New synthetic metals based on a thiadiazole network

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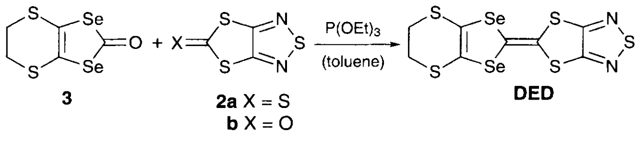
The charge transfer salts of newly synthesized donor thiadiazolo(ethylenedisulfanyl)diselenadithiafulvalene (DED) exhibit metallic behaviour down to low temperatures with a unique crystal structure and small S---N distances in addition to an inter-chalcogen network.

The pursuit of molecular-based conducting or magnetic materials is a subject of current interest.[1–7] The key point of designing a new material with these properties is how to achieve the desired intermolecular interaction. Although there are many atoms that can be expected to enhance intermolecular interactions when incorporated into molecules, most of the known synthetic metals depend solely on a chalcogen network for metallic conduction. Heterocycles including alternate sulfur and nitrogen atoms and their isomers are known to form a close S---N network in the solid state.[8–12] Such a network will favour a conduction pathway. Yet in spite of many trials,[8,11–15] there have been no reports of any well-defined compound containing conjugated thiazyl linkages that exhibit metallic conductivity. For example, both symmetrical and asymmetrical donors incorporating 1,2,5-thiadiazole sub-units have been studied but have not yielded metallic charge transfer salts to date.[12,16] In the meantime, bis(ethylenedisulfanyl)tetraselenafulvalene (BETS) has been reported to produce many stable metallic charge transfer salts.[17–20] Therefore a combination of the two conjugated systems, for example part of BETS together with 1,2,5-thiadiazole, could be a promising candidate for a donor to give rise to new synthetic metals. Here we report the synthesis, crystal structure and electrical properties of metallic charge transfer salts of the above-mentioned new donor, thiadiazole-ethylenedisulfanyldiselenadithiafulvalene (**DED**).

The synthetic route to **DED** is outlined in Scheme 1. The thione **2a**[16,21] and ketone **3**[17] were prepared according to literature procedures. Ketone **3** was treated with thione **2a** (1.1 equiv.) in the presence of excess triethyl phosphite in refluxing toluene under a nitrogen atmosphere to afford **1**[†] as brilliant red plates in 25–30% yield with very little contamination by the two self-coupling products. A similar reaction of the corresponding 1,3-dithiol-2-one **2b**[16] and **3** in a large excess of triethyl phosphite with or without toluene also produced **1**, but in lower yield (7–11%) together with the self-coupling products. Purification was carried out by fractional crystallization from toluene–ethanol.

Single crystals of the charge transfer salts were obtained as black rhombic plates by the galvanostatic (2.5 μA) electrolysis of **1** (*ca.* 0.4 mmol dm^{-3}) with an appropriate tetrabutylammonium salt (2–6 mmol dm^{-3}) in THF at room temperature.



Scheme 1

The resistivities of [(**DED**)$_2$X(THF)$_2$ (X = PF$_6$, AsF$_6$)] decrease down to *ca.* 20 K and then increase at lower temperatures (Fig. 1). The TaF$_6$ salt also exhibits similar behaviour except that the resistivity minimum is at *ca.* 35 K. X-Ray structure analysis revealed that the PF$_6$ salt exhibits a unique crystal structure[‡] (Fig. 2). The crystallographically independent molecules are two donors (**I** and **II**), two solvents (THF1, THF2; the latter is disordered) and one anion. The two donor molecules form a dimer with direct overlap and the same orientation. The dimers and anions pack alternately to form a donor–anion-mixed layer in the *ac* plane. The solvent molecules also make parallel sheets to sandwich the mixed layer. As a result the structure can be considered to consist of alternating solvent and the mixed sheets running parallel to the (010) plane. As shown in Fig. 2(*b*), two adjacent dimers hold a PF$_6$ anion approximately in the centre, which leaves room for a third dimer to interpose the thiadiazole rings between the two dimers towards the anion. The donors are connected by many short contacts centred around the heteroatoms in the thiadiazole rings. The X-ray photographs together with a preliminary X-ray study proved that the remaining salts are all isostructural to the PF$_6$ salt. In this structure there are no distinct donor columns or sheets, which have always been observed in previous synthetic conducting materials. Instead the overlap between the thiadiazole rings provides a two dimensional network of S---N interactions in addition to S---S(Se) interactions. Accordingly the thiadiazole network can be thought to afford a conduction path for the observed metallic conductivity. In fact the calculated overlap integrals and tight-binding band (Fig. 3) indicate significant interactions in the corresponding directions. Moreover, the interdimer interaction is so strong that the large band-gap characteristic of the dimerized system is not found in this system. As far as we know these are unique examples of metallic charge transfer salts based on conjugated thiazyl linkages. In spite of the calculated quasi-one-dimensional Fermi surface (Fig. 3), X-ray photographs (by Imaging Plate on the

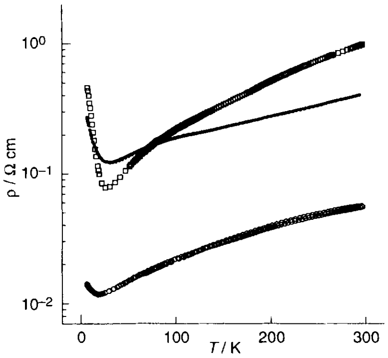


Fig. 1 Temperature dependences of the electrical resistivity of single crystals of (**DED**)$_2$X(solv)$_2$ {X = PF$_6$ (○), AsF$_6$ (□), solv = THF; X = TaF$_6$ (●), solv = C$_6$H$_5$Cl and/or 1,1,2-C$_2$H$_3$Cl$_3$}

PF_6 salt) demonstrated that their crystal structures are stable down to 11 K.

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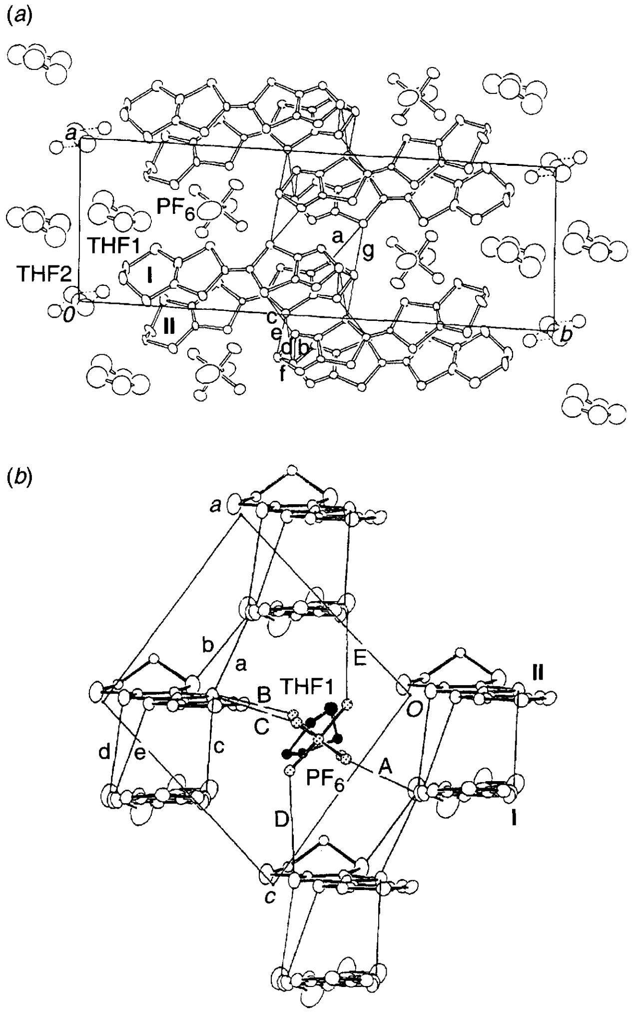

Fig. 2 Crystal structure of (**DED**)$_2$PF$_6$(THF)$_2$. (*a*) Particular close (S---N <3.35 Å; S---S <3.65 Å) intermolecular contacts mediated by the thiadiazole group are indicated by thin lines from a to g; (*b*) Particularly close (Se---F <3.3 Å; Se---Se <3.70; Se---S <3.70 Å) intermolecular contacts between donor and anion, or between chalcogen atoms are shown by thin lines with suffixes from A to E (Se---F) and a to e [Se---S(e)].

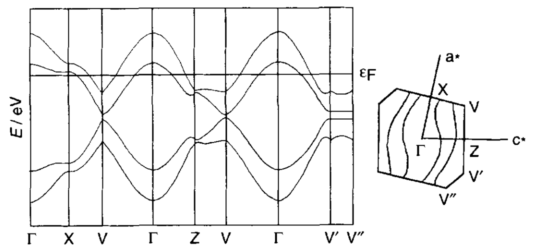

Fig. 3 The calculated tight-binding band structure of (**DED**)$_2$PF$_6$(THF)$_2$

Footnotes

† MS *m*/*z* (relative intensity) 446 (M^+, 100%). Anal. calcd. for $C_8H_4N_2S_5Se_2$: C, 21.52; H, 0.90; N, 6.28; S, 35.92 and Se, 35.38. Found: C, 21.40; H, 0.98; N, 6.35; S, 35.80 and Se, 34.05%.

‡ *Crystal data* for (**DED**)$_2$PF$_6$(THF)$_2$: $Se_4S_{10}PF_6N_4C_{24}H_{24}O_2$, M = 1181.95, black plate, crystal dimensions 0.30 × 0.40 × 0.10 mm^3, triclinic, space group $P\bar{1}$ (No. 2), a = 8.760(1), b = 25.006(3), c = 8.395(2) Å, α = 97.56(2), β = 101.96(2), γ = 91.61(1)°, V = 1780.5(6) Å^3, Z = 2, D_{calc} = 2.182 g cm^{-3}. Rigaku AFC5R, graphite monochromated Mo-Kα (λ = 0.71069 Å), ω–2θ scan with scan rate of 10.0°/min^{-1} (in ω) up to 3 scans, scan width = (0.73 + 0.30 tanθ)°, μ(Mo-Kα) = 48.02 cm^{-1}, F_{000} = 1130.00. 25 reflections used for unit cell determination ($26.9 \leqslant 2\theta \leqslant 30.9°$). No. of reflections measured; total: 8766, unique: 8227 (R_{int} = 0.052). $2\theta_{max}$ = 55.2° at 23.0 °C; Lorentz-polarization and absorption corrections were made; structure solution was carried out by direct methods (SHELXS86) and refinement by full-matrix least-squares; function minimized: $\Sigma\omega(|F_o| - |F_c|)^2$ and least squares weights: $1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$, 3998 observations with $I > 3.00\sigma(I)$ and 399 variables. All non-hydrogen atoms were refined anisotropically, R = 0.068 and R_w = 0.075. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallograpic Data Centre. See Informations for Authors, Issue No. 1.

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