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A new organic superconductor, $(DODHT)_2BF_4{\cdot}H_2O$

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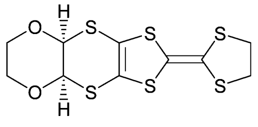
In addition to two organic superconductors $(DODHT)_2X$ [DODHT = (1,4-dioxane-2,3-diyldithio)dihydrotetrathiafulvalene; X = PF_6 and AsF_6] previously reported by us, the BF_4 salt of DODHT containing one water molecule [$(DODHT)_2BF_4{\cdot}H_2O$] has been found to undergo a superconducting transition at 3.2 K under a hydrostatic pressure of 15.5 kbar.

We have found that the DODHT donor, which has a *cis*-fused dioxane ring and a reduced π-electron system, produces superconducting salts with octahedral anions PF_6^- and AsF_6^-.[1] This is thought to originate in the destabilization of the extremely stable metallic state that occurs, for example, with the use of donor systems with extended π-conjugation such as bis-fused TTFs.[2] Such a destabilization is crucial in achieving superconductivity, as suggested by a series of studies of the phase diagrams of TMTSF (tetramethyltetraselenafulvalene) and BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene] superconductors that the superconducting state lies immediately adjacent to the antiferromagnetic insulating state.[3] Our design of donor molecules to destabilize the metallic state is based on the following requirements: (i) an increase in the on-site Coulombic repulsion energy by reducing the π-system of the TTF and bis-fused TTF cores and (ii) a decrease in the intermolecular interaction by introducing σ-bond frameworks into the donor molecules.[4] The DODHT molecule fulfils these requirements. Therefore, a successful search for superconducting salts of DODHT derived from other anions would support the validity of our molecular design for achieving superconductivity. We report here a new superconducting hydrate composed of DODHT and the tetrahedral anion BF_4^-, $(DODHT)_2BF_4{\cdot}H_2O$.



DODHT

The BF_4 salt was prepared by the constant current (0.5 μA) electrocrystallization method in PhCl containing $^nBu_4NBF_4$ at 25 °C, the electrical resistivity of which was measured by the conventional four-probe dc method along the *a*-axis. Measurement under hydrostatic pressure was carried out using a standard clamp cell with olefin oil (Daphne 7373, IDEMITSU) as the pressure medium.

Fig. 1 shows the temperature dependence of the resistivity at pressures of up to 15.5 kbar. At ambient pressure, this salt exhibited semiconductive behavior with an activation energy of 50 meV (σ_{rt} = 2.8 S cm^{-1}), and a clear transition to another semiconducting (or insulating) state at 270 K. The temperature of this transition decreased as pressure was increased and at 10 kbar, this salt became metallic down to 70 K. Furthermore, at 15.5 kbar, an abrupt decrease in resistivity attributable to a superconducting transition was observed at 3.2 K. A similar large pressure dependence of the resistive behavior was also seen in $(DODHT)_2X$ (X = PF_6 and AsF_6). In order to confirm the superconductivity of this salt, the temperature dependence of the resistivity under magnetic fields of up to 1.6 T was measured at 15.5 kbar. As shown in Fig. 2, the superconducting transition was completely suppressed under 1.6 T.

X-Ray structural analysis† revealed that this salt crystallizes in the triclinic space group $P\bar{1}$. As shown in Fig. 3, the donor arrangement belongs to the β″-type category,[5] similarly to those of $(DODHT)_2X$ (X = PF_6 and AsF_6). However, the length of the *c*-axis of this salt is almost twice that of the *c*-axis of the PF_6 and AsF_6 salts because of the lack of an inversion center in the BF_4^- anion. There exist two crystallographically independent donor molecules in this salt, the bond lengths of which are

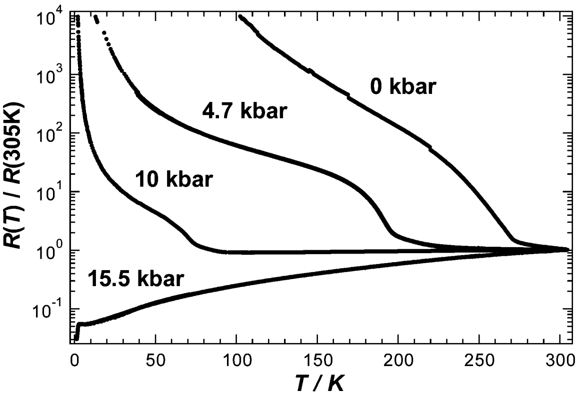


Fig. 1 Temperature dependence of the resistivity for $(DODHT)_2BF_4{\cdot}H_2O$ at pressures of 0 to 15.5 kbar.

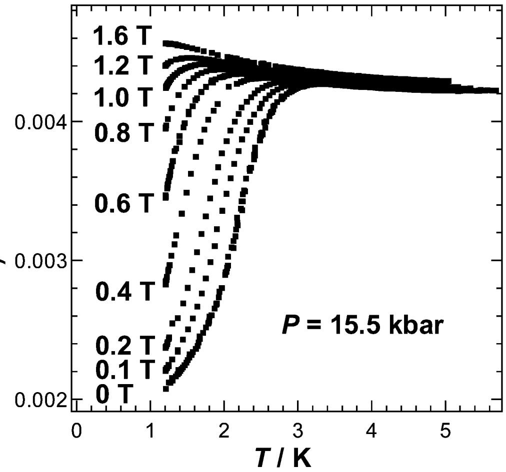


Fig. 2 Magnetic field dependence of the superconducting transition of $(DODHT)_2BF_4{\cdot}H_2O$ at 15.5 kbar.

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almost the same within experimental error, suggesting that no charge separation occurs. The conducting layers formed by the donor molecules are separated by an insulating layer consisting of the BF_4^- anions and water molecules.‡ The BF_4^- anion shows a disordered orientation due to a large thermal motion around the boron atom at 293(2) K. Donor molecules are stacked along the [$\bar{1}$01] direction with a four-folded period in a head-to-tail manner and dimerized with interplanar distances of 3.57, 3.85 and 3.81 Å (Fig. 3(a)). There are several intermolecular S···S contacts shorter than the sum of the van der Waals radii (3.70 Å) between stacks, whereas no short S···S contact is observed within a stack. This S···S contact pattern reflects the calculated overlap integrals,[6] which indicates that the interaction between stacks is much stronger than that within a stack (Fig. 3(b)); the same can be said for the PF_6 and AsF_6 salts of DODHT. However, unlike the PF_6 and AsF_6 salts, the respective absolute values of the overlap integrals within two types of cyclic-like donor pairs (c_2 = 1.99 and c_3 = 1.89 × 10^{-3}) in this salt are larger than that between these pairs (c_1 = 0.77 × 10^{-3}). This is probably due to the slightly different deviations of overlaps along both the molecular long and short axes, which cause a change in the effective area of the π-system of the DODHT molecule that is capable of overlapping. Thus, in the DODHT superconductors, such a subtle difference among the molecular arrangements has a marked influence on the intermolecular interaction and, consequently, would lead to various aspects of the pressure-induced resistive behavior. In order to clarify the role of the water molecule in this salt, we are preparing a BF_4 salt of DODHT containing no water molecule for comparison.

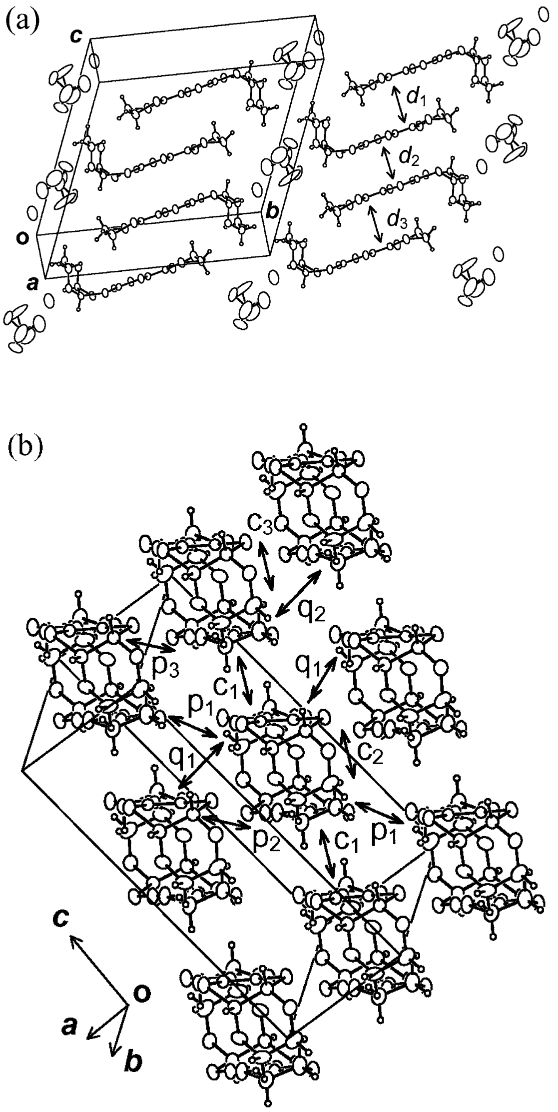

Fig. 3 Crystal structure of $(DODHT)_2BF_4{\cdot}H_2O$. (a) Intermolecular distances: d_1 = 3.85, d_2 = 3.57 and d_3 = 3.81 Å. (b) Intermolecular overlap integrals (× 10^{-3}) c_1, c_2, c_3, q_1, q_2, p_1, p_2 and p_3 are 0.77, −1.99, −1.89, −10.84, −12.35, 11.04, −9.81 and −8.54, respectively.

In conclusion, we have discovered a new superconductor, $(DODHT)_2BF_4{\cdot}H_2O$, with a superconducting transition temperature of 3.2 K at 15.5 kbar, which is one of the few superconducting salts to contain water.[7,8] Even the BEDT-TTF donor, which is known to produce the largest number of organic superconductors,[9] has so far produced only a limited number of superconducting hydrates.[7] Therefore, it is possible to obtain other types of superconductors from DODHT. Further work on this is ongoing in our laboratories.

Notes and references

† *Crystal data* for $(DODHT)_4(BF_4)_2(H_2O)_2$: $C_{40}H_{44}S_{24}O_{10}B_2F_8$, M = 1627.97, triclinic, space group $P\bar{1}$, a = 5.8088(9), b = 16.095(3), c = 17.193(3) Å, α = 72.109(3)°, β = 87.783(3)°, γ = 86.951(3)°, V = 1527.1(4) Å^3, T = 293(2) K, Z = 1, μ(Mo-Kα) = 0.917 mm^{-1}, D_c = 1.770 g cm^{-3}. Data collection was carried out by a Bruker SMART APEX three-circle diffractometer equipped with a CCD area detector (graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å, ω-scan mode (0.3° steps), semi-empirical absorption correction on Laue equivalents). A total of 5510 reflections were collected. The refinement converges with R_1 = 0.0440 for 2144 [$I_O \geqslant 2\sigma(I_O)$], $_wR_2$ = 0.1173 for 3894 ($2\theta_{max}$ = 46.54°), GOF = 0.869. The structures were solved by a direct method and refined by full-matrix-least-squares against F^2 with all data, using SHELXTL software (Bruker AXS, Inc.). Non-H atoms were refined anisotropically and all H atoms were refined in isotropic approximation. CCDC 197872. See http://www.rsc.org/suppdata/cc/b2/b211275b/ for crystallographic files in CIF or other electronic format.

‡ Elemental analysis supports the existence of a water molecule in this salt. Anal. Calcd. for $C_{20}H_{22}O_5S_{12}BF_4$: C, 29.51; H, 2.72%. Found: C, 29.46; H, 2.71%.

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