Evaluating the structural features of Bis(triphenylphosphine)nickel(II)complex using Avogadro

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1. Introduction

Coordination chemistry is basic chemistry of metal ions which accepts electron pairs from ligands around it. Coordination compounds provide a wide range of colours and coordination numbers of the metal ions exhibited their structure. Nickel is one of the transition metals and abundant in nature as nickel(II). This is because it is more stable than nickel (0), nickel(I), nickel(III), and nickel(IV). The geometries formed by the nickel (II) complexes varies, including square planar, tetrahedral, trigonal bipyramidal, and octahedral. The most common geometries of the nickel (II) complex are square planar and octahedral. Each nickel(II) ion complexes with certain ligands and shows different physical and chemical properties, thus making their investigation very interesting and challenging.

The Nickel (II) ion forms many stable complexes as predicted by the Irving Williams series. Nickel is a chemical element with the chemical symbol Ni and atomic number 28. It is a silvery-white lustrous metal with a slight golden tinge. Nickel belongs to the transition metals and is hard and ductile. In its compounds nickel exhibits oxidation states of −1, 0, +1, +2, +3, and +4, though the +2 state is by far the most common. Nickel (II) commonly forms a large number of complexes with three different geometries. These are octahedral, tetrahedral (PPh3)2, and square planar. Some five-coordinate complexes are known but are rare. Nickel(II) is a $3d^8$ system, so octahedral and tetrahedral complexes will have 2 unpaired electrons and square planar complexes usually will have none. Since square planar nickel(II) complexes usually have no unpaired electrons they are diamagnetic and thus have a magnetic moment of zero. Nickel compounds are suspected carcinogens and phosphines are irritants.

Bis(triphenylphosphine)nickel(II) complex is a widely used reagent in organic synthesis as a catalyst or intermediate in various reactions such as hydroformylation, hydrogenation, and cross-coupling reactions. It is also a good ligand for transition metal complexes and is used to prepare other coordination compounds. It is relatively stable and can be stored in the solid state

for prolonged periods under dry conditions. It is not hygroscopic, so it does not absorb water from air, but it should be kept away from moisture and air.

In addition, Ni(PPh3)2 can be used as a ligand in coordination chemistry. Its phosphine ligands can coordinate with a transition metal central ion, to form a coordination complex. These complexes are often used as catalysts in chemical reactions and have a wide range of applications. It is also used as a precursor in catalytic hydrogenation reactions, where it acts as a source of the Ni(0) catalytic species. The complex can also be used as an intermediate in the cross-coupling reactions where it acts as a source of Ni(0) catalytic species.

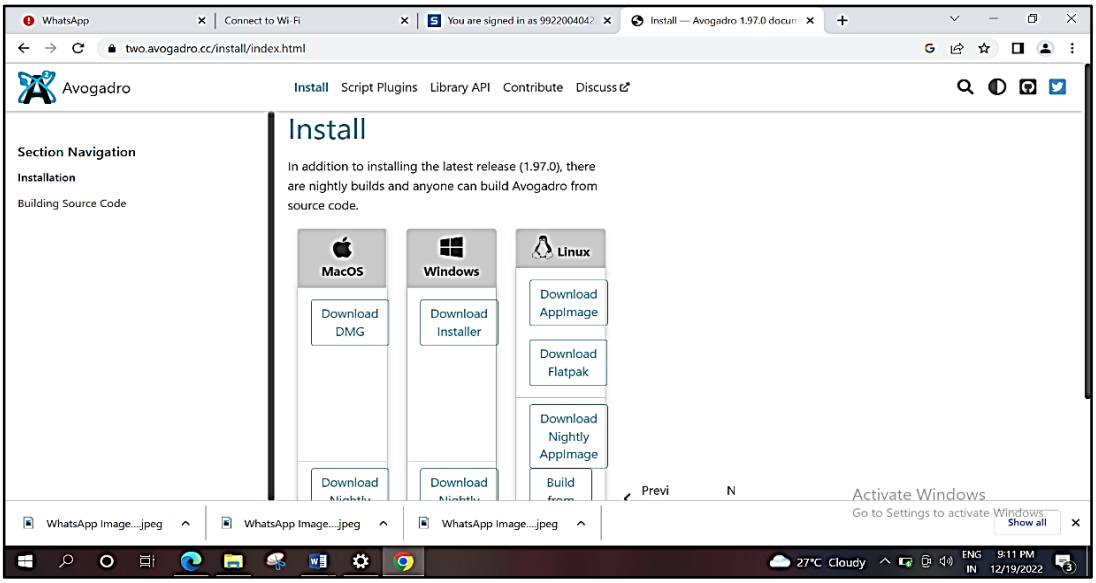
2. Objectives

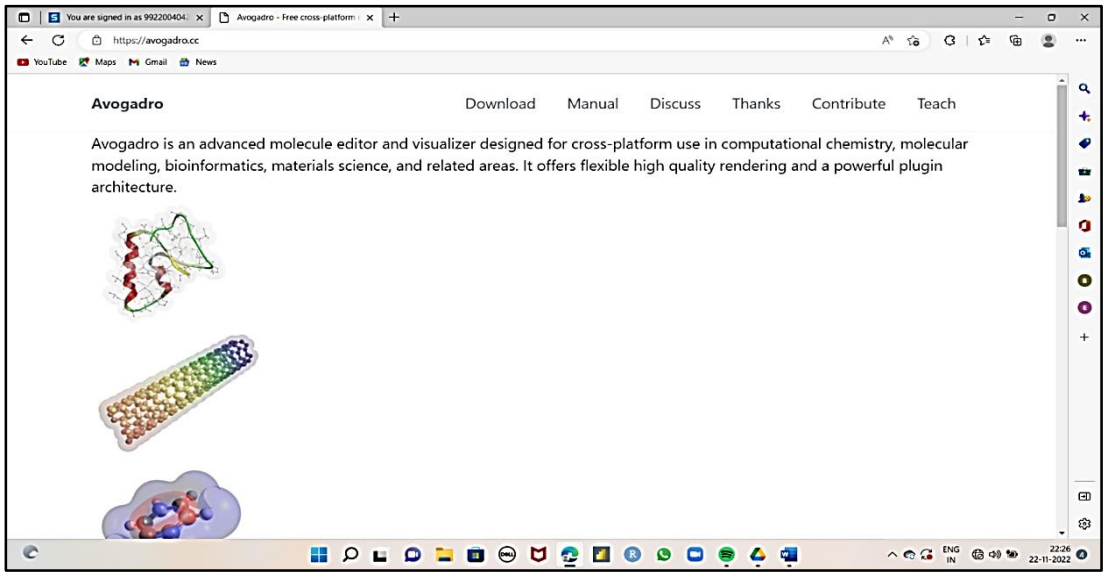
- Drawing the structure of Bis-Triphenyl Phosphine Nickel(II) complex in Avogadro interface.
- Analysing the structure of Bis-Triphenyl Phosphine Nickel(II) complex by changing the ligand to iodine.
- Analysing the structure of Bis-Triphenyl Phosphine Nickel(II) complex by changing the central metal atom.
- Interpreting the changes in the properties of the complex with changes in the metal atom and ligand.

3. INSTALLATION OF AVOGADRO

3.1. Procedure for installation

- Avogadro is an open-source software so it can be installed for free.
- Go to browser and search Avogadro in search bar, a webpage opens showing us the link **https://avogadro.cc**
- The download option is available at the top of the page, click on that option to download.
- After downloading, install the package in the system.
- At the time of installing the software click on the option saying Add Icon to Home Screen.
- Now we can open the Avogadro software from the Desktop by clicking on the icon.

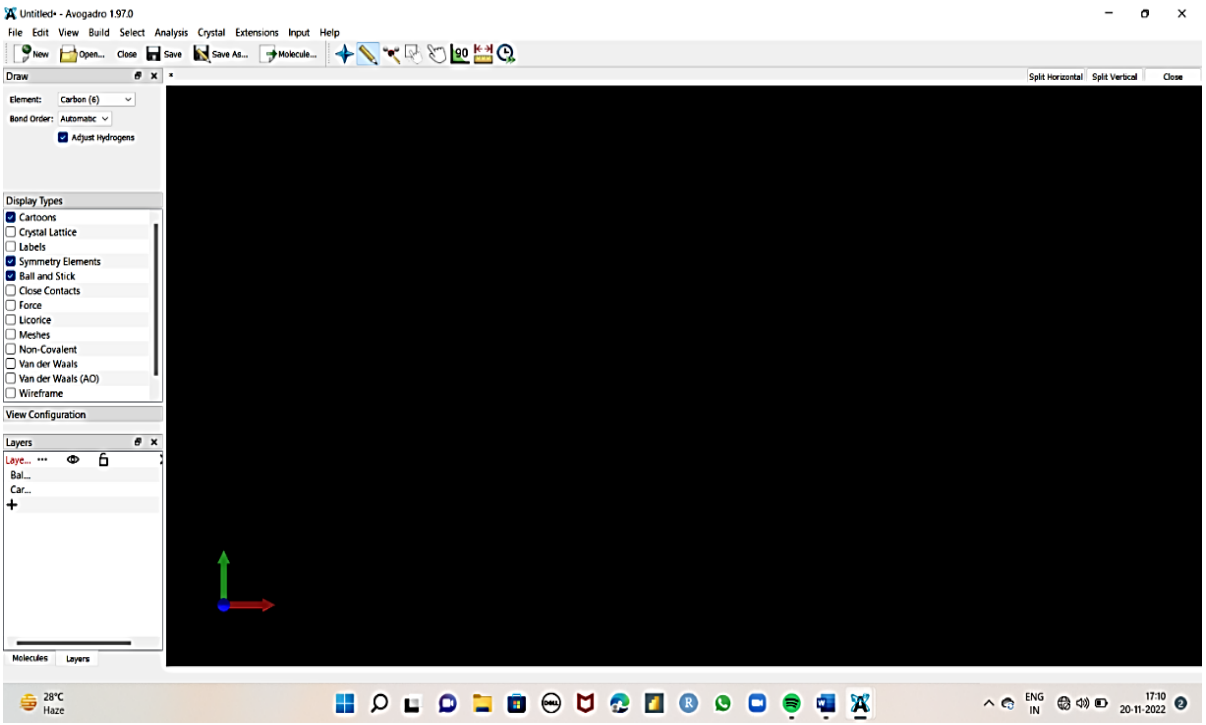




3.2. Overview of Avogadro

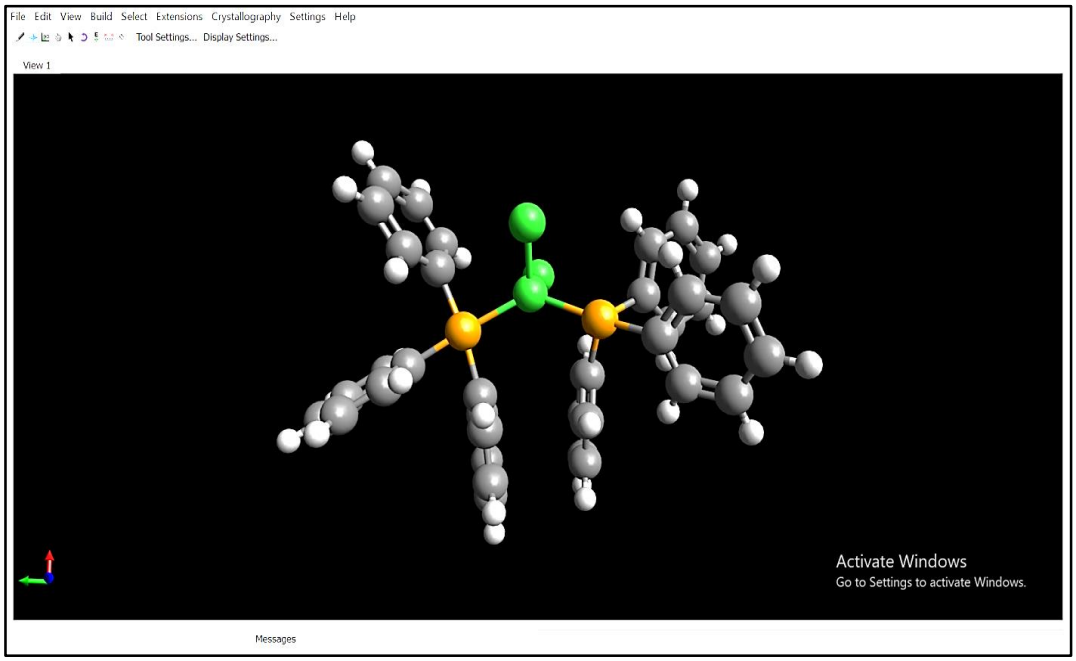
- Right click on the Avogadro icon on the Desktop to open Avogadro software.
- A window opens with different options on the top and blank space in the middle to create the structures.
- Learnt the basic commands and tools in Avogadro by watching tutorials from Spoken Tutorial website.
- Link for the Spoken Tutorial is provided here **https://spoken-tutorial.org**

- Practised the software by building some structures and analysing their properties using different options in the software.
- Learnt how to save the files in the Avogadro software and we should save the files by using **.cml**

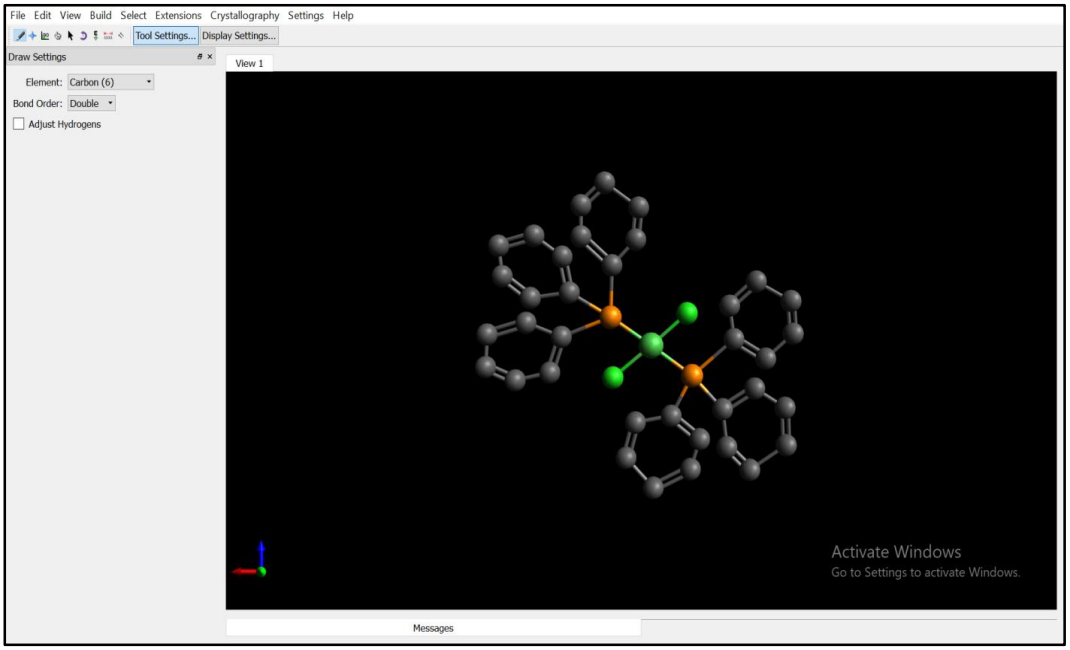


3.3. Procedure for drawing the structure of Bis-triphenyl Phosphine Nickel(II) complex

- From the toolbar on the top of the screen select the **Draw** tool and a menu appears on the left side of the screen named Draw Settings.
- Select Ni from the element selector option where we can see whole periodic table
- Now attach two chlorine atoms to the Ni atom and also attach two phosphorous atoms to Ni atom.
- Now for each phosphorous atom attach three phosphine compounds.
- Now our structure is built and go to Auto Optimization Tool which is in the toolbar present at the top.
- The Auto Optimization Settings menu appears on the left side of the screen.
- Select Force field as UFF and click on the start button.
- Wait for few seconds to optimize and now our structure is optimized**.**



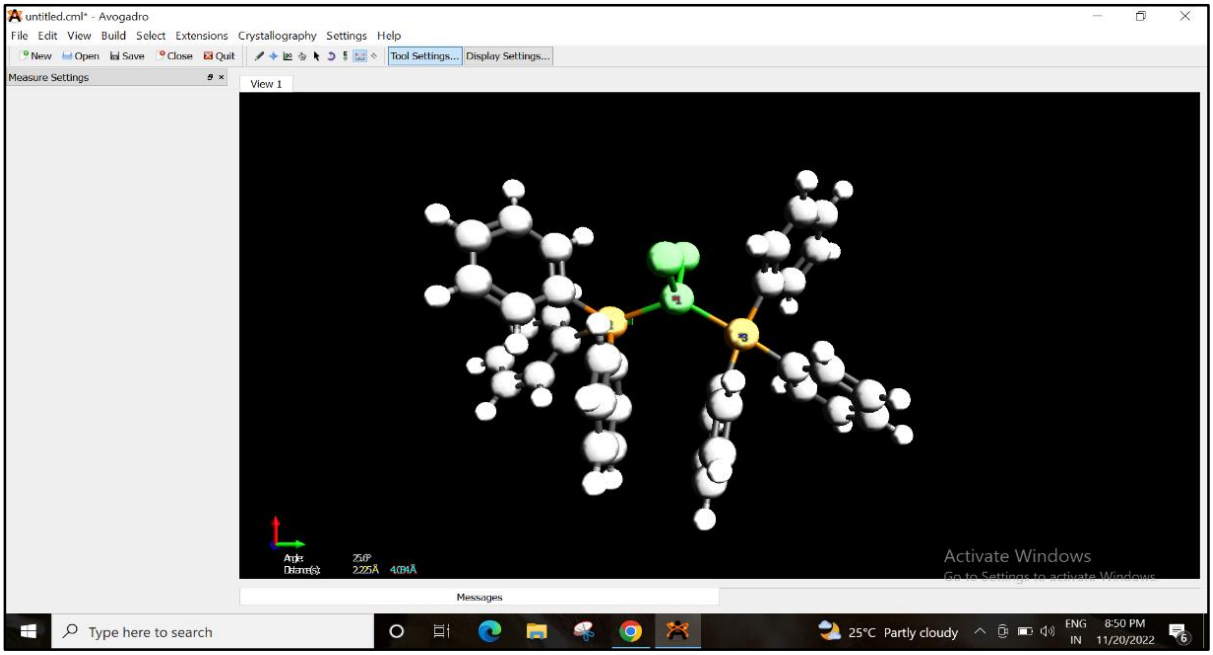
Bis-Triphenyl Phosphine Nickel (II) Complex Cis Isomer



Bis –Triphenyl Phosphine Nickel (II) Complex Trans Isomer

3.4. Procedure for measuring the distance and bond angle

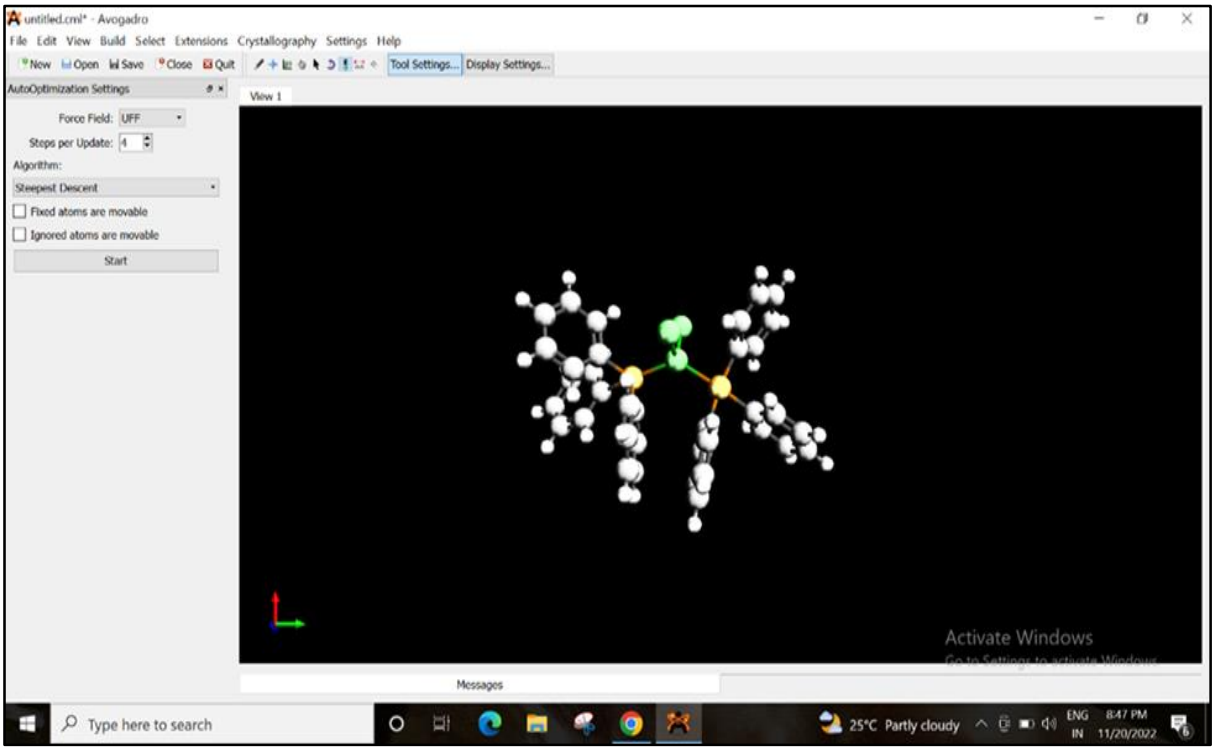
- There is an option known as **Click to Measure** on the toolbar, select that option.
- Now first click on an atom and then on other one to measure the distance between them.
- The parameters we measured were displayed at the bottom of the screen (arrow mark represents them)



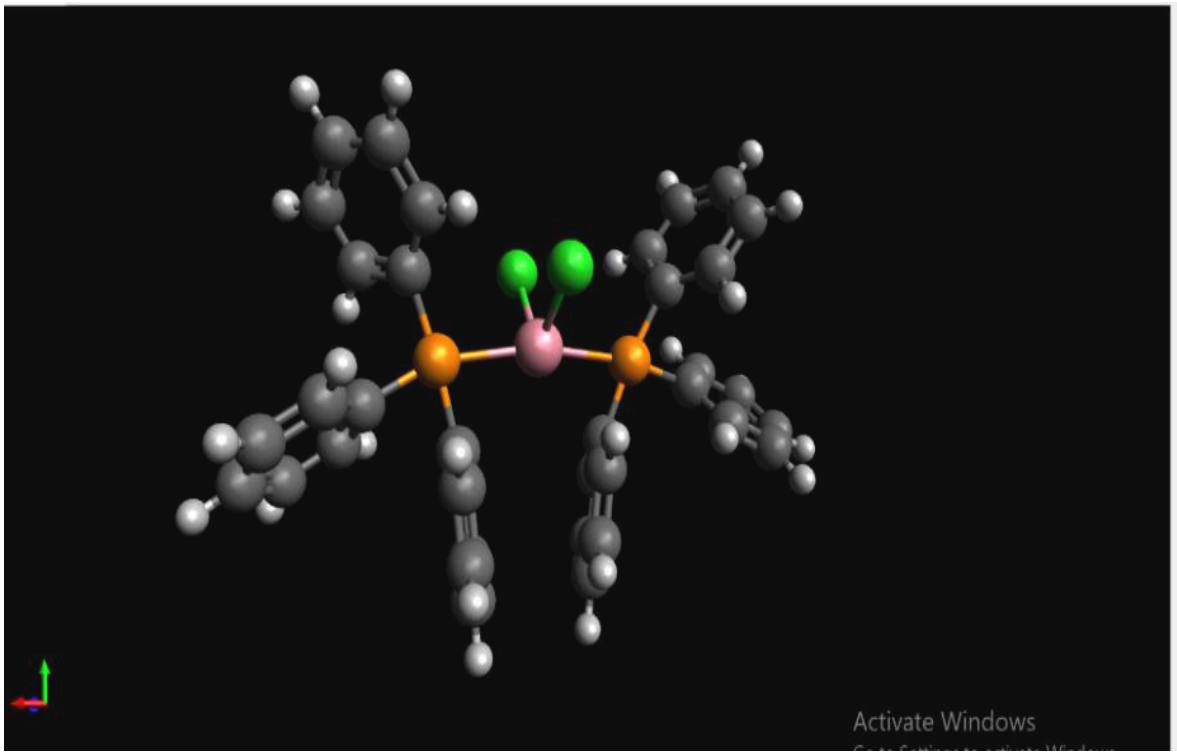
3.5. Procedure for measuring the bond length

- To measure bond length, go to **view** option available on the taskbar.
- In **view menu** there are different options available, select the **properties** option.
- In properties select the **bond properties** and by selecting it a table displays showing the bond properties, like that we can find the different properties by using the various options. Here are some reference pictures of various properties options mentioned below

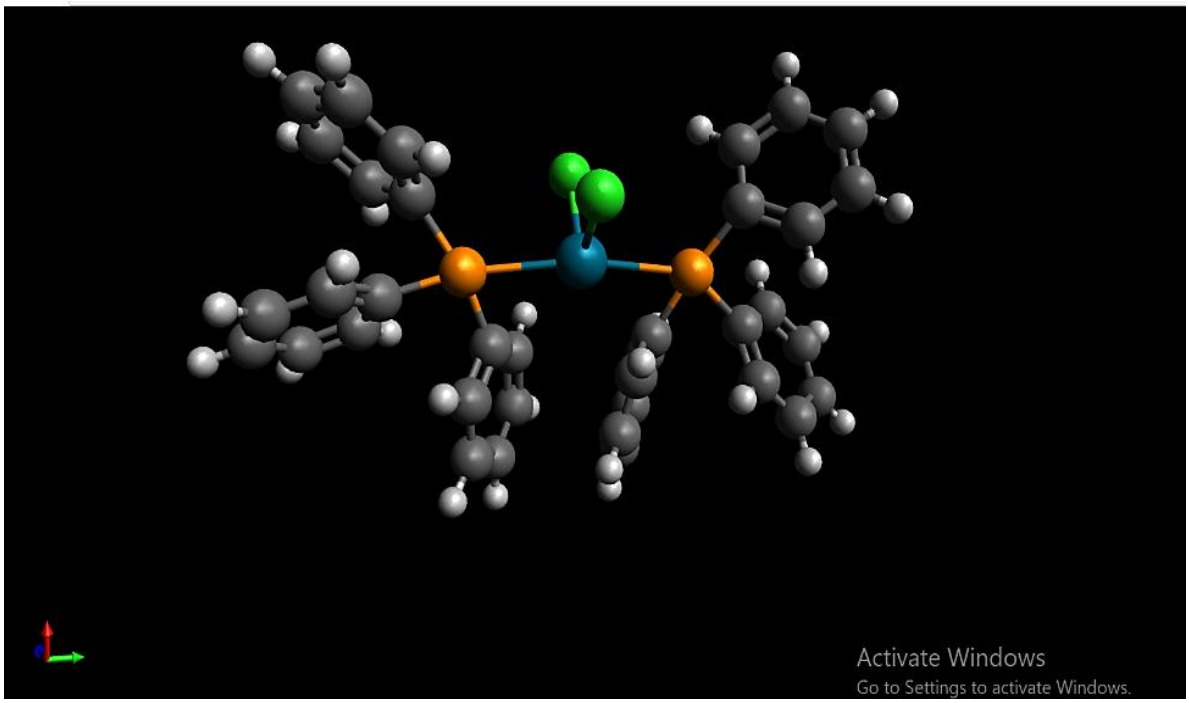
3.6. The 3D structure of the Bis –Triphenyl Phosphine Nickel (II) Complex with Iodine ligand



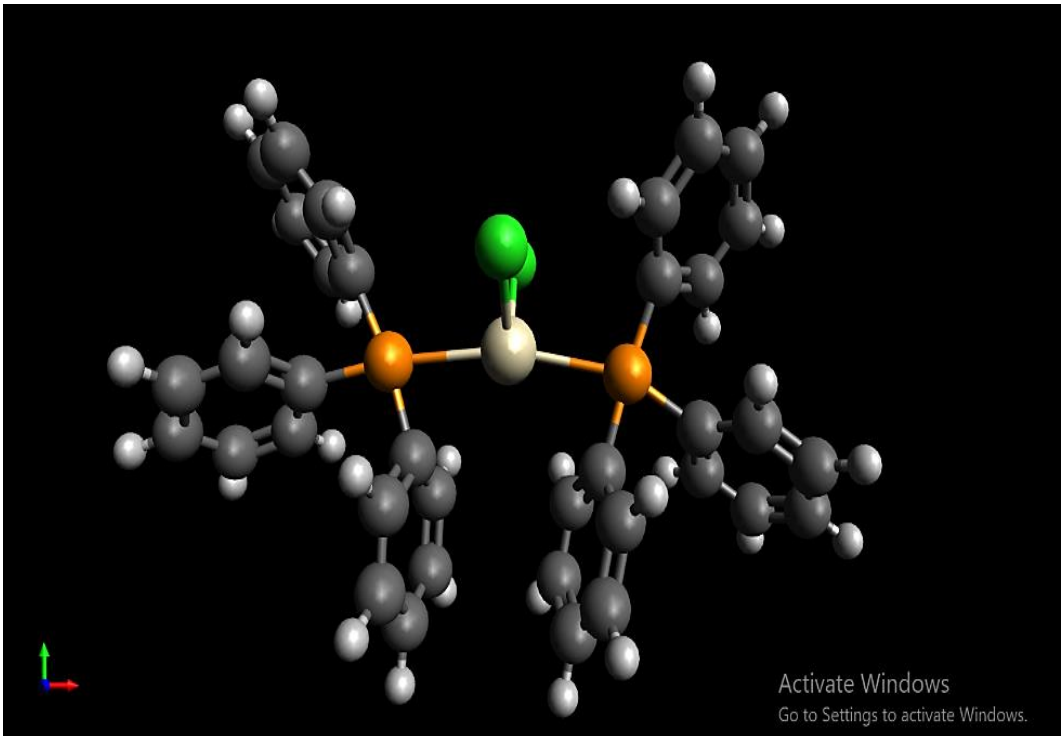
3.7.The 3D structure of the Bis Triphenyl Phosphine Cobalt Complex



3.8.The 3D structure of the Bis Triphenyl Phosphine Palladium Complex



3.9.The 3D structure of the Bis Triphenyl Phosphine Platinum Complex



4. Result and Discussion

4.1 Information regarding the Bis triphenyl phosphine Nickel(II) complex

- Dichloro bis(triphenylphosphine)nickel(II) refers to a pair of metal phosphine complexes with the formula $NiCl_2[P(C_6H_5)_3]_2$
- Molecular Weight of the complex is 656.2 g/mol.
- IUPAC Name of the complex is Triphenyl phosphonium.
- The compound exists as two isomers, a paramagnetic dark blue solid and a diamagnetic red solid.
- These complexes function as catalysts for organic synthesis.
- Appearance of complex purple-blue (tetrahedral) or red (square planar).
- It is in the form of Crystals or Powder.
- Storage: Inert atmosphere, Room Temperature.
- Soluble in water.

4.2. Structure of Bis triphenyl phosphine Nickel(II) complex

- The complex is prepared by treating hydrated nickel chloride with triphenylphosphine in alcohol or glacial acetic acid.
- When allowed to crystallize from chlorinated solvents, the tetrahedral isomer converts to the square planar isomer.
- The square planar form is red and diamagnetic.
- The phosphine ligands are trans with respective Ni-P and Ni-Cl distances of 2.24 and 2.17 Å.
- The blue form is paramagnetic and features tetrahedral Ni(II) centres.
- In this isomer, the Ni-P and Ni-Cl distances are elongated at 2.32 and 2.21 Å.
- As illustrated by the title complexes, tetrahedral and square planar isomers coexist in solutions of various four-coordinated nickel(II) complexes.
- Weak field ligands, as judged by the spectrochemical series, favour tetrahedral geometry and strong field ligands favour the square planar isomer.
- Both weak field (Cl^-) and strong field (PPh_3) ligands comprise $NiCl_2(PPh_3)_2$, hence this compound is borderline between the two geometries.
- Steric effects also affect the equilibrium; larger ligands favouring the less crowded tetrahedral geometry.

4.3. Applications of the complexes

- Used as a solvent in the production of active pharmaceutical ingredients.
- Used as a catalyst for cross-coupling of Grignard reagents, hydrosilylations, hydrogenation and polymerization.

4.4. Catalytic Activity

- The complex was first described by Walter Reppe who popularized its use in alkyne trimerizations and carbonylation’s
- Dichlorobis(triphenylphosphine)nickel(II) is a catalyst in Suzuki reactions, although usually inferior in terms of activity.

4.5. The change in colour of the complex by replacing the central metal atom

4.5.1. Bis triphenyl phosphine cobalt chloride

- This complex is typically yellow-brown in colour due to the presence of cobalt(II) in its coordination sphere.
- Cobalt (II) is a transition metal that exhibits a d^6 electronic configuration , meaning it has six electrons in its outermost shell.
- This electronic configuration gives cobalt (II) the ability to absorb visible light, thus resulting in the yellow-brown coloration of the complex.

4.5.2. Bis triphenyl phosphine platinum chloride

- The cis isomer is a white crystalline powder, while the trans isomer is yellow
- The colour of the compound is due to the absorption of the light in the visible region of the electromagnetic spectrum by the Platinum (II) ions in the compound.
- The colour is influenced by the presence of the triphenyl phosphine ligands, which can affect the electronic structure of the platinum ions and influence the absorption of the light.

4.5.3. Bis triphenyl phosphine palladium chloride

- It is the orange-red coloured compound.
- The colour of the compound is due to the absorption of light in the visible region of the electromagnetic spectrum by the palladium (II) ions in the compound.
- The colour is also influenced by the presence of the triphenyl phosphine ligands, which can affect the electronic structure of the palladium ions and influence the absorption of light.
- The colour of the compound is also a result of the d-d electronic transitions and the crystal field effect in the complex.

4.5.4. Bis triphenyl phosphine nickel (II) complex with iodine ligand

- The colour of the bis triphenyl phosphine nickel (II) complex with iodine ligand is typically brownish-red.
- This colour is due to the absorption of light in the visible spectrum by the d-d electronic transitions of the nickel ion in the complex.

- The energy levels of the d-orbitals and the nature of the ligands (i.e., iodine) in the complex result in the specific colour that is observed.
- The colour of this complex can also be affected by factors such as the crystal field and the solvent in which the complex is dissolved.

5. Conclusion

The colour of bis triphenyl phosphine nickel (II) complex is due to the d-d electronic transitions in the complex. The complex contains a metal ion, nickel (II), which has an unpaired electron in its d-orbital. When light of a certain energy is absorbed by the complex, this electron is excited from a lower energy d-orbital to a higher energy d-orbital. This transition results in the absorption of light in the visible region, causing the complex to appear a certain colour. The specific colour observed is determined by the energy difference between the d-orbitals involved in the transition and the ligands present in the complex.

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