Cs$_2$[WS$_4$]

Bikshandarkoil R. Srinivasan, Christian Näther and Wolfgang Bensch

Cs₂[WS₄]

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The title compound, dicaesium tetrathiotungstate(VI), was obtained from a dilute aqueous solution containing equimolar quantities of Cs_2CO_3 and $(NH_4)_2[WS_4]$. The compound crystallizes in the orthorhombic space group *Pnma* and is isotypic with $Cs_2[MoS_4]$, $Rb_2[WS_4]$, $(NH_4)_2[WS_4]$ and $K_2[MoS_4]$. The structure contains discrete slightly distorted tetrahedral $[WS_4]^{2-}$ anions (*m* symmetry), separated by Cs^+ cations. One of the two unique Cs^+ cations (both located on mirror planes) is surrounded by nine S atoms and the other by ten S atoms.

Related literature

The title compound has previously been characterized by X-ray powder diffraction (Müller & Sievert, 1974). For isotypic structures see: $Cs_2[MoS_4]$ (Raymond *et al.*, 1995), $K_2[MoS_4]$ (Emirdag-Eanes & Ibers, 2001), $Rb_2[MoS_4]$ (Ellermeier *et al.*, 1999), $Rb_2[WS_4]$ (Yao & Ibers, 2004) and $(NH_4)_2[WS_4]$ (Srinivasan *et al.*, 2004). Various tetrathiotungstates with organic ammonium counter cations were characterized by Srinivasan *et al.* (2007).

Experimental

Crystal data

$Cs_2[WS_4]$	$V = 929.70\ (12)$ Å³
$M_r = 577.91$	$Z = 4$
Orthorhombic, $Pnma$	Mo $K\alpha$ radiation
$a = 10.0579\ (9)$ Å	$\mu = 20.95$ mm⁻¹
$b = 7.2362\ (5)$ Å	$T = 170\ (2)$ K
$c = 12.7740\ (9)$ Å	$0.08 \times 0.07 \times 0.04$ mm

Data collection

Stoe IPDSI diffractometer	11509 measured reflections
Absorption correction: numerical (X-$SHAPE$; Stoe & Cie, 1998)	1492 independent reflections
	1322 reflections with $I > 2\sigma(I)$
$T_{min} = 0.211,\ T_{max} = 0.442$	$R_{int} = 0.060$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$	41 parameters
$wR(F^2) = 0.069$	$\Delta\rho_{max} = 2.31$ e Å⁻³
$S = 1.03$	$\Delta\rho_{min} = -2.62$ e Å⁻³
1492 reflections	

Table 1
Selected geometric parameters (Å, °).

W1—S3	2.1915 (12)	Cs1—S2ᵛⁱⁱ	3.7072 (5)
W1—S3ⁱ	2.1915 (12)	Cs2—S1ᵛⁱⁱⁱ	3.6564 (4)
W1—S1	2.1935 (18)	Cs2—S1ⁱˣ	3.6564 (4)
W1—S2	2.2079 (18)	Cs2—S3ˣ	3.7170 (15)
Cs1—S1ⁱⁱ	3.451 (2)	Cs2—S3ᵛⁱⁱⁱ	3.7170 (15)
Cs1—S1	3.5331 (19)	Cs2—S3ˣⁱ	3.7384 (14)
Cs1—S3ⁱⁱⁱ	3.5502 (14)	Cs2—S3ˣⁱⁱ	3.7384 (14)
Cs1—S3ⁱᵛ	3.5502 (14)	Cs2—S2ˣⁱⁱⁱ	3.7527 (19)
Cs1—S3ᵛ	3.5680 (14)	Cs2—S2	3.926 (2)
Cs1—S3ᵛⁱ	3.5680 (14)	Cs2—S3	4.0448 (16)
Cs1—S2ⁱⁱ	3.579 (2)	Cs2—S3ⁱ	4.0448 (16)
Cs1—S2ⁱᵛ	3.7072 (5)		
S3—W1—S3ⁱ	108.86 (7)	S3—W1—S2	109.65 (4)
S3—W1—S1	108.92 (5)	S1—W1—S2	110.82 (8)

Symmetry codes: (i) $x, -y + \frac{1}{2}, z$; (ii) $x - \frac{1}{2}, y, -z + \frac{1}{2}$; (iii) $-x + \frac{3}{2}, y + \frac{1}{2}, z - \frac{1}{2}$; (iv) $-x + \frac{3}{2}, -y, z - \frac{1}{2}$; (v) $-x + 1, y + \frac{1}{2}, -z + 1$; (vi) $-x + 1, -y, -z + 1$; (vii) $-x + \frac{3}{2}, -y + 1, z - \frac{1}{2}$; (viii) $-x + \frac{3}{2}, -y, z + \frac{1}{2}$; (ix) $-x + \frac{3}{2}, -y + 1, z + \frac{1}{2}$; (x) $-x + \frac{3}{2}, y + \frac{1}{2}, z + \frac{1}{2}$; (xi) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{3}{2}$; (xii) $x + \frac{1}{2}, y, -z + \frac{3}{2}$; (xiii) $x - \frac{1}{2}, y, -z + \frac{3}{2}$.

Data collection: *DIF4* (Stoe & Cie, 1998); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *XCIF* in *SHELXTL* (Bruker, 1998).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2130).

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supplementary materials

Cs$_2$[WS$_4$]

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Comment

As part of an ongoing research programme, we are investigating the synthesis and structural characterization of organic ammonium tetrathiometalates of the group VI metals Mo and W (Srinivasan *et al.*, 2007). While several tetrathiotungstates containing organic ammonium cations are known (Srinivasan *et al.*, 2007, and literature therein), the structures of only two tetrathiotungstates with inorganic counter cations, *viz.* Rb$_2$[WS$_4$] (Yao & Ibers, 2004) and (NH$_4$)$_2$[WS$_4$] (Srinivasan *et al.*, 2004) are reported so far. Here we describe the structure of dicesium tetrathiotungstate(VI) (I) which is isotypic with the corresponding Mo compounds Cs$_2$[MoS$_4$] (Raymond *et al.*, 1995), K$_2$[MoS$_4$] (Emirdag-Eanes & Ibers, 2001), Rb$_2$[MoS$_4$] (Ellermeier *et al.*, 1999), and with the aforementioned Rb$_2$[WS$_4$] and (NH$_4$)$_2$[WS$_4$]. The lattice parameters of (I) are consistent with a previous determination from X-ray powder data (a = 10.05 Å, b = 7.24 Å, c = 12.85 Å and V = 935.4 Å^3; Müller & Sievert, 1974).

The structure of (I) consists of discrete tetrahedral [WS$_4$]$^{2-}$ ions (*m* symmetry), separated by Cs$^+$ cations (Fig. 1). The [WS$_4$] tetrahedron is slightly distorted with S—W—S angles between 108.86 (7) and 110.82 (8) ° (Table 1). The W—S bond lengths range from 2.1915 (12) to 2.2079 (18) Å with an average value of 2.196 Å which is comparable with the bond lengths ranging from 2.1710 (17) to 2.2053 (14) Å in the lighter homologue Rb$_2$[WS$_4$] (Yao & Ibers, 2004). Interestingly, the difference Δ between the longest and the shortest W—S bond of 0.0164 Å in (I) is comparable to the Δ value of 0.0134 Å in (NH$_4$)$_2$[WS$_4$] (Srinivasan *et al.*, 2004), but much less than the Δ value of 0.0343 Å for the isotypic Rb$_2$[WS$_4$]. Two crystallographically independent Cs$^+$ cations are present in the asymmetric unit and both are coordinated by S atoms leading to irregular polyhedra. The packing of the structure is illustrated in Fig. 2. The Cs1—S distances range from 3.451 (2) to 3.7072 (5) Å (average 3.579 Å) while the Cs2—S distances vary between 3.6564 (4) and 4.0448 (16) Å. The mean Cs2—S distance (3.799 Å) is significantly longer than the average Cs1—S distance. Cs1 is surrounded by six symmetry related [WS$_4$]$^{2-}$ tetrahedra *via* nine S atoms (Fig. 3), while Cs2 is surrounded by five symmetry related [WS$_4$]$^{2-}$ tetrahedra *via* ten S atoms.

Experimental

The title compound was crystallized from a very dilute aqueous solution (90 ml) containing equimolar quantities of (NH$_4$)$_2$[WS$_4$] (174 mg, 0.5 mmol) and Cs$_2$CO$_3$ (163 mg, 0.5 mmol). It is to be noted that the use of more concentrated solutions leads to the formation of microcrystalline products. The crystals were filtered, washed with ice-cold water (2 ml), followed by 2-propanol (10 ml) and diethyl ether (10 ml), and air dried. The yield of the air stable yellow crystals was approximately 50%. The mid IR spectrum of (I) exhibits no signals above 500 cm^{-1}. The intense signal at 460 cm^{-1} can be assigned to the triply degenerate asymmetric stretching vibration of the [WS$_4$]$^{2-}$ tetrahedron. The Raman spectrum shows intense signals at 481 and 179 cm^{-1} and a weak signal at 460 cm^{-1}, as expected for the tetrathiotungstate anion.

supplementary materials

Refinement

The largest peak in the residual electron density map is located at a distance of 0.68 Å from Cs2 and the deepest hole 0.78 Å from W1.
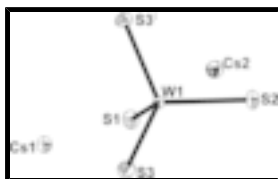
Figures

Fig. 1. Part of the crystal structure of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $x, -y + 1/2, z$]
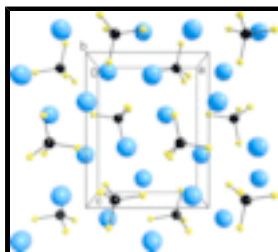

Fig. 2. A perspective view of the crystal packing of (I) along the b axis. Cs atoms are represented as blue spheres, W atoms as black spheres and S atoms as yellow spheres.

Fig. 3. A view of the surroundings of the Cs1 cation showing Cs1 linked to six different $[WS_4]^{2-}$ units *via* nine S atoms (Cs···S distances are shown as dashed lines). [Symmetry codes: (ii) $x - 1/2, y, -z + 1/2$; (iii) $-x + 3/2, y + 1/2, z - 1/2$; (iv) $-x + 3/2, -y, z - 1/2$; (v) $-x + 1, y + 1/2, -z + 1$; (vi) $-x + 1, -y, -z + 1$; (vii) $-x + 3/2, -y + 1, z - 1/2$.]

dicaesium tetrathiotungstate(VI)

Crystal data

$Cs_2[WS_4]$	$F_{000} = 992$
$M_r = 577.91$	$D_x = 4.129$ Mg m^{-3}
Orthorhombic, *Pnma*	Mo *Kα* radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2ac 2n	Cell parameters from 8000 reflections
$a = 10.0579$ (9) Å	$\theta = 3.0–30.0º$
$b = 7.2362$ (5) Å	$\mu = 20.95$ mm^{-1}
$c = 12.7740$ (9) Å	$T = 170$ (2) K
$V = 929.70$ (12) Å^3	Block, yellow
$Z = 4$	$0.08 \times 0.07 \times 0.04$ mm

Data collection

STOE IPDS 1	1492 independent reflections

sup-2

diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

T = 170(2) K

φ–scans

Absorption correction: numerical
(X-SHAPE; Stoe & Cie, 1998)

T_{min} = 0.211, T_{max} = 0.442

11509 measured reflections

1322 reflections with $I > 2\sigma(I)$

R_{int} = 0.060

θ_{max} = 30.4º

θ_{min} = 2.6º

$h = -14 \rightarrow 14$

$k = -10 \rightarrow 10$

$l = -17 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.027

$wR(F^2)$ = 0.069

S = 1.03

1492 reflections

41 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

$w = 1/[\sigma^2(F_o^2) + (0.0492P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001

$\Delta\rho_{max}$ = 2.31 e Å^{-3}

$\Delta\rho_{min}$ = −2.62 e Å^{-3}

Extinction correction: SHELXL97,
$Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.00164 (18)

Special details

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 $F^2 > 2sigma(F^2)$ 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 ($Å^2$)

	x	y	z	$U_{iso}*/U_{eq}$
W1	0.75191 (3)	0.2500	0.57843 (2)	0.00972 (10)
Cs1	0.53579 (4)	0.2500	0.16913 (3)	0.01439 (12)
Cs2	0.84172 (5)	0.2500	0.89664 (4)	0.01797 (12)
S1	0.7079 (2)	0.2500	0.41025 (14)	0.0169 (3)
S2	0.96862 (18)	0.2500	0.60598 (15)	0.0169 (3)
S3	0.66310 (14)	0.00367 (16)	0.64964 (12)	0.0186 (3)

supplementary materials

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
W1	0.00771 (15)	0.00837 (14)	0.01308 (15)	0.000	0.00028 (8)	0.000
Cs1	0.0121 (2)	0.01475 (19)	0.0163 (2)	0.000	−0.00075 (15)	0.000
Cs2	0.0160 (2)	0.0149 (2)	0.0230 (2)	0.000	0.00236 (17)	0.000
S1	0.0167 (9)	0.0187 (8)	0.0153 (8)	0.000	−0.0041 (6)	0.000
S2	0.0094 (7)	0.0197 (8)	0.0215 (8)	0.000	−0.0022 (6)	0.000
S3	0.0164 (6)	0.0125 (5)	0.0268 (7)	−0.0011 (4)	0.0048 (5)	0.0056 (4)

Geometric parameters (Å, °)

W1—S3	2.1915 (12)	Cs2—S1^v	3.6564 (4)
W1—S3^i	2.1915 (12)	Cs2—S1^{iv}	3.6564 (4)
W1—S1	2.1935 (18)	Cs2—S3^{xii}	3.7170 (15)
W1—S2	2.2079 (18)	Cs2—S3^v	3.7170 (15)
W1—Cs2^{ii}	4.1380 (7)	Cs2—S3^{xiii}	3.7384 (14)
W1—Cs2	4.1640 (6)	Cs2—S3^{xiv}	3.7384 (14)
W1—Cs1^{iii}	4.2606 (6)	Cs2—S2^{ii}	3.7527 (19)
W1—Cs1^{iv}	4.3580 (4)	Cs2—S2	3.926 (2)
W1—Cs1^v	4.3580 (4)	Cs2—S3	4.0448 (16)
W1—Cs2^{vi}	4.4011 (4)	Cs2—S3^i	4.0448 (16)
W1—Cs2^{vii}	4.4011 (4)	Cs2—W1^{xiv}	4.1380 (7)
Cs1—S1^{viii}	3.451 (2)	S1—Cs1^{iii}	3.451 (2)
Cs1—S1	3.5331 (19)	S1—Cs2^{vi}	3.6564 (4)
Cs1—S3^{ix}	3.5502 (14)	S1—Cs2^{vii}	3.6564 (4)
Cs1—S3^{vi}	3.5502 (14)	S2—Cs1^{iii}	3.579 (2)
Cs1—S3^x	3.5680 (14)	S2—Cs1^{iv}	3.7072 (5)
Cs1—S3^{xi}	3.5680 (14)	S2—Cs1^v	3.7072 (5)
Cs1—S2^{viii}	3.579 (2)	S2—Cs2^{xiv}	3.7527 (19)
Cs1—S2^{vi}	3.7072 (5)	S3—Cs1^v	3.5502 (14)
Cs1—S2^{vii}	3.7072 (5)	S3—Cs1^{xi}	3.5680 (14)
Cs1—W1^{viii}	4.2606 (6)	S3—Cs2^{vi}	3.7170 (15)
Cs1—W1^{vii}	4.3580 (4)	S3—Cs2^{ii}	3.7384 (14)
Cs1—W1^{vi}	4.3580 (4)		
S3—W1—S3^i	108.86 (7)	S3^x—Cs1—W1^{vi}	150.96 (2)
S3—W1—S1	108.92 (5)	S3^{xi}—Cs1—W1^{vi}	91.15 (2)
S3^i—W1—S1	108.92 (5)	S2^{viii}—Cs1—W1^{vi}	80.295 (18)
S3—W1—S2	109.65 (4)	S2^{vi}—Cs1—W1^{vi}	30.43 (3)
S3^i—W1—S2	109.65 (4)	S2^{vii}—Cs1—W1^{vi}	139.31 (3)
S1—W1—S2	110.82 (8)	W1^{viii}—Cs1—W1^{vi}	97.530 (9)
S3—W1—Cs2^{ii}	64.00 (4)	W1^{vii}—Cs1—W1^{vi}	112.242 (12)

S3^i—W1—Cs2^{ii}	64.00 (4)	S1^v—Cs2—S1^{iv}	163.39 (6)
S1—W1—Cs2^{ii}	82.76 (5)	S1^v—Cs2—S3^{xii}	116.46 (4)
S2—W1—Cs2^{ii}	166.41 (5)	S1^{iv}—Cs2—S3^{xii}	57.87 (3)
S3—W1—Cs2	71.53 (4)	S1^v—Cs2—S3^v	57.87 (3)
S3^i—W1—Cs2	71.53 (4)	S1^{iv}—Cs2—S3^v	116.46 (4)
S1—W1—Cs2	179.12 (6)	S3^{xii}—Cs2—S3^v	59.19 (4)
S2—W1—Cs2	68.30 (5)	S1^v—Cs2—S3^{xiii}	126.67 (4)
Cs2^{ii}—W1—Cs2	98.115 (10)	S1^{iv}—Cs2—S3^{xiii}	69.74 (4)
S3—W1—Cs1^{iii}	125.54 (4)	S3^{xii}—Cs2—S3^{xiii}	85.03 (4)
S3^i—W1—Cs1^{iii}	125.54 (4)	S3^v—Cs2—S3^{xiii}	112.60 (2)
S1—W1—Cs1^{iii}	53.73 (5)	S1^v—Cs2—S3^{xiv}	69.74 (4)
S2—W1—Cs1^{iii}	57.09 (5)	S1^{iv}—Cs2—S3^{xiv}	126.67 (4)
Cs2^{ii}—W1—Cs1^{iii}	136.492 (11)	S3^{xii}—Cs2—S3^{xiv}	112.60 (2)
Cs2—W1—Cs1^{iii}	125.393 (12)	S3^v—Cs2—S3^{xiv}	85.03 (4)
S3—W1—Cs1^{iv}	139.88 (4)	S3^{xiii}—Cs2—S3^{xiv}	56.95 (4)
S3^i—W1—Cs1^{iv}	54.13 (4)	S1^v—Cs2—S2^{ii}	82.19 (3)
S1—W1—Cs1^{iv}	111.06 (3)	S1^{iv}—Cs2—S2^{ii}	82.19 (3)
S2—W1—Cs1^{iv}	58.259 (13)	S3^{xii}—Cs2—S2^{ii}	89.70 (4)
Cs2^{ii}—W1—Cs1^{iv}	117.909 (7)	S3^v—Cs2—S2^{ii}	89.70 (4)
Cs2—W1—Cs1^{iv}	68.543 (7)	S3^{xiii}—Cs2—S2^{ii}	149.68 (2)
Cs1^{iii}—W1—Cs1^{iv}	82.470 (9)	S3^{xiv}—Cs2—S2^{ii}	149.68 (2)
S3—W1—Cs1^v	54.13 (4)	S1^v—Cs2—S2	95.12 (3)
S3^i—W1—Cs1^v	139.88 (4)	S1^{iv}—Cs2—S2	95.12 (3)
S1—W1—Cs1^v	111.06 (3)	S3^{xii}—Cs2—S2	145.74 (3)
S2—W1—Cs1^v	58.259 (13)	S3^v—Cs2—S2	145.74 (3)
Cs2^{ii}—W1—Cs1^v	117.909 (7)	S3^{xiii}—Cs2—S2	64.49 (3)
Cs2—W1—Cs1^v	68.543 (7)	S3^{xiv}—Cs2—S2	64.49 (3)
Cs1^{iii}—W1—Cs1^v	82.470 (8)	S2^{ii}—Cs2—S2	108.46 (3)
Cs1^{iv}—W1—Cs1^v	112.242 (12)	S1^v—Cs2—S3	62.64 (3)
S3—W1—Cs2^{vi}	57.53 (4)	S1^{iv}—Cs2—S3	114.37 (4)
S3^i—W1—Cs2^{vi}	143.17 (4)	S3^{xii}—Cs2—S3	152.884 (17)
S1—W1—Cs2^{vi}	55.946 (9)	S3^v—Cs2—S3	117.054 (10)
S2—W1—Cs2^{vi}	107.18 (3)	S3^{xiii}—Cs2—S3	118.09 (2)
Cs2^{ii}—W1—Cs2^{vi}	80.054 (9)	S3^{xiv}—Cs2—S3	92.90 (2)
Cs2—W1—Cs2^{vi}	124.159 (7)	S2^{ii}—Cs2—S3	63.19 (3)
Cs1^{iii}—W1—Cs2^{vi}	75.627 (8)	S2—Cs2—S3	53.61 (3)
Cs1^{iv}—W1—Cs2^{vi}	158.065 (11)	S1^v—Cs2—S3^i	114.37 (4)
Cs1^v—W1—Cs2^{vi}	64.062 (9)	S1^{iv}—Cs2—S3^i	62.64 (3)
S3—W1—Cs2^{vii}	143.17 (4)	S3^{xii}—Cs2—S3^i	117.054 (10)
S3^i—W1—Cs2^{vii}	57.53 (4)	S3^v—Cs2—S3^i	152.884 (17)
S1—W1—Cs2^{vii}	55.946 (9)	S3^{xiii}—Cs2—S3^i	92.90 (2)

S2—W1—Cs2^{vii}	107.18 (3)	S3^{xiv}—Cs2—S3^{i}	118.09 (2)
Cs2^{ii}—W1—Cs2^{vii}	80.054 (9)	S2^{ii}—Cs2—S3^{i}	63.19 (3)
Cs2—W1—Cs2^{vii}	124.159 (7)	S2—Cs2—S3^{i}	53.61 (3)
Cs1^{iii}—W1—Cs2^{vii}	75.627 (8)	S3—Cs2—S3^{i}	52.30 (3)
Cs1^{iv}—W1—Cs2^{vii}	64.062 (9)	S1^{v}—Cs2—W1^{xiv}	97.60 (3)
Cs1^{v}—W1—Cs2^{vii}	158.065 (11)	S1^{iv}—Cs2—W1^{xiv}	97.60 (3)
Cs2^{vi}—W1—Cs2^{vii}	110.588 (13)	S3^{xii}—Cs2—W1^{xiv}	86.91 (2)
S1^{viii}—Cs1—S1	136.42 (4)	S3^{v}—Cs2—W1^{xiv}	86.91 (2)
S1^{viii}—Cs1—S3^{ix}	142.64 (3)	S3^{xiii}—Cs2—W1^{xiv}	31.796 (19)
S1—Cs1—S3^{ix}	69.10 (4)	S3^{xiv}—Cs2—W1^{xiv}	31.796 (19)
S1^{viii}—Cs1—S3^{vi}	142.64 (3)	S2^{ii}—Cs2—W1^{xiv}	176.10 (3)
S1—Cs1—S3^{vi}	69.10 (4)	S2—Cs2—W1^{xiv}	75.44 (3)
S3^{ix}—Cs1—S3^{vi}	62.27 (4)	S3—Cs2—W1^{xiv}	120.19 (2)
S1^{viii}—Cs1—S3^{x}	69.81 (4)	S3^{i}—Cs2—W1^{xiv}	120.19 (2)
S1—Cs1—S3^{x}	73.08 (4)	S1^{v}—Cs2—W1	90.97 (3)
S3^{ix}—Cs1—S3^{x}	104.94 (3)	S1^{iv}—Cs2—W1	90.97 (3)
S3^{vi}—Cs1—S3^{x}	142.16 (2)	S3^{xii}—Cs2—W1	147.771 (19)
S1^{viii}—Cs1—S3^{xi}	69.81 (4)	S3^{v}—Cs2—W1	147.77 (2)
S1—Cs1—S3^{xi}	73.08 (4)	S3^{xiii}—Cs2—W1	91.90 (3)
S3^{ix}—Cs1—S3^{xi}	142.16 (2)	S3^{xiv}—Cs2—W1	91.90 (3)
S3^{vi}—Cs1—S3^{xi}	104.94 (3)	S2^{ii}—Cs2—W1	76.96 (3)
S3^{x}—Cs1—S3^{xi}	61.92 (4)	S2—Cs2—W1	31.50 (3)
S1^{viii}—Cs1—S2^{viii}	62.03 (4)	S3—Cs2—W1	30.924 (18)
S1—Cs1—S2^{viii}	161.55 (5)	S3^{i}—Cs2—W1	30.924 (18)
S3^{ix}—Cs1—S2^{viii}	95.29 (4)	W1^{xiv}—Cs2—W1	106.942 (12)
S3^{vi}—Cs1—S2^{viii}	95.29 (4)	W1—S1—Cs1^{iii}	95.44 (7)
S3^{x}—Cs1—S2^{viii}	122.10 (4)	W1—S1—Cs1	162.32 (9)
S3^{xi}—Cs1—S2^{viii}	122.10 (4)	Cs1^{iii}—S1—Cs1	102.24 (5)
S1^{viii}—Cs1—S2^{vi}	85.68 (3)	W1—S1—Cs2^{vi}	94.25 (3)
S1—Cs1—S2^{vi}	101.28 (3)	Cs1^{iii}—S1—Cs2^{vi}	96.68 (3)
S3^{ix}—Cs1—S2^{vi}	119.97 (4)	Cs1—S1—Cs2^{vi}	83.78 (3)
S3^{vi}—Cs1—S2^{vi}	59.36 (3)	W1—S1—Cs2^{vii}	94.25 (3)
S3^{x}—Cs1—S2^{vi}	129.54 (4)	Cs1^{iii}—S1—Cs2^{vii}	96.68 (3)
S3^{xi}—Cs1—S2^{vi}	68.43 (4)	Cs1—S1—Cs2^{vii}	83.78 (3)
S2^{viii}—Cs1—S2^{vi}	77.53 (3)	Cs2^{vi}—S1—Cs2^{vii}	163.39 (6)
S1^{viii}—Cs1—S2^{vii}	85.68 (3)	W1—S2—Cs1^{iii}	91.71 (6)
S1—Cs1—S2^{vii}	101.28 (3)	W1—S2—Cs1^{iv}	91.31 (3)
S3^{ix}—Cs1—S2^{vii}	59.36 (3)	Cs1^{iii}—S2—Cs1^{iv}	102.47 (3)
S3^{vi}—Cs1—S2^{vii}	119.97 (4)	W1—S2—Cs1^{v}	91.31 (3)
S3^{x}—Cs1—S2^{vii}	68.43 (4)	Cs1^{iii}—S2—Cs1^{v}	102.47 (3)
S3^{xi}—Cs1—S2^{vii}	129.54 (4)	Cs1^{iv}—S2—Cs1^{v}	154.83 (6)

S2^{viii}—Cs1—S2^{vii}	77.53 (3)	W1—S2—Cs2^{xiv}	170.32 (8)
S2^{vi}—Cs1—S2^{vii}	154.83 (6)	Cs1^{iii}—S2—Cs2^{xiv}	78.61 (4)
S1^{viii}—Cs1—W1^{viii}	30.83 (3)	Cs1^{iv}—S2—Cs2^{xiv}	90.80 (3)
S1—Cs1—W1^{viii}	167.25 (4)	Cs1^{v}—S2—Cs2^{xiv}	90.80 (3)
S3^{ix}—Cs1—W1^{viii}	121.31 (3)	W1—S2—Cs2	80.20 (5)
S3^{vi}—Cs1—W1^{viii}	121.31 (3)	Cs1^{iii}—S2—Cs2	171.91 (6)
S3^{x}—Cs1—W1^{viii}	96.08 (3)	Cs1^{iv}—S2—Cs2	77.90 (3)
S3^{xi}—Cs1—W1^{viii}	96.08 (3)	Cs1^{v}—S2—Cs2	77.90 (3)
S2^{viii}—Cs1—W1^{viii}	31.20 (3)	Cs2^{xiv}—S2—Cs2	109.48 (5)
S2^{vi}—Cs1—W1^{viii}	80.24 (3)	W1—S3—Cs1^{v}	95.85 (4)
S2^{vii}—Cs1—W1^{viii}	80.24 (3)	W1—S3—Cs1^{xi}	156.39 (6)
S1^{viii}—Cs1—W1^{vii}	112.968 (15)	Cs1^{v}—S3—Cs1^{xi}	99.60 (3)
S1—Cs1—W1^{vii}	89.53 (2)	W1—S3—Cs2^{vi}	92.64 (5)
S3^{ix}—Cs1—W1^{vii}	30.016 (19)	Cs1^{v}—S3—Cs2^{vi}	79.44 (3)
S3^{vi}—Cs1—W1^{vii}	89.58 (2)	Cs1^{xi}—S3—Cs2^{vi}	107.62 (3)
S3^{x}—Cs1—W1^{vii}	91.15 (2)	W1—S3—Cs2^{ii}	84.20 (4)
S3^{xi}—Cs1—W1^{vii}	150.96 (2)	Cs1^{v}—S3—Cs2^{ii}	174.41 (5)
S2^{viii}—Cs1—W1^{vii}	80.296 (18)	Cs1^{xi}—S3—Cs2^{ii}	82.13 (3)
S2^{vi}—Cs1—W1^{vii}	139.31 (3)	Cs2^{vi}—S3—Cs2^{ii}	94.97 (3)
S2^{vii}—Cs1—W1^{vii}	30.43 (3)	W1—S3—Cs2	77.54 (4)
W1^{viii}—Cs1—W1^{vii}	97.530 (8)	Cs1^{v}—S3—Cs2	78.13 (3)
S1^{viii}—Cs1—W1^{vi}	112.968 (15)	Cs1^{xi}—S3—Cs2	88.26 (3)
S1—Cs1—W1^{vi}	89.53 (2)	Cs2^{vi}—S3—Cs2	154.38 (4)
S3^{ix}—Cs1—W1^{vi}	89.58 (2)	Cs2^{ii}—S3—Cs2	107.29 (3)
S3^{vi}—Cs1—W1^{vi}	30.016 (19)		

Symmetry codes: (i) x, $-y+1/2$, z; (ii) $x-1/2$, y, $-z+3/2$; (iii) $x+1/2$, y, $-z+1/2$; (iv) $-x+3/2$, $-y+1$, $z+1/2$; (v) $-x+3/2$, $-y$, $z+1/2$; (vi) $-x+3/2$, $-y$, $z-1/2$; (vii) $-x+3/2$, $-y+1$, $z-1/2$; (viii) $x-1/2$, y, $-z+1/2$; (ix) $-x+3/2$, $y+1/2$, $z-1/2$; (x) $-x+1$, $y+1/2$, $-z+1$; (xi) $-x+1$, $-y$, $-z+1$; (xii) $-x+3/2$, $y+1/2$, $z+1/2$; (xiii) $x+1/2$, $-y+1/2$, $-z+3/2$; (xiv) $x+1/2$, y, $-z+3/2$.
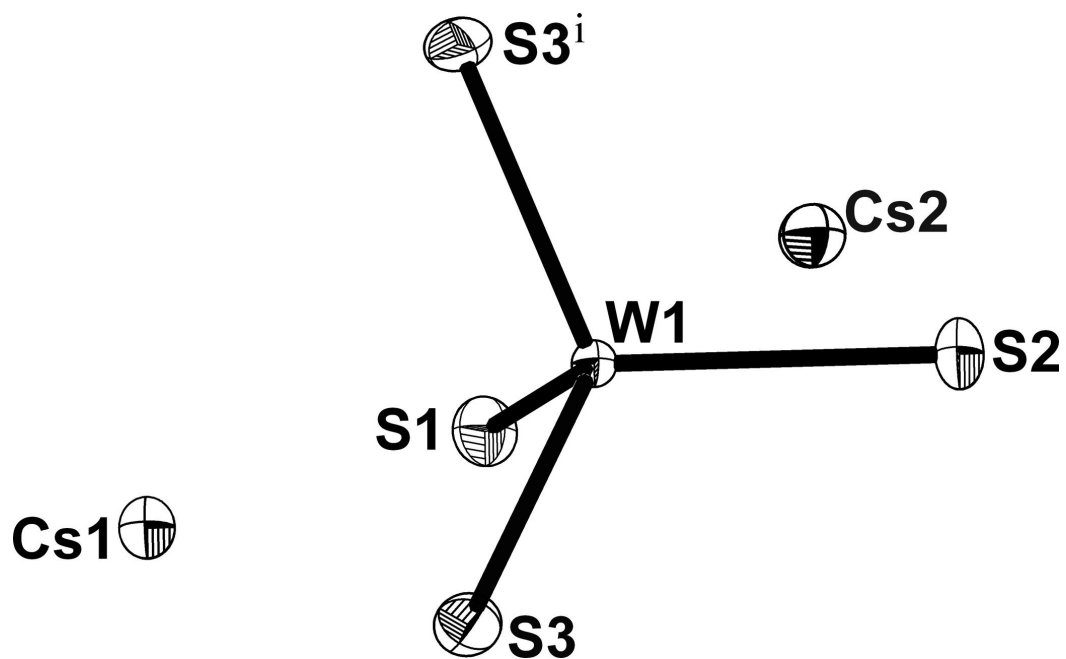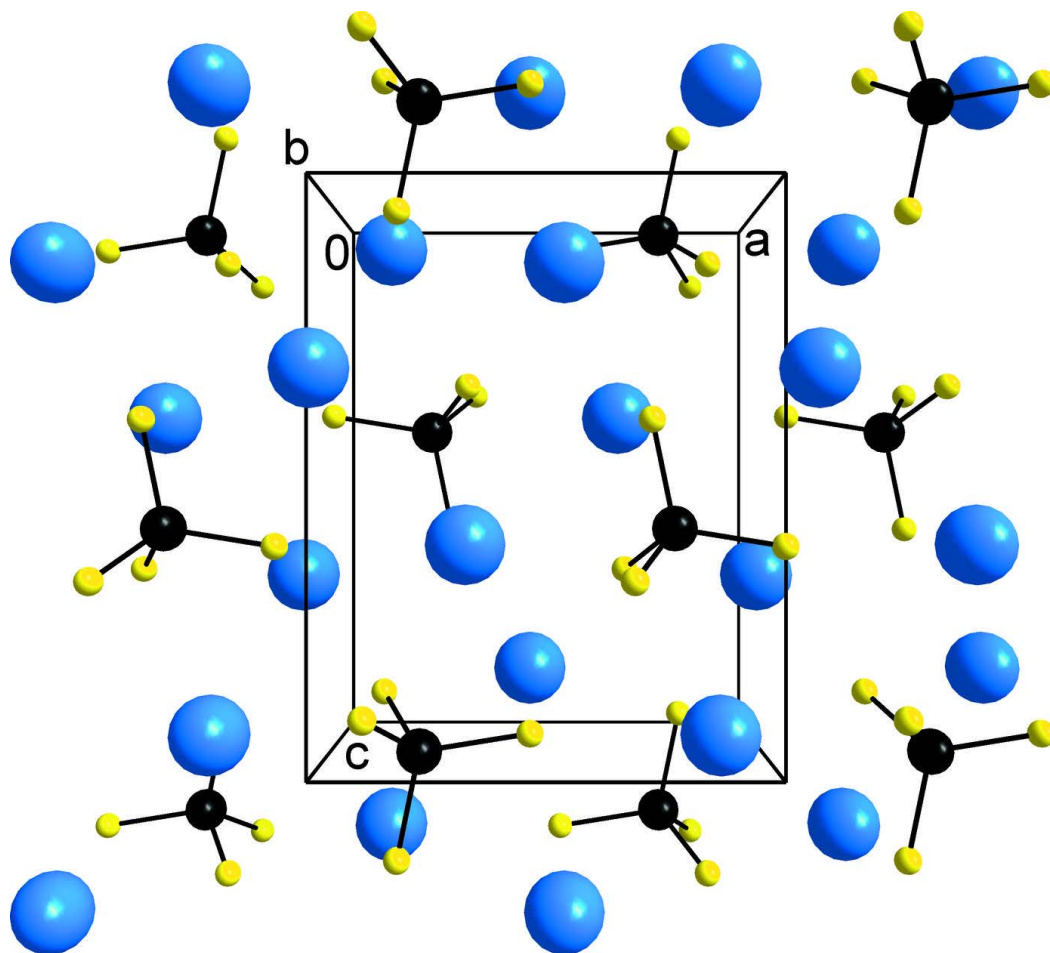
Fig. 1

Fig. 2

Fig. 3