Polysulfonylamines, CLXXXIX [1]. Weitere Beispiele für die O-Protonierung von Harnstoffen mit Di(organosulfonyl)aminen: Bildung und Kristallstrukturen von 1,1-Dimethyluronium-di(4-fluorbenzolsulfonyl)amid und Di(1-methylharnstoff)-hydrogen(I)-di(4-fluorbenzolsulfonyl)amid

Polysulfonylamines, CLXXXIX. Additional Examples of the O-Protonation of Ureas by Di(organosulfonyl)amines: Formation and Crystal Structures of 1,1-Dimethyluronium Di(4-fluorobenzenesulfonyl)amide and Di(1-methylurea)hydrogen(I) Di(4-fluorobenzenesulfonyl)amide

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Co-crystallization of N-methyl-substituted ureas with di(organosulfonyl)amines, (RSO₂)₂NH, leads unpredictably to either molecular co-crystals or, via proton transfer, to uronium salts. As a sequel to former reports, this communication describes the formation and the crystal structures of the new ionic compounds 1,1-dimethyluronium di(4-fluorobenzenesulfonyl)amide (1, monoclinic, space group $P₂_1/c$, $Z' = 1$) and di(1-methylurea)hydrogen(I) di(4-fluorobenzenesulfonyl)amide (2, triclinic, $P\overline{1}$, $Z' = 1$); both salts were obtained from dichloromethane/petroleum ether. In the structure of 2, the urea moieties of the cationic homoconjugate are connected by a very short [O–H···O]$^+$ hydrogen bond [$d(\text{O–H}···\text{O}) = 244.6(2)$ pm, $\theta(\text{O–H}···\text{O}) \approx 170^\circ$, bridging H atom asymmetrically disordered over two positions]. The O-protonation induces a specific elongation of the C–O bond lengths to 131.2(2) pm in 1 or 129.5(2) and 127.4(2) pm in 2, as compared to literature data of ca. 126 pm for the unprotonated ureas. Both crystal structures are dominated by conventional two- and three-centre hydrogen bonds, which involve the OH and all NH donors and give rise to one-dimensional cation-anion arrays. In particular, the ionic entities of 1 are alternatingly associated into simple chains propagated by glide-plane operations parallel to the c axis, whereas the donor-richer structure of 2 displays inversion symmetric dimers of formula units, which are further hydrogen-bonded into strands propagated by translation parallel to the a axis.

Key words: Hydrogen Bonding, [O–H···O]$^+$ Homoconjugate, N-Methyl Ureas, N-Methyl Uronium Cations, Sulfonamides