

A new molecular metal based on Pd(dmit)₂: synthesis, structure and electrical properties of (C₇H₁₃NH)[Pd(dmit)₂]₂ (dmit²⁻ = 2-thioxo-1,3-dithiole-4,5-dithiolate)

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Air-oxidation of the acetone–acetic acid solution of (C₇H₁₃NH)₂[Pd(dmit)₂] yielded black shiny platelets of (C₇H₁₃NH)[Pd(dmit)₂]₂. The crystal structure was characterized by a criss-cross columnar structure, which has been often observed in M(dmit)₂-based (M = Ni, Pd) superconductors. Although the quinuclidinium cation (C₇H₁₃NH)⁺ is found to be orientationally disordered on a 2-fold axis, the crystal exhibited metallic conductivity down to ~40 K. Under ambient pressure the room temperature conductivity is around 22 S cm⁻¹ and the resistivity gradually decreased with decreasing temperature down to 200 K, where it suddenly started to decrease more rapidly and kept decreasing down to ~40 K, where it started to increase steeply. At ca. 200 K the structural transition occurred, yet the crystal and molecular structures remained practically unaffected including the cation site disorder and the strong dimerization of the Pd(dmit)₂ molecules. The electrical behaviour under high pressure was rather unusual but could be compared with structurally related Pd(dmit)₂-based superconductors.

Among the metal-dithiolene complexes, the [M(dmit)₂] (M = Ni, Pd, Pt, Au, *etc.*) salts in particular have been most intensively studied to develop conducting or magnetic materials.¹ In spite of the structural similarity to the chalcogen donor molecules such as BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene), most of the crystal structures of the [M(dmit)₂] salts consist of stacking structures and do not diversify much compared with the chalcogen donor salts.² This means that crystal structure determining factors of the [M(dmit)₂] salts can be more easily derived at least for the salts with some particular class of cation species. In addition most of the reports deal with ammonium and related bulky cation salts of [M(dmit)₂]. As a result, when we make a close examination of the previous reports, a relationship might emerge between the arrangement of [M(dmit)₂] molecules in the solid state and the structural feature of the cation. Since the [M(dmit)₂] molecular arrangement determines the physical properties of the solid state, a full understanding of such a relationship could help us to design further advanced and novel functional materials based on the [M(dmit)₂] molecules. In other words the [M(dmit)₂] salts are the system of choice for a case study of the structure–property relationship, or more generally for crystal designing.

There have been reported two patterns of typical molecular arrangement of the [M(dmit)₂] salts which achieve stable metallic or superconducting states: one is called the “spanning overlap” type where the [M(dmit)₂] molecules stack in such a way that one [M(dmit)₂] molecule spans over two [M(dmit)₂] molecules,³ and the other is called the “solid crossing columns” type where columns in the same sheet are parallel but lie criss-cross with those in a neighbouring sheet (Fig. 1).⁴ The former structure leads to two-dimensional intermolecular interaction with wholly metallic properties,⁵ while the latter often leads to metallic or superconducting states.^{6–12}

It has been known^{1,3–12} that a series of structurally related cations such as (CH₃)₄N⁺, (CH₃)₂(C₂H₅)₂N⁺, C₅H₁₀NH₂⁺

and C₄H₈NH₂⁺ yield the charge transfer salts of either of the criss-cross column or the spanning overlap type. Due to the molecular structural similarity to the above-mentioned series of cations, quinuclidinium ion (shown in Scheme 1) can be thought to make the M(dmit)₂ molecules arrange in either way mentioned above. Therefore it would be interesting to synthesize the quinuclidinium–M(dmit)₂ salts and investigate their structural and electrical properties. We report herein the synthesis, structure and electrical properties of a new partially oxidized [Pd(dmit)₂] salt.¹³

Experimental

Synthesis

Acetone and acetonitrile were purified by following the literature in ref. 14. Other reagents were purchased and used as received. Basically we followed the reported general procedure¹⁵ for the syntheses of the M(dmit)₂ salts to prepare (C₇H₁₃NH)₂[Pd(dmit)₂] with the following modification (Scheme 2). All procedures were carried out in a nitrogen atmosphere unless noted otherwise. All solvents were deaerated by bubbling nitrogen gas through them for 20 min immediately before use.

(C₇H₁₃NH)₂[Pd(dmit)₂]. Sodium (0.36 g; 15.66 mmol) and dmit(COPh)₂ (**1**) (2.75 g; 6.76 mmol)¹⁵ were placed in a three-necked flask (500 ml) equipped with a dropping funnel, a condenser and a three-way valve in a nitrogen atmosphere. Methanol (100 ml) was carefully added to prepare the crimson solution of the disodium salt Na₂(dmit). PdCl₂ (0.61 g; 3.44 mmol) in NH₃ aq. (25–28%) (200 ml) and quinuclidine hydrochloride (1.00 g; 6.76 mmol) in methanol (80 ml) were successively added with stirring and the mixture was stirred overnight at room temperature. The volatile solvent was

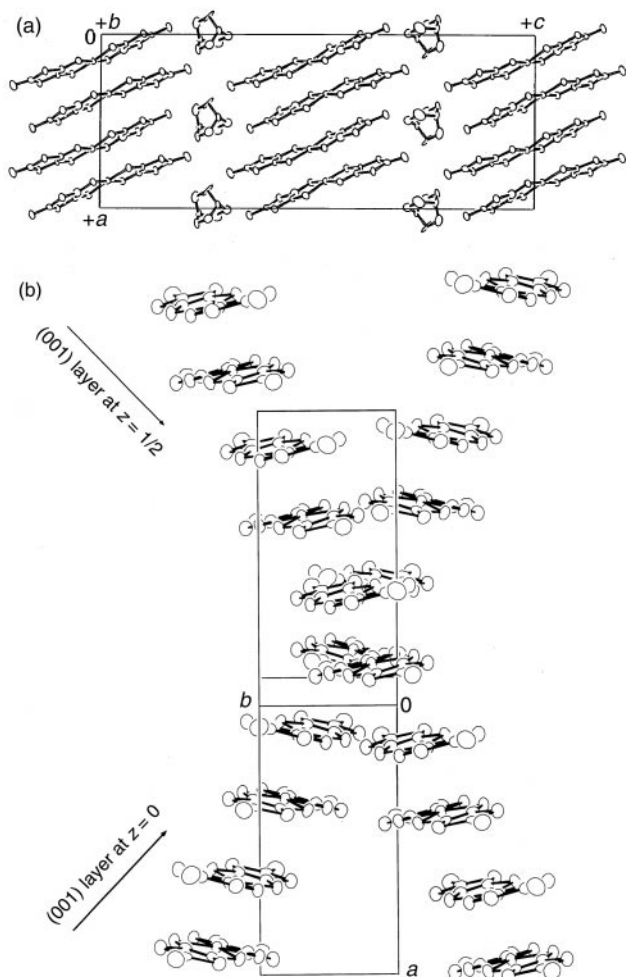
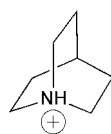
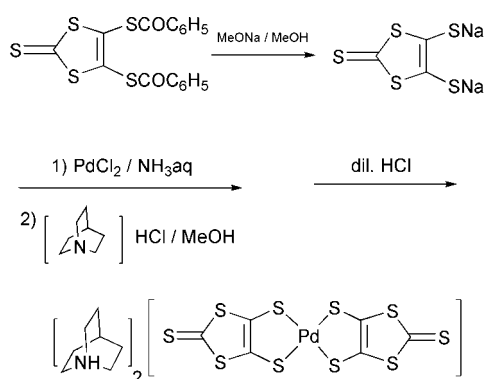


Fig. 1 (a) The crystal structures of $(\text{C}_7\text{H}_{13}\text{NH})[\text{Pd}(\text{dmit})_2]_2$ at 298 K. (b) Criss-cross columns parallel to (110) and $(\bar{1}10)$ (298 K).

removed to about a third of the original volume under reduced pressure and the residual mixture was neutralized with 10% HCl until the solution turned slightly acidic. The resultant precipitates were filtered off with suction and washed with methanol and diethyl ether, then dried *in vacuo*. The crude



Scheme 1



Scheme 2

products were dissolved in acetone or methanol then filtered to remove insoluble residues. The filtrate was evaporated under reduced pressure at room temperature to nearly saturated solution then chilled at -40°C for 30 min. The black crystals were collected, washed with methanol then diethyl ether, and dried *in vacuo*. Yield: 1.26 g (51.7%). IR/ cm^{-1} : 1456.0, 1054.9, 895.8, 465.7. UV/nm: 554.0, 390.5, 326.0, 208.0. Elemental analysis $\text{C}_{20}\text{H}_{28}\text{N}_2\text{S}_{10}\text{Pd}$ (calc) C 33.20; H 3.90; N 3.87 (found) C 35.43; H 4.41; N 3.56%.

$(\text{C}_7\text{H}_{13}\text{NH})[\text{Pd}(\text{dmit})_2]_2$. (A) Electrochemical method; $(\text{C}_7\text{H}_{13}\text{NH})_2[\text{Pd}(\text{dmit})_2]$ was weighed (9.86 mg) in a dry-box and placed in an H-tube with a glass-frit (G2 or G3) between the anode and cathode compartments, which was well purged with a dry nitrogen stream in advance. 15 ml of acetone-acetonitrile (1:1 vol) or acetonitrile was added and Pt-electrodes (1 mm diameter) were immersed. After the complex was completely dissolved with an ultrasonic device, the H-tube was allowed to stand still overnight at 18°C then a constant current of 0.3–3.0 μA was applied for a week. Supporting electrolytes were not added.

(B) Chemical method; 15–20 mg of $(\text{C}_7\text{H}_{13}\text{NH})_2[\text{Pd}(\text{dmit})_2]$ was dissolved in a mixed solution of acetone (10–20 ml) and acetic acid (0.5–4.0 ml) in a 50 ml Erlenmeyer flask and loosely sealed, then allowed to evaporate gradually in air at a constant temperature (0 – 20°C). Single crystals of good quality and large size were obtained from the following conditions; the complex (16.4 mg) in acetone (20 ml) and acetic acid (4.0 ml) stood for 7 days at 18°C .

IR/ cm^{-1} : 1292.3, 1058.9, 1025.3, 513.6. Elemental analysis $\text{C}_{19}\text{H}_{14}\text{NS}_{20}\text{Pd}_2$ (calc) C 20.55; H 1.27; N 1.26 (found) C 20.65; H 1.45; N 1.28%.

Resistivity measurement

The electrical resistivity was measured on a single crystal using a standard 4-probe method and a home-made cryostat over the temperature range 4–300 K. Gold wires (20 μm ϕ) and gold paste were used as the electrical contacts. The electrical resistivity under high pressure (0–12.0 kbar) was measured using a clump-type Cu/Be cell and Daphne oil 7373 (Idemitsu Co., Ltd.) as a pressure medium.

X-Ray structural analysis

X-Ray structural analysis was carried out at room (298 K) and low (150 K) temperatures. An automated Mac Science MXC 18 diffractometer with graphite-monochromated Mo-K α radiation was used for all the data collections. Three standard reflections, which were monitored every 100 data measurements, showed no significant deviation in intensities and no decay correction was applied. An empirical absorption correction was carried out by azimuthal (ψ -) scans of several reflections. The data were corrected for Lorentz and polarization effects.

The structure at 298 K was solved by a direct method (SHELXS-86¹⁶), and the hydrogen atoms were placed at the calculated ideal positions. A full-matrix least-squares technique with anisotropic thermal parameters for non-hydrogen atoms and isotropic ones for hydrogen atoms (positional parameters are constrained to the attached carbons) was employed for the structure refinement. The refinement and production of the publication material were carried out using SHELXL-97.¹⁷ In the refinement all non-H atoms were refined anisotropically and H atoms placed in calculated positions and refined with a riding model. The disorder of the cation around a 2-fold crystallographic axis was modelled on the basis of a connected set of atoms with overall SOF 0.5 but with C/N pairs of atoms with SOF 0.25 in the C9 and C12 sites.

Table 1 The crystal data of $(C_7H_{13}NH)[Pd(dmit)_2]_2$

Temperature/K, T	298(2)	150(2)
Chemical formula	$C_{19}H_{14}NS_{20}Pd_2$	$C_{19}H_{14}NS_{20}Pd_2$
Formula weight, M	1110.31	1110.31
Crystal system	Monoclinic	Monoclinic
$a/\text{\AA}$	14.603(3)	14.50(2)
$b/\text{\AA}$	6.3722(11)	6.333(9)
$c/\text{\AA}$	36.335(6)	36.13(5)
$\beta/^\circ$	90.020(10)	90.14(10)
$V/\text{\AA}^3$	3381.1(11)	3318(8)
Space group	$C2/c$ (no. 15)	$C2/c$ (no. 15)
Z	4	4
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	2.32	2.36
No. of reflections measured	2876	3600
No. of independent reflections	2673	3416
No. of reflections observed	2414	2844
$[I > 2\sigma(I)]$		
R_{int}	0.0187	0.0330
The final R values ^a		
$R(F)$, $wR(F)$	0.0766, 0.2465	0.1247, 0.3151

^aFor observed data.

The structure at 150 K was solved by a direct method¹⁸ and expanded using Fourier techniques.¹⁹ The refinement was carried out based on the same model as the 298 K structure but only the Pd and S atoms were refined anisotropically to eliminate non-positive definite anisotropic thermal displacement ellipsoid tensors for a number of C atoms.²⁰ Atom scattering factors and the values for the mass attenuation coefficients were taken from the literature.²¹ The refinement and production of the publication material were carried out using SHELXL-97.¹⁷

CCDC reference numbers 163763–163764. See <http://www.rsc.org/suppdata/jm/b1/b102260c/> for crystallographic files in .cif or other format.

Results and discussion

Synthesis

None of the quinuclidinium salt $(C_7H_{13}NH)_2[Pd(dmit)_2]$ was obtained when the appropriate chloride was added as a suspension in methanol instead of an NH_3 aq. solution. When the neutralization with dil. HCl was omitted the desired product was not obtained either. The former fact suggests that the metal chlorides are required to dissolve completely for the ligand exchange reaction, while the latter can be explained by the fact that the quinuclidinium cation can easily release the proton in the strongly alkaline condition which is required for the removal of the protecting groups from $dmit^{2-}$, and a slightly HCl-acidic condition is necessary to restore the quinuclidinium cation. On the recrystallization of the crude $(C_7H_{13}NH)_2[Pd(dmit)_2]$ isopropyl alcohol appeared to be an unfavorable solvent because the complex changed in color the instant that isopropyl alcohol was added; the resultant residue was different from the corresponding 1:1 salt. $(C_7H_{13}NH)_2[Pd(dmit)_2]$ is sensitive to air-oxidation and it requires a strictly inert atmosphere throughout the purification. The UV–VIS absorption spectra showed that the addition of some drops of triethylamine to the solution turned out to be effective in preventing the air-oxidation as previously reported for the related complexes.¹⁵

As for the partially oxidized salt $(C_7H_{13}NH)[Pd(dmit)_2]_2$ the electrochemical method gave small single crystals, while the chemical method gave black irregular-shaped shiny platelets of a typical size of *ca.* $1 \times 0.1 \times 0.015 \text{ mm}^3$. The 1:2 salt was always obtained in powder form even when single crystals were also formed, and the most important factor for obtaining large single crystals appeared to be the control of the rate of air-oxidation as well as the evaporation of the solvent; the lower

the temperature and the use of less acetic acid often gave better results.

Molecular and crystal structure of $(C_7H_{13}NH)[Pd(dmit)_2]_2$

The unit cell of $(C_7H_{13}NH)[Pd(dmit)_2]_2$ at room temperature is shown in Fig. 1(a). The crystallographic data are summarized in Table 1. The molecular and crystal structures of this salt hardly change at lower temperature, including the disorder of the cation. Therefore we shall first discuss the common features of the structure by looking at the high-temperature phase.

The molecular and crystal structures of $Pd(dmit)_2$ in this salt share many of the basic structural features with other isostructural compounds.^{6,7,9,22} The dimerized $Pd(dmit)_2$ molecules stack to form columns parallel to (110) and $(\bar{1}10)$ (Fig. 1(b)). The intra- and interdimer distances are 3.050 and 3.831 Å, respectively, which are normal compared with the related compounds.^{6,7,9,22,23} The molecular overlap is eclipsed within a dimer, while slipped between the neighboring dimers. This stacking feature implies that the dimerization could be very strong. In fact the Pd–Pd distance within the dimer is 3.140(3) Å, which is as short as those reported on some isostructural $Pd(dmit)_2$ compounds^{6,7,9,22} and such a strong Pd–Pd interaction was regarded as a chemical bond by some researchers.²² In compensation for the resultant ligand–ligand repulsion the central Pd atom deviates from the mean molecular plane of the coordinating four sulfur atoms (by 0.069 Å) more markedly than the $Ni(dmit)_2$ complexes,⁶ where such dimerization is very weak.^{24–29} The Pd–S bond lengths (mean 2.303 Å) and S–Pd–S bond angles (mean 89.9°) are comparable to other related $Pd(dmit)_2$ complexes. Within a $Pd(dmit)_2$ column and between the adjacent columns are found sulfur–sulfur contacts which are shorter than the van der Waals distance (3.70 Å), and those columns are connected by such interatomic contacts to form a conduction sheet in the *ab*-plane (Fig. 1(b)). The two columns in the same sheet are parallel but those in the neighboring sheets are criss-cross (Fig. 1(b)). The quinuclidinium cations are located on 2-fold axes, and thus orientationally disordered: for clarity only one orientation is depicted in Fig. 1(a). Some of the metallic or superconducting $M(dmit)_2$ ($M = Ni, Pd$) salts such as β -(Me_4N)[$Pd(dmit)_2$] are isostructural with this salt (see Table 2).^{4,6–10} The interrelation between the $M(dmit)_2$ dimers and the cations divides this series of isostructural $M(dmit)_2$ salts into two classes and this crystal structure should be called β -type rather than β' -type.³⁰ Another high-pressure superconductor $(CH_3)_2(C_2H_5)_2N[Pd(dmit)_2]_2$ with a different crystal structure also has conduction sheets with the same $Pd(dmit)_2$ arrangement.^{5a,31} Since the electrical properties of the $M(dmit)_2$ salts substantially depend on the charge and molecular arrangement of the $M(dmit)_2$ species, the electrical behaviour of this salt under high pressure is intriguing, which will be discussed below.

In the low-temperature phase, the nitrogen and carbon atoms of the cation could still not be distinguished from the X-ray study, and thus we can not say anything definite about the possibility of disorder between the two atoms (C9 and C12) at the present stage. However the PLATON³² geometry program indicates the presence of possible N–H \cdots S H-bond formation as indicated in Table 3. These results suggest that N has a preference for the C12 site because this results in a stronger H-bond but they do not preclude the presence of some N in the C9 site. The crystal data and the molecular arrangement are almost unchanged through the transition (Table 1). For example, the Pd–S bond lengths (mean 2.30 Å), the S–Pd–S bond angles (mean 89.9°), the central Pd atom deviations from the mean molecular plane of the coordinating four sulfur atoms (0.073 Å) and the Pd–Pd distance within a dimer (3.114(5) Å) are comparable to those at room temperature, as well as both intra- and interdimer distances (3.043 Å and 3.790 Å, respectively). There have been many arguments as to whether the

Table 2 Selected M(dmit)₂ complexes having criss-cross columns or related structures

Chemical formula ^a	$\sigma(\text{RT})^b$	Electrical behaviour ^c	References
(Me ₄ N)[Ni(dmit) ₂] ₂	50	10 K, $T_c = 5$ K (7 kbar)	4, 6, 24–28
β -(Me ₄ N)[Pd(dmit) ₂] ₂	50	$T_c = 6.2$ K (6.5 kbar)	7, 8
(Me ₂ Et ₂ N)[Pd(dmit) ₂] ₂	50	$T_c = 4$ K (2.4 kbar)	31
(C ₇ H ₁₃ NH)[Pd(dmit) ₂] ₂	22	~40 K	This work
Cs[Pd(dmit) ₂] ₂	100–200	56.5 K	9, 29
(Me ₄ N)[Pt(dmit) ₂] ₂	10	~220 K	10
(Me ₄ As)[Pd(dmit) ₂] ₂	1	Semiconductive	7
β' -(Me ₂ Et ₂ P)[Pd(dmit) ₂] ₂	10	$T_c = 4.0$ – 1.8 K (6.9–10.4 kbar)	11
β' -(Me ₄ Sb)[Pd(dmit) ₂] ₂	20–30 ^d	Semiconductive	12
(Me ₄ P)[Pd(dmit) ₂] ₂	20	Semiconductive	22

^aMe = CH₃, Et = C₂H₅. ^bConductivity at room temperature/S cm⁻¹. ^cSuperconducting transition temperatures (T_c 's) are listed with the critical pressures in parentheses, otherwise the lowest temperatures where metallic behaviour was observed at ambient pressure are listed. ^dThe value is not explicitly described in the literature and read from the graph.

dimerization of Pd(dmit)₂ would become weak or not under high pressure and at low temperature, especially around superconducting transitions, for such a difference can be directly associated with whether the conduction band would be mainly of HOMO (highest occupied molecular orbital) or LUMO (lowest unoccupied molecular orbital) of the Pd(dmit)₂ molecule.^{11,12,30,33} In this salt it is clear that reduction in temperature from 298 to 150 K has only a small effect on the intradimer separation and Pd–Pd distance but a somewhat larger but still small effect on the interdimer separation which is comparable with the effect on the S···S contacts between the Pd(dmit)₂ columns within a sheet parallel to (001) *e.g.* (150 K distances in square brackets) S4···S3 3.493(7) [3.453(9)], S4···S5 3.540(7) [3.512(9)], S7···S6 3.585(7) [3.544(9)] and S7···S8 3.535(7) [3.494(9)]. Thus it seems that the reduction in temperature has not had much effect on the dimers themselves but has caused them to pack together more closely. Reflectance spectra as well as a tight-binding band calculation would give us useful information about the electronic structures of both phases.

Electrical behaviour of (C₇H₁₃NH)[Pd(dmit)₂]₂

The temperature dependence of the electrical resistivity of (C₇H₁₃NH)[Pd(dmit)₂]₂ obtained by way of the chemical method (air-oxidation) under ambient and high pressures is shown in Fig. 2. Fig. 2(a) is a result of ambient pressure measurement of a sample, and Fig. 2(b) shows the result of a series of measurements on increasing pressure from 0 to 12 kbar using a different sample from that of Fig. 2(a). Under ambient pressure the room temperature conductivity is around 22 S cm⁻¹ and the resistivity gradually decreased with decreasing temperature down to 200 K, where it suddenly started to decrease more rapidly and kept decreasing down to ~40 K, where it started to increase steeply. Comparing the two figures in Fig. 2, one can notice a sample-dependence about the temperature (T_{\min}) where the resistivity takes the minimum, but the anomaly at 200 K is not sample-dependent. There was a trend that a broader resistivity minimum was observed at higher temperatures on the sample which was of poor quality judging from its X-ray photographs. This fact suggests that T_{\min} may not be associated with a transition.

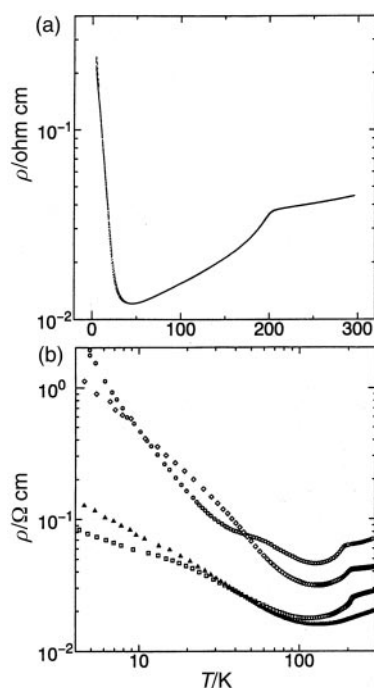
Table 3 Specified hydrogen bonds (with esd's except fixed and riding H)

	D–H ^a	H···A ^a	D···A ^a	$\angle(\text{DHA})^b$	Involved atoms
298 K	0.98	2.48	3.27(4)	137.5	C12–H12···S10 ^c
	0.98	2.68	3.37(4)	127.8	C9–H9···S1 ^d
150 K	1.00	2.54	3.33(4)	136.2	C12–H12···S10 ^c
	1.00	2.56	3.28(5)	129.2	C9–H9···S1 ^d

^aInteratomic distances in Å. ^bBond angles in degrees. ^cSymmetry operation: 2–x, 1–y, –z. ^dSymmetry operation: $\frac{1}{2}$ –x, $-\frac{1}{2}$ +y, $\frac{1}{2}$ –z

There have been reported more than 100 kinds of charge transfer salts of M(dmit)₂ complexes with a variety of closed-shell cations which were designed as conducting crystalline materials.^{1,2} Yet at ambient pressure most of them are semiconducting from room temperature and require a high pressure to realize metallic properties. All of such metallic M(dmit)₂ salts have either criss-cross or “spanning overlap” structures except for one, Na[Ni(dmit)₂]₂,³⁴ of which the crystal structure is not yet known. Therefore this new salt (C₇H₁₃NH)[Pd(dmit)₂]₂ adds an important and interesting entry to the list.

Fig. 2(b) shows how the resistivity decreases on increasing pressure. The temperature dependence as a whole became smaller and smaller on going from atmospheric pressure up to 12 kbar, where the anomaly at 200 K was completely suppressed. The electrical behaviour under 12 kbar is unusual; the slope of the resistivity increase at lower temperature became steeper under 12 kbar than under 5.3 kbar. Generally speaking higher pressure compels a molecular crystal to have a higher density and thus enhances intermolecular interaction, which broadens the band width, which in turn stabilizes the metallic state rather than the insulating state. Yet in this case the disappearance of the anomaly at 200 K might imply that the

**Fig. 2** The temperature dependence of the electrical resistivity of (C₇H₁₃NH)[Pd(dmit)₂]₂ obtained by way of the chemical method (air-oxidation) under ambient (a) and high pressures (circles: 1 bar, diamonds: 1.8 kbar, squares: 5.3 kbar and triangles: 12.0 kbar) (b).

electrical behaviour at low temperature could originate from a different phase from that under pressures lower than 12 kbar. Dimensional crossover associated with a gradual interchange between HOMO and LUMO of the Pd(dmit)₂ molecule as a conduction band could also have something to do with the behaviour.^{11,12,30,33} However, such puzzling pressure and temperature dependence has also been observed in a high pressure superconductor (CH₃)₂(C₂H₅)₂N[Pd(dmit)₂]₂, which has a similar Pd(dmit)₂ arrangement in the conduction sheet to this salt.^{5a,31} What is more, around the critical pressure under which the superconducting transition was observed β-(Me₄N)[Pd(dmit)₂]₂ as well as (CH₃)₂(C₂H₅)₂N[Pd(dmit)₂]₂ exhibited resistivity anomalies at 50–60 K, which appear very similar to the anomaly at 200 K in (C₇H₁₃NH)[Pd(dmit)₂]₂. At the same time the superconducting transitions of the compounds above are always observed in a narrow pressure range. Therefore a closer examination of electrical behaviour of (C₇H₁₃NH)[Pd(dmit)₂]₂ under 5–12 kbar is intriguing for the possibility of finding a superconducting transition.

Concluding remarks

In spite of the molecular structural similarity to the chalcogen donors, Pd(dmit)₂ complexes have been known to take a rather limited variety of crystal structures, yet exhibit unique electrical properties, which are sometimes contrary to those of the chalcogen donor salts. Examples include positive pressure dependence of superconducting transition temperatures,^{7,8} high-pressure induced non-metallic behaviour,^{5a,11,12,31} and possibly dimensional crossover^{12,30} or a two-band system,^{11,12} which have been often observed in the salts with criss-cross-column structures. Although such phenomena are certainly intriguing and important for research and development of molecular (super)conductors, the high pressure and low temperature which such phenomena require to occur have made most experiments too demanding thus far. Accordingly additional examples, which exhibit properties similar to one or more of the above under more ambient conditions, have been highly desired. In the meantime, the number of Pd(dmit)₂ complexes with a clear metallic property under atmospheric pressure is still very small. We obtained such a Pd(dmit)₂ complex utilizing the quinuclidinium cation, of which the structure can be expected to contain an arrangement of the Pd(dmit)₂ molecules in the criss-cross way, deducing from the previous reports. The new Pd(dmit)₂ complex reported herein could provide useful information for this and further studies.

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