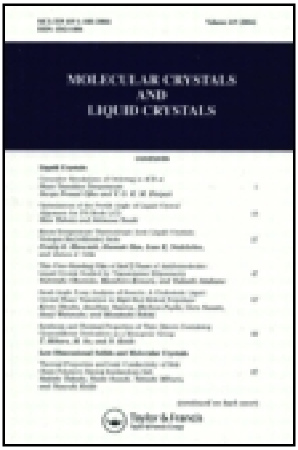

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 14 Oct 2011.

To cite this article: J. P. Stokes , T. J. Emge , W. A. Bryden , J. S. Chappell , D. O. Cowan , T. O. Poehler , A. N. Bloch & T. J. Kistenmacher (1982): $(TMTSF)_2$(2,5-Tcnqbr2): Structure and Physical Properties, Molecular Crystals and Liquid Crystals, 79:1, 683-692

To link to this article: http://dx.doi.org/10.1080/00268948208071012

Mol. Cryst. Liq. Cryst., 1982, Vol. 79, pp. 327–336
0026-8941/82/7901-0327$06.50/0

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

$(TMTSF)_2$(2,5-TCNQBr2): STRUCTURE AND PHYSICAL PROPERTIES

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Submitted for publication August 31, 1981

The 2:1 charge-transfer salt $(TMTSF)_2$(2,5-TCNQBr2) has been prepared and its physical properties investigated. Its crystal structure consists of segregated stacks of TMTSF donors (ring-over-bond overlap pattern; mean interplanar spacing of 3.6A) and chains of edge-on and disordered 2,5-TCNQBr2 acceptors. Infrared data are suggestive of unit charge on the 2,5-TCNQBr2 molecule and, therefore, half charge on the TMTSF donor. Resistivity data are successfully interpreted on the basis of a percolation construction. Magnetic data are also presented.

INTRODUCTION

Since the pioneering work of Wheland and Gillson,[1] halogenated derivatives of the electron acceptor TCNQ have played an important role in the understanding and extension of the solid-state chemistry and physics of organic

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charge-transfer salts.* Of the various halogenated analogs presently available, the symmetric 2,5-dihalo derivatives appear to be most versatile in that salts of these acceptors populate all classes into which organic charge-transfer complexes are commonly categorized. As examples, we note the following salts and their classification:

A) 1:1 mixed-stack semiconductors - DBTTF-2,5-TCNQF2;[2]

B) 1:1 segregated-stack metals - TTF-2,5-TCNQBr2,[1] DBTTF-2,5-TCNQCℓ2,[3] TMTTF-2,5-TCNQCℓ2;[4]

C) 1:1 segregated-stack Mott-Hubbard insulators - TTF-2,5-TCNQCℓ2,[1] TTF-2,5-TCNQF2,[5] TMTTF-2,5-TCNQF2,[4] HMTSF-2,5-TCNQF2.[4]

In this report we extend this list of donor-2,5-dihaloTCNQ salts with the introduction of a class of 2:1 salts typified by $(TMTSF)_2(2,5\text{-}TCNQC\ell 2)$[4] and $(TMTSF)_2$-(2,5-TCNQBr2). The latter of these two salts and its physical properties will be discussed in detail here.

EXPERIMENTAL

Large needles of $(TMTSF)_2(2,5\text{-}TCNQBr2)$, dark brown in color, were grown in a straight tube by slow diffusion through solvents at room temperature: TMTSF in chlorobenzene and 2,5-TCNQBr2 in acetonitrile.

$(TMTSF)_2(2,5\text{-}TCNQBr2)$ crystallizes in the monoclinic system, space group C2/c, with: a = 7.936(3)A, b = 20.140(9)A, c = 22.749(5)A, $\beta = 92.70(3)^{\circ}$, V = 3632A^3, D(measd) = 2.29(1) g cm^{-3}, D(calcd) = 2.301 g cm^{-3}, Z = 4. The TMTSF donors lie in general positions, while the 2,5-TCNQBr2 acceptors lie on positions of two-fold symmetry. Reflection data were collected on a Syntex P$\bar{1}$ diffractometer to 55° in 2θ. An absorption correction was applied. Refinement was by least squares and led to a final R value

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*Acceptor abbreviations: TCNQ, tetracyanoquinodimethane; DMTCNQ, 2,5-dimethyltetracyanoquinodimethane; the 2,5-dihalo derivatives are exemplified by 2,5-TCNQBr2, 2,5-dibromotetracyanoquinodimethane.
Donor abbreviations: TTF, tetrathiafulvalene; TMTTF, tetramethyltetrathiafulvalene; DBTTF, dibenzotetrathiafulvalene; HMTSF, hexamethylenetetraselenafulvalene; TMTSF, tetramethyltetraselenafulvalene; NMP, N-methylphenazine

0.14. The Se and Br atoms were treated anisotropically while all other atoms were treated isotropically. All structure factors, including those affected by diffuse streaking, were included in the analysis.

DC resistivity data were obtained by two- and four-probe techniques and microwave data by the cavity perturbation method. Single-crystal EPR spectra were recorded at X-band frequency with the applied field perpendicular to the TMTSF stacking axis. Infrared data were collected on pressed pellets in KBr.

RESULTS AND DISCUSSION

Crystallography

The crystal structure of $(TMTSF)_2(2,5\text{-}TCNQBr2)$ has been determined by single-crystal X-ray methods. X-Ray photographic data showed that the crystals were not well-ordered as the resulting photographs contained characteristic disorder diffuse scattering. The crystal selected for data acquisition possessed these imperfections to a much lesser degree than all others examined. The general aspects of the derived model (from Patterson-Fourier methods) are in good agreement with the observed structure factors. The disorder diffuse streaking is dominant on levels with odd h index which arise mainly from the 2,5-TCNQBr2 subcell (C2/c; $\underline{a}$, $\underline{b}$, $\underline{c}$). Consistent with this observation, we find residual electron density in the region of the 2,5-TCNQBr2 acceptor of up to 2.4 e/A^3. This residual density is possibly interpretable in terms of positional, librational and substitutional (Br atom) disorder, but we have yet to make a quantitative evaluation. The TMTSF subcell (A2/m; $\underline{a}' = \underline{a}/2$, $\underline{b}' = \underline{b}/2$, $\underline{c}' = \underline{c}$) appears to be less disordered.

The novel crystal structure of $(TMTSF)_2(2,5\text{-}TCNQBr2)$ is depicted in the unit-cell projections of Figure 1. The structure consists of segregated stacks of TMTSF molecules which are isolated from other donor stacks by chains of edge-on 2,5-TCNQBr2 acceptors. Each TMTSF column has four chains of acceptors as nearest neighbors and *vice versa* (see Figure 1). Within the TMTSF columns, there are four Se···Se contacts at distances shorter by 0.05A to 0.18A than the van der Waals sum (4.0A). The overlap pattern displayed in Figure 1 is nominally of the ring-over-bond type; the mean separation between molecular planes is ca. 3.6A, a value very similar to those in the uniform stack

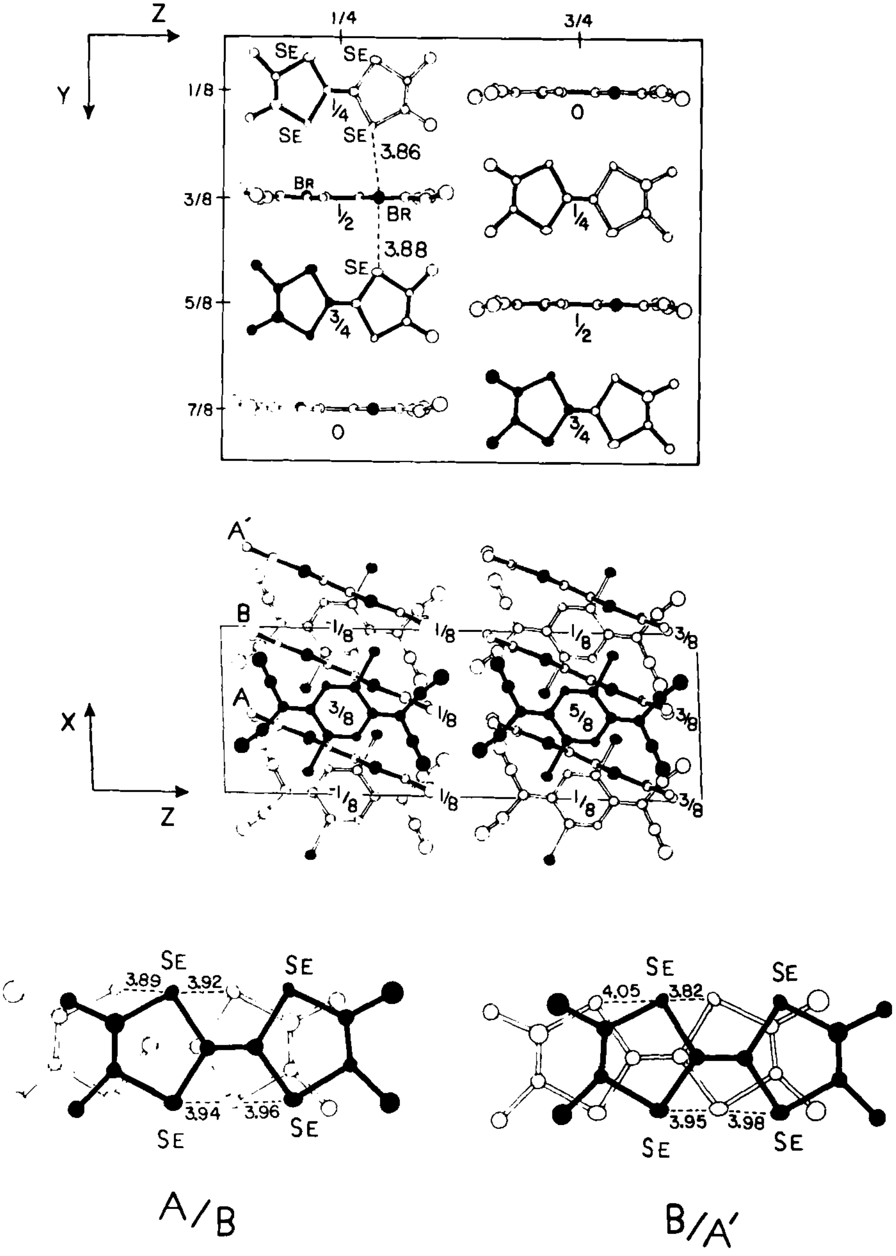

FIGURE 1 Basic elements of the crystal structure

systems TMTSF-TCNQ (3.60A)[6] and TMTSF-DMTCNQ (3.64A)[7] and the dimerized donor stacks in the PF_6^-, AsF_6^- and $C\ell O_4^-$ salts of TMTSF.[8] In contrast, the intermolecular forces in the acceptor chains appear to be soft. The only close contact is between Br atoms at 4.04A - a value measurably longer than the van der Waals sum (3.9A). Thus, the absence of strong intermolecular coupling within the acceptor chain is consistent with the observed structural disorder.

Of particular interest are the interactions between the columns of TMTSF donors and the chains of 2,5-TCNQBr2 acceptors. While there are two Se···Br contacts which are ca. 0.10A shorter than the van der Waals sum, the overall structural motif (Figure 1) is not suggestive of optimal interaction between the TMTSF columns and 2,5-TCNQBr2 chains. Thus, from a structural perspective, $(TMTSF)_2$-(2,5-TCNQBr2) can be characterized as consisting of quasi 1-D columns of TMTSF donors separated from each other by disordered chains of 2,5-TCNQBr2 acceptors.

Charge Transfer

We have recently established that a linear correlation exists between the stretching frequency (ω_0) of the nitrile groups and the charge (z) on the TCNQ acceptor in many of its charge-transfer salts.[9] Extension of this analysis to 2,5-TCNQBr2 and some of its salts, including $(TMTSF)_2$-(2,5-TCNQBr2), is presented in Table 1. The spectroscopic data are strongly suggestive of unit charge on the acceptor and, therefore, half charge on the donor in $(TMTSF)_2$(2,5-TCNQBr2).

Conductivity

From a one-electron band structure point of view, the crystal structure analysis and charge-transfer study suggest that $(TMTSF)_2$(2,5-TCNQBr2) should be metallic and electrically similar to the 2:1 inorganic salts of TMTSF.[10] However, this is not the case: as is apparent from Figure 2, the dc conductivity is activated. The activation is much weaker than observed in Mott insulators such as HMTSF-TCNQF4 and HMTSF-2,5-TCNQF2.[4] It is not too strong to be associated with a weak Peierls distortion[11] of the lattice, but the associated gap would be inconsistent with the magnetic susceptibility data of the next section. Nor do we observe any such distortion in the X-ray analysis.

TABLE 1 Nitrile Stretching Frequency Data

Material	ω_0(cm^{-1})	z
(a) "Knowns"		
2,5-TCNQBr2	2219	0
K(2,5-TCNQBr2)	~2179	1
(b) 1:1 salts#		
DBTTF-2,5-TCNQBr2	~2195	~0.60
TTF-2,5-TCNQBr2	2183	0.90
TMTTF-2,5-TCNQBr2	2178	1.0
(c) 2:1 salts#		
(HMTTF)$_2$(2,5-TCNQBr2)	2184	0.88
(HMTSF)$_2$(2,5-TCNQBr2)	2182	0.93
(TMTSF)$_2$(2,5-TCNQBr2)	2179	1.0

#Stoichiometry determined by chemical analysis.

On the other hand, what is apparent from the X-ray work is that structural disorder is inherent to the material. Where the associated random potentials are sufficiently large and the band structure sufficiently one-dimensional, such disorder can lead to weak localization of the electronic states.[12-15] In that case, dc conduction occurs exclusively, and ac conduction principally, through phonon-assisted hopping. The frequency dependence of the conductivity, evident in Figure 2, is consistent with such a description, though not as strong as in other disordered organic conductors.[14] The dc hopping conductivity in such systems in general obeys a law of the form[12,13]

$$\sigma = \sigma_0(T)\exp-[(T_m/T)^{1/m}] \quad , \tag{1}$$

where m is a strongly varying function of the temperature, depending on the detailed anisotropy of the conducting percolation network. One fit to such a law is shown in Figure 3, strongly reminiscent of Shante's[13] treatment of disordered samples of NMP-TCNQ. In the temperature region 220 K > T > 130 K, the resistivity is activated (m = 1), with an activation energy of 0.06 eV. In the temperature

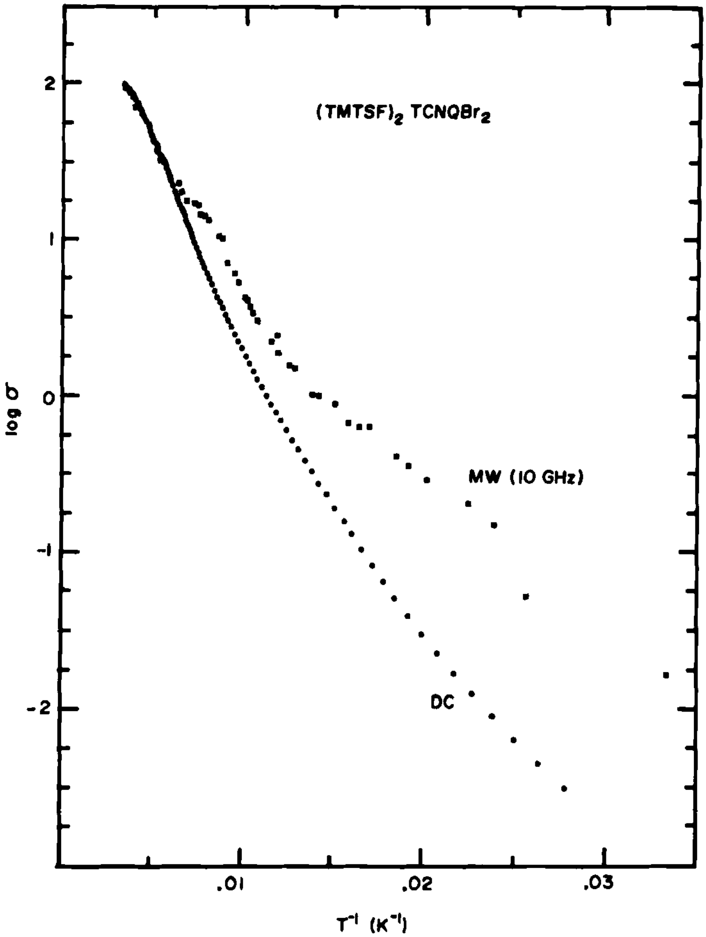

FIGURE 2 DC and mw conductivity data

regions 130 K > T > 48 K and 48 K > T > 35 K (below which the resistivity is too high to measure), the resistivity has the general form of equation (1) with m = 2.91 and 3.87 and $T_m = 2.91 \times 10^5$ and 1.37×10^7, respectively.

Magnetism

The relative spin susceptibility (Figure 4) for $(TMTSF)_2$-(2,5-TCNQBr2) in contrast with the conductivity is not activated. Instead, it is Pauli-like at high temperatures and Curie-like at low temperatures, consistent with a high

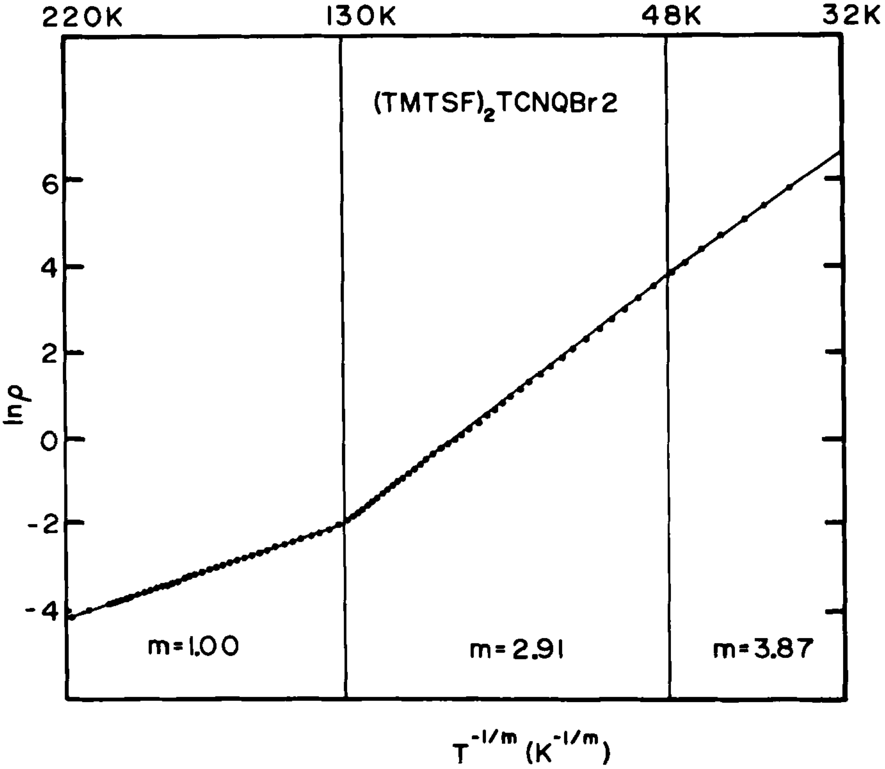

FIGURE 3 A plot of the dc resistivity data using the model proposed by Shante[13]

density of localized states at the Fermi level. In this regard, the behavior is similar to other disordered organic conductors.[12,14-15] On the other hand, the magnetism of (TMTSF)$_2$(2,5-TCNQBr2) is more complicated in that it must involve strongly-localized unpaired spins on the anion molecules as well as the weakly localized-spins in the conduction band. The presence of but one EPR line suggests strong exchange coupling between the two spin populations.

Figure 4 shows no dramatic transition in the magnetic behavior as a function of temperature. Instead, the g-factor and linewidth monotonically decrease with decreasing temperature. The room-temperature g-factor is not unlike that of other charge-transfer salts involving TMTSF and organic acceptors such as TCNQ[16] and DMTCNQ.[17] It is somewhat smaller than in (TMTSF)$_2$PF$_6$.[18] The temperature

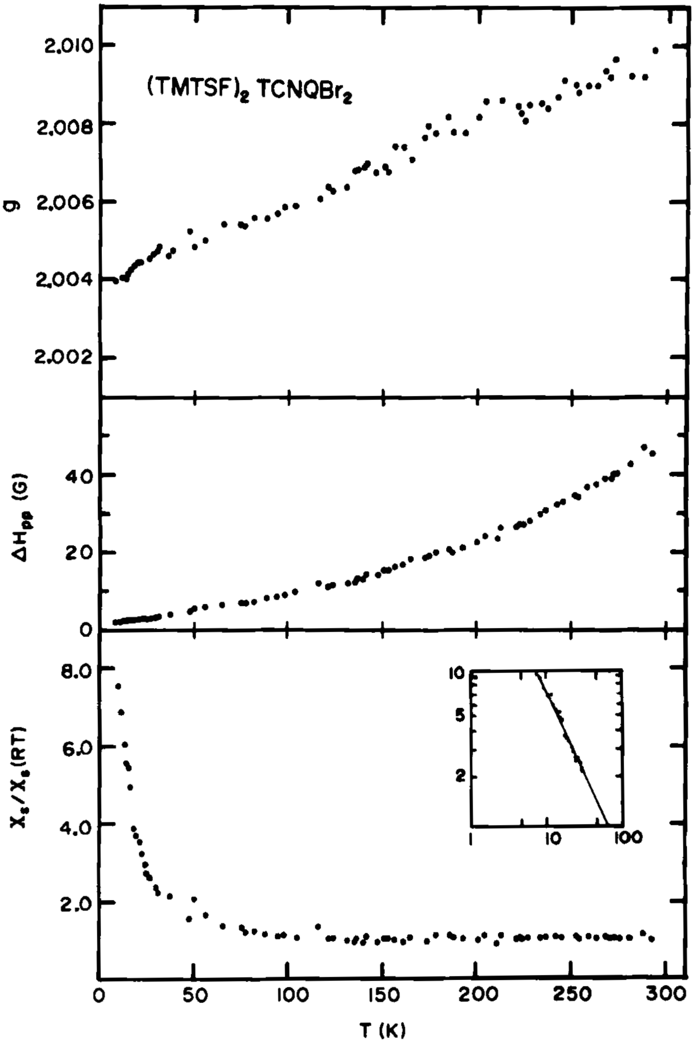

FIGURE 4 Single-crystal spin resonance data

dependent g-values imply that the nearly temperature-independent susceptibility above 100 K is associated largely with the cation stack and the low-temperature Curie susceptibility (insert of Figure 4) with the anion molecules, in accord with the above discussion. A detailed analysis of the fractional susceptibilities associated with each species is underway.

In summary, we report here on the organic salt $(TMTSF)_2(2,5\text{-}TCNQBr2)$. The crystal structure consists of stacks of donors separated by chains of acceptors perpendicular to the donor stacks. The dc and mw conductivities and the spin susceptibility can be understood in terms of a disordered nearly one-dimensional system.

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