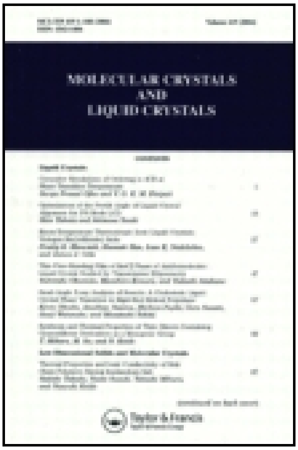

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NEW ORGANIC SUPERCONDUCTORS FROM A NON-TTF DONOR, BDA-TTP

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A new π-electron donor, 2,5-bis(1,3-dithian-2-ylidene)-1,3,4,6-tetrathia-pentalene (BDA-TTP), which contains no tetrathiafulvalene (TTF) molecule, produces a series ambient-pressure superconductors β-(BDA-TTP)$_2$X (X^- = SbF_6^-, AsF_6^-, and PF_6^-), in which the values of intermolecular overlap integrals suggest loose donor packing motifs.

Keywords: organic superconductors; new π-electron donor; magnetic susceptibility; electrical conductivity; crystal structures

INTRODUCTION

Following the discovery of superconductivity in organic cation-radical salts (TMTSF)$_2$X (TMTSF = tetramethyltetraselenafulvalene, X = monovalent anions) [1], a good number of molecular-based organic superconductors have been developed over the past two decades [2]. These superconductors, excluding fullerene superconductors, are composed of organic donor components, which are classified into two categories: (i) π-electron donors such as bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF), dimethyl(ethylenedithio)diselenadithiafulvalene (DMET), and bis(ethylenedithio)tetraselenafulvalene (BETS), which directly contribute to the superconductivity; (ii) organic counter cations such as R_4N^+ in M(dmit)$_2$ (M = Ni and Pd; dimt = isotrithionedithiolate) superconductors, which can

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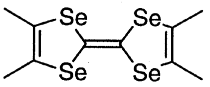
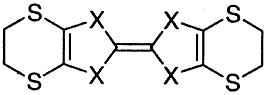
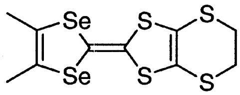
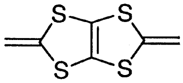
*Corresponding author. E-mail: yamada@sci.himeji-tech.ac.jp not participate in electrical conduction [3]. However, all the known π-electron donors belonging to the former category contain the tetrachalcogenafulvalene molecule. Therefore, the very important and challenging question in this field of whether or not the production of superconductors from a new organic π-electron donor containing no tetrachalcogenafulvalene molecule was feasible remained unsolved. The settlement of this long-standing issue would change the way of thinking of molecular designers for the design of an organic superconductor.

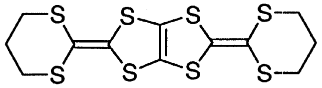
We describe here that BDA-TTP, which contains the bis-fused 1,3-dithiole-2-ylidene (BDY) unit instead of the tetrachalcogenafulvalene molecule as a π-electron system, provides three superconducting salts β-(BDA-TTP)$_2$X (X = SbF_6^-, AsF_6^-, and PF_6^- anions).


TMTSF


BEDT-TTF (X = S)
BETS (X = Se)


DMET


BDY unit


BDA-TTP

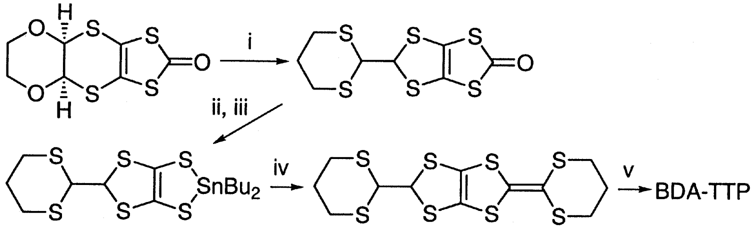
RESULT AND DISCUSSION

Synthesis

The synthesis of BDA-TTP was carried out as shown in Scheme 1, in analogy with the synthetic route to its dithiolane analogue reported by us earlier [4]. Plate-like single crystals of the BDA-TTP salts with SbF_6^-, AsF_6^-, and PF_6^- anions were prepared by the controlled-current electrocrystallization method [5] in 1,1,2-trichloroethane.

Magnetic and Electrical Properties

The zero-field-cooled (ZFC) temperature dependence of the dc magnetization for the SbF_6, AsF_6, and PF_6 salts of BDA-TTP, which was measured using multiple single crystals under an applied magnetic field of 1 Oe, revealed that the onset of diamagnetic transition occurs at temperatures of 6.9 K for the SbF_6 salt and of 5.9 K for both the AsF_6 and PF_6 salts (Figure 1). Based on their ZFC susceptibility curve at 2 K, we estimated



Reagents and conditions: i, 1,3-propanedithiole, $BF_3{\cdot}OEt_2$, $CHCl_3$, rt, 1 d (70%); ii, MeMgBr, THF, rt, 2 h; iii, Cl_2SnBu_2, THF, –78 °C → 0 °C; iv, ethyl 1,3-dithiane-2-carboxylate, Me_3Al, CH_2Cl_2, –78 °C → rt, overnight (41% overall yield); v, DDQ, toluene, reflux, 40 min (80%).

SCHEME 1 Synthesis of BDA-TTP.

ca. 15%, 20%, and 15% bulk superconductivities for the SbF_6, AsF_6, and PF_6 salts, respectively.

Figure 2 shows the resistivities of the SbF_6 and AsF_6 salts as a function of temperature under ambient pressure. The room-temperature conductivities were 1.5 S cm^{-1} for the SbF_6 salt and 2.9 S cm^{-1} for the AsF_6 salt. On the resistive behavior of the SbF_6 salt, the resistivity increased as that in a semiconductor on cooling from room temperature to near 150 K, and then exhibited metallic behavior down to 7.5 K. Below this temperature, the resistivity displayed an abrupt drop and became almost zero below 6.5 K. The onset of superconducting transition observed in the subsequent heating process (the inset in Figure 2) was at 7.5 K, which is

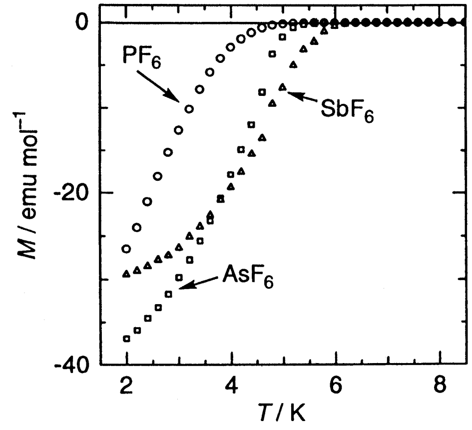


FIGURE 1 Temperature dependence of the ZFC dc magnetization for the SbF_6, AsF_6, and PF_6 salts.

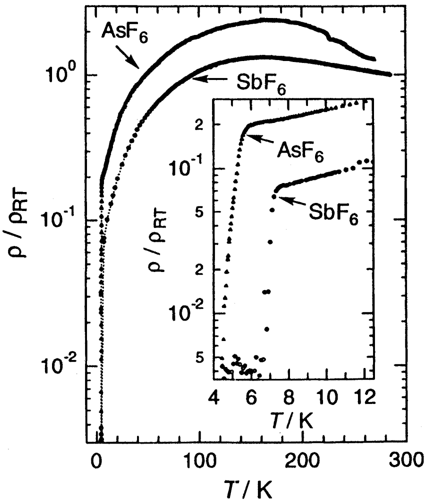


FIGURE 2 Temperature dependence of the relative resistivity for the SbF_6 and AsF_6 salts.

slightly higher than that in the magnetization measurement. Similar resistive maximum and superconductive behavior were found in the temperature dependence of the resistivity of the AsF_6 salt. Below near 160 K, the resistivity of this salt decreased with decreasing temperatures down to a superconducting transition with onset at 5.8 K which is comparable to that of the magnetic transition, and almost zero resistance was observed below 4.4 K. Although we carried out resistive measurements on numerous single crystals of the PF_6 salt (a representative room-temperature conductivity, 3.8 S cm^{-1}), all the crystal specimens were found to disintegrate at temperatures in the range of 110–140 K. Owing to the fragile nature of the crystals, superconducting transition of this salt could not be determined by resistive measurements.

Crystal Structures

All these superconductors crystallized in the triclinic space group $P\bar{1}$, and they are isostructural. Figure 3 shows the crystal structure of (BDA-TTP)$_2$SbF$_6$, in which the molecular packing mode is very similar to that in β-(BEDT-TTF)$_2$I$_3$ [6]. The molecular structure of BDA-TTP in this salt is nonplanar, and its two outer dithiane rings favor chair conformations, though nonequivalent, with dihedral around the intramolecular sulfur-to-sulfur axis of 47.9° and 33.2°, respectively. The BDA-TTP molecules are stacked along the [101] direction and somewhat dimerized: the donor

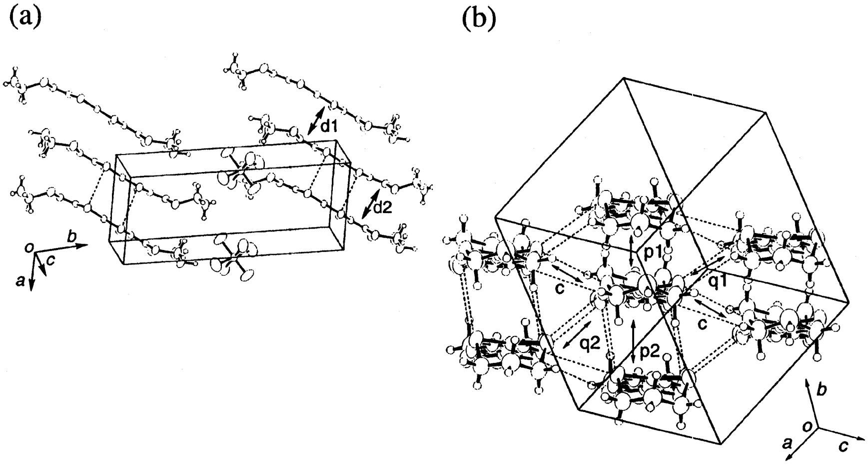


FIGURE 3 Crystal Structure of $(BDA\text{-}TTP)_2SbF_6$. Intermolecular S···S contacts (< 3.70 Å) are indicated by dotted lines. In (b), the values of intermolecular overlap integrals are $c = -0.44$, $p1 = 14.7$, $p2 = 6.26$, $q1 = 8.14$, and $q2 = 8.89$ ($\times 10^{-3}$).

molecules alternate at the average interplanar distances of 3.52 Å (d1 in Figure 3a) and 3.80 Å (d2 in Figure 3a). The two donor molecules being 3.52 Å apart are mutually shifted, while one pair with interplanar spacing of 3.80 Å has a nearly eclipsed arrangement.

There are several intermolecular S···S contacts shorter than the sum of van der Waals radii (3.70 Å) between stacks, but within a stack, fewer S···S contacts are observed. This contact pattern reflects the small anisotropy of the intermolecular overlap integral in the *ac* plane (Figure 3b), resulting in the two-dimensional electronic structure peculiar to the β-structure. Furthermore, it is noteworthy that the largest overlap integrals in all three BDA-TTP superconductors (14.7, 14.8, and 13.9×10^{-3} for the SbF_6, AsF_6, and PF_6 salts, respectively) are roughly half of those in the known organic superconductors such as β-$(BEDT\text{-}TTF)_2I_3$ (24.5×10^{-3})[7] and κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ (25.7×10^{-3}),[8] suggesting that they are characterized as a superconductor system with loose donor packing.

REFERENCES

[1] Bechgaard, K., Carneiro, K., Rasmussen, F. B., Olsen, M., Rindorf, G., Jacobsen, C. S., Pedersen, H. J., & Scott, J. C. (1981). ***J. Am. Chem. Soc.***, ***103***, 2440, and references therein.

[2] Ishiguro, T., Yamaji, K., & Saito, G. (1998). ***Organic Superconductors*** (2nd ed.). Berlin: Springer; Williams, J. M., Ferraro, J. R., Thorn, R. J. Carlson, K. D., Geiser, U., Wang,

H. H., Kini, A. M., & Whangbo, M.-H. (1992). *Organic Superconductors (Including Fullerenes)*. Prentice Hall: Englewood Cliffs.

[3] Kobayashi, A., & Kobayashi, H. In *Handbook of Organic Conductive Molecules and Polymers* Chichester: John Wily & Sons, 1997, **2**, 249.

[4] Yamada, J., Watanabe, M., Anzai, H., Nishikawa, H., Ikemoto, I., & Kikuchi, K. (1999). *Angew. Chem. Int. Ed.*, *38*, 810.

[5] Anzai, H., Delrieu, J. M., Takasaki, S., Nakatsuji, S., & Yamada, J. (1995). *J. Cryst. Growth*, *154*, 145; Nishikawa, H., Ishikawa, H., Sato, T., Kodama, T., Ikemoto, I., Kikuchi, K., Tanaka, S., Anzai, H., & Yamada, J. (1998). *J. Mater. Chem.*, *8*, 1321.

[6] Williams, J. M., Emge, T. J., Wang, H. H., Beno, M. A., Copps, P. T., Hall, L. N., Carlson, K. D. & Crabtree, G. W. (1984). *Inorg. Chem.*, *23*, 2560.

[7] Mori, T., Kobayashi, A., Sasaki, Y., Kobayashi, H., Saito, G., & Inokuchi, H. (1984). *Chem. Lett.*, 957.

[8] Oshima, K., Mori, T., Inokuchi, H., Urayama, H., Yamochi, H., & Saito, G. (1988). *Phys. Rev.*, *B38*, 938.