

Supporting information for “Hands-on Inquiry-Based Qualitative Identification of Metals in Coins Utilizing Atmospheric Pressure Chemical Ionization Mass Spectrometry”

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A202: Metal Chelate Complexes – Synthesis and Analysis

Length of Practical: 12 Hours over 2 Days

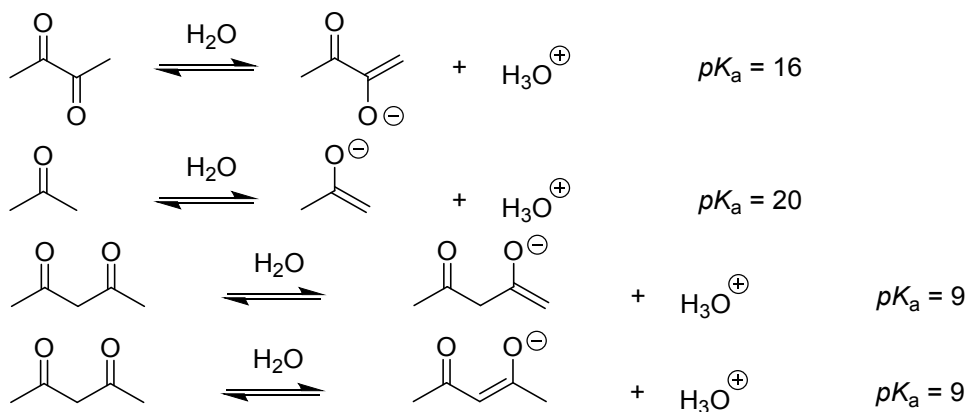
Objectives

- To investigate two different methods for the synthesis of a series of transition metal complexes.
- To practice using balloons of nitrogen gas for the execution of an anhydrous reaction.
- To employ mass spectrometry in the analysis of transition metal complexes.
- To design and carry out an experiment to determine the metal composition of a coin.

Pre-Lab Assessment

Complete a COSHH assessment for all of the chemicals (including products) associated with this practical. You will need to bring this with you and have it checked by a demonstrator before starting in the lab. In addition, having read through the lab manual, answer the following questions:

Q1. Which of the following is the correct representation of the basicity of the acetylacetonate anion, acac:



Q2. Iron has three major isotopes: 54, 56 and 57. Carbon has two major isotopes: 12 and 13. Using ChemDraw to predict m/z values (View > Show Analysis Window), predict which values you would expect to see for the following ions in a mass spectrum, together with their relative abundances:

- a) $[\text{Fe}(\text{acetylacetonate})_2]^+$
- b) $[\text{Fe}(\text{acetylacetonate})_3 + \text{H}^+]$

Q3. Why is a salt like $[\text{Bu}_4\text{N}][\text{PF}_6]$ needed for the electrolysis?

- a) Acetylacetone is a poor conductor and does not enable transport of electrons or ions
- b) Salts suppress unwanted side-reactions
- c) An organic cation (Bu_4N^+) helps dissolve the salt, due to favourable organic solvent-solute interactions.
- d) The hexafluorophosphate anion (PF_6^-) is large and helps to solubilise the metal.
- e) The hexafluorophosphate anion (PF_6^-) is stable to electrolysis

Q4. Which electrode do you expect to be oxidised to form the complex?

- a) Anode
- b) Cathode
- c) Neither

Q5. Why is a large potential difference ($>32\text{ V}$) used for the electrochemical synthesis of transition metal acetylacetonates?

- a) To increase the rate of the reaction
- b) To increase the yield of the reaction
- c) To heat the reaction up
- d) To reduce the risk of ignition of the flammable organic solvent

Q6. Compare and contrast salt metathesis and electrosynthesis in terms of their “green” credentials.

Introduction

Acetylacetone ($\text{CH}_3\text{COCH}_2\text{COCH}_3$), or acacH , is a weak carbon-acid which, when it is deprotonated, can form complexes with metal cations. These complexes are of the form $\text{M}(\text{acac})_3$, where the metal is in an oxidation state of +3. Other metal oxidation states give different stoichiometries. In the conventional synthesis of metal acac complexes, treating acetylacetone with a weak base such as ammonia, sodium carbonate, or sodium acetate, removes a proton from between the two carbonyl groups, generating a delocalised anion which can then act as a bidentate ligand for a metal cation (Figure 1).

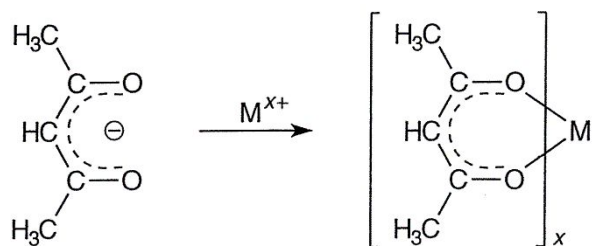


Figure S1: An illustration of how a delocalised anion may act as a bidentate ligand.

If there are three acac ligands around a metal centre, such as Co^{3+} , the complex will have a structure similar to that shown in Figure 2. For a doubly charged ion, such as Cu^{2+} , only two ligands will coordinate and various geometries are possible, including tetrahedral and square planar. However, if the binding of two acac ligands leaves the ion coordinatively unsaturated, solvent molecules may also bind and raise the coordination number; this solvent coordination occurs in $\text{Zn}(\text{acac})_2(\text{H}_2\text{O})_2$, for example. It should be noted that, in the solid state, molecular packing may affect the detailed coordination geometries of the metal centres, resulting in the possibility of crystal polymorphs.

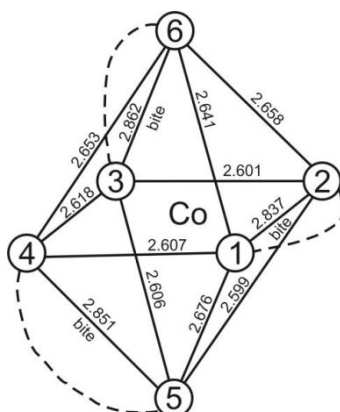


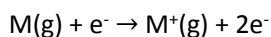
Figure S2: A representation of the structure of $\text{Co}(\text{acac})_3$. Bond distances are shown in Å.

Metal-acac complexes can be produced using conventional synthesis methods, but it is possible to synthesise the complexes electrochemically. In this method, electrodes of the metal are dipped into a mixture of acetylacetone dissolved in acetone, together with a small amount of supporting electrolyte (tetra-*n*-butylammonium hexafluorophosphate). Passing an electric current through this mixture results in the oxidation of the metal and the formation of the complex.

Electron Impact & Atmospheric Pressure Chemical Ionisation Mass Spectrometry

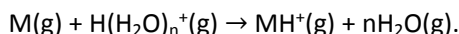
Mass spectrometry is a technique in which ions derived from compounds are subjected to separation and their mass:charge (m/z) ratio is measured. In this practical, you will use atmospheric pressure chemical ionisation (APCI) to form ions.

In EI-MS, molecular species in the gas phase, $\text{M}(\text{g})$, are bombarded with high energy electrons. Electron-molecule collisions result in the formation of positively charged ions, the majority of which carry a 1+ charge:



Subsequent fragmentation of the molecular ion often occurs, giving rise to daughter ions of lower m/z values.

In APCI-MS, an electric field first ionises nitrogen gas molecules to form $N_4^+(g)$ ions. These then react with atmospheric water vapour to form ions such as $H(H_2O)_n^+(g)$, where n is a small integer. These ions, which are essentially water molecules clustered around a proton, are able to protonate the molecule of interest, which then can then be analysed *via* the spectrometer:



This ionisation technique sometimes results in heavier ions where solvent molecules can coordinate to the $MH^+(g)$ ions to form more complex species such as $MH(solvent)_x^+(g)$.

Procedure

Day 1

You should work in pairs during this practical. During the first day each pair should choose one compound from **Group A** and one compound from **Group B** to synthesise *via* salt metathesis. In addition, each pair should choose one metal from Fe, Cu, or Zn to generate the corresponding metal acetylacetonate complex using electrochemical synthesis. The whole lab cohort should collaborate on these syntheses so at least one sample of each compound is made by both conventional and electrochemical synthesis

The transition metal acetylacetonate complexes to be synthesised by salt metathesis are:

Group A

$V(acac)_3$
 $Cr(acac)_3$
 $Mn(acac)_3$

Group B

$Fe(acac)_3$
 $Cu(acac)_2$
 $Zn(acac)_2$

The demonstrator will assign your group one complex from **Group A** and one complex from **Group B**. You will then gather all data together to draw up a table linking the $M(acac)_x$ complex to its characteristic mass spectrum. Detailed procedures for these syntheses are provided below.

You should read through Parts I and II, below, and plan how you will perform these two experiments (three syntheses) concurrently in a manner that will allow you to complete everything in the first day.

Part I: Conventional Syntheses of Transition Metal Complexes

Group A

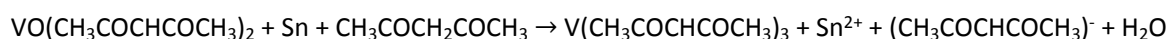
Synthesis of $V(acac)_3$

In order to avoid oxidation of V(III), the preparation should be performed under nitrogen in a fume hood. V(III) is formed by the reduction of V(IV) using metallic tin.

Place bis(acetylacetonato)oxovanadium(IV), (1.33 g, 5 mmol) in a two-necked, round-bottomed flask (100 mL) together with acetylacetone (10 mL). Attach a reflux condenser and purge the flask with nitrogen by attaching a nitrogen balloon to the side arm *via* a suba-seal. Allow the nitrogen to pass from the balloon, into the flask, up the condenser, and out, *via* an additional needle and suba-seal. Once the first balloon has been emptied of nitrogen, attach a full balloon to the needle at the tip of the condenser and replace the suba-seal on the side arm by a glass stopper.

Add tin powder (0.60 g, 5 mmol) *via* the side arm of the flask and heat under reflux for 3 hours, maintaining the atmosphere of nitrogen gas. If the balloon empties, replace it with a full one. After this time, allow any excess tin powder to settle and decant the solution into a beaker (50 mL). Allow the solution to cool to room temperature.

Collect the brown crystals of the product by vacuum filtration using a Büchner funnel and filter paper. Record the yield and calculate the percentage yield, using the following equation (you will need to balance the equation first!):



Record the yield of your product.

Synthesis of Cr(acac)₃

Dissolve 1.40 g (0.0053 mol) of chromium(III) chloride hexahydrate in 50 cm³ of deionised water in a 100 cm³ round bottomed flask with a stirrer bar. Add 10.00 g of urea in three or four portions to the deep green solution, shaking well after each addition. Add 3 cm³ of acetylacetone using a Pasteur pipette and swirl the resulting mixture. Fit the flask with a condenser and heat the mixture to 80-90 °C on a hotplate for 1.5 hours.

The solution is initially almost black in appearance but as complexation proceeds deep maroon plate-like crystals should form. Remove the flask from the hotplate and allow the mixture to cool in air for 15 minutes before cooling in an ice bath for a further 20 minutes.

Collect the product by vacuum filtration using a Büchner funnel and filter paper and dry the sample with further suction. Record the yield and calculate the percentage yield using the following equation (you will need to balance it first):



Recrystallise a portion of your product by dissolving 0.4 g in about 70 cm³ of boiling cyclohexane in a fume hood, stirring with a glass rod to aid dissolution. After removing any remaining solid by gravity hot filtration, allow the filtrate to cool, collect the red-wine coloured needles by vacuum filtration and allow to dry under suction.

Record the yield of your product.

Synthesis of Mn(acac)₃

In this synthesis trivalent manganese is formed by the oxidation of Mn(II) with Mn(VII).

Dissolve 2.60 g (13.1 mmol) of MnCl₂·4H₂O and 6.80 g of sodium acetate trihydrate in 100 mL of deionised water in a round bottomed flask (250 mL) containing a stirrer bar. Prepare a solution of

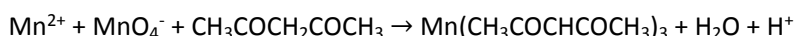
0.52 g (3.28 mmol) of KMnO_4 in 25 mL of deionised water and ensure that the solid is completely dissolved. Add 10 mL of acetylacetone to the MnCl_2 solution and swirl the mixture before adding the solution of KMnO_4 portion-wise with stirring. Use a dropping pipette for the addition, which should take around 10-15 minutes.

Stir for a further 10 minutes and then add, in a similar manner, a further solution of 6.3 g of sodium acetate trihydrate in 25 mL of deionised water.

Fit the flask with a condenser and, while still stirring, heat the resulting dark mixture on a hotplate to 60-70 °C for 15 minutes and then allow to cool to room temperature in air.

Collect the almost black product by vacuum filtration using a sinter funnel, wash with 60 mL of cold, deionised water and allow the sample to suck dry for 15 minutes. Dry the product further in a vacuum desiccator overnight.

Weigh the dried product and calculate the percentage yield, according to the following equation (you will need to balance this equation first!):



Recrystallise a portion of your product by adding about 0.2 g of the crude material in a 125 mL conical flask, add 12 mL of cyclohexane and heat to boiling on a hotplate, set at 90 °C, for 2 minutes, using a small glass funnel in the neck of the flask to control evaporation. Remove any undissolved solid *via* hot filtration into a clean conical flask (125 mL) and then add 40 mL of 40-60 petroleum ether. Leave to cool to room temperature in air and then transfer to an ice bath for 20 minutes. Collect the product by vacuum filtration using a sinter funnel, wash with 10 mL of cold petroleum ether, and allow the sample to suck dry for 15 minutes. Record the yield.

Record the yield of your product.

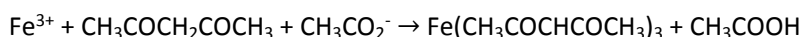
Group B

Synthesis of $\text{Fe}(\text{acac})_3$

Dissolve finely ground $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (12.2 mmol) in deionised water (25 mL). Over a period of 10-15 minutes (using a glass pipette), add a solution of acetylacetone (4 mL) in methanol (10 mL). Stir throughout the addition using a large magnetic stirring bar.

To the resultant blood-red mixture, add a solution of sodium acetate trihydrate (5.0 g) in deionised water (15 mL), over a period of 5 minutes, maintaining stirring throughout. Heat the mixture rapidly to about 80 °C on a hotplate. Maintain the temperature with rapid stirring for 15 minutes. **Continuously monitor the reaction and do not allow the mixture to boil.** Allow the reaction to cool to room temperature in air and then transfer it to an ice bath.

Collect the product by vacuum filtration using a sintered funnel, wash with cold deionised water (100 mL), and allow the sample to suck dry for 15 minutes. Transfer the product to a pre-weighed sample tube and dry in a vacuum desiccator for 15 minutes. Determine the crude percentage yield using the following equation (you will need to balance it first):



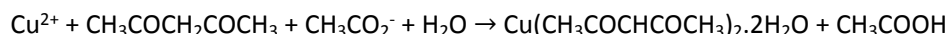
Recrystallise about 0.2 g of the dried product in a 10 or 25 mL conical flask, add 3 mL of deionised water. Gently warm the flask on a hotplate at 50 °C adding methanol dropwise (using a glass pipette) until the crude product just dissolves – about 3 mL of methanol will be required. Cool in an ice bath for 30 minutes. Collect the product by vacuum filtration using a sintered funnel, and suck dry for 15 minutes. Transfer to a pre-weighed sample tube and dry in a vacuum desiccator for 15 minutes.

Record the yield of your product.

Synthesis of $\text{Cu}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$

Dissolve copper(II) chloride dihydrate (23.5 mmol) in deionised water (25 mL) in a 250 mL conical flask. Add a solution of acetylacetone (5 mL) in methanol (10 mL), with stirring, over a period of 20 minutes using a glass dropping pipette. In a similar manner, transfer a solution of sodium acetate trihydrate (6.00 g) in deionised water (15 mL) to the stirred mixture over a period of 5 minutes and then heat at 80 °C on a hotplate for 15 minutes.

Leave the mixture to cool to room temperature in air before transferring it to an ice bath. Collect the product by vacuum filtration using a Büchner funnel and filter paper, wash with 100 mL of deionised water, and dry under suction for 15 minutes. Transfer the product to a pre-weighed sample tube and dry in a vacuum desiccator for 15 minutes. Determine the percentage yield, assuming two waters of crystallisation and using the equation below (you will need to balance it first):



To approximately 0.2 g of the dried crude product contained in a 125 mL conical flask, add methanol (25 mL) and a few anti-bumping granules. Reflux the mixture for 5 min, using standard reflux apparatus.

Using a clean 125 mL conical flask containing hot methanol (5 mL), a fluted filter paper and funnel, perform a hot filtration to separate the solution from any solid residue. Leave the azure blue solution to cool naturally to room temperature. Collect the product by vacuum filtration using a Büchner funnel and filter paper, washing with ice-cold methanol (10 mL), and allow the product to suck dry for 15 minutes. Transfer to a pre-weighed sample tube.

Record the yield of your product.

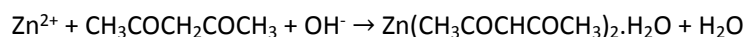
In-lab question: Why is bumping during reflux hazardous? How can you reduce the risk?

Synthesis of $\text{Zn}(\text{acac})_2 \cdot \text{H}_2\text{O}$

To a solution of acetylacetone (25.0 mmol) and sodium hydroxide (25.0 mmol) in water (15 mL), slowly add a solution of 3.60 g of zinc sulfate heptahydrate (12.5 mmol) in water (15 mL), with stirring. Allow the suspension to stand for 1 hour, collect the product by vacuum filtration using a Büchner funnel and filter paper, wash with deionised water (10 mL), and allow the sample to suck dry for 15 minutes.

Dissolve the crude product in a mixture of hot ethyl acetate (25 mL) : acetylacetone (1.5 mL). Remove any solid decomposition products by hot filtering the solution into a clean flask. Cool the resultant solution to obtain the hydrated $\text{Zn}(\text{acac})_2$ as needles.

Collect the product by vacuum filtration using a Büchner funnel and filter paper and allow the sample to suck dry for 10 minutes. Transfer the product to a pre-weighed sample tube and dry in a vacuum desiccator for 15 minutes. Determine the percentage yield, assuming one water of crystallisation and using the equation below (you will need to balance it first):



Record the yield of your product.

Part II: Electrochemical Syntheses of Transition Metal Complexes

Note: This part of the experiment involves the use of **hazardous voltages**. Pay particular attention to **all of the instructions given and never touch any apparatus that is connected to a live electrical supply. If in doubt, ask a demonstrator.**

Add acetylacetone (50 mL) and acetone (15 mL) to a clamped, tall 250 mL beaker containing a stirrer bar. Add tetra-*n*-butylammonium hexafluorophosphate (0.05 g) to the solution, with stirring.

Take two electrodes made of the metal whose complex you wish to make and rub them with sandpaper to remove any surface impurities. Then immerse these electrodes sequentially in 2 M HCl, 2 M NaOH and then rinse them with deionised water, allowing 1 minute for each rinsing step. Finally, rinse them with acetone and allow them to dry. Once cleaned, do not touch the surface of the electrodes and handle them with gloves.

Available metals: Zinc (sheet), Copper (foil), Iron (screws)

Attach the electrodes to the crocodile. Submerge the electrodes in the electrolyte solution but make sure that the crocodile clips are clear of the electrolyte. The plastic divider is designed to keep the electrodes apart. An illustration of the set-up is provided in Figure 3.

Note: The electrodes must not touch during this experiment as this may cause a fire. Make sure that you are confident that the electrodes are secure and separate. **Check with a demonstrator.**

Attach the leads to a constant voltage power pack, set to deliver 0 V. Switch on the power pack and, when you are convinced that the apparatus is stable, increase the voltage slowly to 150 V or 32 V (see label on top of power pack).

Note: Under no circumstances should you touch any part of the apparatus when the power pack is switched on. In case of emergency, switch the power pack off at the mains socket before doing anything else.

After several minutes, you should see a colour forming in the solution (if using a transition metal). Leave the experiment running for 90 minutes. After this time, turn the voltage to 0 V and then switch off the power supply, and unplug it. **Only then**, dismantle your apparatus.

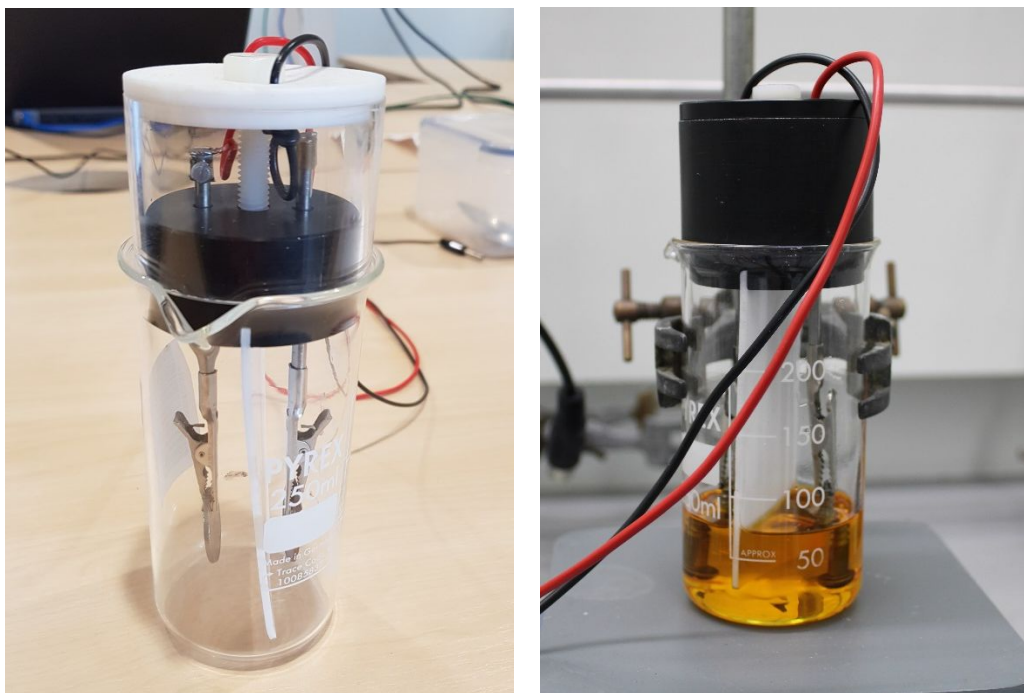


Figure S3: General apparatus set-up for electrochemical syntheses.

If the metal(acac) complex has precipitated, collect it by filtration using a Büchner funnel and filter paper and wash twice with acetone – this will remove the tetrabutylammonium hexafluorophosphate. Allow the solid to suck dry.

If the complex has not formed a precipitate, decant the solution into a round-bottomed flask and remove the solvent on a rotary evaporator. After the acetone has been removed (water bath at 40 °C), you will need to reduce the pressure to 50 mmHg and increase the temperature of the water bath to 70 °C, as the boiling point of acetylacetone is 140 °C at atmospheric pressure. (You can use the nomograph in your lab manual to estimate boiling temperatures at reduced pressure, or use the interactive nomograph to be found at:

<https://www.sigmaaldrich.com/chemistry/solvents/learning-center/nomograph.html>

Cool the resultant oil until it crystallises. Resuspend the solids in a small volume of THF (approx. 1 mL) to remove the tetrabutylammonium hexafluorophosphate and then collect the complex by filtration using a small Hirsch funnel and filter paper. Wash the solid with a small volume (approx. 1 mL) of THF and allow to dry in air.

Record the mass recovery of your product.

Part III: Mass spectrometric analysis

Analysis by mass spectrometry requires very dilute samples (~ 1 mg/mL) for the acquisition of high-quality spectra. Prepare your solution by adding a spatula tip of $M(\text{acac})_x$ complex to approximately 2 mL of MeOH or acetone.

***In-lab question:** Why might a high concentration reduce the quality of the spectra obtained?*

A demonstrator will show you the proper use of the mass spectrometer and data acquisition. A spreadsheet of possible fragments masses will be generated which can be compared to the peaks observed in your mass spectra for successful characterisation of the metal complexes. You are provided with a spreadsheet of atomic masses and abundances of all naturally occurring isotopes of the elements. Use these data to determine the masses for the possible fragments of $M(\text{acac})_2$ and $M(\text{acac})_3$:

$[M(\text{acac})_2 + \text{H}]^+$	$[M(\text{acac})_2]^+$	$[M(\text{acac})_3 + \text{H}]^+$
$[M(\text{acac})_2 + \text{H} + \text{H}_2\text{O}]^+$	$[M(\text{acac})_2 + \text{H}_2\text{O}]^+$	$[M(\text{acac})_3 + \text{H} + \text{H}_2\text{O}]^+$
$[M(\text{acac})_2 + \text{H} + \text{MeOH}]^+$	$[M(\text{acac})_2 + \text{MeOH}]^+$	$[M(\text{acac})_3 + \text{H} + \text{MeOH}]^+$
$[M(\text{acac})_2 + \text{H} + \text{CH}_3\text{COCH}_3]^+$	$[M(\text{acac})_2 + \text{CH}_3\text{COCH}_3]^+$	$[M(\text{acac})_3 + \text{H} + \text{CH}_3\text{COCH}_3]^+$

For the $M(\text{acac})_x$ complexes you have identified by mass spectrometry, analysis of the relative isotopic ratio provides further insight into the identity of the fragment. The theoretical relative isotopic abundances can be calculated in ChemDraw. For the relevant metal acetylacetonate complex, draw the charged species in ChemDraw (Figure 4), obtain its isotopic composition (View → Show Analysis Window), and compare this to the observed composition.

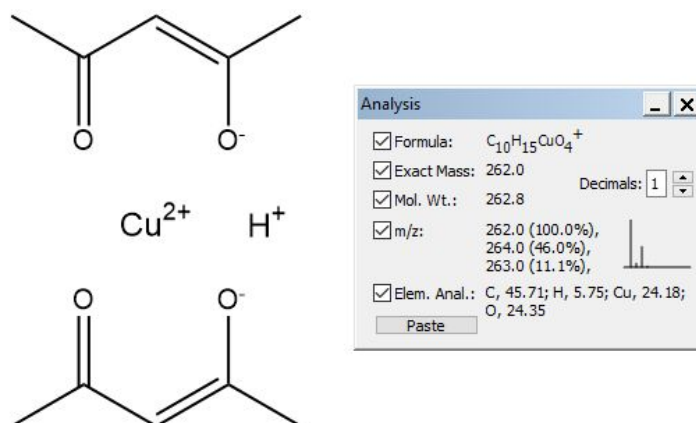


Figure S4. Example isotopic analysis of $\text{Cu}(\text{acac})_2$.

Once you have fully characterised your metal complexes by mass spectrometry, share your data with your lab group so a full picture of the $M(\text{acac})_x$ compounds can be built up.

Day 2

During the second day you will design an experiment which probes the metal composition of a coin. You will be provided with the same equipment and chemicals as on Day 1.

Part IV: What metals are coins made of?

Analysis of unknowns is an essential tool for scientists in all fields of research. Using the synthetic and analytical techniques you explored on Day 1, design an experiment to determine the possible metal components within a coin of your choosing. Factors you may want to consider are:

- Whether salt metathesis or electrochemical synthesis best suit this problem
 - If salt metathesis, what reagents will be necessary?
 - If electrochemical synthesis, how will the coins behave at the cathode/anode?
- If the coin is an alloy, how will you isolate the mixture of metals from the reaction?
- How will you analyse the pure/mixed compound(s) obtained?

Before beginning your research, consult a demonstrator to discuss your proposed solution. Record the coin you use for your analysis (country, year, denomination).

Post-Lab

Provide a complete report of your experimental work, including the following points:

- A brief method outlining the particular syntheses that you personally carried out.
- Why is Sn used for the synthesis of $V(acac)_3$? Why not Zn?
- The mass spectrometry data obtained for the compounds that you synthesised. Make sure to address the isotope distribution pattern, where relevant. You do not have to identify the species responsible for every peak observed.
- A calculated percentage yield for each of your products synthesised by salt metathesis, using the observed molecular ion peak as a guide for the exact compounds you have synthesised.
- An analysis of the metal content in the coins analysed. Do any observed isotopic distribution patterns support your conclusions?
- Using an online database, obtain the actual composition of the coin you used. Does your analysis agree with the database?