Organic Metals. A New Series of Radical-cation Salts based on an Unsymmetrically Alkylated Tetraselenafulvalene Molecule

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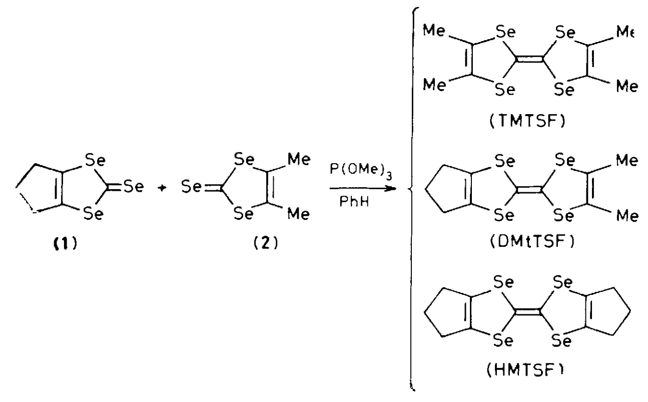
A new series of radical-cation salts of 2-(4,5-dimethyl-1,3-diselenole-2-ylidene)-5,6-dihydro-4*H*-cyclopenta-1,3-diselenole has been prepared by electro-oxidation, and the temperature dependence of the d.c. electrical conductivities of the salts is reported; very high conductivities are observed with no sign of either a metal–insulator or a superconducting phase transition even at very low temperature (0.1 K).

The recent discoveries of antiferromagnetism (AF) and superconductivity (SC) of tetramethyltetra-selena- and -thiafulvalene (TMTSF and TMTTF) radical-cation salts[1] have stimulated extensive investigation into these compounds. They have the same stoicheiometry (TMTSF or TMTTF)$_2$X (where X is a monovalent anion) and 'zig-zag'-type stacking of molecules which seem to stabilize the observed low temperature ground states.[2] Synthesis of new compounds with the TTF/TSF backbone but with different substituents on the fulvalene rings is necessary for the study of the AF



Scheme 1

and SC states. Recently, we prepared new radical-cation salts by oxidation of dimethyl(trimethylene)tetrathiafulvalene (DMtTTF) which are isomorphous and isostoicheiometric with the TMTTF salts and have an AF ground state at low temperature.[3] There is probably little chance of observing the SC state at ambient pressure in this DMtTTF series owing to an electronic localization found at low temperature as already reported for the TMTTF salts.[4] We have synthesized the selenium analogues of the salts DMtTTF which we hoped would be highly conducting at low temperatures.

Dimethyl(trimethylene)tetraselenafulvalene (DMtTSF) [2-(4,5-dimethyl-1,3-diselenole-2-ylidene)-5,6-dihydro-4*H*-cyclopenta-1,3-diselenole] was prepared as shown in Scheme 1 from equimolar amounts of the appropriate 1,3-diselenole-2-selones (**1**) and (**2**).[5,6,7] The coupling was neatly performed, using two equivalents of trimethyl phosphite in refluxing benzene.[5] After 10—12 h the reaction was complete and the crude mixture was cooled, filtered, and then washed with diethyl ether.

The resulting violet solid contained the three expected tetraselenafulvalenes TMTSF, DMtTSF, and HMTSF, the R_F's of which were respectively *ca.* 0.6, 0.7, and 0.8 (t.l.c. SiO_2, CS_2 as eluant). The residue was recrystallized from cyclohexane to give violet plates of a mixture of mainly DMtTSF and TMTSF which was further purified [removal of (**2**)] by chromatography on a SiO_2 column (Kieselgel 60 Merck with CS_2 as eluant). The violet substance isolated was sublimed at 110 °C under reduced pressure (*P ca.* 10^{-2} Torr). The purity of this final compound (m.p. 257 °C) was checked by t.l.c. (SiO_2–CS_2, R_F *ca.* 0.7), ^{1}H n.m.r. (CS_2–Me_4Si) 1.95 (s) and 2.40 (m) (both the singlet and multiplet have integral curves with the same ratios), and mass spectroscopy. The main peaks in the mass spectrum corresponding to DMtTSF were observed but because of the isotopes of selenium, the spectra of DMtTSF and TMTSF can not be completely separated and the occurrence of a very small amount of TMTSF was not excluded (up to 1%). Electrochemical half-wave potentials of DMtTSF were measured *vs.* the saturated Calomel electrode at a Pt electrode in 1,1,2-trichloroethane–tetrabutylammonium perchlorate (10^{-1} M) ($E^1_{\frac{1}{2}} = +0.48$, $E^2_{\frac{1}{2}} = +0.87$ V).

Three radical-cation salts of DMtTSF with the anions ClO_4, PF_6, and AsF_6 were then prepared by electro-oxidation using a constant current (10 μA) at the first half-wave potential with 1,1,2-trichloroethane as the electrolytic solvent. Single crystals were grown as small, shiny, black platelets (dimensions 4000—200 × 100—80 × *ca.* 20 μm).

The stoicheiometry of the perchlorate salt was confirmed by electronic microprobe spectroscopy. We compared the *X*-ray emission lines of Se and Cl in both $(DMtTSF)_2ClO_4$ and $(TMTSF)_2ClO_4$. The stoicheiometry appeared identical and preliminary *X*-ray data indicated that the crystallographic structures are triclinic and similar to those already found for the TMTSF salts.[8] From this we assumed that we had made a new isostructural series of salts $(DMtTSF)_2X$ (X = ClO_4, PF_6, and AsF_6).

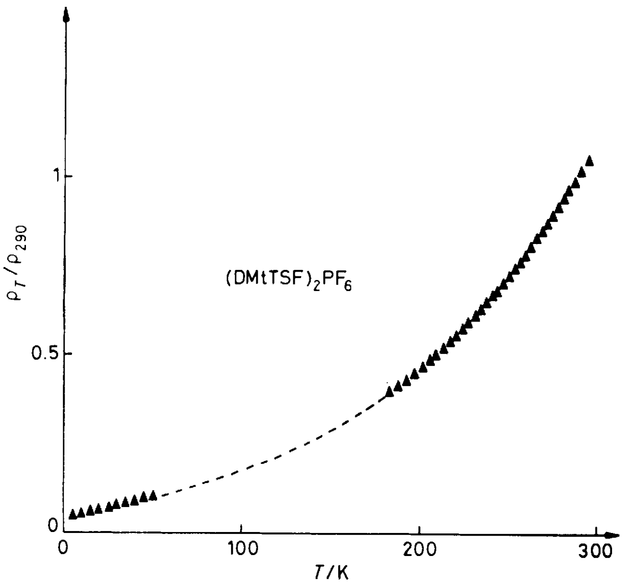


Figure 1. Temperature dependence of the d.c. electrical resistivity normalized to the room temperature value for the $(DMtTSF)_2$-PF_6 salt.

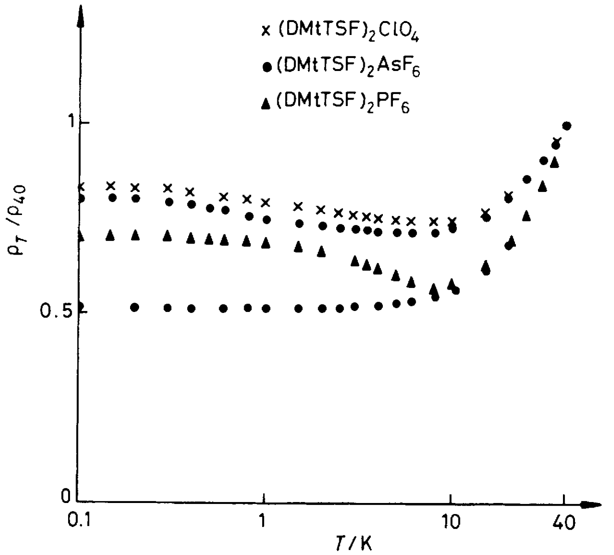


Figure 2. D.c. electrical resistivity normalized to the 40 K value for the series $(DMtTSF)_2X$ *vs.* the logarithm of the temperature between 40 and 0.1 K.

The d.c. conductivity of the $(DMtTSF)_2X$ salts were were measured using the standard four probe method. Because of the very small cross-section of the samples, only estimates of the room temperature conductivities were made (X = ClO_4, $\sigma_{\parallel}$ = 1000—1300; AsF_6, 1200—1500; PF_6, 500—800 Ω^{-1} cm^{-1} at 290 K). The values obtained seem to be dependent on the anion and they are higher than for the corresponding TMTSF salts. When the crystals were cooled, metallic behaviour was first observed and then cracks, as already observed in the TMTSF or TMTTF series,[4] prevented continuous measurements down to low temperature. However below 50 K, these cracks disappeared, and metallic behaviour was again observed for the three salts. An estimation of the complete curve for the PF_6 salt is given in Figure 1 (the dashed curve indicates the presence of cracks in the crystals). Within the limited accuracy of this determination the behaviour of the three salts was similar between 10 and 300 K.

The very low temperature data, obtained using a $^4He/^3He$ dilution refrigerator, are summarized in Figure 2. The resistivity saturates for all the compounds below 1 K and a very high conductivity remains at *T ca.* 0.1 K (σ *ca.* $10^4\ \Omega^{-1}\ cm^{-1}$ estimated from the extrapolated plot in Figure 1). No sign of either insulating or superconducting ground states were observed down to this temperature. Between 1 and 10 K a slight increase in the resistivity was generally observed. However this effect is sample dependent: we have reported in Figure 2 the behaviour of two crystals of the AsF_6 salt from the same batch. A resistivity increase was detected for one of the crystals whereas the other one remained metallic at all temperatures.

These preliminary results possibly indicate an extrinsic contribution to the resistivity at very low temperatures. One explanation might be that there is a very small amount of TMTSF in the crystals. The reported results would then correspond to DMtTSF–TMTSF alloys. The fluctuations in behaviour within a batch of crystals may correspond to differing amounts of uncontrolled doping. TMTSF and DMtTSF are both formed in the preparation (see Scheme 1) and even though purification of DMtTSF leaves a very small amount of TMTSF this molecule may remain and be incorporated during the electro-oxidation. New preparations of very pure compounds are in progress to clarify this point. The physical properties of very lightly doped samples have been shown to be close to those of the pristine salts (neglecting the superconducting state).[9] Thus the properties of very pure DMtTSF salts are probably very similar to those presented in this paper.

In conclusion, we have shown that the DMtTSF salts are very promising materials. Preliminary studies have shown that they are isomorphous with the TMTSF series and highly metallic behaviour is found down to very low temperatures. This study with that of the sulphur analogue[3] shows that highly conducting salts can be prepared from unsymmetrical precursor molecules.

Received, 12th September 1983; Com. 1218

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