# Tetracyanomuconitritebis(tetrathiafulvalene): The First Complex Salt of Tetrathiafulvalene

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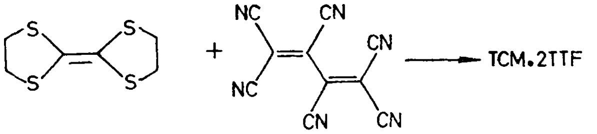
*Summary* The isolation and structure determination of a complex salt of tetrathiafulvalene are described; tetracyanomuconitrilebis(tetrathiafulvalene) contains tetrathiafulvalene in two formal oxidation states (0 and +1), exhibits a low room temperature resistivity ($10^{-3}\ \Omega$ cm) and (in the solid state) shows *anti* Curie–Weiss law behaviour in the temperature range 400—95 K with a sudden change in slope ("transition") at 140 K.

WE have reported unusual properties of tetrathiafulvalene (TTF), (**1**)[1] and prepared a large number of its derivatives[2] and salts.[2] TTF·TCNQ (TCNQ = tetracyanoquinodimethane) was the most interesting of these salts with respect to electrical conductivity[3,4] and magnetic properties,[3–4] and the conductivity of substituted TTF salts was always lower than that of the parent system.[2] Thus, TTF was probably the best donor and new acceptors (other than TCNQ,[3,4,2] DDQ,[2] $I_2$,[2] TCNE,[2] trinitrobenzene,[2] etc.) had to be tested first with TTF and then with its substituted derivatives.



(1) (2) (3)

We now report that tetracyanomuconitrile (TCM), (**2**)[5] forms an unusual complex salt (**3**) with TTF.

In compound (**3**) TTF exists in two formal oxidation states (0 and +1) like the complex salts of TCNQ,[6] (elemental analysis, e.s.r., and optical spectroscopy).

Compound (**3**) crystallizes from acetonitrile in long, narrow, dark blue needles (m.p. > 270°). Its i.r. (KBr pellet) spectrum exhibits two very broad bands at 2·5—6·9 and 6·9—16 $\mu$m, the latter having its maximum intensity at 7·5 $\mu$m. Superimposed on these bands are spikes and shoulders at 3·23, 4·6, 7·25, 7·5, 8·05, 9·15, 9·9, 12·3, 13·7, and 15 $\mu$m. Its solution u.v. spectrum is dominated by the absorptions[5] of $TCM^{\cdot-}$. In dilute acetonitrile solution the u.v.-visible spectrum of (**3**) is practically identical to that of $TCM^{\cdot-}Na^{+}$ with the exception of weak absorptions at 290 and 310 $\mu$m in the spectrum of the former. These could be due to neutral TTF.[7]

The e.s.r. spectrum of (**3**) (DMSO) shows two signals (relative intensity 1 : 1) with hyperfine structure due to $TTF^{+}$ (5 lines, $g = 2{\cdot}0086$)[7] and $TCM^{2\cdot-}$ (9 lines, presumably envelopes of 5 lines each,[5] $g = 2{\cdot}0032$).

Compound (**3**) (in solution) does not consist of $TCM^{2\cdot-}$-$2TTF^{+}$ since (a) its optical spectra match those[5] of $TCM^{\cdot-}$ and not $TCM^{2-}$ and (b) its solution e.s.r. spectrum exhibits a strong signal (*ca.* 100% relative to DPPH) due to $TCM^{\cdot-}$ ($TCM^{2-}$ should be diamagnetic). Hence, by stoicheiometry and electroneutrality, compound (**3**) (in solution) must contain the species: TTF°, $TCM^{\cdot-}$, $TTF^{\cdot+}$.

This complex salt exhibits a room temperature resistivity‡ of *ca.* $10^{-3}$ $\Omega$ cm; *i.e.*, approximately the same room temperature resistivity as TTF·TCNQ.[3,4]

In its solid state temperature dependent e.s.r. spectrum, the complex salt (**3**) shows the unusual behaviour depicted in the Figure. Concomitant with the loss in magnetic susceptibility (with decreasing temperature) we observe line narrowing. The shape of the line does not change with temperature. Finally, the rate of loss of magnetic susceptibility is not a continuous process but exhibits unusual reversibly reproducible behaviour at 240—290 K and 95—*ca.* 140 K (Figure). Below 95 K, the signal intensity increases with decreasing temperature up to 4 K.§ The temperature dependent e.s.r. behaviour of TCM·2TTF is similar to that of TTF·TCNQ, except for the narrowing of the e.s.r. line and the change in rate of e.s.r. signal loss at or near 140 K.

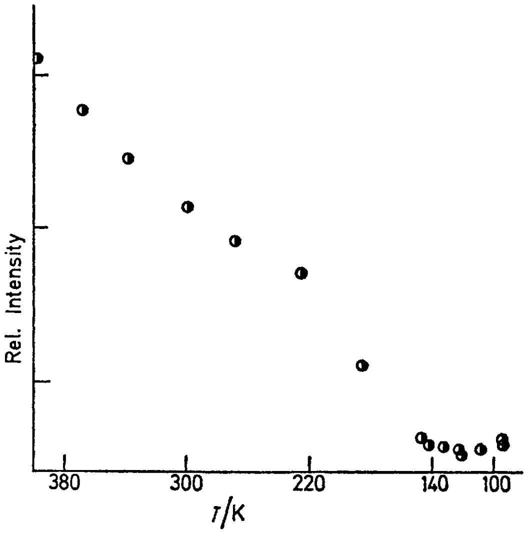


FIGURE. Relative intensity is in arbitrary units (planimeter integration). The behaviour between 290 and 240 K was reproducible. Arbitrary units relative to highest intensity peak.

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‡ Single-crystal conductivity determinations are being carried out in collaboration with G. A. Thomas and D. E. Schafer.

§ The temperature dependent magnetic susceptibility and e.s.r. spectroscopy of this and other similar materials at lower than 95 K are currently being determined in collaboration with Professor E. Wasserman and Dr. F. DiSalvo, Bell Laboratories. We thank R. S. Hutton for preliminary results.

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