Crystal structure of *S*-[4-(2,6-dimethylphenylselenide)-3,5-dimethylphenyl]-dibenzothiophenium bis(triflate) hydrate, $[C_{20}H_{16}SSe_{0.5}]_2 \cdot (CF_3O_3S)_2 \cdot 2.78H_2O$

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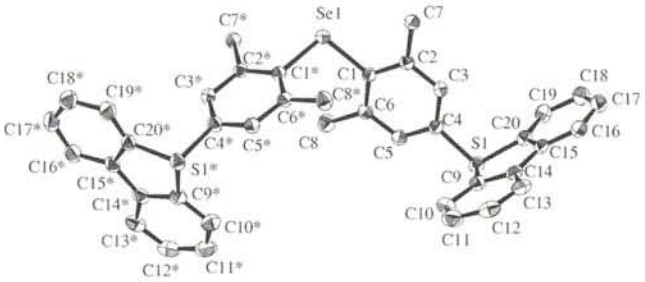

Abstract

$C_{42}H_{39.56}F_6O_{8.78}S_4Se$, monoclinic, *C*12/*c*1 (No. 15), $a = 21.993(5)$ Å, $b = 13.639(4)$ Å, $c = 16.042(5)$ Å, $\beta = 107.95(2)°$, $V = 4577.8$ Å^3, $Z = 4$, $R_{gt}(F) = 0.066$, $wR_{all}(F) = 0.092$, $T = 296$ K.

Source of material

The title compound was prepared from diaryl selenide on treatment with a two molar equivalent of dibenzothiophene S-oxide in dry dichloromethane at 213 K. This structure analysis is part of the preparation and study of hyper-valent sulfur compounds [1]. Single crystals of the compound were obtained by slow recrystallization from chloroform at room temperature.

Discussion

The related *S*-alkylthiophenium salt [2] was first prepared in 1964 and subsequently such salts and their reactivities [3] have been reported in detail. However, to date only a few *S*-arylthiophenium salts have been reported [4]. Recently, we have successfully prepared the bis-*S*-arylthiophenium salt in one step.

The structure plot (50% probability ellipsoids) excludes the two triflate counter ions per molecule and water for simplicity. The hydrogen atoms of the water molecules were not localized. The selenium atom is on the two-fold axis of symmetry and the coordinates of the atoms with asterisks are equal to $-x, y, 1/2-z$ with respect to the corresponding unique atom coordinates at x, y, z. The Se—C bond distances are normal at 1.936(5) Å, as is the C(1)–S(1)–C(1)* bond angle of 102.3(3)°. The respective positive charge is located on the sulfur atoms and influences their bonding nature. The sulfur atoms are in a pyramidal environment with the bond distances S(1)—C(4), S(1)—C(9) and S(1)—C(20) equal to 1.785(5) Å, 1.794(6) Å and 1.775(6) Å, respectively. All the other bond distance and bond angles are in the normal range.

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Table 1. Data collection and handling.

Crystal:	colorless, prismatic, size 0.4 × 0.5 × 0.6 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	9.86 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC7R, ω/2θ
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5216, 5100
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 3\ \sigma(I_{obs})$, 3572
$N(param)_{refined}$:	287
Programs:	SIR92 [5], teXsan [6], DIFABS [7], ORTEP-II [8]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
O(4)	8*f*	0.35	0.3941(8)	0.424(1)	0.192(1)	0.089(5)
O(5)	8*f*	0.26	0.422(1)	0.390(2)	0.153(2)	0.098(7)
O(6)	8*f*	0.32	0.4987(9)	0.423(1)	0.281(1)	0.075(4)
O(7)	8*f*	0.26	0.460(1)	0.373(2)	0.216(2)	0.083(6)
O(8)	8*f*	0.20	0.487(1)	0.295(2)	0.217(2)	0.080(8)
H(1)	8*f*		0.6107	0.0217	0.0484	0.050
H(2)	8*f*		0.6502	0.1775	0.2760	0.053
H(3)	8*f*		0.5064	–0.1510	0.1021	0.055
H(4)	8*f*		0.5056	–0.0892	0.0183	0.055
H(5)	8*f*		0.5648	–0.1572	0.0643	0.055
H(6)	8*f*		0.6263	0.0714	0.4026	0.067
H(7)	8*f*		0.5679	0.1437	0.3649	0.067
H(8)	8*f*		0.5555	0.0301	0.3725	0.067
H(9)	8*f*		0.5661	0.3327	0.1194	0.076
H(10)	8*f*		0.4886	0.4138	–0.0078	0.085
H(11)	8*f*		0.5006	0.3972	–0.1526	0.082
H(12)	8*f*		0.5857	0.2976	–0.1789	0.072
H(13)	8*f*		0.6663	0.1753	–0.1802	0.070
H(14)	8*f*		0.7537	0.0532	–0.1554	0.077
H(15)	8*f*		0.8082	–0.0089	–0.0062	0.079
H(16)	8*f*		0.7777	0.0541	0.1219	0.071

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Se(1)	4*e*	1/2	–0.10149(6)	1/4	0.0523(5)	0.0333(4)	0.0494(5)	0	0.0247(4)	0
S(1)	8*f*	0.67666(7)	0.2016(1)	0.1206(1)	0.0507(9)	0.0494(8)	0.0469(9)	–0.0139(7)	0.0191(7)	–0.0062(7)
S(2)	8*f*	0.83504(9)	0.1484(2)	0.3303(1)	0.059(1)	0.092(1)	0.052(1)	–0.011(1)	0.0153(9)	0.005(1)
F(2)	8*f*	0.8407(3)	0.2793(6)	0.4508(4)	0.122(5)	0.231(8)	0.110(4)	–0.085(5)	0.056(4)	–0.097(5)
F(3)	8*f*	0.7556(3)	0.1939(5)	0.4154(4)	0.091(4)	0.173(6)	0.115(4)	–0.040(4)	0.058(3)	–0.045(4)
F(4)	8*f*	0.7675(4)	0.3053(5)	0.3288(5)	0.160(6)	0.113(5)	0.162(6)	0.029(5)	0.051(5)	–0.029(5)
O(1)	8*f*	0.8674(3)	0.0815(5)	0.3991(4)	0.079(4)	0.132(5)	0.095(4)	0.003(4)	0.017(3)	0.054(4)
O(2)	8*f*	0.8766(2)	0.2074(4)	0.2971(3)	0.078(4)	0.105(4)	0.063(3)	–0.018(3)	0.027(3)	0.008(3)
O(3)	8*f*	0.7796(2)	0.1080(4)	0.2646(3)	0.061(3)	0.104(4)	0.068(3)	–0.016(3)	–0.004(3)	–0.024(3)
C(1)	8*f*	0.5556(2)	–0.0124(4)	0.2136(3)	0.037(3)	0.035(3)	0.040(3)	0.002(2)	0.013(2)	0.003(2)
C(2)	8*f*	0.5641(2)	–0.0305(4)	0.1323(3)	0.032(3)	0.035(3)	0.042(3)	0.003(2)	0.010(2)	0.001(2)
C(3)	8*f*	0.6033(3)	0.0325(4)	0.1042(4)	0.044(3)	0.043(3)	0.042(3)	0.001(2)	0.019(3)	–0.001(2)
C(4)	8*f*	0.6327(3)	0.1101(4)	0.1573(4)	0.041(3)	0.043(3)	0.045(3)	–0.005(3)	0.016(3)	0.001(3)
C(5)	8*f*	0.6266(3)	0.1249(4)	0.2391(4)	0.047(3)	0.044(3)	0.042(3)	–0.007(3)	0.014(3)	–0.007(2)
C(6)	8*f*	0.5884(3)	0.0630(4)	0.2696(3)	0.042(3)	0.042(3)	0.037(3)	0.000(2)	0.011(3)	–0.003(2)
C(7)	8*f*	0.5322(3)	–0.1145(4)	0.0742(4)	0.057(4)	0.041(3)	0.045(3)	–0.008(3)	0.022(3)	–0.008(3)
C(8)	8*f*	0.5842(3)	0.0785(5)	0.3603(4)	0.065(4)	0.063(4)	0.043(3)	–0.012(3)	0.020(3)	–0.009(3)
C(9)	8*f*	0.6155(3)	0.2653(4)	0.0381(4)	0.048(3)	0.042(3)	0.050(4)	–0.009(3)	0.011(3)	–0.003(3)
C(10)	8*f*	0.5691(4)	0.3237(5)	0.0544(5)	0.074(5)	0.049(4)	0.072(5)	0.000(3)	0.030(4)	–0.008(3)
C(11)	8*f*	0.5264(4)	0.3697(5)	–0.0168(6)	0.075(5)	0.047(4)	0.092(6)	0.006(4)	0.025(5)	0.000(4)
C(12)	8*f*	0.5337(4)	0.3591(5)	–0.0980(5)	0.070(5)	0.048(4)	0.083(5)	–0.003(4)	0.013(4)	0.011(4)
C(13)	8*f*	0.5806(3)	0.3024(5)	–0.1145(4)	0.072(5)	0.044(3)	0.057(4)	–0.015(3)	0.014(4)	0.003(3)
C(14)	8*f*	0.6220(3)	0.2521(4)	–0.0440(4)	0.057(4)	0.039(3)	0.052(4)	–0.014(3)	0.018(3)	–0.001(3)
C(15)	8*f*	0.6725(3)	0.1827(4)	–0.0447(4)	0.055(4)	0.042(3)	0.053(4)	–0.017(3)	0.026(3)	–0.004(3)
C(16)	8*f*	0.6906(3)	0.1482(5)	–0.1147(4)	0.067(4)	0.055(4)	0.055(4)	–0.014(3)	0.027(3)	–0.005(3)
C(17)	8*f*	0.7393(4)	0.0800(5)	–0.1006(5)	0.070(5)	0.066(5)	0.065(4)	–0.018(4)	0.035(4)	–0.017(4)
C(18)	8*f*	0.7708(3)	0.0451(5)	–0.0157(5)	0.058(4)	0.065(4)	0.081(5)	–0.005(3)	0.030(4)	–0.008(4)
C(19)	8*f*	0.7537(3)	0.0789(5)	0.0557(5)	0.053(4)	0.062(4)	0.065(4)	–0.006(3)	0.022(3)	0.000(3)
C(20)	8*f*	0.7047(3)	0.1459(4)	0.0394(4)	0.048(3)	0.047(3)	0.055(4)	–0.012(3)	0.026(3)	–0.005(3)
C(21)	8*f*	0.7986(4)	0.2339(9)	0.3845(6)	0.069(6)	0.133(9)	0.072(6)	–0.020(6)	0.019(5)	–0.028(6)

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