A New Series of Organomineral Conductors prepared from BEDT-TTF and Di-anions of Transition Metal Chlorides

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New organomineral materials have been prepared electrochemically from bis(ethylene dithio)-tetrathiafulvalene (BEDT-TTF) and inorganic anions of transition (and non transition) metal chlorides; all the compounds investigated are good conductors, and the copper salt shows metallic behaviour.

In the search for new conducting molecular materials, several attempts have been made to assemble together blocks of organic and inorganic molecules.[1] Recently, investigations of radical cation salts derived from tetrathiafulvalene (TTF) have suggested that the counter ions might play a key role. The introduction of a transition metal chloride, in place of a diamagnetic mono anion, promised to cause a change in the physical properties of the material. Such assemblies would form materials with magnetic chains or clusters capable of interacting with one-dimensional electronic systems.

Recently we have shown that it is possible to insert inorganic anions such as MX_3^- or MX_4^{2-} (M = transition metal, X = Cl) into organic mixed valence stacks, *i.e.*, TTF^+/TTF^0.[2] In extending this investigation to bis(ethylenedithio)tetrathiafulvalene (BEDT–TTF) it was necessary to overcome the problem of the different solubilities of BEDT–

Table 1. Physical properties of BEDT–TTF$(MX_4)_x$.

Compounds BEDT-TTF$(MX_4)_x$[a]	Magnetic susceptibility[b] C_{exp}[d] emu cgs mole^{-1} K^{-1}	Electrical conductivity at RT (σ S cm^{-1})	
BEDT–TTF$(MnCl_4)_{0.3-0.4}$	$C_{exp} = 1.30$ ($4 < T(K) < 300$, $\theta = -1K, \chi = 0.25$)[b]	0.5	S.C.[c]
$(CoCl_4)_{0.3-0.4}$	$C_{exp} = 0.87$ ($4 < T(K) < 300$, $\theta = -1.3K, \chi = 0.33$)	0.5	S.C.
$(ZnCl_4)_{0.3-0.4}$[e]	Weak Pauli type paramagnetism	0.06	S.C.
BEDT–TTF$^+(CuCl_4)_{0.25}$	$C_{exp} = 0.23$ ($80 < T(K) < 300$, $\theta = -65K, \chi = 0.20$)	50—100	metallic behaviour to low *T*

[a] Stoicheiometry obtained from elemental analysis and confirmed by magnetism experiments; [b] Measured on a SQUID magnetometer; [c] S.C. = semi-conductor; [d] Curie–Weiss law observed, characterised by the Curie constant (C_{exp}) and the Weiss temperature (θ); [c] The zinc chloride salt has a spin susceptibility owing to the organic radical cation, as confirmed by preliminary e.s.r. experiments.

TTF and the inorganic salts in commonly used solvents: acetonitrile, tetrahydrofuran, and chlorinated hydrocarbons.

We describe here the electrochemical synthesis† of new complexes prepared from BEDT–TTF and inorganic anions in a mixture of benzonitrile and acetonitrile (1:1), both compounds being reasonably soluble in this solvent mixture at 30 °C. Experiments were performed at constant d.c. current, a high intensity current (i = 40 μA) being necessary to cause formation of small black platelets of the Mn, Co, and Zn salts within 48 h. A low intensity current synthesis took several days, during which re-equilibration of the inorganic salts occurred [equation (1)] and gave rise to a mixture of products. Typically, a solution of BEDT–TTF (2×10^{-3} mol dm^{-3}) was treated with a 3—5 fold excess of the transition metal chloride (as the ammonium salt), $MX_4(NR_4)_2$ (M = Mn, Co, Zn, Cu; R = Me, Et). The new salts formed in the high intensity electrosynthesis were assigned the general formula BEDT–TTF$(MX_4)_{0.3-0.4}$ by elemental analysis.

$$MX_4{}^{2-} \rightleftarrows MX_3{}^{-} + X^{-} \rightleftarrows MX_2 + 2X^{-} \qquad (1)$$

Until recently most 'organocopper conductors' have been prepared by the chemical oxidation of organic molecules such as TTF or its dibenzo- or tetramethyl-derivatives (DBTTF, TMTTF) by copper halides. Chemical oxidation often gives rise to powders which can be classed as insulators, or display poor electrical conductivity.[3] In an attempt to prepare an organocopper charge transfer complex by oxidation of TTF with $CuCl_2$ in acetonitrile or nitromethane, we found that the black powder obtained was, in fact, a mixture of products, one of which was characterised as $TTFCl_{0.7}$, the yield of which increased considerably with a trace of moisture in the solvent.

Owing to the high redox potential of BEDT–TTF^{+}/BEDT–TTF^{0} [+0.53 V *vs.* standard calomel electrode (S.C.E.)][4] with respect to the lower potential of Cu^{2+}/Cu^{+} (+0.17 V), there is no reaction between BEDT–TTF and copper salts at room temperature. This is in contrast to the case of TTF which has a redox potential of +0.33 V.[5] At a higher temperature (50 °C) oxidation of BEDT–TTF by the copper salt occurs readily to yield a black powder of stoicheiometry BEDT–TTF$(CuCl_4)_{0.3}$.

Electrolysis of the copper salt at a current of *ca.* 30 μA yielded black platelets with the same composition as the black powder formed by oxidation of BEDT–TTF by $CuCl_2$. A second phase, red in colour, was seen to be forming at a current of 45 μA, but was not identified.

The magnetic and transport properties of the new compounds are presented in Table 1. The Mn, Co, and Zn salts can be classed as good semi-conductors, exhibiting temperature dependent conductivity analogous to that observed for TTF salts. The organocopper salt, however, is metallic in nature, with magnetic susceptibility values not exhibiting temperature dependence according to the sample Curie–Weiss law.

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† Experimental procedure: a 100 cm^3 U-shaped cell with the two electrolytic compartments separated by a sintered glass wall (porosity 3) was used. The electrodes consisted of a 1 cm^2 Pt sheet for the cathode and a 1 mm diameter Pt rod for the anode. The anodic compartment contained BEDT–TTF (1.3×10^{-4} mol) dissolved in boiling benzonitrile (15 cm^3), to which was added dry acetonitrile (45 cm^3) under an argon atmosphere; the ammonium salt was dissolved in the cathodic compartment at room temperature. Electrodes were immersed in the solution, to a depth of 2.5 cm, through air tight stoppers. The synthesis was carried out at constant d.c. current (30—45 μA) at 30 °C over 48 h.