

Overview of synthesis and preparation experiments



**ASSIGN
BUSTER**

Introduction:

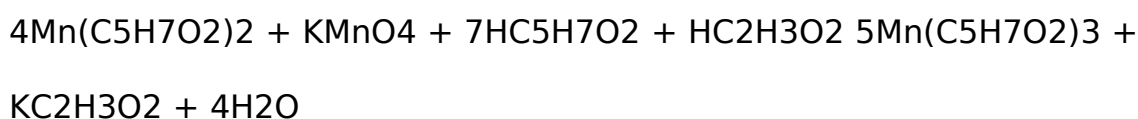
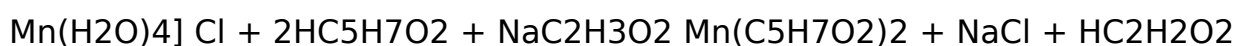
As we know, Manganese is found in the first row of transition metal with the electron configuration [Ar] 3d⁵ 4s². Besides that, Manganese has different type of oxidation states when it appears as a compound and the oxidation state is from Mn(-III) until Mn(VII). So, we know that the compounds of manganese range in the oxidation number have a different of 10 electrons. In the experiment 1, we prepare tris(acetylacetonato)manganese(III), Mn(acac)₃ by using manganese(II) chloride tetrahydrate and potassium permanganate act as oxidation agent to oxidise manganese(II) chloride to acetylacetonemanganese(III).

Manganese(III) acetylacetonate is an one- electron oxidant. Manganese(III) acetylacetonate

is high spin. It has also a distorted octahedral structure. This distortion is due to the Jahn-Teller effect. (Absolute Astronomy, 2009). The structure of Manganese(III) acetylacetonate is shown as below:-

(Source: Tcieurope. com)

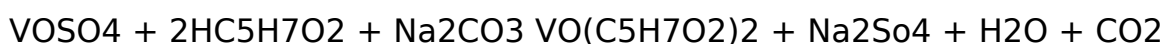
The equation is as follow:-



Furthermore, bis(acetylacetonato)oxovanadium(IV) is also known as Vanadyl acetylacetonate, $\text{VO}(\text{acac})_2$. As we know, it is a blue green complex.

bis(acetylacetonato)oxovanadium(IV) has a vanadyl group, VO_2^+ . The vanadyl group is bonded to 2 acetylacetonate anions and the structure of the compound is as follow:-

This complex can be made from vanadium(IV) or vanadium(V). In our experiment, bis(acetylacetonato)oxovanadium(IV) was prepared from vanadium(V) oxide and the equation is as follow:-



(Absolute Astronomy, 2009)

Besides that, both of the acetylacetonato (acac) groups of bis(acetylacetonato)oxovanadium(IV) are able to be exchanged with organic ligands having coordinating atoms of different potentialities. (Maurya, 2003)

Both Manganese(III) acetylacetonate and bis(acetylacetonato)oxovanadium(IV) are bond with acetylacetonate which known as ligand. The precursor for acetylacetonate is acetylacetone with formula $\text{C}_5\text{H}_8\text{O}_2$. However, acetylacetonate is an anion. It can bind to corresponding cation but it very hard to exist as a free ion in solution.

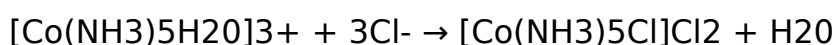
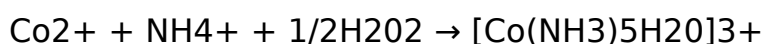
In addition, Cobalt is a hard, gray metal. It has a proton number 27. Besides that, there are two types of cobalt ions namely Co^{2+} and Co^{3+} . First, Co^{3+} ion is more weaker than the Co^{2+} ion. However, the complex ion formed

with higher oxidation state is more stable. (°zmir Institute of Technology, n. d.). So that, Cobalt(III) complexes are kinetically inert.

Co³⁺ can undergo a process known as ligand exchange reactions slowly which compared to Co²⁺ complexes. The cobalt(III) complexes are usually in octahedral shape. In the experiment, chloropentaamminecobalt(III) chloride is being synthesized. The structure is as follow:-

(Source: Chemicalbook. com)

The complex is prepared by the oxidation of ammoniacal solution of cobalt(II) salts by using hydrogen peroxide. The formula is as follow:-



(°zmir Institute of Technology, n. d.)

Materials and Methods:

Experiment one,

5g of MnCl₂ · 4H₂O

1. 3g of NaC₂H₃O₂ · 3H₂O NaC₂H₃O₂ · 3H₂O

Dissolved in 200cm³ of distilled water.

21cm³ of 2HC₅H₇O₂ slowly added

1g of KMnO₄

Present of two-phase layer

Solution A added in with stirring

Dissolved in 50cm³ of distilled water.

13g of NaC₂H₃O₂ · 3H₂O

Solution B added in

Solution A

Solution B

Dissolved in 50cm³ of distilled water.

Heated with 60°C for 30 minutes

Complex washed with acetone

Solid complex filtered by suction

Resultant solution was cooled with ice-cold water

Experiment 2

Experiment 3

5 cm³ distilled water

4 cm³ concentrated H₂SO₄

10 cm³ ethanol

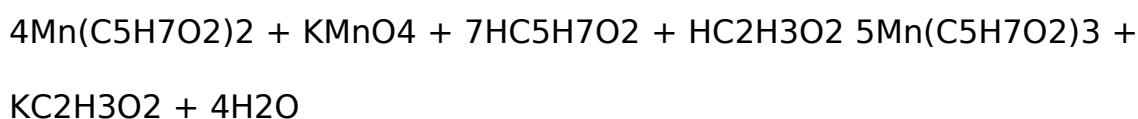
Were added in.

Recrystallise

Results :

For experiment 1,

from the equation below, I can get the theoretical mass of the $\text{Mn}(\text{acac})_3$ solid complex by :



From the equation, we know that 1 mol of $\text{Mn}(\text{H}_2\text{O})_4] \text{Cl} = 1$ mol of $\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_2$.

So, 5 g of $\text{Mn}(\text{H}_2\text{O})_4] \text{Cl} = 0.0308$ mol is also = 0.0308 mol of $\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_2$.

From the second equation, 4 mol of $\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_2 = 5$ mol of $\text{Mn}(\text{acac})_3$

0.0308 mol of $\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_2 = 0.0385$ mol.

So, theoretical weight of $\text{Mn}(\text{acac})_3 = 0.0385 \text{ mol} \times 252.938 \text{ g/mol}$

theoretical weight of $\text{Mn}(\text{acac})_3 = 9.7381 \text{ g}$

The following shows the method to get our experimental weight:

Weight of Sample tube

14. 8180 g

Weight of Sample tube + solid complex , $\text{Mn}(\text{acac})_3$

18. 7785 g

So, the experimental weight of $\text{Mn}(\text{acac})_3$ complexes were 3. 9605 g

Percentage yield of $\text{Mn}(\text{acac})_3$ complexes we get was = 3. 9605 g / 9. 7381 g X 100 %

= 40. 67 %

Next, Magnetic moment of $\text{Mn}(\text{acac})_3$ complexes were calculated as follow :

$$m = 0. 9278\text{g} - 0. 8193\text{g}$$

$$= 0. 1085\text{g}$$

$$R_o = -33$$

$$L = 2. 4\text{cm}$$

$$R = 1165 \text{ (paramagnetic)}$$

$$C_{\text{Bal}} = 1$$

$$X(g) = [C_{\text{Bal}} \times L \times (R - R_o)] / 109 \times m$$

$X(g)$ of $\text{Mn}(\text{acac})_3$ complexes = 2. 65 X 10⁻⁵

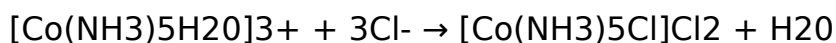
So, $\text{Mn}(\text{acac})_3$ complexes are paramagnetic

Interpretation of IR spectrum for complexes will be written in discussion.

For experiment 2,

from the equation below, I can get the theoretical mass of the

[Co(NH₃)₅Cl]Cl₂ solid complex by :



From the above equation, 1 mol of Co²⁺ = 1 mol of [Co(NH₃)₅H₂O]³⁺

12g of Co²⁺ = 0.0504 mol

So 0.0504 mol of [Co(NH₃)₅H₂O]³⁺ = 0.0504 mol of [Co(NH₃)₅Cl]Cl₂

Theoretical weight of [Co(NH₃)₅Cl]Cl₂ solid complexes = 0.0504 mol X 250.433 g/mol

= 12.6218 g

The following shows the method to get our experimental weight:

Weight of Sample tube

14.9285 g

Weight of Sample tube + solid complex, Mn(acac)₃

22.3723 g

So, the experimental weight of [Co(NH₃)₅Cl]Cl₂ solid complexes = 7.4438 g

Percentage yield of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ complexes = $7.4438 \text{ g} / 12.6218 \text{ g} \times 100 \%$

= 58.98 %

Next, Magnetic moment of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ complexes were calculated as follow :

$$m = 0.9264\text{g} - 0.8207\text{g}$$

$$= 0.1057\text{g}$$

$$R_o = -36$$

$$L = 2.1\text{cm}$$

$$R = -41 \text{ (diamagnetic)}$$

$$C_{\text{Bal}} = 1$$

$$X(g) = [C_{\text{Bal}} \times L \times (R - R_o)] / 109 \times m$$

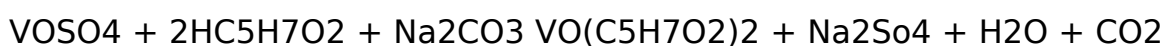
$X(g)$ of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ complexes = -9.9338×10^{-8}

So, $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ complexes are diamagnetic

For experiment 3,

from the equation below, I can get the theoretical mass of the

$[\text{V}(\text{acac})_2(\text{H}_2\text{O})]$ solid complex by :



From the above equation, 1 mol of V_2O_5 = 2 mol of $VOSO_4$

2g of V_2O_5 = 0.011 mol = 0.022 mol of $VOSO_4$

2 mol of $VOSO_4$ = 2 mol of $VO(C_5H_7O_2)_2$

Theoretical weight of $VO(C_5H_7O_2)_2$ = 0.022 mol X 264.94 g/mol

= 5.8287 g

The following shows the method to get our experimental weight:

Weight of Sample tube

14.8445 g

Weight of Sample tube + solid complex, $Mn(acac)_3$

18.5818 g

So, the experimental weight of $VO(C_5H_7O_2)_2$ = 3.7373 g

Percentage yield of $VO(C_5H_7O_2)_2$ = 3.7373 g / 5.8287 g X 100%

= 64.12%

Next, Magnetic moment of impure $VO(C_5H_7O_2)_2$ complexes were calculated as follow :

$m = 0.8880g - 0.8244 g$

= 0.0636g

Ro = -34

<https://assignbuster.com/overview-of-synthesis-and-preparation-experiments/>

$$L = 2.5 \text{ cm}$$

$$R = 72 \text{ (paramagnetic)}$$

$$C_{\text{Bal}} = 1$$

$$X(g) = [C_{\text{Bal}} \times L \times (R - R_0)] / 109 \times m$$

$$X(g) \text{ of impure } \text{VO}(\text{C}_5\text{H}_7\text{O}_2)_2 \text{ complexes} = 4.17 \times 10^{-6}$$

So, $\text{VO}(\text{C}_5\text{H}_7\text{O}_2)_2$ complexes are paramagnetic

Magnetic moment of pure $\text{VO}(\text{C}_5\text{H}_7\text{O}_2)_2$ complexes were calculated as follow :

$$m = 0.8947 \text{ g} - 0.8211$$

$$= 0.0736 \text{ g}$$

$$R_0 = -33$$

$$L = 2.3 \text{ cm}$$

$$R = 144 \text{ (paramagnetic)}$$

$$C_{\text{Bal}} = 1$$

X(g) of pure $\text{VO}(\text{C}_5\text{H}_7\text{O}_2)_2$ complexes = 5.53×10^{-6}

Discussion :

**Interpretation of IR spectrum for
tris(acetylacetonato)manganese(III):**

Wavenumber (cm^{-1})

Description of bands

2921.1 – 2959.7

-relative intensity : weak

CH stretching of CH_3

1593.9

1508.0

-relative intensity : strong

-(C= C) stretching

-(C= CH) deformation

1387.2

-relative intensity : strong

-(CH_3)- symmetric C-H deformation

1253.5

-relative intensity : strong

-(C= C) stretching

-(C-CH₃) stretching

1016. 8

-relative intensity : strong

-(CH₃) out-of plane bending

923. 2

-relative intensity : strong

-(C-CH₃) stretching

777. 0

-relative intensity : strong

-(C-H)deformation

678. 1

-relative intensity : medium/ strong

-(C-CH₃)stretching,(O= C-CH₃) deformation

-(Mn-O) stretching indicates metal-ligand bond

460. 1

- relative intensity : weak

- (C= C) stretching,(C-CH₃) stretching

-(Mn-O) stretching that also indicates metal-ligand bond

Interpretation of IR spectrum for chloropentaamminecobalt(III) chloride:

Wavenumber (cm⁻¹)

Description of bands

3258. 0

-relative intensity : strong

NH₃ stretch

1576. 2

-relative intensity : medium

-degenerate asymmetric NH₃ stretching

1307. 8

-relative intensity : strong

-symmetric NH₃ angle deformation

844. 9

-relative intensity : strong

-NH₃ rocking

487. 6

-(Co-Cl) stretching indicates metal-ligand bond

Interpretation of IR spectrum for impure bis(acetylacetonato)oxovanadium(IV):

Wavenumber (cm⁻¹)

Description of bands

1556. 8

1521. 0

-relative intensity : medium

- (C= O) stretching

-(C= C),(C= CH) stretching

1418. 7

-relative intensity : medium

-(CH₃) deformation

1374. 0

1357. 6

-relative intensity : strong

-(C= O) stretching

-(CH₃) deformation mode

1286. 6

-relative intensity : strong

-(C= C= C) stretching

998. 2

-relative intensity : strong and sharp

-stretching of V= O bond

-it also indicates the metal-ligand bond.

1018. 6

-relative intensity : strong

-(CH₃) rocking

936. 1

-relative intensity : strong

-(C-CH₃) stretching

-(C= O) stretching

798. 6

-relative intensity : medium

-(C-H) out-of-plane bending

685. 9

657. 2

-relative intensity : medium/ weak

-(ring) deformation

- out-of-plane bending for:

609. 2

-(ring) deformation

Interpretation of IR spectrum for pure bis(acetylacetonato)oxovanadium(IV):

FTIR is known as Fourier Transform Infrared Spectroscopy. This FTIR can be used to identify different types of chemical bond which is either organic compound or inorganic compound. So no two different compounds will have same spectrum. However, FTIR may cause destructive to our sample compare to magnetic susceptibility which is non-destructive. Besides that, magnetic susceptibility can be group by paramagnetic, diamagnetic and ferromagnetic. Paramagnetic substance is those attracted by strong magnetic field but those repelled by magnetic field are diamagnetic substances.

Besides that, we can also confirm the shape by using magnetic susceptibility. The Cobalt ion to form Chloropentaamminecobalt(III) chloride has 6 electron in d orbital.

Magnetic Susceptibility for chloropentaamminecobalt(III) chloride is -9.9338×10^{-8} and it is diamagnetic. Only the low-spin octahedral shape shows diamagnetic properties, so the shape of chloropentaamminecobalt(III) chloride is octahedral.

Magnetic Susceptibility for tris(acetylacetonato)manganese(III) is 2.65×10^{-5} and it is paramagnetic. So the shape of tris(acetylacetonato)manganese(III) is octahedral. However we cannot determine whether is low-spin or high-spin in this situation because we are not calculating the pairing energy for the complex.

In addition, there is only one electron in d orbital for vanadium ion of bis(acetylacetonato)oxovanadium(IV). Magnetic susceptibility for it is 4.17×10^{-6} and it is paramagnetic.

Moreover, oxovanadium complexes act as insulin mimetics, nucleolytic and anticancer.

To recognize insulin- mimetic complexes, a simple and fast in-vitro assay is developed. Besides that, an accurate assessment of the cells taken up of glucose, in-vitro assay with Ehrlich can be used. The oxovanadium complexes can cleave DNA without the present of hydrogen peroxide. Then, its nucleolytic efficiency is also greater but it is affected by the choice of

buffer and pH. The oxovanadium complexes is also an anticancer agent against human ovarian cancer.

Actually, I have acquired a lot of new knowledge among these three experiments. First, experiment one and two are easier to carry out compared to experiment three. This is because experiment one and two involved oxidation which Mn^{2+} was oxidized to Mn^{3+} ; Co^{2+} was oxidized to Co^{3+} . Whereas experiment 3 involved reduction which reduced VO_5^{+} to VO_4^{+} . At the beginning of each experiments, we heated up the sample in open air. It is easier to oxidize the compound than reduce the compound in the presence of oxygen. So, we need more time to heated the V_2O_5 .

During the first time of experiment three, I failed to get a blue color solid powder. This is because I heated the sample in the open air and I failed to control the heater. So, after the filtration process, I got a white solid powder. Therefore, I learnt from the mistake and during the second time I used reflux method. This time I can control the heating process well. The ethanol was not evaporated much. After filtration, I got quite a lot of blue solid powder. So, I knew that, for reduction process, we cannot heat the sample too quickly and heat too long. If we heated too long, most of the product will evaporate.

Next, from the FTIR spectrum, I can observe that the spectrum from the first and third experiment are quite similar. This is because, the peak from the spectrum are mostly from the acetylacetonato (acac). However, spectrum from experiment two is quite different from other experiment because mostly the peaks come from Cl compared to other experiments.

The percentage yield of the complexes from all the three experiment that I have calculate out was not so high. This is maybe due to the washing of the product with acetone, some of the product was dissolved and washed away. However, there are other factors which cause problem to our results. First, most of the heating plate we used cannot function well. I changed many heating plate during the experiment. Next, we have kept our half way done sample for more than 7 days. The results may not be so accurate anymore. Another factor maybe due to the volume and amount of the sample and other material we measure are not accurate. Our product may contain some impurities.

However, some of the precaution was taken during the experiment. In these experiments, some of the chemical was corrosive and poisonous such as concentrated HCl and H₂SO₄. So, we poured the chemical carefully in the fume board. Next, before using any instrument, we read through the manual to understand the steps to function the magnetic susceptibility balance. We also taken down some important steps to function the FTIR spectrophotometer. I have asked some help from lab assistant on where to get the material for experiment.

Conclusion

The percentage yield for tris(acetylacetonato)manganese(III) is 40. 67%, chloropentaamminecobalt(III) chloride is 58. 98% and (acetylacetonato)oxovanadium(IV) is 64. 12%.

For tris(acetylacetonato)manganese(III), the peak for two Mn-O bond are at the region approximately 678. 1 cm⁻¹ and 458. 3 cm⁻¹. For

chloropentaamminecobalt(III) chloride, the peak for Co-N bond is at 669. 2 cm-1 while Co-Cl bond is at 486. 2 cm-1. For

bis(acetylacetonato)oxovanadium(IV), the peak for V= O bond is at 997. 4 cm-1 region.

Magnetic Susceptibility for tris(acetylacetonato)manganese(III) is 2.65×10^{-5} and it is paramagnetic. Besides, Magnetic Susceptibility for chloropentaamminecobalt(III) chloride is -9.93×10^{-8} and is diamagnetic. For bis(acetylacetonato)oxovanadium(IV), magnetic susceptibility for impure complex and pure complex are 4.17×10^{-6} and 5.53×10^{-6} respectively. They are paramagnetic.