Non-Dimerized Chains in the Tetragonal Halide Salts of *o*-DMTTF

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The electrocrystallization of *o*-dimethyltetrathiafulvalene in the presence of halide anions affords 2:1 salts formulated as $[o\text{-DMTTF}]_2X$, (X = Cl, Br, I). The three salts are isomorphous, crystallizing in the tetragonal system, space group I–42d, with the halide anion on the –4 site and the *o*-DMTTF molecule along a two-fold axis, forming strictly uniform stacks along *c*, and further stabilised by C–H•••X hydrogen bonds [1]. The evolution of the structure was thoroughly investigated upon variation of temperature, within the halide series and within solid solutions such as $[o\text{-DMTTF}]_2(Br)_x(I)_{1-x}$, and $[o\text{-DMTTF}]_2(Br)_x(Cl)_{1-x}$, $0 < x < 1$.

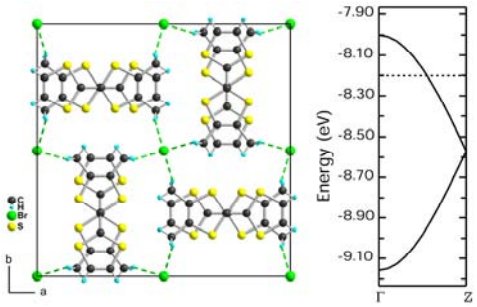

Figure 1. Projection view of the tetragonal unit cell of $[o\text{-DMTTF}]_2Br$

Physical investigations performed on the bromide salt show that it exhibits a metallic behaviour down to T_{MI} = 50K, while application of pressure moves the metal insulator transition to 39 K at 7.9 kbar. Band structure calculations indicate a strong one-dimensional character, also confirmed by the anisotropy ratio of the conductivity, $\sigma_{//}/\sigma_{\perp}$ = 500, as determined by two independent methods (four contact low frequency transport measurements and analysis of the anisotropy of the Dysonian EPR line). The iodide salt experiences a first-order phase transition with a strong hysteresis around 200–250 K. Low temperature X-ray studies will be also presented to understand the nature of the observed phase transitions.

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[1] M. Fourmigué, E. W. Reinheimer, K. R. Dunbar, P. Auban-Senzier, C. Pasquier, C. Coulon, Dalton Trans. 2008, 4652.