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First radical cation salts from the symmetrical outer S-position isomer of BEDT-TTF

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The X-ray crystal structures and physical characterizations of the first radical cation salts obtained from the symmetrical S-position isomer of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF), are presented in this work. The unusual feature of this new π-donor **D1**, involved in the described salts $(\mathbf{D1})_3\cdot(ClO_4)_2$, $(\mathbf{D1})_3\cdot(BF_4)_2$ and $\mathbf{D1}\cdot Cu(SCN)_2$, is the presence of two disulfide bridges, allowing weak intermolecular S···S interactions. The influence of these outer sulfur atoms on the network of related materials is also discussed in relation to the first physical characterizations which have been carried out.

Introduction

Since the discovery of the first series of organic superconductors obtained from tetramethyltetraselenafulvalene (TMTSF) (Fig. 1a),[1,2] considerable efforts have been devoted to the search for molecular superconductors presenting higher critical temperatures (T_c). In this field, the development of new π-donors derived from families related to tetraselenafulvalene (TSF) or tetrathiafulvalene (TTF) has been of particular interest in the synthesis of organic metals[3] that exhibit relevant physical properties. Taking advantage of the large synthetic versatility, one of the most promising strategies consists of introducing additional sulfur atoms at the periphery of the TTF-skeleton. Thus, the synthesis of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) (Fig. 1b) was a giant step in organic metals research. At least 20 superconductors have been prepared from this π-donor and the following BEDT-TTF kappa phases, κ-$(BEDT\text{-}TTF)_2\cdot Cu(SCN)_2$ ($T_c = 10.4$ K under ambient pressure),[4] κ-$(BEDT\text{-}TTF)_2\cdot CuN(CN)_2Br$ ($T_c = 11.6$ K, under ambient pressure)[5] and κ-$(BEDT\text{-}TTF)_2\cdot CuN(CN)_2Cl$ ($T_c = 12.8$ K, $P = 0.3$ kbar)[6] still hold the record for superconducting transition temperatures in the series. All these highly conducting salts present a quasi-two-dimensional electronic structure, this increase of electronic dimensionality constituting a requisite for stabilization of the metallic state at low temperature.[3] Moreover, the prominent role of the outer sulfur atoms of BEDT-TTF in this 2D character has been clearly proved with the intermolecular chalcogen–chalcogen interactions.[7] Such S···S intermolecular contacts have also been found in other π-electron donors that present peripheral sulfur atoms.[8] In this context, the symmetrical[9] and dissymmetrical[10] S-position isomers of BEDT-TTF (**D1** and **D2** respectively) and a more soluble unsymmetrical derivative **D3**[10] have been recently synthesized (Fig. 2). These π-donors are characterized by the presence of one or two disulfide bridges giving rise to significant S···S intermolecular contacts. The solid-state properties of organic salts are a direct consequence of the packing of radical cations in the crystallographic network. Thus, it appears of great interest to study the influence of these peripheral sulfur atoms on the structural organization of the corresponding salts. For this purpose, we have focused on the preparation of radical-cation salts from **D1**, **D2** and **D3**. As described in previous papers,[9,10] these new π-donors display very similar electrochemical properties to those of BEDT-TTF (as a reminder, oxidation potentials of **D1** are $E_{ox}^1 = 0.54$ V and $E_{ox}^2 = 0.99$ V *vs.* SCE in a solution of $Bu_4N^+PF_6^-$ 0.1 M solubilized in CH_2Cl_2), which makes them good candidates for obtaining promising new molecular materials.

In this work, we present the chemical preparation, X-ray crystal structures and preliminary physical characterizations of the salts $(\mathbf{D1})_3\cdot(ClO_4)_2$ (**1**), $(\mathbf{D1})_3\cdot(BF_4)_2$ (**2**) and $\mathbf{D1}\cdot Cu(SCN)_2$ (**3**), which stem from the symmetrical outer S-position isomer of BEDT-TTF, **D1**. More particularly, concerning the discussion of the role of terminal disulfide bridges in the structural arrangement, the organization of donor arrays in the described compounds will be compared to those usually observed in current BEDT-TTF salts.

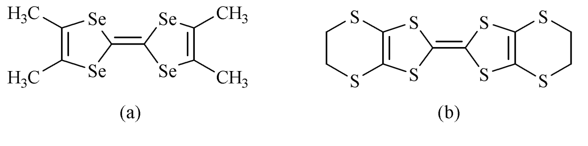


Fig. 1 a) Tetramethyltetraselenafuvalene (TMTSF); b) bis(ethylenedithio)tetrathiafuvalene (BEDT-TTF).

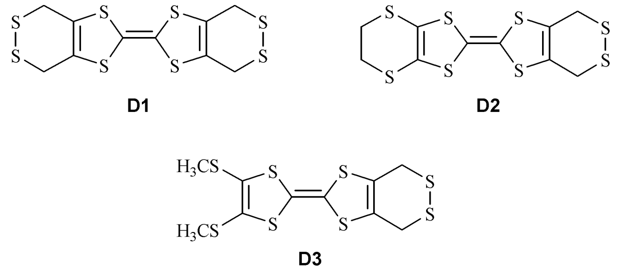


Fig. 2 The symmetrical S-position isomer of BEDT-TTF (**D1**), the dissymmetrical S-position isomer of BEDT-TTF (**D2**) and the unsymmetrical derivative (**D3**).

Table 1 Crystallographic data of **D1** salts **1**, **2** and **3** at ambient temperature

Chemical formula	$C_{15}H_{12}O_4S_{12}Cl$ (**1**)	$C_{15}H_{12}F_4S_{12}B$ (**2**)	$C_{12}H_8S_{10}N_2Cu$ (**3**)
Crystal system	Monoclinic	Monoclinic	Monoclinic
M/g mol^{-1}	676.48	663.84	564.39
a/Å	11.953(4)	11.910(8)	5.417(7)
b/Å	14.701(2)	14.579(8)	17.75(1)
c/Å	13.917(4)	13.771(2)	20.71(1)
β/degrees	93.77(2)	94.28(2)	96.94(2)
V/Å^3	2440(1)	2384(3)	1976(4)
Temperature/K	294	294	294
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
Z	4	4	4
λ/Å	0.71073	0.71073	0.71073
D_c/g cm^{-3}	1.86	1.85	1.881
μ(Mo-Kα)/cm^{-1}	11.82	10.94	21.249
Reflections measured	5719	4589	4040
$I > 3\sigma(I)$	3910	3407	1353
No of variables	307	307	174
$R(F)$	0.051	0.048	0.056
$R_w(F)$	0.080	0.050	0.069

Experimental

Sample preparation

The described radical cation salts **1**, **2** and **3** have been obtained by electrocrystallization. Single crystals were grown on a platinum wire anode by anodic oxidation of **D1** at constant low-current density (1 μA cm^{-2}).

For salts **1** and **2**, solutions of Bu_4NClO_4 and Bu_4NBF_4 (0.1 mol L^{-1}) in a chlorobenzene–acetonitrile medium (9 : 1 v/v ratio) were respectively used as supporting electrolytes. Crystal growth of **3** was carried out in a chlorobenzene–acetonitrile medium (7 : 3 v/v ratio) containing **D1**, KSCN, Cu(SCN) and 18-crown-6 ether used to capture potassium ions in the electrochemical preparation.

X-Ray structure determination†

Intensity measurements were collected on an Enraf-Nonius MACH3 diffractometer equipped with graphite monochromatized Mo-Kα (0.71073 Å) radiation. The unit cell parameters were determined and refined from 25 carefully centered reflections corresponding to $\theta > 10°$. Data were collected using the ω-scan technique. Intensities were corrected for Lorentz polarization and absorption effect using the DIFABS procedure.[11] Structures were resolved by direct methods and successive Fourier difference synthesis. The refinement on F was performed by the full matrix least-squares method.[12] Hydrogen atoms placed at computer positions were not refined. All calculations were performed on a DEC 3000AXP 300LX computer using the MolEN package programs.[13] The crystallographic data of described salts are collected in Table 1. Bond lengths and angles are given in Tables 2 and 3.

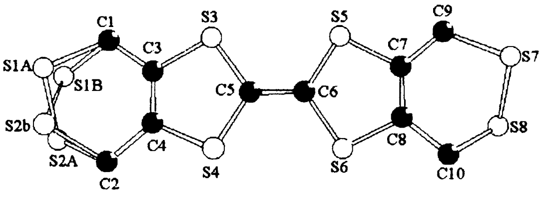
Physical characterizations

The d.c. electrical conductivity measurements over the range 100–295 K were performed on single crystals by the standard four probe method. The electrical contacts were made directly with gold wire using silver paint. Electron paramagnetic resonance (EPR) experiments were realized with a Bruker ESP 300E spectrometer equipped with a helium cryostat. Single crystals were mounted with silicone grease on a quartz rod. The field was measured using diphenylpicrylhydrazyl (DPPH, $g = 2.0036$) as a stable free radical marker.

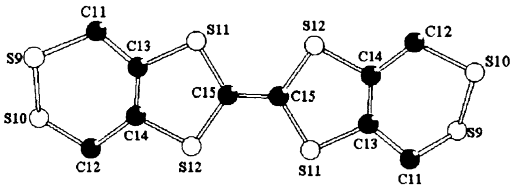
Optical absorption spectra were recorded in the near IR–visible range on a FTIR 750 Nicolet spectrometer (using the classical technique with diluted compounds inside a pressed KBr pellet).

Results and discussion

Firstly, the association of the symmetrical S-position isomer **D1** with ClO_4^- and BF_4^- anions affords radical cation salts presenting the same [3 : 2] stoichiometry as those formed from BEDT-TTF, γ-(BEDT-TTF)$_3$·$(ClO_4)_2$[14] and γ-(BEDT-TTF)$_3$·$(BF_4)_2$.[15] Salts **1** and **2**, (**D1**)$_3$·$(ClO_4)_2$ and (**D1**)$_3$·$(BF_4)_2$ respectively, are isostructural and both of them crystallize in the $P2_1/n$ space group. Crystal structures are built of respectively ClO_4^- and BF_4^- anions in general positions and of two independent donor molecules, denoted by **A** and **B**.



Molecule A



Molecule B

Molecule **A** is located in a general position and presents a conformation close to that of the BEDT-TTF neutral molecule (Fig. 3). Its TTF core is strongly bent and both disulfide bridges adopt a twisted conformation. A position disorder is also observed for one of the two terminal groups and the corresponding sulfur atoms are found together in two positions with an occupation ratio of 75 : 25 for S_{1a}/S_{1b} and S_{2a}/S_{2b} respectively. Molecule **B** is located on the symmetry center at the origin of the lattice and presents a planar TTF core (Fig. 4). A twisted conformation also characterizes the disulfide bridges, which are in this case perfectly ordered. Thus, as was reported for BEDT-TTF, this symmetrical S-position isomer is flexible enough to allow different conformations.

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†CCDC reference number 1145/200. See http://www.rsc.org/suppdata/jm/a9/a908843a for crystallographic files in .cif format.

Table 2 Bond distances (Å) in **(D1)**$_3$·(ClO$_4$)$_2$ (**1**), **(D1)**$_3$·(BF$_4$)$_2$ (**2**) and **D1**·Cu(SCN)$_2$ (**3**) salts

(D1)$_3$·(ClO$_4$)$_2$							
Cl–O1	1.430(5)	S4–C4	1.751(4)	S9–S10	2.053(2)	C3–C4	1.381(6)
Cl–O2	1.382(5)	S4–C5	1.723(4)	S9–C11	1.850(5)	C5–C6	1.372(6)
Cl–O3	1.435(4)	S5–C6	1.727(4)	S10–C12	1.793(5)	C7–C8	1.321(6)
Cl–O4	1.366(6)	S5–C7	1.768(4)	S11–C13	1.753(5)	C7–C9	1.489(6)
S1–S2	2.048(2)	S6–C6	1.742(4)	S11–C15	1.722(4)	C8–C10	1.514(6)
S1–C1	1.836(5)	S6–C8	1.769(4)	S12–C14	1.751(5)	C11–C13	1.505(6)
S2–C2	1.838(5)	S7–S8	2.051(2)	S12–C15	1.726(4)	C12–C14	1.521(6)
S3–C3	1.749(4)	S7–C9	1.810(4)	C1–C3	1.505(6)	C13–C14	1.341(6)
S3–C5	1.752(4)	S8–C10	1.821(5)	C2–C4	1.502(6)	C15–C15′	1.380(6)
(D1)$_3$·(BF$_4$)$_2$							
F1–B	1.355(8)	S4–C4	1.755(5)	S9–S10	2.039(2)	C3–C4	1.340(7)
F2–B	1.361(9)	S4–C5	1.717(5)	S9–C11	1.793(6)	C5–C6	1.366(7)
F3–B	1.299(9)	S5–C6	1.733(5)	S10–C12	1.795(6)	C7–C8	1.335(7)
F4–B	1.322(8)	S5–C7	1.748(5)	S11–C13	1.742(5)	C7–C9	1.504(8)
S1–S2	2.031(3)	S6–C6	1.730(5)	S11–C15	1.714(5)	C8–C10	1.490(8)
S1–C1	1.814(6)	S6–C8	1.740(5)	S12–C14	1.736(6)	C11–C13	1.495(8)
S2–C2	1.842(6)	S7–S8	2.039(2)	S12–C15	1.721(5)	C12–C14	1.497(8)
S3–C3	1.745(5)	S7–C9	1.802(6)	C1–C3	1.505(8)	C13–C14	1.345(7)
S3–C5	1.734(5)	S8–C10	1.789(6)	C2–C4	1.499(8)	C15–C15′	1.395(6)
D1·Cu(SCN)$_2$							
Cu1–S10	2.576(4)	S1–S2	2.044(6)	S5–C6	1.70(1)	C2–C4	1.52(2)
Cu1–N1	1.858(9)	S1–C1	1.85(1)	S5–C7	1.73(1)	C3–C4	1.33(2)
Cu1–N2	1.839(9)	S2–C2	1.82(1)	S6–C6	1.72(1)	C5–C6	1.40(1)
S9–C11	1.61(1)	S3–C3	1.75(1)	S6–C8	1.74(1)	C7–C8	1.32(1)
S10–C12	1.60(1)	S3–C5	1.70(1)	S7–C9	1.77(1)	C7–C9	1.53(2)
N1–C11	1.16(1)	S4–C4	1.73(1)	S8–C10	1.80(1)	C8–C10	1.50(2)
N2–C12	1.18(1)	S4–C5	1.71(1)	C1–C3	1.51(2)	—	—

These two donor molecules are organized in centrosymmetrical trimers [**ABA**′], which are stacked along the [100] direction (Fig. 5). The [3 : 2] stoichiometry of salts **1** and **2** suggests that each trimer is carrying a charge of +2. Thus, we have studied its distribution on the two independent molecules, taking into account the donor geometry. A correlation between charge transfer and bond lengths of the TTF core recently established for BEDT-TTF salts[16] is applied to molecules **A** and **B**. The bond lengths of each donor are first averaged in the D_{2h} symmetry and it appears that the centrosymmetric molecule **B** is close to a fully oxidized state whereas the charge on **A** and on its centrosymmetric related molecule **A**′

Table 3 Angles in **(D1)**$_3$·(ClO$_4$)$_2$ (**1**), **(D1)**$_3$·(BF$_4$)$_2$ (**2**) and **D1**·Cu(SCN)$_2$ (**3**) salts

(D1)$_3$·(ClO$_4$)$_2$							
O1–Cl–O2	105.9(3)	S7–S8–C10	98.5(2)	S5–C6–C5	122.8(3)	C14–S12–C15	96.3(2)
O1–Cl–O3	111.1(3)	S1–C1–C3	112.2(3)	S6–C6–C5	122.1(3)	S9–C11–C13	111.0(3)
O1–Cl–O4	112.6(3)	S2–C2–C4	113.0(3)	S5–C7–C8	116.3(3)	S10–C12–C14	113.9(3)
O2–CL–O3	112.3(4)	S3–C3–C1	115.8(3)	S5–C7–C9	114.3(3)	S11–C13–C11	114.8(3)
O2–Cl–O4	109.3(4)	S3–C3–C4	116.4(3)	C8–C7–C9	129.4(4)	S11–C13–C14	116.9(3)
O3–Cl–O4	105.7(3)	C1–C3–C4	127.7(4)	S6–C8–C7	117.7(3)	C11–C13–C14	128.3(4)
S2–S1–C1	99.4(2)	S4–C4–C2	115.5(3)	S6–C8–C10	113.5(3)	S12–C14–C12	115.0(3)
S1–S2–C2	98.0(2)	S4–C4–C3	115.6(3)	C7–C8–C10	128.8(4)	S12–C14–C13	116.0(3)
C3–S3–C5	95.8(2)	C2–C4–C3	128.8(4)	S7–C9–C7	111.9(3)	C12–C14–C13	128.9(4)
C4–S4–C5	96.8(2)	S3–C5–S4	114.0(2)	S8–C10–C8	112.8(3)	S11–C15–C15′	123.2(3)
C6–S5–C7	95.8(2)	S3–C5–C6	122.9(3)	S10–S9–C11	98.0(2)	S12–C15–C15′	122.0(3)
C6–S6–C8	94.8(2)	S4–C5–C6	123.0(3)	S9–S10–C12	99.2(2)	S11–C15–S12	114.8(2)
S8–S7–C9	98.7(2)	S5–C6–S6	115.1(2)	C13–S11–C15	95.9(2)	—	—
(D1)$_3$·(BF$_4$)$_2$							
F1–B–F2	109.7(6)	S7–S8–C10	98.3(2)	S5–C6–C5	122.9(4)	C14–S12–C15	95.9(2)
F1–B–F3	107.9(6)	S1–C1–C3	112.6(4)	S6–C6–C5	122.7(4)	S9–C11–C13	112.8(4)
F1–B–F4	110.8(6)	S2–C2–C4	110.7(4)	S5–C7–C8	117.5(4)	S10–C12–C14	114.4(4)
F2–B–F3	108.6(6)	S3–C3–C1	114.5(4)	S5–C7–C9	114.9(4)	S11–C13–C11	116.3(4)
F2–B–F4	109.3(6)	S3–C3–C4	115.9(4)	C8–C7–C9	127.6(5)	S11–C13–C14	116.3(4)
F3–B–F4	110.5(6)	C1–C3–C4	129.6(5)	S6–C8–C7	116.1(4)	C11–C13–C14	127.4(5)
S2–S1–C1	98.5(2)	S4–C4–C2	113.9(4)	S6–C8–C10	115.2(4)	S12–C14–C12	115.5(4)
S1–S2–C2	99.8(2)	S4–C4–C3	117.2(4)	C7–C8–C10	128.6(5)	S12–C14–C13	116.7(4)
C3–S3–C5	95.8(2)	C2–C4–C3	128.9(5)	S7–C9–C7	113.8(4)	C12–C14–C13	127.8(5)
C4–S4–C5	95.2(2)	S3–C5–S4	114.5(3)	S8–C10–C8	113.3(4)	S11–C15–C15′	123.2(4)
C6–S5–C7	95.4(2)	S3–C5–C6	122.0(4)	S10–S9–C11	97.6(2)	S12–C15–C15′	121.5(4)
C6–S6–C8	96.4(2)	S4–C5–C6	123.4(4)	S9–S10–C12	98.4(2)	S11–C15–S12	115.1(3)
S8–S7–C9	99.0(2)	S5–C6–S6	114.3(3)	C13–S11–C15	96.0(2)	—	—
D1·Cu(SCN)$_2$							
S10–Cu1–N1	108.8(3)	C4–S4–C5	96.5(5)	C1–C3–C4	130.(1)	S6–C6–C5	121.5(9)
S10–Cu1–N1	96.3(3)	C6–S5–C7	95.7(5)	S4–C4–C2	114.6(8)	S5–C7–C8	117.7(8)
N1–Cu1–N2	154.9(5)	C6–S6–C8	95.5(5)	S4–C4–C3	116.4(8)	S5–C7–C9	116.0(8)
Cu1–N1–C11	177(1)	S8–S7–C9	97.7(4)	C2–C4–C3	128.1(1)	C8–C7–C9	126.(1)
Cu1–N2–C12	173(1)	S7–S8–C10	99.3(5)	S3–C5–S4	114.8(6)	S6–C8–C7	115.8(8)
Cu1–S10–C12	92.8(4)	S1–C1–C3	108.8(8)	S3–C5–C6	122.0(9)	S6–C8–C10	114.7(8)
S2–S1–C1	98.6(4)	S2–C2–C4	111.3(8)	S4–C5–C6	123.1(9)	C7–C8–C10	129(1)
S1–S2–C2	98.0(4)	S3–C3–C1	113.3(8)	S5–C6–C5	115.2(5)	S7–C9–C7	114.6(8)
C3–S3–C5	95.8(5)	S3–C3–C4	116.3(8)	S5–C6–C5	123.2(9)	S8–C10–C8	112.5(8)

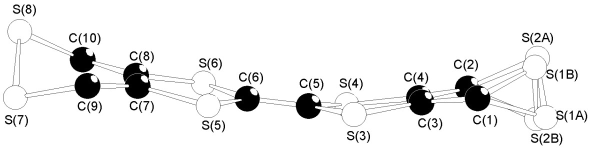


Fig. 3 $(\mathbf{D1})_3\cdot(ClO_4)_2$ salt: conformation of the **A**-molecule.

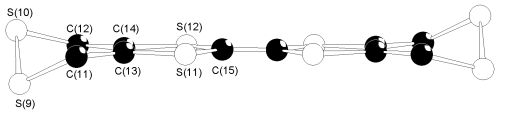


Fig. 4 $(\mathbf{D1})_3\cdot(ClO_4)_2$ salt: conformation of the **B**-molecule.

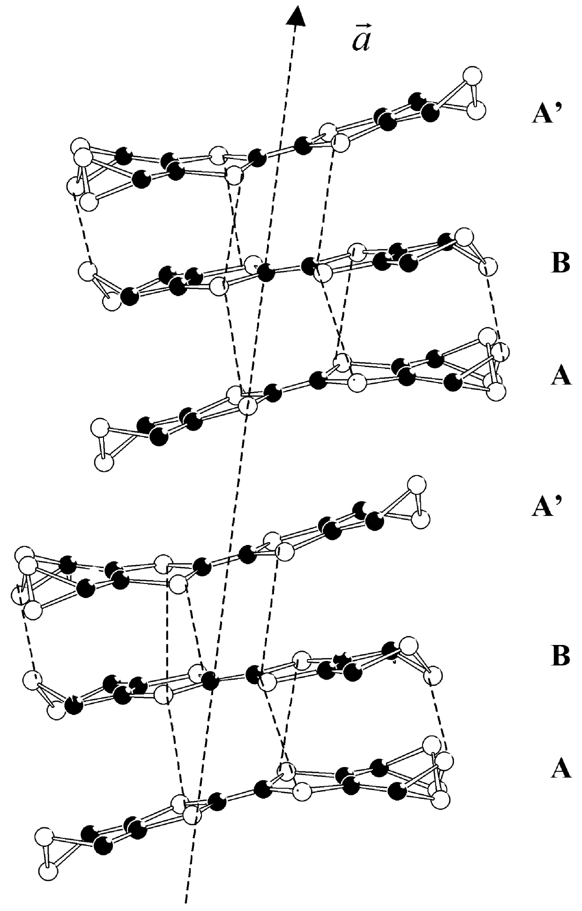
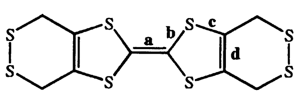


Fig. 5 $(\mathbf{D1})_3\cdot(ClO_4)_2$ salt: representation of trimerized donors stacking along the [100] direction.

Table 4 Calculation[a] of donor charge in $(\mathbf{D1})_3\cdot(ClO_4)_2$ (**1**) and in $(\mathbf{D1})_3\cdot(BF_4)_2$ (**2**). D_{2h} symmetry has been imposed



Salts	$(\mathbf{D1})_3\cdot(ClO_4)_2$	$(\mathbf{D1})_3\cdot(BF_4)_2$
$Q_A = Q_{A'}$	0.61	0.57
Q_B	0.93	0.97
$Q_B + 2Q_A$	2.15	2.09

[a] Using the relation[16] $Q_{calc} = 6.347 - 7.463\delta$ with $\delta = (b+c) - (a+d)$.

is assumed to be +0.5 (Table 4). Unlike γ-(BEDT-TTF)$_3\cdot(ClO_4)_2$, in which all donor molecules bear an average charge of +0.67, it seems that donors are not in a delocalized mixed valence state in these two salts **1** and **2**. In fact, we have supposed that **B** bears a charge of +1 and the second is probably located either on **A** or on **A′** with the same probability, *i.e.* 0.5, giving rise to a site localization phenomenon. Interplanar short distances (3.33 Å) and some short S···S contacts inside a trimer provide evidence of strong interactions between donors (Table 5). Probably due to steric hindrance, the molecular overlap is not very important. On the other hand, shorter distances between trimers are 3.745(2) and 3.698(2) Å for **1** and **2** respectively. Consequently, the molecular overlap also appears very weak, indicating that interactions between trimers are probably not important.

The general structural arrangement of BEDT-TTF salts, characterized by an alternance of donor and anion layers, is not observed in this case. In fact, the donor array is organized in trimerized stacks and the organic columns are oriented in the lattice in order to engage sulfur atoms of terminal bridges in van der Waals contacts. As was previously observed in **D3** salts, $\mathbf{D3}\cdot ClO_4$,[10] $\mathbf{D3}\cdot PF_6$[10] and $(\mathbf{D3})_2\cdot CuCl_4$,[17] molecules of **D1** of two neighbouring columns are perpendicular (Fig. 6). Thus, it appears that the salts prepared from this new π-donor **D1**, as was the case for **D3**, are characterized by an original association mode of the network, not usually observed for other TTF derivatives and probably related to the presence of the terminal disulfide bridges.

Many BEDT-TTF based kappa phase salts were derived from polymeric anions and led to the most exciting conducting and superconducting salts in the TTF family. Considering the

Table 5 Intermolecular intratrimer contacts in $(\mathbf{D1})_3\cdot(ClO_4)_2$ and $(\mathbf{D1})_3\cdot(BF_4)_2$

Bonds	$(\mathbf{D1})_3\cdot(ClO_4)_2$/Å	$(\mathbf{D1})_3\cdot(BF_4)_2$/Å
$S_{1a}{}^{i}–S_9{}^{i} = S_{1a}{}^{ii}–S_9{}^{ii}$	3.226(2)	3.31(2)
$S_5{}^{i}–S_{11}{}^{i} = S_5{}^{ii}–S_{11}{}^{ii}$	3.555(1)	3.545(2)
$S_4{}^{i}–S_{11}{}^{i} = S_4{}^{ii}–S_{11}{}^{ii}$	3.615(1)	3.635(2)
$S_3{}^{i}–S_{12}{}^{i} = S_3{}^{ii}–S_{12}{}^{ii}$	3.648(1)	3.647(2)

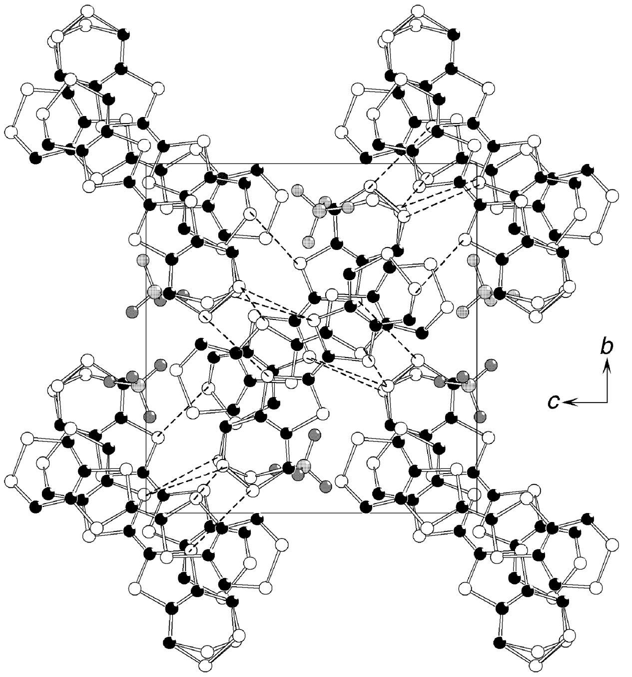


Fig. 6 Projection onto the (*bc*) plane of the crystal structure of $(\mathbf{D1})_3\cdot(ClO_4)_2$. S···S contacts smaller than the sum of van der Waals radii are represented by dashed lines.

structural similarities of **D1** with the BEDT-TTF skeleton, many attempts were also made to associate this donor with a polymeric anion and we succeeded in the preparation of a radical cation salt, associating **D1** with the $Cu(SCN)_2^-$ anion. The corresponding salt **3** presents a [1 : 1] stoichiometry and crystallizes in the $P2_1/n$ space group.

The unit cell contains one independent donor molecule, which is located in a general position. Its TTF core is roughly planar and both disulfide bridges present a twisted conformation (Fig. 7). A position disorder is displayed also for one of the two peripheral S–S groups and the corresponding sulfur atoms are found together in two positions with the refined occupation ratio of 75 : 25 for S_{1a}/S_{1b} and S_{2a}/S_{2b} respectively. Nevertheless, in contrast to $(BEDT\text{-}TTF)_2{\cdot}Cu(SCN)_2$,[6] kappa type packing of donor molecules is not observed in salt **3**. In this case, **D1** molecules form regular stacking parallel to the *a* axis (Fig. 8). Moreover, some S···S contacts between donors are shown inside organic columns and successive molecules present a bond–cycle type overlap. According to the [1 : 1] stoichiometry of this salt and after averaging in the D_{2h} symmetry, bond lengths of the donor are in good agreement with those of the corresponding BEDT-TTF radical cation.[18]

The anion array is organized in infinite zig-zag chains of $Cu(SCN)_2^-$ along the *a* axis. The anion is also coordinated by the copper atom as a pendant with the terminal sulfur atom S(10), the distance Cu(1)–S(10) being 2.576(4) Å (Fig. 9).

Compared to $(BEDT\text{-}TTF)_2{\cdot}Cu(SCN)_2$, the salt **3** presents a very different crystallographic organization. Thus, the molecular arrangement of **3** consists of an alternation along the [010] and [001] directions of infinite donor stackings and chains of polymeric anions (Fig. 10). This particular organization could result from the presence of disulfide bridges of donors. Nevertheless, the influence of terminal sulfur atoms on the network is very discrete and the arrangement of organic arrays, previously noted for other **D1** or **D3** salts, is not displayed in this salt.

Along the *b*-axis, some S···S contacts between donor and anion arrays are observed involving sulfur atoms of the TTF core but not sulfur atoms of disulfide bridges (Fig. 11). On the other hand, along the $(a+c)$ direction, as shown in Fig. 12, the spatial arrangement of donors is appropriate for considering intermolecular contacts between terminal sulfur atoms of **D1** and sulfur atoms of $Cu(SCN)_2^-$. However, only the S(1a)–

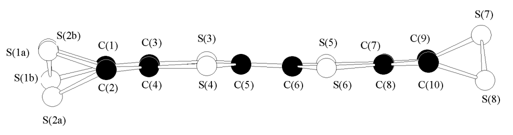


Fig. 7 Conformation of the π-donor in $\mathbf{D1}{\cdot}Cu(SCN)_2$.

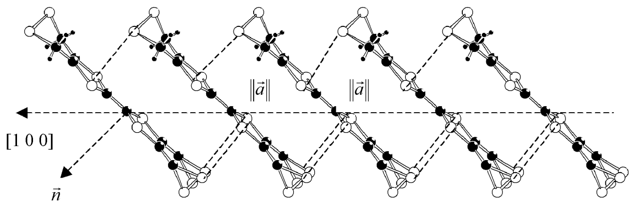


Fig. 8 Donors stacking in $\mathbf{D1}{\cdot}Cu(SCN)_2$.

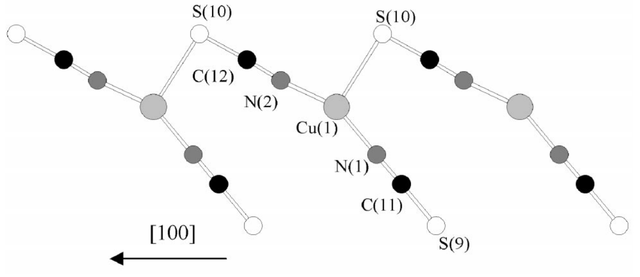


Fig. 9 Linear organization of the $Cu(SCN)_2^-$ anion.

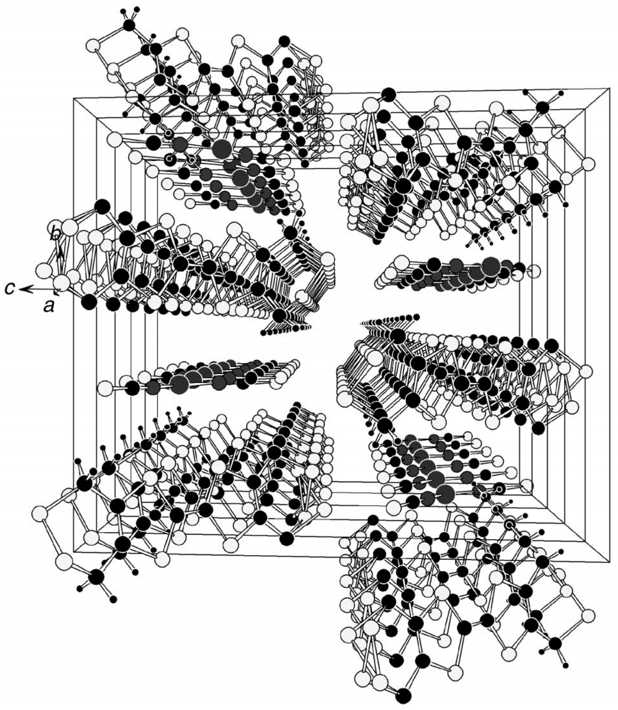


Fig. 10 Structural organization of $\mathbf{D1}{\cdot}Cu(SCN)_2$.

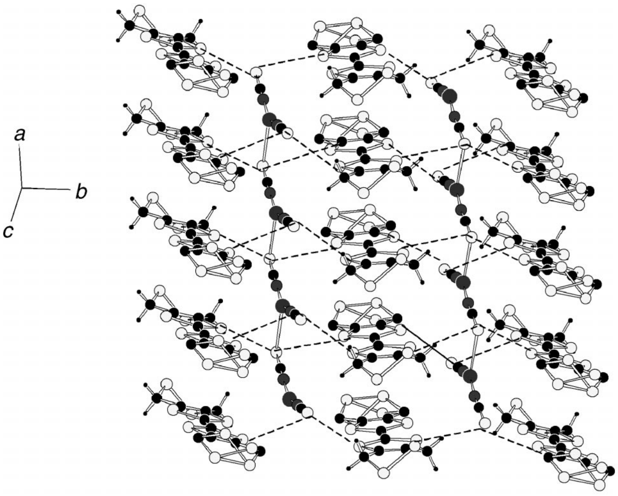


Fig. 11 S···S contacts between organic and anion arrays in [010] direction (represented by dashed lines).

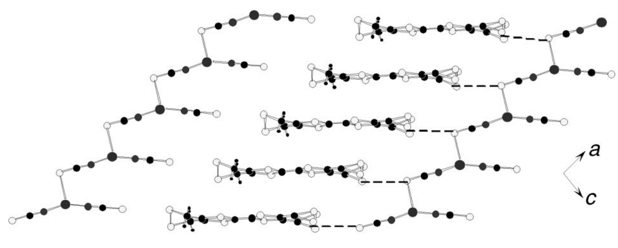


Fig. 12 Projection onto the (*ac*) plane of the crystal structure of $\mathbf{D1}{\cdot}Cu(SCN)_2$. S···S distances shorter than twice the van der Waals radius of the S-atom, in the $(a+c)$ direction, are represented by dashed lines.

S(10) distance (d S(1a)–S(10) = 3.648(5) Å) is shorter than twice the van der Waals radius of the S-atom (1.85 Å).

The influence of the shape and the size of anions on the crystal structures of BEDT-TTF salts has been widely studied. It is well known that small tetrahedral anions, such as ClO_4^- and BF_4^-, generally do not influence the structural arrangement of the radical cation salts of BEDT-TTF, whereas polymeric anions always lead to kappa phase salts. In this latter case, anionic arrays play a decisive role in the crystallographic network and the physical properties of the corresponding salts. By analogy, the differences in structural organization between **3** and the two other isostructural salts **1** and **2** could be attributed to polymeric anions. Probably because of the presence of $Cu(SCN)_2^-$ chains, located between organic columns, donors could not adopt the special arrangement previously observed for other **D1** salts.

A few physical properties have been investigated for these radical-cation salts. The d.c. electrical conductivity and EPR experiments have been carried out on single crystals, IR absorption spectra on powder samples. These last experiments are usually powerful in characterizing mixed valence systems. In charge transfer salts, two significant features are usually recognized:[19] i) the charge transfer bands characteristic of a fully ionized salt (band B) or of a mixed valence state (band A in Torrance's classification); ii) the presence of a normally IR inactive mode, revealed by the electron–molecular vibration coupling and called vibronic modes.

Isostructural [3 : 2] salts **1** and **2** exhibit very similar properties; these are semiconductors with an absolute room temperature electrical conductivity of about 10^{-2} S cm^{-1} and an associated activation energy $\Delta E \cong 0.12$ eV.

A weak and narrow EPR line is detected for a g-factor value around 2.005. The intensity of this room temperature signal decreases quickly when the crystal is cooled down indicating the probable presence of a classical excited triplet state at room temperature.[20] The recorded absorption spectra are in agreement with this behavior and the presence of two intense charge transfer bands located respectively at 11 000 and 16 000 cm^{-1}. The less energetic band is attributed to a 'B band' type, characteristic of a doubly occupied site, which is associated with both an intra- and an inter-trimer charge excitation.[21] Besides, in the IR range, a vibronic a_g mode detected at 1325 cm^{-1} is due to the central stretching vibration of the TTF type molecule as in similar compounds based on TMTTF or BEDT-TTF salts.[19]

As evidenced by d.c. conductivity measurements the [1 : 1] salt **3** is also a semiconductor ($\sigma = 10^{-4}$ S cm^{-1}) with an energy gap $\Delta E = 0.22$ eV and this result is classical for such a valence molecular conductor with one privileged stacking direction. In this narrow electronic band, for systems in which electronic repulsions compete with Coulombic repulsions, a metal–insulator transition exists. When a coulombic intrasite term (U) is about the same value or larger than the electronic bandwidth, a Mott–Hubbard gap is present.[22] This is the case for this salt for which the stacking distance is rather large ($d = 3.7$ Å) indicating a small transfer integral and a narrow electronic band. The EPR temperature dependence allows us to deepen this behavior. Indeed, by integration of the EPR signal ($\Delta H = 6.6$ G in the a direction), we demonstrate the spin susceptibility temperature dependence (Fig. 13). A strong decrease is detected below 200 K indicating the occurrence of a phase transition; for the low temperature phase, the spin susceptibility is almost zero because of the opening of a gap at the Fermi level. Similar behavior has already been observed in other TTF-type salts.[23] This is characteristic of some stacking instability which gives rise to some kind of spin-Peierls like transition. This behavior could be completed later by some more detailed low temperature studies.

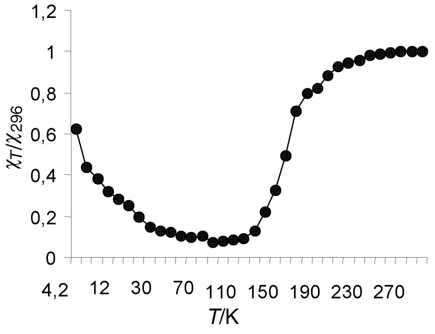


Fig. 13 The spin susceptibility temperature dependence of the salt **D1**·$Cu(SCN)_2$.

In complement to these studies, the room temperature absorption spectrum has been recorded: it shows a very intense electronic band around 13 000 cm^{-1}, which is attributed to a B band. This result confirms the presence of large Coulomb interactions. Indeed, in a first approximation, the intrasite Coulomb term is given by the position of the charge transfer 'B-band', *i.e.* around 1 eV. We are therefore in the presence of a Mott–Hubbard insulator as already described for other 1 : 1 salts.[24]

Conclusions

In search of new charge transfer salts, we have shown that this symmetrical isomer of BEDT-TTF is a promising π-donor. Its molecular symmetry can give rise to a well defined crystal structure without any stacking disorder as observed for non centrosymmetric molecules.

Indeed, two types of structural organizations have been evidenced, the most interesting one resulting from the association of **D1** with the polymeric anion $Cu(SCN)_2^-$. The corresponding salt gives rise to a regular stacking of donors stabilized by a gain of covalent energy. In this [1 : 1] radical cation salt, there is a competition between the steric influence and the electronic effects. On the one hand, the **D1** molecule presents non-planar outer rings which induce some hindrance to the stacking effect as in BEDT-TTF salts. On the other hand, the electronic charge distribution is rather similar to the one encountered in TTF radical cations as evidenced by preliminary extended Hückel calculations.[19] It appears that the presence of methylene groups in **D1** gives a weak electronic density on the outer sulfur atoms. This is a delicate balance between two driving forces which are at the origin of the supposed structural instability observed below 200 K.

Indeed, this symmetrical isomer of BEDT-TTF appears to behave differently but a rich polymorphism can arise as evidenced here with two examples. Taking advantage of the wide variety of possible anions, other cation radical salts presenting 2D and even 3D structural organizations should be prepared in the future from this new donor.

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