Polysulfonylamines, CXCII. Polynäre Verbindungen aus Di(4-fluorobenzolsulfonyl)amin (FAH), 1,1,3-Trimethylharnstoff (TrMU) und Dimethylamin (Me₂NH): Bildung und Strukturen des Cokristalls FAH·TrMU (Z' = 1), des Salzes Me₂NH₂⁺·FA⁻ (Z' = 6) und des Salz-Cokristalls FAH·TrMU·Me₂NH₂⁺·FA⁻ (Z' = 1). Bemerkungen zur Oxophobie von C–F-Gruppen in Kristallstrukturen

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Cocrystallization of di(4-fluorobenzenesulfonyl)amine, (4-F-C₆H₄SO₂)₂NH (= FAH), with 1,3,3-trimethylurea (TrMU) from dichloromethane/petroleum ether afforded the molecular cocrystal FAH·TrMU (1, monoclinic, P₂₁/n, Z' = 1) and the salt cocrystal FAH·TrMU·Me₂NH₂⁺·FA⁻ (2, monoclinic, P2₁, Z' = 1). The minor product 2 resulted from a hydrolysis reaction of TrMU and was obtained by serendipity. The salt component of 2, Me₂NH₂⁺·FA⁻ (3, monoclinic, C2, Z' = 6), was prepared by metathesis of [Me₂NH₂]Cl with Ag[FA] and is not isomorphous to its previously reported congeners Me₂NH₂⁺·(4-X-C₆H₄SO₂)₂N⁻ (4–7 for X = Cl, Br, I or Me, all monoclinic, Cc, Z' = 1). The three new structures display one-dimensional arrays (catemers) based upon classical two- or three-centre hydrogen bonds that use N–H or N⁺–H groups as donors and S=O, C=O or N⁻ groups as acceptors. In 1, the catemers consist of alternating FAH and TrMU molecules, in 3 of alternating Me₂NH₂⁺ and FA⁻ ions (six independent formula units), in 2 of alternating Me₂NH₂⁺ and FA⁻ ions (one independent unit) and FAH···TrMU··· heterodimers acting as side-groups to the ionic polymer. The packings of 1–3 are completely devoid of short fluorne-oxygen contacts below the van der Waals limit, as are all the known crystal structures containing FAH or FA⁻ entities (“oxophobia” of the C–F groups). The Z’ = 6 structure of 3 may be interpreted as a stratagem to avoid short F···O contacts, in contrast to the Z’ = 1 structures of 4–6, which exhibit hydrogen-bonded ion catemers similar to the catemer of 3, and two halogen bonds C–X···O=S per formula unit.

Key words: Cocrystals, Catemers via Hydrogen Bonding, Halogen Bonding, Oxophobia of C–F Groups, Sulfonamides