Crystal structure of di[bis(ethylenedithio)tetrathiafulvalene] bromide trihydrate, $(C_{10}H_8S_8)_2Br \cdot 3H_2O$

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Source of material: Crystals were prepared by the electrochemical oxidation of BEDT-TTF [BEDT-TTF, or ET = bis(ethylenedithio)tetrathiafulvalene] in a mixed solvent of 1,1,2-trichloroethane, acetonitrile and water (volume ratio = 10 : 20 : 1) containing 1 mmol ET, 10 mmol CuBr, 10 mmol KBr and 10 mmol 18-crown-6 with 0.5 to 2.0 μ A current.

The bromide structure is isostructural to the corresponding chloride salt (see ref. 1) and consists of two-dimensional sheets of BEDT-TTF cations which are separated along the crystallographic *a* axis by two dimensional hydrogen bonded network formed between water molecules and bromide anions. The distances of 3.07 Å for O1–Br, 3.02 Å for O1–O2 and 3.32 Å for Br–O2 suggest that O1 water molecules make hydrogen bonds with both bromide anions and O2 water molecules. There could be weaker hydrogen bonding between Br and O2 water molecules. The shortest interstack and intrastack S–S distances are 3.48 Å and 3.74 Å respectively, similar to those found in the isostructural salt, (BEDT-TTF)₂Cl · 3H₂O (see ref. 1). Two ethylene groups are disordered as shown by relatively large thermal parameters of C(7) to C(10). Such a disorder is common among BEDT-TTF salts (see ref. 2).

$C_{20}H_{22}BrO_3S_{16}$, orthorhombic, *Pcca* (No. 54), $a = 32.83(1)$ Å, $b = 6.725(2)$ Å, $c = 15.020(5)$ Å, $V = 3316.1$ Å³, $Z = 4$, $R(F) = 0.059$, $R_w(F^2) = 0.173$.

Table 1. Parameters used for the X-ray data collection

Crystal:	black needle, size 0.07 x 0.25 x 0.60 mm
Wavelength:	Mo K_{α} radiation (0.71073 Å)
μ :	22.74 cm ⁻¹
Diffractometer:	Enraf-Nonius CAD4
Scan mode:	$\theta/2\theta$
$T_{\text{measurement}}$:	293 K
$2\theta_{\text{max}}$:	45°
$N(hkl)_{\text{unique}}$:	1322
Criterion for I_o :	$I_o > 3 \sigma(I_o)$
$N(\text{param})_{\text{refined}}$:	183
Programs:	SDP, SHELXS-86, SHELXL-93

Table 2. Final atomic coordinates and displacement parameters (in Å²)

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}
H(7A)	8f	0.2035(5)	−0.223(2)	0.448(1)	0.152
H(7B)	8f	0.1847(5)	−0.086(2)	0.375(1)	0.152
H(8A)	8f	0.2165(4)	0.089(2)	0.477(1)	0.144
H(8B)	8f	0.1901(4)	−0.005(2)	0.552(1)	0.144
H(9A)	8f	−0.1763(5)	0.283(2)	0.246(2)	0.230
H(9B)	8f	−0.1689(5)	0.306(2)	0.347(2)	0.230
H(10A)	8f	−0.1639(4)	0.574(2)	0.304(1)	0.160
H(10B)	8f	−0.1447(4)	0.513(2)	0.213(1)	0.160
H(1)	8f	0.2336	0.4302	0.3299	0.118
H(21)	8f	0.2564	0.2716	0.218	0.125
H(22)	8f	0.2554	0.0842	0.2261	0.125

Table 3. Final atomic coordinates and displacement parameters (in Å²)

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br	4e	1/4	1/2	0.0535(2)	0.083(2)	0.086(2)	0.088(2)	0.004(1)	0	0
S(1)	8f	0.05279(9)	−0.1012(4)	0.4032(2)	0.042(2)	0.029(2)	0.065(2)	0.001(1)	−0.010(2)	−0.004(1)
S(2)	8f	0.07178(8)	0.3156(4)	0.4376(2)	0.028(2)	0.029(2)	0.071(2)	0.003(1)	−0.006(2)	−0.004(1)
S(3)	8f	−0.03929(8)	0.0194(4)	0.3488(2)	0.035(2)	0.028(1)	0.063(2)	0.000(1)	−0.011(1)	−0.003(1)
S(4)	8f	−0.01842(9)	0.4398(4)	0.3714(2)	0.037(2)	0.028(1)	0.068(2)	−0.000(1)	−0.007(1)	−0.004(1)

Table 3. (Continued)

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
S(5)	8f	0.1347(1)	-0.2485(5)	0.4493(3)	0.052(2)	0.034(2)	0.094(2)	0.013(2)	-0.026(2)	-0.006(2)
S(6)	8f	0.15708(9)	0.2493(5)	0.4893(3)	0.032(2)	0.042(2)	0.101(3)	0.005(1)	-0.013(2)	-0.014(2)
S(7)	8f	-0.12358(9)	0.0926(4)	0.2886(2)	0.032(2)	0.040(2)	0.070(2)	0.000(1)	-0.015(2)	-0.007(1)
S(8)	8f	-0.0964(1)	0.5933(5)	0.3103(3)	0.047(2)	0.033(2)	0.132(3)	0.006(2)	-0.024(2)	0.001(2)
C(1)	8f	0.0355(3)	0.140(2)	0.4050(7)	0.032(7)	0.036(6)	0.039(6)	-0.003(5)	0.002(5)	0.000(5)
C(2)	8f	-0.0028(3)	0.192(2)	0.3789(7)	0.042(8)	0.035(6)	0.044(7)	-0.002(5)	0.004(5)	-0.002(5)
C(3)	8f	0.1015(3)	-0.048(2)	0.4412(7)	0.019(6)	0.035(7)	0.052(6)	0.010(5)	-0.005(5)	-0.004(5)
C(4)	8f	0.1108(3)	0.144(2)	0.4565(7)	0.027(6)	0.030(6)	0.051(7)	0.008(5)	-0.002(5)	-0.005(5)
C(5)	8f	-0.0769(3)	0.192(2)	0.3230(6)	0.020(6)	0.036(6)	0.041(6)	-0.001(5)	-0.004(5)	-0.003(5)
C(6)	8f	-0.0674(3)	0.384(2)	0.3318(7)	0.048(7)	0.032(6)	0.038(6)	0.001(5)	0.003(5)	-0.002(5)
C(7)	8f	0.1822(5)	-0.127(2)	0.436(1)	0.09(1)	0.05(1)	0.17(2)	0.027(9)	-0.01(1)	-0.01(1)
C(8)	8f	0.1893(4)	0.042(2)	0.491(1)	0.05(1)	0.042(9)	0.20(2)	0.007(6)	-0.04(1)	-0.02(1)
C(9)	8f	-0.1553(5)	0.307(2)	0.290(2)	0.07(1)	0.034(9)	0.36(4)	0.006(8)	-0.05(2)	-0.01(1)
C(10)	8f	-0.1431(4)	0.491(2)	0.277(1)	0.05(1)	0.06(1)	0.20(2)	0.006(9)	-0.06(1)	-0.00(1)
O(1)	4e	1/4	1/2	0.349(1)	0.062(8)	0.074(9)	0.10(1)	0.026(7)	0	0
O(2)	8f	0.2693(3)	0.177(2)	0.2154(7)	0.090(7)	0.068(6)	0.092(7)	-0.010(6)	0.007(6)	0.007(5)

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