Analysis of the structural determination nickel complexes

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Abstract. The sets of bands in the IR and UV -- spectra are the same specific a characteristic of a substance, like a person's fingerprint. According to these spectra, the substance it can be identified if its vibrational spectrum is already known. In addition, by IR and UV -spectra determine the symmetry and structure of unexplored molecules. Frequencies the main vibrations found from the spectra are necessary for calculating thermodynamic properties of substances. Measuring the intensity of bands in the spectra allows you to quantitative analysis, study chemical equilibria and kinetics of chemical reactions, monitor the progress of technological processes. Nickel (II) ion forms many stable complexes. This work is devoted to the preparation and study of the stereochemistry of nickelphosphine complexes. We obtained nickelphosphine complexes NiBr₂(PPh₃)₂; NiBr₂(PCy₃)₂, and analysed to determine the structure. We studied the magnetic moments of solids from the following spectra in UV-visible (electronic spectra), infrared spectrum (normal range) and far infrared spectrum.

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 (PPh₃)₂, and square planar. Some five-coordinate complexes are known but are rare. Nickel (II) is a 3d⁸ 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 [1-5].

Tricyclohexylphosphine is the tertiary phosphine with the formula P(C₆H₁₁)₃. Commonly used as a ligand in organometallic chemistry, it is often abbreviated to PCy₃, where Cy stands for cyclohexyl. It is not air stable, so the preparation was carried out under nitrogen.

NiBr₂ is a metal, however (PPh₃)₂ and (PCy₃)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 hydroisolation reactions (the adding of a silane across a double bond).

The general reaction for this experiment:

NiBr₂+2P→[ NiBr₂(P)₂],

where P=PPh₃ or PCy₃ (Ph=phenyl,C₆H₅; Cy= cyclohexyl,C₆H₁₁).
2. Methods and results

The preparation of the [NiBr$_2$(PPh$_3$)$_2$] - 4g of NiBr$_2$.3H$_2$O, dissolved in 15 ml in pure ethanol. The flask with the solution was heated, a yellow to green color change occurred. Then, a substance of 2.8 g of PPh$_3$, which is white crystals / flakes, was taken, dissolved in 30 ml of colorless propan-2-ol. A few convex shavings were added to avoid overfilling, and the mixture was heated; when the mixture was heated, it gave a clear solution.

When the phosphine was dissolved, turn off the fire and poured a warm solution of nickel bromide into the condenser. A precipitate form immediately. The reaction proceeds quickly and takes on a color from green to dark green. The flask was cooled and then placed in an ice bath for 20 minutes to completely precipitate. The solid product is filtered off and washed with ethanol and then with diethyl ether. The range of melting temperatures was 190-194 °C [6].

The preparation of NiBr$_2$(PCy$_3$)$_2$ - 4 g of NiBr$_2$.3H$_2$O, a dark yellow substance, was dissolved in 15 ml of pure ethanol in a small conical flask and heated. And then 1.5 g of PCy$_3$, which looks like white sugar powder, is dissolved in 20 ml of ethanol. A few convex shavings were added to avoid overfilling, and the mixture was heated. PCy$_3$ is more phosphoric than PPh$_3$ salt dissolved faster. Filtered of the solid products and washed by ethanol and then diethyl ether. Allow the products to dry. The final product was black color. Weighed the product and it was 0.15g. The melting point of the product was determined. The melting point range was 145-167 °C.

Analysis of the Nickel Complexes-Structural determination – measurement of the Magnetic Moments NiBr$_2$(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. Pushed the empty sample tube into the apparatus and took the reading Ro, -029. Glass is diamagnetic. The sample tube was weighed. Weight was 0.9501 g. Insert the handset into the device and take the reading R 187. The room temperature was 21 °C, and the calibration constant C was 1.1260 [7].

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

UV/VIS Spectra – 11.1 mg of NiBr$_2$ (PPh$_3$)$_2$ was dissolved in 10 cm$^3$ of dichloromethane using a small volumetric flask. Measurements were taken in spectra between 700 – 400 nm in a quartz cell.

15.6 mg of NiBr$_2$ (PCy$_3$)$_2$ was dissolved in 10 cm$^3$ of dichloromethane using a small volumetric flask a spectral value between 700 – 400 nm in a quartz cell was also observed [8]. Infrared Spectra (4000cm$^{-1}$ to 600cm$^{-1}$). Done by a laboratory supervisor are Infrared Spectra. These are given in the laboratory book. Magnetic Momentum Measurement - Johnson Matthey Formula (JMC):

$$\chi_w = \frac{C \cdot l \cdot (R - R_D)}{10^9 \cdot m}$$

Use $\chi_w$ to evaluate $\chi_w$

The mass susceptibility for NiBr$_2$(PPh$_3$)$_2$ is calculated as followed,

where, Ro 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 centimeters. C is the calibration constant

$$\chi_w = \frac{C \cdot l \cdot (R - R_D)}{10^9 \cdot m} = \frac{1.1260 \cdot 2.9 \cdot 187 - (-029)}{109 \cdot (0.9501 - 0.8275)} = \frac{1.1260 \cdot 2.9 \cdot 216}{109 \cdot 0.1226} = \frac{5.753 \cdot 10^{-6}}{Xw}$$

$$Xw = 5.753 \cdot 10^{-6}$$
The R readings are negative for NiBr$_2$(PCy$_3$)$_2$, so it is impractical to continue further calculations. Evaluate $\chi_m$ where $\chi_m = \chi_w M$ and $M = \text{the relative molecular mass of the complex}$

$$\chi_m = 5.753 \times 10^{-6} \times 743.075$$

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

$$\chi_m = 4.275 \times 10^{-3}$$

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.]

$$\chi_m^{\text{para}} = 173.904275$$

Calculate the magnetic moment from $\mu = 2.83 \sqrt{\chi_m^{\text{para}}} T$, where T is in K.

$$\mu = 2.83 \sqrt{173.904275 \times 294.15}$$

$21^\circ C = 294.15 k$$

$\mu = 2.83 \times 226.172$

$\mu = 640.067$

UV/VIS Spectra

We calculate the molar absorption coefficient ($\varepsilon$), with units, for any bands using the Beer-Lambert law:

$$A = \varepsilon cl$$

where: $A = \text{absorbance}$

$c = \text{concentration in mol dm}^{-3}$

$l = \text{path length of cell in cm}$

Bands where $\varepsilon$ is between 0 - 5000 are most likely to be $d$-$d$ transitions

$$A = \varepsilon cl$$

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

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

$$c = \frac{(n \times 1000)}{743.075} = 1.49 \times 10^{-3} \text{ mol dm}^{-3}$$

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

$\varepsilon = 233.56$
3. Conclusion

In conclusion, we present the results of a study of the nickel (II) ion and the stereochemistry of nickel phosphine complexes forming a set of stable complexes, as predicted by the Irving Williams series. These complexes were analyzed for structural determination by the magnetic moments of solids, UV-visible, infrared and far-infrared spectra. Considering metal compounds, we have already noted the stabilizing effect of certain ligands, especially tertiary phosphines, on the α-bonds between carbon and transition metals. This is most pronounced in metals in their divalent state. Spectrophotometric methods allow working in a narrow area of optimal light absorption. Thus, it significantly increases the sensitivity and accuracy of quantitative determination, which is very important.

![Structural model complex NiBr₂(PPh₃)₂ (left) and NiBr₂(PCy₃)₂ (right).](image)

Observing «figure 1» in the infrared (IR) spectra for part 1, it is shown that the Ni-Br stretching for NiBr₂(PPh₃)₂ occurred at 3053 cm⁻¹, and when considering the infrared spectra for part 2, it was observed that the Ni-Br stretch for NiBr₂(PCy₃)₂ is between 3000-2500 cm⁻¹. However, the tutorial practical guide notes the far infrared spectra, and shows that the Ni-Br stretching for NiBr₂(PPh₃)₂ is between 250-300 cm⁻¹, and for NiBr₂(PCy₃)₂ is between 200-250 cm⁻¹.

The mass susceptibility for NiBr₂(PPh₃)₂ is \( \chi_w = 5.753 \times 10^{-6} \). The reading R is negative for NiBr₂(PCy₃)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.

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