

# Development of the first methyl antimony bridged tetrachalcogenafulvalene systems

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For the creation of new crystal and electronic structures in molecular conductors, dimeric tetrathiafulvalene (TTF) and tetraselenafulvalenes (TSFs) **1-3** linked by single or double methyl antimony bridge(s) have been prepared.

The present compounds were easily prepared by a one-step reaction via lithiation of the corresponding tetrachalcogenafulvalene (Scheme 1). The doubly linked compounds **2** were obtained as cis/trans mixtures, and then the singly linked compound **3** was also isolated. Subsequently, cis/trans mixtures of **2** were separated by means of gel-permeation column chromatography with CS<sub>2</sub> as an eluent after recycled purification. These molecules exhibit unique and favourable donor character for preparing charge-transfer (CT) salts. Singly linked compounds **1** and **3** show three pairs of reversible redox couples and the first two stages are successive. In contrast, doubly bridged compounds cis-**2** and trans-**2** show two pairs of reversible waves as well as the parent TSF.

Crystal structures of **1**, cis-**2**, and trans-**2** have been determined by X-ray diffraction method. The molecular structure of **1** with the pyramidal antimony atom is reminiscent of a flying hawk. In the crystal of **1**, there are some intermolecular short Sb...S and S...S contacts shorter than the sum of the van der Waals radii. As a result, these interactions make the three-dimensional network in the crystal. (Figure 1). Two isomers, cis-**2** and trans-**2** exhibit entirely different types of crystals. The crystal of cis-**2** has stacks linked with the side-by-side intermolecular Se...Se short contacts, whereas the trans-**2** forms dimerized structure containing CS<sub>2</sub> solvent, where the doubly bridged methyl antimony atoms are disordered. The preparation of conducting CT salts will be also reported.

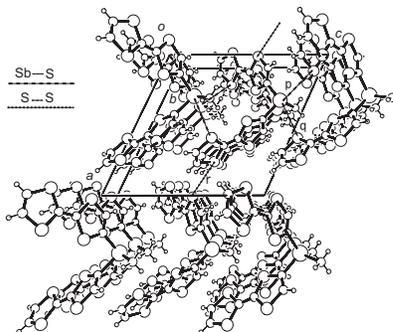
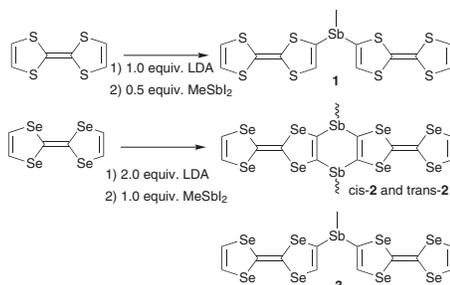


Fig. 1 Crystal structure of 1