Organic Metals: A New Series of Radical-cation Salts based on an Alkylated Tetrathiafulvalene

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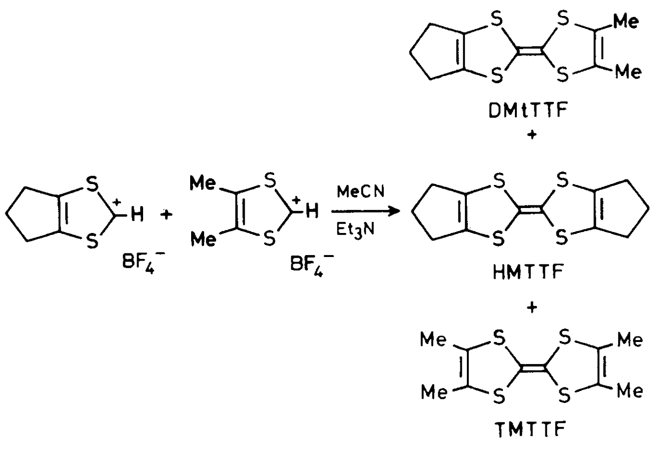
A new series of radical-cation salts, prepared by electro-oxidation, of 2-(4,5-dimethyl-1,3-dithiol-2-ylidene)-5,6-dihydro-4*H*-cyclopenta-1,3-dithiole exhibit very promising d.c. electrical conductivity and e.s.r. characteristics (linewidth and *g*-factor); an antiferromagnetic state probably exists at low temperature.

Quasi-one-dimensional organic conductors currently constitute a rapidly expanding field because of the recent discoveries of antiferromagnetic (AF) and superconducting (SC) states at low temperature.[1] These discoveries have been initiated by the synthesis of a new class of compounds, the radical-cation salts from tetramethyltetra-selena- and -thia-fulvalenes (TMTSF and TMTTF),[2,3] which show common salient features necessary to prevent (in certain cases) a periodic lattice



Scheme 1

distortion and therefore to favour another low-temperature ground state (AF or SC). These salts have the stoicheiometry $(TMTTF)_2X$ (where X is a halogen or pseudo-halogen counter-ion) and the weakly dimerized stacking of the radical cations exhibits both electronic transverse interactions through S . . . S or Se . . . Se contacts and cavities, formed by the methyl groups, where the counter-ions lie.

The synthesis of new compounds with these structural characteristics is necessary for the study of the AF and SC states which may thus be stabilised at higher temperatures and under atmospheric pressure. We present in this communication a promising new series of compounds based on an unsymmetric alkylated TTF derivative DMtTTF which we have synthesized following the classical procedure[4] shown in Scheme 1. Coupling of the dithiolium salts yielded a mixture of three tetrathiafulvalenes which were separated by successive crystallizations in hexane and acetonitrile. The unsymmetrical DMtTTF was then purified by high performance liquid chromatography [Waters-500 chromatograph with hexane–benzene (7:3) as eluant]. The purity of the final compound was verified by n.m.r. and mass spectroscopy and the electrochemical half-wave potentials were measured *vs.* S.C.E. at a Pt electrode in MeCN–$Bu^n_4NBF_4$ (10^{-1} M) ($E^1_{1/2}$ = + 0.255 V, $E^2_{1/2}$ = + 0.610 V, S.C.E. = saturated calomel electrode).

Three radical-cation salts were then prepared by electro-oxidation following the techniques used by Bechgaard,[5] using a constant current (10 μA) at room temperature with acetonitrile and 1,1,2-trichloroethane as the electrolytic solvents. For the three salts, the elemental analysis gave the expected 2 : 1 stoicheiometry *i.e.* $(DMtTTF)_2$ X with X = ClO_4^-, BF_4^-, and PF_6^-. Preliminary *X*-ray data[6] indicate that the crystallographic structure is triclinic with similar unit cell parameters to those of the TMTTF salts.[3]

The single-crystal physical properties *i.e.* d.c. electrical conductivity and e.s.r. characteristics (linewidth and *g*-factor) were examined for the three salts. The electrical conductivity along the needle axis exhibits both a room temperature (295 K) value of σ *ca.* 80 Ω^{-1} cm^{-1} and a thermal dependence more metallic than that observed for the corresponding TMTTF salts[7] (Figure 1). As already noted for these compounds, incurable cracks occur during the thermal cycling of the samples and it was impossible to get continuous data between 4 and 300 K. Thus, the dashed curve in Figure 1 is indicative only of the behaviour of the ClO_4 salt and T_{max} = 150 K may be an over-estimated value for the minimum resistivity temperature. For the two other salts only partial temperature dependences have been obtained and these exhibit similar characteristics.

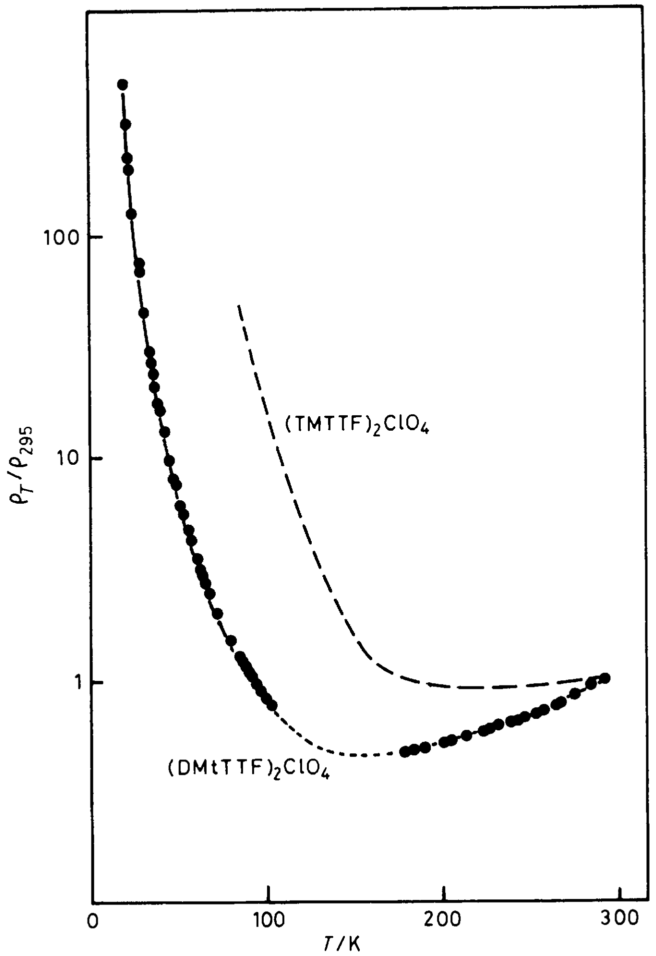


Figure 1. Temperature dependence of d.c. electrical resistivity normalized to the room temperature value. The temperature dependence of $(TMTTF)_2ClO_4$ (ref. 7) (dotted line) is shown for comparison.

The *g*-factor and linewidth temperature dependence of the e.s.r. signal are also similar, above 30 K, to those already observed for TMTTF salts.[7] Results obtained when the needle axis of the crystals is parallel to the static magnetic field are given in Figure 2. Two special features are observed at low temperature, as follows. (i) The linewidth value no longer decreases with *T* but turns over at *ca.* 25 K and increases very quickly down to 10 K where the resonance line disappears almost completely. (ii) The *g*-factor, which is constant, as expected, over a large temperature range increases at temperatures below 25 K and shows a maximum at *ca.* 15 K.

The divergence of the linewidth and the shift of the *g*-factor have already been observed above the condensation of an antiferromagnetic ground state in quasi-one-dimensional systems and are attributed to the onset of short-range magnetic order.[8,9] Therefore our e.s.r. results suggest that an AF state should appear at *ca.* 10 K for all three PF_6, BF_4, and ClO_4 DMtTTF salts.

A comparison of properties of the three TMTTF, TMTSF, and DMtTTF salts allows us to discuss the role of the anion symmetry. In the TMTTF or TMTSF series order–disorder transitions are generally observed for non-centrosymmetrical anions[10] which may be observed through resistivity or e.s.r. measurements.[7] As may be seen from Figure 2 the linewidth of the BF_4 and ClO_4 salts (non-centrosymmetrical anions) is larger at high temperature. This property may be related to an

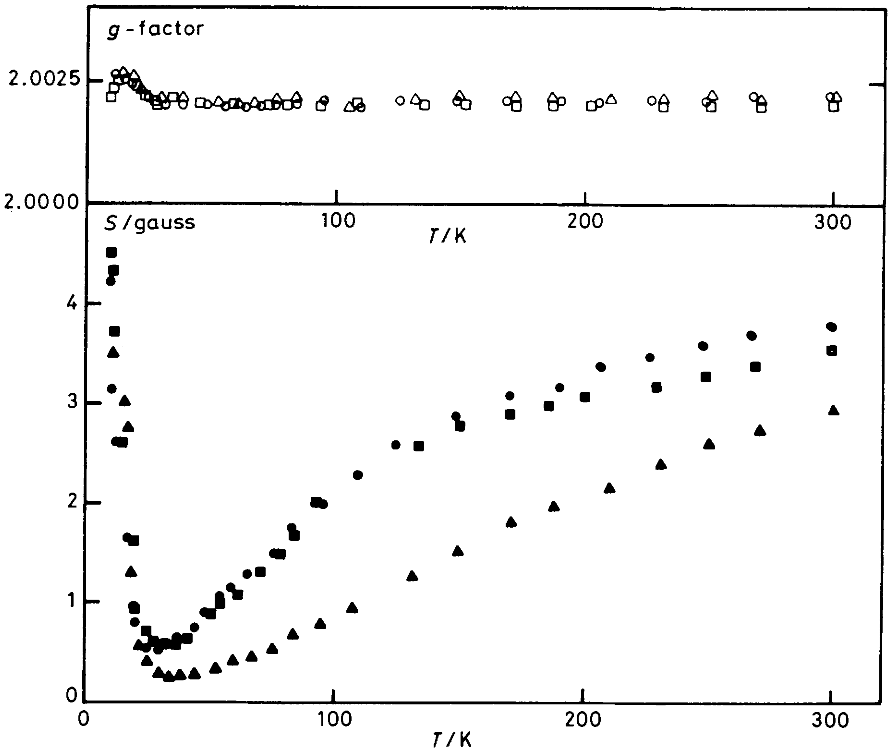


Figure 2. Temperature dependence of one component of the *g*-factor and the linewidth tensors (the magnetic field is parallel to the crystal needle axis of highest conductivity) for the three DMtTTF salts. ○,● $(DMtTTF)_2ClO_4$; □,■ $(DMtTTF)_2BF_4$; △,▲ $(DMtTTF)_2PF_6$. 1 gauss = 10^{-4} T.

anion disorder but no evidence has been obtained to date for such order–disorder phase transitions.

In conclusion, this new series of salts which appears to be isostoicheiometric and isomorphous with the TMTTF/TMSTF series is very promising and may allow us to find a ground state which should be AF or even superconducting. A detailed study of their crystal structures and physical properties will be reported elsewhere.

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