

(BETS)₂[Fe(tdas)₂]₂: a new metal in the molecular conductor family

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The structure of bis[4,5-ethylenedithio-2-(4,5-ethylenedithio-1,3-diselenacyclopent-4-en-2-ylidene)-1,3-diselenacyclopent-4-enium] bis(μ -1,2,5-thiadiazole-3,4-dithiolato- $\kappa^3S^4, S^5; S^4$)bis-[(1,2,5-thiadiazole-3,4-dithiolato- κ^2S^4, S^5)iron(III)], (BETS)₂[Fe(tdas)₂]₂ [BETS is alternatively called bis(ethylenedithio)-tetraselenafulvalenium] or (C₁₀H₈S₄Se₄)₂{[Fe(C₂N₂S₃)₂]₂}, consists of segregated columns of dimers of BETS and columns of dimers of [Fe(tdas)₂]. Each dimer displays inversion symmetry. Numerous chalcogen–chalcogen contacts are observed within and between the columns, producing a network of interactions responsible for the metal-like behaviour of the compound.

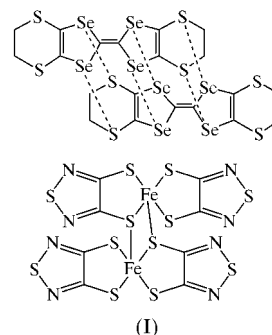
Comment

In the chemistry of molecular solids, and after the discovery of numerous molecular conductors (Williams *et al.*, 1992) and several ferromagnets (Cassoux & Miller, 1998), the quest for materials exhibiting two physical properties in the same lattice, *e.g.* conductivity and magnetism, has become a new challenge. Indeed, such hybrid molecular solids will allow studies of the competition and/or the possible interplay between the two properties and could even show new physical properties. The BETS molecule, bis(ethylenedithio)-tetraselenafulvalenium, seems to be an appropriate candidate for the synthesis of such hybrid materials, since it is involved in a large number of magnetic conductors. For example, in the λ -(BETS)₂FeCl₄ phase, conduction electrons interact with localized spins, and a field-induced restoration of a highly conducting state is observed at low temperature (Brossard *et al.*, 1998), as well as a field-induced superconducting state (Uji *et al.*, 2001). As another example, the mixed-composition compounds (BETS)₂Fe_xGa_{1-x}Cl_{4-y}Br_y are the first molecular antiferromagnetic superconductors, and these compounds also

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display unprecedented superconductor–insulator and superconductor–metal transitions (Kobayashi *et al.*, 2000).

In the same way, metal–bisdithiolene complexes have been intensively studied, because of their ability to form molecular metals and superconductors (Faulmann & Cassoux, 2002). Among them, (*n*-Bu₄N)[Fe(tdas)₂] (tdas is 1,2,5-thiadiazole-3,4-dithiolate) occupies a peculiar position, since it also exhibits unusual magnetic properties (Takahashi *et al.*, 1996). [Fe(tdas)₂][−] has been used as a counter-ion for the sulfur-rich tetrathiafulvalene (TTF) donor, and two salts, (TTF)_x[Fe(tdas)₂], have been obtained (Underhill *et al.*, 1996). Both are semiconductors; for $x = 2$, the compound exhibits thermally activated magnetic behaviour, while for $x = \frac{3}{2}$, Curie-type behaviour has been observed. More recently, the X-ray crystal structure determination and magnetic susceptibility measurement of the above salt with $x = 2$ (Robertson *et al.*, 1998) have indicated that this structure possesses anti-ferromagnetic [Fe(tdas)₂]₂[−] dimers and a co-existence of delocalized and localized unpaired electrons.



An increase in the number of S atoms in the donor should increase the intermolecular interactions in stacked charge-

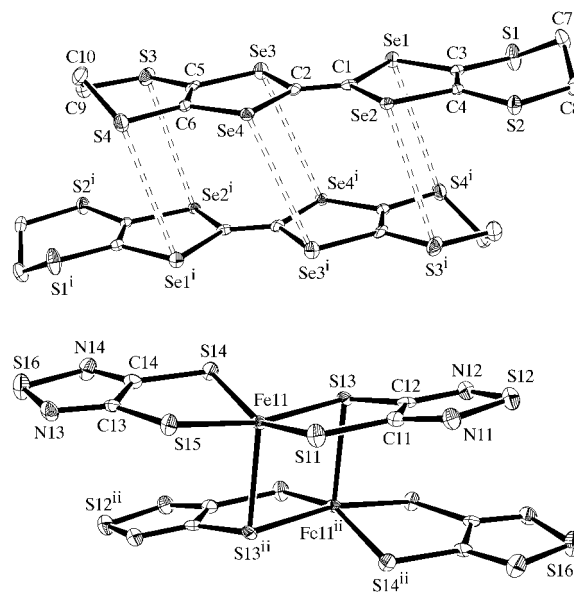


Figure 1

The molecular structure of (I), showing the dimerization of each entity. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity [symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $1-x, 1-y, -z$].

transfer salts, leading to metal-like behaviour. When bis-(ethylenedithio)tetrathiafulvalene (ET) is used as donor, the $(\text{ET})_2[\text{Fe}(\text{tdas})_2]$ salt thus obtained exhibits room-temperature conductivity about two orders of magnitude higher than the corresponding TTF salt, but still shows semiconducting behaviour over the whole temperature range (Deplano *et al.*, 2002). Substitution of the S atoms by Se is expected to result in increased polarizabilities and orbital overlap between molecules, leading to stable metallic states. Thus, by using BETS, where four of the eight atoms of ET are replaced by Se, metal-like behaviour should be achieved. Therefore, the combination of BETS and $\text{Fe}(\text{tdas})_2$ in the same compound, such as in the title compound, (I), is expected to result in conductive and magnetic materials.

The asymmetric unit of (I) contains one $\text{Fe}(\text{tdas})_2$ unit and one BETS molecule, each of them being dimerized (Fig. 1). Apart from the terminal CH_2CH_2 groups, the BETS molecule is almost planar (maximum deviation of 0.15 Å for atom S1). The dimerization of the BETS molecules occurs through the formation of short $\text{S}\cdots\text{Se}$ and $\text{Se}\cdots\text{Se}$ contacts which are shorter than the sum of the van der Waals radii (Pauling, 1960) [$\text{Se}1\cdots\text{S}4^{\text{i}}$ 3.742 (2), $\text{Se}2\cdots\text{S}3^{\text{i}}$ 3.698 (2) and $\text{Se}3\cdots\text{Se}4^{\text{i}}$ 3.7522 (8) Å; symmetry code: (i) $-x, 1-y, 1-z$]. The dimers are not in an eclipsed configuration, since one BETS molecule is displaced along its long axis by such a distance that the S atoms are approximately above the Se atoms of the other BETS molecule. The dimers are also connected to each other

through short chalcogen–chalcogen contacts [$\text{Se}2\cdots\text{Se}2^{\text{ii}}$ 3.6012 (9), $\text{Se}2\cdots\text{Se}4^{\text{ii}}$ 3.5603 (8), $\text{Se}4\cdots\text{S}2^{\text{ii}}$ 3.529 (1) and $\text{S}2\cdots\text{S}4^{\text{ii}}$ 3.580 (2) Å; symmetry code: (ii) $1-x, 1-y, 1-z$].

The $\text{Fe}(\text{tdas})_2$ entities are dimerized (Fig. 1) through the formation of two $\text{Fe}-\text{S}$ bonds of 2.466 (1) Å, involving atom S13, leading to a short $\text{Fe}\cdots\text{Fe}$ contact of 3.078 (1) Å. As seen from Table 1, the bond lengths involving atom S13 are slightly longer than those involving atoms S11, S14 and S15, whereas no significant differences are observed in the bond angles. Within the dimer, short $\text{S}\cdots\text{S}$ contacts are also observed [$\text{S}11\cdots\text{S}13^{\text{iii}}$ 3.600 (2), $\text{S}13\cdots\text{S}13^{\text{iii}}$ 3.579 (2) and $\text{S}13\cdots\text{S}15^{\text{iii}}$ 3.434 (2) Å; symmetry code: (iii) $1-x, 1-y, -z$; Fig. 2]. The $\text{Fe}(\text{tdas})_2$ unit is bent around the Fe atom, with an angle of 27.18 (6)° between the $\text{Fe}11/\text{S}11/\text{S}13$ and $\text{Fe}11/\text{S}14/\text{S}15$ planes, thus giving a square-pyramidal configuration at the Fe atom. As in the BETS stacking, some short contacts between dimers are also observed [$\text{S}12\cdots\text{S}13^{\text{iv}}$ 3.685 (2) and $\text{S}16\cdots\text{S}16^{\text{v}}$ 3.237 (2) Å; symmetry codes: (iv) $2-x, 1-y, -z$; (v) $1-x, 2-y, 1-z$; Fig. 2].

The BETS dimers form an angle of 83.2 (4)° with the $\text{Fe}(\text{tdas})_2$ dimers, while the angle between monomers is 53.73 (4)°. Each of these dimers stacks along the a direction, but their mean plane is strongly tilted with respect to this direction; the a axis forms an angle of 55.3° with the $[\text{Fe}(\text{tdas})_2]_2$ dimer and an angle of 51.3° with the BETS dimer.

The two stacks are not isolated, since there are some short contacts between the dimers of $\text{Fe}(\text{tdas})_2$ and those of BETS (Table 2 and Fig. 2). The chalcogen–chalcogen contacts create a conduction network, responsible for the high room-temperature conductivity of (I) (0.2 S cm^{-1}) and the metallic character which is observed down to *ca* 200 K.

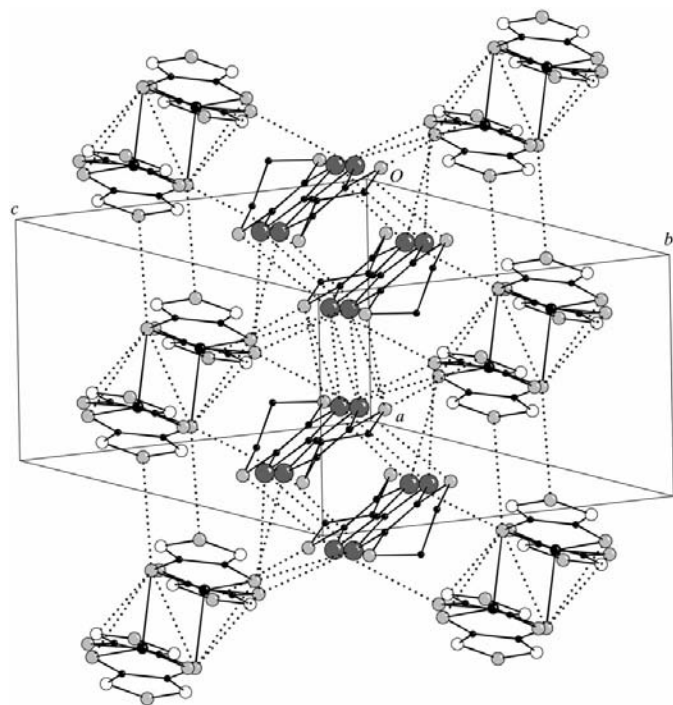


Figure 2

A view of the structure of (I) along the central $\text{C}=\text{C}$ bond of BETS, showing two BETS dimers surrounded by six $[\text{Fe}(\text{tdas})_2]$ dimers. Dotted lines indicate chalcogen–chalcogen contacts shorter than the sum of their van der Waals radii. Fe atoms are indicated by medium black spheres, Se by large dark-grey spheres, S by medium grey spheres, C by small black spheres and N by open spheres.

Experimental

Compound (I) was obtained after electrocrystallization of a solution of nitrobenzene/ethanol (90/10) containing the neutral donor BETS and $(n\text{-Bu}_4\text{N})[\text{Fe}(\text{tdas})_2]$ (Awaga *et al.*, 1994). After a period of three weeks, thin black lozenges of (I) were harvested on the Pt anode, washed with nitrobenzene/ethanol (90/10) and dried under vacuum.

Crystal data

$(\text{C}_{10}\text{H}_8\text{S}_4\text{Se}_4)_2[\{\text{Fe}(\text{C}_2\text{N}_2\text{S}_3)_2\}_2]$
 $M_r = 1849.06$
 Triclinic, $P\bar{1}$
 $a = 8.5466$ (12) Å
 $b = 12.1018$ (16) Å
 $c = 12.9993$ (16) Å
 $\alpha = 109.293$ (14)°
 $\beta = 99.966$ (16)°
 $\gamma = 95.140$ (10)°
 $V = 1234.2$ (3) Å³

$Z = 1$
 $D_x = 2.488$ Mg m^{-3}
 Mo $K\alpha$ radiation
 Cell parameters from 8000 reflections
 $\theta = 2\text{--}25.9^\circ$
 $\mu = 7.37$ mm^{-1}
 $T = 160$ (2) K
 Block, black
 $0.15 \times 0.12 \times 0.10$ mm

Data collection

Stoe IPDS diffractometer
 φ scans
 Absorption correction: refined on ΔF (Parkin *et al.*, 1995), cubic fit to $\sin\theta/\lambda$ with 24 parameters, correction applied to the full data set
 $T_{\min} = 0.429$, $T_{\max} = 0.478$

13 154 measured reflections
 4503 independent reflections
 3449 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.061$
 $\theta_{\max} = 26.1^\circ$
 $h = -10 \rightarrow 10$
 $k = -14 \rightarrow 14$
 $l = 0 \rightarrow 15$

Table 1

Selected geometric parameters (Å, °).

Fe11—S15	2.2282 (15)	S11—C11	1.735 (5)
Fe11—S11	2.2460 (12)	S13—C12	1.753 (4)
Fe11—S14	2.2473 (12)	S14—C14	1.737 (5)
Fe11—S13	2.2500 (14)	S15—C13	1.734 (4)
<hr/>			
C11—S11—Fe11	102.66 (16)	C14—S14—Fe11	101.42 (14)
C12—S13—Fe11	102.29 (17)	C13—S15—Fe11	101.75 (17)

Table 2

 Chalcogen–chalcogen contacts (Å) between (BETS)₂ dimers and [Fe(tdac)₂]₂ dimers.

Se1···S11 ⁱ	3.622 (1)	Se4···S15 ⁱⁱ	3.519 (1)
Se3···S15 ⁱ	3.850 (1)	S2···S16 ⁱⁱ	3.585 (2)
Se2···S15 ⁱⁱ	3.399 (1)	Se1···S13 ⁱⁱⁱ	3.624 (2)
Se4···S11 ⁱⁱ	3.660 (2)		

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

Refinement

 Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.073$
 $S = 0.98$

4503 reflections

298 parameters

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0374P)^2]$

 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.89 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.82 \text{ e } \text{Å}^{-3}$

The H atoms of the terminal ethylene groups of the BETS molecule were placed geometrically at distances of 0.99 Å and treated as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *IPDS* (Stoe & Cie, 1996); cell refinement: *IPDS*; data reduction: *IPDS*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1495). Services for accessing these data are described at the back of the journal.

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