Polysulfonylamine, CLXXXVII [1]. Strukturvielfalt in (Acetonitril)silber(I)-di(arensulfonyl)amiden: Zwei Molekülkristalle mit $Z' = 1$, ein Ionenkristall mit $Z' = 2$ und zwei auf Halogenbrücken C–Br···O=S beruhende molekulare Polymorphe mit $Z' = 1$ beziehungsweise $Z' = 2$ in der gleichen Raumgruppe

Polysulfonylamines, CLXXXVII. Structural Diversity in (Acetonitrile)silver(I) Di(arenesulfonyl)-amides: Two Molecular $Z' = 1$ Crystals, an Ionic $Z' = 2$ Crystal, and Two Molecular Polymorphs Based upon C–Br···O=S Halogen Bonds and Featuring $Z' = 1$ or $Z' = 2$ in the Same Space Group

Christoph Wölper[a], Alejandra Rodríguez-Gimeno[a], Katherine Chulvi Iborra[a], Helene Kuhn[a], Anne Kristin Lüttig[a], Sabrina Moll[a], Christin Most[a], Matthias Freytag[a], Ina Dix[b], Peter G. Jones[a] und Armand Blaschette[a]

[a] Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany
[b] Institut für Anorganische Chemie, Universität Göttingen, Tammannstraße 4, 37077 Göttingen, Germany

Reprint requests to Prof. Dr. P. G. Jones. E-mail: p.jones@tu-bs.de

Z. Naturforsch. **2009**, *64b,* 952 – 968; received June 3, 2009

Herrn Professor Reinhard Schmutzler zum 75. Geburtstag gewidmet

Crystallization of silver di(4-methylbenzenesulfonyl)amide [Ag(MA)], silver di(4-nitrobenzenesulfonyl)amide [Ag(NA)], silver di(4-bromobenzenesulfonyl)amide [Ag(BA)] or silver di(4-fluorobenzenesulfonyl)amide [Ag(FA)] from acetonitrile solutions under slightly different conditions afforded single crystals of the following complexes, which were structurally authenticated by X-ray diffraction at low temperatures: (MeCN)Ag(MA) (**1**, triclinic, space group $P\bar{1}$, $Z' = 1$), $(MeCN)_2$Ag(NA) (**2**, monoclinic, $P2_1/c$, $Z' = 1$), $(MeCN)_2$Ag(BA) (**3**, monoclinic, $P2_1/c$, $Z' = 1$), $(MeCN)_2$Ag(BA) (**4**, monoclinic, $P2_1/c$, $Z' = 2$), and $[(MeCN)_3Ag][Ag(FA)_2]\cdot MeCN$ (**5**, triclinic, $P\bar{1}$, $Z' = 1$). In each structure, the inner coordination sphere of silver is formed by the ligand nitrogen atoms, leading to a linear NAgN core for the molecular complex **1** and the complex anion of **5**, or to a trigonal planar AgN_3 core for the molecular complex **2**, the molecular polymorphs **3** and **4**, and the complex cation of **5**. The flexible di(arenesulfonyl)amide ligands adopt extended pseudo-C_2 symmetric conformations in **1**, **2** and **5**, but folded pseudo-mirror symmetric conformations in **3** and **4**. The molecules of **1** are associated into inversion-symmetric dimers *via* a short Ag···O contact; the dimers form stacks by translation along the *a* axis, causing the silver ions to segregate in zigzag chains. The arrangement of the molecules in **2** is controlled mainly by a centered C–H···Ph hydrogen bond, a dipolar nitro-nitro and a dipolar nitro-sulfonyl interaction, giving rise to layers oriented parallel to the *bc* plane. The packing motifs of polymorphs **3** and **4** are very similar. Both forms consist of layers in which the molecules act as 4-connecting nodes in a network based upon C–Br···O=S halogen bonds. In the $Z' = 1$ structure of **3**, the layers are generated by 2_1 screw axes and display one short and one long halogen bond, whereas in the $Z' = 2$ structure of **4**, the layers are realized by glide planes and are based on four independent halogen bonds that are all reasonably short. The packing of **5** exhibits alternating layers comprised of complex anions or of complex cations and acetonitrile solvent molecules, respectively. This $Z' = 2$ structure may be viewed as a kinetic polymorph of a more symmetric $Z' = 1$ crystal.

Key words: Acetonitrile, Halogen Bonding, Polymorphism, Silver, Sulfonamides