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Molecular Interactions, Band Structure, and BEDT-TTF Oxidation States in the Molecular Conductor $(\text{BEDT-TTF})_3[\text{V(dmit)}_3]_2$

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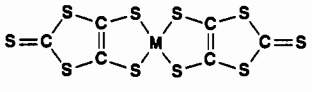
The discovery of superconductivity under pressure in $\text{TTF-[Ni(dmit)}_2]_2$[1,2] triggered an extensive investigation into the physics and chemistry of molecular conductors based on M(dmit)_2 (**1**)



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as well as other transition-metal bis(dithiolene) acceptors. Some of these materials exhibit interesting physical and structural properties such as charge density waves,[3] metal–insulator transitions,[4] and superconductivity.[5,6] The properties of these materials are to a large extent determined by the nature of their band electronic structures, which in turn are imposed by crystal packing, often determined by multiple hydrogen bonding.[7] A logical progression for the synthesis of new charge-transfer materials with interesting properties is the use of transition-metal tris(dithiolene) acceptors. The preassembling of the planar chalcogen-containing units in a different geometry is expected to yield new structural arrangements for both the acceptor and the donor stacks.[8] Salts of this type such as $X_3[\text{V(dmit)}_3]_2$ (X = BEDT-TTF, TMTSF)[9] and $\text{TTF[V(dddt)}_3]$[10] have been recently prepared.

The structure of $(\text{BEDT-TTF})_3[\text{V(dmit)}_3]_2$ is shown in Figure 1a.[9] The V(dmit)_3 acceptor forms an interlocking herringbone network along *b*, where two of its dmit units are used in face-to-face interactions with dmit units of adjacent acceptors while the third one interpenetrates the BEDT-TTF stacks. This leads to two crystallographically independent BEDT-TTF molecules: those of the double chains along *a* (see Figure 1a,c) and those of the single chains (see Figure 1a,b). Hereafter, these two types of BEDT-TTF molecules will be referred to as $\text{BEDT-TTF}_{\text{DC}}$ and $\text{BEDT-TTF}_{\text{SC}}$, respectively. Both V(dmit)_3 and BEDT-TTF interact with adjacent molecules along the needle axis (*a*). This material was previously shown[9] to be semiconducting although exhibiting quite high conductivity along *a*.

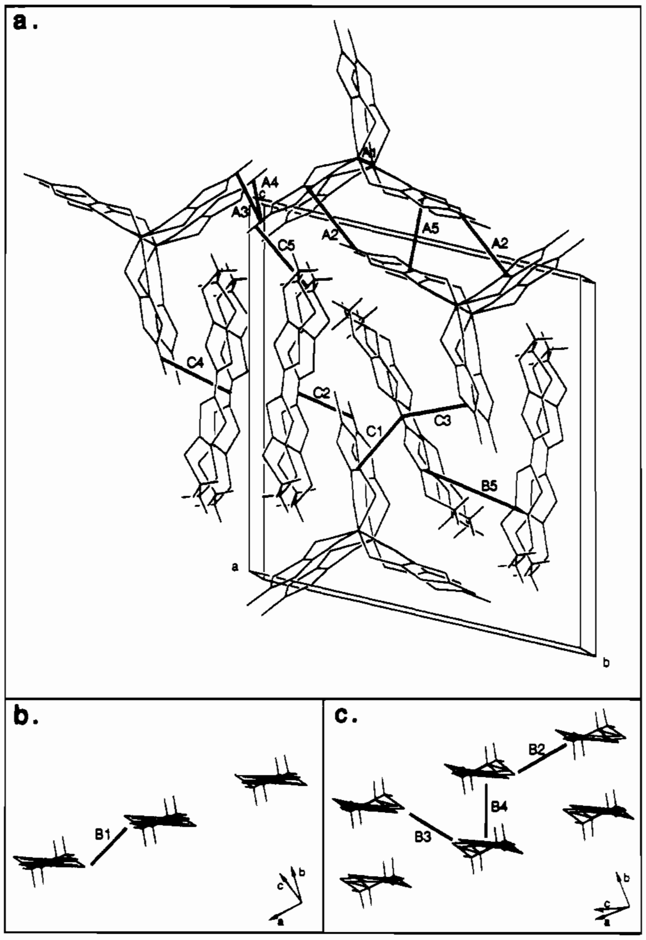

Figure 1. Crystal structure of $(\text{BEDT-TTF})_3[\text{V(dmit)}_3]_2$: (a) View down the *a* axis; (b) BEDT-TTF single chains; (c) BEDT-TTF double chains. The different types of interaction, i.e., $\text{V(dmit)}_3\cdots\text{V(dmit)}_3$ (A1–A5), BEDT-TTF···BEDT-TTF (B1–B5), and $\text{V(dmit)}_3\cdots$BEDT-TTF (C1–C5), are shown.

Because of the stoichiometry, two electrons per three BEDT-TTF molecules are transferred to the V(dmit)_3 acceptors. This raises the question as to what is the oxidation state of the two different types of BEDT-TTF molecules in the structure. In principle, three different possibilities must be considered. First, if the interactions between single and double chains are negligible and those between pairs of BEDT-TTF molecules in the parallel double chains are weak, $\text{BEDT-TTF}_{\text{DC}}$ and $\text{BEDT-TTF}_{\text{SC}}$ can be assumed to be in +1 and 0 oxidation states, respectively. In such a case the electrons of the double chain would be localized. Second, if the former interactions are weak but the latter are strong, the same oxidation states can be assumed but there will be no electron localization in the double chains. Third, if both types of interactions are non-negligible, one can assume an oxidation state of $+^2/_3$ for both $\text{BEDT-TTF}_{\text{DC}}$ and $\text{BEDT-TTF}_{\text{SC}}$. The first possibility seems to be unlikely on the basis of both magnetic susceptibility and EPR measurements.[9] Since the two types of BEDT-TTF molecules in the structure are very similar, the second possibility also seems to be ruled out. In view of the local arrangement of single and double chains, extensive delocalization among them, as required by the third possibility, seems however quite unlikely unless it is mediated through V(dmit)_3 acceptors. In this note we report the results of our extended

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(1) Abbreviations used: dmit^{2-} = 2-thioxo-1,3-dithiole-4,5-dithiolato, dddt^{2-} = 5,6-dihydro-1,4-dithiin-2,3-dithiolato, TTF = tetrathiafulvalene, BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene, TMTSF = tetramethyltetraselenafulvalene.

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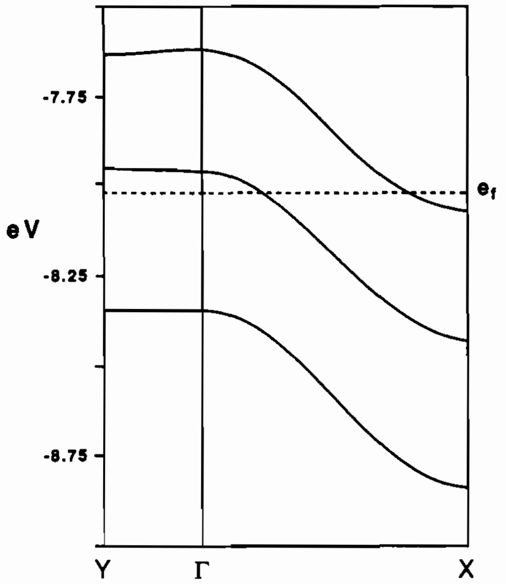

Figure 2. Band structure for the BEDT-TTF sublattice in (BEDT-TTF)$_3$[V(dmit)$_3$]$_2$. The dashed line indicates the Fermi level and Γ, *X*, and *Y* refer to the wave vectors (0,0), ($a^*/2$, 0), and (0, $b^*/2$), respectively.

Hückel tight-binding[11] analysis of the electronic structure of (BEDT-TTF)$_3$[V(dmit)$_3$]$_2$.

Our calculations for the 3D network of (BEDT-TTF)$_3$[V(dmit)$_3$]$_2$ show that for the bands implicated in the charge transfer, the band structure of this material is the superposition of the band structures of the V(dmit)$_3$ and BEDT-TTF sublattices. Although there are obvious V(dmit)$_3$···BEDT-TTF interactions, they do not affect the nature and dispersion of these bands which determine the physical properties of the material. The band structure of the BEDT-TTF sublattice is shown in Figure 2. The middle band is almost exclusively built from the highest occupied molecular orbital (HOMO) of BEDT-TTF$_{SC}$, whereas the upper and lower bands are built from the HOMO's of BEDT-TTF$_{DC}$. All these bands are one-dimensional (1D), indicating that the single and double chains do not interact. Although they are not relevant for the discussion below, it should be noted that the bands built from the singly occupied molecular orbital of V(dmit)$_3$ (i.e., the acceptor bands of the V(dmit)$_3$ sublattice) have also 1D character along the *a* direction. Consequently, although on the basis of the S···S contacts (BEDT-TTF)$_3$[V(dmit)$_3$]$_2$ is a 3D material, it is only 1D from the viewpoint of its electronic structure.

Before considering the implications of the band structure of Figure 2, it is important to examine how these results are related to the crystal structure of the material. Taking into account all S···S contacts smaller than 3.8 Å, there are 15 different types of intermolecular contacts per unit cell. These contacts are shown in Figure 1 with labels A1–A5 for V(dmit)$_3$···V(dmit)$_3$, B1–B5 for BEDT-TTF···BEDT-TTF, and C1–C5 for V(dmit)$_3$···BEDT-TTF. The S···S distances and the corresponding overlap integrals associated with each interaction are listed in Table I. The strongest interaction (B4) occurs between pairs of BEDT-TTF molecules in the adjacent stacks of the double chain (i.e., the repeat unit of the double chain). This results in bonding (Ψ_+) and antibonding (Ψ_-) combinations of the two HOMO's, which lead to the lower and upper bands of Figure 2, respectively. Since the two types of BEDT-TTF molecules are structuraly similar and the B1 and B2 interactions are almost identical, the band of the single chain lies just halfway in between the two bands of the double chain and the three bands have an almost identical dispersion. Within the BEDT-TTF sublattice, the B5 contact could lead to some 2D character of the bands. However, the calculated overlap integral is quite small. This is because the B5 S···S contacts are associated with the outer sulfur atoms of both molecules, which exhibit only a weak contribution to the BEDT-TTF HOMO.[12] In addition, because of the strong interaction B4, the difference in energies of the Ψ_+ and Ψ_- orbitals and that of the BEDT-TTF$_{SC}$ HOMO is such that the interaction energy is very weak. The BEDT-TTF molecules of the single and double chains could in principle interact through the C1/C2 and/or C3/C4 pairs of interactions. However, as shown in Table I, the overlap integrals for C2 and C4 are very small and this prevents any possible communication. Although there are other possible pathways for the interaction of the single and double BEDT-TTF chains through V(dmit)$_3$, all of them involve some of the contacts with very small overlap integrals. In consequence, the band structure of the BEDT-TTF sublattice can be considered to be the superposition of the single- and double-chain band structures.

Table I. S···S Distances Smaller Than 3.8 Å and Overlap Integrals ($\times 10^{-3}$) Associated with the Different V(dmit)$_3$···V(dmit)$_3$, BEDT-TTF···BEDT-TTF, and V(dmit)$_3$···BEDT-TTF Interactions in (BEDT-TTF)$_3$[V(dmit)$_3$]$_2$[a]

interaction type	S···S dist (Å)	overlap integral ($\times 10^{-3}$)
	V(dmit)$_3$···V(dmit)$_3$	
A1	3.392, 3.449, 3.493, 3.513, 3.565, 3.652, 3.682, 3.721, 3.756	4.6
A2	3.516 (×2)	2.8
A3	3.438, 3.745 (×2)	0.3
A4	3.591 (×2)	1.2
A5	3.628	0.2
	BEDT-TTF···BEDT-TTF	
B1	3.582 (×2)	7.0
B2	3.585, 3.609, 3.681	6.7
B3	3.800 (×2)	1.1
B4	3.657 (×2), 3.671 (×2)	28.2
B5	3.741, 3.766	1.9
	V(dmit)$_3$···BEDT-TTF	
C1	3.530, 3.552, 3.735, 3.752	1.1
C2	3.696	0.2
C3	3.757, 3.771	1.6
C4	3.557, 3.599, 3.651	0.1
C5	3.442	1.4

[a] See Figure 1 for labeling.

As shown in Figure 2, the middle and upper bands of the BEDT-TTF sublattice overlap. Since the stoichiometry (BEDT-TTF)$_3$[V(dmit)$_3$]$_2$ provides four electrons to fill the HOMO bands of the BEDT-TTF sublattice, the Fermi level cuts both the middle and upper bands. Because of the purely 1D character of these bands the charge associated with the two different BEDT-TTF molecules of (BEDT-TTF)$_3$[V(dmit)$_3$]$_2$ can readily be assigned. If k_f and k_f' are the Fermi wave vectors associated with the middle and upper bands, respectively (see **2**), the charge of a BEDT-TTF$_{SC}$ molecule will be $4k_f/a^*$ and that of a BEDT-TTF$_{DC}$ molecule will be $^1/_2[2 - 4(a^*/2 - k_f')/a^*]$. Since $k_f = a^*/2 - k_f'$, the charge of a BEDT-TTF$_{DC}$ molecule is given by $1 - (2k_f/a^*)$. According to our calculations (see Figure 2), these charges are near $+^1/_2$ (i.e., 0.44) and $+^3/_4$ (i.e., 0.78), respectively. Consequently, there are two different BEDT-TTF molecules in (BEDT-TTF)$_3$[V(dmit)$_3$]$_2$ although the charges are not different enough so as to be structurally detected. It is worthy of note that the charges on the two different BEDT-TTF molecules are similar inspite of the lack of transfer integrals strongly coupling the single and double BEDT-TTF chains.

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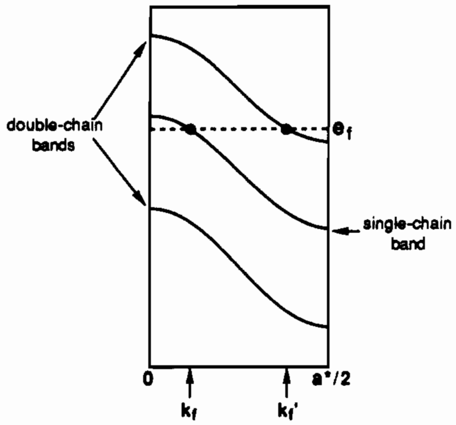

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Another important implication of the band structure of the BEDT-TTF sublattice of (BEDT-TTF)$_3$[V(dmit)$_3$]$_2$ is that if the band overlap occurs (and this is required in order to avoid the charges 0 and +1, which would be inconsistent with the reported X-ray crystal structure[9]), the system should be metallic. Since the two Fermi wave vectors of **2** are related by the relation $2k_f = a^* - 2k_f'$, a single charge density wave (CDW) distortion with wave vector $q = a^* - 2k_f'$ can open energy gaps in both partially filled bands of Figure 2. The semiconducting character of the material suggests that the CDW distortion has already occurred at room temperature and that the reported crystal structure[9] of (BEDT-TTF)$_3$[V(dmit)$_3$]$_2$ is in fact an average of the modulated structure. Thus, it would be very interesting to undertake X-ray diffuse scattering measurements in order to look for the superlattice reflections in the room-temperature structure of this material. By analogy with other molecular conductors like (BEDT-TTF)$_2$ReO$_4$[13] and α'-TTF[Pd(dmit)$_2$]$_2$,[14] if the existence of a modulated structure is confirmed, it would be interesting to see if the metallic state of (BEDT-TTF)$_3$[V(dmit)$_3$]$_2$ could be stabilized by applying pressure.

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