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Comparison of the electronic structures of isostructural (BEDT-TTF)₃(HSO₄)₂ and [Ni(dddt)₂]₃(HSO₄)₂ molecular metals

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Abstract. — The isostructural charge transfer salts (BEDT-TTF)₃(HSO₄)₂ and [Ni(dddt)₂]₃(HSO₄)₂ are metallic at room temperature and exhibit metal to insulator transitions at 130 K and 25 K, respectively. X-ray diffuse scattering measurements for (BEDT-TTF)₃(HSO₄)₂ and tight-binding band structure calculations for both salts suggest that these transitions are most likely due to slight structural modifications, probably donor displacements, which suppress the semi-metallic overlap in these 3:2 salts. Although the Fermi surface of (BEDT-TTF)₃(HSO₄)₂ is made of closed loops, our study suggests that this salt has remarkable pseudo-1D properties. We show that even when they are isostructural, the BEDT-TTF and Ni(dddt)₂ salts can be electronically quite different, because the LUMO of the latter donor is not too far in energy from the HOMO. Consequently, the LUMO of Ni(dddt)₂ can mix into the partially filled bands of their charge transfer salts, which are based on the HOMO of the donor. This feature can change noticeably the topology of the band structure and the Fermi surface. We show that this actually happens in [Ni(dddt)₂]₃(HSO₄)₂ and that it can be the clue to understand the differences in physical properties of the (BEDT-TTF)₃(HSO₄)₂ and [Ni(dddt)₂]₃(HSO₄)₂ salts.

Many metallic charge transfer salts of BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene, 1) have been reported [1] although in only a few of them the donor molecules have an average oxidation state of + 2/3. (BEDT-TTF)₃Cl₂·2 H₂O, which is metallic at room temperature, undergoes a metal to insulator transition at 100 K and becomes superconducting at 2 K under an applied pressure of 16 kbar [2, 3]. (BEDT-TTF)₃CuCl₄·H₂O [4, 5] and (BEDT-TTF)₃NiCl₄·H₂O [6] are both metallic at room temperature but whereas the first salt retains the metallic conductivity until 0.2 K, the second seems to undergo some irreversible

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structural change around 150 K which destroys its metallic character. A series of salts like $(\text{BEDT-TTF})_3(\text{IO}_4)_2$ [7], $\gamma\text{-(BEDT-TTF)}_3(\text{ReO}_4)_2$ [7], $(\text{BEDT-TTF})_3(\text{BF}_4)_2$ [7], $(\text{BEDT-TTF})_3(\text{ClO}_4)_2$ [8], $(\text{BEDT-TTF})_3(\text{BrO}_4)_2$ [9], $(\text{BEDT-TTF})_3\text{Br}_2 \cdot 2\text{H}_2\text{O}$ [10] and $(\text{BEDT-TTF})_3(\text{HSO}_4)_2$ [11, 12], adopt the so-called γ -type structure and, except for the first two which are insulators, are metallic at room temperature and undergo a metal to insulator transition at 150 K, 170 K, 210 K, 185 K and 130 K, respectively. The metal to insulator transition in $(\text{BEDT-TTF})_3(\text{ClO}_4)_2$ is lowered from 170 K to 100 K under an applied pressure of 10 kbar [13] and in the case of $(\text{BEDT-TTF})_3(\text{HSO}_4)_2$ the transition is completely suppressed under 7.5 kbar [14]. However, superconductivity could not be observed. It is this last salt which is the object of the present study.

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Several charge transfer salts of $\text{M}(\text{dddt})_2$ (2) where $\text{M} = \text{Ni}, \text{Pd}, \text{Pt}, \text{Au}$ and dddt^{2-} is 5,6-dihydro-1,4-dithiin-2,3-dithiolato, have been prepared [15]. Recently, the first of them to be metallic, $[\text{Ni}(\text{dddt})_2]_3(\text{HSO}_4)_2$, has been reported [16]. This salt, which is isostructural [17] with $(\text{BEDT-TTF})_3(\text{HSO}_4)_2$ [11, 12], also exhibits a metal to insulator transition but only at ~ 25 K. Thus, the metallic state of $[\text{Ni}(\text{dddt})_2]_3(\text{HSO}_4)_2$ seems to be quite more stable than that of $(\text{BEDT-TTF})_3(\text{HSO}_4)_2$. In addition, recent thermopower measurements show that there are notable differences between the two salts [18]. Consequently, it seems that despite the similarity in crystal structures, the substitution of Ni^{2+} for the central $\text{C}=\text{C}$ bond of BEDT-TTF has a significant effect on the electronic structure of these molecular metals.

In fact, it has been recently shown [19] that BEDT-TTF and $\text{M}(\text{dddt})_2$ ($\text{M} = \text{Pt}, \text{Pd}$) charge transfer salts with similar crystal structures can be electronically quite different. The reason is that whereas the HOMO (highest occupied molecular orbital) of BEDT-TTF lies very far apart from the LUMO (lowest unoccupied molecular orbital), this is not the case for $\text{M}(\text{dddt})_2$. Consequently, only the HOMO of the donor plays a major role in the conduction bands of the BEDT-TTF charge transfer salts but both the HOMO and LUMO of the donor can be involved in those of the $\text{M}(\text{dddt})_2$ charge transfer salts. This peculiar feature was first noticed [20] for charge transfer salts of the $\text{M}(\text{dmit})_2$ ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$) acceptors and has a strong influence on their transport properties [21]. Thus in the present work we compare the band structures and Fermi surfaces of the isostructural $(\text{BEDT-TTF})_3(\text{HSO}_4)_2$ and $[\text{Ni}(\text{dddt})_2]_3(\text{HSO}_4)_2$ salts in order to understand the origin of their metal to insulator transitions and to gain some understanding of the differences and similarities among isostructural BEDT-TTF and $\text{M}(\text{dddt})_2$ charge transfer salts. Our tight-binding band structure calculations [22] use an extended Hückel type Hamiltonian [23] and a double- ζ basis set [24] for all atoms except

hydrogen. The exponents, contraction coefficients and parameters were taken from previous work [25].

Crystal structure.

The crystal structures of $(\text{BEDT-TTF})_3(\text{HSO}_4)_2$ [11] and $[\text{Ni}(\text{dddt})_2]_3(\text{HSO}_4)_2$ [17] contain donor layers alternating along the c direction with layers of HSO_4^- anions. A perspective view of a donor molecule layer of $(\text{BEDT-TTF})_3(\text{HSO}_4)_2$ in the crystallographic ab plane is shown in figure 1. Each donor molecule in figure 1 is viewed approximately along the direction of its central $\text{C}=\text{C}$ bond and for clarity the hydrogen atoms are not shown. The repeat unit of this slab contains three donor molecules, two of which are related by an inversion center. Thus, the unit cell contains two crystallographically independent donors.

The slab of figure 1 can be described either, as a series of parallel inclined stacks running approximately along the $(a+b)$ direction (hereafter designated as the d_1 direction), or as a

Fig. 1. — Perspective view of a BEDT-TTF layer of $(\text{BEDT-TTF})_3(\text{HSO}_4)_2$. Each molecule is viewed approximately along its central $\text{C}=\text{C}$ bond. The hydrogen atoms are not shown for simplicity.

Table I. — $\text{S}\cdots\text{S}$ distances shorter than $4.0 \text{ \AA}$ and absolute values of the $\beta_{\text{HOMO-HOMO}}$ interaction energies (eV) for the different donor-donor interactions in $(\text{BEDT-TTF})_3(\text{HSO}_4)_2$ (see Fig. 1 for labelling).

Interaction type	$\text{S}\cdots\text{S}$ distances ($\text{\AA}$)	$\beta_{\text{HOMO-HOMO}}$
A	3.823, 3.838, 3.901 ($\times 2$),	0.0451
B	3.922, 3.949, 3.913	0.0450
C	3.421 ($\times 2$), 3.535 ($\times 2$), 3.869 ($\times 2$), 3.912	0.1263
D	3.416, 3.423, 3.513, 3.523, 3.899,	0.1330
	3.953, 3.957	
E	3.650, 3.677, 3.752, 3.843, 3.961,	0.2577
	3.987, 3.992	
F	3.706 ($\times 2$), 3.762 ($\times 2$), 3.800 ($\times 2$), 3.938	0.2935

Table II. — S...S distances shorter than 4.0 Å and absolute values of the $\beta_{\text{HOMO-HOMO}}$ and $\beta_{\text{LUMO-LUMO}}$ interaction energies (eV) for the different donor-donor interactions in $[\text{Ni}(\text{dddt})_2]_3(\text{HSO}_4)_2$ (see Fig. 1 for labelling).

Interaction type	S...S distances (Å)	$\beta_{\text{HOMO-HOMO}}$	$\beta_{\text{LUMO-LUMO}}$
A	3.765, 3.828, 3.893, 3.904, 3.905, 3.946, 3.970	0.2574	0.2229
B	3.933 ($\times 2$)	0.0173	0.0786
C	3.529 ($\times 2$), 3.601 ($\times 2$), 3.775 ($\times 2$) 3.781	0.0855	0.0775
D	3.536, 3.605, 3.635, 3.747, 3.896, 3.969	0.0723	0.0622
E	3.512, 3.539, 3.577, 3.687, 3.768, 3.827	0.2584	0.2079
F	3.536 ($\times 2$), 3.570 ($\times 2$), 3.637 ($\times 2$) 3.685	0.2110	0.1932

series of step-chains running along the d_2 direction. This arrangement gives rise to six different types of interactions between donor molecules noted A-F in figure 1. As shown in table I, short S...S intermolecular distances smaller than 4.0 Å are associated with all these interactions. This leads to sequences of -A-A-B-A-A- donor-donor interactions along the d_1 direction, -E-E-F-E-E- donor-donor interactions along the d_2 direction and -D-D-C-D-D- donor-donor interactions along the d_3 direction (see Fig. 1).

As mentioned before, $(\text{BEDT-TTF})_3(\text{HSO}_4)_2$ and $[\text{Ni}(\text{dddt})_2]_3(\text{HSO}_4)_2$ are isostructural so that the previous description applies also to the later salt. The short S...S distances in $[\text{Ni}(\text{dddt})_2]_3(\text{HSO}_4)_2$ are reported in table II. Crystallographically, the only difference between the two salts concerns a possible orientational disorder of the outer ethylene groups. In $(\text{BEDT-TTF})_3(\text{HSO}_4)_2$ all the ethylene groups are ordered and the two different donors have a staggered conformation [11, 12]. In $[\text{Ni}(\text{dddt})_2]_3(\text{HSO}_4)_2$ an ethylene group of one of the donors exhibits conformational disorder [17]. Thus, one of the $[\text{Ni}(\text{dddt})_2]$ donors exists in two equally probable conformations : staggered and eclipsed. The second type of donors has no disorder problems and exhibits the staggered conformation.

Electronic structure.

A. $(\text{BEDT-TTF})_3(\text{HSO}_4)_2$. — The repeat unit of the donor slabs in $(\text{BEDT-TTF})_3(\text{HSO}_4)_2$ contains three BEDT-TTF molecules so that there will be three HOMO bands. With the formal oxidation required by the stoichiometry, $(\text{BEDT-TTF})_3^{2+}$, there are four electrons per unit cell to fill these three bands. Thus, in principle, the system could be either a semimetal or a band gap semiconductor. The calculated band structure for the $(\text{BEDT-TTF})_3^{2+}$ slabs in $(\text{BEDT-TTF})_3(\text{HSO}_4)_2$ is shown in figure 2. It is clear that the upper and middle bands slightly overlap so that the system is a semi-metal. Although the donor slabs contain two different BEDT-TTF molecules, their internal geometries are very similar (for instance, the central C = C distances are 1.381 and 1.384 Å [11] and consequently, the HOMO energies are almost identical (i.e., the energy difference is of the order of 0.05 eV). Thus the HOMO bands of the donor layers result from a strong mixing of the HOMOs of both types of donors. The calculated

Fig. 2. — Dispersion relations for the HOMO bands of the donor slabs in $(\text{BEDT-TTF})_3(\text{HSO}_4)_2$ where the dashed line refers to the Fermi level. Γ , X, Y, M and S are the wave vectors $(0, 0)$, $(a^*/2, 0)$, $(0, b^*/2)$, $(a^*/2, b^*/2)$ and $(-a^*/2, b^*/2)$, respectively.

Fermi surface contains two different hole pockets centered at Y and M (Fig. 3a) and two electron pockets related by symmetry (Fig. 3b). The three different hole and electron pockets are closed so that $(\text{BEDT-TTF})_3(\text{HSO}_4)_2$ should have 2D semi-metallic conductivity.

Before considering the possible origin of the metal to insulator transition it is important to analyze how the crystal and electronic structures of this salt are related. Usually, the simplest way to do it is by calculating the so called $\beta_{\text{HOMO-HOMO}}$ interaction energies [26]. These interaction energies are a measure of the strength of the interaction between a pair of BEDT-TTF HOMOs in adjacent sites of the crystal and give important insight concerning the correlation between the crystal and electronic structures of molecular solids [27]. The absolute values of $\beta_{\text{HOMO-HOMO}}$ interaction energies for the six different donor-donor intermolecular interactions shown in figure 1 as well as the associated S...S distances are reported in table I. These interaction energies can be clearly classified into three different groups according to the strength of the interaction: those along the d_2 direction (step-chains) are strong (~ 0.25 - 0.30 eV), those along the d_1 direction (inclined stacks), are small (~ 0.05 eV) and those along the d_3 direction (see Fig. 1) are intermediate (~ 0.13 eV). The small values of the

Fig. 3. — Calculated Fermi surface for $(\text{BEDT-TTF})_3(\text{HSO}_4)_2$ (a) hole pockets, (b) electron pockets and (c) combined Fermi surface.

interactions along d_1 can be attributed to the long S...S distances. However this is only a part of the story because in other BEDT-TTF salts with columnar donor stacks like BEDT-TTF₂ReO₄ [28] and β -BEDT-TTF₂X (X = I₃, IBr₂) [26a], some of the stronger donor...donor interactions (~ 0.25 eV) are associated with S...S distances even longer than those considered here. Clearly, it is the orientation of the interacting sulfur p-orbitals, different for columnar and inclined stacks, which plays the major role. The interactions along the d_3 direction are those associated with the shortest S...S distances and yet the interaction energies are only intermediate. This is again a consequence of the not very favorable orientation of the interacting sulfur p-orbitals which, for this geometry, can make only π -type overlaps. By contrast, the donors of the step layers along d_2 are oriented in such a way that the interacting sulfur p-orbitals make very good σ -type overlaps. Thus, the associated interaction energies are strong. The fundamental role of the orientation of the interacting sulfur p-orbitals can be once more illustrated by comparing interactions E and F which are of the same type : although E is associated with the shorter S...S distances it is F which has the stronger interaction energy. Thus, from the electronic viewpoint, the BEDT-TTF slabs of (BEDT-TTF)₃(HSO₄)₂ seem to be best described as a series of step-chains along the d_2 direction interacting through weaker π - and σ -type contacts along the other directions of the slab. It is also important to point out that from a pure consideration of the S...S distances, the chains along d_1 appear to be made of groups of three donors (i.e., the three donors linked by interactions of type A in Fig. 1), so that from a purely structural viewpoint the donor slab could be considered to be built from these trimeric donor units. However, as shown in table I the intra-trimer interaction energy (A) is quite small so that, from an electronic viewpoint, these trimeric units have no real meaning.

The final outcome of the discussion above is that if we had to single out BEDT-TTF chains in the donor slabs of (BEDT-TTF)₃(HSO₄)₂, it is the step-chains along d_2 which would be chosen and not the inclined stacks along d_1 . Also, the calculated values of the interaction energies suggest that the step-chains should play a relevant role in the electronic structure of this salt. At first sight this conclusion seems to be in conflict with the Fermi surfaces of figures 3a and b. Since these surfaces are closed, we would conclude that (BEDT-TTF)₃(HSO₄)₂ is a 2D semi-metallic conductor and consequently, one could argue that from the electronic viewpoint no chains can be singled out in these slabs. The fact that the step-chains play an important role in the transport properties of this salt can be readily appreciated when the hole and electron Fermi surfaces are combined together and represented in an extended zone scheme as shown in figure 3c. The combined Fermi surface is a series of small closed loops arranged in wavy patterns perpendicular to the step-chain direction. It is important

to note that within each wavy pattern the sequence of closed loops is of the type $\cdot$ -electron (e)-hole (h)-electron (e)-hole (h)- $\cdot$ and that within the first Brillouin zone there are three of these wavy patterns. Thus the Fermi surface of $(\text{BEDT-TTF})_3(\text{HSO}_4)_2$ can be viewed as the result of an imperfect nesting of the warped open quasi-1D Fermi surface associated with a one-third empty band of an ideal donor lattice. This is schematically illustrated in 3 for a rectangular lattice. Thus, although the Fermi surface of $(\text{BEDT-TTF})_3(\text{HSO}_4)_2$ is made of a series of closed loops, the system should be anisotropic and be better conducting along the direction of the step-chains.

Let us now consider the possible origin of the metal to insulator transition. An electronic localization is ruled out by the fact that the transition is quite abrupt which suggests a structural origin. With the Fermi surface of figure 3c it could be speculated that the transition results from an excitonic-like instability due to the coupling of the electron and hole pockets. In other words, with the introduction of some new periodicity the electron pocket and the largest hole pockets could hybridize so as to open a gap between the « bonding » and « antibonding » combinations of these hybrids. This type of mechanism, proposed in the sixties by Kohn [29], Halperin and Rice [30], was recognized to occur for the first time in an organic charge transfer salt in the case of $\text{Cs}[\text{Pd}(\text{dmit})_2]_2$ [31]. The driving force for the distortion would be the gain of electronic energy resulting from the opening of an hybridization gap between the electron and largest hole pockets of figure 3c. This mechanism should lead to the formation of a new unit cell for the slab and thus to the appearance of additional reflections in the low temperature X-ray patterns of this salt. Consequently we carried out X-ray diffuse scattering experiments until 25 K in order to detect such additional reflections. Our attempts were however unsuccessful so that we believe that the excitonic mechanism does not occur. Consequently, the only remaining possibility is that the transition is the result of a lattice distortion which suppresses the small semi-metallic overlap between the upper and middle bands of figure 2 while keeping the same unit cell. In other words, the distortion would just slightly change the intermolecular interactions among the three donors of the unit cell and, in contrast with the previous mechanism, the X-ray pattern will not show any additional periodicity after the distortion. The situation could be similar to that proposed to occur in semi-metallic $(\text{BEDT-TTF})_3(\text{ClO}_4)_2$ for which Enoki *et al.* [32] have recently suggested that the 170 K metal to insulator transition could be associated with BEDT-TTF displacements induced by changes in the hydrogen bonding network between donors and acceptors. It is worth mentioning that both the lower transition temperature and the fact that only for $(\text{BEDT-TTF})_3(\text{HSO}_4)_2$ the transition is suppressed under pressure [14], suggests that these structural modifications are smaller in $(\text{BEDT-TTF})_3(\text{HSO}_4)_2$ than in $(\text{BEDT-TTF})_3(\text{ClO}_4)_2$. A low temperature structural refinement is thus essential in order to determine what type of donor displacements (translations and/or rotations) lead to the suppression of the semi-metallic overlap. Since the metal to insulator transition is suppressed under pressure, we suggest that magnetoresistance measurements under pressure would be very interesting. If pressure does not significantly modify the Fermi surface of the material, there should be three different Shubnikov-de Haas frequencies such that the area associated with two of the pockets should be equal to twice the area associated with the third one. Also a detailed study of the conductivity anisotropy in the ab plane would be very interesting in order to test our Fermi surface topology.

B. $[\text{Ni}(\text{dddt})_2]_3(\text{HSO}_4)_2$. — As mentioned in the introduction, the HOMO and LUMO of $\text{Ni}(\text{dddt})_2$ are not far apart in energy so that the LUMO can play an important role in the electronic structure of the $\text{Ni}(\text{dddt})_2$ salts even if it behaves as a donor. The HOMO and LUMO of $\text{Ni}(\text{dddt})_2$ are shown in 4 and the HOMO of BEDT-TTF in 5. In terms of the sulfur contributions, the HOMOs of BEDT-TTF and $\text{Ni}(\text{dddt})_2$ are similar and have the same nodal properties. The nodal properties of the LUMO of $\text{Ni}(\text{dddt})_2$ are however different. Conse-

quently, if two BEDT-TTF and $\text{Ni}(\text{dddt})_2$ salts with the same anion are isostructural, their electronic structures and transport properties will be similar only if the LUMO of $\text{Ni}(\text{dddt})_2$ does not mix into the partially filled HOMO bands, because such a mixing can affect quite strongly the topology of the band structure and the Fermi surface.

The calculated band structure for the $[\text{Ni}(\text{dddt})_2]_3^-$ slabs in $[\text{Ni}(\text{dddt})_2]_3(\text{HSO}_4)_2$ is shown in figure 4, where both the HOMO and LUMO bands are plotted. It is obvious that there is no clear energy separation between the three HOMO and the three LUMO bands. The second and third bands from bottom slightly overlap so that we have again the same semi-metallic situation. The Fermi surface for $[\text{Ni}(\text{dddt})_2]_3(\text{HSO}_4)_2$ is shown in figure 5. It contains electron

Fig. 4. — Dispersion relations for the HOMO and LUMO bands of the donors slabs in $[\text{Ni}(\text{dddt})_2]_3(\text{HSO}_4)_2$, where the dashed line refers to the Fermi level. Γ , X , Y , M and S are the wave vectors $(0, 0)$, $(a^*/2, 0)$, $(0, b^*/2)$, $(a^*/2, b^*/2)$ and $(-a^*/2, b^*/2)$, respectively.

Fig. 5. — Calculated Fermi surface for $[\text{Ni}(\text{dddt})_2]_3(\text{HSO}_4)_2$

pockets around Y and hole pockets at approximately the midpoint of the $\Gamma \rightarrow S$ direction. There are similarities but also marked differences with respect to the Fermi surface of $(\text{BEDT-TTF})_3(\text{HSO}_4)_2$ (Fig. 3c). The combined Fermi surface of figure 5 can also be seen as a series of closed loops forming an almost straight linear pattern perpendicular to the step-chain direction. However, there are two clear differences. First, there are only two of these almost linear patterns of closed loops in the first Brillouin zone. Second, the semimetallic overlap of the two bands is smaller so that the linear patterns perpendicular to the step-chain direction are more difficult to recognize. Consequently, with the Fermi surface of figure 5 it is not likely that $[\text{Ni}(\text{dddt})_2]_3(\text{HSO}_4)_2$ will exhibit the anisotropy expected for $(\text{BEDT-TTF})_3(\text{HSO}_4)_2$. According to our results $[\text{Ni}(\text{dddt})_2]_3(\text{HSO}_4)_2$ should be a more 2D semi-metal.

The previous results clearly prove that despite their similar crystal structures the two salts differ appreciably in their electronic structure. A careful look at the band structures of figures 2 and 4 shows that although there are similarities in the topology of the two partially filled bands for the two systems (for instance, the same band shape along the $\Gamma \rightarrow S$ and $\Gamma \rightarrow X$ directions), they are also important differences. For instance, along $\Gamma \rightarrow Y$ the second band from bottom in figure 2 is dispersive and the third band is quite flat. The second band from bottom has the same shape in figures 2 and 4 but it is the fourth band of figure 4 which is quite flat. The third band of figure 4 (which crosses the Fermi level) has a downward slope unlike the two partially filled bands of figure 2 along this direction. Thus, it seems that a LUMO band is overlapping with the HOMO bands in the vicinity of the Fermi level. Thus, we analyzed in detail the nature of the band orbitals for different wave vectors of the Brillouin zone. At Γ and X , the main character of the three lowest crystal orbitals is that of the HOMO of the donors. In contrast, only the first and fourth bands at Y are dominated by the HOMOs. The second and third bands at Y exhibit a very strong mixing of the HOMOs and LUMOs. This means that a LUMO band, which at Γ is very near the top of the upper HOMO band (i.e., the fourth band from bottom), intends to go down along $\Gamma \rightarrow Y$ undergoing avoided crossings with the second and third HOMO bands. In that way a substantial LUMO character is introduced in the second and third bands from bottom and the shape of the Fermi surface is significantly changed. It is then expected that the two salts exhibit noticeable differences in their transport properties.

We should now turn back to the second point raised in the introduction : why the transition of $[\text{Ni}(\text{dddt})_2]_3(\text{HSO}_4)_2$ occurs at a considerably lower temperature than that of $(\text{BEDT-TTF})_3(\text{HSO}_4)_2$ (25 K vs. 130 K) ? It is not clear at all what could be the effect of the $[\text{Ni}(\text{dddt})_2]_3(\text{HSO}_4)_2$ conformational disorder on the kind of structural transition we propose to occur here. We note however that even if such disorder has some role in lowering T_{M-1} , the decrease seems to be too large to be solely due to it. We rather believe the strong lowering of T_{M-1} originates from the clear electronic differences between the two salts noted before. In fact a likely explanation can be proposed when the interaction energies of tables I and II are compared. Since both the HOMO and LUMO of $\text{Ni}(\text{dddt})_2$ play a role in the electronic structure of the slabs, both $\beta_{\text{HOMO-HOMO}}$ and $\beta_{\text{LUMO-LUMO}}$ for the six different types of interactions (see Fig. 1) have been reported in table II. Except for the interaction B the two sets of values are qualitatively similar. As it was the case for the BEDT-TTF salt, the interactions along the step-chain (E and F) are among the strongest, but now one of the interactions along the inclined stacks (A) is very strong whereas it was among the weakest for the BEDT-TTF salt. This means that, from an electronic viewpoint, the step-chains are quite strongly connected in $[\text{Ni}(\text{dddt})_2]_3(\text{HSO}_4)_2$ whereas they are much less in $(\text{BEDT-TTF})_3(\text{HSO}_4)_2$. Incidentally, since in the $\text{Ni}(\text{dddt})_2$ salt interaction A is strong and interaction B is considerably weaker, it appears that, in contrast with the situation in the BEDT-TTF salt both structurally and electronically one can consider there are trimer donor units along the d_1 direction. The existence of these trimeric units along d_1 is what strongly connects the step-chains in the

Fig. 6. — Projection view of interaction A in (BEDT-TTF)₃(HSO₄)₂ (a) and [Ni(dddt)₂]₃(HSO₄)₂ (b).

present salt. This has two consequences for the physical properties of [Ni(dddt)₂]₃(HSO₄)₂. First, its Fermi surface should be less anisotropic, as actually found. Second, since it is clear that any electronic effect strengthening the intermolecular interactions will make the small displacements which we propose to be at the origin of the metal to insulator transition more difficult to achieve, the metallic state should be more stable.

In conclusion, the substitution of Ni²⁺ for the central C = C in BEDT-TTF has two important effects for the electronic structure of these salts. Firstly, it brings along an additional orbital, the LUMO of Ni(dddt)₂, which can mix into the HOMO partially filled bands. Secondly, the nickel d-orbitals can interact with the sulfur p-orbitals if the overlap mode, dictated mostly by the rest of the molecule, is favorable. This effect mostly affects the filled levels of the system (i.e., they implicate Ni(dddt)₂ orbitals other than the HOMO which have strong contributions from the metal which tries to establish the maximum bonding interactions with other atoms), but these are the levels which substantially contribute to the cohesion energy of the crystal. These subtle modifications, which do not change the global structure, have a slight effect in changing the orbital orientation of the sulfur p-orbitals and thus can indirectly modify the strength of the HOMO-HOMO interactions. This is the case for interaction A, where a decrease of nearly 0.06 Å in one of the S...S distances, the increase in the number of S...S short distances (see Fig. 6) and a small change in the donor orientation are responsible for the increase of the interaction and thus of the coupling between step-chains. This kind of subtle structural modifications are to be generally expected in the Ni(dddt)₂ salts with respect to the BEDT-TTF analogs. Because of these two reasons, although charge transfer salts of Ni(dddt)₂ can be isostructural with those of BEDT-TTF, the physical properties of these materials will not necessarily be similar to those of the parent BEDT-TTF salts.

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(β) should not be confused with the conventional transfer integrals (t). Although the two quantities are obviously related and have the same physical meaning, the absolute values of β are somewhat greater than those of t .

[27] For some examples of this type of analysis see :

(a) references [26a, b].

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