Preparation of bis(sulphato)-μ-superoxido-bis(pentaammine-cobalt(III)) hydrogen sulphate trihydrate

Bis(sulphato)-μ-superoxido-bis(pentaamine-cobalt(III)) hydrogen sulphate trihydrate is a dark green crystalline substance containing dinuclear μ-superoxido-bis(pentaammine-cobalt(III)) cations $[(NH_3)_5Co(O_2)Co(NH_3)_5]^{5+}$ with a non-planar bridging group Co–O–O–Co. An unpaired electron is delocalized, hence both cobalt atoms are equivalent. The complex cation $[(NH_3)_5Co(O_2)Co(NH_3)_5]^{5+}$ may be prepared by the one-electron oxidation of μ-peroxido-bis(pentaammine-cobalt(III)) cation $[(NH_3)_5Co(O_2)Co(NH_3)_5]^{4+}$ with peroxo-disulphate anion.

$$\mathbf{2\ CoSO_4(aq) + 10\ NH_3(aq) + O_2(g) \xrightarrow{(NH_4)_2SO_4} [(NH_3)_5Co(O_2)Co(NH_3)_5](SO_4)_2(aq)}$$

$$\mathbf{2\ [(NH_3)_5Co^{III}(O_2)^{-II}Co^{III}(NH_3)_5](SO_4)_2(aq) + (NH_4)_2S_2O_8(aq) + 3\ H_2O(l) \longrightarrow}$$

$$\mathbf{\longrightarrow 2\ [(NH_3)_5Co^{III}(O_2)^{-I}Co^{III}(NH_3)_5](HSO_4)(SO_4)_2 \cdot 3\ H_2O(s) + 2\ NH_3(aq)}$$

As an oxidizing agents also cerium(IV) salts or potassium permanganate can be used.

Work

Prepare bis(sulphato)-μ-superoxido-bis(pentaammine-cobalt(III)) hydrogen sulphate trihydrate from 0,0200 moles of cobalt(II) sulphate.

Chemicals

- cobalt(II) sulphate heptahydrate $CoSO_4 \cdot 7\ H_2O$, dark pink crystalline substance,
- ammonia, NH_3 concentrated water solution, $w(NH_3) = 0{,}26$,
- ammonium sulphate $(NH_4)_2SO_4$, white crystalline substance,
- ammonium peroxo-disulphate $(NH_4)_2S_2O_8$, white crystalline substance,
- sulphuric acid H_2SO_4, concentrated water solution, $w = 0{,}96$,
- ethanol CH_3CH_2OH, denaturised spirit.

Procedure

Built up the same apparatus as in previous synthesis (Fig. 1).
Use equivalent quantities of cobalt(II) sulphate heptahydrate and ammonium sulphate instead of cobalt(II) nitrate hexahydrate and ammonium nitrate.
During the air bubbling, dissolve the calculated amount of ammonium peroxo-disulphate with a 25 % excess in small volume of water.
Once the oxidation is finished, add the ammonium sulphate solution to the reaction mixture in the gas-washing bottle. Shake the closed gas-washing bottle intensively for about three minutes. Let settle the precipitated dark green product (superoxido complex) in the gas-washing bottle cooled in an ice bath. Filter out the product on filter funnel with glass frit. Wash it with cool ammonia solution from the first gas-washing bottle and with ethanol. Dry the product in an air stream on the frit.

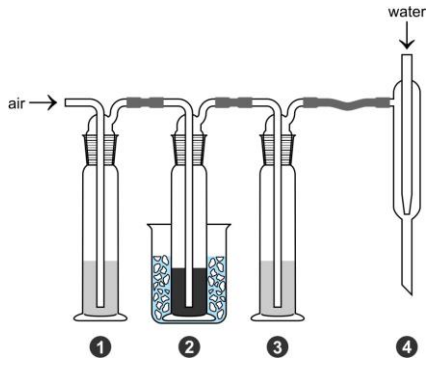

Fig. 1 Apparatus for oxidation with oxygen.

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

Safety instructions

***Cobalt(II) sulphate heptahydrate* – $CoSO_4 \cdot 7H_2O$**

R22	Harmful if swallowed.
R49	May cause cancer by inhalation.
R42/43	May cause sensitization by inhalation and skin contact.
R50/53	Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
S22	Do not breathe dust.
S45	In case of accident or if you feel unwell seek medical advice immediately (show the label where possible).
S53	Avoid exposure – Obtain special instructions before use.
S60	This material and its container must be disposed of as hazardous waste.
S61	Avoid release to the environment. Refer to special instructions/safety data sheet.

***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.

***Ammonium sulphate* – $(NH_4)_2SO_4$**

R22	Harmful if swallowed.
S22	Do not breathe dust
S24/25	Avoid contact with skin and eyes.

***Ammonium peroxo-disulphate* – $(NH_4)_2S_2O_8$**

R8	Contact with combustible material may cause fire.
R22	Harmful if swallowed.
R36/37/38	Irritating to eyes, respiratory system and skin.
R42/43	May cause sensitization by inhalation and skin contact.
S22	Do not breathe dust.
S24	Avoid contact with skin.
S26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S37	Wear suitable gloves.

***Oxygen* – O_2**

S21	When using do not smoke.

***Sulphuric acid* – H_2SO_4**

R23	Toxic by inhalation.
R34	Causes burns.
R49	May cause cancer by inhalation.
S23	Do not breathe gas/fumes/vapour/spray (appropriate wording to be specified by the manufacturer)
S45	In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
S36/37/39	Wear suitable protective clothing, gloves and eye/face protection.

***Ethyl alcohol* – C_2H_5OH**

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