

Polysulfonylamine, 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 *P*2₁/*c*, *Z*' = 1) and di(1-methylurea)hydrogen(I) di(4-fluorobenzenesulfonyl)amide (**2**, triclinic, *P*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*(O···O) = 244.6(2) pm, θ (O–H···O) \approx 170°, 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