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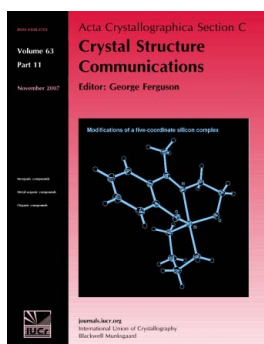
# An ethanol-solvated centrosymmetric dimer of bismuth(III) and thiosaccharinate resulting from 'semicoordination' contacts

**Mariana Dennehy, Ricardo M. Ferullo, Eleonora Freire and Ricardo Baggio***Acta Cryst.* (2014). **C70**, 627–631

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# An ethanol-solvated centrosymmetric dimer of bismuth(III) and thiosaccharinate resulting from 'semicoordination' contacts

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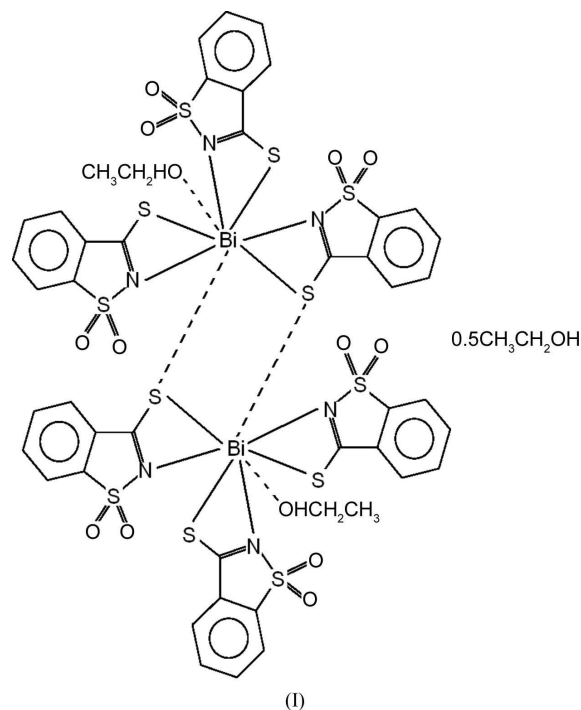
In the title compound, bis( $\mu$ -1,1-dioxo-1,2-benzothiazole-3-thiolato)- $\kappa^3N,S,S$ ;  $\kappa^3S:N,S$ -bis[(1,1-dioxo-1,2-benzothiazole-3-thiolato- $\kappa^2N,S$ )(ethanol- $\kappa O$ )bismuth(III)] ethanol hemisolvate,  $[\text{Bi}_2(\text{C}_7\text{H}_4\text{NO}_2\text{S}_2)_6(\text{C}_2\text{H}_5\text{OH})_2] \cdot 0.5\text{C}_2\text{H}_5\text{OH}$ , three independent thiosaccharinate (tsac) anions chelate the metal centre through the endocyclic N and exocyclic S atoms. The complex also presents two 'semicoordination' contacts, one from a pendant ethanol solvent molecule and a second one from an S atom of a centrosymmetrically related molecule. This latter interaction complements two  $\pi$ - $\pi$  interactions between tsac rings to form a dimeric entity which is the elemental unit that builds up the crystal structure. These dinuclear units are connected to each other *via* a second type of  $\pi$ - $\pi$  interaction, generating chains along  $[1\bar{1}1]$ . Two ethanol molecules, one of them of full occupancy at a general position and semicoordinated to the central cation, and a second one depleted and disordered around a symmetry centre, stabilize the structure. The complex was studied theoretically and the vibrational assignments were confirmed by employing theoretical density functional theory (DFT) methods.

**Keywords:** crystal structure; bismuth compounds; thiones; DFT calculations; thiosaccharin.

## 1. Introduction

Thionates, *i.e.* anions produced by the deprotonation of heterocyclic thioamides, can coordinate to metals to produce a variety of structures, from simple mononuclear to complex polynuclear species. Over the years, we have developed a sustained interest in the coordination behaviour of hetero-

cyclic thiones in general, and thiosaccharine [the thione form of saccharin, 1,2-benzothiazole-3(2*H*)-thione 1,1-dioxide,  $\text{C}_6\text{H}_4\text{SO}_2\text{NHCS}$ ] in particular. Like other thioamides, it is a versatile ligand. Its anion (hereinafter tsac) has the ability to coordinate to metal centres in many different ways (Dennehy *et al.*, 2007). We have studied metal thiosaccharinates with heavy metals (Dennehy *et al.*, 2012, 2011, and references therein). Because bismuth compounds are known to be safe to humans, in recent decades efforts have been made to synthesize bismuth complexes (Briand & Burford, 2000). Within the chemistry of  $\text{Bi}^{\text{III}}$ , bismuth(III) thiolates (containing a Bi-S bond) are some of the most studied bismuth compounds. Exploring the coordination chemistry of bismuth could be advantageous in synthesizing biologically important compounds. Therefore, the structural characterization of bismuth complexes is interesting and meaningful (Andrews *et al.*, 2011).



Despite the great number of metal-thionate complexes reported in the last decade or so, bismuth(III) thiosaccharinates have not received much attention, and the only crystal structure reported so far of a bismuth(III) thiosaccharinate complex is  $[\text{Ph}_2\text{Bi}(\text{tsac})]$  (Andrews *et al.*, 2011). In the same paper, the authors claim to have synthesized bismuth thiosaccharinate,  $\text{Bi}(\text{tsac})_3$ , but they were unsuccessful in their attempts to crystallize it, so no direct crystallographic evidence of its structure is available. In spite of this, the authors presented the complex as a polymeric chain,  $[\text{Bi}(\text{tsac})_3]_n$ , and based on the analysis of their vibrational data they proposed a coordination mode through the exocyclic S atom. In trying to elucidate this crystal structure, we have developed a different synthetic pathway which ended up with the  $\text{Bi}(\text{tsac})_3$  phase reported here, (I). Accordingly, this is the first structural work on a Bi-tsac complex crystallized without the presence of any facilitator ancillary ligand.

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## 2. Experimental

### 2.1. Synthesis and crystallization

Solid thiosaccharin (Htsac) in its  $\alpha$ -form was prepared by the reaction of saccharin (3.00 g; Mallindkrodt Pharmaceuticals) with Lawesson's reagent (3.64 g; Fluka) in toluene (25 ml), following the technique published by Schibye *et al.* (1978), and characterized by melting point and IR spectroscopic analysis (Grupče *et al.*, 1994). The title complex, (I), was synthesized by dropwise addition of a yellow solution of Htsac (15 mg, 0.075 mmol) in ethanol–acetone (1:1 *v/v*, 5 ml) to another solution of  $\text{Bi}(\text{NO}_3)_3$  (10 mg, 0.025 mmol of  $\text{Bi}^{3+}$ ) in ethanol–acetone (4 ml) with mechanical stirring. A saturated solution of the complex in ethanol–acetone was allowed to evaporate slowly at room temperature. After 24 h, yellow single crystals of (I) suitable for X-ray diffraction had formed. The crystals were washed with diethyl ether and were air stable.

The IR spectra were obtained in a KBr dispersion. The IR spectrum of (I) confirms the presence of thiosaccharinate anions and molecules of the crystallization solvent (Dennehy *et al.*, 2007). Selected anion bands for (I) ( $\nu$ ,  $\text{cm}^{-1}$ ): 1472 (*m*), 1409 (*m*), 1341/1326 (*m*), 1239 (*m*), 1180/1167 (*s*), 1016 (*w*), 997 (*m*), 794 (*m*), 736 (*w*), 627 (*w*), 586 (*m*), 557 (*m*), 532 (*m*), 425 (*m*). Selected anion bands for (II) [as reported by Andrews *et al.* (2011)] ( $\nu$ ,  $\text{cm}^{-1}$ ): 1325 (*m*), 1419 (*m*), 1156 (*m*), 1001 (*m*), 805 (*w*).

### 2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. There are two ethanol solvent molecules in the structure, one with full occupancy at a general position and a second, depleted and disordered around a symmetry centre, whose occupation factor was fixed at 0.25. Due to problems in the independent refinement of this

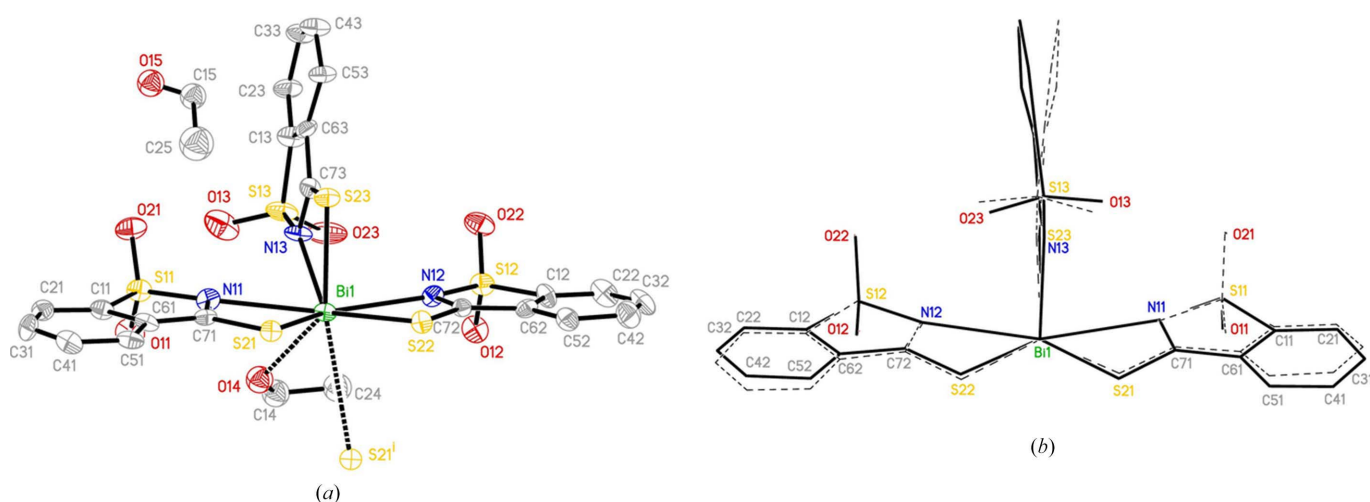
**Table 1**

Experimental details.

Crystal data	
Chemical formula	$[\text{Bi}_2(\text{C}_7\text{H}_4\text{NO}_2\text{S}_2)_6(\text{C}_2\text{H}_6\text{O})_2] \cdot 0.5\text{C}_2\text{H}_6\text{O}$
$M_r$	1722.52
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	295
$a, b, c$ (Å)	8.1979 (6), 14.0424 (16), 14.1697 (10)
$\alpha, \beta, \gamma$ (°)	70.779 (8), 80.031 (6), 79.353 (8)
$V$ (Å <sup>3</sup> )	1502.6 (2)
$Z$	1
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	6.33
Crystal size (mm)	0.18 × 0.05 × 0.05
Data collection	
Diffractometer	Oxford Gemini S Ultra CCD area-detector diffractometer
Absorption correction	Multi-scan ( <i>CrysAlis PRO</i> ; Oxford Diffraction, 2009)
$T_{\text{min}}, T_{\text{max}}$	0.68, 0.74
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	19073, 7115, 5631
$R_{\text{int}}$	0.102
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.688
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.068, 0.189, 1.23
No. of reflections	7115
No. of parameters	371
No. of restraints	3
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	2.75, -1.38

Computer programs: *CrysAlis PRO* (Oxford Diffraction, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXTL* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2003).

latter ethanol molecule, it was refined with similarity restraints to the fully occupied molecule, both in coordinates and in anisotropic displacement parameters. H atoms in fully occupied hosts were identified in a difference Fourier map, but were further idealized and allowed to ride, with methyl  $\text{C}-\text{H} = 0.96$  Å and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ , and aromatic  $\text{C}-\text{H} =$


**Figure 1**

(a) A molecular view of the monomeric unit in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. Dashed lines indicate the semicoordination bonds. (b) A least-squares fit of a monomer and its pseudo-mirror-related image. [Symmetry code: (i)  $-x + 1, -y + 2, -z + 1$ .]

**Table 2**  
 Selected bond distances (Å).

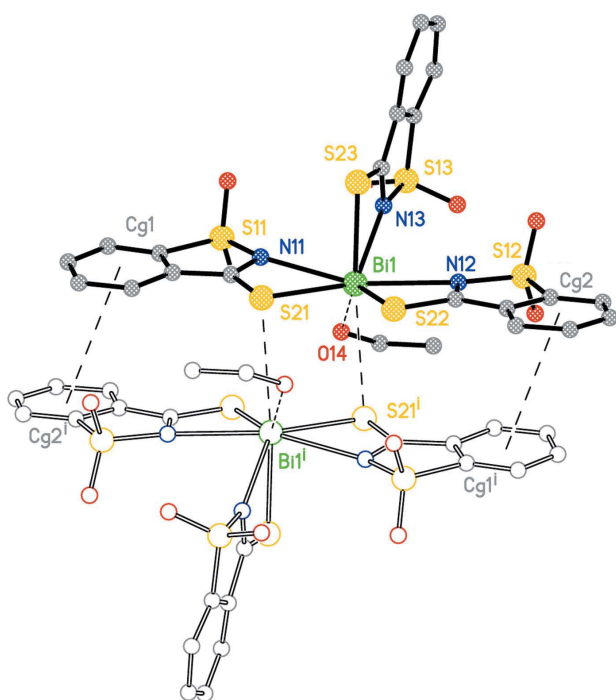
	Experimental	Calculated
Bi1—S23	2.613 (3)	2.664
Bi1—N13	2.723 (8)	2.574
Bi1—N12	2.617 (9)	2.580
Bi1—N11	2.661 (9)	2.595
Bi1—S21	2.701 (2)	2.854
Bi1—S22	2.715 (3)	2.849
Bi1—O14	2.926 (9)	2.747
Bi1—S21 <sup>i</sup>	3.364 (3)	

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

0.93 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . As expected, the presence of the heavy  $\text{Bi}^{3+}$  cation produced some disruptive effects, *viz.* large peaks in the difference maps (2.76 and 2.54  $e \text{ \AA}^{-3}$ ) at distances slightly less than 1 Å from the metal centre, and ill-defined methyl H atoms, which oscillated during refinement and had finally to be kept fixed at a reasonable position.

### 3. Results and discussion

The monomeric unit of (I) is presented in Fig. 1(a), which shows the most relevant characteristics of the Bi coordination environment. To a first-order approximation, this is constituted by three tsac anions acting in a  $\kappa^2N,S$ -chelating mode, with coordination lengths spanning the ranges 2.613 (3)–2.715 (3) (Bi—S) and 2.617 (9)–2.723 (8) Å (Bi—N) (for more details see Table 2), and S—Bi—N chelating angles lying between 58.18 (16) and 59.04 (18)° (for more details see Table 3). The three ligands are disposed in a rather symmetric

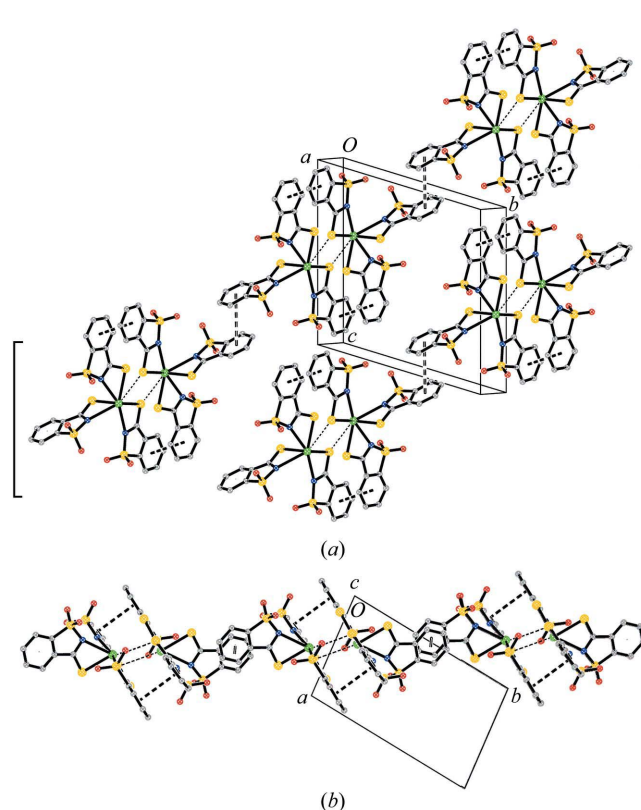

**Figure 2**

The centrosymmetric dimeric unit of (I). Dashed lines indicate the various intermolecular interactions. Cg indicates a ring centroid; see Table 4 for definitions. [Symmetry code: (i)  $-x + 1, -y + 2, -z + 1$ .]

**Table 3**  
 Selected bond angles (°).

	Experimental	Calculated
S23—Bi1—N12	84.7 (2)	82.78
S23—Bi1—N11	83.9 (2)	85.30
N12—Bi1—N11	160.0 (3)	160.1
S23—Bi1—S21	90.68 (8)	91.34
N12—Bi1—S21	138.42 (19)	138.4
N11—Bi1—S21	58.18 (16)	57.58
S23—Bi1—S22	88.00 (9)	91.35
N12—Bi1—S22	58.57 (19)	57.59
N11—Bi1—S22	137.17 (16)	138.43
S21—Bi1—S22	80.01 (8)	81.37
S23—Bi1—N13	59.04 (18)	58.29
N12—C72—C62	116.1 (8)	115.39
N12—C72—S22	118.4 (8)	119.97
C62—C72—S22	125.5 (8)	124.64
O13—S13—O23	118.8 (7)	119.47

fashion, mimicking a mirror plane relating units tsac1 and tsac2 [mean least-squares deviation for these groups = 0.14 (2) Å; the number identifies the different tsac moieties and corresponds to the trailing number in the atom and centroid labels] and leaving tsac3 slightly offset from its pseudo-mirror image [by 0.37 (9) Å; Fig. 1b]. The three tsac ligands (O atoms excluded) are planar [maximum deviations from the least-squares plane are 0.021 (9) Å for atom C61 (tsac1), 0.021 (12) Å for atom C22 (tsac2) and 0.052 (11) Å for


**Figure 3**

(a) A packing view of (I). Shown between brackets and running from bottom left to upper right is one isolated  $[1\bar{1}1]$  chain. (b) A complementary projection rotated 90° from the view in (a), showing the resulting (110) planes. Dashed lines indicate the various intermolecular interactions.

**Table 4**
 $\pi$ - $\pi$  contacts ( $\text{\AA}$ ,  $^\circ$ ).

$Cg1$  is the centroid of the C11–C61 ring,  $Cg2$  that of the C12–C62 ring and  $Cg3$  that of the C13–C63 ring. CCD is the centroid-to-centroid distance, DA the dihedral angle between rings, SA the slippage angle or (mean) angle subtended by the intercentroid vector to the plane normals, and IPD the interplanar distance or (mean) distance from one plane to the neighbouring centroid; for details, see Janiak (2000).

Group 1...group 2	CCD ( $\text{\AA}$ )	DA ( $^\circ$ )	SA ( $^\circ$ )	IPD ( $\text{\AA}$ )
$Cg1 \cdots Cg2^i$	3.765 (7)	5.1 (6)	22.4 (2)	3.510 (5)
$Cg3 \cdots Cg3^{ii}$	4.077 (7)	0	28.3	3.590 (5)

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

**Table 5**

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O14–H14...O11	0.86	2.34	3.185 (14)	166
C21–H21...O21 <sup>i</sup>	0.93	2.33	3.192 (16)	153
C33–H33...O22 <sup>ii</sup>	0.93	2.55	3.454 (17)	165
C41–H41...O12 <sup>iii</sup>	0.93	2.56	3.475 (14)	166

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

atom C63 (tsac3)], while the interplanar angles in the coordination polyhedron are 4.5 (3) (tsac1–tsac2), 97.8 (2) (tsac1–tsac3) and 98.2 (2) $^\circ$  (tsac2–tsac3).

Within this picture, the formal coordination number of Bi would be 6, but there are in addition two rather long ‘semi-coordination’ distances to be taken into account (dashed lines in Fig. 2), a Bi...O one involving the fully occupied ethanol molecule [ $Bi \cdots O14 = 2.926$  (9)  $\text{\AA}$ ] and one between two centrosymmetrically related complex molecules [ $Bi \cdots S21^i = 3.364$  (3)  $\text{\AA}$ ; symmetry code: (i)  $-x + 1, -y + 2, -z + 1$ ]. Even though they are unusually long for standard Bi...S(O) distances, simple inspection of Fig. 1(a) discloses the need to take these interactions into account, given the rather bizarre geometry around the metal that the chelating ligands alone give rise to; a very crude idea is given by the baricentre of the three S/N pairs, which lies 0.787 (2)  $\text{\AA}$  from the cation. A rather more elaborate argument is provided by a bond-valence calculation (Brown, 2002), as performed with PLATON (Spek, 2009), which gives for atom Bi1, in the biased sixfold coordination, a bond valence of 2.744 valence units (v.u.) (expected value 3.00 v.u.), while the complete eight-coordination raises this value to 2.974 v.u.

The above-mentioned Bi...S21<sup>i</sup> contact, together with two  $\pi$ - $\pi$  interactions involving the tsac1 and tsac2 rings (Table 4, first entry), define the dimeric entities represented in Fig. 2 and which can be considered the supramolecular unit from which the crystal structure builds up. This dimeric binding leads to a Bi...Bi<sup>i</sup> distance of 4.3846 (8)  $\text{\AA}$ .

These dimers are in turn connected by a second type of  $\pi$ - $\pi$  interaction, now involving only symmetry-related tsac3 rings (Table 4, second entry). This leads to the formation of chains running along  $[1\bar{1}1]$ , shown in Fig. 3(a).

Finally, there are a few C–H...O contacts (Table 5, entries 2–4) linking the chains into a planar array parallel to (110)

**Table 6**

 Selected FT–IR spectroscopic bands ( $\text{cm}^{-1}$ ).

Definitions:  $\nu$  = stretching,  $\delta$  = in-plane deformation, as = asymmetric, s = symmetric,  $\varphi$  = benzene ring, s = strong, m = medium and w = weak.

	Experimental	Calculated
$\nu(\text{CN}), \nu(\varphi\text{S})$	1409 (m)	1441/1446
$\nu_{\text{as}}(\text{SO}_2)$	1341/1326 (m)	1312/1289
$\nu_{\text{as}}(\varphi\text{CN}), \delta(\text{CH})$	1239 (m)	1271
$\nu_s(\text{SO}_2), \delta(\varphi\text{SN})$	1180/1167 (s)	1114/1125
$\nu(\text{CC}) \nu(\text{CO}) \text{EtOH}$	1038 (w)	1055
$\nu(\text{CS}), \delta(\text{CNS})$	997 (m)/1016 (w)	1014/1019
$\nu(\text{NS}), \delta(\text{CCC})$	794 (m)	791

(Fig. 3b). Interplanar contacts are of a much weaker van der Waals nature. The first entry in Table 5 corresponds to an interaction between the fully occupied ethanol molecule and the molecular core, involving the same OH group which ‘semicoordinates’ to Bi1.

As mentioned above, Andrews *et al.* (2011) reported the synthesis of a bismuth thiosaccharinate phase, (II), which the authors, through a spectroscopic characterization, finally formulated as a one-dimensional polymer,  $[\text{Bi}(\text{tsac})_3]_n$ . Unfortunately, no crystallographic data (neither powder nor single-crystal X-ray diffraction) are available for this compound to be compared with the corresponding data for (I). However, comparison of the vibrational frequencies in both compounds (see *Experimental* section for details) suggests the weakly dimeric compound presented here, (I), to be different from that reported for (II).

In order to check the assignments of the vibrational frequencies, quantum-mechanical calculations were performed using density functional theory (DFT) analysis at the B3LYP/Lan12dz(Bi);6-31G\*\*(CHNOS) level. Computations were carried out using the GAUSSIAN09 suite of programs (Frisch *et al.*, 2010) running under LINUX. The calculated parameters reproduced the crystal structure reasonably (see comparative values in Tables 2 and 3). As previously reported by Soran *et al.* (2010), calculated Bi–S distances undergo elongations and the Bi–N distances are correspondingly shortened. The computed bond angles are very accurate. The theoretical vibrational analysis performed with the optimized geometry of the complex at the DFT level yields vibrational spectra in good agreement with the experimental spectra (Table 6). The most interesting bands to be observed in these complexes are those related to the five-membered ring of the thiosaccharinate anions, located between 1500 and 400  $\text{cm}^{-1}$ . The absorption band at 794  $\text{cm}^{-1}$ , attributable to the  $\nu(\text{NS})+\delta(\text{CCC})$  vibration (C–N stretching vibrations coupled with aromatic ring motions), has a computed value of 791  $\text{cm}^{-1}$ . The experimental  $\nu(\text{CS})+\delta(\text{CNS})$  at 997 (m)/1016 (w)  $\text{cm}^{-1}$  has a calculated frequency of 1014/1019  $\text{cm}^{-1}$ . Thus, the experimental-to-computed frequency ratio is good when compared with literature values.

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tometer. MD and RMF thank SGCyT-UNS for financial support of Project M24/Q025.

Supporting information for this paper is available from the IUCr electronic archives (Reference: sk3545).

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## supplementary materials

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## An ethanol-solvated centrosymmetric dimer of bismuth(III) and thio-saccharinate resulting from 'semicoordination' contacts

Mariana Dennehy, Ricardo M. Ferullo, Eleonora Freire and Ricardo Baggio

### Computing details

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO* (Oxford Diffraction, 2009); data reduction: *CrysAlis PRO* (Oxford Diffraction, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2003).

### Bis[tris(1,2-benzisothiazol-3-thionato-1,1-dioxide- $\kappa$ N, $\kappa$ S)(ethanol)bismuth(III)] ethanol hemisolvate

#### Crystal data

[Bi(C<sub>7</sub>H<sub>4</sub>NO<sub>2</sub>S<sub>2</sub>)<sub>3</sub>(C<sub>2</sub>H<sub>6</sub>O)]<sub>2</sub>·0.5C<sub>2</sub>H<sub>6</sub>O

*M<sub>r</sub>* = 1722.52

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

Hall symbol: -P 1

*a* = 8.1979 (6) Å

*b* = 14.0424 (16) Å

*c* = 14.1697 (10) Å

$\alpha$  = 70.779 (8)°

$\beta$  = 80.031 (6)°

$\gamma$  = 79.353 (8)°

*V* = 1502.6 (2) Å<sup>3</sup>

*Z* = 1

*F*(000) = 837

*D<sub>x</sub>* = 1.904 Mg m<sup>-3</sup>

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

Cell parameters from 4557 reflections

$\theta$  = 3.9–26.5°

$\mu$  = 6.33 mm<sup>-1</sup>

*T* = 295 K

Plate, light yellow

0.18 × 0.05 × 0.05 mm

#### Data collection

Oxford Gemini S Ultra CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega$  scans, thick slices

Absorption correction: multi-scan

(*CrysAlis PRO*; Oxford Diffraction, 2009)

*T<sub>min</sub>* = 0.68, *T<sub>max</sub>* = 0.74

19073 measured reflections

7115 independent reflections

5631 reflections with *I* > 2 $\sigma$ (*I*)

*R<sub>int</sub>* = 0.102

$\theta_{\max}$  = 29.3°,  $\theta_{\min}$  = 3.6°

*h* = -10→11

*k* = -17→18

*l* = -18→18

#### Refinement

Refinement on *F*<sup>2</sup>

Least-squares matrix: full

*R*[*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.068

*wR*(*F*<sup>2</sup>) = 0.189

*S* = 1.23

7115 reflections

371 parameters

3 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

$$w = 1/[\sigma^2(F_o^2) + (0.092P)^2]$$

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

$$\Delta\rho_{\max} = 2.75 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -1.38 \text{ e } \text{\AA}^{-3}$$

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Bi1	0.63193 (4)	0.87818 (3)	0.61397 (3)	0.03910 (16)	
S11	0.4875 (4)	0.6604 (2)	0.5100 (2)	0.0485 (7)	
S21	0.6864 (3)	0.92945 (19)	0.41108 (18)	0.0401 (6)	
N11	0.5693 (11)	0.7601 (6)	0.5150 (6)	0.042 (2)	
O11	0.3189 (11)	0.6666 (7)	0.5546 (6)	0.069 (3)	
O21	0.6010 (11)	0.5696 (6)	0.5464 (7)	0.067 (3)	
C11	0.5035 (13)	0.6995 (8)	0.3757 (8)	0.045 (2)	
C21	0.4659 (15)	0.6529 (9)	0.3130 (9)	0.051 (3)	
H21	0.4244	0.5909	0.3374	0.062*	
C31	0.4931 (16)	0.7031 (9)	0.2118 (9)	0.057 (3)	
H31	0.4679	0.6742	0.1666	0.068*	
C41	0.5544 (14)	0.7917 (10)	0.1756 (8)	0.055 (3)	
H41	0.5679	0.8235	0.1064	0.066*	
C51	0.5986 (12)	0.8379 (9)	0.2394 (7)	0.046 (3)	
H51	0.6425	0.8991	0.2138	0.055*	
C61	0.5752 (11)	0.7898 (8)	0.3406 (7)	0.040 (2)	
C71	0.6038 (12)	0.8199 (7)	0.4256 (8)	0.039 (2)	
S12	0.7069 (4)	0.9237 (2)	0.88089 (19)	0.0491 (7)	
S22	0.8000 (3)	1.0394 (2)	0.57304 (17)	0.0424 (6)	
N12	0.7115 (11)	0.9325 (6)	0.7581 (6)	0.044 (2)	
O12	0.5364 (10)	0.9355 (7)	0.9248 (6)	0.059 (2)	
O22	0.8138 (12)	0.8356 (7)	0.9293 (7)	0.075 (3)	
C12	0.8041 (14)	1.0351 (9)	0.8546 (8)	0.049 (3)	
C22	0.8409 (16)	1.0759 (12)	0.9222 (9)	0.064 (4)	
H22	0.8140	1.0491	0.9915	0.077*	
C32	0.9197 (17)	1.1585 (13)	0.8795 (11)	0.072 (4)	
H32	0.9513	1.1874	0.9227	0.086*	
C42	0.9576 (16)	1.2038 (11)	0.7787 (11)	0.066 (3)	
H42	1.0121	1.2612	0.7549	0.079*	
C52	0.9115 (14)	1.1607 (10)	0.7115 (9)	0.054 (3)	
H52	0.9318	1.1899	0.6422	0.065*	
C62	0.8357 (12)	1.0743 (8)	0.7522 (8)	0.041 (2)	
C72	0.7828 (12)	1.0133 (8)	0.7000 (7)	0.038 (2)	
S13	0.6004 (4)	0.5960 (3)	0.8533 (3)	0.0616 (9)	
S23	0.9197 (3)	0.7609 (2)	0.6282 (2)	0.0461 (6)	
N13	0.6621 (10)	0.6911 (7)	0.7545 (7)	0.049 (2)	
O13	0.4965 (13)	0.5430 (8)	0.8236 (9)	0.095 (4)	
O23	0.5379 (11)	0.6350 (9)	0.9363 (8)	0.090 (4)	
C13	0.7984 (14)	0.5292 (9)	0.8662 (9)	0.058 (3)	
C23	0.8483 (15)	0.4371 (9)	0.9410 (10)	0.060 (3)	
H23	0.7726	0.4016	0.9911	0.071*	
C33	1.0180 (16)	0.4043 (9)	0.9335 (10)	0.063 (4)	
H33	1.0588	0.3448	0.9807	0.075*	



C43	1.1277 (15)	0.4561 (10)	0.8594 (11)	0.066 (4)	
H43	1.2395	0.4276	0.8550	0.079*	
C53	1.0810 (14)	0.5482 (9)	0.7911 (9)	0.054 (3)	
H53	1.1587	0.5871	0.7465	0.065*	
C63	0.9118 (14)	0.5793 (8)	0.7926 (8)	0.046 (2)	
C73	0.8212 (13)	0.6748 (8)	0.7310 (8)	0.043 (2)	
O14	0.2919 (11)	0.8258 (8)	0.6748 (7)	0.073 (3)	
H14	0.2913	0.7759	0.6520	0.109*	
C14	0.1947 (19)	0.8115 (14)	0.7679 (11)	0.080 (4)	
H14A	0.0803	0.8413	0.7569	0.096*	
H14B	0.1948	0.7392	0.8020	0.096*	
C24	0.250 (2)	0.8557 (14)	0.8320 (11)	0.086 (5)	
H24A	0.3704	0.8455	0.8256	0.129*	
H24B	0.2071	0.8240	0.9006	0.129*	
H24C	0.2107	0.9273	0.8132	0.129*	
O15	1.009 (5)	0.445 (3)	0.552 (3)	0.073 (3)	0.25
H15	1.1043	0.4238	0.5257	0.109*	0.25
C15	1.016 (7)	0.536 (3)	0.566 (3)	0.080 (4)	0.25
H15A	1.1190	0.5366	0.5883	0.096*	0.25
H15B	0.9261	0.5482	0.6155	0.096*	0.25
C25	1.011 (9)	0.618 (3)	0.472 (4)	0.086 (5)	0.25
H25A	1.0124	0.6828	0.4813	0.129*	0.25
H25B	1.1013	0.6064	0.4227	0.129*	0.25
H25C	0.9066	0.6181	0.4502	0.129*	0.25

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Bi1	0.0345 (2)	0.0432 (2)	0.0314 (2)	-0.00218 (15)	0.00001 (13)	-0.00424 (15)
S11	0.0521 (16)	0.0426 (14)	0.0391 (13)	-0.0114 (12)	-0.0005 (11)	0.0032 (11)
S21	0.0401 (13)	0.0415 (13)	0.0328 (12)	-0.0099 (10)	0.0030 (9)	-0.0048 (10)
N11	0.049 (5)	0.041 (5)	0.025 (4)	-0.011 (4)	0.007 (3)	0.001 (3)
O11	0.062 (5)	0.085 (6)	0.050 (5)	-0.026 (5)	0.014 (4)	-0.009 (5)
O21	0.072 (6)	0.042 (4)	0.061 (5)	0.000 (4)	-0.003 (4)	0.011 (4)
C11	0.043 (6)	0.043 (6)	0.038 (5)	-0.004 (4)	-0.006 (4)	0.001 (4)
C21	0.054 (7)	0.039 (6)	0.058 (7)	-0.005 (5)	-0.015 (5)	-0.007 (5)
C31	0.074 (8)	0.060 (7)	0.048 (6)	-0.009 (6)	-0.004 (5)	-0.034 (6)
C41	0.042 (6)	0.080 (9)	0.033 (5)	-0.006 (6)	0.003 (4)	-0.010 (5)
C51	0.031 (5)	0.057 (6)	0.033 (5)	0.004 (4)	0.003 (4)	-0.001 (5)
C61	0.026 (5)	0.050 (6)	0.030 (5)	-0.005 (4)	-0.001 (3)	0.005 (4)
C71	0.033 (5)	0.032 (5)	0.043 (5)	0.002 (4)	-0.003 (4)	-0.004 (4)
S12	0.0577 (17)	0.0513 (16)	0.0298 (12)	-0.0062 (12)	-0.0047 (11)	-0.0021 (11)
S22	0.0474 (15)	0.0490 (14)	0.0277 (11)	-0.0116 (11)	0.0024 (9)	-0.0088 (10)
N12	0.055 (5)	0.037 (5)	0.034 (4)	-0.006 (4)	-0.004 (4)	-0.005 (4)
O12	0.049 (5)	0.081 (6)	0.042 (4)	-0.025 (4)	0.016 (3)	-0.014 (4)
O22	0.078 (6)	0.072 (6)	0.059 (5)	0.003 (5)	-0.031 (5)	0.004 (5)
C12	0.051 (6)	0.065 (7)	0.035 (5)	-0.015 (5)	-0.011 (4)	-0.015 (5)
C22	0.056 (8)	0.093 (10)	0.038 (6)	-0.021 (7)	0.001 (5)	-0.010 (6)
C32	0.052 (8)	0.101 (11)	0.071 (9)	-0.012 (8)	-0.027 (6)	-0.027 (8)

C42	0.059 (8)	0.071 (9)	0.071 (9)	-0.024 (6)	-0.006 (6)	-0.017 (7)
C52	0.047 (7)	0.065 (8)	0.051 (6)	-0.010 (5)	-0.006 (5)	-0.017 (6)
C62	0.033 (5)	0.042 (5)	0.046 (6)	0.000 (4)	0.007 (4)	-0.019 (5)
C72	0.040 (5)	0.040 (5)	0.030 (5)	0.001 (4)	-0.007 (4)	-0.011 (4)
S13	0.0325 (14)	0.0606 (18)	0.0632 (19)	-0.0031 (13)	0.0008 (12)	0.0139 (15)
S23	0.0346 (13)	0.0455 (14)	0.0448 (14)	-0.0035 (11)	0.0042 (10)	-0.0018 (11)
N13	0.025 (4)	0.046 (5)	0.055 (5)	0.003 (4)	-0.003 (4)	0.005 (4)
O13	0.072 (7)	0.090 (7)	0.104 (8)	-0.038 (6)	-0.018 (6)	0.016 (6)
O23	0.049 (5)	0.101 (8)	0.073 (6)	0.015 (5)	0.017 (4)	0.009 (6)
C13	0.045 (6)	0.046 (6)	0.060 (7)	-0.010 (5)	0.001 (5)	0.012 (5)
C23	0.053 (7)	0.042 (6)	0.064 (8)	0.004 (5)	-0.009 (6)	0.005 (6)
C33	0.054 (7)	0.047 (7)	0.070 (8)	0.001 (5)	-0.019 (6)	0.007 (6)
C43	0.040 (7)	0.066 (8)	0.078 (9)	0.012 (6)	-0.009 (6)	-0.011 (7)
C53	0.036 (6)	0.047 (6)	0.064 (7)	0.006 (5)	-0.003 (5)	-0.006 (5)
C63	0.049 (6)	0.035 (5)	0.052 (6)	0.009 (4)	-0.005 (5)	-0.020 (5)
C73	0.037 (6)	0.039 (5)	0.049 (6)	-0.013 (4)	-0.005 (4)	-0.004 (5)
O14	0.059 (6)	0.084 (6)	0.079 (6)	-0.020 (5)	0.006 (4)	-0.032 (5)
C14	0.070 (9)	0.126 (13)	0.063 (8)	-0.048 (9)	0.001 (6)	-0.040 (9)
C24	0.093 (11)	0.102 (12)	0.057 (8)	-0.009 (9)	0.005 (7)	-0.026 (8)
O15	0.059 (6)	0.084 (6)	0.079 (6)	-0.020 (5)	0.006 (4)	-0.032 (5)
C15	0.070 (9)	0.126 (13)	0.063 (8)	-0.048 (9)	0.001 (6)	-0.040 (9)
C25	0.093 (11)	0.102 (12)	0.057 (8)	-0.009 (9)	0.005 (7)	-0.026 (8)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Bi1—S23	2.613 (3)	C42—H42	0.9300
Bi1—N12	2.617 (9)	C52—C62	1.373 (16)
Bi1—N11	2.661 (9)	C52—H52	0.9300
Bi1—S21	2.701 (2)	C62—C72	1.461 (15)
Bi1—S22	2.715 (3)	S13—O13	1.423 (12)
Bi1—N13	2.723 (8)	S13—O23	1.434 (12)
Bi1—S21 <sup>i</sup>	3.364 (3)	S13—N13	1.664 (9)
Bi1—O14	2.926 (9)	S13—C13	1.725 (12)
S11—O11	1.417 (9)	S23—C73	1.740 (10)
S11—O21	1.432 (8)	N13—C73	1.286 (13)
S11—N11	1.685 (10)	C13—C63	1.368 (15)
S11—C11	1.787 (11)	C13—C23	1.420 (15)
S21—C71	1.731 (11)	C23—C33	1.379 (17)
N11—C71	1.286 (12)	C23—H23	0.9300
C11—C21	1.366 (17)	C33—C43	1.360 (18)
C11—C61	1.400 (15)	C33—H33	0.9300
C21—C31	1.373 (16)	C43—C53	1.371 (16)
C21—H21	0.9300	C43—H43	0.9300
C31—C41	1.337 (17)	C53—C63	1.374 (15)
C31—H31	0.9300	C53—H53	0.9300
C41—C51	1.398 (17)	C63—C73	1.482 (14)
C41—H41	0.9300	O14—C14	1.391 (16)
C51—C61	1.365 (13)	O14—H14	0.8638
C51—H51	0.9300	C14—C24	1.43 (2)
C61—C71	1.467 (15)	C14—H14A	0.9700

S12—O22	1.421 (8)	C14—H14B	0.9700
S12—O12	1.432 (8)	C24—H24A	0.9600
S12—N12	1.697 (9)	C24—H24B	0.9600
S12—C12	1.787 (12)	C24—H24C	0.9600
S22—C72	1.699 (9)	O15—C15	1.37 (2)
N12—C72	1.331 (13)	O15—H15	0.8500
C12—C22	1.365 (18)	C15—C25	1.45 (3)
C12—C62	1.368 (14)	C15—H15A	0.9600
C22—C32	1.34 (2)	C15—H15B	0.9600
C22—H22	0.9300	C25—H25A	0.9601
C32—C42	1.365 (19)	C25—H25B	0.9601
C32—H32	0.9300	C25—H25C	0.9600
C42—C52	1.416 (19)		
S23—Bi1—N12	84.7 (2)	C52—C42—H42	121.1
S23—Bi1—N11	83.9 (2)	C62—C52—C42	117.8 (11)
N12—Bi1—N11	160.0 (3)	C62—C52—H52	121.1
S23—Bi1—S21	90.68 (8)	C42—C52—H52	121.1
N12—Bi1—S21	138.42 (19)	C12—C62—C52	119.3 (11)
N11—Bi1—S21	58.18 (16)	C12—C62—C72	112.2 (9)
S23—Bi1—S22	88.00 (9)	C52—C62—C72	128.4 (10)
N12—Bi1—S22	58.57 (19)	N12—C72—C62	116.1 (8)
N11—Bi1—S22	137.17 (16)	N12—C72—S22	118.4 (8)
S21—Bi1—S22	80.01 (8)	C62—C72—S22	125.5 (8)
S23—Bi1—N13	59.04 (18)	O13—S13—O23	118.8 (7)
N12—Bi1—N13	82.0 (3)	O13—S13—N13	109.4 (6)
N11—Bi1—N13	78.0 (3)	O23—S13—N13	108.5 (6)
S21—Bi1—N13	129.7 (2)	O13—S13—C13	111.4 (7)
S22—Bi1—N13	131.4 (2)	O23—S13—C13	111.2 (7)
O11—S11—O21	119.6 (5)	N13—S13—C13	94.8 (5)
O11—S11—N11	108.5 (5)	C73—S23—Bi1	87.4 (4)
O21—S11—N11	108.4 (5)	C73—N13—S13	110.1 (7)
O11—S11—C11	111.9 (5)	C73—N13—Bi1	93.1 (6)
O21—S11—C11	110.5 (5)	S13—N13—Bi1	156.4 (5)
N11—S11—C11	94.9 (5)	C63—C13—C23	121.6 (11)
C71—S21—Bi1	85.6 (4)	C63—C13—S13	110.0 (8)
C71—N11—S11	110.2 (8)	C23—C13—S13	128.3 (9)
C71—N11—Bi1	97.0 (7)	C33—C23—C13	114.7 (11)
S11—N11—Bi1	151.9 (4)	C33—C23—H23	122.7
C21—C11—C61	123.0 (10)	C13—C23—H23	122.7
C21—C11—S11	130.2 (8)	C43—C33—C23	122.3 (11)
C61—C11—S11	106.7 (8)	C43—C33—H33	118.9
C11—C21—C31	116.0 (10)	C23—C33—H33	118.9
C11—C21—H21	122.0	C33—C43—C53	123.0 (11)
C31—C21—H21	122.0	C33—C43—H43	118.5
C41—C31—C21	122.6 (11)	C53—C43—H43	118.5
C41—C31—H31	118.7	C43—C53—C63	115.6 (11)
C21—C31—H31	118.7	C43—C53—H53	122.2
C31—C41—C51	121.5 (10)	C63—C53—H53	122.2

C31—C41—H41	119.3	C13—C63—C53	122.2 (10)
C51—C41—H41	119.3	C13—C63—C73	108.1 (9)
C61—C51—C41	117.7 (11)	C53—C63—C73	129.1 (10)
C61—C51—H51	121.1	N13—C73—C63	117.0 (9)
C41—C51—H51	121.1	N13—C73—S23	120.1 (8)
C51—C61—C11	119.0 (11)	C63—C73—S23	122.9 (8)
C51—C61—C71	130.6 (10)	C14—O14—H14	110.4
C11—C61—C71	110.3 (8)	O14—C14—C24	113.4 (12)
N11—C71—C61	117.8 (9)	O14—C14—H14A	108.6
N11—C71—S21	118.8 (9)	C24—C14—H14A	108.9
C61—C71—S21	123.3 (7)	O14—C14—H14B	109.5
O22—S12—O12	117.7 (6)	C24—C14—H14B	108.6
O22—S12—N12	110.0 (5)	H14A—C14—H14B	107.6
O12—S12—N12	109.0 (5)	C14—C24—H24A	109.8
O22—S12—C12	110.2 (6)	C14—C24—H24B	109.3
O12—S12—C12	112.8 (6)	H24A—C24—H24B	109.5
N12—S12—C12	94.8 (5)	C14—C24—H24C	109.3
C72—S22—Bi1	85.5 (4)	H24A—C24—H24C	109.5
C72—N12—S12	109.4 (7)	H24B—C24—H24C	109.5
C72—N12—Bi1	97.5 (6)	C15—O15—H15	108.6
S12—N12—Bi1	152.8 (5)	O15—C15—C25	111 (3)
C22—C12—C62	125.0 (11)	O15—C15—H15A	112.4
C22—C12—S12	127.6 (9)	C25—C15—H15A	104.0
C62—C12—S12	107.4 (8)	O15—C15—H15B	109.8
C32—C22—C12	113.8 (12)	C25—C15—H15B	111.2
C32—C22—H22	123.1	H15A—C15—H15B	109.0
C12—C22—H22	123.1	C15—C25—H25A	112.4
C22—C32—C42	126.1 (15)	C15—C25—H25B	111.5
C22—C32—H32	116.9	H25A—C25—H25B	109.5
C42—C32—H32	116.9	C15—C25—H25C	104.3
C32—C42—C52	117.9 (12)	H25A—C25—H25C	109.5
C32—C42—H42	121.1	H25B—C25—H25C	109.5

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O14—H14 $\cdots$ O11	0.86	2.34	3.185 (14)	166
C21—H21 $\cdots$ O21 <sup>ii</sup>	0.93	2.33	3.192 (16)	153
C33—H33 $\cdots$ O22 <sup>iii</sup>	0.93	2.55	3.454 (17)	165
C41—H41 $\cdots$ O12 <sup>iv</sup>	0.93	2.56	3.475 (14)	166

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

$\pi-\pi$  contacts ( $\text{\AA}$ ,  $^\circ$ )

Group 1 $\cdots$ group 2	CCD ( $\text{\AA}$ )	DA ( $^\circ$ )	SA ( $^\circ$ )	IPD ( $\text{\AA}$ )
Cg1 $\cdots$ Cg2 <sup>i</sup>	3.765 (7)	5.1 (6)	22.4 (2)	3.510 (5)

Cg3...Cg3<sup>ii</sup> 4.077 (7) 0 28.3 3.590 (5)

Symmetry codes: (i) 1 - x, 2 - y, 1 - z; (ii) 2 - x, 1 - y, 2 - z. Cg1 is the centroid of the C11–C61 ring, Cg2 that of the C12–C62 ring and Cg3 that of the C13–C63 ring. CCD is the centroid-to-centroid distance, DA the dihedral angle between rings, SA the slippage angle or (mean) angle subtended by the intercentroid vector to the plane normals, and IPD the interplanar distance or (mean) distance from one plane to the neighbouring centroid. For details, see Janiak (2000).

*Selected bond distances (Å)*

	Experimental	Calculated
Bi1—S23	2.613 (3)	2.664
Bi1—N13	2.723 (8)	2.574
Bi1—N12	2.617 (9)	2.580
Bi1—N11	2.661 (9)	2.595
Bi1—S21	2.701 (2)	2.854
Bi1—S22	2.715 (3)	2.849
Bi1—O14	2.926 (9)	2.747
Bi1—S21 <sup>i</sup>	3.364 (3)	

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

*Selected bond angles (°)*

	Experimental	Calculated
S23—Bi1—N12	84.7 (2)	82.78
S23—Bi1—N11	83.9 (2)	85.30
N12—Bi1—N11	160.0 (3)	160.1
S23—Bi1—S21	90.68 (8)	91.34
N12—Bi1—S21	138.42 (19)	138.4
N11—Bi1—S21	58.18 (16)	57.58
S23—Bi1—S22	88.00 (9)	91.35
N12—Bi1—S22	58.57 (19)	57.59
N11—Bi1—S22	137.17 (16)	138.43
S21—Bi1—S22	80.01 (8)	81.37
S23—Bi1—N13	59.04 (18)	58.29
N12—C72—C62	116.1 (8)	115.39
N12—C72—S22	118.4 (8)	119.97
C62—C72—S22	125.5 (8)	124.64
O13—S13—O23	118.8 (7)	119.47

*Selected FT-IR spectroscopic bands (cm<sup>-1</sup>)*

	Experimental	Calculated
$\nu(\text{CN}), \nu(\varphi\text{S})$	1409 (m)	1441/1446
$\nu_{\text{as}}(\text{SO}_2)$	1341/1326 (m)	1312/1289
$\nu_{\text{as}}(\varphi\text{CN}), \delta(\text{CH})$	1239 (m)	1271
$\nu_{\text{s}}(\text{SO}_2), \delta(\varphi\text{SN})$	1180/1167 (s)	1114/1125
$\nu(\text{CC}) \nu(\text{CO}) \text{EtOH}$	1038 (w)	1055
$\nu(\text{CS}), \delta(\text{CNS})$	997 (m)/1016 (w)	1014/1019
$\nu(\text{NS}), \delta(\text{CCC})$	794 (m)	791

$\nu$ : stretching;  $\delta$ : in-plane deformation; as: asymmetric; s: symmetric;  $\varphi$ : benzenic ring; s: strong; m: medium; w: weak.