'Organic Metals'. Isostructural Tetrathia- and Tetraselena-fulvalene Salts of 2,5-Diethyltetracyano-*p*-quinodimethane

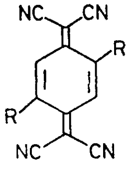
By Jan R. Andersen,*† Robert A. Craven, James E. Weidenborner, and Edward M. Engler*
(*IBM T. J. Watson Research Center, Yorktown Heights, New York* 10598)

Summary Replacement of the sulphur atoms in the charge transfer salt tetrathiafulvalene (TTF)-2,5-diethyltetracyano-*p*-quinodimethane (DETCNQ) with selenium yields the isostructural and better conducting analogue tetraselenafulvalene (TSeF)-DETCNQ, in which the Peierls transition temperature is decreased.

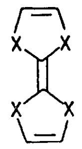
Since the discovery of unusual metal-like properties in tetrathiafulvalene (TTF)-tetracyanoquinodimethane (TCNQ) [(IIa)-(Ia)], numerous new derivatives of this charge transfer salt have appeared.[1] For the majority of these systems, the crucial data for the identification of the organic metallic state, *e.g.* single crystal conductivity, phase transition temperature, and crystal structure, are lacking. Where data are available, differences in crystal structure complicate comparisons between the molecular modifications and the resulting solid state properties. Studies of the isostructural selenium analogue of TTF-TCNQ, tetraselenafulvalene (TSeF)-TCNQ [(IIb)-(Ia)], and their alloys[2] have simplified such comparisons. Unfortunately the substitution of sulphur by selenium in TTF-TCNQ derivatives does not necessarily result in isostructural compounds.[3]

We report here the second example where such a modification does not disturb the crystal structure appreciably. Replacement of sulphur in the charge transfer salt TTF-2,5-diethyltetracyano-*p*-quinodimethane (DETCNQ) [(IIa)-(Ib)][4] with selenium yields the isostructural salt TSeF-DETCNQ [(IIb-Ib)].

DETCNQ[5] was prepared from 2,5-diethylcyclohexane-1,4-dione which was obtained by diethylation of diethyl 2,5-dioxocyclohexane-1,4-dicarboxylate[6] followed by hydrolysis and decarboxylation. TSeF was prepared according to the literature.[7] Both compounds were purified by multiple recrystallizations followed by gradient sublimation on to Teflon. Single crystals of TSeF-DETCNQ were obtained as black needles by slow evaporation of solvent from a solution of the components in acetonitrile. If this solution was quickly cooled, a red, insulating crystal-habit was obtained instead. The optical spectrum indicated[8] that it consisted of stacks with alternating donor and acceptor molecules.



(I)
a; R = H
b; R = Et



(II)
a; X = S
b; X = Se

The conducting form of TSeF-DETCNQ crystallizes in space group $P\bar{1}$, and X-ray powder measurements indicate it has essentially the same unit cell dimensions [a = 13·954(12); b = 3·878(2); c = 10·061(10) Å; α = 96·16(9)°; β =

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† IBM Postdoctoral Fellow; permanent address: Chemistry Department, Research Establishment, RISØ, DK-4000 Denmark.

95·85(8)°; $\gamma = 84{\cdot}96(15)°$] as those found for TTF–DETCNQ.[4]

Four-probe d.c. electrical conductivity measurements on single crystals of TSeF–DETCNQ gave a room temperature value of *ca.* 800 Ω^{-1} cm^{-1}. The conductivity increased by *ca.* 50% as the temperature was lowered and a broad maximum was observed at 200 K. On further cooling a phase transition at 100 K was observed compared to 110 K in TTF–DETCNQ. The qualitative changes in the conductivity achieved by replacing the sulphur atoms with selenium in the heterofulvalene–DETCNQ salts are comparable to what was reported for the corresponding TCNQ salts.[7] In both cases selenium seems to stabilize the metallic state, since the metal to semiconductor transition occurs at a lower temperature than that of the sulphur analogue. We also observe an increase in the conductivity of *ca.* 100% with the introduction of selenium.

These features are common in spite of the different crystal packings of the two kinds of materials. The TCNQ salts crystallize in a monoclinic lattice, in which the stacks of donors and acceptors are tilted against each other to form a herring-bone pattern with each acceptor molecule having two nearest donor molecules and *vice versa*.[9] On the other hand, the DETCNQ analogues are triclinic, with all stacks tilted in the same direction and each acceptor being surrounded by four nearest donors.[4]

For the TTF and TSeF salts of TCNQ it was suggested that a major factor involved in lowering the phase transition temperature in the selenium containing compound was increased electronic overlap between donor and acceptor stacks.[2,10] Enhanced linewidth broadening in the e.s.r. spectrum of TSeF–TCNQ was interpreted as evidence for this interaction.[10]

Introduction of alkyl groups on the acceptor molecule in TSeF–TCNQ appeared to be an effective means of modifying interstack coupling in an identifiable manner. Electronically 'insulating' alkyl groups should serve as 'spacers,' *i.e.* push donor and acceptor stacks apart. The narrower linewidth in the e.s.r. spectrum of TSeF–DETCNQ (*ca.* 175 G) compared to that of TSeF–TCNQ (*ca.* 550 G) suggests that these interstack interactions are indeed decreased, and this may account for part of the increase in phase transition temperature.‡

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‡ The role of differences in charge transfer, intra- and inter-stack distances, *etc.* will be discussed in a forthcoming paper.

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