

Oxalato complexes

The oxalate anion is derived from oxalic acid, systematically named ethanedioic acid HOOC–COOH. As a ligand, it acts commonly as a tetradentate ligand, bridging two metal atoms (Fig. 1). In mononuclear complexes it is bidentately coordinated, forming five-membered chelate rings (Fig. 2). Oxalate ligand is also rarely tridentately coordinated, where the oxygen atom of chelate ring is simultaneously bonded to another metal atom.

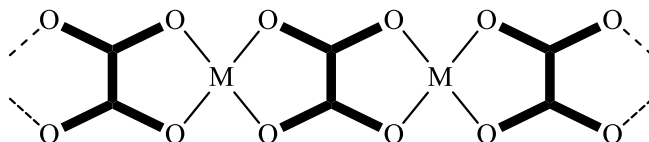


Fig. 1 Schematic representation of tetradentately coordinated oxalate anion.

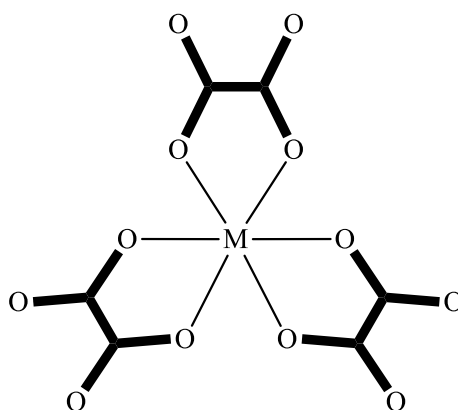


Fig. 2 Schematic representation of bidentately coordinated oxalate anion.

Preparation of potassium tris(oxalato) aluminate trihydrate

Potassium tris(oxalato) aluminate trihydrate $K_3[Al(C_2O_4)_3] \cdot 3H_2O$ is a colourless crystalline substance, well soluble in water and insoluble in ethanol. In its structure, three oxalate ligands are coordinated to aluminium atom by six oxygen atoms, forming three chelate rings. The central aluminium atom has coordination number 6. The complex anion $[Al(C_2O_4)_3]^{3-}$ has octahedral geometry.

Potassium tris(oxalato) aluminate trihydrate may be prepared by a two-step synthesis.

In the first step, aluminium reacts with strong alkali potassium hydroxide solution (eq. 5). Gaseous hydrogen is excluded in the reaction.



In the second step, hydroxido ligands of the formed tetrahydroxido aluminate anion $[Al(OH)_4]^-$ are replaced by oxalate ligands (eq. 6).



Work

Prepare potassium tris(oxalato) aluminate trihydrate from 1,00 g of aluminium.

Chemicals

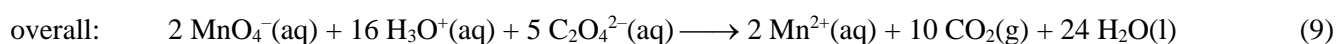
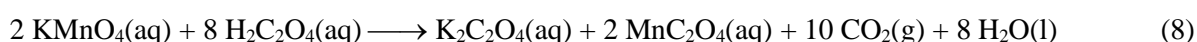
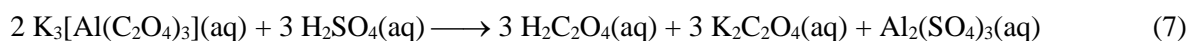
- aluminium, Al, finely powdered,
- potassium hydroxide, KOH, white crystalline substance granules or flakes,
- oxalic acid dihydrate, $(COOH)_2 \cdot 2H_2O$, white crystalline substance,
- ethanol, CH_3CH_2OH , denaturised spirit.

Procedure

Prepare 11,0 wt% potassium hydroxide solution containing three-times more hydroxide than necessary for the reaction 5. Add slowly 1,0 g of finely powdered aluminium in very small portions (!) to the potassium hydroxide solution. When no more bubbles of hydrogen are visible heat the solution to a boil and filter the hot solution on the fluted filter paper. Add slowly the calculated amount of oxalic acid dihydrate to the hot filtrate. Let the reaction mixture boil until the formed precipitate dissolves. Filter the solution, cool it to room temperature and add 50 cm³ of ethanol. Put the mixture to an ice bath. Filter out the excluded crystals of K₃[Al(C₂O₄)₃]·3H₂O on Büchner funnel, wash them with ethanol and dry them freely on open air.

Evidence of oxalate anions

Put few miligrams of the product K₃[Al(C₂O₄)₃] · 3H₂O to a test tube with acidified potassium permanganate solution. Slightly heat the test tube. In acidified solution the complex decomposes (eq. 7) and free oxalate anions are subsequently oxidized by permanganate anions forming gaseous carbon dioxide (eq. 8). The originally violet solution changes to colourless.



Safety instructions

Aluminium – Al

- R15** Contact with water liberates extremely flammable gases.
- R17** Spontaneously flammable in air.
- S7/8** Keep container tightly closed and dry.
- S43** In case of fire use .. (indicate in the space the precise type of fire-fighting equipment. If water increases the risk add: Never use water).

Potassium hydroxide – KOH

- R35** Causes severe burns.
- S26** In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
- S37/39** Wear suitable gloves and eye/face protection.

Oxalic acid dihydrate = Ethanedioic acid dihydrate – (COOH)₂ · 2H₂O

- R21/22** Harmful in contact with skin and if swallowed.
- S2** Keep out of the reach of children.
- S24/25** Avoid contact with skin and eyes.