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# Fe<sup>III</sup> in a low-spin state in caesium bis[3-ethoxysalicylaldehyde 4-methylthiosemicarbazonato(2-)-κ<sup>3</sup>O<sup>2</sup>,N<sup>1</sup>,S]-ferrate(III) methanol monosolvate

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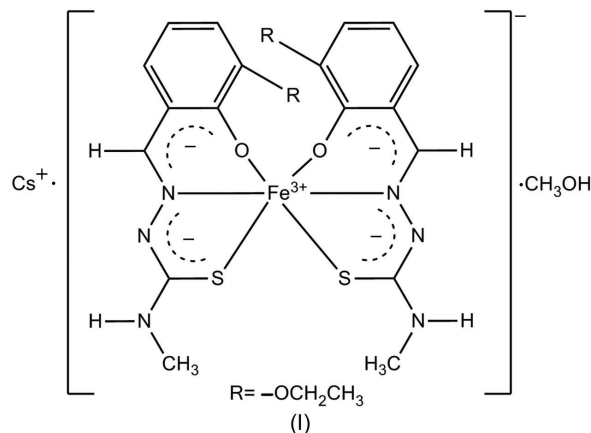
The synthesis and crystal structure (at 100 K) of the title compound, Cs[Fe(C<sub>11</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>S<sub>2</sub>)<sub>2</sub>].CH<sub>3</sub>OH, is reported. The asymmetric unit consists of an octahedral [Fe<sup>III</sup>(L<sub>2</sub>)<sub>2</sub>]<sup>-</sup> fragment, where L<sup>2-</sup> is 3-ethoxysalicylaldehyde 4-methylthiosemicarbazonato(2-) {systematic name: [2-(3-ethoxy-2-oxido-benzylidene)hydrazin-1-ylidene](methylamino)methanethiolate}, a caesium cation and a methanol solvent molecule. Each L<sup>2-</sup> ligand binds through the thiolate S, the imine N and the phenolate O atoms as donors, resulting in an Fe<sup>III</sup>S<sub>2</sub>N<sub>2</sub>O<sub>2</sub> chromophore. The O,N,S-coordinating ligands are orientated in two perpendicular planes, with the O and S atoms in *cis* positions and the N atoms in *trans* positions. The Fe<sup>III</sup> cation is in the low-spin state at 100 K.

**Keywords:** crystal structure; thiosemicarbazones; iron(III); low-spin structures; chromophores; switching behaviour; Fe<sup>III</sup> spin-crossover behaviour.

## 1. Introduction

Transition metal fragments displaying switching behaviour are appealing materials, which may be used in a functional way in research and technology (Létard *et al.*, 2004; Gütllich *et al.*, 2004; Gütllich & Goodwin, 2004; van Koningsbruggen *et al.*, 2004; van Koningsbruggen, 2004). It is now established that some molecular species containing transition metal ions may exhibit a crossover between states having different magnetic moments. Among these, iron(III) occupies a unique position in the development of the spin-crossover area, since it was with iron(III) tris(dithiocarbamates) that the temperature-induced phenomenon was first discovered (Cambí & Szegő, 1931, 1933). The magnetic interconversion between the low-

spin ( $S = \frac{1}{2}$ ) and high-spin ( $S = \frac{5}{2}$ ) states in Fe<sup>III</sup> systems has now been found to be triggered by a change in temperature or pressure or by light irradiation (Hayami *et al.*, 2000, 2009; van Koningsbruggen *et al.*, 2004).



Scheme 1

The generation of Fe<sup>III</sup> spin-crossover behaviour has been demonstrated for a variety of ligand systems (van Koningsbruggen *et al.*, 2004). Among these, particular interest has been focused on Fe<sup>III</sup> entities containing two tridentate O,N,S-coordinating thiosemicarbazone ligands, which exhibit a thermal spin transition (Zelentsov *et al.*, 1973; Ryabova *et al.*, 1978, 1982; Ryabova, Ponomarev, Zelentsov & Atovmyan, 1981; Ryabova, Ponomarev, Zelentsov, Shipilov & Atovmyan, 1981; Floquet *et al.*, 2003, 2006, 2009; Li *et al.*, 2013; Zelentsov, 1983). In our research we first focused on using derivatives of pyridoxal-4-*R*-thiosemicarbazone for generating Fe<sup>III</sup> spin-crossover, resulting in the octahedral Fe<sup>III</sup>S<sub>2</sub>N<sub>2</sub>O<sub>2</sub> entity [Fe<sup>III</sup>(HL)(L)]·2H<sub>2</sub>O, where HL<sup>-</sup> and L<sup>2-</sup> are the mono- and dianionic forms of pyridoxal-4-methyl-thiosemicarbazone, respectively (Yemeli Tido *et al.*, 2008). The crystal structure of this compound has been determined at 100 K and, from the values of the geometric parameters, it could be inferred that the Fe<sup>III</sup> cation is in the low-spin state. Temperature-dependent magnetic susceptibility measurements (5–300 K) showed that this spin state is retained over this temperature range. Complete dehydration of the compound results in an Fe<sup>III</sup> high-spin material (Yemeli Tido *et al.*, 2008). Furthermore, it appeared that varying the pH during the synthesis of the Fe<sup>III</sup> entities leads to the formation of Fe<sup>III</sup> compounds differing in the degree of deprotonation of the ligand (Yemeli Tido, 2010). In addition, we have identified a photo-induced spin transition through light-induced excited spin-state trapping (LIESST) of Fe<sup>III</sup> in [Fe<sup>III</sup>(HL)(L)]·*x*H<sub>2</sub>O, where HL<sup>-</sup> = 5-chlorosalicylaldehyde thiosemicarbazonato(1-) and L<sup>2-</sup> = 5-chlorosalicylaldehyde thiosemicarbazonato(2-) (*x* = 1), or HL<sup>-</sup> = 5-bromosalicylaldehyde thiosemicarbazonato(1-) and L<sup>2-</sup> = 5-bromosalicylaldehyde thiosemicarbazonato(2-) (*x* =  $\frac{1}{2}$ ) (Yemeli Tido, 2010). We report here the title novel Fe<sup>III</sup> compound, Cs[Fe(L)<sub>2</sub>].CH<sub>3</sub>OH, (I), containing two dianionic tridentate 3-ethoxysalicylaldehyde 4-methylthiosemicarbazonato(2-) (L<sup>2-</sup>) ligands (Scheme 1), and the determination of its structure at 100 K.

**Table 1**  
 Experimental details.

Crystal data	
Chemical formula	Cs[Fe(C <sub>11</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> S) <sub>2</sub> ].CH <sub>4</sub> O
<i>M<sub>r</sub></i>	723.40
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.486 (3), 9.078 (3), 19.875 (7)
$\alpha$ , $\beta$ , $\gamma$ (°)	100.629 (5), 91.549 (5), 113.674 (5)
<i>V</i> (Å <sup>3</sup> )	1369.5 (8)
<i>Z</i>	2
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	2.06
Crystal size (mm)	0.04 × 0.02 × 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>	0.711, 1.000
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	15188, 4844, 3414
<i>R</i> <sub>int</sub>	0.082
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.596
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, 0.122, 0.92
No. of reflections	4844
No. of parameters	377
No. of restraints	5
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	1.84, -0.62

Computer programs: *CrystalClear-SM Expert* (Rigaku, 2013), *SUPERFLIP* (Palatinus & Chapuis, 2007; Palatinus & van der Lee, 2008; Palatinus *et al.*, 2012), *SHELXL97* (Sheldrick, 2008), *ORTEP-3* (Farrugia, 2012) and *OLEX2* (Dolomanov *et al.*, 2009).

## 2. Experimental

### 2.1. Synthesis and crystallization

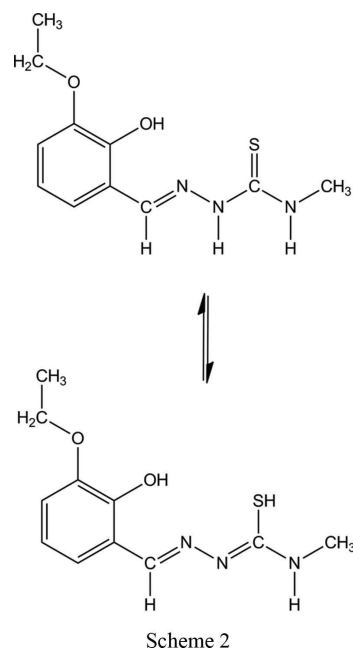
FeCl<sub>3</sub>·6H<sub>2</sub>O (1.0 mmol, 0.27 g) was dissolved in methanol (5 ml). 3-Ethoxysalicylaldehyde 4-methylthiosemicarbazone (1.0 mmol, 0.25 g) was dissolved in methanol (30 ml) with the addition of CsOH·H<sub>2</sub>O (4.0 mmol, 0.67 g). To this mixture, the methanolic Fe<sup>III</sup> salt solution was added with constant stirring. The resulting dark-green solution was stirred and heated at 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 H atoms on secondary amine atoms N13 and N23 were located in difference Fourier maps and refined with restrained N–H distances of 0.88 (2) Å and with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(N). The H atom attached to atom O3 of the methanol molecule was located in a difference Fourier map and refined with an O–H distance restraint of 0.84 (2) Å and with *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(O). The remaining H atoms were included in the refinement in calculated positions and treated as riding on their parent atoms, with C–H = 0.95 Å and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C) for aryl (–CH=) H atoms, C–H = 0.99 Å and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C) for methylene

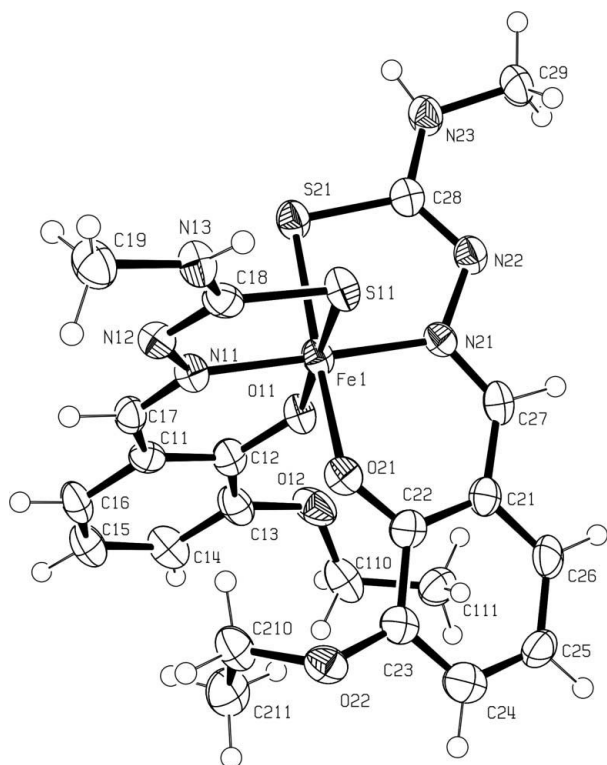
(–CH<sub>2</sub>–) H atoms, and C–H = 0.98 Å and *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(C) for methyl (–CH<sub>3</sub>) H atoms.

The ethoxy group of one of the ligands shows positional disorder. Two different sets of positions for the methyl and methylene C atoms were identified in the difference Fourier synthesis, *i.e.* C111 and C110, and C113 and C112, respectively, which were refined with inversely proportional occupancy factors [0.552 (17) and 0.448 (17)]. Similarity restraints were applied to the chemically equivalent bonds within the two disordered conformations. The residual density on a difference Fourier map included a quadrilateral of peaks near Cs of height 1.21–1.84 e Å<sup>-3</sup>. Unreasonably close contacts to some ligand atoms, which persisted after refinement, ruled out an attribution of these peaks to disorder of the Cs site. Twinning was also considered and rejected; three possible twin laws were provided by *ROTAX* (Cooper *et al.*, 2002), but refinement in *SHELXL97* (Sheldrick, 2008) led to a negligible scale factor for each such twin component. Therefore the peaks, which represent a small fraction of the 54 electrons in the Cs<sup>+</sup> cation, were assumed to arise from limitations of the data.



## 3. Results and discussion

In solution, the free ligand 3-ethoxysalicylaldehyde 4-methylthiosemicarbazone (H<sub>2</sub>L) exists in two tautomeric forms, *i.e.* the thione and thiol forms, as illustrated in Scheme 2. Consequently, in Fe<sup>III</sup> compounds, the ligand may be present in either of the possible tautomers, and may be neutral, anionic or dianionic. Referring to the thiol tautomer, neutral H<sub>2</sub>L has H atoms located on the phenol O atom and the thiol S atom. The first deprotonation step involving the phenol group results in the formation of 3-ethoxysalicylaldehyde 4-methylthiosemicarbazionate(1–) (abbreviated as HL<sup>–</sup>). Subsequent deprotonation yields 3-ethoxysalicylaldehyde 4-methylthiosemicarbazionate(2–) (abbreviated as L<sup>2–</sup>).



**Figure 1**  
The molecular structure and atom-numbering scheme for (I). The  $\text{Cs}^+$  cation,  $\text{CH}_3\text{OH}$  solvent molecule and an alternative orientation for  $\text{C110}-\text{C111}$  have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

The structure of (I) (Fig. 1) was determined at 100 K. It crystallizes in the triclinic system in the space group  $P\bar{1}$ . The asymmetric unit consists of one formula unit,  $\text{Cs}[\text{Fe}(\text{L})_2] \cdot \text{CH}_3\text{OH}$ , with no atom on a special position. The  $\text{Fe}^{\text{III}}$  cation is coordinated by two dianionic  $O,N,S$ -tridentate thiosemicarbazone ligands, displaying a distorted octahedral  $\text{Fe}^{\text{III}}-\text{S}_2\text{N}_2\text{O}_2$  geometry. Selected geometric parameters are listed in Table 2.

The donor atoms of the ligands are situated in two perpendicular planes, with the O and S atoms in *cis* positions and the N atoms in *trans* positions. These features are corroborated by the bond angles involving the Fe1 atom and the donor atoms (Table 2).

The bond distances involving the Fe1 atom and the donor atoms (Table 2) suggest that (I) contains low-spin  $\text{Fe}^{\text{III}}$  at 100 K. Typical distances for Fe–S, Fe–O and Fe–N bonds are 2.23–2.31, 1.93–1.95 and 1.88–1.96 Å, respectively, for low-spin  $\text{Fe}^{\text{III}}$  compounds of this family, and 2.40–2.44, 1.96–1.99 and 2.05–2.15 Å, respectively, for the corresponding high-spin  $\text{Fe}^{\text{III}}$  compounds (van Koningsbruggen *et al.*, 2004). It is noteworthy that both Fe–O distances in (I) are shorter than the typical values quoted for low-spin  $\text{Fe}^{\text{III}}$ . Two reasons may be invoked for this occurrence. Firstly, the low-spin Fe–O reference values are mainly taken from X-ray crystal structures determined at temperatures higher than that at which the structure of (I) was determined (100 K), hence it may be anticipated that the range of actual low-spin Fe–O distances at 100 K will be slightly shorter than the cited values. Secondly,

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

Fe1–S11	2.2686 (19)	Fe1–S21	2.265 (2)
Fe1–O11	1.904 (4)	Fe1–O21	1.918 (4)
Fe1–N11	1.933 (5)	Fe1–N21	1.939 (5)
O11–Fe1–S11	177.83 (14)	S21–Fe1–S11	89.61 (7)
O11–Fe1–N11	94.37 (19)	O21–Fe1–S11	89.34 (13)
O11–Fe1–S21	92.56 (14)	O21–Fe1–N11	87.4 (2)
O11–Fe1–O21	88.49 (18)	O21–Fe1–S21	178.01 (13)
O11–Fe1–N21	85.55 (18)	O21–Fe1–N21	93.7 (2)
N11–Fe1–S11	85.55 (15)	N21–Fe1–S11	94.57 (15)
N11–Fe1–S21	94.17 (16)	N21–Fe1–S21	84.71 (16)
N11–Fe1–N21	178.9 (2)		

it is significant to note that the Fe–O distances seem to be less sensitive to a change in  $\text{Fe}^{\text{III}}$  spin state than the Fe–N and Fe–S distances, which may be related to the  $\pi$ -acceptor capability of the N- and S-donor atoms opposed to the  $\pi$ -donor capability of the O-donor atoms. This is of particular significance when  $\text{Fe}^{\text{III}}$  is in the low-spin state, as increased back-bonding will lead to comparatively more pronounced shortening of the Fe–N and Fe–S bonds than of the Fe–O bonds.

The tridentate ligands in (I) are coordinated to the  $\text{Fe}^{\text{III}}$  cation by the thiolate S, phenolate O and imine N atoms, forming six- and five-membered chelate rings. As might be expected, the five-membered chelate ring involves a significantly less restricted bite angle [ $\text{O11}-\text{Fe1}-\text{N11} = 94.37 (19)^\circ$  and  $\text{O21}-\text{Fe1}-\text{N21} = 93.7 (2)^\circ$ ] than the six-membered chelate ring [ $\text{S11}-\text{Fe1}-\text{N11} = 85.55 (15)^\circ$  and  $\text{S21}-\text{Fe1}-\text{N21} = 84.71 (16)^\circ$ ]. Further stabilization arises from the near alternation of single and double bonds in the different electronic forms, allowing a high degree of  $\pi$ -electron delocalization throughout both of the chelate rings. H atoms could not be located on the phenolate O and thiolate S atoms, which implies that both ligands are in the dianionic form. This is concomitant with the presence of a trivalent iron cation together with a monovalent caesium cation. Ryabova, Ponomarev, Zelentsov & Atovmyan (1981) reported the related compound  $\text{Cs}[\text{Fe}(\text{L})_2]$  [where  $\text{L}^{2-} = \text{salicylaldehyde thiosemicarbazone}(2-)$ ], although this contains high-spin  $\text{Fe}^{\text{III}}$ .

The binding of the twofold deprotonated ligand of (I) to the  $\text{Fe}^{\text{III}}$  cation involves electron delocalization within the chelate ring, which is evident from the geometric parameters. The  $\text{C18}-\text{S11}$  bond length of 1.742 (7) Å and the  $\text{C28}-\text{S21}$  bond length of 1.759 (6) Å suggest partial electron delocalization of these bonds. This corresponds well with the C–S bond length of 1.750 (6) Å for the low-spin  $\text{Fe}^{\text{III}}$  compound  $\text{NH}_4[\text{Fe}(\text{L})_2]$  [where  $\text{L}^{2-} = 5\text{-chlorosalicylaldehyde thiosemicarbazone}(2-)$ ] at 135 K (Ryabova *et al.*, 1978). Similarly, a bond order larger than 1 can be inferred for the C–N bond involving the deprotonated hydrazinic N atom. The  $\text{C17}-\text{N11}$  and  $\text{C27}-\text{N21}$  bond lengths in (I) are 1.302 (7) and 1.291 (8) Å, respectively, which correlates with the value reported by Ryabova *et al.* (1978), *i.e.* a C–N bond length of 1.265 (8) Å for  $\text{NH}_4[\text{Fe}(\text{L})_2]$  at 135 K. Moreover, for (I), the  $\text{N11}-\text{N12}$  and  $\text{N21}-\text{N22}$  bond lengths are 1.398 (7) and 1.406 (7) Å, respectively, indicating some electron delocalization.

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

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N13—H13···S11 <sup>i</sup>	0.87 (2)	2.97 (6)	3.505 (6)	122 (5)
N23—H23···S21 <sup>ii</sup>	0.87 (2)	2.70 (5)	3.416 (6)	141 (6)
O3—H3···N12	0.85 (2)	2.04 (4)	2.852 (7)	160 (8)

Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $-x, -y + 1, -z + 1$ .

The hydrogen-bonding interactions of (I) are listed in Table 3 and displayed in Fig. 2. N13—H13···S11( $-x + 1, -y + 1, -z + 1$ ) interactions paired about the inversion centre at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  create  $R_2^2(8)$  rings (Bernstein *et al.*, 1995), as do N23—H23···S21( $-x, -y + 1, -z + 1$ ) contacts about  $(0, \frac{1}{2}, \frac{1}{2})$ . In this manner, successive Fe<sup>III</sup> entities are linked in the *a* direction. Atom O3 of the CH<sub>3</sub>OH solvent molecule forms an O3—H3···N12 contact with hydrazinic atom N12. In turn, hydrazinic atom N12 is bonded to imine atom N11, which is coordinated to the Fe<sup>III</sup> cation centre. However, the Fe1—N11 bond length [1.933 (5) Å] is virtually identical to the Fe1—N21 bond length [1.939 (5) Å] involving the other ligand, which is devoid of hydrogen-bonding interactions. The Cs<sup>+</sup> cations link the anions into chains along [100].

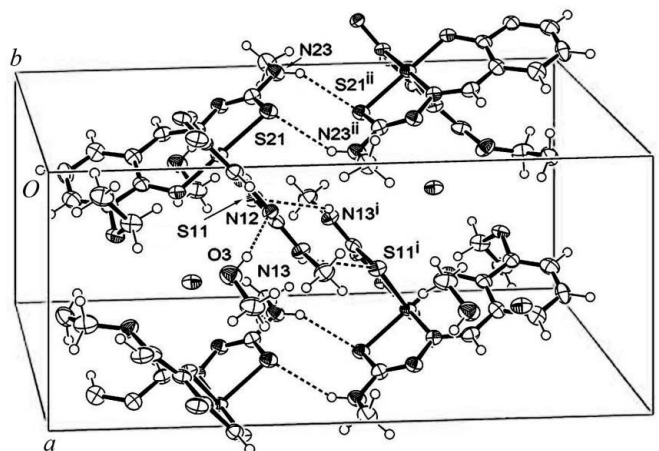
This study has focused on the synthesis and characterization of (I) and it has shown that the Fe<sup>III</sup> cation is in the low-spin state in this compound at 100 K. We are currently in the process of further investigating new members of this Fe<sup>III</sup> bis(ligand) system, while tuning the spin state of Fe<sup>III</sup> by varying the degree of deprotonation of the ligand, as well as varying the *R*- and *R'*-substituents of the *R*-salicylaldehyde *R'*-thiosemicarbazone ligand.

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Supporting information for this paper is available from the IUCr electronic archives (Reference: SF3227).

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**Figure 2**

A projection showing the unit cell of (I). An alternative orientation for C110—C111 has been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate hydrogen bonds. [Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $-x, -y + 1, -z + 1$ .]

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## supplementary materials

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## Fe<sup>III</sup> in a low-spin state in caesium bis[3-ethoxysalicylaldehyde 4-methylthio-semicarbazonato(2-)- $\kappa^3O^2,N^1,S$ ]ferrate(III) methanol monosolvate

Robyn E. Powell, Carl H. Schwalbe, Graham J. Tizzard and Petra J. van Koningsbruggen

### 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: SUPERFLIP (Palatinus & Chapuis, 2007; Palatinus & van der Lee, 2008; Palatinus *et al.*, 2012); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 2012); software used to prepare material for publication: OLEX2 (Dolomanov *et al.*, 2009).

### Caesium bis[[2-(3-ethoxy-2-oxidobenzylidene)hydrazin-1-ylidene](methylamino)methanethiolato- $\kappa^2O^2,N^1,S$ ]ferrate(III) methanol monosolvate

#### Crystal data

Cs[Fe(C<sub>11</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>S)<sub>2</sub>] $\cdot$ CH<sub>4</sub>O

$M_r = 723.40$

Triclinic, *P* $\bar{1}$

$a = 8.486$  (3) Å

$b = 9.078$  (3) Å

$c = 19.875$  (7) Å

$\alpha = 100.629$  (5)°

$\beta = 91.549$  (5)°

$\gamma = 113.674$  (5)°

$V = 1369.5$  (8) Å<sup>3</sup>

$Z = 2$

$F(000) = 726$

$D_x = 1.754$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71075$  Å

Cell parameters from 2733 reflections

$\theta = 2.5$ – $25.0$ °

$\mu = 2.06$  mm<sup>-1</sup>

$T = 100$  K

Plate, green

$0.04 \times 0.02 \times 0.01$  mm

#### Data collection

Rigaku AFC12 four-circle  $\kappa$  diffractometer

Radiation source: Rotating anode, Rotating anode

Confocal mirrors, VHF Varimax monochromator

Detector resolution: 28.5714 pixels mm<sup>-1</sup> profile data from  $\omega$  scans

Absorption correction: multi-scan (*CrystalClear*-SM Expert; Rigaku, 2013)

$T_{\min} = 0.711$ ,  $T_{\max} = 1.000$

15188 measured reflections

4844 independent reflections

3414 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.082$

$\theta_{\max} = 25.1$ °,  $\theta_{\min} = 2.5$ °

$h = -10 \rightarrow 10$

$k = -10 \rightarrow 10$

$l = -23 \rightarrow 22$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

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

$wR(F^2) = 0.122$

$S = 0.92$

4844 reflections

377 parameters

5 restraints

Primary atom site location: iterative  
 Hydrogen site location: mixed  
 H atoms treated by a mixture of independent  
 and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0635P)^2]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 1.84 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.62 \text{ e } \text{\AA}^{-3}$

*Special details*

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

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cs1	0.57891 (5)	0.28483 (5)	0.26270 (2)	0.03559 (16)	
Fe1	0.08110 (11)	0.30324 (9)	0.31166 (5)	0.0266 (2)	
S11	0.3264 (2)	0.44993 (18)	0.38549 (9)	0.0319 (4)	
O11	-0.1195 (5)	0.1797 (4)	0.2469 (2)	0.0282 (10)	
O12	-0.3529 (7)	0.0646 (6)	0.1372 (3)	0.0448 (13)	
N11	0.1004 (6)	0.1112 (6)	0.3326 (3)	0.0268 (12)	
N12	0.2322 (6)	0.1243 (6)	0.3803 (3)	0.0272 (12)	
N13	0.4747 (7)	0.3043 (6)	0.4520 (3)	0.0317 (13)	
H13	0.556 (6)	0.403 (4)	0.466 (3)	0.038*	
C11	-0.1382 (8)	-0.0921 (7)	0.2500 (3)	0.0281 (14)	
C12	-0.1862 (8)	0.0187 (7)	0.2223 (3)	0.0293 (15)	
C13	-0.3131 (8)	-0.0478 (7)	0.1652 (4)	0.0372 (17)	
C14	-0.3949 (8)	-0.2141 (8)	0.1380 (4)	0.0393 (17)	
H14	-0.4804	-0.2547	0.0994	0.047*	
C15	-0.3516 (9)	-0.3233 (8)	0.1675 (4)	0.0402 (18)	
H15	-0.4101	-0.4386	0.1500	0.048*	
C16	-0.2252 (8)	-0.2630 (7)	0.2213 (4)	0.0349 (16)	
H16	-0.1942	-0.3376	0.2403	0.042*	
C17	0.0002 (8)	-0.0410 (7)	0.3039 (3)	0.0290 (15)	
H17	0.0204	-0.1248	0.3200	0.035*	
C18	0.3411 (8)	0.2772 (7)	0.4062 (3)	0.0302 (15)	
C19	0.5001 (9)	0.1727 (8)	0.4766 (4)	0.0415 (18)	
H19A	0.5236	0.1023	0.4382	0.062*	
H19B	0.3954	0.1068	0.4954	0.062*	
H19C	0.5984	0.2206	0.5127	0.062*	
C110	-0.3870 (19)	0.0423 (14)	0.0647 (6)	0.047 (5)	0.552 (17)
H11A	-0.5119	-0.0267	0.0506	0.056*	0.552 (17)
H11B	-0.3219	-0.0177	0.0413	0.056*	0.552 (17)
C111	-0.338 (2)	0.2021 (19)	0.0411 (10)	0.043 (4)	0.552 (17)
H11C	-0.3722	0.1788	-0.0086	0.065*	0.552 (17)
H11D	-0.2126	0.2665	0.0508	0.065*	0.552 (17)
H11E	-0.3977	0.2648	0.0657	0.065*	0.552 (17)
C112	-0.2503 (16)	0.1287 (14)	0.0901 (7)	0.023 (4)	0.448 (17)
H11F	-0.2773	0.0453	0.0466	0.027*	0.448 (17)
H11G	-0.1270	0.1659	0.1072	0.027*	0.448 (17)
C113	-0.286 (2)	0.2708 (18)	0.0784 (10)	0.029 (4)	0.448 (17)

H11H	-0.2307	0.3088	0.0385	0.043*	0.448 (17)
H11I	-0.2388	0.3606	0.1193	0.043*	0.448 (17)
H11J	-0.4110	0.2364	0.0699	0.043*	0.448 (17)
S21	-0.0784 (2)	0.32882 (18)	0.39898 (9)	0.0316 (4)	
O21	0.2202 (5)	0.2897 (5)	0.2382 (2)	0.0290 (10)	
O22	0.3242 (5)	0.1540 (5)	0.1222 (2)	0.0336 (11)	
N21	0.0586 (6)	0.4957 (5)	0.2920 (3)	0.0265 (12)	
N22	0.0018 (7)	0.5926 (6)	0.3401 (3)	0.0306 (13)	
N23	-0.1254 (7)	0.6013 (6)	0.4403 (3)	0.0352 (13)	
H23	-0.128 (9)	0.582 (8)	0.4817 (17)	0.042*	
C21	0.1506 (8)	0.4674 (7)	0.1771 (3)	0.0306 (15)	
C22	0.2078 (7)	0.3420 (7)	0.1814 (3)	0.0291 (15)	
C23	0.2581 (8)	0.2713 (7)	0.1211 (3)	0.0299 (15)	
C24	0.2536 (8)	0.3237 (8)	0.0606 (4)	0.0385 (17)	
H24	0.2869	0.2734	0.0205	0.046*	
C25	0.2016 (9)	0.4479 (7)	0.0573 (4)	0.0381 (17)	
H25	0.2020	0.4852	0.0157	0.046*	
C26	0.1487 (8)	0.5181 (7)	0.1152 (4)	0.0365 (17)	
H26	0.1106	0.6022	0.1126	0.044*	
C27	0.0929 (8)	0.5449 (7)	0.2350 (4)	0.0317 (16)	
H27	0.0786	0.6416	0.2310	0.038*	
C28	-0.0599 (8)	0.5248 (7)	0.3910 (4)	0.0313 (15)	
C29	-0.1007 (10)	0.7715 (7)	0.4438 (4)	0.0411 (18)	
H29A	-0.1756	0.7753	0.4064	0.062*	
H29B	0.0206	0.8386	0.4391	0.062*	
H29C	-0.1303	0.8148	0.4882	0.062*	
C210	0.2056 (9)	-0.0007 (7)	0.1370 (4)	0.0395 (17)	
H21A	0.1604	0.0214	0.1814	0.047*	
H21B	0.2691	-0.0696	0.1418	0.047*	
C211	0.0565 (9)	-0.0936 (8)	0.0815 (4)	0.047 (2)	
H21C	-0.0028	-0.0235	0.0747	0.071*	
H21D	-0.0249	-0.1927	0.0951	0.071*	
H21E	0.0997	-0.1252	0.0384	0.071*	
O3	0.3902 (7)	-0.0555 (6)	0.2962 (3)	0.0464 (13)	
H3	0.337 (10)	-0.021 (10)	0.326 (3)	0.070*	
C31	0.4608 (10)	-0.1567 (8)	0.3210 (4)	0.0467 (19)	
H31A	0.4769	-0.2306	0.2819	0.070*	
H31B	0.3813	-0.2219	0.3499	0.070*	
H31C	0.5728	-0.0869	0.3483	0.070*	

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cs1	0.0301 (2)	0.0342 (2)	0.0458 (3)	0.01752 (17)	0.00371 (19)	0.00666 (17)
Fe1	0.0238 (5)	0.0223 (4)	0.0343 (6)	0.0105 (4)	0.0035 (4)	0.0056 (4)
S11	0.0298 (9)	0.0232 (7)	0.0413 (11)	0.0104 (6)	0.0003 (8)	0.0057 (7)
O11	0.022 (2)	0.023 (2)	0.039 (3)	0.0092 (17)	-0.0014 (19)	0.0060 (18)
O12	0.056 (3)	0.047 (3)	0.040 (3)	0.036 (3)	-0.007 (3)	-0.002 (2)
N11	0.021 (3)	0.026 (3)	0.034 (3)	0.011 (2)	0.002 (2)	0.006 (2)
N12	0.025 (3)	0.029 (3)	0.027 (3)	0.012 (2)	-0.001 (2)	0.004 (2)



N13	0.027 (3)	0.027 (3)	0.039 (4)	0.010 (2)	-0.004 (3)	0.006 (2)
C11	0.026 (3)	0.031 (3)	0.028 (4)	0.013 (3)	0.006 (3)	0.004 (3)
C12	0.019 (3)	0.027 (3)	0.041 (4)	0.007 (3)	0.008 (3)	0.009 (3)
C13	0.031 (4)	0.030 (3)	0.054 (5)	0.017 (3)	0.010 (3)	0.006 (3)
C14	0.026 (4)	0.035 (4)	0.053 (5)	0.013 (3)	-0.003 (3)	0.001 (3)
C15	0.033 (4)	0.025 (3)	0.058 (5)	0.010 (3)	0.004 (4)	0.003 (3)
C16	0.031 (4)	0.023 (3)	0.055 (5)	0.015 (3)	0.011 (3)	0.010 (3)
C17	0.031 (4)	0.027 (3)	0.035 (4)	0.016 (3)	0.008 (3)	0.011 (3)
C18	0.029 (4)	0.032 (3)	0.031 (4)	0.015 (3)	0.009 (3)	0.003 (3)
C19	0.044 (4)	0.037 (4)	0.046 (5)	0.022 (3)	-0.001 (4)	0.006 (3)
C110	0.044 (10)	0.032 (7)	0.064 (11)	0.019 (7)	0.002 (8)	0.002 (6)
C111	0.046 (10)	0.045 (9)	0.045 (11)	0.020 (8)	0.017 (8)	0.017 (7)
C112	0.009 (8)	0.018 (6)	0.034 (9)	0.000 (6)	0.000 (6)	0.004 (6)
C113	0.030 (9)	0.026 (8)	0.032 (11)	0.013 (7)	0.002 (8)	0.007 (7)
S21	0.0303 (9)	0.0273 (8)	0.0402 (11)	0.0139 (7)	0.0072 (8)	0.0094 (7)
O21	0.023 (2)	0.031 (2)	0.034 (3)	0.0133 (18)	0.002 (2)	0.0055 (19)
O22	0.025 (2)	0.037 (2)	0.039 (3)	0.0149 (19)	0.007 (2)	0.004 (2)
N21	0.025 (3)	0.022 (2)	0.029 (3)	0.009 (2)	0.001 (2)	0.002 (2)
N22	0.030 (3)	0.026 (3)	0.038 (3)	0.013 (2)	0.007 (3)	0.008 (2)
N23	0.039 (3)	0.031 (3)	0.045 (4)	0.021 (2)	0.013 (3)	0.012 (3)
C21	0.026 (3)	0.022 (3)	0.037 (4)	0.002 (3)	0.006 (3)	0.008 (3)
C22	0.017 (3)	0.027 (3)	0.035 (4)	0.001 (2)	0.004 (3)	0.006 (3)
C23	0.021 (3)	0.028 (3)	0.032 (4)	0.004 (3)	0.000 (3)	0.002 (3)
C24	0.027 (4)	0.035 (4)	0.043 (5)	0.006 (3)	0.005 (3)	0.001 (3)
C25	0.042 (4)	0.031 (3)	0.032 (4)	0.004 (3)	0.010 (3)	0.010 (3)
C26	0.035 (4)	0.021 (3)	0.047 (5)	0.003 (3)	0.007 (3)	0.010 (3)
C27	0.029 (4)	0.024 (3)	0.044 (5)	0.012 (3)	0.001 (3)	0.011 (3)
C28	0.031 (4)	0.028 (3)	0.035 (4)	0.012 (3)	0.002 (3)	0.007 (3)
C29	0.055 (5)	0.029 (3)	0.048 (5)	0.024 (3)	0.015 (4)	0.011 (3)
C210	0.036 (4)	0.028 (3)	0.051 (5)	0.012 (3)	0.004 (3)	0.003 (3)
C211	0.035 (4)	0.041 (4)	0.061 (6)	0.010 (3)	0.010 (4)	0.012 (3)
O3	0.048 (3)	0.043 (3)	0.057 (4)	0.025 (2)	0.014 (3)	0.016 (2)
C31	0.042 (4)	0.037 (4)	0.067 (6)	0.021 (3)	0.011 (4)	0.012 (4)

*Geometric parameters (Å, °)*

Cs1—O11 <sup>i</sup>	3.075 (4)	C110—C111	1.508 (15)
Cs1—O12 <sup>i</sup>	3.117 (5)	C111—H11C	0.9800
Cs1—C12 <sup>i</sup>	3.701 (6)	C111—H11D	0.9800
Cs1—C13 <sup>i</sup>	3.725 (6)	C111—H11E	0.9800
Cs1—C18	3.533 (6)	C112—H11F	0.9900
Cs1—O21	3.089 (4)	C112—H11G	0.9900
Cs1—O22	3.205 (5)	C112—C113	1.492 (15)
Cs1—N21 <sup>i</sup>	3.712 (5)	C113—Cs1 <sup>ii</sup>	3.862 (19)
Cs1—N22 <sup>i</sup>	3.622 (5)	C113—H11H	0.9800
Cs1—C28 <sup>i</sup>	3.578 (6)	C113—H11I	0.9800
Cs1—C210	3.686 (7)	C113—H11J	0.9800
Cs1—O3	3.065 (5)	S21—Cs1 <sup>ii</sup>	3.767 (2)
Cs1—H3	3.22 (8)	S21—C28	1.759 (6)
Fe1—Cs1 <sup>ii</sup>	4.2755 (18)	O21—C22	1.320 (8)

Fe1—S11	2.2686 (19)	O22—C23	1.391 (8)
Fe1—O11	1.904 (4)	O22—C210	1.451 (7)
Fe1—N11	1.933 (5)	N21—Cs1 <sup>ii</sup>	3.712 (5)
Fe1—S21	2.265 (2)	N21—N22	1.406 (7)
Fe1—O21	1.918 (4)	N21—C27	1.291 (8)
Fe1—N21	1.939 (5)	N22—Cs1 <sup>ii</sup>	3.622 (5)
S11—C18	1.742 (7)	N22—C28	1.293 (8)
O11—Cs1 <sup>ii</sup>	3.075 (4)	N23—H23	0.87 (2)
O11—C12	1.324 (7)	N23—C28	1.357 (8)
O12—Cs1 <sup>ii</sup>	3.117 (5)	N23—C29	1.462 (8)
O12—C13	1.393 (8)	C21—C22	1.420 (9)
O12—C110	1.423 (13)	C21—C26	1.392 (9)
O12—C112	1.346 (12)	C21—C27	1.439 (9)
N11—N12	1.398 (7)	C22—C23	1.412 (9)
N11—C17	1.302 (7)	C23—C24	1.378 (10)
N12—C18	1.314 (7)	C24—H24	0.9500
N13—H13	0.87 (2)	C24—C25	1.377 (10)
N13—C18	1.347 (8)	C25—H25	0.9500
N13—C19	1.459 (8)	C25—C26	1.385 (9)
C11—C12	1.414 (9)	C26—H26	0.9500
C11—C16	1.417 (8)	C27—H27	0.9500
C11—C17	1.433 (9)	C28—Cs1 <sup>ii</sup>	3.578 (6)
C12—Cs1 <sup>ii</sup>	3.701 (6)	C29—H29A	0.9800
C12—C13	1.405 (9)	C29—H29B	0.9800
C13—Cs1 <sup>ii</sup>	3.725 (6)	C29—H29C	0.9800
C13—C14	1.374 (9)	C210—H21A	0.9900
C14—H14	0.9500	C210—H21B	0.9900
C14—C15	1.398 (10)	C210—C211	1.501 (10)
C15—H15	0.9500	C211—H21C	0.9800
C15—C16	1.358 (10)	C211—H21D	0.9800
C16—H16	0.9500	C211—H21E	0.9800
C17—H17	0.9500	O3—H3	0.85 (2)
C19—H19A	0.9800	O3—C31	1.428 (9)
C19—H19B	0.9800	C31—H31A	0.9800
C19—H19C	0.9800	C31—H31B	0.9800
C110—H11A	0.9900	C31—H31C	0.9800
C110—H11B	0.9900		
O11 <sup>i</sup> —Cs1—O12 <sup>i</sup>	50.71 (12)	C15—C14—H14	120.1
O11 <sup>i</sup> —Cs1—C12 <sup>i</sup>	19.92 (11)	C14—C15—H15	120.3
O11 <sup>i</sup> —Cs1—C13 <sup>i</sup>	38.88 (13)	C16—C15—C14	119.4 (6)
O11 <sup>i</sup> —Cs1—C18	126.17 (14)	C16—C15—H15	120.3
O11 <sup>i</sup> —Cs1—O21	160.79 (10)	C11—C16—H16	119.0
O11 <sup>i</sup> —Cs1—O22	110.91 (11)	C15—C16—C11	122.0 (6)
O11 <sup>i</sup> —Cs1—N21 <sup>i</sup>	44.01 (10)	C15—C16—H16	119.0
O11 <sup>i</sup> —Cs1—N22 <sup>i</sup>	63.92 (11)	N11—C17—C11	125.3 (6)
O11 <sup>i</sup> —Cs1—C28 <sup>i</sup>	66.84 (13)	N11—C17—H17	117.3
O11 <sup>i</sup> —Cs1—C210	109.83 (13)	C11—C17—H17	117.3
O11 <sup>i</sup> —Cs1—H3	95.6 (11)	S11—C18—Cs1	84.4 (2)

O12 <sup>i</sup> —Cs1—C12 <sup>i</sup>	39.63 (14)	N12—C18—Cs1	91.4 (4)
O12 <sup>i</sup> —Cs1—C13 <sup>i</sup>	21.20 (15)	N12—C18—S11	124.8 (5)
O12 <sup>i</sup> —Cs1—C18	143.96 (14)	N12—C18—N13	118.3 (6)
O12 <sup>i</sup> —Cs1—O22	60.30 (12)	N13—C18—Cs1	94.4 (4)
O12 <sup>i</sup> —Cs1—N21 <sup>i</sup>	83.74 (12)	N13—C18—S11	116.9 (4)
O12 <sup>i</sup> —Cs1—N22 <sup>i</sup>	105.65 (13)	N13—C19—H19A	109.5
O12 <sup>i</sup> —Cs1—C28 <sup>i</sup>	115.91 (14)	N13—C19—H19B	109.5
O12 <sup>i</sup> —Cs1—C210	62.24 (15)	N13—C19—H19C	109.5
O12 <sup>i</sup> —Cs1—H3	94.3 (7)	H19A—C19—H19B	109.5
C12 <sup>i</sup> —Cs1—C13 <sup>i</sup>	21.81 (15)	H19A—C19—H19C	109.5
C12 <sup>i</sup> —Cs1—N21 <sup>i</sup>	63.92 (12)	H19B—C19—H19C	109.5
C12 <sup>i</sup> —Cs1—H3	80.9 (9)	O12—C110—H11A	108.9
C13 <sup>i</sup> —Cs1—H3	79.6 (6)	O12—C110—H11B	108.9
C18—Cs1—C12 <sup>i</sup>	122.28 (15)	O12—C110—C111	113.2 (10)
C18—Cs1—C13 <sup>i</sup>	128.55 (15)	H11A—C110—H11B	107.8
C18—Cs1—N21 <sup>i</sup>	118.74 (13)	C111—C110—H11A	108.9
C18—Cs1—N22 <sup>i</sup>	100.47 (13)	C111—C110—H11B	108.9
C18—Cs1—C28 <sup>i</sup>	82.85 (15)	C110—C111—H11C	109.5
C18—Cs1—C210	95.74 (16)	C110—C111—H11D	109.5
C18—Cs1—H3	49.9 (6)	C110—C111—H11E	109.5
O21—Cs1—O12 <sup>i</sup>	110.99 (12)	H11C—C111—H11D	109.5
O21—Cs1—C12 <sup>i</sup>	142.14 (12)	H11C—C111—H11E	109.5
O21—Cs1—C13 <sup>i</sup>	121.97 (13)	H11D—C111—H11E	109.5
O21—Cs1—C18	63.41 (14)	O12—C112—H11F	110.4
O21—Cs1—O22	51.74 (11)	O12—C112—H11G	110.4
O21—Cs1—N21 <sup>i</sup>	151.27 (10)	O12—C112—C113	106.5 (11)
O21—Cs1—N22 <sup>i</sup>	134.09 (11)	H11F—C112—H11G	108.6
O21—Cs1—C28 <sup>i</sup>	132.31 (13)	C113—C112—H11F	110.4
O21—Cs1—C210	50.96 (13)	C113—C112—H11G	110.4
O21—Cs1—H3	78.6 (14)	Cs1 <sup>ii</sup> —C113—H11H	159.8
O22—Cs1—C12 <sup>i</sup>	98.06 (13)	Cs1 <sup>ii</sup> —C113—H11I	50.8
O22—Cs1—C13 <sup>i</sup>	76.39 (14)	Cs1 <sup>ii</sup> —C113—H11J	78.0
O22—Cs1—C18	110.36 (13)	C112—C113—Cs1 <sup>ii</sup>	84.3 (9)
O22—Cs1—N21 <sup>i</sup>	129.96 (11)	C112—C113—H11H	109.5
O22—Cs1—N22 <sup>i</sup>	141.63 (12)	C112—C113—H11I	109.5
O22—Cs1—C28 <sup>i</sup>	162.18 (13)	C112—C113—H11J	109.5
O22—Cs1—C210	22.98 (13)	H11H—C113—H11I	109.5
O22—Cs1—H3	92.3 (16)	H11H—C113—H11J	109.5
N21 <sup>i</sup> —Cs1—C13 <sup>i</sup>	80.59 (13)	H11I—C113—H11J	109.5
N21 <sup>i</sup> —Cs1—H3	126.2 (16)	Fe1—S21—Cs1 <sup>ii</sup>	86.49 (6)
N22 <sup>i</sup> —Cs1—C12 <sup>i</sup>	83.55 (12)	C28—S21—Cs1 <sup>ii</sup>	70.2 (2)
N22 <sup>i</sup> —Cs1—C13 <sup>i</sup>	102.00 (13)	C28—S21—Fe1	94.3 (2)
N22 <sup>i</sup> —Cs1—N21 <sup>i</sup>	22.07 (11)	Fe1—O21—Cs1	122.27 (19)
N22 <sup>i</sup> —Cs1—C210	163.06 (15)	C22—O21—Cs1	110.5 (3)
N22 <sup>i</sup> —Cs1—H3	125.5 (16)	C22—O21—Fe1	122.8 (4)
C28 <sup>i</sup> —Cs1—C12 <sup>i</sup>	83.85 (14)	C23—O22—Cs1	105.1 (3)
C28 <sup>i</sup> —Cs1—C13 <sup>i</sup>	105.22 (15)	C23—O22—C210	115.9 (5)
C28 <sup>i</sup> —Cs1—N21 <sup>i</sup>	35.96 (13)	C210—O22—Cs1	97.5 (4)
C28 <sup>i</sup> —Cs1—N22 <sup>i</sup>	20.68 (13)	Fe1—N21—Cs1 <sup>ii</sup>	92.97 (16)

C28 <sup>i</sup> —Cs1—C210	173.95 (15)	N22—N21—Cs1 <sup>ii</sup>	75.4 (3)
C28 <sup>i</sup> —Cs1—H3	105.4 (16)	N22—N21—Fe1	121.3 (4)
C210—Cs1—C12 <sup>i</sup>	92.00 (15)	C27—N21—Cs1 <sup>ii</sup>	100.8 (4)
C210—Cs1—C13 <sup>i</sup>	71.05 (16)	C27—N21—Fe1	123.8 (4)
C210—Cs1—N21 <sup>i</sup>	144.62 (14)	C27—N21—N22	114.9 (5)
C210—Cs1—H3	69.5 (15)	N21—N22—Cs1 <sup>ii</sup>	82.6 (3)
O3—Cs1—O11 <sup>i</sup>	83.41 (12)	C28—N22—Cs1 <sup>ii</sup>	77.8 (4)
O3—Cs1—O12 <sup>i</sup>	79.58 (14)	C28—N22—N21	113.1 (5)
O3—Cs1—C12 <sup>i</sup>	67.03 (13)	C28—N23—H23	121 (5)
O3—Cs1—C13 <sup>i</sup>	64.40 (14)	C28—N23—C29	120.9 (6)
O3—Cs1—C18	64.93 (14)	C29—N23—H23	110 (5)
O3—Cs1—O21	87.47 (13)	C22—C21—C27	122.1 (6)
O3—Cs1—O22	88.26 (13)	C26—C21—C22	119.8 (6)
O3—Cs1—N21 <sup>i</sup>	120.17 (13)	C26—C21—C27	118.1 (6)
O3—Cs1—N22 <sup>i</sup>	126.29 (13)	O21—C22—Cs1	50.3 (3)
O3—Cs1—C28 <sup>i</sup>	108.60 (15)	O21—C22—C21	124.3 (6)
O3—Cs1—C210	65.61 (15)	O21—C22—C23	118.1 (6)
O3—Cs1—H3	15.2 (6)	C21—C22—Cs1	140.5 (4)
S11—Fe1—Cs1 <sup>ii</sup>	141.53 (5)	C23—C22—Cs1	81.3 (4)
O11—Fe1—Cs1 <sup>ii</sup>	40.12 (12)	C23—C22—C21	117.5 (6)
O11—Fe1—S11	177.83 (14)	O22—C23—Cs1	54.3 (3)
O11—Fe1—N11	94.37 (19)	O22—C23—C22	120.9 (6)
O11—Fe1—S21	92.56 (14)	C22—C23—Cs1	77.2 (4)
O11—Fe1—O21	88.49 (18)	C24—C23—Cs1	140.9 (4)
O11—Fe1—N21	85.55 (18)	C24—C23—O22	117.9 (6)
N11—Fe1—Cs1 <sup>ii</sup>	119.22 (14)	C24—C23—C22	121.1 (6)
N11—Fe1—S11	85.55 (15)	C23—C24—H24	119.6
N11—Fe1—S21	94.17 (16)	C25—C24—C23	120.9 (7)
N11—Fe1—N21	178.9 (2)	C25—C24—H24	119.6
S21—Fe1—Cs1 <sup>ii</sup>	61.59 (5)	C24—C25—H25	120.2
S21—Fe1—S11	89.61 (7)	C24—C25—C26	119.5 (7)
O21—Fe1—Cs1 <sup>ii</sup>	118.58 (13)	C26—C25—H25	120.2
O21—Fe1—S11	89.34 (13)	C21—C26—H26	119.5
O21—Fe1—N11	87.4 (2)	C25—C26—C21	121.1 (7)
O21—Fe1—S21	178.01 (13)	C25—C26—H26	119.5
O21—Fe1—N21	93.7 (2)	N21—C27—C21	126.2 (6)
N21—Fe1—Cs1 <sup>ii</sup>	60.11 (14)	N21—C27—H27	116.9
N21—Fe1—S11	94.57 (15)	C21—C27—H27	116.9
N21—Fe1—S21	84.71 (16)	S21—C28—Cs1 <sup>ii</sup>	82.2 (2)
Fe1—S11—Cs1	90.32 (6)	N22—C28—Cs1 <sup>ii</sup>	81.5 (4)
C18—S11—Cs1	68.4 (2)	N22—C28—S21	124.3 (5)
C18—S11—Fe1	94.6 (2)	N22—C28—N23	119.8 (6)
Fe1—O11—Cs1 <sup>ii</sup>	116.35 (16)	N23—C28—Cs1 <sup>ii</sup>	104.0 (4)
C12—O11—Cs1 <sup>ii</sup>	107.8 (3)	N23—C28—S21	115.8 (5)
C12—O11—Fe1	126.1 (4)	N23—C29—H29A	109.5
C13—O12—Cs1 <sup>ii</sup>	104.8 (4)	N23—C29—H29B	109.5
C13—O12—C110	120.8 (6)	N23—C29—H29C	109.5
C110—O12—Cs1 <sup>ii</sup>	133.0 (6)	H29A—C29—H29B	109.5
C112—O12—Cs1 <sup>ii</sup>	122.2 (6)	H29A—C29—H29C	109.5

C112—O12—C13	114.7 (7)	H29B—C29—H29C	109.5
N12—N11—Fe1	121.8 (3)	Cs1—C210—H21A	72.6
C17—N11—Fe1	125.4 (4)	Cs1—C210—H21B	78.0
C17—N11—N12	112.7 (5)	O22—C210—Cs1	59.6 (3)
N11—N12—Cs1	92.7 (3)	O22—C210—H21A	109.2
C18—N12—Cs1	68.4 (3)	O22—C210—H21B	109.2
C18—N12—N11	113.3 (5)	O22—C210—C211	112.1 (6)
C18—N13—H13	120 (5)	H21A—C210—H21B	107.9
C18—N13—C19	123.2 (5)	C211—C210—Cs1	171.0 (5)
C19—N13—H13	116 (5)	C211—C210—H21A	109.2
C12—C11—C16	119.0 (6)	C211—C210—H21B	109.2
C12—C11—C17	123.6 (5)	C210—C211—H21C	109.5
C16—C11—C17	117.4 (6)	C210—C211—H21D	109.5
O11—C12—Cs1 <sup>ii</sup>	52.3 (3)	C210—C211—H21E	109.5
O11—C12—C11	124.2 (6)	H21C—C211—H21D	109.5
O11—C12—C13	118.4 (6)	H21C—C211—H21E	109.5
C11—C12—Cs1 <sup>ii</sup>	141.1 (4)	H21D—C211—H21E	109.5
C13—C12—Cs1 <sup>ii</sup>	80.1 (4)	Cs1—O3—H3	93 (6)
C13—C12—C11	117.4 (5)	C31—O3—Cs1	129.1 (4)
O12—C13—Cs1 <sup>ii</sup>	54.0 (3)	C31—O3—H3	111 (6)
O12—C13—C12	116.2 (5)	O3—C31—H31A	109.5
C12—C13—Cs1 <sup>ii</sup>	78.1 (3)	O3—C31—H31B	109.5
C14—C13—Cs1 <sup>ii</sup>	138.2 (5)	O3—C31—H31C	109.5
C14—C13—O12	121.3 (7)	H31A—C31—H31B	109.5
C14—C13—C12	122.5 (7)	H31A—C31—H31C	109.5
C13—C14—H14	120.1	H31B—C31—H31C	109.5
C13—C14—C15	119.7 (7)		
Cs1—S11—C18—N12	-87.8 (5)	C13—O12—C110—C111	-150.5 (9)
Cs1—S11—C18—N13	92.1 (5)	C13—O12—C112—C113	-167.5 (9)
Cs1 <sup>ii</sup> —O11—C12—C11	-131.7 (5)	C13—C14—C15—C16	-2.1 (11)
Cs1 <sup>ii</sup> —O11—C12—C13	48.2 (6)	C14—C15—C16—C11	1.7 (10)
Cs1 <sup>ii</sup> —O12—C13—C12	-50.2 (6)	C16—C11—C12—Cs1 <sup>ii</sup>	106.4 (7)
Cs1 <sup>ii</sup> —O12—C13—C14	129.6 (6)	C16—C11—C12—O11	176.8 (6)
Cs1 <sup>ii</sup> —O12—C110—C111	45.2 (15)	C16—C11—C12—C13	-3.0 (9)
Cs1 <sup>ii</sup> —O12—C112—C113	-39.0 (12)	C16—C11—C17—N11	175.3 (6)
Cs1—N12—C18—S11	84.1 (5)	C17—N11—N12—Cs1	108.1 (5)
Cs1—N12—C18—N13	-95.8 (5)	C17—N11—N12—C18	175.6 (5)
Cs1 <sup>ii</sup> —C12—C13—O12	39.4 (5)	C17—C11—C12—Cs1 <sup>ii</sup>	-76.6 (8)
Cs1 <sup>ii</sup> —C12—C13—C14	-140.3 (7)	C17—C11—C12—O11	-6.2 (10)
Cs1 <sup>ii</sup> —C13—C14—C15	-110.5 (8)	C17—C11—C12—C13	174.0 (6)
Cs1 <sup>ii</sup> —S21—C28—N22	-74.2 (5)	C17—C11—C16—C15	-176.3 (6)
Cs1 <sup>ii</sup> —S21—C28—N23	101.9 (5)	C19—N13—C18—Cs1	-96.8 (6)
Cs1—O21—C22—C21	-130.3 (5)	C19—N13—C18—S11	177.3 (5)
Cs1—O21—C22—C23	48.3 (6)	C19—N13—C18—N12	-2.8 (9)
Cs1—O22—C23—C22	-41.5 (6)	C110—O12—C13—Cs1 <sup>ii</sup>	-168.2 (9)
Cs1—O22—C23—C24	134.5 (5)	C110—O12—C13—C12	141.6 (9)
Cs1—O22—C210—C211	176.2 (5)	C110—O12—C13—C14	-38.6 (11)
Cs1 <sup>ii</sup> —N21—N22—C28	73.3 (5)	C110—O12—C112—C113	82.2 (12)

Cs1 <sup>ii</sup> —N21—C27—C21	-100.4 (6)	C112—O12—C13—Cs1 <sup>ii</sup>	136.7 (8)
Cs1 <sup>ii</sup> —N22—C28—S21	74.5 (5)	C112—O12—C13—C12	86.5 (9)
Cs1 <sup>ii</sup> —N22—C28—N23	-101.4 (6)	C112—O12—C13—C14	-93.7 (9)
Cs1—C22—C23—O22	33.4 (5)	C112—O12—C110—C111	-53.4 (11)
Cs1—C22—C23—C24	-142.4 (5)	O21—C22—C23—Cs1	-35.6 (4)
Cs1—C23—C24—C25	-108.7 (8)	O21—C22—C23—O22	-2.1 (8)
Fe1—S11—C18—Cs1	88.53 (10)	O21—C22—C23—C24	-178.0 (5)
Fe1—S11—C18—N12	0.8 (6)	O22—C23—C24—C25	-175.3 (5)
Fe1—S11—C18—N13	-179.4 (5)	N21—N22—C28—Cs1 <sup>ii</sup>	-76.3 (4)
Fe1—O11—C12—Cs1 <sup>ii</sup>	144.3 (5)	N21—N22—C28—S21	-1.8 (8)
Fe1—O11—C12—C11	12.6 (9)	N21—N22—C28—N23	-177.7 (5)
Fe1—O11—C12—C13	-167.5 (4)	N22—N21—C27—C21	-179.1 (6)
Fe1—N11—N12—Cs1	-70.0 (4)	C21—C22—C23—Cs1	143.2 (5)
Fe1—N11—N12—C18	-2.4 (7)	C21—C22—C23—O22	176.6 (5)
Fe1—N11—C17—C11	2.3 (9)	C21—C22—C23—C24	0.8 (8)
Fe1—S21—C28—Cs1 <sup>ii</sup>	84.70 (10)	C22—C21—C26—C25	0.1 (9)
Fe1—S21—C28—N22	10.6 (6)	C22—C21—C27—N21	-12.1 (10)
Fe1—S21—C28—N23	-173.4 (5)	C22—C23—C24—C25	0.7 (9)
Fe1—O21—C22—Cs1	156.7 (5)	C23—O22—C210—Cs1	-110.9 (5)
Fe1—O21—C22—C21	26.4 (7)	C23—O22—C210—C211	65.4 (7)
Fe1—O21—C22—C23	-155.0 (4)	C23—C24—C25—C26	-1.7 (9)
Fe1—N21—N22—Cs1 <sup>ii</sup>	-84.5 (3)	C24—C25—C26—C21	1.3 (9)
Fe1—N21—N22—C28	-11.2 (7)	C26—C21—C22—Cs1	110.3 (7)
Fe1—N21—C27—C21	0.7 (9)	C26—C21—C22—O21	177.5 (5)
O11—C12—C13—Cs1 <sup>ii</sup>	-36.8 (5)	C26—C21—C22—C23	-1.1 (8)
O11—C12—C13—O12	2.6 (9)	C26—C21—C27—N21	167.6 (6)
O11—C12—C13—C14	-177.1 (6)	C27—N21—N22—Cs1 <sup>ii</sup>	95.3 (5)
O12—C13—C14—C15	-180.0 (6)	C27—N21—N22—C28	168.6 (5)
O12—C112—C113—Cs1 <sup>ii</sup>	25.6 (8)	C27—C21—C22—Cs1	-70.0 (8)
N11—N12—C18—Cs1	-83.3 (4)	C27—C21—C22—O21	-2.8 (9)
N11—N12—C18—S11	0.8 (8)	C27—C21—C22—C23	178.6 (5)
N11—N12—C18—N13	-179.1 (5)	C27—C21—C26—C25	-179.6 (6)
N12—N11—C17—C11	-175.7 (5)	C29—N23—C28—Cs1 <sup>ii</sup>	-98.9 (6)
C11—C12—C13—Cs1 <sup>ii</sup>	143.1 (5)	C29—N23—C28—S21	173.1 (5)
C11—C12—C13—O12	-177.5 (6)	C29—N23—C28—N22	-10.7 (10)
C11—C12—C13—C14	2.7 (10)	C210—O22—C23—Cs1	106.3 (5)
C12—C11—C16—C15	0.9 (10)	C210—O22—C23—C22	64.9 (7)
C12—C11—C17—N11	-1.8 (10)	C210—O22—C23—C24	-119.2 (6)
C12—C13—C14—C15	-0.2 (11)		

Symmetry codes: (i)  $x+1, y, z$ ; (ii)  $x-1, y, z$ .

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N13—H13 $\cdots$ S11 <sup>iii</sup>	0.87 (2)	2.97 (6)	3.505 (6)	122 (5)
N23—H23 $\cdots$ S21 <sup>iv</sup>	0.87 (2)	2.70 (5)	3.416 (6)	141 (6)
O3—H3 $\cdots$ N12	0.85 (2)	2.04 (4)	2.852 (7)	160 (8)

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