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CRYSTAL STRUCTURE OF A NEW MOLECULAR CONDUCTOR (DBTTF)[Ni(dmit)$_2$]

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The crystal of (DBTTF)[Ni(dmit)$_2$] contains uniform, segregated stacks of cations and anions. A three dimensional network of closely spaced molecules leads to intermolecular overlap integrals of the HOMO and LUMO with small anisotropy. This compound is highly conductive and signs of overlap integrals along the two segregated stacks suggest that this compound is the first two-chain system with parallel band structure.

Recent studies of the BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) compounds have renewed an understanding of the molecular conductors which were formerly assumed to be one-dimensional. The multi-dimensional intermolecular S···S contacts observed in these compounds are closely related to the stabilization of the metallic state down to very low temperature.[1] Our attempt is to couple the organo sulfur donor with the metal dithiolate with a view to extend the dimensionality.[2] We report here the structure of (DBTTF)[Ni(dmit)$_2$] (DBTTF= dibenzotetrathiafulvalene, dmit=isotrithionedithiolate) and consider the effect of the interchain coupling on the band structure.

Black fine needles of (DBTTF)[Ni(dmit)$_2$] were obtained by galvanostatic electrolysis of a 1,2-dichloroethane solution containing DBTTF and [(n-Bu)$_4$N][Ni(dmit)$_2$]. Elemental anal. Found: C, 31.81; H, 1.61; S,59.38%. Calcd for $C_{20}H_8S_{14}Ni$: C, 31.78; H, 1.07; S, 59.38%. Crystal data: triclinic, space group $P\bar{1}$, a=14.29(1), b=3.830(5), c=12.256(7) Å, α=90.03(5), β=106.26(5), γ=89.84(5)°, V=643.994 Å^3, Z=1. All the crystals examined by X-ray diffraction method were twinned, which could not be revealed by the Weissenberg and oscillation photographs. Since the lattice parameters α and γ are very close to 90.0° , the data collection was performed assuming the monoclinic unit cell. The structure was solved by the Patterson method and refined to the conventional R value of 0.090. Final positional parameters are given in Table 1.[3]

In the crystal of (DBTTF)[Ni(dmit)$_2$], the DBTTF and Ni(dmit)$_2$ units form segregated columns along the b axis (Fig. 1). Within the columns, the units repeat by a unit translation b. The normal to the DBTTF molecular plane is tilted 23° with respect to the stacking axis. The tilt of the Ni(dmit)$_2$ molecular plane with respect to the stacking axis is 22°, and opposite in direction to

Table 1. Fractional atomic coordinates (x 10^3). The e.s.d.'s are given in parentheses

	x	y	z
Ni	0	0	0
S1	54(4)	-168(5)	177(5)
S2	-140(5)	139(6)	18(5)
S3	-46(6)	-191(6)	362(6)
S4	-222(6)	117(6)	218(6)
S5	-212(8)	-54(9)	455(8)
S6	547(5)	663(6)	176(6)
S7	363(5)	364(6)	36(5)
C1	-47(19)	-81(22)	227(19)
C2	-135(20)	44(24)	151(22)
C3	-163(23)	-74(23)	350(22)
C4	484(16)	485(19)	38(17)
C5	457(17)	626(17)	240(18)
C6	463(26)	684(38)	350(25)
C7	381(22)	642(24)	396(23)
C8	295(21)	521(19)	329(20)
C9	287(19)	471(18)	217(19)
C10	369(20)	470(21)	174(20)

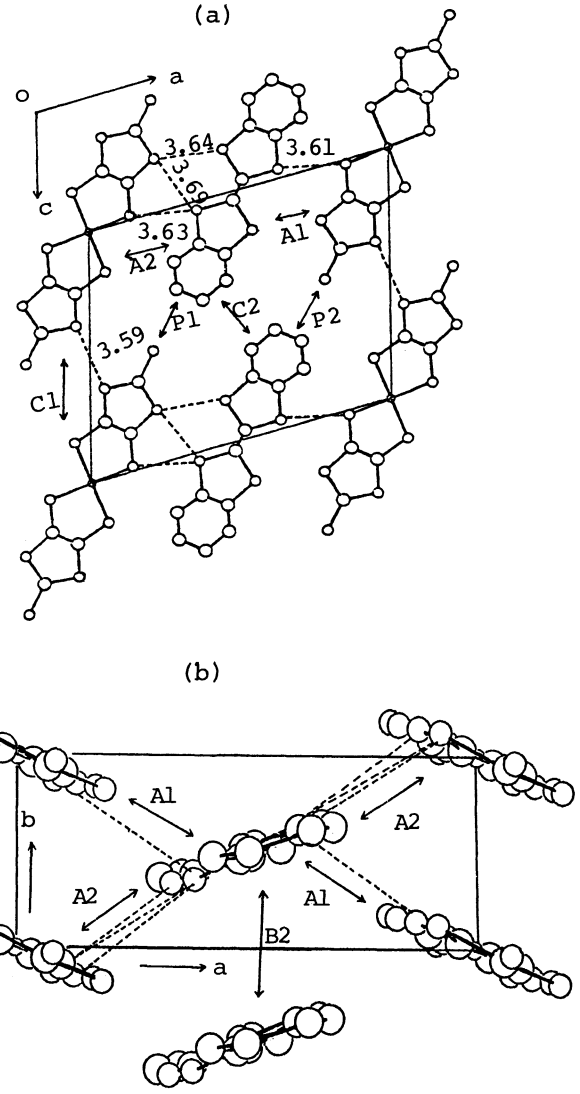
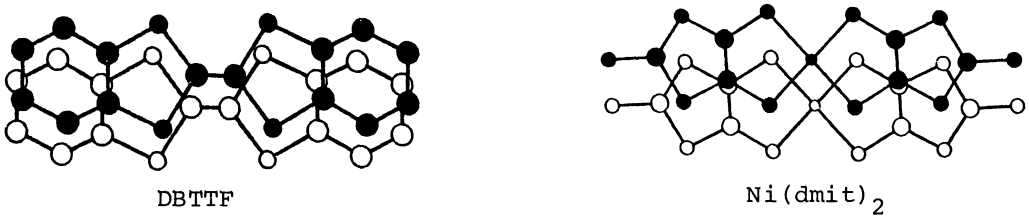


Fig. 1. Crystal structure of (DBTTF)[Ni(dmit)$_2$].

the tilt of the DBTTF unit (Fig. 1b). Therefore, the cations and anions are not coplanar, but form a dihedral angle of 135°. The molecular stacking within the two separate columns of the DBTTF and Ni(dmit)$_2$ units is shown in Fig. 2. Overlap displacement in the direction perpendicular to the long molecular axis is observed in both columns. The interplanar stacking distances are 3.53 Å in the DBTTF columns and 3.55 Å in the Ni(dmit)$_2$ columns. None of the interatomic S···S distances between adjacent molecules in both columns is shorter than the van der Waals distance (3.70 Å).

On the other hand, short S···S distances are found between the DBTTF and Ni(dmit)$_2$ units in the adjacent columns along the a axis, such that a two-



DBTTF Ni(dmit)$_2$

Fig. 2. Molecular stacking within the two separate columns of the DBTTF and Ni(dmit)$_2$ units.

dimensional network is formed parallel to the ab plane. Such interchain S···S contacts are similar to those in $(BMDT\text{-}TTF)_3ClO_4(1,2\text{-dichloroethane})$.[4)]

Table 2. Overlap integrals (x 10^3) of the HOMO (DBTTF) and LUMO ($Ni(dmit)_2$) illustrated in Fig. 1

Intrachain		Interchain			
B1	-12.72	A1	0.878	P1	-0.307
B2	-9.46	A2	0.731	P2	-0.119
		C1	-0.208		
		C2	0.358		

The cations and anions align themselves along the c axis in such a way the long molecular axis is tilted relative to the c axis, respectively. In this direction, short S···S distance is also observed between the $Ni(dmit)_2$ units.

Intermolecular overlap integrals of the HOMO (DBTTF) and the LUMO ($Ni(dmit)_2$) illustrated in Fig. 1 are shown in Table 2.[5)] The values of the intrachain overlap integrals B1 and B2 (therefore, band widths) are comparable to those in TTF-TCNQ.[6)] In addition, $S_{//b}$(intrastack)/$S_{//a}$(interstack) ratios ($\approx$10) are smaller than those in TTF-TCNQ($\approx 10^2$), close to those in $(TMTSF)_2X$.[7)] Evenly appreciable overlap integrals are also found along the c axis, extending the range of effective electronic interactions in the third direction.

The above results provide the question whether such interchain couplings stabilize the metallic state. For two-chain donor-acceptor system with non-interacting segregated columns, there are two possible band structures (Fig. 3), depending on the sign of the intrachain transfer integral.[8)] The one is the "crossed" band structure which contains normal and inverted one-dimensional tight-binding bands and the other is the "parallel" one where both bands are normal (or inverted). TTF-TCNQ and other charge transfer compounds are considered to take the former one.[6)] In 1:1 compounds with the crossed band structure, the Fermi energy is where the bands cross. If interchain coupling between unlike chains (donor-acceptor) are effectively strong, a covalency gap develops at the Fermi surface, yielding "zero-gap semiconductor".[9)] In TTF-TCNQ, the TCNQ units slip-stack in such a way the phases always match across the length of the molecule. Although the LUMO of the $Ni(dmit)_2$ has the same symmetry as that of TCNQ, the $Ni(dmit)_2$ units in $(DBTTF)[Ni(dmit)_2]$ stack in anti-phase mode. Thus, the DBTTF

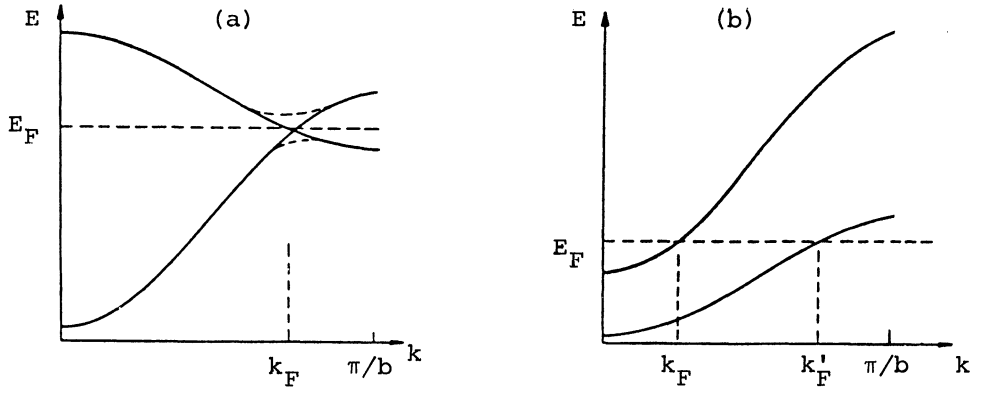


Fig. 3. The (a) "crossed" and (b) "parallel" band structures for two-chain donor-acceptor system (very schematic).

and $Ni(dmit)_2$ chains have intrachain overlap integrals with the same sign, leading to the parallel band structure (both bands are inverted). In this case, interchain coupling between unlike chains would not form the gap, despite the 1:1 composition. This is the most important feature of (DBTTF)[$Ni(dmit)_2$]. That is, this compound is the first two-chain system with the parallel band structure. The metallic state of this compound is expected to be stable against the interchain coupling between unlike chains, and the low-temperature behavior of the electrical properties will be of special interest. Preliminaly electrical conductivity measurements indicate that this compound is highly conductive ($\sigma_{R.T.} \approx$ 300 S cm^{-1}, along the b axis) and temperature dependence of $\sigma_{//b}$ is very small around the room temperature.

Various types of two-chain conductors can be designed by coupling cations and anions, both of which form the conduction pathway and interact to each other. But, it should be recalled that strong interchain coupling between unlike chains would form the energy gap in some cases. In order to avoid this unfavorable situation for electrical conductivity, detailed consideration including the symmetry of the monomer HOMO and LUMO , the stacking mode and the cation/anion ratio will be required.

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