

# Two new cation radical bis(ethylenedithio)tetraselenafulvalene (BETS) salts, $\alpha$ -(BETS)<sub>6</sub>Bi<sub>3</sub>Cl<sub>12</sub>·PhCl and (BETS)<sub>2</sub>Bi<sub>2</sub>Cl<sub>8</sub>: synthesis, structure and conducting properties. First characterisation of the new trinuclear anion [Bi<sub>3</sub>Cl<sub>12</sub>]<sup>3-</sup>

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Two new radical cation salts, (BETS)<sub>6</sub>Bi<sub>3</sub>Cl<sub>12</sub>·PhCl **1** and (BETS)<sub>2</sub>Bi<sub>2</sub>Cl<sub>8</sub> **2**, where BETS is bis(ethylenedithio)tetraselenafulvalene, have been obtained and their structures and conducting properties studied. Salt **1** has a layered structure, consisting of radical cation layers of the  $\alpha$  type, and segregated anion sheets containing discrete [Bi<sub>3</sub>Cl<sub>12</sub>]<sup>3-</sup> trinuclear anions and PhCl solvent molecules. It is metallic down to 180 K. The crystal structure of salt **2** consists of stacks of BETS radical cations, with polymeric [(Bi<sub>2</sub>Cl<sub>8</sub>)<sub>n</sub>]<sup>2n-</sup> anion chains arranged in a chessboard fashion. The compound **2** exhibits semiconducting properties.

Superconductivity in molecular compounds was discovered more than 16 years ago.<sup>1</sup> Today, the number of molecular superconductors approaches one hundred. Most known radical cation superconducting salts are based on the bis(ethylenedithio)tetrathiafulvalene (ET) donor molecule. Within this series, the extensively studied  $\kappa$ -(ET)<sub>2</sub>X salts where X is a polymeric anion consisting of planar organometallic complexes of Cu<sup>+</sup> with pseudo-halogen ligands such as NCS, N(CN)<sub>2</sub>Cl, N(CN)<sub>2</sub>Br or N(CN)<sub>2</sub>CN, are the record holders with a superconducting transition temperature ( $T_c$ ) up to 10 K.<sup>2-4</sup> Bis(ethylenedithio)tetraselenafulvalene (BETS) is a close analogue of ET and may be considered as deriving from it by substituting four selenium for four sulfur atoms in the central tetrachalcogenafulvalene fragment. The probability of obtaining molecular superconductors is also quite high when using BETS as a donor molecule for preparing radical cation salts. Representative examples are  $\lambda$ -(BETS)<sub>2</sub>GaCl<sub>4</sub> with  $T_c = 8-10$  K<sup>5,6</sup> and  $\lambda$ -(BETS)<sub>2</sub>GaCl<sub>3</sub>Br with  $T_c = 7-8$  K.<sup>7</sup> A new series of BETS-based superconductors with mixed-halide gallium anions, such as GaCl<sub>3</sub>F, GaBr<sub>0.5</sub>Cl<sub>3.5</sub> and GaBr<sub>1.5</sub>Cl<sub>2.5</sub>, has recently been synthesized.<sup>8</sup> These salts are isostructural to  $\lambda$ -(BETS)<sub>2</sub>GaCl<sub>4</sub>. Interestingly, some correlations between  $T_c$  and the unit-cell volume  $U$  of these salts, such as the simultaneous increase of  $T_c$  and  $U$ , seem to exist.<sup>8</sup> However, substitution of the gallium atom in the tetrahalide tetrahedral anion by other elements similar in size (for example Fe, In or Al) results in a loss of superconductivity as in the case of  $\lambda$ -(BETS)<sub>2</sub>FeCl<sub>4</sub><sup>9</sup> and even in a change of the crystal structure of the indium and aluminium salts.<sup>10</sup> Thus, any change in the anion size and the unit-cell volume of the radical cation salts may be reflected by changes in their conducting (or superconducting) properties. In order better to understand the correlation between conducting properties, structures and compositions of the BETS-based salts, it seems necessary to enlarge the available data set by preparing new compounds in this series. Recently, the new (BETS)<sub>4</sub>Cu<sub>2</sub>Cl<sub>6</sub>, (BETS)<sub>2</sub>Fe<sub>0.75</sub>Ga<sub>0.25</sub>Cl<sub>4</sub><sup>11</sup> and (BETS)<sub>4</sub>Hg<sub>3</sub>I<sub>8</sub> phases<sup>12</sup> have been obtained and studied.

The present paper describes the synthesis of two new salts

derived from BETS and obtained by using a [BiCl<sub>4</sub>]<sup>-</sup> anion salt, *i.e.*  $\alpha$ -(BETS)<sub>6</sub>Bi<sub>3</sub>Cl<sub>12</sub>·PhCl **1** and (BETS)<sub>2</sub>Bi<sub>2</sub>Cl<sub>8</sub> **2**, their structure and conducting properties. The new trinuclear anion [Bi<sub>3</sub>Cl<sub>12</sub>]<sup>3-</sup> has been characterised in the structure of **1**.

## Experimental

### Synthesis

Crystals of salts **1** and **2** were obtained by electrocrystallisation of BETS in a chlorobenzene–ethanol mixture (10% absolute ethanol v/v) under galvanostatic conditions ( $I = 0.5$   $\mu$ A) at 70 °C with PPh<sub>4</sub>BiCl<sub>4</sub> as supporting electrolyte. The rather poor solubility of BETS in chlorobenzene and the poor quality of the resulting crystals prepared at 20 °C (boat-like needles and very thin plates) made it necessary to proceed with the electrocrystallisation process at higher temperatures (50 °C) than usual. After 7–10 d, long or wide, thin plate- and parallelogram-shaped black crystals were collected at the anode. The long plates are designated salt **1** and have been characterised by X-ray diffraction methods as the  $\alpha$ -(BETS)<sub>6</sub>Bi<sub>3</sub>Cl<sub>12</sub>·PhCl phase, whereas the wide plates are designated salt **2** and have been characterised as the (BETS)<sub>2</sub>Bi<sub>2</sub>Cl<sub>8</sub> phase.

### Crystallography

**Crystal data.**  $\alpha$ -(BETS)<sub>6</sub>Bi<sub>3</sub>Cl<sub>12</sub>·PhCl **1**, C<sub>66</sub>H<sub>53</sub>Bi<sub>3</sub>Cl<sub>13</sub>S<sub>24</sub>Se<sub>24</sub>,  $M = 4598.36$ , triclinic,  $a = 19.46(2)$ ,  $b = 11.280(9)$ ,  $c = 14.98(1)$  Å,  $\alpha = 67.32(8)$ ,  $\beta = 85.55(7)$ ,  $\gamma = 82.29(7)^\circ$ ,  $U = 3006(4)$  Å<sup>3</sup> (by least-squares refinement on diffractometer angles for 20 automatically centred reflections in the range  $38 < 2\theta < 83^\circ$ ,  $\lambda = 1.54051$  Å), space group  $P1$ ,  $Z = 1$ ,  $D_c = 2.540$  g cm<sup>-3</sup>,  $F(000) = 2119$ . Black long thin plates, crystal size  $0.40 \times 0.20 \times 0.05$  mm;  $\mu(\text{Cu-K}\alpha) = 23.66$  mm<sup>-1</sup>.

(BETS)<sub>2</sub>Bi<sub>2</sub>Cl<sub>8</sub> **2**, C<sub>20</sub>H<sub>16</sub>Bi<sub>2</sub>Cl<sub>8</sub>S<sub>8</sub>Se<sub>8</sub>,  $M = 1846.05$ , monoclinic,  $a = 24.67(1)$ ,  $b = 22.73(1)$ ,  $c = 7.508(4)$  Å,  $\beta = 98.56(5)^\circ$ ,  $U = 4165(4)$  Å<sup>3</sup> (by least-squares refinement on diffractometer angles for 20 automatically centred reflections in the range

11 < 2θ < 33°, λ = 0.709 26 Å, space group  $P2_1/n$  (alt.  $P2_1/c$ , no. 14),  $Z = 4$ ,  $D_c = 2.944 \text{ g cm}^{-3}$ ,  $F(000) = 3352$ . Black wide thin plates, crystal size 0.24 × 0.14 × 0.02 mm,  $\mu(\text{Mo-K}\alpha) = 16.37 \text{ mm}^{-1}$ .

**Data collection and processing.** In both cases, two standard reflections monitored after every 50 showed no significant variations. The X-ray studies were carried out using a four-circle automatic KM-4 KUMA DIFFRACTION diffractometer at 298 K. For  $\alpha\text{-(BETS)}_6\text{Bi}_3\text{Cl}_{12}\cdot\text{PhCl}$  **1**,  $\omega\text{-}2\theta$  scan,  $\omega\text{-scan}$  width = 0.60 + 0.35 tan θ,  $\omega\text{-scan}$  speed = 2.6–6.6° min<sup>-1</sup>, graphite-monochromated Cu-Kα radiation, 8138 collected unique reflections,  $2\theta_{\text{max}} = 160.58^\circ$ ,  $-24 \leq h \leq 24$ ,  $-12 \leq k \leq 13$ ,  $0 \leq l \leq 11$ , 3422 observed reflections with  $I > 2\sigma(I)$ ; maximum, minimum transmission factors 0.73, 0.11. For  $(\text{BETS})_2\text{Bi}_2\text{Cl}_8$  **2**,  $\omega\text{-}2\theta$  scan,  $\omega\text{-scan}$  width = 0.60 + 0.35 tan θ, scan speed = 3.0–6.8° min<sup>-1</sup>, graphite-monochromated Mo-Kα radiation, 5523 collected unique reflections,  $2\theta_{\text{max}} = 67.86^\circ$ ,  $-34 \leq h \leq 38$ ,  $0 \leq k \leq 34$ ,  $0 \leq l \leq 8$ , 1220 observed reflections with  $I > 2\sigma(I)$ , maximum, minimum transmission factors 0.73, 0.12. In both cases absorption corrections were applied during the final refinement using the program SHELX 76<sup>13</sup> with the real forms of the crystals.

**Structure analysis and refinement.** The crystal structures of compounds **1** and **2** were solved by direct methods and Fourier-difference maps with programs SHELXS 86<sup>14</sup> and SHELXL 93.<sup>15</sup> The Bi and Se atoms for **1** and **2** were refined by full-matrix least squares in anisotropic approximation, the other non-hydrogen atoms in isotropic approximation, using  $F$ . No hydrogen atoms were included in the calculation.

Although the BETS molecule and the  $\text{Bi}_3\text{Cl}_{12}$  anion both contain a centre of symmetry, attempts to solve structure **1** in the space group  $P\bar{1}$  failed, due to the presence of the lone chlorobenzene molecule and led to polymeric BETS molecules with short Se...Se contacts ( $\approx 2 \text{ \AA}$ ).

The final  $R$  factors were 0.082 for compound **1** and 0.077 for **2**. Mean shift/e.s.d. in the final refinement 0.098 for **1** and 0.125 for **2**. Maximum and minimum residual densities in the final difference maps were 2.26,  $-3.31 \text{ e \AA}^{-3}$  for **1** and 2.75,  $-2.43 \text{ e \AA}^{-3}$  for **2**.

All calculations were performed on a AT-486 personal computer.

CCDC reference number 186/831.

### Conductivity

The crystal conductivity was measured by the standard four-probe method with a d.c. current. Contacts to the sample were made by graphite paste using 10 μm diameter platinum wires.

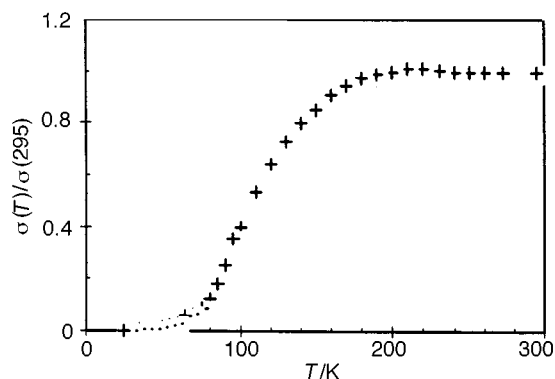
### Results and Discussion

The room-temperature conductivities of  $\alpha\text{-(BETS)}_6\text{Bi}_3\text{Cl}_{12}\cdot\text{PhCl}$  **1** and  $(\text{BETS})_2\text{Bi}_2\text{Cl}_8$  **2** are 20–25 and 0.1–0.4 S cm<sup>-1</sup>, respectively.

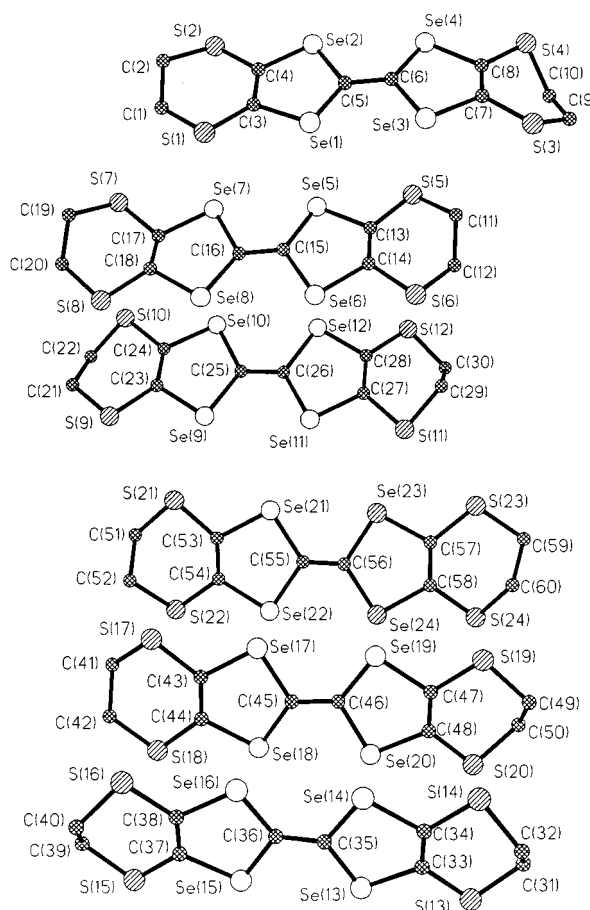
The temperature dependence of the normalised conductivity of  $\alpha\text{-(BETS)}_6\text{Bi}_3\text{Cl}_{12}\cdot\text{PhCl}$  **1** is shown in Fig. 1. The conductivity of this phase weakly varies upon cooling from room temperature down to 180 K and begins to decrease below this temperature. The compound becomes a semiconductor and a semiconductor-to-insulator transition takes place at  $\approx 90 \text{ K}$ .

The crystals of the  $(\text{BETS})_2\text{Bi}_2\text{Cl}_8$  salt exhibit a semiconducting temperature-dependent behaviour over the whole temperature range measured. As will be discussed below, the observed conductivity properties of this salt are well explained by its stoichiometry and the packing arrangement of columnar stacking.

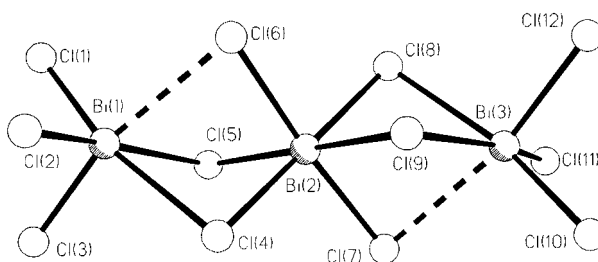
The asymmetric unit of compound **1** contains six crystallographically independent BETS moieties (Fig. 2) and one dis-



**Fig. 1** Temperature dependence of the normalised conductivity of  $\alpha\text{-(BETS)}_6\text{Bi}_3\text{Cl}_{12}\cdot\text{PhCl}$  **1**



**Fig. 2** Atom-labelling scheme for the BETS molecules in  $\alpha\text{-(BETS)}_6\text{Bi}_3\text{Cl}_{12}\cdot\text{PhCl}$  **1**



**Fig. 3** Atom-labelling scheme for the  $[\text{Bi}_3\text{Cl}_{12}]^{3-}$  anion in  $\alpha\text{-(BETS)}_6\text{Bi}_3\text{Cl}_{12}\cdot\text{PhCl}$  **1**

crete trinuclear anion  $[\text{Bi}_3\text{Cl}_{12}]^{3-}$  (Fig. 3). The BETS moieties (designated A, B, C, D, E and F) are packed in two stacks (A, B, C and D, E, F, respectively) in  $\alpha$ -type fashion<sup>16</sup> (Fig. 4). Salt **1** has a layered structure (Fig. 5), consisting of radical cation

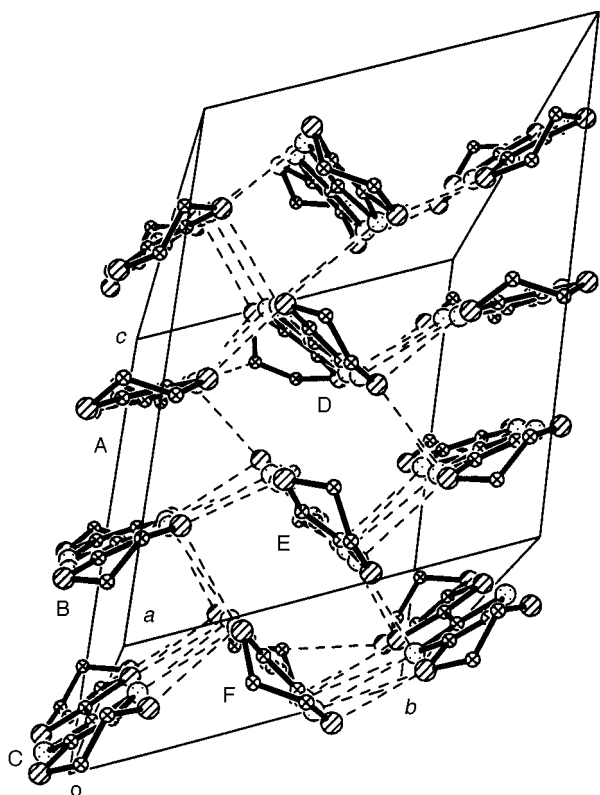


Fig. 4 View of the packing of the BETS molecules in  $\alpha$ -(BETS)<sub>6</sub>Bi<sub>3</sub>Cl<sub>12</sub>·PhCl **1**. Dashed lines indicate chalcogen–chalcogen contacts shorter than the sum of their van der Waals radii

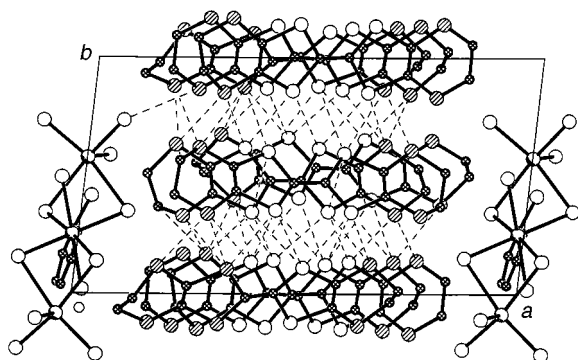


Fig. 5 Projection of the structure of  $\alpha$ -(BETS)<sub>6</sub>Bi<sub>3</sub>Cl<sub>12</sub>·PhCl **1** in the *ab* plane. Dashed lines indicate chalcogen–chalcogen and S...Cl contacts shorter than the sum of their van der Waals radii

layers of the so-called  $\alpha$ -type<sup>16</sup> and segregated anion sheets containing [Bi<sub>3</sub>Cl<sub>12</sub>]<sup>3-</sup> trinuclear anions and PhCl solvent molecules. The layers consisting of radical cations (BETS)<sup>+1/2</sup> alternate along the *a* axis with the inorganic layers containing the anions and the PhCl molecules. The dihedral angles between the average planes of the BETS molecules from neighbouring stacks vary from 53.9 to 79.7° because the BETS molecules belonging to the same stack are not parallel to each other (Fig. 4, Table 1). The type of molecule overlap in the (A, B, C) stack [Fig. 6(a)] is different from that in the (D, E, F) stack [Fig. 6(b)]. However, both overlap modes consist of (i) a transverse shift of the molecular plane of A, B and C and D, E and F BETS molecules, respectively, and (ii) a transverse and longitudinal shift between A and C [Fig. 6(a)] and between D and F [Fig. 6(b)]. Short Se...Se, Se...S and S...S intermolecular contacts are observed between molecules belonging to adjacent stacks but not within a stack. These interactions are shown in Figs. 4 and 5 and listed in Table 2.

The most striking novelty in this structure is the presence of the discrete [Bi<sub>3</sub>Cl<sub>12</sub>]<sup>3-</sup> trinuclear anion (Fig. 2). Indeed, many bismuth chloride complexes have been previously reported,

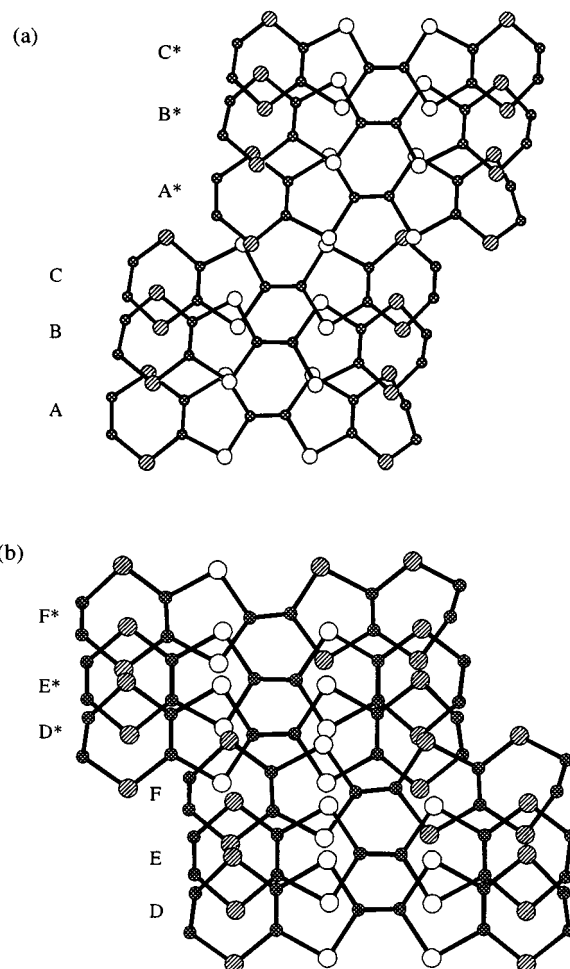


Fig. 6 Molecular overlap of the BETS molecule in  $\alpha$ -(BETS)<sub>6</sub>Bi<sub>3</sub>Cl<sub>12</sub>·PhCl **1** (a) within the (A, B, C) stacks, (b) within the (D, E, F) stacks

Table 1 Dihedral angles (°) between averaged cation planes in  $\alpha$ -(BETS)<sub>6</sub>Bi<sub>3</sub>Cl<sub>12</sub>·PhCl **1**

	B	C	D	E	F
A	6.4	7.1	53.9	61.7	72.8
B		3.5	60.1	67.9	79.0
C			60.7	68.5	79.7
D				7.8	19.0
E					11.2

including [Bi<sub>2</sub>Cl<sub>8</sub>]<sup>2-</sup> and [BiCl<sub>5</sub>]<sup>2-</sup>,<sup>6</sup> [BiCl<sub>6</sub>]<sup>3-</sup>,<sup>7</sup> [Bi<sub>2</sub>Cl<sub>9</sub>]<sup>3-</sup>,<sup>8</sup> [Bi<sub>4</sub>Cl<sub>16</sub>]<sup>4-</sup>,<sup>17</sup> [Bi<sub>2</sub>Cl<sub>11</sub>]<sup>5-</sup><sup>18</sup> and [Bi<sub>4</sub>Cl<sub>18</sub>]<sup>6-</sup>,<sup>10</sup> but the anion [Bi<sub>3</sub>Cl<sub>12</sub>]<sup>3-</sup> observed in the structure of  $\alpha$ -(BETS)<sub>6</sub>Bi<sub>3</sub>Cl<sub>12</sub>·PhCl **1** is, to our knowledge, the first *trinuclear* bismuth chloride anion of this kind ever reported.

Each trinuclear bismuth(III) unit consists of three non-equivalent six-co-ordinated bismuth atoms involving terminal Bi–Cl bonds with lengths in the range 2.464(9)–2.68(1) Å and two kinds of bridging Bi–Cl bonds with lengths in the range 2.697(8)–3.273(7) Å (Table 3). The co-ordination polyhedra of the Bi atoms in the anion are distorted octahedra. The configuration of the Bi(2) atom is the less distorted, probably because its octahedron involves only bridging Bi–Cl bonds [2.697(8)–2.91(1) Å]. Atoms Bi(1) and Bi(3) are bonded to three terminal chlorine atoms in the *fac* configuration [2.464(9), 2.54(1), 2.59(1) Å for Bi(1), and 2.530(8), 2.50(1), 2.68(1) Å for Bi(3)], and to three bridging chlorine atoms [3.039(8), 3.01(1), 3.273(7) Å for Bi(1) and 3.026(8), 3.052(9), 3.195(6) Å for Bi(3)]. Some similarities could be found when comparing this structure with that of the [Mg(MeCN)<sub>2</sub>]<sub>2</sub>[Bi<sub>4</sub>Cl<sub>16</sub>] compound<sup>17</sup>

**Table 2** Short Se...Se ( $r \leq 4.00$  Å), Se...S ( $r \leq 3.84$  Å), S...S ( $r \leq 3.68$  Å) and Cl...S ( $r \leq 3.74$  Å) contacts in (BETS)<sub>6</sub>Bi<sub>3</sub>Cl<sub>12</sub>·PhCl **1**

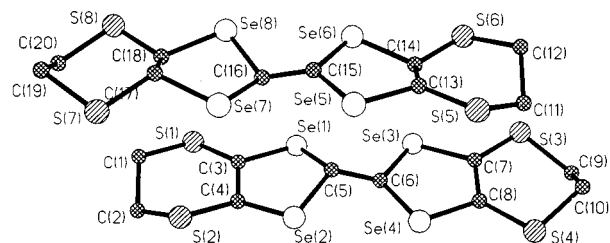
Se(1)...Se(14 <sup>a</sup> )	3.796(6)	Se(1)...Se(16 <sup>a</sup> )	3.703(6)
Se(2)...Se(9 <sup>b</sup> )	3.927(6)	Se(2)...Se(13)	3.882(6)
Se(2)...Se(15)	3.861(6)	Se(2)...Se(22 <sup>b</sup> )	3.954(6)
Se(2)...Se(22 <sup>b</sup> )	3.621(8)	Se(3)...Se(14 <sup>a</sup> )	3.658(6)
Se(3)...Se(19 <sup>a</sup> )	3.988(6)	Se(3)...S(14 <sup>a</sup> )	3.47(1)
Se(4)...Se(11 <sup>b</sup> )	3.936(7)	Se(4)...Se(13)	3.845(7)
Se(4)...Se(22 <sup>b</sup> )	3.895(6)	Se(4)...S(13)	3.55(1)
Se(5)...Se(13)	3.986(6)	Se(5)...Se(18)	3.876(6)
Se(5)...Se(20)	3.801(6)	Se(6)...Se(17 <sup>a</sup> )	3.869(6)
Se(6)...Se(19 <sup>a</sup> )	3.925(6)	Se(6)...Se(23 <sup>a</sup> )	3.644(9)
Se(7)...Se(18)	3.764(6)	Se(7)...S(18)	3.491(9)
Se(8)...Se(17 <sup>a</sup> )	3.976(6)	Se(8)...Se(21 <sup>a</sup> )	3.758(6)
Se(8)...S(17 <sup>a</sup> )	3.68(1)	Se(9)...Se(21 <sup>a</sup> )	3.893(6)
Se(9)...S(21 <sup>a</sup> )	3.57(1)	Se(10)...Se(18)	3.857(6)
Se(10)...Se(22)	3.798(6)	Se(10)...S(18)	3.707(9)
Se(10)...S(22)	3.69(1)	Se(11)...Se(21 <sup>a</sup> )	3.900(6)
Se(11)...Se(14 <sup>a</sup> )	3.969(6)	Se(11)...Se(23 <sup>a</sup> )	3.829(6)
Se(12)...Se(18)	3.865(6)	Se(12)...Se(20)	3.860(6)
Se(12)...Se(22)	3.913(6)	Se(12)...Se(24)	3.822(6)
Se(13)...S(5)	3.562(8)	Se(15)...S(2)	3.65(1)
Se(16)...S(1 <sup>d</sup> )	3.64(1)	Se(16)...S(9 <sup>e</sup> )	3.806(9)
Se(19)...S(6 <sup>d</sup> )	3.68(1)	Se(20)...S(5)	3.78(1)
Se(23)...S(6 <sup>d</sup> )	3.755(9)	Se(23)...S(11 <sup>d</sup> )	3.79(1)
Se(24)...S(12)	3.57(1)	Se(24)...S(4 <sup>f</sup> )	3.797(9)
S(1)...S(17 <sup>a</sup> )	3.65(1)	S(1)...S(16 <sup>a</sup> )	3.66(1)
S(2)...S(15)	3.61(1)	S(3)...S(14 <sup>a</sup> )	3.54(1)
S(4)...S(13)	3.55(1)	S(5)...S(13)	3.57(1)
S(7)...S(18)	3.52(1)	S(9)...S(21 <sup>a</sup> )	3.54(1)
S(11)...S(23 <sup>a</sup> )	3.63(1)	S(12)...S(24)	3.66(1)
Cl(1)...S(11 <sup>e</sup> )	3.574(9)	Cl(4)...S(2)	3.625(9)
Cl(8)...S(20 <sup>b</sup> )	3.68(1)	Cl(11)...S(19 <sup>b</sup> )	3.553(9)

a  $x, 1+y, z$ ; b  $x, y, 1+z$ ; c  $x, 1+y, -1+z$ ; d  $x, -1+y, z$ ; e  $x, -1+y, 1+z$ ; f  $x, y, -1+z$ ; g  $1+x, -1+y, 1+z$ ; h  $1+x, y, z$ ; i  $1+x, 1+y, z$ .

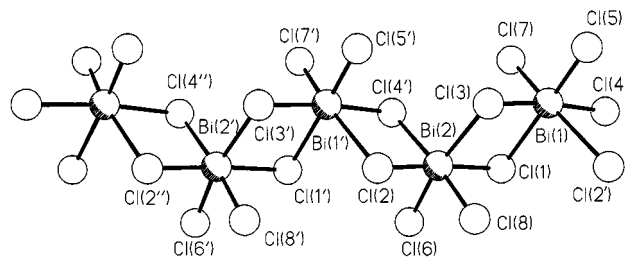
**Table 3** Selected bond lengths (Å) and angles (°) in  $\alpha$ -(BETS)<sub>6</sub>Bi<sub>3</sub>Cl<sub>12</sub>·PhCl **1**

Bi(1)–Cl(1)	2.464(9)	Bi(1)–Cl(2)	2.54(1)
Bi(1)–Cl(3)	2.59(1)	Bi(1)–Cl(4)	3.039(8)
Bi(1)–Cl(5)	3.01(1)	Bi(1)...Cl(6)	3.273(7)
Bi(2)–Cl(4)	2.697(8)	Bi(2)–Cl(5)	2.91(1)
Bi(2)–Cl(6)	2.73(1)	Bi(2)–Cl(7)	2.73(1)
Bi(2)–Cl(8)	2.775(8)	Bi(2)–Cl(9)	2.82(1)
Bi(3)...Cl(7)	3.195(6)	Bi(3)–Cl(8)	3.026(8)
Bi(3)–Cl(9)	3.052(9)	Bi(3)–Cl(10)	2.530(8)
Bi(3)–Cl(11)	2.50(1)	Bi(3)–Cl(12)	2.68(1)
Cl(1)–Bi(1)–Cl(2)	95.0(3)	Cl(1)–Bi(1)–Cl(3)	94.6(3)
Cl(1)–Bi(1)–Cl(4)	166.8(3)	Cl(1)–Bi(1)–Cl(5)	96.9(3)
Cl(2)–Bi(1)–Cl(3)	95.2(3)	Cl(2)–Bi(1)–Cl(4)	90.9(3)
Cl(2)–Bi(1)–Cl(5)	166.1(2)	Cl(3)–Bi(1)–Cl(4)	96.6(3)
Cl(3)–Bi(1)–Cl(5)	90.8(3)	Cl(4)–Bi(1)–Cl(5)	75.9(2)
Cl(4)–Bi(2)–Cl(5)	83.0(3)	Cl(4)–Bi(2)–Cl(6)	86.8(3)
Cl(4)–Bi(2)–Cl(8)	94.9(3)	Cl(4)–Bi(2)–Cl(8)	178.0(3)
Cl(4)–Bi(2)–Cl(9)	93.3(3)	Cl(5)–Bi(2)–Cl(6)	89.9(3)
Cl(5)–Bi(2)–Cl(7)	95.8(3)	Cl(5)–Bi(2)–Cl(8)	98.7(3)
Cl(5)–Bi(2)–Cl(9)	175.8(3)	Cl(6)–Bi(2)–Cl(7)	174.2(3)
Cl(6)–Bi(2)–Cl(8)	92.2(3)	Cl(6)–Bi(2)–Cl(9)	88.0(3)
Cl(7)–Bi(2)–Cl(8)	85.9(3)	Cl(7)–Bi(2)–Cl(9)	86.3(3)
Cl(8)–Bi(2)–Cl(9)	85.0(2)	Cl(8)–Bi(3)–Cl(9)	76.9(2)
Cl(8)–Bi(3)–Cl(10)	166.5(2)	Cl(8)–Bi(3)–Cl(11)	92.5(3)
Cl(8)–Bi(3)–Cl(12)	95.4(3)	Cl(9)–Bi(3)–Cl(10)	91.7(3)
Cl(9)–Bi(3)–Cl(11)	165.3(3)	Cl(9)–Bi(3)–Cl(12)	94.8(3)
Cl(10)–Bi(3)–Cl(11)	97.4(3)	Cl(10)–Bi(3)–Cl(12)	92.7(3)
Cl(11)–Bi(3)–Cl(12)	96.3(4)		

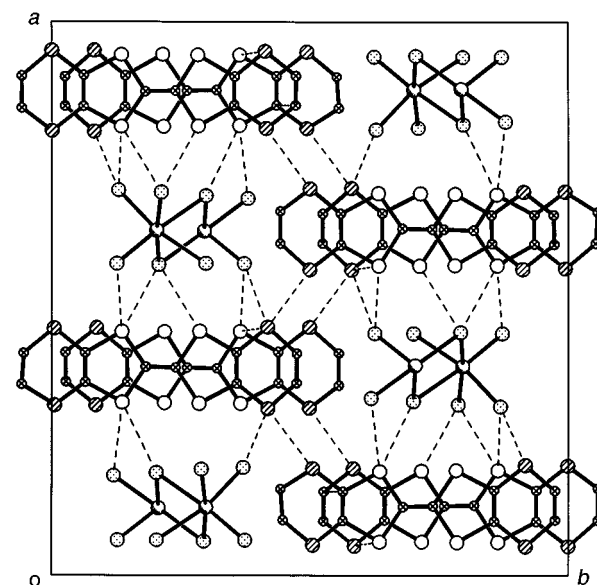
which contains a tetranuclear bismuth(III) anion with terminal Bi–Cl bond lengths in the range 2.43(2)–2.55(2) Å and bridging Bi–Cl bond lengths in the range 2.68(2)–3.01(2) Å. In  $\alpha$ -(BETS)<sub>6</sub>Bi<sub>3</sub>Cl<sub>12</sub>·PhCl **1** the [Bi<sub>3</sub>Cl<sub>12</sub>]<sup>3-</sup> anion is associated with a solvent molecule of chlorobenzene with a short contact of 3.743(6) Å between Cl(1) and Cl(13).



**Fig. 7** Atom-labelling scheme for the BETS molecules in (BETS)<sub>2</sub>-Bi<sub>2</sub>Cl<sub>8</sub> **2**



**Fig. 8** Atom-labelling scheme for the polymeric [(Bi<sub>2</sub>Cl<sub>8</sub>)<sub>n</sub>]<sup>2n-</sup> anion in (BETS)<sub>2</sub>Bi<sub>2</sub>Cl<sub>8</sub> **2**



**Fig. 9** Projection of the structure of (BETS)<sub>2</sub>Bi<sub>2</sub>Cl<sub>8</sub> **2** in the  $ab$  plane. Dashed lines indicate chalcogen-chalcogen, S...Cl and Se...Cl contacts shorter than the sum of their van der Waals radii

The 2:1 stoichiometry in  $\alpha$ -(BETS)<sub>6</sub>Bi<sub>3</sub>Cl<sub>12</sub>·PhCl, resulting in a formal charge on each BETS moiety of  $\frac{1}{2}$ , and the presence of (BETS)<sup>1/2</sup> containing layers clearly account for the experimentally observed metal-like behaviour of this compound.

The asymmetric unit of compound **2** contains two crystallographically independent BETS moieties (Fig. 7) and one polymeric [(Bi<sub>2</sub>Cl<sub>8</sub>)<sub>n</sub>]<sup>2n-</sup> anion (Fig. 8). The crystal structure consists of stacks of BETS radical cations, with polymeric [(Bi<sub>2</sub>Cl<sub>8</sub>)<sub>n</sub>]<sup>2n-</sup> anion chains arranged in a chessboard fashion (Fig. 9). The cation stacks and the polymeric chains [(Bi<sub>2</sub>Cl<sub>8</sub>)<sub>n</sub>]<sup>2n-</sup> alternate along the  $a$  and  $b$  axes. Each BETS stack is surrounded by four [(Bi<sub>2</sub>Cl<sub>8</sub>)<sub>n</sub>]<sup>2n-</sup> chains. The structure of the anionic [(Bi<sub>2</sub>Cl<sub>8</sub>)<sub>n</sub>]<sup>2n-</sup> polymeric chain (Fig. 8) is reminiscent of that of the polymeric [(BiCl<sub>4</sub>)<sub>n</sub>]<sup>n-</sup> anion in [NH<sub>2</sub>Et<sub>2</sub>][BiCl<sub>4</sub>]<sup>19</sup> and also of that of the [(BiI<sub>4</sub>)<sub>n</sub>]<sup>n-</sup> anionic chain in the (ET)BiI<sub>4</sub> molecular semiconductor.<sup>20</sup> The [(Bi<sub>2</sub>Cl<sub>8</sub>)<sub>n</sub>]<sup>2n-</sup> polymeric anion contains BiCl<sub>6</sub> octahedra sharing edges, in such a way that the terminal chlorine ligands are in a *cis* configuration. The [(Bi<sub>2</sub>Cl<sub>8</sub>)<sub>n</sub>]<sup>2n-</sup> chains are parallel to the  $c$  axis. As in some other tetrachlorobismuthate(III) salts,<sup>19</sup> three types of Bi–Cl distances

**Table 4** Selected bond lengths (Å) and angles (°) in (BETS)<sub>2</sub>Bi<sub>2</sub>Cl<sub>8</sub> **2**

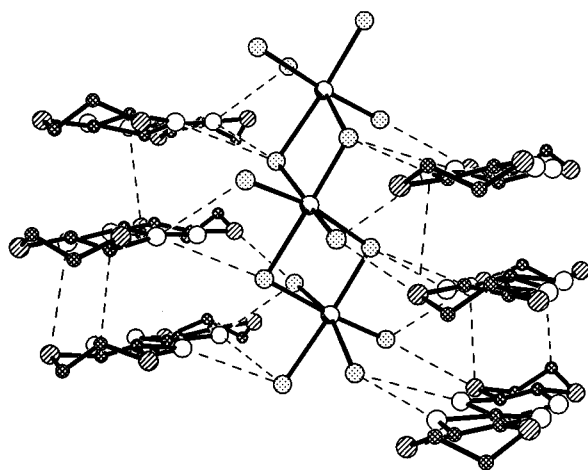
Bi(1)–Cl(1)	3.008(6)	Bi(1)–Cl(2 <sup>a</sup> )	3.077(6)
Bi(1)–Cl(3)	2.689(6)	Bi(1)–Cl(4)	2.859(6)
Bi(1)–Cl(5)	2.473(6)	Bi(1)–Cl(7)	2.597(6)
Bi(2)–Cl(1)	2.830(7)	Bi(2)–Cl(2)	2.547(6)
Bi(2)–Cl(3)	2.890(5)	Bi(2)–Cl(4 <sup>a</sup> )	2.958(6)
Bi(2)–Cl(6)	2.590(6)	Bi(2)–Cl(8)	2.479(6)
Cl(1)–Bi(1)–Cl(2 <sup>a</sup> )	88.08(8)	Cl(1)–Bi(1)–Cl(3)	82.6(3)
Cl(1)–Bi(1)–Cl(4)	91.4(2)	Cl(1)–Bi(1)–Cl(5)	174.3(2)
Cl(1)–Bi(1)–Cl(7)	87.0(2)	Cl(3)–Bi(1)–Cl(2 <sup>a</sup> )	99.01(7)
Cl(3)–Bi(1)–Cl(4)	173.4(3)	Cl(3)–Bi(1)–Cl(5)	92.2(2)
Cl(3)–Bi(1)–Cl(7)	95.7(2)	Cl(4)–Bi(1)–Cl(2 <sup>a</sup> )	78.04(6)
Cl(4)–Bi(1)–Cl(5)	93.7(2)	Cl(4)–Bi(1)–Cl(7)	86.7(2)
Cl(5)–Bi(1)–Cl(2 <sup>a</sup> )	90.09(8)	Cl(5)–Bi(1)–Cl(7)	95.8(2)
Cl(7)–Bi(1)–Cl(2 <sup>a</sup> )	163.77(7)	Cl(1)–Bi(2)–Cl(2)	176.8(2)
Cl(1)–Bi(2)–Cl(3)	82.4(3)	Cl(1)–Bi(2)–Cl(4 <sup>a</sup> )	96.2(2)
Cl(1)–Bi(2)–Cl(6)	86.3(2)	Cl(1)–Bi(2)–Cl(8)	86.9(3)
Cl(2)–Bi(2)–Cl(3)	100.0(2)	Cl(2)–Bi(2)–Cl(4 <sup>a</sup> )	85.7(2)
Cl(2)–Bi(2)–Cl(6)	91.1(2)	Cl(2)–Bi(2)–Cl(8)	91.0(2)
Cl(3)–Bi(2)–Cl(4 <sup>a</sup> )	96.4(2)	Cl(3)–Bi(2)–Cl(6)	167.8(2)
Cl(3)–Bi(2)–Cl(8)	88.9(3)	Cl(6)–Bi(2)–Cl(4 <sup>a</sup> )	89.2(3)
Cl(6)–Bi(2)–Cl(8)	86.0(2)	Cl(8)–Bi(2)–Cl(4 <sup>a</sup> )	174.1(2)

Symmetry transformations used to generate equivalent atoms: 1  $x, y, z + 1$ ; 2  $x, y, z - 1$ .

**Table 5** Short Se...Cl ( $r \leq 3.90$  Å), Se...S ( $r \leq 3.84$  Å), Cl...S ( $r \leq 3.74$  Å) and S...S ( $r \leq 3.68$  Å) contacts in (BETS)<sub>2</sub>Bi<sub>2</sub>Cl<sub>8</sub> **2**

Se...Cl(2 <sup>a</sup> )	3.692(6)	Se(1)...Cl(3 <sup>b</sup> )	3.874(6)
Se(2)...Cl(1)	3.863(6)	Se(2)...Cl(4)	3.620(6)
Se(3)...Cl(2 <sup>a</sup> )	3.585(6)	Se(3)...Cl(8 <sup>a</sup> )	3.566(6)
Se(3)...S(6)	3.780(7)	Se(4)...Cl(4)	3.673(6)
Se(4)...Se(5 <sup>e</sup> )	3.814(7)	Se(5)...Cl(1 <sup>b</sup> )	3.847(6)
Se(5)...Cl(4)	3.787(6)	Se(5)...Cl(7 <sup>b</sup> )	3.874(6)
Se(6)...Cl(3 <sup>a</sup> )	3.662(6)	Se(7)...Cl(1 <sup>b</sup> )	3.725(6)
Se(7)...Cl(6 <sup>b</sup> )	3.656(6)	Se(7)...S(2)	3.846(6)
Se(8)...Cl(3 <sup>a</sup> )	3.657(6)	Se(8)...Cl(5 <sup>a</sup> )	3.511(6)
Cl(5)...S(1 <sup>a</sup> )	3.465(8)	Cl(6)...S(2 <sup>e</sup> )	3.710(7)
Cl(7)...S(5 <sup>e</sup> )	3.352(8)	Cl(8)...S(6 <sup>f</sup> )	3.426(8)
S(2)...S(4 <sup>e</sup> )	3.391(8)	S(5)...S(7 <sup>d</sup> )	3.398(8)

a  $0.5 + x, 0.5 - y, -0.5 + z$ ; b  $x, y, -1 + z$ ; c  $0.5 - x, -0.5 + y, 1.5 - z$ ; d  $0.5 - x, 0.5 + y, 0.5 - z$ ; e  $-0.5 + x, 0.5 - y, -0.5 + z$ ; f  $-0.5 + x, 0.5 - y, 0.5 + z$ ; g  $x, y, 1 + z$ .

**Fig. 10** View of the structure of (BETS)<sub>2</sub>Bi<sub>2</sub>Cl<sub>8</sub> **2**. Dashed lines indicate chalcogen–chalcogen, S...Cl and Se...Cl contacts shorter than the sum of their van der Waals radii

are present within the BiCl<sub>6</sub> groups (Table 4): two short terminal [2.473(6), 2.597(6) Å for Bi(1) and 2.479(6), 2.590(6) Å for Bi(2)], two medium bridging [2.689(6), 2.859(6) Å for Bi(1) and 2.547(6), 2.830(7) Å for Bi(2)] and two long bridging distances corresponding to the *trans* positions to the terminal

bonds [3.008(6), 3.077(6) Å for Bi(1) and 2.958(6), 2.890(5) Å for Bi(2)]. A similar distribution of Bi–Cl bond lengths has been previously observed in [(Me<sub>2</sub>N)<sub>3</sub>PSeSeP(NMe<sub>2</sub>)<sub>3</sub>][BiCl<sub>4</sub>]<sub>2</sub> [2.474(9)–2.528(9) Å for the terminal bonds, 2.65(1)–3.04(1) Å for the bridging bonds].<sup>21</sup> Such [(Bi<sub>2</sub>Cl<sub>8</sub>)<sub>n</sub>]<sup>2n-</sup> chains have been also observed in [Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>][BiCl<sub>4</sub>], in which the Bi–Cl terminal bond lengths are 2.50(1) and 2.52(1) Å and the Bi–Cl bridging distances are in the range 2.70(1)–3.10(1) Å.<sup>22</sup> Such a six-co-ordinated chain structure involving bridging halogen atoms seems to be rather common in [BiX<sub>4</sub>]<sup>-</sup> anions (X = Cl or Br).<sup>23,24</sup>

In (BETS)<sub>2</sub>Bi<sub>2</sub>Cl<sub>8</sub> the BETS molecules in the stacks are almost parallel and equidistant (Fig. 10): the dihedral angle between their planes is 1.7°, and the interplanar distances are 3.76 and 3.75 Å. There are short intermolecular contacts between cations, as well as between cation and anion, within the stacks as well as between molecules belonging to adjacent stacks (Table 5). However, the 1:1 stoichiometry of this salt, resulting in a full charge transfer (*i.e.* the formal charge of each BETS moiety is +1), and the absence of any conducting layer account for the experimentally observed semiconducting behaviour of compound **2**.

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