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

# Chemistry of New Charge Transfer Complexes

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Version of record first published: 28 Mar 2007.

To cite this article: F. Wudl , G. A. Thomas , D. E. Schafer & W. M. Walsh Jr (1976): Chemistry of New Charge Transfer Complexes, Molecular Crystals and Liquid Crystals, 32:1, 147-150

To link to this article: http://dx.doi.org/10.1080/15421407608083642

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*Mol. Cryst. Liq. Cryst.*, 1976, Vol. 32, pp. 147–150
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# Chemistry of New Charge Transfer Complexes

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This presentation will be divided into two parts: (I) new TTF salts and (II) new donors and acceptors.

## I NEW TTF SALTS

This section is divided into two parts: (1) effect of counterions on solid state structure and properties and (2) transition metal compounds of TTF.

### 1 Effect of counterions

The purpose of this study is to ascertain the importance of size, shape, polarizability and dipole moment of anions on the solid state structure, electrical conductivity, electron spin resonance (esr), and magnetic susceptibility of TTF salts.

The best approach appeared to be to examine series of (a) spherical, (b) cylindrical, and (c) planar anions, *e.g.*,

(a) spherical: $F^-$, $Cl^-$, $Br^-$, $I^-$
(b) cylindrical: $^-OCN$, $^-SCN$, $^-SeCN$, $^-TeCN$, $N_3^-$, $NC\bar{N}CN$
(c) planar: TCNQ, TCM, Dithiolenides, Krogmann

In this presentation we will restrict ourselves to the second category and to isostructural series.

In order to be able to draw valid conclusions from this study, two major constraints had to be met:

1. All salts within a series had to be isomorphous and iso-stoichiometric.
2. All members of a series had to exist as relatively large, single crystals.

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We prepared $TTF_{11}(SCN)_6$ and $TTF_{11}(SeCN)_6$. However, we could not prepare $TTF_x(OCN)_y$, $TTF_x(N_3)_y$, and $TTF_x(NCNCN)_y$.

Single crystal x-ray structure determination of the SCN, SeCN, and I salts indicated these to be all isomorphous.

Figures 1 and 2 show the arrangement of the molecules in the crystal lattice. Figure 2 is a view down the (c) axis (stacking axis) and Figure 1 is an ORTEP drawing of three unit cells.

Figure 3 represents a study of single crystal DC electrical conductivity of these three TTF salts as a function of temperature. The most striking result is that the SeCN salt is a semiconductor whereas the SCN salt is a "metal" (between room temperature and $\sim 220°K$).

It will be shown that when the hopping mode applies, the hopping electrons are more strongly influenced by the dipole moment of the counterion than by its polarizability.

## 2 Transition metal compounds of TTF

There are three types of compounds expected from reactions of TTF with transition and metal salts. These are (1) TTF acts as a ligand, (2) TTF acts as a cation, and (3) TTF acts as both ligand and cation. We believe we prepared at least one compound of each type. Thus, $TTF[Pt(acac)_2]_2$,

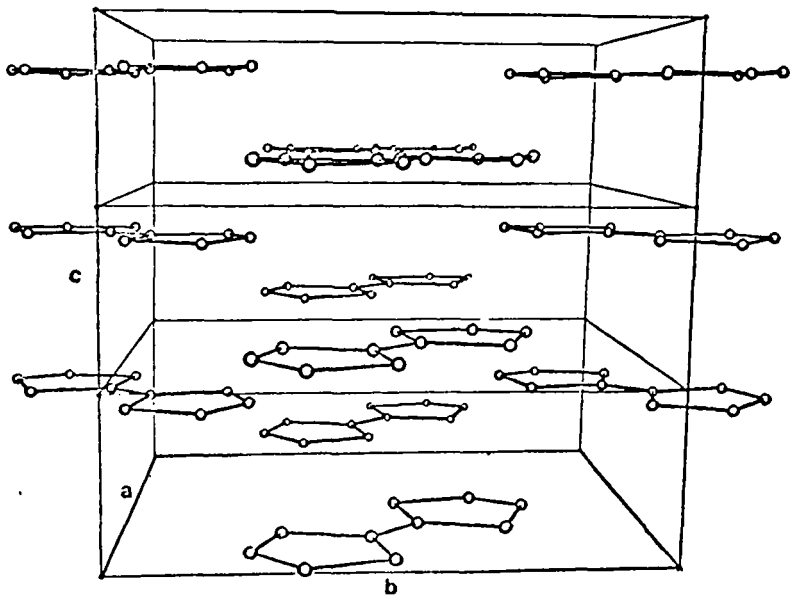


FIGURE 1

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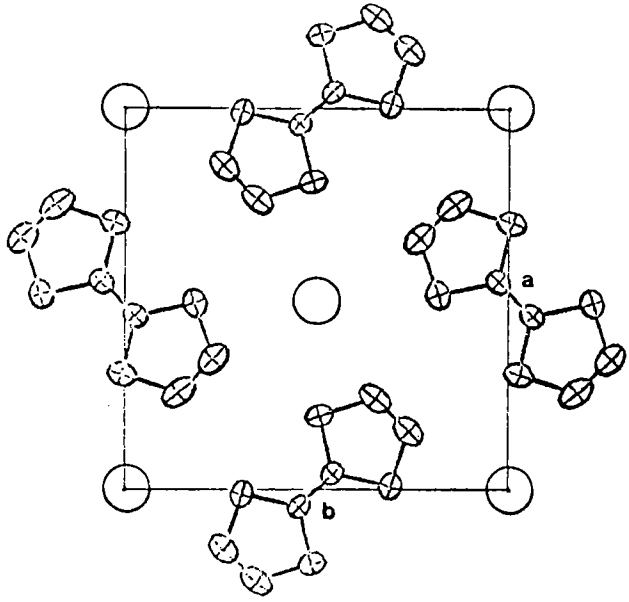


FIGURE 2

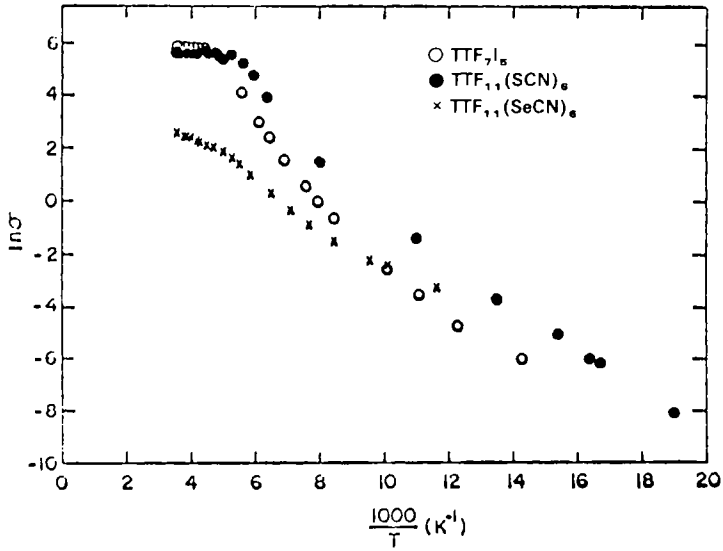


FIGURE 3

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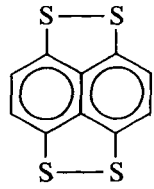
$TTFM(Mnt)_2$(M = Ni, Pd, Pt; Mnt = maleonitriledithiolato), and $TTF_6Co_2Cl_7O_2$ and $TTF_5Pt_2Cl_{10.6}$ are examples which will be discussed.

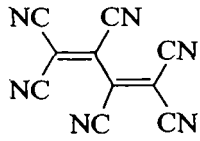
## II NEW DONORS AND ACCEPTORS

The new donor TTN (**1**) was



**1**

recently prepared by us. A TCNQ salt of it was prepared and will be described. The use of TCM (**2**) as a new acceptor will be mentioned.



**2**

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