

## The conductivity and band structure of some synthetic semiconductors based on $M(dmit)_2$ ( $M = Ni, Pd, Pt$ )

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## The conductivity and band structure of some synthetic semiconductors based on $M(\text{dmit})_2$ ( $M = \text{Ni}, \text{Pd}, \text{Pt}$ )

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**Abstract.** The conductivity of the following six new low-dimensional compounds is reported:  $(\text{Me}_4\text{N})[\text{Ni}(\text{dmit})_2]$ ,  $(\text{Et}_4\text{N})[\text{Ni}(\text{dmit})_2]$ ,  $(\text{Pr}_4\text{N})[\text{Ni}(\text{dmit})_2]$ ,  $(\text{Bu}_4\text{N})[(\text{Ni}(\text{dmit})_2)]$ ,  $(\text{Bu}_4\text{N})[\text{Pt}(\text{dmit})_2]$  and  $(\text{Et}_4\text{N})_{0.5}[\text{Pd}(\text{dmit})_2]$ . Semiconducting behaviour is found for all the compounds investigated, with activation energies between 0.1 and 0.5 eV. The crystal structures have been established by x-ray diffraction. Using these, the band structure has been determined. It is shown that the compounds investigated are semiconductors each having a correlation gap resulting from an effective electron–electron repulsion of 1.0 eV.

### 1. Introduction

Charge-transfer compounds based on bis(1,3-dithiole-2-thione-4,5-dithiolato)-niccolate(III) (henceforth  $\text{Ni}(\text{dmit})_2$ ) have recently attracted much attention. With different donor molecules, various research groups have synthesised compounds that display either superconductivity ( $\text{TTF}[\text{Ni}(\text{dmit})_2]_2$ , Brossard *et al* (1986);  $(\text{Me}_4\text{N})_{0.5}[\text{Ni}(\text{dmit})_2]$ , Kajita *et al* (1988)), metallic conductivity (e.g.  $[(n\text{-Bu})_4]_{0.29}[\text{Ni}(\text{dmit})_2]$ , Valade *et al* (1983)) or semiconductivity (this paper and, e.g., for  $\text{TTF}[\text{Pd}(\text{dmit})_2]_2$  and  $\text{TTF}[\text{Pt}(\text{dmit})_2]_3$ , Bousseau *et al* (1986)). In this paper we study the conductivity of six compounds within the series  $(\text{R}_4\text{N})_x[\text{M}(\text{dmit})_2]$  ( $M = \text{Ni}, \text{Pd}, \text{Pt}$ ;  $\text{R} =$  methyl (Me), ethyl (Et), propyl (Pr) and butyl (Bu); and  $x = 0.5, 1$ ):  $(\text{Me}_4\text{N})[\text{Ni}(\text{dmit})_2]$ ,  $(\text{Et}_4\text{N})[\text{Ni}(\text{dmit})_2]$ ,  $(\text{Pr}_4\text{N})[\text{Ni}(\text{dmit})_2]$ ,  $(\text{Bu}_4\text{N})[\text{Ni}(\text{dmit})_2]$ ,  $(\text{Bu}_4\text{N})[\text{Pt}(\text{dmit})_2]$  and  $(\text{Et}_4\text{N})_{0.5}[\text{Pd}(\text{dmit})_2]$ , all of which display semiconducting behaviour. For all six compounds the crystal structure has been determined. This allows us to calculate the wavefunction overlap between valence orbitals of adjacent  $M(\text{dmit})_2$  ions, which is proportional to the transfer integral. The purpose of this paper is to relate the observed activation energy for the conductivity to the outcome of the tight-binding band-structure calculations. We will show that, under the assumption that the on-site Coulomb repulsion is much larger than the band width, the activation energies can be explained.

The organisation of the paper is as follows. First, the crystal structures will be discussed, with special emphasis on the  $M(\text{dmit})_2$  groups (§ 2). In § 3, the experimental results of the conductivity measurements are presented. In § 4 the band structures are

calculated. The last two sections are devoted to a comparison of observed and calculated gap values.

## 2. The preparation and crystal structure of $(R_4N)_x[M(dmit)_2]$

The dianionic salts  $(R_4N)_2[M(dmit)_2]$  were prepared following a synthesis route described in the literature (Steimecke *et al* 1979, Kato *et al* 1984, Valade *et al* 1985). From this, the  $(R_4N)_x[M(dmit)_2]$  ( $x = 1, 0.5$ ) coordination compounds are synthesised either by oxidation with iodine, or by autoxidation as described by Steimecke *et al* (1979).

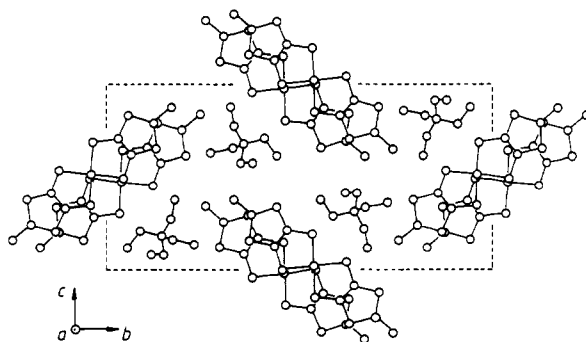
As details regarding the crystal structure have been or will be published elsewhere we restrict ourselves to features relevant to the electronic structure.  $M(dmit)_2$  compounds exhibit widely different forms of molecular packing (see, e.g., Kobayashi *et al* (1987) and references therein). Within the series considered in this paper, we encounter both 3D networks, 2D sheets and linear chains.

$(Me_4N)[Ni(dmit)_2]$  (Van Diemen *et al* 1988) features two crystallographically inequivalent  $Ni(dmit)_2$  groups, which are intricately stacked to form a structure resembling a winding staircase. There are no important Ni–S contacts between the anions: the shortest distance (3.98 Å) is significantly larger than the van der Waals radius (3.48 Å). The anions are stacked, side by side, in pairs with the central Ni atoms at relatively large distances. Inter-molecular contacts between the  $[Ni(dmit)_2]^-$  ions are formed by S–S contacts varying from 3.231 to 3.697 Å in distance, i.e. shorter than the corresponding van der Waals radius (3.70 Å).

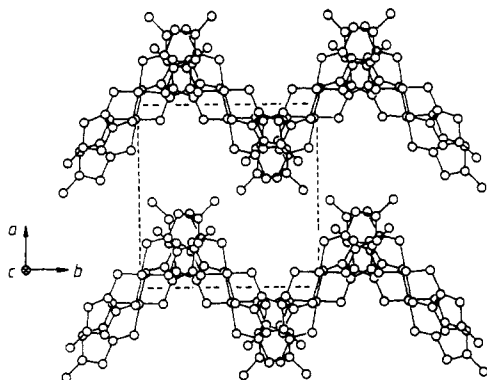
$(Et_4N)[Ni(dmit)_2]$  (Groeneveld *et al* 1986, Kramer *et al* 1987) is a one-dimensional system with zig-zag chains separated by the donor groups (see figure 1). The structure contains quasi-planar  $[Ni(dmit)_2]^-$  ions, stacked face to face with alternating Ni–Ni distances of 4.163 and 4.243 Å. Several short inter-molecular S–S contacts between the  $[Ni(dmit)_2]^-$  ions within the chain were found from 3.660 to 3.711 Å. Also a short Ni–S contact within a ‘dimer’ exists of 3.506 Å.

$(Pr_4N)[Ni(dmit)_2]$  (Van Diemen *et al* 1988) contains dimers of anions with short S–S contacts (3.496 Å). The dimers themselves are arranged in layers separated by the  $(Pr_4N)^+$  ions (see figure 2).

The structure of  $(Bu_4N)[Ni(dmit)_2]$  (Lindquist *et al* 1982) can be described as a 2D network of S–S contacts (3.514–3.611 Å). There are no short inter-molecular S–S



**Figure 1.** The structure of  $(Et_4N)[Ni(dmit)_2]$ . The stacking axis is normal to the  $bc$  plane. The broken line is the projection of the unit cell.



**Figure 2.** The structure of  $(\text{Pr}_4\text{N})[\text{Ni}(\text{dmit})_2]$ . The projection is along the  $c$  axis. The layer of dimers lies in the  $bc$  plane. The  $\text{Pr}_4\text{N}$  groups have been omitted for clarity.

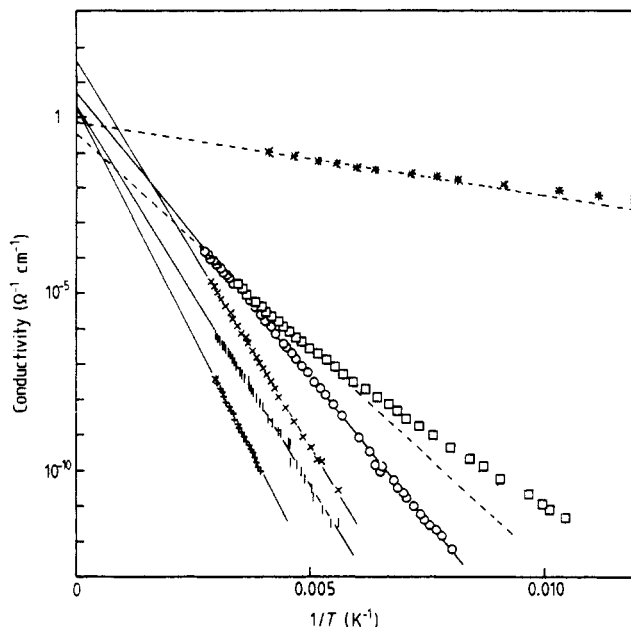
contacts in the direction perpendicular to this plane. The ‘isolated’ layers of anionic molecules are separated by the large  $(\text{Bu}_4\text{N})^+$  ions.

$(\text{Bu}_4\text{N})[\text{Pt}(\text{dmit})_2]$  (Von Marinelli *et al* 1988) consists of monomeric units, in which the Pt(III) ions are positioned at centres of symmetry. One important feature of this structure is the exclusive side-by-side intra-chain stacking of the completely planar units along the  $z$  axis, in contrast to the face-to-face stacking found in, e.g.,  $(\text{Et}_4\text{N})[\text{Ni}(\text{dmit})_2]$ . The anionic chains are separated from each other by chains formed by the  $[(\text{C}_4\text{H}_9)_4\text{N}]^+$  ions. Within the chain, formed by the  $\text{Pt}(\text{dmit})_2^-$  ions, the neighbouring anions are rotated by approximately  $75^\circ$  with respect to each other. The shortest inter-stack S–S distance is  $3.557 \text{ \AA}$ .

$(\text{Et}_4\text{N})_{0.5}[\text{Pd}(\text{dmit})_2]$  (Groeneveld *et al* 1988) has a stoichiometry differing from that of the above compounds. The unit cell comprises two  $\text{Pd}(\text{dmit})_2$  ions, with a total charge of minus one, which are arranged in sheets separated by a layer of tetra-ethylammonium cations. Within these sheets a chain can be identified with Pd–Pd distances of  $3.231$  and  $5.284 \text{ \AA}$  while S–S distances range from  $3.26$  to  $3.72 \text{ \AA}$ . This difference arises because in this compound, in contrast to the ones mentioned above, the anion is not flat. The two dmit ligands have an inclination of about  $7^\circ$  with one another, making the molecular unit V-shaped.

### 3. Conductivity experiments

Conductivity experiments were performed on single crystals with typical dimensions of  $1 \times 0.1 \times 0.1 \text{ mm}^3$ . Thin gold wires,  $30 \mu\text{m}$  in diameter, were glued to the crystals with silver paint (Electrodag 1415). All measurements were made in a two-probe configuration since the impedances are so high that it is not necessary to perform four-probe measurements. Temperatures between  $50$  and  $400 \text{ K}$  were obtained in a continuous-flow cryostat (Oxford Instruments), or in a conventional He bath cryostat. The temperature stability was better than  $1 \text{ K}$ . The data were taken at a cooling (warm-up) rate of approximately  $1 \text{ K min}^{-1}$ . The conductivity was measured with a Keithley model 617 electrometer using a constant voltage of  $1 \text{ V}$ . This enabled us to measure impedances up to  $10^{13} \Omega$ .



**Figure 3.** The temperature dependence of the conductivity for  $(\text{Me}_4\text{N})[\text{Ni}(\text{dmit})_2]$  (circles),  $(\text{Et}_4\text{N})[\text{Ni}(\text{dmit})_2]$  (squares),  $(\text{Pr}_4\text{N})[\text{Ni}(\text{dmit})_2]$  (bars),  $(\text{Bu}_4\text{N})[\text{Ni}(\text{dmit})_2]$  (plus signs),  $(\text{Bu}_4\text{N})[\text{Pr}(\text{dmit})_2]$  (crosses) and  $(\text{Et}_4\text{N})_{0.5}[\text{Pd}(\text{dmit})_2]$  (asterisks).

Figure 3 shows the conductivity of the six compounds under consideration. The temperature dependence of the conductivity may be expressed as

$$\sigma(T) = \sigma_0 \exp(-E_a/k_B T). \quad (3.1)$$

The values of the activation energy  $E_a$  and the conductivity prefactor  $\sigma_0$  are listed in table 1. As seen from figure 3, for  $(\text{Et}_4\text{N})[\text{Ni}(\text{dmit})_2]$  and  $(\text{Et}_4\text{N})_{0.5}[\text{Pd}(\text{dmit})_2]$  there are deviations from the simple semiconductor expression (3.1). In the latter case the behaviour is described by

$$\sigma(T) = \sigma_0 \exp[-(E'_a/k_B T)^{1/2}]. \quad (3.2)$$

Such a temperature dependence can be interpreted as regular semiconducting behaviour with a temperature-dependent gap  $E_a = (E'_a/T)^{1/2}$ , but often it is associated with dis-

**Table 1.** Conductivity parameters of  $(\text{R}_4\text{N})_x[\text{M}(\text{dmit})_2]$ .

Compound	$E_a$ (eV)	$\sigma_0$ ( $\Omega^{-1} \text{cm}^{-1}$ )
$(\text{Me}_4\text{N})[\text{Ni}(\text{dmit})_2]$	0.32	4.8
$(\text{Et}_4\text{N})[\text{Ni}(\text{dmit})_2]$	0.25†	0.4
$(\text{Pr}_4\text{N})[\text{Ni}(\text{dmit})_2]$	0.43	2.1
$(\text{Bu}_4\text{N})[\text{Ni}(\text{dmit})_2]$	0.51	1.8
$(\text{Bu}_4\text{N})[\text{Pt}(\text{dmit})_2]$	0.43	38
$(\text{Et}_4\text{N})_{0.5}[\text{Pd}(\text{dmit})_2]$	0.10†	0.7

† Since the gap is temperature dependent, the room-temperature value is given.

order (Bloch *et al* 1972). We will use the room-temperature activation energy for comparison with the calculations of the electronic structure.

With regard to the values of  $\sigma_0$ , one observes that they vary relatively modestly, i.e. within two orders of magnitude. This value (roughly  $5 \Omega^{-1} \text{cm}^{-1}$ ) can be associated with the carrier mobility, using

$$\sigma_0 = n_0 q \mu \quad (3.3)$$

where  $n_0$  is the total electron density,  $q$  the electron charge and  $\mu$  the mobility;  $n_0 \approx 8 \times 10^{20} \text{ electrons cm}^{-3}$ , resulting in a mobility of  $0.01\text{--}0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . Similar values are found for semiconductors within the series of substituted morpholinium  $\text{TCNQ}_2$  (Visser *et al* 1982). For typical 1D metals like  $\text{TTF-TCNQ}_2$  the mobility is two orders of magnitude higher (Cohen *et al* 1974).

#### 4. Band-structure calculations

In this section the results of a band-structure calculation for the above-mentioned compounds are presented. The calculation of the band structure of an organic (semi)conductor is always a two-stage process: firstly the valence molecular orbitals of the molecules have to be calculated and only thereafter can one calculate the overlap between neighbouring molecules, which in turn enables one to calculate the band structure. This division is necessary since the energy scale of chemical bonding within the molecule is a few orders of magnitude higher than the transfer integrals linking them together.

We will assume that the electron Hamiltonian for the system is of the form

$$\mathcal{H} = \sum_{i \neq j, \sigma} t_{ij} (c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma}) + \sum_{i, \alpha} \varepsilon_\alpha c_{i\alpha}^\dagger c_{i\alpha} + \sum_i U c_{i\downarrow}^\dagger c_{i\downarrow} c_{i\uparrow}^\dagger c_{i\uparrow} \quad (4.1)$$

where  $t_{ij}$  is the transfer integral,  $\varepsilon_\alpha$  is a site-dependent Madelung energy ( $\alpha$  denotes crystallographically different sites) and  $U$  is the on-site (Hubbard) electron–electron repulsion. We note that the transfer integrals and local potentials are different for all systems, whereas the value of the Hubbard parameter  $U$  is approximately constant for a given acceptor molecule and a fixed band filling. The Hubbard Hamiltonian is in general insoluble, but its limits are well known: if  $U \ll W$  where  $W$  is the band width, a half-filled system is metallic with Pauli-like susceptibility. If, on the other hand,  $U$  exceeds the band width, the system is an insulator with weak antiferromagnetic exchange  $J = 4t^2/U$ ; the band is split in two identical parts with an energy separation  $U$ . The task we set ourselves in this section is to calculate the transfer integrals.

Molecular orbitals of neutral  $\text{Ni}(\text{dmit})_2$  and  $\text{Pt}(\text{dmit})_2$  units were obtained from an extended Hückel calculation (Howell *et al* 1980). The atomic orbitals are of Slater type:

$$|\varphi^{\text{AO}}\rangle = (2\xi)^{n+1/2} [(2n)!]^{-1/2} r^{n-1} e^{-\xi r} Y_{lm}(\theta, \varphi). \quad (4.2)$$

For the different atoms, the radii and principal quantum numbers are listed in table 2. The resulting molecular orbitals, linear combinations of (4.2), are shown in figure 4. The differences between Ni and Pt molecules are minor and mainly affect the metal atom; the ligand orbitals hardly change at all. Since no parameters were known for Pd, we have used for the latter the average of Ni and Pt. The  $\text{Ni}(\text{dmit})_2$  orbital is quite similar to the ones obtained by Kobayashi *et al* (1987).

The overlap between molecular orbitals on adjacent  $M(\text{dmit})_2$  units can be calculated

**Table 2.** Slater orbital data.

Atom	Orbital	Coefficient	$\zeta$ ( $\text{\AA}^{-1}$ )
C	$2p_z$		3.072
S	$3p_z$		3.445
Ni†	$3d_{xz}$	0.610	10.87
		0.512	4.91
Pd†	$4d_{xz}$	0.619	11.31
		0.529	4.94
Pt†	$5d_{xz}$	0.633	11.37
		0.551	5.10

† The  $d_{xz}$  orbitals are contracted (Basch and Gray 1966).

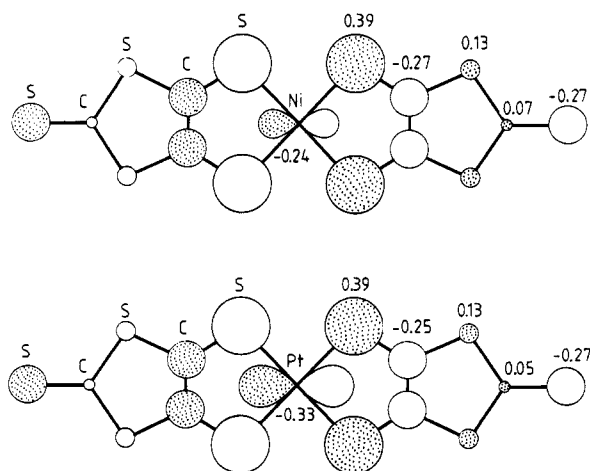
numerically, using a scheme developed by Roothaan (1951). The overlap,  $S$ , is proportional to the transfer integrals (Berlinsky *et al* 1974, Grant 1983):

$$t_{ij} = KS_{ij}(E_i + E_j)/2 \quad (4.3)$$

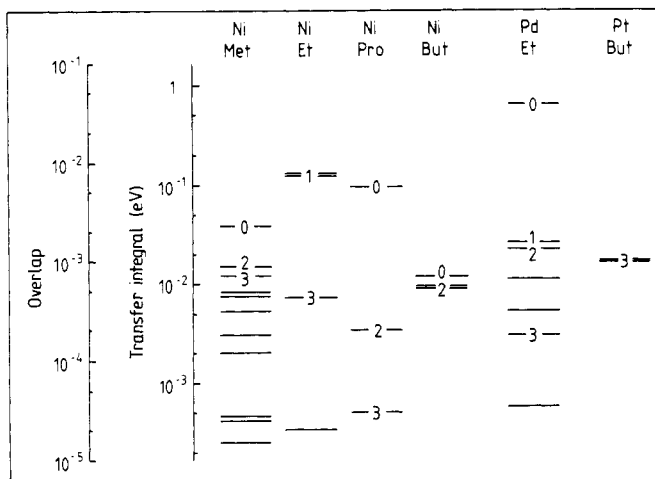
where  $E_i$  and  $E_j$  are the ionisation energies of the relevant orbital, i.e. the LUMO of the neutral molecule, and  $K$  is a constant between 1 and 2 (usually taken as 1.75). The calculated ionisation energy is 9.5 eV, both for Ni(dmit)<sub>2</sub> and Pt(dmit)<sub>2</sub>. Therefore, we also use

$$t_{ij} = 17 S_{ij} \text{ (eV)}. \quad (4.4)$$

Our values for  $S_{ij}$  are systematically larger by a factor of 1.7 than those obtained by Kobayashi *et al* (1987). The origin of this discrepancy is not known; we can merely state that our wavefunctions are properly normalised and that the configurational dependence of the overlap is the same as obtained by Kobayashi and co-workers.



**Figure 4.** Molecular orbitals of Ni(dmit)<sub>2</sub> and Pt(dmit)<sub>2</sub>. Carbon and sulphur orbitals are of the  $p_z$  type, while those of nickel and platinum are of the  $d_{xz}$  type. Radii and quantum numbers are listed in table 2.

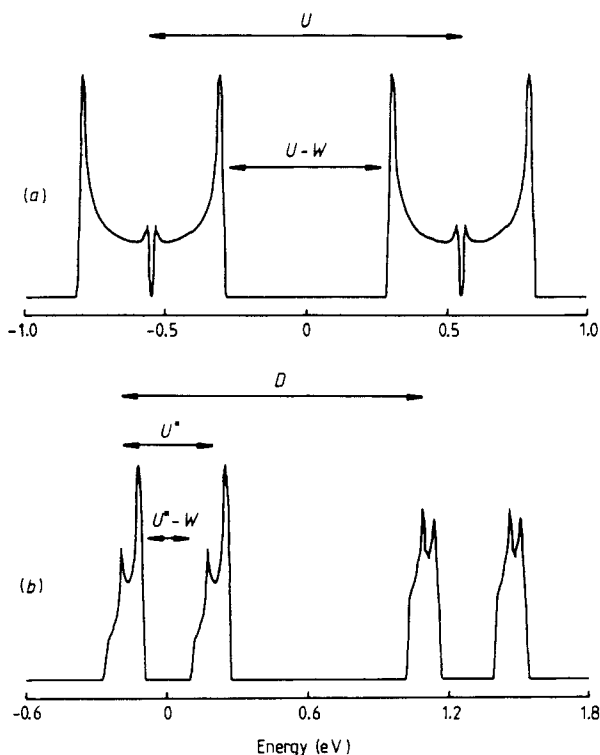


**Figure 5.** Inter-molecular overlaps for six  $(R_4N)_x[M(\text{dmit})_2]$  compounds. The heading gives the metal atom and the alkyl group;  $x = 1$  for all except  $(Et_4N)_{0.5}[Pd(\text{dmit})_2]$ . The numbers associated with the overlaps denote the dimensionality of the system if smaller transfer integrals are neglected: 0 implies a dimer, 1 a chain etc (see the text).

All overlaps have been calculated for the six compounds. Overlaps exceeding  $10^{-5}$  are shown graphically in figure 5. The numbers assigned to the overlaps denote the dimensionality of the system if the smaller overlaps are neglected.  $(Et_4N)_{0.5}[Pd(\text{dmit})_2]$  is taken as an example: a large transfer integral (0.63 eV) couples two  $Pd(\text{dmit})_2$  groups to dimers, denoted by 0. Two subsequent transfer integrals (0.026 and 0.022 eV) interconnect these dimers. The first one occurs twice as often as the second and forms chains (1); with the second a 2D network is constructed (2). Two extra transfer integrals strengthen this layer. The first transfer integral that couples neighbouring layers (3) has a value of  $2.9 \times 10^{-3}$  eV. The transfer integrals were used to determine the electronic density of states (DOS) in the interactionless limits  $U = 0$  and  $U \gg W$  ( $W$  denotes the band width). In the first case, the band is half-filled (quarter-filled for the Pd compound). In the limit where  $U$  exceeds  $W$ , one has two identical bands, separated by an energy  $U$  (Hubbard 1965). The lower one is then completely filled (half-filled for Pd). The results are shown in figure 6. For  $(Me_4N)[Ni(\text{dmit})_2]$  the result lacks the unambiguity of the other DOS pictures, since in this case two crystallographically independent sites are present. This gives rise to the possibility of different site energies (see equation (1)), which broaden and split the band. The effect is shown in figure 6(a). Table 3 lists the band widths and the dimensionality of the electronic system. The calculated anisotropies are in agreement with what might have been anticipated on the basis of the structural descriptions given in § 2. From examination of the values of atom-to-atom overlaps it was found that the S-S contacts determine the total molecule-to-molecule overlap.

All  $M(\text{dmit})_2$  species, with the exception of  $Pd(\text{dmit})_2$ , are flat. In the latter case we have performed two different calculations to study the effect of the molecular bending. First the  $z$  axis of the reference frame for the atomic  $p_z$  and  $d_{xz}$  orbitals was taken to be the mean of the two normal vectors of the dmit planes. In a second calculation, the two dmit groups were handled separately, each with their own reference frame. The difference amounted to only a few per cent. In the above, the (probably more important) changes in the MO of  $Pd(\text{dmit})_2$  upon bending have been neglected.





**Figure 6.** The density of states in arbitrary units: the full trace is the DOS assuming equal on-site energies for the different Ni(dmit)<sub>2</sub> molecules; the broken trace is the DOS if  $E_1 = 0.1$  eV and  $E_2 = -0.1$  eV, for (Me<sub>4</sub>N)[Ni(dmit)<sub>2</sub>] (a), (Et<sub>4</sub>N)[Ni(dmit)<sub>2</sub>] (b), (Pr<sub>4</sub>N)[Ni(dmit)<sub>2</sub>] (c), (Bu<sub>4</sub>N)[Ni(dmit)<sub>2</sub>] (d), (Bu<sub>4</sub>N)[Pt(dmit)<sub>2</sub>] (e) and (Et<sub>4</sub>N)<sub>0.5</sub>[Pd(dmit)<sub>2</sub>] (f). The energies are relative to the centre of the band.

## 5. Discussion

In this section the link will be established between the activation energies obtained from the conductivity experiments and the band-structure data. As noted previously, one assumes the Hubbard  $U$ -term to be determined primarily by the type of acceptor molecule and band filling.

As can be seen from table 1 and figure 6, the proper limit is  $U \gg W$ , since otherwise one would expect metallic or semimetallic behaviour. If  $U \gg W$ , the gap  $\Delta (=2E_a)$  is  $U - W$  (see figure 7). We have used the same  $U$ -value for all compounds with a 1:1 donor to acceptor ratio. In table 4 experimental and calculated gaps are compared with each other, assuming  $U$  equal to  $1.05 \pm 0.1$  eV. Note that this value can also be used for the Pt compound, reflecting the minor importance of the metal atom in the determination of electronic properties. Comparison between theory and experiment is most difficult for (Me<sub>4</sub>N)[Ni(dmit)<sub>2</sub>] as a consequence of the already mentioned possibility of different site energies. Therefore, only a lower bound for the band width can be given. It would seem that the difference is quite appreciable with respect to the transfer integrals. The value of  $E_1 - E_2$  can be estimated to be  $\approx 0.2$  eV. The agreement thus obtained between theory and experiment is satisfactory.

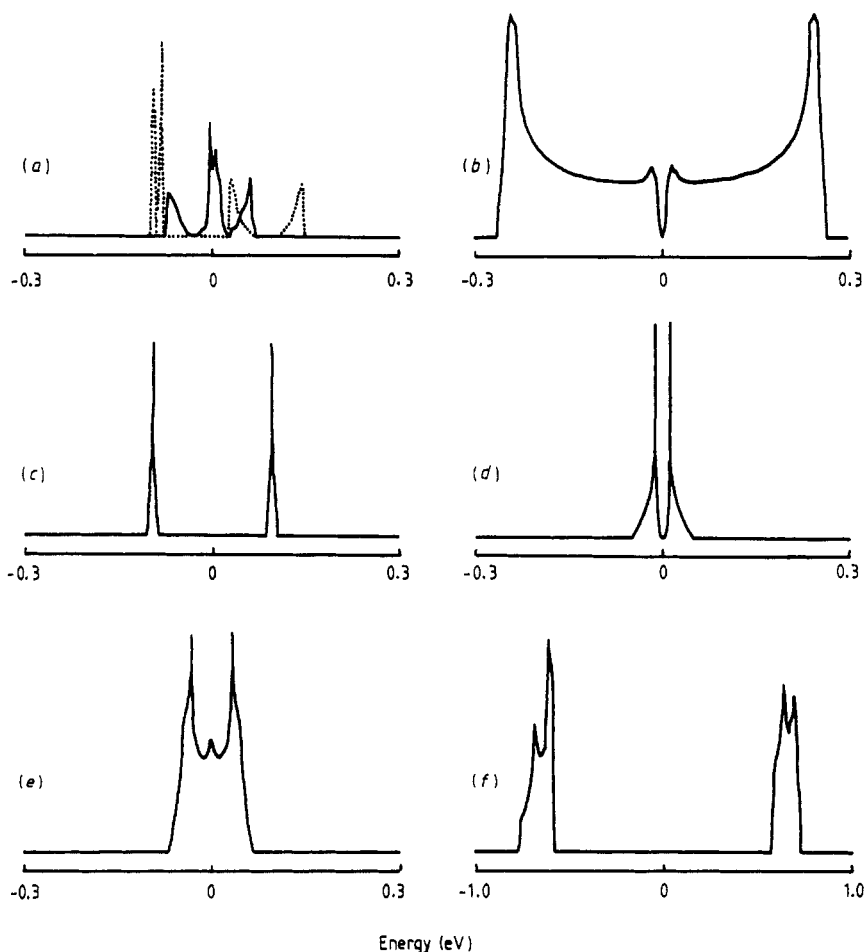
**Table 3.** Calculated band-structure parameters of  $(R_4N)_x[M(\text{dmit})_2]$ .

Compound	Electronic structure	$W_{1D}:W_{2D}:W_{3D}^\dagger$	Bandwidth ( $10^3$ S)
$(\text{Me}_4\text{N})[\text{Ni}(\text{dmit})_2]$	3D	1:1:0.5	$>8.6^\ddagger$
$(\text{Et}_4\text{N})[\text{Ni}(\text{dmit})_2]$	1D	1:0.05:0.05	31.5
$(\text{Pr}_4\text{N})[\text{Ni}(\text{dmit})_2]$	Sheet of dimers	1:1:0.2	12.3
$(\text{Bu}_4\text{N})[\text{Ni}(\text{dmit})_2]$	2D	1:1:0.01(?)	5.8
$(\text{Bu}_4\text{N})[\text{Pt}(\text{dmit})_2]$	3D	1:1:1	8.0
$(\text{Et}_4\text{N})_{0.5}[\text{Pd}(\text{dmit})_2]$	Anisotropic dimer system	1:0.4:0.05	10.4§

$^\dagger$  Relative band widths in three crystallographic directions.

$^\ddagger$  The quoted value neglects the difference in site energy (see text).

$^\S$  The band width of the bonding dimer band.



**Figure 7.** The density of states in the  $U \gg W$  limit for  $(\text{Et}_4\text{N})[\text{Ni}(\text{dmit})_2]$  (a) and for  $(\text{Et}_4\text{N})_{0.5}[\text{Pd}(\text{dmit})_2]$  (b).  $D$  is the dimer splitting.

**Table 4.** Experimental and theoretical gap values.

Compound	$\Delta_{\text{exp}} = 2E_a$ (eV)	$\Delta_{\text{calc}}$ (eV)	$U$ (eV)
(Me <sub>4</sub> N)[Ni(dmit) <sub>2</sub> ]	0.64	<0.90	1.05
(Et <sub>4</sub> N)[Ni(dmit) <sub>2</sub> ]	0.50	0.51	1.05
(Pr <sub>4</sub> N)[Ni(dmit) <sub>2</sub> ]	0.86	0.84	1.05
(Bu <sub>4</sub> N)[Ni(dmit) <sub>2</sub> ]	1.02	0.95	1.05
(Bu <sub>4</sub> N)[Pt(dmit) <sub>2</sub> ]	0.86	0.91	1.05
(Et <sub>4</sub> N)[Pd(dmit) <sub>2</sub> ]	0.20	0.20	0.37

A special place is taken by (Et<sub>4</sub>N)<sub>0.5</sub>[Pd(dmit)<sub>2</sub>]. As seen above, this compound consists of dimers. The dimer splitting  $D$  (figure 7) is 1.3 eV, making it the largest band-structure parameter. This means that all electrons occupy the bonding dimer wavefunction, which has a band width of 0.17 eV. This turns the system into an effectively half-filled band system, like the compounds considered previously. The effective Coulomb repulsion is now that for a dimer:  $U^* = 0.35 \pm 0.05$  eV—substantially less than the value for a single M(dmit)<sub>2</sub> ion.

We now return to the temperature dependence of the semiconductor gap in (Et<sub>4</sub>N)[Ni(dmit)<sub>2</sub>] and (Et<sub>4</sub>N)<sub>0.5</sub>[Pd(dmit)<sub>2</sub>]. It was seen that the gap has a value  $U - W$ . If the temperature is lowered, the transfer integrals increase as a consequence of the decrease in length of the crystal axes. This increases the band width and hence reduces the correlation gap  $U - W$ . We have estimated the magnitude of this effect, using an estimated thermal expansion parameter  $\alpha \approx 10^{-4} \text{ K}^{-1}$ , suitable for organic materials. The increase in band width is of the order of 10 to 20% going from 300 to 100 K. The smaller the values of  $U - W$ , the larger the temperature dependence of the gap—this explains why the gap variation is only seen in the compounds with the smallest gaps. This effect, however, is much smaller than that found experimentally (70%). In a later paper we will show that the  $T^{-1/2}$  behaviour of the conductivity can be explained if one takes into account the large thermal motion of the anions.

## 6. Conclusion

We have analysed the semiconductor gap in a series of M(dmit)<sub>2</sub> compounds with large cationic 'donor' molecules (tetra-alkylammonium). The gap is determined by the difference between the correlation  $U$  and the band width. These systems have band widths of 0.1 to 0.5 eV, which is small compared with the on-site Coulomb repulsion ( $U$ ), for which we found 1.0 eV. This value was found to be independent of what the compound was for all 1:1 complexes. Additionally, we have examined one 1:2 compound, which consists of dimeric units. In this case, the electron–electron interaction could be described by a dimer  $U$  for which a value of 0.35 eV was found.

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