

Electrocrystallization, X-ray structure and electronic properties of the dmit-based salt $[\text{MePh}_3\text{P}][\text{Ni}(\text{dmit})_2]_3$

Anthony E. Pullen,^a Hsiang-Lin Liu,^b D. B. Tanner,^b Khalil A. Abboud^a and John R. Reynolds^{*a}

^aDepartment of Chemistry, Center for Macromolecular Science and Engineering, University of Florida, P.O. Box 117200, Gainesville, Florida 32611-7200, USA

^bDepartment of Physics, University of Florida, P.O. Box 118440, Gainesville, Florida 32611-8440, USA

Electrooxidation of $[\text{Ni}(\text{dmit})_2]^-$ ($\text{dmit} = \text{C}_3\text{S}_5^{2-} = 4,5\text{-dithiolate-2-thione-1,3-dithiole}$) in 3:1 acetonitrile–acetone at a Pt wire anode in the presence of methyltriphenylphosphonium bromide electrolyte yields the radical anion salt complex $[\text{MePh}_3\text{P}][\text{Ni}(\text{dmit})_2]_3$. Black shiny platelet crystals were harvested. They belong to the monoclinic space group $P2_1/c$, $M = 1631.41$, $a = 21.0872(1)$, $b = 17.4930(2)$, $c = 15.7203(2)$ Å, $\beta = 107.072(1)^\circ$, $V = 5543.4(1)$ Å³ and $Z = 4$. The crystal packing structure consists of columns of $\text{Ni}(\text{dmit})_2$ units of width one unit separated by columns of MePh_3P^+ counter-ions. The $\text{Ni}(\text{dmit})_2$ columns are composed of dimers of $\text{Ni}(\text{dmit})_2$ units with non-bonding interactions with six other pairs of $\text{Ni}(\text{dmit})_2$ units. The arrangement of the dimers with respect to each other in the columns has been seen in other phosphonium-based $\text{Ni}(\text{dmit})_2$ complexes and is similar to the packing of $\kappa\text{-BEDT-TTF}$ radical cation salts which have shown superconductivity. Single-crystal temperature-dependent conductivity measurements have shown that this material is semiconducting with a room-temperature conductivity of 0.1 S cm^{-1} and a thermal activation energy of 0.22 eV .

Since the reported synthesis of the dmit ($\text{dmit} = \text{C}_3\text{S}_5^{2-} = 4,5\text{-dithiolate-2-thione-1,3-dithiole}$) ligand,¹ it has been utilized in an extensive amount of research along with the development of a number of analogues. The research has encompassed the areas of coordination chemistry,² organic chemistry³ and materials chemistry.⁴ Bis-chelate dmit complexes using square-planar coordinating metals (*i.e.* Ni^{II} , Pd^{II} , Pt^{II}) have been used in the assembly of semiconducting, metallic and even superconducting materials. The planar structure and sulfur-rich nature of dmit allows it to form stackable close-packing structures when using square-planar coordinating metals. Also, the large sulfur atomic orbitals allows for intermolecular non-bonding orbital interactions.⁴ Currently seven different dmit-based systems are known to have superconducting electrical properties. The complex $\alpha\text{-[EDT-TTF][Ni}(\text{dmit})_2]$ is the latest dmit-based complex to show such electrical properties, with a T_c of 1.3 K at ambient pressure.⁵

The primary methods used in the search for dmit-based conducting materials has been to change the counter-ion and the metal centre, with the $\text{Ni}(\text{dmit})_2$ system and the alkylammonium-based cations being the most widely studied.⁶ The complex $[\text{Me}_4\text{N}][\text{Ni}(\text{dmit})_2]_2$ shows superconducting behaviour under 7 kbar pressure with a T_c of 5.0 K .⁵ One class of closed-shell cations not thoroughly studied are the phosphonium-based cations.^{6,7} The first $\text{Ni}(\text{dmit})_2$ non-integer oxidation state complex to be electrocrystallized using a phosphonium-based cation was $[\text{Me}_4\text{P}][\text{Ni}(\text{dmit})_2]_2$ by Kato and co-workers.⁶ The structure is composed of columns of dimers of $\text{Ni}(\text{dmit})_2$ units separated by columns of Me_4P^+ cations. The salt exhibits semiconductivity with a single-crystal room-temperature conductivity of 0.6 S cm^{-1} . Recently we, along with Nakamura *et al.*,⁷ have synthesized and studied the 3:1 tetraphenylphosphonium-based complex $[\text{Ph}_4\text{P}][\text{Ni}(\text{dmit})_2]_3$. This complex exhibits a unique packing array of $\text{Ni}(\text{dmit})_2$ units. The packing is characterized by stacks of $\text{Ni}(\text{dmit})_2$ units separated by orthogonal $\text{Ni}(\text{dmit})_2$ spacer units. The salt displays semiconducting behaviour with a single-crystal room-temperature conductivity of $7\text{--}10 \text{ S cm}^{-1}$. To further the understanding of phosphonium-based $\text{Ni}(\text{dmit})_2$ radical anion salts, we have synthesized the similar 3:1 complex $[\text{MePh}_3\text{P}][\text{Ni}(\text{dmit})_2]_3$ by electrocrystallization. Similar to

Ph_4P^+ , we have replaced a phenyl group on the cation with a methyl group in order to study, not only the structural differences, but also the electronic properties. Herein, we report the synthesis, X-ray structure analysis and temperature-dependent conductivity of $[\text{MePh}_3\text{P}][\text{Ni}(\text{dmit})_2]_3$ and compare its properties to the $[\text{Me}_4\text{P}][\text{Ni}(\text{dmit})_2]_2$, $[\text{Ph}_4\text{P}][\text{Ni}(\text{dmit})_2]_3$ and $[(\text{PhCH}_2)\text{Ph}_3\text{P}][\text{Ni}(\text{dmit})_2]_3$ salts.^{6,7}

Experimental

Synthesis of $[\text{MePh}_3\text{P}][\text{Ni}(\text{dmit})_2]_3$

$[\text{Bu}_4\text{N}][\text{Ni}(\text{dmit})_2]$ was synthesized following the procedures described by Hansen *et al.*⁸ The radical anion salt $[\text{MePh}_3\text{P}][\text{Ni}(\text{dmit})_2]_3$ was synthesized *via* constant-current electrocrystallization in a two-compartment glass H-cell equipped with Pt wire electrodes. A saturated solution of $[\text{Bu}_4\text{N}][\text{Ni}(\text{dmit})_2]$ was electrooxidized in 3:1 acetonitrile–acetone with 0.06 mol dm^{-3} MePh_3PBr under an argon atmosphere. A current density of $0.9 \mu\text{A cm}^{-2}$ was applied over a period of 18 days. Black, shiny chunk-like and platelet crystals were harvested. All solvents were degassed thoroughly prior to use. Acetone was used as received (Aldrich) and acetonitrile was dried over type 4A molecular sieves (Fisher).

X-Ray structure determination

Crystallographic data for $[\text{MePh}_3\text{P}][\text{Ni}(\text{dmit})_2]_3$ 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 ($0.23 \times 0.1 \times 0.08 \text{ mm}^3$) was chosen for study.

The diffractometer was equipped with a graphite monochromator utilizing $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Cell parameters were refined using 8192 reflections. A hemisphere of data (1381 frames) was collected using the ω -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 $I < 1\%$). Psi-scan absorption corrections were applied based on the entire data set.

The structure was solved by direct methods in SHELXTL, and refined using full-matrix least-squares procedures. The

Table 1 Crystallographic data for [MePh₃P][Ni(dmit)₂]₃

chemical formula	C ₃₇ H ₁₈ Ni ₃ PS ₃₀
formula mass	1631.41
space group	P2 ₁ /c
<i>a</i> /Å	21.0872(1)
<i>b</i> /Å	17.4930(2)
<i>c</i> /Å	15.7203(2)
β/degrees	107.072(1)
<i>V</i> /Å ³	5543.4(1)
<i>Z</i>	4
<i>D_c</i> /g cm ⁻³	1.955
<i>F</i> (000)	3276
μ(Mo-Kα)/cm ⁻¹	22.0
2θ _{max} /degrees	55.0
range of <i>h, k, l</i>	−28–25; 0–22; 0–20
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b	0.034; 0.065
goodness-of-fit	1.131
Δρ _{max} /e Å ⁻³	0.545
Δρ _{min} /e Å ⁻³	−0.499

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

non-H atoms were treated anisotropically, whereas the hydrogen atoms were refined with isotropic thermal parameters. 713 Parameters were refined in the final cycle of refinement using 9941 reflections [with $I > 2\sigma(I)$] to yield R_1 of 3.40%, and 12219 reflections to yield wR_2 of 6.48%, respectively. Refinement was carried out using F^2 .

Molecular numbering schemes for the three crystallographically independent Ni(dmit)₂ units of [MePh₃P][Ni(dmit)₂]₃ are shown in Fig. 1. Selected bond lengths and angles are located in Table 2 for [MePh₃P][Ni(dmit)₂]₃.

Conductivity measurements

Temperature-dependent (300–150 K) resistances were measured by a four-probe method using an ac technique. Two single-crystal platelets of [MePh₃P][Ni(dmit)₂]₃ (typically 0.91 × 0.46 × 0.09 mm³) were measured in this study. Narrow-gauge (0.02 mm diameter) gold wires were affixed to the crystal using fast drying gold paint. 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 has been deter-

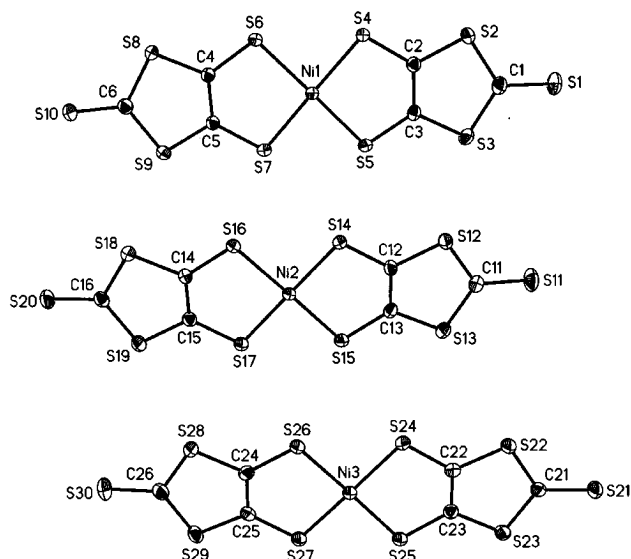


Fig. 1 Thermal ellipsoid drawings (50% probability) and numbering schemes for the three crystallographically independent Ni(dmit)₂ moieties in [MePh₃P][Ni(dmit)₂]₃

mined to be ±0.2 K or better over the temperature range measured.

Results and Discussion

Crystal structure of [MePh₃P][Ni(dmit)₂]₃

The crystal structure of [MePh₃P][Ni(dmit)₂]₃ † consists of one MePh₃P⁺ cation and three crystallographically independent Ni(dmit)₂ units. The packing is characterized by columns of Ni(dmit)₂ dimers separated by columns of MePh₃P⁺ counter-ions. The Ni(dmit)₂ units are arranged in a dimeric fashion in the *bc* plane with the long axis of Ni(dmit)₂ molecules in the *a* direction, as shown in Fig. 2. Each dimer is surrounded by six other dimers. Each of the dimers forms dihedral angles of 44.5(1)° and 51.2(1)° with four other dimers along the *c* direction and 6.7(1)° with two other dimers along the *b* direction. This packing motif is quite similar to both [Me₄P][Ni(dmit)₂]₂,⁶ and the κ-phase BEDT-TTF salts. Currently the complex κ-[BEDT-TTF]₂{Cu[N(CN)₂]Cl} with this packing array has the highest superconducting transition temperature measured to date of a molecular material of 12.8 K.⁴ The Me₄P⁺ complex also forms dimers of Ni(dmit)₂ units but in this instance, dihedral angles of 60° with four other adjacent dimers and 0° with two other pairs of the six total surrounding dimers are observed. There are extensive S...S non-bonding interdimer orbital interactions in a two-dimensional array resulting from close contacts with distances less than the sum of the van der Waals radii (3.70 Å). The S...S distances range from 3.440 Å resulting from thiolate–thiolate [S(4)–S(14)] interactions to 3.658 Å due to thiolate–thiole [S(18)–S(25)] interactions. There are also several Ni d₂₂...S non-bonding interdimer interactions observed in the crystal lattice. These range from 3.232 Å due to Ni d₂₂–thiole [Ni(3)–S(9)] orbital overlap to 3.856 Å due to Ni d₂₂–thiolate [Ni(2)–S(24)] orbital interactions.

Within the dimers, the Ni(dmit)₂ units stack in an eclipsed fashion. Two of the three crystallographically independent Ni(dmit)₂ units are in dimers with the units being slightly slipped (transverse offset) from perfectly eclipsed, as shown by the view down the *c* axis in Fig. 3. These Ni(dmit)₂ units form dimers with intradimer spacings ranging from 3.443 to 3.652 Å. The third crystallographically independent Ni(dmit)₂ forms a dimer with a perfectly eclipsed stacking motif. This is mediated by strong Ni d₂₂...Ni d₂₂ orbital interactions which is shown by the solid line in the packing diagram in Fig. 2. The distance is only 2.7837(7) Å between the Ni atoms. This results in a fold-like dmit–Ni–dmit dihedral angle of 13.0° of the dmit ligand planes from 0° for a perfectly square-planar complex. To our knowledge, this very short Ni...Ni interaction resulting from dimers arranged in an eclipsed fashion is unique among Ni(dmit)₂-based complexes. This has been observed in several instances with Pd(dmit)₂^{4–6,9} and Pt(dmit)₂-based materials.^{4,10}

The above-described packing of the anions and cations in [MePh₃P][Ni(dmit)₂]₃ is significantly different from the other similar 3:1 phosphonium-based complexes [Ph₄P][Ni(dmit)₂]₃ and [(PhCH₂)₃P][Ni(dmit)₂]₃ but very similar to the 2:1 salt [Me₄P][Ni(dmit)₂]₂.^{6,7} The Ph₄P⁺ salt displays a unique packing scheme amongst the Ni(dmit)₂ complexes, with stacks of Ni(dmit)₂ units separated by orthogonal spacer Ni(dmit)₂ units. By simply adding a methylene spacer to one of the phenyl groups, all of the Ni(dmit)₂ molecules of [(PhCH₂)₃P][Ni(dmit)₂]₃ are arranged in parallel planes. By replacing a phenyl group with a methyl

† Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/25.

Table 2 Bond lengths (Å) and angles (degrees) for the crystallographically independent Ni(dmit)₂ units of [MePh₃P][Ni(dmit)₂]₃

Ni(1)–S(7)	2.1856(8)	S(9)–C(6)	1.732(3)	S(15)–C(13)	1.707(3)	S(22)–C(21)	1.730(3)
Ni(1)–S(4)	2.1871(8)	S(9)–C(5)	1.737(3)	S(16)–C(14)	1.700(3)	S(22)–C(22)	1.750(3)
Ni(1)–S(5)	2.1890(8)	S(10)–C(6)	1.640(3)	S(17)–C(15)	1.697(3)	S(23)–C(21)	1.741(3)
Ni(1)–S(6)	2.2106(8)	C(2)–C(3)	1.390(4)	S(18)–C(16)	1.737(3)	S(23)–C(23)	1.744(3)
Ni(1)–Ni(1) ^a	2.7837(7)	C(4)–C(5)	1.394(4)	S(18)–C(14)	1.743(3)	S(24)–C(22)	1.713(3)
S(1)–C(1)	1.634(3)	Ni(2)–S(14)	2.1595(8)	S(19)–C(16)	1.735(3)	S(25)–C(23)	1.715(3)
S(2)–C(1)	1.740(3)	Ni(2)–S(15)	2.1660(8)	S(19)–C(15)	1.739(3)	S(26)–C(24)	1.696(3)
S(2)–C(2)	1.745(3)	Ni(2)–S(17)	2.1614(8)	S(20)–C(16)	1.641(3)	S(27)–C(25)	1.697(3)
S(3)–C(3)	1.739(3)	Ni(2)–S(16)	2.1614(8)	C(12)–C(13)	1.382(4)	S(28)–C(26)	1.738(3)
S(3)–C(1)	1.746(3)	S(11)–C(11)	1.650(3)	C(14)–C(15)	1.388(4)	S(28)–C(24)	1.741(3)
S(4)–C(2)	1.693(3)	S(12)–C(11)	1.729(3)	Ni(3)–S(26)	2.1615(8)	S(29)–C(26)	1.740(3)
S(5)–C(3)	1.690(3)	S(12)–C(12)	1.745(3)	Ni(3)–S(27)	2.1670(8)	S(29)–C(25)	1.742(3)
S(6)–C(4)	1.695(3)	S(13)–C(11)	1.741(3)	Ni(3)–S(25)	2.1712(8)	S(30)–C(26)	1.641(3)
S(7)–C(5)	1.686(3)	S(13)–C(13)	1.745(3)	Ni(3)–S(24)	2.1749(8)	C(22)–C(23)	1.372(4)
S(8)–C(4)	1.744(3)	S(14)–C(12)	1.705(3)	S(21)–C(21)	1.654(3)	C(24)–C(25)	1.393(4)
S(8)–C(6)	1.746(3)						
S(7)–Ni(1)–S(4)	170.92(3)	C(2)–C(3)–S(3)	116.6(2)	S(11)–C(11)–S(12)	123.3(2)	C(21)–S(22)–C(22)	97.44(14)
S(7)–Ni(1)–S(5)	85.21(3)	S(5)–C(3)–S(3)	122.0(2)	S(11)–C(11)–S(13)	122.9(2)	C(21)–S(23)–C(23)	97.11(14)
S(4)–Ni(1)–S(5)	92.20(3)	C(5)–C(4)–S(6)	121.5(2)	S(12)–C(11)–S(13)	113.7(2)	C(22)–S(24)–Ni(3)	101.69(10)
S(7)–Ni(1)–S(6)	92.29(3)	C(5)–C(4)–S(8)	115.1(2)	C(13)–C(12)–S(14)	120.9(2)	C(23)–S(25)–Ni(3)	102.18(10)
S(4)–Ni(1)–S(6)	88.89(3)	S(6)–C(4)–S(8)	123.4(2)	C(13)–C(12)–S(12)	115.6(2)	C(24)–S(26)–Ni(3)	102.94(10)
S(5)–Ni(1)–S(6)	170.71(3)	C(4)–C(5)–S(7)	121.8(2)	S(14)–C(12)–S(12)	123.5(2)	C(25)–S(27)–Ni(3)	102.76(10)
S(7)–Ni(1)–Ni(1) ^a	101.01(3)	C(4)–C(5)–S(9)	116.7(2)	C(12)–C(13)–S(15)	120.9(2)	C(26)–S(28)–C(24)	97.17(14)
S(4)–Ni(1)–Ni(1) ^a	87.95(3)	S(7)–C(5)–S(9)	121.5(2)	C(12)–C(13)–S(13)	116.2(2)	C(26)–S(29)–C(25)	97.27(14)
S(5)–Ni(1)–Ni(1) ^a	97.09(3)	S(10)–C(6)–S(9)	121.9(2)	C(15)–C(13)–S(13)	122.9(2)	S(21)–C(21)–S(22)	123.8(2)
S(6)–Ni(1)–Ni(1) ^a	92.16(3)	S(10)–C(6)–S(8)	124.4(2)	C(15)–C(14)–S(16)	121.1(2)	S(21)–C(21)–S(23)	122.8(2)
C(1)–S(2)–C(2)	97.53(14)	S(9)–C(6)–S(8)	113.7(2)	C(15)–C(14)–S(18)	116.0(2)	S(22)–C(21)–S(23)	113.5(2)
C(3)–S(3)–C(1)	97.02(14)	S(14)–Ni(2)–S(15)	93.11(3)	S(16)–C(14)–S(18)	122.9(2)	C(23)–C(22)–S(24)	122.0(2)
C(2)–S(4)–Ni(1)	102.45(10)	S(14)–Ni(2)–S(17)	177.89(3)	S(16)–C(14)–S(18)	122.9(2)	C(23)–C(22)–S(22)	115.6(2)
C(3)–S(5)–Ni(1)	102.51(10)	S(15)–Ni(2)–S(17)	85.64(3)	C(14)–C(15)–S(17)	121.1(2)	C(22)–C(23)–S(25)	120.8(2)
C(4)–S(6)–Ni(1)	101.61(10)	S(14)–Ni(2)–S(16)	88.13(3)	C(14)–C(15)–S(19)	115.7(2)	C(22)–C(23)–S(23)	116.3(2)
C(5)–S(7)–Ni(1)	102.47(10)	S(15)–Ni(2)–S(16)	177.90(3)	S(17)–C(15)–S(19)	123.2(2)	S(25)–C(23)–S(23)	122.9(2)
C(4)–S(8)–C(6)	97.34(14)	S(17)–Ni(2)–S(16)	93.07(3)	S(20)–C(16)–S(19)	123.1(2)	C(25)–C(24)–S(26)	120.8(2)
C(6)–S(9)–C(5)	97.14(14)	C(11)–S(12)–C(12)	97.50(14)	S(20)–C(16)–S(18)	123.3(2)	C(25)–C(24)–S(28)	116.1(2)
S(1)–C(1)–S(2)	123.3(2)	C(11)–S(13)–C(13)	96.16(14)	S(19)–C(16)–S(18)	113.6(2)	S(26)–C(24)–S(28)	123.1(2)
S(1)–C(1)–S(3)	123.2(2)	C(12)–S(14)–Ni(2)	102.50(10)	S(26)–Ni(3)–S(27)	92.66(3)	C(24)–C(25)–S(27)	120.8(2)
S(2)–C(1)–S(3)	113.5(2)	C(13)–S(15)–Ni(2)	102.44(10)	S(26)–Ni(3)–S(25)	178.64(3)	C(24)–C(25)–S(29)	115.7(2)
C(3)–C(2)–S(4)	121.4(2)	C(14)–S(16)–Ni(2)	102.24(10)	S(27)–Ni(3)–S(25)	86.35(3)	S(27)–C(25)–S(29)	123.5(2)
C(3)–C(2)–S(2)	115.3(2)	C(15)–S(17)–Ni(2)	102.51(10)	S(26)–Ni(3)–S(24)	87.78(3)	S(30)–C(26)–S(28)	122.7(2)
S(4)–C(2)–S(2)	123.2(2)	C(16)–S(18)–C(14)	97.09(14)	S(27)–Ni(3)–S(24)	176.61(3)	S(30)–C(26)–S(29)	123.5(2)
C(2)–C(3)–S(5)	121.4(2)	C(16)–S(19)–C(15)	97.44(14)	S(25)–Ni(3)–S(24)	93.26(3)	S(28)–C(26)–S(29)	113.8(2)

^aSymmetry transformations used to generate equivalent atoms: $-x, -y, -z+2$.

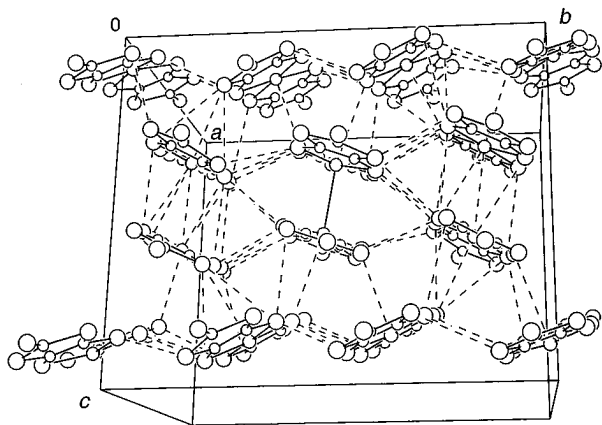


Fig. 2 View along the long axis of the Ni(dmit)₂ moieties showing a dimeric packing arrangement in [MePh₃P][Ni(dmit)₂]₃ [MePh₃P⁺ cations have been omitted for clarity]. Also shown are extensive S...S and Ni d₂₂...S (---) and Ni d₂₂...Ni d₂₂ (—) non-bonding orbital interactions.

group, the material [MePh₃P][Ni(dmit)₂]₃ results with the same stoichiometry but with a very different packing. The complex [Me₄P][Ni(dmit)₂]₂ with a 2:1 stoichiometry due to the small size of the cation, has a packing of the Ni(dmit)₂ moieties identical to that of [MePh₃P][Ni(dmit)₂]₃.

Electrical conductivity

The temperature dependence of the four-probe is shown in Fig. 4. Semiconducting behaviour is illustrated as the conduc-

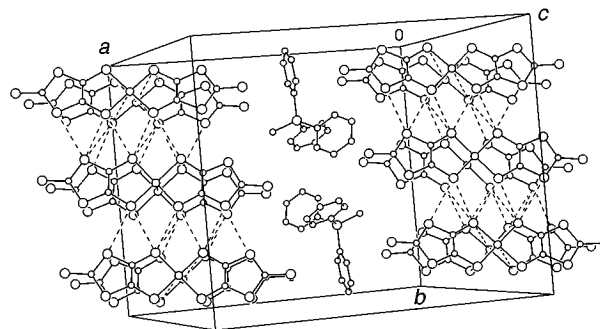


Fig. 3 View perpendicular to the Ni(dmit)₂ moieties showing intra-dimer quasi-eclipsed stacking arrangements of the moieties of [MePh₃P][Ni(dmit)₂]₃. Also shown are the dimers packed in a columnar arrangement separated by MePh₃P⁺ cations. Dashed lines represent S...S distances less than the sum of the van der Waals radii.

tivity decreases rapidly from its 300 K value of 0.1 S cm⁻¹ with decreasing temperature. The temperature-dependent conductivity is well fit by eqn. (1),

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

with a thermal activation energy E_a of 220 meV. The room-temperature conductivity is two orders of magnitude smaller than that of [Ph₄P][Ni(dmit)₂]₃⁷ and similar to the value reported for [(PhCH₂)Ph₃P][Ni(dmit)₂]₃ (0.2 S cm⁻¹) and [Me₄P][Ni(dmit)₂]₂ (0.6 S cm⁻¹).⁶ Moreover, the value of the thermal activation energy is about 20 times larger than that of [Ph₄P][Ni(dmit)₂]₃. Thus, although both [MePh₃P][Ni(dmit)₂]₃ and [Ph₄P][Ni(dmit)₂]₃ have the same stoichio-

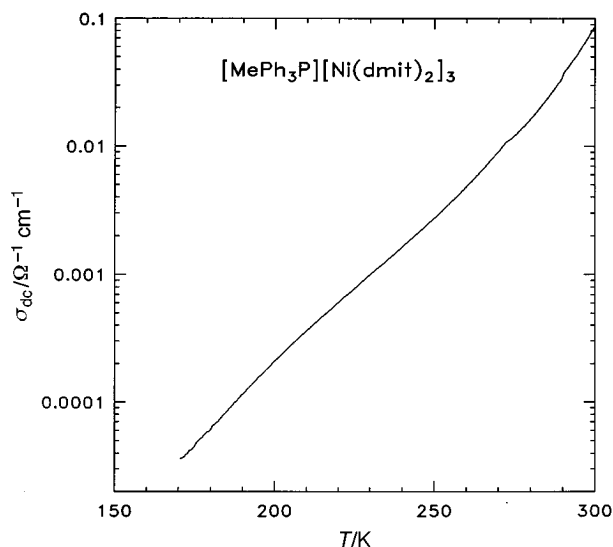


Fig. 4 Dc conductivity for $[\text{MePh}_3\text{P}][\text{Ni}(\text{dmit})_2]_3$ as a function of temperature

metry, the electrical properties of these materials are dominated by the differences in packing caused by differences in counterion structure.

It has long been advocated that molecular systems are advantageous owing to their tailorability by the chemist to 'fine tune' a system to potentially yield improved material properties. We have seen from the results for $[\text{MePh}_3\text{P}][\text{Ni}(\text{dmit})_2]_3$, $[(\text{PhCH}_2)_3\text{P}][\text{Ni}(\text{dmit})_2]_3$, $[\text{Me}_4\text{P}][\text{Ni}(\text{dmit})_2]_2$ and $[\text{Ph}_4\text{P}][\text{Ni}(\text{dmit})_2]_3$ that although the components of the materials, such as the counter-ion, can be changed only slightly, very different unexpected and unpredictable structural and electrical properties may result. This has been seen not only in this series of phosphonium-based $\text{Ni}(\text{dmit})_2$ salts, but also within other families (*i.e.* ammonium, sulfonium) of $\text{Ni}(\text{dmit})_2$ salts.^{4,6,7}

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