



# Crystal structure of bis(ethylenedithio)tetrathiafulvalenium $\mu_2$ -acetato-bis[tribromidorhenate(III)] 1,1,2-trichloroethane hemisolvate

Alexander A. Golichenko,<sup>a\*</sup> Andrey V. Kravchenko,<sup>b</sup> Irina V. Omelchenko,<sup>c</sup> Denis M. Chudak,<sup>b</sup> Vladimir A. Starodub,<sup>d</sup> Boleslaw Barszcz<sup>e</sup> and Alexander V. Shtemenko<sup>a</sup>

Received 20 March 2016

Accepted 11 April 2016

Edited by C. Rizzoli, Università degli Studi di Parma, Italy

**Keywords:** crystal structure; radical cation salt; bis(ethylenedithio)tetrathiafulvalene; rhenium; quadruple metal–metal bond.

**CCDC reference:** 1473493

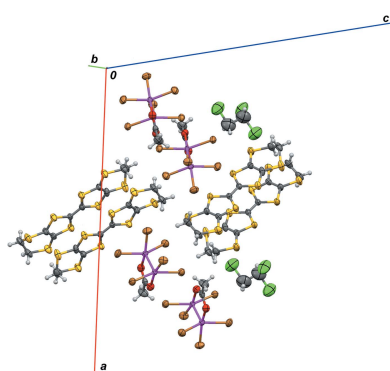
**Supporting information:** this article has supporting information at journals.iucr.org/e

<sup>a</sup>Department of Inorganic Chemistry, Ukrainian State University of Chemical Technology, Gagarin Ave. 8, Dnipropetrovsk 49005, Ukraine, <sup>b</sup>Applied Chemistry Department, V. N. Karazin Kharkiv National University, 4 Svoboda Square, Kharkiv, 61022, Ukraine, <sup>c</sup>SSI "Institute for Single Crystals" NAS of Ukraine, 60 Nauky Ave., Kharkiv, 61072, Ukraine, <sup>d</sup>Institute of Chemistry, Jan Kochanowski University, 25-406 Kielce, Poland, and <sup>e</sup>Institute of Molecular Physics, Polish Academy of Sciences, 60-179 Poznan, Poland. \*Correspondence e-mail: golichenko\_alex@i.ua

The asymmetric unit of the title salt,  $(C_{10}H_8S_8)[Re_2Br_6(CH_3COO)] \cdot 0.5C_2H_3Cl_3$ , contains one bis(ethylenedithio)tetrathiafulvalene (ET) radical cation, one  $\mu_2$ -acetato-bis[tribromidorhenate(III)] anion and a 1,1,2-trichloroethane molecule with half-occupancy disordered about a twofold rotation axis. The tetrathiafulvalene fragment adopts an almost planar configuration typical of the ET radical cation. The C atoms of both ethylenedithio fragments in the cation are disordered over two orientations with occupancy factors 0.65:0.35 and 0.77:0.23. In the anion, six Br atoms and a  $\mu_2$ -acetate ligand form a strongly distorted cubic  $O_2Br_6$  coordination polyhedron around the  $Re_2$  dinuclear centre. In the crystal, centrosymmetrically related ET cations and  $Re_2O_2Br_6$  anions are linked into dimers by  $\pi$ – $\pi$  stacking interactions [centroid-to-centroid distance = 3.826 (8) Å] and by pairs of additional  $Re \cdots Br$  contacts [3.131 (3) Å], respectively. The dimers are further packed into a three-dimensional network by non-directional interionic electrostatic forces and by C–H  $\cdots$  Br and C–H  $\cdots$  S hydrogen bonds. The disordered 1,1,2-trichloroethane molecules occupy solvent-accessible channels along the *b* axis.

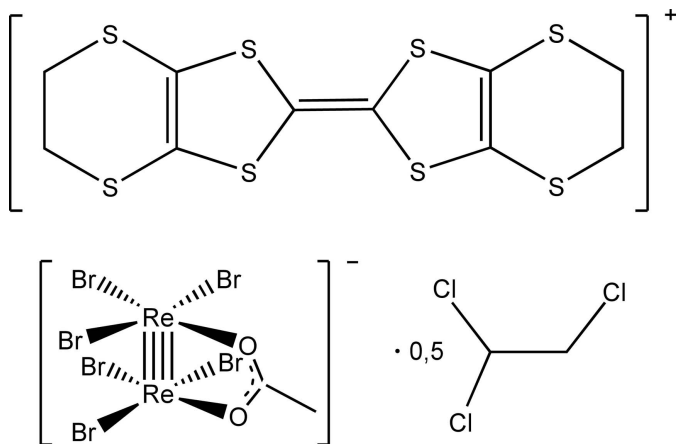
## 1. Chemical context

In the past few decades, molecular low-dimensional conducting materials have attracted much interest owing to their physical properties, in particular their electrical, magnetic and spectroscopic properties. The packing of radical cations in the crystal and the properties of radical cation salts depend substantially on the type of anions involved (Mori *et al.*, 1999; Mori, 1999). Labile equatorial chloride or bromide groups around the  $Re_2^{6+}$  cluster unit are the reactive centres in interactions with other chemical compounds and biological macromolecules (Shtemenko *et al.*, 2013, 2015). Only one radical cation salt containing a rhenium–rhenium quadruple bond has been described so far  $\{(ET)_2[Re_2Cl_8]$  [ET = bis(ethylenedithio)tetrathiafulvalene]; Reinheimer *et al.*, 2008]. In this context, we present the synthesis and crystal structure of a new radical cation salt of ET with the dirhenium(III) anion  $[Re_2Br_6(CH_3COO)]^-$ . Neither acetic acid nor acetate was used in the synthesis of this radical cation salt. Evidently, the acetate ligand arose by hydrolysis of  $CH_3CN$  (Cotton *et al.*, 1991). Complex compounds of dirhenium(III) with one equatorial carboxylato ligand are not well studied, the struc-



OPEN ACCESS

ture of only three such rhenium compounds having been reported to date (Lau *et al.*, 2000; Vega *et al.*, 2002; Beck & Zink, 2011).



## 2. Structural commentary

The title compound (Fig. 1) consists of bis(ethylenedithio)tetrathiafulvalene (ET) radical cations,  $\mu_2$ -acetato-bis[tribromidorhenate(III)] anions and 1,1,2-trichloroethane molecules in the stoichiometric molar ratio of 1:1:0.5. The solvent molecule is disordered over two orientations of equal occupancy about a twofold rotation axis intersecting the midpoint of the C—C ethane bond. The tetrathiafulvalene fragment adopts an almost planar configuration (r.m.s. deviation = 0.033 Å) that is typical for ET radical cations. The dihedral angle between the five-membered rings is 0.3 (6)°. The carbon atoms of both ethylenedithio fragments (C4/C5 and C9/C10)

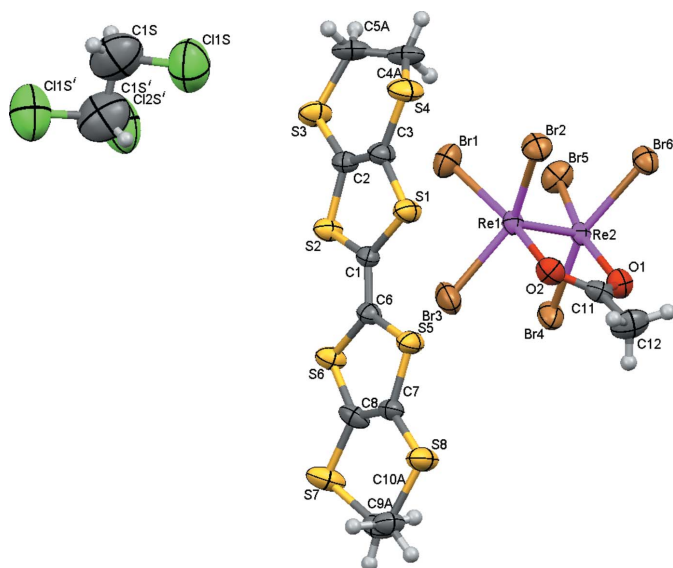


Figure 1

The asymmetric unit of the title compound, with displacement ellipsoids drawn at the 50% probability level. [Symmetry code: (i)  $-\frac{1}{2} - x, y, -z$ .] Only one component of the disordered 1,1,2-trichloroethane molecule and the major component of the ET cation are shown. Colour codes: C, grey; H, white; O, red; S, yellow; Cl, green; Br, brown, Re, violet.

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C5B-H5BA\cdots Br1$	0.98	2.77	3.63 (8)	147
$C9A-H9AA\cdots Br6^i$	0.97	2.80	3.60 (3)	140
$C9B-H9BA\cdots S4^{ii}$	0.97	2.75	3.46 (10)	130
$C9B-H9BB\cdots Br6^i$	0.96	2.61	3.40 (11)	140
$C10A-H10A\cdots Br4^{iii}$	0.97	2.92	3.83 (4)	156
$C10A-H10B\cdots S3^{ii}$	0.97	2.81	3.57 (3)	136
$C10B-H10D\cdots Br4^{iii}$	0.98	2.67	3.61 (11)	161

Symmetry codes: (i)  $x, -y - \frac{1}{2}, z - \frac{1}{2}$ ; (ii)  $-x, -y - 1, -z$ ; (iii)  $-x + \frac{1}{2}, y - 1, -z$ .

are disordered over two sets of sites with occupancy ratios of 0.65:0.35 and 0.77:0.23, respectively.

In the anion, each  $Re^{III}$  atom is coordinated by three Br atoms forming  $ReBr_3$  units which are linked by a Re—Re multiple bond [2.2174 (10) Å] and a bridging  $\mu_2$ -acetate ligand, forming a strongly distorted cubic  $O_2Br_6$  coordination polyhedron around the  $Re_2$  core. The length of the Re—Re bond is very close to the mean value of 2.222 Å for quadruple bonds (Groom *et al.*, 2016), and the six bromine ligands are arranged into an eclipsed conformation. It is also known that the presence of *O,O*-bridging ligands in such structures has a negligible effect on the Re—Re bond length [it varies in the range 2.2067 (7)–2.2731 (9) Å for compounds with no bridging ligands and in the range 2.2168 (8)–2.2532 (2) Å for compounds with *O,O*-bridging ligands (Poineau *et al.*, 2015)]. Thus, the structure of the  $Re_2Br_6CH_3COO^-$  anion corresponds to the typical structure of compounds with quadruple Re—Re bonds in an  $Re_2^{6+}$  core (Cotton *et al.*, 2005). The Re—Br and Re—O bonds vary in the ranges 2.435 (3)–2.451 (3) Å and 2.009 (15)–2.040 (16) Å, respectively. The distortion from an ideal cubic geometry is mainly due to the short distance between the O atoms of the acetate group [2.24 (2) Å], while the  $Br\cdots Br$  separations between adjacent Br atoms vary in the range 3.411 (3)–3.553 (4) Å.

## 3. Supramolecular features

In the crystal (Fig. 2), pairs of centrosymmetrically related ET cations are linked in a ‘head-to-tail’ manner into dimers by  $\pi$ – $\pi$  stacking interactions, with centroid-to-centroid separations of 3.836 (8) Å, perpendicular interplanar distances of 3.518 (6) Å and offsets of 1.52 (2) Å. Pairs of  $Re_2O_2Br_6$  anions are also linked into dimers by additional pairwise  $Re\cdots Br$  contacts [ $Br6\cdots Re2 = 3.131$  (3) Å]. Cationic and anionic dimers are packed into a three-dimensional network by non-directional intermolecular electrostatic forces and by C—H $\cdots$ Br and C—H $\cdots$ S hydrogen bonds (Table 1). Solvent-accessible channels along the *b* axis are occupied by the disordered 1,1,2-trichloroethane molecules.

## 4. Database survey

A search of the Cambridge Structural Database (Version 5.36; last update February 2015; Groom *et al.*, 2016) for related

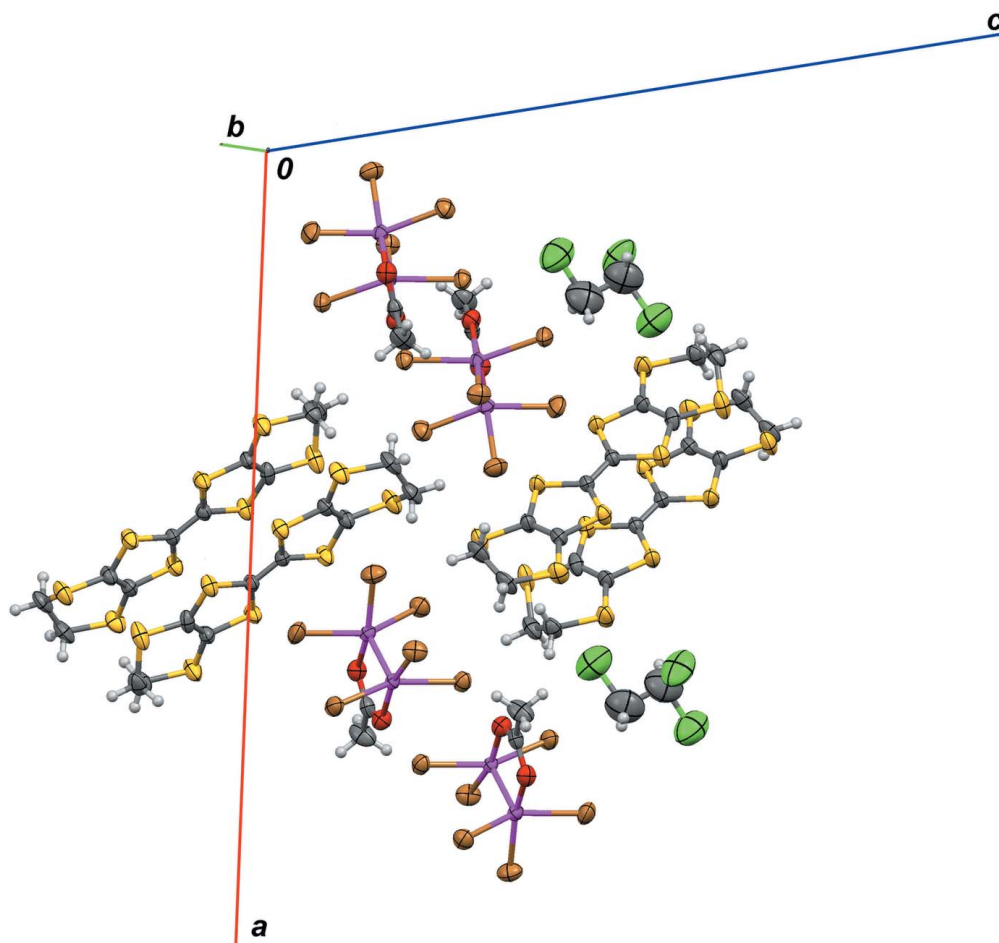


Figure 2

Partial crystal packing of the title compound, with displacement ellipsoids shown at the 50% probability level. Only one component of the disordered 1,1,2-trichloroethane molecule and the major component of the ET molecule are shown. Colour codes: C, grey, H, white, O, red, S, yellow, Cl, green, Br, brown, Re, violet.

compounds of bis(ethylenedithio)tetrathiafulvalene with simple Re-containing anions resulted in eight hits, amongst which one closely related structure containing the ET cation and  $\text{Re}_2\text{Cl}_8$  anion (Reinheimer *et al.*, 2008). A search for  $\text{Re}_2\text{Hal}_x\text{L}_y$  anionic moieties, where Hal is a halogen atom and  $L$  is the  $\mu_2$ -carboxylic group, resulted in nine hits. Some closely related patterns were found, *e.g.* one containing the ( $\mu_2$ -acetato)-hexachloridodirhenate anion exhibiting the same structure of the title compound (Vega *et al.*, 2002), and one containing the di- $\mu_2$ -acetato-bis(dibromidorhenate) anion (Koz'min *et al.*, 1981).

## 5. Synthesis and crystallization

The synthesis of the radical cation title salt was performed by galvanostatic anodic oxidation of ET ( $0.002 \text{ mol l}^{-1}$ ) in a two-electrode U-shaped glass cell with platinum electrodes. The initial current intensity of  $0.1 \mu\text{A}$  was increased by  $0.05 \mu\text{A}$  per day to a final value of  $0.45 \mu\text{A}$ . A mixture of 1,1,2-trichloroethane/acetonitrile (12:1 *v/v*) was used as solvent.  $[(\text{C}_4\text{H}_9)_4\text{N}]_2[\text{Re}_2\text{Br}_8]$  ( $0.008 \text{ mol l}^{-1}$ ) was used as electrolyte.

After a period of 6–7 weeks, black shiny plate-shaped crystals of the title salt suitable for X-ray analysis were formed.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All hydrogen atoms were placed in idealized positions and refined using a riding-model approximation, with  $\text{C-H} = 0.96\text{--}0.97 \text{ \AA}$ , and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or  $1.5U_{\text{eq}}(\text{C})$  for methyl H atoms. The 1,1,2-trichloroethane molecule is disordered over two sets of sites about a twofold rotation axis with equal occupancy. The C4–C5 and C9–C10 groups of the ET cations are disordered over two orientations with occupancy factors of 0.65/0.35 and 0.77/0.23, respectively. These occupancies were initially obtained as free variables by the full-matrix refinement, and were then fixed in the final refinement cycles. The C–C and C–Cl bond lengths in the solvent molecule were constrained to be  $1.52(1)$  and  $1.80(1) \text{ \AA}$ , respectively, and the C–Cl bonds of the solvent molecule were restrained to have the same lengths to within  $0.01 \text{ \AA}$ . The C–S and C–C bonds of the disordered fragments of the ET cation were also restrained

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	(C <sub>10</sub> H <sub>8</sub> S <sub>8</sub> )[Re <sub>2</sub> Br <sub>6</sub> (C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> )]·0.5C <sub>2</sub> H <sub>3</sub> Cl <sub>3</sub>
<i>M<sub>r</sub></i>	1362.24
Crystal system, space group	Monoclinic, <i>I2/a</i>
Temperature (K)	298
<i>a</i> , <i>b</i> , <i>c</i> (Å)	27.1825 (5), 8.53737 (13), 26.0667 (5)
$\beta$ (°)	100.8440 (17)
<i>V</i> (Å <sup>3</sup> )	5941.21 (18)
<i>Z</i>	8
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	16.93
Crystal size (mm)	0.4 × 0.4 × 0.1
Data collection	
Diffractometer	Agilent Xcalibur Sapphire3
Absorption correction	Multi-scan ( <i>CrysAlis PRO</i> ; Agilent, 2014)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.067, 1.000
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	36051, 6755, 6304
<i>R<sub>int</sub></i>	0.039
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.650
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.052, 0.137, 1.14
No. of reflections	6755
No. of parameters	334
No. of restraints	99
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	1.77, -1.90

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

to have the same lengths to within 0.005 Å. The atoms of each disordered fragment, including the solvent molecule, were restrained to have approximately the same displacement parameters to within 0.02–0.04 Å<sup>2</sup>. DELU restraints to within 0.01 Å<sup>2</sup> were applied to atoms C4B, C5B, C9B, C10B, C1S and Cl2S. In addition, all non-hydrogen atoms of the solvent molecule were restrained to be approximately isotropic to within 0.03–0.06 Å<sup>2</sup>. Several outlier reflections (67) that were believed to be affected by the contribution of several unresolved minor twin domains were omitted from the final cycles of refinement, reducing the *R* factor from 0.061 to 0.052. Attempts to refine the structure using a two-component twin

model were unsuccessful. Moreover, the crystals of the title compound are stable but show a strong tendency to splicing. The poor quality of the available crystal may account for the rather low bond precision of the C—C bonds and the presence of several large residual density peaks.

## Acknowledgements

This work was supported by a grant for Science Research (No. 0111U000111) from the Ministry of Education and Science of Ukraine. We also thank COST Action CM1105 for supporting this study.

## References

- Agilent (2014). *CrysAlis PRO*. Agilent Technologies, Yarnton, England.
- Beck, J. & Zink, G. (2011). *J. Chem. Crystallogr.* **41**, 1185–1189.
- Cotton, F. A., DeCanio, E. C., Kibala, P. A. & Vidyasagar, K. (1991). *Inorg. Chim. Acta*, **184**, 221–228.
- Cotton, F. A., Murillo, C. A. & Walton, R. A. (2005). *Multiple Bonds between Metal Atoms*, 3rd ed., pp. 271–376. New York: Springer Science and Business Media Inc.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Koz'min, P. A., Surazhskaya, M. D. & Larina, T. B. (1981). *Russ. J. Inorg. Chem.* **26**, 57–60.
- Lau, S. S., Fanwick, P. E. & Walton, R. A. (2000). *Inorg. Chim. Acta*, **308**, 8–16.
- Mori, T. (1999). *Bull. Chem. Soc. Jpn.*, **72**, 2011–2027.
- Mori, T., Mori, H. & Tanaka, Sh. (1999). *Bull. Chem. Soc. Jpn.*, **72**, 179–197.
- Poineau, F., Sattelberger, A. P., Lu, E. & Liddle, S. T. (2015). *Molecular Metal–Metal Bonds: Compounds, Synthesis, Properties*, edited by S. T. Liddle, pp. 205–216. Weinheim: Wiley-VCH.
- Reinheimer, E. W., Galán-Mascarós, J. R., Gómez-García, C. J., Zhao, H., Fourmigué, M. & Dunbar, K. R. (2008). *J. Mol. Struct.* **890**, 81–89.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Shtemenko, N. I., Chifotides, H. T., Domasevitch, K. V., Golichenko, A. A., Babiy, S. A., Li, Z., Paramonova, K. V., Shtemenko, A. V. & Dunbar, K. R. (2013). *J. Inorg. Biochem.* **129**, 127–134.
- Shtemenko, A. V., Chifotides, H. T., Yegorova, D. E., Shtemenko, N. I. & Dunbar, K. R. (2015). *J. Inorg. Biochem.* **153**, 114–120.
- Vega, A., Calvo, V., Manzur, J., Spodine, E. & Saillard, J.-Y. (2002). *Inorg. Chem.* **41**, 5382–5387.

## supporting information

*Acta Cryst.* (2016). E72, 712-715 [doi:10.1107/S2056989016006058]

## Crystal structure of bis(ethylenedithio)tetrathiafulvalenium $\mu_2$ -acetato-bis-[tribromidorhenate(III)] 1,1,2-trichloroethane hemisolvate

Alexander A. Golichenko, Andrey V. Kravchenko, Irina V. Omelchenko, Denis M. Chudak, Vladimir A. Starodub, Boleslaw Barszcz and Alexander V. Shtemenko

### Computing details

Data collection: *CrysAlis PRO* (Agilent, 2014); cell refinement: *CrysAlis PRO* (Agilent, 2014); data reduction: *CrysAlis PRO* (Agilent, 2014); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

### Bis(ethylenedithio)tetrathiafulvalenium $\mu_2$ -acetato-bis[tribromidorhenate(III)] 1,1,2-trichloroethane hemisolvate

#### Crystal data

(C<sub>10</sub>H<sub>8</sub>S<sub>8</sub>)[Re<sub>2</sub>Br<sub>6</sub>(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)]·0.5C<sub>2</sub>H<sub>3</sub>Cl<sub>3</sub>

$M_r = 1362.24$

Monoclinic, *I*2/a

$a = 27.1825$  (5) Å

$b = 8.53737$  (13) Å

$c = 26.0667$  (5) Å

$\beta = 100.8440$  (17)°

$V = 5941.21$  (18) Å<sup>3</sup>

$Z = 8$

$F(000) = 4960$

$D_x = 3.046$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 18811 reflections

$\theta = 2.9\text{--}30.7^\circ$

$\mu = 16.93$  mm<sup>-1</sup>

$T = 298$  K

Block, metallic dark violet

0.4 × 0.4 × 0.1 mm

#### Data collection

Agilent Xcalibur Sapphire3  
diffractometer

Radiation source: Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 16.1827 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan  
(*CrysAlis PRO*; Agilent, 2014)

$T_{\min} = 0.067$ ,  $T_{\max} = 1.000$

36051 measured reflections

6755 independent reflections

6304 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.039$

$\theta_{\max} = 27.5^\circ$ ,  $\theta_{\min} = 2.9^\circ$

$h = -35 \rightarrow 35$

$k = -11 \rightarrow 9$

$l = -33 \rightarrow 33$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.052$

$wR(F^2) = 0.137$

$S = 1.14$

6755 reflections

334 parameters

99 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0534P)^2 + 229.8497P]$$

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

$$\Delta\rho_{\max} = 1.77 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -1.90 \text{ e } \text{\AA}^{-3}$$

### Special details

**Experimental.** Absorption correction: *CrysAlisPro* (Agilent, 2014) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

**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.

**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  $F^2 > 2\sigma(F^2)$  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 ( $\text{\AA}^2$ )

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
S1	0.0279 (2)	-0.3844 (7)	0.1248 (2)	0.0486 (13)	
S2	-0.0188 (2)	-0.1562 (6)	0.0484 (2)	0.0411 (11)	
S3	-0.0801 (3)	-0.0100 (7)	0.1157 (3)	0.0532 (14)	
S4	-0.0284 (3)	-0.2886 (8)	0.2057 (2)	0.0602 (17)	
S5	0.0889 (2)	-0.5248 (8)	0.0393 (2)	0.0484 (13)	
S6	0.0408 (2)	-0.2918 (6)	-0.0354 (2)	0.0436 (12)	
S7	0.0915 (3)	-0.3875 (7)	-0.1204 (2)	0.0586 (17)	
S8	0.1502 (3)	-0.6653 (9)	-0.0297 (2)	0.0590 (16)	
C1	0.0209 (7)	-0.313 (2)	0.0627 (7)	0.034 (4)	
C2	-0.0374 (7)	-0.152 (2)	0.1079 (8)	0.037 (4)	
C3	-0.0160 (8)	-0.262 (3)	0.1431 (8)	0.043 (5)	
C4	-0.065 (3)	-0.122 (6)	0.220 (3)	0.064 (11)	0.35
H4A	-0.1001	-0.1537	0.2165	0.077*	0.35
H4B	-0.0538	-0.0909	0.2563	0.077*	0.35
C4A	-0.0391 (15)	-0.084 (3)	0.2196 (15)	0.056 (8)	0.65
H4AA	-0.0440	-0.0750	0.2554	0.067*	0.65
H4AB	-0.0094	-0.0242	0.2166	0.067*	0.65
C5A	-0.0822 (16)	-0.015 (5)	0.1850 (9)	0.060 (9)	0.65
H5AA	-0.0864	0.0909	0.1965	0.072*	0.65
H5AB	-0.1118	-0.0737	0.1893	0.072*	0.65
C5B	-0.062 (3)	0.011 (9)	0.1862 (9)	0.061 (12)	0.35
H5BA	-0.0272	0.0463	0.1933	0.073*	0.35
H5BB	-0.0817	0.0950	0.1967	0.073*	0.35
C6	0.0472 (7)	-0.372 (2)	0.0258 (7)	0.035 (4)	
C7	0.1061 (8)	-0.523 (2)	-0.0214 (8)	0.039 (4)	
C8	0.0834 (9)	-0.415 (2)	-0.0558 (8)	0.044 (5)	
C9A	0.1534 (9)	-0.479 (4)	-0.1154 (13)	0.057 (8)	0.77
H9AA	0.1634	-0.4736	-0.1492	0.068*	0.77
H9AB	0.1777	-0.4205	-0.0908	0.068*	0.77
C9B	0.134 (4)	-0.548 (10)	-0.130 (4)	0.05 (2)	0.23

H9BA	0.1153	-0.6449	-0.1362	0.060*	0.23
H9BB	0.1493	-0.5262	-0.1596	0.060*	0.23
C10A	0.1547 (13)	-0.643 (4)	-0.0988 (9)	0.051 (7)	0.77
H10A	0.1857	-0.6902	-0.1045	0.061*	0.77
H10B	0.1272	-0.6987	-0.1202	0.061*	0.77
C10B	0.173 (4)	-0.566 (13)	-0.083 (3)	0.05 (2)	0.23
H10C	0.1860	-0.4639	-0.0715	0.059*	0.23
H10D	0.2006	-0.6266	-0.0923	0.059*	0.23
Re1	0.12639 (3)	0.02771 (9)	0.15999 (3)	0.0325 (2)	
Re2	0.18894 (3)	0.19389 (8)	0.18533 (3)	0.0285 (2)	
Br1	0.05027 (9)	0.1855 (3)	0.15459 (12)	0.0621 (7)	
Br2	0.10600 (9)	-0.1027 (3)	0.23712 (10)	0.0541 (6)	
Br3	0.11180 (11)	0.0172 (4)	0.06499 (10)	0.0623 (7)	
Br4	0.20677 (9)	0.2898 (3)	0.10198 (9)	0.0529 (6)	
Br5	0.15056 (10)	0.4496 (3)	0.19753 (11)	0.0560 (6)	
Br6	0.20369 (9)	0.1635 (3)	0.28134 (8)	0.0476 (5)	
O1	0.2381 (6)	0.0139 (18)	0.1841 (6)	0.047 (3)	
O2	0.1742 (6)	-0.1510 (17)	0.1587 (6)	0.046 (3)	
C11	0.2221 (8)	-0.129 (2)	0.1733 (7)	0.039 (4)	
C12	0.2582 (11)	-0.260 (3)	0.1768 (12)	0.066 (7)	
H12A	0.2756	-0.2551	0.1480	0.100*	
H12B	0.2404	-0.3578	0.1756	0.100*	
H12C	0.2819	-0.2533	0.2090	0.100*	
Cl1S	-0.1993 (6)	0.0569 (19)	0.0673 (6)	0.150 (6)	
Cl2S	-0.2811 (11)	0.288 (3)	0.0317 (11)	0.140 (10)	0.50
C1S	-0.2592 (9)	0.090 (4)	0.0257 (5)	0.15 (2)	
H1S	-0.2848	0.0099	0.0239	0.180*	
H1SA	-0.2718	0.1918	0.0336	0.180*	0.50

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.052 (3)	0.062 (3)	0.035 (2)	0.022 (3)	0.013 (2)	0.012 (2)
S2	0.053 (3)	0.036 (2)	0.037 (2)	0.010 (2)	0.016 (2)	0.008 (2)
S3	0.064 (4)	0.044 (3)	0.055 (3)	0.018 (3)	0.022 (3)	0.001 (2)
S4	0.080 (4)	0.065 (4)	0.043 (3)	0.015 (3)	0.032 (3)	0.013 (3)
S5	0.049 (3)	0.065 (4)	0.034 (2)	0.018 (3)	0.014 (2)	0.010 (2)
S6	0.062 (3)	0.036 (2)	0.036 (2)	0.009 (2)	0.017 (2)	0.0036 (19)
S7	0.102 (5)	0.041 (3)	0.040 (3)	0.018 (3)	0.032 (3)	0.006 (2)
S8	0.064 (4)	0.075 (4)	0.042 (3)	0.028 (3)	0.020 (3)	0.008 (3)
C1	0.033 (9)	0.043 (10)	0.028 (8)	0.000 (8)	0.008 (7)	0.002 (7)
C2	0.040 (10)	0.038 (10)	0.036 (9)	-0.002 (8)	0.015 (8)	0.000 (8)
C3	0.049 (11)	0.050 (12)	0.033 (9)	0.010 (9)	0.015 (8)	0.007 (9)
C4	0.071 (17)	0.065 (16)	0.061 (15)	0.002 (14)	0.025 (14)	-0.003 (12)
C4A	0.070 (18)	0.053 (15)	0.057 (15)	0.000 (14)	0.040 (14)	-0.015 (13)
C5A	0.074 (19)	0.059 (17)	0.058 (15)	0.008 (16)	0.043 (14)	-0.007 (14)
C5B	0.066 (18)	0.061 (16)	0.060 (16)	0.000 (14)	0.023 (13)	-0.004 (12)
C6	0.039 (10)	0.039 (10)	0.030 (8)	-0.002 (8)	0.011 (7)	0.002 (7)

C7	0.042 (10)	0.045 (11)	0.031 (9)	0.004 (8)	0.012 (8)	-0.004 (8)
C8	0.067 (14)	0.036 (10)	0.030 (9)	-0.010 (10)	0.014 (9)	-0.007 (8)
C9A	0.07 (2)	0.061 (19)	0.050 (17)	-0.023 (17)	0.030 (16)	-0.004 (15)
C9B	0.05 (2)	0.05 (3)	0.05 (2)	0.000 (17)	0.013 (15)	0.001 (17)
C10A	0.058 (18)	0.050 (17)	0.050 (16)	0.014 (15)	0.025 (14)	0.003 (14)
C10B	0.05 (2)	0.05 (3)	0.05 (2)	0.000 (17)	0.013 (15)	-0.001 (17)
Re1	0.0300 (4)	0.0326 (4)	0.0333 (4)	-0.0033 (3)	0.0025 (3)	0.0011 (3)
Re2	0.0294 (4)	0.0276 (3)	0.0275 (3)	-0.0007 (2)	0.0027 (3)	0.0040 (2)
Br1	0.0443 (12)	0.0641 (15)	0.0752 (17)	0.0068 (11)	0.0042 (11)	0.0085 (13)
Br2	0.0564 (13)	0.0555 (13)	0.0517 (12)	-0.0093 (10)	0.0140 (10)	0.0070 (10)
Br3	0.0602 (15)	0.0809 (18)	0.0408 (11)	-0.0144 (13)	-0.0036 (10)	-0.0037 (11)
Br4	0.0481 (12)	0.0703 (15)	0.0389 (11)	-0.0074 (11)	0.0047 (9)	0.0135 (10)
Br5	0.0561 (13)	0.0389 (11)	0.0737 (16)	0.0048 (10)	0.0142 (12)	0.0065 (11)
Br6	0.0513 (12)	0.0517 (12)	0.0388 (10)	-0.0108 (10)	0.0056 (9)	0.0051 (9)
O1	0.050 (9)	0.041 (8)	0.048 (8)	0.002 (7)	0.005 (7)	0.004 (7)
O2	0.056 (9)	0.034 (7)	0.048 (8)	-0.001 (6)	0.009 (7)	-0.004 (6)
C11	0.056 (12)	0.033 (9)	0.031 (9)	0.005 (9)	0.014 (8)	-0.001 (8)
C12	0.074 (18)	0.048 (14)	0.085 (19)	0.023 (13)	0.034 (15)	0.014 (13)
Cl1S	0.133 (11)	0.148 (12)	0.153 (12)	0.021 (9)	-0.014 (9)	-0.014 (10)
Cl2S	0.15 (2)	0.115 (17)	0.14 (2)	0.048 (16)	-0.024 (17)	0.005 (15)
C1S	0.15 (4)	0.12 (2)	0.19 (4)	0.02 (3)	0.05 (3)	-0.01 (3)

*Geometric parameters (Å, °)*

S1—C1	1.708 (19)	C7—C8	1.35 (3)
S1—C3	1.72 (2)	C9A—H9AA	0.9700
S2—C1	1.71 (2)	C9A—H9AB	0.9700
S2—C2	1.72 (2)	C9A—C10A	1.46 (5)
S3—C2	1.72 (2)	C9B—H9BA	0.9700
S3—C5A	1.82 (2)	C9B—H9BB	0.9700
S3—C5B	1.82 (2)	C9B—C10B	1.46 (14)
S4—C3	1.74 (2)	C10A—H10A	0.9700
S4—C4	1.82 (2)	C10A—H10B	0.9700
S4—C4A	1.82 (2)	C10B—H10C	0.9700
S5—C6	1.72 (2)	C10B—H10D	0.9700
S5—C7	1.73 (2)	Re1—Re2	2.2174 (10)
S6—C6	1.716 (19)	Re1—Br1	2.451 (3)
S6—C8	1.72 (2)	Re1—Br2	2.451 (2)
S7—C8	1.75 (2)	Re1—Br3	2.435 (3)
S7—C9A	1.84 (2)	Re1—O2	2.009 (15)
S7—C9B	1.84 (2)	Re2—Br4	2.454 (2)
S8—C7	1.75 (2)	Re2—Br5	2.465 (2)
S8—C10A	1.84 (2)	Re2—Br6	2.473 (2)
S8—C10B	1.84 (2)	Re2—O1	2.040 (16)
C1—C6	1.40 (3)	O1—C11	1.30 (3)
C2—C3	1.36 (3)	O2—C11	1.30 (3)
C4—H4A	0.9700	C11—C12	1.48 (3)
C4—H4B	0.9700	C12—H12A	0.9600



C4—C5B	1.46 (4)	C12—H12B	0.9600
C4A—H4AA	0.9700	C12—H12C	0.9600
C4A—H4AB	0.9700	C11S—C1S	1.800 (16)
C4A—C5A	1.46 (4)	C12S—C1S	1.81 (2)
C5A—H5AA	0.9700	C12S—H1SA	0.8557
C5A—H5AB	0.9700	C1S—C1S <sup>i</sup>	1.515 (18)
C5B—H5BA	0.9700	C1S—H1S	0.9700
C5B—H5BB	0.9700	C1S—H1SA	0.9703
C1—S1—C3	94.9 (10)	C10A—C9A—H9AA	108.9
C1—S2—C2	95.6 (9)	C10A—C9A—H9AB	108.9
C2—S3—C5A	104.3 (14)	S7—C9B—H9BA	109.6
C2—S3—C5B	97 (3)	S7—C9B—H9BB	109.6
C5A—S3—C5B	19 (3)	H9BA—C9B—H9BB	108.1
C3—S4—C4	108 (2)	C10B—C9B—S7	110 (7)
C3—S4—C4A	97.4 (15)	C10B—C9B—H9BA	109.6
C4A—S4—C4	25 (3)	C10B—C9B—H9BB	109.6
C6—S5—C7	94.9 (9)	S8—C10A—H10A	109.0
C6—S6—C8	94.9 (10)	S8—C10A—H10B	109.0
C8—S7—C9A	98.9 (13)	C9A—C10A—S8	113 (2)
C8—S7—C9B	103 (3)	C9A—C10A—H10A	109.0
C9A—S7—C9B	26 (4)	C9A—C10A—H10B	109.0
C7—S8—C10A	102.8 (12)	H10A—C10A—H10B	107.8
C7—S8—C10B	96 (4)	S8—C10B—H10C	109.1
C10B—S8—C10A	28 (4)	S8—C10B—H10D	109.1
S1—C1—S2	116.1 (11)	C9B—C10B—S8	112 (7)
C6—C1—S1	122.7 (15)	C9B—C10B—H10C	109.1
C6—C1—S2	121.1 (15)	C9B—C10B—H10D	109.1
S3—C2—S2	116.0 (12)	H10C—C10B—H10D	107.9
C3—C2—S2	115.7 (15)	Re2—Re1—Br1	104.91 (8)
C3—C2—S3	128.3 (16)	Re2—Re1—Br2	108.99 (7)
S1—C3—S4	116.6 (12)	Re2—Re1—Br3	107.19 (7)
C2—C3—S1	117.5 (15)	Br1—Re1—Br2	88.73 (10)
C2—C3—S4	125.9 (17)	Br3—Re1—Br1	89.29 (11)
S4—C4—H4A	109.2	Br3—Re1—Br2	143.01 (9)
S4—C4—H4B	109.2	O2—Re1—Re2	91.6 (4)
H4A—C4—H4B	107.9	O2—Re1—Br1	163.4 (4)
C5B—C4—S4	112 (5)	O2—Re1—Br2	85.2 (5)
C5B—C4—H4A	109.2	O2—Re1—Br3	86.4 (4)
C5B—C4—H4B	109.2	Re1—Re2—Br4	102.59 (6)
S4—C4A—H4AA	108.8	Re1—Re2—Br5	106.59 (7)
S4—C4A—H4AB	108.8	Re1—Re2—Br6	101.74 (6)
H4AA—C4A—H4AB	107.7	Br4—Re2—Br5	88.72 (9)
C5A—C4A—S4	114 (3)	Br4—Re2—Br6	155.47 (8)
C5A—C4A—H4AA	108.8	Br5—Re2—Br6	87.39 (9)
C5A—C4A—H4AB	108.8	O1—Re2—Re1	88.9 (4)
S3—C5A—H5AA	108.1	O1—Re2—Br4	89.9 (5)
S3—C5A—H5AB	108.1	O1—Re2—Br5	164.3 (4)

C4A—C5A—S3	117 (2)	O1—Re2—Br6	87.4 (5)
C4A—C5A—H5AA	108.1	C11—O1—Re2	120.9 (14)
C4A—C5A—H5AB	108.1	C11—O2—Re1	119.9 (13)
H5AA—C5A—H5AB	107.3	O1—C11—C12	120 (2)
S3—C5B—H5BA	107.3	O2—C11—O1	118.4 (18)
S3—C5B—H5BB	107.3	O2—C11—C12	121 (2)
C4—C5B—S3	120 (5)	C11—C12—H12A	109.5
C4—C5B—H5BA	107.3	C11—C12—H12B	109.5
C4—C5B—H5BB	107.3	C11—C12—H12C	109.5
H5BA—C5B—H5BB	106.9	H12A—C12—H12B	109.5
S6—C6—S5	116.3 (11)	H12A—C12—H12C	109.5
C1—C6—S5	122.5 (15)	H12B—C12—H12C	109.5
C1—C6—S6	121.2 (15)	C1S—C12S—H1SA	8.9
S5—C7—S8	114.5 (12)	C11S—C1S—C12S	112 (2)
C8—C7—S5	116.4 (16)	C11S—C1S—H1S	118.6
C8—C7—S8	129.0 (16)	C11S—C1S—H1SA	109.2
S6—C8—S7	115.3 (13)	C12S—C1S—H1S	114.7
C7—C8—S6	117.5 (16)	C12S—C1S—H1SA	7.8
C7—C8—S7	127.2 (18)	C1S <sup>i</sup> —C1S—C11S	97 (2)
S7—C9A—H9AA	108.9	C1S <sup>i</sup> —C1S—C12S	104.2 (12)
S7—C9A—H9AB	108.9	C1S <sup>i</sup> —C1S—H1S	108.0
H9AA—C9A—H9AB	107.7	C1S <sup>i</sup> —C1S—H1SA	112.0
C10A—C9A—S7	114 (2)	H1S—C1S—H1SA	111.3
S1—C1—C6—S5	0 (3)	C7—S8—C10A—C9A	40 (3)
S1—C1—C6—S6	-177.4 (11)	C7—S8—C10B—C9B	-63 (7)
S2—C1—C6—S5	177.7 (11)	C8—S6—C6—S5	0.2 (14)
S2—C1—C6—S6	0 (2)	C8—S6—C6—C1	178.1 (17)
S2—C2—C3—S1	2 (3)	C8—S7—C9A—C10A	58 (3)
S2—C2—C3—S4	-178.8 (14)	C8—S7—C9B—C10B	-42 (7)
S3—C2—C3—S1	-177.1 (13)	C9A—S7—C8—S6	158.8 (15)
S3—C2—C3—S4	2 (3)	C9A—S7—C8—C7	-22 (2)
S4—C4—C5B—S3	58 (9)	C9A—S7—C9B—C10B	42 (6)
S4—C4A—C5A—S3	-61 (4)	C9B—S7—C8—S6	-175 (4)
S5—C7—C8—S6	1 (2)	C9B—S7—C8—C7	4 (4)
S5—C7—C8—S7	-178.2 (13)	C9B—S7—C9A—C10A	-43 (8)
S7—C9A—C10A—S8	-71 (3)	C10A—S8—C7—S5	174.5 (16)
S7—C9B—C10B—S8	77 (9)	C10A—S8—C7—C8	-4 (3)
S8—C7—C8—S6	179.3 (13)	C10A—S8—C10B—C9B	43 (6)
S8—C7—C8—S7	0 (3)	C10B—S8—C7—S5	-158 (4)
C1—S1—C3—S4	176.8 (14)	C10B—S8—C7—C8	23 (4)
C1—S1—C3—C2	-4 (2)	C10B—S8—C10A—C9A	-40 (8)
C1—S2—C2—S3	-179.7 (12)	Re1—Re2—O1—C11	-3.2 (15)
C1—S2—C2—C3	0.9 (19)	Re1—O2—C11—O1	-6 (2)
C2—S2—C1—S1	-3.7 (13)	Re1—O2—C11—C12	175.2 (17)
C2—S2—C1—C6	178.7 (17)	Re2—Re1—O2—C11	3.0 (15)
C2—S3—C5A—C4A	22 (4)	Re2—O1—C11—O2	6 (3)
C2—S3—C5B—C4	-61 (7)	Re2—O1—C11—C12	-175.0 (17)

C3—S1—C1—S2	4.6 (14)	Br1—Re1—Re2—Br4	-90.90 (10)
C3—S1—C1—C6	-177.8 (18)	Br1—Re1—Re2—Br5	1.54 (11)
C3—S4—C4—C5B	-19 (7)	Br1—Re1—Re2—Br6	92.30 (10)
C3—S4—C4A—C5A	63 (3)	Br1—Re1—Re2—O1	179.4 (5)
C4—S4—C3—S1	168 (3)	Br1—Re1—O2—C11	-174.7 (11)
C4—S4—C3—C2	-11 (4)	Br2—Re1—Re2—Br4	175.23 (10)
C4—S4—C4A—C5A	-54 (6)	Br2—Re1—Re2—Br5	-92.32 (10)
C4A—S4—C3—S1	144.9 (18)	Br2—Re1—Re2—Br6	-1.56 (10)
C4A—S4—C3—C2	-34 (3)	Br2—Re1—Re2—O1	85.6 (5)
C4A—S4—C4—C5B	50 (4)	Br2—Re1—O2—C11	-105.9 (15)
C5A—S3—C2—S2	-169.7 (19)	Br3—Re1—Re2—Br4	3.05 (11)
C5A—S3—C2—C3	10 (3)	Br3—Re1—Re2—Br5	95.49 (11)
C5A—S3—C5B—C4	53 (6)	Br3—Re1—Re2—Br6	-173.75 (10)
C5B—S3—C2—S2	-152 (3)	Br3—Re1—Re2—O1	-86.6 (5)
C5B—S3—C2—C3	28 (3)	Br3—Re1—O2—C11	110.1 (15)
C5B—S3—C5A—C4A	-48 (8)	Br4—Re2—O1—C11	-105.8 (15)
C6—S5—C7—S8	-179.3 (12)	Br5—Re2—O1—C11	169.2 (11)
C6—S5—C7—C8	-0.5 (19)	Br6—Re2—O1—C11	98.6 (15)
C6—S6—C8—S7	178.5 (13)	O2—Re1—Re2—Br4	89.8 (5)
C6—S6—C8—C7	-0.6 (19)	O2—Re1—Re2—Br5	-177.8 (5)
C7—S5—C6—S6	0.1 (14)	O2—Re1—Re2—Br6	-87.0 (5)
C7—S5—C6—C1	-177.7 (18)	O2—Re1—Re2—O1	0.1 (6)

Symmetry code: (i)  $-x-1/2, y, -z$ .

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C5B—H5BA $\cdots$ Br1	0.98	2.77	3.63 (8)	147
C9A—H9AA $\cdots$ Br6 <sup>ii</sup>	0.97	2.80	3.60 (3)	140
C9B—H9BA $\cdots$ S4 <sup>iii</sup>	0.97	2.75	3.46 (10)	130
C9B—H9BB $\cdots$ Br6 <sup>ii</sup>	0.96	2.61	3.40 (11)	140
C10A—H10A $\cdots$ Br4 <sup>iv</sup>	0.97	2.92	3.83 (4)	156
C10A—H10B $\cdots$ S3 <sup>iii</sup>	0.97	2.81	3.57 (3)	136
C10B—H10D $\cdots$ Br4 <sup>iv</sup>	0.98	2.67	3.61 (11)	161

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