EPR investigation of the electronic states in β'-type [Pd(dmit)₂]₂ compounds (where dmit is 2-thioxo-1,3-dithiole-4,5-dithiolate)

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Magnetic investigations of organic conductors, β'-type [Pd(dmit)₂]₂, have been performed by Electron Paramagnetic Resonance (EPR) measurements. We found that most of them except one compound underwent antiferromagnetic transitions. Although they are isostructural with little differences in lattice parameters, their spin–spin correlations and antiferromagnetic transition temperatures show strong counter ion dependence. The EPR g-values of Pd(dmit)₂ cannot be explained within the framework of isolated radical description which is a good approximation for conventional organic conductors. The electronic structures of a series of molecular conductors based on Pd(dmit)₂ at ambient pressure are discussed from microscopic points of view.

Research on metal dithiolene complexes M(dmit)₂, where dmit (C₃S₅) is 2-thioxo-1,3-dithiole-4,5-dithiolate, is one of the major trends in the development of organic conductors with new functions. Although several metallic phases are found in Ni(dmit)₂ compounds even at ambient pressure, most Pd(dmit)₂ compounds (especially the β'-type one) are paramagnetic insulators at ambient pressure. Since the crystal structure of the Pd(dmit)₂ system is based on stacks of strongly dimerized Pd(dmit)₂ molecules, the energy levels of the antibonding HOMO band become higher than those of the bonding LUMO. As a result, it is considered that the conduction band is formed by the two-dimensional half-filled HOMO band. Although the mechanism of the charge localization of β'-type Pd(dmit)₂ compounds has not been clear, the above consideration suggests that the non-metallic state at ambient pressure is a Mott–Hubbard insulator. In previous ¹H-NMR measurements on the analogous Pd(dmise)₂ based compounds, where dmise (C₃S₅Se, 2-seleno-1,3-dithiole-4,5-dithiolate) is one of the selenium-containing analogues of dmit, we found that they underwent antiferromagnetic transitions. The large local magnetization in antiferromagnetic states ruled out the possibility of spin–spin correlations and antiferromagnetic transition temperatures show strong counter ion dependence. The EPR g-values of Pd(dmit)₂ cannot be explained within the framework of isolated radical description which is a good approximation for conventional organic conductors. The electronic structures of a series of molecular conductors based on Pd(dmit)₂ at ambient pressure are discussed from microscopic points of view.

Results and discussion

We have performed EPR measurements of Pd(dmit)₂ compounds with a counter cation of Me₂Z (Z = As and Sb) and Et₃Me₂Z (Z = P, As and Sb). Although the structural difference is small among these compounds, the EPR properties are quite different. In this paper, we present the experimental results of the typical three compounds, (1) β'-Et₃Me₂P[Pd(dmit)₂]₂, (2) β'-Et₃Me₂Sb[Pd(dmit)₂]₂ and (3) β'-Me₅As[Pd(dmit)₂]₂ (hereafter we abbreviate them as Et₃Me₂P, Et₃Me₂Sb and Me₅As, respectively).

Et₃Me₂P exhibits a superconducting transition in the...
Table 1 Determined \( T_N \) of the \( \beta' \)-type \( \text{Pd(dmit)}_2 \) compounds

<table>
<thead>
<tr>
<th>Cation</th>
<th>( \text{Et}_2\text{Me}_2\text{Sb} )</th>
<th>( \text{Et}_2\text{Me}_2\text{As} )</th>
<th>( \text{Et}_2\text{Me}_2\text{P} )</th>
<th>( \text{Me}_4\text{Sb} )</th>
<th>( \text{Me}_4\text{As} )</th>
<th>( \text{Me}_4\text{P} )</th>
<th>( \text{Me}_4\text{N} )</th>
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<tbody>
<tr>
<td>( T_N )</td>
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<td>18</td>
<td>18</td>
<td>35</td>
<td>35</td>
<td>12</td>
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Fig. 1 Temperature dependence of EPR parameters of \( \beta' \)-\( \text{Et}_2\text{Me}_2\text{P}[\text{Pd(dmit)}_2]_2 \). (a) \( \zeta_{\text{spin}} \) determined by EPR intensity, (b) \( \Delta H_{\text{pp}} \), and (c) \( g \) values (\( H^* \)(square), \( H^0 \)(circle), \( H^c \)(triangle)).

pressure region of 6.9–10.4 kbar with \( T_c = 4.0–1.8 \) K. \(^\text{11}\) Measurements of EPR parameters of \( \text{Et}_2\text{Me}_2\text{P} \) were performed for 10 aligned crystals. Fig. 1(a) shows the temperature dependence of the spin susceptibility, \( \zeta_{\text{spin}} \), determined by the EPR intensity. The absolute value of \( 5.0 \times 10^{-4} \) emu mol\(^{-1} \) at 40 K is almost the same as, or slightly larger than that determined by SQUID magnetometry in a previous report. \(^\text{10}\) Scattering of data at high temperatures is due to weak EPR signals associated with huge broadening of the linewidth. Gradual decrease of \( \zeta_{\text{spin}} \) below 50 K with a broad hump around 80 K was also observed in the SQUID measurements. Sudden disappearance of the EPR signal below 18 K indicates a phase transition. Fig. 1(b) shows the temperature dependence of the peak-to-peak linewidth, \( \Delta H_{\text{pp}} \). The \( \Delta H_{\text{pp}} \) decreases as temperature decreases. At low temperatures, divergence of the \( \Delta H_{\text{pp}} \) with a minimum around 20 K was observed, indicating magnetic long-range fluctuation. Hence we concluded that the origin of the phase transition at 18 K is magnetic ordering (\( T_N = 18 \) K). Fig. 1(c) shows the temperature dependence of the \( g \)-values of \( \text{Et}_2\text{Me}_2\text{P} \) when applying the external static field along the orthogonal three axes. The anisotropy of the \( g \)-values is huge even in the case of the external field applied in the conduction plane. These features are different from TTF based organic conductors where the in-plane anisotropy of the \( g \)-values is small and the \( g \)-value shows a maximum when the external field is applied perpendicular to the conducting plane. Detailed analyses of the \( g \)-tensor will be discussed in the following section. The \( g \)-values are almost temperature independent. The EPR properties of \( \beta' \)-\( \text{Et}_2\text{Me}_2\text{As}[\text{Pd(dmit)}_2]_2 \) and \( \beta' \)-\( \text{Et}_2\text{Me}_2\text{Sb}[\text{Pd(dmit)}_2]_2 \) are very similar to those of \( \text{Et}_2\text{Me}_2\text{P} \). Hence we omit these results here. The \( T_N \)'s of both compounds were determined as 18 K. The \( T_N \)'s determined by EPR measurement in this study are summarized in Table 1. Recently \( \text{Me}_2\text{Sb} \) was found to undergo a superconducting transition under pressure. \(^\text{11}\) The \( \text{Et}_2\text{Me}_2\text{P} \) and \( \text{Me}_4\text{Sb} \) compounds mentioned above show various electronic phases as pressure increases, non-metal—superconductor—metal—insulator. On the other hand, \( \beta' \)-\( \text{Et}_2\text{Me}_2\text{Sb}[\text{Pd(dmit)}_2]_2 \) exhibits neither superconducting nor second insulating phases even at high pressures. \(^\text{10}\) Only a non-metal—metal transition was observed as pressure increases. (The \( \text{Et}_2\text{Me}_2\text{As} \) compound shows similar pressure dependence. It may be located on its boundary.)

Fig. 2 shows the temperature dependence of the EPR parameters of \( \text{Et}_2\text{Me}_2\text{Sb} \). The reliable absolute value of \( \zeta_{\text{spin}} \) cannot be estimated because of the small mass of the crystal, but it is almost the same as that of \( \text{Et}_2\text{Me}_2\text{P} \). Fig. 2(a) shows the relative temperature dependence of \( \zeta_{\text{spin}} \) determined by the EPR intensity. The EPR signal remained down to the lowest temperature, indicating the absence of the antiferromagnetic transition at least down to 4.3 K. \( \zeta_{\text{spin}} \) shows almost temperature independent behavior with a slight increase below 10 K. The \( \Delta H_{\text{pp}} \) monotonically decreases as temperature decreases down to the lowest temperature as seen in Fig. 2(b). The absolute values of the \( \Delta H_{\text{pp}} \) for each axis are larger than those of \( \text{Et}_2\text{Me}_2\text{P} \). Fig. 2(c) shows the temperature dependence of the \( g \)-values of \( \text{Et}_2\text{Me}_2\text{Sb} \). Roughly speaking, the \( g \)-values of each axis are almost temperature independent, and close to those of \( \text{Et}_2\text{Me}_2\text{P} \). As temperature decreases, they gradually decrease.

The third group of compounds, \( \text{Me}_4\text{P} \) and \( \text{Me}_4\text{As} \), show no metallic behavior even under high pressure. \(^\text{10}\) Fig. 3 shows the temperature dependence of the EPR parameters of \( \text{Me}_4\text{As} \). The abrupt decrease of \( \zeta_{\text{spin}} \) and the divergence of \( \Delta H_{\text{pp}} \) around 35 K obviously show the existence of the magnetic order. We determined \( T_N \) of the \( \text{Me}_4\text{As} \) compound as 35 K. An abrupt change of the \( g \)-values is considered to be an apparent phenomenon due to demagnetization in the proximity of the antiferromagnetic transition. At high temperatures, the \( g \)-values show appreciable temperature dependence especially along the \( b^* \) axis.

One of the questions that arises from above results is “Why the \( T_N \)’s of \( \text{Pd(dmit)}_2 \) show crucial counter ion dependence?” Recently Rouziere et al. discussed variations in the electronic structures in relation to the structural changes and with the influence of the cation on the crystal from the point of view of X-ray diffraction investigation. \(^\text{9}\) Considering the strong dimerization of \( \text{Pd(dmit)}_2 \), they estimated intermolecular overlap integrals. They show that the electronic degree of dimerization increases as counter cation size becomes larger. The difference of the \( T_N \)’s may be due to the degree of dimerization. Actually, there is a trend that compounds with

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large counter cations possess lower $T_N$'s. However no linear relationship was found. The counter cation size and dimerization effect are also important for the dimensionality of electronic structure. The HOMO band has two-dimensional character, while the LUMO is one-dimensional. As a result, the dimerization enhances the two-dimensional character of the HOMO through HOMO–LUMO level-crossing. Here we try to consider inter-dimer interaction between stacks. In this paper, we estimated the inter-dimer interaction between stacks as the overlap integral. Fig. 4 shows the relationship of the inter-dimer interaction versus the $T_N$. The parameters, $A$, $B$ and $r$, are adopted as those given at room temperature in previous papers.3,8,9,12 Here we denote the 'inter'-dimer interaction within stacks normalized 'intra'-dimer interaction as $B/A$, the 'inter'-dimer interaction between stacks normalized 'intra'-dimer interaction as $r/A$, and anisotropy of the inter-dimer interaction as $r/B$. Previous results determined by $^1$H-NMR, $[^\beta$-Me$_2$N]$[\text{Pd(dmit)}]_2$ ($T_N = 12 \text{ K}$), $[^\beta$-Me$_2$P]$[\text{Pd(dmit)}]_2$ ($T_N = 35 \text{ K}$), $[^\beta$-Me$_2$N]$[\text{Pd(dmise)}]_2$ ($T_N = 14 \text{ K}$) and $[^\beta$-Me$_2$P]$[\text{Pd(dmise)}]_2$ ($T_N = 40 \text{ K}$), are also included in this figure.5,6

Rouziere et al. pointed out the possibility of magnetic frustration within conduction layers at low temperature with the anisotropy of the interaction between the Pd(dmit)$_2$ dimers.9 Recently theoretical investigation of effective exchange interactions for dimerized systems was performed by Mori et al.13 Assuming that the HOMO levels are dominant for magnetic interactions, the calculated $T_N$ and magnitude of local moments for Pd(dmit)$_2$ are qualitatively in agreement with EPR and $^1$H-NMR results.

![Fig. 2 Temperature dependence of EPR parameters of $[^\beta$-Et$_2$Me$_2$Sb]$[\text{Pd(dmit)}]_2$. (a) $T_{\text{sym}}$ determined by EPR intensity, (b) $\Delta H_{pp}$, and (c) $g$ values ($i/a^*$ (square), $j/b^*$ (circle), $k/c^*$ (triangle)).](image1)

![Fig. 3 Temperature dependence of EPR parameters of $[^\beta$-Me$_2$As]$[\text{Pd(dmit)}]_2$. (a) $T_{\text{sym}}$ determined by EPR intensity, (b) $\Delta H_{pp}$ and (c) $g$ values ($i/a^*$ (square), $j/b^*$ (circle), $k/c^*$ (triangle)).](image2)

![Fig. 4 Relationship of the inter-dimer interaction versus the $T_N$. The parameters, $A$, $B$ and $r$, which are schematically shown in the insets, are the same in refs. 3,8,9,12. $\triangle = r/A$ (H-H), $\square = B/A$ (H-H), $\bullet = r/B$. The broken line is a guide to the eye.](image3)
Lastly we present the results of the g-tensor analyses, and discuss the symmetry of the wave-function. We performed angular dependence of the g-values of Et₂Me₂P at 25 K in order to perform the g-tensor analyses to provide significant information. When the static magnetic field was applied in the midway angle within the a₁* plane, the resonance line was split into two. The ratio of the relative intensity is approximately 6:4. Since the crystal structure is monoclinic and we used 10 aligned crystals for the measurement, two arrangements are possible when we put the a₁* plane of the crystals parallel to the EPR sample stage. Assuming this, we can evaluate the principal values and axes of the g-tensor by least squares fit to the measured data assuming an anisotropic g-value.

Fig. 5 shows the determined principal axes and values on the actual Pd(dmit)₂: arrangements. One of the principal axes, g₁, lies along the b-axis, which is roughly the direction of the molecular short axis. The principal axis, g₂, lies along the molecular long axis, and g₃ is close to the direction normal to the molecular plane. The principal axes are well explained as the average of the molecular axes of Pd(dmit)₂ radicals with solid crossing columns: we can treat the directions of them as in the framework for conventional organic conductors. On the other hand, the principal values of Pd(dmit)₂ show characteristic features. The large shift from g₂ of the g₁ and g₂ are remarkable, although the small shift of g₃ is explained by the fact that HOMO and/or LUMO are mainly composed of orbitals elongated in the z direction. Considering the huge shift of g₁, it seems likely that the Pd d₃z²-r² orbital is also composed of the wave-function besides the pₓ orbital of C and S. It is noted that the principal value shows its maximum for the molecular short axis, while the maximum principal values of TTF derivatives are along the molecular long axes. This fact suggests that there is only a small contribution of the Pd d orbital along the molecular long axis. However, an isolated Pd(dmit)₂ possesses a HOMO without d contribution because of its symmetry according to the extended Hückel molecular orbital calculation. Moreover, the average of the principal values, (gₐₙₓ) (2.038), of β-Et₂Me₂[Pd(dmit)₂] does not agree with that of a 1:1 radical, Bu₄[N][Pd(dmit)₂] (Bu = butyl) solution, (g) (= 2.0191). The observed g-tensor cannot be explained by that of an isolated Pd(dmit)₂ molecule.

For conventional organic conductors, the principal values and axes of the crystal are well explained by taking into account the principal values and the axes of the g-tensor of the radical and the geometry of the molecular stacking in the crystal. According to the above consideration is also available even in the paramagnetic states of an antiferromagnet with strong “dimer” structure, κ-(BEDT-TTF)₂Cu[N(CN)₂]Cl. Recent first-principle calculations by Miyazaki et al. including the actual dimer effect suggest that the HOMO of Pd(dmit)₂ has appreciable contributions from the Pd d₃z²-r² orbitals. This expectation coincided with the EPR results. It is likely that the discrepancy of the g-tensor from the isolated radical is due to the deformation of the wave-function with the strong dimer structure of the Pd(dmit)₂ system.

In conclusion, we investigated the low temperature electronic states and determined the Tₐ's of the series of β-Pd(dmit)₂ compounds. The EPR ΔHₗ and Tₐ's show crucial ion dependence, and we found a close relationship between the Tₐ's and 'inter'-stack interaction. It is proposed that possible frustration of local moments on triangle dimers reduces the Tₐ's and magnitude of the local moments. The EPR g-values of Pd(dmit)₂ are found to be beyond one radical description; we should consider the wave-function [Pd(dmit)₂] supramolecules. These experimental facts from the view point of magnetic investigation are evidence that compounds of this family are Mott–Hubbard insulators with a dimer as a unit. Recently we succeeded in synthesizing ¹³C substituted Pd(dmit)₂ molecules, and started ¹³C-NMR measurements. Further ¹³C-NMR investigations are in progress.

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