Bis[(dimethyl-\(\lambda^4\)-sulfanylidene)oxonium] hexabromidotellurate(IV) dimethyl sulfoxide disolvate

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Crystal data

2C2H6OS2·Br6Te62−·2C2H6OS

Mw = 921.59
Triclinic, P
α = 8.0087 (2) Å
β = 9.2428 (2) Å
γ = 10.5249 (3) Å

y = 66.340 (1)°
V = 639.98 (3) Å³
Z = 1

Cu Kα radiation
μ = 23.30 mm⁻¹
T = 100 (2) K

0.23 × 0.20 × 0.16 mm

Data collection

Bruker APEX2 CCD detector
Absorption correction: numerical
[SADABS (Bruker, 2005)]

Tmin = 0.075, Tmax = 0.118
5232 measured reflections
2112 independent reflections
2112 reflections with I > 2σ(I)
Rint = 0.023

Refinement

R[F² > 2σ(F²)] = 0.021
wR(F²) = 0.056
S = 1.15
2112 reflections
159 parameters

Hydrogen-bond geometry (Å, °).

Table 1

D—H···A        D—H        H···A        D···A        D—H···A

O2—H2O···O1    0.83 (7)    1.62 (8)    2.448 (4)    175 (7)

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT; program(s) used to solve structure: XS in SHELXL (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: XP (Bruker, 1998); software used to prepare material for publication: X CIF in SHELXL (Sheldrick, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2262).

References

supplementary materials
The structure of (I) consists of two units of two H⁺ hydrogen bonded dimethylsulfoxide molecules, Fig. 1, and a centrosymmetric hexabromotellurate(IV) anion, Fig. 2. At 2.448 (4) Å, the O1···O2 distance is relatively short, and is consistent with the presence of a moderately strong hydrogen bond (Keefer et al., 1988). The IR spectrum reveals peaks typical for the [(dmso)₂H]⁺ cation with a strong band at 731 cm⁻¹. This is in line with similar samples in which the same cation has been analyzed (Jaswal et al., 1990). A closely related tellurium complex, [(dmso)₂H][TeCl₆] has been structurally reported at room temperature (Viossat et al., 1981) and at low temperature (Laitinen et al., 2002). The cation in the latter experiment shows a O1···O2 distance of 2.435 (3) Å and the authors describe this as "a relatively strong hydrogen bond".

The hexabromotellurate(IV) anion in (I) shows an approximately octahedral geometry as expected. A review of some related structures shows that there are packing factors that slightly distort the geometry. One example where [TeBr₆]²⁻ shows deviations away from the regular octahedral geometry indicates that there is a 0.024Å difference between the longest and shortest bond Te—Br bond lengths (Borgias et al., 1985). In that report, the Te atom is located in a general position. In other literature, the Te is located at a center of inversion and displays a larger angular deviation from 90° [87.56 (3) - 92.44 (3)°] (Abriel & du Bois, 1989) which is greater than those reported here [less than 0.9° away from 90°]. A review of structural data for MX₆E²⁻ compounds (M = Se, Te and X = Cl, Br, I) was published to provide an explanation of the stereochemistry of the lone pair electrons (Abriel, 1987).

The unit cell shows, Fig. 3, the pairs of hydrogen bonded dmso molecule and dmso-H ions and anions, Table 1.

### Experimental

Compound (I) was prepared by the slow cooling to room temperature of a hot solution (333 K) of tellurium dioxide (0.30 g, 0.19 mmol) dissolved in hydrobromic acid (1 mL) to which dimethylsulfoxide (5 mL) had been added. After 2 weeks, a crop of orange crystals formed although they are prone to solvent loss and decomposition. Analysis found: C 10.57; H 2.91; C₈H₂₆Br₆O₄S₄Te requires: C 10.42, H 2.84. The IR spectrum showed strong bands at 3392, 1056, 731 cm⁻¹.

### Refinement

The maximum and minimum electron density peaks of 1.01 and -0.68 e Å⁻³, respectively, are located 0.88 and 1.53 Å, respectively, from the Te atom. Hydrogen atoms positions were refined freely with C-H = 0.83 (7) - 1.03 (6) Å.
Bis[(dimethyl-\(\lambda^4\)-sulfanylidene)oxonium] hexabromoditellurate(IV) dimethyl sulfoxide disolvate

Crystal data

\[
\begin{align*}
2\text{C}_2\text{H}_7\text{OS}^+\cdot\text{Br}_6\text{Te}^{2-}\cdot2\text{C}_2\text{H}_6\text{OS} & \quad Z = 1 \\
M_r = 921.59 & \quad F_{000} = 432 \\
\text{Triclinic, } P\bar{1} & \quad D_x = 2.391 \text{ Mg m}^{-3} \\
\text{Hall symbol: } -P 1 & \quad \text{Melting point: } 343 \text{ K} \\
a = 8.0087 (2) \text{ Å} & \quad \text{Cu } K\alpha \text{ radiation} \\
b = 9.2428 (2) \text{ Å} & \quad \lambda = 1.54178 \text{ Å} \\
c = 10.5249 (3) \text{ Å} & \quad \text{Cell parameters from 4736 reflections} \\
\alpha = 66.280 (1)^\circ & \quad 0 = 5^\circ-66^\circ \\
\beta = 70.732 (1)^\circ & \quad \mu = 23.30 \text{ mm}^{-1} \\
\gamma = 66.340 (1)^\circ & \quad T = 100 (2) \text{ K} \\
V = 639.98 (3) \text{ Å}^3 & \quad \text{Block, orange} \\
& \quad 0.23 \times 0.20 \times 0.16 \text{ mm} \\
\end{align*}
\]

Data collection

Bruker APEX2 CCD detector 
\text{diffractometer} 
\text{Radiation source: fine-focus sealed tube} 
\text{2112 independent reflections} 
\text{2112 reflections with } I > 2\sigma(I)
Monochromator: graphite  
\( T = 100(2) \) K  
\( \omega \) scans  
Absorption correction: numerical  
[based on real shape of the crystal; absorption correction followed by the application of SADABS (Bruker, 2005)]  
\( T_{\text{min}} = 0.075, \ T_{\text{max}} = 0.118 \)  
5232 measured reflections

Reefinement

Hydrogen site location: difference Fourier map  
Least-squares matrix: full  
\( R[F^2 > 2\sigma(F^2)] = 0.021 \)  
\( wR(F^2) = 0.056 \)  
\( S = 1.15 \)  
2112 reflections  
159 parameters  
Primary atom site location: structure-invariant direct methods  
Secondary atom site location: difference Fourier map

Special details

Experimental. Analysis found: C 10.57; H 2.91; C~8--H~26--Br~6Õ~4~S~4~Te requires: C 10.42, H 2.84

Geometry. All e.s.d.’s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.’s are taken into account individually in the estimation of e.s.d.’s in distances, angles and torsion angles; correlations between e.s.d.’s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.’s is used for estimating e.s.d.’s involving l.s. planes.

Reefinement. Refinement of F² against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F², conventional R-factors R are based on F, with F set to zero for negative F². The threshold expression of F² > 2σ(F²) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F² are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

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supplementary materials

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Geometric parameters (Å, °)

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sup-4
C1—H1C  0.97 (5)  C4—H4C  1.01 (5)
C2—H2A  0.98 (5)
Br1—Te1—Br1  180.0  H1B—Cl1—H1C  117 (4)
Br1—Te1—Br3  89.604 (11)  S1—C2—H2A  107 (3)
Br1—Te1—Br3  90.395 (11)  S1—C2—H2B  110 (3)
Br1—Te1—Br3\textsuperscript{i}  90.397 (11)  H2A—C2—H2B  110 (4)
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Br3—Te1—Br3  179.999 (11)  H2A—C2—H2C  112 (4)
Br1—Te1—Br3\textsuperscript{i}  89.151 (11)  H2B—C2—H2C  114 (4)
Br1—Te1—Br2\textsuperscript{i}  90.849 (11)  O2—S2—C3  102.38 (19)
Br3—Te1—Br2\textsuperscript{i}  89.485 (12)  O2—S2—C4  102.5 (2)
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Br3—Te1—Br2\textsuperscript{i}  89.485 (12)  H3A—C3—H3B  104 (4)
Br2—Te1—Br2\textsuperscript{i}  180.0  S2—C3—H3C  107 (3)
O1—S1—C2  103.95 (17)  H3A—C3—H3C  115 (4)
O1—S1—C1  104.47 (17)  H3B—C3—H3C  116 (5)
C2—S1—C1  98.62 (19)  S2—C4—H4A  114 (3)
S1—C1—H1A  108 (3)  S2—C4—H4B  107 (4)
S1—C1—H1B  106 (3)  H4A—C4—H4B  108 (5)
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S1—C1—H1C  106 (3)  H4A—C4—H4C  110 (4)
H1A—C1—H1C  108 (4)  H4B—C4—H4C  111 (5)
Symmetry codes: (i) \(-x+1, -y, -z+1\).

**Hydrogen-bond geometry (Å, °)**

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<tr>
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Fig. 2
supplementary materials

Fig. 3