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'Organic Metals': Complex Formation of 1,2-Dithiole Derivatives with Tetracyanoquinodimethane or Tetrathiosquarate Salts

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Summary Some organic charge-transfer complexes have been prepared with 1,2-dithiolylium derivatives and tetracyanoquinodimethane (TCNQ) or tetrathiosquarate salts; the complexes with TCNQ have a conductivity of *ca.* $0.4 \Omega^{-1} \text{cm}^{-1}$.

THE search for more effective 'organic metals' has led to a vast number of tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) derivatives which differ primarily in the nature of substituents on either the TTF ring or the TCNQ unit. However, only a limited number of such charge-transfer salts show high conductivity. In spite of extensive recent work, it is still difficult to specify detailed molecular requirements which would give rise to, and increase conductivity in, organic materials.¹⁻³

1,2-Dithiole salts⁴ have received some attention.⁵⁻⁷ They possess extensive electronic delocalisation and some aromatic character. We have already prepared some organic charge-transfer complexes involving 1,2-dithiole

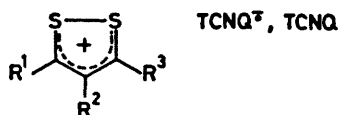
salts (*e.g.* 3,5-diphenyl-1,2-dithiolylium tetracyanopropenide: $\sigma 10^{-12} \Omega^{-1} \text{cm}^{-1}$), and we have now obtained charge-transfer complexes of the type 1,2-dithiole-TCNQ (stoichiometry 1:2) (Scheme 1) with a compaction conductivity of *ca.* $1.0 \Omega^{-1} \text{cm}^{-1}$, which is comparable to the conductivity of complexes already obtained with two molecules of TCNQ.⁸ It has not yet been possible to grow single crystals suitable for crystallographic or d.c. resistance measurements. An analogous 3,5-diamino-1,2-dithiolylium-TCNQ complex has also been prepared, stoichiometry *ca.* 2:3 (m.p. 230 °C; $\sigma 0.6 \Omega^{-1} \text{cm}^{-1}$).

The spectra of these TCNQ complexes, measured for KBr discs in the wavenumber range 40,000–2000 cm^{-1} , are similar to those described by Torrance *et al.*⁹ for TCNQ complexes including less than one unpaired electron (weak peaks at 11,800, 8500, and 2800 cm^{-1}). The absorption spectra in acetonitrile (40,000–11,400 cm^{-1}) show a peak at 11,900 cm^{-1} characteristic of TCNQ⁻.⁹ The peak intensities are in agreement with the stoichiometry given for the complexes.

We have also attempted to find new acceptor salts. High symmetry, high polarisability, small molecular size, and molecular planarity² are among the factors which seem to favour high conductivity; dipotassium tetrathiosquarate (TTS²⁻ 2K⁺) should comply with these requirements.¹⁰

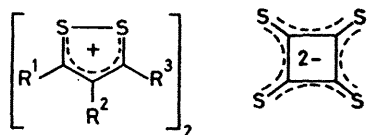
We have discovered that dipotassium tetrathiosquarate reacts with 1,2-dithiolylium salts to give black, shiny 2:1 complexes, in the microcrystalline powder state (Scheme 2). The room temperature compaction conductivity is low ($10^{-10} \Omega^{-1} \text{cm}^{-1}$), however.

The metathesis between donor and acceptor salts probably involves almost complete electron transfer, leading to



SCHEME 1

R ¹	R ²	R ³	Yield (%)	M.p. (θ/°C)	$\sigma/\Omega^{-1} \text{cm}^{-1}$
Ph	H	H	23	202	0.18
Ph	H	Ph	25	250	0.4
H	Ph	H	50	234	0.4



SCHEME 2

R ¹	R ²	R ³	Yield (%)	M.p. (θ/°C)
H	H	H	50	350
Ar ^a	H	H	90	156
H	Ph	H	55	162—165
Ar ^a	H	Ar ^a	85	185—188

^a Ar = *p*-MeOC₆H₄

considerable electrostatic repulsion in the solid which may partially explain the low conductivity of these salts. Similar comments apply to the system TTF-Br.¹

We have also tried to obtain charge-transfer complexes between TTS²⁻ 2K⁺ and tetramethyltetrathiafulvalene monochloride and dichloride salts but unfortunately these salts appear to be unreactive in charge-transfer complex formation.

The complexes in Schemes 1 and 2 were obtained in an analytically pure state (C, H, and S microanalysis) by mixing the dithiolylium iodide in acetonitrile with a solution of TCNQ in the same solvent or of the tetrathiosquarate salt in aqueous alcoholic solution at room temperature.

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