

A new organic superconductor, β -(BDA-TTP) $_2$ GaCl $_4$ [BDA-TTP = 2,5-(1,3-dithian-2-ylidene)-1,3,4,6-tetrathiapentalene]

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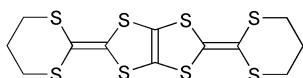
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The preparation, crystal structure and physical properties of β -(BDA-TTP) $_2$ GaCl $_4$ has been investigated; the salt exhibits superconductivity at 3.1 K (onset) under a hydrostatic pressure of 7.6 kbar.

The majority of organic superconductors have so far been based on tetrachalcogenafulvalene donors, such as TMTSF (tetramethyltetraselenafulvalene), BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene], DMET [dimethyl(ethylenedithio)diselenadithiafulvalene] and BETS [bis(ethylenedithio)tetraselenafulvalene].¹ Meanwhile, we have found that BDA-TTP, which comprises the bis-fused 1,3-dithiol-2-ylidene (BDY) unit as a π -electron system, gives ambient-pressure superconductors β -(BDA-TTP) $_2$ X (X = SbF $_6$, AsF $_6$, PF $_6$).² Further characterisation of β -(BDA-TTP) $_2$ SbF $_6$ revealed that this superconductor has the largest value of the effective cyclotron mass ($m_c^* = 12.4 \pm 1.1 m_e$) yet found in an organic superconductor.³ In addition to our continued interest in the development of new organic superconductors,^{4,5} this result prompted us to undertake the pursuit of other BDA-TTP-based superconductors. In this communication, we report the discovery of superconductivity in β -(BDA-TTP) $_2$ GaCl $_4$ under pressure.



BDA-TTP

(BDA-TTP) $_2$ GaCl $_4$ was obtained by the controlled-current electrocrystallization method⁶ in 5% acetone-PhCl (60 mL) containing BDA-TTP (0.08 mmol) and Et $_4$ NGaCl $_4$ (0.43 mmol) and was accompanied by a small amount of the solvated (BDA-TTP) $_3$ GaCl $_4$ ·PhCl. The structures of these GaCl $_4$ salts of BDA-TTP were determined by X-ray analyses.[†]

The crystal structure of (BDA-TTP) $_2$ GaCl $_4$ was found to be isostructural to that of β -(BDA-TTP) $_2$ FeCl $_4$,⁷ featuring layers of BDA-TTP donor molecules alternating with anion layers as shown in Fig. 1(a). The unit cell consists of one GaCl $_4$ ⁻ anion and two crystallographically independent BDA-TTP molecules. The structures of two independent BDA-TTP molecules, including the conformation of the two outer dithiane rings and the orientation of the two trimethylene end groups with respect to the molecular plane, are almost the same with each other. The donor molecules alternate at interplanar distances of 3.56 and 3.90 Å to form a slipped stack. No significant differences of both the pattern of intermolecular S...S contacts shorter than the sum of the van der Waals radii (3.70 Å) and the values of the intermolecular overlap integrals could be discerned between the donor layers of the GaCl $_4$ and FeCl $_4$ salts (Fig. 1(b)).

The temperature dependence of the resistivity of β -(BDA-TTP) $_2$ GaCl $_4$ indicated metallic behaviour from room temperature ($\sigma_{300} = 53 \text{ S cm}^{-1}$) to 118 K, at which temperature a

sharp metal-to-insulator (MI) transition occurred (Fig. 2). Surprisingly, the temperature of the MI transition decreased as pressure was increased and at 7.6 kbar, a trace of the MI transition followed by an abrupt drop in resistivity attributable to a superconducting transition with an onset of 3.1 K were observed. With further increases in the pressure up to 9.7 kbar, the MI transition was completely suppressed, but the superconducting transition still remained, the temperature of which gradually decreased at 9.0 and 9.7 kbar, respectively, as is found in most of the organic superconductors.¹ Similarly, we could ascertain the suppression of the MI transition and the appearance of the superconducting transition in the pressure-induced conducting behaviour of two different samples. As shown in Fig. 3, the magnetoresistance of β -(BDA-TTP) $_2$ GaCl $_4$ measured at various temperatures under an applied pressure of 8.3

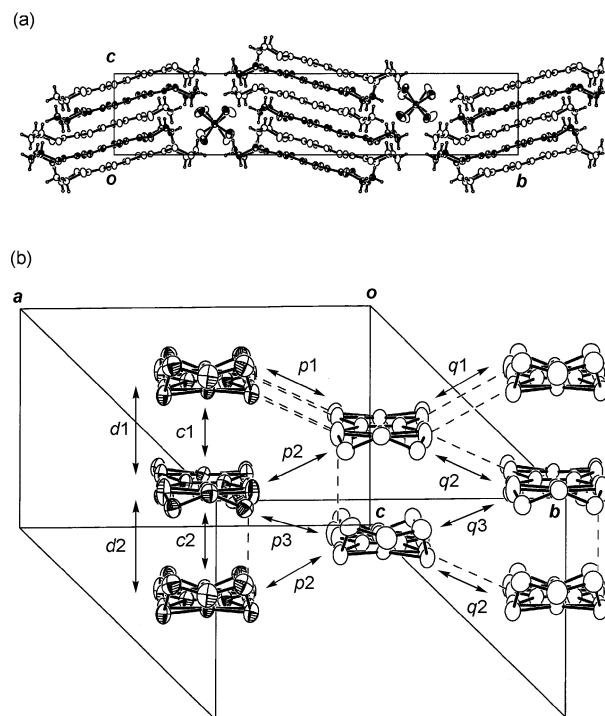


Fig. 1 (a) Crystal structure of β -(BDA-TTP) $_2$ GaCl $_4$ viewed along the a -axis; open circles indicate the back molecules. (b) Structure of the donor layer in β -(BDA-TTP) $_2$ GaCl $_4$. Hydrogen atoms are omitted for clarity. Intermolecular face-to-face distances of the BDA-TTP column are 3.56 ($d1$) and 3.90 ($d2$) Å. Short intermolecular S...S contacts (< 3.70 Å) are drawn by broken lines. Intermolecular overlap integrals $c1$, $c2$, $p1$, $p2$, $p3$, $q1$, $q2$ and $q3$ are 14.8, 13.4, 2.40, -7.03, 3.05, 6.92, -5.30 and 5.48×10^{-3} , respectively.

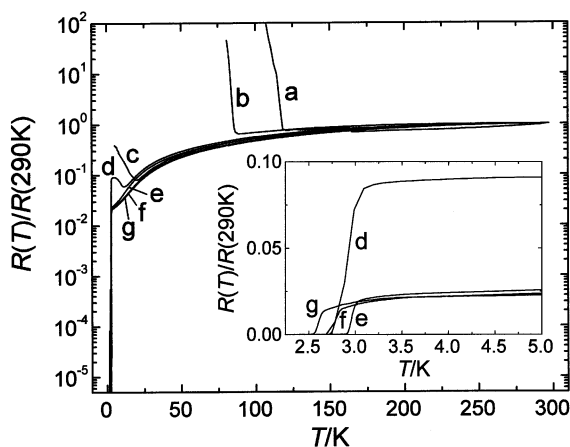


Fig. 2 Temperature dependence of the resistivity for β -(BDA-TTP) $_2$ GaCl $_4$ at 0 (a), 2.8 (b), 5.7 (c), 7.6 (d), 8.3 (e), 9.0 (f) and 9.7 (g) kbar, respectively. The inset shows the relative resistivity in the low-temperature region.

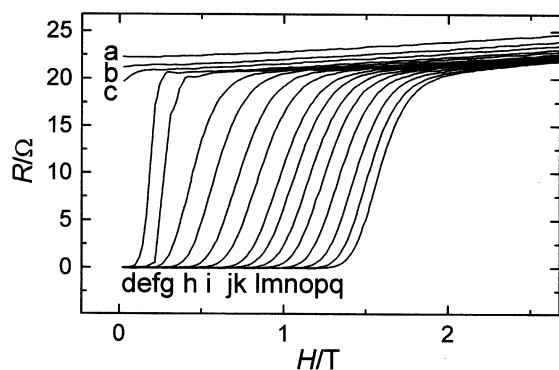


Fig. 3 Magnetoresistance of β -(BDA-TTP) $_2$ GaCl $_4$ under 8.3 kbar at 4.2 (a), 3.5 (b), 3.0 (c), 2.5 (d), 2.2 (e), 1.9 (f), 1.7 (g), 1.5 (h), 1.3 (i), 1.2 (j), 1.1 (k), 1.0 (l), 0.9 (m), 0.8 (n), 0.7 (o), 0.6 (p) and 0.48 (q) K, respectively.

kbar clearly indicated that the resistivity at all temperatures below 3.0 K was restored by increasing magnetic field, which adds to the superconductivity of this salt.

On the other hand, the resistivity of the solvated (BDA-TTP) $_3$ GaCl $_4$ ·PhCl showed a semiconductive temperature dependence with an activation energy of 150 meV around room temperature ($\sigma_{\text{rt}} = 3.3 \times 10^{-3}$ S cm $^{-1}$). The crystal structure of the solvated salt is isomorphous to that of (BDA-TTP) $_3$ FeCl $_4$ ·PhCl.⁷

In conclusion, we have discovered a new superconductor, β -(BDA-TTP) $_2$ GaCl $_4$, with a superconducting transition temperature of 3.1 K at 7.6 kbar, which is the first BDA-TTP salt to exhibit pressure-induced superconductivity. This discovery provides evidence that BDA-TTP can produce superconductors under pressure as well as at ambient pressure. Therefore, we are actively examining the pressure-induced conducting behaviour of our reported BDA-TTP salts and simultaneously preparing new BDA-TTP salts.

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Notes and references

† Crystal data for (BDA-TTP) $_2$ GaCl $_4$: C $_24$ H $_24$ Cl $_4$ GaS $_{16}$, $M = 1036.95$, monoclinic, space group $P2_1/a$, $a = 12.4693(11)$ Å, $b = 38.768(5)$ Å, $c = 7.7351(2)$ Å, $\beta = 91.1990(4)^\circ$, $U = 3738.4(6)$ Å 3 , $Z = 4$, $D_c = 1.84$ g cm $^{-3}$, $\mu(\text{Mo-K}\alpha) = 1.937$ mm $^{-1}$, $T = 298$ K, $R = 0.055$ and $R_w = 0.053$ for 5603 observed reflections with $I > 3\sigma(I)$ from 8344 unique reflections ($0.52^\circ \leq \theta \leq 27.51^\circ$). Max./min. residual electron density 0.569/−0.525 e Å $^{-3}$. GOF = 1.1052. Crystal data for (BDA-TTP) $_3$ GaCl $_4$ ·PhCl: C $_42$ H $_41$ Cl $_5$ GaS $_{24}$, $M = 1562.21$, monoclinic, space group $P2_1$, $a = 9.7552(9)$ Å, $b = 35.599(4)$ Å, $c = 8.840(2)$ Å, $\beta = 92.12(1)^\circ$, $U = 3067.9(6)$ Å 3 , $Z = 2$, $D_c = 1.691$ g cm $^{-3}$, $\mu(\text{Mo-K}\alpha) = 1.516$ mm $^{-1}$, $T = 298$ K, $R = 0.062$ and $R_w = 0.054$ for 5465 observed reflections with $I > \sigma(I)$ from 7508 unique reflections ($2.58^\circ \leq \theta \leq 27.51^\circ$). Max./min. residual electron density 0.81/−0.66 e Å $^{-3}$. GOF = 1.630. The data were collected on a Rigaku Quantum CCD X-ray system for (BDA-TTP) $_2$ GaCl $_4$ and on a Rigaku AFC5R four-circle diffractometer for (BDA-TTP) $_3$ GaCl $_4$ ·PhCl. The structures were solved by direct methods and refined by full-matrix least-square analysis (anisotropic for non-hydrogen atoms). The structure of (BDA-TTP) $_3$ GaCl $_4$ ·PhCl was refined as a racemic twin with the Flack parameter refining to 0.158(1). All diagrams and calculations were performed using the teXsan and CRYSTALS crystallographic software packages. CCDC 212143–212144. See <http://www.rsc.org/suppdata/cc/b3/b306314c/> for crystallographic data in .cif or other electronic format.

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