

Access Reading

Study Skills Session, Supporting Documents

Thursday 4th April 2024

Name:

PhD tutor:

Daniel

Subject Strand:

Sciences (Chemistry and Food and Nutritional Science)

Critical thinking:

Critical thinking can be defined as the process of working out **what** you think and **why** you think this.

Critical thinking is essential to all subject disciplines at university study. It is very common for new university students to receive feedback that they need to think thus write more critically to develop their essays and ultimately receive higher grades.

At university critical thinking also involves:

- Identifying **what you want to know**, and **why**.
- Sourcing **relevant and reliable** information.
- Grounding your thinking in this **evidence**.
- Addressing **contradictions** in wider academic thinking.

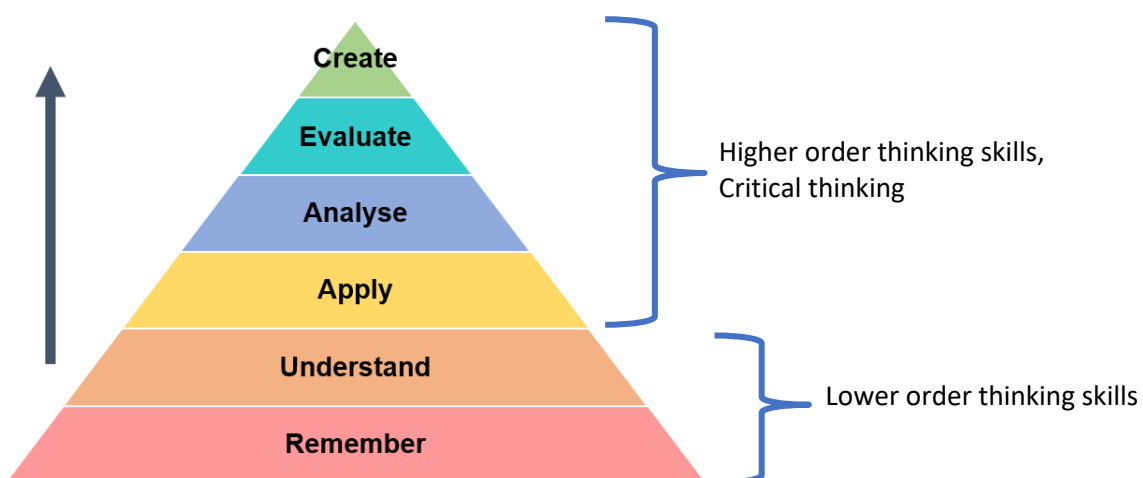
Critical thinking is an important study skill that you will develop at university, practising this skill before enrolling at university to help you make a smoother transition academically.

Bloom's Taxonomy:

To help establish how critical we are being we can utilise Bloom's Taxonomy. Through Bloom's Taxonomy we can see the stages of learning as a hierarchy of critical analysis.

"Remember" requires the least amount of critical thinking and "Create" requires the most. The higher your university work sits on the pyramid the more critical you are being. This means when you analyse and evaluate academic literature you are seen to be more critical than those which simply describe theories and claims without questioning their validity.

To achieve a higher level on the pyramid you still need to undertake everything beneath it but be sure not to get trapped there!



Stages	Description	Examples of words associated with this level
Create	Produce new or original work.	Design, construct, develop, formulate, investigate
Evaluate	Justify a stand or decision.	Argue, defend, support, critique, weigh
Analyse	Draw connections among ideas.	Relate, compare, contrast, examine, question
Apply	Use information in new situations.	Execute, implement, solve, use, demonstrate
Understand	Explain ideas of concepts.	Describe, discuss, classify, recognise, paraphrase
Remember	Recall facts and basic concepts.	Define, state, memorise, repeat, quoting

Health and Safety Discussion Questions

What health and safety considerations do we need to be aware of in a university lab-based environment?

What processes need to be undertaken to ensure health and safety procedures are followed?

A. COSHH Assessment																				
Please Mark relevant hazards and control measures with an X																				
Hazards											How might they cause harm (including routes of exposure)		Control measures (please specify types of eye protection/gloves)							
Substance (include process by-products)	Form	Volumes used g/L	C Corrosive	Xi Irritant	Xn Harmful	T Toxic	Ca Carcinogenic	O Oxidising	F Flammable	Ex Explosive	Env Environmental	List how these cause harm and routes of exposure	WEL	Fume cupboard FC	Microbiological safety cabinet MSC	Laboratory coat Coat	Eye protection Eyes	Gloves Gloves	Respiratory protection RPE	Other /details*
Acetylacetone	L	5mL											mgm ⁻³							
KMnO ₄ (Potassium Permanganate)	S	0.2g											mgm ⁻³							
H ₂ SO ₄ (Sulphuric Acid)	L	200 mL											mgm ⁻³							

Sodium Carbonate (anhydrous)	S	5g	X								H319 – Causes serious eye irritation	N/A			X	X	X		P305+P351+P338 – If in eyes, rinse with water, remove contact lenses
CH ₃ COONa.3H ₂ O	S	2.6g									No associated hazards	N/A			X	X	X		Wear ppe
Toluene	L	1mL	X	X				X			H225 – Highly flammable liquid and vapour H304 – May be fatal if swallowed and enters airways H315 – Causes skin irritation H336 – May cause drowsiness or dizziness H361d – Suspected of damaging the unborn child H373 – May cause damage to organs through prolonged or repeated exposure	192 mgm ⁻³	X		X	X	X		P210 – Keep away from sources of ignition P260 – Do not breathe fume/spray P280 – Wear ppe P301+P310 – If swallowed, call a poison centre or physician P370+P378 – In case of fire, use dry powder or dry sand P403+P235 – Store in a well-ventilated place, keep cool
Pyridine	L	1mL	X	X				X			H225 – Highly flammable liquid and vapour H302+H312+H332 – Harmful if swallowed, in contact with skin or if inhaled H315 – Causes skin irritation H319 – Causes serious eye irritation	15 mgm ⁻³	X		X	X	X		P210 – Keep away from sources of ignition P280 – Wear ppe P305+P351+P338 – If in eyes, rinse with water, remove contact lenses
VO(SO ₄).6H ₂ O	S	5g		X							H302 – Harmful if swallowed	N/A			X	X	X		Wear ppe
[VO(acac) ₂]	S	-	X	X							H302 – Harmful if swallowed H315 – Causes skin irritation H319 – Causes serious eye irritation H335 – May cause respiratory irritation	N/A	X		X	X	X		P261 – Avoid breathing dust P305+P351+P338 – If in eyes, rinse with water, remove contact lenses
[Mn(acac) ₃]	S	-	X	X							H302 – Harmful if swallowed H315 – Causes skin irritation H319 – Causes serious eye irritation H335 – May cause respiratory irritation	N/A	X		X	X	X		P261 – Avoid breathing dust P305+P351+P338 – If in eyes, rinse with water, remove contact lenses



Please feel free to make notes in this area:



B. Assessing the level of risk and further action needed <i>(please check relevant box)</i>					
7.1 How severe is any injury or health effect likely to be?	Tick one box (S =score given in brackets)	Minor <input type="checkbox"/> (1)	Serious <input checked="" type="checkbox"/> (2)	Major <input type="checkbox"/> (3)	Fatal <input type="checkbox"/> (4)
7.2. How likely is exposure to the hazard?	Tick one box (P =score given in brackets)	Very unlikely <input type="checkbox"/> (1)	Unlikely <input checked="" type="checkbox"/> (2)	Possible <input type="checkbox"/> (3)	Likely <input type="checkbox"/> (4)
7.3. Calculate the risk score by multiplying the 2 scores in Q7.1 & 7.2	Risk Score (S x P) =	Low <input type="checkbox"/> (1–3)	Medium <input checked="" type="checkbox"/> (4–6)	High <input type="checkbox"/> (8–9)	Very High <input type="checkbox"/> (12–16)

C. Waste disposal

Please provide details on disposal of chemical and/or biological waste including any special requirements.
Dispose of any waste into the correctly labelled waste containers. Vanadium and Manganese complexes are to be disposed of in the heavy metals waste container. Acetylacetone and sodium acetate trihydrate solutions are to be disposed of in the non-halogenated waste container.

Chemical Safety Data Sheet (SDS) for COSHH Activity:

Acetylacetone

Pictogram	
Signal Word	Danger
Hazard statement(s)	
H226	Flammable liquid and vapor.
H302	Harmful if swallowed.
H311 + H331	Toxic in contact with skin or if inhaled.
Precautionary statement(s)	
P210	Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.
P233	Keep container tightly closed.
P280	Wear protective gloves/ protective clothing/ eye protection/ face protection.
P301 + P312	IF SWALLOWED: Call a POISON CENTER/ doctor if you feel unwell.
P303 + P361 + P353	IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water.
P304 + P340 + P311	IF INHALED: Remove person to fresh air and keep comfortable for breathing. Call a POISON CENTER/ doctor.
Supplemental Hazard Statements	none
Reduced Labeling (<= 125 ml)	
Pictogram	
Signal Word	Danger
Hazard statement(s)	
H311 + H331	Toxic in contact with skin or if inhaled.
Precautionary statement(s)	
P304 + P340 + P311	IF INHALED: Remove person to fresh air and keep comfortable for breathing. Call a POISON CENTER/ doctor.
Supplemental Hazard Statements	none

Derived No Effect Level (DNEL)			
Application Area	Routes of exposure	Health effect	Value
Workers	Skin contact	Long-term systemic effects	12mg/kg BW/d
Workers	Inhalation	Long-term systemic effects	84 mg/m ³

KMnO₄ (Potassium Permanganate)

Labelling according Regulation (EC) No 1272/2008 as amended by GB-CLP Regulation, UK SI 2019/720, and UK SI 2020/1567

Pictogram



Signal Word Danger

Hazard statement(s)

H272 May intensify fire; oxidizer.
H302 Harmful if swallowed.
H314 Causes severe skin burns and eye damage.
H361d Suspected of damaging the unborn child.
H373 May cause damage to organs (Brain) through prolonged or repeated exposure if inhaled.
H410 Very toxic to aquatic life with long lasting effects.

Precautionary statement(s)

P210 Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.
P260 Do not breathe dust.
P273 Avoid release to the environment.
P280 Wear protective gloves/ protective clothing/ eye protection/ face protection.
P303 + P361 + P353 IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water.
P305 + P351 + P338 IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

Supplemental Hazard Statements

none

Reduced Labeling (<= 125 ml)

Pictogram



Signal Word Danger

Hazard statement(s)

H314 Causes severe skin burns and eye damage.
H361d Suspected of damaging the unborn child.

Precautionary statement(s)

P260 Do not breathe dust.
P280 Wear protective gloves/ protective clothing/ eye protection/ face protection.
P303 + P361 + P353 IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water.

P305 + P351 + P338 IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

Supplemental Hazard Statements



none

Ingredients with workplace control parameters

Component	CAS-No.	Control parameters	Value	Basis
Potassium permanganate	7722-64-7	TWA	0.2 mg/m3 inhalable fraction	Europe. Commission Directive 2017/164/EU establishing a fourth list of indicative occupational exposure limit values
	Remarks	Indicative		
		TWA	0.05 mg/m3 Respirable fraction	Europe. Commission Directive 2017/164/EU establishing a fourth list of indicative occupational exposure limit values
		Indicative		

		TWA	0.2 mg/m3 Inhalable	UK. EH40 WEL - Workplace Exposure Limits
		TWA	0.05 mg/m3 Respirable fraction	UK. EH40 WEL - Workplace Exposure Limits

H₂SO₄ (Sulphuric Acid)

Pictogram	
Signal Word	Danger
Hazard statement(s)	
H290	May be corrosive to metals.
H314	Causes severe skin burns and eye damage.
Precautionary statement(s)	
P234	Keep only in original packaging.
P280	Wear protective gloves/ protective clothing/ eye protection/ face protection.
P303 + P361 + P353	IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water.
P304 + P340 + P310	IF INHALED: Remove person to fresh air and keep comfortable for breathing. Immediately call a POISON CENTER/ doctor.
P305 + P351 + P338	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
P363	Wash contaminated clothing before reuse.
Supplemental Hazard Statements	none
Reduced Labeling (<= 125 ml)	
Pictogram	
Signal Word	Danger
Hazard statement(s)	
H314	Causes severe skin burns and eye damage.
Precautionary statement(s)	
P280	Wear protective gloves/ protective clothing/ eye protection/ face protection.
P303 + P361 + P353	IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water.
P304 + P340 + P310	IF INHALED: Remove person to fresh air and keep comfortable for breathing. Immediately call a POISON CENTER/ doctor.
P305 + P351 + P338	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
P363	Wash contaminated clothing before reuse.
Supplemental Hazard Statements	none

Component	CAS-No.	Control parameters	Value	Basis
sulphuric acid	7664-93-9	TWA	0.05 mg/m3 Mist	Europe. COMMISSION DIRECTIVE 2009/161/EU establishing a third list of indicative occupational exposure limit values in implementation of Council Directive 98/24/EC and amending Commission Directive 2000/39/EC
	Remarks	Indicative TWA	0.05 mg/m3 Mist, thoracic fraction	UK. EH40 WEL - Workplace Exposure Limits

Additional SDS Links:

Acetylacetone: <https://www.sigmaaldrich.com/GB/en/sds/sigald/p7754?userType=anonymous>

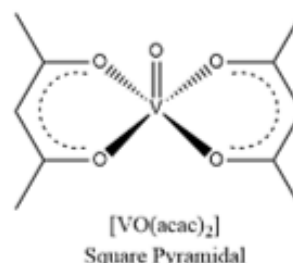
KMnO₄: <https://www.sigmaaldrich.com/GB/en/sds/sigald/399124?userType=anonymous>

H₂SO₄: <https://www.sigmaaldrich.com/GB/en/sds/sigald/258105?userType=anonymous>

Lab report discussion:

Introduction

The aims of the experiment was to synthesise two metal acetylacetonate complexes, $[\text{VO}(\text{acac})_2]$ and $[\text{Mn}(\text{acac})_3]$, where UV-Visible was to be employed for both complexes in toluene and pyridine and IR spectroscopy was also employed to both respective complexes. The UV-Visible spectroscopy was to find if the complexes had possible d-d transitions and the IR spectroscopy was to confirm the correct structure was produced. The magnetic moments were to be used to find the number of unpaired electrons within the complex. The percentage yield for each respective complex was also to be determined along with a titration of the resulting synthesised complex, $[\text{VO}(\text{acac})_2]$ against potassium permanganate (KMnO_4) solution to calculate the percentage of Vanadium within the complex.



Experimental

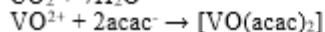
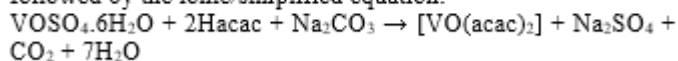
Synthesis of $[\text{Mn}(\text{acac})_3]$

To prepare tris(2,4-pentanedionate)manganese(III) or $[\text{Mn}(\text{acac})_3]$, a solution of manganese(II) chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) (1.0163g), water (40mL) and sodium acetate trihydrate ($\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$) (2.6356g) was produced, where acetylacetone (4mL) was then added. The solution was stirred continuously using a magnetic stirrer for around 35 minutes, followed by potassium permanganate (KMnO_4) (0.2007g), where stirring was then continued. A solution of $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ (2.6040g) and water (10mL) was then prepared. This solution was then added slowly in small quantities to the manganese solution over 5 minutes, while still stirring. The overall solution was then heated to 60°C for approximately 15 minutes, where it was then cooled in an ice bath. The black crystals were then filtered off by suction and washed with water (300mL), and was kept under suction until the crystals were dry.

Results and Discussion

The Reactions for the Preparation of each of the Complexes

To prepare $[\text{VO}(\text{acac})_2]$ from $\text{VOSO}_4 \cdot 6\text{H}_2\text{O}$. Note: Hacac is used for acetylacetone and acac is its respective anion (due to deprotonation of Hacac). The overall equation is shown first followed by the ionic/simplified equation.



Percentage Yield

Thus using these equations the percentage yields of both complexes could be calculated.

$[\text{VO}(\text{acac})_2]$

The starting material $\text{VOSO}_4 \cdot 6\text{H}_2\text{O}$, had a mass of 5.0358g, where the molecular mass is 271.092g mol^{-1} .

$5.0358\text{g} \div 271.092\text{g mol}^{-1} = 0.01858\text{mol VOSO}_4 \cdot 6\text{H}_2\text{O}$
 The assumption is a 1:1 ratio of reactant to product and thus there should be the same number of moles $[\text{VO}(\text{acac})_2]$, as $\text{VOSO}_4 \cdot 6\text{H}_2\text{O}$, where the molecular mass of the product is 265.159g mol^{-1} .
 Hence $0.01858\text{mol} [\text{VO}(\text{acac})_2]$
 $0.01858\text{mol} \times 265.159\text{g mol}^{-1} = 4.92559\text{g}$
 $(4.0851 \div 4.92559) \times 100\% = 82.94\%$

Abstract

The aims of the experiment were to synthesise $[\text{VO}(\text{acac})_2]$ (square pyramidal) and $[\text{Mn}(\text{acac})_3]$ (distorted octahedral), measure them spectroscopically using IR and UV-Visible, interpret the magnetic moments and determine the percentage of vanadium in its respective complex. It was found that the percentage yields for the acetylacetonate vanadium and manganese complexes were 82.94% and 8.56% respectively. The IR spectra confirmed these structures were produced due to specific peaks such as V=O stretch 997.12 and Mn-O 575.23cm^{-1} . The UV-Visible spectra confirmed d-d transitions were present due to the respective one (V) and four (Mn) valence d electrons, and $[\text{VO}(\text{acac})_2]$ in the pyridine solvent showed there was a charge transfer. Each of the λ_{max} obtained corresponded to the colour of the solution transmitted. The magnetic moments (1.73 and $4.95\mu_B$ respectively) confirmed the number of valence electrons. A titration of the vanadium complex against potassium permanganate solution resulted in an average of 16.98% of vanadium in its complex.

Conclusions

Preparation of the complexes $[\text{VO}(\text{acac})_2]$ and $[\text{Mn}(\text{acac})_3]$ and conducting a series of spectroscopic analysis techniques resulted in evidence of the correct respective structures being produced, with percentage yields of 82.94% and 8.56% respectively. The IR spectra both provided evidence by significant peaks such as the V=O stretch at 997.12cm^{-1} and the other respective peaks provided that the acetylacetonate ligand was present.

The experiment also showed that $[\text{Mn}(\text{acac})_3]$ was a High Spin complex, providing that the splitting parameter was relatively small and that it was paramagnetic and that $[\text{VO}(\text{acac})_2]$ was also paramagnetic where the complexes had 4 and 1 valence d electrons respectively. The UV-Visible spectra showed that there were d-d transitions in all four complexes and that the maximum wavelengths absorbed corresponded to the colour of the solution, but $[\text{VO}(\text{acac})_2]$ also undertook charge transfer when in pyridine, resulting in a deeper colour.

My thoughts...

What information is in each section?

What does it contribute to the overall structure?

What is the importance of each section?

Critical Reading notes:

Remember you don't have to answer all the questions, use them in a way that you find useful. If you wish to apply these questions to the **Lab Report** discussed, please do. If you want to apply these questions to a new piece of **Academic Literature**, then this is in the "Further Resources".

<p>What are the key features of each section?</p> <p>I.e. Introduction "sets the scene".</p>	
<p>What is the overall language or tone of a lab report / academic literature?</p> <p>Think the tense, does it include "I" or "we"?</p>	
<p>What are the key quantities, times or observations in the Experimental Section that would help you to repeat this experiment?</p>	
<p>In the Results and Discussion, how is each statement supported with literature or a suitable explanation?</p>	
<p>Are there any flaws, gaps or limitations to the descriptions that could be improved?</p>	
<p>How does the Abstract and Conclusion explain the aims or reason for this experiment?</p>	

<p>How does this scientific text relate to other ideas I have read and/or my personal experience?</p> <p>Does it agree, contradict, or challenge my current knowledge?</p>	
<p>How does the author reference other scientists' work?</p> <p>Consider figures, tables, previous literature.</p>	

Further resources:

Academic Literature Example:

P. K. Baker and S. G. Fraser, *Inorganica Chimica Acta.*, **1986**, 116, L3-L4

Can the Abstract, Introduction, Experimental and Results and Discussion sections be observed?

Inorganica Chimica Acta, 116 (1986) L3-L4

L3

The Reactions of $[M_2(CO)_3(NCMe)_2]$ ($M = Mo$ and W).

Part 3. The Synthesis and Spectral Properties of the Seven-coordinate Complexes $[M_2(CO)_3(L-L)]$ ($M = Mo$ and W ; $L-L = py_2$, 2,2'-bipyridyl and 1,10-phenanthroline)

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(Received December 2, 1985)

In a previous paper in this series [1] we described a new high-yielding synthesis of the complexes $[M_2(CO)_3L_2]$ ($M = Mo$ and W ; $L = PPh_3$, $AsPh_3$ and $SbPh_3$). Although the molybdenum dichloro and dibromo complexes containing nitrogen donor ligands $[MoX_2(CO)_3(L-L)]$ ($X = Cl$ and Br ; $L-L = py_2$, 2,2'-bipyridyl and 1,10-phenanthroline) have been reported by Colton and Tomkins [2], and the tungsten bispyridine compounds $[WX_2(CO)_3(py)_2]$ ($X = Cl$ and Br) by Westland and Muriithi [3], to date there has been no report of the diiodo complexes with the exception of the tungsten compounds $[W_2(CO)_3(L-L)]$ ($L-L = py_2$ [3] and 2,2'-bipyridyl [4]) which have been prepared by reacting the zerovalent complexes $[W(CO)_4(L-L)]$ with iodine. The small number of diiodide complexes known is almost certainly due to the difficulty of synthesising the iodide bridged dimers $[M(\mu-I)(CO)_4]_2$ ($M = Mo$ and W) [5,6]. We now wish to report a new high-yielding synthesis of the complexes $[M_2(CO)_3(L-L)]$ ($M = Mo$ and W ; $L = py_2$, 2,2'-bipyridyl and 1,10-phenanthroline), from the reaction of $[M_2(CO)_3(NCMe)_2]$ with the appropriate nitrogen donor ligand.

Experimental

$[M_2(CO)_3(NCMe)_2]$ were prepared according to literature methods [7], an pyridine, 2,2'-bipyridyl and 1,10-phenanthroline were purchased from Aldrich Chemical Company. CH_2Cl_2 was dried and distilled before use.

1H NMR spectra were recorded on a Jeol FX60 NMR spectrometer (all spectra were calibrated against tetramethylsilane). Infrared spectra were recorded on a Perkin-Elmer 197 infrared spectrophotometer. Elemental analyses for carbon, hydrogen and nitrogen were recorded on a Carlo Erba Elemental Analyser MOD1106 (using a helium carrier gas).

*Author to whom correspondence should be addressed.

$[MoI_2(CO)_3(py)_2]/CH_2Cl_2$ (1)

To $MoI_2(CO)_3(NCMe)_2$ (0.27 g, 0.523 mmol) dissolved in CH_2Cl_2 (15 cm³) with continuous stirring under a stream of dry argon was added pyridine (0.083 g, 1.049 mmol), and the mixture was left stirring for 4 min. Removal of the solvent *in vacuo* afforded the analytically pure brown crystalline complex $[MoI_2(CO)_3(py)_2]CH_2Cl_2$ (yield = 0.23 g, 65%): 1H NMR δ $\{(CD_3)_2SO\}$ 8.83 (d, 2H), 8.27 (m, 2H), 7.89 (d, 1H), 5.73 (s, 2H, CH_2Cl_2).

$WI_2(CO)_3(py)_2$ (2)

To $WI_2(CO)_3(NCMe)_2$ (0.229 g, 0.379 mmol) dissolved in CH_2Cl_2 (15 cm³) with continuous stirring under a stream of dry argon was added pyridine (0.06 g, 0.759 mmol), and the mixture was left stirring for 10 min. Removal of the solvent *in vacuo* afforded the analytically pure brown crystalline complex $[WI_2(CO)_3(py)_2]$ (yield = 0.21 g, 82%): 1H NMR δ $\{(CD_3)_2SO\}$ 8.79 (d, 2H), 8.28 (m, 2H), 7.73 (d, 1H).

$MoI_2(CO)_3(bipy)$ (3)

To $MoI_2(CO)_3(NCMe)_2$ (0.33 g, 0.640 mmol) dissolved in CH_2Cl_2 (15 cm³) with continuous stirring under a stream of dry argon was added 2,2'-bipyridyl (0.10 g, 0.640 mmol), and the mixture was left stirring for 5 min. Removal of the solvent *in vacuo* afforded the analytically pure brown crystalline complex $[MoI_2(CO)_3(bipy)]$ (yield = 0.32 g, 85%): 1H NMR δ $\{(CD_3)_2SO\}$ 9.5 (d, 2H), 8.67 (m, 4H), 7.88 (d, 2H).

$WI_2(CO)_3(bipy)$ (4)

To $WI_2(CO)_3(NCMe)_2$ (0.34 g, 0.563 mmol) dissolved in CH_2Cl_2 (15 cm³) with continuous stirring under a stream of dry argon was added 2,2'-bipyridyl (0.088 g, 0.563 mmol), and the mixture was left stirring for 5 min. Removal of the solvent *in vacuo* afforded the analytically pure brown crystalline complex $[WI_2(CO)_3(bipy)]$ (yield = 0.29 g, 76%): 1H NMR δ $\{(CD_3)_2SO\}$ 9.69 (d, 2H), 8.71 (m, 4H), 7.91 (d, 2H).

$[MoI_2(CO)_3(phen)]/CH_2Cl_2$ (5)

To $MoI_2(CO)_3(NCMe)_2$ (0.26 g, 0.504 mmol) dissolved in CH_2Cl_2 (15 cm³) with continuous stirring under a stream of dry argon was added 1,10-phenanthroline (0.091 g, 0.505 mmol), and the mixture was left stirring for 10 min. Removal of the solvent *in vacuo* afforded the analytically pure brown crystalline complex $[MoI_2(CO)_3(phen)]CH_2Cl_2$ (yield = 0.24 g, 68%): 1H NMR δ $\{(CD_3)_2SO\}$ 10.01 (m, 2H), 9.23 (m, 2H), 8.44 (m, 4H), 5.79 (s, 2H, CH_2Cl_2).

TABLE I. Analytical (C, H and N)^a and IR Data^b for [MI₂(CO)₃(L-L)]

Complex		Analysis (%) ^a	$\nu(\text{CO})^b$ (cm ⁻¹)
[MoI ₂ (CO) ₃ (py) ₂][CH ₂ Cl ₂]	(1)	C 24.92 (24.84) H 2.06 (1.79) N 4.17 (4.14)	2015(s), 1934(s) and 1900(m)
[WI ₂ (CO) ₃ (py) ₂]	(2)	C 22.82 (22.97) H 1.46 (1.48) N 3.89 (4.12)	2005(s), 1920(s) and 1905(s)
[MoI ₂ (CO) ₃ (bipy)]	(3)	C 26.53 (26.47) H 1.46 (1.37) N 4.62 (4.75)	2035(s), 1960(s) and 1912(s)
[WI ₂ (CO) ₃ (bipy)]	(4)	C 23.50 (23.03) H 1.49 (1.19) N 4.11 (4.13)	2025(s), 1945(s) and 1895(s)
[MoI ₂ (CO) ₃ (phen)][CH ₂ Cl ₂]	(5)	C 27.06 (27.50) H 1.60 (1.44) N 4.00 (4.01)	2040(s), 1963(s) and 1934(s)
[WI ₂ (CO) ₃ (phen)][CH ₂ Cl ₂]	(6)	C 24.35 (24.42) H 1.35 (1.28) N 3.53 (3.56)	2020(s), 1940(s) and 1915(s)

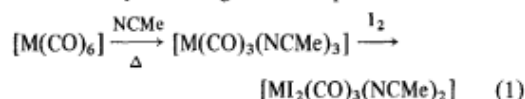
^aCalculated values in parenthesis.^bSpectra recorded in CHCl₃ unless stated, m, medium, s, strong.*[WI₂(CO)₃(phen)][CH₂Cl₂] (6)*

To WI₂(CO)₃(NCMe)₂ (0.268 g, 0.444 mmol) dissolved in CH₂Cl₂ (15 cm³) with continuous stirring under a stream of dry argon was added 1,10-phenanthroline (0.08 g, 0.444 mmol), and the mixture was left stirring for 11 min. Removal of the solvent *in vacuo* afforded the analytically pure brown crystalline complex [WI₂(CO)₃(phen)][CH₂Cl₂] (yield = 0.27 g, 77%): ¹H NMR δ [(CD₃)₂SO] 10.12 (d, 2H), 9.21 (d, 2H), 8.32 (m, 4H), 5.75 (s, 2H, CH₂-Cl₂).

Results and Discussion

Elemental analysis (C, H and N) and infrared spectroscopy (Table I) and ¹H NMR spectroscopy (see 'Experimental') support the formulation of the complexes [MI₂(CO)₃(L-L)] (M = Mo and W; L-L = py₂, 2,2'-bipyridyl, and 1,10-phenanthroline). Two acetonitrile ligands are readily replaced from [MI₂(CO)₃(NCMe)₂] by nitrogen donor ligands. The complexes are both air and light sensitive and are stored under argon in the dark.

Since the complexes [MI₂(CO)₃(NCMe)₂] can be synthesised in high yield (>90% based on M(CO)₆) by the reaction sequence shown in eqn. (1) [7] and the reaction of these compounds with nitrogen donors also gives very good yields (see 'Experimental'), this has proved to be an excellent method of synthesising these complexes.



It is interesting to note that Stiddard [4] reported that reaction of I₂ with [Mo(CO)₄(bipy)] in CHCl₃ gave the iodide bridged dimer [Mo(μ -I)I(CO)₃(bipy)]₂ with the 2,2'-bipyridyl ligand bonded as a monodentate ligand to the molybdenum. The infrared spectrum of this complex (CHCl₃) showed bands [4] at $\nu(\text{CO})$ cm⁻¹ = 2040, 2018, 1976, 1935, and 1888, which is different from our product [MoI₂(CO)₃(bipy)] from reaction of [MoI₂(CO)₃(NCMe)₂] and 2,2'-bipyridyl in CH₂Cl₂ showing carbonyl stretching bands (CHCl₃) at $\nu(\text{CO})$ cm⁻¹ = 2035(s), 1960(s) and 1912(s) typical of mononuclear seven-coordinate complexes of molybdenum(II) and tungsten(II).

Acknowledgement

S.G.F. thanks the S.E.R.C. for support.

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- 3 A. D. Westland and N. Muriithi, *Inorg. Chem.*, **12**, 2356 (1973).
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- 6 R. Colton, *Coord. Chem. Rev.*, **6**, 269 (1971).
- 7 P. K. Baker, S. G. Fraser and E. M. Keys, *J. Organomet. Chem.*, in press.

Within your plastic wallet, you have two additional resources that you can read in your free time to help you feel more prepared for university study.

- 1) Overton et al., *Study and communication skills for the chemical sciences*, Oxford University Press, Oxford, 2011, ch. 8, pp.107-126.
- 2) University of Reading, Department of Chemistry, *Keeping a Lab Notebook and Writing A Lab Report: What you need to know*.

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accessreading@reading.ac.uk

Lab Report (in full)

Experimental

The aims of the experiment was to synthesise two metal acetylacetonate complexes, $[\text{VO}(\text{acac})_2]$ and $[\text{Mn}(\text{acac})_3]$, where UV-Visible was to be employed for both complexes in toluene and pyridine and IR spectroscopy was also employed to both respective complexes. The UV-Visible spectroscopy was to find if the complexes had possible d-d transitions and the IR spectroscopy was to confirm the correct structure was produced. The magnetic moments were to be used to find the number of unpaired electrons within the complex. The percentage yield for each respective complex was also to be determined along with a titration of the resulting synthesised complex, $[\text{VO}(\text{acac})_2]$ against potassium permanganate (KMnO_4) solution to calculate the percentage of Vanadium within the complex.

The experiment was completed to understand the preparation, properties and experimental techniques used for transition metal complexes, specifically in this case the acetylacetonate ligand (usually referred to as Hacac) and Vanadium/Manganese metal centres. Acetylacetonate is a bidentate ligand consisting of a di-ketone structure, where deprotonation results in the anion (acac) as shown in *Figure 1* where the negative charge is delocalised across the five central atoms (three carbons and the two oxygens), which can then donate four electrons to the metal centre forming two coordinate bonds. This is due to the structure undergoing tautomerisation, which favours the enol form due to internal hydrogen bonding.

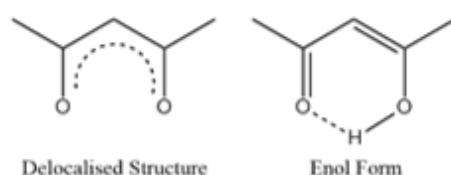


Figure 1: The delocalised structure and enol form (with internal hydrogen bonding) of the acetylacetonate ligand.

The experimental techniques employed were to determine the specific stretches (the wavenumbers) of the Infra-red spectrum and then the d-d transitions that occur due to excitation of electrons in the ground state to the excited state, found from the UV-Visible spectrum. The magnetic moments of the Vanadium and Manganese complex were stated as 1.73 and $4.95\mu_B$ respectively, which were then used to calculate the number of unpaired electrons, which relate closely with the d-d transitions. The UV-Visible spectra were to also help determine if the complex was to be high or low spin as the wavelength absorbed relates to the energy of the transition between the orbitals and therefore can be stated as the splitting parameter, Δ . The elemental analysis techniques were used to confirm the structures of both complexes.

Synthesis of $[\text{Mn}(\text{acac})_3]$

To prepare tris(2,4-pentanedionate)manganese(III) or $[\text{Mn}(\text{acac})_3]$, a solution of manganese(II) chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) (1.0163g), water (40mL) and sodium acetate trihydrate ($\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$) (2.6356g) was produced, where acetylacetone (4mL) was then added. The solution was stirred continuously using a magnetic stirrer for around 35 minutes, followed by potassium permanganate (KMnO_4) (0.2007g), where stirring was then continued. A solution of $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ (2.6040g) and water (10mL) was then prepared. This solution was then added slowly in small quantities to the manganese solution over 5 minutes, while still stirring. The overall solution was then heated to 60°C for approximately 15 minutes, where it was then cooled in an ice bath. The black crystals were then filtered off by suction and washed with water (300mL), and was kept under suction until the crystals were dry.

Titration of $[\text{VO}(\text{acac})_2]$

Potassium hydrogen sulphate (KHSO_4) (2.0147g) was added to $[\text{VO}(\text{acac})_2]$ (0.9969g) in a crucible, which was then heated using a Bunsen burner, supported by a clay triangle and tripod setup. The mixture was heated until it melted and the effervescence finished, however the mixture was ensured that it did not combust directly (set alight). Once the reaction had finished another five portions of KHSO_4 were added to the crucible and heated (individually, where the previous reaction was finished the next quantity was added), of mass around 1g (the masses 1.0135g, 1.0204g, 1.0089g, 1.0712g and 1.0778g were used).

The crucible was then allowed to cool, where the solid was then dissolved in H_2SO_4 (200mL, 2mol dm^{-3}). A microspatula-end-full of sodium sulphite (Na_2SO_3) was then added and the solution was then heated to boiling, where it was kept for approximately 2 minutes at this temperature, where the solution was then cooled to room temperature. This solution, may contain soot particulates and if necessary the solution could be filtered, where the solution was then retained. A sample of this solution (20mL) was pipetted and then titrated against potassium permanganate solution (0.02mol dm^{-3}). A second titration was also carried out, and thus from these results the vanadium content percentage of $[\text{VO}(\text{acac})_2]$ was then calculated.

Result and discussion

The preparation of $[\text{VO}(\text{acac})_2]$ and $[\text{Mn}(\text{acac})_3]$ and analysis resulted in the structure being determined along with the stretches (IR) and the splitting parameter from the ground to excited state (UV-Visible). The prepared complexes were blue crystals and black crystals respectively.

Molecular Structures and Magnetic Moments

The metal complexes have different geometries to each other due to the coordination number being five in the vanadium and six in the manganese complex. Thus it could be determined that $[\text{VO}(\text{acac})_2]$, would have a square pyramidal structure as shown in Figure 2 and $[\text{Mn}(\text{acac})_3]$ would have an octahedral structure. However once the number of d-orbital electrons was determined this structure may be found to be incorrect.

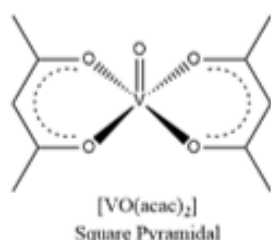


Figure 2: The square pyramidal structure of $[\text{VO}(\text{acac})_2]$.

The oxidation state of vanadium was found to be V^{4+} (due to the oxide ligand contributing a -2 charge and each of the acac ligands a -1 charge) and therefore has d^1 electrons (due to being a group 5 transition metal). Once, on the other hand, the oxidation state for manganese was determined to be Mn^{3+} (due to the three anionic acac ligands), it was found that there would be d^4 electrons present in the valence orbital.

The magnetic moments support this calculation of d-orbital electrons, as shown below using the Spin-Only Formula (Equation 1). The magnetic moment depends on the number of unpaired electrons.

$$\text{Equation 1: } \mu = \sqrt{n(n+2)}$$

Where μ = Magnetic Moment (μ_B or Bohr Magnetons)
 n = Number of unpaired electrons

Rearranging this equation gives $n = -1 + \sqrt{1 + \mu^2}$

$$\begin{aligned} [\text{VO}(\text{acac})_2] &= 1.73\mu_B \\ \sqrt{1(1+2)} &= 1.73\mu_B \\ -1 + \sqrt{1+1.73^2} &= 1 \text{ unpaired electron} \end{aligned}$$

Thus in the vanadium complex there is one unpaired electron, evidence for the previous calculation that there is only d^1 electrons present. Thus the splitting diagram for a square pyramidal structure with one d electron present is shown in Figure 3.

Square Pyramidal

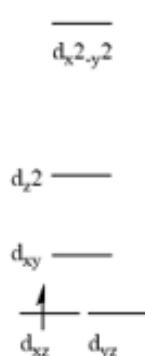
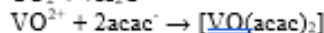
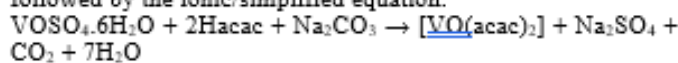


Figure 3: The splitting diagram for a square pyramidal structure such as $[\text{VO}(\text{acac})_2]$.

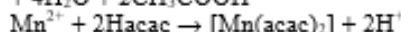
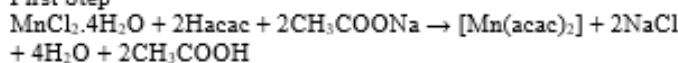
The Reactions for the Preparation of each of the Complexes

To prepare $[\text{VO}(\text{acac})_2]$ from $\text{VOSO}_4 \cdot 6\text{H}_2\text{O}$. Note: Hacac is used for acetylacetone and acac is its respective anion (due to deprotonation of Hacac). The overall equation is shown first followed by the ionic/simplified equation.

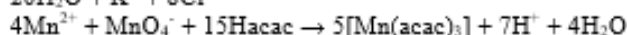
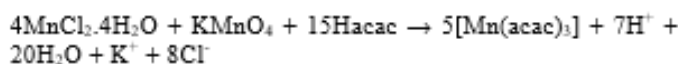
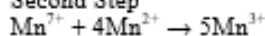


To prepare $[\text{Mn}(\text{acac})_3]$ from $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$. The overall production of the final complex is produced via two steps, where the first step a substitution occurs and the second step oxidises the Mn^{2+} to Mn^{3+} .

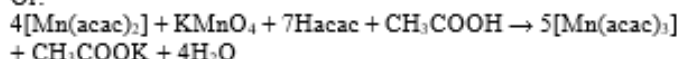
First Step



Second Step



Or:



The titration consisted of a solution consisting of sulfuric acid and the vanadium complex against potassium permanganate solution.



Percentage Yield

Thus using these equations the percentage yields of both complexes could be calculated.

$[\text{VO}(\text{acac})_2]$

The starting material $\text{VOSO}_4 \cdot 6\text{H}_2\text{O}$, had a mass of 5.0358g, where the molecular mass is 271.092g mol^{-1} .

$$5.0358\text{g} \div 271.092\text{g mol}^{-1} = 0.01858\text{mol } \text{VOSO}_4 \cdot 6\text{H}_2\text{O}$$

The assumption is a 1:1 ratio of reactant to product and thus there should be the same number of moles $[\text{VO}(\text{acac})_2]$, as $\text{VOSO}_4 \cdot 6\text{H}_2\text{O}$, where the molecular mass of the product is 265.159g mol^{-1} .

Hence $0.01858\text{mol } [\text{VO}(\text{acac})_2]$

$$0.01858\text{mol} \times 265.159\text{g mol}^{-1} = 4.92559\text{g}$$

$$(4.0851 \div 4.92559) \times 100\% = 82.94\%$$

$[\text{Mn}(\text{acac})_3]$

The starting material $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, had a mass of 1.0163g, where the molecular mass is 197.904g mol^{-1} .

$$1.0163\text{g} \div 197.904\text{g mol}^{-1} = 5.1353 \times 10^{-3}\text{mol } \text{MnCl}_2 \cdot 4\text{H}_2\text{O}$$

The assumption (using the reaction equation above) is a 4:5 ratio of reactant to product, where the molecular mass of the product is 352.265g mol^{-1} .

$$5.1353 \times 10^{-3}\text{mol} \times 1.25 = 6.4191 \times 10^{-3}\text{mol } [\text{Mn}(\text{acac})_3]$$

$$6.4191 \times 10^{-3}\text{mol} \times 352.265\text{g mol}^{-1} = 2.26124\text{g}$$

$$(0.1935 \div 2.26124) \times 100\% = 8.56\%$$

Abstract

The aims of the experiment were to synthesise $[\text{VO}(\text{acac})_2]$ (square pyramidal) and $[\text{Mn}(\text{acac})_3]$ (distorted octahedral), measure them spectroscopically using IR and UV-Visible, interpret the magnetic moments and determine the percentage of vanadium in its respective complex. It was found that the percentage yields for the acetylacetonone vanadium and manganese complexes were 82.94% and 8.56% respectively. The IR spectra confirmed these structures were produced due to specific peaks such as V=O stretch 997.12 and Mn-O 575.23cm^{-1} . The UV-Visible spectra confirmed d-d transitions were present due to the respective one (V) and four (Mn) valence d electrons, and $[\text{VO}(\text{acac})_2]$ in the pyridine solvent showed there was a charge transfer. Each of the λ_{max} obtained corresponded to the colour of the solution transmitted. The magnetic moments (1.73 and $4.95\mu\text{B}$ respectively) confirmed the number of valence electrons. A titration of the vanadium complex against potassium permanganate solution resulted in an average of 16.98% of vanadium in its complex.

Conclusion

Preparation of the complexes $[\text{VO}(\text{acac})_2]$ and $[\text{Mn}(\text{acac})_3]$ and conducting a series of spectroscopic analysis techniques resulted in evidence of the correct respective structures being produced, with percentage yields of 82.94% and 8.56% respectively. The IR spectra both provided evidence by significant peaks such as the V=O stretch at 997.12cm^{-1} and the other respective peaks provided that the acetylacetonone ligand was present.

The experiment also showed that $[\text{Mn}(\text{acac})_3]$ was a High Spin complex, providing that the splitting parameter was relatively small and that it was paramagnetic and that $[\text{VO}(\text{acac})_2]$ was also paramagnetic where the complexes had 4 and 1 valence d electrons respectively. The UV-Visible spectra showed that there were d-d transitions in all four complexes and that the maximum wavelengths absorbed corresponded to the colour of the solution, but $[\text{VO}(\text{acac})_2]$ also undertook charge transfer when in pyridine, resulting in a deeper colour.