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NEW EXAMPLES OF TERNARY ORGANIC CONDUCTORS : SULFONIUM ION RADICAL SALTS

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Although several inorganic conductors are known as tertiary component materials, for instance chalcogenides, scarce are the conductors formed by the association of three organic entities.

Only one example has been reported by Delhaes (1) and Miller (2) for the iodine contained ternary ammonium quinodimethanide salts $R_3NH\ (TCNQ^{2/3-})(I_3^-)_{1/3}$

We now investigate a novel series of ion radical salts exhibiting a ternary composition of well defined stoichiometry.

SYNTHESIS

These complexes contain TCNQ, iodine and various sulfonium ions. They can be easily prepared by two methods:

1- partial reduction of TCNQ° by a slight excess of organic sulfonium iodides in acetonitrile.

$$R\ Me_2S^+\ I^-\ +\ TCNQ^\circ \xrightarrow[70^\circ C]{CH_3CN} R\ Me_2S^+(TCNQ\text{-}I)^-$$

R = Me and Et

2- partial oxidation of $TCNQ^-$ by stoichiometric organic sulfonium tri-iodides in ethanol. This new method seems to be a general route to obtain needle-like crystals of good quality.

$$R\,Me_2S^+\,I_3^- + TCNQ^- \underset{40°C}{\overset{EtOH}{\rightleftharpoons}} R\,Me_2(TCNQ\text{-}I)^- + I_2$$

The resulting complexes are generaly less soluble in alcohol than in acetonitrile,the reverse reaction can be avoided.However when sulfur atom is hindered by large substituents,both reactions give rise to the formation of binary complexes.

$$Et_2Me\,S^+\,I^- \xrightarrow{TCNQ^\circ} Et_2Me\,S^+(TCNQ_2)^-$$

$$Et_3S^+\,I^- \longrightarrow Et_3\,S^+\,(TCNQ_2)^-$$

PHYSICAL PROPERTIES

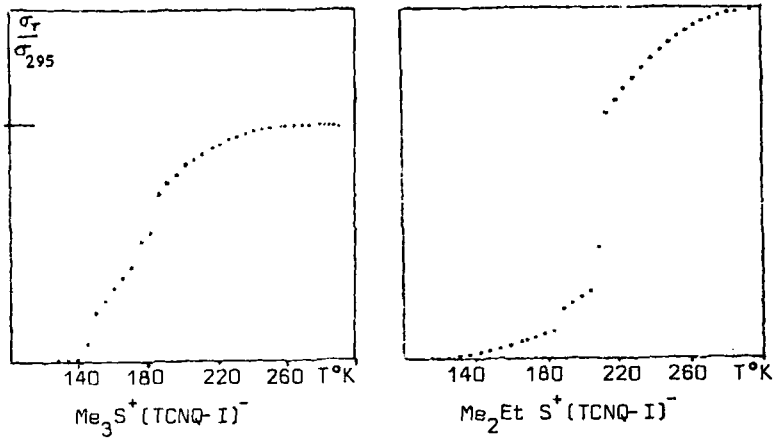
Ternary complexes exhibit interesting physical properties compare to binary salts.The single crystal anisotropic d.c. conductivity measured along the needle axis,shows that conductivity of ternary salts is larger than that of binary salts by several orders of magnitude.

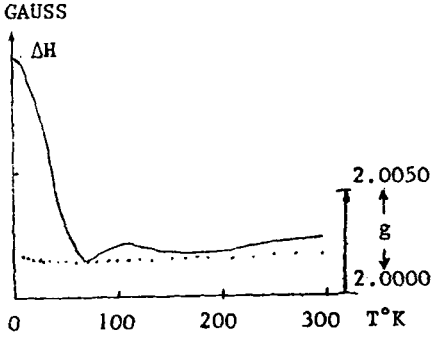
			$\sigma_{295}\,\Omega^{-1}cm^{-1}$	T_c° K
Ternary salts	$Me_3S^+(TCNQ\text{-}I)^-$	I	40	138
	$EtMe_2S^+(TCNQ\text{-}I)^-$	II	90	216
Binary salts	$Et_2MeS^+(TCNQ_2)^-$	III	4.10^{-3}	
	$Et_3S^+(TCNQ_2)^-$	IV	$1.5\ 10^{-4}$	

The temperature dependence of rationalized conductivity curves indicates a semi-conducting behaviour with a metal-insulator phase transition at 138°K for I and 216°K for II.

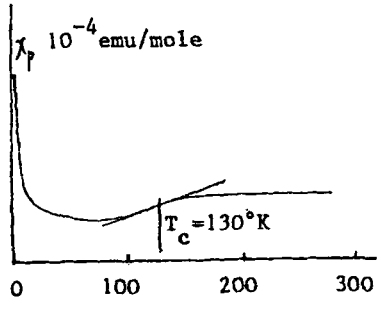
Magnetic susceptibility vs. temperature of I confirms this metal-insulator phase transition around 130°K (which is not observed for II) whereas E&R line width (ΔH) reveals a second transition at 70°K which could be assigned to a structural rearrangement. g values remain constant as expected for one chain conductors. (g = 2.0020)

Temperature dependence of normalized conductivity





Temperature independent g factor. The line width curve suggests a second phase transition at 70°K

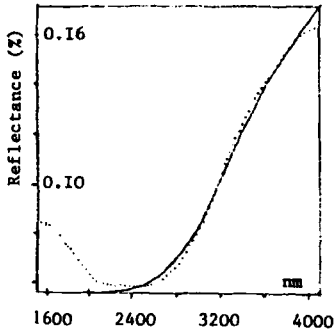


Magnetic susceptibility vs. temperature. T_c = 130°K Impurities should be at the origin of Curie "tail" at low temperature.

Experimental reflectance is in agreement with the theoritical curve calculated according to the Drude model with the following parameters :

$\omega_p = 0.57$ eV ; $\hbar/\tau = 0.15$ eV ; $\varepsilon_\infty = 2$; $C^{te} = 0.05$

from which the electronic bandwidth is found : $\Delta = 0.5$ eV



Optical reflectivity of $Me_3S^+(TCNQ\text{-}I)^-$

The X ray structure determination is in progress, however, the first results give evidence that I and II are isostructural with ammonium complexes. The unit cell parameters of the monoclinic system are the following :

Cations	a(Å)	b(Å)	c(Å)	β
Me_3NH^+ (1)	20.35	6.46	13.92	115.0
Me_3S^+	20.45	6.50	14.55	117.6
$EtMe_2S^+$	20.57	6.55	15.16	116.0

This work is now currently extended to the Se and P salts.

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