VNIVERSITAT DE VALÈNCIA
Facultat de Química
Departament de Química Inorgànica

Inorganic Chemistry Laboratory - II

Grau en Química

LQI-II PRACTICAL PROGRAMME

1. COMPARATIVE STUDY OF THE CHEMICAL BEHAVIOUR OF METAL IONS OF THE FIRST TRANSITION ROW.

2. STUDY OF THE CHEMICAL BEHAVIOUR OF VANADIUM. SYNTHESIS OF VANADIUM ACETYLACETONATE COMPLEX.

3. CHROME (II) ACETATE. SYNTHESIS AND REACTIVITY.

4. PREPARATION OF Cu (I) AND Cu (II) COMPOUNDS.

SPECTROCHEMICAL SERIES.

5. SYNTHESIS AND CHARACTERISATION OF OXALATE COMPLEXES $[Fe(C_2O_4)(H_2O)_2]$ AND $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$. A REACTIVITY STUDY.

6. OXYGEN UPTAKE BY A Co (II) COMPLEX.

7. SYNTHESIS AND PURIFICATION OF ACETYLFERROCENE, $[Fe(\eta5\text{-}C_5H_5)(\eta5\text{-}C_5H_4COCH_3)]$. SYNTHESIS OF FERROCENE.

8. PREPARATION AND RESOLUTION OF $[Co(en)_3]^{3+}$ ENANTIOMERS.

9. SYNTHESIS AND STUDY OF SOME PROPERTIES OF SEVERAL COBALT (III) COMPLEXES.

Inorganic Chemistry Laboratory Rules

1- Cleaning in the laboratory

Laboratory work requires scrupulous cleaning of both the material used and the laboratory table. The material will be cleaned before use and immediately after each operation. *At the end of each session, students must clean their workplace before leaving the laboratory.*

Cleaning an item will begin by eliminating solid waste (if any) using a glass rod. Do not throw solid products into the sink even if they are soluble in water. Deposit them in the waste container.

When there are traces of organic products on the item to be cleaned, dissolve them with acetone, pouring the solution into the waste bottle. In other cases, it may be necessary to use acids to eliminate waste. Before doing so consult the lecturer. Wash with water and detergent. Rinse with tap water and then with deionised water. If any material is not clean repeat the previous treatment.

The clean material is left to drain and if necessary it is dried with paper or on the stove.

Volumetric material will **never** dry on the stove. Once clean, it is homogenised with the solution to be measured.

Water is a scarce commodity. Avoid unnecessary use.

2 - Basic safety measures in the laboratory

PERSONAL RULES

1. During sessions in the laboratory students must wear **mandatory** safety goggles and a lab coat. **Contact lenses** can be highly dangerous. **Gloves** should be used when handling caustics.

2. Long hair must be gathered and tied.

3. Backpacks, coats, and bags must not be left in the laboratory – use the lockers.

4. It is strictly forbidden to smoke or consume food or drinks in the laboratory. No chemical products should be brought to the mouth for tasting, nor touched with hands.

5. Wash your hands and take off your lab coat before leaving the laboratory.

RULES FOR THE USE OF CHEMICALS

6. Avoid chemical contact with the skin. Use funnels and propipets to transfer liquids (not your mouth).

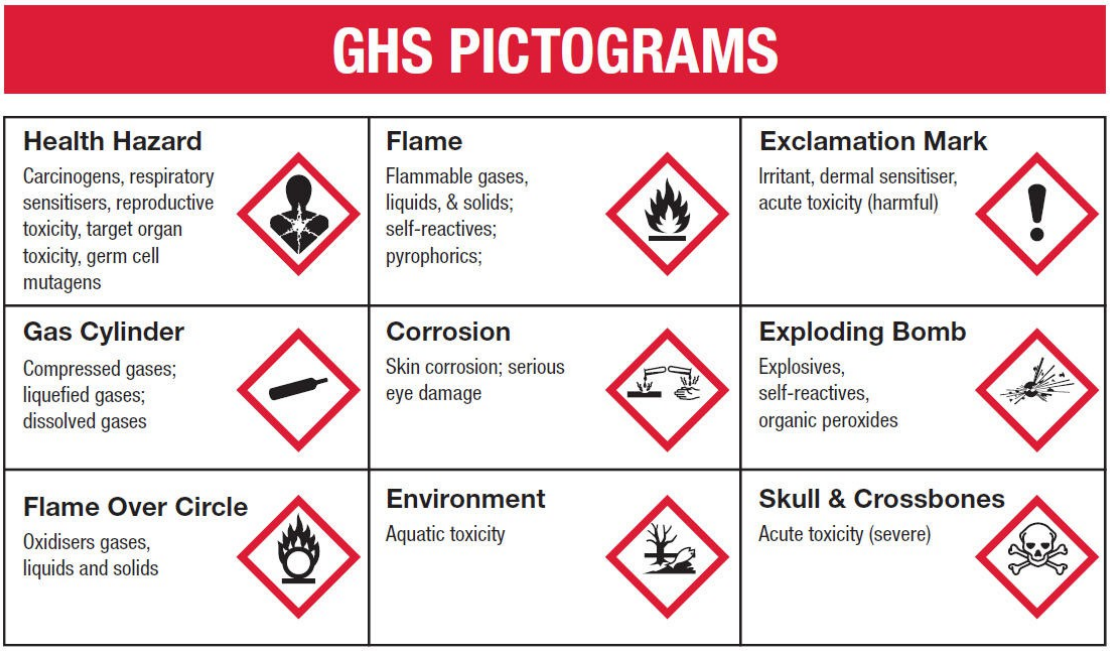
7. If an acid or other corrosive chemical is accidentally spilled, consult the lecturer.

8. To detect the smell of a substance, your face must not be placed directly over the container: use your open hand as a screen and let a small amount of vapour reach your nose. Jars must be closed immediately after use.

9. When preparing solutions, stir gently in a controlled manner to avoid splashing.

10. Acids require special care. Handle them with caution in the case. When diluting them, never pour water on acids: always add acid to water rather than water to acid.

11. Before using any product, look at the safety pictograms on the label and take appropriate preventive measures.



12. When a substance is heated in a test tube, the open end of the tube should not be directed at any nearby person to avoid accidents. Take extra precautions when lighting burners, and extinguish the flame when not in use.

13. It should be assumed that all chemicals are toxic, and that all organic solvents are flammable and should be kept away from flames.

RULES FOR THE USE OF INSTRUMENTS

14. When determining the mass of chemical products with scales, a suitable container must be used.

15. The place where any instrument is located must be kept perfectly clean and dry, especially those instruments with electrical contacts. Read the instructions for use of instruments.

16. Glass material should be checked for possible cracks, especially before use under vacuum or pressure.

17. When heating with a heating blanket, a wooden jack or block must be used underneath. Never turn on blankets or heating plates without a container for heating.

18. In reflux and distillation assemblies, the porous plate must be added cold, and the ground joints must be well adjusted. Never leave the experiment while any reaction, distillation, or measurement is being carried out.

RULES FOR WASTE

19. In the laboratory, there are properly labelled containers for the waste generated.

EMERGENCY RULES

20. If it is necessary to evacuate the laboratory, close the gas taps, and leave in an orderly manner following the instructions given by the lecturer. At the beginning of the practice session, locate the various items of emergency equipment in the laboratory: D - showers and eyewash; E - fire extinguishers; M - fire blankets; B - first aid kit; AB - spill absorber; AL- emergency alarm; S- emergency exit; and V- container for broken glass.

Students must read and agree to observe all laboratory safety rules to ensure their own safety, and that of fellow students, instructors, and staff. Students must fully cooperate to maintain a safe laboratory. Students will follow all written and oral instructions given by the instructor. Any violation of these rules may result in not being allowed to participate in the laboratory experiment, receiving a warning, and/or dismissal from the course.

(Sign on the sheet as instructed by the lecturer) .

PRACTICE 1

COMPARATIVE STUDY OF THE CHEMICAL BEHAVIOUR OF METAL IONS OF THE FIRST TRANSITION ROW

INTRODUCTION

We can strictly define transition elements as those with partially filled *d* orbitals. However, from a chemical point of view it is more appropriate to expand this definition and also consider those elements with partly filled *d* orbitals in their ground state or in any of their oxidation states. This definition justifies the inclusion of Cu, Ag, and Au as transition metals. By this definition, Zn, Cd, and Hg are excluded from transition metals, as they have a d^{10} configuration. However, being the end members of the series, they are often considered together with the transition elements.

Thus, of the 118 elements characterised so far, 68 are transition elements. It is evident that in such a large group of elements, one cannot expect a homogeneous chemical behaviour; however, all transition elements exhibit some general features in common: a) all are metals; b) nearly all are tough, ductile, and malleable, with high boiling and melting points, and are good conductors of heat and electricity, in other words, they possess the *typical properties of metals*; c) all form alloys with one another and with the metallic main group elements; d) many are sufficiently electropositive to react with mineral acids to form salts, although some are rather inert in this respect; e) with few exceptions, they exhibit a wide variety of oxidation states (variable valence).

Many form coloured compounds in one, if not in all, oxidation states. Because of partly filled *d* orbitals, some transition metal ions containing odd number of electrons form paramagnetic compounds.

Attending to the nature of their partially occupied energetic levels, transition elements can be divided in three main groups: i) transition elements or elements from *d*-block; ii) lanthanides; iii) actinides.

The elements from *d*-block are divided into three large periods: 1st, 2nd, and 3rd transition rows. The chemistry of these elements is of great importance, but also quite complex. The abundance of *d*-block elements in the Earth's crust varies considerably. The most abundant transition metal in the Earth's solid crust is iron, which is fourth among all the elements and second (to aluminium) among metals in crustal abundance (5% weight). Titanium and manganese are also quite abundant. Some of the heavier transition metals such as ruthenium (Ru), rhodium (Rh), iridium (Ir), palladium (Pd), osmium (Os) and platinum (Pt) are rather rare. Technetium is a synthetic element.

Iron is a metal of great technological importance, as well as all metals from the first transition row. Transition metals as elements, or some of their compounds, constitute a large number of catalysts for many industrial processes. In addition, transition elements (mainly iron, zinc, copper but also manganese, nickel, cobalt, and molybdenum) play important roles in our daily life and in keeping organisms alive.

OBJECTIVES

1. Comparative study of the behaviour of metal ions from the first transition row (Cr (III), Mn (II), Fe (II), Co (II), Ni (II), Cu (II) and Zn (II))) against general reagents such as NH_3 (aq.), NaOH (aq.), H_2O_2 (aq.), etc.

2. Verification of the complex formation in basic media of metallic ions from the first transition row.

3. Assessment of the different trends for the oxidation of metallic ions Cr (III), Mn (II), Fe (II), Co (II), Ni (II), Cu (II) and Zn (II); as well as the influence of pH, solubility, and complex formation reactions in the stabilisation of certain oxidation states.

PRELIMINARY QUESTIONS

1. Write down the electronic configurations of elements from the first transition series and the M^{2+} and M^{3+} ions of the first transition row.

2. Which oxidation states show the elements of the first transition row? Indicate in each case those that are most stable.

3. From the standard potential data E^0 ($M^{2+}_{aq.}/M$) and E^0 ($M^{3+}_{aq.}/M^{2+}_{aq.}$) for the elements of the first transition row, discuss the reactivity of the metals to mineral acids, as well as the relative stability of oxidation states II/III in an acidic medium.

EXPERIMENTAL PROCEDURE

Reagents and materials

Materials	Reagents
Rack with 14 test tubes	0.1M solutions of salts of:
Watch glass	Mn(II), Ni(II), Co(II), Cu(II) and Zn(II)
Chlorine generator (Kipp's apparatus)	Iron(II) sulphate (solid)
10 mL volumetric cylinder	Chromium (III) sulphate (solid)
	Potassium hydroxide (solid)
	NaOH 3M solution free of carbonates
	3M ammonia
	Ammonium chloride (solid)
	Concentrated HCl
	6% hydrogen peroxide
	$KMnO_4$ (solid)

Safety remarks

- Basic concentrated solutions are caustic, so use gloves and safety goggles to avoid spills.
- Chlorine is a toxic gas. Thus, assays with this gas must be done under supervision of the lecturer in a fume hood.

Reactions in solution. Assays.

Since Fe(II) solutions are unstable, prepare for the entire group, 100 mL of a solution 0.1M from the sulphate, at the time of the practice. Add 4 drops of diluted H_2SO_4 to that solution.

Assay #1

Add 1 mL (20 drops) of each one of the metal ion solutions Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) in a properly labelled test tube. The tube with the Mn(II) solution is heated to the boiling point for 30 seconds. Add then to each of the test tubes 1 mL of a solution 3M NaOH free of carbonates drop by drop. After a quick mixing, write down the appearance: a) immediately; b) after few minutes; c) after 2

hours. Afterwards, add to each tube 1 mL of H_2O_2 6% and carefully heat until boiling. Write down the changes produced before and after heating the solution.

Assay #2

Add 1 mL (20 drops) of each one of the metal ion solutions Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) in a test tube properly labelled. Then add 1 mL of 3M NH_3 and mix gently. Observe any change that occurs. Successively add to each tube 0.2 g of NH_4Cl, (shake every tube) and observe if a redissolution of the precipitate takes place.

Add 1 mL of H_2O_2 6 % and carefully heat until boiling.

Assay #3

Add 1 mL (20 drops) of each of the metal ion solutions Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) in a properly labelled test tube. Add 1g (approximately 10-12 beads) KOH in each one of the test tubes.

(Caution: very corrosive solution). Heat the solution while stirring and observe the changes produced.

(Attention: assays with Cl_2 will be done in the fume hood under supervision of the lecturer). Bubble Cl_2 in the solution of each of the tubes during several minutes. Write down the changes observed. Finally, dilute each solution with water to double their volumes.

(The lecturer will generate Cl_2 using a Kipp's apparatus).

Waste management: discard all the solutions of this practice in the waste disposal labelled for 'Transition Metals'.

ADDITIONAL QUESTIONS

1. Write down in a table all the changes observed – such as the presence of a precipitate, transparent solution, loss of precipitate, colour changes, or absence of colour. Use the columns for the reagents added to the process in each of the assays and the rows for the transition metals.

2. Interpret and justify the previous observations, as well as point out trends in oxidation and the formation of complexes in basic mediums.

3. The corresponding species for the oxidation state VI for Cr are formulated in acidic media as $Cr_2O_7^{2-}$ or CrO_4^{2-} in basic media. Can you explain this difference?

4. The most stable oxidation state for manganese is 2+, however, during the practical session there is a spontaneous oxidation of Mn(II) to Mn(III). In which conditions is this observed?

5. Why does $Cu(OH)_2$ not precipitate in assay #2?

ADDITIONAL BIBLIOGRAPHY

A. W. L. Dudeney; J. Chem. Ed., 1971, 48, 376-381.

B. A. Burke, D.A. Davenport, T. J. Smith, R. A. Walton; J. Chem. Ed., 1977, 54, 360-361.

PRACTICE 2

STUDY OF THE CHEMICAL BEHAVIOUR OF VANADIUM. SYNTHESIS OF VANADIUM ACETYLACETONATE COMPLEX

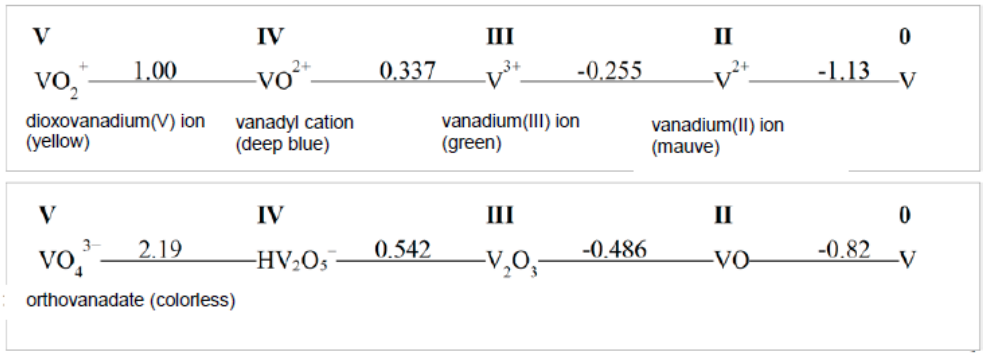
INTRODUCTION

A) Vanadium was originally discovered by Andrés Manuel del Río in a Mexican lead ore in 1801 by analysing the mineral vanadinite, and named it erythronium. Four years later, however, he was convinced by other scientists that erythronium was identical to chromium. In 1831, the Swedish chemist, Nils Gabriel Sefström, rediscovered the element in a new oxide he found while working with iron ores from a mine in Sweden. Sefström named it vanadium after Vanadis, the Scandinavian goddess of beauty. Both names (erythronium and vanadium) were attributed to the wide range of colours found in vanadium compounds.

Vanadium (V, Z = 23, [Ar] $3d^3 4s^2$) can be presented in a large number of different oxidation states (from -3 to +5). It is the transition element that presents most variety of colours and tones in its compounds. Except the oxidation state +5 (d^0), the other stable states (from +4 to +2) exhibit one, two, or three unpaired electrons, respectively, so that its compounds tend to be paramagnetic.

The most important compound is vanadium pentoxide (V_2O_5), a brick red solid, from which derive most of the compounds of this element. In addition, it is an effective catalyst for oxidation of SO_2 to SO_3 during the industrial process of obtaining sulfuric acid (H_2SO_4). Moreover, various vanadates are used as catalysts for the reductive desulphurisation of oil. The majority of vanadium produced is used in the manufacture of alloys such as vanadium-steel, which it is the most resistant alloy of iron known.

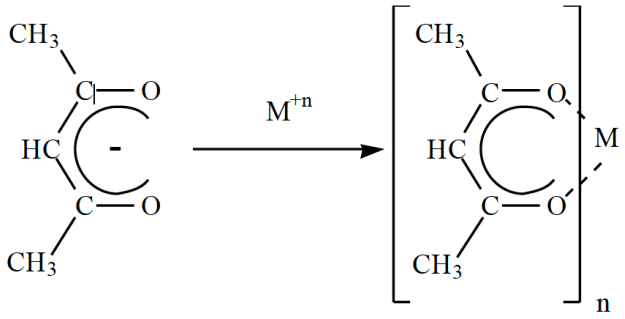
The Latimer diagrams of Vanadium in acidic and basic medium are respectively (see Annexes):



B) **Acetylacetone** (pentane-2,4-dione = $CH_3COCH_2COCH_3$ = Hacac)* is a β-diketone that can be ionised in aqueous solutions behaving as weak acids:

$$CH_3COCH_2COCH_3 \longrightarrow H^+ + [CH_3COCHCOCH_3]^-$$

The resulting anion (acetylacetonate = $acac^-$) can act as a ligand for metal ions, typically forming a bidentate complex where the metal is bound to the two oxygen atoms, thus forming a 6-membered ring chelate.



In general, the complexes that are formed are neutral crystalline solids since the metal acetylacetonate complex has a stoichiometry $[M(acac)_n]$, in which n is the metal charge. Thus, metal ions with charge +3 (Al, Co, Cr, Mn, Fe) form complexes of stoichiometry 3:1 where the metal is coordinated to three $acac^-$ ligands in an octahedral environment. Vanadyl ion (VO^{2+}) forms a complex with a 2:1 stoichiometry where

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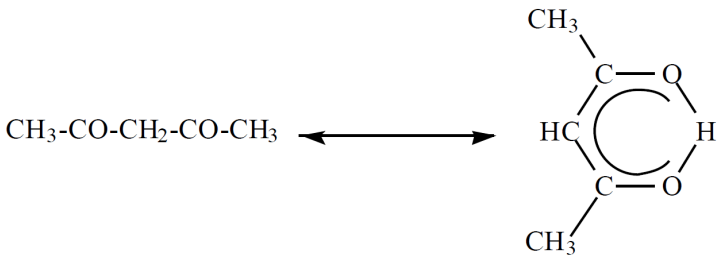
* In pure state or in nonpolar organic solvents, the diketone form is in equilibrium with the cyclic enol form:



vanadium (+4) is surrounded by five atoms of oxygen in an environment square pyramid (Annex IV). Copper (Cu^{2+}) forms a square planar complex with a 2:1 stoichiometry.

The coordinated ligand $acac^-$ forms a planar 6-membered ring (1M + 2O+ 3C) which has six π electrons: one of each atom of the ring, except the metal one, plus the delocalised electron (see equilibrium formation of the bond $acac^-$-M above). This planar ring of six members can be considered as a weak aromatic ring which confers extra stability to the complex $[M(acac)_n]$ by the formation of n weakly aromatic rings.

PRELIMINARY QUESTIONS

1. Draw the flowchart diagrams for each one of the assays performed in this practice.

2. Using Frost diagrams for vanadium in acidic and basic media (see Annex 1), predict the stability of the different oxidation states in aqueous solution.

3. Vanadium pentoxide (V_2O_5) under certain conditions of concentration and pH may give rise to polyvanadates. What is the nature of these ions? What other transition elements lead to similar compounds?

OBJECTIVES

1. Approach the redox chemistry of vanadium: reduction of V(V) to V(IV), V(III) and V(II) with several reducing agents. Qualitative assays with V(V) in solution (attending to changes as a function of pH) and in solid state (calcination assay).

2. Stabilisation of V(IV) through the formation of a complex: synthesis of the vanadium complex $[VO(acac)_2]$.

EXPERIMENTAL PROCEDURE

Reagents and materials

Materials	Reagents
Rack with test tubes	Zn powder
Pipette	Na_2CO_3
100 mL beaker	Saturated solution of Na_2CO_3
50 mL volumetric cylinder	Acetylacetone (MW = 100.11; ρ = 0.973)

25 mL volumetric cylinder	NH_4VO_3
10 mL volumetric cylinder	NaOH 6 M
Spatula	KI
Conical funnel	HCl concentrated
Heating plate	V_2O_5 (MW = 181.88)
Vacuum filtering flask	HCl 4 M
Büchner funnel	H_2SO_4 1 M and 0.05 M
50 mL beaker	Na_2SO_4
Filter adapter cone (rubber)	NH_4VO_3 0.05 M
Watch glass	pH indicator paper
Porcelain capsule	
Test tube lid	
Glass rod	

Caution

- Avoid all personal contact, including inhalation of V_2O_5.
- All residues in this practice must be disposed in the container labelled as 'V residues'. The synthetised complex must be introduced in the bottle labelled as $[VO(acac)_2]$.

Experimental

1 **V(IV): V(V) → V(IV)**

Synthesis of $[VO(acac)_2]$ (This experiment must be done in the hood).

1. Weigh 0.8 g of vanadium pentoxide (V_2O_5) in a 100 mL beaker. Add 12 mL of water and 6 mL of concentrated HCl to V_2O_5.

2. Heat and stir the suspension on a heating plate (cover the beaker with the watch glass) and add while heating 1.8 g of sodium sulphite (Na_2SO_3) in small portions. The orange-brown suspension changes to a deep blue solution.

3. Once finished the addition of sodium sulphite and the blue solution is formed, cool it to room temperature.

4. Add 2.5 mL of acetylacetone (Hacac) to the blue solution and stir.

5. Add anhydrous sodium carbonate (Na_2CO_3) in small portions while stirring vigorously until effervescence is completed and a dark blue-greenish precipitate begins to appear (around 3.5-4.0 g is necessary). At this point, slowly add a saturated solution of sodium carbonate until the end of the precipitation (estimated required volume: 3 mL). Check with pH indicator paper that the pH is around 10 (if it is lower than 10, keep adding sodium carbonate solution). Remove the magnetic stirring bar.

6. Cool down the resulting solution in an ice bath during at least 15 minutes (it is recommended to move to other assays). Filter the obtained product in a filtering plate (without vacuum at the beginning). Wash with two portions of 10 mL each of cold water and then a small portion of ethanol. Leave to dry in air stream during several minutes.

7. Transfer the product to a tared small watch glass and dry it on the stove at 60 ºC until constant weight. Determine the yield of the synthesis.

Waste management: Dispose the product synthesised in the bottle labelled 'Recover $[VO(acac)_2]$'.

2 **V(III): V(V) → V(III). (This experiment must be done in the hood).**

1. Pour 5 mL of a 0.05 M solution of ammonium metavanadate (NH_4VO_3) in a test tube and add 1 mL of H_2SO_4 1 M.

2. Add a spatula tip of solid KI (enough to cover the bottom of the test tube) and write down the changes observed.

3. Change the solution to a small beaker (50 mL) and cover it with a watch glass. Carefully heat the solution in a heating plate until the violet vapours stop and the solution loses its initial colour (the process may last 15-20 minutes). **ENSURE THAT THE SOLUTION DOES NOT BECOME DRY.** Add a small portion of distilled water if it is becoming dry. Write down the changes observed.

3 **V(II): V(V) → V(II).**

1. Pour 3 mL of a 0.05 M solution of ammonium metavanadate (NH_4VO_3) in a test tube, add 10 drops of HCl 4 M and boil for 2 minutes to remove the O_2 dissolved in the solution.

2. **Immediately afterwards,** add a tip of spatula of Zn powder to the test tube and close it rapidly with a rubber lid to avoid air entering. Pay attention to the subsequent changes of colour that appear. Write down the changes observed.

4 V(V) Formation of polyvanadates

1. Take two test tubes and add 3 mL of a 0.05 M solution of ammonium metavanadate (NH_4VO_3) in each tube.

2. To the first test tube: slowly add 10 drops of H_2SO_4 0.05 M and gently shake the test tube to mix. Write down the changes observed. Then add 20 drops of H_2SO_4 1 M. Write down the changes observed.

3. To the second test tube: slowly add 2 mL of NaOH 6 M and gently shake the test tube to mix. Wait 5-10 minutes and write down the final appearance of the solution.

Waste management: Discard all solutions from assays 2, 3 and 4 in the container labelled as 'V waste'.

5 V(V) Calcination assay. (This experiment must be done in the hood).

Cover the bottom of a porcelain capsule with solid ammonium metavanadate (NH_4VO_3) (approximately 0.5 g). Place the capsule over a grid with a Bunsen burner and heat while stirring the solid with a glass rod. Stop the heating as soon as an orange-brown compound appears. Check that ammonium is released with a wet pH indicator paper.

Waste management: Introduce the obtained product in the waste container labelled as 'Recover V_2O_5'.

ADDITIONAL QUESTIONS

Section 1. Synthesis of $[VO(acac)_2]$.

1. What is the oxidation state of vanadium in the complex $[VO(acac)_2]$? What is the oxidation state of vanadium in the starting vanadium pentoxide (V_2O_5)?

2. What is the role of Na_2SO_3 in the first part of the synthesis?

3. Why is a Na_2CO_3 solution added in the 5th step of the synthesis? Which gas appears during effervescence?

4. Write and adjust all the reactions that take place during the synthesis.

5. Determine the yield of the synthesis of $[VO(acac)_2]$.

Section 2.

1. Which compound is responsible of the colour change of the solution after adding KI? Which compound is present in the violet vapours that appear? Which species remain in solution after heating? What is the oxidation state of vanadium in this compound?

2. Write and adjust all the reactions that take place during the assay.

Section 3.

1. Which vanadium species is formed in the final solution? Which is the oxidation state of this species?

2. Write and adjust all the reactions that take place during the assay.

Section 4.

1. Write all the changes observed and explain them using the distribution diagram in Annex V.

Section 5.

1. Which compound is formed after thermic decomposition? What is the oxidation state of vanadium in this compound?

2. Write and adjust the reaction that takes place during the assay.

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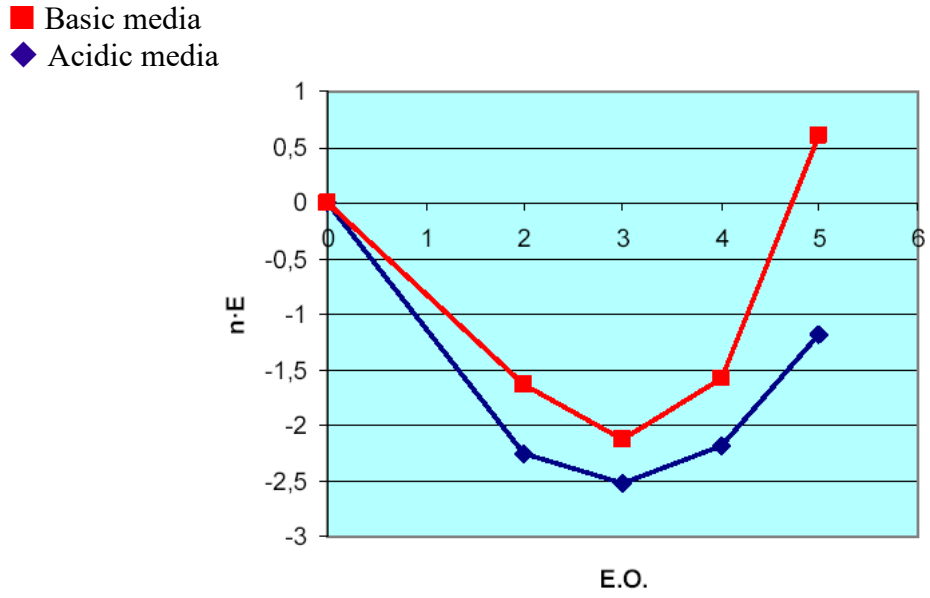
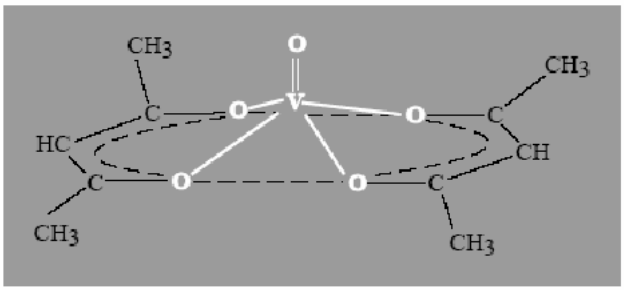
Annex I Frost diagram for vanadium



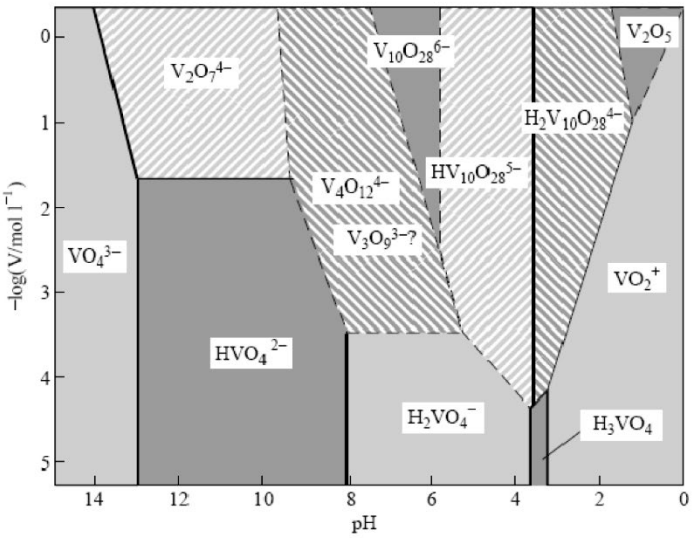
Annex II Colour of the different oxidation states of vanadium

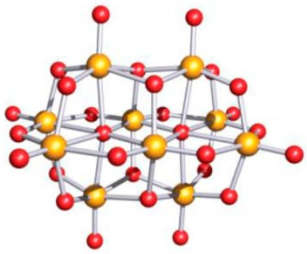
+5 **+4** **+3** **+2**

Annex III [VO(acac)$_2$] structure



Annex IV Distribution diagram of vanadium (+5): vanadates and polyvanadates present in solution as a function of pH and the total concentration of vanadium





Structure of $[V_{10}O_{28}]^{6-}$ anion

PRACTICE 3

CHROME (II) ACETATE. SYNTHESIS AND REACTIVITY.

INTRODUCTION

Hydrated chromium (II) acetate synthesis was first reported by Eugene-Melchior Danger (1811-1890) who also proposed the formula $CrC_4H_4O_5$ for the new compound. This empirical formula is correct except for the fact that at that time hydrogen was erroneously assigned an atomic mass of 2.

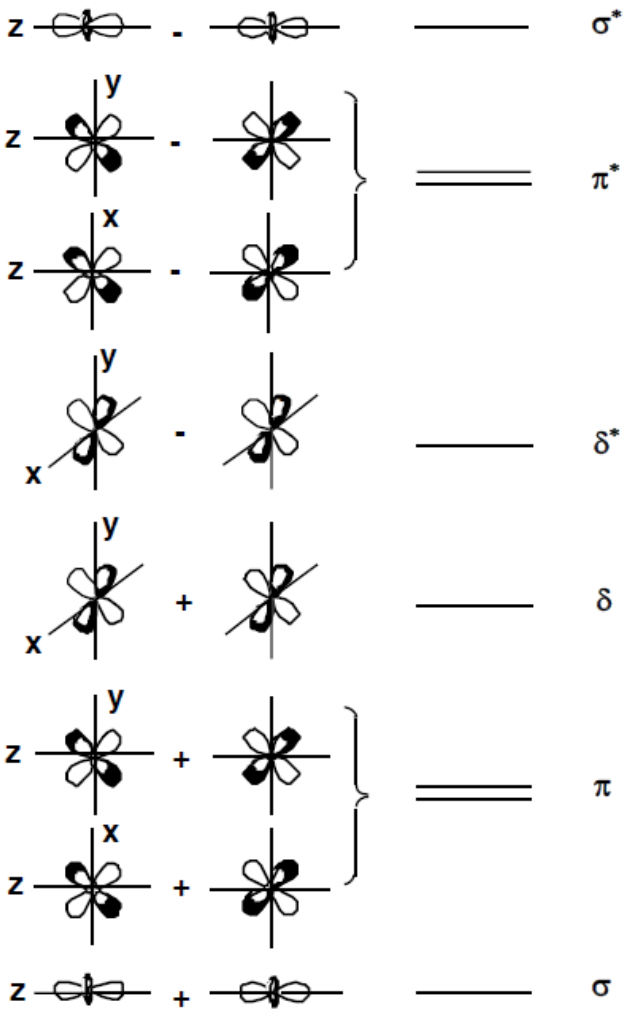
In 1950 King and Garner (*J. Chem. Phys.*, **1950**, *18*, 689) performed magnetic susceptibility measurements on chromium acetate and found that it was diamagnetic, which means that this compound possesses unpaired electrons. This observation contrasted with the fact that hydrated Cr(II) ion, $[Cr(H_2O)_6]^{2+}$ has four missing electrons.

The crystalline structure was resolved in 1970 (Cotton *et al*. in *J. Am. Chem. Soc.,* **1970**, *93*, 2926) and shows that two chromium atoms are at a distance of 2,362(1) Å and four acetate groups act as bridge ligands. That short distance was indicative of a Cr-Cr link. The two water molecules are coordinated in axial positions in the direction of the Cr-Cr link.

The diamagnetism of chromium (II) acetate is due to the existence of a metal-metal bond, which results in the overlapping of the *d* orbitals of the chromium atoms. The following figure shows the overlapping diagram of the *d* orbitals and the corresponding energy levels.

Even though σ and π interactions are well known, δ interaction is unknown for the representative elements.

The energy order of the bonds is $\sigma > \pi >> \delta$. In the case of Cr (II) with electron configuration $3d^4$, there are a total of 8 electrons leading to an electronic structure $\sigma^2\pi^4\ \delta^2$ whereas the Cr-Cr bond order is estimated to be 4.



OBJECTIVES

1. Obtaining chromium (II) acetate from potassium dichromate. This requires three consecutive reactions.

a) First step consists of a reduction reaction from Cr (VI) to Cr (III) using ethanol.

b) Second reduction from Cr (III) to Cr (II) with Zn in acidic medium.

c) The addition of the $[Cr(H_2O)_6]^{2+}$ solution to an excess of sodium acetate produces the precipitation of $[Cr_2(CH_3COO)_4\ (H_2O)_2]$.

Cr(II) is rapidly and irreversibly oxidised by air at room temperature, so all manipulations must be carried out in the total absence of oxygen.

2. Comparing the reactivity of solutions of $[Cr(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{3+}$.

$$[M(H_2O)_6]^{n+} + L\text{-}L^- \xrightarrow{k_1} [M(H_2O)_4(L\text{-}L)]^{(n-1)+} + 2H_2O$$

$$[M(H_2O)_4(L\text{-}L)]^{(n-1)+} + L\text{-}L \xrightarrow{k_2} [M(H_2O)_2(L\text{-}L)_2]^{(n-2)+} + 2H_2O$$

$$[M(H_2O)_2(L\text{-}L)_2]^{(n-2)+} + L\text{-}L \xrightarrow{k_3} [M(L\text{-}L)_3]^{(n-3)+} + 2H_2O$$

First order rate constants for substitution reactions vary greatly from one ion to another. Those ions in coordination compounds for which such substitution reactions are rapid (with large rate constants 10^2-10^9 s^{-1}), are called labile, whereas those for which such substitution reactions proceed slowly (with small rate constants 10^{-3}-10^{-6} s^{-1}) are called inert. In particular $[Cr(H_2O)_6]^{2+}$, d^4, is a very labile ion while $[Cr(H_2O)_6]^{3+}$, d^3, is an inert ion (see Purcell-Kotz textbook, Chapter 13). In this practice, we will study this difference of reactivity for Cr (II) and Cr (III).

a) $[Cr(H_2O)_6]^{2+}$ will react rapidly with an excess of sodium acetylacetonate (Na^+ $acac^-$), at room temperature to form $Cr(acac)_2$ and then oxidise to $Cr(acac)_3$. The formation of $Cr(acac)_3$ from hydrated $CrCl_3$ and sodium acetylacetonate requires heating the solution to 100ºC for more than one hour.

b) $[Cr(H_2O)_6]^{3+}$ solutions react very slowly at room temperature in the presence of Cl^- to form $[CrCl(H_2O)_5]^{2+}$.

PRELIMINARY QUESTIONS

1. Calculate the amount of ethanol (ρ = 0.789 $g \cdot cm^{-3}$ and purity = 96%) stoichiometrically necessary to complete the reduction of 3g of potassium dichromate.

2. What is the value of the reduction potential of the Cr(III)/Cr(II) pair? Are Cr(II) solutions stable on air? According to the value of the reduction potential of the Cr(III)/Cr(II) pair, can you say that Cr(II) ions are stable in aqueous solution in the absence of oxygen?

3. Sketch the structure of $Cr_2(CH_3CO_2)_4(H_2O)_2$.

EXPERIMENTAL PROCEDURE

Reagents and materials

Materials	Reagents
Three neck round bottom flask	$K_2Cr_2O_7$
Dropping funnel	Concentrated HCl
100 mL conical flask	96% ethanol
2 beakers (100 mL)	Zn powder
Frit glass filter	Acetylacetone

Vacuum filtering flask	Na_2CO_3 anhydrous
10 mL volumetric cylinder	H_2O_2 1%
5 mL pipette	Sodium acetate trihydrate
	Ether

Chromium (II) acetate synthesis.

A) Obtention of Cr(III) solution. (This experiment must be done in the hood).

1. Weigh 3g of potassium dichromate and place it in a three-neck round bottom flask (**C** in Figure 1).

2. Add 15 mL of concentrated HCl and stir.

3. Gradually add 2 mL of 96% ethanol while stirring on the heating plate. Observe changes of colour as they occur.

4. Allow the solution to stand until the initial yellow colour disappears. At that time, the reduction is considered to be concluded. Add 15 mL of distilled water that has been previously boiled.

5. Remove 5 mL (measured with the 5 mL pipette) of the solution and store it in a vial. Use the rest for the next stage of reduction to Cr (II).

B) Obtention of Cr(II) solution. (This experiment must be done in the hood)

Set up the device depicted in Figure 1, which preserves an oxygen-free environment. Check that the ground joints close tightly, use petroleum jelly or silicone stopcock grease if necessary.

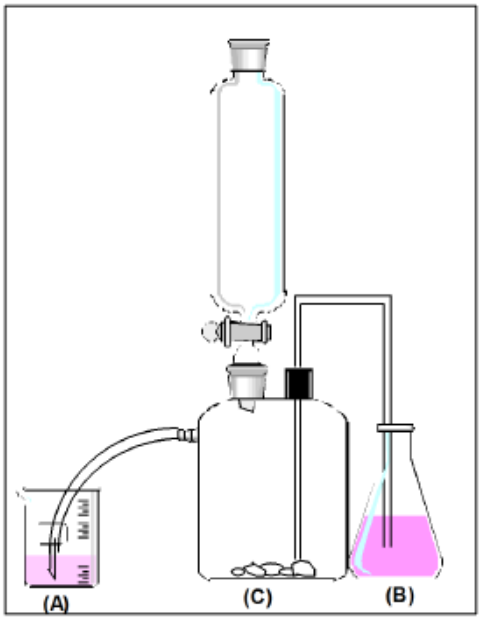
1. Put water in a beaker (A) and connect a side outlet of the flask (C) to the glass (A), using a rubber tube and an eyedropper. Be sure that tube B is just below the surface of the water in the beaker.

2. Introduce 25g of sodium acetate dissolved in 25 mL of distilled water that has been previously boiled in a 100 mL conical flask (B). Stir until complete dissolution. Cover with a stopper.

3. Using the powder funnel, place 3g of zinc powder and 1g of solid Na_2CO_3 into the three-neck round bottom flask (C), which contains the solution of Cr (III). Shake the flask content (C) with a magnetic stirrer.

4. Close the assembly by placing the addition funnel with the key closed and a cap. Adjust the U-shaped glass tube so it does not touch the solution of (C), placing the long part of the tube in (C). Gas evolution must occur through the outlets.

5. Keep the mixture in reaction for (10-15) minutes until the reduction is complete. The initial green colour of Cr(III) solution is changed to a very intense blue colour of Cr(II). If after 15 minutes of reaction you do not observe a permanent clear blue colour, carefully add a few millilitres of concentrated HCl dropwise to flask C using the addition funnel. Take care during the addition that no solution rises into the U-shaped glass tube leading to flask B. Observe the colour change of the solution and compare it with that of the Cr (III) sample previously separated.



C) Obtention of Cr(II) acetate. (This experiment must be done in the hood)

1. When the solution is blue, indicating the presence of Cr(II), introduce the U-shaped glass tube into the solution (flask C) checking that the other end is inside the sodium acetate solution (flask B). Pinch off the rubber tubing at the side-arm with a Mohr clamp, add 5mL of conc. HCl from the funnel and allow the positive pressure of the hydrogen gas to carry the Cr(II) solution through the glass tubing into the beaker containing the sodium acetate solution. Transfer as much of the solution as possible without allowing the glass transfer tube to touch the sodium acetate solution. Deep red chromium acetate should immediately form.

2. Close the conical flask with a cap and immerse it in an ice bath for a few minutes to complete the precipitation of chromium (II) acetate.

3. Filter the cold deep red solution using the frit glass filter and the vacuum filtering flask – making certain to avoid oxidation by not sucking too much air through the sample. As soon as the liquid is no longer visible, break the vacuum and wash the red crystalline solid with boiled distilled water (free of O_2), then with ethanol (two or three times) and finally with ether.

During filtration and washing, ensure that no air passes through the solid and that the surface of the solid is always covered with liquid until the last wash.

Note: The oxidation of chromium (II) acetate during the filtering and drying process produces a darkening of the product surface.

4. Break the vacuum, collect the sample, and spread it out on a filter paper to allow the remaining ether to evaporate. Weigh the solid to determine the yield of product.

Waste management: Dispose the product synthesised in the bottle labelled 'Recover chromium acetate (II)'. Introduce the filter paper into the disposal labelled 'Waste filter paper with Cr'. Enter the contents of the three-neck round bottom flask into the bottle labelled 'Zn Waste'.

Reactivity Assays.

A) Substitution reaction in Cr(III) (ac).

1. Introduce a small amount of chromium (II) acetate in two test tubes A and B and add 1 mL of distilled water that has been previously boiled. Add several drops of diluted hydrogen peroxide and observe the colour of the solutions.

2. Add two drops of concentrated HCl into one of the tubes (A), keeping the other tube (B) as reference. Observe if there is any colour change. Leave tubes at room temperature for 10 minutes. Compare the colour of both solutions.

3. Heat the tube A in the burner. Observe any colour change. Heat tube B using the same procedure. Observe any changes.

B) Substitution reaction synthesis of $Cr(acac)_3$

1. Weigh 1g of sodium carbonate in a 100 mL beaker and dissolve the solid in the minimum of distilled water (repeat this twice). Add 1 mL of acetylacetone to each beaker and stir for a few minutes.

2. Add 0.5 g of chromium (II) acetate to the first beaker and stir for a few minutes. Extract with acetone or chloroform and observe the coloration.

Waste management: introduce the product obtained in the waste disposal labelled 'Recover chromium acetate (III)'.

3. Add 5 mL of the aqueous solution of Cr (III) (which was separated previously) to the second beaker. Stir for a few minutes and observe any reaction. Add some acetone or chloroform and write down the observations.

Waste management: Discard all solutions of this practice that contain Cr in the waste container labelled 'Cr Waste'.

ADDITIONAL QUESTIONS

1. Write down all the reactions that take place during the synthesis of chromium (II) acetate. In the reduction process from Cr (III) to Cr (II), what is the purpose of adding sodium carbonate? What is the purpose of adding HCl?

2. Write down the interpretation of events observed in Section A of the reactivity assays.

3. Write the reactions that take place when mixing chromium (II) acetate and sodium acetylacetonate.

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PRACTICE 4

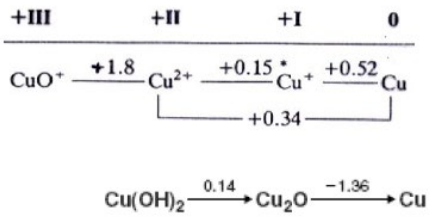
PREPARATION OF Cu (I) AND Cu (II) COMPOUNDS. SPECTROCHEMICAL SERIES

INTRODUCTION

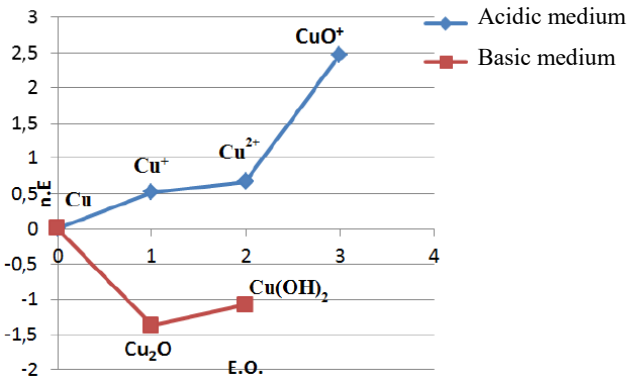
Copper is a transition metal with electronic configuration [Ar]$3d^{10}4s^{1}$. It is a soft, malleable, and ductile metal with very high electrical and thermal conductivities that are only surpassed by pure silver. It possesses a distinctive reddish metallic colour, and it has been known since prehistoric time. It was probably the first metal used by men in its elemental state since it is found in nature in an elemental form.

The chemistry of copper is dominated by the +2 oxidation state, with electronic configuration [Ar]$3d^{9}$, which is the most stable oxidation state; however, there is a substantial chemistry of the +1 oxidation state, and copper(I) compounds ([Ar]$3d^{10}$) can be stabilised by some ligands. When copper is exposed to moist air for a long time, it develops a waterproof green layer on its surface. Copper reacts with oxygen in the air to form copper oxide, which then combines with carbon dioxide to make poisonous copper carbonate, which gives it a green colour.

The Latimer diagrams of copper in acidic and basic media are respectively:



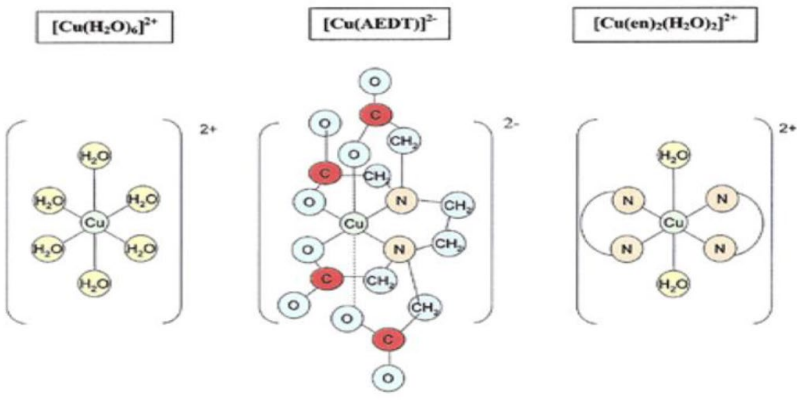
The Frost diagrams obtained from those of Latimer are presented below:



Both diagrams (Latimer and Frost) show that $Cu^{+}_{aq.}$ undergoes a disproportionation reaction in acidic medium to give $Cu^{2+}_{aq.}$ and Cu; it is, therefore, an unstable oxidation state in this medium, but it can be stabilised by the formation of insoluble salts or complexes (remember that the values of the potentials vary in these cases). In contrast, in basic medium Cu (I) it can be stabilised by the formation of Cu_2O.

The Cu (I) ion has a d^{10} configuration and salts and complexes are diamagnetic and colourless except when the counter-ion is coloured, or when the charge transfer absorptions occur in the visible region. There are a few coloured compounds, e.g., Cu_2O (yellow-red), $Cu_2(CO_3)$ yellow, and CuI brown.

State (II) is the most stable and important oxidation state for copper. Cu (II) has an electronic configuration of d^9 with one unpaired electron; thus, Cu (II) compounds are coloured and exhibit paramagnetism. Most Cu (II) complexes possess octahedral geometry with tetragonal distortion due to the Jahn-Teller effect. Cu (II) compounds are green or blue because of an absorption band in the 600-900 nm region of the electromagnetic spectrum. They are generally asymmetrical bands and include several transitions, which are close to each other due to the Jahn-Teller effect. Most copper (II) salts are dissolved in water to form the aqua ion, $[Cu(H_2O)_6]^{2+}$. By adding different ligands to these aqueous solutions, it is possible to successively displace water molecules, although it is extremely difficult to replace the six coordinated molecules. Ammonia can replace up to five water molecules; the sixth molecule can only be replaced using liquid ammonia. Similarly, with ethylenediamine ($H_2NCH_2CH_2NH_2$, $C_2N_2H_8$), the entire replacement of all water molecules is only achieved with a large excess of amine. A large number of amine complexes are blue because of the displacement of the absorption band at higher energies. In this practice, we observe this displacement by modifying the copper hexacoordinate environment: O_6, N_2O_4 and N_4O_2 forming complexes with EDTA and ethylenediamine.



PRELIMINARY QUESTIONS

1. Draw the flowchart diagrams for each of the assays performed in this practice.

2. Using Latimer and Frost diagrams for copper in acidic and basic media, discuss the stability of the different oxidation states in aqueous solution. Does copper (I) $_{aq.}$ disproportionate? Under what conditions? Write and adjust the disproportion reaction. Could you have an aqueous solution of Cu (I)? How could you stabilise this oxidation state? Why?

3. Write and adjust the synthesis reaction of CuCl (s) using the reagents as indicated in the experimental part.

4. Write and adjust the $[Cu(en)_2\ (H_2O)_2]\ I_2$ (s) synthesis reaction from the reagents indicated in the experimental part.

5. The most common stereochemistry for Cu (II) complexes is octahedral geometry with tetragonal distortion. Using the crystal field theory, draw the diagram of energy levels for this stereochemistry and determine an approximated value of the magnetic moment.

6. What is the Jahn-Teller effect?

7. Are Cu (II) coloured compounds? And Cu (I) compounds? Why?

8. What is the spectrochemical series?

OBJECTIVES

1. Stabilisation of the oxidation state (I) of copper. Preparation of CuCl and reactivity assays.

2. Synthesis of di aquabis(ethylenediamine)copper (II) iodide. Characterisation by IR spectroscopy.

3- Synthesis and solution characterisation by UV-visible spectroscopy of three Cu (II) hexacoordinate complexes: $[Cu(H_2O)_6]^{2+}$, $[Cu(EDTA)]^{2+}$ and $[Cu(en)_2(H_2O)_2]^{2+}$. Analysis of the crystal field splitting for octahedral complexes depending on the nature of the ligands present in the metal coordination sphere (spectrochemical series).

en: $H_2NCH_2CH_2NH_2$; $EDTA^{4-}$: $[(OOCCH_2)_2NCH_2CH_2N(CH_2COO)_2]^{4-}$

EXPERIMENTAL PROCEDURE

Reagents and materials

Materials	Reagents
Rack with tube tests	$CuCl_2 \cdot H_2O$
Dropper	Laminated metal copper
50, 100, and 250 mL beakers	Cu (II) acetate monohydrate
25 and 50 mL graduated cylinders	HCl concentrated
10 and 25 mL volumetric flasks	HCl 6M
Spatula	NaOH 4M
Conical funnel	NH_3 0,1M
Vacuum filtering flask	NH_3 6M
Büchner filtration funnel	KI
Filter adapter cone (rubber)	ethylenediamine
Glass rod	$CuSO_4 \cdot 5H_2O$
Magnetic bar	Na_2H_2EDTA
Heating plate	
Multi-position heating plate	
UV-vis spectrophotometer	
Quartz cuvettes	

Caution: **Ethylenediamine** is **flammable and toxic** (harmful if inhaled, swallowed, or touched). Please handle inside the fume hood.

(It is recommended to start with procedure 2a and when the reaction is in the ice bath, proceed with section 1).

1.- Copper (I) chloride synthesis. (This experiment must be done in the hood).

Put the water into the bath and heat to about 90ºC. Weigh 2.1 grams of $CuCl_2.2H_2O$ and place it in a round-bottom flask; add 8 mL of H_2O and then immerse the flask in the water bath. Add the magnetic bar and stir the mixture until dissolved. Then add to the dissolution 1.6 g of metallic Cu cut into small pieces. Take 16 mL of HCl (conc) and add it to the reaction mixture. Connect the condenser. Stir the solution using the magnetic stirrer and maintain the reaction temperature at 90ºC for 30 min, until the

solution becomes yellow. Decant the solution while hot (to separate the copper that has not reacted), pouring it over 200 mL of cold water. Dilution will make a suspended white solid appear: (copper (I) chloride. Allow the precipitate to settle, and decant most of the supernatant solution. Then filter through a Buchner and wash with ethanol and ether. Calculate yield. Observe if the precipitate changes colour over time. The copper that has not reacted must be removed from the reaction mixture, then washed and recycled.

Waste management: Discard the product obtained in the waste disposal labelled 'Recover copper (I) chloride'. Filter papers with Cu should be introduced in the container labelled 'Filter paper with Cu'.

Assays

Introduce a small amount of the precipitated CuCl into 4 test tubes.

A) In the first tube, add 1mL of HCL 1M and observe the solubility.
B) In the second tube, add 1 mL of HCl 6 M and observe any changes that occur. Add 1.5 mL of 4 M NaOH until the appearance of a precipitate. Compare with the precipitate formed when you dissolve $CuCl_2 \cdot 2H_2O$ (pick up a small amount of $CuCl_2 \cdot 2H_2O$ on the tip of the spatula and dissolve in 2-3 mL water) with 1.5 mL of NaOH 4 M
C) In the third tube, add 1 mL of 0.1M NH_3. Note the changes.
D) In the fourth tube, add 1 mL of 6 M NH_3. Observe the changes.

Waste management: Discard all the dissolutions of the assays A, B, C and D of this practice in the waste disposal labelled as 'Waste Cu'.

2.- Hexacoordinate copper (II) complexes.

2a.- ***Preparation diaquabis(ethylenediamine) copper (II) (This experiment must be done in the hood).***

Dissolve 0.9 g of copper acetate (II) monohydrate in 3 mL of water in a 50 mL beaker. Add drops of 1 mL of ethylenediamine while stirring until the solution becomes purple. Then add a solution of KI (2.1 g of solid in approximately 3.5 mL of distilled water).

Heat the reaction mixture to 60°C for 10 min on the hotplate stirrer. Use the temperature probe to obtain an accurate control of the temperature. Cool the solution in an ice bath during 1-2 h – a purple crystalline product in the form of needles will appear. The solid crystals are collected by Büchner filtration and the filtrate is discarded. Wash the

crystals carefully with small amounts of cold ethanol, leave them in the filter funnel and draw air through them for several minutes. Finally, dry the crystals in air by leaving them to stand uncovered for several minutes. Calculate the yield.

Waste management: Dispose the product obtained diaquabis(ethylenediamine) copper (II) in the waste container labelled as 'Recovering Cu (II)-en'.

2b.- Spectrochemical series. Preparation of solutions.

- **Preparation of $[Cu(H_2O)_6]^{2+}$ of chromophore CuO_6**

Prepare an aqueous solution by dissolving 0.200 g of $CuSO_4 \cdot 5H_2O$ and dilute to the mark in the 10 mL volumetric flask.

- **Preparation of $[Cu(EDTA)]^{2-}$ of chromophore CuN_2O_4**

Prepare an aqueous solution by dissolving 0.0350 g of copper (II) acetate monohydrate and 0.1 g of Na_2H_2EDTA and dilute to the mark in the 25 mL volumetric flask.

- **Preparation of $[Cu(en)_2(H_2O)_2]^{2+}$ of chromophore CuN_4O_2**

Prepare an aqueous solution by dissolving 0.125 g of $[Cu(en)_2(H_2O)_2]I_2$ previously synthesised and dilute to the mark in the 25 mL volumetric flask.

Obtain the UV-Vis spectra for the three complexes ranging from 400 to 900 nm. Determine the wavelength of maximum absorbance in each case.

Waste management: Discard all solutions in the waste container labelled 'Cu waste'.

ADDITIONAL QUESTIONS

Section 1

1. Calculate the percentage yield obtained in the process of synthesis of CuCl. Describe the appearance and colour of each of the reactants and products participating in the reaction.

2. Explain using chemical reactions what is observed in assays A, B, C, and D.

Section 2a

3. Calculate the percent yield obtained in the process of synthesis of $[Cu(en)_2(H_2O)_2]I_2$. Describe the appearance and colour of each of the reactants and products participating in the reaction.

Section 2b

4. Describe, using the appropriate chemical reactions, the preparation of the aqueous solutions containing the complexes $[Cu(H_2O)_6]^{2+}$, $[Cu(EDTA)]^{2-}$, and $[Cu(en)_2(H_2O)_2]^{2+}$ used to register their UV-vis spectra. What colours do they exhibit? Calculate the concentration of these solutions. Do they all have the same concentration? Explain why.

5. From the measurements of the absorbance of these solutions in the range of 400–900 nm, determine the wavelength of maximum absorbance for each of the three complexes. What does this value represent?

6. Compare the λ_{max} values obtained for the three complexes and explain why the maxima of the visible spectra of the Cu (II) complexes move by changing the ligands attached to the metal. Sort all three ligands according to the ability of ligands to split d orbital energy levels, to the magnitude of Δ_o (spectrochemical series).

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PRACTICE 5

SYNTHESIS AND CHARACTERISATION OF OXALATE COMPLEXES $[Fe(C_2O_4)(H_2O)_2]$ AND $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$. A REACTIVITY STUDY

INTRODUCTION

Iron, the most important of all metals, is also one of the most abundant elements in the lithosphere. Its most important minerals are hematite (Fe_2O_3), magnetite (Fe_3O_4), and siderite ($FeCO_3$). The element has a great biological relevance: hemoglobin and myoglobin carry oxygen; the cytochromes (involved in the conversion of the adenosine diphosphate into adenosine triphosphate with the energy released during glucose oxidation) are electronic transfer agents; and the nitrogenase enzymatic system (used in nitrogen fixation in biological systems) contains iron. The most common oxidation states of iron in its compounds are divalent and trivalent. The redox value for $Fe^{2+}(ac)/Fe(s)$ under standard conditions (pH = 0 and T = 25°C) is -0.44 V and the couple $Fe^{3+}(ac)/Fe^{2+}(ac)$ 0.77 V. Therefore, Fe(s) is attacked by dilute mineral acids forming salts of Fe(II) that can be oxidised to Fe(III) in the presence of oxygen from the air. Concentrated nitric acid and other energetic oxidisers passivate it. Lower oxidation states can be found in their complexes with carbonyl ligands while high oxidation states (Fe(IV) and Fe(VI)) are rarer and have only been observed in a small number of compounds.

This practice addresses the synthesis of two oxalate complexes, one with Fe(II) (with formula $[Fe(C_2O_4)(H_2O)_2]$) and another with Fe(III) (the mononuclear complex with formula $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$), and there is evidence of the different modes of coordination of the oxalate ligand using infrared spectroscopy. The practice is finished with several reactivity assays of isolated complexes.

OBJECTIVES

1. Synthesis of two oxalate complexes of iron, one with Fe(II) and the other with Fe(III), with formulas $[Fe(C_2O_4)(H_2O)_2]$ and $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$.

2. Determination of the formula of the potassium salt through thermal drying and conductivity measurements in aqueous solution.

3. Reactivity assays of Fe(III) complex (unstable in sunlight and reduced to Fe(II)).

4. Study of the thermal behaviour of Fe(II) oxalate.

5. Characterisation of the coordination arrangements for the oxalate ligand (bidentate and bis-bidentate) in the complexes by IR spectroscopy.

PRELIMINARY QUESTIONS

1. Draw a flow diagram for the synthesis carried out during this practice. Calculate the moles of reagents used in each step.

2. Write the Lewis structure of oxalate ion. What are the coordination modes?

3. Why is the synthesis of Fe(II) oxalate carried out in acidic media?

4. What is the concentration of a hydrogen peroxide solution of 20 volumes?

5. Why ethanol is added in step B.4 in the synthesis of $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$?

EXPERIMENTAL PROCEDURE

Reagents and materials

Materials	Reagents
Glass rod	Acetone[7]
Magnetic stirrer	96% ethanol
10 and 50 mL volumetric cylinders	1.10-fenanthroline 2% in ethanol
Beakers: 250 mL (x1)	Oxalic dihydrate acid (solid) and 10%
150 mL (x2)	aqueous solution
100 mL (x2)	Potassium oxalate monohydrated
Filtering flask	20 vol. hydrogen peroxide
50 mL volumetric flask	Glacial acetic acid

Crushed ice bath Magnetic stirrer Agate mortar and pestle Glass capsule Glass funnel Aluminium foil Watch glass Test tube rack and test tubes Evans balance IR-ATR equipment UV lamp	Mohr's salt (iron(II) sulphate and ammonium hexahydrate)

A) Synthesis of compound trans-diaqua(μ-oxalate)iron(II), [Fe(C_2O_4)(H_2O)$_2$].

(It is recommended to heat by Bunsen burner 100 mL of distilled water to be used throughout the synthesis)

1. Weigh 7.5 g of ammonium iron(II) sulphate (Mohr's salt) in a 100 mL beaker and dissolve it in 25 mL of warm water acidified with 1 mL of H_2SO_4 3 M.

2. Slowly add to the resulting solution 3.75 g of oxalic dihydrate acid dissolved in 40 mL of water and heat to boiling while stirring continuously. Keep stirring the solution until a yellow solid appears as agitation will avoid splashes. The solid formed is iron (II) oxalate, FeC_2O_4. Allow the solid to settle.

3. Decant off the supernatant solution and add 15 mL of warm water to the suspension while stirring. Filter through a Buchner, wash the solid with small portions of warm water, acetone, and finally air-dry. Weigh the dry solid and determine the yield.

Waste management: Introduce the obtained product in the bottle labelled as 'Recover [Fe(C_2O_4)(H_2O)$_2$] *'.*

B) *Synthesis of compound potassium tris(oxalate)ferrate(III)trihidrate, $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$.*

1. Dissolve 2.5 g of potassium oxalate monohydrate in 8 mL of water in a 100 mL beaker. Add 1.8 g of the Fe(II) oxalate (obtained in the previous step A) to this solution and heat the mixture at 40 °C.

2. Slowly add 7 mL of 20 vol. H_2O_2 to the resulting suspension while continuously stirring. Then heat to boiling.

3. Add drops of a 10% solution of oxalic acid until the green precipitate previously formed dissolves (Approximately 7-8 mL).

4. If a precipitate appears, filter the warm solution on a conical funnel using a filter paper.

5. Add 15 mL of ethanol to the filtrate solution. Let it cool down in darkness (covered with aluminium foil) first at room temperature and later in an ice bath.

6. Filter off the crystals obtained and wash them with a mixture of ethanol:water (1:1), then with acetone, and finally air dry. Weigh the solid and calculate the yield.

Waste management: Introduce the obtained product in the bottle labelled as 'Recover $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$*'.*

C) Determination of potassium salt formula

1. Grind approximately 1.5 g of the dry potassium salt obtained previously and then weigh accurately 1.000 g in a tared watch glass. Heat on a stove to 110 °C until the weight remains constant and write down the amount lost. Determine the number of water molecules of hydration in the initial compound.

2. Determine the molar conductance of the potassium salt dissolved in water:

a) Prepare 50 mL of aqueous solution 10^{-3} M.

b) Measure the specific conductance or conductivity (Λ) of the solution immediately after being prepared.

c) Calculate the value of the molar conductance (Λ_M) using the following expression:

$$\Lambda_M = 10^3 \Lambda / M$$

where M is the concentration of the solution and its Λ specific conductance in S/cm.

d) Compare the results with the data from Annex I and determine the type of electrolyte.

D) Reactivity assays of the synthetised oxalate complexes

1. Weigh 0.25 g of the dry product from step B and dissolve it in 5 mL of water with 10 drops of a solution of glacial acetic acid. Stir to favour the dissolution and leave the tube exposed to the UV light from the lamp. Observe the changes produced over time.

2. Dissolve a little of the same salt in water and divide the solution in two parts (use two test tubes). One of the tubes is kept in darkness (cover it with aluminium foil) and the other is exposed to light. After 15 minutes, add one drop of the phenanthroline solution in ethanol (Fe^{2+} reagent) to each of the tubes and compare the results.

3. Introduce about 0.5 g of Fe(II) oxalate (yellow solid) in a Pyrex dry tube and hold it with a clamp in a vertical position in a stand. Heat with the flame of a burner, first gently and later at higher temperature and observe the thermic decomposition. Leave the solid residue to cool down. Carefully take the tube, close it with a glass capsule and flip it immediately – leaving the solid exposed to the air. Observe the changes that occur. Finally, bring a magnetic bar towards the bottom of the capsule and observe what occurs.

Waste management: Place all solutions of this practice in bottle labelled 'Waste Fe'.

E) IR spectra of synthetised oxalate complexes.

1. Record the IR spectra of each of the samples and print them following the instructions from the equipment.

F) Magnetic moment determination of the synthetised oxalate complexes (optional).

Using the magnetic balance determine the magnetic moment of Fe(II) and Fe(III) complexes. Compare the results, calculate the number of unpaired electrons in each case, and determine if it is a high or low spin complex.

ADDITIONAL QUESTIONS

1. Write and adjust the chemical reactions that take place in steps A and B. Which could be the insoluble intermediate product that is formed in the synthesis of the Fe(III) complex.

2. Justify the different solubility in water of the two synthetised complexes.

3. Interpret the measurements in step C.

4. What is the result of the exposure to light to tris(oxalate)ferrate(III) anion? Write a chemical reaction that explains this phenomenon.

5. Write and adjust the chemical reaction corresponding to the thermal decomposition of the Fe(II) oxalate. Which are the decomposition products? What happens to the residue of the decomposition when in contact with air? Explain this.

6. According to the recorded IR spectra, what conclusion can be drawn about the modes of coordination of the oxalate ligand in the two iron complexes isolated? Propose possible structures for both compounds according to the results obtained during the practice.

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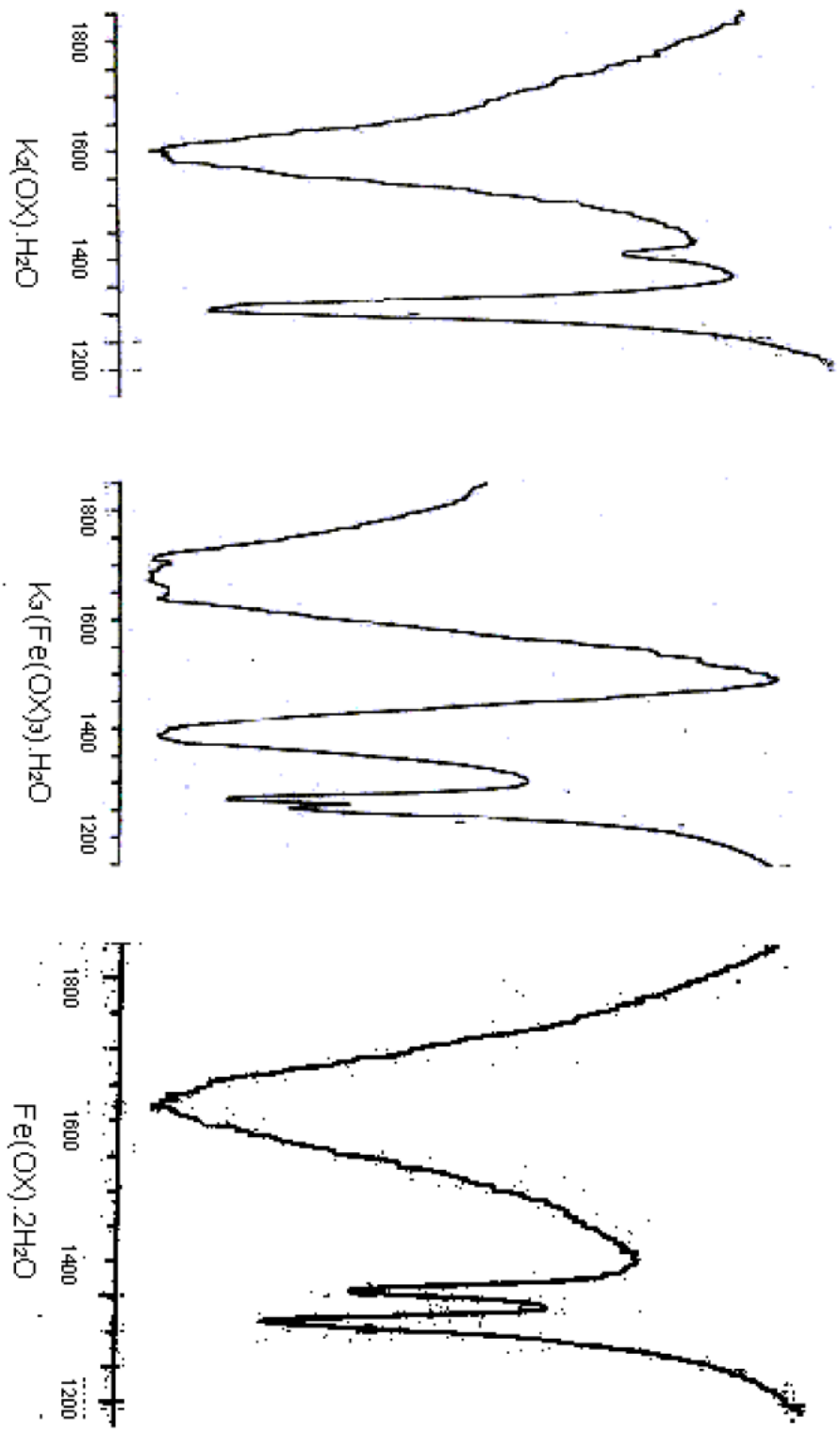
ANNEX I. Ranges of molar conductances (Λ_M) that should be expected for electrolytes of 2, 3, 4 and 5 ions (~10^{-3} M) in common solvents at 25 °C

Solvent	Dielectric constant	Type of electrolyte			
		1:1	2:1	3:1	4:1
Water	78,4	118-131	235-273	408-435	~560
Nitromethane	35,9	75-95	150-180	220-260	290-330
Nitrobenzene	34,8	20-30	50-60	70-82	90-100
Acetone	20,7	100-140	160-200		
Acetonitrile	36,2	120-160	220-300	340-420	
Dimethylformamide	36,7	65-90	130-170	200-240	
Methanol	32,6	80-115	160-220		
Ethanol	24,3	35-45	70-90		

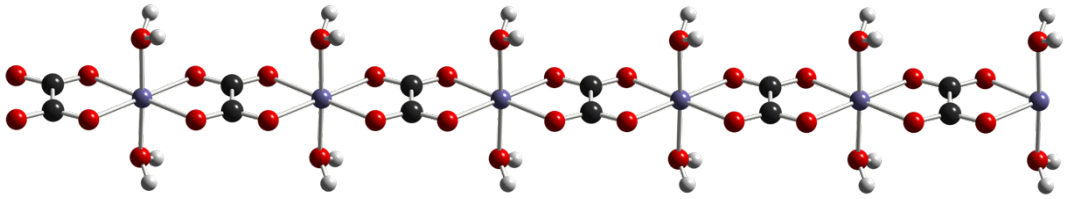
Units of all molar conductances are $\Omega^{-1}cm^2mol^{-1}$.


1800
1600
1400
1200
K2(OX).H2O
1800
1600
1400
1200
K3(Fe(OX)3).H2O
1800
1600
1400
1200
Fe(OX).2H2O

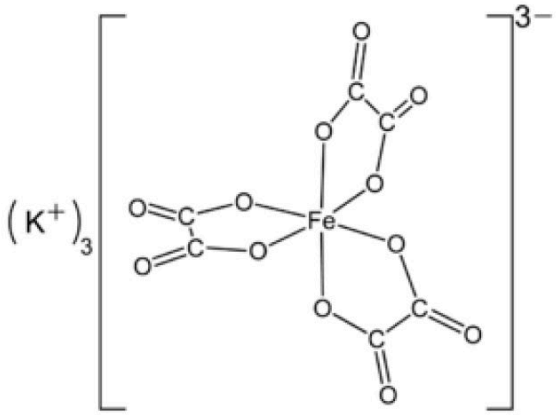
IR SPECTRA

ADDITIONAL MATERIAL

$[Fe(C_2O_4)(H_2O)_2]$ structure



$K_3[Fe(C_2O_4)_3]$ structure and enantiomeric forms



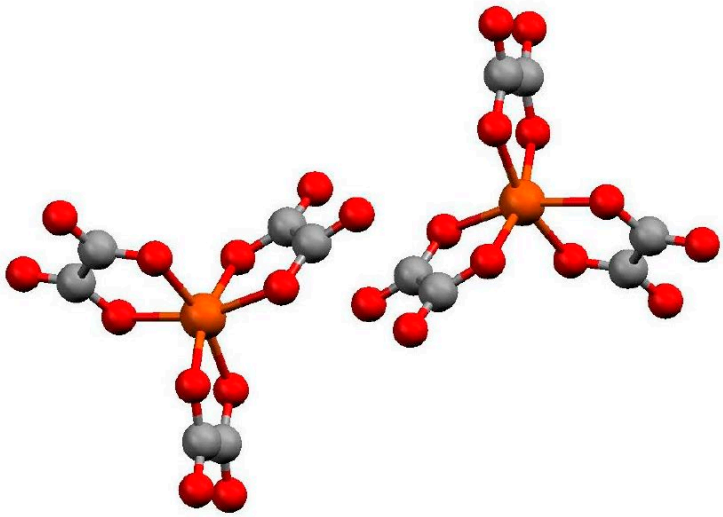


Table 1. Assignment of the vibrational spectra of the two modifications of $Fe(C_2O_4)\cdot 2H_2O$ (band positions in cm^{-1})

α-$Fe(C_2O_4)\cdot 2H_2O$		β-$Fe(C_2O_4)\cdot 2H_2O$		Assignment
IR	Raman	IR	Raman	
3343 vs,br		3342 vs,br		ν(OH)(H_2O)
1625 vs		1625 vs		ν(C-O)
	1489vs,1450sh		1490vs,1450sh	ν(C-O)
1361 s		1361 s		ν(C-O)
1317 vs		1317 vs		ν(C-O)
	913 s		907 s	ν(C-C)
822 s		820 s		δ(O-C-O) + ν(C-C)
765/718 w		755/714 w		ρ(H_2O)
531 m	580/520 m	540 m	590/528 m	δ_{ring}
493 s		493 s		ν(Fe-O) (?)

Band intensities: vs, very strong; s, strong; m, medium; w, weak; br, broad; sh, shoulder.

Table 2

Raman and infrared spectra and vibrational assignments for solid potassium oxalate

Infrared (cm^{-1})	Raman (cm^{-1})	Approximate assignment of vibrational mode
	1747 w	
1600 vs, br	1605 w	ν_6 ν(CO)
	1496 vs	ν_1 ν(CO) symmetric
1406 w	1449 vs	ν(CO)
1309 ms	1348 w	ν_9 ν(CO)
	888 vs	ν_2 ν(CC)
768 m		
725 w		
618 mw		
525 m		
	476 s	ν_3 δ(CO_2) symmetric
	316 w	ν_{10} ρ(CO_2)

TABLE III-23. Frequencies and Band Assignments of Chelating Oxalato Complexes (cm^{-1})[383]

$K_2[Zn(ox)_2]\cdot 2H_2O$	$K_2[Cu(ox)_2]\cdot 2H_2O$	$K_2[Pd(ox)_2]\cdot 2H_2O$	$K_2[Pt(ox)_2]\cdot 3H_2O$	$K_3[Fe(ox)_3]\cdot 3H_2O$	$K_3[V(ox)_3]\cdot 3H_2O$	$K_3[Cr(ox)_3]\cdot 3H_2O$	$K_3[Co(ox)_3]\cdot 3H_3O$	$K_3[Al(ox)_3]\cdot 3H_2O$	$[Cr(NH_3)_4(ox)]\cdot Cl$	Band Assignment	
1632	(1720) 1672	1698	1709	1712	1708	1708	1707	1722	1704	ν_a(C=O)	ν_7
—	1645	1675, 1657	1674	1677, 1649	1675, 1642	1684, 1660	1670	1700, 1683	1668	ν_a(C=O)	ν_1
1433	1411	1394	1388	1390	1390	1387	1398	1405	1393	ν_s(CO) + ν(CC)	ν_2
1302	1277	1245 (1228)	1236	1270, 1255	1261	1253	1254	1292, 1269	1258	ν_s(CO) + δ(O—C=O)	ν_8
890	886	893	900	885	893	893	900	904	914, 890	ν_s(CO) + δ(O—C=O)	ν_3
785	795	818	825	797, 785	807, 797	810, 798	822, 803	820, 803	804	δ(O—C=O) + ν(MO)	ν_9
622	593	610	—	580	581	595	—	—	—	Crystal water?	
519	541	556	575, 559	528	531	543	565	587	545	ν(MO) + ν(CC)	ν_4
519	481	469	469	498	497	485	472	436	486, 469	Ring. def. + δ(O—C=O)	ν_{10}
428, 419	420	417	405	366	368	415	446	485	366	ν(MO) + ring def.	ν_{11}
377, 364	382, 370	368	370	340	336	358	364	364	347	δ(O—C=O) + ν(CC)	ν_5
291	339	350	328	—	—	313	332	—	328	π	

PRACTICE 6

OXYGEN UPTAKE BY A Co (II) COMPLEX.

INTRODUCTION

Natural proteins responsible for oxygen transport and storage contain a transition metal coordinated reversibly to oxygen. These metals are usually iron (in the form of ferrous heme in proteins such as myoglobin and hemoglobin), copper (hemocyanin), and vanadium (hemovanadin). There are a number of coordination compounds that reversibly coordinate molecular oxygen, and for that reason, they have been extensively studied as 'model compounds' of biological processes. Co (II) complexes are among the most studied.

Co (II) forms some square planar complexes. Among them the most studied are those that form Co(II) with Schiff bases; these are tetradentate ligands with N and O as donor atoms located in such a way that reinforces the planar square stereochemistry. (Figure 1). Some of these complexes have the particularity of being able to absorb O_2 at room temperature. One of the best-known cobalt(II) 'oxygen carriers' is [Co(salen)], where H_2salen represents N,N'-bis(salicylaldehyde)ethylenediamine acid. Schematic molecular formula of species [Co(salen)] is represented in Figure 2.

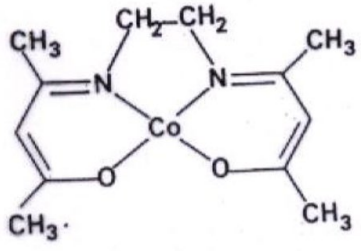


Figure 1: Square planar Co (II) complex with N and O as donor atoms.

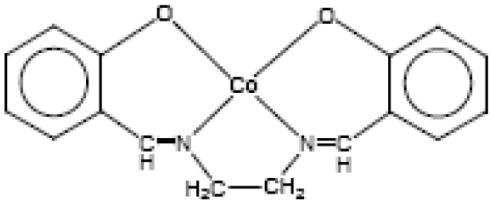


Figure 2: Schematic molecular formula of species [Co(salen)].
H_2salen = N,N'-bis(salicylaldehyde)ethylenediamine

[Co(salen)] complex exists in two different solid forms, depending on the synthetic process that has been followed for its preparation. There is a dark red form inactive towards oxygen absorption, and a brown active form. The inactive form (red) consists of dimeric [Co(salen)] units located one above the other, but slightly displaced, in which the Co atom of one molecule interacts with an O-atom of the second leading to a square pyramid geometry. The distance (Co-O) between the two dimeric units is

2.26Å, which is too short to allow the entry of O_2 molecules (Figure 3a). The crystal structure of inactive [Co(salen)] is shown in Figure 4.

The active form (brown) also has [Co(salen)] dimeric units, but with one Co atom directly above the other. The shortest distance between the two units, 3.45Å, is large enough to allow oxygen to enter easily. The active form absorbs oxygen at room temperature, and releases it at higher temperatures. This cycle may be repeated many times, although owing to decomposition the activity of the compound towards oxygen uptake slowly decreases on continued cycling.

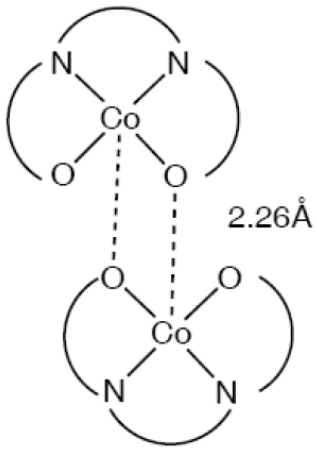


Figure 3a. [Co(salen)] inactive form, red dark colour.

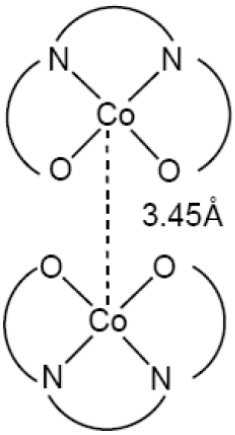


Figure 3b. [Co(salen)] active form, brown colour.

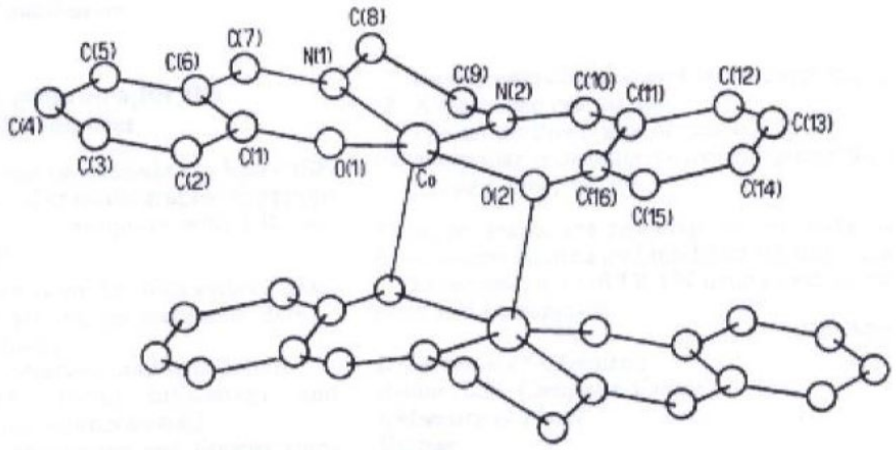


Figure 4. Inactive form of [Co(salen)]. Dimeric unit scheme with all atoms labelled.

When Co(salen) is dissolved in donor solvents (e.g., dimethylsulfoxide DMSO, dimethylformamide DMF, pyridine) in the presence of oxygen, it rapidly forms adducts. In DMSO, a dark brown solid with molecular formula $[(DMSO)Co(salen)]_2O_2$ precipitates. This compound is diamagnetic and formally contains two atoms of Co(III)

with a peroxo bridge between the two metal centres. The most probable structure for the adduct $[(DMSO)Co(salen)]_2O_2$ is shown in Figure 5.

$$\underset{\text{Inactive, red}}{2\,[Co^{II}(salen)]} + 2L + O_2 \longrightarrow [(L)Co^{III}(salen)]_2O_2 \text{ (DIAMAGNETIC)}$$

L = DMSO, Py, DMF ...

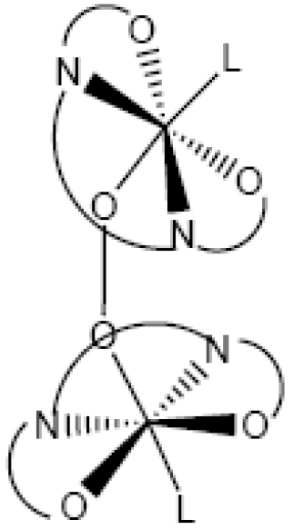


Figure 5. Structure of adduct species $[(L)Co(salen)]_2O_2$ with the oxygen bound.

In this experiment, the inactive form of Co(salen) is prepared by an adaptation of the Bailes and Calvin method (5). An aqueous solution of cobalt(II) acetate is added to a hot ethanol solution of H_2salen under nitrogen (Fig. 2). A mixture of active and inactive forms is initially obtained, which is entirely converted to the inactive form when heated in ethanol. Once inactive Co(salen) has been formed, and it may be filtered off and handled in air without worrying about decomposition.

OBJECTIVES

1. Synthesis of tetradentate ligand N,N'-bis(salicylaldehyde)ethylenediamine acid (H_2salen).

2. Synthesis of the complex formed with this ligand and Co(II), [Co(salen)], red form inactive toward absorption of oxygen.

3. Activation of inactive form of [Co(salen)] by adduct formation with DMSO. The uptake of dioxygen is then investigated for the complex in a DMSO solution to determine the number of moles of O_2 absorbed per mol of [Co(salen)].

PRELIMINARY QUESTIONS

1. Write and adjust the reaction between salicylaldehyde and ethylenediamine to obtain H_2salen.

2. Carefully read the experimental procedure and draw the flowchart diagram for the synthesis of [Co(salen)].

3. Write and adjust the reaction for the synthesis of [Co(salen)]. Why is it necessary to bubble N_2 (gas) during the procedure?

4. Draw the flowchart diagram for the experimental section #3.

5. The most frequent stereochemistry for Co (II) complexes are octahedral (high spin) and tetrahedral. A remarkable aspect of cobalt (II) complexes is that in certain occasions square planar complexes are formed. Using the crystal field theory, draw the energy level diagram for the geometries mentioned above and determine the magnetic moment value for each.

6. Give a reasoned explanation for the fact that almost all Co(III) complexes are octahedral (low spin). What magnetic moment do they exhibit?

EXPERIMENTAL PROCEDURE

Caution

Handle carefully salicylaldehyde and DMSO; the latter is absorbed through the skin.

Materials and reagents

Materials	**Reagents**
50, 100, and 250 mL beakers	Salicylaldehyde
Funnel	96% ethanol
10 mL graduated cylinder	Ethylenediamine
2 10 mL pipettes	Co (II) acetate tetrahydrate
Vacuum filtering system	Dimethylsulfoxide (DMSO)
Magnetic stirrer and heating plate	N_2 (g) and O_2 (g)
Three-neck round bottom flask with cap	
Condenser	
Water bath	
Thermometer	

Oven Test tube with side arm and lid Small test tube

1.- Synthesis of N,N'-bis(salicylaldehyde)ethylenediamine acid (H_2salen). (This experiment must be done in the hood).

Add 1.6 mL of salicylaldehyde to 25 mL of hot 96% ethanol in a beaker. While stirring, heat this solution on a heating plate, then add 0.5 ml of ethylenediamine in small portions. Stir the solution for approximately 3 min. Remove the beaker from the hot plate and allow it to cool in an ice bath. Then collect the bright yellow flaky crystals on a Büchner funnel using the vacuum. Wash the crystals with a small amount of cold ethanol, then air-dry the product thoroughly. Determine the yield of your product.

Waste management: discard filtrate solutions in the waste disposal labelled 'Waste: Ethylenediamine + Salicylic acid'.

Waste management: discard the synthesised product in the waste disposal labelled 'Recover H_2salen'.

2.- Synthesis of [N,N'-bis(salicylaldehyde)ethylenediamino]cobalt(II), Co(salen), the inactive form.

Heat water in a bath to 60ºC. Add approximately 1.17 g of dry previously synthesised H_2salen in a 3-neck round bottom flask fitted with a magnetic stir bar. Add 60 ml of 96% ethanol and flush the apparatus with nitrogen while stirring for 5-10 min. Connect the condenser, adjust the nitrogen flow to a steady rate (1 bubble each 5 seconds) and immerse the flask in a 70-80°C water bath while providing a slow steady flow of cool water through the condenser. H_2salen will be dissolved.

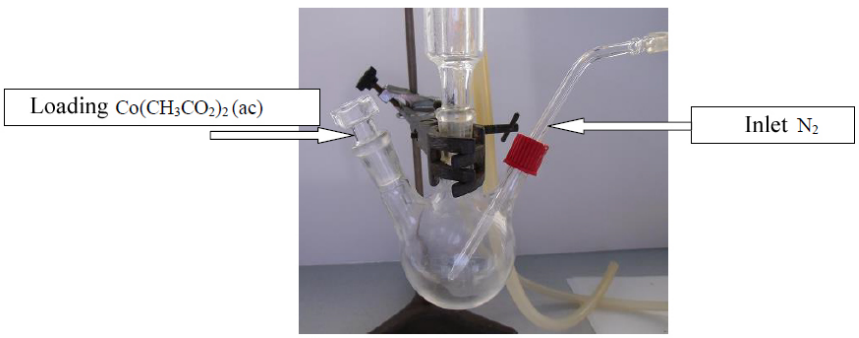


Figure 6. Apparatus for [Co(salen)] preparation.

Weigh out 1.09 g of cobalt (II) acetate, $Co(CH_3CO_2)_2 \cdot 4H_2O$, transfer the solid to a beaker and dissolve it in approximately 7.5 mL of hot water. Add the cobalt (II) acetate solution to the 3-neck round bottom flask after all of the H_2salen is dissolved. Use the side neck. Immediately a dark gelatinous precipitate is formed. After the addition of cobalt is complete, reflux for 1 hour during which the precipitate becomes dark red.

Then allow the solution to cool under N_2. Discontinue the nitrogen flow and collect the product on a Büchner funnel in air (no vacuum at the beginning of filtration). Rinse the product three times with the minimum amount of water and then with 96% ethanol. Leave the product in the filter funnel and suck air through it for several minutes, and then allow to air dry. If further drying is necessary, use a vacuum desiccator. Determine the yield of the Co(salen) product.

Waste management: Discard filtrate the synthesised product in the waste disposal labelled 'Waste Co'.
Waste management: Discard the filter paper in the waste container labelled as 'Filter paper with Co'.
Waste management: Discard the remaining product after oxygen binding studies in the waste disposal labelled 'Recover [Co(salen)]'.

Determination of the number of moles of oxygen absorbed per mole of complex

Accurately weigh out 0.100 g of completely dry [Co(salen)] and place in a dry side-arm test tube fitted with a ground-glass stopper. Introduce 5 mL of DMSO in a small beaker and bubble oxygen for 2 minutes until saturation **(handle DMSO carefully since it is readily absorbed by the skin and can easily carry other compounds through the skin with it)**. Transfer DMSO solution to a small test tube until it is filled to within 2 cm of the top. Lower the tube carefully inside the side-arm test tube that contains [Co(salen)] without spillage.

Connect the tube with a rubber to a system consisting of two pipettes. Check that the water level reaches approximately 7 in the pipette connected to the tube. Insert a tightly fitting ground-glass stopper in the mouth of the tube and adjust the movable arm to make the water levels equal on both sides (Figure 7). Record the water level in the pipette connected to the tube (V_1). Finally, invert the side-arm tube being careful not to spill any of the mixture into the Tygon connecting tube. DMSO forms an adduct with [Co(salen)] that absorb O_2. As oxygen is absorbed, the water level inside the pipette

should rise. Note the changes occurring in the tube. Continue shaking until no further changes occur (10 to 20 minutes) and record the level of water (V_2). Adjust the moveable arm before the reading so that the water levels in the tubes are again equal (ensuring that the pressure within the apparatus is atmospheric). From the decrease in volume (V_2-V_1) at room temperature and constant pressure, the number of moles of oxygen absorbed per mole of [Co(salen)] can be calculated.

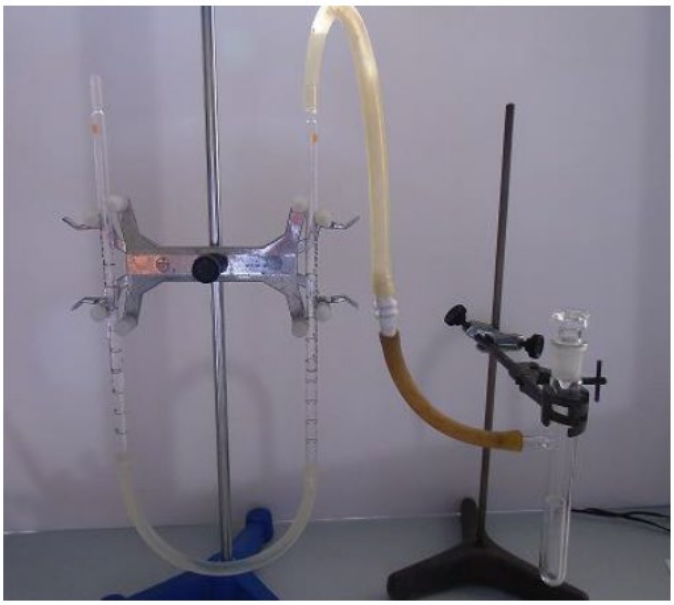


Figure 7. Apparatus to be used for oxygen binding studies.

Waste management: Discard the solution in the waste disposal labelled 'Waste [Co(salen)]+DMSO'.

ADDITIONAL QUESTIONS

Section 1

1. Calculate the percent yield obtained in the process of synthesis of H_2salen. Data: density of salicylaldehyde = 1.164 g/mL; density of ethylendiamine = 0.895 g/mL.

2. Calculate the percent yield obtained in the synthesis of [Co(salen)].

3. Determine the number moles of oxygen absorbed by [Co(salen)] in the presence of DMSO. What is the ratio Co:O_2?

4. According to the results in the previous question, write down the chemical reaction for obtaining the adduct between [Co(salen)], DMSO and oxygen. Draw a

structure for the oxygenated product and describe it. What is the oxidation state of cobalt and oxygen in this adduct?

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PRACTICE 7

SYNTHESIS AND PURIFICATION OF ACETYLFERROCENE, [Fe(η^5-C_5H_5)(η^5-$C_5H_4COCH_3$)]. SYNTHESIS OF FERROCENE

INTRODUCTION

The chemical behaviour of ferrocene reveals the aromatic characteristic of the coordinated cyclopentadienyl rings which experience electrophilic substitution reactions more easily than benzene. In addition, the ferrocene is thermally stable and is not attacked by oxygen in the air or water at room temperature and pressure. However, it can lose an electron easily and produce the ferrocene cation, $[Fe(\eta^5\text{-}C_5H_5)_2]^+$ with a reduction potential of E^O = +0.40 V.

In this practice we are going to firstly study the reaction of acetylation that takes place with acetic anhydride in the presence of phosphoric acid as a catalyst; and secondly, we will synthesise the hexafluorophosphate of ferrocene. The extent to which the reaction of acetylation is produced depends on the experimental conditions: temperature; reaction time; amount of catalyst; etc. The reaction is usually never complete and so you obtain a mixture of ferrocene and acetylferrocene to be separated later.

OBJECTIVES

1. Perform the acetylation reaction that takes place between ferrocene and acetic anhydride using phosphoric acid as catalyst.

2. Follow the progress of the reaction using thin layer chromatography.

3. Perform the purification of acetylferrocene with column chromatography.

4. Perform the oxidation reaction of ferrocene-to-ferrocene cation.

EXPERIMENTAL PROCEDURE

Material	Reagents
Glass rod	Ferrocene
100 mL conical flask	Acetic anhydride
Magnetic stirrer	Phosphoric acid
Beakers: 250 mL (x1)	Hexane
100 mL (x3)	Ethyl acetate
50 mL (x1)	Sodium bicarbonate
Pipettes	Chloroform
Thermometer	Silica gel
Separating funnel	Iron(III) chloride hexahydrate
Chromatography plates	Potassium hexafluorophosphate
Glasswool	Acetone
Chromatography column	NaOH 6M
Clamps	
Capillaries	
Glass funnel	
Büchner flask and Büchner funnel	

A) Synthesis of acetylferrocene, [Fe(η^5-C_5H_5)(η_5-$C_5H_4COCH_3$)](in fume hood)

In a 100 mL conical flask, dissolve 0.45 g of ferrocene in 9 mL of acetic anhydride. Carefully add 6 drops of phosphoric acid (85%) and heat the reaction mixture in a hot water bath to 60-70 °C for 45 minutes while stirring. Follow the progress of the reaction with thin layer chromatography using hexane-ethyl acetate (10:1) as eluent at different times (0, 25 and 45 minutes). Afterwards, pour the resulting mixture onto 20 g of crushed ice. When all the ice has melted, neutralise the solution with 6M NaOH (approximately 15 mL) and sodium hydrogencarbonate until effervescence stops. Cool for a further 5 minutes and extract three times with 5 mL of chloroform using a separating funnel. Evaporate the chloroform solution to dryness overnight with an air stream (in the hood). Collect the solids by filtering on a Buchner funnel, wash with water, and press the solids as dry as possible between sheets of filter paper.

B) Acetylferrocene purification. (In fume hood)

Acetylferrocene is purified by column chromatography using a silica gel column chromatography and a mixture of hexane:ethyl acetate (10:1) as eluent. The crude product obtained in the previous step is dissolved in a minimum of chloroform and the solution is added carefully to the top of the column. Using the above eluent, acetylferrocene elutes more slowly than ferrocene. Collect the fractions of both compounds and evaporate to dryness on the rotary evaporator to yield an orange solid. Collect the solid, and record the yield.

Waste management: Remove chloroform in the bottle labelled as 'Halogenated solvents: chloroform'.

Waste management: Remove the rest of solvents in the bottle labelled as 'Non-halogenated solvents'.

Waste management: Remove silica gel in the bottle labelled as 'Contaminated silica gel'.

C) IR spectra of the synthetised compounds

Record the IR spectra of ferrocene and acetylferrocene, print them, and compare following the instructions.

D) Synthesis of hexafluorophosphate ferrocene.

Dissolve 0.22 g of ferrocene in 5 mL of acetone in a 50 mL beaker using the sonicator. Meanwhile, in another 100 mL beaker, dissolve 0.35 g of iron (III) chloride in 15 mL of water. Add the ferrocene solution in drops to that of the iron (III) chloride while continuously stirring with a magnetic stirrer. Once the addition has finished and a dark colour solution appears, keep stirring during several minutes until all the ferrocene reacts.

The resulting solution is filtered with a pleated paper filter and collected in a 100 mL beaker. Add to this solution 0.25 g of KPF_6 dissolved in 10 mL of water. The resulting solution is left on an ice bath until a complete crystallisation of the desired

product forms dark-violet needles. The solid obtained is vacuum filtered with two paper filters, rinsed with a small amount of cold water and finally air dried. Determine the yield.

E) Magnetic moment determination of ferrocene and hexafluorophosphate of ferrocene. (Optional)

Use the magnetic balance to determine the magnetic moment of ferrocene and hexafluorophosphate ferrocene. Compare the results.

Waste management: Introduce the obtained product in the bottle labelled as 'ferrocenium hexafluorophosphate'

ADDITIONAL QUESTIONS

1. Write the equation of the acetylferrocene reaction.

2. What is the role of the catalyst? Propose an equation that proves it.

3. Which compound elutes first: $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4COCH_3)]$ or $[Fe(\eta^5\text{-}C_5H_5)_2]$? Why?

4. If the eluted products are colourless, how can their location on a chromatographic plate be established? Which methods can be used to detect the elution of colourless products in a chromatographic column?

5. Write the equation for the ferrocene.

6. Determine its equilibrium constant. Will it be obtained quantitatively?

7. What is the electronic configuration of both complexes? (Ref. 3)

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PRACTICE 8

PREPARATION AND RESOLUTION OF $[Co(en)_3]^{3+}$ ENANTIOMERS.

INTRODUCTION

In 1813 Jean Baptiste Biot noticed that plane-polarised light was rotated either to the right or the left when it passed through single crystals of quartz or aqueous solutions of tartaric acid or sugar. In 1848 Louis Pasteur was able to separate using laboratory methods two different kinds of crystals from tartaric acid. The solution of one crystal deviated polarised light clockwise, while the other deviated to the left.

Substances that can rotate plane-polarised light are said to be optically active. Those that rotate the plane clockwise (to the right) are said to be dextrorotatory (Latin dexter, 'right'). Those that rotate the plane counterclockwise (to the left) are called levorotatory (Latin laevus, 'left'). These directions are designed (+) and (-) (or sometimes, *d* and *l*), respectively. Substances that are composed only of one of these forms are called ***chiral***. A pair of such objects that are mirror images of each are called ***enantiomers*** or ***optical isomers***. The magnitude of the rotations observed for a pair of enantiomers is always the same. The only difference between these compounds is the direction in which they rotate plane-polarised light. If equal amounts of the two enantiomers are present in a sample, we obtain a ***racemic mixture***.

The direction and magnitude of rotation can be measured experimentally with a polarimeter. A polarimeter consists of a light source, two prisms, and a cell containing the solution of the optically active compound. A sodium lamp is usually used as the light source and the wavelength of its D line is 589.3 nm. The light provided by the source is not polarised, after passing through a polarising lens (prism), the only light remaining is oscillating in one plane (polarised plane). This light is then passed through a solution of an optically active compound, which results in a rotation of the plane of oscillation. A second polarising lens (prism) is used in combination with a detector to find the angle of rotation (Figure 1).

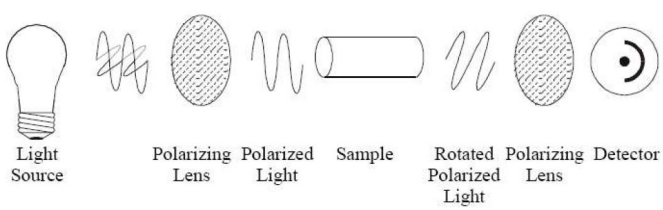


Figure 1

The magnitude of the rotation is not only determined by the intrinsic properties of the molecule, but also by the concentration, path length, and wavelength of light. To standardise the optical rotations reported in the literature, a parameter has been defined as the specific rotation $[\alpha]_\lambda$ (equation (1)):

$$[\alpha]_\lambda^T = \frac{\alpha}{lc} \quad (1)$$

α = rotation angle measured by the polarimeter in degrees

λ = wavelength used to measure the rotation in nanometres (D line of sodium, 589.3 nm)

l = path length (usually 1 dm)

c = concentration measured in g/mL

Normally $[\alpha]_\lambda$ values are quoted in the literature at 20 ºC. There is a slight temperature dependence on optical rotation, which can be corrected using equation (2).

$$[\alpha]_\lambda^{20} = [\alpha]_\lambda^T \cdot [1 + 0.0001\,(T - 20)] \quad (2)$$

Generally, when we intend to compare several compounds, we use molecular rotation, $[M]_\lambda$ that is defined in equation (3):

$$[M]_\lambda = M \cdot [\alpha]_\lambda / 100 \quad (3)$$

where M represents the molecular mass.

The percent optical purity (x) of a material is the ratio of the measured specific rotation, $[\alpha]_{\lambda\ \text{measured}}$, to the standard pure specific rotation, $[\alpha]_{\lambda\ \text{standard}}$ (equation (4)):

$$X = \frac{[\alpha]_\lambda\ measured}{[\alpha]_\lambda\ standard} \times 100 \quad (4)$$

The percentage of the major enantiomer in a mixture of enantiomers can be calculated as (equation (5)):

$$\%\ enantiomer = x + \frac{(100 - x)}{2}$$

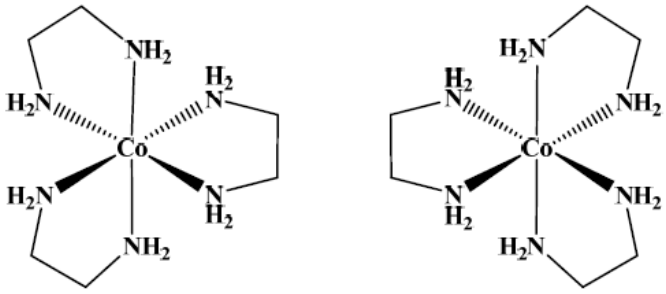
Thus, if a sample is an equal mixture of (+) and (-) enantiomers, the measured rotation is zero and $X = 0$, so the % (major enantiomer) = 50%.

Pasteur correctly reasoned that the rotatory property of the tartaric acid must lie in the structure of the molecule itself since the crystals dissolved to produce solutions

that rotated the light. Optical activity is usually associated with organic molecules containing asymmetric carbon. However, optical activity is a general property that can be found in any molecule that cannot be superimposed on its mirror image. Inorganic molecules may be chiral based on asymmetric nitrogen, and phosphorus or sulphur atoms, but a larger number of chiral inorganic compounds do not have asymmetric atoms. Instead, the chirality of these molecules is due to the overall molecular symmetry, specifically the absence of an improper rotation axis S_n. Since S1 is equivalent to a symmetry plane and S2 is equivalent to a centre of symmetry, enantiomers do not necessarily contain a symmetric plane or an inversion centre.

Optical activity in octahedral transition metal complexes in which the metal centre is coordinated to three bidentate ligands is an extensively studied example of chirality. These compounds are included in point group D_3.

A well-known example of chirality in the octahedral metal complex is that of cation tris(ethylenediamine)cobalt(III), $[Co(en)_3]^{3+}$ (Figure 2). Alfred Werner isolated (or resolved) the mirror image form of this cation in 1912. Although it was known that $(+)[Co(en)_3]^{3+}$ must have one of the structures shown in Figure 2, it was not until 1954 that the absolute structure was determined to be the one on the left. The designation by the Greek letters Λ and Δ are similar to the R and S descriptors used in organic chemistry. There is no correlation of Λ and Δ with dextrorotatory or levorotatory.



Λ (+) enantiomer **Δ (–) enantiomer**

Figure 2

The separation (resolution) of enantiomers in a racemic mixture constitutes a challenge since these compounds exhibit identical physical and chemical properties: solubility, reactivity, melting points, etc. In fact, the only differences between these compounds are: a) the direction in which they rotate plane polarised light, equal but opposite angles; and b) the ability to interact/react differently with other enantiomers. These differences are sufficient to allow their separation and analysis.

One of the more common pathways to the resolution of enantiomers is the method called ‘asymmetric induction of second order’. An optically active compound reacts with the molecules of the racemic mixture and gives compounds (diastereomers) with different solubilities, which could be separated by precipitation, crystallisation, and filtration.

OBJECTIVES

This practice aims to synthesise a cobalt (III) complex $[Co(en)_3]Cl_3$ (en = ethylenediamine) and to proceed with the resolution and characterisation of its optical isomers. Furthermore, racemization of one enantiomer will be achieved using activated charcoal.

The practice will be carried out in two laboratory sessions.

GENERAL PROCEDURE

The complex $[Co(en)_3]^{2+}$, formed in situ from $CoCl_2 \cdot 6H_2O$ and an excess of ethylenediamine, will be oxidised with 30% H_2O_2 to give the inert complex $[Co(en)_3]Cl_3$ isolated as a mixture of the two optical isomers. These isomers will then be resolved as diastereomers by crystallisation in the presence of the optically active anion (+)tartrate.

Two diastereomers, [(+) $Co(en)_3$][(+) tart]Cl and [(-) $Co(en)_3$][(+) tart]Cl, can be formed when L (+) tartrate is added to the racemic solution of the cobalt complex; these have, of course, different physical properties, and in particular, different solubilities. With a proper choice of conditions, it is possible to fractionally crystallise one diastereomer. In this case [(+) $Co(en)_3$][(+) tart]Cl, which happens to be the least soluble, is obtained from solution as the pentahydrate and can be isolated through filtration (the other diastereomer remaining in solution).

The optical isomer, [(+) $Co(en)_3$]$I_3 \cdot H_2O$ ($[\alpha]_{589.3} = +89^o$), is obtained directly by adding I^- to the solution from which [(+) $Co(en)_3$][(+) tart]$Cl \cdot 5H_2O$ was previously obtained.

The other isomer, [(-) $Co(en)_3$]$I_3 \cdot$H2O, is obtained by adding I^- to the solution from which the (+) isomer was previously precipitated. The solid that precipitates with I^- is a mixture of crystals of the racemate [(±) $Co(en)_3$]$I_3 \cdot H_2O$ and pure [(-) $Co(en)_3$]$I_3 \cdot H_2O$. The latter is much more soluble in warm water than the racemate and may be extracted into solution. On cooling, the desired enantiomer [(-) $Co(en)_3$]$I_3 \cdot H_2O$ precipitates with $[\alpha]_{589.3} = -89^o$.

EXPERIMENTAL PROCEDURE

Reagents and materials

Materials	Reagents
Polarimeter	$CoCl_2 \cdot 6H_2O$
50, 100 and 150 mL beakers	L (+) tartaric acid
5 Ml pipette	Ethylenediamine
10, 50, and 100 mL graduated cylinders	30% H_2O_2
25 mL volumetric flask	NaOH (beads)
Stirring heating plate	NaI
Vacuum filtering flask	NH_3 0,1M
Frit glass filter	6M and 12M HCl
Büchner filtration funnel	Activated charcoal
Thermometer	Ethanol
Conical funnel	Acetone
Mortar and pestle	
Watch glass	
Parafilm ®	

A) Synthesis of tris(ethylenediamine)cobalt(III) chloride, $[Co(en)_3]Cl_3$ (This experiment must be done in the hood).

1. Weigh 9.0 g of CoCl2·6H2O in a 20 mL beaker, dissolve the solid in 20 mL of distilled water while stirring with a magnetic stir bar.

2. In a 250 mL beaker, prepare a solution adding 7.6 mL of ethylenediamine in 10 mL of distilled water. After cooling the solution in an ice bath, add 4.0 mL of 6M HCl. Then add this solution to the previously prepared cobalt solution and maintain the mixture in an ice bath.

3. Add 10 mL of 30% H_2O_2 in small portions while constantly stirring. Be careful since a vigorous effervescence can occur.

4. Once the addition has finished, take the beaker from the ice and continue stirring until no effervescence appears (this process could take few minutes).

5. Heat the resulting solution in a water bath at a constant temperature 60-80ºC while stirring in the heating plate. Concentrate the solution to a 40 mL volume. This process will take one hour approximately. Use the temperature probe to control heat.

6. Place the beaker in an ice bath. When the reaction mixture has been cooled, carefully add 30 mL of concentrated HCl (12M) in small amounts and 60 mL of ethanol. Agitate with a glass rod during the addition. Maintain the solution in the ice bath to let the compound precipitate (30 minutes approximately).

7. When the reaction mixture has been cooled for the specified amount of time, take the beaker from the ice, and quickly filter the orange needles that have formed. It is important to filter the solution while it is cold to improve the yield. Wash the crystals with small amounts of cold ethanol and acetone. Leave the product in the filter funnel and suck air through it for several minutes, and then allow to air dry.

8. Collect the precipitate in a watch glass, weigh the amount obtained and determine the yield of the reaction.

B) Resolution of the tris (ethylenediamine) cobalt (III) complex cation

B-1. Optical Activity of L (+) – tartaric acid

To become familiar with the measurements of the optical activity we will proceed previously with the measurement of L (+) - tartaric acid. The following procedure is be followed:

1. Weigh 5.000 g of acid and dissolve in the minimum of distilled water. Transfer this solution to a 25 mL volumetric flask and dilute to mark with distilled water.

2. Before measuring the solution, adjust the polarimeter to 0 by introducing distilled water in the sample holder. Discard then the water from the sample holder and fill the sample holder with your prepared solution. Fill the sample holder to the top and ensure no bubbles are present; if there are bubbles; tilt the sample holder to ensure the bubbles are in the curved part of the holder and not in the top or bottom of the sample holder.

3. Open the hatch of the polarimeter, place the sample holder in the tube, and then close the hatch again. Measure the sign and magnitude of rotation following the instructions provided by the polarimeter, do not forget to write down the temperature. Determine $[\alpha]_D$ value for L (+) tartaric acid.*

* Data: $[\alpha]_D$ value for L (+) tartaric acid at 20ºC ranges from +12.0 and +12.8º.

B-2. Synthesis of [(+) $Co(en)_3$][(+) tart]$Cl \cdot 5H_2O$.

1. Weigh 7.2 g (21 mmol) of the complex $[Co(en)_3]Cl_3$ and 3.9 g (26.1 mmol) of L (+) tartaric acid in a 100 mL beaker. Add 25 mL of distilled water and stir for about one minute.
2.- Weigh 2.1 g (52.5 mmol) of NaOH in a watch glass and add to the stirring solution. Cover the beaker with the watch glass and gently heat the solution (this part must be done in the hood) until all of the solids are dissolved. Check that the pH of the solution is basic; if not, add one or two NaOH beads.
3. Remove the beaker from the heat, quickly remove the stir bar, and let the solution cool slowly to room temperature. Cover with Parafilm® and leave the beaker undisturbed overnight (end of the first session).
4. Set up a Buchner funnel for vacuum filtration and filter off the orange crystals. Save the dark orange solution into a conical flask, cover it with Parafilm (this solution should contain primarily your other (–) enantiomer), and store it in your drawer for later. **CAUTION! Save the filtrate solution before washing the crystals.** Rinse the crystals with 1:1 water/acetone solution (total volume 20 mL) and then pure acetone. Pull air through the product and weigh the solid when dry.

Grind the crystals in a mortar to facilitate their dissolution and set aside for experiments B-3 and B-4

B-3. Optical activity of diasteromer [(+) $Co(en)_3$][(+) tart]$Cl \cdot 5H_2O$.

1. To determine the specific rotation of this diastereomer, dissolve approximately 0.300g of the complex in 10 mL water, transfer this solution to a 25 mL volumetric flask and dilute to mark with distilled water.
2. Calibrate the polarimeter with distilled water. Fill the sample holder with the previous diastereomer solution. Ensure minimal bubbles are present, and that any bubbles are in the curved portion of sample holder. Place the sample holder back in the machine and begin to take the reading.

3. Measure the sign and magnitude of rotation following the instructions provided by the polarimeter, do not forget to write down the temperature. Determine $[\alpha]_D$ value for the [(+) $Co(en)_3$][(+) tart]$Cl \cdot 5H_2O$ enantiomer.

B-4. Preparation and measurement of the optical activity of enantiomers [(+) $Co(en)_3]I_3 \cdot H_2O$ and [(-) $Co(en)_3]I_3 \cdot H_2O$.

[(+) $Co(en)_3]I_3 \cdot H_2O$

1. Weigh 2.0 g (3.9 mmol) of [(+) $Co(en)_3$][(+) tart]$Cl \cdot 5H_2O$ in a 50 mL beaker. Then add one bead of sodium hydroxide and 15 mL of distilled water.
2. Dissolve the solid using the heating plate for a few minutes with constant stirring. Caution: If the solution is heated for more than five minutes, racemization will occur.
3. Add 3.6 g (24 mmol) of NaI to the previous solution while heating and stir for one more minute.
4. After cooling in an ice bath, filter through a Buchner and rinse the crystals with an ice-cold solution of NaI (3 g NaI in 10 mL water) to remove the tartrate. Rinse then with 10 mL ethanol, and finally with 10 mL acetone. Allow the [(+)-Co(en)3]I3·H2O to air-dry and determine the yield.
5. Measure its $[\alpha]_D$ by dissolving approximately 0.300 g in 25 mL water.

[(-) $Co(en)_3]I_3 \cdot H_2O$

1. Dilute to 30 mL the filtrate solution from which [(+) $Co(en)_3$][(+) tart]$Cl \cdot 5H_2O$ was precipitated in the fourth point of Section B-2. Add one bead of NaOH and gently heat the solution by stirring until it is dissolved.
2. Heat the solution and add 8.5 g (57 mmol) of NaI while stirring.
3. Upon cooling in an ice bath, impure [(-) $Co(en)_3]I_3 \cdot H_2O$ precipitates. Filter through a Buchner and rinse with a cold solution of NaI (3 g NaI in 10 mL water).
4. Collect the wet solid and dissolve the precipitate by stirring in 35 mL water at 50 ºC in a 50 mL beaker. Filter off the undissolved racemate while warm and add 5 g of NaI to the filtrate solution.
5. Crystallisation of [(-) $Co(en)_3]I_3 \cdot H_2O$ occurs on cooling the filtrate solution in an ice bath. Filter the precipitate, rinse with ethanol, then acetone, and finally air-dry. Weigh the solid and determine the yield and $[\alpha]_D$ by dissolving approximately 0.300 g in 25 mL water.

B-5. Racemization of [(+) $Co(en)_3]I_3 \cdot H_2O$ or [(-) $Co(en)_3]I_3 \cdot H_2O$

1. Dissolve approximately 1 g of [(+) $Co(en)_3]I_3 \cdot H_2O$ or [(-) $Co(en)_3]I_3 \cdot H_2O$ in the minimum volume of warm water (4-5 mL). Add a small amount of activated charcoal and boil the solution for approximately 30 min covering the beaker with a watch glass. Do not allow the solution to dry, and add water if necessary.
2. Filter the solution while hot, adding a few grams of NaI to the solution filtrate (until it becomes clear) to aid precipitation of the racemate.
3. Filter the solid through a Buchner, wash with alcohol, acetone, and finally air-dry. Determine $[\alpha]_D$ of the racemized product.

Waste management: Discard all products obtained in the waste disposal.
Waste management: Discard all solutions in the waste container labelled 'Waste Co-en'
Waste management: Filter papers should be introduced in the container labelled 'Filter paper with Co'.

ADDITIONAL QUESTIONS

1. Write down all the reactions that take place in this practice.

2. Determine the yield of all isolated products. Comment on the results obtained.

3. In the purification of both (+) and (-) $[Co(en)_3]I_3 \cdot H_2O$, the compounds were washed with water containing NaI. What was the purpose of the NaI?

4. If $[\alpha]_D$ of pure [(+) $Co(en)_3]I_3 \cdot H_2O$ is +89º, what percentage of this enantiomer is present in the sample? Assume that the only impurity is [(-) $Co(en)_3]I_3 \cdot H_2O$. Do the same for the other enantiomer. Use these data to recalculate the yields obtained for each synthesised enantiomer.

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PRACTICE 9

SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

INTRODUCTION

Cobalt (III) complexes are inert to the replacement of the ligand and its synthesis is kinetically controlled. This enables isolating more coordination compounds of Co(IlI) that for other more labile metal ions, as well as obtaining and separating isomers of various classes.

This practice illustrates important aspects of the coordination chemistry of this metal ion through the synthesis of four of its complexes (the last two being bond isomers) and the study of some of its properties.

OBJECTIVES

1. Obtention of four mononuclear complexes of Co(III).

2. Characterisation by IR spectroscopy: ligand identification and binding modes.

PRELIMINARY QUESTIONS

A-1. Why does the general method for synthesis of a Co(III) complex generally begin from Co(II) salts?

A-2. Is it possible to oxidise Co^{2+} (aq) with hydrogen peroxide?

A-3. How is the carbonate anion coordinated with the metal ion? (see step D-2)

EXPERIMENTAL PROCEDURE

Materials and reagents

Material	Reagents
Glass rod	Concentrated HCl

Magnetic stirrer	Concentrated NH_3
Volumetric cylinders: 50, 25 and 10 mL	96% ethanol
(one of each)	HCl 6 M, 4 M and 2 M
Beakers: 250 mL (x1),	$[Co(CO_3)(NH_3)_4]NO_3$
150 mL (x2) and 100 mL (x2)	Activated charcoal
Filtering plate	$NaNO_2$
Filtering flask	
Conical funnel	
Crushed ice bath	
IR spectrophotometer	
Agate or kaolin mortar and pestle	
Test tubes and rack	
2 watch glasses	
Clamps for test tubes	

A) Synthesis of $[CoCl(NH_3)_5]Cl_2$ (in fume hood)

1. Weigh 5 g of the $[Co(CO_3)(NH_3)_4]NO_3$ complex in a 250 mL beaker and dissolve in 50 mL of water. Then add drops of 4 mL of concentrated hydrochloric acid until all the CO_2 is expelled.

2. Add 10 mL of concentrated NH_3 to the resulting solution and heat to 60-70 °C for 20 minutes. Regulate the heat to prevent the solution from boiling over, but be sure to continue heating for 20 minutes. Then add drops of 80 mL of concentrated hydrochloric acid.

3. Cool down the solution to room temperature and purple-red crystals ($[CoCl(NH_3)_5]Cl_2$) will appear. Separate the crystals and wash the product several times, by decantation, with small amounts of ice-cold distilled water. Then filter through a water aspirator vacuum with glass fritted funnel. Wash with cold ethanol and let the solid dry on the stove at 120ºC. Calculate the yield.

B) Synthesis of $[Co(NH_3)_6]Cl_3$ (in fume hood)

1. Proceed as in the previous synthesis using **$[Co(CO_3)(NH_3)_4]NO_3$** as starting reagent and a 100 mL beaker. The amounts of reagents are reduced by half (2.5 g **$[Co(CO_3)(NH_3)_4]NO_3$**, 25 mL of water and 2 mL of HCl) and 0.5 g of activated charcoal and 10 mL of concentrated ammonia are added.

2. Gently warm (60-70 °C) for 30-45 minutes. When half-time heating, determine the pH of the solution with indicator paper and if the solution is not basic add more concentrated ammonia until basic pH (in contrast to the previous A synthesis, **no more HCl is added** during heating). It is recommended to cover the beaker with a watch glass.

3. Activated charcoal is removed by filtration over **filter paper, never on a filtering plate**. Slowly add concentrated hydrochloric acid to the orange filtrate solution until the formation of a precipitate (1-3 mL).

4. Cool the solution in an ice bath and filter the precipitate on a filtering plate with vacuum. The solid is rinsed with a few millilitres of 4 M HCl and ethanol. Leave it to dry in air, weigh, and calculate the yield.

ADDITIONAL QUESTIONS TO STEPS A AND B

STEP A: $[CoCl(NH_3)_5]Cl_2$

A-4. Write and adjust all the reactions that take place in this synthesis.

A-5. If Co(III) complexes are inert for the ligand substitution, why is an instant release of CO_2 is observed when the complex carbonate solution is acidified?

A-6. Why is there only one additional ligand of NH_3 in the coordination sphere of the metal?

STEP B

B-1. What is the role of activated charcoal in this synthesis?

C) Synthesis of the chloro isomers of pentaamminenitritecobalt(III) and pentaamminenitrocobalt(III) chloride and their interconversion.

C-1 Synthesis of $[Co(ONO)(NH_3)_5]Cl_2$ (In fume hood)

1. Weigh 1.5 g of $[CoCl(NH_3)_5]Cl_2$ in a 100 mL beaker and dissolve in a mixture of 5 mL of concentrated NH_3 and 50 mL of water. Gently heat to dissolve. Filter with pleated paper filter if turbidity appears and let the filtrate cool to 10 °C.

2. Slowly acidify with 2 M HCl until approximately pH 6.5 while stirring and maintaining the solution in cold.

3. Add 1.5 g of $NaNO_2$ to the previous solution and once dissolved, add 1.5 mL of 6 M HCl.

4. Cool in an ice bath about half an hour. The formed solid is filtered on a filtering plate with vacuum and is rinsed with cold water and ethanol and dried with a stream of air. Calculate the yield.

C-2 Synthesis of $[Co(NO_2)(NH_3)_5]Cl_2$ (In fume hood)

1. Weigh 1.0 g of the compound from the previous step in a 100 mL beaker and dissolve with 20 mL of warm water containing 6-7 drops of concentrated NH_3 (cover the beaker with a watch glass and gently warm until a colour change (to ochre) is observed.

2. Cool the resulting solution on an ice bath and add 10 mL of concentrated HCl. Let the solution crystallise. Filter the product and rinse it with ethanol letting it dry in an air stream.

C-3 Isomers interconversion

1. Prepare a dilute solution of each of the two isomers. Divide the solution of the nitrite complex in two test tubes and heat one of them on a water bath observing any change that appears.

2. Acidify slightly the nitrite complex solution with 4 M HCl and irradiate it with ultraviolet light during half an hour (it is better to place several drops of the nitrite

solution on a watch glass to facilitate irradiation according to the experimental device in use). What is observed?

D) IR spectra of the Co(III) compounds synthetised

1. Record the IR spectra of each of the samples and print them following the equipment instructions.

Waste management: introduce all the obtained products in the corresponding bottles.
Waste management: remove all solutions in the bottle labelled as 'Waste Co-en'.
Waste management: introduce all filters in the bottle labelled as 'Filter paper with Co'.

ADDITIONAL QUESTIONS TO STEPS C AND D

STEP C

C-1. Which of the two isomers is more stable?

C-2. Why is the nitrite complex obtained first?

STEP D

D-1. Assign the peaks corresponding to the ligands by consulting the bibliography below.

D-2. In the case of the carbonate complex, indicate which is the preferent mode of coordination.

D-3. Compare the spectra of the complexes containing nitro and nitrite ligands and indicate any differences between them.

ADDITIONAL BIBLIOGRAPHY

1. R. J. Angelici, *Técnica y Síntesis en Química Inorgánica*, ed. Reverté, 1979, pp 181-194.

2. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley and Sons, 4th de., New York, 1986 (general).

3. K. Nakamoto, J. Fujita y H. Murata, *J. Am. Chem. Soc.*, **1958**, *80*, 4817-4823.