Metal acetylacetonate complexes synthesis

FTIR (Fourier Transform Infrared Spectroscopy) is useful for identifying types of chemical bonds in an organic or inorganic molecule such as its functional group by producing an IR (infrared) absorption spectrum. FTIR can be used for qualitative analysis for known compound and quantitative analysis for unknown compound that is either in solid, liquid or gaseous state. However, FTIR alone is insufficient to identify an unknown compound. Though, FTIR can still be used by supporting other techniques such as nuclear magnetic resonance, emission spectroscopy and mass spectroscopy in identifying unknown compound. FTIR is essentially useful in identifying the functional groups of a molecule. The IR spectrum obtained from analyzing a compound can be divided into two areas. The area between wavelength 4000 and 1000 cm-1 of the spectrum is the region where most of the functional groups show absorption bands, also known as the functional group region. On the other hand, the area between wavelength 1000 and 400 cm-1 of the spectrum is known as the fingerprint region. The chemical bonds in a molecule can be determined by interpreting the IR spectrum.

Generally, all substances can be classified into either one of three groups based on their magnetic properties. They are paramagnetic, diamagnetic and ferromagnetic. Those can be attracted to a magnetic field are known as paramagnetic. While those that repel a magnetic field are known as diamagnetic. The magnetic properties of the diamagnetic and paramagnetic substances can only be measured and observed when they are subjected to a magnetic field that is applied externally. Unlike paramagnetic and diamagnetic substances, ferromagnetic substances are able to retain their own permanent magnetic field.

Procedure

- To prepare tris(acetylacetonato)manganese(III), Mn(acac)3

5g (0. 025 mol) manganese(II) chloride tetrahydrate (M. W. 197. 90) and 1. 3g(0. 0095mol) sodium acetate trihydrate (MW 136. 08) were dissolved in 200 cm^3 distilled water.

21 cm^3 of acetyacetone was added to the solution slowly.

The two phase system was treated with 1g/(50 cm^3 of water) of potassium permanganate solution.

After a few minutes, 13g/(50 cm^3 of water) of sodium acetate solution was added into the solution.

The solution was heated with stirring at 60°C for 30 minutes.

The resultant solution was cooled in ice-cold water and then the solid complex formed was filtered by suction filtration.

The complex was washed with acetone and it was dried by suction.

- To prepare chloropentaamminecobalt(III) chloride, [CoCl(NH3)5]Cl2

6g ammonium chloride was dissolved in 40 cm^3 conc. Ammonia in a 250 cm^3 flask.

The solution was stirred continually. At the same time, 12g of finely powdered CoCl2. 6H2O was added in small portions

The slurry in fume cupboard was warmed and 10cm^3 of 30% hydrogen peroxide was added slowly from a burette with vigorous swirling.

When effervescence had ceased, 40 cm^3 of concentration hydrochloride acid was added slowly.

The product was heated on a stream bath for 15 minutes.

The product was cooled, filtered and washed with 25 cm^3 of ice water, then with 25 cm^3 of 6M HCl and then alcohol.

The product was dried at 110°C for an hour.

- To prepare aquabis(acetylacetonato)oxovanadium(IV), [VO(acac)2(H2O)].

2 g of vanadium(V) oxide was weighed out into a 250 cm^3 conical flask.

A mixture of 5 cm^3 of distilled water, 4 cm^3 of concentrated sulphuric acid and 10cm^3 absolute ethanol were added into the vanadium oxide.

The mixture was heated under reflux for around 1 hour.

The solution was filtered and the filtrate was transfer into a 250 cm^3 beaker.

5 cm^3 of acetylacetone was added into the solution and then the solution was neutralize by adding 16% w/v of sodium carbonate.

The precipitate was washed with cold methylated spirits and cold ethanol using suction filtration.

The product was dried by suction and the yield was measured.

Half of the product was used for recrystallization.

The half product that for recrystallization was dissolved in a minimum volume of dichloromethane.

The impurities were filtered and diethyl ether was added until precipitation had occurred.

The product was filtered and it was washed with ether and also air dried.

Result

Mass and molar susceptibility, and of samples:

Ï‡g (Mn(acac)3) =

=

= 2. 3756 ¨¯10-5 erg G-2 g-1

Ï‡m (Mn(acac)3) = 2. 3756 ¨¯10-5 erg G-2 g-1 Ã- 355. 286 g mol-1

= 0. 00844 erg G-2 mol-1

Ï‡g ([CoCl(NH3)5]Cl2) =

= – 2. 1516 ¨¯ 10-7 erg G-2 g-1

Ï‡m ([CoCl(NH3)5]Cl2) = – 2. 1516 ¨¯ 10-7 erg G-2 g-1 Ã- 250. 445 g mol-1

= – 5. 3886 ¨¯ 10-5 erg G-2 mol-1

Ï‡g (Impure [VO(acac)2(H2O)]) =

= 3. 7340 ¨¯ 10-6 erg G-2 g-1

Ï‡m (Impure [VO(acac)2(H2O)]) = 3. 7340 ¨¯ 10-6 erg G-2 g-1 Ã- 283. 16 g mol-1

= 1. 0573 ¨¯ 10-3 erg G-2 mol-1

Ï‡g (Pure [VO(acac)2(H2O)]) =

= 3. 9175 ¨¯ 10-6 erg G-2 g-1

Ï‡m (Pure [VO(acac)2(H2O)]) = 3. 9175 ¨¯ 10-6 erg G-2 g-1 Ã- 283. 16 g mol-1

= 1. 1093 ¨¯ 10-3 erg G-2 mol-1

The paramagnetic susceptibility of Mn(acac)3 is greater than [VO(acac)2(H2O)] complex. This shows that Mn(acac)3 complex has more unpaired electron in the t2g and eg orbitals than the [VO(acac)2(H2O)] complex. On the other hand, [CoCl(NH3)5]Cl2 with negative paramagnetic susceptibility shows that the complex is a diamagnetic compound.

Discussion

tris(acetylacetonato)manganese(III), Mn(acac)3

The resonance forms of acetylacetonate are

Resonance of acetylacetonate

Structure of tris(acetylacetonato)manganese(III), Mn(acac)3

Figure 1. 0 shows the predicted structure for Mn(acac)3. It is an octahedral complex with 3 acetylacetonate bonded to it as ligands to the manganese.

Experimental data shows that Mn(acac)3 is a paramagnetic compound. Based on Valence Bond Theory, the electrons arrangement in low spin complex of Mn(acac)3 produce diamagnetic compound and therefore our Mn(acac)3 product is not a low spin complex. As for the high spin complex, there are unpaired electrons in 3d orbital which give rise to a paramagnetic compound. Thus, our Mn(acac)3 product is a high spin complex.

From Valence Bond Theory, we know that Mn(acac)3 compound is a high spin complex. First, we consider this octahedral complex have no Ï€ bonding. Out of nine orbitals in the valence shell of the manganese ion, only six (s, p and dx2-y2 and dz2 orbitals) are suitable for Ïƒ bonding, while the other three (dxy, dxz, dyz) which are directed between the ligands are not suitable. The predicted Ligand Field Theory for Mn(acac)3 compound is as illustrated in Figure 1. 1 above.

Chloropentaamminecobalt(III) chloride, [CoCl(NH3)5]Cl2

Structure of Chloropentaamminecobalt(III) chloride, [CoCl(NH3)5]Cl2

Figure 2. 0 shows the predicted structure for [CoCl(NH3)5]Cl2. It is an octahedral complex with a chlorine atom and 5 ammonia bonded to cobalt as ligands and a chlorine molecule bonded to the complex as anion.

Experimental data shows that [CoCl(NH3)5]Cl2 is a diamagnetic compound. Based on Valence Bond Theory, the electrons arrangement in low spin complex of [CoCl(NH3)5]Cl2 produce diamagnetic compound and therefore our [CoCl(NH3)5]Cl2 product is a low spin complex. As for the high spin complex, there are unpaired electrons in 3d orbital which give rise to a paramagnetic compound that does not match our experimental data. Hence, our $[CoCl(NH_3)_5]Cl_2$ product is not a high spin complex.

From Valence Bond Theory, we know that $[CoCl(NH_3)_5]Cl_2$ compound is a low spin complex. The predicted Ligand Field Theory for $[CoCl(NH_3)_5]Cl_2$ compound is as illustrated in Figure 2. 1 above.

aquabis(acetylacetonato)oxovanadium(IV), $[VO(acac)_2(H_2O)]$

Structure of aquabis(acetylacetonato)oxovanadium(IV), $[VO(acac)_2(H_2O)]$.

Figure 3. 0 shows the predicted structure for $[VO(acac)_2(H_2O)]$. It is an octahedral complex with oxygen, 2 acetylacetate and one water molecule bonded to vanadium as ligands.

Experimental data shows that $[VO(acac)_2(H_2O)]$ is a paramagnetic compound. Based on Valence Bond Theory, the electrons arrangement in either low spin or high spin for $[VO(acac)_2(H_2O)]$ complex will produce a paramagnetic compound. Thus, our $[VO(acac)_2(H_2O)]$ product is still a low spin complex.

From Valence Bond Theory, we know that $[VO(acac)_2(H_2O)]$ compound is a low spin complex. The predicted Ligand Field Theory for $[VO(acac)_2(H_2O)]$ compound is as illustrated in Figure 3. 1 above.

Literature for oxovanadium complexes:

Insulin-mimetic

There has been a major problem in treating diabetic patients with insulin which is the risk of hypoglycemia, low blood glucose level. However, administration of same amount of vanadium lowers diabetic hyperglycemia does not greatly lower glood glucose level to cause clinical hypoglycemia which is a major advantage of vanadium therapy. The ligand also greatly influence in the determination of antidiabetic or cytotoxic properties of vanadium complexes. For example, the vanadium complex (4-hydroxypyridine-2, 6-dicarboxylato)oxovanadate(V) was reported to have antidiabetic properties in rats and cytotoxic effects in Saccharomyces cerevisiae. Other complexes such as dipicolinic acid transtition metal (cobalt, chromium, iron, molybdenum, manganese, nickel, tungsten and vanadium) complexes show greatest insulin-enhancing effect in rat with STZ-induced diabetes and greatest cytotoxic effects on rat myoblasts. Therefore, the design of ligated vanadium complexes should maintain insulin-enhancing activity while having lower toxicity in animals. (Alan S. Tracey, 2007)

Nucleolytic

Vanadium compounds induce cytotoxic effects (antineoplatic cell-cycle arrest) via plasma membrane lipoperoxidation reactions, DNA fragmentation and cleavage. Studies show that the inhibition of the growth of the cancer cell lines is more difficult as the anti-diabetic vanadium compounds also inhibit cell growth in mammals. (Alan S. Tracey, 2007)

Anticancer

In 1979, the metalocene compound, biscyclopentadienyldichloro-Vanadium(IV), (C5H5)VCl2 was found to have anti-tumor activity. This compound inhibited the growth of various cancer cells and activity of solid tumors in vivo. Furthermore, Vanadium(V) peroxocomplexes with insulin-mimetic activity were shown to have anti-tumor activity against murine leukemia cells at that time. The vanadocene compounds are known to induce apoptosis in cell lines now whereby the apoptotic signal is different from that of cisplatin, the most widely used metal cancer therapeutic agent. Apoptotic signal from cisplatin triggers primary DNA damage and involves p53 induction. This p53 protein is a tumor suppressor that usually functions in the processes of apoptosis, cell cycle control and maintenance of genomic stability. Vanadium(V) metallocenes were the most potent cytotoxic compounds when tested against human testicular cancer cell lines in contrast with four other metallocenes dichlorides (titanium, zirconium, molybdenum and hafnium). (Alan S. Tracey, 2007)

Mn(acac)3 has similar absorption bands to [CoCl(NH3)5]Cl2 and [VO(acac)2 (H2O)] at about 2900 to 3000 cm-1 with 3 peaks, 1500 to 1600 cm-1 with 2 peaks, 1300 to 1400 cm-1 with 2 peaks and 1200 to 1300 cm-1 with one peak. These absorption bands observed are most likely from the acac ligands that bonded to Mn and V. Besides, the oxygen bonded as a ligand to different transition element also gives a different absorption band for different transition metal accordingly.

Conclusion

The percentage yield and molar susceptibility for Mn(acac)3, [CoCl(NH3)5]Cl2, and [VO(acac)2(H2O)] complexes are 33. 33% and 0. 00844 erg G-2 mol-1; 52. 29% and – 5. 3886 ¨¯ 10-5 erg G-2 mol-1; 131. 48% and 1. 1093 ¨¯ 10-3 erg G-2 mol-1 respectively.