



Crystal structure of bis[octakis(dimethyl sulfoxide- κ O)ytterbium(III)] pentabromidoplumbate(II) tribromide dimethyl sulfoxide monosolvate: a ytterbium-doped lead halide perovskite precursor

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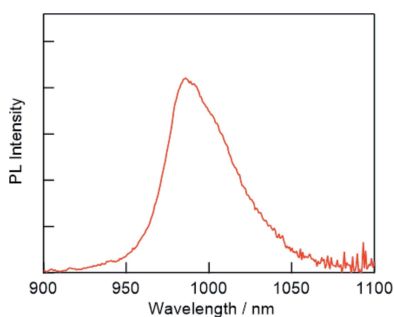
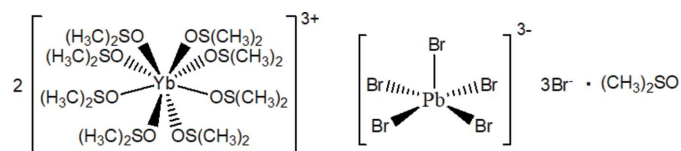
Keywords: lead halide perovskite; ytterbium; photoluminescence; crystal structure.**CCDC reference:** 2251523**Supporting information:** this article has supporting information at journals.iucr.org/e

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A mixture of PbBr_2 and $\text{YbBr}_3 \cdot n\text{H}_2\text{O}$ in a dimethyl sulfoxide (DMSO) solution yielded single crystals of a lead halide perovskite precursor with ytterbium, bis[octakis(dimethyl sulfoxide)ytterbium(III)]pentabromidoplumbate(II) tribromide with dimethyl sulfoxide as co-crystallite, $[\text{Yb}(\text{C}_2\text{H}_6\text{OS})_8][\text{PbBr}_5]_{0.5}\text{Br}_{1.5} \cdot 0.5\text{C}_2\text{H}_6\text{OS}$. The complex ions PbBr_5^{3-} and $\text{Yb}(\text{DMSO})_8^{3+}$ are present in the crystal together with three Br^- ions and DMSO molecules. X-ray crystallography revealed that the Br^- ions in YbBr_3 are replaced by the solvent and bound to a Pb^{II} atom or remain free. The presence of PbBr_5^{3-} units, which are molecular ions with a square-pyramidal structure, is also observed. These single crystals react with a caesium chloride solution, exhibiting near-infrared (NIR) luminescence by visible photoexcitation, suggesting the formation of Yb^{3+} -doped lead halide perovskites ($\text{CsPbBr}_{3-x}\text{Cl}_x \cdot \text{Yb}^{3+}$).

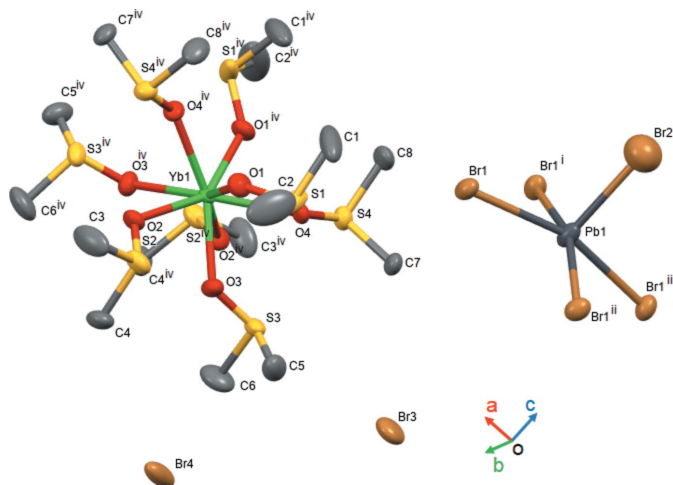
1. Chemical context

Lead halide perovskite crystals have attracted considerable attention in the fields of solar cells and optoelectronics (Lee *et al.*, 2012; Burschka *et al.*, 2013; Fu *et al.*, 2019). Lead halide perovskite crystals have been investigated extensively owing to their facile solution-phase fabrication, high energy-conversion efficiency, and characteristic photoresponse. Lead halide perovskites can easily be prepared by spin coating microcrystalline thin films in solution.



Highly polar solvents, such as dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), are used in fabricating perovskite thin films by solution processing. Typically, these solvents are removed by thermal annealing using a hot plate or air drying after spin coating, and crystal growth proceeds as the solvent becomes supersaturated. The crystal morphology and crystalline phase depend on the annealing temperature and treatment time (Tenailleau *et al.*, 2019; Bi *et al.*, 2014; Xiao *et al.*, 2014; Jung *et al.*, 2019). The morphology of perovskite films, such as the film thickness and grain boundaries, signifi-




Figure 1

Arrangement of $[\text{Yb}(\text{DMSO})_8]^{3+}$, $[\text{PbBr}_5]^{2-}$ and free Br^- anions in the precursor crystal, with displacement ellipsoids at the 50% probability level. The disordered DMSO molecule is omitted for clarity. Symmetry codes: (i) $y, \frac{1}{2} - x, z$; (ii) $\frac{1}{2} - y, x, z$; (iii) $\frac{1}{2} - x, \frac{1}{2} - y, z$; (iv) $\frac{3}{2} - x, \frac{1}{2} - y, z$.

cantly affects the performance of solar cells. Complex formation between Pb atoms and solvent molecules in the perovskite precursor solution significantly influences the film morphology (Ozaki *et al.*, 2017; Wakamiya *et al.*, 2014; Ozaki *et al.*, 2019). The addition of $\text{CH}_3\text{NH}_3\text{I}$ dissolved in 2-propanol to 1D crystals displaced the DMF solvent, forming a 3D perovskite structure. The addition of $\text{CH}_3\text{NH}_3\text{I}$ dissolved in 2-propanol to these 1D crystals suspended in DMF solvent forms a 3D perovskite structure (Wakamiya *et al.*, 2014). The $\text{CH}_3\text{NH}_3\text{I}$ -PbI₂-DMF intermediate formed by $\text{CH}_3\text{NH}_3\text{I}$ addition was also observed during thermal annealing. DMF coordination with the intermediate is thought to be responsible for Ostwald ripening (Guo *et al.*, 2016). Additionally, when DMSO was used as the solvent, a PbI_2 -(DMSO)₂ complex was formed, in which DMSO was more strongly coordinated to PbI_2 than DMF (Miyamae *et al.*, 1980).

Lead halide perovskite thin films have been investigated extensively for solar cells and various other fields, including optoelectronics. Recently, the efficient luminescence of rare-earth elements using a lead halide perovskite as an optical absorption antenna was reported by doping ytterbium into a 3D $\text{CsPbBr}_x\text{Cl}_{3-x}$ perovskite (Kroupa *et al.*, 2018; Erickson *et al.*, 2019). However, the crystal structure of lead halide perovskites doped with rare-earth elements and their mechanism of formation remains unclear. In this study, precursor single-crystals of a lead halide perovskite doped with rare-earth elements, bis[octakis(dimethyl sulfoxide)-ytterbium(III)] pentabromidoplumbate(II) tribromide dimethyl sulfoxide solvate, were successfully prepared, and the structure of the precursor crystal was determined.

2. Structural commentary

The obtained structure exhibits an alternating sequence of PbBr_5^{3-} and $2[\text{Yb}(\text{DMSO})_8]^{3+}$ units (Figs. 1 and 2). The

$[\text{Yb}(\text{DMSO})_8]^{3+}$ unit is considered to possess three Br^- (Br3, Br4) ions as counter-anions. Interestingly, the PbBr_5^{3-} unit exhibits a square-pyramidal structure. Lead halide compounds often show lead-centered octahedral structures, and there have been no previous reports of the PbBr_5^{3-} molecular ion with a square-pyramidal geometry. The free atom Br3 is located on the straight line of the Br2—Pb1 bond, and the Pb1...Br3 distance is 6.781 (9) Å (Fig. 1). The free Br3 atom is located at a distance more than twice that of Br2 in the Pb1—Br2 bond [2.814 (4) Å], suggesting that there is no Pb1—Br3 interaction.

The DMSO molecule as co-crystallite is disordered, and the exact configuration was difficult to determine. Thermogravimetric analysis (TG-DTA) of the crystals revealed a weight loss of 3.4% at approximately 410 K, with an endothermic peak, corresponding to a dissociation of 0.5 equivalents of

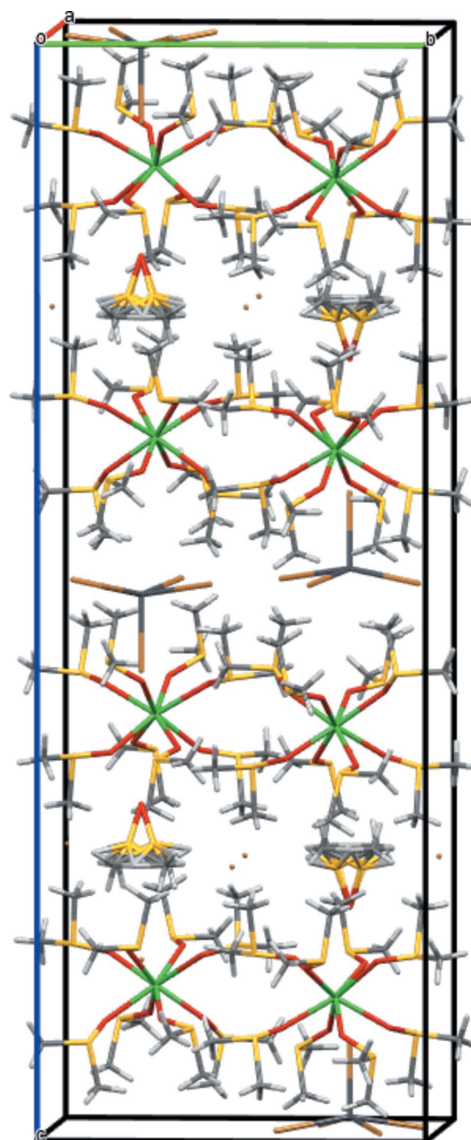


Figure 2
Perspective view of the precursor crystal structure along [100].

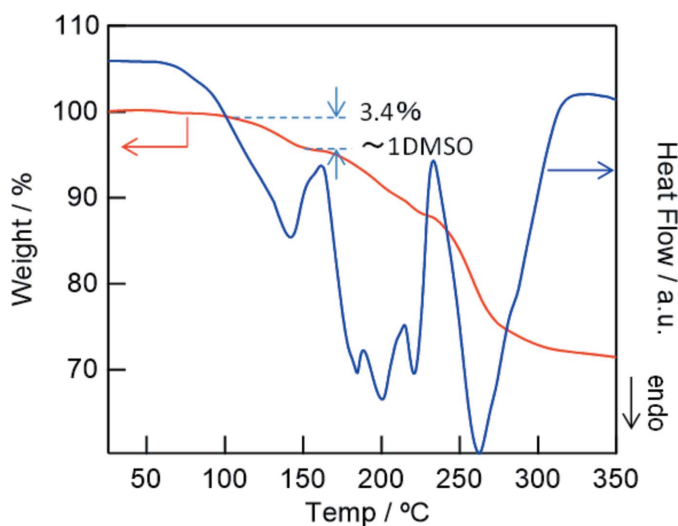


Figure 3
TG-DTA curves acquired under a nitrogen atmosphere.

DMSO relative to Yb (theoretical value 3.1 wt%) (Fig. 3). The crystal structure resembles that of a 1D perovskite with a series of (PbX_5^{3-}) units (Wang *et al.*, 1995). However, the weak interactions between the Br^- ions and DMSO molecules in the gaps between the (PbX_5^{3-}) units prevents the 1D perovskite from bridging. All halogen ions were lost when YbBr_3 was added, and DMSO is coordinated to the Yb^{III} atom instead. Several Br^- ions react with PbBr_2 to form PbBr_5^{3-} , and therefore YbBr_3 has served as a source of halogen ions in the lead halide perovskite framework.

3. Photophysical analysis

The precursor crystal did not exhibit any luminescence upon irradiation with visible light. In contrast, the dropwise addition of a methanol solution containing caesium chloride to the

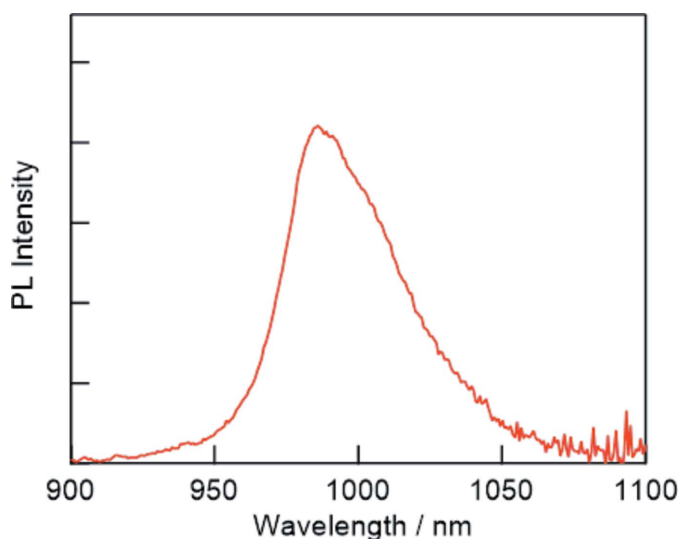


Figure 4
Near-infrared emission from Yb^{3+} after treatment of the precursor crystals with a CsCl methanol solution.

precursor crystals, followed by annealing at 473 K for 5 min, resulted in the formation of light-yellow microcrystals. The microcrystals exhibited Yb^{3+} -derived near-infrared (NIR) emission at 980 nm upon photoexcitation at 400 nm (Fig. 4). This indicates that the precursor crystals reacted with caesium chloride, and Yb^{3+} -doped 3D lead halide perovskite crystals ($\text{CsPbBr}_{3-x}\text{Cl}_x\cdot\text{Yb}^{3+}$) (Erickson *et al.*, 2019) were formed. The NIR luminescence of doped Yb^{3+} was observed, in addition to the visible-light absorption of the lead halide perovskite crystals.

4. Database survey

The Inorganic Crystal Structure Database (ICSD) (ICSD, 2023) did not include any closely related structures. For $[\text{Yb}(\text{DMSO})_8]^{3+}$ units, tetrakis[1,4-bis(phenylsulfinyl)butane]ytterbium(III) triperchlorate (Li *et al.*, 2004) and *catena*-[octakis(dimethyl sulfoxide)ytterbium heptakis(dimethyl sulfoxide)ytterbium hexakis(μ_3 -sulfido)dodecakis(μ_2 -sulfido)hexasulfidohexasilverhexatungsten] (Zhang *et al.*, 2011) are present in the database.

5. Synthesis and crystallization

PbBr_2 and $\text{YbBr}_3\cdot n\text{H}_2\text{O}$ were dissolved in DMSO (anhydrous, Fujifilm Wako Pure Chemicals) to prepare a 0.5 M solution. The solution was heated to 373 K using a hot plate; acetone was added gradually to obtain colourless needle-like crystals (Fig. 5).

6. Refinement

The crystal data, data collection, and structural refinement details are summarized in Table 1. Because the precursor crystals contain numerous heavy atoms, it was difficult to analyze the residual electrons of these atoms; therefore, an empirical absorption correction using spherical harmonics was applied. The residual electron densities $\Delta\rho_{\text{max}}$ and $\Delta\rho_{\text{min}}$ of 8.97 and $-1.78 \text{ e } \text{\AA}^{-3}$ are located 0.912 and 0.918 \AA , respectively, from the Pd atom. H atoms were positioned geom-

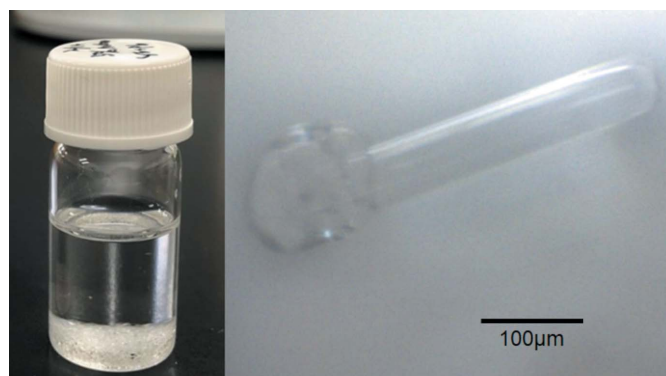


Figure 5
Photographs of crystals in solution and of the single crystal used for the measurement.

Table 1
Experimental details.

Crystal data	
Chemical formula	[Yb(C ₂ H ₆ OS) ₈][PbBr ₅] _{0.5} Br _{1.5} ·0.5·0.5C ₂ H ₆ OS
<i>M_r</i>	1260.36
Crystal system, space group	Tetragonal, <i>P4/ncc</i>
Temperature (K)	93
<i>a</i> , <i>c</i> (Å)	14.3940 (2), 40.6538 (8)
<i>V</i> (Å ³)	8422.9 (3)
<i>Z</i>	8
Radiation type	Cu Kα
<i>μ</i> (mm ⁻¹)	16.57
Crystal size (mm)	0.50 × 0.36 × 0.04
Data collection	
Diffractometer	XtaLAB Synergy, Dualflex, HyPix
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2019)
<i>T_{min}</i> , <i>T_{max}</i>	0.195, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	23286, 4274, 3579
<i>R_{int}</i>	0.108
(sin θ/λ) _{max} (Å ⁻¹)	0.626
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.080, 0.225, 1.08
No. of reflections	4274
No. of parameters	203
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	8.97, -1.78

Computer programs: *CrysAlis PRO* (Rigaku OD, 2019), *OLEX2.solve* (Bourhis *et al.*, 2015), *SHELXL2018/3* (Sheldrick, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

etrically (C–H = 0.98 Å) and refined as riding with *U*_{iso}(H) = 1.5*U*_{eq}(C). Various atoms were refined with fixed occupancies: S5 (0.25) C9 (0.5) H9A (0.5) H9B (0.5) H9C (0.5).

Acknowledgements

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Computing details

Data collection: *CrysAlis PRO* 1.171.40.43a (Rigaku OD, 2019); cell refinement: *CrysAlis PRO* 1.171.40.43a (Rigaku OD, 2019); data reduction: *CrysAlis PRO* 1.171.40.43a (Rigaku OD, 2019); program(s) used to solve structure: *olex2.solve* (Bourhis *et al.*, 2015); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015); molecular graphics: *Olex2* 1.5 (Dolomanov *et al.*, 2009); software used to prepare material for publication: *Olex2* 1.5 (Dolomanov *et al.*, 2009).

Bis[octakis(dimethyl sulfoxide- κ O)ytterbium(III)] pentabromidoplumbate(II) tribromide dimethyl sulfoxide monosolvate

Crystal data

[Yb(C₂H₆OS)₈][PbBr₅]_{0.5}Br_{1.5}·0.5C₂H₆OS
 M_r = 1260.36
 Tetragonal, *P4/ncc*
 a = 14.3940 (2) Å
 c = 40.6538 (8) Å
 V = 8422.9 (3) Å³
 Z = 8
 $F(000)$ = 4864

D_x = 1.988 Mg m⁻³
 Cu $K\alpha$ radiation, λ = 1.54184 Å
 Cell parameters from 8591 reflections
 θ = 4.4–74.7°
 μ = 16.57 mm⁻¹
 T = 93 K
 Plate, colourless
 0.50 × 0.36 × 0.04 mm

Data collection

XtaLAB Synergy, Dualflex, HyPix
 diffractometer
 Detector resolution: 10.0000 pixels mm⁻¹
 ω scans
 Absorption correction: multi-scan
 (CrysAlisPro; Rigaku OD, 2019)
 T_{\min} = 0.195, T_{\max} = 1.000
 23286 measured reflections

4274 independent reflections
 3579 reflections with $I > 2\sigma(I)$
 R_{int} = 0.108
 θ_{max} = 74.9°, θ_{min} = 2.2°
 h = -16→17
 k = -12→17
 l = -35→50

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)]$ = 0.080
 $wR(F^2)$ = 0.225
 S = 1.08
 4274 reflections

203 parameters
 0 restraints
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.152P)^2 + 25.6573P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 8.97 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -1.78 \text{ e } \text{Å}^{-3}$$

Special details

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

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Pb1	0.250000	0.250000	0.50704 (2)	0.0340 (3)	
Yb1	0.750000	0.250000	0.37362 (2)	0.0190 (3)	
Br1	0.43356 (6)	0.34068 (6)	0.49553 (2)	0.0349 (3)	
Br3	0.250000	0.250000	0.34023 (5)	0.0559 (6)	
Br4	0.49813 (6)	0.50187 (6)	0.250000	0.0608 (7)	
S4	0.54958 (13)	0.14251 (13)	0.40874 (5)	0.0303 (4)	
S3	0.53965 (14)	0.27929 (16)	0.33522 (5)	0.0345 (5)	
S2	0.76666 (17)	0.46366 (15)	0.33661 (5)	0.0377 (5)	
S1	0.64007 (15)	0.41439 (19)	0.42370 (6)	0.0500 (7)	
O3	0.6392 (4)	0.3125 (4)	0.33952 (15)	0.0344 (12)	
O1	0.7248 (4)	0.3778 (4)	0.40597 (15)	0.0356 (12)	
O4	0.6108 (4)	0.2258 (4)	0.40211 (14)	0.0284 (11)	
O2	0.8176 (4)	0.3738 (4)	0.34489 (14)	0.0314 (12)	
C7	0.4353 (5)	0.1886 (7)	0.4131 (2)	0.0363 (18)	
H7A	0.435947	0.238849	0.429408	0.055*	
H7B	0.393082	0.139411	0.420479	0.055*	
H7C	0.414022	0.212997	0.391917	0.055*	
C4	0.7484 (6)	0.4587 (9)	0.2931 (3)	0.048 (3)	
H4A	0.807678	0.446497	0.281992	0.071*	
H4B	0.723157	0.518084	0.285400	0.071*	
H4C	0.704475	0.408721	0.287950	0.071*	
O5	0.750000	0.750000	0.3018 (5)	0.100 (9)	
C8	0.5663 (7)	0.1162 (8)	0.4512 (3)	0.050 (2)	
H8A	0.628770	0.090851	0.454460	0.075*	
H8B	0.520014	0.070349	0.458222	0.075*	
H8C	0.559160	0.173003	0.464263	0.075*	
C5	0.4723 (7)	0.3819 (8)	0.3353 (3)	0.052 (3)	
H5A	0.476672	0.411699	0.356951	0.078*	
H5B	0.407268	0.366359	0.330720	0.078*	
H5C	0.495481	0.424428	0.318416	0.078*	
C6	0.5276 (11)	0.2517 (8)	0.2925 (3)	0.060 (3)	
H6A	0.532561	0.308699	0.279429	0.090*	
H6B	0.466864	0.222907	0.288694	0.090*	
H6C	0.576829	0.208406	0.285983	0.090*	
C3	0.8528 (10)	0.5533 (7)	0.3366 (3)	0.065 (4)	
H3A	0.888786	0.550183	0.357047	0.097*	

H3B	0.822330	0.614034	0.335028	0.097*	
H3C	0.894404	0.544800	0.317779	0.097*	
C1	0.6579 (9)	0.3911 (13)	0.4651 (3)	0.080 (5)	
H1A	0.659188	0.323712	0.468536	0.119*	
H1B	0.607311	0.418331	0.478018	0.119*	
H1C	0.717213	0.418025	0.472066	0.119*	
C2	0.6643 (11)	0.5360 (10)	0.4257 (4)	0.095 (6)	
H2A	0.731670	0.545755	0.425340	0.143*	
H2B	0.638504	0.561609	0.446075	0.143*	
H2C	0.636020	0.567247	0.406771	0.143*	
S5	0.7808 (8)	0.7165 (8)	0.2655 (2)	0.0300 (17)	0.25
C9	0.684 (2)	0.686 (2)	0.2475 (5)	0.075 (11)	0.5
H9A	0.697334	0.666771	0.224902	0.113*	0.5
H9B	0.641419	0.739136	0.247289	0.113*	0.5
H9C	0.655988	0.634559	0.259618	0.113*	0.5
Br2	0.250000	0.250000	0.57625 (11)	0.0958 (12)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb1	0.0241 (3)	0.0241 (3)	0.0539 (5)	0.000	0.000	0.000
Yb1	0.0228 (3)	0.0217 (3)	0.0124 (4)	-0.00053 (15)	0.000	0.000
Br1	0.0260 (4)	0.0325 (5)	0.0460 (5)	-0.0026 (3)	-0.0052 (3)	0.0051 (3)
Br3	0.0723 (10)	0.0723 (10)	0.0233 (10)	0.000	0.000	0.000
Br4	0.0775 (10)	0.0775 (10)	0.0274 (8)	0.0460 (12)	0.0088 (6)	0.0088 (6)
S4	0.0305 (9)	0.0285 (8)	0.0320 (10)	-0.0019 (7)	0.0069 (7)	0.0006 (7)
S3	0.0304 (9)	0.0498 (11)	0.0235 (9)	-0.0071 (8)	-0.0053 (7)	0.0102 (9)
S2	0.0557 (12)	0.0316 (10)	0.0257 (10)	-0.0024 (8)	-0.0002 (9)	0.0059 (8)
S1	0.0289 (10)	0.0675 (15)	0.0536 (14)	0.0111 (9)	-0.0110 (9)	-0.0388 (12)
O3	0.027 (3)	0.043 (3)	0.033 (3)	-0.001 (2)	-0.006 (2)	0.010 (2)
O1	0.042 (3)	0.037 (3)	0.028 (3)	0.004 (3)	0.002 (3)	-0.010 (2)
O4	0.026 (3)	0.033 (3)	0.025 (3)	-0.006 (2)	0.003 (2)	0.008 (2)
O2	0.037 (3)	0.031 (3)	0.026 (3)	-0.001 (2)	-0.001 (2)	0.010 (2)
C7	0.021 (3)	0.050 (5)	0.038 (4)	-0.002 (3)	0.004 (3)	0.009 (4)
C4	0.044 (5)	0.065 (7)	0.035 (5)	0.001 (4)	-0.013 (4)	0.016 (5)
O5	0.137 (14)	0.137 (14)	0.026 (9)	0.000	0.000	0.000
C8	0.039 (5)	0.069 (6)	0.041 (5)	-0.005 (4)	0.005 (4)	0.027 (5)
C5	0.041 (5)	0.068 (7)	0.048 (6)	0.020 (5)	0.010 (4)	0.011 (5)
C6	0.088 (9)	0.063 (7)	0.030 (5)	-0.009 (5)	-0.015 (6)	-0.008 (4)
C3	0.099 (9)	0.042 (5)	0.053 (6)	-0.036 (6)	-0.018 (6)	0.013 (5)
C1	0.067 (7)	0.139 (13)	0.033 (5)	-0.054 (8)	0.013 (5)	-0.018 (7)
C2	0.088 (10)	0.074 (9)	0.124 (13)	0.039 (8)	-0.033 (9)	-0.066 (9)
S5	0.030 (7)	0.026 (7)	0.034 (4)	0.008 (2)	-0.006 (3)	0.005 (3)
C9	0.10 (2)	0.11 (2)	0.018 (9)	-0.06 (2)	0.002 (10)	-0.030 (11)
Br2	0.1033 (18)	0.1033 (18)	0.081 (3)	0.000	0.000	0.000

Geometric parameters (Å, °)

Pb1—Br1	2.9839 (9)	C7—H7A	0.9800
Pb1—Br1 ⁱ	2.9840 (9)	C7—H7B	0.9800
Pb1—Br1 ⁱⁱ	2.9840 (9)	C7—H7C	0.9800
Pb1—Br1 ⁱⁱⁱ	2.9840 (9)	C4—H4A	0.9800
Pb1—Br2	2.814 (4)	C4—H4B	0.9800
Yb1—S3 ^{iv}	3.4324 (19)	C4—H4C	0.9800
Yb1—S3	3.4325 (19)	O5—S5	1.616 (18)
Yb1—S2 ^{iv}	3.432 (2)	C8—H8A	0.9800
Yb1—S2	3.432 (2)	C8—H8B	0.9800
Yb1—O3	2.297 (5)	C8—H8C	0.9800
Yb1—O3 ^{iv}	2.297 (5)	C5—H5A	0.9800
Yb1—O1	2.290 (6)	C5—H5B	0.9800
Yb1—O1 ^{iv}	2.290 (6)	C5—H5C	0.9800
Yb1—O4	2.341 (5)	C6—H6A	0.9800
Yb1—O4 ^{iv}	2.341 (5)	C6—H6B	0.9800
Yb1—O2 ^{iv}	2.342 (5)	C6—H6C	0.9800
Yb1—O2	2.342 (5)	C3—H3A	0.9800
S4—O4	1.512 (6)	C3—H3B	0.9800
S4—C7	1.783 (8)	C3—H3C	0.9800
S4—C8	1.784 (10)	C1—H1A	0.9800
S3—O3	1.521 (6)	C1—H1B	0.9800
S3—C5	1.767 (10)	C1—H1C	0.9800
S3—C6	1.790 (11)	C2—H2A	0.9800
S2—O2	1.525 (6)	C2—H2B	0.9800
S2—C4	1.792 (11)	C2—H2C	0.9800
S2—C3	1.789 (10)	S5—C9	1.63 (3)
S1—O1	1.511 (6)	C9—H9A	0.9800
S1—C1	1.734 (13)	C9—H9B	0.9800
S1—C2	1.786 (15)	C9—H9C	0.9800
Br1—Pb1—Br1 ⁱⁱⁱ	161.96 (5)	O4—S4—C8	105.2 (4)
Br1 ⁱ —Pb1—Br1 ⁱⁱ	161.96 (5)	C7—S4—C8	96.1 (4)
Br1—Pb1—Br1 ⁱ	88.591 (8)	O3—S3—Yb1	32.3 (2)
Br1 ⁱⁱⁱ —Pb1—Br1 ⁱⁱ	88.591 (8)	O3—S3—C5	104.7 (5)
Br1—Pb1—Br1 ⁱⁱ	88.591 (8)	O3—S3—C6	105.8 (6)
Br1 ⁱⁱⁱ —Pb1—Br1 ⁱ	88.591 (8)	C5—S3—Yb1	125.8 (4)
Br2—Pb1—Br1 ⁱⁱ	99.02 (3)	C5—S3—C6	97.8 (6)
Br2—Pb1—Br1	99.02 (3)	C6—S3—Yb1	120.0 (5)
Br2—Pb1—Br1 ⁱⁱⁱ	99.02 (3)	O2—S2—Yb1	34.6 (2)
Br2—Pb1—Br1 ⁱ	99.02 (3)	O2—S2—C4	104.8 (5)
S3 ^{iv} —Yb1—S3	125.90 (7)	O2—S2—C3	106.2 (5)
S2—Yb1—S3 ^{iv}	81.32 (5)	C4—S2—Yb1	112.8 (4)
S2 ^{iv} —Yb1—S3 ^{iv}	75.66 (5)	C3—S2—Yb1	134.0 (4)
S2—Yb1—S3	75.66 (5)	C3—S2—C4	97.5 (5)
S2 ^{iv} —Yb1—S3	81.32 (5)	O1—S1—C1	106.0 (6)
S2—Yb1—S2 ^{iv}	128.01 (8)	O1—S1—C2	101.9 (6)

O3 ^{iv} —Yb1—S3	112.72 (15)	C1—S1—C2	96.7 (8)
O3—Yb1—S3 ^{iv}	112.72 (15)	S3—O3—Yb1	126.9 (3)
O3 ^{iv} —Yb1—S3 ^{iv}	20.75 (15)	S1—O1—Yb1	133.0 (4)
O3—Yb1—S3	20.74 (15)	S4—O4—Yb1	134.8 (4)
O3 ^{iv} —Yb1—S2	92.18 (16)	S2—O2—Yb1	123.8 (3)
O3—Yb1—S2	55.45 (15)	S4—C7—H7A	109.5
O3 ^{iv} —Yb1—S2 ^{iv}	55.45 (15)	S4—C7—H7B	109.5
O3—Yb1—S2 ^{iv}	92.18 (16)	S4—C7—H7C	109.5
O3 ^{iv} —Yb1—O3	105.8 (3)	H7A—C7—H7B	109.5
O3—Yb1—O4 ^{iv}	146.6 (2)	H7A—C7—H7C	109.5
O3—Yb1—O4	76.3 (2)	H7B—C7—H7C	109.5
O3 ^{iv} —Yb1—O4 ^{iv}	76.3 (2)	S2—C4—H4A	109.5
O3 ^{iv} —Yb1—O4	146.6 (2)	S2—C4—H4B	109.5
O3—Yb1—O2	71.92 (18)	S2—C4—H4C	109.5
O3 ^{iv} —Yb1—O2 ^{iv}	71.92 (18)	H4A—C4—H4B	109.5
O3 ^{iv} —Yb1—O2	73.06 (19)	H4A—C4—H4C	109.5
O3—Yb1—O2 ^{iv}	73.05 (19)	H4B—C4—H4C	109.5
O1—Yb1—S3 ^{iv}	119.98 (17)	S4—C8—H8A	109.5
O1 ^{iv} —Yb1—S3	119.98 (17)	S4—C8—H8B	109.5
O1—Yb1—S3	91.31 (17)	S4—C8—H8C	109.5
O1 ^{iv} —Yb1—S3 ^{iv}	91.31 (17)	H8A—C8—H8B	109.5
O1—Yb1—S2 ^{iv}	163.81 (17)	H8A—C8—H8C	109.5
O1 ^{iv} —Yb1—S2 ^{iv}	62.82 (16)	H8B—C8—H8C	109.5
O1—Yb1—S2	62.82 (16)	S3—C5—H5A	109.5
O1 ^{iv} —Yb1—S2	163.81 (17)	S3—C5—H5B	109.5
O1—Yb1—O3 ^{iv}	140.5 (2)	S3—C5—H5C	109.5
O1 ^{iv} —Yb1—O3 ^{iv}	85.5 (2)	H5A—C5—H5B	109.5
O1—Yb1—O3	85.5 (2)	H5A—C5—H5C	109.5
O1 ^{iv} —Yb1—O3	140.5 (2)	H5B—C5—H5C	109.5
O1 ^{iv} —Yb1—O1	109.9 (3)	S3—C6—H6A	109.5
O1 ^{iv} —Yb1—O4	74.4 (2)	S3—C6—H6B	109.5
O1 ^{iv} —Yb1—O4 ^{iv}	72.5 (2)	S3—C6—H6C	109.5
O1—Yb1—O4	72.5 (2)	H6A—C6—H6B	109.5
O1—Yb1—O4 ^{iv}	74.4 (2)	H6A—C6—H6C	109.5
O1 ^{iv} —Yb1—O2 ^{iv}	75.0 (2)	H6B—C6—H6C	109.5
O1 ^{iv} —Yb1—O2	146.2 (2)	S2—C3—H3A	109.5
O1—Yb1—O2	75.0 (2)	S2—C3—H3B	109.5
O1—Yb1—O2 ^{iv}	146.2 (2)	S2—C3—H3C	109.5
O4 ^{iv} —Yb1—S3 ^{iv}	59.21 (14)	H3A—C3—H3B	109.5
O4 ^{iv} —Yb1—S3	164.14 (15)	H3A—C3—H3C	109.5
O4—Yb1—S3	59.21 (14)	H3B—C3—H3C	109.5
O4—Yb1—S3 ^{iv}	164.14 (15)	S1—C1—H1A	109.5
O4 ^{iv} —Yb1—S2	91.35 (15)	S1—C1—H1B	109.5
O4 ^{iv} —Yb1—S2 ^{iv}	114.21 (15)	S1—C1—H1C	109.5
O4—Yb1—S2 ^{iv}	91.35 (15)	H1A—C1—H1B	109.5
O4—Yb1—S2	114.22 (15)	H1A—C1—H1C	109.5
O4 ^{iv} —Yb1—O4	120.7 (3)	H1B—C1—H1C	109.5
O4 ^{iv} —Yb1—O2 ^{iv}	135.7 (2)	S1—C2—H2A	109.5

O4—Yb1—O2	135.7 (2)	S1—C2—H2B	109.5
O4 ^{iv} —Yb1—O2	77.2 (2)	S1—C2—H2C	109.5
O4—Yb1—O2 ^{iv}	77.2 (2)	H2A—C2—H2B	109.5
O2 ^{iv} —Yb1—S3 ^{iv}	92.66 (14)	H2A—C2—H2C	109.5
O2—Yb1—S3 ^{iv}	60.01 (15)	H2B—C2—H2C	109.5
O2—Yb1—S3	92.66 (14)	O5—S5—C9	104.8 (10)
O2 ^{iv} —Yb1—S3	60.00 (15)	S5—C9—H9A	109.5
O2—Yb1—S2 ^{iv}	119.48 (15)	S5—C9—H9B	109.5
O2 ^{iv} —Yb1—S2 ^{iv}	21.68 (15)	S5—C9—H9C	109.5
O2 ^{iv} —Yb1—S2	119.48 (15)	H9A—C9—H9B	109.5
O2—Yb1—S2	21.68 (15)	H9A—C9—H9C	109.5
O2—Yb1—O2 ^{iv}	120.2 (3)	H9B—C9—H9C	109.5
O4—S4—C7	105.1 (4)		
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C7—S4—O4—Yb1	-151.3 (5)	C6—S3—O3—Yb1	-121.5 (5)
C4—S2—O2—Yb1	-108.9 (5)	C3—S2—O2—Yb1	148.6 (5)
C8—S4—O4—Yb1	107.9 (5)	C1—S1—O1—Yb1	105.7 (6)
C5—S3—O3—Yb1	135.8 (5)	C2—S1—O1—Yb1	-153.7 (7)

Symmetry codes: (i) $y, -x+1/2, z$; (ii) $-y+1/2, x, z$; (iii) $-x+1/2, -y+1/2, z$; (iv) $-x+3/2, -y+1/2, z$.