Organic Metals: Synthesis of *sym*-Diselenadithiafulvalene

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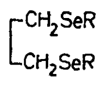
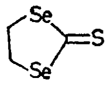
Summary A novel synthesis of *sym*-diselenadithiafulvalene (**7**) is reported as well as its reaction with tetracyanoquinodimethane to give a salt having high electrical conductivity.

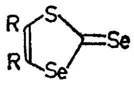
The observation of superconducting phenomena[1] in the fluctuation region in the organic metal, tetrathiafulvalene–7,7,8,8-tetracyanoquinodimethane (TTF–TCNQ) has led to increasing interest in π-donors for use with TCNQ. As discussed earlier,[2] several important donor properties, including electronic polarizability, are required for achieving metallic conduction in organic charge-transfer salts. Because of this, selenium analogues of TTF, such as tetraselenafulvalene (TSeF)[3] and its tetramethyl derivative,[4] have been synthesized. We now report the synthesis of *sym*-diselenadithiafulvalene (DSeDTF), the first mixed sulphur–selenium analogue of TTF, and the corresponding organic metal DSeDTF–TCNQ.[5]



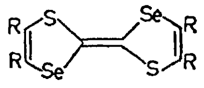
(1) R = CN
(2) R = H



(3)



(4) R = CO$_2$Me



(5) R = CO$_2$Me
(6) R = CO$_2$H
(7) R = H

Hypophosphorous acid reduction of 1,2-ethylenediselenocyanate[6] (**1**) gave the unknown oily ethane-1,2-diselenol (**2**) which was treated directly with thiocarbonyldi-imidazole[7] to give the orange 1,3-diselenolane-2-thione (**3**), m.p. 74° (30%). Reaction of the thione (**3**) with dimethylacetylenedicarboxylate in toluene gave the red selone ester (**4**), m.p. 105° (70%), which in turn was converted by triphenylphosphine in benzene into the red DSeDTF tetraester (**5**), m.p. 138° (50%). Alkaline hydrolysis of the ester (**5**) afforded the corresponding black tetracarboxylic acid (**6**), m.p. $>$ 280° (98%); copper-catalysed decarboxylation of (**6**) in hot hexamethylphosphoramide gave (25%) DSeDTF (**7**) as orange-red prisms, m.p. 118°; λ_{max} (cyclohexane) 210 (log ϵ 3·95), 235 sh (3·57), 285 (3·96), 298 (3·99), 325 sh (3·77), 375 (2·99), and 470 (2·30) nm.‡

Reaction of equimolar amounts of DSeDTF and TCNQ in hot MeCN gave, upon cooling, black crystals of DSeDTF–TCNQ. The d.c. electrical conductivity was 700 ± 300 Ω^{-1} cm^{-1} at room temperature and has negative temperature coefficient upon cooling (*cf.* TTF–TCNQ: 500—1000 Ω^{-1} cm^{-1} at room temp.)[1] The solid state properties of DSeDTF–TCNQ will be reported in detail elsewhere.[8]

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‡ The stereochemistry of (**7**) is arbitrarily assigned.

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