

Structure of the silver imidodi(sulphuryl fluoride)–benzene solvate $\text{AgN}(\text{SO}_2\text{F})_2 \cdot \text{C}_6\text{H}_6$

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Abstract

The structure of the monobenzene solvate of silver imidodi(sulphuryl fluoride), $\text{AgN}(\text{SO}_2\text{F})_2 \cdot \text{C}_6\text{H}_6$, was determined from single crystal X-ray data. The asymmetric unit contains one quarter of the formula unit with the silver and nitrogen atoms lying at the intersection of two mirror planes; the sulphur and one of the oxygen atoms, O(2), lie on the same mirror plane. The remaining substituent at sulphur is in a general position that must be occupied equally by oxygen and fluorine and is designated as O/F (1). The bonding between silver and benzene is of a new type, in which each benzene is symmetrically η^2 -coordinated (Ag–C 2.490(7) Å) to each of two silver atoms to give infinite chains parallel to the *c* axis. A weak C(1)–H(1)···O/F(1) hydrogen bond (C···O/F 3.47 Å) was located, which cross-links these chains in the *b* direction, and probably accounts for the fact that the more electronegative fluorine atom predominantly occupies the general position.

Key words: Silver; Crystal structure; Benzene; Imidodi(sulphuryl fluoride); Addition compound

1. Introduction

There continues to be great interest in imidodi(sulphuryl fluoride) and related compounds, such as $\text{HN}(\text{SO}_2\text{CF}_3)_2$ [1] and $\text{HN}(\text{SO}_2\text{CF}_3)(\text{SO}_2\text{C}_4\text{F}_9)$ [2]. This stems, *inter alia*, from their value in preparing compounds containing xenon–nitrogen bonds [3–7] and from the reactivity of the *N*-fluoro derivatives [8].

The silver salt of imidodi(sulphuryl fluoride) has been known for many years and can be isolated as a monobenzene solvate [9]. Molecular weight determinations in benzene point to strong association in solution, and a structure similar to that of $\text{AgClO}_4 \cdot \text{C}_6\text{H}_6$ has been suggested [10]. The only crystallographic data available at present for imidodi(sulphuryl fluoride) derivatives are for an ionic tetraphenylarsonium salt

[11] and two xenon compounds, $\text{FXeN}(\text{SO}_2\text{F})_2$ [5,6] and $[\text{XeN}(\text{SO}_2\text{F})_2][\text{Sb}_3\text{F}_{16}]$ [4]. To extend information in this field and investigate the benzene–silver interaction, we have determined the crystal structure of $\text{AgN}(\text{SO}_2\text{F})_2 \cdot \text{C}_6\text{H}_6$.

2. Experimental

2.1. Preparation of silver imidodi(sulphuryl fluoride)–benzene

The compound was prepared in benzene solution from imidodi(sulphuryl fluoride) [12] and silver oxide (BDH) as described previously [9]. Recrystallization from dichloromethane gave white crystals, m.p. 121–122°C. Anal. Found: C, 19.6, H, 1.6, N, 3.8, F, 10.5, Ag, 29.5; $\text{C}_6\text{H}_6\text{AgF}_2\text{NO}_4\text{S}_2$ calc.: C, 19.7, H, 1.6, N, 3.8, F, 10.4, Ag, 29.5%. For a solution in a CH_2Cl_2 – CD_2Cl_2 mixture the ^1H NMR spectrum showed a signal at 7.58 ppm for the coordinated benzene and the ^{19}F spectrum a singlet at 52.6 ppm.

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2.2. Crystal structure

2.2.1. Crystal data

$C_6H_6AgF_2NO_4S_2$, $M = 365.9$, orthorhombic, $Cmcm$, from systematic absences and subsequent refinement, $a = 11.885$ (5), $b = 8.279$ (4), $c = 10.830$ (4) Å, $V = 1065.6$ Å³, $Z = 4$, $D_c = 2.28$ g cm⁻³, Mo $K\alpha$ radiation (graphite monochromator), $\lambda = 0.7107$ Å, $\mu = 21.9$ cm⁻¹, $F(000) = 712$, $T = 294$ K, crystal size $0.8 \times 0.3 \times 0.25$ mm³.

2.2.2. Structure determination

Data were measured for 1121 reflections, 474 of which were unique with $I > 3\sigma(I)$. These were corrected for Lorentz and polarization effects but an absorption correction was not applied. The initial ambiguity in the space group ($Ama2$, $Cmc2_1$ or $Cmcm$) was removed by successful refinement in $Cmcm$. Crystallographic calculations used the CRYSTALS programs [13] and scattering factors were those for neutral atoms [14].

The asymmetric unit contains one quarter of the formula unit. From a three-dimensional Patterson synthesis, the silver atom was placed at 0, 0.02, 0.25, at the intersection of two mirror planes. Successive difference Fourier syntheses then revealed positions for the nitrogen atom (also lying at the intersection of the two mirror planes), the sulphur, lying on a mirror plane, and two further atoms, one lying on the same mirror plane and the second in a general position. C(2) of the benzene ring lies on a twofold axis and there is a mirror plane perpendicular to this, bisecting opposite C–C bonds.

During refinement, it became clear that the oxygen and fluorine atom positions were disordered, and in an attempt to define this more closely, both types of atom were considered to be oxygen. The occupation factors were then refined, within the constraint that the total electron density at the combined positions should not exceed 25, *i.e.* the sum of the electron counts for two oxygen atoms and one fluorine atom. Refined values for the occupation factors were 1.050 (9) and 0.504 (17), respectively, at the O(1) and O(2) positions, giving electron counts of 8.40(7) and 8.06(23), respectively. This shows that, although fluorine is disordered between both sites, there is predominant fluorine occupation at the O(1) site, now designated O/F(1). The original model would have given electron counts of 8.5 and 8.0 at O(1) and O(2), respectively.

Refinement was continued with anisotropic thermal parameters and the two independent hydrogen atoms placed at calculated positions (C–H = 1.00 Å). This showed large anisotropic thermal parameters for both O(2) and O/F(1) as a result of the disorder, but the

TABLE 1. Atomic coordinates, with estimated standard deviations in parentheses, for $Ag[N(SO_2F)_2] \cdot benzene$

Atom	x/a	y/b	z/c	U (equiv.)
Ag(1)	0.0000	0.0197(2)	0.2500	0.0868
S(1)	0.1145(2)	0.3874(4)	0.2500	0.0761
N(1)	0.0000	0.293(1)	0.2500	0.0560
O/F(1)	0.1192(5)	0.482(2)	0.142(1)	0.1389
O(2)	0.2032(7)	0.276(2)	0.2500	0.1303
C(1)	-0.0573(8)	-0.123(1)	0.0576(7)	0.0738
C(2)	-0.1108(9)	0.0000	0.0000	0.0833
H(1)	-0.1025	-0.2115	0.0991	
H(2)	-0.1966	0.0000	0.0000	

vibration of O(2) along the S(1)–O(2) bond was small, confirming that this site is predominantly oxygen. For O/F(1), on the other hand, the “vibration” parallel to the bond was large, as expected with the type of disorder present. A weighting scheme based on a four-coefficient Chebyshev polynomial was then applied and refinement converged at a final R of 5.67% ($R_w = 7.35\%$). The maximum shift to e.s.d. was 0.01 and maximum and minimum residual electron densities were 0.68 and -0.17 e Å⁻³, respectively. A table of anisotropic thermal parameters has been deposited with the Cambridge Crystallographic Data Centre. Structure factor listings can be obtained from D.B.S.

3. Discussion

Table 1 lists the atomic coordinates and important bond distances and angles are listed in Table 2. A diagram showing the molecular structure and atom numbering scheme is given in Fig. 1 and, as shown in Fig. 2, the compound is polymeric, with silver atoms linked by benzene molecules into infinite chains parallel to the c axis.

The benzene molecules act as symmetrical bis- η^2 ligands and the symmetry requires the four Ag–C distances to be equal (2.490(7) Å). This value is similar to those (2.48 and 2.50 Å) in $[AuAg(C_6F_5)_2(C_6H_6)]$ [15], where benzene is a simple η^2 group, and should be compared with the shorter Ag–C separation (2.40 Å) for the η^1 -coordinated benzene in a silver carborene complex [16]. Again, for symmetry reasons, there are only two independent C–C distances within the aromatic molecule (1.35(1) and 1.36(2) Å), which are equal within the errors of the determination, but the two independent C–C–C angles (118.0(5) and 123.9(10)°) are significantly different, probably a consequence of coordination to silver. Simple η^2 -coordination has also been observed in a number of silver complexes with other aromatic molecules [17,18] but both the Ag–C distances and the C–C separations in

TABLE 2. Bond lengths (Å) and angles (deg), with estimated standard deviations in parentheses for $\text{Ag}[\text{N}(\text{SO}_2\text{F})_2] \cdot \text{benzene}$

Bond lengths	
Ag(1)–N(1)	2.26(1)
Ag(1)–C(1)	2.490(7)
S(1)–N(1)	1.571(6)
S(1)–O/F(1)	1.407(8)
S(1)–O(2)	1.403(10)
C(1)–C(2)	1.35(1)
C(1)–C(1')	1.36(2)
Bond angles	
N(1)–Ag(1)–C(1)	118.3(2)
C(1)–Ag(1)–C(1')	113.6(3)
C(1)–Ag(1)–C(1')	31.8(4)
C(1)–Ag(1)–C(1'')	123.4(4)
O/F(1)–S(1)–O/F(1')	112.2(12)
N(1)–S(1)–O/F(1)	108.2(4)
N(1)–S(1)–O(2)	108.7(6)
O/F(1)–S(1)–O(2)	109.7(6)
S(1)–N(1)–S(1')	120.1(7)
Ag(1)–N(1)–S(1)	120.0(4)
Ag(1)–C(1)–C(2)	99.0(4)
Ag(1)–C(1)–C(1')	74.1(2)
C(2)–C(1)–C(1')	118.0(5)
C(1)–C(2)–C(1'')	123.9(10)

Atoms carrying single, double, triple and quadruple primes are related by the symmetry operations $-x, y, z, x, y, 0.5-z, -x, y, 0.5-z$ and $x, -y, -z$, respectively.

the coordinated aromatic are usually unequal. Bis- η^2 behaviour is much rarer but occurs in the silver perchlorate-benzene solvate [10], although in that case the silver atoms are disordered and asymmetrically bonded to benzene. The present compound, therefore, appears to be the first example of benzene behaving as a symmetrical bis- η^2 ligand; the silver atom is fivefold coordinated to four carbon atoms and the nitrogen of the imidodisulphuryl fluoride group.

The nitrogen atom in this moiety is in trigonal planar coordination with ideal 120° angles. The Ag–N

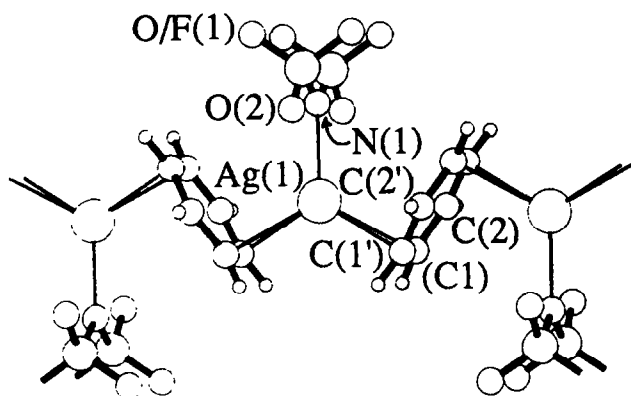


Fig. 1. Structure of $\text{AgN}(\text{SO}_2\text{F})_2 \cdot \text{C}_6\text{H}_6$ showing the atom numbering scheme.

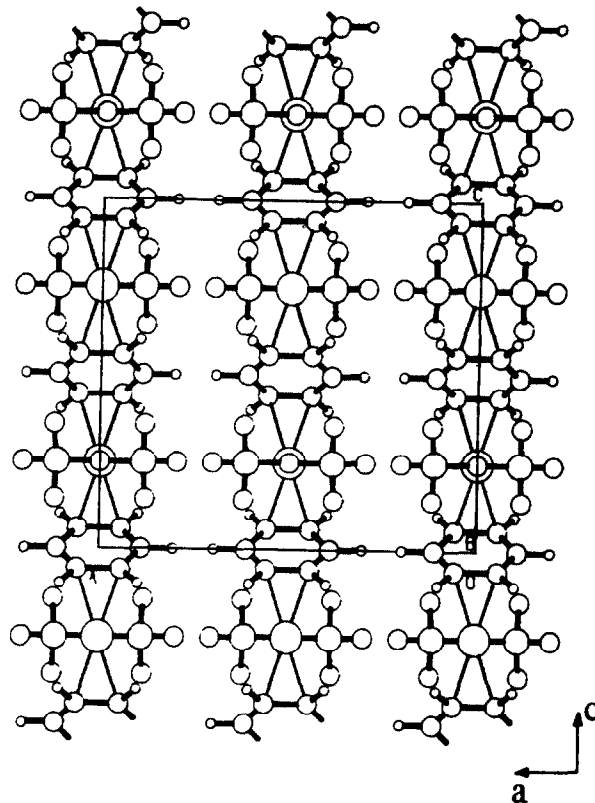


Fig. 2. Projection of the unit cell contents down the b axis.

separation (2.26(1) Å) is, not surprisingly, longer than in the two-coordinate cationic species $[\text{Ag}(\text{NCCl})_2]^+$, 2.140(4) Å [19], and $[\text{Ag}(\text{NCH})_2]^+$, 2.130(3) Å [20], but is comparable to the mean value in the four-coordinate species $[\text{Ag}(\text{NCMe})_4]^+$, 2.18(3)–2.33(2) Å [21].

An important feature of the structure is the near equality of the distances between sulphur and the oxygen/fluorine substituents, indicating disorder in the system. Such disorder is also found in one of the SO_2F groups of $[\text{XeN}(\text{SO}_2\text{F})_2]^+$ (S–O, 1.34 and 1.37, S–F, 1.40 Å), although distances in the second (ordered) group are more normal (S–O, 1.39 and 1.40, S–F 1.518 Å) [4]. The anion in $\text{Ph}_4\text{As}[\text{N}(\text{SO}_2\text{F})_2]$ is also disordered at room temperature [11], but at 112 K it shows a staggered conformation (approximately C_2 symmetry) with mean S–O and S–F distances of 1.415 and 1.574 Å, respectively. The mean S–N distance (1.568 Å) is comparable to that in the present compound (1.571(6) Å), pointing in both cases to some degree of multiple bonding.

There is a short interatomic contact (3.47 Å) between C(1) and a symmetry related O/F(1) atom ($-x, y-1, z$) and, although this is close to the sum of the van der Waals' radii, it can be interpreted as a C–H...O/F hydrogen bond. The separation is comparable to those previously reported for bonds of this type

[22] and, more importantly, the contact is correctly oriented, with a wide C(1)-H(1)···O/F(1) angle (146°). Further, the H(1)···O/F(1)-S(1) angle (134°) is such that participation by one of the O/F lone pairs is possible. This weak interaction serves to cross-link the polymeric chains in the *b* direction.

Symmetry arguments would suggest that the single fluorine atom would occupy the O(2) site on the mirror plane while random disorder between the O(1) and O(2) positions would lead to electron counts of 8.33. Neither of these alternatives is, in fact, observed and the fluorine disorder is such that there is predominantly fluorine character at the O(1) positions. Weak C-H···X interaction of the type observed here will, on electronegativity grounds, be stronger to fluorine than to oxygen, and this probably accounts for the specific disorder observed in the imidodisulphuryl group.

References

- 1 J. Foropoulos, Jr., and D.D. DesMarteau, *Inorg. Chem.*, **23** (1984) 3720.
- 2 S. Singh and D.D. DesMarteau, *Inorg. Chem.*, **29** (1990) 2982.
- 3 D.D. DesMarteau, R.D. LeBlond, S.F. Harrison and D. Nothe, *J. Am. Chem. Soc.*, **103** (1981) 7734.
- 4 R. Faggiani, D.K. Kennepohl, C.J.L. Lock and G.J. Schrobilgen, *Inorg. Chem.*, **25** (1986) 563.
- 5 J.F. Sawyer, G.J. Schrobilgen and S.J. Sutherland, *Inorg. Chem.*, **21** (1982) 4064.
- 6 G.A. Schumacher and G.J. Schrobilgen, *Inorg. Chem.*, **22** (1983) 2178.
- 7 J. Foropoulos, Jr., and D.D. DesMarteau, *J. Am. Chem. Soc.*, **104** (1982) 4260.
- 8 S. Singh, D.D. DesMarteau, S.S. Zuberi, M. Witz and H.N. Huang, *J. Am. Chem. Soc.*, **109** (1987) 7194.
- 9 J.K. Ruff, *Inorg. Chem.*, **4** (1965) 1446.
- 10 H.G. Smith and R.E. Rundle, *J. Am. Chem. Soc.*, **80** (1958) 5075.
- 11 W. Isenberg, M. Noltemeyer and G.M. Sheldrick, *Acta Crystallogr., Sect. B*, **38** (1982) 2887.
- 12 J.K. Ruff and M. Lustig, *Inorg. Synth.*, **11** (1968) 138.
- 13 D.J. Watkins, J.R. Carruthers and D.W. Betteridge, *CRYSTALS Users Guide*, Chemical Crystallography Laboratory, University of Oxford, Oxford, 1985.
- 14 *International Tables for X-Ray Crystallography*, Vol. 4, Kynoch Press, Birmingham, UK, 1974.
- 15 R. Uson, A. Laguna, M. Laguna, B.R. Manzano, P.G. Jones and G.M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, (1984) 285.
- 16 K. Shelly, D.C. Finster, Y.T. Lee, W.R. Scheidt and C.A. Reed, *J. Am. Chem. Soc.*, **107** (1985) 5955.
- 17 R.W. Turner and E.L. Amma, *J. Am. Chem. Soc.*, **88** (1966) 3243.
- 18 R. Uson, J. Fornies, M. Tomas and I. Ara, *J. Chem. Soc., Dalton Trans.*, (1990) 3151.
- 19 H.W. Roesky, J. Schimkowiak, P.G. Jones, M. Noltemeyer and G.M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, (1988) 2507.
- 20 P.G. Jones, H.W. Roesky and J. Schimkowiak, *J. Chem. Soc., Chem. Commun.*, (1988) 730.
- 21 K. Nilsson and Å. Oskarsson, *Acta Chem. Scand., Ser. A*, **38** (1984) 79.
- 22 G.R. Desiraju, *Acc. Chem. Res.*, **24** (1991) 290.