Mono- and binuclear tris(3-*tert*-butyl-2-sulfanylidene-1*H*-imidazol-1-yl)hydroborate bismuth(III) dichloride complexes: a soft scorpionate ligand can coordinate to *p*-block elements

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Tris(pyrazolyl)hydroborate ligands have been utilized in the fields of inorganic and coordination chemistry due to the ease of introduction of steric and electronic substitutions at the pyrazole rings. The development and use of the tris(pyrazolyl)hydroborate ligand, called a ‘scorpionate’, were pioneered by the late Professor Swiatoslaw Trofimenko. He developed a second generation for his ligand system by the introduction of 3-*tert*-butyl and 3-phenyl substituents and this new ligand system accounted for many remarkable developments in inorganic and coordination chemistry in stabilizing monomeric species while maintaining an open coordination site. Bismuth is remarkably harmless among the toxic heavy metal *p*-block elements and is now becoming popular as a replacement for highly toxic metal elements, such as lead. Two bismuth(III) complexes of the anionic sulfur-containing tripod tris(3-*tert*-butyl-2-sulfanylidene-1*H*-imidazol-1-yl)hydroborate ligand were prepared. By recrystallization from MeOH/CH₂Cl₂, orange crystals of dichlorido(methanol- κ O)[tris(3-*tert*-butyl-2-sulfanylidene-1*H*-imidazol-1-yl- κ S)hydroborato]bismuth(III), [Bi(C₂₁H₃₄BN₆S₃)Cl₂(CH₄O)], (I), were obtained, manifesting a mononuclear structure. By using a noncoordinating solvent, red crystals of the binuclear structure with bridging Cl atoms were obtained, namely di- μ -chlorido-bis[chlorido[tris(3-*tert*-butyl-2-sulfanylidene-1*H*-imidazol-1-yl- κ S)hydroborato]bismuth(III)], [Bi₂(C₂₁H₃₄BN₆S₃)₂Cl₄], (II). These complexes show {Bi^{III}S₃Cl₂O} and {Bi^{III}S₃Cl₃} coordination geometries with average Bi^{III}–S bond lengths of 2.73 and 2.78 Å in (I) and (II), respectively. The overall Bi^{III} coordination geometry is distorted octahedral due to stereochemically active lone pairs. The three Bi^{III}–S bond lengths are almost equal in (I) but show considerable differences in (II), with one long and two shorter distances that also correlate with changes in the UV–Vis and ¹H NMR spectra. For direct measurements of the Bi–S/Cl coordination, ligand K-edge X-ray absorption measurements were carried out in combination with ground and excited-state electronic structure analyses. For *p*-block elements, these sulfur-containing ligands are useful for preparing the appropriate complexes due to their flexible coordination geometry.

1. Introduction

The N3-type ligands, such as tris(pyrazolyl)hydroborate, have been utilized in the fields of inorganic and coordination chemistry (Trofimenko 1999; Pettinari, 2008). The reason for their general use is the ease of introduction of steric and electronic substitutions at the pyrazole rings (Elguero, 1984, 1996; Yet, 2008; Fustero *et al.*, 2011). The history of the development and use of the tris(pyrazolyl)hydroborate ligand, called a ‘scorpionate’, has been outlined by the founder of this chemistry, the late Professor Swiatoslaw Trofimenko (Trofimenko, 2004). His first use of his boron–pyrazole chemistry

was for the 4,4,8,8-tetrakis(pyrazolyl)pyrazabole ligand, which was envisioned as dialkylboronium acetylacetonate by Professor M. Frederick Hawthorne (Hawthorne & Reintjes, 1964). This year is the 50th anniversary of the discovery of scorpionate ligands which began with Professor Trofimenko's first publication on boron–pyrazole chemistry in 1966 (Trofimenko, 1966). He developed a second generation for his ligand system by the introduction of 3-*tert*-butyl and 3-phenyl substituents in 1986 (Calabrese *et al.*, 1986; Trofimenko *et al.*, 1987). This latter ligand system became quite popular, accounting for many remarkable developments in inorganic and coordination chemistry in stabilizing monomeric species while maintaining an open coordination site. Before introducing bulky substituents, mainly coordinatively saturated complexes [L_2M in this case, with tris(pyrazolyl)hydroborate denoted by L] were synthesized, which still maintained the N_6 coordination geometry without any notable reactivity. In Trofimenko's historical account (Trofimenko, 2004), newer ligand architectures were proposed by the introduction of other heteroatoms, such as oxygen, sulfur and phosphorus.

Bismuth is remarkably harmless among the toxic heavy metal p -block elements (Mohan, 2010); thus, it used to be widely available as a medicine for the treatment of stomach disorders. Moreover, bismuth is now becoming popular as a replacement for highly toxic metal elements, such as lead. More recently, bismuth and its compounds with a formal Bi^{III} oxidation state and an electron configuration of $[Xe]4f^{14}5d^{10}6s^26p^0$ have found significant catalytic applications as green Lewis acids in organic and organometallic chemistry (Suzuki *et al.*, 1997; Suzuki & Matano, 2001; Leonard *et al.*, 2002; Ollevier, 2013). We report here the crystal structures of two Bi^{III} complexes with the tris(3-*tert*-butyl-2-sulfanylidene-1H-

imidazol-1-yl)hydroborate ligand (denoted Tm^{tBu}) as soft tris(pyrazolyl)hydroborate derivatives in the mono- and binuclear forms, namely $[Bi(Tm^{tBu})Cl_2(MeOH)]$, (I), and $[Bi(Tm^{tBu})Cl(\mu-Cl)]_2$, (II). Moreover, we discuss the role of Bi–S/Cl bonding, a stereochemically active lone pair that contributes to the distorted geometries by ligand K-edge X-ray spectroscopic analysis and electronic structure calculations.

2. Experimental

2.1. Synthesis and crystallization

2.1.1. Chemicals. The preparation and handling of both title complexes were performed under an argon atmosphere using standard Schlenk techniques. The dichloromethane and n -heptane solvents were purified by distillation according to published methods (Armarego & Chai, 2012). Other reagents are available commercially and were used without further purification. The soft scorpionate ligand Tm^{tBu} and its thallium(I) complex, *i.e.* $[Tl(Tm^{tBu})]$, were obtained according to the literature method of Mihalcić *et al.* (2004).

2.1.2. Sample characterization. IR spectra (4000 – 400 cm^{-1}) were recorded in KBr pellets using a JASCO FT-IR 6300 spectrophotometer. Abbreviations used in the description of vibration data are as follows: s = strong, m = medium and w = weak. 1H and ^{13}C NMR spectra (500 and 125 MHz, respectively) were obtained on a Bruker AVANCE-500 NMR spectrometer at room temperature (298 K) in $CDCl_3$. 1H and ^{13}C chemical shifts were reported as δ values relative to residual solvent peaks. The elemental analyses (C, H and N) were performed by the Chemical Analysis Centre of Ibaraki University.

2.1.3. Preparation of complex (I). Complex (I) was obtained by metathesis from the thallium(I) complex. A solution of $[Tl(Tm^{tBu})]$ (0.0700 g, 0.103 mmol) in dichloromethane (5 ml) was added to a solution of $BiCl_3$ (0.0315 g, 0.100 mmol) in degassed acetone (5 ml) and the resulting solution stirred at 243 K for 2 h under an argon atmosphere. After allowing the reaction to proceed overnight, the solvent was removed under reduced pressure and the resulting solid was extracted into dichloromethane. Single crystals of (I) were obtained by slow evaporation from a saturated dichloromethane/degassed methanol (2:1 v/v) solution as orange crystals (yield: 0.0608 g, 0.0770 mmol, 77%).

Elemental analysis calculated for $C_{22}H_{38}BBiCl_2N_6OS_3$: C 33.47, H 4.85, N 10.67%; found: C 33.49, H 4.83, N 10.66%. IR (KBr, cm^{-1}): 3175 (m , C–H), 3145 (m , C–H), 2977 (m , C–H), 2927 (m , C–H), 2404 (w , B–H), 1559 (m), 1418 (m), 1358 (s), 1193 (s), 1175 (s), 1011 (m), 755 (m), 737 (m). UV–vis (CH_2Cl_2 , 298 K; λ_{max} , nm) (ϵ , $\times 10^3\text{ M}^{-1}\text{ cm}^{-1}$): 238 (30), 275 (32), 314 (16, sh), 458 (5). 1H NMR ($CDCl_3$, 298 K): 1.81 (s , 27H, CH_3), 3.49 (s , 3H, CH_3OH), 6.84 (d , 3H, $J = 2\text{ Hz}$, imidazole H), 6.97 (d , 3H, $J = 2\text{ Hz}$, imidazole H); the protons of the BH group and the OH group of methanol were not observed. ^{13}C NMR ($CDCl_3$, 298 K): 30.3 (CCH_3), 50.4

Table 1
Experimental details.

	[Bi(Tm ^{tBu})Cl ₂ (MeOH)]	[Bi(Tm ^{tBu})Cl(μ-Cl)] ₂
Crystal data		
Chemical formula	[Bi(C ₂₁ H ₃₄ BN ₆ S ₃)Cl ₂ (CH ₄ O)]	[Bi ₂ (C ₂₁ H ₃₄ BN ₆ S ₃) ₂ Cl ₄]
<i>M_r</i>	789.46	1514.83
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	179	179
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.2899 (5), 10.6653 (4), 15.9818 (10)	10.8009 (11), 11.3698 (14), 11.8690 (13)
α , β , γ (°)	72.157 (6), 83.838 (8), 67.742 (7)	95.125 (4), 91.947 (4), 99.549 (3)
<i>V</i> (Å ³)	1545.08 (16)	1429.9 (3)
<i>Z</i>	2	1
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	6.10	6.58
Crystal size (mm)	0.24 × 0.16 × 0.07	0.23 × 0.15 × 0.15
Data collection		
Diffractometer	Rigaku XtaLAB P200	Rigaku XtaLAB P200
Absorption correction	Numerical (NUMABS; Rigaku, 1999)	Numerical (NUMABS; Rigaku, 1999)
<i>T</i> _{min} , <i>T</i> _{max}	0.465, 0.653	0.270, 0.373
No. of measured, independent and observed [<i>F</i> ² > 2.0σ(<i>F</i> ²)] reflections	51186, 7083, 6768	39709, 6115, 5816
<i>R</i> _{int}	0.037	0.034
(sin θ/λ) _{max} (Å ⁻¹)	0.650	0.650
Refinement		
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.012, 0.032, 1.01	0.013, 0.033, 1.04
No. of reflections	7083	6115
No. of parameters	327	307
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	1.03, -0.66	0.59, -0.85

Computer programs: *CrystalClear-SM Expert* (Rigaku, 2013), *SIR2011* (Burla *et al.*, 2012), *Il Milione* (Burla *et al.*, 2007), *SHELXL2014* (Sheldrick, 2015) and *CrystalStructure* (Rigaku, 2015).

(CH₃OH), 61.1 (CCH₃), 119.2 (imidazole C₄ or C₅), 123.5 (imidazole C₄ or C₅), 151.8 (imidazole C=S).

2.1.4. Preparation of complex (II). Complex (II) was obtained by metathesis from the thallium(I) complex. A solution of [Tl(Tm^{tBu})] (0.0708 g, 0.104 mmol) in dichloromethane (5 ml) was added to a solution of BiCl₃ (0.0403 g, 0.128 mmol) in degassed acetone (5 ml), and the resulting solution stirred at 243 K for 3 h under an argon atmosphere. After allowing the reaction to proceed overnight at room temperature, the solvent was removed under reduced pressure and the resulting solid was extracted into dichloromethane. Single crystals of (II) were obtained by slow evaporation from a saturated dichloromethane/*n*-heptane (2:1 *v/v*) solution as red crystals (yield: 0.0607 g, 0.0396 mmol, 76%). The structure of this complex was reported previously (Bao *et al.*, 2004). However, the measurement temperature [153 (2) K] is different in this case, so we used our own structural parameters for comparison with the structure of mononuclear complex (I).

Elemental analysis calculated for C₄₂H₆₈B₂Bi₂Cl₄N₁₂S₆·H₂O: C 32.91, H 4.60, N 10.97%; found: C 33.20, H 4.71, N 10.63%. IR (KBr, cm⁻¹): 3182 (*m*, C—H), 3149 (*m*, C—H), 2976 (*s*, C—H), 2926 (*m*, C—H), 2382 (*w*, B—H), 1562 (*m*), 1420 (*m*), 1356 (*s*), 1195 (*s*), 1176 (*s*), 821 (*w*), 730 (*m*), 686 (*m*). UV–vis (CH₂Cl₂, 298 K; λ_{max}, nm) (ε, × 10³ M⁻¹ cm⁻¹): 276 (14), 326 (6, *sh*), 471 (2). ¹H NMR (CDCl₃, 298 K): 1.78 (*s*, 18H, CH₃), 1.80 (*s*, 36H, CH₃), 6.77 (*d*, 2H, *J* = 2 Hz, imidazole H), 6.79 (*d*, 4H, *J* = 2 Hz, imidazole H), 6.84 (*d*, 2H, *J* = 2 Hz, imidazole H), 6.93 (*d*, 4H, *J* = 2 Hz, imidazole H). ¹³C NMR

was not measured since complicated signals would be expected.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms were placed in calculated idealized geometry at distances of 0.98–1.00 Å from the attached heavy atoms. They were treated as rigid centres and constrained with *U*_{iso}(H) = 1.2–1.5 times *U*_{eq} of the neighbouring atom.

2.3. Experimental and theoretical electronic structure analyses

2.3.1. Ligand K-edge X-ray absorption spectroscopy. Sulfur and chlorine K-edge X-ray absorption spectroscopic measurements were carried out at beamline 14-3 (BL14-3) of Stanford Synchrotron Radiation Lightsource. BL14-3 is a 20-pole 2.0 T Wiggler beamline equipped with a liquid-nitrogen-cooled Si(111) double-crystal monochromator. This experimental set-up provides tuneable access to the tender X-ray energy range (2–4 keV), where the S K- (2.4–2.7 keV) and Cl K-edges (2.7–3.0 keV) are located. The energy scale for S K-edge was calibrated to the first peak (2472.0 eV) of the Na₂S₂O₃·5H₂O spectrum. For the Cl K-edge, the Cs₂[CuCl₄] salt was used as the calibrant, where the energy position of the pre-edge feature was set at 2820.2 eV. The spectra were collected in fluorescence detection mode using a Passivated Implanted

Plana Silicon (PIPS) detector (Canberra). The beam path was purged with He. The incident beam intensity was measured by an ionization chamber operating at 1800 V. The samples were ground with BN and pasted onto S- or Cl-contaminant-free Kapton tape (CERTIPREP). The samples faced the detector and were 45° rotated relative to the incoming X-ray beam.

2.3.2. XAS data normalization and fitting. For both edges, at least three spectra were averaged, baseline subtracted (using a BN standard) and normalized using our in-house code ADRP (Gardenghi, 2011) (see full energy range spectra in Fig. S1 of the *Supporting information*). The fitting of the spectral features was carried out using *PeakFit* (Seasolve). The first and second derivative spectra shown in the *Supporting information* (Fig. S2) were used to obtain the energy positions of the rising-edge inflection points and the pre-edge/rising-edge spectral features, respectively. The individual fits with the least number of Gaussian/Lorentzian amplitude functions were determined from the number of resolved peaks from the second derivative spectra (see *Supporting information*). The conversion of spectral intensities to orbital compositions was carried out as described earlier for terminal and bridging chloride (Barton *et al.*, 2015) and sulfur ligands (Queen *et al.*, 2013).

2.3.3. Electronic structure calculations. Ground and core-level excited-state analyses were carried out using *GAUSSIAN09* (Frisch *et al.*, 2009). Given the intense spectral features at the ligand K-edges, we used a pure density functional theory (DFT), meta-GGA density functional (BP86; Becke, 1988, Perdew, 1986) that provides a covalent electronic structure description. For an adequate representation of the orbitals, we used a triple- ζ -quality basis set with polarization function def2TZVP (Schaefer *et al.*, 1992; Weigend & Ahlrichs, 2005) that can be considered as saturated with

respect to the electronic structure. The TD-DFT formalism for core-level excitations implemented in *GAUSSIAN09* was utilized to assist the assignment of the pre-edge and rising-edge features and correlated with the ground-state frontier orbital compositions. Relativistic effects were considered by requesting molecular integral evaluations employing the Douglas–Kroll–Hess 4th order relativistic correction including spin-orbit terms. The connection between the experimental and calculated Bi–S/Cl bond covalency was derived using the transition dipole expression (Solomon *et al.*, 2005), as detailed in Barton *et al.* (2015) and Queen *et al.* (2013). The H-atom positions for the sodium salt of the Tm^{tBu} anion and complexes (I) and (II) were refined by structural optimizations. The atomic positional coordinates used for all calculations are given in the *Supporting information*.

3. Results and discussion

Bismuth(III) complexes with original unsubstituted tris(pyrazolyl)hydroborate ligands have been reported as $[\text{Bi}^{\text{III}}\text{Cl}\{\text{HB}(\text{pz})_3\}_2(\text{pzH})]$ (pzH is pyrazole) (Dodds *et al.*, 2004). Therefore, we aimed to prepare Bi^{III} complexes with sterically hindered tris(pyrazolyl)hydroborate ligands to obtain mononuclear coordinatively unsaturated complexes. However, we obtained a black solid (bismuth metal), identified by the disappearance of B–H stretching in its IR spectrum. This combination of ligand and metal ion thus did not produce any stable mononuclear complex, likely due to the larger ionic radius of the Bi^{III} ion (1.03 Å in a six-coordinate compound) compared with the first or second row transition metal ions (Shannon, 1976). Therefore, we hypothesized the use of a more flexible ligand for complexation. Bismuth as a soft Lewis acid coordinates well to a soft-base donor, such as sulfur or phosphorus. Thus, we chose the tris(2-sulfanylidene-1*H*-imidazol-1-yl)hydroborate (Tm) ligand, which is the sulfur analogue of the original tris(pyrazolyl)hydroborates (Garner

Figure 1
The molecular structure of $[\text{Bi}(\text{Tm}^{\text{tBu}})\text{Cl}_2(\text{CH}_3\text{OH})]$, (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

Figure 2
The molecular structure of $[\text{Bi}(\text{Tm}^{\text{tBu}})\text{Cl}(\mu\text{-Cl})]_2$, (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. [Symmetry code: (i) $-x + 1, y + 1, -z + 2$.]

Table 2

Selected bond lengths (Å) and bond angles (°) in (I) and (II).

	(I)		(II)
Bi1—S1	2.6463 (6)	Bi1—S1	2.9128 (5)
Bi1—S2	2.8307 (5)	Bi1—S2	2.7222 (5)
Bi1—S3	2.7242 (4)	Bi1—S3	2.6931 (5)
Bi1—Cl1	2.6933 (5)	Bi1—Cl1	2.9401 (6)
Bi1—Cl2	2.7499 (4)	Bi1—Cl1 ⁱ	2.8915 (5)
Bi1—O1	2.8023 (14)	Bi1—Cl2	2.5949 (5)
		Bi1...Bi1 ⁱ	4.1858 (5)
S1—Bi1—Cl1	100.115 (14)	S1—Bi1—Cl1	92.814 (16)
S2—Bi1—Cl1	160.302 (13)	S2—Bi1—Cl1	166.327 (14)
S3—Bi1—Cl1	76.546 (13)	S3—Bi1—Cl1	102.541 (15)
S1—Bi1—Cl2	74.926 (13)	S1—Bi1—Cl1 ⁱ	108.598 (16)
S2—Bi1—Cl2	103.836 (14)	S2—Bi1—Cl1 ⁱ	79.020 (15)
S3—Bi1—Cl2	160.381 (14)	S3—Bi1—Cl1 ⁱ	160.787 (15)
S1—Bi1—S2	90.300 (14)	S1—Bi1—Cl2	164.283 (15)
S1—Bi1—S3	88.960 (13)	S2—Bi1—Cl2	97.312 (17)
S2—Bi1—S3	87.065 (14)	S3—Bi1—Cl2	77.787 (16)
Cl1—Bi1—Cl2	95.046 (14)	S1—Bi1—S2	86.582 (15)
S1—Bi1—O1	152.76 (4)	S1—Bi1—S3	86.949 (15)
S2—Bi1—O1	74.07 (3)	S2—Bi1—S3	91.074 (15)
S3—Bi1—O1	111.80 (4)	Cl1—Bi1—Cl2	86.939 (18)
Cl1—Bi1—O1	101.73 (3)	Cl1—Bi1—Cl1 ⁱ	88.262 (15)
Cl2—Bi1—O1	87.10 (4)	Cl1 ⁱ —Bi1—Cl2	87.108 (17)

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

et al., 1996; Reglinski, Garner *et al.*, 1999). Bi^{III} complexes ligated by the Tm ligand have been reported previously (Spicer & Reglinski, 2009; Reglinski *et al.*, 2015). Binuclear Bi^{III} complexes with methyl-substituted (Tm^{Me}) and *tert*-butyl-substituted [Tm^{tBu}; tris(3-*tert*-butyl-2-sulfanylidene-1*H*-imidazol-1-yl)hydroborate] Tm ligands have also been reported as [Bi(Tm^{Me})Cl(μ -Cl)]₂ and [Bi(Tm^{tBu})Cl(μ -Cl)]₂ by the reaction of Tm^{Me} or Tm^{tBu} with BiCl₃ at low temperature (Reglinski, Spicer *et al.*, 1999; Bao *et al.*, 2004).

We repeated the above reactions using the [Ti(Tm^{tBu})] complex as the starting material. After recrystallization from a dichloromethane/methanol solution, orange crystals were obtained. X-ray structure analysis reveals a mononuclear structure, (I), as shown in Fig. 1. This complex is the first example of a mononuclear structure ligated by Tm^{tBu} ligands. It has a distorted octahedral geometry with a {Bi^{III}S₃Cl₂O} ligand donor set. Moreover, it has three acute angles [S3—Bi1—Cl2 = 160.381 (14)°, S2—Bi1—Cl1 = 160.302 (13)° and S1—Bi1—O1 152.76 (4)°] due to a stereochemically active lone pair, which makes the S3—Bi1—O1 angle of 111.80 (4)° the most obtuse (Table 2). The presence of a stereochemically active lone pair at the Bi^{III} centre is expected due to a formal electronic configuration of 6s², which would result in a distorted octahedral coordination geometry (Wheeler & Kumar, 1992; Lawton *et al.*, 1974). Despite the differences in S—Bi—X bond angles, the average Bi—S bond length in (I) is 2.734 (6) Å, for a full range of 2.6463 (5)–2.8307 (5) Å. The Bi—S bond opposite to the weakly coordinated methanol ligand is the shortest. It is also remarkable that a close to 0.1 Å difference exists between the Bi—S bond lengths *trans* to the chloride ligands.

On the other hand, after recrystallization from dichloromethane/*n*-heptane solution, red crystals were obtained. X-ray

diffraction analysis revealed a binuclear structure, (II), where the Bi^{III} centres are bridged by two chloride ions, as shown in Fig. 2. This structure shows much similarity to a previously reported structure (Bao *et al.*, 2004). Complex (II) also has a distorted octahedral coordination geometry at each Bi^{III} centre, displaying {Bi^{III}S₃Cl₃} ligand donor sets. Once again, it has three acute angles [S1—Bi1—Cl2 = 164.283 (15)°, S2—Bi1—Cl1 = 166.327 (14)° and S3—Bi1—Cl1ⁱ = 160.787 (15)°; symmetry code: (i) $-x + 1, -y + 1, -z + 2$]. Therefore, the presence of a stereochemically active lone pair makes the S1—Bi1—Cl1ⁱ angle the most obtuse [108.598 (16)°]. In contrast to mononuclear complex (I), the average Bi—S bond lengths in (II) is longer [2.776 (6) Å; range 2.6931 (5)–2.9128 (5) Å]. The three Bi—S bonds again differ greatly from each other, similar to the situation in complex (I). One of the bonds *trans* to the terminal chloride ligand is the longest, while the other two are approximately equal (within 0.03 Å). The differences in the Bi—S bond lengths for complex (II) correlate with the two pairs of clearly observed ¹H NMR signals with an integration ratio of almost 1:2. Notably, the binuclear structure remains intact in noncoordinating CDCl₃ solution during NMR measurements. For complex (I), only a single pattern of ¹H NMR signals was observed. Due to the differences between the mono- and binuclear coordination geometries, the colours of the crystals were also different, being orange and red for (I) and (II), respectively, as was also observed from the differences in their UV–Vis spectra.

A direct experimental measure of the covalent nature of the Bi–ligand bonds can be obtained from ligand K-edge X-ray absorption spectroscopy. The pre-edge features at the sulfur and chlorine K-edges below the ionization threshold appear to be due to a mixing of the vacant Bi 6*p* orbitals with the filled 3*p* donor orbitals of the S and Cl ligands. The rising-edge features superimposed on the ionization edge-jump for the Tm^{tBu} ligand are informative about changes in the S—C bonding (Queen *et al.*, 2013). The appearance of multiple pre-edge features at the Cl K-edge is indicative of the different chemical environments of the terminal and bridging chloride ligands (Barton *et al.*, 2015).

Fig. 3 compares the spectral differences between the free/uncoordinated ligand or ligand salt and the Bi^{III} coordinated ligands for binuclear complex (II) at the S (Fig. 3*a*) and Cl (Fig. 3*b*) K-edges. The spectra were renormalized to take into account the different number of absorbers per molecule. The S K-edge spectra in Fig. 3(*a*) shows considerable spectral differences between the free and coordinated Tm^{tBu} ligands. Upon coordination to the formally Bi^{III} centre, a well-resolved pre-edge feature appears at 2471.5 eV, which is due to the mixing of the S-donor orbitals (3*p*-based lone pairs) and the Bi 6*p* vacant orbitals. The *Supporting information* contains details of the spectral fits (Fig. S3 and Table S1), which show that the pre-edge intensity of 1.01 unit corresponds to approximately 0.95 e donation from the six sulfur ligands into the 12 electron holes of the double Bi 6*p* set when using an S 1*s*→3*p* transition dipole integral of 19.3 for an N-conjugated sulfur ligand (see Table S2 in the *Supporting information*). This corresponds to approximately 0.08 e per hole, which is an

Figure 3
Renormalized (A) sulfur and (B) chlorine K-edge spectra of complex (II) with free ligands.

indication for the presence of a covalent bonding interaction. The Cl K-edge spectra in Fig. 3(b) show the emergence of two well-resolved pre-edge features at 2821.8 and 2823.1 eV, which are due to the presence of terminal and bridging chloride ligands, respectively. The bridging chloride ligand formally forms two covalent bonds with the adjacent Bi^{III} centres; thus it has a greater extent of Cl→Bi electron donation in comparison to the terminal chloride ligand and a more positive effective nuclear charge. As a result, the Cl K-edge spectrum of compound (II) has two ionization thresholds that are superimposed on top of each other (see fitting data in the *Supporting information*; Table S1). Since the Cl 1s electrons are excited into the same set of Bi 6p frontier orbitals, the energy shift between the binding energy of the Cl 1s in the terminal (lower energy) and bridging (higher energy) chlorine absorbers can be correlated with the splitting of the pre-edge features (1.3 eV). Using the Cl 1s→3p transition dipole integrals developed for the (Et₄N)₂[Pd₂Cl₆] complex with both terminal (26.4 units) and bridging (29.7 units) chloride ligands (see Table S2 in the *Supporting information*), the pre-edge intensities of 1.60 and 0.89 units will correspond to a total Cl→Bi^{III} donation of 0.36 and 0.18 e. Thus, the terminal Cl–Bi bonding appear to be twice as covalent, which is understandable given the considerably longer bridging Bi1–Cl1/Cl1ⁱ distances compared with terminal Bi1–Cl2 (Table 2). However, the total electron donation from the Cl ligands per Bi–Cl bond (9%) is greater than for the Cu–Cl bond in the covalent Cs₂[CuCl₄] complex (7%). The Bi–Cl bonding is anticipated to be dominantly ionic, as seen from the shift in

Figure 4
Highest-occupied molecular orbitals (HOMOs) for complexes (I) and (II), showing the stereochemically active Bi 6s² lone pairs (Bi purple, Cl light green, N dark blue, C gray and H white). (A) Front and rear views of the HOMOs for (I); (B) +/- combinations of the two Bi 6s orbitals.

Figure 5
Lowest unoccupied frontier molecular orbitals for complex (I) that illustrate the covalent interaction between the Bi^{III} centre and the S/Cl ligands.

the rising-edge positions between the NaCl uncoordinated ligand spectrum and the binuclear complex. However, it also has a considerable covalent character from an intensity analysis of the pre-edge features. The less covalent bridging Bi—Cl interaction in comparison to the terminal one suggests the preference for the site of attack by coordinating solvent molecules, such as methanol, that can lead to the formation of a stable mononuclear complex.

The above experimental electronic structure analysis from ligand K-edge spectroscopy can be complemented with electronic structure calculations using a covalent density functional theory and saturated basis set with respect of electronic structure properties. The highest occupied molecular orbitals (HOMOs) of complexes (I) and (II) are shown in Fig. 4(a), which clearly demonstrate the presence of a polarized Bi 6s orbital due to the differences between the apical S and basal S₂Cl₂ ligand environments for both the mono- and binuclear complexes. These HOMOs also demonstrate the predominantly σ -bonding interactions between the Tm^tBu and chloride ligands with the Bi^{III} centre.

The covalent interactions between the Bi^{III} ion and the S/Cl ligand orbitals as experimentally probed by ligand K-edge XAS are graphically illustrated in Fig. 5 for the lowest unoccupied frontier molecular orbitals (LUMO). For the sake of brevity, the LUMOs of the mononuclear complex (I) are shown here, while the corresponding double sets of LUMOs for binuclear complex (II) are given in the *Supporting infor-*

mation (Fig. S4). If we choose the orientation of the methanol O atom, the Bi^{III} ion and one of the S atoms of the Tm^tBu ligand in a *trans* position to the methanol ligand for the *z* direction, the LUMO corresponds to the predominantly σ^* combination of S 3*p*, Cl 3*p*, O 2*p* and the π^* combination of Cl 3*p* at the righthand side and the Bi^{III} 6*p_z* orbital. It is also notable that the S-atom lone pair is extensively delocalized into the π^* system of the pyrazole ring, thus any substitution on the ring will be transmitted to the Bi—S bonding. LUMO+1 and LUMO+2 correspond exclusively to σ^* interactions between the Bi 6*p_x* and S/Cl 3*p* ligand orbitals. It is important to highlight that the structural distortions in the Bi^{III} inner-sphere environment allows for off-axis σ/σ^* interactions between the Bi and S/Cl/O orbitals, as can be clearly seen from the contour plots of the LUMO+1 and LUMO+2 orbitals. Thus, the stereochemically active 6*s*² lone pair enables more extensive covalent interactions than anticipated for an ideal octahedral coordination environment.

The core-level time-dependent DFT spectra for the free ligand and the two complexes (see Fig. S5 in the *Supporting information*) provided justification for the assignment of the resolved pre-edge features at both the S and Cl K-edges in Fig. 3 to the first set of LUMOs. It is important to highlight that the S and Cl K-edge spectra are expected to show a high similarity for the mono- and binuclear complexes, with the exception of the double edge jump due to the presence of the bridging chloride ligands. The quantitation of the orbital

compositions at the BP86/def2TZVP level of theory using Mulliken population analysis defines LUMO as Bi $6p^{0.38}$ S $3p^{0.03}$ Cl $3p^{0.04}$ O $2p^{0.01}$, LUMO+1 as Bi $6p^{0.23}$ S $3p^{0.03}$ Cl $3p^{0.06}$, and LUMO+2 as Bi $6p^{0.28}$ S $3p^{0.04}$ Cl $3p^{0.08}$ for complex (I), while the rest is composed of ligand C, N and H contributions. Summation of the individual S $3p$ and Cl $3p$ contributions gives S $\rightarrow$ Bi and Cl $\rightarrow$ Bi total electron donations for the first three LUMOs with 6 electron holes of 0.20 e S $3p$ and 0.36 e Cl $3p$ contributions, respectively. The small Bi contributions of 0.23–0.38 per electron hole indicate that the valence $6p$ orbital contributions also present in higher lying unoccupied orbitals as various additional combinations of ligand donor/Bi $6p$ orbitals are possible. These contribute to the ill-resolved rising-edge features along both the S K- and Cl K-edges above the pre-edge features that are not analyzed here quantitatively. A similar analysis for binuclear complex (II) gives total S $\rightarrow$ Bi and Cl $\rightarrow$ Bi donations for the first six LUMOs (see Fig. S6 in the *Supporting information*) of 0.28 e S $3p$ and 0.34 e Cl $3p$, which are again indicative for the presence of covalent Bi–S and Bi–Cl interactions. The corresponding experimental values from S K- and Cl K-edge XAS measurements are 0.95 e for the Tm^{tBu} ligand and 0.36/0.38 e for the Cl^t/Cl^b ligands (t is terminal and b is bridging). While the Cl $3p$ contributions show a remarkable agreement between theory and experiment, the calculated S $3p$ contribution overly underestimates the experimental values, which suggests that higher lying Bi–S(Tm^{tBu}) orbitals may also contribute to the first pre-edge feature. The considerable S/Cl $\rightarrow$ Bi electron donation numbers validate the use of a covalent DFT description for the electronic structure of the Bi(Tm^{tBu})(Cl) L complexes.

4. Conclusion

Chemical synthesis with combined X-ray diffraction, X-ray spectroscopic, and theoretical electronic structure investigations have provided a comprehensive geometric and electronic structural overview of the composition, structure and stability relationships in mono- and binuclear bismuth(III) complexes with an anionic sulfur-containing tripod ligand. The molecular structural analysis from XRD data already indicated a strong interaction between the p -block element and the soft chelating ligand environment. Furthermore, the distortion of the inner-sphere bond angles around the central Bi^{III} ion suggested the presence of a stereochemically active Bi $6s^2$ lone pair. Ligand K-edge X-ray absorption spectroscopic measurements at the S $1s$ and Cl $1s$ excitation energies provided well-resolved pre-edge features and structured rising-edge features. Upon coordination to the Bi^{III} ion, the spectral features of the free S-ligand changes significantly, which is an experimental indication of the presence of a significant S $\rightarrow$ Bi electron donation or covalency. The Cl K-edge spectra shows two resolved pre-edge features for the terminal and the bridging chloride environment with large intensities, which again are indicative of significant Cl $\rightarrow$ Bi covalency. Complementary electronic structure calculations using density functionals that generally give covalent bonding further supports the significant inter-

actions between Bi^{III} and the soft tripodal ligand. The chloride ligands provide additional stability through covalent Bi–Cl bonding. It is interesting to note that the weak Bi^{III}–O(methanol) interaction is sufficient to stabilize the mononuclear complex over a period of time; however, extended storage can result in the loss of the methanol ligand and dimerization taking place. We have observed this behaviour for the samples during the XAS measurements, when the spectra of an old (kept at room temperature for more than six months) mononuclear complex turned out to be identical to that of the binuclear complex. The molecular orbital analysis shows the magnitude with which the S $3p$ orbitals become involved with the σ - and π -system of the pyrazole ligands. This provides a rationale for the future functionalization of the scorpionate ligand with electron withdrawing/donating groups that can enable or hinder specific S-metal ligand interactions and tune the reactivity of the Tm-ligand-coordinated metal site.

Acknowledgements

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supporting information

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Mono- and binuclear tris(3-*tert*-butyl-2-sulfanylidene-1*H*-imidazol-1-yl)hydroborate bismuth(III) dichloride complexes: a soft scorpionate ligand can coordinate to *p*-block elements

Kiyoshi Fujisawa, Ayaka Kuboniwa, Mercedesz Kiss and Robert K. Szilagy

Computing details

For both compounds, 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: *SIR2011* (Burla *et al.*, 2012) for BiTmCl₂; Il Milione (Burla *et al.*, 2007) for BiTmClm-Cl₂. For both compounds, program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *CrystalStructure* (Rigaku, 2015); software used to prepare material for publication: *CrystalStructure* (Rigaku, 2015).

(BiTmCl₂) Dichlorido(methanol- κ O)[tris(3-*tert*-butyl-2-sulfanylidene-1*H*-imidazol-1-yl)- κ S]hydroborato]bismuth(III)

Crystal data

[Bi(C₂₁H₃₄BN₆S₃)Cl₂(CH₄O)]

$M_r = 789.46$

Triclinic, $P\bar{1}$

$a = 10.2899$ (5) Å

$b = 10.6653$ (4) Å

$c = 15.9818$ (10) Å

$\alpha = 72.157$ (6)°

$\beta = 83.838$ (8)°

$\gamma = 67.742$ (7)°

$V = 1545.08$ (16) Å³

$Z = 2$

$F(000) = 780.00$

$D_x = 1.697$ Mg m⁻³

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

Cell parameters from 6399 reflections

$\theta = 3.0\text{--}27.5^\circ$

$\mu = 6.10$ mm⁻¹

$T = 179$ K

Block, orange

$0.24 \times 0.16 \times 0.07$ mm

Data collection

Rigaku XtaLAB P200

diffractometer

Detector resolution: 5.814 pixels mm⁻¹

ω scans

Absorption correction: numerical

(NUMABS; Rigaku, 1999)

$T_{\min} = 0.465$, $T_{\max} = 0.653$

51186 measured reflections

7083 independent reflections

6768 reflections with $F^2 > 2.0\sigma(F^2)$

$R_{\text{int}} = 0.037$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.0^\circ$

$h = -13 \rightarrow 13$

$k = -13 \rightarrow 13$

$l = -20 \rightarrow 20$

*Refinement*Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.012$ $wR(F^2) = 0.032$ $S = 1.01$

7083 reflections

327 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0201P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.008$ $\Delta\rho_{\max} = 1.03 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.66 \text{ e } \text{\AA}^{-3}$ *Special details*

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

Refinement. Refinement was performed using all reflections. The weighted R-factor (wR) and goodness of fit (S) are based on F^2 . R-factor (gt) are based on F. The threshold expression of $F^2 > 2.0 \sigma(F^2)$ is used only for calculating R-factor (gt).

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Bi1	0.36354 (2)	1.04501 (2)	0.67383 (2)	0.01603 (2)
Cl1	0.25103 (5)	1.26183 (4)	0.53006 (3)	0.02523 (8)
Cl2	0.50213 (4)	1.17929 (5)	0.73128 (3)	0.02968 (9)
S1	0.20113 (4)	1.14394 (4)	0.79687 (3)	0.01864 (8)
S2	0.45474 (4)	0.76840 (4)	0.79180 (2)	0.02165 (8)
S3	0.15003 (4)	0.98696 (4)	0.62743 (2)	0.01790 (7)
O1	0.62244 (15)	0.89575 (17)	0.61046 (10)	0.0438 (4)
H1D	0.6395	0.8542	0.5713	0.053*
N1	-0.08146 (13)	1.24077 (14)	0.75734 (9)	0.0191 (3)
N2	0.01419 (13)	1.00946 (14)	0.81002 (9)	0.0187 (3)
N3	0.43620 (14)	0.78152 (14)	0.96219 (9)	0.0214 (3)
N4	0.23275 (15)	0.82784 (14)	0.90396 (8)	0.0202 (3)
N5	0.22948 (14)	0.69860 (13)	0.65939 (9)	0.0188 (3)
N6	0.15131 (14)	0.77211 (14)	0.77630 (8)	0.0198 (3)
C1	-0.0224 (2)	1.4371 (2)	0.65160 (12)	0.0338 (4)
H1A	-0.0408	1.5388	0.6351	0.041*
H1B	0.0776	1.3839	0.6658	0.041*
H1C	-0.0477	1.4138	0.6024	0.041*
C2	-0.2653 (2)	1.4796 (2)	0.70769 (15)	0.0388 (5)
H2A	-0.2849	1.5815	0.6909	0.047*
H2B	-0.2884	1.4551	0.6584	0.047*
H2C	-0.3224	1.4546	0.7585	0.047*
C3	-0.0764 (2)	1.4329 (2)	0.81079 (13)	0.0340 (4)
H3A	-0.0940	1.5343	0.7954	0.041*
H3B	-0.1363	1.4082	0.8600	0.041*
H3C	0.0224	1.3786	0.8278	0.041*

C4	−0.10966 (17)	1.39816 (17)	0.73153 (11)	0.0243 (3)
C5	0.04038 (15)	1.13061 (16)	0.78764 (10)	0.0166 (3)
C6	−0.18439 (17)	1.18594 (18)	0.75890 (11)	0.0226 (3)
H6	−0.2794	1.2387	0.7404	0.027*
C7	−0.12563 (17)	1.04496 (18)	0.79122 (11)	0.0228 (3)
H7	−0.1722	0.9803	0.7998	0.027*
C8	0.6598 (2)	0.57980 (19)	0.97319 (12)	0.0316 (4)
H8A	0.7612	0.5455	0.9837	0.038*
H8B	0.6190	0.5192	1.0177	0.038*
H8C	0.6429	0.5773	0.9146	0.038*
C9	0.6141 (2)	0.7329 (2)	1.07119 (13)	0.0374 (5)
H9A	0.7149	0.7009	1.0828	0.045*
H9B	0.5673	0.8292	1.0762	0.045*
H9C	0.5745	0.6693	1.1140	0.045*
C10	0.6543 (2)	0.8316 (2)	0.91306 (14)	0.0427 (5)
H10A	0.7553	0.7982	0.9245	0.051*
H10B	0.6391	0.8335	0.8531	0.051*
H10C	0.6086	0.9272	0.9195	0.051*
C11	0.59183 (18)	0.73193 (18)	0.97865 (11)	0.0243 (3)
C12	0.37182 (17)	0.79315 (16)	0.88797 (10)	0.0187 (3)
C13	0.33391 (19)	0.81150 (19)	1.02439 (11)	0.0278 (4)
H13	0.3487	0.8122	1.0819	0.033*
C14	0.20998 (19)	0.83945 (19)	0.98888 (10)	0.0267 (4)
H14	0.1216	0.8632	1.0171	0.032*
C15	0.14735 (19)	0.7795 (2)	0.50545 (11)	0.0292 (4)
H15A	0.1754	0.7766	0.4453	0.035*
H15B	0.0738	0.7396	0.5242	0.035*
H15C	0.1114	0.8778	0.5074	0.035*
C16	0.39551 (19)	0.7470 (2)	0.54034 (12)	0.0288 (4)
H16A	0.4245	0.7434	0.4804	0.035*
H16B	0.3646	0.8448	0.5427	0.035*
H16C	0.4749	0.6871	0.5809	0.035*
C17	0.3252 (2)	0.53949 (19)	0.56530 (13)	0.0338 (4)
H17A	0.3546	0.5344	0.5057	0.041*
H17B	0.4049	0.4820	0.6060	0.041*
H17C	0.2488	0.5035	0.5832	0.041*
C18	0.27423 (17)	0.69314 (17)	0.56696 (10)	0.0214 (3)
C19	0.17947 (16)	0.81433 (16)	0.68941 (10)	0.0171 (3)
C20	0.23340 (19)	0.58114 (17)	0.72914 (11)	0.0258 (4)
H20	0.2646	0.4861	0.7271	0.031*
C21	0.18492 (19)	0.62702 (17)	0.79991 (11)	0.0264 (4)
H21	0.1752	0.5694	0.8570	0.032*
C22	0.7500 (2)	0.8917 (2)	0.63949 (15)	0.0427 (5)
H22A	0.7306	0.9713	0.6633	0.051*
H22B	0.8142	0.8984	0.5899	0.051*
H22C	0.7931	0.8026	0.6853	0.051*
B1	0.1064 (2)	0.8501 (2)	0.84775 (12)	0.0208 (4)
H1	0.0452	0.8058	0.8891	0.025*

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

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Bi1	0.01464 (3)	0.01767 (3)	0.01733 (3)	−0.00662 (2)	0.00094 (2)	−0.00655 (2)
Cl1	0.0344 (2)	0.02018 (19)	0.02140 (18)	−0.01082 (17)	0.00152 (16)	−0.00566 (15)
Cl2	0.0225 (2)	0.0394 (2)	0.0369 (2)	−0.01774 (19)	0.00175 (17)	−0.01666 (19)
S1	0.01422 (17)	0.0227 (2)	0.02320 (18)	−0.00741 (15)	0.00018 (14)	−0.01156 (15)
S2	0.02088 (19)	0.0249 (2)	0.01456 (16)	−0.00174 (16)	−0.00040 (14)	−0.00753 (15)
S3	0.02191 (19)	0.01311 (17)	0.01865 (17)	−0.00623 (15)	−0.00488 (14)	−0.00307 (14)
O1	0.0377 (8)	0.0580 (10)	0.0466 (9)	−0.0171 (7)	0.0138 (7)	−0.0353 (8)
N1	0.0140 (6)	0.0211 (7)	0.0227 (6)	−0.0048 (5)	0.0013 (5)	−0.0097 (5)
N2	0.0154 (6)	0.0216 (7)	0.0210 (6)	−0.0076 (5)	0.0014 (5)	−0.0082 (5)
N3	0.0235 (7)	0.0213 (7)	0.0170 (6)	−0.0028 (6)	−0.0029 (5)	−0.0079 (5)
N4	0.0239 (7)	0.0206 (7)	0.0143 (6)	−0.0059 (6)	0.0016 (5)	−0.0059 (5)
N5	0.0224 (7)	0.0144 (6)	0.0207 (6)	−0.0071 (5)	−0.0036 (5)	−0.0048 (5)
N6	0.0248 (7)	0.0160 (6)	0.0191 (6)	−0.0087 (6)	−0.0022 (5)	−0.0031 (5)
C1	0.0318 (10)	0.0274 (10)	0.0328 (10)	−0.0069 (8)	0.0053 (8)	−0.0022 (8)
C2	0.0221 (9)	0.0264 (10)	0.0568 (13)	0.0016 (8)	0.0000 (9)	−0.0098 (9)
C3	0.0388 (11)	0.0251 (9)	0.0414 (11)	−0.0087 (8)	0.0064 (8)	−0.0201 (8)
C4	0.0208 (8)	0.0193 (8)	0.0307 (9)	−0.0041 (7)	0.0037 (7)	−0.0094 (7)
C5	0.0138 (7)	0.0198 (8)	0.0185 (7)	−0.0055 (6)	0.0017 (5)	−0.0099 (6)
C6	0.0134 (7)	0.0298 (9)	0.0263 (8)	−0.0078 (7)	0.0015 (6)	−0.0110 (7)
C7	0.0168 (8)	0.0305 (9)	0.0272 (8)	−0.0126 (7)	0.0032 (6)	−0.0126 (7)
C8	0.0298 (10)	0.0283 (10)	0.0304 (9)	0.0019 (8)	−0.0097 (7)	−0.0124 (8)
C9	0.0402 (11)	0.0391 (11)	0.0317 (10)	−0.0031 (9)	−0.0153 (8)	−0.0175 (9)
C10	0.0388 (11)	0.0449 (12)	0.0423 (11)	−0.0219 (10)	−0.0124 (9)	0.0028 (10)
C11	0.0248 (8)	0.0240 (9)	0.0224 (8)	−0.0049 (7)	−0.0080 (6)	−0.0067 (7)
C12	0.0225 (8)	0.0150 (7)	0.0152 (7)	−0.0031 (6)	−0.0017 (6)	−0.0040 (6)
C13	0.0345 (10)	0.0299 (9)	0.0149 (7)	−0.0050 (8)	0.0008 (7)	−0.0095 (7)
C14	0.0298 (9)	0.0299 (9)	0.0161 (7)	−0.0060 (8)	0.0058 (6)	−0.0087 (7)
C15	0.0316 (9)	0.0337 (10)	0.0250 (8)	−0.0094 (8)	−0.0067 (7)	−0.0129 (7)
C16	0.0241 (9)	0.0283 (9)	0.0361 (10)	−0.0099 (8)	0.0037 (7)	−0.0128 (8)
C17	0.0451 (11)	0.0225 (9)	0.0370 (10)	−0.0115 (8)	0.0067 (9)	−0.0160 (8)
C18	0.0243 (8)	0.0195 (8)	0.0225 (8)	−0.0071 (7)	−0.0011 (6)	−0.0097 (6)
C19	0.0174 (7)	0.0151 (7)	0.0198 (7)	−0.0066 (6)	−0.0038 (6)	−0.0043 (6)
C20	0.0352 (9)	0.0149 (8)	0.0271 (8)	−0.0102 (7)	−0.0042 (7)	−0.0029 (6)
C21	0.0383 (10)	0.0174 (8)	0.0236 (8)	−0.0131 (7)	−0.0036 (7)	−0.0008 (6)
C22	0.0408 (12)	0.0457 (13)	0.0449 (12)	−0.0117 (10)	0.0046 (9)	−0.0241 (10)
B1	0.0218 (9)	0.0207 (9)	0.0212 (8)	−0.0092 (8)	0.0022 (7)	−0.0066 (7)

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

Bi1—S1	2.6463 (5)	C3—H3B	0.9800
Bi1—Cl1	2.6933 (5)	C3—H3C	0.9800
Bi1—S3	2.7242 (4)	C6—C7	1.340 (2)
Bi1—Cl2	2.7499 (4)	C6—H6	0.9500
Bi1—S2	2.8307 (5)	C7—H7	0.9500
Bi1—O1	2.8023 (14)	C8—C11	1.531 (2)

S1—C5	1.7381 (15)	C8—H8A	0.9800
S2—C12	1.7193 (16)	C8—H8B	0.9800
S3—C19	1.7283 (15)	C8—H8C	0.9800
O1—C22	1.419 (3)	C9—C11	1.524 (2)
O1—H1D	0.8400	C9—H9A	0.9800
N1—C5	1.361 (2)	C9—H9B	0.9800
N1—C6	1.3852 (19)	C9—H9C	0.9800
N1—C4	1.518 (2)	C10—C11	1.527 (3)
N2—C5	1.3528 (19)	C10—H10A	0.9800
N2—C7	1.383 (2)	C10—H10B	0.9800
N2—B1	1.558 (2)	C10—H10C	0.9800
N3—C12	1.3702 (19)	C13—C14	1.342 (3)
N3—C13	1.383 (2)	C13—H13	0.9500
N3—C11	1.509 (2)	C14—H14	0.9500
N4—C12	1.352 (2)	C15—C18	1.526 (2)
N4—C14	1.387 (2)	C15—H15A	0.9800
N4—B1	1.562 (2)	C15—H15B	0.9800
N5—C19	1.359 (2)	C15—H15C	0.9800
N5—C20	1.389 (2)	C16—C18	1.532 (2)
N5—C18	1.511 (2)	C16—H16A	0.9800
N6—C19	1.3580 (19)	C16—H16B	0.9800
N6—C21	1.386 (2)	C16—H16C	0.9800
N6—B1	1.545 (2)	C17—C18	1.528 (2)
C1—C4	1.524 (2)	C17—H17A	0.9800
C1—H1A	0.9800	C17—H17B	0.9800
C1—H1B	0.9800	C17—H17C	0.9800
C1—H1C	0.9800	C20—C21	1.342 (2)
C2—C4	1.529 (2)	C20—H20	0.9500
C2—H2A	0.9800	C21—H21	0.9500
C2—H2B	0.9800	C22—H22A	0.9800
C2—H2C	0.9800	C22—H22B	0.9800
C3—C4	1.528 (2)	C22—H22C	0.9800
C3—H3A	0.9800	B1—H1	1.0000
S1—Bi1—C11	100.115 (14)	H8A—C8—H8C	109.5
S1—Bi1—S3	88.960 (13)	H8B—C8—H8C	109.5
C11—Bi1—S3	76.546 (13)	C11—C9—H9A	109.5
S1—Bi1—C12	74.926 (13)	C11—C9—H9B	109.5
C11—Bi1—C12	95.046 (14)	H9A—C9—H9B	109.5
S3—Bi1—C12	160.381 (14)	C11—C9—H9C	109.5
S1—Bi1—S2	90.300 (14)	H9A—C9—H9C	109.5
C11—Bi1—S2	160.302 (13)	H9B—C9—H9C	109.5
S3—Bi1—S2	87.065 (14)	C11—C10—H10A	109.5
C12—Bi1—S2	103.836 (14)	C11—C10—H10B	109.5
S1—Bi1—O1	152.76 (4)	H10A—C10—H10B	109.5
S2—Bi1—O1	74.07 (3)	C11—C10—H10C	109.5
S3—Bi1—O1	111.80 (4)	H10A—C10—H10C	109.5
C11—Bi1—O1	101.73 (3)	H10B—C10—H10C	109.5

C12—Bi1—O1	87.10 (4)	N3—C11—C9	108.59 (14)
C5—S1—Bi1	106.38 (5)	N3—C11—C10	110.33 (14)
C12—S2—Bi1	103.20 (5)	C9—C11—C10	108.58 (16)
C19—S3—Bi1	104.44 (5)	N3—C11—C8	108.13 (14)
C22—O1—H1D	109.5	C9—C11—C8	108.76 (14)
C5—N1—C6	108.00 (13)	C10—C11—C8	112.36 (17)
C5—N1—C4	128.36 (13)	N4—C12—N3	107.91 (13)
C6—N1—C4	123.51 (13)	N4—C12—S2	126.54 (12)
C5—N2—C7	107.75 (13)	N3—C12—S2	125.54 (12)
C5—N2—B1	133.83 (13)	C14—C13—N3	107.66 (14)
C7—N2—B1	118.40 (13)	C14—C13—H13	126.2
C12—N3—C13	108.05 (14)	N3—C13—H13	126.2
C12—N3—C11	127.23 (14)	C13—C14—N4	108.47 (15)
C13—N3—C11	124.50 (13)	C13—C14—H14	125.8
C12—N4—C14	107.90 (13)	N4—C14—H14	125.8
C12—N4—B1	132.50 (13)	C18—C15—H15A	109.5
C14—N4—B1	119.57 (14)	C18—C15—H15B	109.5
C19—N5—C20	108.25 (13)	H15A—C15—H15B	109.5
C19—N5—C18	127.58 (13)	C18—C15—H15C	109.5
C20—N5—C18	124.16 (13)	H15A—C15—H15C	109.5
C19—N6—C21	107.34 (13)	H15B—C15—H15C	109.5
C19—N6—B1	132.76 (13)	C18—C16—H16A	109.5
C21—N6—B1	119.59 (13)	C18—C16—H16B	109.5
C4—C1—H1A	109.5	H16A—C16—H16B	109.5
C4—C1—H1B	109.5	C18—C16—H16C	109.5
H1A—C1—H1B	109.5	H16A—C16—H16C	109.5
C4—C1—H1C	109.5	H16B—C16—H16C	109.5
H1A—C1—H1C	109.5	C18—C17—H17A	109.5
H1B—C1—H1C	109.5	C18—C17—H17B	109.5
C4—C2—H2A	109.5	H17A—C17—H17B	109.5
C4—C2—H2B	109.5	C18—C17—H17C	109.5
H2A—C2—H2B	109.5	H17A—C17—H17C	109.5
C4—C2—H2C	109.5	H17B—C17—H17C	109.5
H2A—C2—H2C	109.5	N5—C18—C15	108.87 (13)
H2B—C2—H2C	109.5	N5—C18—C17	108.59 (13)
C4—C3—H3A	109.5	C15—C18—C17	108.52 (14)
C4—C3—H3B	109.5	N5—C18—C16	109.45 (13)
H3A—C3—H3B	109.5	C15—C18—C16	112.53 (14)
C4—C3—H3C	109.5	C17—C18—C16	108.80 (15)
H3A—C3—H3C	109.5	N6—C19—N5	108.29 (13)
H3B—C3—H3C	109.5	N6—C19—S3	125.46 (12)
N1—C4—C1	109.70 (14)	N5—C19—S3	126.22 (12)
N1—C4—C3	108.27 (14)	C21—C20—N5	107.17 (14)
C1—C4—C3	112.34 (15)	C21—C20—H20	126.4
N1—C4—C2	108.68 (14)	N5—C20—H20	126.4
C1—C4—C2	108.85 (15)	C20—C21—N6	108.95 (14)
C3—C4—C2	108.92 (15)	C20—C21—H21	125.5
N2—C5—N1	108.14 (13)	N6—C21—H21	125.5

N2—C5—S1	126.07 (12)	O1—C22—H22A	109.5
N1—C5—S1	125.79 (12)	O1—C22—H22B	109.5
C7—C6—N1	107.55 (14)	H22A—C22—H22B	109.5
C7—C6—H6	126.2	O1—C22—H22C	109.5
N1—C6—H6	126.2	H22A—C22—H22C	109.5
C6—C7—N2	108.53 (14)	H22B—C22—H22C	109.5
C6—C7—H7	125.7	N6—B1—N2	112.52 (13)
N2—C7—H7	125.7	N6—B1—N4	112.92 (14)
C11—C8—H8A	109.5	N2—B1—N4	112.23 (13)
C11—C8—H8B	109.5	N6—B1—H1	106.2
H8A—C8—H8B	109.5	N2—B1—H1	106.2
C11—C8—H8C	109.5	N4—B1—H1	106.2
C5—N1—C4—C1	65.0 (2)	C11—N3—C13—C14	−174.35 (15)
C6—N1—C4—C1	−119.63 (17)	N3—C13—C14—N4	−0.2 (2)
C5—N1—C4—C3	−57.9 (2)	C12—N4—C14—C13	−0.3 (2)
C6—N1—C4—C3	117.46 (17)	B1—N4—C14—C13	177.98 (15)
C5—N1—C4—C2	−176.10 (16)	C19—N5—C18—C15	−62.95 (19)
C6—N1—C4—C2	−0.7 (2)	C20—N5—C18—C15	116.96 (17)
C7—N2—C5—N1	1.47 (17)	C19—N5—C18—C17	179.07 (15)
B1—N2—C5—N1	179.71 (15)	C20—N5—C18—C17	−1.0 (2)
C7—N2—C5—S1	−179.10 (12)	C19—N5—C18—C16	60.4 (2)
B1—N2—C5—S1	−0.9 (2)	C20—N5—C18—C16	−119.66 (16)
C6—N1—C5—N2	−1.59 (17)	C21—N6—C19—N5	−0.02 (17)
C4—N1—C5—N2	174.36 (14)	B1—N6—C19—N5	173.38 (15)
C6—N1—C5—S1	178.98 (12)	C21—N6—C19—S3	177.76 (12)
C4—N1—C5—S1	−5.1 (2)	B1—N6—C19—S3	−8.8 (2)
Bi1—S1—C5—N2	71.57 (14)	C20—N5—C19—N6	−0.30 (17)
Bi1—S1—C5—N1	−109.10 (13)	C18—N5—C19—N6	179.63 (14)
C5—N1—C6—C7	1.10 (18)	C20—N5—C19—S3	−178.05 (12)
C4—N1—C6—C7	−175.09 (14)	C18—N5—C19—S3	1.9 (2)
N1—C6—C7—N2	−0.20 (19)	Bi1—S3—C19—N6	76.69 (13)
C5—N2—C7—C6	−0.78 (18)	Bi1—S3—C19—N5	−105.93 (13)
B1—N2—C7—C6	−179.34 (14)	C19—N5—C20—C21	0.51 (19)
C12—N3—C11—C9	−178.53 (16)	C18—N5—C20—C21	−179.42 (14)
C13—N3—C11—C9	−4.6 (2)	N5—C20—C21—N6	−0.5 (2)
C12—N3—C11—C10	62.6 (2)	C19—N6—C21—C20	0.34 (19)
C13—N3—C11—C10	−123.47 (18)	B1—N6—C21—C20	−174.09 (15)
C12—N3—C11—C8	−60.7 (2)	C19—N6—B1—N2	31.8 (2)
C13—N3—C11—C8	113.28 (18)	C21—N6—B1—N2	−155.42 (14)
C14—N4—C12—N3	0.63 (18)	C19—N6—B1—N4	−96.48 (19)
B1—N4—C12—N3	−177.31 (15)	C21—N6—B1—N4	76.27 (18)
C14—N4—C12—S2	−179.10 (13)	C5—N2—B1—N6	−100.67 (19)
B1—N4—C12—S2	3.0 (3)	C7—N2—B1—N6	77.43 (17)
C13—N3—C12—N4	−0.75 (18)	C5—N2—B1—N4	28.0 (2)
C11—N3—C12—N4	174.00 (14)	C7—N2—B1—N4	−153.90 (13)
C13—N3—C12—S2	178.99 (12)	C12—N4—B1—N6	23.5 (2)
C11—N3—C12—S2	−6.3 (2)	C14—N4—B1—N6	−154.27 (14)

Bi1—S2—C12—N4	70.01 (14)	C12—N4—B1—N2	−104.98 (19)
Bi1—S2—C12—N3	−109.68 (13)	C14—N4—B1—N2	77.27 (18)
C12—N3—C13—C14	0.58 (19)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O1—H1D $\cdots$ Cl1 ⁱ	0.84	2.28	3.0969 (18)	164

Symmetry code: (i) $-x+1, -y+2, -z+1$.**(BiTmClm-Cl2) Di- μ -chlorido-bis{chlorido[tris(3-*tert*-butyl-2-sulfanylidene-1*H*-imidazol-1-yl)- κ S]hydroborato]bismuth(III)}***Crystal data*[Bi₂(C₂₁H₃₄BN₆S₃)₂Cl₄] $M_r = 1514.83$ Triclinic, *P*1 $a = 10.8009$ (11) Å $b = 11.3698$ (14) Å $c = 11.8690$ (13) Å $\alpha = 95.125$ (4)° $\beta = 91.947$ (4)° $\gamma = 99.549$ (3)° $V = 1429.9$ (3) Å³ $Z = 1$ $F(000) = 744.00$ $D_x = 1.759$ Mg m^{−3}Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å

Cell parameters from 6052 reflections

 $\theta = 3.0$ – 27.5° $\mu = 6.58$ mm^{−1} $T = 179$ K

Block, orange

 $0.23 \times 0.15 \times 0.15$ mm*Data collection*

Rigaku XtaLAB P200

diffractometer

Detector resolution: 5.814 pixels mm^{−1} ω scans

Absorption correction: numerical

(NUMABS; Rigaku, 1999)

 $T_{\min} = 0.270$, $T_{\max} = 0.373$

39709 measured reflections

6115 independent reflections

5816 reflections with $F^2 > 2.0\sigma(F^2)$ $R_{\text{int}} = 0.034$ $\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.0^\circ$ $h = -14 \rightarrow 14$ $k = -14 \rightarrow 14$ $l = -14 \rightarrow 15$ *Refinement*Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.013$ $wR(F^2) = 0.033$ $S = 1.04$

6115 reflections

307 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

 $w = 1/[\sigma^2(F_o^2) + (0.019P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 0.59$ e Å^{−3} $\Delta\rho_{\min} = -0.85$ e Å^{−3}*Special details*

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

Refinement. Refinement was performed using all reflections. The weighted R-factor (wR) and goodness of fit (S) are based on F^2 . R-factor (gt) are based on F. The threshold expression of $F^2 > 2.0 \text{ sigma}(F^2)$ is used only for calculating R-factor (gt).

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Bi1	0.39969 (2)	0.41301 (2)	0.85362 (2)	0.01774 (3)
Cl1	0.37944 (5)	0.61914 (5)	1.01595 (4)	0.03186 (11)
Cl2	0.54822 (4)	0.56134 (4)	0.74438 (5)	0.02943 (11)
S1	0.18081 (4)	0.26572 (4)	0.93598 (4)	0.02185 (10)
S2	0.45110 (4)	0.20689 (4)	0.74473 (4)	0.01891 (9)
S3	0.24933 (4)	0.44487 (4)	0.67720 (4)	0.02081 (10)
N1	0.22072 (14)	0.03193 (13)	0.93270 (12)	0.0190 (3)
N2	0.16688 (14)	0.08266 (13)	0.76597 (12)	0.0181 (3)
N3	0.43753 (14)	0.20501 (13)	0.51162 (12)	0.0184 (3)
N4	0.25221 (14)	0.17310 (13)	0.58613 (12)	0.0190 (3)
N5	0.00025 (13)	0.41876 (13)	0.73377 (13)	0.0206 (3)
N6	0.06462 (13)	0.24855 (13)	0.68614 (12)	0.0189 (3)
C1	0.3749 (2)	0.1261 (2)	1.08680 (19)	0.0363 (5)
H1A	0.3979	0.1279	1.1676	0.044*
H1B	0.4434	0.1038	1.0420	0.044*
H1C	0.3598	0.2055	1.0700	0.044*
C2	0.1451 (2)	0.06199 (19)	1.12597 (17)	0.0303 (5)
H2A	0.1674	0.0635	1.2069	0.036*
H2B	0.1258	0.1402	1.1099	0.036*
H2C	0.0713	0.0000	1.1053	0.036*
C3	0.2806 (2)	−0.0901 (2)	1.08051 (18)	0.0344 (5)
H3A	0.3033	−0.0900	1.1612	0.041*
H3B	0.2047	−0.1495	1.0601	0.041*
H3C	0.3497	−0.1103	1.0354	0.041*
C4	0.25550 (17)	0.03418 (17)	1.05699 (15)	0.0231 (4)
C5	0.19061 (16)	0.12427 (15)	0.87656 (15)	0.0174 (4)
C6	0.21619 (19)	−0.06658 (16)	0.85467 (16)	0.0250 (4)
H6	0.2336	−0.1429	0.8703	0.030*
C7	0.18299 (18)	−0.03572 (16)	0.75342 (16)	0.0237 (4)
H7	0.1723	−0.0865	0.6845	0.028*
C8	0.6337 (2)	0.35132 (18)	0.54280 (18)	0.0300 (5)
H8A	0.7244	0.3657	0.5323	0.036*
H8B	0.5942	0.4089	0.5036	0.036*
H8C	0.6187	0.3610	0.6238	0.036*
C9	0.63882 (18)	0.13017 (18)	0.54876 (17)	0.0268 (4)
H9A	0.7292	0.1440	0.5368	0.032*
H9B	0.6254	0.1357	0.6302	0.032*
H9C	0.6010	0.0502	0.5142	0.032*
C10	0.59799 (19)	0.21018 (19)	0.36664 (16)	0.0287 (4)
H10A	0.6883	0.2227	0.3543	0.034*
H10B	0.5595	0.1293	0.3351	0.034*

H10C	0.5591	0.2693	0.3291	0.034*
C11	0.57765 (17)	0.22470 (17)	0.49425 (15)	0.0216 (4)
C12	0.37782 (16)	0.19445 (15)	0.61077 (14)	0.0170 (3)
C13	0.34632 (18)	0.19420 (18)	0.42468 (16)	0.0241 (4)
H13	0.3609	0.1999	0.3467	0.029*
C14	0.23349 (18)	0.17415 (18)	0.47038 (15)	0.0243 (4)
H14	0.1543	0.1627	0.4300	0.029*
C15	0.0832 (2)	0.6027 (2)	0.8588 (2)	0.0394 (5)
H15A	0.0791	0.6879	0.8752	0.047*
H15B	0.0593	0.5604	0.9252	0.047*
H15C	0.1691	0.5935	0.8405	0.047*
C16	0.0232 (2)	0.61294 (19)	0.6516 (2)	0.0388 (5)
H16A	0.0189	0.6983	0.6667	0.047*
H16B	0.1079	0.6038	0.6294	0.047*
H16C	−0.0380	0.5771	0.5901	0.047*
C17	−0.1409 (2)	0.5614 (2)	0.7884 (2)	0.0424 (6)
H17A	−0.1470	0.6462	0.8046	0.051*
H17B	−0.1991	0.5261	0.7245	0.051*
H17C	−0.1626	0.5191	0.8553	0.051*
C18	−0.00674 (17)	0.55006 (17)	0.75832 (18)	0.0262 (4)
C19	0.10116 (16)	0.36878 (16)	0.70073 (15)	0.0182 (4)
C20	−0.09990 (17)	0.32700 (18)	0.74195 (17)	0.0263 (4)
H20	−0.1817	0.3358	0.7646	0.032*
C21	−0.06013 (17)	0.22343 (17)	0.71200 (17)	0.0250 (4)
H21	−0.1095	0.1458	0.7091	0.030*
B1	0.13545 (19)	0.14250 (19)	0.65828 (17)	0.0199 (4)
H1	0.0750	0.0805	0.6102	0.024*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Bi1	0.01588 (4)	0.01547 (4)	0.02072 (4)	0.00196 (3)	−0.00091 (3)	−0.00250 (3)
Cl1	0.0333 (3)	0.0311 (3)	0.0322 (3)	0.0143 (2)	−0.0045 (2)	−0.0054 (2)
Cl2	0.0192 (2)	0.0237 (2)	0.0458 (3)	0.00227 (18)	0.0058 (2)	0.0070 (2)
S1	0.0284 (2)	0.0156 (2)	0.0213 (2)	0.00477 (18)	0.00527 (19)	−0.00240 (18)
S2	0.0203 (2)	0.0211 (2)	0.0155 (2)	0.00582 (18)	−0.00146 (17)	−0.00098 (17)
S3	0.0129 (2)	0.0214 (2)	0.0285 (2)	0.00180 (17)	0.00229 (18)	0.00610 (19)
N1	0.0211 (8)	0.0175 (8)	0.0191 (8)	0.0043 (6)	0.0044 (6)	0.0016 (6)
N2	0.0201 (8)	0.0158 (7)	0.0181 (8)	0.0032 (6)	0.0033 (6)	−0.0007 (6)
N3	0.0189 (7)	0.0209 (8)	0.0164 (7)	0.0070 (6)	0.0012 (6)	0.0006 (6)
N4	0.0192 (7)	0.0214 (8)	0.0167 (7)	0.0060 (6)	−0.0002 (6)	−0.0003 (6)
N5	0.0128 (7)	0.0205 (8)	0.0280 (8)	0.0025 (6)	0.0004 (6)	0.0003 (6)
N6	0.0147 (7)	0.0192 (8)	0.0225 (8)	0.0020 (6)	0.0007 (6)	0.0026 (6)
C1	0.0299 (11)	0.0471 (14)	0.0296 (12)	−0.0004 (10)	−0.0033 (9)	0.0063 (10)
C2	0.0334 (11)	0.0360 (12)	0.0245 (10)	0.0101 (9)	0.0109 (9)	0.0074 (9)
C3	0.0416 (12)	0.0369 (12)	0.0303 (11)	0.0172 (10)	0.0049 (9)	0.0126 (9)
C4	0.0243 (10)	0.0261 (10)	0.0198 (9)	0.0057 (8)	0.0026 (8)	0.0047 (8)
C5	0.0156 (8)	0.0153 (9)	0.0208 (9)	0.0011 (7)	0.0045 (7)	0.0003 (7)

C6	0.0319 (11)	0.0150 (9)	0.0292 (11)	0.0067 (8)	0.0057 (8)	0.0007 (8)
C7	0.0293 (10)	0.0159 (9)	0.0249 (10)	0.0033 (8)	0.0057 (8)	−0.0045 (8)
C8	0.0295 (11)	0.0245 (10)	0.0340 (12)	−0.0007 (8)	0.0105 (9)	−0.0006 (9)
C9	0.0199 (9)	0.0291 (11)	0.0329 (11)	0.0080 (8)	0.0010 (8)	0.0033 (9)
C10	0.0265 (10)	0.0378 (12)	0.0246 (10)	0.0134 (9)	0.0075 (8)	0.0013 (9)
C11	0.0195 (9)	0.0244 (10)	0.0218 (10)	0.0058 (8)	0.0044 (7)	0.0011 (8)
C12	0.0191 (9)	0.0144 (8)	0.0177 (9)	0.0051 (7)	0.0002 (7)	−0.0013 (7)
C13	0.0262 (10)	0.0325 (11)	0.0153 (9)	0.0095 (8)	0.0001 (8)	0.0027 (8)
C14	0.0241 (10)	0.0336 (11)	0.0159 (9)	0.0091 (8)	−0.0034 (7)	−0.0001 (8)
C15	0.0335 (12)	0.0329 (12)	0.0480 (14)	0.0044 (10)	−0.0063 (10)	−0.0128 (10)
C16	0.0380 (12)	0.0279 (12)	0.0550 (15)	0.0147 (10)	0.0028 (11)	0.0102 (10)
C17	0.0238 (11)	0.0320 (12)	0.0696 (17)	0.0077 (9)	0.0081 (11)	−0.0139 (11)
C18	0.0180 (9)	0.0203 (10)	0.0397 (12)	0.0050 (7)	0.0001 (8)	−0.0035 (8)
C19	0.0137 (8)	0.0215 (9)	0.0191 (9)	0.0028 (7)	−0.0004 (7)	0.0018 (7)
C20	0.0122 (9)	0.0283 (10)	0.0377 (12)	0.0010 (8)	0.0043 (8)	0.0022 (9)
C21	0.0149 (9)	0.0235 (10)	0.0351 (11)	−0.0014 (7)	0.0016 (8)	0.0043 (8)
B1	0.0191 (10)	0.0196 (10)	0.0195 (10)	0.0015 (8)	−0.0012 (8)	−0.0015 (8)

Geometric parameters (Å, °)

Bi1—Cl2	2.5949 (5)	C3—H3A	0.9800
Bi1—S3	2.6931 (5)	C3—H3B	0.9800
Bi1—S2	2.7222 (5)	C3—H3C	0.9800
Bi1—Cl1 ⁱ	2.8915 (5)	C6—C7	1.336 (3)
Bi1—S1	2.9128 (5)	C6—H6	0.9500
Bi1—Cl1	2.9401 (6)	C7—H7	0.9500
Cl1—Bi1 ⁱ	2.8915 (5)	C8—C11	1.520 (3)
S1—C5	1.7188 (18)	C8—H8A	0.9800
S2—C12	1.7354 (18)	C8—H8B	0.9800
S3—C19	1.7326 (18)	C8—H8C	0.9800
N1—C5	1.369 (2)	C9—C11	1.530 (3)
N1—C6	1.381 (2)	C9—H9A	0.9800
N1—C4	1.507 (2)	C9—H9B	0.9800
N2—C5	1.356 (2)	C9—H9C	0.9800
N2—C7	1.381 (2)	C10—C11	1.536 (3)
N2—B1	1.554 (2)	C10—H10A	0.9800
N3—C12	1.366 (2)	C10—H10B	0.9800
N3—C13	1.385 (2)	C10—H10C	0.9800
N3—C11	1.517 (2)	C13—C14	1.344 (3)
N4—C12	1.355 (2)	C13—H13	0.9500
N4—C14	1.383 (2)	C14—H14	0.9500
N4—B1	1.558 (2)	C15—C18	1.525 (3)
N5—C19	1.364 (2)	C15—H15A	0.9800
N5—C20	1.385 (2)	C15—H15B	0.9800
N5—C18	1.510 (2)	C15—H15C	0.9800
N6—C19	1.352 (2)	C16—C18	1.528 (3)
N6—C21	1.381 (2)	C16—H16A	0.9800
N6—B1	1.549 (2)	C16—H16B	0.9800

C1—C4	1.529 (3)	C16—H16C	0.9800
C1—H1A	0.9800	C17—C18	1.527 (3)
C1—H1B	0.9800	C17—H17A	0.9800
C1—H1C	0.9800	C17—H17B	0.9800
C2—C4	1.529 (3)	C17—H17C	0.9800
C2—H2A	0.9800	C20—C21	1.342 (3)
C2—H2B	0.9800	C20—H20	0.9500
C2—H2C	0.9800	C21—H21	0.9500
C3—C4	1.529 (3)	B1—H1	1.0000
C12—Bi1—S3	77.787 (16)	C11—C8—H8B	109.5
C12—Bi1—S2	97.312 (17)	H8A—C8—H8B	109.5
S3—Bi1—S2	91.074 (15)	C11—C8—H8C	109.5
C12—Bi1—C11 ⁱ	87.108 (17)	H8A—C8—H8C	109.5
S3—Bi1—C11 ⁱ	160.787 (15)	H8B—C8—H8C	109.5
S2—Bi1—C11 ⁱ	79.020 (15)	C11—C9—H9A	109.5
C12—Bi1—S1	164.283 (15)	C11—C9—H9B	109.5
S3—Bi1—S1	86.949 (15)	H9A—C9—H9B	109.5
S2—Bi1—S1	86.582 (15)	C11—C9—H9C	109.5
C11 ⁱ —Bi1—S1	108.598 (16)	H9A—C9—H9C	109.5
C12—Bi1—C11	86.939 (18)	H9B—C9—H9C	109.5
S3—Bi1—C11	102.541 (15)	C11—C10—H10A	109.5
S2—Bi1—C11	166.327 (14)	C11—C10—H10B	109.5
C11 ⁱ —Bi1—C11	88.262 (15)	H10A—C10—H10B	109.5
S1—Bi1—C11	92.814 (16)	C11—C10—H10C	109.5
Bi1 ⁱ —C11—Bi1	91.738 (15)	H10A—C10—H10C	109.5
C5—S1—Bi1	103.01 (6)	H10B—C10—H10C	109.5
C12—S2—Bi1	105.95 (6)	N3—C11—C8	108.35 (15)
C19—S3—Bi1	106.11 (6)	N3—C11—C9	110.42 (14)
C5—N1—C6	108.04 (15)	C8—C11—C9	112.19 (16)
C5—N1—C4	127.44 (15)	N3—C11—C10	108.72 (15)
C6—N1—C4	124.51 (14)	C8—C11—C10	109.60 (16)
C5—N2—C7	108.25 (14)	C9—C11—C10	107.50 (15)
C5—N2—B1	133.29 (15)	N4—C12—N3	108.17 (15)
C7—N2—B1	118.34 (15)	N4—C12—S2	126.23 (13)
C12—N3—C13	107.79 (14)	N3—C12—S2	125.59 (13)
C12—N3—C11	128.24 (14)	C14—C13—N3	107.74 (16)
C13—N3—C11	123.97 (14)	C14—C13—H13	126.1
C12—N4—C14	107.80 (15)	N3—C13—H13	126.1
C12—N4—B1	133.49 (15)	C13—C14—N4	108.45 (16)
C14—N4—B1	118.60 (15)	C13—C14—H14	125.8
C19—N5—C20	108.11 (15)	N4—C14—H14	125.8
C19—N5—C18	127.96 (15)	C18—C15—H15A	109.5
C20—N5—C18	123.93 (15)	C18—C15—H15B	109.5
C19—N6—C21	107.90 (15)	H15A—C15—H15B	109.5
C19—N6—B1	133.39 (15)	C18—C15—H15C	109.5
C21—N6—B1	118.46 (15)	H15A—C15—H15C	109.5
C4—C1—H1A	109.5	H15B—C15—H15C	109.5

C4—C1—H1B	109.5	C18—C16—H16A	109.5
H1A—C1—H1B	109.5	C18—C16—H16B	109.5
C4—C1—H1C	109.5	H16A—C16—H16B	109.5
H1A—C1—H1C	109.5	C18—C16—H16C	109.5
H1B—C1—H1C	109.5	H16A—C16—H16C	109.5
C4—C2—H2A	109.5	H16B—C16—H16C	109.5
C4—C2—H2B	109.5	C18—C17—H17A	109.5
H2A—C2—H2B	109.5	C18—C17—H17B	109.5
C4—C2—H2C	109.5	H17A—C17—H17B	109.5
H2A—C2—H2C	109.5	C18—C17—H17C	109.5
H2B—C2—H2C	109.5	H17A—C17—H17C	109.5
C4—C3—H3A	109.5	H17B—C17—H17C	109.5
C4—C3—H3B	109.5	N5—C18—C15	109.08 (15)
H3A—C3—H3B	109.5	N5—C18—C16	108.88 (16)
C4—C3—H3C	109.5	C15—C18—C16	112.63 (18)
H3A—C3—H3C	109.5	N5—C18—C17	108.47 (16)
H3B—C3—H3C	109.5	C15—C18—C17	109.27 (18)
N1—C4—C1	109.13 (15)	C16—C18—C17	108.43 (17)
N1—C4—C3	108.54 (16)	N6—C19—N5	107.98 (15)
C1—C4—C3	109.24 (17)	N6—C19—S3	125.53 (13)
N1—C4—C2	109.24 (15)	N5—C19—S3	126.47 (14)
C1—C4—C2	112.29 (18)	C21—C20—N5	107.37 (16)
C3—C4—C2	108.33 (16)	C21—C20—H20	126.3
N2—C5—N1	107.40 (15)	N5—C20—H20	126.3
N2—C5—S1	126.30 (13)	C20—C21—N6	108.63 (16)
N1—C5—S1	126.29 (14)	C20—C21—H21	125.7
C7—C6—N1	107.97 (16)	N6—C21—H21	125.7
C7—C6—H6	126.0	N6—B1—N2	111.95 (15)
N1—C6—H6	126.0	N6—B1—N4	114.25 (15)
C6—C7—N2	108.34 (16)	N2—B1—N4	112.26 (14)
C6—C7—H7	125.8	N6—B1—H1	105.9
N2—C7—H7	125.8	N2—B1—H1	105.9
C11—C8—H8A	109.5	N4—B1—H1	105.9
C5—N1—C4—C1	−61.3 (2)	C11—N3—C13—C14	178.21 (16)
C6—N1—C4—C1	117.48 (19)	N3—C13—C14—N4	0.5 (2)
C5—N1—C4—C3	179.70 (17)	C12—N4—C14—C13	0.9 (2)
C6—N1—C4—C3	−1.5 (2)	B1—N4—C14—C13	−175.76 (16)
C5—N1—C4—C2	61.8 (2)	C19—N5—C18—C15	−63.0 (2)
C6—N1—C4—C2	−119.41 (19)	C20—N5—C18—C15	117.0 (2)
C7—N2—C5—N1	−0.31 (19)	C19—N5—C18—C16	60.3 (2)
B1—N2—C5—N1	−176.07 (17)	C20—N5—C18—C16	−119.7 (2)
C7—N2—C5—S1	−178.81 (13)	C19—N5—C18—C17	178.08 (18)
B1—N2—C5—S1	5.4 (3)	C20—N5—C18—C17	−1.9 (3)
C6—N1—C5—N2	0.53 (19)	C21—N6—C19—N5	−0.84 (19)
C4—N1—C5—N2	179.50 (15)	B1—N6—C19—N5	−174.81 (17)
C6—N1—C5—S1	179.03 (14)	C21—N6—C19—S3	−179.12 (14)
C4—N1—C5—S1	−2.0 (3)	B1—N6—C19—S3	6.9 (3)

Bi1—S1—C5—N2	−72.74 (15)	C20—N5—C19—N6	1.25 (19)
Bi1—S1—C5—N1	109.03 (15)	C18—N5—C19—N6	−178.75 (16)
C5—N1—C6—C7	−0.6 (2)	C20—N5—C19—S3	179.52 (14)
C4—N1—C6—C7	−179.56 (16)	C18—N5—C19—S3	−0.5 (3)
N1—C6—C7—N2	0.4 (2)	Bi1—S3—C19—N6	−75.54 (16)
C5—N2—C7—C6	0.0 (2)	Bi1—S3—C19—N5	106.49 (15)
B1—N2—C7—C6	176.46 (16)	C19—N5—C20—C21	−1.2 (2)
C12—N3—C11—C8	−70.0 (2)	C18—N5—C20—C21	178.81 (17)
C13—N3—C11—C8	110.14 (19)	N5—C20—C21—N6	0.7 (2)
C12—N3—C11—C9	53.2 (2)	C19—N6—C21—C20	0.1 (2)
C13—N3—C11—C9	−126.62 (18)	B1—N6—C21—C20	175.12 (16)
C12—N3—C11—C10	170.92 (16)	C19—N6—B1—N2	99.4 (2)
C13—N3—C11—C10	−8.9 (2)	C21—N6—B1—N2	−74.0 (2)
C14—N4—C12—N3	−1.89 (19)	C19—N6—B1—N4	−29.6 (3)
B1—N4—C12—N3	174.02 (17)	C21—N6—B1—N4	156.96 (16)
C14—N4—C12—S2	177.92 (14)	C5—N2—B1—N6	−29.7 (3)
B1—N4—C12—S2	−6.2 (3)	C7—N2—B1—N6	154.84 (15)
C13—N3—C12—N4	2.19 (19)	C5—N2—B1—N4	100.3 (2)
C11—N3—C12—N4	−177.66 (15)	C7—N2—B1—N4	−75.1 (2)
C13—N3—C12—S2	−177.62 (13)	C12—N4—B1—N6	104.3 (2)
C11—N3—C12—S2	2.5 (3)	C14—N4—B1—N6	−80.2 (2)
Bi1—S2—C12—N4	−68.38 (16)	C12—N4—B1—N2	−24.6 (3)
Bi1—S2—C12—N3	111.39 (14)	C14—N4—B1—N2	150.95 (16)
C12—N3—C13—C14	−1.6 (2)		

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