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# Electrocrystallization and characterization of phosphonium-based radical anion salts $[MePh_3P][Pd(dmit)_2]_3$ and $[Ph_4P][Pd(dmit)_2]_3$ (dmit = 1,3-dithiole-2-thione-4,5-dithiolate). Comparison with related Pd and Ni isologues

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**Abstract**

The two new radical anion salts $[MePh_3P][Pd(dmit)_2]_3$ (**1**) (dmit = $C_3S_5^{2-}$ = 1,3-dithiole-2-thione-4,5-dithiolate) and $[Ph_4P][Pd(dmit)_2]_3$ (**2**) have been synthesized and characterized by X-ray diffraction, elemental analysis and temperature-dependent conductivity measurements. Complexes **1** and **2** were prepared via electrooxidation of $[Pd(dmit)_2]^{2-}$ in acetonitrile–acetone solvent mixtures at a Pt wire anode in the presence of methyltriphenylphosphonium bromide and tetraphenylphosphonium bromide electrolytes, respectively. For $[MePh_3P][Pd(dmit)_2]_3$ (**1**), black shiny needle and platelet crystals suitable for X-ray analysis were obtained. The crystal packing structure consists of layers of $Pd(dmit)_2$ units separated by layers of $MePh_3P^+$ counterions. The $Pd(dmit)_2$ layers are composed of dimers of $Pd(dmit)_2$ units as a result of strong Pd···Pd interactions. Extensive S···S nonbonding interdimer interactions are observed, with each dimer interacting with six other adjacent dimers. For $[Ph_4P][Pd(dmit)_2]_3$ (**2**), black shiny flat needles were harvested and the stoichiometry confirmed by elemental analysis. Single-crystal temperature-dependent conductivity measurements show that **1** behaves as a semiconductor with a room-temperature conductivity of 13 S cm$^{-1}$ and a thermal activation energy of 100 meV. Compound **2** also displays semiconducting behavior with a room-temperature conductivity of 0.8–1 S cm$^{-1}$ and a thermal activation energy of 55 meV. 

*Keywords:* Electrocrystallization; Crystal structures; Palladium complexes; Phosphonium complexes; Dithiolate complexes

## 1. Introduction

One family of molecular conductors that have shown superconductivity is made up of the $M(dmit)_2$-based ($M = Ni^{II}$, $Pd^{II}$; dmit = $C_3S_5^{2-}$ = 1,3-dithiole-2-thione-4,5-dithiolate) non-integer oxidation state (NIOS), radical-anion salts [1]. To date, these remain the only transition-metal-containing organic materials that have shown superconductivity. Currently, eight different $M(dmit)_2$ systems have shown such behavior [2]. The planar, fully delocalized, sulfur-rich dmit ligand in combination with square planar coordinating metal centers such as $Ni^{II}$ or $Pd^{II}$, allows for close-packed arrangements. Both closed-shell and open-shell counterions have been used to assemble such systems. Closed-shell cations from the ammonium family have been observed in $M(dmit)_2$-based superconductors and have been the most widely studied [1–3].

One group of compounds that has received less attention than the more thoroughly studied ammonium- or sulphonium-based cations, are the phosphonium-based cations [2–4]. We have electrocrystallized and studied two $Ni(dmit)_2$ compounds with phosphonium cations $[MePh_3P][Ni(dmit)_2]_3$ (**3**) and $[Ph_4P][Ni(dmit)_2]_3$ (**4**). Compound **4** has also been reported by Nakamura et al. [4] and both complexes are semiconductors with room-temperature conductivities in the range 0.1–10 S cm$^{-1}$. Both display crystal

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packing features unique among the dmit ligand family of NIOS materials with both closed- and open-shell counterions. $[Ph_4P][Ni(dmit)_2]_3$ (**4**) exhibits a unique packing array of $Ni(dmit)_2$ units while in $[MePh_3P][Ni(dmit)_2]_3$ (**3**) the $Ni(dmit)_2$ units form eclipsed dimers. This results in extremely short intermolecular Ni···Ni distances of 2.7837(7) Å leading to fold-like, dmit–Ni–dmit dihedral angles of 13.0° [4], previously observed only in $Pd^{II}$- and $Pt^{II}$-containing NIOS complexes of the dmit family [1–5]. Therefore, because of the very interesting structural properties these two complexes have exhibited, we decided to synthesize their $Pd^{II}$ isologues. Here we report the synthesis, characterization and electrical properties of $[MePh_3P][Pd(dmit)_2]_3$ (**1**) and $[Ph_4P][Pd(dmit)_2]_3$ (**2**) and compare them with the previously reported phosphonium cation-based $Ni^{II}$ and $Pd^{II}$ compounds.

## 2. Experimental

### 2.1. Synthesis of $[MePh_3P][Pd(dmit)_2]_3$ (1)

$[Bu_4N]_2[Pd(dmit)_2]$ was synthesized following the procedures described by Hansen et al. [6]. The radical anion salt $[MePh_3P][Pd(dmit)_2]_3$ (**1**) was prepared via constant-current electrocrystallization in a two-compartment H-cell equipped with Pt wire electrodes. A saturated solution of $[Bu_4N]_2[Pd(dmit)_2]$ was electrooxidized in 3:1 acetonitrile–acetone in the presence of 0.06 mol $dm^{-3}$ $MePh_3PBr$ under an argon atmosphere. A current density of 1 μA $cm^{-2}$ was applied over a period of 8 days. Black shiny needle and platelet crystals were harvested from the anode and thoroughly washed with acetonitrile, methanol and diethyl ether. *Anal.* Found: C, 24.90; H, 1.00; S, 54.10. Calc. for $C_{37}H_{18}Pd_3PS_{30}$: C, 25.04; H, 1.02; Pd, 17.99; P, 1.75; S, 54.20%. All solvents used for electrocrystallization were degassed thoroughly prior to use. Acetone was used as received (Aldrich) and acetonitrile was dried over type 4A molecular sieves (Fisher).

### 2.2. Synthesis of $[Ph_4P][Pd(dmit)_2]_3$ (2)

The radical anion salt $[Ph_4P][Pd(dmit)_2]_3$ (**2**) was prepared via constant-current electrocrystallization similarly to $[MePh_3P][Pd(dmit)_2]_3$ (**1**). A saturated solution of $[Bu_4N]_2[Pd(dmit)_2]$ was electrooxidized in 1:1 acetonitrile–acetone in the presence of 0.65 mol $dm^{-3}$ $Ph_4PBr$ under an argon atmosphere. A current density of 0.9 μA $cm^{-2}$ was applied over a period of 15 days. Black, shiny flat needles were harvested from the anode and washed and isolated similar to the procedures described for $[MePh_3P][Pd(dmit)_2]_3$ (**1**). *Anal.* Found: C, 27.40; H, 1.08; S, 52.20. Calc. for $C_{42}H_{20}Pd_3PS_{30}$: C, 27.47; H, 1.10; Pd, 17.38, P, 1.69; S, 52.37%.

### 2.3. X-ray structure determination

Crystallographic data for $[MePh_3P][Pd(dmit)_2]_3$ (**1**) are shown in Table 1. Data were collected at 173 K on a Siemens Smart Platform equipped with a CCD area detector. A black, shiny platelet crystal (0.39×0.30×0.01 mm) was chosen for study. The diffractometer was equipped with a graphite monochromator utilizing Mo Kα radiation ($\lambda$=0.71073). Cell parameters were refined using 8192 reflections. A hemisphere of data (1381 frames) was collected using the $\omega$-scan method (0.3° frame width). The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability (maximum correction on $I<1\%$). Empirical absorption corrections were applied based on the entire data set.

The structure was solved by direct methods in SHELXTL5, and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in the ideal positions and were riding on their respective carbon atoms. The asymmetric unit contains three $[Pd(dmit)_2]$ complexes and one methyltriphenylphosphonium cation. Two of the complexes pack as dimers while the third acts as a dimer with another complex related by a center of inversion. 641 parameters were refined in the final cycle of refinement using 9252 reflections with $I>2\sigma(I)$ to yield $R_1$ of 3.17% and $wR_2$ of 6.42%, respectively. Refinement was done using $F^2$.

Thermal ellipsoid drawings of the three independent $Pd(dmit)_2$ units are shown in Fig. 1. Selected bond lengths and angles for $[MePh_3P][Pd(dmit)_2]_3$ (**1**) are presented in Table 2.

A crystal structure for $[Ph_4P][Pd(dmit)_2]_3$ (**2**) could not be obtained because repeated electrocrystallizations yielded samples of inferior quality.

Table 1
Crystallographic data for $[MePh_3P][Pd(dmit)_2]_3$ (1)

| | |
|---|---|
| Chemical formula | $C_{37}H_{18}Pd_3PS_{30}$ |
| Formula mass | 1774.48 |
| Space group | $P2_1/c$ |
| $a$ (Å) | 21.2688(6) |
| $b$ (Å) | 17.7723(6) |
| $c$ (Å) | 15.5029(5) |
| β (°) | 108.647(1) |
| $V$ (Å$^3$) | 5552.4(3) |
| $Z$ | 4 |
| $D_c$ (g $cm^{-3}$) | 2.123 |
| $F(000)$ | 3492 |
| $\mu$(Mo Kα) ($cm^{-1}$) | 21.5 |
| $2\theta_{max}$ (°) | 55.0 |
| Range of $h, k, l$ | −28 to 26; −24 to 23; −20 to 18 |
| $R_1$ [a]; $wR_2$ [b] | 0.032; 0.064 |
| Goodness-of-fit | 1.004 |
| $\Delta\rho_{max}$ (e Å$^{-3}$) | 0.750 |
| $\Delta\rho_{min}$ (e Å$^{-3}$) | −1.026 |

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$.
[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0370p)^2 + 0.31p]$, $p = [\max(F_o^2, 0) + 2F_c^2]/3$.

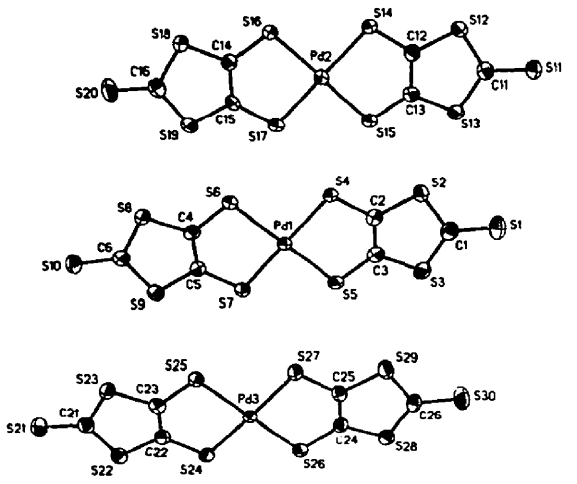


Fig. 1. Thermal ellipsoids drawings (50% probability) and numbering schemes for the three crystallographically independent $Pd(dmit)_2$ units of $[MePh_3P][Pd(dmit)_2]_3$ (**1**).

Table 2
Bond lengths (Å) and angles (°) for the three crystallographically independent $Pd(dmit)_2$ units of $[MePh_3P][Pd(dmit)_2]_3$ (**1**)

| | | | |
|---|---|---|---|
| Pd1–S5 | 2.2980(9) | S15–C13 | 1.703(3) |
| Pd1–S7 | 2.3055(8) | S16–C14 | 1.702(3) |
| Pd1–S4 | 2.3119(8) | S17–C15 | 1.691(3) |
| Pd1–S6 | 2.3255(8) | S18–C16 | 1.735(3) |
| Pd1–Pd1 [a] | 2.9194(5) | S18–C14 | 1.753(3) |
| S1–C1 | 1.639(4) | S19–C16 | 1.740(4) |
| S2–C2 | 1.744(3) | S19–C15 | 1.749(3) |
| S2–C1 | 1.744(4) | S20–C16 | 1.644(4) |
| S3–C1 | 1.737(4) | C12–C13 | 1.391(4) |
| S3–C3 | 1.737(3) | C14–C15 | 1.393(4) |
| S4–C2 | 1.699(3) | Pd3–S24 | 2.2954(8) |
| S5–C3 | 1.685(3) | Pd3–S26 | 2.2961(9) |
| S6–C4 | 1.693(3) | Pd3–S27 | 2.3061(8) |
| S7–C5 | 1.688(3) | Pd3–S25 | 2.3071(9) |
| S8–C6 | 1.743(3) | S21–C21 | 1.641(3) |
| S8–C4 | 1.749(3) | S22–C21 | 1.739(4) |
| S9–C6 | 1.731(3) | S22–C22 | 1.745(3) |
| S9–C5 | 1.748(3) | S23–C21 | 1.728(3) |
| S10–C6 | 1.644(3) | S23–C23 | 1.750(3) |
| C2–C3 | 1.406(4) | S24–C22 | 1.696(3) |
| C4–C5 | 1.399(4) | S25–C23 | 1.702(3) |
| Pd2–S17 | 2.3033(8) | S26–C24 | 1.704(3) |
| Pd2–S15 | 2.3061(9) | S27–C25 | 1.702(3) |
| Pd2–S16 | 2.3101(8) | S28–C26 | 1.735(3) |
| Pd2–S14 | 2.3197(8) | S28–C24 | 1.744(3) |
| S11–C11 | 1.653(3) | S29–C26 | 1.731(3) |
| S12–C11 | 1.740(3) | S29–C25 | 1.758(3) |
| S12–C12 | 1.751(3) | S30–C26 | 1.650(3) |
| S13–C11 | 1.730(3) | C22–C23 | 1.388(4) |
| S13–C13 | 1.747(3) | C24–C25 | 1.390(4) |
| S14–C12 | 1.710(3) | Pd2–Pd3 | 3.0956(4) |

(*continued*)

Table 2 (*continued*)

| | | | |
|---|---|---|---|
| S5–Pd1–S7 | 87.94(3) | S11–C11–S13 | 123.3(2) |
| S5–Pd1–S4 | 89.51(3) | S11–C11–S12 | 123.6(2) |
| S7–Pd1–S4 | 173.89(3) | S13–C11–S12 | 113.1(2) |
| S5–Pd1–S6 | 173.81(3) | C13–C12–S14 | 123.6(3) |
| S7–Pd1–S6 | 89.68(3) | C13–C12–S12 | 115.1(2) |
| S4–Pd1–S6 | 92.29(3) | S14–C12–S12 | 121.2(2) |
| S5–Pd1–Pd1 [a] | 92.09(3) | C12–C13–S15 | 123.1(3) |
| S7–Pd1–Pd1 [a] | 97.16(2) | C12–C13–S13 | 115.9(2) |
| S4–Pd1–Pd1 [a] | 88.48(2) | S15–C13–S13 | 121.0(2) |
| S6–Pd1–Pd1 [a] | 93.87(2) | C15–C14–S16 | 123.3(3) |
| C2–S2–C1 | 97.6(2) | C15–C14–S18 | 115.3(2) |
| C1–S3–C3 | 97.7(2) | S16–C14–S18 | 121.4(2) |
| C2–S4–Pd1 | 102.18(11) | C14–C15–S17 | 123.1(2) |
| C3–S5–Pd1 | 102.42(12) | C14–C15–S19 | 116.0(2) |
| C4–S6–Pd1 | 101.34(11) | S17–C15–S19 | 120.9(2) |
| C5–S7–Pd1 | 101.92(11) | S20–C16–S18 | 122.7(2) |
| C6–S8–C4 | 97.6(2) | S20–C16–S19 | 123.7(2) |
| C6–S9–C5 | 97.4(2) | S18–C16–S19 | 113.7(2) |
| S1–C1–S3 | 123.6(2) | S24–Pd3–S26 | 87.80(3) |
| S1–C1–S2 | 122.9(2) | S24–Pd3–S27 | 175.39(3) |
| S3–C1–S2 | 113.4(2) | S26–Pd3–S27 | 90.22(3) |
| C3–C2–S4 | 122.3(3) | S24–Pd3–S25 | 90.1[illegible](3) |
| C3–C2–S2 | 115.3(2) | S26–Pd3–S25 | 175.47(3) |
| S4–C2–S2 | 122.3(2) | S27–Pd3–S25 | 91.52(3) |
| C2–C3–S5 | 123.5(3) | S24–Pd3–Pd2 | 98.49(2) |
| C2–C3–S3 | 115.9(3) | S26–Pd3–Pd2 | 97.14(2) |
| S5–C3–S3 | 120.6(2) | S27–Pd3–Pd2 | 85.88(2) |
| C5–C4–S6 | 123.4(3) | S25–Pd3–Pd2 | 87.15(2) |
| C5–C4–S8 | 115.1(2) | C21–S22–C22 | 97.5(2) |
| S6–C4–S8 | 121.5(2) | C21–S23–C23 | 97.7(2) |
| C4–C5–S7 | 123.6(3) | C22–S24–Pd3 | 101.73(11) |
| C4–C5–S9 | 116.0(2) | C23–S25–Pd3 | 101.22(12) |
| S7–C5–S9 | 120.4(2) | C24–S26–Pd3 | 101.69(11) |
| S10–C6–S9 | 122.1(2) | C25–S27–Pd3 | 101.30(11) |
| S10–C6–S8 | 124.2(2) | C26–S28–C24 | 97.3(2) |
| S9–C6–S8 | 113.7(2) | C26–S29–C25 | 97.8(2) |
| S17–Pd2–S15 | 87.96(3) | S21–C21–S23 | 123.8(2) |
| S17–Pd2–S16 | 89.65(3) | S21–C21–S22 | 122.7(2) |
| S15–Pd2–S16 | 175.40(3) | S23–C21–S22 | 113.5(2) |
| S17–Pd2–S14 | 174.54(3) | C23–C22–S24 | 123.4(3) |
| S15–Pd2–S14 | 89.99(3) | C23–C22–S22 | 115.7(3) |
| S16–Pd2–S14 | 92.04(3) | S24–C22–S22 | 120.9(2) |
| S17–Pd2–Pd3 | 97.20(2) | C22–C23–S25 | 123.4(3) |
| S15–Pd2–Pd3 | 98.01(2) | C22–C23–S23 | 115.5(2) |
| S16–Pd2–Pd3 | 86.19(2) | S25–C23–S23 | 121.0(2) |
| S14–Pd2–Pd3 | 88.09(2) | C25–C24–S26 | 122.9(3) |
| C11–S12–C12 | 97.9(2) | C25–C24–S28 | 116.4(2) |
| C11–S13–C13 | 97.9(2) | S26–C24–S28 | 120.6(2) |
| C12–S14–Pd2 | 101.18(11) | C24–C25–S27 | 123.6(3) |
| C13–S15–Pd2 | 101.93(11) | C24–C25–S29 | 114.7(2) |
| C14–S16–Pd2 | 101.69(11) | S27–C25–S29 | 121.7(2) |
| C15–S17–Pd2 | 102.19(11) | S30–C26–S29 | 123.2(2) |
| C16–S18–C14 | 97.7(2) | S30–C26–S28 | 123.1(2) |
| C16–S19–C15 | 97.4(2) | S29–C26–S28 | 113.7(2) |

[a] Symmetry transformations used to generate equivalent atoms: $-x+1, -y+1, -z+2$.

### 2.4. Conductivity measurements

Temperature-dependent resistances for single-crystals of $[MePh_3P][Pd(dmit)_2]_3$ (**1**) (300–70 K) and $[Ph_4P][Pd(dmit)_2]_3$ (**2**) (300–215 K) were measured by a four-probe method using an ac technique. For compound **1**, a

needle-like crystal of dimensions $1.60 \times 0.09 \times 0.01$ mm$^3$ was chosen and the crystal for **2** was $1.28 \times 0.46 \times 0.02$ mm$^3$. Narrow-gauge (0.02 mm diameter) gold wires were affixed to the crystal using fast drying gold paint. For $[MePh_3P][Pd(dmit)_2]_3$ (**1**), the sample was mounted on a Motorola printed circuit and was placed in an Oxford Instruments, model CF 200, continuous-flow cryostat. Data were obtained during cooling and warming cycles of the sample. For $[Ph_4P][Pd(dmit)_2]_3$ (**2**), the sample was anchored thermally to the cold head of a closed-cycle refrigerator (CTI Cryogenics). A typical run was performed by first cooling the sample to the lowest temperature, and then taking the data while warming. Temperature reproducibility was determined to be $\pm 0.2$ K or better over the entire temperature range measured for both measurements.

## 3. Results and discussion

### 3.1. Crystal structure of $[MePh_3P][Pd(dmit)_2]_3$ (1)

The crystal structure of $[MePh_3P][Pd(dmit)_2]_3$ (**1**) is similar to that of the previously reported complex $[MePh_3P][Ni(dmit)_2]_3$ (**3**) [4]. The structure of **1** is composed of three crystallographically independent $Pd(dmit)_2$ units and one $MePh_3P^+$ cation. As can be seen in Fig. 2, the crystal packing is formed from columns of $Pd(dmit)_2$ units separated by columns of isolated $MePh_3P^+$ cations. The columns of $Pd(dmit)_2$ moieties are composed of dimers formed from strong intermolecular Pd···Pd interactions and denoted by solid lines. Also illustrated in Fig. 2, is a side-on view of the $Pd(dmit)_2$ units showing fold-like dmit–Pd–dmit dihedral angles of the dmit ligand planes as a result of the Pd···Pd interactions. Each crystallographically independent $Pd(dmit)_2$ unit is characterized by a different dihedral angle of 6.9° containing Pd(1), 7.5° for Pd(2) and 9.5° for the Pd(3) unit. These metal–metal interactions were also observed in $[MePh_3P][Ni(dmit)_2]_3$ (**3**) for the first time for $Ni(dmit)_2$-based complexes. The dihedral angle was reported at 13.0° [4]. This type of metal–metal interaction though has been seen in other instances involving $Pt(dmit)_2$ and $Pd(dmit)_2$-based anion–radical salts [1].

The end-on view of the dimeric arrangements of the $Pd(dmit)_2$ units of $[MePh_3P][Pd(dmit)_2]_3$ (**1**) stacked along the *c* direction, is shown in Fig. 3. All $Pd(dmit)_2$ moieties in **1** are found in dimers, whereas in $[MePh_3P][Ni(dmit)_2]_3$ (**3**), half of the $Ni(dmit)_2$ units are found in dimers. In $[MePh_3P][Pd(dmit)_2]_3$ (**1**), the Pd···Pd interdimer distances range from 2.9194(5) to 3.0956(4) Å. In **3**, the Ni···Ni intradimer distance is smaller at 2.7837(7) Å. Each dimer interacts with six other adjacent dimers in a two-dimensional array (denoted by dotted lines). The S···S interdimer orbital distances are less than the sum of the van der Waals radii of 3.70 Å, ranging from a closest distance of 3.327 Å due to thiole–thiole [S(4)–S(27)] to the highest of 3.655 Å, as a result of thiolate–thiolate [S(3)–S(29)] orbital

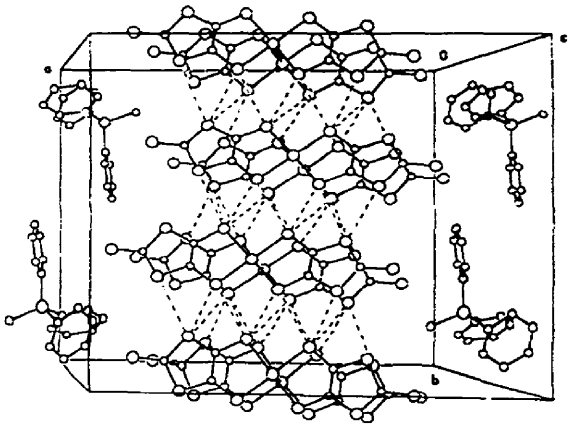

Fig. 2. View perpendicular to the $Pd(dmit)_2$ units of $[MePh_3P][Pd(dmit)_2]_3$ (**1**) showing columns of $Pd(dmit)_2$ units separated by columns of $MePh_3P^+$ cations. The dihedral angle of the dmit ligand planes formed from strong intermolecular Pd···Pd interactions can also be seen.

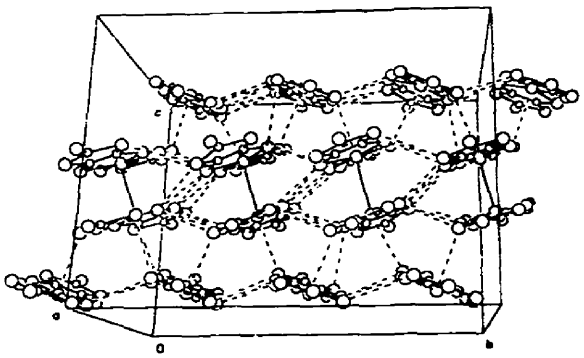

Fig. 3. End-on view of the $Pd(dmit)_2$ units of $[MePh_3P][Pd(dmit)_2]_3$ (**1**). Extensive interdimer S···S and Pd···S non-bonding orbital interactions are observed and denoted by dotted lines.

interactions. Also, Pd···S distances are also observed and range from 3.306 Å due to Pd–thiole [Pd(2)–S(9)] to 3.676 Å as a result of Pd–thiolate [Pd(1)–S(24)] orbital interactions. Each $Pd(dmit)_2$ dimer forms dihedral angles of approximately 4.6° with two other dimers along the *b* direction and dihedral angles of approximately 37.2° with four other dimers along the *c* direction. This packing motif is very similar to that observed for $[MePh_3P][Ni(dmit)_2]_3$ (**3**) and the κ-phase BEDT–TTF (bisethylenedithiotetrathiafulvalene) salts that have exhibited superconductivity [1].

In the compound $[Me_4P][Pd(dmit)_2]_2$ (**5**) with a small phosphonium cation, dimers are also formed but are at 0° with respect to each other [5]. In $[MePh_3P][Pd(dmit)_2]_3$ (**1**) with a larger phosphonium cation, the dimers are tilted with respect to each other. In the related compound, $[Ph_4P][Ni(dmit)_2]_3$ (**4**), with the largest of the phosphonium-based cations structurally characterized by X-ray diffraction, the $Ni(dmit)_2$ units are at 90° with respect to each

other [4], the only time such an arrangement has been seen for M(dmit)$_2$-based compounds.

Other Pd(dmit)$_2$-based complexes have been electrocrystallized with large phosphonium-based cations and resulting 3:1 stoichiometries. Although not structurally characterized by X-ray analysis, the compounds [BTP][Pd(dmit)$_2$]$_3$ (**6**) (BTP = benzyltriphenylphosphonium) and [PPN][Pd(dmit)$_2$]$_3$ (**7**) [PPN = bis(triphenylphosphoranylidene)] have been reported with their stoichiometries determined by elemental analysis [3]. As can be concluded, large phosphonium-based cations induce the formation of 3:1 stoichiometries and unusual packing arrangements.

### 3.2. Electrical conductivity measurements

Fig. 4 shows the temperature dependence of log $\sigma$ of the four-probe measurements for [MePh$_3$P][Pd(dmit)$_2$]$_3$ (**1**) and [Ph$_4$P][Pd(dmit)$_2$]$_3$ (**2**). Semiconducting behavior is observed for both materials. Compound **1** has the higher 300 K conductivity, 13 S cm$^{-1}$. This value is approximately two orders of magnitude greater than the 0.1 S cm$^{-1}$ value observed in [MePh$_3$P][Ni(dmit)$_2$]$_3$ (**3**) [4]. The thermal activation energy $E_a$ of [MePh$_3$P][Pd(dmit)$_2$]$_3$ (**1**) is 100 meV; compound **3** has a value of 220 meV [4]. Although the crystal structure of **1** has a more dimerized packing array of the M(dmit)$_2$ units, the conductivity is much higher than **3**.

In the Ph$_4$P$^+$-based compounds the conductivity values are reversed compared with the MePh$_3$P$^+$ materials when looking at the role of the metal center (Table 3). For [Ph$_4$P][Pd(dmit)$_2$]$_3$ (**2**), the 300 K value of the conductivity is approximately 1 S cm$^{-1}$ whereas its Ni isologue, [Ph$_4$P][Ni(dmit)$_2$]$_3$ (**4**), has a value an order of magnitude greater at 10 S cm$^{-1}$ [4]. The thermal activation energy of **2** is 55 meV which is roughly three times greater than its Ni isologue (**4**) value of 17 meV [4]. The semiconducting compounds [BTP][Pd(dmit)$_2$]$_3$ (**6**) and [PPN][Pd(dmit)$_2$]$_3$ (**7**) have the highest room temperature conductivities for phosphonium-based compounds: 80 and 62 S cm$^{-1}$, respectively [3].

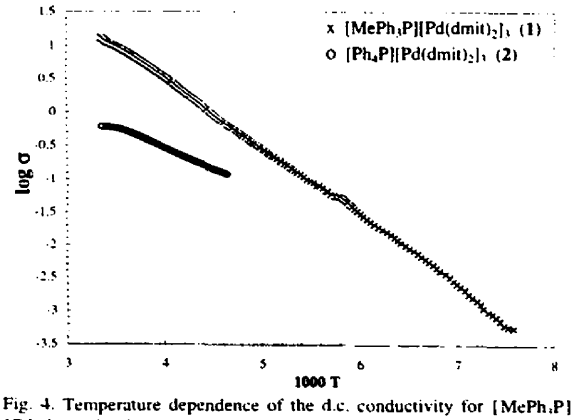


Fig. 4. Temperature dependence of the d.c. conductivity for [MePh$_3$P][Pd(dmit)$_2$]$_3$ (**1**) (×) and [Ph$_4$P][Pd(dmit)$_2$]$_3$ (**2**) (○). Data are shown as $\log_{10}\sigma$ as a function of 1000/$T$.

Table 3
Conductivity parameters for various phosphonium cation-based, 3:1 stoichiometric Ni and Pd(dmit)$_2$ compounds (**1–4**, **6–9**)

| Compound | $\sigma_{RT}$ (S cm$^{-1}$) | $E_a$ (meV) | Ref. |
|---|---|---|---|
| [MePh$_3$P][Pd(dmit)$_2$]$_3$ (**1**) | 13 | 100 | This work |
| [Ph$_4$P][Pd(dmit)$_2$]$_3$ (**2**) | 1 | 55 | This work |
| [MePh$_3$P][Ni(dmit)$_2$]$_3$ (**3**) | 0.1 | 220 | [4] |
| [Ph$_4$P][Ni(dmit)$_2$]$_3$ (**4**) | 10 | 17 | [4] |
| [BTP][Pd(dmit)$_2$]$_3$ (**6**) | 80 | NR | [3] |
| [PPN][Pd(dmit)$_2$]$_3$ (**7**) | 62 | 50 | [3] |
| [BTP][Ni(dmit)$_2$]$_3$ (**8**) | 0.2 | NR | [3] |
| [PPN][Ni(dmit)$_2$]$_3$ (**9**) | 45 | NR | [3] |

NR = Not reported.

## 4. Conclusions

As one can see, these are widely varying results for compounds with the same stoichiometry (3:1) and similar compositions. Along with the differences previously discussed in conductivity values and crystal packing structures of [MePh$_3$P][Pd(dmit)$_2$]$_3$ (**1**) and [MePh$_3$P][Ni(dmit)$_2$]$_3$ (**3**), it once again illustrates the unpredictability of the resulting properties of metal bisdithiolene-type, anion radical molecular materials.

## 5. Supplementary material

Text presenting full tables of crystallographic data, hydrogen atomic coordinates and isotropic thermal parameters, bond lengths and angles, and anisotropic thermal parameters (11 pages) are available from the authors on request.

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