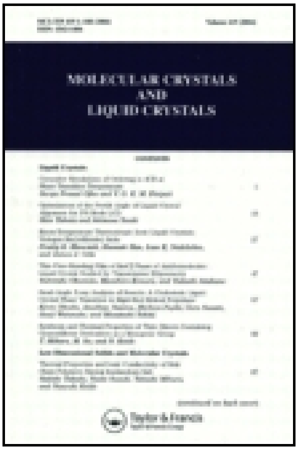

Molecular Crystals and Liquid Crystals

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Tellurium Containing Organic Metals

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TELLURIUM CONTAINING ORGANIC METALS*

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Abstract The electrical conductivity as a function of temperature is reported for single crystals of HMTTeF-TCNQ and HMTTeF-DMTCNQ. The crystal structure for one form of the DMTCNQ salt of HMTTeF is described and a procedure is outlined that could ultimately produce TMTTeF.

I. INTRODUCTION

In the past 12 years, our group has been involved, as have others, in the systematic preparation and examination of organic metals derived from π-donors containing sulfur, selenium, or most recently tellurium. In the sulfur series, Ferraris[1,2] (1972) prepared and studied TTF-TCNQ and TMTTF-TCNQ; Krug[3] (1977) prepared what is now called BEDT-TTF as well as the methylene-bridged analog; Hu[4]

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(1977) prepared acenaphtho-TTF and phenanthro-TTF; Shu and Chiang[5] (1981) prepared the dithieno-TTF or DTTTF; Lerstrup[6] (1983) prepared BDMT-TTF. Our selenium series was initiated when Bechgaard[7] (1974) prepared TMTSF, HMTSF, OMTSF as well as other donors which did not form conducting salts. Lerstrup[8,9] (1982) has more recently prepared dibenzo-TSF (DBTSF) and bisdimethylthieno-TSF (BDMT-TSF) and in addition initiated our tellurium work[8,9] with the preparation of dibenzo-TTeF (DBTTeF) and bis-dimethylthieno-TTeF (BDMT-TTeF). While it is not possible to adequately reference all of the work on the sulfur and selenium compounds, only five tellurium analogues of TTF have been prepared (see Figure 1). In addition to DBTTeF

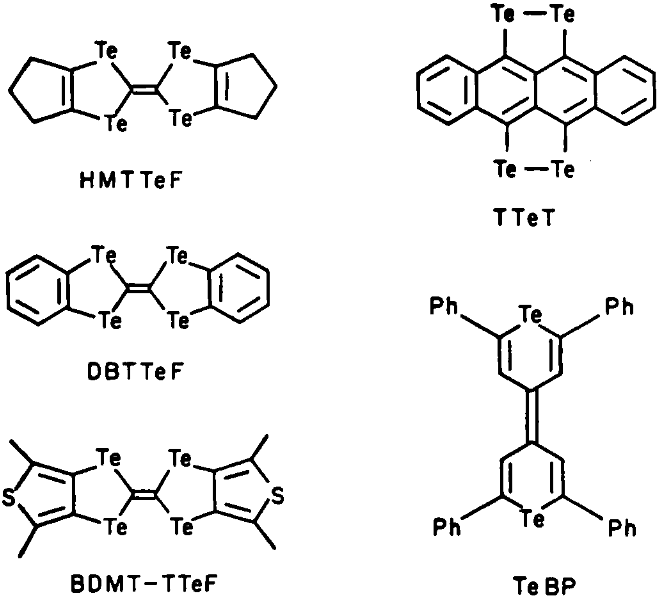

FIGURE 1

and BDMT-TTeF prepared by Lerstrup, HMTTeF was first prepared by Wudl[10] and Aharon-Shalom, TTeF was prepared by Sandman[11] as well as by a Russian group, and TeBP was prepared by Detty.[12] Three important trends are observed as we replace sulfur with selenium in the organic π-donors. The conduction bandwidth is increased in the organic metal salts, the interchain interaction is also increased, reducing the likelihood that these materials will undergo high temperature metal-to-insulator phase transitions, and the molecules tend to be more polarizable, thus reducing the on-site coulomb repulsion. All of these factors should stabilize the tellurium salts and improve their electrical properties. However, until very recently no single crystal conductivity studies were reported.[13] In this paper we will describe our conductivity measurements on HMTTeF-TCNQ and HMTTeF-DMTCNQ, give the crystal structure for one form of the DMTCNQ complex with HMTTeF and outline a procedure that we hope will ultimately produce TMTTeF.

II. STUDY OF HMTTeF SALTS

A. Preparation and Electrical Conductivity

Dark greenish-black crystals of HMTTeF-TCNQ and HMTTeF-DMTCNQ were grown by diffusion in H-cells. The solvents, previously treated with P_2O_5, were distilled under argon and stored over molecular sieves until use. The H-cell assembly was performed in an argon atmosphere. Approximately 3 mg of HMTTeF, dissolved in 3 ml of carbon disulfide, was placed in one sidearm while in the other arm was 5 mg of the acceptor dissolved in 7 ml of chlorobenzene. The two solutions were allowed to slowly diffuse at room temperature. After two to eight weeks, crystals suitable for physical measurements were formed. Both semiconducting and conducting crystal forms were obtained from the same batch.

The single crystals used in the four probe dc conductivity work were measured along the needlelike stacking axis. The dimensions were roughly 2 to 4 mm in length with typical cross-sectional values of 0.1 by 0.04 mm. Silver, gold and palladium contact pastes were tested to insure that there were no unwanted reactions between the crystal and paste. In addition, contactless microwave conductivity measurements were well within the experimental dc findings. (See Table.) The samples were also tested for ohmic behavior at room temperature. Measuring currents of 0.1 to 1.0 milliamps were used for the temperature profiles. Cooling rates were 0.2-0.4 K/min and the conductivity data was collected at every 0.1 K.

The data for both HMTTeF-TCNQ and HMTTeF-DMTCNQ show that the conductivities increase from the room temperature value down to the lowest temperature measured. At temperatures below 100 K, thermal stresses which are not uncommon for these brittle materials apparently cause a discontinuity in the temperature profile.‡ Similar transitions have been seen in salts such as (BDMT-TTF)$_2$ReO$_4$. (See Figures 2 and 3)

There is considerable disparity between the conductivity data reported here and the data previously reported by Saito[13] in two regards. First, Saito's conductivity results show a broad maximum at 243 K (TCNQ salt) and 130 K (DMTCNQ salt). Our results show no maximum for both these samples. Instead, the conductivities are observed to be increasing even at our lowest measured temperatures. Second, the room temperature

HMTTeF SALTS: ELECTRICAL PROPERTIES

ACCEPTOR	PHASE	ELECTRODE	σ_{295K} (1)	σ_{77K} (1)	COMMENTS
TCNQ	SEMICOND.	Ag PASTE	3.4×10^{-6}	——	E_A=0.36eV
	METAL	Ag PASTE	550	910	σ INCREASING AT 73K
		————	1400	600	BROAD MAXIMUM AT 243K (2)
DMTCNQ	METAL	Ag PASTE	460	1000 (3)	σ INCREASING AT 83K
		————	1800	2600	BROAD MAXIMUM AT 130K (2)
		Pd PASTE	450	——	————
		Au PASTE	390	——	————
		MICROWAVE	290,410	——	————

(1) $(\text{ohm-cm})^{-1}$

(2) SAITO, G., TO BE PUBLISHED

(3) T=83K FOR THIS MEASUREMENT

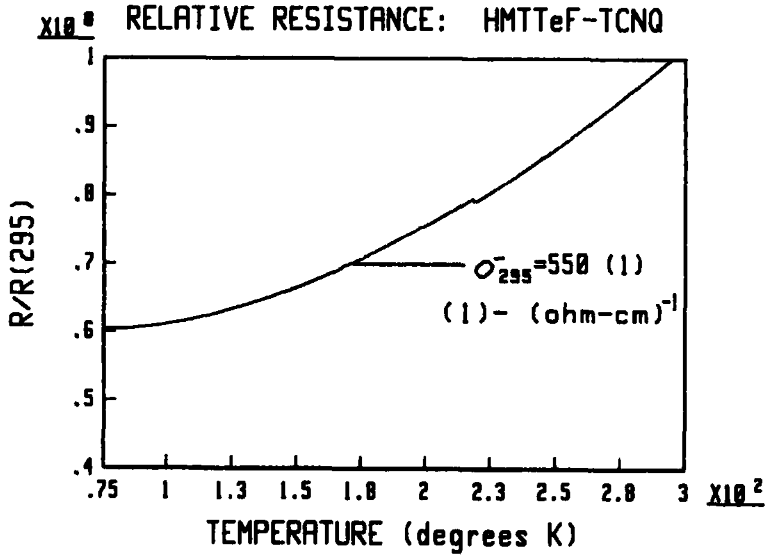

FIGURE 2

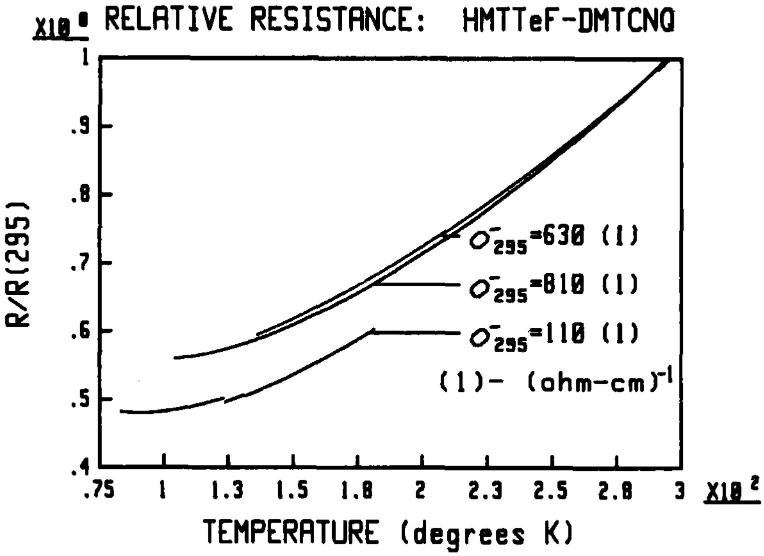

FIGURE 3

conductivities measured by Saito are larger than those found in our group; 2.5 and 4.5 times larger for HMTTeF-TCNQ and HMTTeF-DMTCNQ, respectively. Two obvious explanations for the differences are: (1) differences in crystal quality, and (2) differences in composition, i.e. stoichiometric variations between the donor and acceptor. In the BEDT series, this kind of variation has been noted within a single batch of crystals.[14] Without the complete crystallographic data from both groups, neither explanation can be ruled out.

It is interesting to note that for the quasi-one-dimensional organic metals, the conductivity profiles go through a broad maximum at low temperatures. Typical conductivity ratios between the conductivity maximum and the room-temperature value are on the order of 20-100.[15] However, when the material exhibits higher dimensionality (HMTSF and HMTTF salts, and $(BEDT\text{-}TTF)_2ReO_4$[14]) this ratio is significantly less. While our work is still in the early stages, the HMTTeF salts may also show more two-dimensional character since the conductivity ratio (σ_{LT}/σ_{RT}) for both salts is about 2. The preliminary two-probe sample measurements for the crystal in the perpendicular directions confirm this.

B. Structural Studies

Oscillation photographs (Cr Kα radiation) about the needle axis for a number of the highly conducting specimens showed only poorly developed zero- and first-order layer lines. The repeat distance along the needle axis is 4.10(5)Å, indicative of a segregated stack. Further crystallization experiments are in progress to see if high-quality crystals of this phase can be obtained.

The second phase crystallizes as grey-green needles belonging to the monoclinic system, space group I2/m (an alternate setting of C2/m), with a = 13.019(8), b = 7.254(4), c = 15.828(9)Å, β = 93.25(5)°, V = 1492.3Å^3. Intermediate-resolution intensity data (Nicolet P3m X-ray diffractometer, graphite-monochromatized Mo Kα radiation, $\bar{\lambda}$ = 0.71069Å) have been collected on this phase by the θ-2θ scan technique to a maximum 2θ of 30°. Estimated standard deviations for the collected intensities were assigned as $\sigma_I = (\sigma_c{}^2 + (0.03I)^2)^{1/2}$, where σ_c was derived from counting statistics.[16] The intensity data were corrected for Lorentz and polarization effects, but no absorption correction was applied.

The structural solution was initiated from a Patterson synthesis, with vector-superposition methods yielding positions for the Te and C atoms of the HMTTeF donor. A subsequent difference-Fourier synthesis gave coordinates for the DMTCNQ acceptor and a CS_2 molecule of solvation. All molecular components of this phase, HMTTeF-DMTCNQ(CS_2), are required to have 2/m (C_{2h}) symmetry, with the terminal methylene groups of the HMTTeF donor being disordered. Isotropic least-squares refinement, minimizing $\Sigma w(|F_o| - |F_c|)^2$, where $w = 4F_o{}^2/\sigma^2(F_o{}^2)$, has lead to an R value ($\Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.075, a weighted residual ($\{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$) of 0.061, and a goodness-of-fit value ($\{\Sigma w(|F_o| - |F_c|)^2/(NO - NV)\}^{1/2}$, where NO = 301 observations and NV = 56 variables) of 2.2.

The crystal structure of HMTTeF-DMTCNQ(CS_2) is illustrated in Figure 4. The dominant elements of the crystalline motif are the formation of layers normal to b and the presence of mixed stacks of donors and acceptors

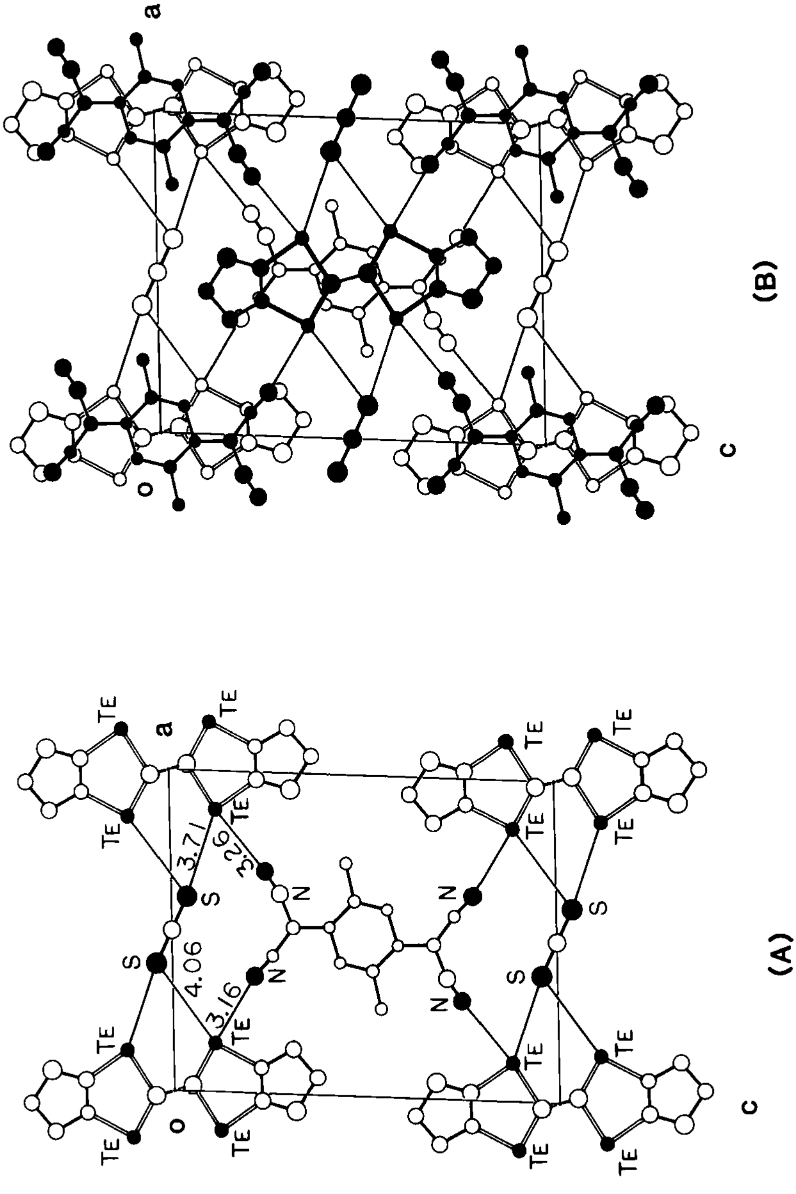

FIGURE 4 A,B

FIGURE 4:
Illustrations of the mixed -stack crystalline motif of HMTTeF-DMTCNQ(CS_2). (A) Donor-acceptor and donor-solvate interactions in the y = 0 plane; (B) the y = 1/2 plane superimposed on the y = 0 plane; (C) the mixed donor-acceptor stack viewed normal to its propagation direction.

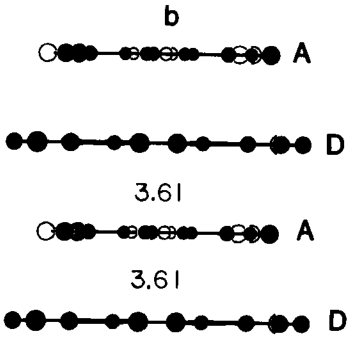

FIGURE 4C

along $\underline{b}$. The mean separation between molecular planes along the mixed stack at 3.61Å ($|\underline{b}|/2$) is slightly (~0.10Å) larger than, for example, that found in the mixed-stack array in the semiconducting form of TMTSF-TCNQ.[17] The pattern of molecular overlap within the DA stack is such that (by symmetry) the centroids of the HMTTeF donor (000) and the DMTCNQ acceptor (0,1/2,0) are coincident in projection. However, there is a measurable tilt (~13°) of the in-plane axis system of the acceptor relative to the donor (and vice versa), which may well add a covalent component to the cohesive energy of the columnar stack.

The interaction between mixed stacks is very extensive, see Figure 4. First, there are four very short Te...N contacts per DA pair, which at 3.16(2) and 3.26(2)Å are some 0.5Å less than the sum of the van der Waals radii (3.70Å)[18] of Te and N. In addition, there are two relatively close Te...S(CS_2) contacts, one (4.06(1)Å) near and one (3.71(1)Å) about 0.3Å less than the sum of the van der Waals radii (4.05Å)[3] of Te and S.

III. STRATEGY FOR THE SYNTHESIS OF TMTTeF

The tellurium donors HMTTeF and BDMT-TTeF were prepared in a similar five-step sequence starting with a cyclic 1,2 vinylic dibromide. In this sequence two equivalents of t-butyllithium are used for the metal-halogen exchange reaction followed by the addition of elemental tellurium. After all of the tellurium has reacted, the entire procedure is repeated. The tellurium dianion is then allowed to react with tetrachloroethylene to form the tellurium donor. However, there are problems in trying to extend this method to the synthesis of TMTTeF since should one attempt the metal halogen exchange with an acylic dibromide the product will be an acetylene owing to the elimination of LiBr. In fact, this elimination reaction even takes place with small ring compounds at elevated temperatures. We propose that it should be possible to prepare TMTTeF using the same type of reaction sequence providing the incipient methyl groups are part of a ring structure which is destroyed at the end of the synthetic scheme. One potential intermediate is the organosilicon compound shown in Figure 5. If this intermediate withstands the conditions of the metal-halogen exchange, then it should be possible to prepare the organosilicon substituted tetratellurafulvalene shown in the figure. This compound when treated with fluoride ion under protic conditions should produce TMTTeF. We are working on the synthesis of the 3,4-dibromo-1-sila-3-cyclopentene as well as other cyclic precursors.

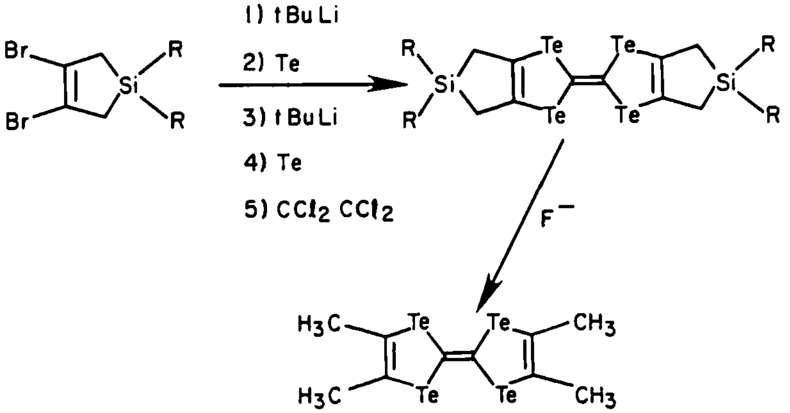

FIGURE 5

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‡ Microwave conductivity as a function of temperature has very recently been measured on single crystals of HMTTeF-DMTCNQ. The data exhibit a break in the conductivity near 110 K. This is strongly suggestive that the discontinuity results from a first-order phase transition.

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