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THE CRYSTAL STRUCTURE OF [BEDT-TTF][Ni(dmit)$_2$]. A NEW ROUTE TO DESIGN OF ORGANIC CONDUCTORS

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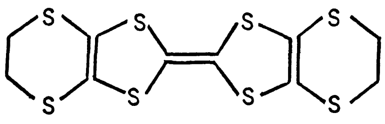
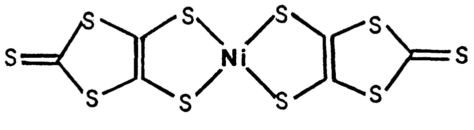
In the crystal of the charge transfer complex, [BEDT-TTF][Ni(dmit)$_2$], BEDT-TTF and Ni(dmit)$_2$ molecules are loosely stacked to form mixed-stacking columns. However, the intermolecular transverse interaction indicates that the BEDT-TTF molecules form a side-by-side chain. [BEDT-TTF][Ni(dmit)$_2$] suggests a new route to design of organic metals, despite of its semiconductive behavior.

Since Mulliken's charge transfer theory, the mixed-stacking structure of the planar π-donor and π-acceptor molecules is the most familiar mode of the charge transfer complexes. Despite of a number of salient optical and magnetic properties, the mixed-stacking complexes have not been regarded as electrically important materials because of the insulating properties. Since the high conductivity has been considered to require segregated regular stackings of donor and/or accepter molecules, the one-dimensionality has been believed to be the most fundamental character of the organic conductors. However, recent studies on the complexes of bis(ethylenedithio)tetrathiafulvalene(BEDT-TTF) have revealed that molecular stacking is not an indispensable condition for high conductivity.$^{1)}$ This fact contributes greatly to expand the field of the synthetic metals.

In this paper, we report the crystal structure of [BEDT-TTF][Ni(dmit)$_2$], which suggests a way to design a new type organic conductors (dmit= isotrithionedithiolate).



BEDT-TTF



Ni(dmit)$_2$

The crystals of [BEDT-TTF][Ni(dmit)$_2$] were obtained by the electrochemical method from a 1,2-dichloroethane solution of BEDT-TTF and [(n-C_4H_9)$_4$N]-[Ni(dmit)$_2$]. The lustrous black crystal with dimensions of about 0.4x0.2x0.02 mm^3 was used for the X-ray diffraction experiments. The crystal belongs to triclinic system with space group $P\bar{1}$. The lattice constants are: a=15.031(5), b=7.355(3), c=6.667(3) Å, α=109.91(5), β=97.69(4), γ=93.43(3)°, Z=1, V=682.3 $Å^3$. Intensities were measured on a Rigaku automated four-circle diffractometer with Mo-Kα radiation. The number of independent reflections ($2\theta<60^\circ$, $|Fo|>3\sigma(|Fo|)$) is 1814. The structure was solved by the direct method and the block-diagonal least-squares refinement reduced the R value to 0.084.

The structure is shown in Figs. 1 and 2. The atomic coordinates are listed in Table 1.

$Ni(dmit)_2$ and BEDT-TTF molecules are centrosymmetric. They are on the positions (0,0,0) and (0,0.5,0.5), respectively. $Ni(dmit)_2$ and BEDT-TTF are stacked alternately along [011]. The mode of the intermolecular overlapping along the stack can be seen in Fig. 1. The short intermolecular S...S contacts (<3.70 Å) are given in Figs. 1 and 2 and Table 2. Despite of the apparent intermolecular overlapping configuration along [011], there is no short intermolecular contact along this direction. This is mainly due to the steric repulsion of the ethylene groups of BEDT-TTF. Many short contacts along [001] suggests that the tendency to form the side-by-side arrangement of BEDT-TTF found in almost all the BEDT-TTF compounds[2)] persists also in this complex.

The d.c. electrical resistivities in the (100) plane were measured by four-probe method over the temperature range 300-80 K. The room-temperature resistivity along the direction approximately parallel to [001] ($\rho_{//}$) is 500 Ω cm. The ratio of the resistivities approximately parallel and perpendicular to [001] ($\rho_{//}/\rho_{\perp}$) is about 1.5 at room temperature. The resistivities increase with decreasing temperature. The activation energies of $\rho_{//}$ and $\rho_{\perp}$ are almost the same (0.28 eV). To our knowledge, all the charge transfer complexes without segregated stacks are insulating. In this sense, the observed resistivity of [BEDT-TTF][$Ni(dmit)_2$] is unusually small. It may be of interest to examine the origin of the fairly small electrical resistivity.

Consider a linear chain along the c axis, where donor(D) and acceptor(A) molecules are stacked alternately (Fig. 3a). Based on the simple tight-binding approximation, the one-dimensional energy bands formed from the frontier orbitals (HOMO of the donor and LUMO of the acceptor) are written as,

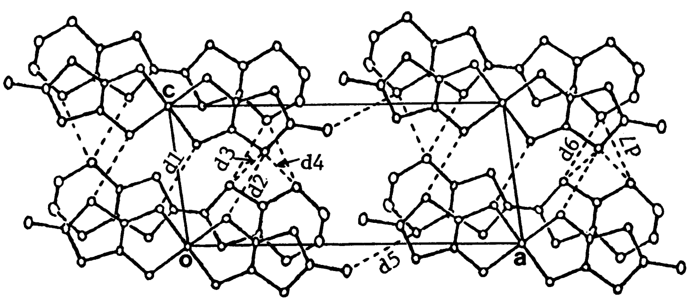


Fig. 1. Structure projected to the plane parallel to $Ni(dmit)_2$ molecule. Broken lines indicate short S...S contacts (see Table 2).

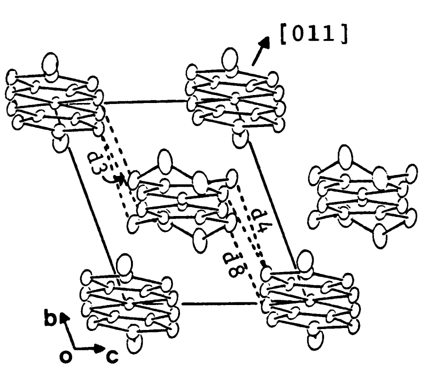


Fig. 2. Molecular arrangement.

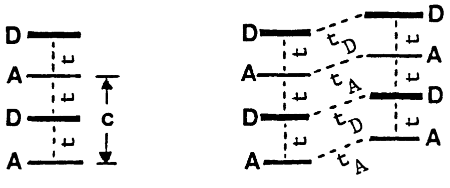
Table 1. Fractional atomic coordinates (x 10^4). The e.s.d's are given in parentheses

	x	y	z
Ni	0	0	0
S1	656(2)	622(5)	-2408(5)
S2	1258(2)	316(6)	2147(6)
S3	2626(2)	1576(6)	-2519(5)
S4	3190(2)	1197(6)	1612(6)
S5	4561(3)	2340(8)	-655(8)
C1	1767(8)	970(19)	-1236(19)
C2	2012(7)	797(18)	658(21)
C3	3498(8)	1713(22)	-510(23)
S6	1295(2)	5457(6)	7058(6)
S7	803(2)	5552(6)	2766(6)
S8	3248(2)	6377(7)	7359(7)
S9	2646(2)	6350(7)	2101(7)
C4	447(8)	5190(19)	4951(20)
C5	2180(8)	5979(20)	5828(21)
C6	1945(8)	5977(21)	3825(21)
C7	3963(11)	6263(34)	5359(31)
C8	3674(11)	7305(34)	3915(30)

Table 2. Short S...S contacts(3.70 Å)

d1(S1...S2)[a]	3.53 Å	d5(S5...S8)	3.58
d2(S2...S3)	3.65	d6(S6...S9)	3.52
d3(S3...S6)	3.65	d7(S8...S9)	3.41
d4(S3...S8)	3.63	d8(S2...S9)	3.68

a) see Figs. 1 and 2. The standard deviations are 0.03-0.10 Å.



(a) (b)

Fig. 3. Models of the molecular arrangements in charge transfer complexes.

$$E(k)=[E_A+E_D\pm((E_A-E_D)^2+16t^2\cos^2 kc/2)^{1/2}]/2, \tag{1}$$

where E_D and E_A are the energies of HOMO and LUMO, t is the transfer energy between adjacent A and D molecules and c is the repeating unit of the structure. As seen from Eq. 1, this system has an energy gap of (E_A-E_D). The intermolecular interaction does not reduce the magnitude of the band gap. Therefore, it is quite natural that the mixed-stacking complexes are insulating.

Next, let us consider a system with two-dimensional interaction (Fig. 3b). The energy band can be written as,

$$E(k)=((E_A+E_D)+2(t_A+t_D)\cos kb\pm B^{1/2})/2, \tag{2}$$

where $B=(E_A-E_D+2(t_A-t_D)\cos kb)^2+16t^2\cos^2(kc/2)$.

If t_A, t_D>>t,

$$E(k)=\begin{cases} E_A + 2t_A\cos kb \\ E_D + 2t_D\cos kb \end{cases} \tag{3}$$

Equation 3 implies that D and A molecules form segregated bands along the transvese direction(//b), when the transverse interactions are much larger than the parallel interaction.

Owing to the anisotropy of the π-orbital, the transverse intermolecular interaction has been considered to be a minor interaction in organic conductors. However, recent examination of the band parameters shows that the transverse (and/or oblique) interactions are not always small in the BEDT-TTF compounds.[3)] Table 3 shows the intermolecular overlap integrals(S).[4)] Since the symmetry of HOMO of BEDT-TTF is different from that of LUMO of $Ni(dmit)_2$, the intermolecular overlap integrals along [011](B...Ni) is almost cancelled. The overlap integral between BEDT-TTF molecules along the side-by-side direction($B...B_{001}$) is largest and is twice of the second largest one. Thus, it may be said that the BEDT-TTF molecules form a segregated arrangement along the transverse direction.

If the partial charge transfer occurs from D to A and the side-by-side interaction between the adjacent BEDT-TTF molecules is sufficiently large, the system will be a new type of organic metals. Unfortunately, the overlap integral is not so large. The intermolecular overlap integral between BEDT-TTF molecules is strongly dependent on the "configuration parameters", D and ϕ defined in Ref. 3. The magnitude of S in the ambient superconductor, β-(BEDT-TTF)$_2$I$_3$ is about 5-10 times larger than that of [BEDT-TTF][Ni(dmit)$_2$].$^{5)}$ The electron correlation may be important in this system and the electron will be localized. Therefore, the semiconductive behavior of this compound is not inconsistent with the simple discussion described above.

Table 3. Intermolecular overlap integrals(x10^3) of the frontier orbitals of BEDT-TTF and Ni(dmit)$_2$

B...B$_{001}$$^{a)}$	2.26	Ni...Ni$_{001}$	0.28
B...Ni$_{001}$	1.14	B....Ni$_{110}$	0.11
B...Ni	0.75		

a)B$_{lmn}$(Ni$_{lmn}$) indicates the BEDT-TTF (Ni(dmit)$_2$) related to the original molecule(B(Ni)) by the translation vector (**l**a+**m**b+**n**c).

In conclusion, in the crystal of [BEDT-TTF][Ni(dmit)$_2$], BEDT-TTF and Ni(dmit)$_2$ are stacked alternately along [011] but much closer side-by-side contacts of BEDT-TTF indicate that BEDT-TTF molecules have a strong tendency to form a segregated arrangement along the transverse direction. The crystal structure of [BEDT-TTF][Ni(dmit)$_2$] presents a new route to design organic metals. If the transverse (or oblique) intermolecular interactions could be sufficiently enhanced, the system would be a new type of organic meatals.

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