

## Conductive Mixed-halide Adducts of Tetrathiafulvalene obtained by Electrocrystallisation

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*Summary* The electrocrystallised mixed-halide  $\text{TTFBr}_{0.23}\text{I}_{0.46}$  and  $\text{TTFBr}_{0.47}\text{I}_{0.24}$  (TTF = tetrathiafulvalene) have Br:I ratios which are dependent on the solution composition, with the total halide stoichiometries approximating the single-halide values in  $\text{TTFBr}_{0.76}$  and  $\text{TTFI}_{0.71}$ , the maximum conductivities at 25 °C being intermediate between the single-halide values of 1600 and

42.5  $\Omega^{-1} \text{cm}^{-1}$ , respectively (*cf.* 2800 and 34  $\Omega^{-1} \text{cm}^{-1}$ , respectively); single-axis structure data are comparable throughout.

NON-STOICHEIOMETRIC halide (X) adducts<sup>1-8</sup> of tetrathiafulvalene (TTF),  $\text{TTFX}_n$  with  $n$  particularly in the range 0.69—0.79, have been widely studied mainly because of

their high conductivities. The bromide and iodide have been made by electrocrystallisation<sup>2</sup> (as well as by other methods<sup>3</sup>) and can be almost isomorphous. We thus attempted to electrocrystallise mixed bromide-iodide adducts, as follows. Galvanostatic electrocrystallisation<sup>2</sup> of a solution of TTF, tetraethylammonium bromide, and tetrabutylammonium iodide at a current density of 0.64 mA cm<sup>-2</sup> gave compounds of composition TTFBr<sub>p</sub>I<sub>q</sub> with *p* 0.47 and *q* 0.24 when the Br<sup>-</sup>:I<sup>-</sup> ratio was initially 2, and *p* 0.23 and *q* 0.46 when the ratio was 0.5. The parent monohalides were also prepared and zero-level Weissenberg and oscillation photographs gave the data in the Table which also includes conductivity measurements.

spacing and *c<sub>x</sub>* is the halide spacing. The occurrence of only two sub-lattices with the bromide + iodide adducts might indicate that Br and I are mutually randomly located, but similar atomic scattering factors must qualify this conclusion. Well defined high-angle reflexions indicate the otherwise well established intrinsic order and good quality of the crystals. The *c*-axis superlattice (the distant regularity associated with non-stoichiometry) has dimensions *ca.* 3, 4, or 5 times *c<sub>x</sub>*, presumably correlating with the small variations in the overall stoichiometries.

The conductivities are not critically dependent on the structure or composition. The experiments nevertheless establish the possibility of doping, to an extent closely

TABLE. Conductivity and structure data.

Compound	$\sigma/\Omega^{-1} \text{ cm}^{-1}$ (25 °C) <sup>a</sup>	Monoclinic cell edges (Å) <sup>b</sup>			<i>n</i> (Calc.)	<i>n</i> (Found)
		<i>a</i>	<i>b</i>	<i>c</i> <sup>c</sup>		
TTFBr <sub>0.76</sub>	820(L2), 833(L2), 2800(L4), 32(L4), 0.018(T2)	11.11	11.31	14.59 4.99 3.51	0.71 ± 0.03	0.76 ± 0.01
TTFI <sub>0.71</sub>	7.4(L2), 7.5(L2), 7.6(L2), 18(L4), 33.6(L4), 0.01(T2)	11.43	11.36	24.63 4.99 3.51	0.71 ± 0.03	0.71 ± 0.01
TTFBr <sub>0.23</sub> I <sub>0.46</sub>	38(L2), 102(L2), 509(L4), 1600(L4), 0.0012(T2)	11.76	11.43	24.96 4.90 3.51	0.73 ± 0.02	0.69 ± 0.02
TTFBr <sub>0.47</sub> I <sub>0.24</sub>	0.22(L2), 0.67(L2), 11.4(L4), 42.5(L4), 0.0028(T2)	11.27	11.27	19.97 4.90 3.51	0.73 ± 0.02	0.71 ± 0.02

<sup>a</sup> L2 and L4 are longitudinal measurements made with 2 and 4 contact methods, respectively. T2 are transverse, 2 contacts  
<sup>b</sup> Monoclinic  $\beta$  undetermined. <sup>c</sup> The *c*-axis values refer to superlattice and 2 sub-lattices.

Only *c*-axis mountings were employed, with the initial aim of establishing that single crystals were formed. However, further conclusions may be drawn. The monohalide structure data agree, within the expected error, with literature values.<sup>3</sup> Furthermore, following precedent, the total-halide stoichiometry *n*, from analysis, can be checked from the *c*-axis sub-lattice parameters,<sup>3</sup> using  $n = (3.51 \pm 0.08 \text{ Å})/c_x$  where the term in parentheses is the TTF

governed by the composition of the crystallisation solution, and it is notable that some Br content added to the iodine compound can enhance the conductivity substantially.

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