Competitive Effect in Metallic κ-Type DHOT-TTP [2-(1,3-Dithiolan-2-ylidene)-5-(1,3-oxathiolan-2-ylidene)-1,3,4,6-tetrathiapentalene] Salts

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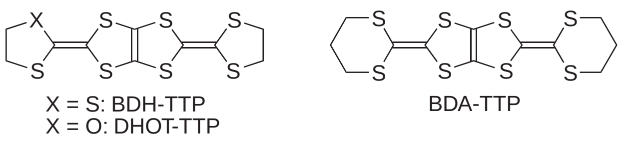
The preparation of κ-(DHOT-TTP)$_2$X (X = PF$_6$, AsF$_6$, and FeCl$_4$) has been accomplished, which exhibit metallic conducting behavior down to low temperatures. A comparison of the values of the intermolecular overlap integrals calculated on the donor layers of these salts with those of the corresponding isomorphous BDH-TTP [2,5-bis(1,3-dithiolan-2-ylidene)-1,3,4,6-tetrathiapentalene] salts suggests that DHOT-TTP, like BDH-TTP, has the ability to form tight packing motifs.

The development of new organic superconductors is undoubtedly a major focus of attention in the field of molecular conductors.[1] Our conceptually guided design of π-electron donors to produce organic superconductors originates in the destabilization of the stable metallic state that occurs, for instance, with the use of the BDH-TTP donor (Chart 1) by reducing intermolecular interaction.[2] One successful strategy in this regard is an increase of steric bulk on the periphery of BDH-TTP by extending the σ-bond framework. Indeed, the BDA-TTP [2,5-bis(1,3-dithian-2-ylidene)-1,3,4,6-tetrathiapentalene] donor, in which the outer dithiolane rings of BDH-TTP are replaced with dithiane rings capable of adopting chair conformations, gives rise to a series of superconducting salts.[3] Meanwhile, we have reported that DHOT-TTP, in which one sulfur atom in the outer dithiolane ring of BDH-TTP is substituted by oxygen, gives the semiconducting I$_3$ and BF$_4$ salts, but with the AuI$_2$ anion forms the metallic α-(DHOT-TTP)$_2$(AuI$_2$)$_{0.87}$ salt.[4] A point worth noting is that the oxygen atom of DHOT-TTP in the AuI$_2$ salt has an extremely small HOMO (highest occupied molecular orbital) coefficient relative to the sulfur atoms. So, this chalcogen substitution might be recognized as an alternative strategy for leading to a decrease of interaction between donor molecules. In order to gain more information on the effect of the introduced oxygen atom on the formation of intermolecular interaction, we undertook the preparation and investigation of the DHOT-TTP salts with other anions. In this paper, we describe the physical properties and structural aspects of κ-(DHOT-TTP)$_2$X (X = PF$_6$, AsF$_6$, and FeCl$_4$).

Electrocrystallization of DHOT-TTP with n-Bu$_4$NX (X = PF$_6$ and AsF$_6$, 4 equiv.) in 1,1,2-trichloroethane and with Et$_4$NFeCl$_4$ (4 equiv.) in 5% acetone/PhCl by the controlled-current method[5] gave (DHOT-TTP)$_2$X (X = PF$_6$ and AsF$_6$) and (DHOT-TTP)$_2$FeCl$_4$, respectively.



X = S: BDH-TTP
X = O: DHOT-TTP

BDA-TTP

Chart 1.

The room-temperature conductivities (σ_{rt}'s) of the PF$_6$ and AsF$_6$ salts were 2.4 and 31 S cm^{-1}, respectively. By variable-temperature resistivity measurements, these salts were found to retain the metallic state down to 1.5 K (Figure 1). A similar metallic behavior has been found in κ-(BDH-TTP)$_2$PF$_6$.[6] On the other hand, the temperature dependence of the resistivity of the FeCl$_4$ salt ($\sigma_{\mathrm{rt}} = 6.1$ S cm^{-1}) showed some jumps in the cooling process and a large hump in the heating process (Figure 1), which are probably attributed to microcracks caused by the stress of the resistance-measuring probes. In addition, unlike κ-(BDH-TTP)$_2$FeCl$_4$ that remains metallic all the way down to 1.5 K,[7] a small upturn in the resistivity was observed at ca. 5 K. The magnetic susceptibility of the FeCl$_4$ salt obeyed the Curie–Weiss law from 300 to 2 K, giving a Curie constant (C) of 4.33 emu K mol^{-1} and a Weiss constant (θ) of -0.50 K. The fitted C is close to the value of 4.38 emu K mol^{-1} expected for a high-spin Fe^{3+} ion ($S = 5/2$, $g = 2.0$), so it is clear that the Fe atom dominates the measured magnetization. The small negative θ implies a very weak antiferromagnetic interaction between the Fe centers.

X-ray crystallographic analyses of the PF$_6$ and AsF$_6$ salts revealed that both salts crystallize isostructurally[8] and, additionally, are isostructural to κ-(BDH-TTP)$_2$PF$_6$.[6] Figure 2 shows the donor packing motif of κ-(DHOT-TTP)$_2$PF$_6$, in which the DHOT-TTP molecule has orientational disoder among the oxygen and three sulfur atoms located in the outer oxathiolane and dithiolane rings. There are several short (less than the van der Waals distance of 3.70 Å) S···S contacts between donor pairs, whereas no short S···S contact is observed within a donor pair. The S···S contact pattern is somewhat different from that observed in κ-(BDH-TTP)$_2$PF$_6$, where each BDH-TTP donor molecule is linked by short intrapair and interpair S···S contacts. Owing to the disorder, intermolecular overlap integrals were calculated by fixing the oxygen atom at the position with the largest

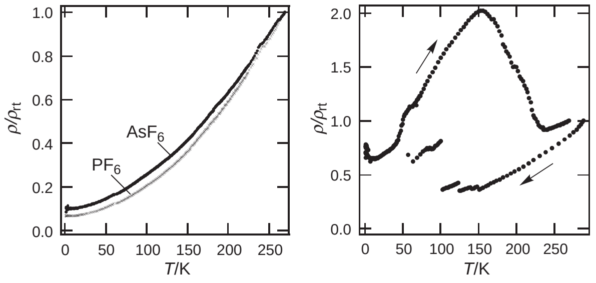


Figure 1. Temperature dependence of the relative resistivities of (DHOT-TTP)$_2$X (X = PF$_6$ and AsF$_6$) (left) and (DHOT-TTP)$_2$FeCl$_4$ (right).

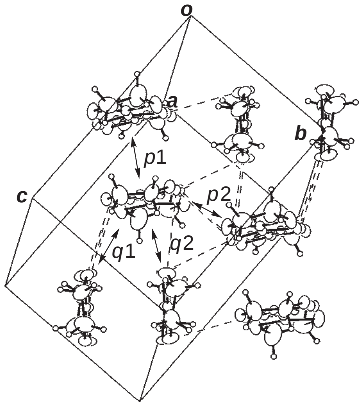


Figure 2. Donor arrangement in κ-(DHOT-TTP)$_2$PF$_6$. Broken lines indicate short S···S contacts (< 3.70 Å). The respective values ($\times 10^{-3}$) of overlap integrals $p1$, $p2$, $q1$, and $q2$ are 20.5, 22.3, 6.22, and -5.07, whereas those in κ-(DHOT-TTP)$_2$AsF$_6$ are 20.1, 22.3, 6.36, and -4.97.

occupancy factor (0.28).[9,10] Despite no short intrapair S···S contact, large values are estimated within a donor pair ($p1 = 20.5 \times 10^{-3}$) as well as between donor pairs ($p2 = 22.3 \times 10^{-3}$), each of which is very close or close to the corresponding value (20.7 or 19.6×10^{-3}) found in κ-(BDH-TTP)$_2$PF$_6$:[6] the same can be said for the isostructural κ-(DHOT-TTP)$_2$AsF$_6$. Therefore, κ-(DHOT-TTP)$_2$X (X = PF$_6$ and AsF$_6$) and κ-(BDH-TTP)$_2$PF$_6$ would show analogous metallic behavior.

The structure of the FeCl$_4$ salt of DHOT-TTP was confirmed by X-ray analysis[11] to be isostructural to that of κ-(BDH-TTP)$_2$FeCl$_4$.[7] As is the case in κ-(BDH-TTP)$_2$FeCl$_4$, short S···S contacts occur between donor pairs rather than within a donor pair (Figure 3). Since the orientational disorder of four outer chalcogen atoms of DHOT-TTP is observed in the FeCl$_4$ salt, the calculation of overlap integrals was performed by the same manner as used for κ-(DHOT-TTP)$_2$PF$_6$.[9,10] In this case, the largest occupancy factor for the oxygen atom is 0.37. There are no remarkable differences between the $p1$, $p2$, $q1$, and $q2$ values and the corresponding values (19.3, 15.7, 6.36, and -6.79×10^{-3}) found in κ-(BDH-TTP)$_2$FeCl$_4$,[7] suggesting that the metallic state of κ-(DHOT-TTP)$_2$FeCl$_4$ is intrinsically stable down to low temperatures.

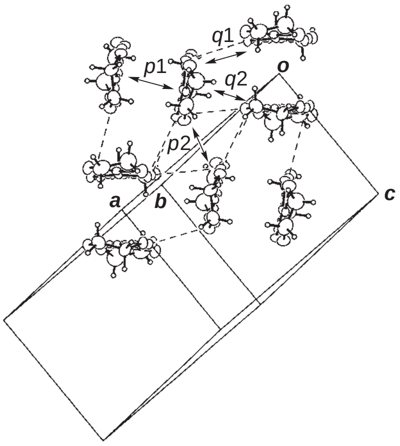


Figure 3. Donor arrangement in κ-(DHOT-TTP)$_2$FeCl$_4$. Broken lines indicate short S···S contacts (< 3.70 Å). The values ($\times 10^{-3}$) of overlap integrals $p1$, $p2$, $q1$, and $q2$ are 17.8, 17.9, 6.24, and -4.65, respectively.

In summary, it has been found that the DHOT-TTP donor in all κ-type salts reported here displays its cohesive force comparable to that of BDH-TTP. The replacement of the sulfur atom in BDH-TTP with oxygen holds two conflicting effects: (i) a decrease of overlap between donor molecules caused by a very small HOMO coefficient of the oxygen atom and (ii) an increase of chemical pressure induced by the smaller size of the oxygen atom. Considering an orthogonal packing of donor dimers in the κ-salts, it is likely that both effects are in competition with each other in these salts. On the other hand, the former effect is expected to preferentially occur in columnar packing motifs in which the side-by-side interaction between donor molecules plays an important role. In such a case, combination of the substitution with oxygen and the extension of σ-framework may bring about a fine tuning of intermolecular interaction to develop superconductivity. Work currently in progress is addressing this question.

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References and Notes

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8 Crystal data for (DHOT-TTP)$_2$PF$_6$: C$_{20}$H$_{16}$O$_2$S$_{14}$PF$_6$, $M_r = 882.15$, monoclinic, space group $C2/c$, $a = 35.594(11)$, $b = 7.856(11)$, $c = 11.035(9)$ Å, $\beta = 98.55(4)^\circ$, $V = 3052(5)$ Å^3, $T = 299$ K, $Z = 4$, $\mu(\text{Mo K}\alpha) = 11.10\,\text{cm}^{-1}$, $D_\text{calcd} = 1.92\,\text{g cm}^{-3}$, $R = 0.066$ and $R_\text{w} = 0.047$ for 2242 observed reflections with $I > 3\sigma(I)$ from 33771 unique reflections; Crystal data for (DHOT-TTP)$_2$AsF$_6$: C$_{20}$H$_{16}$O$_2$S$_{14}$AsF$_6$, $M_r = 926.10$, monoclinic, space group $C2/c$, $a = 35.734(5)$, $b = 7.878(6)$, $c = 11.024(3)$ Å, $\beta = 98.396(19)^\circ$, $V = 3070(2)$ Å^3, $T = 299$ K, $Z = 4$, $\mu(\text{Mo K}\alpha) = 21.21\,\text{cm}^{-1}$, $D_\text{calcd} = 2.004\,\text{g cm}^{-3}$, $R = 0.046$ and $R_\text{w} = 0.053$ for 2687 observed reflections with $I > 3\sigma(I)$ from 3529 unique reflections.

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10 According to the calculation, the HOMO coefficient for the fixed oxygen atom of DHOT-TTP is very small, close to that for the oxygen atom of the disorder-free DHOT-TTP donor molecule in α-(DHOT-TTP)$_2$(AuI$_2$)$_{0.87}$.

11 Crystal data for (DHOT-TTP)$_2$FeCl$_4$: C$_{20}$H$_{16}$O$_2$S$_{14}$FeCl$_4$, $M_r = 934.84$, orthorhombic, space group $Pnma$, $a = 11.065(5)$, $b = 37.181(5)$, $c = 8.060(6)$ Å, $V = 3316(2)$ Å^3, $T = 299$ K, $Z = 4$, $\mu(\text{Mo K}\alpha) = 16.82\,\text{cm}^{-1}$, $D_\text{calcd} = 1.872\,\text{g cm}^{-3}$, $R = 0.055$ and $R_\text{w} = 0.052$ for 1922 observed reflections with $I > 2\sigma(I)$ from 4360 unique reflections.

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