Order Versus Disorder in Chiral Tetrathiafulvalene-Oxazoline Radical-Cation Salts: Structural and Theoretical Investigations and Physical Properties

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Résumé en anglais	Electrocrystallization experiments with the chiral ethylenedithio-tetrathiafulvalene-methyl-oxazoline (EDT-TTF-OX) donors (R)-, (S)-, and (rac)-1 have provided two series of mixed-valence salts with the PF6− and [Au(CN)2]− anions. Within each series the cell parameters are the same for the three R, S, and rac compounds, except for the space group, which is centrosymmetric triclinic P1 for the racemic forms and noncentrosymmetric P1 for the enantiopure salts. In the racemic salt [(rac)-1]2PF6 the two enantiomers crystallize disordered on the same crystallographic site with a site occupational factor of 0.6:0.4, whereas this type of disorder is not possible in the enantiopure salts. Both s-cis and s-trans conformations, when taking into account the mutual orientation of the TTF and oxazoline moieties, are present in this first series. In sharp contrast, in the series of salts [1]2[Au(CN)2], only the s-trans conformation is observed with no structural disorder. Theoretical calculations at the DFT level of theory revealed a very small energy difference between the two stable planar s-cis and s-trans conformations, which are both energy minima in either neutral or oxidized states. Single-crystal conductivity measurements showed metallic-like behavior for all the salts down to 220–250 K with a smooth increase in resistivity at lower temperatures. The conductivity at room temperature is 5 S cm−1 for [(rac)-1]2PF6, in which disorder was observed, whereas for [(R)-1]2PF6 and [(S)-1]2PF6 the average value is around 100 S cm−1. In the second series of salts the conductivity at room temperature is 125–130 S cm−1 for [(rac)-1]2[Au(CN)2] and [(R)-1]2[Au(CN)2]. Extended Hückel band structure calculations revealed identical features for the three salts of the [1]2[Au(CN)2] series and are consistent with the electronic structures of quasi-one-dimensional conductors.
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