*Kirk-Othmer Encyclopedia of Chemical Technology.*


# FLUORINE COMPOUNDS, INORGANIC, COPPER

## 1. Copper(II) Fluorides

Copper(II) forms several stable fluorides, eg, cupric fluoride [7789-19-7], $CuF_2$, copper(II) fluoride dihydrate [13454-88-1],], $CuF_2{\cdot}2H_2O$, and copper hydroxyfluoride [13867-72-6], CuOHF, all of which are interconvertible. When $CuF_2$ is exposed to moisture, it readily forms the dihydrate, and when the latter is heated in the absence of HF, $CuOHF{\cdot}H_2O$ results. The colorless crystals of anhydrous $CuF_2$ are triclinic in structure and are moisture sensitive, turning blue when exposed to moist air. Physical properties of $CuF_2$ are listed in Table 1. $CuF_2$ reacts with ammonia to form $CuF_2{\cdot}5NH_3$.

Copper(I) fluoride is believed to be unstable (1) and no evidence for its existence has been found using mass spectrometry (2).

### 1.1. Manufacture

Several methods of synthesis for anhydrous $CuF_2$ have been reported, the most convenient and economical of which is the reaction of copper carbonate and anhydrous hydrogen fluoride to form the monohydrate, $CuF_2{\cdot}H_2O$. Part of the water content from the monohydrate is removed by addition of excess HF. The excess HF is decanted and the remaining mass transferred to a Teflon-lined tray and dried under an atmosphere of hydrogen fluoride. The decanted material may also be dehydrated in a nickel or copper tray under an atmosphere of fluorine at 150–300°C. Both routes have successfully resulted in ultrapure (99.95%) white $CuF_2$ in good yields. The other method for the preparation of high purity anhydrous copper(II) fluoride is by the direct fluorination of commercially available CuOHF (3), or the action of a mixture of HF and $BF_3$ on $CuF_2{\cdot}2H_2O$ (4).

### 1.2. Uses

Copper(II) fluoride is used as a fluorinating reagent (5–7) in the fluorination of partially hydrogenated silanes; in superconductors (8–10); as a cathode material for high energy density primary and secondary batteries (qv) (11–14); for the skeletal rearrangements of olefins (15); low temperature isomerization of pentane and hexane (16); as a selective herbicide (17); as a termite repellant (18); as a fungicide (19); in the manufacturing of conductive bicomponent fibers for electromagnetic shields (20); as a catalyst for the removal of nitrogen oxides from flue gases (21), and for the synthesis of heterocyclic tetraaromatics (22). The dihydrate is used in the casting of gray iron.

The high purity anhydrous copper(II) fluoride must be stored in a tightly closed or sealed container under an atmosphere of argon. The dihydrate may be stored in polyethylene-lined fiber drums. The ACGIH (1992–1993) adopted toxicity value for copper as Cu is 1 mg/m$^3$, and for fluorides a $F^-$, 2.5 mg/m$^3$.

In spite of the many applications for copper(II) fluoride, demand is restricted to 1 to 10 kg lots. It is available in the United States from Advance Research Chemicals, Aldrich Chemicals, Atomergic, Aesar,

**Table 1. Physical Properties of $CuF_2$**

| Property | Value |
|---|---|
| molecular weight | 101.54 |
| melting point, °C | $785 \pm 10$ |
| boiling point, °C | 1676 |
| solubility, g/100 g | |
| water | 4.75 |
| anhydrous HF | 0.01 |
| aqueous 21.2% HF | 12.1 |
| density, g/cm$^3$ | 4.85 |
| $\Delta H_f$, kJ/mol[a] | −539 |
| $\Delta G_f$, kJ/mol[a] | −492 |
| $S$, J/(mol K)[a] | 77.45 |
| $C_p$, J/(mol K)[a] | 65.55 |

[a] To convert from J to cal, divide by 4.184.

Johnson/Matthey, Cerac Corp., and PCR Corp. The 1993 price for the anhydrous copper(II) fluoride varied from $400 to $600/kg depending on the amount required. The dihydrate is available at $22/kg.

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DAYAL T. MESHRI
Advance Research Chemicals, Inc.

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