# Structural and Physical Properties of $\lambda$-(BEST)$_2$MCl$_4$ (BEST = Bis(ethylenediseleno)tetrathiafulvalene; M = Fe, Ga) and Analogous Magnetic Organic Conductor

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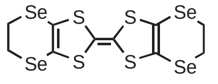
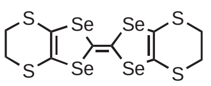
In contrast to $\lambda$-(BETS)$_2$MCl$_4$ (M = Fe, Ga) with superconducting (Ga) or $\pi$–d coupled antiferromagnetic insulating (Fe) ground states, $\lambda$-(BEST)$_2$MCl$_4$ (M = Ga, Fe) are semiconducting at ambient pressure despite of the close similarity of the crystal structures. There exists another triclinic modification of BEST conductor with FeBr$_4^-$ exhibiting metal-insulator and antiferromagnetic transitions.

Recently, the development of magnetic organic conductors has attracted a considerable interest because unprecedented organic conductors such as antiferromagnetic organic superconductor, $\kappa$-(BETS)$_2$FeBr$_4$, magnetic field-induced superconductor, $\lambda$-(BETS)$_2$FeCl$_4$ and ferromagnetic organic metal, (ET)$_3$-[MnCr(C$_2$O$_4$)$_3$](CH$_2$Cl$_2$) have been discovered (BETS = bis(ethylenedithio)tetraselenafulvalene; ET = (ethylenedithio)-tetrathiafulvalene).[1–3] However, no conductor except BETS systems exhibits distinct dual-functional electro-magnetic properties originated from the interplay of $\pi$ metal electrons and localized 3d magnetic moments. Considering that the close contacts between chalcogen atoms and magnetic anions are essential to enhance the $\pi$–d interaction, $\pi$ donor molecule, BEST (bis(ethylenediseleno)tetrathiafulvalene) with protruded Se atoms in the six-membered rings might be a suitable $\pi$ donor to construct new magnetic organic conductors. Since fascinating magnetic organic conductors have been found in BETS conductors with $\lambda$- and $\kappa$-type structures, we have tried to prepare similar crystals by using BEST, an isomer of BETS.

In contrast to BETS conductors, BEST conductors hitherto developed are mostly nonmetallic.[4] Among them, $\kappa$-(BEST)$_2$-Cu[N(CN)$_2$]Br with two-dimensional metallic bands exhibited a metal–insulator transition at 25 K at ambient pressure and a superconducting transition at 7.5 K around 1.5 k bar.[5] Similar $\kappa$-type conductors, $\kappa$-(D)$_2$Cu[N(CN)$_2$]Br [D = ET,[6] MT (bis(methylenedithio)tetrathiafulvalene),[7] BETS[8]] are superconducting or metallic down to low temperatures at ambient pressure. Compared with $\kappa$-type salts, $\lambda$-type conductors are hardly obtainable owing to the inflexible accommodation space for the anion.[9] If the $\lambda$-type crystal of (BEST)$_2$FeCl$_4$ can be obtained, it will provide a crucial information to make clear the reason why the unique $\pi$–d coupled electro-magnetic properties could be realized in $\lambda$-(BETS)$_2$FeCl$_4$.

**Table 1.** The lattice constants of $\lambda$-type BEST salts. Those of $\lambda$-(BETS)$_2$FeCl$_4$ are also presented for comparison[11,12]


BEST


BETS

| | $\lambda$-(BEST)$_2$GaCl$_4$ | $\lambda$-(BEST)$_2$FeCl$_4$ | $\lambda$-(BETS)$_2$FeCl$_4$ |
|---|---|---|---|
| $a$ | 16.362(4) Å | 16.399(5) | 16.164 |
| $b$ | 18.226(4) | 18.178(5) | 18.538 |
| $c$ | 6.724(2) | 6.725(2) | 6.593 |
| $\alpha$ | 97.205(2)° | 97.185(3) | 98.40 |
| $\beta$ | 97.831(2) | 97.797(3) | 96.67 |
| $\gamma$ | 112.263(2) | 112.230(3) | 112.52 |
| $V$ | 1803.8(7) Å$^3$ | 1804.1(9) | 1773.0 |

BEST was prepared according to the literature method.[10] Similar to the case of BETS conductors, the black needle crystals of MCl$_4^-$ salts (M = Fe, Ga) were grown electrochemically. X-ray diffraction experiments revealed that the crystals have $\lambda$-type lattices. The lattice constants are listed in Table 1. The final $R(R_w)$ factors are 0.033(0.029) and 0.032(0.031) for M = Fe and Ga, respectively. The unit cell volumes ($V$) of these two BEST salts are almost equal to each other but about 30 Å$^3$ larger than the unit cell volume of $\lambda$-(BETS)$_2$FeCl$_4$, which is a serious disadvantage for $\lambda$-type BEST salts because it is well known that the "negative chemical pressure" due to the Br/Cl exchange in $\lambda$-(BETS)$_2$MBr$_x$Cl$_{4-x}$ makes the system insulating. For example, $\lambda$-(BETS)$_2$MBrCl$_3$ with unit cell volume about 15 Å$^3$ larger than that of $\lambda$-(BETS)$_2$MCl$_4$ is an insulator.[13,14] Moreover, unlike $\lambda$-(BETS)$_2$MBr$_x$Cl$_{4-x}$, where the lattice constants $b$ and $c$ are almost independent of $x$, the lattice constant $b$ of $\lambda$-(BEST)$_2$MCl$_4$ is smaller than that of $\lambda$-(BETS)$_2$MCl$_4$, which means the "negative chemical pressure" is considered to be fairly large in the $ac$ conduction plane of $\lambda$-(BEST)$_2$MCl$_4$. The crystal structure is shown in Figure 1. There are two crystallographically independent BEST molecules (A, B), which are stacked to form the tetrameric colums along the $a$ axis. Similar to $\lambda$-(BETS)$_2$MCl$_4$, each tetrahalide anion is surrounded by the donor molecules. There are many short Cl···Se (S) contacts (see the caption of Figure 1). The short contact between Cl atom and chalcogen atom (S) of inner five-membered ring is one of the characteristic structural features of $\lambda$-type salt. The four-probe resistivity measurements were made along the $c$ axes (// needle axes of the crystals). The both salts showed almost the same resistivity behavior: $\sigma(\mathrm{RT}) = 10^{-1}\,\mathrm{S\,cm^{-1}}$ and $E_a = 0.13\,\mathrm{eV}$ (Figure 2). The conventional extended Hückel tight-binding band calculations were performed.[15] The amplitude of the highest occupied molecular orbital (HOMO) of molecule A was very small at the Se atoms where BEST molecule is strongly bent from the average molecular plane (Figure 3). Similar to $\lambda$-(BETS)$_2$FeBr$_x$Cl$_{4-x}$ ($x > 0.8$), $\lambda$-(BEST)$_2$FeCl$_4$ is semiconducting despite of the calculated Fermi surfaces. The magnetic susceptibility measurements by SQUID magnetometer down to 2 K showed the Curie–Weiss behavior of the localized magnetic moments of Fe$^{3+}$ ions ($S = 5/2$). The Weiss temperature was

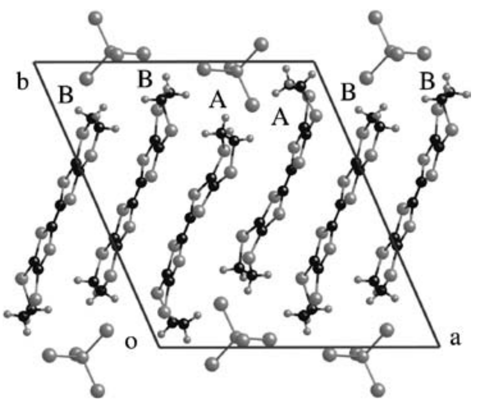
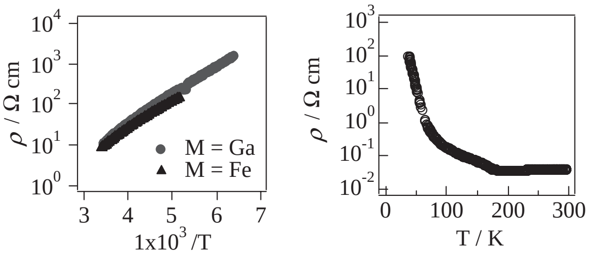
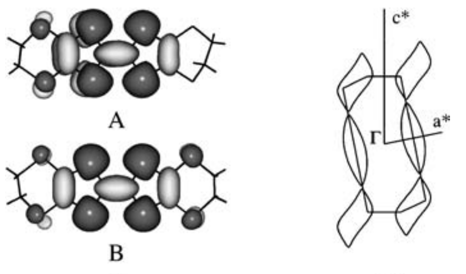


**Figure 1.** Crystal structure of $\lambda$-(BEST)$_2$FeCl$_4$. The intermolecular short contacts (Å) less than the corresponding van der Waals distances are: Se···Se, 3.539, 3.588, 3.594, 3.683, 3.707, 3.943, 3.996; Se···S, 3.563, 3.631, 3.738, 3.757; S···S, 3.568, 3.624; Se···Cl, 3.287, 3.540, 3.586, 3.736, 3.748; S···Cl, 3.641. $\lambda$-(BEST)$_2$GaCl$_4$ has almost the same crystal structure.



(a) (b)

**Figure 2.** (a) Resistivity of $\lambda$-(BEST)$_2$MCl$_4$ (M = Fe, Ga) and (b) (BEST)$_2$FeBr$_4$.



(a) (b)

**Figure 3.** (a) HOMO of two independent molecules A and B of $\lambda$-(BEST)$_2$FeCl$_4$. (b) Fermi surface of $\lambda$-(BEST)$_2$FeCl$_4$ calculated by extended Hückel tight-binding approximation.

$\theta = -8.2$ K. Preliminary high-pressure resistivity measurements up to about 10 kbar showed large resistivity decrease but the system was still semiconducting. Further studies will be made in near future.

We have also obtained another triclinic modification, (BEST)$_2$FeBr$_4$. The lattice constants are: $a = 6.175(3)$, $b = 8.335(4)$, $c = 33.32(2)$ Å, $\alpha = 89.426(11)$, $\beta = 89.148(11)$, $\gamma = 94.634(19)°$, $V = 1856.4(16)$ Å$^3$, $Z = 2$. The unit cell volume is almost equal to that of $\lambda'$-(BETS)$_2$GaBr$_4$ with modified $\lambda$-type structure ($V = 1851.5$ Å$^3$).[16] There are two independent weakly dimeric columns along the $b$ axis. As shown in Figure 2, the resistivity showed a metallic behavior ($\sigma$(RT) = 25 S cm$^{-1}$) but exhibited a transition around 180 K where the resistivity showed an anomaly and began to increase gradually with lowering temperature. Below about 60 K, the resistivity was increased rapidly. The magnetic susceptibility measurements on polycrystalline sample down to 1.9 K showed a slight maximum around 4 K, suggesting the antiferromagnetic ordering of Fe$^{3+}$ moments ($T_N \approx 4$ K). An isostructural (BEST)$_2$InBr$_4$ also showed a metallic behavior around the room temperature.

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## References and Notes

1 E. Ojima, H. Fujiwara, K. Kato, H. Kobayashi, H. Tanaka, A. Kobayashi, M. Tokumoto, and P. Cassoux, *J. Am. Chem. Soc.*, **121**, 5581 (1999); H. Fujiwara, E. Ojima, Y. Nakazawa, B. Zh. Narymbetov, K. Kato, H. Kobayashi, A. Kobayashi, M. Tokumoto, and P. Cassoux, *J. Am. Chem. Soc.*, **123**, 306 (2001).

2 S. Uji, H. Shinagawa, T. Terashima, C. Terakura, T. Yakabe, Y. Terai, M. Tokumoto, A. Kobayashi, H. Tanaka, and H. Kobayashi, *Nature*, **410**, 908 (2001); H. Fujiwara, H. Kobayashi, E. Fujiwara, and A. Kobayashi, *J. Am. Chem. Soc.*, **124**, 6816 (2002).

3 E. Coronado, J. R. Galán-Mascarós, C. J. Gómez-García, and V. Laukhin, *Nature*, **408**, 447 (2000).

4 For example, H. H. Wang, L. K. Montgomery, U. Geiser, L. C. Porter, K. D. Carlson, J. R. Ferraro, J. M. Williams, C. S. Cariss, R. L. Rubinstein, J. R. Whitworth, M. Evain, J. Novoa, and M.-H. Whangbo, *Chem. Mater.*, **1**, 140 (1989); R. N. Lyubovskaya, E. I. Zhilyaeva, S. A. Torunova, O. A. Bogdanova, S. V. Konovalikhin, O. A. Dyachenko, and R. B. Lyubovskii, *Synth. Met.*, **85**, 1581 (1997).

5 J. Sakata, H. Sato, A. Miyazaki, T. Enoki, Y. Okano, and R. Kato, *Solid State Commun.*, **108**, 377 (1998).

6 A. M. Kini, U. Geiser, H. H. Wang, K. D. Carlson, J. M. Williams, W. K. Kwok, K. G. Vandervoort, J. E. Thompson, D. L. Stupka, D. Jung, and M.-H. Whangbo, *Inorg. Chem.*, **29**, 2555 (1990).

7 T. Naito, K. Bun, A. Miyamoto, H. Kobayashi, H. Sawa, R. Kato, and A. Kobayashi, *Synth. Met.*, **56**, 2234 (1993).

8 The resistivity behavior and the lattice constants of $\kappa$-(BETS)$_2$-Cu[N(CN)$_2$]Br were reported by Montgomery et al. (L. K. Montgomery, T. Burgin, J. C. Huffman, K. D. Carlson, J. D. Dudek, G. A. Yaconi, L. A. Megna, P. R. Mobley, W. K. Kwok, J. M. Williams, J. E. Schirber, D. L. Overmyer, J. Ren, C. Rovira, and M.-H. Whangbo, *Synth. Met.*, **56**, 2090 (1993)). Despite of the sample dependence, one sample showed $\kappa$-(BETS)$_2$Cu[N(CN)$_2$]-Br to be metallic down to low temperature.

9 H. Kobayashi, H. Cui, and A. Kobayashi, *Chem. Rev.*, **104**, 5256 (2004).

10 V. Y. Lee, *Synth. Met.*, **20**, 161 (1987).

11 A. Kobayashi, T. Udagawa, H. Tomita, T. Naito, and H. Kobayashi, *Chem. Lett.*, **1993**, 2179.

12 H. Kobayashi, H. Tomita, T. Naito, A. Kobayashi, F. Sakai, T. Watanabe, and P. Cassoux, *J. Am. Chem. Soc.*, **118**, 368 (1996).

13 H. Kobayashi, H. Akutsu, E. Arai, H. Tanaka, and A. Kobayashi, *Phys. Rev.*, **B56**, R8526 (1997); H. Tanaka, A. Kobayashi, A. Sato, H. Akutsu, and H. Kobayashi, *J. Am. Chem. Soc.*, **121**, 760 (1999).

14 H. Akutsu, K. Kato, E. Ojima, H. Kobayashi, H. Tanaka, A. Kobayashi, and P. Cassoux, *Phys. Rev.*, **B58**, 9294 (1998).

15 The exponents $\zeta$ and the ionizatiom potential (eV) for atomic orbitals are: Se 4s, 2.122, −20.0; Se 4p, 1.827, −11.0; S 3s, 2.122, −22.0; S 3p, 1.827, −10.5; C 2s, 1.625, −21.4; C 2p, 1.625, −11.4; H 1s, 1.0, −13.6.

16 H. Tanaka, A. Kobayashi, and H. Kobayashi, *Chem. Lett.*, **1999**, 133.

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