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# Caesium bis(5-bromosalicylaldehyde thiosemicarbazonato- $\kappa^3 O,N,S$ )-ferrate(III): supramolecular arrangement of low-spin $Fe^{III}$ complex anions mediated by $Cs^+$ cations

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The synthesis and crystal structure determination (at 293 K) of the title complex,  $Cs[Fe(C_8H_6BrN_3OS)_2]$ , are reported. The compound is composed of two dianionic  $O,N,S$ -tridentate 5-bromosalicylaldehyde thiosemicarbazonato(2<sup>-</sup>) ligands coordinated to an  $Fe^{III}$  cation, displaying a distorted octahedral geometry. The ligands are orientated in two perpendicular planes, with the O- and S-donor atoms in *cis* positions and the N-donor atoms in *trans* positions. The complex displays intermolecular  $N-H \cdots O$  and  $N-H \cdots Br$  hydrogen bonds, creating  $R_4^4(18)$  rings, which link the  $Fe^{III}$  units in the *a* and *b* directions. The  $Fe^{III}$  cation is in the low-spin state at 293 K.

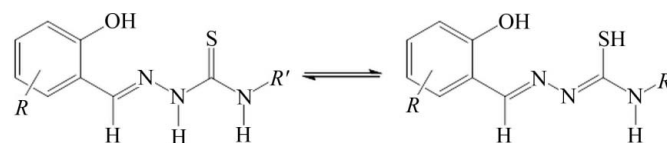
**Keywords:** spin-crossover behaviour; low-spin state  $Fe^{III}$ ; crystal structure; caesium salt; salicylaldehyde thiosemicarbazone;  $Fe^{III}$  coordination compound.

## 1. Introduction

It is recognised that octahedral metal complexes with  $3d^4-3d^7$  configurations with specific ligands can exhibit spin-crossover behaviour, *i.e.* the magnetic interconversion between low-spin and high-spin states, dependent upon external perturbations of temperature, pressure or light irradiation (Gütlich & Goodwin, 2004). In recent years, particular interest has been focused on  $Fe^{III}$  ( $3d^5$ ) complexes of substituted derivatives of  $R$ -salicylaldehyde 4- $R'$ -thiosemicarbazone (Floquet *et al.*, 2003, 2006, 2009; Li *et al.*, 2013; Yemeli Tido *et al.*, 2008; Yemeli Tido, 2010; Powell *et al.*, 2014) for generating  $Fe^{III}$  spin-crossover. The spin-crossover properties of this class of  $Fe^{III}$  bis(ligand) complexes have been found to be sensitive to the

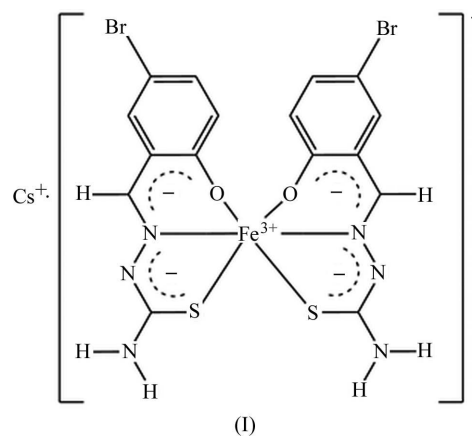
presence of a particular counter-ion, the degree of solvation and the nature of the  $R$ - and  $R'$ -substituted ligands (van Koningsbruggen *et al.*, 2004; Yemeli Tido *et al.*, 2008). Furthermore, it has been established that varying the pH during the synthesis of the  $Fe^{III}$  bis(ligand) units leads to the formation of  $Fe^{III}$  compounds differing in the degree of deprotonation of the ligand, whereby the complex unit can be neutral, monocationic, tricationic or monoanionic (Floquet *et al.*, 2009; Yemeli Tido *et al.*, 2010; Yemeli Tido, 2010).

In  $Fe^{III}$  compounds, it is possible for the tridentate  $R$ -salicylaldehyde 4- $R'$ -thiosemicarbazone ligand ( $H_2L$ ) to exist in tautomeric forms, and the ligand may also be present in its neutral, anionic or dianionic form. Free  $H_2L$  in solution exists in two tautomeric forms, *i.e.* the thione (left) and thiol (right) forms illustrated in Scheme 1.



Scheme 1

We recently reported the structure (at 100 K) of  $Cs[Fe(L1)_2] \cdot CH_3OH$ , where  $L1^{2-} = 3$ -ethoxysalicylaldehyde 4-methylthiosemicarbazonato(2<sup>-</sup>) (Powell *et al.*, 2014). Both of the ligands were found to be twofold deprotonated, as no H atoms were located on the phenolate O or thiolate S atoms. From the values of the geometric parameters, it was established that the  $Fe^{III}$  cation is in the low-spin state. Continuing our research, we have varied the  $R$  and  $R'$  substituents of the ligand and studied the structural and electronic properties of the resulting  $Fe^{III}$  coordination compounds. Herein, we report the room-temperature structure of the title  $Fe^{III}$  salt,  $Cs[Fe(L2)_2]$ , (I), containing two dianionic tridentate 5-bromosalicylaldehyde thiosemicarbazonato(2<sup>-</sup>) ( $L2^{2-}$ ) ligands.



## 2. Experimental

### 2.1. Synthesis and crystallization

5-Bromosalicylaldehyde thiosemicarbazone was synthesized according to the procedure described in the literature by Yemeli Tido (2010). 5-Bromosalicylaldehyde (98%, 49 mmol)

**Table 1**

Experimental details.

Crystal data	
Chemical formula	Cs[Fe(C <sub>8</sub> H <sub>6</sub> BrN <sub>3</sub> OS) <sub>2</sub> ]
<i>M<sub>r</sub></i>	733.02
Crystal system, space group	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>c</i>
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	20.2500 (14), 12.0868 (8), 9.0389 (5)
$\beta$ (°)	90.337 (1)
<i>V</i> (Å <sup>3</sup> )	2212.3 (2)
<i>Z</i>	4
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	6.13
Crystal size (mm)	0.08 × 0.08 × 0.01
Data collection	
Diffractometer	Rigaku AFC12 four-circle Kappa diffractometer
Absorption correction	Multi-scan ( <i>CrystalClear-SM Expert</i> ; Rigaku, 2013)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.640, 0.941
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	29088, 5073, 4211
<i>R</i> <sub>int</sub>	0.045
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.649
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>	0.033, 0.086, 1.04
No. of reflections	5073
No. of parameters	272
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.88, -0.85

Computer programs: *CrystalClear-SM Expert* (Rigaku, 2013), *ROTAX* (Cooper *et al.*, 2002), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008) and *ORTEP-3 for Windows* (Farrugia, 2012).

was dissolved in ethanol (80 ml) with constant stirring and then added to thiosemicarbazide (99%, 49 mmol) dissolved in ethanol (40 ml). The mixture was refluxed for 120 min. After the mixture had been allowed to cool to room temperature, a yellow solid, *i.e.* 5-bromosalicylaldehyde thiosemicarbazone, was isolated by filtration and dried.

FeCl<sub>3</sub>·6H<sub>2</sub>O (1.0 mmol, 0.27 g) was dissolved in methanol (10 ml). 5-Bromosalicylaldehyde thiosemicarbazone (2.0 mmol, 0.54 g) was dissolved in methanol (60 ml) with the addition of CsOH·H<sub>2</sub>O (4.0 mmol, 0.67 g). To this mixture, the methanolic Fe<sup>III</sup> salt solution was added with constant stirring. The resulting dark-green solution was stirred and heated to 353 K for approximately 10 min. The solution was then allowed to stand at room temperature until crystals were formed. Dark-green microcrystals of (I) were isolated by filtration and dried.

## 2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The structure of (I) was solved routinely by direct methods and refined by least squares, with H atoms placed in anticipated positions and non-H atoms given anisotropic displacement parameters. However, the refined parameters did not match the quality of the data set, since the unweighted discrepancy index *R*<sub>1</sub> of 0.092 was much higher than the *R*<sub>int</sub> value of 0.045. Since all 50 of the reflections with the worst discrepancy had *F*<sub>obs</sub> > *F*<sub>calc</sub>, twinning was suspected, and the closeness of the unit-cell  $\beta$  angle to 90° suggested a mechanism for pseudo-merohedral twinning. Application of *ROTAX* (Cooper *et al.*, 2002) indi-

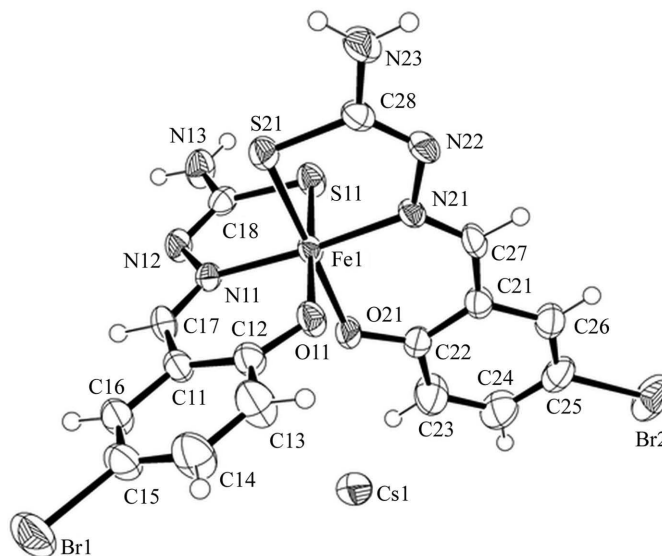
cated 180° rotation about the *a* axis as the likely twin law. Repeating the refinement with this twin law drastically reduced the discrepancy indices.

Now, all polar H atoms were omitted from the model and sought in a difference Fourier map. The H atoms on the secondary atoms N13 and N23 were located in a difference Fourier map at peak heights between 0.60 and 0.70 e Å<sup>-3</sup>, while no comparable peaks appeared adjacent to N11, N12, N21, N22 or any O or S atom. In subsequent refinements, the amino H atoms thus established were treated as riding, with N–H = 0.86 Å and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(N). The remaining H atoms were included in the refinement in calculated positions and treated as riding on their parent atoms, with C–H = 0.93 Å and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C) for aryl (–CH=) H atoms. After final refinement, *R*<sub>1</sub> reached 0.033 and *wR*<sub>2</sub> was equal to 0.086, and a fractional contribution of 0.1306 (8) from the minor twin component was indicated.

## 3. Results and discussion

The crystal structure of (I) (Fig. 1) was determined at 293 K. Compound (I) crystallizes in the monoclinic system in the space group *P*<sub>2</sub><sub>1</sub>/*c*. The asymmetric unit corresponds to the formula unit Cs[Fe(L2)<sub>2</sub>] [L2<sup>2-</sup> is 5-bromosalicylaldehyde thiosemicarbazone(2–)] with no atom on a special position. The central Fe<sup>III</sup> cation is hexacoordinated by two dianionic *O,N,S*-tridentate L2<sup>2-</sup> ligands, displaying a distorted octahedral Fe<sup>III</sup> S<sub>2</sub>N<sub>2</sub>O<sub>2</sub> geometry. Deprotonation occurs for the phenol O and thiol S atoms. Selected geometric parameters are listed in Table 2.

The Fe<sup>III</sup> S<sub>2</sub>N<sub>2</sub>O<sub>2</sub> unit is distorted from ideal octahedral geometry, as indicated by the bond angles (Table 2) of the donor atoms and atom Fe1 (see below). The tridentate L2<sup>2-</sup> ligands are coordinated to the Fe<sup>III</sup> cation by the O- and S-donor atoms, which are situated in two perpendicular planes in


**Figure 1**

The molecular structure and atom-numbering scheme for (I). Displacement ellipsoids are drawn at the 50% probability level.

**Table 2**  
Selected geometric parameters (Å, °).

Fe1—S11	2.2321 (11)	Fe1—O21	1.956 (3)
Fe1—S21	2.2422 (11)	Fe1—N11	1.947 (3)
Fe1—O11	1.942 (3)	Fe1—N21	1.938 (3)
Cs1—S11 <sup>i</sup>	3.7159 (11)	Cs1—N12 <sup>ii</sup>	3.326 (3)
Cs1—S21 <sup>i</sup>	3.5564 (11)	Cs1—N22 <sup>iii</sup>	3.470 (3)
Cs1—O11	3.220 (3)	Cs1—N23 <sup>i</sup>	3.699 (4)
Cs1—O21	3.129 (3)		
S11—Fe1—S21	93.66 (4)	O11—Fe1—N21	89.20 (12)
S11—Fe1—N11	86.01 (9)	O21—Fe1—N11	89.40 (11)
S11—Fe1—O11	177.50 (9)	O21—Fe1—N21	93.78 (12)
S11—Fe1—O21	89.78 (10)	N11—Fe1—N21	175.33 (12)
S11—Fe1—N21	90.57 (9)	C18—S11—Fe1	95.12 (13)
S21—Fe1—O11	88.81 (9)	C28—S21—Fe1	94.61 (14)
S21—Fe1—O21	176.56 (10)	N11—N12—C18	113.5 (3)
S21—Fe1—N11	90.96 (9)	N21—N22—C28	113.6 (3)
S21—Fe1—N21	86.07 (9)	N12—C18—S11	124.3 (3)
O11—Fe1—O21	87.75 (12)	N22—C28—S21	124.8 (3)
O11—Fe1—N11	94.35 (12)	O21—Cs1—N23 <sup>i</sup>	137.96 (7)
O11—Cs1—S11 <sup>i</sup>	176.98 (5)	N12 <sup>ii</sup> —Cs1—S11 <sup>i</sup>	85.01 (6)
O11—Cs1—S21 <sup>i</sup>	129.54 (5)	N12 <sup>ii</sup> —Cs1—S21 <sup>i</sup>	103.23 (6)
O11—Cs1—N12 <sup>ii</sup>	92.97 (7)	N12 <sup>ii</sup> —Cs1—N22 <sup>iii</sup>	156.35 (8)
O11—Cs1—N22 <sup>iii</sup>	65.82 (7)	N12 <sup>ii</sup> —Cs1—N23 <sup>i</sup>	143.33 (8)
O11—Cs1—N23 <sup>i</sup>	100.65 (7)	N22 <sup>iii</sup> —Cs1—S11 <sup>i</sup>	115.72 (6)
O11—Cs1—O21	50.34 (7)	N22 <sup>iii</sup> —Cs1—S21 <sup>i</sup>	98.64 (6)
O21—Cs1—S11 <sup>i</sup>	126.82 (5)	N22 <sup>iii</sup> —Cs1—N23 <sup>i</sup>	56.10 (8)
O21—Cs1—S21 <sup>i</sup>	178.78 (5)	N23 <sup>i</sup> —Cs1—S11 <sup>i</sup>	82.29 (6)
O21—Cs1—N12 <sup>ii</sup>	75.63 (7)	N23 <sup>i</sup> —Cs1—S21 <sup>i</sup>	42.99 (6)
O21—Cs1—N22 <sup>iii</sup>	82.42 (7)	S21 <sup>i</sup> —Cs1—S11 <sup>i</sup>	53.27 (2)

Symmetry codes: (i)  $x, y, z - 1$ ; (ii)  $x, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (iii)  $x, -y + \frac{3}{2}, z - \frac{1}{2}$ .

the *cis* positions, such that the N-donor atoms are situated in mutually *trans* positions.

X-ray structural data of similar Fe<sup>III</sup> bis(ligand) compounds containing dianionic thiosemicarbazonate(2-) ligands show that the Fe—S, Fe—O and Fe—N bond distances are in the ranges 2.23–2.31, 1.93–1.95 and 1.88–1.96 Å, respectively, for low-spin Fe<sup>III</sup> compounds, and 2.40–2.44, 1.96–1.99 and 2.05–2.15 Å, respectively, for corresponding high-spin Fe<sup>III</sup> compounds (van Koningsbruggen *et al.*, 2004). Comparison of the bond distances of (I) involving the Fe<sup>III</sup> atom and the donor atoms (Table 2) suggests that the present compound contains low-spin Fe<sup>III</sup> at 293 K.

The distortion of the Fe<sup>III</sup> S<sub>2</sub>N<sub>2</sub>O<sub>2</sub> unit results from the constraints imposed by the five- and six-membered chelate rings formed. The six-membered chelate ring involves a significantly wider bite angle than the ideal octahedral value of 90° [O11—Fe—N11 = 94.35 (12)° and O21—Fe—N21 = 93.78 (12)°], while the bite angle is narrowed in the five-membered chelate ring [S11—Fe—N11 = 86.01 (9)° and S21—Fe—N21 = 86.07 (9)°]. There is no major strain relief through puckering: the r.m.s. deviations from the least-squares planes of the atoms comprising the six-membered Fe1/N11/C17/C11/C12/O11 and Fe1/N21/C27/C21/C22/O21 chelate rings are 0.034 and 0.038 Å, respectively; the corresponding values for the five-membered Fe1/N11/N12/C18/S11 and Fe1/N21/N22/C28/S21 rings are 0.014 and 0.009 Å, respectively. Compared with the 120° angles in a regular hexagon, the O—Fe—N bite angle is deficient by *ca* 26°, and each of the remaining angles in the six-membered rings is within 2° of 125°. Because the angle at the vertex of a regular pentagon is only 108°, the S—Fe—N bite angles are deficient by only 22°. However, the C—S—Fe

angles are only about 95°, providing an additional deficiency of 13° and a total which could be neatly offset by increasing the other angles to *ca* 120°. (In fact, the N—N—C angles are <120° and the N—C—S angles are >120°.) Such 120° angles are consistent with *sp*<sup>2</sup> hybridization at the C and N atoms. The stability of the Fe<sup>III</sup> complex is enhanced by the high degree of electron delocalization throughout the chelated ligands.

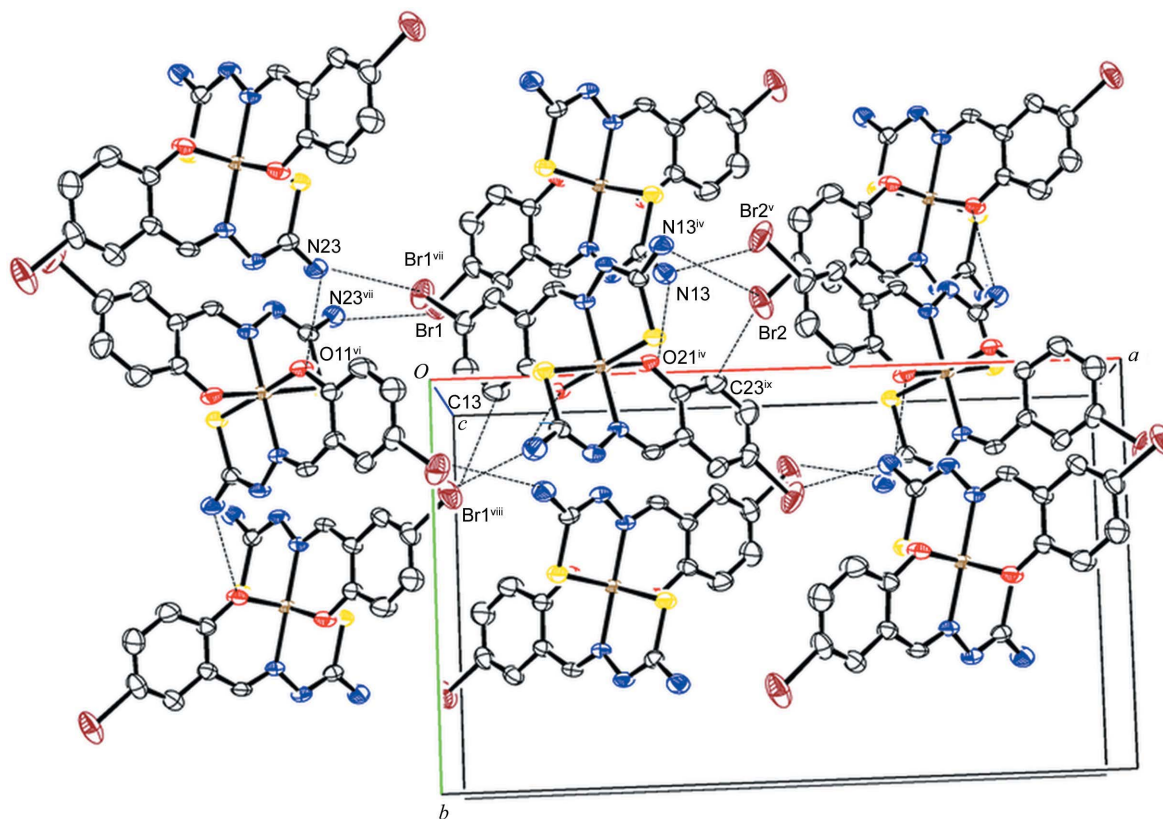
The bond distances of the ligands coordinated to the Fe<sup>III</sup> cation in (I) can be related to bond order. The C—S, C—N and N—N bonds obtained for (I) show characteristics of a bond order between a single and a double bond. As expected, the C18—S11 bond distance of 1.750 (4) Å and the C28—S21 bond distance of 1.753 (4) Å suggest a partial electron delocalization of these bonds. Ryabova, Ponomarev, Zelentsov, Shipilov & Atovmyan (1981) reported the related low-spin compound NH<sub>4</sub>[Fe(L2)<sub>2</sub>] at 298 K, which crystallizes in the centrosymmetric space group *Pnca* with *Z'* = 0.5. Thus, the ligands coordinated around the Fe<sup>III</sup> cation are related by symmetry. The C—S bond distances of (I) correspond with the C—S bond distance of 1.750 (9) Å for NH<sub>4</sub>[Fe(L2)<sub>2</sub>], suggesting the occurrence of partial electron delocalization in both compounds. Furthermore, the electron delocalization of the ligands is confirmed by a bond order larger than 1 for the C—N bond involving the deprotonated hydrazinic N atom. The bond distances for the C17—N11 and C27—N21 bonds in (I) are 1.281 (5) and 1.296 (5) Å, respectively, which are similar to the C—N bond distance of 1.292 (10) Å reported for NH<sub>4</sub>[Fe(L2)<sub>2</sub>]. In addition, the N—N bond distances of (I) are N11—N12 = 1.394 (4) Å and N21—N22 = 1.401 (4) Å, indicating partial electron delocalization.

The Cs<sup>+</sup> cation of (I) is at the centre of an irregular seven-donor atom polyhedron, the donor atoms of which originate from symmetry-related equivalents of both symmetry-independent ligands. Selected geometric parameters are listed in Table 2.

Several donor atoms coordinated to the Fe<sup>III</sup> atom of (I) form interactions with the Cs<sup>+</sup> cation in the second coordination sphere, modulating the electron density of the Fe-donor-atom bonds and hence influencing the electronic state of the Fe<sup>III</sup> cation.

The phenolate O11 and O21 Fe<sup>III</sup> donor atoms bind to the Cs<sup>+</sup> cation within the same Fe<sup>III</sup> unit. The Cs—O distances are Cs1—O11 = 3.220 (3) Å and Cs1—O21 = 3.129 (3) Å, somewhat longer than the mean Cs—O bond length of 3.074 (1) Å in the hydrated Cs<sup>+</sup> cation (Mähler & Persson, 2012). The small O11—Cs1—O21 bond angle of 50.34 (7)° is a corollary of the closeness of the two ligands bound to Fe<sup>III</sup>. The Cs1...Fe separation involving the  $\mu$ -diphenolate bridge is 4.2703 (6) Å and the Cs—O—Fe bond angles are Cs1—O11—Fe = 109.12 (11)° and Cs1—O21—Fe = 112.16 (11)°.

The thiolate S11<sup>i</sup> and S21<sup>i</sup> [symmetry code: (i)  $x, y, z - 1$ ] Fe<sup>III</sup> donor atoms coordinate to the Cs<sup>+</sup> cation with bond distances of 3.7159 (11) and 3.5564 (11) Å, respectively. Moreover, the terminal N23<sup>i</sup> atom of the same Fe<sup>III</sup> unit forms a bond with the Cs<sup>+</sup> cation, with a Cs1—N23<sup>i</sup> bond distance of 3.699 (4) Å. The proximity of atoms N23 and S21 is shown by the small N23<sup>i</sup>—Cs1—S21<sup>i</sup> bond angle of 42.99 (6)°, whereas


**Figure 2**

A projection showing the unit cell of (I). The Cs<sup>+</sup> cation has been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate hydrogen bonds. [Symmetry codes: (iv)  $x, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (v)  $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (vi)  $x, -y + \frac{3}{2}, z + \frac{1}{2}$ ; (vii)  $-x + 2, y + \frac{1}{2}, -z + \frac{3}{2}$ ; (viii)  $-x + 2, y + \frac{1}{2}, -z + \frac{1}{2}$ ; (ix)  $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$ ]

the small S21<sup>i</sup>—Cs1—S11<sup>i</sup> bond angle of 53.27 (2) Å is related to the vicinity of the two ligands bound to Fe<sup>III</sup>. Furthermore, the thiolate S-donor atoms coordinate to the Cs<sup>+</sup> cation, as well as to the Fe<sup>III</sup> cation, which gives rise to the Cs1···Fe<sup>i</sup> separation of 4.7695 (6) Å [symmetry code: (i)  $x, y, z - 1$ ]. The Cs—S—Fe bond angles involving the  $\mu$ -dithiolate bridge are Cs1—S11<sup>i</sup>—Fe = 103.80 (4)° and Cs1—S21<sup>i</sup>—Fe = 108.55 (4)°. In addition, atoms N12<sup>ii</sup> and N22<sup>iii</sup> [symmetry codes: (ii)  $x, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (iii)  $x, -y + \frac{3}{2}, z - \frac{1}{2}$ ] next to the imine N-donor atoms in the first coordination sphere of Fe<sup>III</sup> are also coordinated to the Cs<sup>+</sup> cation (see Table 2).

The Cs<sup>+</sup>···Cs<sup>+</sup> separations of 7.4530 (5) Å for Cs1···Cs1( $x, -y + \frac{3}{2}, z + \frac{1}{2}$ ) and 7.6404 (5) Å for Cs1···Cs1( $x, -y + \frac{1}{2}, z - \frac{1}{2}$ ) do correlate with the shortest Fe<sup>III</sup>···Fe<sup>III</sup> separations in (I). These are 7.5369 (9) Å for Fe···Fe( $x, -y + \frac{3}{2}, z + \frac{1}{2}$ ) and 7.5559 (6) Å for Fe···Fe( $x, -y + \frac{1}{2}, z - \frac{1}{2}$ ).

The previously reported compound Cs[Fe(L1)<sub>2</sub>].CH<sub>3</sub>OH [L1 is 3-ethoxysalicylaldehyde 4-methylthiosemicarbazate(2-)] displays Fe<sup>III</sup>···Fe<sup>III</sup>( $x + 1, y, z$ ) separations of 8.486 (3) Å (Powell *et al.*, 2014). The absence of any solvent molecule in (I) allows the Fe<sup>III</sup> units to be closer to each other in the crystal structure than in the former compound. Furthermore, the *R* and *R'* substituents of the ligands coordinated to the Fe<sup>III</sup> atom, *i.e.* *R* = 5-Br and *R'* = H in (I), and *R* = 3-EtO and *R'* = 4-Me in Cs[Fe(L1)<sub>2</sub>].CH<sub>3</sub>OH, might have some effect on how the Fe<sup>III</sup> units are assembled in the crystal

structure. The sizes and positions of the *R* and *R'* substituents are different, as (I) contains a Br substituent on the C15/C25 atom of the salicylaldehyde group, whereas Cs[Fe(L1)<sub>2</sub>].CH<sub>3</sub>OH contains a relatively bulky ethoxy group on the C13/C23 atom of the salicylaldehyde group, as well as a methyl substituent on the terminal N atom of the thiosemicarbazide group. In addition, the Br substituent of one Fe<sup>III</sup> unit of (I) provides a hydrogen-bonding interaction with an amino group of a neighbouring Fe<sup>III</sup> unit (see below). The occurrence of intermolecular hydrogen-bonding interactions between Fe<sup>III</sup> units in (I) contributes to the arrangement of the Fe<sup>III</sup> entities in the unit cell.

The hydrogen-bonding interactions of (I) are listed in Table 3 and displayed in Fig. 2. The main features of the molecular packing of (I) are the N—H···O and N—H···Br hydrogen bonds. Although the latter are weak, their grip on the Br atoms is augmented by C—H···Br interactions at similar H···Br contact distances. The N13—H13B···Br2<sup>v</sup> and N13—H13A···O21<sup>iv</sup> (see Table 3 for symmetry codes) contacts form hydrogen bonds to two different ring systems. In turn, atom O21 in the former system and atom Br2 in the latter accept hydrogen bonds from inversion-related atom N13( $-x + 1, -y, -z + 2$ ), giving rise to *R*<sub>4</sub><sup>4</sup>(18) rings (Bernstein *et al.*, 1995). In a similar manner, the N23—H23B···Br1<sup>vii</sup> and N23—H23A···O11<sup>vi</sup> contacts create *R*<sub>4</sub><sup>4</sup>(18) rings with inversion-related atom N23( $-x + 2, -y + 2, -z + 2$ ). The ring

**Table 3**  
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N13—H13A $\cdots$ O21 <sup>iv</sup>	0.86	2.08	2.907 (4)	161
N13—H13B $\cdots$ Br2 <sup>v</sup>	0.86	2.72	3.557 (4)	163
N23—H23A $\cdots$ O11 <sup>vi</sup>	0.86	2.10	2.952 (5)	171
N23—H23B $\cdots$ Br1 <sup>vii</sup>	0.86	2.95	3.590 (4)	133
C13—H13 $\cdots$ Br1 <sup>viii</sup>	0.93	2.83	3.578 (5)	139
C23—H23 $\cdots$ Br2 <sup>ix</sup>	0.93	2.86	3.623 (5)	141

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

systems created by the hydrogen bonding between the Fe<sup>III</sup> units link them in the *a* and *b* directions. Furthermore, the Cs<sup>+</sup> cations link the Fe<sup>III</sup> complex anions into a chain along [010].

Compound (I) does not contain any solvent molecules in the crystal lattice. This feature has also been observed for the following Fe<sup>III</sup> compounds: Cs[Fe(ths<sub>a</sub>)<sub>2</sub>] (H<sub>2</sub>ths<sub>a</sub> is salicylaldehyde thiosemicarbazone; Ryabova, Ponomarev, Zelentsov & Atovmyan, 1981), NH<sub>4</sub>[Fe(5-Br-ths<sub>a</sub>)<sub>2</sub>] (Ryabova, Ponomarev, Zelentsov, Shipilov & Atovmyan, 1981) and NH<sub>4</sub>[Fe(5-Cl-ths<sub>a</sub>)<sub>2</sub>] (Ryabova *et al.*, 1978), for which relevant data are compiled in Table 4. This table shows the nonsolvated Fe<sup>III</sup> bis(ligand) compounds together with the spin state of the Fe<sup>III</sup> cation at the temperature at which the crystal structure was determined. The crystallographic data of (I) will now be compared with similar Fe<sup>III</sup> bis(ligand) type compounds (Table 4), all of which are nonsolvated compounds.

The Fe<sup>III</sup> cation in the compound Cs[Fe(ths<sub>a</sub>)<sub>2</sub>] is in a high-spin state at both 103 and 298 K, whereas the Fe<sup>III</sup> cation in NH<sub>4</sub>[Fe(5-Cl-ths<sub>a</sub>)<sub>2</sub>] is in a low-spin state at both 135 and 298 K (Table 4). Furthermore, in NH<sub>4</sub>[Fe(5-Br-ths<sub>a</sub>)<sub>2</sub>], the Fe<sup>III</sup> cation is in a low-spin state at 298 K, while the Fe<sup>III</sup> cation in (I) is in a low-spin state at 293 K. A transition from low-spin to high-spin Fe<sup>III</sup> has been detected for similar materials with increasing temperature (Ryabova *et al.*, 1982), but crystallographic data are not available for these nonsolvated materials. Noting that (I) contains low-spin Fe<sup>III</sup> at 293 K, perhaps it may exhibit a change in spin state above room temperature.

The generation of any spin transition is governed by the energy difference between the high-spin and low-spin electronic states. This energy gap can be tuned by variation of the ligand field strength. The features of the second coordination sphere, such as the arrangement of Fe<sup>III</sup> units within a unit cell belonging to a particular crystal system, also influence the

ligand field characteristics. The packing of Fe<sup>III</sup> units is evidenced by symmetry requirements, which are embedded within the space group in which the material crystallizes. X-ray structural analysis has revealed that the Fe<sup>III</sup> bis(ligand) type compounds (Table 4) adopt different crystal systems and space groups compared with (I). Compound (I) displays a monoclinic crystal system and crystallizes in the space group *P2<sub>1</sub>/c* with *Z* = 4, or alternatively *Z'* = 1. In contrast, the nonsolvated Fe<sup>III</sup> bis(ligand) compounds listed in Table 4 all exhibit an orthorhombic crystal system, although in some cases their space groups differ. For example, Cs[Fe(ths<sub>a</sub>)<sub>2</sub>] crystallizes in the space group *Pna2<sub>1</sub>* with *Z'* = 1, whereas NH<sub>4</sub>[Fe(5-Br-ths<sub>a</sub>)<sub>2</sub>] in its tabular form crystallizes in the space group *Pnca* with *Z'* = 0.5. The compound NH<sub>4</sub>[Fe(5-Cl-ths<sub>a</sub>)<sub>2</sub>] also crystallizes in the space group *Pnca*, also with *Z'* = 0.5. The Fe<sup>III</sup> bis(ligand) entities present variances with respect to their symmetry; in some instances, a value for *Z'* of 0.5 is encountered, which for space group *Pnca* implies that the ligands coordinated to the Fe<sup>III</sup> cation are related by twofold rotational symmetry. Interestingly, Ryabova, Ponomarev, Zelentsov, Shipilov & Atovmyan (1981) reported that NH<sub>4</sub>[Fe(5-Br-ths<sub>a</sub>)<sub>2</sub>] crystallizes in two different forms, one crystallizing as tabular plates and the other as mica-like crystals. It was established that these two different polymorphs exhibit a spin-crossover at different temperatures, *i.e.* the mica-like crystals in the region around 200 K and the tabular plate crystals in the region around 300 K. It appears that the crystallographic data analysed so far for this family of materials do not reveal a relation between Fe<sup>III</sup> spin state and the crystal system and space group.

It is widely recognized that significant changes in the electronic state of Fe<sup>III</sup> bis(ligand) compounds may arise from the associated cation in the complex system, the *R* substituents at the benzene ring of the salicylaldehyde group or the introduction of *R'* substituents into the thioamide group of the thiosemicarbazide group, and the Fe<sup>III</sup> S<sub>2</sub>N<sub>2</sub>O<sub>2</sub> geometry. The main difference observed between the compounds (Table 4) compared with (I) is the varying size of the associated cation (either NH<sub>4</sub><sup>+</sup> or Cs<sup>+</sup>) in the crystal structure and the variation in the slight distortions of the octahedral Fe<sup>III</sup> S<sub>2</sub>N<sub>2</sub>O<sub>2</sub> coordination sphere. It appears that the variation of the associated cation in the Fe<sup>III</sup> bis(ligand) compounds may have an indirect impact on the spin state of Fe<sup>III</sup> by influencing the crystal packing. In addition to the difference in size between NH<sub>4</sub><sup>+</sup>

**Table 4**  
Selected average Fe—donor-atom bond distances for nonsolvated Fe<sup>III</sup> bis(ligand) complexes of *R*-salicylaldehyde *R'*-thiosemicarbazone.

Compound†	Temperature (K)	Space group and <i>Z'</i>	Fe—S (Å)	Fe—N (Å)	Fe—O (Å)	Spin state‡	Reference
Cs[Fe(ths <sub>a</sub> ) <sub>2</sub> ]	298	<i>Pna2<sub>1</sub></i> , <i>Z'</i> = 1	2.44	2.12	1.96	HS	Ryabova, Ponomarev, Zelentsov & Atovmyan (1981)
	103	<i>Pna2<sub>1</sub></i> , <i>Z'</i> = 1	2.44	2.15	1.96	HS	Ryabova, Ponomarev, Zelentsov & Atovmyan (1981)
NH <sub>4</sub> [Fe(5-Br-ths <sub>a</sub> ) <sub>2</sub> ]	298	<i>Pnca</i> , <i>Z'</i> = 0.5	2.23	1.93	1.95	LS	Ryabova, Ponomarev, Zelentsov, Shipilov & Atovmyan (1981)
NH <sub>4</sub> [Fe(5-Cl-ths <sub>a</sub> ) <sub>2</sub> ]	298	<i>Pnca</i> , <i>Z'</i> = 0.5	2.24	1.95	1.93	LS	Ryabova <i>et al.</i> (1978)
	135	<i>Pnca</i> , <i>Z'</i> = 0.5	2.23	1.96	1.94	LS	Ryabova <i>et al.</i> (1978)

† The ligands are defined as follows: H<sub>2</sub>ths<sub>a</sub> is salicylaldehyde thiosemicarbazone, H<sub>2</sub>-5-Br-ths<sub>a</sub> is 5-bromosalicylaldehyde thiosemicarbazone and H<sub>2</sub>-5-Cl-ths<sub>a</sub> is 5-chlorosalicylaldehyde thiosemicarbazone. ‡ The spin states are defined as low-spin (LS) and high-spin (HS). § Determined for crystals of tabular form.

and Cs<sup>+</sup> cations, the former may engage in directed interactions through hydrogen bonding, while the latter presents a more uniform electrostatic field without a preferred direction for hydrogen bonds. The *R* and *R'* substituents of the ligand may exhibit steric and electronic effects [including being involved in hydrogen bonding, *via* the Br substituents in (I)], but at this stage it is unclear how these features may be harnessed to induce a particular spin state for Fe<sup>III</sup>.

The Fe<sup>III</sup> S<sub>2</sub>N<sub>2</sub>O<sub>2</sub> coordination spheres of the compounds are slightly distorted from ideal octahedral geometry. It has been acknowledged that there are subtle differences in the Fe<sup>III</sup> coordination geometry among the members of this particular type of compound. Clearly, the stabilization of Fe<sup>III</sup> in a particular spin state is governed by a subtle balance of geometric parameters, as is implied by the fact that a single compound, *i.e.* NH<sub>4</sub>[Fe(5-Br-thsa)<sub>2</sub>], exists in slightly different polymorphs, each with its own distinct magnetic behaviour. The latter example shows that it is too early to derive a possible relation between Fe<sup>III</sup> spin state and Fe<sup>III</sup> S<sub>2</sub>N<sub>2</sub>O<sub>2</sub> geometry and crystal packing (the latter evidenced by crystal system and space group).

The development of a strategy towards the synthesis of Fe<sup>III</sup> bis(ligand) compounds with a predetermined spin state will require the measurement and analysis of crystallographic data from a larger number of Fe<sup>III</sup> compounds of this family, including these having different *R* and/or *R'* substituents and a variety of associated cations. Other parameters that we are currently considering in our studies are the alteration of the degree of solvation and the tuning of the deprotonation characteristics of the *R*-salicylaldehyde *R'*-thiosemicarbazone ligand.

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## supporting information

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## Caesium bis(5-bromosalicylaldehyde thiosemicarbazonato- $\kappa^3O,N,S$ )ferrate(III): supramolecular arrangement of low-spin Fe<sup>III</sup> complex anions mediated by Cs<sup>+</sup> cations

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### Computing details

Data collection: *CrystalClear-SM Expert* (Rigaku, 2013); cell refinement: *CrystalClear-SM Expert* (Rigaku, 2013); data reduction: *CrystalClear-SM Expert* (Rigaku, 2013); program(s) used to solve structure: ROTAX (Cooper *et al.*, 2002), *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

### Caesium bis(5-bromosalicylaldehyde thiosemicarbazonato- $\kappa^3O,N,S$ )ferrate(III)

#### Crystal data

Cs[Fe(C<sub>8</sub>H<sub>6</sub>BrN<sub>3</sub>OS)<sub>2</sub>]  
 $M_r = 733.02$   
 Monoclinic,  $P2_1/c$   
 Hall symbol: -P 2ybc  
 $a = 20.2500$  (14) Å  
 $b = 12.0868$  (8) Å  
 $c = 9.0389$  (5) Å  
 $\beta = 90.337$  (1)°  
 $V = 2212.3$  (2) Å<sup>3</sup>  
 $Z = 4$

$F(000) = 1396$   
 $D_x = 2.201$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation,  $\lambda = 0.71075$  Å  
 Cell parameters from 26513 reflections  
 $\theta = 2.6$ – $27.5$ °  
 $\mu = 6.13$  mm<sup>-1</sup>  
 $T = 293$  K  
 Plate, green  
 $0.08 \times 0.08 \times 0.01$  mm

#### Data collection

Rigaku AFC12 four-circle Kappa  
 diffractometer  
 Radiation source: fine-focus sealed tube  
 Graphite monochromator  
 Detector resolution: 28.5714 pixels mm<sup>-1</sup>  
 profile data from  $\omega$  scans  
 Absorption correction: multi-scan  
 (*CrystalClear-SM Expert*; Rigaku, 2013)  
 $T_{\min} = 0.640$ ,  $T_{\max} = 0.941$

29088 measured reflections  
 5073 independent reflections  
 4211 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.045$   
 $\theta_{\max} = 27.5$ °,  $\theta_{\min} = 3.0$ °  
 $h = -26 \rightarrow 25$   
 $k = -15 \rightarrow 15$   
 $l = -11 \rightarrow 11$

#### Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.033$   
 $wR(F^2) = 0.086$   
 $S = 1.04$   
 5073 reflections  
 272 parameters

0 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  
 $w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 1.5804P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.88 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.85 \text{ e } \text{\AA}^{-3}$

### Special details

**Geometry.** All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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  $F^2 > 2\sigma(F^2)$  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 ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cs1	0.751537 (18)	0.50484 (2)	0.23503 (3)	0.05227 (10)
Br1	1.01607 (3)	0.26269 (5)	0.25045 (6)	0.06040 (16)
Br2	0.48231 (3)	0.80167 (6)	0.31594 (7)	0.06880 (19)
Fe1	0.74977 (3)	0.50049 (4)	0.70739 (5)	0.02473 (11)
S11	0.67238 (5)	0.45208 (8)	0.86988 (11)	0.0343 (2)
S21	0.82731 (5)	0.52595 (8)	0.88220 (12)	0.0337 (2)
O11	0.81413 (14)	0.5428 (2)	0.5594 (3)	0.0341 (6)
O21	0.68600 (14)	0.4811 (2)	0.5460 (3)	0.0350 (6)
N11	0.77067 (15)	0.3435 (2)	0.6968 (3)	0.0267 (6)
N12	0.73750 (16)	0.2668 (2)	0.7844 (4)	0.0317 (7)
N13	0.65757 (18)	0.2458 (3)	0.9599 (4)	0.0426 (9)
H13A	0.6658	0.1760	0.9637	0.051*
H13B	0.6274	0.2738	1.0152	0.051*
C11	0.86003 (19)	0.3619 (3)	0.5187 (4)	0.0314 (8)
C12	0.8591 (2)	0.4775 (3)	0.5013 (5)	0.0328 (8)
C13	0.9081 (2)	0.5247 (4)	0.4112 (6)	0.0529 (13)
H13	0.9097	0.6012	0.4021	0.063*
C14	0.9531 (2)	0.4625 (4)	0.3369 (6)	0.0549 (12)
H14	0.9842	0.4963	0.2765	0.066*
C15	0.9522 (2)	0.3487 (4)	0.3522 (5)	0.0418 (10)
C16	0.9071 (2)	0.2994 (4)	0.4412 (5)	0.0383 (9)
H16	0.9074	0.2228	0.4511	0.046*
C17	0.81546 (19)	0.3017 (3)	0.6145 (5)	0.0335 (8)
H17	0.8198	0.2251	0.6163	0.040*
C18	0.69182 (19)	0.3110 (3)	0.8677 (4)	0.0298 (8)
N21	0.72844 (15)	0.6554 (2)	0.7352 (3)	0.0267 (6)
N22	0.76224 (16)	0.7196 (3)	0.8402 (4)	0.0327 (7)
N23	0.84049 (18)	0.7187 (3)	1.0217 (4)	0.0439 (9)
H23A	0.8311	0.7864	1.0420	0.053*
H23B	0.8708	0.6848	1.0711	0.053*
C21	0.63791 (19)	0.6633 (3)	0.5574 (4)	0.0321 (8)
C22	0.64042 (19)	0.5535 (3)	0.5056 (4)	0.0331 (8)

C23	0.5922 (3)	0.5206 (4)	0.4022 (6)	0.0547 (13)
H23	0.5923	0.4478	0.3689	0.066*
C24	0.5447 (2)	0.5919 (4)	0.3480 (6)	0.0547 (12)
H24	0.5132	0.5672	0.2803	0.066*
C25	0.5446 (2)	0.7003 (4)	0.3957 (5)	0.0451 (11)
C26	0.5898 (2)	0.7354 (4)	0.4990 (5)	0.0394 (9)
H26	0.5887	0.8085	0.5312	0.047*
C27	0.68104 (19)	0.7074 (3)	0.6680 (5)	0.0333 (8)
H27	0.6745	0.7809	0.6945	0.040*
C28	0.80755 (19)	0.6654 (3)	0.9119 (4)	0.0310 (8)

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cs1	0.0839 (2)	0.04022 (16)	0.03278 (14)	0.01202 (14)	0.00531 (16)	0.00140 (11)
Br1	0.0472 (3)	0.0737 (4)	0.0604 (3)	0.0188 (2)	0.0121 (2)	-0.0177 (3)
Br2	0.0481 (3)	0.0909 (4)	0.0674 (4)	0.0290 (3)	0.0013 (3)	0.0313 (3)
Fe1	0.0313 (2)	0.0162 (2)	0.0268 (2)	0.00079 (19)	0.0026 (2)	0.00010 (18)
S11	0.0395 (5)	0.0238 (4)	0.0398 (5)	0.0007 (4)	0.0103 (4)	0.0019 (4)
S21	0.0390 (5)	0.0256 (4)	0.0365 (5)	0.0029 (4)	-0.0060 (4)	-0.0031 (4)
O11	0.0434 (15)	0.0211 (13)	0.0380 (15)	0.0036 (11)	0.0130 (12)	0.0031 (11)
O21	0.0472 (16)	0.0209 (13)	0.0368 (15)	0.0060 (11)	-0.0101 (13)	-0.0040 (11)
N11	0.0355 (15)	0.0183 (14)	0.0261 (15)	0.0005 (12)	-0.0011 (12)	0.0017 (11)
N12	0.0400 (17)	0.0183 (14)	0.0369 (18)	-0.0004 (12)	0.0034 (14)	0.0057 (12)
N13	0.046 (2)	0.0313 (18)	0.051 (2)	0.0027 (16)	0.0128 (17)	0.0141 (16)
C11	0.0359 (19)	0.0259 (19)	0.0325 (19)	0.0046 (15)	0.0046 (16)	-0.0021 (15)
C12	0.037 (2)	0.0273 (19)	0.034 (2)	0.0011 (16)	0.0053 (16)	0.0002 (15)
C13	0.060 (3)	0.035 (2)	0.064 (3)	-0.001 (2)	0.031 (3)	0.005 (2)
C14	0.052 (3)	0.051 (3)	0.061 (3)	0.002 (2)	0.026 (2)	0.002 (2)
C15	0.037 (2)	0.049 (3)	0.040 (2)	0.0086 (19)	0.0058 (18)	-0.0081 (19)
C16	0.039 (2)	0.035 (2)	0.042 (2)	0.0081 (18)	0.0012 (18)	-0.0053 (17)
C17	0.040 (2)	0.0176 (17)	0.043 (2)	0.0045 (15)	0.0007 (17)	-0.0018 (15)
C18	0.0337 (19)	0.0271 (19)	0.0285 (18)	-0.0026 (15)	-0.0037 (15)	0.0046 (14)
N21	0.0345 (15)	0.0186 (14)	0.0268 (15)	-0.0008 (12)	0.0032 (12)	-0.0024 (11)
N22	0.0413 (18)	0.0221 (15)	0.0347 (17)	-0.0020 (13)	-0.0006 (14)	-0.0082 (13)
N23	0.048 (2)	0.037 (2)	0.046 (2)	0.0021 (16)	-0.0102 (17)	-0.0144 (16)
C21	0.035 (2)	0.0272 (19)	0.034 (2)	0.0026 (16)	0.0036 (15)	0.0030 (15)
C22	0.038 (2)	0.028 (2)	0.033 (2)	0.0036 (16)	-0.0042 (16)	0.0017 (16)
C23	0.063 (3)	0.036 (2)	0.065 (3)	0.000 (2)	-0.024 (3)	-0.007 (2)
C24	0.049 (3)	0.061 (3)	0.054 (3)	0.004 (2)	-0.019 (2)	0.000 (2)
C25	0.038 (2)	0.056 (3)	0.041 (2)	0.012 (2)	-0.0009 (18)	0.014 (2)
C26	0.040 (2)	0.037 (2)	0.042 (2)	0.0086 (18)	0.0032 (19)	0.0056 (17)
C27	0.041 (2)	0.0173 (16)	0.041 (2)	0.0030 (15)	0.0010 (17)	-0.0029 (15)
C28	0.038 (2)	0.0261 (18)	0.0294 (18)	-0.0035 (15)	0.0035 (15)	-0.0040 (14)

*Geometric parameters (Å, °)*

Fe1—S11	2.2321 (11)	C11—C12	1.406 (5)
Fe1—S21	2.2422 (11)	C11—C16	1.407 (5)
Fe1—O11	1.942 (3)	C11—C17	1.450 (6)
Cs1—S11 <sup>i</sup>	3.7159 (11)	C12—C13	1.407 (6)
Cs1—S21 <sup>i</sup>	3.5564 (11)	C13—C14	1.362 (6)
Cs1—O11	3.220 (3)	C13—H13	0.9300
Cs1—O21	3.129 (3)	C14—C15	1.382 (7)
Fe1—O21	1.956 (3)	C14—H14	0.9300
Fe1—N11	1.947 (3)	C15—C16	1.359 (6)
Fe1—N21	1.938 (3)	C16—H16	0.9300
Cs1—C12	3.254 (4)	C17—H17	0.9300
Cs1—N12 <sup>ii</sup>	3.326 (3)	N21—C27	1.296 (5)
Cs1—C22	3.385 (4)	N21—N22	1.401 (4)
Cs1—N22 <sup>iii</sup>	3.470 (3)	N22—C28	1.298 (5)
Cs1—C13	3.547 (6)	N22—Cs1 <sup>vi</sup>	3.470 (3)
Cs1—C23	3.577 (6)	N23—C28	1.356 (5)
Cs1—C28 <sup>i</sup>	3.691 (4)	N23—Cs1 <sup>iv</sup>	3.699 (4)
Cs1—N23 <sup>i</sup>	3.699 (4)	N23—H23A	0.8600
Br1—C15	1.900 (4)	N23—H23B	0.8600
Br2—C25	1.897 (4)	C21—C26	1.407 (5)
S11—C18	1.750 (4)	C21—C22	1.408 (5)
S11—Cs1 <sup>iv</sup>	3.7159 (11)	C21—C27	1.427 (6)
S21—C28	1.753 (4)	C22—C23	1.406 (6)
S21—Cs1 <sup>iv</sup>	3.5564 (11)	C23—C24	1.379 (7)
O11—C12	1.317 (5)	C23—H23	0.9300
O21—C22	1.322 (5)	C24—C25	1.380 (7)
N11—C17	1.281 (5)	C24—H24	0.9300
N11—N12	1.394 (4)	C25—C26	1.372 (7)
N12—C18	1.310 (5)	C26—H26	0.9300
N12—Cs1 <sup>v</sup>	3.326 (3)	C27—Cs1 <sup>vi</sup>	3.807 (4)
N13—C18	1.343 (5)	C27—H27	0.9300
N13—H13A	0.8600	C28—Cs1 <sup>iv</sup>	3.691 (4)
N13—H13B	0.8600		
S11—Fe1—S21	93.66 (4)	Fe1—S11—Cs1 <sup>iv</sup>	103.80 (4)
S11—Fe1—N11	86.01 (9)	C28—S21—Cs1 <sup>iv</sup>	80.30 (13)
S11—Fe1—O11	177.50 (9)	Fe1—S21—Cs1 <sup>iv</sup>	108.55 (4)
S11—Fe1—O21	89.78 (10)	C12—O11—Fe1	125.8 (2)
S11—Fe1—N21	90.57 (9)	C12—O11—Cs1	79.7 (2)
S21—Fe1—O11	88.81 (9)	Fe1—O11—Cs1	109.12 (11)
S21—Fe1—O21	176.56 (10)	C22—O21—Fe1	125.7 (2)
S21—Fe1—N11	90.96 (9)	C22—O21—Cs1	89.4 (2)
S21—Fe1—N21	86.07 (9)	Fe1—O21—Cs1	112.16 (12)
O11—Fe1—O21	87.75 (12)	C17—N11—N12	114.4 (3)
O11—Fe1—N11	94.35 (12)	C17—N11—Fe1	124.6 (3)
O11—Cs1—S11 <sup>i</sup>	176.98 (5)	N12—N11—Fe1	121.0 (2)

O11—Cs1—S21 <sup>i</sup>	129.54 (5)	C18—N12—Cs1 <sup>v</sup>	122.8 (2)
O11—Cs1—N12 <sup>ii</sup>	92.97 (7)	N11—N12—Cs1 <sup>v</sup>	122.6 (2)
O11—Cs1—N22 <sup>iii</sup>	65.82 (7)	C18—N13—H13A	120.0
O11—Cs1—N23 <sup>i</sup>	100.65 (7)	C18—N13—H13B	120.0
O11—Cs1—O21	50.34 (7)	H13A—N13—H13B	120.0
O21—Cs1—S11 <sup>i</sup>	126.82 (5)	C12—C11—C16	119.1 (4)
O21—Cs1—S21 <sup>i</sup>	178.78 (5)	C12—C11—C17	123.9 (3)
O21—Cs1—N12 <sup>ii</sup>	75.63 (7)	C16—C11—C17	117.0 (4)
O21—Cs1—N22 <sup>iii</sup>	82.42 (7)	C12—C11—Cs1	57.6 (2)
O21—Cs1—N23 <sup>i</sup>	137.96 (7)	C16—C11—Cs1	107.5 (3)
O11—Fe1—N21	89.20 (12)	C17—C11—Cs1	105.8 (2)
O21—Fe1—N11	89.40 (11)	O11—C12—C11	124.0 (4)
O21—Fe1—N21	93.78 (12)	O11—C12—C13	118.6 (4)
N11—Fe1—N21	175.33 (12)	C11—C12—C13	117.3 (4)
C18—S11—Fe1	95.12 (13)	O11—C12—Cs1	76.8 (2)
C28—S21—Fe1	94.61 (14)	C11—C12—Cs1	101.1 (3)
N11—N12—C18	113.5 (3)	C13—C12—Cs1	90.1 (3)
N21—N22—C28	113.6 (3)	C14—C13—C12	122.5 (4)
N12—C18—S11	124.3 (3)	C14—C13—Cs1	109.9 (4)
N22—C28—S21	124.8 (3)	C12—C13—Cs1	66.5 (3)
N12 <sup>ii</sup> —Cs1—S11 <sup>i</sup>	85.01 (6)	C14—C13—H13	118.7
N12 <sup>ii</sup> —Cs1—S21 <sup>i</sup>	103.23 (6)	C12—C13—H13	118.7
N12 <sup>ii</sup> —Cs1—N22 <sup>iii</sup>	156.35 (8)	Cs1—C13—H13	93.4
N12 <sup>ii</sup> —Cs1—N23 <sup>i</sup>	143.33 (8)	C13—C14—C15	119.4 (4)
N22 <sup>iii</sup> —Cs1—S11 <sup>i</sup>	115.72 (6)	C13—C14—H14	120.3
N22 <sup>iii</sup> —Cs1—S21 <sup>i</sup>	98.64 (6)	C15—C14—H14	120.3
N22 <sup>iii</sup> —Cs1—N23 <sup>i</sup>	56.10 (8)	C16—C15—C14	120.3 (4)
N23 <sup>i</sup> —Cs1—S11 <sup>i</sup>	82.29 (6)	C16—C15—Br1	120.5 (3)
N23 <sup>i</sup> —Cs1—S21 <sup>i</sup>	42.99 (6)	C14—C15—Br1	119.1 (3)
S21 <sup>i</sup> —Cs1—S11 <sup>i</sup>	53.27 (2)	C15—C16—C11	121.3 (4)
O21—Cs1—C12	67.16 (9)	C15—C16—H16	119.4
O11—Cs1—C12	23.47 (8)	C11—C16—H16	119.4
C12—Cs1—N12 <sup>ii</sup>	81.82 (9)	N11—C17—C11	126.5 (3)
O21—Cs1—C22	22.99 (8)	N11—C17—H17	116.8
O11—Cs1—C22	64.99 (8)	C11—C17—H17	116.8
C12—Cs1—C22	85.89 (9)	N12—C18—N13	119.1 (3)
N12 <sup>ii</sup> —Cs1—C22	90.97 (9)	N13—C18—S11	116.6 (3)
C12—Cs1—N22 <sup>iii</sup>	81.64 (9)	C27—N21—N22	114.0 (3)
C22—Cs1—N22 <sup>iii</sup>	71.09 (9)	C27—N21—Fe1	124.9 (3)
O21—Cs1—C13	89.17 (9)	N22—N21—Fe1	121.0 (2)
O11—Cs1—C13	40.15 (9)	C28—N22—Cs1 <sup>vi</sup>	131.6 (2)
C12—Cs1—C13	23.37 (10)	N21—N22—Cs1 <sup>vi</sup>	108.5 (2)
N12 <sup>ii</sup> —Cs1—C13	94.77 (10)	C28—N23—Cs1 <sup>iv</sup>	79.1 (2)
C22—Cs1—C13	105.07 (10)	C28—N23—H23A	120.0
N22 <sup>iii</sup> —Cs1—C13	76.00 (10)	Cs1 <sup>iv</sup> —N23—H23A	116.4
C12—Cs1—S21 <sup>i</sup>	112.34 (7)	C28—N23—H23B	120.0
C22—Cs1—S21 <sup>i</sup>	158.08 (7)	Cs1 <sup>iv</sup> —N23—H23B	75.2
C13—Cs1—S21 <sup>i</sup>	90.50 (8)	H23A—N23—H23B	120.0

O21—Cs1—C23	40.25 (10)	C26—C21—C22	119.0 (4)
O11—Cs1—C23	87.66 (10)	C26—C21—C27	116.8 (4)
C12—Cs1—C23	107.16 (11)	C22—C21—C27	124.2 (4)
N12 <sup>ii</sup> —Cs1—C23	85.29 (10)	O21—C22—C23	118.6 (4)
C22—Cs1—C23	23.09 (10)	O21—C22—C21	123.9 (4)
N22 <sup>iii</sup> —Cs1—C23	83.58 (9)	C23—C22—C21	117.5 (4)
C13—Cs1—C23	127.81 (11)	O21—C22—Cs1	67.6 (2)
S21 <sup>i</sup> —Cs1—C23	140.36 (9)	C23—C22—Cs1	86.1 (3)
O21—Cs1—C28 <sup>i</sup>	153.27 (7)	C21—C22—Cs1	115.4 (3)
O11—Cs1—C28 <sup>i</sup>	121.63 (8)	C24—C23—C22	122.7 (4)
C12—Cs1—C28 <sup>i</sup>	115.54 (9)	C24—C23—Cs1	120.8 (4)
N12 <sup>ii</sup> —Cs1—C28 <sup>i</sup>	130.71 (8)	C22—C23—Cs1	70.8 (3)
C22—Cs1—C28 <sup>i</sup>	133.56 (9)	C24—C23—H23	118.6
N22 <sup>iii</sup> —Cs1—C28 <sup>i</sup>	72.13 (8)	C22—C23—H23	118.6
C13—Cs1—C28 <sup>i</sup>	92.40 (10)	Cs1—C23—H23	79.0
S21 <sup>i</sup> —Cs1—C28 <sup>i</sup>	27.92 (6)	C23—C24—C25	119.0 (4)
C23—Cs1—C28 <sup>i</sup>	126.05 (10)	C23—C24—H24	120.5
C12—Cs1—N23 <sup>i</sup>	97.50 (9)	C25—C24—H24	120.5
C22—Cs1—N23 <sup>i</sup>	125.66 (9)	C26—C25—C24	120.3 (4)
C13—Cs1—N23 <sup>i</sup>	75.54 (10)	C26—C25—Br2	119.9 (4)
C23—Cs1—N23 <sup>i</sup>	128.77 (10)	C24—C25—Br2	119.8 (3)
C28 <sup>i</sup> —Cs1—N23 <sup>i</sup>	21.14 (8)	C25—C26—C21	121.4 (4)
C12—Cs1—S11 <sup>i</sup>	157.37 (7)	C25—C26—H26	119.3
C22—Cs1—S11 <sup>i</sup>	112.74 (7)	C21—C26—H26	119.3
C13—Cs1—S11 <sup>i</sup>	142.19 (8)	N21—C27—C21	126.6 (3)
C23—Cs1—S11 <sup>i</sup>	89.93 (8)	N21—C27—Cs1 <sup>vi</sup>	95.3 (2)
C28 <sup>i</sup> —Cs1—S11 <sup>i</sup>	61.33 (6)	C21—C27—Cs1 <sup>vi</sup>	132.9 (3)
N21—Fe1—Cs1	96.96 (9)	N21—C27—H27	116.7
O11—Fe1—Cs1	45.44 (9)	C21—C27—H27	116.7
N11—Fe1—Cs1	87.70 (9)	N22—C28—N23	118.0 (4)
O21—Fe1—Cs1	42.73 (9)	N23—C28—S21	117.2 (3)
S11—Fe1—Cs1	132.16 (3)	N22—C28—Cs1 <sup>iv</sup>	116.2 (2)
S21—Fe1—Cs1	133.86 (3)	N23—C28—Cs1 <sup>iv</sup>	79.8 (2)
C18—S11—Cs1 <sup>iv</sup>	94.66 (13)	S21—C28—Cs1 <sup>iv</sup>	71.78 (12)
O21—Cs1—Fe1—N21	-88.03 (14)	Fe1—O11—C12—Cs1	106.2 (2)
O11—Cs1—Fe1—N21	81.96 (14)	C16—C11—C12—O11	174.6 (4)
C12—Cs1—Fe1—N21	110.71 (14)	C17—C11—C12—O11	-6.4 (7)
N12 <sup>ii</sup> —Cs1—Fe1—N21	-162.21 (11)	Cs1—C11—C12—O11	81.5 (4)
C22—Cs1—Fe1—N21	-61.58 (13)	C16—C11—C12—C13	-2.8 (6)
N22 <sup>iii</sup> —Cs1—Fe1—N21	16.75 (11)	C17—C11—C12—C13	176.2 (4)
C13—Cs1—Fe1—N21	98.26 (12)	Cs1—C11—C12—C13	-95.9 (4)
S21 <sup>i</sup> —Cs1—Fe1—N21	94.76 (10)	C16—C11—C12—Cs1	93.1 (4)
C23—Cs1—Fe1—N21	-73.36 (12)	C17—C11—C12—Cs1	-87.8 (4)
C28 <sup>i</sup> —Cs1—Fe1—N21	43.14 (14)	O21—Cs1—C12—O11	-39.76 (19)
N23 <sup>i</sup> —Cs1—Fe1—N21	47.78 (11)	N12 <sup>ii</sup> —Cs1—C12—O11	-117.6 (2)
S11 <sup>i</sup> —Cs1—Fe1—N21	-99.68 (10)	C22—Cs1—C12—O11	-26.0 (2)
O21—Cs1—Fe1—O11	-170.00 (16)	N22 <sup>iii</sup> —Cs1—C12—O11	45.5 (2)

C12—Cs1—Fe1—O11	28.75 (15)	C13—Cs1—C12—O11	119.4 (4)
N12 <sup>ii</sup> —Cs1—Fe1—O11	115.83 (12)	S21 <sup>i</sup> —Cs1—C12—O11	141.44 (18)
C22—Cs1—Fe1—O11	-143.55 (15)	C23—Cs1—C12—O11	-35.1 (2)
N22 <sup>iii</sup> —Cs1—Fe1—O11	-65.21 (12)	C28 <sup>i</sup> —Cs1—C12—O11	111.0 (2)
C13—Cs1—Fe1—O11	16.30 (14)	N23 <sup>i</sup> —Cs1—C12—O11	99.5 (2)
S21 <sup>i</sup> —Cs1—Fe1—O11	12.80 (12)	S11 <sup>i</sup> —Cs1—C12—O11	-172.58 (13)
C23—Cs1—Fe1—O11	-155.32 (14)	O21—Cs1—C12—C11	82.9 (2)
C28 <sup>i</sup> —Cs1—Fe1—O11	-38.82 (15)	O11—Cs1—C12—C11	122.7 (4)
N23 <sup>i</sup> —Cs1—Fe1—O11	-34.18 (13)	N12 <sup>ii</sup> —Cs1—C12—C11	5.1 (2)
S11 <sup>i</sup> —Cs1—Fe1—O11	178.36 (12)	C22—Cs1—C12—C11	96.7 (2)
O21—Cs1—Fe1—N11	91.61 (14)	N22 <sup>iii</sup> —Cs1—C12—C11	168.2 (3)
O11—Cs1—Fe1—N11	-98.40 (14)	C13—Cs1—C12—C11	-117.9 (4)
C12—Cs1—Fe1—N11	-69.65 (14)	S21 <sup>i</sup> —Cs1—C12—C11	-95.9 (2)
N12 <sup>ii</sup> —Cs1—Fe1—N11	17.43 (11)	C23—Cs1—C12—C11	87.6 (3)
C22—Cs1—Fe1—N11	118.06 (14)	C28 <sup>i</sup> —Cs1—C12—C11	-126.3 (2)
N22 <sup>iii</sup> —Cs1—Fe1—N11	-163.61 (11)	N23 <sup>i</sup> —Cs1—C12—C11	-137.9 (2)
C13—Cs1—Fe1—N11	-82.10 (13)	S11 <sup>i</sup> —Cs1—C12—C11	-49.9 (4)
S21 <sup>i</sup> —Cs1—Fe1—N11	-85.59 (10)	O21—Cs1—C12—C13	-159.2 (3)
C23—Cs1—Fe1—N11	106.28 (12)	O11—Cs1—C12—C13	-119.4 (4)
C28 <sup>i</sup> —Cs1—Fe1—N11	-137.22 (14)	N12 <sup>ii</sup> —Cs1—C12—C13	123.0 (3)
N23 <sup>i</sup> —Cs1—Fe1—N11	-132.58 (11)	C22—Cs1—C12—C13	-145.4 (3)
S11 <sup>i</sup> —Cs1—Fe1—N11	79.96 (10)	N22 <sup>iii</sup> —Cs1—C12—C13	-74.0 (3)
O11—Cs1—Fe1—O21	170.00 (16)	S21 <sup>i</sup> —Cs1—C12—C13	22.0 (3)
C12—Cs1—Fe1—O21	-161.25 (15)	C23—Cs1—C12—C13	-154.5 (3)
N12 <sup>ii</sup> —Cs1—Fe1—O21	-74.17 (12)	C28 <sup>i</sup> —Cs1—C12—C13	-8.4 (3)
C22—Cs1—Fe1—O21	26.45 (15)	N23 <sup>i</sup> —Cs1—C12—C13	-20.0 (3)
N22 <sup>iii</sup> —Cs1—Fe1—O21	104.78 (12)	S11 <sup>i</sup> —Cs1—C12—C13	68.0 (3)
C13—Cs1—Fe1—O21	-173.71 (14)	O11—C12—C13—C14	-174.4 (5)
S21 <sup>i</sup> —Cs1—Fe1—O21	-177.20 (11)	C11—C12—C13—C14	3.1 (8)
C23—Cs1—Fe1—O21	14.67 (14)	Cs1—C12—C13—C14	-99.4 (6)
C28 <sup>i</sup> —Cs1—Fe1—O21	131.17 (15)	O11—C12—C13—Cs1	-75.0 (4)
N23 <sup>i</sup> —Cs1—Fe1—O21	135.81 (13)	C11—C12—C13—Cs1	102.5 (4)
S11 <sup>i</sup> —Cs1—Fe1—O21	-11.65 (12)	O21—Cs1—C13—C14	136.9 (3)
O21—Cs1—Fe1—S11	9.09 (11)	O11—Cs1—C13—C14	150.3 (4)
O11—Cs1—Fe1—S11	179.09 (12)	C12—Cs1—C13—C14	117.8 (5)
C12—Cs1—Fe1—S11	-152.16 (11)	N12 <sup>ii</sup> —Cs1—C13—C14	61.4 (3)
N12 <sup>ii</sup> —Cs1—Fe1—S11	-65.08 (7)	C22—Cs1—C13—C14	153.7 (3)
C22—Cs1—Fe1—S11	35.54 (11)	N22 <sup>iii</sup> —Cs1—C13—C14	-140.7 (4)
N22 <sup>iii</sup> —Cs1—Fe1—S11	113.87 (7)	S21 <sup>i</sup> —Cs1—C13—C14	-41.9 (3)
C13—Cs1—Fe1—S11	-164.62 (10)	C23—Cs1—C13—C14	149.1 (3)
S21 <sup>i</sup> —Cs1—Fe1—S11	-168.11 (5)	C28 <sup>i</sup> —Cs1—C13—C14	-69.8 (3)
C23—Cs1—Fe1—S11	23.76 (9)	N23 <sup>i</sup> —Cs1—C13—C14	-82.7 (3)
C28 <sup>i</sup> —Cs1—Fe1—S11	140.26 (11)	S11 <sup>i</sup> —Cs1—C13—C14	-26.6 (4)
N23 <sup>i</sup> —Cs1—Fe1—S11	144.91 (8)	O21—Cs1—C13—C12	19.1 (3)
S11 <sup>i</sup> —Cs1—Fe1—S11	-2.55 (4)	O11—Cs1—C13—C12	32.5 (2)
O21—Cs1—Fe1—S21	-179.27 (12)	N12 <sup>ii</sup> —Cs1—C13—C12	-56.4 (3)
O11—Cs1—Fe1—S21	-9.27 (12)	C22—Cs1—C13—C12	35.9 (3)
C12—Cs1—Fe1—S21	19.48 (11)	N22 <sup>iii</sup> —Cs1—C13—C12	101.5 (3)

N12 <sup>ii</sup> —Cs1—Fe1—S21	106.56 (7)	S21 <sup>i</sup> —Cs1—C13—C12	-159.7 (3)
C22—Cs1—Fe1—S21	-152.82 (11)	C23—Cs1—C13—C12	31.3 (3)
N22 <sup>iii</sup> —Cs1—Fe1—S21	-74.49 (7)	C28 <sup>i</sup> —Cs1—C13—C12	172.4 (3)
C13—Cs1—Fe1—S21	7.02 (9)	N23 <sup>i</sup> —Cs1—C13—C12	159.5 (3)
S21 <sup>i</sup> —Cs1—Fe1—S21	3.53 (4)	S11 <sup>i</sup> —Cs1—C13—C12	-144.4 (2)
C23—Cs1—Fe1—S21	-164.60 (10)	C12—C13—C14—C15	-1.5 (9)
C28 <sup>i</sup> —Cs1—Fe1—S21	-48.10 (11)	Cs1—C13—C14—C15	-75.8 (6)
N23 <sup>i</sup> —Cs1—Fe1—S21	-43.45 (8)	C13—C14—C15—C16	-0.4 (8)
S11 <sup>i</sup> —Cs1—Fe1—S21	169.09 (5)	C13—C14—C15—Br1	-179.1 (4)
N21—Fe1—S11—C18	-174.90 (16)	C14—C15—C16—C11	0.6 (7)
N11—Fe1—S11—C18	1.91 (15)	Br1—C15—C16—C11	179.3 (3)
O21—Fe1—S11—C18	91.32 (15)	C12—C11—C16—C15	1.1 (6)
S21—Fe1—S11—C18	-88.80 (13)	C17—C11—C16—C15	-178.1 (4)
Cs1—Fe1—S11—C18	85.17 (13)	Cs1—C11—C16—C15	63.1 (4)
N21—Fe1—S11—Cs1 <sup>iv</sup>	-78.82 (9)	N12—N11—C17—C11	-176.4 (4)
N11—Fe1—S11—Cs1 <sup>iv</sup>	97.99 (9)	Fe1—N11—C17—C11	2.2 (6)
O21—Fe1—S11—Cs1 <sup>iv</sup>	-172.60 (8)	C12—C11—C17—N11	-1.1 (7)
S21—Fe1—S11—Cs1 <sup>iv</sup>	7.28 (4)	C16—C11—C17—N11	177.9 (4)
Cs1—Fe1—S11—Cs1 <sup>iv</sup>	-178.751 (19)	Cs1—C11—C17—N11	-62.4 (5)
N21—Fe1—S21—C28	1.22 (15)	N11—N12—C18—N13	-178.3 (3)
O11—Fe1—S21—C28	90.51 (15)	Cs1 <sup>v</sup> —N12—C18—N13	13.6 (5)
N11—Fe1—S21—C28	-175.16 (15)	N11—N12—C18—S11	0.7 (5)
S11—Fe1—S21—C28	-89.10 (13)	Cs1 <sup>v</sup> —N12—C18—S11	-167.32 (17)
Cs1—Fe1—S21—C28	97.10 (13)	Fe1—S11—C18—N12	-2.1 (3)
N21—Fe1—S21—Cs1 <sup>iv</sup>	82.53 (9)	Cs1 <sup>iv</sup> —S11—C18—N12	-106.4 (3)
O11—Fe1—S21—Cs1 <sup>iv</sup>	171.81 (8)	Fe1—S11—C18—N13	177.0 (3)
N11—Fe1—S21—Cs1 <sup>iv</sup>	-93.86 (9)	Cs1 <sup>iv</sup> —S11—C18—N13	72.7 (3)
S11—Fe1—S21—Cs1 <sup>iv</sup>	-7.79 (4)	O11—Fe1—N21—C27	93.9 (3)
Cs1—Fe1—S21—Cs1 <sup>iv</sup>	178.407 (19)	O21—Fe1—N21—C27	6.2 (3)
N21—Fe1—O11—C12	168.4 (3)	S11—Fe1—N21—C27	-83.6 (3)
N11—Fe1—O11—C12	-8.5 (3)	S21—Fe1—N21—C27	-177.3 (3)
O21—Fe1—O11—C12	-97.7 (3)	Cs1—Fe1—N21—C27	49.0 (3)
S21—Fe1—O11—C12	82.4 (3)	O11—Fe1—N21—N22	-90.0 (3)
Cs1—Fe1—O11—C12	-91.0 (3)	O21—Fe1—N21—N22	-177.7 (3)
N21—Fe1—O11—Cs1	-100.59 (12)	S11—Fe1—N21—N22	92.4 (3)
N11—Fe1—O11—Cs1	82.45 (12)	S21—Fe1—N21—N22	-1.2 (3)
O21—Fe1—O11—Cs1	-6.78 (11)	Cs1—Fe1—N21—N22	-134.9 (2)
S21—Fe1—O11—Cs1	173.33 (8)	C27—N21—N22—C28	176.9 (3)
O21—Cs1—O11—C12	130.0 (2)	Fe1—N21—N22—C28	0.4 (4)
N12 <sup>ii</sup> —Cs1—O11—C12	61.5 (2)	C27—N21—N22—Cs1 <sup>vi</sup>	-27.6 (3)
C22—Cs1—O11—C12	151.2 (2)	Fe1—N21—N22—Cs1 <sup>vi</sup>	155.88 (15)
N22 <sup>iii</sup> —Cs1—O11—C12	-129.3 (2)	Fe1—O21—C22—C23	-170.7 (4)
C13—Cs1—O11—C12	-32.4 (2)	Cs1—O21—C22—C23	72.1 (4)
S21 <sup>i</sup> —Cs1—O11—C12	-48.4 (2)	Fe1—O21—C22—C21	10.8 (6)
C23—Cs1—O11—C12	146.6 (2)	Cs1—O21—C22—C21	-106.4 (4)
C28 <sup>i</sup> —Cs1—O11—C12	-81.5 (2)	Fe1—O21—C22—Cs1	117.2 (3)
N23 <sup>i</sup> —Cs1—O11—C12	-84.3 (2)	C26—C21—C22—O21	175.6 (4)
O21—Cs1—O11—Fe1	5.49 (9)	C27—C21—C22—O21	-5.0 (6)

C12—Cs1—O11—Fe1	-124.5 (3)	C26—C21—C22—C23	-2.9 (6)
N12 <sup>ii</sup> —Cs1—O11—Fe1	-63.05 (11)	C27—C21—C22—C23	176.5 (4)
C22—Cs1—O11—Fe1	26.63 (11)	C26—C21—C22—Cs1	96.5 (4)
N22 <sup>iii</sup> —Cs1—O11—Fe1	106.12 (12)	C27—C21—C22—Cs1	-84.1 (4)
C13—Cs1—O11—Fe1	-156.93 (19)	O11—Cs1—C22—O21	-45.30 (19)
S21 <sup>i</sup> —Cs1—O11—Fe1	-172.93 (7)	C12—Cs1—C22—O21	-34.2 (2)
C23—Cs1—O11—Fe1	22.11 (13)	N12 <sup>ii</sup> —Cs1—C22—O21	47.5 (2)
C28 <sup>i</sup> —Cs1—O11—Fe1	153.92 (10)	N22 <sup>iii</sup> —Cs1—C22—O21	-116.8 (2)
N23 <sup>i</sup> —Cs1—O11—Fe1	151.16 (11)	C13—Cs1—C22—O21	-47.7 (2)
N21—Fe1—O21—C22	-10.1 (3)	S21 <sup>i</sup> —Cs1—C22—O21	178.45 (13)
O11—Fe1—O21—C22	-99.1 (3)	C23—Cs1—C22—O21	123.1 (4)
N11—Fe1—O21—C22	166.5 (3)	C28 <sup>i</sup> —Cs1—C22—O21	-156.09 (18)
S11—Fe1—O21—C22	80.5 (3)	N23 <sup>i</sup> —Cs1—C22—O21	-130.5 (2)
Cs1—Fe1—O21—C22	-106.2 (3)	S11 <sup>i</sup> —Cs1—C22—O21	132.53 (19)
N21—Fe1—O21—Cs1	96.17 (12)	O21—Cs1—C22—C23	-123.1 (4)
O11—Fe1—O21—Cs1	7.12 (11)	O11—Cs1—C22—C23	-168.4 (3)
N11—Fe1—O21—Cs1	-87.26 (12)	C12—Cs1—C22—C23	-157.3 (3)
S11—Fe1—O21—Cs1	-173.27 (8)	N12 <sup>ii</sup> —Cs1—C22—C23	-75.6 (3)
O11—Cs1—O21—C22	123.2 (2)	N22 <sup>iii</sup> —Cs1—C22—C23	120.1 (3)
C12—Cs1—O21—C22	142.5 (2)	C13—Cs1—C22—C23	-170.8 (3)
N12 <sup>ii</sup> —Cs1—O21—C22	-130.4 (2)	S21 <sup>i</sup> —Cs1—C22—C23	55.3 (4)
N22 <sup>iii</sup> —Cs1—O21—C22	58.5 (2)	C28 <sup>i</sup> —Cs1—C22—C23	80.8 (3)
C13—Cs1—O21—C22	134.4 (2)	N23 <sup>i</sup> —Cs1—C22—C23	106.4 (3)
C23—Cs1—O21—C22	-30.6 (2)	S11 <sup>i</sup> —Cs1—C22—C23	9.4 (3)
C28 <sup>i</sup> —Cs1—O21—C22	40.8 (3)	O21—Cs1—C22—C21	118.2 (4)
N23 <sup>i</sup> —Cs1—O21—C22	67.3 (2)	O11—Cs1—C22—C21	72.9 (3)
S11 <sup>i</sup> —Cs1—O21—C22	-58.1 (2)	C12—Cs1—C22—C21	84.0 (3)
O11—Cs1—O21—Fe1	-5.56 (9)	N12 <sup>ii</sup> —Cs1—C22—C21	165.7 (3)
C12—Cs1—O21—Fe1	13.76 (11)	N22 <sup>iii</sup> —Cs1—C22—C21	1.4 (3)
N12 <sup>ii</sup> —Cs1—O21—Fe1	100.81 (12)	C13—Cs1—C22—C21	70.5 (3)
C22—Cs1—O21—Fe1	-128.8 (3)	S21 <sup>i</sup> —Cs1—C22—C21	-63.3 (4)
N22 <sup>iii</sup> —Cs1—O21—Fe1	-70.32 (11)	C23—Cs1—C22—C21	-118.7 (4)
C13—Cs1—O21—Fe1	5.66 (13)	C28 <sup>i</sup> —Cs1—C22—C21	-37.9 (3)
C23—Cs1—O21—Fe1	-159.33 (19)	N23 <sup>i</sup> —Cs1—C22—C21	-12.3 (3)
C28 <sup>i</sup> —Cs1—O21—Fe1	-88.0 (2)	S11 <sup>i</sup> —Cs1—C22—C21	-109.3 (3)
N23 <sup>i</sup> —Cs1—O21—Fe1	-61.43 (16)	O21—C22—C23—C24	-176.8 (5)
S11 <sup>i</sup> —Cs1—O21—Fe1	173.12 (7)	C21—C22—C23—C24	1.8 (8)
O11—Fe1—N11—C17	1.7 (3)	Cs1—C22—C23—C24	-114.9 (5)
O21—Fe1—N11—C17	89.4 (3)	O21—C22—C23—Cs1	-61.8 (3)
S11—Fe1—N11—C17	179.3 (3)	C21—C22—C23—Cs1	116.8 (4)
S21—Fe1—N11—C17	-87.1 (3)	O21—Cs1—C23—C24	147.7 (4)
Cs1—Fe1—N11—C17	46.7 (3)	O11—Cs1—C23—C24	127.8 (4)
O11—Fe1—N11—N12	-179.8 (3)	C12—Cs1—C23—C24	141.0 (4)
O21—Fe1—N11—N12	-92.1 (3)	N12 <sup>ii</sup> —Cs1—C23—C24	-139.1 (4)
S11—Fe1—N11—N12	-2.2 (2)	C22—Cs1—C23—C24	117.3 (5)
S21—Fe1—N11—N12	91.3 (3)	N22 <sup>iii</sup> —Cs1—C23—C24	61.8 (4)
Cs1—Fe1—N11—N12	-134.8 (3)	C13—Cs1—C23—C24	128.5 (4)
C17—N11—N12—C18	-179.9 (3)	S21 <sup>i</sup> —Cs1—C23—C24	-34.0 (4)



Fe1—N11—N12—C18	1.5 (4)	C28 <sup>i</sup> —Cs1—C23—C24	−0.5 (4)
C17—N11—N12—Cs1 <sup>v</sup>	−11.8 (4)	N23 <sup>i</sup> —Cs1—C23—C24	26.0 (4)
Fe1—N11—N12—Cs1 <sup>v</sup>	169.55 (13)	S11 <sup>i</sup> —Cs1—C23—C24	−54.1 (4)
O21—Cs1—C11—C12	−87.8 (2)	O21—Cs1—C23—C22	30.4 (2)
O11—Cs1—C11—C12	−32.1 (2)	O11—Cs1—C23—C22	10.5 (3)
N12 <sup>ii</sup> —Cs1—C11—C12	−174.2 (3)	C12—Cs1—C23—C22	23.8 (3)
C22—Cs1—C11—C12	−82.3 (2)	N12 <sup>ii</sup> —Cs1—C23—C22	103.7 (3)
N22 <sup>iii</sup> —Cs1—C11—C12	−12.0 (3)	N22 <sup>iii</sup> —Cs1—C23—C22	−55.4 (3)
C13—Cs1—C11—C12	34.6 (3)	C13—Cs1—C23—C22	11.3 (3)
S21 <sup>i</sup> —Cs1—C11—C12	93.1 (2)	S21 <sup>i</sup> —Cs1—C23—C22	−151.2 (2)
C23—Cs1—C11—C12	−98.6 (3)	C28 <sup>i</sup> —Cs1—C23—C22	−117.8 (3)
C28 <sup>i</sup> —Cs1—C11—C12	64.9 (3)	N23 <sup>i</sup> —Cs1—C23—C22	−91.3 (3)
N23 <sup>i</sup> —Cs1—C11—C12	46.2 (3)	S11 <sup>i</sup> —Cs1—C23—C22	−171.3 (3)
S11 <sup>i</sup> —Cs1—C11—C12	152.6 (2)	C22—C23—C24—C25	0.6 (9)
O21—Cs1—C11—C16	158.4 (3)	Cs1—C23—C24—C25	−85.2 (6)
O11—Cs1—C11—C16	−145.9 (3)	C23—C24—C25—C26	−2.0 (8)
C12—Cs1—C11—C16	−113.8 (4)	C23—C24—C25—Br2	177.1 (4)
N12 <sup>ii</sup> —Cs1—C11—C16	72.0 (3)	C24—C25—C26—C21	1.0 (7)
C22—Cs1—C11—C16	163.9 (3)	Br2—C25—C26—C21	−178.2 (3)
N22 <sup>iii</sup> —Cs1—C11—C16	−125.8 (3)	C22—C21—C26—C25	1.6 (6)
C13—Cs1—C11—C16	−79.2 (3)	C27—C21—C26—C25	−177.9 (4)
S21 <sup>i</sup> —Cs1—C11—C16	−20.7 (3)	N22—N21—C27—C21	−179.4 (4)
C23—Cs1—C11—C16	147.5 (3)	Fe1—N21—C27—C21	−3.0 (6)
C28 <sup>i</sup> —Cs1—C11—C16	−48.9 (3)	N22—N21—C27—Cs1 <sup>vi</sup>	23.8 (3)
N23 <sup>i</sup> —Cs1—C11—C16	−67.6 (3)	Fe1—N21—C27—Cs1 <sup>vi</sup>	−159.93 (19)
S11 <sup>i</sup> —Cs1—C11—C16	38.7 (3)	C26—C21—C27—N21	−179.8 (4)
O21—Cs1—C11—C17	32.7 (2)	C22—C21—C27—N21	0.8 (7)
O11—Cs1—C11—C17	88.3 (2)	C26—C21—C27—Cs1 <sup>vi</sup>	−32.0 (5)
C12—Cs1—C11—C17	120.4 (4)	C22—C21—C27—Cs1 <sup>vi</sup>	148.6 (3)
N12 <sup>ii</sup> —Cs1—C11—C17	−53.8 (2)	N21—N22—C28—N23	−176.4 (3)
C22—Cs1—C11—C17	38.1 (2)	Cs1 <sup>vi</sup> —N22—C28—N23	35.5 (5)
N22 <sup>iii</sup> —Cs1—C11—C17	108.4 (2)	N21—N22—C28—S21	1.0 (5)
C13—Cs1—C11—C17	155.1 (3)	Cs1 <sup>vi</sup> —N22—C28—S21	−147.2 (2)
S21 <sup>i</sup> —Cs1—C11—C17	−146.5 (2)	N21—N22—C28—Cs1 <sup>iv</sup>	−84.2 (3)
C23—Cs1—C11—C17	21.8 (3)	Cs1 <sup>vi</sup> —N22—C28—Cs1 <sup>iv</sup>	127.6 (2)
C28 <sup>i</sup> —Cs1—C11—C17	−174.6 (2)	Cs1 <sup>iv</sup> —N23—C28—N22	114.3 (3)
N23 <sup>i</sup> —Cs1—C11—C17	166.7 (2)	Cs1 <sup>iv</sup> —N23—C28—S21	−63.3 (2)
S11 <sup>i</sup> —Cs1—C11—C17	−87.0 (2)	Fe1—S21—C28—N22	−1.6 (4)
Fe1—O11—C12—C11	11.7 (6)	Cs1 <sup>iv</sup> —S21—C28—N22	−109.7 (3)
Cs1—O11—C12—C11	−94.6 (4)	Fe1—S21—C28—N23	175.8 (3)
Fe1—O11—C12—C13	−171.0 (4)	Cs1 <sup>iv</sup> —S21—C28—N23	67.7 (3)
Cs1—O11—C12—C13	82.8 (4)	Fe1—S21—C28—Cs1 <sup>iv</sup>	108.05 (4)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N13—H13A $\cdots$ O21 <sup>v</sup>	0.86	2.08	2.907 (4)	161

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N13—H13 <i>B</i> ···Br2 <sup>vii</sup>	0.86	2.72	3.557 (4)	163
N23—H23 <i>A</i> ···O11 <sup>vi</sup>	0.86	2.10	2.952 (5)	171
N23—H23 <i>B</i> ···Br1 <sup>viii</sup>	0.86	2.95	3.590 (4)	133
C13—H13···Br1 <sup>ix</sup>	0.93	2.83	3.578 (5)	139
C23—H23···Br2 <sup>x</sup>	0.93	2.86	3.623 (5)	141

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Symmetry codes: (v)  $x, -y+1/2, z+1/2$ ; (vi)  $x, -y+3/2, z+1/2$ ; (vii)  $-x+1, y-1/2, -z+3/2$ ; (viii)  $-x+2, y+1/2, -z+3/2$ ; (ix)  $-x+2, y+1/2, -z+1/2$ ; (x)  $-x+1, y-1/2, -z+1/2$ .