

Communication

Enantiopure Radical Cation Salt Based on Tetramethyl-Bis(ethylenedithio)-Tetrathiafulvalene and Hexanuclear Rhenium Cluster

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Received: 8 December 2015; Accepted: 31 December 2015; Published: 5 January 2016
 Academic Editor: Helmut Cölfen

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Abstract: Electrocrystallization of the (*S,S,S,S*) enantiomer of tetramethyl-bis(ethylenedithio)-tetrathiafulvalene donor **1** in the presence of the dianionic hexanuclear rhenium (III) cluster $[\text{Re}_6\text{S}_6\text{Cl}_8]^{2-}$ affords a crystalline radical cation salt formulated as $[(S)\text{-1}]_2 \cdot \text{Re}_6\text{S}_6\text{Cl}_8$, in which the methyl substituents of the donors adopt an unprecedented all-axial conformation. A complex set of intermolecular TTF...TTF and cluster...TTF interactions sustain an original tridimensional architecture.

Keywords: chirality; crystal structure; tetrathiafulvalenes; rhenium clusters

1. Introduction

Tetramethyl-bis(ethylenedithio)-tetrathiafulvalene **1** (TM-BEDT-TTF) has in principle several possible stereoisomers, yet the only ones which have been properly described are the (*S,S,S,S*) (Figure 1) and (*R,R,R,R*) enantiomers [1–3], henceforth abbreviated (*S*)-**1** and (*R*)-**1**, respectively.

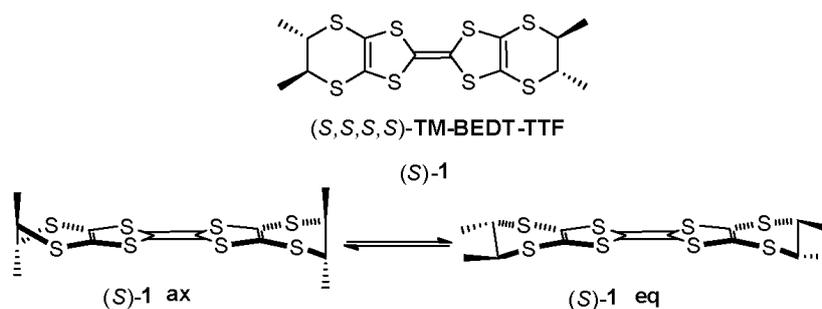


Figure 1. (*S*) enantiomer of tetramethyl-bis(ethylenedithio)-tetrathiafulvalene (TM-BEDT-TTF) **1** with its axial and equatorial conformers.

(*S*)-**1** represents the first example of a chiral TTF derivative [4], and its synthesis allowed the preparation of several TTF based chiral conducting radical cation salts by electrocrystallization [1,5], including the ferromagnetic metal $[\text{TM-BEDT-TTF}]_x[\text{MnCr}(\text{ox})_3]$ (ox = oxalate) [6] or the paramagnetic semiconductor $[\text{TM-BEDT-TTF}]_3(\text{PPh}_4)[\text{K}^{\text{I}}\text{Fe}^{\text{III}}(\text{Cl}_2\text{An})_3]$ (Cl_2An = dichloroanilate) [7]. The latter was also described as (*R*) enantiomer and racemate. The interest in chiral TTF precursors and derived materials [8] is mainly related to the combination of chirality with conducting properties through the electrical magneto-chiral anisotropy effect [9], recently described for enantiopure crystalline metallic salts of the dimethyl-ethylenedithio-tetrathiafulvalene (DM-EDT-TTF) donor [10]. Nevertheless, differences in conducting properties between the enantiopure and racemic counterparts were also

observed as a consequence of the structural disorder in TTF-oxazoline [11,12] based conductors [13,14], or the different packings in DM-EDT-TTF salts [15]. Other interests of chiral TTFs are related to the modulation of the chiroptical properties [16,17] or the preparation of electroactive helical fibers [18–21]. Regarding the enantiopure TM-BEDT-TTF donor **1** an important issue is the conformation adopted by the methyl substituents of the dithiin rings, as this strongly influences the packing and intermolecular contacts between the donors, and, consequently, the transport properties. It has been shown by theoretical calculations that in the gas phase the all-axial conformation is slightly more stable than the all-equatorial one, both being in equilibrium in solution [1] (Figure 1). While neutral **1** has been crystallized as both all-ax [2] and all-eq [1] conformers, its radical cation salts show in most cases all-eq conformation [1,2,5,6], very likely as a means to maximize the packing. The same trend was also observed for the closely related donors DM-EDT-TTF [10,15] and DM-BEDT-TTF [22–24]. Only in very few cases mixed (ax,ax,eq,eq) conformations have been found in the solid state structures of **1** for charge transfer complexes with TCNQ [2], radical cation salts with the iron(III) chloroanilate complex anion [7], and a cycloadduct with tetrachlorocatecholate [25], while the all-ax conformation has been never observed. We describe herein the first crystalline enantiopure radical cation salt of TM-BEDT-TTF in which the oxidized donor adopts a (ax,ax,ax,ax) conformation. The counterion is the dianionic hexanuclear rhenium cluster $[\text{Re}_6\text{S}_6\text{Cl}_8]^{2-}$ [26] which provided several series of TTF based radical cation salts [27–30], but has never been used with a chiral donor to the best of our knowledge.

2. Results and Discussion

Electrocrystallization of a (*S*)-**1** [1] solution in acetonitrile at 0.5 μA current intensity, in the presence of $(\text{Bu}_4\text{N})_2\text{Re}_6\text{S}_6\text{Cl}_8$ [28] as supporting electrolyte, afforded small black prismatic crystals of appropriate quality for single crystal X-ray diffraction analysis. The resulting radical cation salt, formulated as $[(\text{S})\text{-1}]_2 \cdot \text{Re}_6\text{S}_6\text{Cl}_8$, crystallizes in the non-centrosymmetric triclinic space group P1 and contains two independent donor molecules and one hexanuclear cluster in the asymmetric unit (Figure 2). As expected, the cluster contains six Re atoms in an octahedral arrangement capped by six $\mu^3\text{-S}$ and two $\mu^3\text{-Cl}$ atoms forming a cube, with Re-S_μ and Re-Cl_μ distances in the normal range [28]. The coordination sphere of each Re ion is completed by an apical Cl ligand, with Re-Cl_{ap} distances ranging between 2.362 and 2.383 Å.

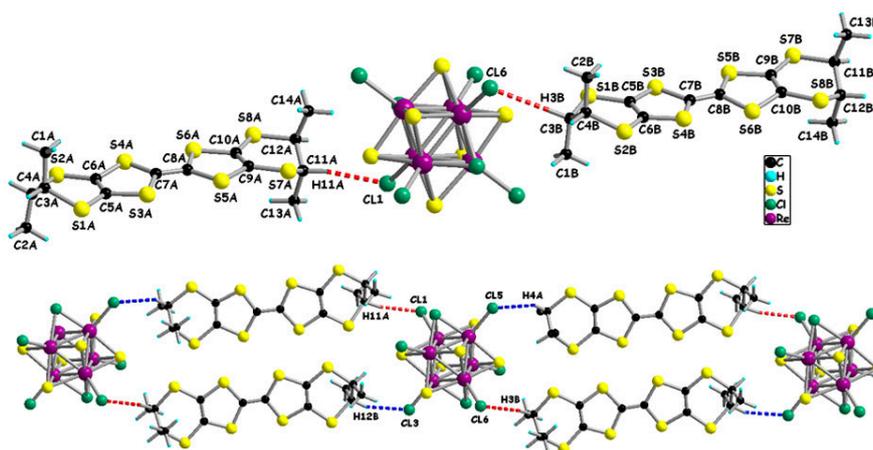


Figure 2. Two independent donor molecules and one rhenium cluster in the structure of $[(\text{S})\text{-1}]_2 \cdot \text{Re}_6\text{S}_6\text{Cl}_8$ together with a partial numbering scheme (top); detail of the hybrid organic-inorganic layer with an emphasis on the shorter ($\text{Cl1} \cdots \text{H11A}$ 2.64 Å; $\text{Cl6} \cdots \text{H3B}$ 2.67 Å; red dotted lines) and longer ($\text{Cl3} \cdots \text{H12B}$ 2.82 Å; $\text{Cl5} \cdots \text{H4A}$ 2.99 Å; blue dotted lines) intermolecular $\text{Cl} \cdots \text{H}$ hydrogen bonding.

Both donors are oxidized into radical cations, as attested by the central $\text{C}=\text{C}$ and C-S bond distances, which show lengthening of $\text{C}=\text{C}$ and shortening of C-S bonds when compared to the neutral

precursor. The completely planar shape of the TTF unit is also in agreement with an oxidation state +1. Interestingly, a complex set of intermolecular interactions establish between the cluster units and the donors which envelop the former. First, hydrogen bonding interactions are observed between four apical Cl ligands and methine H atoms ranging between 2.64 and 2.99 Å (Figure 2).

Then, the clusters further interact with the surrounding donors (Figure 3) through $\text{Cl}_{\text{ap}} \cdots \text{S}$ contacts (3.38–3.72 Å, orange dotted lines) as well as $\text{S}_{\mu} \cdots \text{S}$ contacts (3.44–3.58 Å, green dotted lines), while the donors interact laterally between them through two sets of shorter (3.21–3.30 Å, red dotted lines) and longer (3.59–3.67 Å, blue dotted lines) $\text{S} \cdots \text{S}$ contacts.

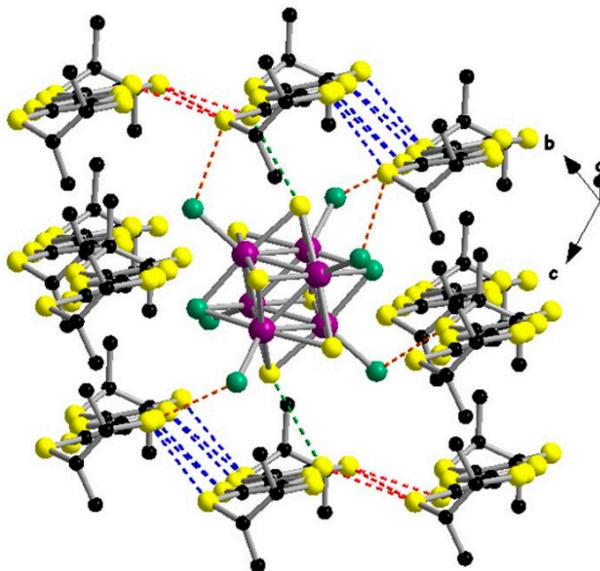


Figure 3. Re cluster encapsulated in a “cage” of donors. Short intermolecular contacts: $\text{S}_{\text{TTF}} \cdots \text{S}_{\text{TTF}}$ 3.21–3.35 Å (red) and 3.59–3.67 Å (blue), $\text{S}_{\text{TTF}} \cdots \text{S}_{\text{cluster}}$ 3.44–3.58 Å (green) and $\text{S}_{\text{TTF}} \cdots \text{Cl}$ 3.38–3.72 Å (orange).

All these intermolecular interactions lead to a three dimensional structure in which layers of donors developing in the *ac* plane are interconnected by cluster units (Figure 4).

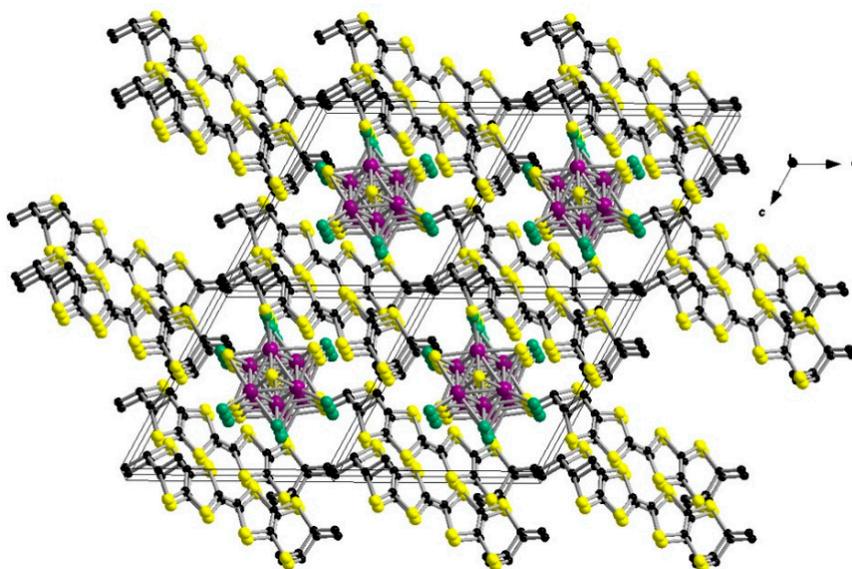


Figure 4. Packing diagram of $[(\text{S}-1)_2] \cdot \text{Re}_6\text{S}_6\text{Cl}_8$ in the *ac* plane.

The most peculiar feature of this structure lies, however, in the conformation of the dithiine rings in both donors. Contrary to what was observed so far in the literature (see above), here the donors adopt all-ax conformations which certainly hamper closer axial S...S intermolecular contacts. The methine carbon atoms show opposite displacements with respect to the planar S–C=C–S motif of the dithiine rings (Table 1), thus leading to sofa-type conformations of the six membered rings [3].

Table 1. Orientations of methyl groups and displacements of methine carbon atoms with respect to the mean plane formed by the other four atoms of the six-membered rings in [(S)-1]₂·Re₆S₆Cl₈ and (R)-1.

Compound	Orientation of Methyl Group	Displacements of CH Atoms/Å
(R)-1-ax [2]	axial	+0.563, −0.331
	axial	+0.285, −0.593
[(S)-1] ₂ ·Re ₆ S ₆ Cl ₈	axial (A)	+0.045, −0.788
	axial (A)	+0.708, −0.118
	axial (B)	+0.109, −0.715
	axial (B)	+0.542, −0.320

One can hypothesize that the occurrence of this unusual all-ax conformation which only allows lateral S...S intermolecular interactions, and not the classical axial σ -type interactions between open-shell species, is strongly favoured by the peculiar nature of the anion which can engage in hydrogen, halogen and chalcogen bonding, as detailed above.

3. Experimental Section

Five milligrams (S)-1 [1], 25 mg (Bu₄N)₂Re₆S₆Cl₈ [28] and 12 mL acetonitrile were used in the electrocrystallization experiment which was conducted at 0.5 μ A at room temperature. Black prismatic crystals were collected in the anodic compartment of the cell after several days. CCDC 1444636 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>.

X-ray structure determination

X-ray diffraction measurements were performed on a Bruker Kappa CCD diffractometer, operating with a MoK α ($\lambda = 0.71073$ Å) X-ray tube with a graphite monochromator. The structure were solved (SHELXS-97) by direct methods and refined (SHELXL-97) by full matrix least-square procedures on F² [31]. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at calculated positions (riding model), included in structure factor calculations but not refined (see Table 2).

Table 2. Crystal Data and Structure Refinement for compound [(S)-1]₂·Re₆S₆Cl₈.

Compound	[(S)-1] ₂ ·Re ₆ S ₆ Cl ₈
empirical formula	C ₂₈ H ₃₂ Cl ₈ Re ₆ S ₂₂
fw	2474.66
T (K)	293(2)
wavelength (Å)	0.71073
crystal system	triclinic
space group	P1

Table 2. Cont.

unit cell dimens	
<i>a</i> (Å)	11.9422(4)
<i>b</i> (Å)	12.2034(5)
<i>c</i> (Å)	12.3025(5)
α (deg)	108.613(4)
β (deg)	110.882(4)
γ (deg)	105.463(3)
<i>V</i> (Å ³)	1433.57(10)
<i>Z</i>	1
<i>D</i> _c (g·cm ^{−3})	2.866
abs coeff (mm ^{−1})	13.817
θ range for data collection (deg)	3.5–34.15
reflns collected	44218
indep reflns	14,253
completeness (%)	99.5
data/restraints/param	22683/4/577
structure Flack parameter	−0.006(8)
GOF on <i>F</i> ²	1.011
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	R1 = 0.039, wR2 = 0.051
<i>R</i> indices (all data)	R1 = 0.093, wR2 = 0.062
largest diff. peak and hole (e·Å ^{−3})	1.071 and −1.207

4. Conclusions

The first example of a crystalline radical cation salt of the enantiopure donor tetramethyl-bis(ethylenedithio)-tetrathiafulvalene (TM-BEDT-TTF) in which the methyl substituents adopt the all-axial arrangement is described. The occurrence of such unprecedented situation is very likely driven by the peculiar nature of the counterion, the hexanuclear rhenium cluster [Re₆S₆Cl₈]^{2−}, which engages in intermolecular hydrogen, halogen and chalcogen bonding interactions with the oxidized donors. This result demonstrates that the association of chiral methylated BEDT-TTF derivatives with chalcogenated rhenium clusters provides original solid state architectures.

Acknowledgments: This work was supported by the National Agency for Research (ANR Inter, ANR-12-IS07-0004-04, CREMM Project), the CNRS and the University of Angers.

Author Contributions: Flavia Pop carried out the synthesis and X-ray characterization of the compound. Patrick Batail provided the rhenium cluster and discussed the project with Narcis Avarvari and Flavia Pop. Narcis Avarvari supervised the project and wrote the manuscript. The three authors discussed the results.

Conflicts of Interest: The authors declare no conflict of interest.

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