Kirk-Othmer Encyclopedia of Chemical Technology.

FLUORINE COMPOUNDS, INORGANIC, COBALT

1. Cobalt Difluoride

Cobalt difluoride [10026-17-2], CoF_2, is a pink solid having a magnetic moment of $4,266 \times 10^{-23}$ J/T (4.6 Bohr magneton) (1) and closely resembling the ferrous (FeF_2) compounds. Physical properties are listed in Table 1. Cobalt(II) fluoride is highly stable. No decomposition or hydrolysis has been observed in samples stored in plastic containers for over three years.

CoF_2 is manufactured commercially by the action of aqueous or anhydrous hydrogen fluoride (see Fluorine compounds, inorganic–hydrogen) on cobalt carbonate (see Cobalt compounds) in a plastic, ie, polyethylene/polypropylene, Teflon, Kynar, rubber, or graphite-lined container to avoid metallic impurities. The partially hydrated mass is lavender pink in color. It is dried at 150–200°C and then pulverized to obtain the anhydrous salt. A very high (99.9%) purity CoF_2 having less than 0.05% moisture content has also been prepared by reaction of $CoCO_3$ and liquid hydrogen fluoride. This is a convenient synthetic route giving quantitative yields of the pure product. The reaction of $CoCl_2$ and anhydrous HF is no longer commercially practical because of environmental considerations. The various hydrates, eg, the cobalt(II) fluoride dihydrate [13455-27-1], $CoF_2 \cdot 2H_2O$, cobalt(II) fluoride trihydrate [13762-15-7], $CoF_2 \cdot 3H_2O$, and cobalt(II) fluoride tetrahydrate [13817-37-3], $CoF_2 \cdot 4H_2O$, have been obtained by the reaction of freshly prepared oxide, hydroxide, or carbonate of cobalt(II) and aqueous hydrogen fluoride (2).

Cobalt difluoride, used primarily for the manufacture of cobalt trifluoride, CoF_3, is available from Advance Research Chemicals, Inc., Aldrich Chemicals, and PCR in the United States, Fluorochem in the UK, and Schuhardt in Germany. The 1993 price varied from $60 to $200/kg depending on the quantity and the price of cobalt metal. CoF_2 is shipped as a corrosive and toxic material in DOT-approved containers.

2. Cobalt Trifluoride

Cobalt(III) fluoride [10026-18-3] or cobalt trifluoride, CoF_3, is one of the most important fluorinating reagents. Physical properties may be found in Table 1. It is classified as a hard fluorinating reagent (3) and has been employed in a wide variety of organic and inorganic fluorination reactions. CoF_3, a light brown, very hygroscopic compound, is a powerful oxidizing agent and reacts violently with water evolving oxygen. It should be handled in a dry box or in a chemical hood and stored away from combustibles, moisture, and heat. The material should not be stored in plastic containers for more than two years. The crystals possess a hexagonal structure.

Cobalt trifluoride is readily prepared by reaction of fluorine (qv) and $CoCl_2$ at 250°C or CoF_2 at 150–180°C. Direct fluorination of CoF_2 leads to quantitative yields of 99.9% pure CoF_3 (4).

CoF_3 is used for the replacement of hydrogen with fluorine in halocarbons (5); for fluorination of xylylalkanes, used in vapor-phase soldering fluxes (6); formation of dibutyl decalins (7); fluorination of alkynes (8); synthesis of unsaturated or partially fluorinated compounds (9–11); and conversion of aromatic compounds to

Table 1. Physical Properties of the Cobalt Fluorides

Parameter	Cobalt difluoride[a]	Cobalt trifluoride
molecular weight	96.93	115.93
melting point, °C	1127	926
solubility, g/100 g[b]		
water	1.36	dec
anhydrous HF	0.036	
density, g/cm^3	4.43	3.88
ΔH_f, kJ/mol[c]	−672	−790
ΔG_f, kJ/mol[c]	−627	−719
S, J/(mol K)[c]	82.4	95
C_p, J/(mol K)[c]	68.9	92

[a] The bp of CoF_2 is 1739°C.
[b] CoF_2 is also soluble in mineral acids.
[c] To convert J to cal, divide by 4.184.

perfluorocyclic compounds (see Fluorine compounds, organic). CoF_3 rarely causes polymerization of hydrocarbons. CoF_3 is also used for the conversion of metal oxides to higher valency metal fluorides, eg, in the assay of uranium ore (12). It is also used in the manufacture of nitrogen fluoride,NF_3, from ammonia (13).

CoF_3 is available from Advance Research Chemicals, Inc., Aldrich Chemicals, Aesar, Johnson/Matthey, PCR, Pfaltz & Bauer, Noah Chemicals, and Strem Chemicals of the United States, Fluorochem of the UK, and Schuhardt of Germany. Demand for cobalt trifluoride varies from 100 to 1500 kg/yr and the 1993 price for smaller quantities ranged from $300 to $350/kg.

The ACGIH adopted TLV/TWA for 1992–1993 for fluorides as F^- is TWA 2.5 mg/m^3, and for cobalt as Co metal dust TWA 0.05 mg/m^3. Dust masks should be used while handling both the cobalt fluorides and all other cobalt compounds. CoF_3 is shipped as an oxidizer and a corrosive material.

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DAYAL T. MESHRI
Advance Research Chemicals, Inc.

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