

At convergence, the additional four parameters lowered the wR^2 factor (all data) compared with the non-disordered model from 12.1 to 11.2%. Anisotropic refinement of O1A did not result in significantly lower residuals. Additionally, the O1A positional and anisotropic displacement parameters exhibited very high (88–96%) correlations. Anisotropic refinement of O1A was abandoned for these reasons. There was no apparent disorder found for the CF_3 groups or the tempo ligand other than the nitroxyl O atom. Positional and isotropic displacement parameters of H atoms were refined without restraints, resulting in C—H distances of 1.03 (3)–0.89 (3) Å and U values of 0.064 (11)–0.025 (7) Å² for the tempo molecule. The corresponding values for the hfac anion C—H were 0.87 (3) Å and 0.030 (7) Å², respectively.

Data collection: *XSCANS* (Siemens, 1990). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990a). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Sheldrick, 1990b). Software used to prepare material for publication: *SHELXTL*.

Support from the Department of Chemistry of Georgetown University, Washington, DC, is gratefully acknowledged. The diffractometer was obtained with a grant from the National Science Foundation. The author thanks Mr Admassu Regassa for his assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1320). Services for accessing these data are described at the back of the journal.

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Polysulfonylamines. LXXXVI.† Silver(I) Bis(4-fluorobenzenesulfonyl)amide Monohydrate‡

ACHIM WEITZE, ARMAND BLASCHETTE AND PETER G. JONES*

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany. E-mail: jones@xray36.anchem.nat.tu-bs.de

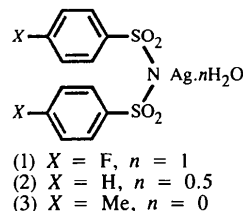
(Received 24 March 1997; accepted 11 April 1997)

Abstract

The title compound, $[\text{Ag}(\text{C}_{12}\text{H}_8\text{F}_2\text{NO}_4\text{S}_2)(\text{H}_2\text{O})]_n$, consists of infinite strands $[(\text{RSO}_2)_2\text{N}-\text{Ag}(\mu\text{-H}_2\text{O})]_\infty$ ($R = 4\text{-fluorophenyl}$), in which Ag extends its coordination number to five by accepting one Ag—O bond from each of the $(\text{RSO}_2)_2\text{N}^-$ ligands in the adjacent repeat units. By means of O—H...O hydrogen bonds, the strands are associated to form parallel layers. These display an inner polar region of Ag atoms, H_2O molecules and $\text{N}(\text{SO}_2)_2$ groups, outer apolar regions of stacked benzene fragments and interlayer regions consisting of F atoms.

Comment

Although silver(I) di(organosulfonyl)amides, $\text{AgN}(\text{SO}_2R)_2 \cdot n\text{H}_2\text{O}$ ($n = 0$ or $n > 0$), have not been studied extensively, even the few crystal structures currently known demonstrate for this class of compounds a rich variety of structural features, e.g. high coordination numbers at and aggregation of Ag centres, various bonding modes of hydrate water towards Ag and apolar–apolar sandwich-type layers (DesMarteau, Zuberi, Pennington & Randolph, 1992; Nèveke *et al.*, 1993; Jones, Hamann, Blaschette, Cammenga & Epple, 1993; Jones, Henschel, Weitze & Blaschette, 1994). The X-ray structure determination of the title compound, (1), is a sequel to our previous studies of silver(I) di(benzenesulfonyl)amide hemihydrate, (2), and anhydrous silver(I) di(4-toluenesulfonyl)amide, (3) (Jones, Henschel,



† Part LXXXV: Moers, Blaschette & Jones (1997).

‡ Alternative name: poly{ $\mu\text{-aqua-O:O-}\mu^3\text{-[bis(4-fluorophenylsulfonyl)amido]-O}^2\text{:N:O}^3\text{-silver(1)}$ }.

Weitze & Blaschette, 1994). The striking relationships between structures (1)–(3) are discussed below.

The asymmetric unit of (1) comprises one formula unit. Glide-plane related units are linked along the *z* axis to form infinite strands displaying a herringbone pattern and Ag atoms with irregular pentacoordination (Fig. 1 and Table 1). A saw-tooth-shaped [Ag(μ -H₂O)]_∞ chain serves as a backbone for the strands; it displays significantly different Ag—O1_w distances, but almost equal angles close to 97° both at Ag and O1_w. The chain is approximately planar, as expressed by the Ag—O1_w—Ag'—O1_w' torsion angles of ±175.2 (1)°; the Ag···Ag' distance, 3.685 (1) Å, is much longer than that in metallic silver (2.88 Å). The silver cation is tightly bonded to the amide N atom; Ag—N 2.278 (2) Å, *cf.* the sum of covalent radii (2.04 Å). Very similar Ag—N distances, 2.269 (3) and 2.260 (3) Å, were observed for the pentacoordinated Ag centres in (2) and (3). In the three structures, the N atoms have moderately distorted trigonal-planar environments, N in (1) being 0.071 (2) Å out of the plane defined by Ag, S1 and S2. Besides the strong Ag—N interaction, the amide ligand in (1) forms two weaker Ag—O bonds, one to each of the adjacent Ag atoms, thus completing the pentacoordination of the metal. The sterically favourable orientation of the coordinating O atoms within the ligand framework is revealed by the *transoid* torsion angles O2—S1—N—S2 −161.1 (2) and O3—S2—N—S1 −170.7 (2)°, the corresponding parameters for the non-coordinating atoms O1 and O4 being −32.0 (2) and 60.2 (2)°, respectively. Moreover, the near equality, close to 140°, of the independent Ag—O—S bond

angles should be noted. The intramolecular bond lengths and angles of the amide ligand are unexceptional.

A strand-building pattern topologically related to that described here was found for lithium dimesylamide monohydrate, LiN(SO₂Me)₂·H₂O (Schomburg, Blaschette & Kassomenakis, 1991). In the [Li(μ -H₂O)]_∞ chain of this structure, alternating Li atoms are N-bonded to two amide anions, the latter again acting as tridentate N,O,O'-ligands bracketing a sequence of three metal atoms. Thus, alternating Li atoms attain a tetrahedral N₂O₂ or an octahedral O₆ coordination, in contrast to the irregular NO₄ pentacoordination of Ag in (1).

In the present structure, strands stacked into layers parallel to the *xz* plane are connected by O—H···O hydrogen bonds originating from the water molecules (Fig. 2). Note that the different bonding functionality of the sulfonyl O atoms, either as a donor atom towards Ag (O3), or as a hydrogen-bond acceptor (O4), or both (O2), or neither (O1), is reflected in a slight graduation of their respective S—O distances. The layered structure shows polar regions of Ag atoms, water molecules and N(SO₂)₂ moieties, apolar regions of stacked benzene fragments and interlayer regions of F atoms, the latter displaying five distances that are shorter than F1···F2 in the asymmetric unit, 4.679 (3) Å, but without exception longer than the van der Waals distance (2.94 Å).

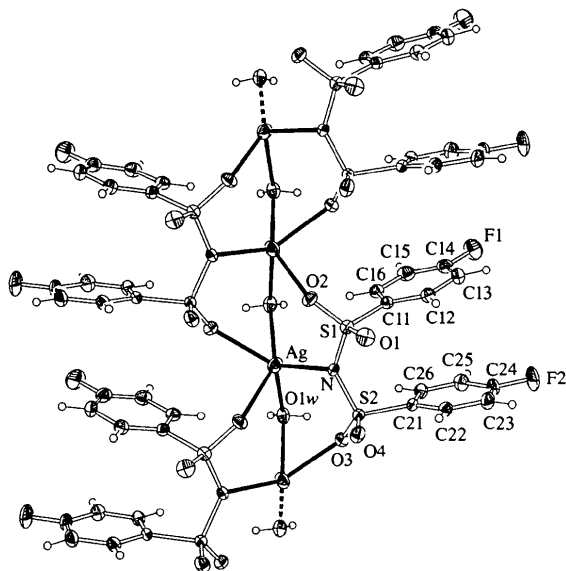


Fig. 1. Packing diagram of (1) viewed along the *x* axis. Note the chains of alternating Ag and water O atoms at *y* ≈ 0.25, 0.75 and the fluorine-containing region at *y* ≈ 0.5. Ellipsoids represent 50% probability levels. H-atom radii are arbitrary.

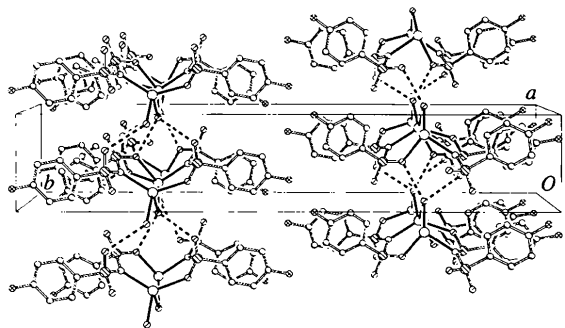


Fig. 2. Packing diagram of (1) viewed along the *z* axis, showing the hydrogen bonds (indicated as broken bonds) linking the strands shown in Fig. 1.

A common feature of structures (1)–(3) are parallel strands, all leading to a silver pentacoordination. Depending on the nature of the aryl group and the H₂O:Ag ratio, different strand-forming bond patterns are observed. Thus, the strands in (2) and (3) do not rely on an infinite backbone as found in (1). Instead they are built up from discrete segments, [(RSO₂)₂N—Ag(μ -H₂O)Ag—N(SO₂R)₂], (2), or [(RSO₂)₂N—Ag—Ag—N(SO₂R)₂], (3), uniquely connected by bonds formed between the amide ligands and Ag atoms in adjacent segments. In the first case, Ag attains pentacoordination by an intrasegmental Ag—O(sulfonyl) bond and

an intersegmental silver–aryl η^2 interaction involving the *m*- and *p*-C atoms of one phenyl group. By means of O—H...O hydrogen bonds, the resulting strands are stacked into layers resembling those in (1). In (3), on the other hand, where the methyl substituent at the *p*-C atom obviously prevents silver–aryl π bonding, the pentacoordination of Ag is completed by one intra- and two intersegmental AgO bonds.

Experimental

Compound (1) was prepared as formerly described (Blaschette *et al.*, 1993) and recrystallized by cooling a solution in hot water to room temperature.

Crystal data

[Ag(C₁₂H₈F₂NO₄S₂)(H₂O)]
M_r = 458.20
 Monoclinic
*P*2₁/*c*
a = 6.0389 (4) Å
b = 32.772 (3) Å
c = 7.3695 (8) Å
 β = 97.750 (8)°
V = 1445.2 (2) Å³
Z = 4
D_x = 2.106 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 63 reflections
 θ = 5.0–12.5°
 μ = 1.731 mm⁻¹
T = 173 (2) K
 Prism
 0.6 × 0.2 × 0.2 mm
 Colourless (some discoloration to grey)

Data collection

Siemens *P4* diffractometer
 ω scans
 Absorption correction:
 ψ scans (*XEMP*; Siemens, 1994a)
 T_{\min} = 0.657, T_{\max} = 0.707
 4065 measured reflections
 3317 independent reflections
 2687 reflections with
 $I > 2\sigma(I)$

*R*_{int} = 0.018
 θ_{\max} = 27.50°
 $h = -7 \rightarrow 7$
 $k = -2 \rightarrow 42$
 $l = -9 \rightarrow 2$
 3 standard reflections every 247 reflections
 intensity decay: 2%

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.066$
 $S = 1.045$
 3317 reflections
 216 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0302P)^2 + 1.4445P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.860 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.895 \text{ e } \text{Å}^{-3}$
 Extinction correction: none
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Ag—N	2.278 (2)	S2—O4	1.442 (2)
Ag—O3 ⁱ	2.420 (2)	S2—N	1.609 (2)
Ag—O1w	2.432 (2)	Ag...Ag ⁱ	3.685 (1)
Ag—O1w ⁱ	2.504 (2)	F1...F2 ^v	4.679 (3)
Ag—O2 ⁱⁱ	2.740 (2)	F1...F2 ⁱⁱⁱ	3.101 (4)

S1—O1	1.437 (2)	F1...F2 ^v	3.554 (3)
S1—O2	1.448 (2)	F2...F2 ^v	3.385 (4)
S1—N	1.604 (2)	F1...F2 ^v	3.889 (3)
S2—O3	1.441 (2)	F2...F2 ^{vi}	3.602 (4)
N—Ag—O3 ⁱ	126.79 (7)	O1w—Ag—O2 ⁱⁱ	94.63 (6)
N—Ag—O1w	106.02 (7)	O1w ⁱ —Ag—O2 ⁱⁱ	151.14 (6)
O3 ⁱ —Ag—O1w	125.69 (7)	S1—N—S2	122.16 (13)
N—Ag—O1w ⁱ	116.15 (7)	S1—N—Ag	117.42 (11)
O3 ⁱ —Ag—O1w ⁱ	72.50 (7)	S2—N—Ag	119.95 (12)
O1w—Ag—O1w ⁱ	96.95 (7)	S1—O2—Ag ⁱ	138.26 (11)
N—Ag—O2 ⁱⁱ	85.56 (7)	S2—O3—Ag ⁱⁱ	139.74 (12)
O3 ⁱ —Ag—O2 ⁱⁱ	79.26 (6)	Ag—O1w—Ag ⁱⁱ	96.60 (7)

Symmetry codes: (i) $x, \frac{3}{2}-y, z-\frac{1}{2}$; (ii) $x, \frac{3}{2}-y, \frac{1}{2}+z$; (iii) $-x, 1-y, -z$; (iv) $-x, 1-y, 1-z$; (v) $x, y, z-1$; (vi) $1-x, 1-y, 1-z$.

Table 2. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
O1w—H01...O2 ⁱ	0.87 (3)	1.97 (3)	2.823 (3)	167 (4)
O1w—H02...O4 ⁱⁱ	0.87 (3)	2.12 (3)	2.929 (3)	153 (4)

Symmetry codes: (i) $x-1, \frac{3}{2}-y, \frac{1}{2}+z$; (ii) $x-1, y, z$.

Water H atoms were refined with distance restraints (command *SADI*), with the other H atoms riding.

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994b). Software used to prepare material for publication: *SHELXL93*.

The authors thank the Fonds der Chemischen Industrie for financial support and Mr A. Weinkauff for technical assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1325). Services for accessing these data are described at the back of the journal.

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