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Stable Molecular Metal $[\text{Pd}(\text{dddt})_2]\text{Ag}_{1.54}\text{Br}_{3.50}$: Synthesis, Crystal Structure, Transport Properties and Electronic Band Structure

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Abstract. — The synthesis, crystal and electronic band structures as well as conducting properties of the new stable molecular metal $[\text{Pd}(\text{dddt})_2]\text{Ag}_{1.54}\text{Br}_{3.50}$ (dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolato) are reported. The crystal structure contains layers of donor cations alternating with layers of silver bromide complex anions along the *a* axis of the unit cell. The Ag and Br atoms are disordered in the anion layer. The conducting layers contain uniform stacks of the translationally equivalent $\text{Pd}(\text{dddt})_2$ cations along the *c*-axis with a Pd · Pd distance of 4.157(2) Å. Within the cation layers there are shortened interstack S · S contacts (3.49(3) and 3.56(3) Å). The temperature dependence of the resistivity exhibits metallic behaviour down to 1.3 K. The resistivity anisotropy (ρ_a^*/ρ_{bc}) at room temperature is about 600 and does not change considerably when decreasing the temperature down to 4.2 K. The origin of the metallic conductivity of $[\text{Pd}(\text{dddt})_2]\text{Ag}_{1.54}\text{Br}_{3.50}$ as well as the stability of this salt with respect to metal-to-insulator transitions is explained on the basis of tight binding band structure calculations.

Introduction

Transition metal complexes of 5,6-dihydro-1,4-dithiin-2,3-dithiol ($\text{M}(\text{dddt})_2$) present considerable interest since they are close structural analogues of the bis(ethylenedithio) tetrathiafulvalene molecule (BEDT-TTF or ET), which is known to form superconducting charge transfer

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salts [1]. Formally, the central C = C bond of ET is substituted by a metal ion in the M(dddt)₂ complexes. Like ET, M(dddt)₂ complexes (M = Ni, Pt, Pd, Au) form conducting charge transfer salts in a partially oxidized state [2-7]. However, although the ET and M(dddt)₂ salts have often similar crystal structures, their electronic band structures can be quite different [8,9]. The reason is that whereas only the HOMO (highest occupied molecular orbital) of ET plays a role in the conduction bands of its charge transfer salts, both the HOMO and LUMO (lowest unoccupied molecular orbital) of M(dddt)₂ can be involved in those of the M(dddt)₂ charge transfer salts [8,10,11]. Such anomalous behaviour is also found in several charge transfer salts of the M(dmit)₂ anion [12,13].

The electronic structure and conducting properties of the M(dddt)₂ salts strongly depend on the packing motif of the M(dddt)₂ cations in the crystal lattice, which, in turn, is determined by nature of the metal (M) and the counterion [2-7]. Therefore, variations in the nature of the metal and/or the anion in the M(dddt)₂ charge transfer salts are of a considerable interest in the search for new molecular metals and superconductors. Recently, we have found that the electrochemical oxidation of Ni(dddt)₂ in the presence of the electrolyte Bu₄NAgBr₂ gives rise to a Ni(dddt)₂ salt with a polymeric silver bromide complex anion, which exhibits high conductivity down to liquid helium temperature [6]. However the crystal structure of this salt could not be solved because of the low quality of the crystals. Thus, it was of interest to synthesize the salts of other M(dddt)₂ complexes with silver bromide anions. In this article we present the synthesis, crystal structure, transport properties and electronic band structure of a salt of Pd(dddt)₂ with a silver bromide complex anion which is a stable molecular metal down to 1.3 K.

Experimental

ELECTROCRYSTALLIZATION. — Crystals of [Pd(dddt)₂]Ag_{1.54}Br_{3.50} were prepared by electrochemical oxidation of the neutral Pd(dddt)₂ complex in nitrobenzene (5×10^{-4} mol/l) on a Pt anode under constant current ($j = 1 \mu\text{A}/\text{cm}^2$) at 24.5 °C. The Bu₄NAgBr₂ salt was used as electrolyte (5×10^{-3} mol/l). The crystals grew up on the anode for one week as bright black very thin plates ($\sim 0.9 \times 0.5 \times 0.01 \text{ mm}^3$). Their composition was deduced from an X-ray study. The Ag/Pd ratio (1.64 ± 0.1) was also determined from X-ray photoelectron spectroscopy and it was found to be close to the value obtained from the X-ray analysis.

CRYSTAL STRUCTURE DETERMINATION. — The main crystal data for C₈H₈Ag_{1.54}Br_{3.50}PdS₈ are as follows: $M = 912.88$, $a = 20.10(2)$, $b = 6.002(5)$, $c = 4.157(2) \text{ \AA}$, $\alpha = 98.01(6)$, $\beta = 94.51(6)$, $\gamma = 96.39(7)^\circ$, $V = 491(1) \text{ \AA}^3$, space group P $\bar{1}$. $Z = 1$, $D_c = 3.09 \text{ g cm}^{-3}$, $F(000) = 424.9$, $\mu = 109.6 \text{ cm}^{-1}$. Refinement of the unit cell dimensions and measurement of 814 non-zero reflections were performed on a four-circle automatic KM-4 (KUMA DIFFRACTION, Poland) diffractometer with monochromatized MoK α radiation, using a $\theta - 2\theta$ scan technique and $2\theta_{\text{max}} = 44.1^\circ$. The structure was solved by direct methods according to the SHELXS-86 program. Refinement of the data was carried out with a full-matrix least-squares method in the anisotropic approximation for all non hydrogen atoms (SHELXL-93 program). The hydrogen atoms were not localized. An absorption correction was not applied. The final value of R (0.076) was determined for 566 reflections at $I > 4\sigma(I)$. The atom coordinates and equivalent isotropic thermal parameters are listed in Table I. The determination of the unit cell dimensions as well as the bond lengths and angles was not too precise because of the poor quality of the crystals. Therefore, except otherwise stated, the values of the bond lengths and angles are not discussed in detail.

Table I. — Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $[\text{Pd}(\text{ddd}t)_2]\text{Ag}_{1.54}\text{Br}_{3.50}$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	$U(\text{eq})$
Pd (1)	5000	5000	5000	39 (2)
S (1)	4093 (4)	3026 (13)	2409 (22)	42 (2)
S (2)	4392 (4)	7894 (13)	6580 (25)	51 (3)
S (3)	2638 (4)	3499 (13)	1659 (22)	43 (2)
S (4)	3060 (4)	8923 (13)	5744 (24)	49 (3)
C (1)	3615 (16)	6936 (46)	5147 (84)	42 (9)
C (2)	3417 (12)	4708 (44)	3116 (68)	25 (7)
C (3)	2304 (18)	7824 (51)	3402 (86)	44 (10)
C (4)	2978 (17)	5322 (49)	3501 (91)	48 (10)
Ag (1) *	975 (9)	1441 (54)	-2741 (41)	237 (19)
Ag (2) *	896 (13)	-1204 (114)	-1518 (33)	351 (43)
Br (1) *	127 (17)	898 (105)	998 (67)	417 (52)
Br (2) *	505 (13)	5248 (58)	-2182 (37)	214 (16)
Br (3) *	-46 (15)	2084 (119)	-3280 (54)	474 (52)

* The partial populations are 0.38 (2) for Ag (1), 0.39 (3) for Ag (2), 0.48 for Br (1), 0.59 (5) for Br (2) and 0.68 for Br (3).

ELECTRICAL TRANSPORT MEASUREMENTS. — Resistance was measured by the standard four probe dc technique in the layer bc plane as well as by a modified Montgomery method [14] approximately along a diagonal in the bc plane (direction of the maximum length of the crystals) and along the a^* axis, *i.e.*, perpendicular to the conducting layers. The ambient temperature conductivity measured in the bc plane for four crystals was $12 - 40 \Omega^{-1}\text{cm}^{-1}$.

BAND STRUCTURE CALCULATIONS. — The tight-binding band structure calculations are based upon the effective one-electron Hamiltonian of the extended Hückel method [15]. The off-diagonal matrix elements of the Hamiltonian were calculated according to the modified Wolfsberg-Helmholz formula [16]. All valence electrons were explicitly taken into account in the calculations. The basis set consisted of Slater type orbitals of double- ζ quality for Pd 4d and of single- ζ quality for Pd 5s and 5p, S 3s and 3p, C 2s and 2p and H 1s. The exponents, contraction coefficients of the double- ζ orbitals and atomic parameters used for the calculations were taken from previous work [12].

Results and Discussion

The crystal structure of $[\text{Pd}(\text{ddd}t)_2]\text{Ag}_{1.54}\text{Br}_{3.50}$ contains alternating layers of donor-cations and non-stoichiometric silver bromide anions parallel to the bc -plane (Fig. 1). The Ag and Br atoms of the anion layer are disordered occupying four and six positions, with total populations of 1.54(5) and 3.50(1), respectively. It appeared impossible to pick out any rational fragments in the anion structure because of the disordering of the Ag and Br atoms.

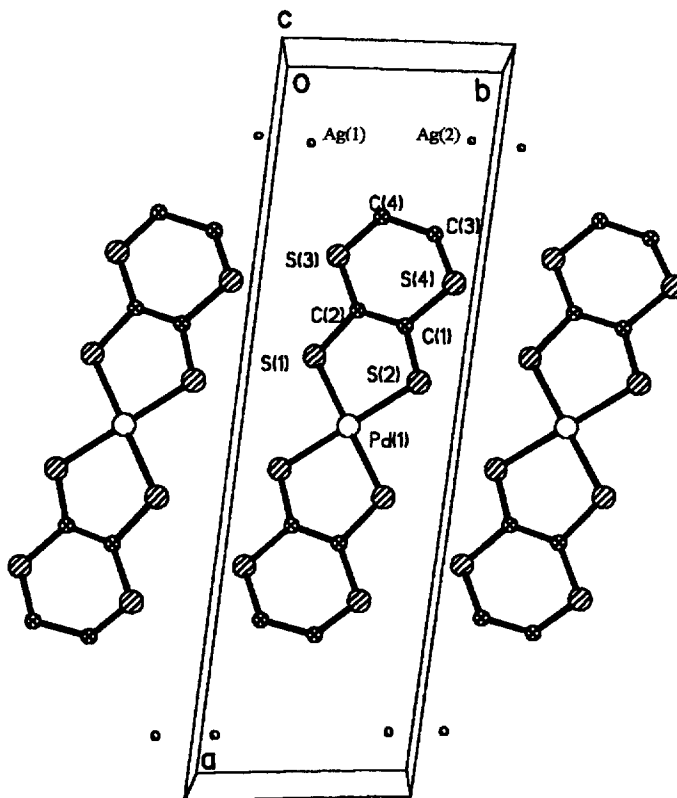


Fig. 1. — Crystal structure of $[\text{Pd}(\text{dddtd})_2]\text{Ag}_{154}\text{Br}_{350}$. The bromine atoms are omitted in the anion layer for clarity.

The $\text{Pd}(\text{dddtd})_2$ cation has C_1 symmetry with the Pd atom located in the center of symmetry. All atoms of the cation (except for the terminal carbons) are located in one plane (the largest deviation from the plane running through the $\text{PdS}(1)\text{S}(2)\text{C}(1)\text{C}(2)\text{S}(3)\text{S}(4)$ atoms is 0.06 \AA). In contrast with most conducting charge transfer salts of the $\text{Pd}(\text{dmit})_2$ anion [17], there is no pyramidalization of the Pd atom in the $\text{Pd}(\text{dddtd})_2$ cation. The six-membered cycles of the donor have an eclipsed conformation (the deviations of the C(3) and C(4) atoms from the mean cation plane are 0.37 and -0.42 \AA , respectively). The Pd-S distances ($2.252(8) \text{ \AA}$ and $2.285(8) \text{ \AA}$) are shorter than the respective distances in the crystals of the $\text{Pd}(\text{dmit})_2$ salts ($2.292(2) \text{ \AA}$ and $2.303(3) \text{ \AA}$ [17]). In the conducting layers of the β -type the translationally equivalent $\text{Pd}(\text{dddtd})_2$ cations form uniform stacks along the c -axis with a $\text{Pd} \cdots \text{Pd}$ distance of $4.157(2) \text{ \AA}$ (Fig. 2). The successive donors of such stacks are displaced along the short axis of the molecule so that the $\text{Pd}(\text{dddtd})_2$ cation layers can be described as a parallel arrangement of inclined donor stacks. The interplanar distances in the $\text{Pd}(\text{dddtd})_2$ stacks are identical and equal to 3.84 \AA . There are S \cdots S interstack contacts as short as $3.49(3) \text{ \AA}$ ($\text{S}(1) \cdots \text{S}(4)$, noted 1 in Fig. 2) and $3.56(3) \text{ \AA}$ ($\text{S}(3) \cdots \text{S}(4)$, noted 2 in Fig. 2). Since the Pd and Pt bis(dithiolates) usually form dimers inside the stacks of their charge transfer salts [3, 4, 10, 17, 18], the existence of uniform $\text{Pd}(\text{dddtd})_2$ chains in the present salt is quite remarkable.

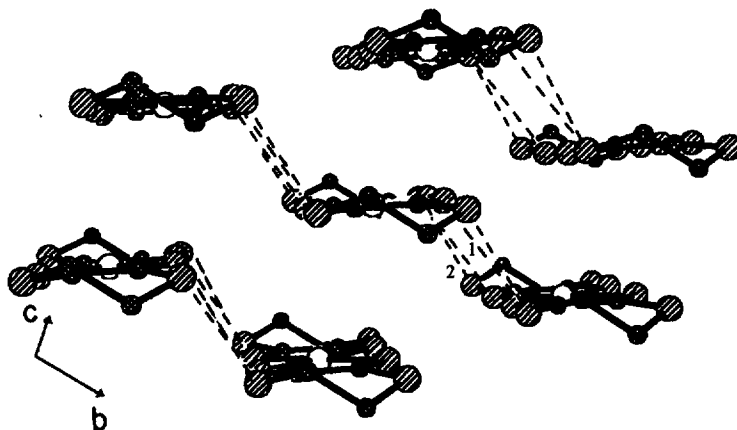


Fig. 2. — Structure of the cation layer in the $[\text{Pd}(\text{dddt})_2]\text{Ag}_{1.54}\text{Br}_{3.5}$ salt where the shortened inter-stack $\text{S}\cdots\text{S}$ contacts are shown.

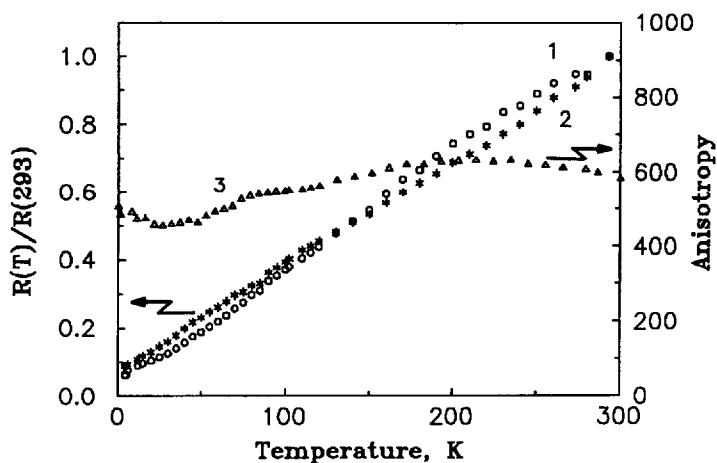


Fig. 3. — Temperature dependence of the normalized resistance along different crystallographic directions and resistance anisotropy for the same $[\text{Pd}(\text{dddt})_2]\text{Ag}_{1.54}\text{Br}_{3.5}$ crystal: 1) along the a^* -axis (ρ_{\perp}); 2) along a diagonal in the bc -plane (ρ_{\parallel}); 3) anisotropy ($\rho_{\perp}/\rho_{\parallel}$)

The temperature dependences of the normalized resistance along the a^* axis (ρ_{\perp}) and approximately along a diagonal in the bc -plane (ρ_{\parallel}) as well as the resistance anisotropy for the same $[\text{Pd}(\text{dddt})_2]\text{Ag}_{1.54}\text{Br}_{3.5}$ crystal are plotted in Figure 3. In spite of the existence of disorder in the structure, the resistance exhibits metallic behavior down to 1.3 K. The values of the room temperature conductivities are $\sigma_a^* = 6 \times 10^{-2} \Omega^{-1}\text{cm}^{-1}$ and $\sigma_{bc} = 35 \Omega^{-1}\text{cm}^{-1}$. From 293 K to 4.2 K σ_{\perp} and σ_{\parallel} decrease sixteen and ten times, respectively. The anisotropy ($\rho_{\perp}/\rho_{\parallel}$) at 293 K is about 600 and is close to those of the quasi-2D metals based on ET salts. The change of this anisotropy down to 4.2 K is small.

After $[\text{Ni}(\text{dddt})_2]_3(\text{AuBr}_2)_2$ [6, 7], $[\text{Pd}(\text{dddt})_2]\text{Ag}_{1.54}\text{Br}_{3.5}$ is the second example of a stable metal among the $\text{M}(\text{dddt})_2$ charge transfer salts. However, because of the different stoichiometry and crystal structure, the electronic structure of the two systems must exhibit some

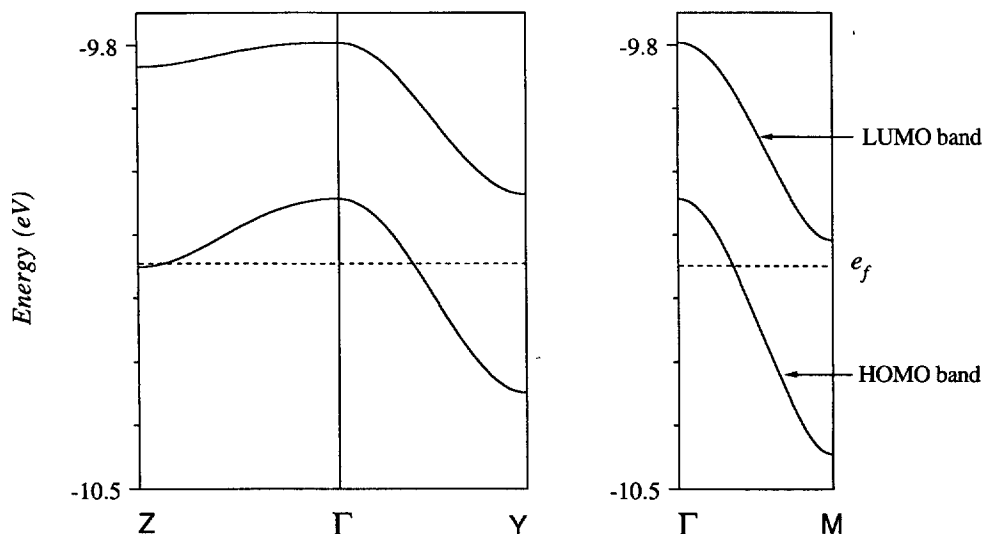


Fig. 4. — Dispersion relations for the HOMO and LUMO bands of the donor slabs in $[\text{Pd}(\text{dddtt})_2]\text{Ag}_{1.54}\text{Br}_{3.50}$. The dashed line refers to the Fermi level assuming a charge transfer of $+0.5$ per donor molecule. Γ , Y , Z and M refer to the wave vectors $(0, 0)$, $(b^*/2, 0)$, $(0, c^*/2)$ and $(-b^*/2, c^*/2)$, respectively.

differences. Thus, in order to gain some understanding about the factors stabilizing the metallic state in $\text{M}(\text{dddtt})_2$ charge transfer salts we have carried out a tight binding band structure study of $[\text{Pd}(\text{dddtt})_2]\text{Ag}_{1.54}\text{Br}_{3.50}$. The HOMO-LUMO gap for the $\text{Pd}(\text{dddtt})_2$ donor is 0.30 eV, a typical value for molecules leading to two-band systems [11]. Since the repeat unit of the $\text{Pd}(\text{dddtt})_2$ layers contains just one donor, the band structure should be very simple, *i.e.*, two overlapping bands originating from the HOMO and LUMO of $\text{Pd}(\text{dddtt})_2$. The calculated band structure of the donor slab in $[\text{Pd}(\text{dddtt})_2]\text{Ag}_{1.54}\text{Br}_{3.50}$ is shown in Figure 4: the HOMO and LUMO bands overlap as expected. However, the calculated Fermi level assuming the silver atoms in the Ag^{2+} oxidation state, *i.e.*, the situation for which the number of holes in the HOMO band is the smallest possible, does not cut the LUMO band. Consequently, although the HOMO and LUMO bands overlap, for any practical matter the system can be considered as a one-band system. The HOMO band of Figure 4 has a dispersion of ~ 0.40 eV which is very similar to the total dispersion of the HOMO bands of metallic $[\text{Ni}(\text{dddtt})_2]_3(\text{AuBr}_2)_2$ [7] and thus it is consistent with the metallic behavior of the present salt. The HOMO band is about three times more dispersive along b^* than along c^* . Thus, although from a structural viewpoint it is appealing to describe the donor slabs of $[\text{Pd}(\text{dddtt})_2]\text{Ag}_{1.54}\text{Br}_{3.50}$ as being build from a series of parallel inclined chains along c , from the viewpoint of the conducting properties they would be better described as a series of interacting step-chains along b (see Fig. 5).

As shown in Figure 5, there are three different types of donor · donor interactions (labeled A, B and C) in the donor slabs of $[\text{Pd}(\text{dddtt})_2]\text{Ag}_{1.54}\text{Br}_{3.50}$. The $\text{S} \cdots \text{S}$ contacts shorter than 4.1 Å as well as the calculated $\beta_{\text{HOMO-HOMO}}$, $\beta_{\text{LUMO-LUMO}}$ and $\beta_{\text{HOMO-LUMO}}$ interaction energies [19] are reported in Table II. The B interaction, which is associated with the shortest $\text{S} \cdots \text{S}$ contacts, has the largest $\beta_{\text{HOMO-HOMO}}$ and $\beta_{\text{LUMO-LUMO}}$ interaction energies. Those for A are quite small. The $\beta_{\text{HOMO-HOMO}}$ and $\beta_{\text{LUMO-LUMO}}$ interaction energies for C are quite large even if the $\text{S} \cdots \text{S}$ contacts are long. This leads to a non negligible dispersion of the HOMO

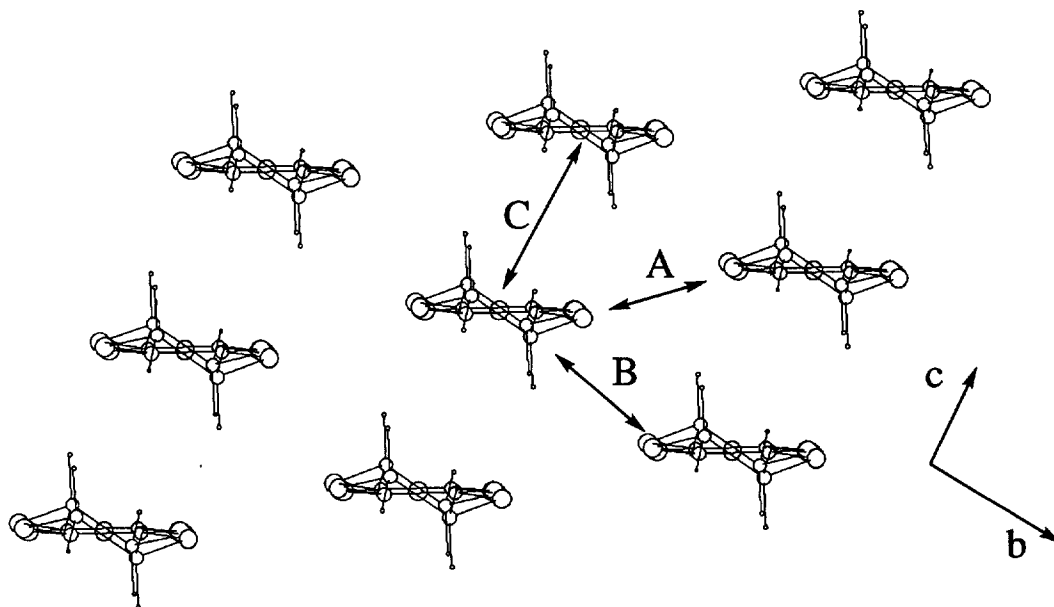


Fig. 5. — Perspective view of a donor layer of $[Pd(dddt)_2]Ag_{1.54}Br_{3.50}$ showing the different types of intermolecular interactions.

Table II. — $S \cdots S$ distances shorter than 4.1 \AA and absolute values of the $\beta_{HOMO-HOMO}$, $\beta_{LUMO-LUMO}$ and $\beta_{HOMO-LUMO}$ interaction energies (eV) for the different donor · donor interactions in $[Pd(dddt)_2]Ag_{1.54}Br_{3.50}$ (see Fig. 5 for labelling).

Interaction	$S \cdots S$ distances (\AA)	$\beta_{HOMO-HOMO}$	$\beta_{LUMO-LUMO}$	$\beta_{HOMO-LUMO}$
A	3.643 ($\times 2$), 3.715 ($\times 2$), 3.810 ($\times 2$) 3.997	0.0138	0.0150	0.0002
B	3.491 ($\times 2$), 3.569 ($\times 2$), 3.761 ($\times 2$) 3.842 ($\times 2$)	0.1318	0.1084	0.0084
C	4.085 ($\times 2$) *	0.0837	0.0430	0.0173

* Shortest $S \cdots S$ contacts for this interaction type. There is also a $Pd \cdots Pd$ distance of 4.157 \AA associated with this interaction.

band along c^* . As a matter of fact the dispersion along c^* for both the HOMO and LUMO bands are smaller than expected on the basis of the interaction energies of Table II. The LUMO band is very flat because of HOMO-LUMO interactions which are non negligible along this direction (see Tab. II) and which push up the LUMO band. The HOMO band is pushed up by lower energy levels which couple with the HOMO. Thus, although the partially filled band is mainly build up from the HOMO of the donor, the fine details of the band dispersion and consequently, of the Fermi surface, can be influenced to a sizable degree by other donor levels. Calculations which do not take into account all the valence levels of the molecule can lead to relatively incorrect descriptions of the electronic structure of these materials. As noted above,

uniform chains such as those exhibited by the present salt are very rare among charge transfer salts of Pd and Pt bis-dithiolates. The only ones from which we are aware in metallic salts are those of α' -TTF[Pd(dmit)₂]₂ [20], although they form a different type of layer. The intrachain mode of overlap is almost identical in both salts but the interaction energies are about four times larger [12] in α' -TTF[Pd(dmit)₂]₂. Thus, in the later salt the HOMO and LUMO bands are very dispersive along the uniform chain direction. The difference between the two salts comes from the presence of the ethylene groups in Pd(dddt)₂ which keeps the two molecules further apart. This is an important difference between the Pd(dmit)₂ and Pd(dddt)₂ systems. Whereas in the Pd(dmit)₂ salts the existence of uniform chains of this type can lead to one-dimensional (1D) metals along the chains, we believe this is not possible for the Pd(dddt)₂ salts. In that case, despite the presence of uniform chains the salts will be either two-dimensional (2D) or 1D along a direction which is not that of the chains, as for instance in some Pd(dmit)₂ salts containing chains of dimeric units [13, 21].

Before looking at the Fermi surface of [Pd(dddt)₂]Ag_{1.54}Br_{3.50}, we must consider the question of the oxidation state of the silver cations. In principle, silver could be either Ag⁺ or Ag²⁺. In the first case, the charge of Pd(dddt)₂ would be around +2 so that the HOMO band will be practically empty and it would be very difficult to understand the high conductivity of the salt. In the second case, the Pd(dddt)₂ charge would be close to +0.5, which seems more likely, and the HOMO band would be one-quarter empty in better agreement with the metallic properties of the salt. In agreement with these considerations, [Pd(dddt)₂]Ag_{1.54}Br_{3.50} gives an intense broad EPR signal which can be assigned to the Ag²⁺ spins (details of the EPR study will be reported elsewhere). The conducting M(dddt)₂ systems as well as the M(dmit)₂ ones do not show an EPR signal. Thus, we believe the charge of Pd(dddt)₂ in the present salt is probably close to +0.5. It should be noted that the electrochemical oxidation of ET in the presence of the Bu₄NAgBr₂ gives the (ET)Ag_{2.4}Br_{3.0} salt, containing a polymeric complex anion with silver as Ag⁺ [22]. The formation of the Ag²⁺ bromide anion during the electrocrystallization of [Pd(dddt)₂]Ag_{1.54}Br_{3.50} can be attributed to the higher oxidation potentials of the neutral M(dddt)₂ complexes (~ 0.9 V for M = Ni, Pt [23]) with respect to ET.

We are now ready to consider the nature of the Fermi surface of [Pd(dddt)₂]Ag_{1.54}Br_{3.50} as well as the related question: why this salt is a stable metal down to 1.3 K? The calculated Fermi surface assuming a charge (q) of +0.5 per donor molecule is shown in Figure 6. It consists of hole pockets of an ellipsoid shape centered at Γ so that [Pd(dddt)₂]Ag_{1.54}Br_{3.50} should be a 2D metal with better conductivity along b . Such Fermi surface does not exhibit any nesting vector. The shape of the Fermi surfaces calculated for values of q slightly larger or smaller than +0.5 — to take into account weak stoichiometry deviations — does not change except for the area readjustment. Consequently, [Pd(dddt)₂]Ag_{1.54}Br_{3.50} is expected to be a stable metal down to very low temperatures. As a matter of fact, since no rational fragments could be found in the structure because of disorder, we can not completely discard the possibility of having both Ag⁺ and Ag²⁺. Thus we have carried out a complete study of the Fermi surface as a function of q . For values of q between +0.25 and +0.55 the Fermi surface has the ellipsoid shape of Figure 6. Then, for q near +0.6 such ellipsoids are large enough to reach the border of the Brillouin zone and the Fermi surface becomes open but un-nested. For q values around +0.9 and until +1.55 the Fermi surfaces are open and well nested by a wave vector having an incommensurate component along b^* and a 1/2 component along c^* . Finally, the Fermi surface closes again for larger values of q . Consequently, if there was an important proportion of silver atoms as Ag⁺ the Fermi surface could be well nested and would be susceptible to exhibit a charge or spin density wave instability which would destroy the metallic character of the salt. We take the fact that such an instability is not observed (as well as the unlikeliness of charges larger than +1 for Pd(dddt)₂) as a further indication that at least a large part of the silver

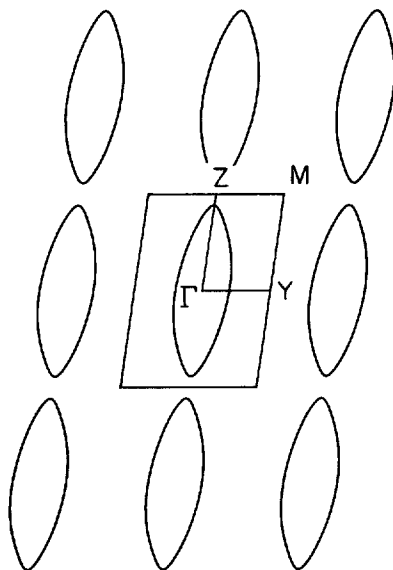


Fig. 6. — Calculated Fermi surface for $[\text{Pd}(\text{dddt})_2]\text{Ag}_{1.54}\text{Br}_{3.5}$ assuming a charge (q) of +0.5 per $\text{Pd}(\text{dddt})_2$.

atoms are present as Ag^{2+} and consequently, that the charge of the $\text{Pd}(\text{dddt})_2$ donor is close to +0.5.

It is clear from the preceding discussion that $[\text{Pd}(\text{dddt})_2]\text{Ag}_{1.54}\text{Br}_{3.50}$ is a stable metal down to 1.3 K because of the existence of moderate donor · · donor interactions within the uniform stacks along c . If it were not for such interactions this salt would be a 1D metal along the step-chain direction (*i.e.*, b) and most probably would undergo a density wave instability destroying its metallic character at low temperature. At this point it is interesting to consider again the other stable metal within the $\text{M}(\text{dddt})_2$ family: $[\text{Ni}(\text{dddt})_2]_3(\text{AuBr}_2)_2$ [6, 7]. Although the two band structures look different, in fact they are very strongly related. In $[\text{Ni}(\text{dddt})_2]_3(\text{AuBr}_2)_2$ there are the same type of uniform chains but because there are three donor molecules per repeat unit the band structure along the step-chains appears as triply folded. Since the three donor molecules are not identical, small gaps open so that the HOMO and LUMO bands lead to three subbands each. It is the overlap between two of the HOMO subbands brought about by the interstep-chain interactions which leads to the metallic character of this salt. Thus, the essential aspect of the electronic structure of $[\text{Ni}(\text{dddt})_2]_3(\text{AuBr}_2)_2$, *i.e.*, the existence of an HOMO band mainly dispersive along the step-chain direction but with nonnegligible interactions along the interstep-chain directions is also found in $[\text{Pd}(\text{dddt})_2]\text{Ag}_{1.54}\text{Br}_{3.50}$. Since the average charge of the donor is +2/3 in the first salt and $\sim +1/2$ in the second, the electron filling of the HOMO band in both salts is not such different neither. The source of the stability of the metallic state of $[\text{Ni}(\text{dddt})_2]_3(\text{AuBr}_2)_2$ was attributed [7] to the existence of uniform chains like those along c in the present salt which provide an elastic force against the small movements of the donors needed to open a gap between the two overlapping HOMO subbands. This elastic force originates from the $\text{M} \cdot \cdot \text{S}$ bonding interactions stabilizing levels lower than the HOMO and which are favored by such uniform chains. This explains why the $[\text{Ni}(\text{dddt})_2]_3(\text{HSO}_4)_2$ salt [24], with donor slabs very similar to those of $[\text{Ni}(\text{dddt})_2]_3(\text{AuBr}_2)_2$ but where the $\text{Ni}(\text{dddt})_2$ uniform chains have been broken into trimeric units, can not keep its

metallic state and undergoes a metal to insulator transition at 25 K. It also explains [8] why (BEDT-TTF)₃(HSO₄)₂ [25], isostructural with [Ni(dddt)₂]₃(HSO₄)₂ but where such M · · S do not exist, undergoes a metal to insulator transition at a much higher temperature (130 K). Usually, the M · · S interactions increase with the size of the transition metal. In the present case, the stronger Pd · · S interactions along the uniform stacks do not only provide such an elastic force against donor movements but also reinforce the HOMO · · HOMO interactions along the uniform stacks. This leads to the closed Fermi surface and thus, ultimately, to the stability of the metallic state of [Pd(dddt)₂Ag_{1.54}Br_{3.50}]. Thus, the existence of uniform chains of M(dddt)₂ donors where the successive units are displaced along the short molecular axis seems to be an important factor in stabilizing the metallic state of these M(dddt)₂ charge transfer salts. Certainly, charge transfer salts of the M(dddt)₂ donors seem to be quite promising in the search for new metals and maybe superconductors.

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