Supporting Information for “Hands-on Inquiry-Based Qualitative Identification of Metals in Coins Utilizing Atmospheric Pressure Chemical Ionization Mass Spectrometry”
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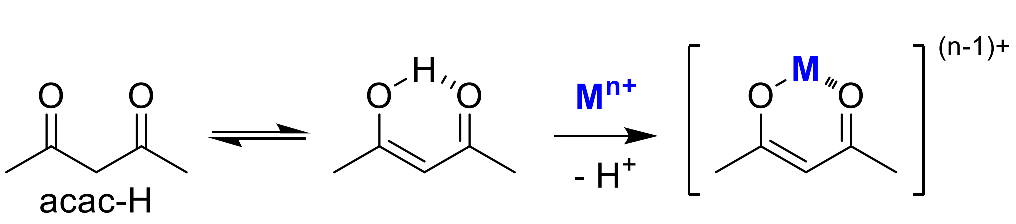
A117: Metal Chelate Complexes – Synthesis and Analysis

Introduction

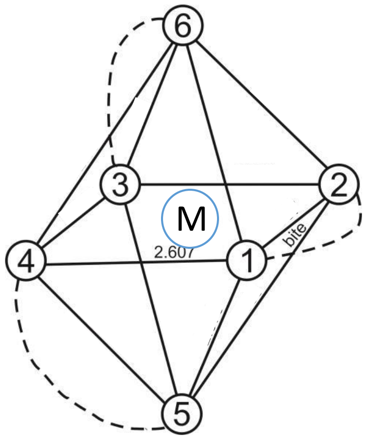
- Acetylacetonate (acac) complexes have varied uses:

e.g. catalysts for polymerisation; $Al(acac)_3$ is used as a molluscocide

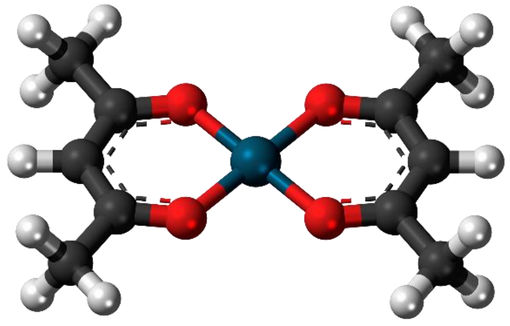
- Traditionally prepared by replacing one ligand with acetylacetonate:



$$MX_m + n \text{ acac}^- \rightarrow M(acac)_n + m\, X^-$$



$M(acac)_3$



$Cu(acac)_2$

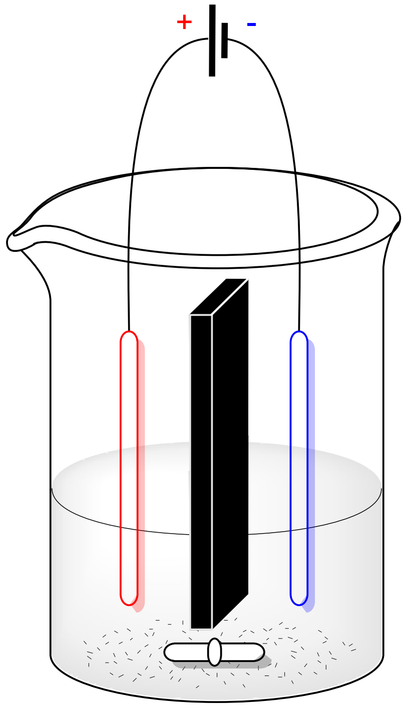
Introduction

- Alternatively, it is possible to prepare the complexes electrochemically:

(+) $M(s) \rightarrow M^{n+} + n\ e^-$

(-) n acac-H + $n\ e^- \rightarrow n$ acac$^-$ + $n/2\ H_2$

$M(s) + n$ acac-H $\rightarrow M(acac)_n + n/2\ H_2$



Undivided cell

Objectives

- To investigate two different methods for the synthesis of a series of acetylacetonate complexes, $M(acac)_n$:

  Salt metathesis and electrochemical synthesis
- To analyse the synthesised $M(acac)_n$ complexes by mass spectrometry
- To develop and investigate a method to identify metals present in coins

Day 1 – Conventional Synthesis (Salt Metathesis)

Each pair should prepare complexes in two categories:

- $Fe(acac)_3$
- $Cu(acac)_2 \cdot 2H_2O$
- $Zn(acac)_2 \cdot H_2O$

These can be prepared using MCl_n or $M(OAc)_n$

NaOAc or NaOH is used as the base to deprotonate acetylacetone → $acac^-$

Also prepare one of the following:

- $V(acac)_3$ **[requires exclusion of air using a balloon of N_2]**
- $Cr(acac)_3$
- $Mn(acac)_3$

Careful control of pH and/or adjustment of oxidation states required from most stable available metal salt

Considerations for Salt Metathesis

Transition metal salts often have variable oxidation states

- Can be sensitive to oxidation in air/solution
- Can be sensitive to pH in aqueous solution, e.g. formation of insoluble $M(OH)_n$

$V(acac)_3$: V^{4+} oxidation state more stable – reduced to V^{3+} using Sn

$Cr(acac)_3$: Cr^{3+} is sensitive to basic aqueous conditions

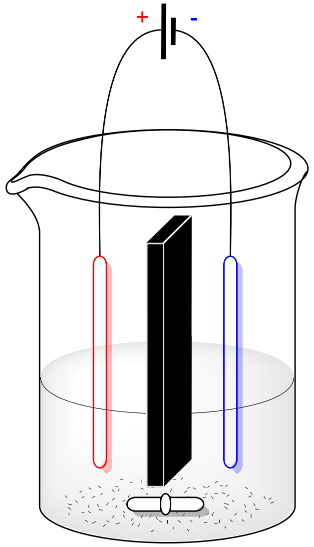
Urea is used to maintain weakly basic conditions: $CO(NH_2)_2$ hydrolysed slowly to NH_3 and CO_2

NH_3 is used as a weak base to deprotonate acetylacetone

$Mn(acac)_3$: Mn^{3+} salts often not available (aerobic stability)

Prepared by oxidation of $Mn(acac)_2$ by MnO_4^-

Electrochemical synthesis



- You will choose one metal from Fe, Cu, and Zn to prepare $M(acac)_n$ electrochemically:

$$M(s) + n\ \text{acac–H} \rightarrow M(\text{acac})_n + n/2\ H_2$$

- NB: Although two electrodes are both the same metal, **oxidation** occurs only at the **anode (+)**, and **H_2 evolution** occurs at the **cathode (–)**
- Acetylacetone is mildly acidic (pK_a ~9 in H_2O); however, not sufficiently conductive
- Need an inert electrolyte to make the system significantly more conductive: $[nBu_4N]\ [PF_6]$

Safety

<u>Chemical safety</u>

- MX_n compounds are corrosive/toxic
- Acetylacetone is flammable; methanol is flammable/toxic
- Keep electrolysis reactions in a fume-hood

<u>Use of high voltage power supply</u>

- Do ***not*** allow the two electrodes to touch when power supply is on (sparks and ignites highly flammable organic solvent)
- Do ***not*** touch electrodes when power supply is turned on

<u>Cleaning metal surfaces:</u>

- HCl(aq) and NaOH are mildly corrosive

Summary

Day 1:

1. Prepare two $M(acac)_n$ complexes using conventional synthesis
2. Prepare one of $Fe(acac)_3$, $Zn(acac)_2$, or $Cu(acac)_2$ electrochemically
3. Analyse $M(acac)_n$ by mass spectrometry

Day 2:

Plan and investigate how to identify metals present in coins

Complete the pro forma report for this practical and submit electronically to Canvas.

A117:
Metal Chelate Complexes – Synthesis and Analysis
Day 2

Mass Spectrometric Analysis

- You will acquire the mass spectra of the synthesised $M(acac)_n$ complexes
- Mass spectrometry is a sensitive technique –
  our instrument can identify individual isotopes of each element to 0.1 Da
- APCI method: Soft ionisation technique. Generally detect solvated adducts, with possibly some fragmentation. Detect charged species of the forms:
- $[M+H]^+$, $[M+H+H_2O]^+$, $[M+H+CH_3OH]^+$, $[M+H+CH_3COCH_3]^+$
  (and higher solvated adducts)

$M(acac)_n \rightarrow [M(acac)_{n-1}(acac\text{-}H)]^+$ *i.e. [complex + H]*$^+$

$M(acac)_n \rightarrow [M(acac)_{n-1}]^+ + [acac]^-$ *i.e. [complex – acac]*$^+$

Also possible: *Charged species* + H_2O; + MeOH; + acetone

Mass Spectrometric Analysis

- You are provided with a spreadsheet of atomic masses and abundances of all naturally-occurring isotopes of the elements, "M"
- Use these data to determine the expected mass for the likely candidates that could be identified by mass spectrometry:

$[M(acac)_2+H]^+$	$[M(acac)_2+H+H_2O]^+$	$[M(acac)_2+H+CH_3OH]^+$	$[M(acac)_2+H+CH_3COCH_3]^+$
$[M(acac)_2]^+$	$[M(acac)_2+H_2O]^+$	$[M(acac)_2+CH_3OH]^+$	$[M(acac)_2+CH_3COCH_3]^+$
$[M(acac)_3+H]^+$	$[M(acac)_3+H+H_2O]^+$	$[M(acac)_3+H+CH_3OH]^+$	$[M(acac)_3+H+CH_3COCH_3]^+$

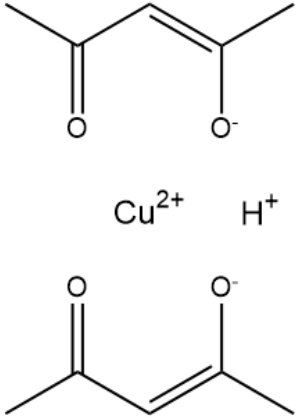
Sample preparation:

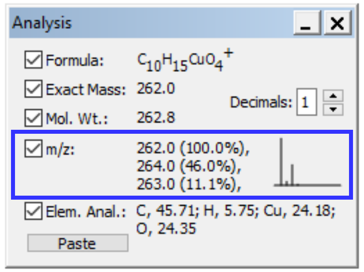
Prepare a very dilute solution of your $M(acac)_n$ in a vial in either MeOH or acetone – this will influence whether you may see +MeOH or +acetone adducts in the mass spectrum

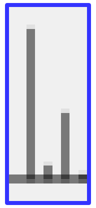
Mass Spectrometric Analysis

- For the synthesised $M(acac)_n$ you believe to have identified using the spreadsheet:
- Draw the structure for its charged species in ChemDraw
- Obtain its expected isotope composition

  (NB. ^{13}C accounts for ~1.1% abundance of all carbon, which is not accounted for by your spreadsheet)
- View $\rightarrow$ Show Analysis Window
  - e.g. $[Cu(acac)_2+H]^+$:







Major *m/z* species:

262.2

264.0

- Confirm the isotope pattern obtained is in agreement with the ChemDraw prediction