

Metallic pigments

Introduction

Coloured compounds are used in a variety of obvious applications. We encounter these in dyes for our cloth, pH indicators and pigments for paints. Dyes are commonly organic compounds, they adhere well to fabric, are nontoxic and inexpensive. However, they tend to fade over time, like indigo, the dye used for blue jeans. For a surface exposed to sunlight for extended periods of time like the paint used for cars this would be a major problem. Traditionally paint pigments are inorganic in nature and often metal based. They are fade resistant, adhere well to surfaces such as metal, but some are also toxic.

Compounds are coloured because they absorb certain wavelength of visible light. For example a compound that absorbs green light will reflect all colours but green and appear red. The absorbed light is used to move electrons from low energy orbitals to high energy orbitals. The energy difference determines which colour is absorbed. Most organic colours have a large energy difference and do not absorb visible light. Consequently they appear colourless. Transition metal compounds have very small energy differences and are often brightly coloured. The colours can be fine-tuned by changing the ligands around the metal. Ligands are covalently attached to the central metal and the resulting ion is written in square brackets. Counter ions are present to balance the charges.

Today we will explore cobalt compounds. Co has several stable oxidation states, the most common are Co^{2+} and Co^{3+} . The oxidation can be achieved by reacting Co^{2+} with O_2 or H_2O_2 . We will bind different ligands to the metal, some as simple as H_2O , others larger organic compounds such as phenanthrene. Some are neutral, others are charged. In all cases, the ligand binds to the metal by making a covalent bond using its free electron pair(s), typically, O or N atoms.

Chemical nomenclature can be very confusing. So that you can find the correct starting materials we will use the bottle labels in the experimental section, but will use the correct way to write the chemical in the equations. For example, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ seems like very wet Cobalt nitrate. In reality this material is a salt composed of a Hexaaquacobalt dication, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and two nitrate ions, NO_3^- and should be written as $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$. The water molecules are covalently bonded to the cobalt and one of the free electron pairs on oxygen is used to make the bond.

Safety

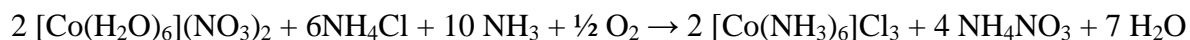
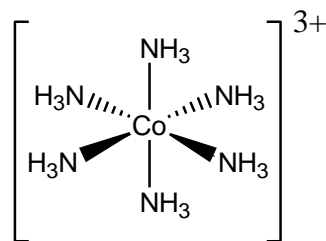
Personal protective equipment including safety goggles, gloves and a lab coat must be worn at all times during the experiment. Long pants should be worn along with close-toed shoes. No food

or drink is allowed in the lab. Always work in the fumehood and do not pour any chemicals down the drain.

Procedures

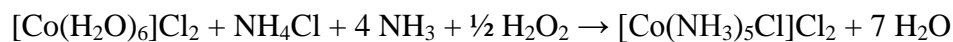
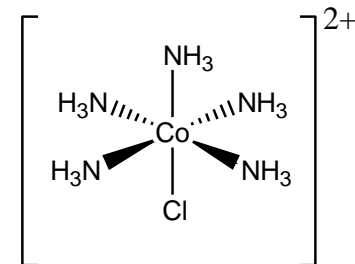
Each group will perform one of the long experiments (**1** or **2**) and all of the short experiments (**3** – **7**). Make sure you start with the long experiment and perform the short experiments while the long reaction is occurring.

Experiment 1: Preparation of Hexaamminecobalt(III)chloride $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$



1. In a 250 mL Erlenmeyer flask, dissolve 2.91 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 1.59 g of NH_4Cl in 15 mL of water.
2. Add 6 mL of concentrated aqueous ammonia and 0.04 g of activated charcoal.
3. Vigorously bubble air through the solution for 1 hour. (Ask instructor for apparatus setup)
4. Isolate the charcoal contaminated precipitate by vacuum filtration using a Buchner funnel
5. In a 50 mL beaker, place 15 mL of water then 6 drops of HCl.
6. Dissolve the charcoal contaminated precipitate in the HCl solution.
7. Heat gently for 10 minutes.
8. Remove the activated charcoal by vacuum filtration.

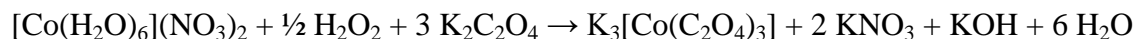
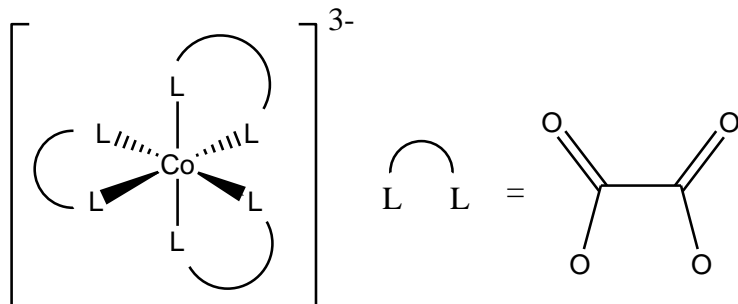
Experiment 2: Preparation of Chloropentaamminecobalt(III) chloride $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$



1. In a 125 mL Erlenmeyer flask, dissolve 2.51 g of NH_4Cl in 15 mL of conc. aq. NH_3 .
2. Slowly add 5 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$.

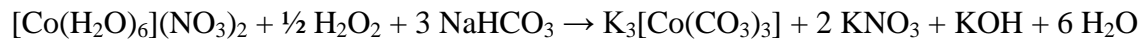
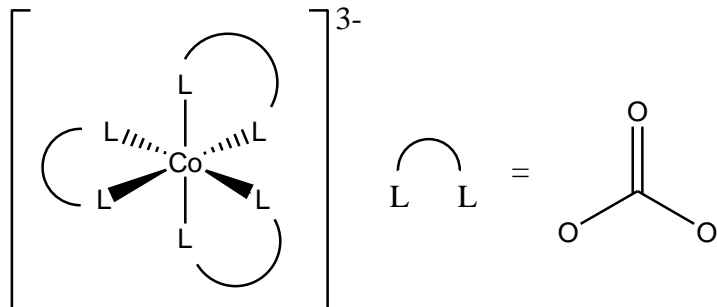
3. Add 5 mL of 30% H₂O₂ dropwise.
4. Slowly add 15 mL of conc. HCl.
5. Heat reaction for 1 hour in a hot water bath using a stirrer/hotplate.
6. Cool reaction in an ice water bath for 15 minutes.
7. Filter the crystals using vacuum filtration with a Buchner funnel and wash with 15 mL of 1:1 HCl:H₂O.
8. Collect both precipitate and filtrate. Observe and record color of both.

Experiment 3: Preparation of Trioxalatocobaltate(III) [Co(ox)₃]³⁻



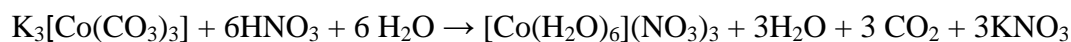
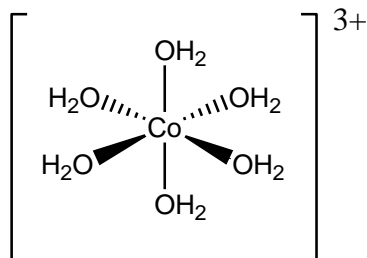
1. In a 100 mL beaker, dissolve 0.10 g of Co(NO₃)₂·6H₂O in 80 mL of deionized water. This stock solution is not a final product and is used in the next reaction. Only one group needs to make this solution for the entire class, maybe your teacher would like to show off their weighing skills!
2. In a 50 mL beaker, add 1.55 g of K₂C₂O₄·H₂O and a magnetic stirbar and 10 mL of the [Co(H₂O)₆]²⁺ stock solution .
3. Add 10 mL of 3% H₂O₂ to oxidize the metal and heat gently to 30-40 °C on the stirrer/hotplate (set at 1) while stirring and continue stirring until a blue-green color is seen (10 to 15 minutes).
4. Observe and record color.

Experiment 4: Preparation of Tricarbonatocobaltate(III) [Co(CO₃)₃]³⁻



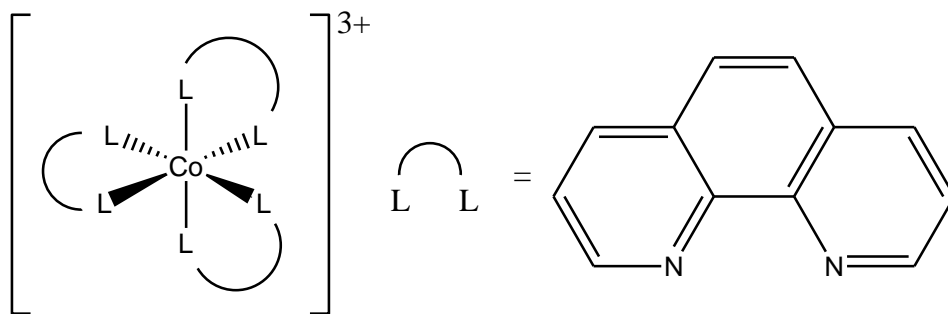
1. In a 50 mL beaker, dissolve 1 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 20 mL of water and add a few drops of 30% H_2O_2 .
2. In a 250 mL Erlenmeyer flask, add 5.66 g of NaHCO_3 and a magnetic stirbar to 20 mL of water and add a few drops of 30% H_2O_2 .
3. Add the contents of the beaker to the E. Flask while stirring. There will be rapid gas evolution so stir for approximately 1 minute until bubbling stops.
4. Observe and record the colour. This solution will be used in experiment 5.

Experiment 5: Preparation of Hexaaquacobalt(III) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$



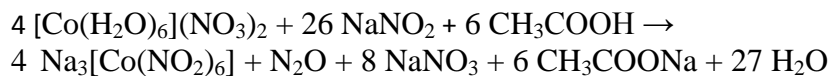
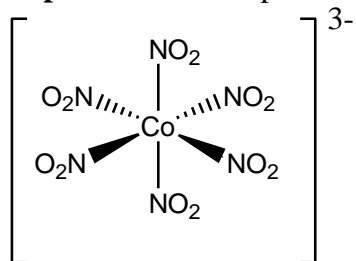
1. In a 250 mL beaker, add 20 mL of the $[\text{Co}(\text{CO}_3)_3]^{3-}$ solution to 80 mL of 4M HNO_3 .
2. Observe and record the colour. This solution is used in experiment 6.

Experiment 6: Preparation of Tris(1,10-phenanthroline)cobalt(III) $[\text{Co}(\text{phen})_3]^{3+}$



1. In a 50 mL beaker, add 0.12 g of 1,10-phenanthroline and 10 mL of the $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ solution.
2. Observe and record the colour.

Experiment 7: Preparation of Hexanitrocobaltate(III) $[\text{Co}(\text{NO}_2)_6]^{3-}$



1. In a test tube, dissolve 0.37 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 3 mL of water.
2. In a second test tube, dissolve 3.08 g of NaNO_2 in 5 mL of water.
3. In a 125 mL Erlenmeyer flask, combine the solutions and add 1.5 mL of glacial acetic acid with a magnetic stirbar.
4. Dilute with water to 50 mL then stir vigorously for 2 minutes.
5. Observe and record colour.

References

Riordan, A.R., Jansma, A., Fleischman, S., Green, D.B., Mulford, D.R., **2005**. *The Chemical Educator*. 10, 115-119