Preparation of *trans*-bis(ethane-1,2-diamine)-dichlorido-cobalt(III) chloride

Trans-bis(ethane-1,2-diamine)-dichlorido-cobalt(III) chloride is a dark green crystalline substance very well soluble in water and almost insoluble in common organic solvents. In aqueous solution it decomposes stepwise:

$$[CoCl_2(en)_2]^+(aq) + H_2O(l) \longrightarrow [CoCl(en)_2(H_2O)]^{2+}(aq) + Cl^-(aq)$$

$$[CoCl(en)_2(H_2O)]^{2+}(aq) + H_2O(l) \longrightarrow [Co(en)_2(H_2O)_2]^{3+}(aq) + Cl^-(aq)$$

By evaporating a neutral solution at 90 – 100 °C the *trans*-isomer is changed to a racemic mixture of the Λ-*cis*-isomer and Δ-*cis*-isomer.
The *trans*-isomer may be prepared by oxidation of cobalt(II) chloride solution containing ethane-1,2-diamine. As an oxidizing agent gaseous oxygen may be used. After adding hydrochloric acid, heating and evaporating, a solid adduct *trans*-$[CoCl_2(en)_2]Cl \cdot HCl$ is formed.

$$\mathbf{4\ CoCl_2(aq) + 8\ en(aq) + O_2(g) + 8\ HCl(aq) \xrightarrow{\Delta T} 4\ \textit{trans}\text{-}[CoCl_2(en)_2]Cl \cdot HCl(s) + 2\ H_2O(l)}$$

By careful and moderate thermal decomposition of the adduct the trans-isomer is prepared.

$$\mathbf{\textit{trans}\text{-}[CoCl_2(en)_2]Cl \cdot HCl(s) \xrightarrow{110\ °C} \textit{trans}\text{-}[CoCl_2(en)_2]Cl(s) + HCl(g)}$$

Work

According to the following procedure prepare *trans*-bis(ethane-1,2-diamine)-dichlorido-cobalt(III) chloride.

Chemicals

- cobalt(II) chloride hexahydrate, $CoCl_2 \cdot 6\ H_2O$, dark violet crystalline substance,
- ethane-1,2-diamine (ethylene diamine), $NH_2CH_2CH_2NH_2$, colourless oily liquid, $\rho = 0{,}898\ g\ cm^{-3}$,
- hydrochloric acid, HCl, concentrated, $w(HCl) = 0{,}36$,
- ethanol, CH_3CH_2OH, denatured spirit,
- diethyl ether, $(C_2H_5)_2O$.

Procedure

Dissolve 5,0 g of finely powdered cobalt(II) chloride hexahydrate in 20 cm^3 of water. Add 2,8 cm^3 (= 2,5 g) of ethane-1,2-diamine. Pour the final solution to a gas-washing bottle and connect it to a water pump (Fig. 1). Bubble the mixture with oxygen for about one hour. Put the reaction mixture to a beaker with hot water to speed up the oxidation reaction. Once the oxidation is finished, transfer the solution from the gas-washing bottle to an empty beaker. Under continuous stirring add 10 cm^3 of concentrated hydrochloric. Bring the mixture in the beaker to a boil and evaporate *cca* half of its volume. Then, cool the mixture with ice. After cooling to room temperature, filter out the green adduct *trans*-$[CoCl_2(en)_2]Cl \cdot HCl$ on a Büchner funnel. Wash the adduct with ethanol and diethyl ether.
Put the adduct into an evaporating dish in thin layer, and heat it moderately over a ceramic wire gauze at temperature 110 – 125 °C for about 30 minutes. Eliminating gaseous hydrogen chloride a green crystalline *trans*-bis(ethane-1,2-diamine)-dichlorido-cobalt(III) chloride will be prepared.

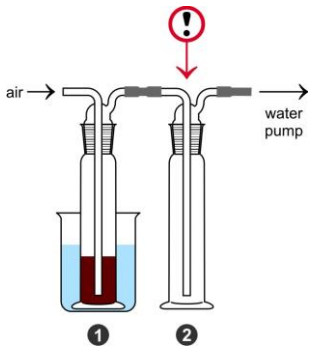


Fig. 1 Apparatus for preparation of *trans*-bis(ethane-1,2-diamine)-dichlorido-cobalt(III) chloride.

1 – reactor heated by hot water,
2 – safety vessel.

Preparation of *cis*-bis(ethane-1,2-diamine)-dichlorido-cobalt(III) chloride

Cis-bis(ethane-1,2-diamine)-dichlorido-cobalt(III) chloride is a violet crystalline substance very well soluble in water and almost insoluble in common organic solvents.
The procedure for preparation of the *cis*-isomer is based on stepwise isomerisation of the *trans*-isomer at higher temperature in a polar solvent.

$$\textit{trans}\text{-}[CoCl_2(en)_2]Cl(solv) \xrightarrow{\Delta T} \textit{cis}\text{-}[CoCl_2(en)_2]Cl(solv)$$

The extent of isomerisation can be determined by various analytical techniques, for example by visible spectroscopy. *Cis*-bis(ethane-1,2-diamine)-dichlorido-cobalt(III) chloride exists in form of two optical isomers (Λ-*cis* and Δ-*cis*) and their separation needs more demanding techniques.

Work

According to the following procedure prepare *cis*-bis(ethane-1,2-diamine)-dichlorido-cobalt(III) chloride.

Chemicals

- *trans*-bis(ethane-1,2-diamine)-dichlorido-cobalt(III) chloride, freshly prepared,
- ethanol, CH_3CH_2OH, denatured spirit,
- diethyl ether, $(C_2H_5)_2O$.

Procedure

In a small beaker dissolve 2,0 g of *cis*-bis(ethane-1,2-diamine)-dichlorido-cobalt(III) chloride in 5 cm^3 of water. Let stand the solution for 5 – 10 minutes. Put the beaker into a pre-heated water bath (Fig. 2). The solution changes its colour to violet. Evaporate *cca* half of its volume. Then, cool the mixture with ice. After cooling, filter out the violet *cis*-$[CoCl_2(en)_2]Cl$ on a filter funnel with glass frit. Wash the product with small amount of cold ethanol and diethyl ether.

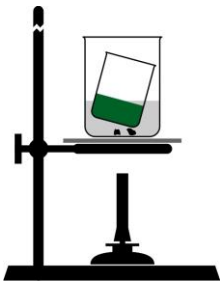
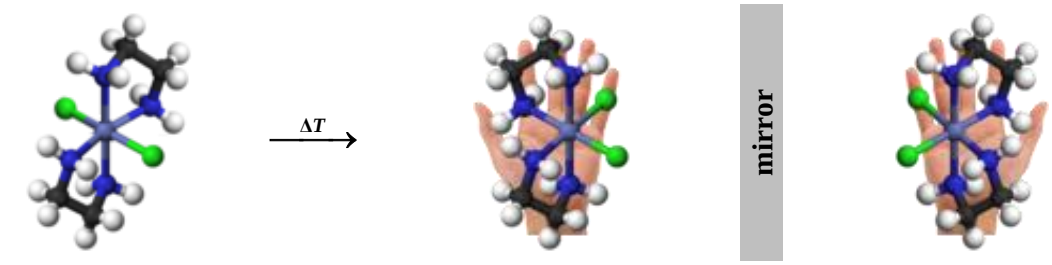


Fig. 2 Apparatus for preparation of *cis*-bis(ethane-1,2-diamine)-dichlorido-cobalt(III) chloride.

<u>*A note on isomerism*</u>: There are two structural (constitutional, geometrical) isomers (*cis*- and *trans*-) of the $[CoCl_2(en)_2]^+$ cation. Additionally, two optical isomers (enantiomers, Λ-*cis*- and Δ-*cis*-) of the *cis*-isomer are known. If we write a chemical equation in which the *cis*-$[CoCl_2(en)_2]Cl$ is a product, we always mean the mixture of two optical isomers, produced in statistically absolutely equal amounts. The final mixture containing the both enantiomers is called *racemic mixture* or *racemate*. A sample with only a single enantiomer is an *enantiomerically pure* or *enantiopure* compound.



trans-$[CoCl_2(en)_2]^+$

Λ-*cis*-$[CoCl_2(en)_2]^+$
Λ = Latin *laevus* = left

Δ-*cis*-$[CoCl_2(en)_2]^+$
Δ = Latin *dexter* = right

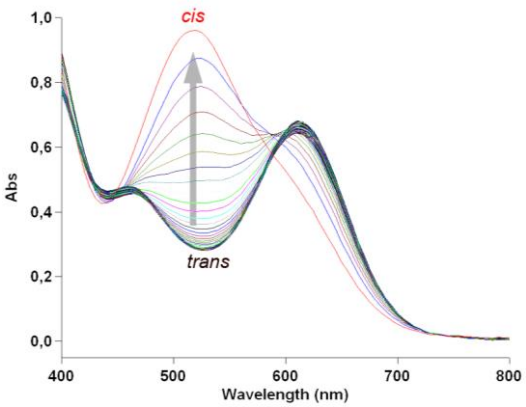


Fig. 3 Visible spectra of isomerization *trans*-$[CoCl_2(en)_2]Cl \rightarrow$ *cis*-$[CoCl_2(en)_2]Cl$. Measured in methanol at 50 °C at the Graz University (Austria).

Safety instructions

***Cobalt(II) chloride hexahydrate* – $CoCl_2 \cdot 6\ H_2O$**

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.

***Ethane-1,2-diamine (Ethylenediamine)* – $NH_2CH_2CH_2NH_2$**

R10	Flammable.
R34	Causes burns.
R21/22	Harmful in contact with skin and if swallowed.
R42/43	May cause sensitization by inhalation and skin contact.
S26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
S45	In case of accident or if you feel unwell seek medical advice immediately (show the label where possible).
S1/2	Keep locked up and out of the reach of children.
S36/37/39	Wear suitable protective clothing, gloves and eye/face protection.

***Hydrochloric acid* – HCl**

R34	Causes burns.
R37	Irritating to respiratory system.
S2	Keep out of the reach of children
S26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice

***Oxygen* – O_2**

S21	When using do not smoke.

Dichlorido-bis(ethane-1,2-diamine)cobalt(III) chloride, $[CoCl_2(en)_2]Cl$

R36/37/38	Irritating to eyes, respiratory system and skin.
S26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S36	Wear suitable protective clothing.

***Ethyl alcohol* – C_2H_5OH**

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

***Diethyl ether* – $(C_2H_5)_2O$**

R12	Extremely flammable.
R19	May form explosive peroxides.
S9	Keep container in a well-ventilated place.
S16	Keep away from sources of ignition – No smoking.
S29	Do not empty into drains.
S33	Take precautionary measures against static discharges.