# Structure and Properties of (DTM-TTP)(TCNQ)(TCE) and the Related Complex

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DTM-TTP (2-(4,5-bisthiomethyl-1,3-dithiol-2-ylidene)-5-(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene) and TCNQ (tetracyanoquinodimethane) form the title 1:1 complex including 1,1,2-trichloroethane (TCE). The crystal structure is composed of segregated stacks. This complex undergoes a metal-insulator transition around 100 K. Thermoelectric power takes small positive values, and the magnetic susceptibility is paramagnetic down to low temperatures.

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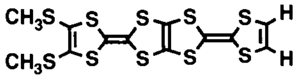
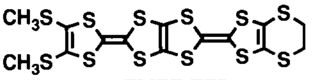
Radical-cation salts of TTP(tetrathiapenetalene)-series donors have afforded many metallic organic conductors,[1,2] whereas their charge-transfer complexes with organic acceptors have been less investigated. Although semiconducting behaviors of some TCNQ complexes have been mentioned,[3-5] no structure analysis has been reported. Here we report the crystal structure and physical properties of (DTM-TTP)(TCNQ)(TCE).

Hot TCE solutions of the donor[3] and TCNQ were mixed, and the solution was allowed to evaporate at room temperature. After several weeks black crystals in the form of needle were harvested. As the donor DTM-TTP and TMET-TTP (2-(4,5-bisthiomethyl-1,3-dithiol-2-ylidene)-5-(4,5-ethylenedithio-1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene) were used.



**DTM-TTP**



**TMET-TTP**

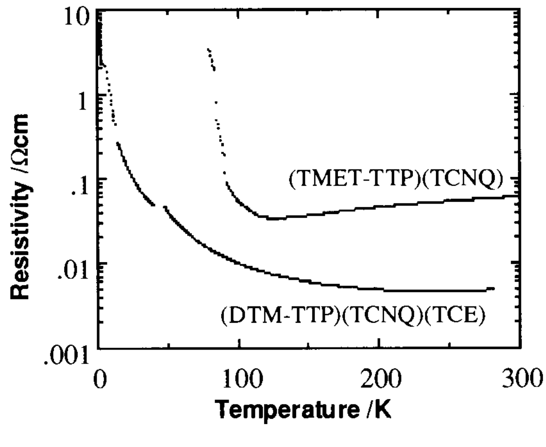


**Figure 1.** Electrical resistivity of (DTM-TTP)(TCNQ)(TCE) and (TMET-TTP)(TCNQ).

Electrical resistivities of (DTM-TTP)(TCNQ)(TCE) and (TMET-TTP)(TCNQ) are shown in Figure 1. The DTM-TTP salt shows high conductivity 200 Scm$^{-1}$ at room temperature. The temperature dependence of the resistivity exhibits a broad minimum around 250 K, below which a gradual increase is observed, but the resistivity is almost flat down to about 100 K. The TMET-TTP salt shows lower conductivity 14 Scm$^{-1}$ at room temperature, but more pronounced metallic dependence, and a definite metal-insulator transition around 100 K. Unfortunately attempts at the structure analysis of the TMET-TTP salt have been unsuccessful.

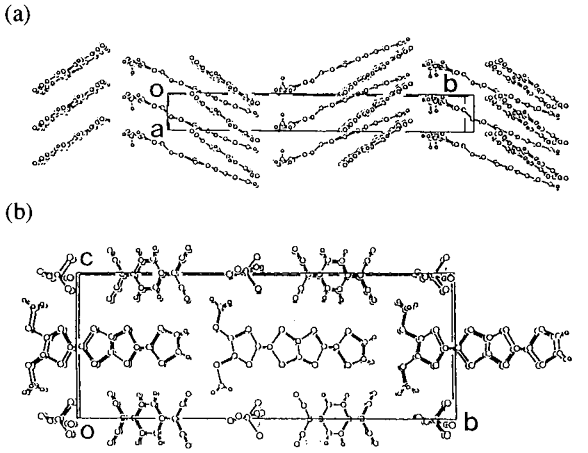


**Figure 2.** Crystal structure of (DTM-TTP)(TCNQ)(TCE), (a) projection along the *c* axis, and (b) projection along the *a* axis.

Crystal structure of (DTM-TTP)(TCNQ)(TCE) is depicted in Figure 2.[6] The structure is made up of segregated columns of DTM-TTP and TCNQ; those are running along the *a* axis. The unsymmetrical donors are aligned in a "head-to-head" manner. Since TCNQ is considerably shorter than DTM-TTP in length, the excess open space at the side of TCNQ is filled by TCE, and the composition is 1:1:1. The interplanar spacings are 3.48 Å and 3.2 Å for DTM-TTP and TCNQ, respectively. The stacking modes of the donors and the acceptors are ordinary ring-over-bond type. The thiomethyl groups of DTM-TTP extend in the molecular plane. The structure analyses of TTM-TTP (2,5-bis(4,5-bisthiomethyl-1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene) salts show that at least one thiomethyl group is out of the molecular plane when the donor charge is less than +1, whereas all methyl groups are in the molecular plane when the donor charge is equal to or larger than +1.[7] The planar structure of the present compound indicates large positive charge ($\geq$1+).[8] From the overlap of HOMO and LUMO the bandwidths are 0.8 eV both for the donor and the acceptor columns.

The CN stretching frequencies of TCNQ are 2191 and 2178 cm$^{-1}$ respectively for the DTM-TTP and TMET-TTP salts. In comparison with the reported frequencies,[9] these values correspond to TCNQ$^{1.14-}$ and TCNQ$^{1.57-}$. These extraordinarily large degrees of charge transfer are surprising because no example of TCNQ exceeding $TCNQ^{1-}$ has been reported (in the above estimation we have simply extrapolated the reported data).[10] Together with the results of structure analysis, it may be concluded that the charge on DTM-TTP is nearly 1+.

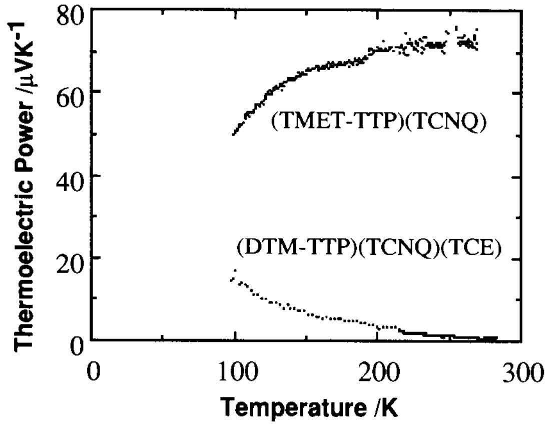


**Figure 3.** Thermoelectric power of (DTM-TTP)(TCNQ)(TCE) and (TMET-TTP)(TCNQ).

Thermoelectric power of (DTM-TTP)(TCNQ)(TCE) takes small positive values (Figure 3).. Positive thermoelectric power usually indicates the dominance of the donor conduction, but in this case, if the degree of charge transfer exceeds one, it suggests the opposite conclusion. The nearly zero thermoelectric power indicates two possibilities: (1) the contributions of the donor and the acceptor bands are comparable, and/or (2) the energy bands are nearly half-filled.

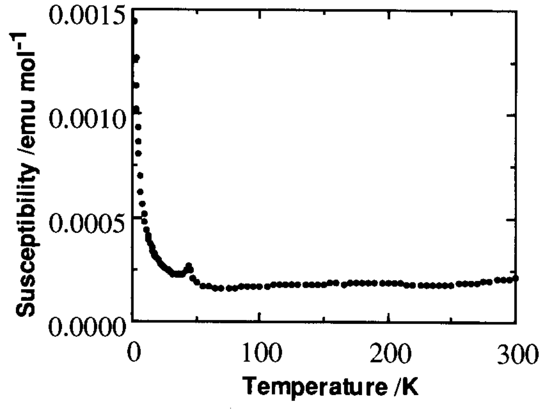


**Figure 4.** Static magnetic susceptibility of (DTM-TTP)(TCNQ)(TCE). Pascal diamagnetic contribution $-3.29 \times 10^{-4}$ emu/mol has been subtracted.

Static magnetic susceptibility (Figure 4) does not show any definite anomaly around 100 K, and is approximately flat down to low temperatures. From this the insulator phase can be attributed to either (1) the $4k_F$ charge density waves or (2) the paramagnetic insulator like the Mott insulator. In both cases the role of electron correlation should be important.

In conclusion the degree of charge transfer in (DTM-TTP)(TCNQ)(TCE) is likely to be nearly 1.0, whereas this complex shows fairly high conductivity. The nature of the insulating phase of this compound has some resemblance to those of $(TTM\text{-}TTP)I_3$ and $(TTM\text{-}TTP)(I_3)_{5/3}$.[7]

## References and Notes

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6 Crystal data of (DTM-TTP)(TCNQ)(TCE): $F_w$=810.45, monoclinic, space group $P2_1$, $a$= 3.803(5), $b$=32.31(3), $c$=12.39(2) Å, $\beta$= 90.6(1) °, $Z$=2, $\rho_{calc}$=1.7684 g $cm^{-3}$, and $V$=1522(5) $Å^3$. The final $R$=0.105 ($R_w$=0.114) for independent 1345 reflections ($I>5\sigma(I)$). The positions of chlorine atoms are disordered; this reduces the accuracy of the structure analysis.

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8 The bond lengths of the DTM-TTP molecule are: the vertical C(7)-C(8) = 1.37 Å at the center of TTP, and the horizontal C(5)-C(6) = 1.38 Å; these values are in accordance with the large positive charge of nearly 1+.[7] The accuracy of TCNQ bond lengths are not good enough for such estimation.

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