intra- and intermolecular interactions. Similar observations were made for complexes 8 and 9, even though they have different silver salts, i.e. $\text{AgNO}_3$ for 8 and $\text{AgClO}_3$ for 9. The counter ions were linked to their cationic part through non-covalent $\text{O}(\text{counter ion})...\text{H(ligand)}$ interactions via either the head or the tail. The torsional behavior of the oxime OH of the ligand $L_1$ was found to freely rotate and the OH group does not coordinate to the silver ion. The counter ions, however, had no major effect in controlling the chelating coordination mode.

Furthermore, all the remaining complexes were examined. For example, in 10, the counter ion ($\text{NO}_3^-$) occupied the axial site of the dimers. They are then connected to the adjacent molecules into chains that enhance the packing of the solid state structures. The $\text{NO}_3^-$ had no significant impact on the complex. In the polymeric chains of 11 and 12, the ligands adopted the most stable bent conformer using intramolecular hydrogen bonding interaction. The interaction of the counter ions (either $\text{NO}_3^-$ or $\text{ClO}_3^-$) were similar. According to the QTAIM calculations, there was a strong interaction of the counter ion with the OH group of the oxime tail, which assisted the torsional behavior of the OH group. Therefore, the counter ions affected the intramolecular interaction of the
ligands by helping in the rotation of the tail and by playing the role of connecting the adjacent chains with the packing of the crystal structure.

In structure 13, the CF₃SO₃⁻ only aided in the completion of the coordination sphere. However, CF₃SO₃⁻ occupies the axial site of the dimeric complex with strong O(counter ion)⋯HO(ligand) interaction similar to 10. The bulky axial ligands prevented the formation of the similar chains of dimers, as observed in 10 (Figure 15). The separate molecules in 13 were connected only via weak hydrogen bonding interactions in the solid state structure.

![Figure 15](image.png)

**Figure 15.** The role of NO₃⁻ counter ions in enhancing the polymeric chain of 10 in the ac-plane.
4 SUMMARY

In this work, various intermolecular and intramolecular interactions in transition metal complexes were studied using DFT and QTAIM methods. It is clear from the studies that understanding the different kinds of interactions that exist between M-M or M-L coordination leads to a definition of the structural composition of solid state structures. The stability of palladium(II) and (III), and silver compounds were confirmed and the details were explained.

This study demonstrated the effect on the stability in benzoato complex when O was substituted with S to form thiobenzoato complexes with Pd(II) and Pd(III). The Pd-O interaction was shown to be stronger than the Pd-S interaction, which may have contributed to the slight instability of 1b. However, the 1b stabilizes itself, for example, by using other weak intramolecular interactions such as the one found between the S atom and the H atom from the nearby phenyl group (S···H-Ph interactions). The axial chlorido ligand attachment to 1a and 1b in the oxidation processes to form 7a and 7b were possible because both oxidized compounds were proven to be more stable. The strength of Pd(III)···Pd(III) interaction and the increasing covalency were similar in 7a and 7b, leading to the shortest Pd(III)-Pd(III) bond distance recorded. Moreover, the structure of a potential pre-catalyst in 2-phenylation of 1-methylenedole and indole with 1a and 1b was verified.

The rich chemistry of Pd(II) and Pd(III) compounds led to the design of new Pd(II)- and Pd(III)-pyrazole and pyrazolate compounds. Here five stable compounds were obtained. Compound 4 showed a longer Pd-Pd bond distance which reduced the strength and covalency of the Pd···Pd interaction. However, 4 stabilizes, for instance by using additional Br···H-Npz intramolecular interactions. In the special case of compounds 5 with heteronuclear tetrahedron Pd2Ag2 core additional M···M interactions were observed. Although these interactions are rather weak, they help to stabilize the molecular structure. Compound 6 was the oxidized product formed from compound 2 and again was shown to be more stable than corresponding Pd(II) compounds.

A systematic study of silver imidazolecarbaldehyde oxime complexes was also performed in this work. The neutral imidazolecarbaldehyde oxime ligands were fully studied. The charge distribution and electron density of the oxime ligands revealed the favorable coordination site of the imidazole oxime ligand, which is the imidazole nitrogen (head) as opposed to the nitrogen of oxime group (tail). The ligands adopted a stable bent or a straight conformer before coordinating to the silver metal. These led to the formation of various coordination modes with silver salts such as; a chelating mononuclear complex 8 and 9, a dinuclear bridging complex 10, a polymeric chain-like complex 11 and 12, and a combination of a bridging and terminal complex 13. The versatile
coordinations of the imidazole oxime ligand were especially achievable due to the free nature of the ligand, that is the torsional behavior of the oxime tail which is affected by any close weak interactions.

Furthermore, in this study it was confirmed that the counter ions had no major influence in the molecular structure but only aided in extending the structure, as in crystal packing through intermolecular non-covalent interactions.
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Albert Ofori
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