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'Organic Metals': a New Class of Conducting Ion-radical Salts Based on 7,7,8,8-Tetracyanoquinodimethane and Iodine

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Summary A new class of conducting ion-radical salts containing parallel chains of TCNQ and I_3^- is described, all of which possess a 1/3 filled electronic band, show metallic properties at high temperatures, and undergo a metal–insulator transition as the temperature is decreased.

QUASI-ONE-DIMENSIONAL 'organic metals' are being extensively studied.[1] The known systems are either ion-radical salts or charge-transfer complexes. Among the former, anion-radical salts based on TCNQ (7,7,8,8-tetracyanoquinodimethane) form the class which has been the most studied but which has also provided the least variety of examples; only a few salts are known to show metallic behaviour (as for example NMP-TCNQ, Q-TCNQ$_2$ and Acr-TCNQ$_2$†).[2] During our study of TCNQ salts with ammonium cations we prepared a novel three-component material containing one-dimensional chains of both TCNQ and I_3^-.[3,4] This salt, the cation of which is trimethylammonium (TMA), exhibits metal-like conductivity at high temperature[5] and around 150 K undergoes a transition to a non-magnetic insulating phase. We at first thought that it was an interesting but exceptional case; however we recently found this is the first example of a new class of materials, on which we here report.

TCNQ anion-radical salts are generally obtained by TCNQ oxidation of iodide salts following the reaction (1),[6]

$$3M^+I^- + 2x\mathrm{TCNQ} \rightarrow 2M^+[\mathrm{TCNQ}]_x^- + M^+I^-_3 \qquad (1)$$

where x most often is equal to 1, 1·5, or 2. In the case of trimethylammonium iodide (TMA^+I^-) this oxidation leads to well developed green crystals of $[\mathrm{TMA}]^+[\mathrm{TCNQ}]^{2/3-}$-$[I_3^-]_{1/3}$ instead of $[\mathrm{TMA}]^+[\mathrm{TCNQ}]_x^-$. A systematic study of substituted ammonium cations has shown that the occurrence in the structure of I_3^- chains together with TCNQ^- is related to the structure of the cation, which must be of the type $\mathrm{RMe_2N^+H}$. For example, we have synthesised the salts shown of the cations (neomenthyl)$\mathrm{Me_2N^+H}$ $(\mathrm{DMNA})^+$, (cyclohexylmethyl)$\mathrm{Me_2N^+H}$ $(\mathrm{DMCA})^+$, $\mathrm{Me_2N^+H[CH_2]_2N^+HMe_2}$ $(\mathrm{TMDDA})^{2+}$, $\mathrm{Me_2N^+H[CH_2]_6N^+HMe_2}$ $(\mathrm{TMHDA})^{2+}$, and $\mathrm{Me_2N^+H[CH_2]_9N^+HMe_2}$ $(\mathrm{TMNDA})^{2+}$.

$$(\mathrm{DMNA})^+(\mathrm{TCNQ})^{2/3-}(I_3^-)_{1/3}\ (\mathrm{DMCA})^+(\mathrm{TCNQ})^{2/3-}(I_3^-)_{1/3}$$
$$(\mathrm{TMDDA})^{2+}\ (\mathrm{TCNQ})_2^{4/3-}(I_3^-)_{2/3}$$
$$(\mathrm{TMHDA})^{2+}\ (\mathrm{TCNQ})_2^{4/3-}(I_3^-)_{2/3}$$
$$(\mathrm{TMNDA})^{2+}\ (\mathrm{TCNQ})_2^{4/3-}(I_3^-)_{2/3}$$

Elemental analyses indicated that the compounds were stoicheiometric, with one halogen atom per TCNQ molecule. Preliminary *X*-ray studies[8] showed that, as in the TMA salt,[4] the iodine atoms are arranged in linear tri-iodide chains parallel to regular TCNQ stacks. These results are consistent with a metallic behaviour which is indeed observed at high temperatures. The Figure depicts the typical dependence of the single-crystal electrical conductivity upon temperature, with the TMHDA salt as example. The

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† NMP = *N*-methylphenazinium; Q = quinolinium; Acr = acridinium.

conductivity increases as the temperature is decreased below room temperature, passes through a broad maximum and then decreases continuously. In agreement with other observations on organic conductors[1] a metal–insulator transition occurs at the temperature corresponding to an inflection point in the lnσ *vs.* $1/T$ plot. Moreover at this temperature the transition is recognizable from the paramagnetic susceptibility behaviour (Figure). The Table summarizes our electrical conductivity data for several salts.

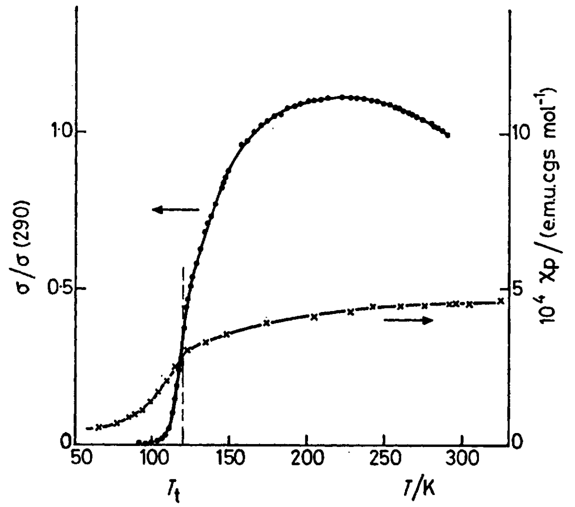

FIGURE. Temperature dependence of electrical conductivity (●) and paramagnetic susceptibility (×) of $[\mathrm{TMHDA}]^{2+}$ $[\mathrm{TCNQ}]_2^{4/3-}$ $[\mathrm{I}_3^-]_{2/3}$. The plotted values of conductivity are normalized to the conductivity at 290 K.

TABLE. Single-crystal conductivity data for compounds of type M^+ $\mathrm{TCNQ}^{2/3-}$ $(\mathrm{I}_3^-)_{1/3}$. T_{max} and $T_{\mathrm{transition}}$ are respectively the temperature of the maximum of conductivity and the temperature of the metal–insulator transition

M	Room temperature conductivity /Ω^{-1} cm^{-1}	T_{max}/K	$T_{\mathrm{transition}}$/K
TMA	30	240	150
TMDDA	50	250	150
TMHDA	40	225	120
DMNA	10	320	220

Owing to their stoicheiometry and the presence in the structure of I_3^- chains these compounds constitute a new class of 'organic metals' possessing an exactly one-third filled band. Thus a detailed study of their crystal structures and physical properties (to be reported elsewhere) is of great interest for an understanding of the competition between the lattice Peierls distortion and the disorder effect due to the I_3^- positions. Although the cation structure cited above is a necessary condition for obtaining a mixture of TCNQ and iodine, it is not a sufficient condition, and the reason why I_3^- ions are retained is as yet obscure.

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[7] P. Dupuis, unpublished work.

[8] C. Hauw, personal communication.