

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

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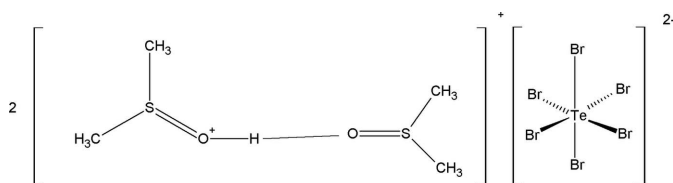
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{S–C}) = 0.005$ Å; R factor = 0.021; wR factor = 0.057; data-to-parameter ratio = 13.3.

The structure of the title salt, $2\text{C}_2\text{H}_7\text{OS}^+\cdot\text{Br}_6\text{Te}^{2-}\cdot 2\text{C}_2\text{H}_6\text{OS}$, displays $\text{O–H}\cdots\text{O}$ hydrogen bonding between one protonated dimethyl sulfoxide molecule and a neighboring dimethyl sulfoxide molecule, and an octahedral geometry for the Te atom; the latter is situated on a center of inversion.

Related literature

For the structure of the related compound $[(\text{dmsO–H})_2]\text{[TeCl}_6]$, see: Laitinen *et al.* (2002); Viossat *et al.* (1981). For related literature, see Abriél (1987); Abriél & du Bois (1989); Borgias *et al.* (1985); Jaswal *et al.* (1990); Keefer *et al.* (1988).



Experimental

Crystal data

$2\text{C}_2\text{H}_7\text{OS}^+\cdot\text{Br}_6\text{Te}^{2-}\cdot 2\text{C}_2\text{H}_6\text{OS}$

$M_r = 921.59$

Triclinic, $P\bar{1}$

$a = 8.0087$ (2) Å

$b = 9.2428$ (2) Å

$c = 10.5249$ (3) Å

$\alpha = 66.280$ (1)°

$\beta = 70.732$ (1)°

$\gamma = 66.340$ (1)°

$V = 639.98$ (3) Å³

$Z = 1$

Cu $K\alpha$ radiation

$\mu = 23.30$ mm⁻¹

$T = 100$ (2) K

$0.23 \times 0.20 \times 0.16$ mm

Data collection

Bruker APEX2 CCD detector
diffractometer

Absorption correction: numerical
[based on real shape of the
crystal; absorption correction
followed by the application of

SADABS (Bruker, 2005)]

$T_{\min} = 0.075$, $T_{\max} = 0.118$

5232 measured reflections

2112 independent reflections

2112 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$

$wR(F^2) = 0.056$

$S = 1.15$

2112 reflections

159 parameters

All H-atom parameters refined

$\Delta\rho_{\text{max}} = 1.02$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.68$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D\text{—H}\cdots A$	$D\text{—H}$	$\text{H}\cdots A$	$D\cdots A$	$D\text{—H}\cdots A$
$\text{O2—H2O}\cdots\text{O1}$	0.83 (7)	1.62 (8)	2.448 (4)	175 (7)

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

This work was supported in part by a University of Wisconsin Colleges Summer Faculty Research Grant. MDR acknowledges Marquette University for the use of X-ray diffraction facilities and the University of Wisconsin - Fox Valley's Professional Development Committee for travel funding.

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

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supplementary materials

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Comment

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]₂[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 0.024 Å 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.

Figures

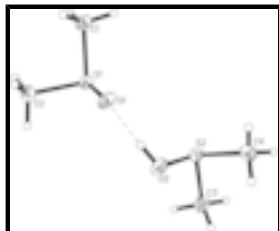


Fig. 1. Numbering Scheme for $[(\text{DMSO})_2\text{H}]^+$ (the hydrogen bond is shown as a dashed line). Displacement ellipsoids are shown at the 50% level.

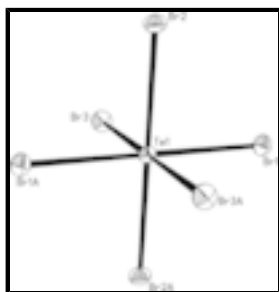


Fig. 2. Numbering Scheme for $[\text{TeBr}_6]^{2-}$. Displacement ellipsoids are shown at the 50% level.

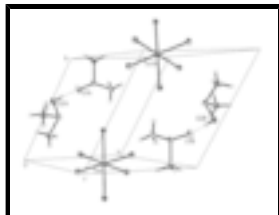


Fig. 3. Hydrogen-bond formation and projection of the unit cell content of $[(\text{DMSO})_2\text{H}]_2[\text{TeBr}_6]$. Symmetry operators: Te1A $[x, y+1, z]$; O1A and O2A $[1-x, 1-y, -z]$; O1B and O2B $[x, y, z+1]$

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Crystal data

$2\text{C}_2\text{H}_7\text{OS}^+ \cdot \text{Br}_6\text{Te}^{2-} \cdot 2\text{C}_2\text{H}_6\text{OS}$

$M_r = 921.59$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 8.0087\ (2)\ \text{\AA}$

$b = 9.2428\ (2)\ \text{\AA}$

$c = 10.5249\ (3)\ \text{\AA}$

$\alpha = 66.280\ (1)^\circ$

$\beta = 70.732\ (1)^\circ$

$\gamma = 66.340\ (1)^\circ$

$V = 639.98\ (3)\ \text{\AA}^3$

$Z = 1$

$F_{000} = 432$

$D_x = 2.391\ \text{Mg m}^{-3}$

Melting point: 343 K

Cu $K\alpha$ radiation

$\lambda = 1.54178\ \text{\AA}$

Cell parameters from 4736 reflections

$\theta = 5\text{--}66^\circ$

$\mu = 23.30\ \text{mm}^{-1}$

$T = 100\ (2)\ \text{K}$

Block, orange

$0.23 \times 0.20 \times 0.16\ \text{mm}$

Data collection

Bruker APEX2 CCD detector
diffractometer

Radiation source: fine-focus sealed tube

2112 independent reflections

2112 reflections with $I > 2\sigma(I)$

Monochromator: graphite $R_{\text{int}} = 0.023$
 $T = 100(2)$ K $\theta_{\text{max}} = 66.8^\circ$
 ω scans $\theta_{\text{min}} = 4.7^\circ$
 Absorption correction: numerical
 [based on real shape of the crystal; absorption correction followed by the application of SADABS (Bruker, 2005)] $h = -8 \rightarrow 9$
 $T_{\text{min}} = 0.075$, $T_{\text{max}} = 0.118$ $k = -9 \rightarrow 10$
 5232 measured reflections $l = 0 \rightarrow 12$

Refinement

Refinement on F^2 Hydrogen site location: difference Fourier map
 Least-squares matrix: full All H-atom parameters refined
 $R[F^2 > 2\sigma(F^2)] = 0.021$ $w = 1/[\sigma^2(F_o^2) + (0.0268P)^2 + 1.1408P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.056$ $(\Delta/\sigma)_{\text{max}} = 0.004$
 $S = 1.15$ $\Delta\rho_{\text{max}} = 1.02 \text{ e } \text{\AA}^{-3}$
 2112 reflections $\Delta\rho_{\text{min}} = -0.68 \text{ e } \text{\AA}^{-3}$
 159 parameters Extinction correction: SHELXL97 (Sheldrick, 2008),
 $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Primary atom site location: structure-invariant direct methods Extinction coefficient: 0.00507 (17)
 Secondary atom site location: difference Fourier map

Special details

Experimental. Analysis found: C 10.57; H 2.91; C~8~H~26~Br~6O~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.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Te1	0.5000	0.0000	0.5000	0.01240 (12)
Br1	0.47203 (5)	0.30103 (4)	0.30479 (4)	0.01875 (12)
Br2	0.13998 (5)	0.11843 (5)	0.62389 (4)	0.01970 (12)
Br3	0.39388 (5)	-0.09389 (5)	0.33507 (4)	0.02004 (12)
S1	0.72250 (12)	0.24280 (11)	-0.11647 (9)	0.0176 (2)
O1	0.8060 (4)	0.2997 (3)	-0.0395 (3)	0.0229 (6)
C1	0.4776 (5)	0.3040 (5)	-0.0455 (4)	0.0213 (8)

supplementary materials

H1A	0.459 (7)	0.246 (6)	0.054 (5)	0.030 (12)*
H1B	0.440 (7)	0.421 (7)	-0.066 (5)	0.032 (13)*
H1C	0.424 (6)	0.263 (6)	-0.088 (5)	0.026 (12)*
C2	0.7743 (6)	0.0237 (5)	-0.0301 (4)	0.0215 (8)
H2A	0.700 (7)	-0.016 (6)	-0.060 (5)	0.027 (11)*
H2B	0.741 (6)	0.002 (6)	0.070 (5)	0.027 (12)*
H2C	0.907 (7)	-0.020 (6)	-0.066 (5)	0.025 (11)*
S2	1.03170 (12)	0.54942 (12)	-0.30476 (10)	0.0219 (2)
O2	1.0726 (4)	0.4039 (4)	-0.1636 (3)	0.0256 (6)
H2O	0.985 (10)	0.364 (9)	-0.123 (8)	0.07 (2)*
C3	1.2525 (6)	0.5183 (6)	-0.4190 (5)	0.0266 (9)
H3A	1.340 (7)	0.519 (6)	-0.369 (5)	0.029 (12)*
H3B	1.245 (7)	0.614 (7)	-0.496 (6)	0.040 (14)*
H3C	1.284 (8)	0.410 (7)	-0.440 (6)	0.049 (15)*
C4	1.0161 (7)	0.7251 (6)	-0.2660 (6)	0.0321 (10)
H4A	1.015 (7)	0.822 (7)	-0.346 (6)	0.040 (14)*
H4B	0.913 (8)	0.747 (7)	-0.207 (6)	0.043 (15)*
H4C	1.125 (7)	0.695 (6)	-0.222 (5)	0.035 (13)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Te1	0.01221 (17)	0.01490 (18)	0.01250 (17)	-0.00478 (12)	-0.00205 (12)	-0.00641 (12)
Br1	0.0217 (2)	0.0180 (2)	0.0169 (2)	-0.00800 (15)	-0.00436 (15)	-0.00352 (15)
Br2	0.0143 (2)	0.0229 (2)	0.0215 (2)	-0.00556 (15)	0.00073 (15)	-0.01025 (16)
Br3	0.0237 (2)	0.0221 (2)	0.0211 (2)	-0.00733 (16)	-0.00826 (16)	-0.01003 (16)
S1	0.0187 (4)	0.0208 (4)	0.0158 (4)	-0.0096 (4)	-0.0020 (3)	-0.0059 (3)
O1	0.0228 (14)	0.0314 (15)	0.0234 (13)	-0.0161 (12)	-0.0018 (11)	-0.0118 (11)
C1	0.0215 (19)	0.026 (2)	0.022 (2)	-0.0115 (17)	-0.0024 (16)	-0.0095 (17)
C2	0.025 (2)	0.0208 (19)	0.021 (2)	-0.0087 (17)	-0.0077 (17)	-0.0047 (16)
S2	0.0167 (4)	0.0226 (5)	0.0279 (5)	-0.0070 (4)	-0.0058 (4)	-0.0075 (4)
O2	0.0243 (15)	0.0295 (15)	0.0261 (14)	-0.0158 (13)	-0.0052 (12)	-0.0042 (12)
C3	0.026 (2)	0.028 (2)	0.028 (2)	-0.0117 (18)	0.0002 (18)	-0.0107 (18)
C4	0.024 (2)	0.025 (2)	0.049 (3)	-0.0039 (18)	-0.002 (2)	-0.021 (2)

Geometric parameters (\AA , $^\circ$)

Te1—Br1 ⁱ	2.6865 (4)	C2—H2B	0.95 (5)
Te1—Br1	2.6865 (4)	C2—H2C	0.97 (5)
Te1—Br3	2.6956 (4)	S2—O2	1.576 (3)
Te1—Br3 ⁱ	2.6956 (4)	S2—C3	1.767 (4)
Te1—Br2 ⁱ	2.7103 (4)	S2—C4	1.776 (4)
Te1—Br2	2.7103 (4)	O2—H2O	0.83 (7)
S1—O1	1.537 (3)	C3—H3A	1.00 (5)
S1—C2	1.787 (4)	C3—H3B	0.92 (6)
S1—C1	1.791 (4)	C3—H3C	1.03 (6)
C1—H1A	0.96 (5)	C4—H4A	0.95 (6)
C1—H1B	0.95 (5)	C4—H4B	0.86 (6)

C1—H1C	0.97 (5)	C4—H4C	1.01 (5)
C2—H2A	0.98 (5)		
Br1 ⁱ —Te1—Br1	180.0	H1B—C1—H1C	117 (4)
Br1 ⁱ —Te1—Br3	89.604 (11)	S1—C2—H2A	107 (3)
Br1—Te1—Br3	90.395 (11)	S1—C2—H2B	110 (3)
Br1 ⁱ —Te1—Br3 ⁱ	90.397 (11)	H2A—C2—H2B	110 (4)
Br1—Te1—Br3 ⁱ	89.604 (11)	S1—C2—H2C	103 (3)
Br3—Te1—Br3 ⁱ	179.999 (1)	H2A—C2—H2C	112 (4)
Br1 ⁱ —Te1—Br2 ⁱ	89.151 (11)	H2B—C2—H2C	114 (4)
Br1—Te1—Br2 ⁱ	90.849 (11)	O2—S2—C3	102.38 (19)
Br3—Te1—Br2 ⁱ	89.485 (12)	O2—S2—C4	102.5 (2)
Br3 ⁱ —Te1—Br2 ⁱ	90.515 (11)	C3—S2—C4	100.2 (2)
Br1 ⁱ —Te1—Br2	90.848 (11)	S2—O2—H2O	112 (5)
Br1—Te1—Br2	89.151 (11)	S2—C3—H3A	106 (3)
Br3—Te1—Br2	90.515 (11)	S2—C3—H3B	107 (3)
Br3 ⁱ —Te1—Br2	89.485 (12)	H3A—C3—H3B	104 (4)
Br2 ⁱ —Te1—Br2	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)
H1A—C1—H1B	113 (4)	S2—C4—H4C	108 (3)
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 ($\text{\AA}, ^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O2—H2O \cdots O1	0.83 (7)	1.62 (8)	2.448 (4)	175 (7)

Fig. 1

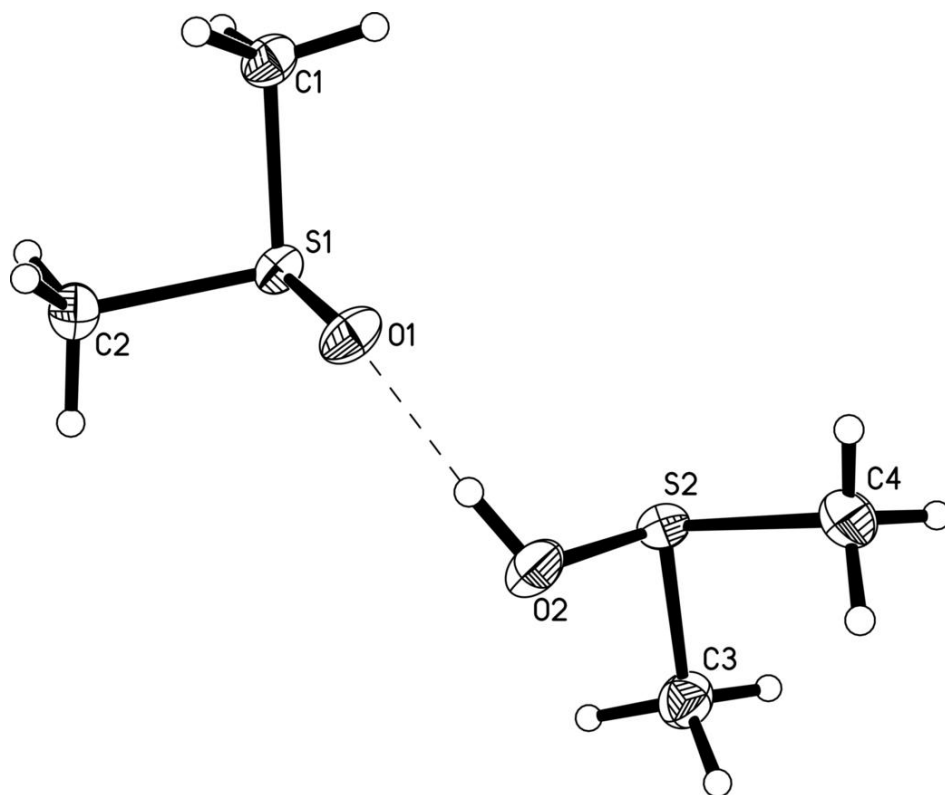


Fig. 2

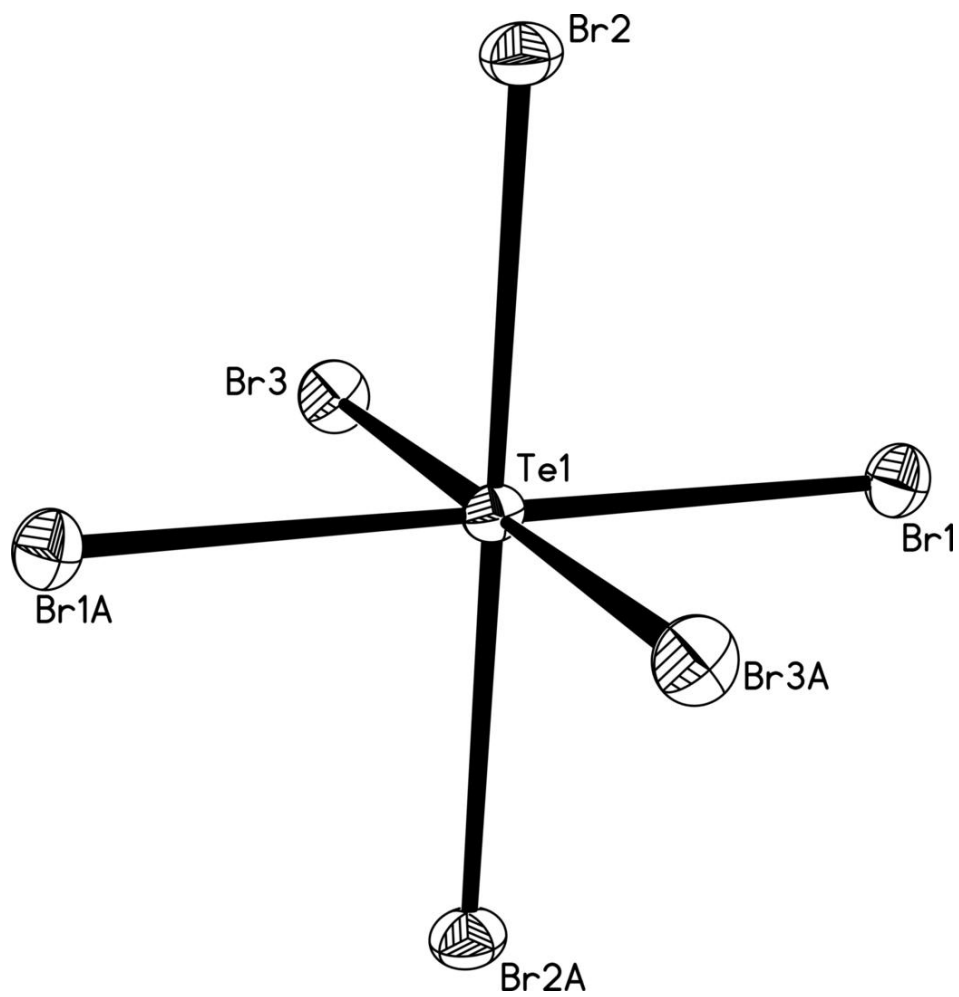


Fig. 3

