Polysulfonylamine, CXCII [1]. Polynäre Verbindungen aus Di(4-fluorbenzolsulfonyl)amin (FAH), 1,1,3-Trimethylharnstoff (TrMU) und Dimethylamin (Me_2NH): Bildung und Strukturen des Cokristalls FAH·TrMU ($Z' = 1$), des Salzes $Me_2NH_2^+ \cdot FA^-$ ($Z' = 6$) und des Salz-Cokristalls FAH·TrMU·$Me_2NH_2^+ \cdot FA^-$ ($Z' = 1$). Bemerkungen zur Oxophobie von C–F-Gruppen in Kristallstrukturen

Polysulfonylamines, CXCII. Polynary Compounds Based upon Di(4-fluorobenzenesulfonyl)amine (FAH), 1,1,3-Trimethylurea (TrMU) and Dimethylamine (Me_2NH): Formation and Structures of the Cocrystal FAH·TrMU ($Z' = 1$), the Salt $Me_2NH_2^+ \cdot FA^-$ ($Z' = 6$) and the Salt Cocrystal FAH·TrMU·$Me_2NH_2^+ \cdot FA^-$ ($Z' = 1$). Comments on the Oxophobia of C–F Groups in Crystal Structures

Christoph Wölper[a], Alejandra Rodríguez-Gimeno[b], Katherine Chulvi Iborra[b], Ina Dix[c], Matthias Freytag[b], Peter G. Jones[b] und Armand Blaschette[b]

[a] Fachbereich Chemie, Universität Duisburg-Essen, Campus Essen, Universitätsstraße 7, 45141 Essen, Germany
[b] Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany
[c] Novartis Pharma AG, Forum 1, Novartis Campus, 4056 Basel, Switzerland

Reprint requests to Prof. Dr. P. G. Jones. Fax: +49-531-391-5387. E-mail: p.jones@tu-bs.de

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Cocrystallization of di(4-fluorobenzenesulfonyl)amine, $(4\text{-F-}C_6H_4SO_2)_2NH$ (= FAH), with 1,3,3-trimethylurea (TrMU) from dichloromethane/petroleum ether afforded the molecular cocrystal FAH·TrMU (**1**, monoclinic, $P2_1/n$, $Z' = 1$) and the salt cocrystal FAH·TrMU·$Me_2NH_2^+ \cdot FA^-$ (**2**, monoclinic, $P2_1$, $Z' = 1$). The minor product **2** resulted from a hydrolysis reaction of TrMU and was obtained by serendipity. The salt component of **2**, $Me_2NH_2^+ \cdot FA^-$ (**3**, monoclinic, $C2$, $Z' = 6$), was prepared by metathesis of $[Me_2NH_2]Cl$ with Ag[FA] and is not isomorphous to its previously reported congeners $Me_2NH_2^+ \cdot (4\text{-X-}C_6H_4SO_2)_2N^-$ (**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 $Me_2NH_2^+$ and FA^- ions (six independent formula units), in **2** of alternating $Me_2NH_2^+$ 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 fluorine-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