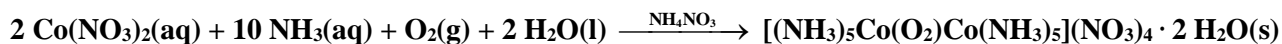


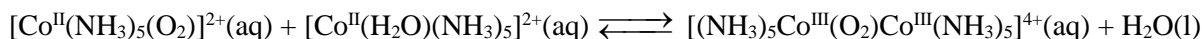
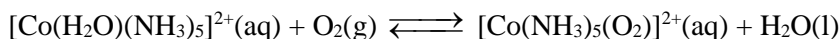
Preparation of μ -peroxido-bis(pentaammine-cobalt(III)) nitrate dihydrate

μ -peroxido-bis(pentaammine-cobalt(III)) nitrate dihydrate is a dark brown crystalline decomposing on air. In solutions it is stable only in the presence of ammonia with concentration over $\approx 7 \text{ mol dm}^{-3}$, in acidic solutions decomposes eliminating gaseous oxygen. The structure contains a bridging ligand Co–O–O–Co with a non-planar arrangement.

μ -peroxido-bis(pentaammine-cobalt(III)) nitrate dihydrate μ -peroxido-bis(pentaammine-cobalt(III)) nitrate dihydrate may be prepared by oxidation of cobalt(II) salt with air oxygen.



Depending on the concentration of ammonia, the various complexes with general formula $[\text{Co}(\text{H}_2\text{O})_{6-x}(\text{NH}_3)_x]^{2+}$ are formed. The main reactant with oxygen is aqua-pentaammine-cobalt(II) cation $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]^{2+}$. Its two-step preparation can be expressed by the equation:



The isolated final product may also contain another cobalt complexes. Their quantity can be diminished by the reaction conditions.

Work

Prepare μ -peroxido-bis(pentaammine-cobalt(III)) nitrate dihydrate from 0,0200 moles of cobalt(II) nitrate.

Chemicals

- cobalt(II) nitrate hexahydrate $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$, dark pink crystalline substance,
- ammonia, NH_3 concentrated water solution, $w(\text{NH}_3) = 0,26$,
- ammonium nitrate NH_4NO_3 , white crystalline substance,
- sulphuric acid H_2SO_4 , concentrated water solution, $w = 0,96$,
- ethanol $\text{CH}_3\text{CH}_2\text{OH}$, denaturated spirit.

Procedure

Built up an apparatus according to the Fig. 1.

① Fill the first gas-washing bottle with diluted (1 : 1) ammonia solution to decrease the losses of ammonia in the reactor caused by the intensive bubbling.

② The second gas-washing bottle will contain reactants. From the calculated amount of cobalt(II) nitrate hexahydrate prepare a 15 wt% aqueous solution. Filter the prepared solution directly to the gas-washing bottle. Add an aqueous solution of ammonium nitrate with concentration 1 mol dm^{-3} . The molar ratio of cobalt(II) and ammonium cations should be $n(\text{Co}(\text{NO}_3)_2) : n(\text{NH}_4\text{NO}_3) = 2 : 1$. Finally, add concentrated ammonia solution, three-times more than necessary according to the reaction. Put the reactor to a wide and high beaker, and fill it with ice.

③ The third gas-washing bottle acts as an absorber of unreacted ammonia. It contains sulphuric acid solution diluted in the volume ratio 1 : 10.

Switch on the water pump and start a moderate bubbling. Oxidation takes about 45 minutes. Let the precipitated product settle for few minutes and filter it out on a filter funnel with glass frit. Wash it with cool ammonia solution from the first gas-washing bottle and with ethanol. Let the product dry freely.

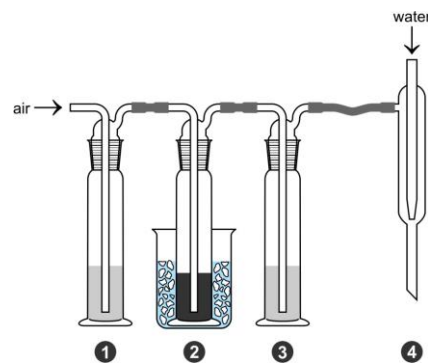
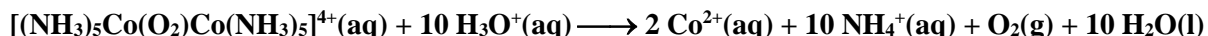


Fig. 1 Apparatus for oxidation with oxygen.

- 1 – ammonia solution (diluted 1 : 1),
 2 – reactor cooled with ice,
 3 – absorber = sulphuric acid solution (diluted 1 : 10),
 4 – water pump.

Determination of oxygen content

The dinuclear μ -peroxido-bis(pentaamine-cobalt(III)) complex cation decomposes in acidified solutions and gaseous oxygen is excluded.



From the measured volume of oxygen at given state conditions, the purity of the prepared product can be determined. The volume of any gas can be measured in an apparatus depicted on Fig. 2.

Work

Determine the purity of the prepared μ -peroxido-bis(pentaamine-cobalt(III)) nitrate dihydrate.

Chemicals

- hydrochloric acid, $c(\text{HCl}) = 0,25 \text{ mol dm}^{-3}$.

Procedure

Weigh about 0,4 g of the prepared product on analytical balances, and put it carefully into a boat in a fraction flask containing 50 cm³ of diluted hydrochloric acid (Fig. 2). Moving the separatory funnel up and down set the water levels in the measuring apparatus to be equal. Note the level of water in the burette.

Turn rapidly the fraction flask to vertical position. The boat with the product sample should sink in acid solution and quickly react to produce oxygen. No unreacted product must remain in the boat. As previously, moving the separatory funnel up and down set the water levels in the measuring apparatus to be equal. Note the level of water in the burette. The difference of water levels before and after the measurement represents the volume of excluded oxygen. Calculate the real quantity of μ -peroxido-bis(pentaamine-cobalt(III)) nitrate dihydrate in the weighted sample and consequently also the purity of the prepared product.

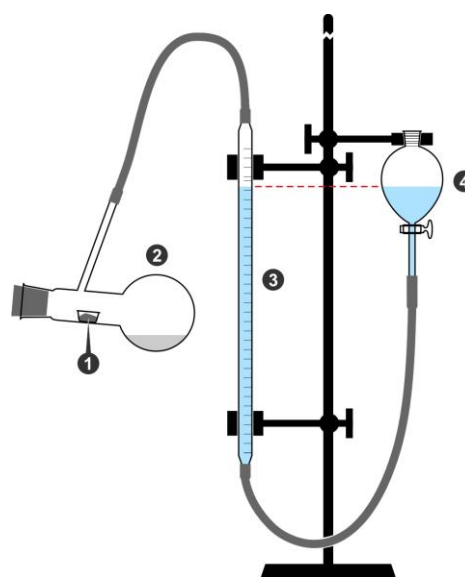


Fig. 2 Apparatus for measuring the volume of oxygen.

- 1 – a boat with the sample,
- 2 – fraction flask with diluted HCl,
- 3 – gas burette filled with water,
- 4 – separatory funnel.

Safety instructions

Cobalt(II) nitrate hexahydrate – $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

- R8** Contact with combustible material may cause fire.
- R20/21/22** Harmful by inhalation, in contact with skin and if swallowed.
- R36/37/38** Irritating to eyes, respiratory system and skin.
- S17** Keep away from combustible material.
- S26** In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
- S36/37/39** Wear suitable protective clothing, gloves and eye/face protection.

Ammonium nitrate – NH_4NO_3

- R8** Contact with combustible material may cause fire.
- R36/37/38** Irritating to eyes, respiratory system and skin.
- S17** Keep away from combustible material.
- S26** In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
- S36** Wear suitable protective clothing.

Ammonia – NH_3

- R10** Flammable.
- R23** Toxic by inhalation.
- S16** Keep away from sources of ignition – No smoking.
- S38** In case of insufficient ventilation wear suitable respiratory equipment.
- S7/9** Keep container tightly closed and in a well-ventilated place.

Oxygen – O_2

- S21** When using do not smoke.

Ethyl alcohol – $\text{C}_2\text{H}_5\text{OH}$

- R11** Highly flammable.
- S7** Keep container tightly closed.
- S16** Keep away from sources of ignition – No smoking.