Preparation and stereochemistry of nickel phosphine complexes

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Abstract. The Nickel (II) ion forms many stable complexes as predicted by the Irving Williams series. This experiment is about preparation and stereochemistry of nickel phosphine complexes. The nickel phosphine complexes, which were prepared are NiBr$_2$(PPh$_3$)$_2$ and NiBr$_2$(PCy$_3$)$_2$. The first part of the experiment is to prepare the nickel complexes. After preparing nickel phosphine complexes NiBr$_2$(PPh$_3$)$_2$ and NiBr$_2$(PCy$_3$)$_2$ the complexes have been analyzed for structural determination. The complexes were analyzed by the Magnetic Moments of solids-The Johnson Matthey Balance, UV-visible (electronic spectra), Infrared spectra (normal range) and Far-infrared spectra (which were supplied in the practical booklet).

1. Introduction
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 (PPh$_3$)$_2$, 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. Square planar nickel (II) complexes usually have no unpaired electrons, are diamagnetic and thus have a magnetic moment of zero. Nickel (II) with 2 unpaired electrons. Nickel compounds are suspected carcinogens and phosphines are irritants [1, 2].

Tricyclohexylphosphine is the tertiary phosphine with the formula P(C$_6$H$_{11}$)$_3$. Commonly used as a ligand in organometallic chemistry, it is often abbreviated to PCy$_3$, where Cy stands for cyclohexyl. It is not air stable, so the preparation was carried out under nitrogen.

NiBr$_2$ is a metal, however (PPh$_3$)$_2$ and (PCy$_3$)$_2$ are ligands. Nickel complexes can be used as catalysts. They are very efficient in the polymerisation of ethene for the formation of polythene (plastics) and in hydrosilation reactions (the adding of a silane across a double bond).

The general reaction for this experiment:

NiBr$_2$+2P→[NiBr$_2$(P)$_2$],

where P=PPh$_3$ or PCy$_3$ (Ph=phenyl,C$_6$H$_5$, Cy=cyclohexyl,C$_6$H$_{11}$)$^{(1)}$. 

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(1)
2. Methods and materials

2.1. The preparation of the $[\text{NiBr}_2(\text{PPh}_3)_2]$  
1.4 g of NiBr$_2$.3H$_2$O, which is dark yellow colour, was dissolved in 15ml of dried absolute ethanol in a small conical flask. As the yellow solution heated in the flask it gradually became green solution. Then, using the reflux apparatus 2.8 g of PPh$_3$, which is white crystals/flakes was dissolved in 30ml of colourless propan-2-ol. Added few bumping chips to avoid the overflow and heated the mixture, by heating the mixture it gave clear solution. When the phosphine was dissolved turned off the heat and poured the warm nickel bromide solution down the condenser. The precipitated formed immediately. The reaction was fast and changed the colour from green to dark green. Allowed the flask to cool down and then placed it in an ice bath for around 20 minutes to complete precipitation. Sat the suction filtration and washed the filter paper with ethanol to avoid the product to become wet with water. Filtered of the solid product and washed by ethanol and then diethyl ether. Allowed the product to dry and weighed the product and it was 2.63 g. The product was stored in a bottle with a label. The melting point of the product was determined. The melting point range was 190–194 °C.

2.2. The preparation of NiBr$_2$(PCy$_3$)$_2$  
1.4g of NiBr$_2$.3H$_2$O, which is dark yellow colour was dissolved in 15 ml dried absolute ethanol in a small conical flask and heated. The reflux/nitrogen apparatus has been flushed with nitrogen gas and then dissolved 1.5g of PCy$_3$, which looks like white sugar powder in 20ml of dried absolute ethanol. Added few bumping chips to avoid the overflow and heated the mixture. PCy$_3$ is more phosphoric than PPh$_3$, so it dissolved faster. While the mixture was refluxing poured, the warm nickel bromide solution down the condenser against a positive stream of nitrogen and the precipitate formed immediately. The precipitate was dark green colour. Allowed the flask to cool down and then placed it in an ice bath for around 20 minutes to complete the precipitation. Sat the suction filtration and washed the filter paper with ethanol to avoid the product to become wet with water. Filtered of the solid products and washed by ethanol and then diethyl ether. Allow the products to dry. The final product was black colour. Weighed the product and it was 0.15 g. The product was stored in a bottle with a label. The melting point of the product was determined. The melting point range was 145–167 °C.

2.3. Analysis of the Nickel complexes-Structural determination

a) Measurement of the Magnetic Moments of Solids – The Johnson Matthey (JMC) Balance:  
$\text{NiBr}_2(\text{PPh}_3)_2$: Weighed the empty sample tube which was 0.8275g. The balance was switched on with the RANGE knob sat to x1 scale. The apparatus has been switched on and sat by a laboratory supervisor. Pushed the empty sample tube into the apparatus and took the reading $R_0$, – 029. It is negative since the glass is diamagnetic. Crushed the sample to a fine powder and inserted into sample tube to 2.9 cm. Weighed the sample tube with sample. The weight was 0.9501g. Pushed the tube into the apparatus as before and took the reading, $R$, 187. The temperature in the room was 21 °C and the calibration constant, C is 1.1260.

$\text{NiBr}_2(\text{PCy}_3)_2$: Followed the same procedure above.  
The empty sample tube weight 0.8170 g. Ro was – 028 the length of the sample was 2.85cm. Weight of the sample tube with sample was 0.9087 g. And R was – 035. The temperature in the room was 21 °C and the calibration constant, C is 1.1260.

b) UV/VIS Spectra

Dissolved 11.1 mg of NiBr$_2$(PPh$_3$)$_2$ in 10 cm$^3$ of dichloromethane using a small volumetric flask. Ran the spectrum between 700–400 nm in a quartz cell.

Dissolved 15.6 mg of NiBr$_2$(PCy$_3$)$_2$ in 10 cm$^3$ of dichloromethane using a small volumetric flask. Ran the spectrum between 700–400 nm in a quartz cell.

c) Infrared Spectra (4000 to 600 cm$^{-1}$): Done by a laboratory supervisor.

d) Far Infrared Spectra: These are given in the laboratory book.
3. Results

3.1. Measurement of the Magnetic Moments of Solids – The Johnson Matthey (JMC) Balance

(a) Use \( \chi_w = \frac{C(R - R_o)}{10^9 m} \) to evaluate \( \chi_w \)

The mass susceptibility for NiBr\(_2\)(PPh\(_3\))\(_2\) is calculated as followed,
Where, \( R_o \) is the reading of the empty tube.
\( R \) is the reading of the tube plus sample.
\( m \) is the mass of the sample in grams
\( l \) is the length of the sample in centimetres
\( C \) is the calibration constant

\[ \chi_w = C \times 1 \times (R - R_o) / 10^9 \times m \]
\[ \chi_w = 1.1260 \times 2.9\text{cm} \times (187 - (-0.029)) / 10^9 \times (0.9501-0.8275) \]
\[ \chi_w = 1.1260 \times 2.9\text{cm} \times 216 / 10^9 \times 0.1226 \]
\[ \chi_w = 5.753 \times 10^{-6} \]

The reading \( R \) is negative for NiBr\(_2\)(PCy\(_3\))\(_2\). So did not proceed any further with the calculation.

(b) Evaluate \( \chi_m \) where \( \chi_m = \chi_w M \) and \( M \) = the relative molecular mass of the complex.

\[ \chi_m = \chi_w M \]
\[ \chi_m = (5.753 \times 10^{-6}) \times 743.075 \]

[The relative molecular mass of NiBr\(_2\)(PPh\(_3\))\(_2\)=743.075 g/mol]

\[ \chi_m = 4.275 \times 10^{-3} \]

(c) We now separate \( \chi_m^{\text{para}} \), the molar susceptibility for the metal ion, from \( \chi_m^{\text{dia}} \) which is the contribution from the ligands.

\[ \chi_m^{\text{para}} = \chi_m - \chi_m^{\text{dia}} \]
\[ \chi_m^{\text{para}} = 4.275 \times 10^{-3} - (-173.9) \]

[\( \chi_m^{\text{dia}} \) value is taken from the table 2 which is given in the practical book.]

\[ \chi_m^{\text{para}} = 173.904275 \]

(d) Calculate the magnetic moment from \( \mu = 2.83 \sqrt{(\chi_m^{\text{para}} T)} \), Where \( T \) is in K.

\[ \mu = 2.83 \sqrt{(173.904275 \times 294.15)} \]
\[ \mu = 2.83 \times 226.172 \]
\[ \mu = 640.067 \]

3.2. UV/VIS Spectra

Calculate the molar absorption coefficient (\( \varepsilon \)), with units, for any bands using the Beer-Lambert law
\( (A = \varepsilon c l) \)

Where \( A = \text{absorbance} \); 
\( c = \text{concentration in mol dm}^{-3} \);
l = path length of cell in cm;
Bands where $\varepsilon$ is between 0–5000 are most likely to be d–d transitions

$$A = \varepsilon cl$$

$$\varepsilon = A / C \times l$$

$$\varepsilon = 0.348 / 1.49 \times 10^{-3} \text{ mol dm}^{-3} \times 1\text{ cm}$$

$$[c=(n \times 1000)/v=1.49 \times 10^{-3} \text{ mol dm}^{-3}]$$

$$(n=0.0111/743.075=1.495 \times 10^{-5} \text{ mol})$$

$$\varepsilon = 233.56(1)(2)$$

4. Conclusion
Looking at the infrared spectra (IR) for part 1 it shows that the Ni-Br stretch for NiBr$_2$(PPh$_3$)$_2$ was observed at 3053 cm$^{-1}$, and looking at the infrared spectra for part 2 it shows that the Ni-Br stretches for NiBr$_2$(PCy$_3$)$_2$ is between 3000–2500 cm$^{-1}$. However, looking at the Far infrared spectra in a practical book it shows that the Ni-Br stretch for NiBr$_2$(PPh$_3$)$_2$ is between 250–300 cm$^{-1}$ and for NiBr$_2$(PCy$_3$)$_2$ is between 200–250 cm$^{-1}$. The mass susceptibility for NiBr$_2$(PPh$_3$)$_2$ is $\chi_w = 5.753 \times 10^{-6}$. The reading R is negative for NiBr$_2$(PCy$_3$)$_2$. So did not proceed any further with the calculation because this will show that the compound is diamagnetic and the magnetic moment is 0.

![NiBr$_2$(PPh$_3$)$_2$](image1.png)

![NiBr$_2$(PCy$_3$)$_2$](image2.png)

References
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