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Organosulfur donor with hydroxy groups and its conducting salt: crystal structures and physical properties

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Abstract

Crystal structures of organosulfur donor 2-(5′,6′-dihydro[1,3]dithiolo[4,5-b][1,4]-dithiin-2′-ylidene)-6,7-di-hydro-5H-[1,3]dithiolo[4,5-b][1,4]dithiepine-6,6-dimethanol (**D**) and its conducting salt $\mathbf{D}_2I_3$ are described. Conductivity properties of $\mathbf{D}_2I_3$ are also discussed.

Keywords: Radical salts; Bis(ethylenedithio)tetrathiafulvalene (ET); Crystal structures; Electrical conductivity

1. Introduction

The radical cation salts based on bis(ethylenedithio)tetrathiafulvalence (ET) are the major class of organic quasi-two-dimensional metals and superconductors [1]. Their conductive properties are highly sensitive to chemical modifications of the ET framework, and considerable efforts have been devoted to the search for molecular superconductors presenting higher critical temperatures (T_c) by the synthetic chemistry methods [2–4]. Most of these chemical modifications were aimed to increase the dimensionality of these materials which can suppress the Peierls distortions at low temperature by favoring the intermolecular interaction among electron donors and acceptors (or counter anions). To introduce the possibility of strong hydrogen bonding some ET derivatives with hydroxy groups have been synthesised [5–9].

We report here the crystal structures of the title donor **D** (Fig. 1) and its conducting salt $\mathbf{D}_2I_3$.

2. Experimental

2.1. Materials and equipment

Unless stated otherwise, all reagents were purchased from commercial sources and used without additional purification. Organosulfur donor (**D**) and the supporting electrolyte n-Bu_4NI_3 were prepared according to literature procedures [6,10]. Conductivity was measured by the four-probe technique on a compressed pellet.

2.2. Synthesis of $\mathbf{D}_2I_3$

The conducting salt $\mathbf{D}_2I_3$ was obtained by electrocrystallization. Single crystals were grown on a platinum wire anode as brown thin plates by anodic oxidation of **D** in the presence of n-Bu_4NI_3 at constant low-current density (1 $\mu A\,cm^{-2}$) in CH_3CN.

2.3. Crystallography

Intensity measurements were collected on a Stoe Image Plate Diffraction System [11] for donor **D** and a Stoe Mark II-Image Plate Diffraction System [12] for its salt $\mathbf{D}_2I_3$, equipped with graphite monochromated Mo

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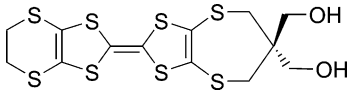

Fig. 1. Organosulfur donor **D**.

Kα radiation ($\lambda = 0.71073$ Å) using the $\omega - 2\theta$ scan technique. The structures were solved by Direct methods using the programme SHELXS 97 [13]. The refinement and all further calculations were carried out using SHELXL 97 [14].

For donor **D**, the H-atoms were either located from Fourier difference maps and refined isotropically or included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. The crystal diffracted weakly and only 1/3 of the reflections can be considered to be observed [$I > 2\sigma(I)$]. Owing to the extremely long *b*-axis, a certain fraction of the reflections (ca. 12%) was overlapped and eliminated from the *hkl* file. The molecule is structurally disordered, with the terminal –C_2H_4 group having two conformations.

For its salt $\mathbf{D}_2I_3$, the hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL 97 default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. An absorption correction was applied using DIFABS [15] ($T_{\min} = 0.325$, $T_{\max} = 0.755$).

Table 1
Crystallographic data for donor **D** and its salt $\mathbf{D}_2I_3$

	D	$\mathbf{D}_2I_3$
Molecular formula	$C_{13}H_{14}O_2S_8$	$C_{26}H_{28}I_3O_4S_{16}$
Molecular weight	458.72	1298.14
Crystal dimensions (mm)	0.40 × 0.40 × 0.10	0.500 × 0.275 × 0.025
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	$Pbn2_1$
Unit cell dimensions		
a (Å)	6.4287(7)	8.2240(5)
b (Å)	42.420(7)	11.7860(7)
c (Å)	7.1209(8)	42.170(3)
β (°)	114.705(12)	90.000(0)
U (Å^3)	1764.2(4)	4087.5(5)
Z	4	4
D_{calc} (g cm^{-3})	1.727	2.109
Absorption coefficient (mm^{-1})	1.016	3.146
R_{int}	0.1316	0.0701
Measured reflections	8562	14 708
Independent reflections	3004	7099
Reflections with $I > 2\sigma(I)$	1110	5762
R_1 (observed)	0.0714	0.0849
wR_2 (all data)	0.2189	0.2372
Goodness-of-fit	0.821	1.026

The crystallographic data of donor **D** and its salt $\mathbf{D}_2I_3$ are collected in Table 1. Selected bond lengths and angles are given in Table 2.

Table 2
Selected bond lengths (Å) and angles (°) for donor **D** and its salt $\mathbf{D}_2I_3$

D		$\mathbf{D}_2I_3$			
Bond lengths					
C(1)–C(4)	1.342(11)	C(1)–C(4)	1.372(16)	C(14)–C(17)	1.369(17)
C(1)–S(1)	1.741(11)	C(1)–S(1)	1.742(10)	C(14)–S(9)	1.744(11)
C(4)–S(4)	1.750(11)	C(4)–S(4)	1.725(13)	C(17)–S(12)	1.740(12)
C(5)–C(6)	1.325(14)	C(5)–C(6)	1.416(17)	C(18)–C(19)	1.370(16)
C(5)–S(4)	1.756(9)	C(5)–S(4)	1.731(12)	C(18)–S(9)	1.721(11)
C(5)–S(1)	1.777(9)	C(5)–S(1)	1.728(11)	C(18)–S(12)	1.744(12)
C(6)–S(5)	1.749(9)	C(6)–S(5)	1.717(12)	C(19)–S(13)	1.744(11)
C(6)–S(8)	1.759(9)	C(6)–S(8)	1.729(11)	C(19)–S(16)	1.750(10)
C(7)–C(11)	1.354(9)	C(7)–C(11)	1.316(18)	C(20)–C(24)	1.364(16)
C(7)–S(5)	1.745(10)	C(7)–S(5)	1.779(11)	C(20)–S(13)	1.726(12)
C(11)–S(8)	1.733(11)	C(11)–S(8)	1.744(11)	C(24)–S(16)	1.735(10)
O(1)–C(12)	1.441(14)	O(1)–C(12)	1.395(17)	O(3)–C(25)	1.416(15)
O(2)–C(13)	1.436(12)	O(2)–C(13)	1.466(15)	O(4)–C(26)	1.403(14)
Bond angles					
C(4)–C(1)–S(1)	116.6(8)	C(4)–C(1)–S(1)	116.7(8)	C(17)–C(14)–S(9)	117.2(9)
C(1)–C(4)–S(4)	118.3(8)	C(1)–C(4)–S(4)	116.8(9)	C(14)–C(17)–S(12)	116.3(9)
S(4)–C(5)–S(1)	113.4(6)	S(1)–C(5)–S(4)	116.2(7)	S(9)–C(18)–S(12)	116.0(7)
S(5)–C(6)–S(8)	113.9(7)	S(5)–C(6)–S(8)	116.6(7)	S(13)–C(19)–S(16)	114.5(6)
C(11)–C(7)–S(5)	115.4(8)	C(11)–C(7)–S(5)	115.2(9)	C(24)–C(20)–S(13)	116.9(9)
C(7)–C(11)–S(8)	118.9(8)	C(7)–C(11)–S(8)	119.4(9)	C(20)–C(24)–S(16)	117.2(8)
O(1)–C(12)–C(9)	111.0(11)	O(1)–C(12)–C(9)	112.0(11)	O(3)–C(25)–C(22)	112.7(10)
O(2)–C(13)–C(9)	115.0(12)	O(2)–C(13)–C(9)	111.3(10)	O(4)–C(26)–C(22)	111.8(11)
C(13)–C(9)–C(12)	115.1(10)	C(13)–C(9)–C(12)	109.9(10)	C(26)–C(22)–C(25)	110.0(10)

3. Results and discussion

3.1. Structure of **D**

Organosulfur donor **D** was recrystallised from THF/CH_3CN to afford single crystals. The X-ray crystal analysis revealed that in the crystal lattice, the molecules are linked by a 1D polymer arrangement of some conventional O–H···O hydrogen bonds (Table 3), so forming zig-zag chains along the *b*-axis (Fig. 2). The donor molecules are quasi-parallel caused by asymmetric hydrogen-bonds and mutually shifted with interplanar distances of 4.17 Å and stacked along the *c*-axis. There are intermolecular S···S contacts in the range of 3.29–3.60 Å.

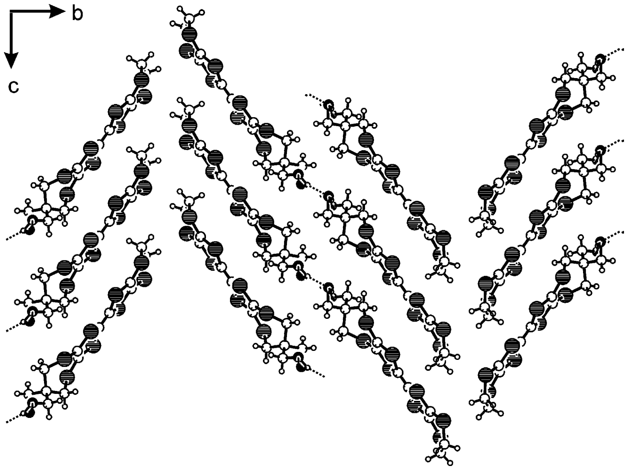

Fig. 2. Crystal packing of the neutral donor **D** showing hydrogen bonding (dashed lines) between stacks.

3.2. Synthesis, conductivity properties and structure of $\mathbf{D_2I_3}$

In order to obtain the conducting salts of **D**, standard electrocrystallizations were examined in the presence of various tetrabutylammonium (TBA) salts as the electrolyte: these included linear (I_3^-), tetrahedral (ClO_4^-), and octahedral (PF_6^-) anions. However, only the electrocrystallization at a constant current (1.0 μA) in CH_3CN with TBA· I_3 gave crystalline salts as brown thin plates. The room-temperature conductivity measured by a four-probe technique on a compressed pellet showed a relatively high conductivity ($\sigma_{rt} = 2.95$ S cm^{-1}). The temperature dependence of the resistivity is shown in Fig. 3. From room temperature to about 240 K, its electrical resistance varies very little. But when the temperature is lowered further, the electrical resistance increases strongly, showing semiconducting behaviour with the activation energy being about 0.35 eV.

The X-ray analyses showed that the charge-transfer complex $\mathbf{D_2}I_3$ crystallises with two positively charged donor molecules A and B and one disordered I_3^- anion per asymmetric unit (Fig. 4). The molecular structures of the two donor units (A and B) are only slightly different. For both units A and B in the salt, the central TTF units are coplanar with deviations from the least-squares plane being less than 0.047 Å. Apparently, in the oxidation state the TTF units show less deviations from planarity

Table 3
Hydrogen bonds (Å, °) for donor **D**

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	D–H···A (°)
O(2)–H(2)···O(1)^{i}	1.05(11)	1.85(11)	2.884(10)	170(11)
O(1)–H(1)···O(2)^{ii}	1.00(13)	1.76(13)	2.719(11)	159(12)

Symmetry transformations used to generate equivalent atoms: (i) $1x - 1,\ y,\ z$; (ii) $-x + 2,\ -y,\ -z + 1$.

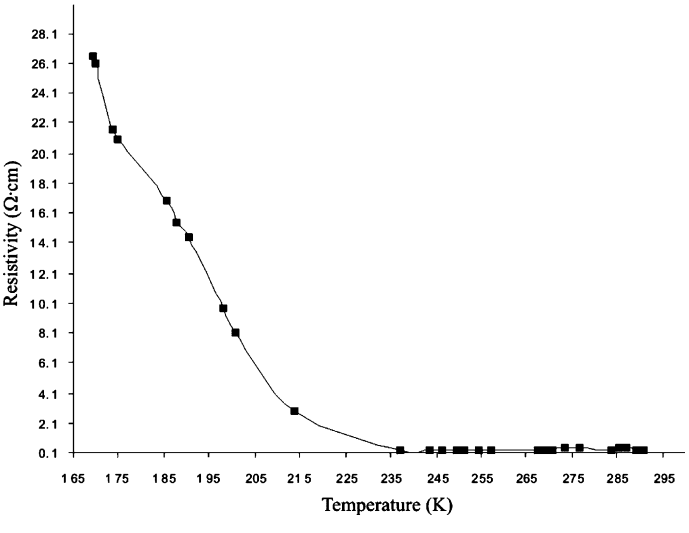

Fig. 3. Temperature dependence of the resistivity for $\mathbf{D_2}I_3$.

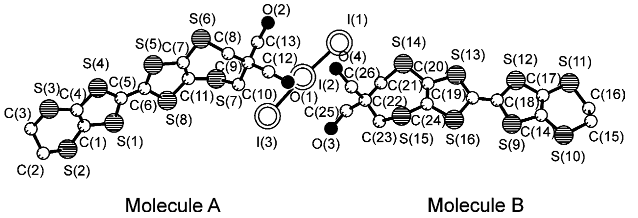

Fig. 4. Crystal structure of the conducting salt $\mathbf{D}_2\mathrm{I}_3$. Hydrogen atoms are omitted for clarity.

than those in the neutral state (largest deviation is 0.064 Å). The bond lengths of the central C═C [C(5)–C(6); C(18)–C(19)] bonds are 1.416 and 1.370 Å, respectively, in the salt (Table 2). As compared to that of the neutral donor **D** (1.325 Å), it can be inferred that the TTF units in salt $\mathbf{D}_2\mathrm{I}_3$ are partially oxidised according to the correlation between the oxidation states of TTF derivatives and bond lengths of the central C═C bonds [16]. As depicted in Fig. 5, the donor molecules are dimerised in 'head-to-head' manner, which might increase the effective overlap area of the molecules and stabilise the electronic state with van der Waals attractive force [17]. Dimers are orthogonally arranged to each other along the *b*-axis. The dihedral angles between the molecules are 84.6° and 72.3° for pairs A–A and B–B, respectively. The donor array of the present salt is classified as the so-called κ-type. There are S···S contacts (3.46–3.62 Å, sum of van der Waals radii 3.70 Å) and weak hydrogen bonds (C–H···S = 3.49–3.76 Å and C–H···O = 2.84–2.91 Å) between neighboring dimers. Whereas between A and B stacks, some conventional O–H···O hydrogen bonds with 1D polymer arrangement (Table 4 and Fig. 5), a short S···I contact (3.63 Å) and weak hydrogen bonds C–H···I (3.74–3.95 Å) are observed.

In both **D** and $\mathbf{D}_2\mathrm{I}_3$, no intramolecular hydrogen bonds are observed which can be explained by strong competition of bimolecular ring motifs [18]. The hydrogen bond pattern in these two compounds is different, as shown by the graph-set analysis following the accepted proposition of Etter et al. [19]. In donor **D**, one kind of hydrogen bond gives rise to chains and two other different kinds of hydrogen bond give rise to rings, which form a higher-order network. Therefore, the graph-set for **D** is $C(6)\ R_4^4(8)\ R_2^2(12)\ R_4^4(16)$. Whereas in its salt, $\mathbf{D}_2\mathrm{I}_3$, one kind of hydrogen bond gives rise to chains and another kind of hydrogen bond gives rise to a ring, two of which make up a higher-order network. Thus, the graph-set for $\mathbf{D}_2\mathrm{I}_3$ is $C(6)\ R_3^3(10)\ R_4^4(16)$.

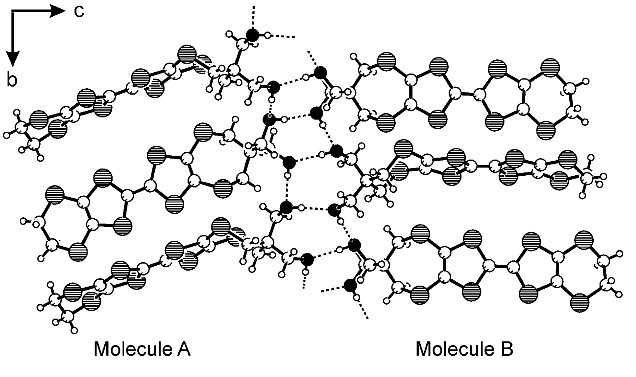

Fig. 5. Crystal packing of the conducting salt $\mathbf{D}_2\mathrm{I}_3$ showing hydrogen bonding (dashed lines). I_3^- anions are omitted for clarity.

Table 4
Hydrogen bonds (Å, °) for $\mathbf{D}_2\mathrm{I}_3$

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	D–H···A (°)
O(1)–H(1)···O(2)^{i}	0.84	1.85	2.664(12)	162.9
O(2)–H(2)···O(3)	0.84	1.88	2.706(12)	167.3
O(3)–H(3)···O(4)^{i}	0.86	1.87	2.728(11)	179.4
O(4)–H(4)···O(1)^{ii}	0.85	1.90	2.744(12)	179.1

Symmetry transformations used to generate equivalent atoms: (i) $-x-3/2,\ y+1/2,\ z$; (ii) $-x-3/2,\ y-1/2,\ z$.

4. Conclusions

In conclusion, the title donor has yielded a conducting salt $\mathbf{D}_2\mathrm{I}_3$ and shows a unique crystal structure. Thus, compound **D** can be expected to be a suitable donor for exploring organic metals in the future.

5. Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 218114–218115 for compounds **D** and $\mathbf{D}_2\mathrm{I}_3$. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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