Bis(ethylenedithio)tetraselenafulvalene: short-cut synthesis, X-ray crystal structure and π-electron density distribution‡

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A convenient one-step reaction for the preparation of 2,3-dihydro-1,4-dithiin, **3**, involved in the synthesis of the organic donor compound bis(ethylenedithio)tetraselenafulvalene (BETS), as well as the crystal structure of this donor as determined by X-ray diffraction, are presented. A qualitative insight into the π-electron density distribution is also discussed.

In addition to bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET), bis(ethylenedithio)tetraselenafulvalene (BEDT-TSeF or BETS) has recently become one of the most used organic donor molecules for the preparation of conducting and superconducting electron transfer salts.[1,2] BETS differs from ET by the substitution of Se for S atoms in the TTF fragment of ET. In the ET-based salts, it is known that the deviation from planarity of the outer six-membered rings and the S···S interactions between these rings are necessary for increasing the dimensionality of these salts and stabilizing the metallic state. Substitution of Se for S atoms increases the possibilities of additional favourable chalcogen–chalcogen interactions owing to the larger size and greater polarizability of selenium compared to sulfur. Following this strategy, a number of $(BETS)_2X$ salts (X = PF_6, BF_4, ClO_4, ReO_4, $HgBr_4$, $GaCl_4$, $FeCl_4$, *etc.*) were prepared and found to exhibit metallic or even superconducting properties.[3,4] In the series of the $(BETS)_2GaX_xY_{4-x}$ (X = F, Cl, Br) salts, no less than six superconductors were characterised.[5] Moreover, a magnetic-field-restored highly conducting state was observed in the λ-$(BETS)_2FeCl_4$ phase.[6] Other reported examples are $(BETS)_2MX_4$ (X = Cl^-, Br^-, CN^-; M = Fe^{3+}, Co^{2+}, Mn^{2+}, Ni^{2+}).[2,7]

Therefore, considering this high ability of BETS to form interesting conductive salts, it appears attractive and advantageous to improve its lengthy and difficult synthesis as previously reported by Kato *et al.*[3] We will also report in this paper the full X-ray crystal structure determination of BETS, as well as the π-electron density distribution of this molecule calculated by the PM3 semiempirical method.

Results and Discussion

In 1983, Schumaker *et al.*[8] reported the first synthesis of BETS with CSe_2 or H_2Se as the starting material. Later on, Kato *et al.*[3] proposed a six-step procedure using the less toxic and easier to handle selenium powder, but also the expensive *cis*-1,2-dichloroethylene, the very malodorous benzyl mercaptan and a large amount of sodium, as starting materials. In their method (Scheme 1, Method A), three steps are needed to synthesize 2,3-dihydro-1,4-dithiin, **3** (involving the isolation of
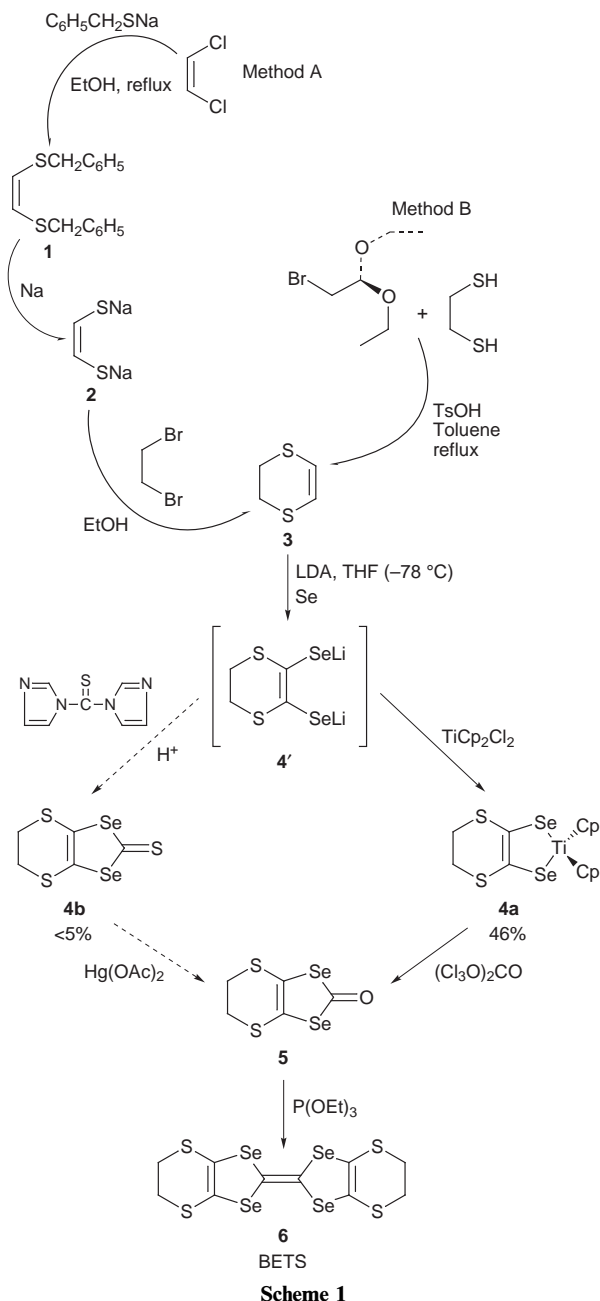
Scheme 1

the very hygroscopic and difficult to purify $C_2S_2H_2Na_2$ intermediate, **2**). Moreover, this lengthy preparation of **3** gives poor irreproducible yields (8–21%). We have perfected a short one-step method (Method B) for the synthesis of **3** based on the previous work of Parham et al.[9] Our method is based on the reaction in stoichiometric amounts of 2-bromo-1,1-diethoxyethane and 1,2-ethanedithiol in toluene (instead of in dilute aqueous chlorhydric acid solution as in ref. 9). Traces of p-toluenesulfonic acid monohydrate are added to the toluene and an azeotropic distillation is performed to remove water from the reaction. After refluxing the reaction mixture for 24 h, extracting with ether and washing with water, a final distillation yields highly pure **3** as a transparent and light yellow liquid with a yield of 38%.

A further improvement in the synthesis of BETS could consist in the preparation of ketone **5** using an organic (dotted) route.[10] The idea is to form thione **4b**, the following transchalcogenation of **4b** into **5** being expected to be quantitative. After quenching diselenolate [**4′**] with glacial acetic acid, the 1,1′-thiocarbonyldiimidazole is added at −70 °C and the solution is allowed to warm up to room temperature over approximately 5 h. After treatment of the organic phase and separation by column chromatography, a disappointingly poor yield of **4b** was obtained (<5%). This is probably due to the formation of several by-products and can be explained by the insufficient reactivity of 1,1′-thiocarbonyldiimidazole at low temperature and the very poor stability of the intermediate diselenol formed after quenching. Thus, the inorganic route towards BETS described by Kato et al.,[3] involving the preparation of the titanocenium complex **4a** and the ketone **5**,

still remains a better method to stabilize the unstable diselenolate intermediate compound [**4′**].

Single crystals (red elongated plates) of BETS were obtained by recrystallisation in benzonitrile, and its crystal structure could be determined by X-ray diffraction methods.[11] Crystal data indicate that the crystals of BETS are isostructural to those of ET[12] and bis(ethylenediseleno)tetrathiafulvalene[13] (BEDSe-TTF or BEST) wherein the outer sulfur atoms of ET are replaced by selenium. It is clear that substitution of the S atoms of ET by larger Se atoms does result in the increase of the molecular distances, as shown in Table 1 [see Fig. 1(a) for numbering scheme] and in the enlargement of the unit cell (1449.6 to 1516.5 Å) as also occurs in BEST (1544 Å³). As in ET and BEST, the molecular packing is composed of pairs of nonplanar BETS molecules [Fig. 1(b)]. The mode of overlap of this pair is shown in Fig. 2. The Se···Se intermolecular contacts within these pairs are 3.736, 3.899 and 3.904 Å for Se(1)—Se(2^i), Se(1)—Se(4^i) and Se(2)—Se(3^i), respectively (see Table 1). No other short Se···S or S···S contacts are found for this pair.

In order to obtain a qualitative insight into the π-electron density distribution in BETS, ET and BEST single-point calculations were performed with the PM3 semiempirical method[14] for all listed compounds, using the atomic coordinates experimentally obtained.[15] The charge density distribution and net charge partitions calculated for BETS, ET and BEST are shown in Fig. 3(a), 3(b) and 3(c), respectively.

As could be expected, in all three studied compounds, the π density is mainly distributed over the C=C bonds of the central TTF or TSeF fragment. When comparing the net

Table 1 Compared intramolecular distances and selected Se(S)···Se(S) intermolecular contacts in BETS, ET and BEST

Atoms[a]	BETS	ET[b]	BEST[b]
Interatomic distances/Å			
Se(S)(1)—C(1)	1.916(5)	1.764	1.758
Se(S)(1)—C(3)	1.905(5)	1.757	1.760
Se(S)(2)—C(4)	1.906(5)	1.747	1.752
Se(S)(2)—C(1)	1.896(5)	1.760	1.765
Se(S)(3)—C(2)	1.898(5)	1.753	1.760
Se(S)(3)—C(5)	1.923(5)	1.755	1.761
Se(S)(4)—C(6)	1.922(5)	1.755	1.754
Se(S)(4)—C(2)	1.901(5)	1.753	1.763
C(1)—C(2)	1.338(7)	1.319	1.329
C(3)—C(4)	1.338(8)	1.335	1.326
C(5)—C(6)	1.328(8)	1.328	1.330
Se(S)(5)—C(3)	1.745(5)	1.727	1.886
Se(S)(5)—C(7)	1.818(6)	1.801	1.954
Se(S)(6)—C(4)	1.745(5)	1.744	1.900
Se(S)(6)—C(8)	1.814(6)	1.803	1.940
Se(S)(7)—C(5)	1.752(5)	1.751	1.903
Se(S)(7)—C(9)	1.805(6)	1.804	1.946
Se(S)(8)—C(6)	1.752(5)	1.747	1.901
Se(S)(8)—C(10)	1.809(6)	1.800	1.931
C(7)—C(8)	1.440(10)	1.430	1.440
C(9)—C(10)	1.502(9)	1.494	1.483
Short intermolecular Se(S)···Se(S) contacts: S···S ⩽ 3.7 Å, S···Se ⩽ 3.85 Å, Se···Se 4 Å			
Se(S)(1)—Se(S)(2^i)	3.736(1)	3.686	3.700
Se(S)(1)—Se(S)(4^i)	3.899(1)	3.887	3.902
Se(S)(2)—Se(S)(3^i)	3.904(1)	3.875	3.904
Se(S)(2)—Se(S)(4^{ii})	3.632(1)	3.629	3.686
Se(S)(3)—Se(S)(8^{iii})	3.445(2)	3.482	3.542
Se(S)(5)—Se(S)(6^{iii})	3.748(2)	3.692	3.784
Se(S)(7)—Se(S)(8^{iii})	3.560(2)	3.545	3.644
Se(S)(1)—Se(S)(2^{iii})	3.816(1)	3.992	4.224
Se(S)(3)—Se(S)(4^{iii})	3.826(1)	3.988	4.231
Se(S)(6)—Se(S)(3^{iv})	3.789(1)	3.813	3.746
Se(S)(5)—Se(S)(7^{v})	3.890(2)	3.892	3.925
Se(S)(7)—Se(S)(7^{vi})	3.785(3)	3.848	3.840

[a] Symmetry operations for second atom: (i) $1 - x$, $-y$, $1 - z$; (ii) $2 - x$, $-y$, $1 - z$; (iii) $x - 1$, y, z; (iv) $\frac{1}{2} + x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$; (v) $\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$; (vi) $1 - x$, $-y$, $-z$. [b] Coordinates taken from ref. 12 and 13 for ET and BEST, respectively; standard deviations: 0.006–0.012 Å.
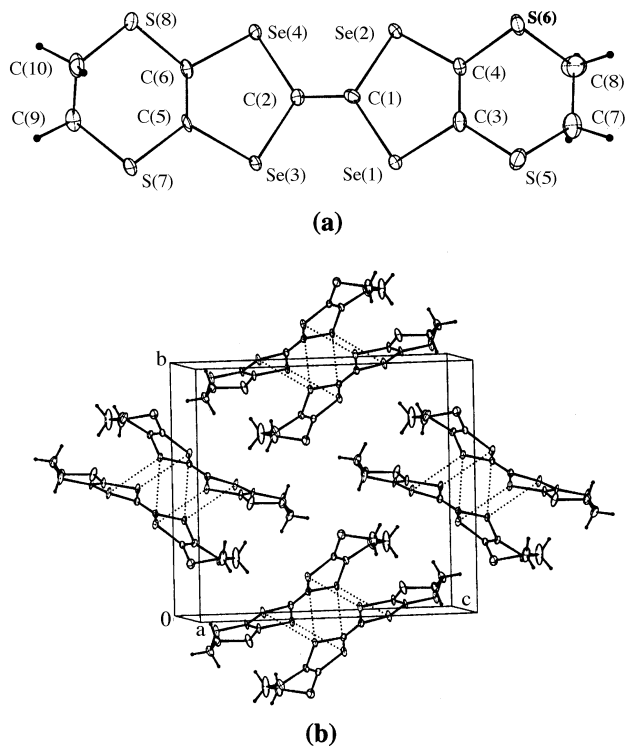
(a)

(b)

Fig. 1 (a) Atom numbering scheme and (b) molecular packing of neutral BETS

charge partitions on Se and S atoms at the same positions in BETS and ET as well as BEST and ET, one may observe that a larger π-electron density remains located on the Se atoms (and, correspondingly, a lower one on the carbon atoms of the C=C bonds). This indicates that the C—Se bonds are less antibonding than the C—S bonds. On the other hand, the differences in the electronic structure and properties between ET and its selenium analogues should be more significant for BETS than for BEST, since the main contribution to the HOMO is coming from the carbon and chalcogen atomic orbitals of the central fragment. Indeed, the calculated HOMO energy of BETS (−8.731 eV) is more than 0.5 eV lower than those of BEST (−8.277 eV) and ET (−8.246 eV), implying a substantially higher stability for BETS. This is experimentally reflected in the significantly higher values of the first and second oxidation potentials reported for BETS
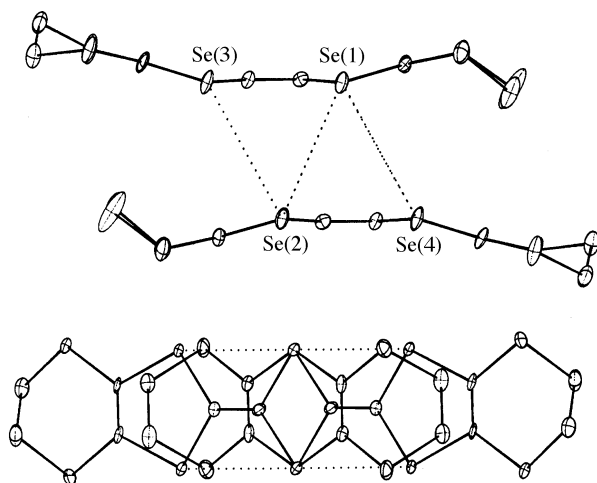

Fig. 2 Mode of overlap of the paired BETS (interaction i) The dotted lines indicate the short Se···Se contacts ($\leqslant 4$ Å). Hydrogen atoms are omitted for clarity
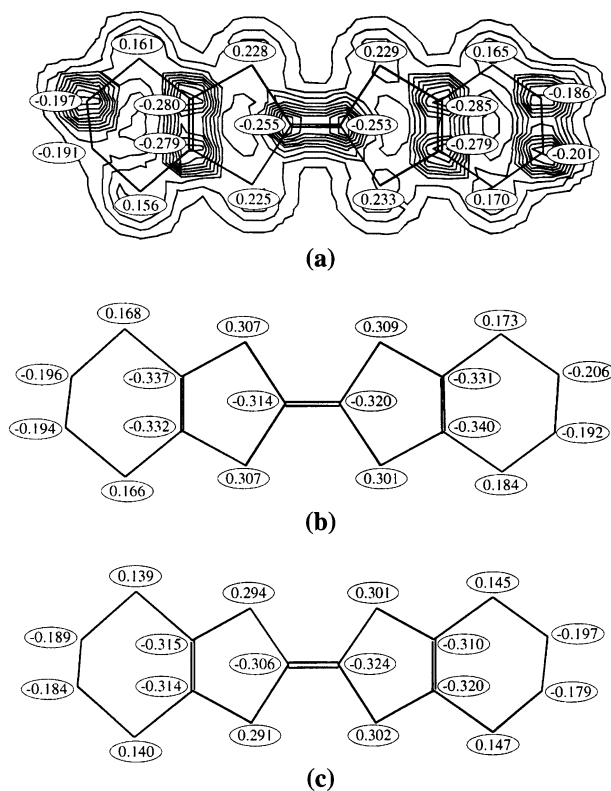

(a)

(b)

(c)

Fig. 3 Charge density distribution (zero plane offset) and net charge partitions of (a) BETS, (b) ET and (c) BEST

(0.27 and 0.49 V measured at a Pt electrode in benzonitrile vs. Ag/AgNO$_3$[16]) in comparison with ET (0.10 and 0.41 V under the same conditions), while the differences in these values for BEST and ET are very small.[17] Having in mind a possible enhancement of the transverse intermolecular overlap in the corresponding cation radical salts, we can conclude that substitution of sulfur atoms by selenium ones is much more efficient for this enhancement in the central five-membered rings than in the peripheral part of the ET molecule, since it strongly changes the HOMO by making it more diffuse.

A few years ago, Kato et al.[18] discussed the steric effects in several similar donor molecules and predicted most favourable molecular arrangements for conductive candidates by comparing the S_o/S_i ratio, where S_o and S_i were experimental (for ET) or estimated (for BETS) outside and inside interatomic distances between the chalcogen atoms in the transverse direction, respectively. The molecules for which the S_o/S_i ratio is close to 1.0 were predicted to be more suitable for enhancing the transverse overlap. However, because of the different ability of the sulfur and selenium atoms to induce intermolecular interaction, the difference in their van der Waals radii ($R_{Se} = 2$ Å, $R_S = 1.85$ Å) should be taken into account. Indeed, this concept was mentioned by Kato et al.[18] when predicting enhanced transverse intermolecular interactions for BETS-based salts. Therefore, instead of the S_o/S_i ratio, another ratio, C, defined as $C = (d_{X_o-X_o} + 2R_{X_o})/(d_{X_i-X_i} + 2R_{X_i})$ (d is the concerned interatomic distance, see Fig. 4; R is the concerned van der Waals radius) seems to be more appropriate in the comparison of the molecular arrangements of ET-derived molecules. The value of C is reflected in the shape of the molecule and three borderline situations can be considered: $C = 1$, which corresponds to a rectangular shape [Fig. 4(a)], $C > 1$ for a butterfly-like shape [Fig. 4(b)] and $C < 1$ for a hexagonal-like shape [Fig. 4(c)].
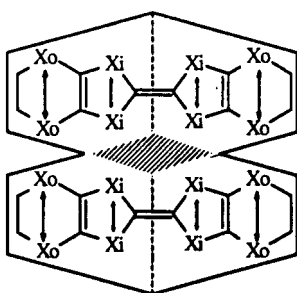
For BETS, the ratio C calculated from the structure described above is 0.99, very close to 1 (rectangular shape). This value seems to be more suitable for a good transverse overlap than that found for ET, 1.07.[19] The situation is even
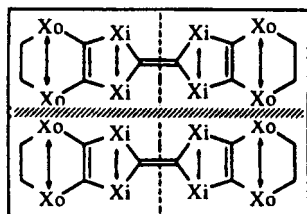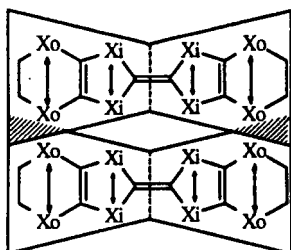
Fig. 4 Molecular shape and intermolecular transverse interaction (filled) area of ET-derived molecules for (a) $C = 1$, (b) $C > 1$, (c) $C < 1$

more pronounced in BEST with a C ratio of 1.14.[19] This larger value of C should not promote a large overlap and may explain the relatively low number of BEST-derived salts reported in the literature, none of which exhibit conducting behaviour down to low temperature or superconducting properties.[17] In BETS, the shortest chalcogen–chalcogen distance is 3.445 Å [Se(3)—S(8^{iii}), Table 1]. The Se—Se distances are very short as well and may also participate in an efficient transverse overlap (Fig. 5). These contacts are much more important than those between chalcogen atoms in ET and even more so than in BEST, where the selenium atoms occupy external positions.
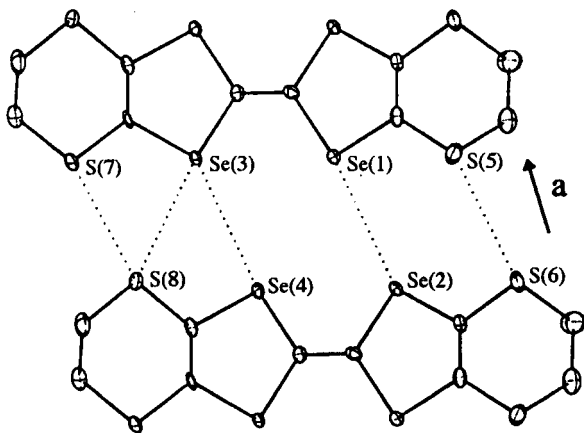

Fig. 5 Molecular arrangement along the a axis (interaction iii) in BETS. Dotted lines indicate the short X···X (X = Se, S) contacts ($\leqslant 3.7$ Å for S···S, $\leqslant 3.85$ Å for Se···S, $\leqslant 4$ Å for Se···Se)

In conclusion, such a detailed steric and electronic examination of the structural features of neutral donors may help in predicting their ability to form conductive electron-transfer salts and in selecting promising new donors.

Experimental

The infrared measurements were performed on a Perkin Elmer 1725X spectrophotometer at room temperature on KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature on a Bruker AC-200 spectrophotometer at 200 and 50 MHz, respectively.

Synthesis of 2,3-dihydro-1,4-dithiin, 3

In a three-neck flask surmounted by a Dean–Stark system, traces of p-toluenesulfonic acid are added to 166 ml of toluene. Azeotropic distillation of water is then performed overnight. The resulting mixture is cooled down to room temperature and the Dean–Stark system replaced by a condenser. 2-Bromo-1,1-diethoxyethane (12.6 ml, 82 mmol) and 7 ml of 1,2-ethanedithiol (83 mmol) are added under N_2. This mixture is warmed up until reflux for 24 h, upon which it rapidly becomes brown and a black precipitate is formed. After cooling down to room temperature, the mixture is treated with 150 ml of water. The product is extracted with three fractions of 150 ml of ether. The organic phase is washed with two fractions of 50 ml of distilled water and dried on $MgSO_4$. The organic phase is filtered and ether is removed by evaporation. A crude brown oil is obtained and distilled under vacuum (84 °C, 15 mm Hg) to give 3.57 g of light yellow and transparent liquid **3**. Yield: 38%. ^{1}H NMR (CDCl$_3$) δ: 6.1 (s, 2H, H—C=); 3.2 (s, 4H, CH$_2$).

Synthesis of BETS, 6

BETS was synthesised from **3** via **4′**, **4a**, **5** and **6** (Scheme 1) following literature methods.[3]

Characterisation of 4. ^{1}H NMR (CD$_2$Cl$_2$) δ: 5.95 and 6.15 (2 s, nonequivalent cyclopentadienyls); 3.25 (s, CH$_2$). ^{13}C NMR (CD$_2$Cl$_2$) δ: 31.5 (s, CH$_2$); 109.4 (s, =C—S); 111.5 (s, Cp). IR (ν, cm^{-1}): 815(vs); 863(m); 919(m); 1013(m); 1278(m); 1410(s); 2911(w); 3066(w).

Characterisation of 5. Mp: 95 °C. ^{1}H NMR (CD$_2$Cl$_2$) δ: 3.47 (s, CH$_2$). ^{13}C NMR (CD$_2$Cl$_2$) δ: 33.2 (s, CH$_2$); 116.9 (s, $C=C$—Se); 185.5 (s, $C=$O). IR (ν, cm^{-1}): 486(w); 696(m); 802(vs); 924(m); 950(m); 1262(m); 1414(s); 1502(w); 1590(w); 1655(vs).

Characterisation of 6. Mp: 275 °C. IR (ν, cm^{-1}): 447(w); 696(w) 807(s); 839(m); 876(m); 918(m); 939(m); 1258(s); 1406(s); 2957(w).

Crystallography

$C_{10}H_8S_4Se_4$, MW = 572.25, monoclinic, space group $P2_1/n$, unit cell at 160 K: $a = 6.668(1)$, $b = 14.094(1)$, $c = 16.161(1)$ Å, $\beta = 93.16(1)°$, $U = 1516.5$ Å^3, $D_c = 2.51$ g cm^{-3} for $Z = 4$. Data with $2.9° \leqslant 2\theta \leqslant 48.4°$ were collected on a STOE IPDS (imaging plate diffraction system) using monochromatic Mo-K$_\alpha$ radiation (λ = 0.710 13 Å), μ$_c$ = 100.9 cm^{-1}, 2218 independent reflections with $I > 0$ σ(I). The structure was solved by direct methods (SHELXS-86). The non-hydrogen atoms were refined anisotropically. Hydrogens atoms were included but not refined. The structure was refined by full-matrix least-squares methods to $R = 0.039$, $R_w = 0.031$.

CCDC reference number 440/028.

Acknowledgements

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