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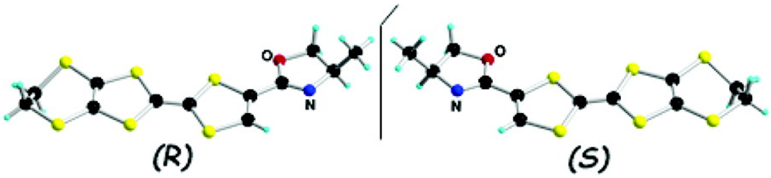

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Chiral Molecular Metals: Syntheses, Structures, and Properties of the AsF_6^- Salts of Racemic (±)-, (*R*)-, and (*S*)-Tetrathiafulvalene−Oxazoline Derivatives

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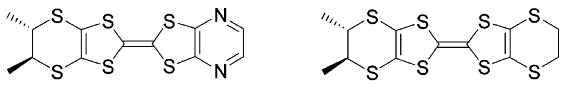
Within the extended series of organic metals and superconductors based on tetrathiafulvalene (TTF) and derivatives, the introduction of chirality offers an invaluable opportunity to evaluate the role of *disorder* on the conductive properties since radical cation salts of enantiopure donors are expected to suffer less from structural disorder than those of racemates, where the crystal structure may tolerate the enantiomers exchanging places.[1] Indeed, disorder in molecular conductors has been shown to strongly influence the electronic conductivity or the superconducting transition temperature, based on the effect of random electrostatic potentials on the carriers in the organic stacks. Chirality in molecular TTF-based conductors can be envisioned through the introduction of at least one chiral element, either on the donor molecule or on the counterion. Following the first report by Dunitz and Wallis of an enantiopure chiral TTF derivative,[2] many other neutral TTF and BEDT−TTF derivatives have been described,[1] albeit very few examples of conducting salts were reported.[3] Note, for example, the chiral and rigid donor molecules of C_2 symmetry incorporating the (*S*,*S*)-dimethylethylenedithio moiety (Chart 1), such as P-(*S*,*S*)-(DMEDT)−TTF in its $AuBr_2^-$ salt,[4] (*S*,*S*)-DMBEDT−TTF in its ClO_4^- salt[5], or the BEDT−TTF salt with the antimony (*L*)-tartrate, $[Sb_2(L\text{-tart})_2]^{2-}$ as chiral counterion.[6]

In any case but one, involving semiconducting PF_6^- salts of (*S*,*S*)-DMBEDT−TTF and its racemic version,[7] only one single isomer was described, preventing useful comparisons between both enantiomers and the racemic compound. Herein, we describe and compare the structural and electronic properties of a first complete series of mixed-valence metallic salts based on chiral tetrathiafulvalenes bearing an (*R*)-, (*S*)-, or racemic (±)-methyl−oxazoline heterocycle.

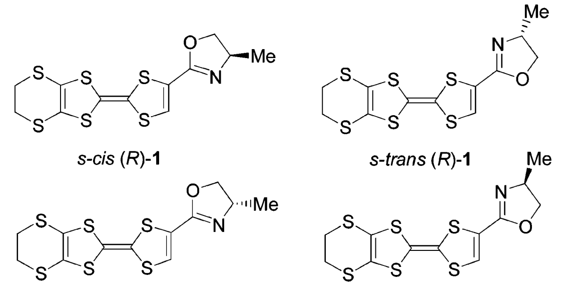
The syntheses of (*R*)-**1**, (*S*)-**1**, and (±)-**1** as intermediates in the preparation of the corresponding phosphino−oxazoline (PHOX) ligands have been recently described.[8] The chirality of the (*R*)-**1** and (*S*)-**1** donor molecules is perfectly controlled and imposed by the chirality of the amino alcohols used as reagents in their synthesis. Note also that contrary to the rigid C_2 symmetry molecules mentioned above, (*R*)-**1**, (*S*)-**1**, and (±)-**1** can adopt two planar *s-cis* and *s-trans* conformations. Electrocrystallization of either (*R*)-**1**, (*S*)-**1**, or racemic (±)-**1** in CH_2Cl_2 solutions containing $(n\text{-Bu})_4NAsF_6$ as electrolyte afforded black needles of the 2:1 salts, formulated as $[(R)\text{-}\mathbf{1}]_2AsF_6$, $[(S)\text{-}\mathbf{1}]_2AsF_6$, and $[(\pm)\text{-}\mathbf{1}]_2AsF_6$, respectively.

Chart 1



P-(*S*,*S*)-DMEDT-TTF **(*S*,*S*)-DMBEDT-TTF**

Chart 2



s-cis (*R*)-**1**
s-trans (*R*)-**1**
s-cis (*S*)-**1**
s-trans (*S*)-**1**

The racemic $[(\pm)\text{-}\mathbf{1}]_2AsF_6$ salt crystallizes in the triclinic system, space group $P\bar{1}$, with the AsF_6^- anion on the inversion center, one donor molecule in general position in the unit cell, and the oxazoline ring almost coplanar with the TTF core but *disordered* on two positions, corresponding to both *R* and *S* enantiomers on the same site, one as *s-cis* and the other as *s-trans* conformers (Figure 1).

Enantiopure $[(R)\text{-}\mathbf{1}]_2AsF_6$ and $[(S)\text{-}\mathbf{1}]_2AsF_6$ are isostructural and crystallize in the chiral space group *P*1 with one anion and two crystallographically independent donor molecules with *s-cis* and *s-trans* conformations, respectively, which also differ by the disorder of the ethylene moiety observed only within the *s-trans* conformer (Figure 2).

In the solid state, the racemic and enantiopure salts adopt closely related layered structures, with stacks of donor molecules along *b*, interacting side-by-side along *a* (Figure 3). Within each stack, the molecules alternate in a head-to-tail manner, with bond-over-ring overlaps. The donor slabs thus adopt the so-called β-type structural motif.[9]

Single crystal conductivity measurements have been performed on all three salts, which exhibit a metallic character at room temperature (Figure 4) with $\sigma_{RT} \approx 100$ S cm^{-1} in the pure enantiomers, while the room temperature conductivity of the (±) salt is 1 order of magnitude lower ($\sigma_{RT} \approx 10$ S cm^{-1}). For all three salts, the resistivity shows a broad minimum around 230 K followed by a localized regime.

Tight-binding calculations for the donor layers of the enantiopure $[(R)\text{-}\mathbf{1}]_2AsF_6$ salt led to the Fermi surface of Figure 5. Those for $[(S)\text{-}\mathbf{1}]_2AsF_6$ and the racemic $[(\pm)\text{-}\mathbf{1}]_2AsF_6$ are essentially identical. Although the layers are of β-type, so that a closed Fermi surface could have been expected,[10] these salts are really quasi one-dimensional (Q1D) metals with the highest conductivity along the *b* stacking axis. The absolute values of the intermolecular interaction energies (β)[9] for $[(R)\text{-}\mathbf{1}]_2AsF_6$ are 0.529 and 0.337 eV for the

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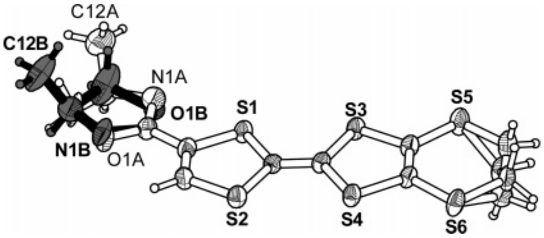

Figure 1. ORTEP view (thermal ellipsoids at 50% probability level) of the donor molecule in [(±)-**1**]$_2$AsF$_6$.

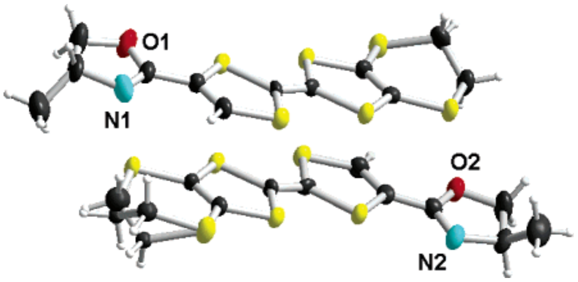

Figure 2. View (thermal ellipsoids at 50% probability level) of the two crystallographically independent (*R*)-**1** donor molecules in [(*R*)-**1**]$_2$AsF$_6$ with *s-cis* (top) and *s-trans* (bottom) conformations.

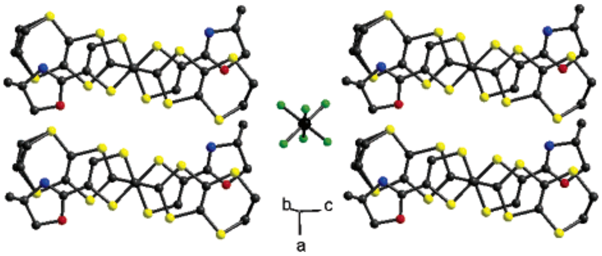

Figure 3. Projection view of the solid-state organization of [(*R*)-**1**]$_2$AsF$_6$.

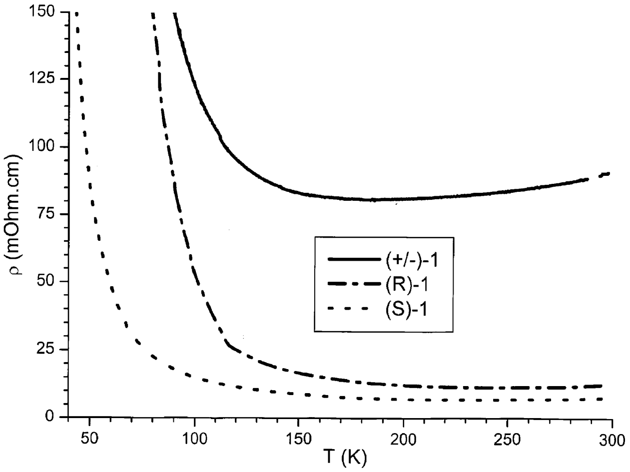

Figure 4. Temperature dependence of the resistivity for [(*R*)-**1**]$_2$AsF$_6$, [(*S*)-**1**]$_2$AsF$_6$, and [(±)-**1**]$_2$AsF$_6$. Breaks observed around 115 K in the curves for [(*R*)-**1**]$_2$AsF$_6$ and [(±)-**1**]$_2$AsF$_6$ are due to microcracks during the measurements.

intrastack interactions and 0.086−0.034 eV for the interstack ones. Those for a typical β-phase-like β-(BEDT−TTF)$_2$I$_3$[9] are 0.439−0.287 eV and 0.164−0.024 eV, respectively. Thus for the present salts, the intrastack interactions are stronger, and the interstack interactions are weaker, both facts favoring the Q1D behavior.

The Fermi surface (Figure 5) consists of a pair of slightly warped and almost perfectly nested lines ($q_{\text{nesting}} = -(1/8)a^* + (1/2)b^*$). This suggests that a charge density wave (CDW) structural modulation could destroy the Fermi surface and be at the origin of the change in the conductivity regime. However, the smoothness of the resistivity increase clearly suggests that this change cannot be associated with a phase transition but is rather due to a 1D Mott localization of the carriers, as observed in (TMTTF)$_2$X salts.[11] The localization occurring here, in which one hole would rest in every dimer, may be also favored by the different sources of disorder in the structure.[12] Indeed, the conductivity of the racemic salt, with the additional source of disorder due to the presence of both *R* and *S* enantiomers on the same site, is approximately 1 order of magnitude smaller than the conductivity of the enantiopure salts, emphasizing the paramount role played by different disorder sources in the conductivity behavior of such cation radical salts.

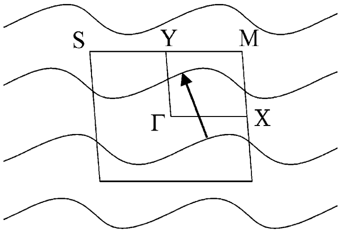

Figure 5. Calculated Fermi surface for the donor layers of [(*R*)-**1**]$_2$AsF$_6$, where $\Gamma = (0, 0)$, $X = (a^*/2, 0)$, $Y = (0, b^*/2)$, $M = (a^*/2, b^*/2)$, and $S = (-a^*/2, b^*/2)$. The black arrow refers to the nesting vector, q_{nesting}, discussed in the text.

In summary, we have synthesized and characterized a first *complete* series of racemic and enantiopure conducting salts with *metallic* character, based here on chiral oxazolines. Despite strongly related crystalline and electronic structures, the higher conductivity of pure enantiomers, lacking the disorder inherent to racemic mixture, demonstrates that this chiral donor route is very promising for the elaboration of other metallic salts, taking into account that the substituent on the oxazoline ring or the nature of the counterion can be easily modified.

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Supporting Information Available: Crystallographic data of [(±)-**1**]$_2$AsF$_6$, [(*R*)-**1**]$_2$AsF$_6$, and [(*S*)-**1**]$_2$AsF$_6$ (CCDC 254823−254825) and experimental (electrocrystallization and conductivity measurements) and computational details (CIF, PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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