JOURNAL OF
Materials
CHEMISTRY
Communication

A new κ-type organic superconductor based on BETS molecules, κ-(BETS)$_2$GaBr$_4$ [BETS = bis(ethylenedithio)tetraselenafulvalene]

Hisashi Tanaka,[a] Emiko Ojima,[a] Hideki Fujiwara,[a] Yasuhiro Nakazawa,[a]
Hayao Kobayashi*[a] and Akiko Kobayashi[b]

[a]*Institute for Molecular Science, Myodaiji-cho, Okazaki 444-8585, Japan*
[b]*Research Centre for Spectrochemistry, Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan*

Received 31st August 1999, Accepted 4th November 1999

Similar to the recently discovered organic conductor κ-(BETS)$_2$FeBr$_4$ exhibiting a transition from an antiferromagnetic metal phase to a superconducting phase at 1.0 K, κ-(BETS)$_2$GaBr$_4$ shows a superconducting transition around 0.5–1.0 K, indicating T_C of κ-(BETS)$_2$MBr$_4$ (M = Fe, Ga) to be almost independent of the existence of magnetic anions; from these findings a way to develop novel organic conductors with controlled antiferromagnetic interactions is suggested.

In recent studies on the development of new organic conductors, the enhancement of dimensionality of the electronic structures has been one of the fundamental guiding principles. In this respect, conductors with so-called 'κ-type structure' have been long regarded as the most promising systems to produce organic superconductors since the first discovery of a κ-type BEDT-TTF superconductor in 1987 [BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene].[1–4]

Bis(ethylenedithio)tetraselenafulvalene (BETS) is a selenium derivative of BEDT-TTF, whose 2 : 1 salts with linear, tetrahedral and octahedral anions such as I_3^-, ClO_4^- and PF_6^- have been studied systematically in the early 1990s with the aim of searching for new series of conductors having stable two-dimensional metal states[5] and many BETS salts prepared at that time were revealed to have stable metallic states down to low temperature.[5–11] Specifically, all the κ-type BETS salts showed metallic states around liquid helium temperature.

Very recently, we have reported that κ-(BETS)$_2$FeBr$_4$ undergoes successive phase transitions with lowering temperature from a paramagnetic metal state to an antiferromagnetic metal state at 2.5 K (T_N) and from an antiferromagnetic metal state to a superconducting state at 1.0 K (T_C).[12] This is the first finding of superconductivity in κ-type BETS salts. Furthermore, it is strongly indicated that antiferromagnetic ordering of Fe^{3+} spins and superconductivity coexist below 1.0 K.[13] Thus, κ-(BETS)$_2$FeBr$_4$ is a unique system, which enables us to study the relation between superconductivity and magnetic order and the role of the interaction between π conduction electrons and localized magnetic moments in organic conductors. We have reported that the resistivity behavior of κ-(BETS)$_2$FeBr$_4$ and κ-(BETS)$_2$GaBr$_4$ at 2–300 K closely resemble each other.[6] Therefore, it may be expected that κ-(BETS)$_2$GaBr$_4$ undergoes a superconducting transition below 2 K. Here, the results of low-temperature resistivity measurements of κ-(BETS)$_2$GaBr$_4$ are presented. The structural and electrical properties of the mixed-halogenogallate anion system, κ-(BETS)$_2$GaBr$_x$Cl$_{4-x}$ ($x \approx 2.0$), are also reported briefly.

Plate-like crystals of κ-(BETS)$_2$GaBr$_x$Cl$_{4-x}$ ($x = 0.0, 2.0, 4.0$) were prepared by electrochemical oxidation of BETS (5 mg) in a mixed solvent (20 ml) of 90% chlorobenzene–10% ethanol containing the (NEt$_4$)GaCl$_4$ and/or (NEt$_4$)GaBr$_4$ electrolyte (total 15–20 mg). For crystallization using the mixed electrolyte, exchange of halogen atoms (Br, Cl) occurred immediately in solution, and mixed-halogenogallate anions, $GaBr_xCl_{4-x}^-$ were formed.[14] The value of x of the mixed-halogenogallate system was estimated by electron probe microanalysis (EPMA) and X-ray diffraction experiments, and was found to be approximately equal to the 1 : 1 ratio of (NEt$_4$)GaCl$_4$ and (NEt$_4$) GaBr$_4$ in the solution. It was essential to dissolve the electrolytes completely and leave the solutions to stand for 12–24 h before starting electrochemical oxidation in order to obtain crystals with the desired compositions.

Crystals of κ-(BETS)$_2$GaBr$_x$Cl$_{4-x}$ belong to the orthorhombic system with space group *Pnma*.[6] Low temperature magnetoresistance experiments showed that κ-(BETS)$_2$GaCl$_4$ has a two-dimensional cylindrical Fermi surface.[15] As reported in a previous paper,[14] the anionic sites of λ-(BETS)$_2$-GaBr$_x$Cl$_{4-x}$ can accommodate only a small number of Br atoms ($0 \leqslant x \leqslant 2$), while κ-(BETS)$_2$GaBr$_xCl_{4-x}$ crystals can adopt any value of $0 \leqslant x \leqslant 4$. Furthermore, we have recently found that larger anions such as $InBr_4^-$ and $TlCl_4^-$ can be also accommodated in κ-type structures owing to the flexibility of the anion space. The tetrahedral anions of κ-(BETS)$_2$-GaBr$_x$Cl$_{4-x}$ lie on mirror planes and the distribution of Br atoms is not completely random. This behavior is similar to that for λ-(BETS)$_2$GaBr$_x$Cl$_{4-x}$ in which Br atoms have preferred positions.[14] Fig. 1 shows the Br population on each halogen site in κ-(BETS)$_2$GaBr$_x$Cl$_{4-x}$ ($x \approx 2.0$), as estimated

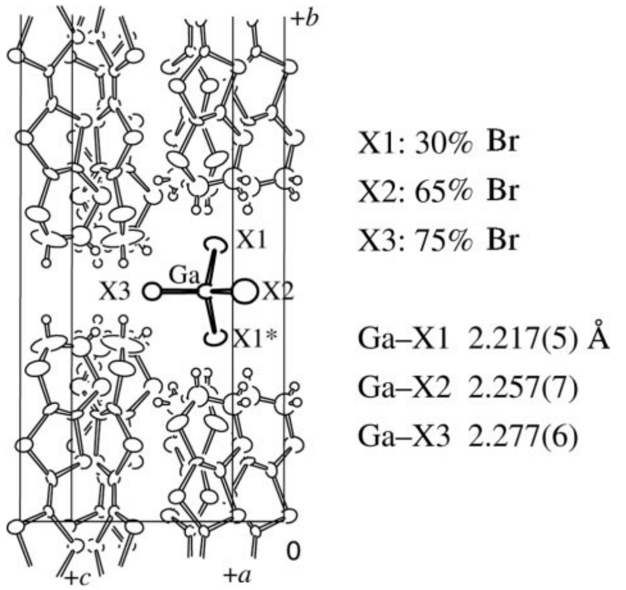

Fig. 1 The occupancy probabilities (%) of Br on each halogen site of an anion and Ga–X bond lengths in κ-(BETS)$_2$GaBr$_x$Cl$_{4-x}$ ($x = 2.0$). Halogen atoms, X2 and X3 and the gallium atom lie on the mirror plane.

from X-ray structure refinements. Br atoms tend to be distributed on X2 and X3 sites, and the largest occupation probability of Br atoms on X3 is consistent with the longest bond length being Ga–X3. A low Br distribution on X1 is due to the closer contacts between X1 and the atoms of surrounding BETS molecules.

Electrical resistivities were measured by the conventional four-probe method along the conduction planes of the crystals (parallel to the *ac* plane). Fig. 2 shows the electrical resistivities of κ-(BETS)$_2$GaBr$_x$Cl$_{4-x}$ ($x = 0.0$, 2.0, 4.0) down to 2 K. The room temperature resistivities are 30–50 S cm^{-1}. As reported previously,[6] unlike κ-(BETS)$_2$GaCl$_4$, which shows a normal metallic behavior, κ-(BETS)$_2$GaBr$_4$ exhibited a characteristic broad resistivity maximum around 70 K, while κ-(BETS)$_2$-GaBr$_2$Cl$_2$ showed an intermediate resistivity behavior. The suppression of the broad resistivity maximum in the system with $x = 2.0$ is reminiscent of the 'chemical pressure effect' on the resistivity of λ-(BETS)$_2$GaBr$_x$Cl$_{4-x}$. However, for λ-type BETS salts, the resistivity is more sensitive to the bromine content and the crystal with $x > 0.8$ adopts an insulating ground state, indicating strong electron correlation in λ-type salts.[14,16] On the other hand, crystals of all the κ-type BETS salts are metallic around liquid helium temperature, which is consistent with the well known high stability of metallic states of κ-type organic conductors.

Since the superconducting transition of the λ-type BETS salts with tetrahalogenogallate seems to be enhanced in systems with larger anions, or 'strong negative chemical pressure',[14,16] κ-(BETS)$_2$GaBr$_4$ is the most promising system to exhibit a superconducting transition in the series κ-(BETS)$_2$GaBr$_x$Cl$_{4-x}$. We measured the resistivity of κ-(BETS)$_2$GaBr$_4$ down to 0.1 K using a ^{3}He–^{4}He dilution system and as shown in Fig. 3, a superconducting transition was observed around 0.5–1.0 K. This is the second observation of superconductivity in κ-type BETS conductors following the recent observation in κ-(BETS)$_2$FeBr$_4$.[12] The magnetic field dependence of the resistivity suggested the onset of the superconducting transition around 1.3 K but compared with the transition of κ-(BETS)$_2$FeBr$_4$, this superconducting transition is not so sharp. The superconducting transition begins to disappear under a weak magnetic field and is completely absent at *ca.* 3.0 kOe.

The discovery of superconductivity in κ-(BETS)$_2$FeBr$_4$ and κ-(BETS)$_2$GaBr$_4$ suggests the importance of a suitable size of anion, *i.e.*, a suitable 'chemical pressure' to realize the superconductivity. T_C values of 1.0–0.5 K for κ-(BETS)$_2$GaBr$_4$ and 1.0 K for κ-(BETS)$_2$FeBr$_4$ indicate that the superconductivities of these systems are almost independent of the magnetic nature of the anions. Similarly to λ-(BETS)$_2$Fe$_x$Ga$_{1-x}$Br$_y$Cl$_{4-y}$ which exhibits many novel transport phenomena such as superconductor-to-metal and superconductor-to-insulator transitions,[17] the electronic properties of κ-type salts with mixed anions will be very interesting. It is suspected that κ-(BETS)$_2$Fe$_x$Ga$_{1-x}$Br$_4$ will undergo a superconducting transition at around 1 K irrespective of the value of x, while the antiferromagnetic interaction will be weakened with increasing Ga content and the antiferromagnetic transition temperature will be lowered. Whether it is possible to observe the antiferromagnetic phase transition below the superconducting transition at a given value of x will be examined in the near future.

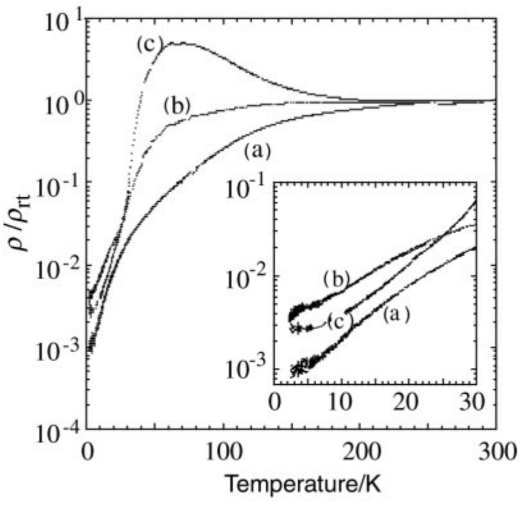

Fig. 2 Resistivity of κ-(BETS)$_2$GaBr$_x$Cl$_{4-x}$ [$x = 0.0$ (a), 2.0 (b) or 4.0 (c)].

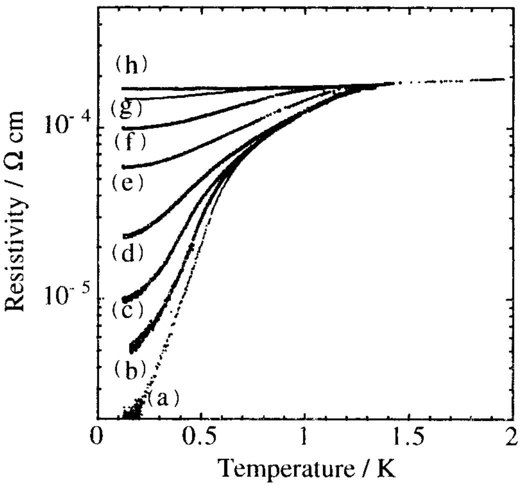

Fig. 3 The magnetic field-dependence of the resistivities of κ-(BETS)$_2$-GaBr$_4$ at (a) 0, (b), 0.02, (c) 0.05, (d) 0.1, (e) 0.3, (f) 0.7, (g) 1.5 and (h) 3.0 kOe. The magnetic field is perpendicular to the *ac* plane.

Notes and references

1 A. Kobayashi, R. Kato, H. Kobayashi, S. Moriyama, Y. Nishio, K. Kajita and W. Sasaki, *Chem. Lett.*, 1987, 459; R. Kato, H. Kobayashi, A. Kobayashi, S. Moriyama, Y. Nishio, K. Kajita and W. Sasaki, *Chem. Lett.*, 1987, 507.

2 H. Urayama, H. Yamochi, G. Saito, K. Nozawa, T. Sugano, M. Kinoshita, S. Sato, K. Oshima, A. Kawamoto and J. Tanaka, *Chem. Lett.*, 1988, 55; K. Oshima, T. Mori, H. Inokuchi, H. Urayama, H. Yamochi and G. Saito, *Phys. Rev. B*, 1988, **38**, 938.

3 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.*, 1990, **29**, 2555.

4 J. M. Williams, A. M. Kini, H. H. Wang, K. D. Carlson, U. Geiser, L. K. Montgomery, G. J. Phyrka, D. M. Watkins, J. M. Kommers, S. J. Boryschuk, A. V. S. Crouch, W. K. Kwok, J. E. Schirber, D. L. Overmyer, D. Jung and M.-H. Whangbo, *Inorg. Chem.*, 1990, **29**, 3272.

5 R. Kato, H. Kobayashi and A. Kobayashi, *Synth. Met.*, 1991, **42**, 2093; A. Kobayashi, R. Kato, T. Naito and H. Kobayashi, *Synth. Met.*, 1993, **56**, 2078.

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

7 L. K. Montgomery, T. Burgin, J. C. Huffman, K. D. Carlson, J. D. Dudek, G. A. Yaconi, L. A. Magna, 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.*, 1993, **55–57**, 2090.

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

9 H. Tanaka, A. Kobayashi and H. Kobayashi, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 3137.

10 N. D. Kushch, L. I. Buravov, S. I. Pesotskii, R. B. Lyubovskii, É. B. Yagubskii, M. G. Kaplunov, E. V. Golubev, B. Narymbetov, S. S. Khasanov, L. V. Zorina, L. P. Rozenberg, R. P. Shibaeva, A. Kobayashi and H. Kobayashi, *J. Mater. Chem.*, 1998, **8**, 897.

11 B. Narymbetov, N. D. Kushch, L. V. Zorina, S. S. Khasanov, R. P. Shibaeva, T. G. Togonidze, A. E. Kovalev, M. V. Kartsovnik,

L. I. Bravov, E. B. Yagubskii, E. Canadell, A. Kobayashi and H. Kobayashi, *Eur. Phys. J. B*, 1998, **5**, 179.

12 E. Ojima, H. Fujiwara, K. Kato, H. Kobayashi, H. Tanaka, A. Kobayashi, M. Tokumoto and P. Cassoux, *J. Am. Chem. Soc.*, 1999, **121**, 5581.

13 Very recently, one of the authors (Y. N.) has found a large anomaly in the heat capacity of κ-$(BETS)_2FeBr_4$ around 2.4 K corresponding to the antiferromagnetic Fe^{3+} spin ordering whereas the anomaly corresponding to the superconducting transition at 1 K was very small. This indicates that the system retains antiferromagnetic ordering even below the superconducting transition temperature. Therefore the antiferromagnetic ordering of Fe^{3+} spins and superconductivity of the π electron system are considered to coexist below 1 K.

14 H. Tanaka, A. Kobayashi, A. Sato, H. Akutsu and H. Kobayashi, *J. Am. Chem. Soc.*, 1999, **121**, 760.

15 H. Tajima, A. Kobayashi, T. Naito and H. Kobayashi, *Solid State Commun.*, 1996, **98**, 755; S. I. Pesotskii, R. B. Lyubovskii, N. D. Kushch, M. V. Kartsovnik, W. Biberacher, K. Andres, H. Kobayashi and A. Kobayashi, *J. Exp. Theor. Phys.*, 1999, **88**, 114.

16 H. Kobayashi, H. Akutsu, E. Arai, H. Tanaka and A. Kobayashi, *Phys. Rev. B*, 1997, **56**, R8526.

17 H. Kobayashi, A. Sato, E. Arai, H. Akutsu, A. Kobayashi and P. Cassoux, *J. Am. Chem. Soc.*, 1997, **117**, 12392; A. Sato, E. Ojima, H. Kobayashi, A. Kobayashi and P. Cassoux, *Chem. Lett.*, 1998, 673; H. Kobayashi, A. Sato, H. Tanaka, A. Kobayashi and P. Cassoux, *Coord. Chem. Rev.*, 1999, **190–192**, 921.

Communication a908789c