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FLUORINE COMPOUNDS, INORGANIC, TIN

The main binary tin fluorides are stannous fluoride and stannic fluoride. Because the stannous ion, Sn^{2+}, is readily oxidized to the stannic ion, Sn^{4+}, most reported tin and fluorine complexes are of tin(IV) and fluorostannates. Stannous fluoroborates have also been reported.

1. Stannous Fluoride

Stannous fluoride [7783-47-3], SnF_2, is a white crystalline salt that has mp 215°C (1), bp 850°C, and is readily soluble in water and hydrogen fluoride. At 20°C stannous fluoride dissolves in water to a concentration of 30–39%; in anhydrous hydrogen fluoride to 72–82% (2–4).

The pH of a freshly prepared 0.4% solution of stannous fluoride is between 2.8 and 3.5. Initially clear aqueous solutions become cloudy on standing owing to hydrolysis and oxidation. The insoluble residue is a mixture containing stannous and stannic species, fluoride, oxide, oxyfluorides, and hydrates.

Stannous fluoride probably was first prepared by Scheele in 1771 and was described by Gay-Lussac and Thenard in 1809. Commercial production of stannous fluoride is by the reaction of stannous oxide and aqueous hydrofluoric acid, or metallic tin and anhydrous hydrogen fluoride (5, 6). SnF_2 is also produced by the reaction of tin metal, HF, and a halogen in the presence of a nitrile (7).

Stannous fluoride is used widely in dentifrices (qv) and other dental preparations because of its anticaries effect (8). The chemistry (9) involved in cavity prevention is thought to be reaction of stannous fluoride and the hydroxyapatite, $Ca_5(PO_4)_3OH$, of the tooth to form the more insoluble fluoroapatite, $Ca_5(PO_4)_3F$. More concentrated solutions of stannous fluoride react with hydroxyapatite to produce $Sn_3F_3PO_4$ [12592-27-7] (10). The role of SnF_2 in reducing acidogenicity of dental plaque *in vivo* has also been studied (11). On heating stannous fluoride under nitrogen with stannic fluoride, Sn_7F_{16}, Sn_3F_8, Sn_2F_6, and $Sn_{10}F_{34}$ are formed (12).

Other uses of SnF_2 are in the synthesis of fluorophosphate glasses having low melting temperatures (13–15), in formation of transparent film (16), and in the preparation of optically active alcohols (17).

2. Fluorostannites and Fluorostannates

Complexes of the type $MSnF_3$, where M is NH_4 [15660-29-4], Na [13782-22-4], K [13782-23-5], and Cs [13782-25-7], have been crystallized from aqueous solutions (18–20). Solutions of these salts deposit tin(II) oxide crystals indicating hydrolysis but not oxidation. From molten mixtures of SnF_2 and NaF, RbF, and CsF, both the $MSnF_3$ (M = Na [13782-22-4], K [13782-23-5], Rb [13782-24-6], and Cs [13782-25-7]) and the fluorostannate salts, $MSnF_5$ (M = Na [58179-42-3], K [58179-40-1], Rb [72264-75-6], and Cs [72264-76-7]) have been obtained (21). Complexes of the type $Cd(H_2O)_6{\cdot}(SnF_3)_2$ [125445-76-3], $Zn(H_2O)_6{\cdot}SnF_3$ [125445-75-2] (22), $SnCl_3{\cdot}SnF_3$ [108632-61-7], $N_2H_6{\cdot}(SnF_3)_2$ [99625-93-1] (23), $N_2H_5{\cdot}SnF_3$ [73953-53-4] (24), $Ca(SnF_3)_2$ [69244-56-0] (25), $Ni(SnF_3)_2$ [26442-44-4] (26), $Co(SnF_3)_2$ [26442-43-3] (26) have also been reported.

3. Stannic Fluoride

Stannic fluoride [7783-62-2], SnF_4, is a white solid that sublimes at 705°C and hydrolyzes in water to form insoluble stannic acid. It can be prepared by reaction of fluorine and probably ClF_3 or BrF_3 with virtually any tin(II) or tin(IV) compound, eg, Sn, SnO, SnO_2, SnS, SnS_2 (27), and $SnCl_2$ (28). Reaction of $SnCl_4$ and HF (29) forms $SnCl_4{\cdot}SnF_4$ which can be decomposed by heating to 750°C where pure SnF_4 sublimes. Stannic fluoride forms numerous complexes as a Lewis acid. The other methods of preparation for stannic fluoride include the oxidation of SnF_2 by a halogen in acetonitrile (30, 31); the reaction of NF_3O and Sn (32); and the reaction of COF_2 and SnO_2 (33). Stannic fluoride is used in the manufacture of glass (qv) (34).

4. Stannous Fluoroborate

Stannous fluoroborate [13814-97-6], $Sn(BF_4)_2$, is prepared in electrochemical cells using tin and fluoroboric acid (35, 36), by reaction of 80% HF and H_3BO_3 followed by reaction with $Sn(OH)_2$ (37); and from the reaction of mossy tin and 30–70% HBF_4 (38). The main use of stannous fluoroborate is in electroplating (qv) (39).

5. Hexafluorostannates

The hexafluorostannate anion [21340-04-5], SnF_6^{2-}, forms readily and is stable over a wide pH range. Numerous hexafluorostannates have been prepared by dissolving stannates in excess hydrofluoric acid, dissolving stannic acid in excess HF and neutralizing, or by reaction of salts and SnF_4. Many of these stable and generally water-soluble hexafluorostannates were prepared as early as 1857. Spectral studies of the SnF_6^{2-} anion have been reported (40). Some of the newer hexafluorostannates are $K{\cdot}NaSnF_6$ [112813-21-5] (41), $CsNa{\cdot}SnF_6$ [112813-23-7], $Rb{\cdot}NaSnF_6$ [112813-22-6] (42), and $N_2H_6{\cdot}SnF_6$ [128493-43-6] (43).

6. Safety, Handling, and Toxicity

Stannous fluoride is used in dentifrices and dental preparations. The OSHA permissible exposure limit (44) and ACGIH (45) established TLV for fluoride is 2.5 mg/m^3 of air.

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