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TOPICAL REVIEW

Variety of valence bond states formed of frustrated spins on triangular lattices based on a two-level system Pd(dmit)$_2$

Masafumi Tamura$^1$ and Reizo Kato$^2$

$^1$ Department of Physics, Faculty of Science and Technology, Tokyo University of Science, Noda, Chiba 278-8510, Japan
$^2$ Condensed Molecular Materials Laboratory, RIKEN, Wako, Saitama 351-0198, Japan
E-mail: qra_tam@ph.noda.tus.ac.jp

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Abstract

Recent studies on the physical properties of the triangular system based on the Pd(dmit)$_2$ salts (dmit $=$ 1,3-dithiole-2-thione-4,5-dithiolate) are reviewed. Quantum chemical architectures of the Pd(dmit)$_2$ molecule and its dimer are introduced with emphasis on the strong dimerization of a two-level system, which provides unique physical properties of the salts. The magnetic properties are outlined in view of the magneto-structural correlation specific to the frustrated spin systems. Some newly discovered ground states and their origins are discussed, for which the valence bond formation plays a key role. Among them, the two-level structure is crucial for the novel charge-separated state found in two salts. The valence bond ordering, similar to the spin-Peierls transition, has been found in a two-dimensional frustrated spin system. The physical aspects and possible relation to the pressure-induced superconductivity are discussed.

Keywords: Pd(dmit)$_2$ salts, triangular lattice, antiferromagnets, frustration, HOMO-LUMO interplay, spin gap, superconductivity

1. Introduction

For a long time, the physics of frustrated quantum spin systems has been a subject of active, mostly theoretical research. Much attention has been paid to the possibility of unconventional quantum states in frustrated systems, such as the resonating valence bond state, particularly in connection with the high-$T_c$ cuprate superconductors near the Mott criticality. Following the extensive developments in 1980s and 1990s of materials with strongly correlated electrons, the situation has noticeably changed in recent years, and a number of such frustrated spin systems, including those based on organic molecules, have become experimentally accessible. The strong electronic correlations in organic superconductors have been reviewed in [1].

Specifically, two-dimensional (2D) triangular antiferromagnets, the prototypical frustrated system, are attained in some organic molecular systems having $S = 1/2$ Heisenberg spins. Two classes of compounds have been hitherto known to give 2D triangular antiferromagnets: the Z[Pd(dmit)$_2$]$_2$ salts [2] (for a comprehensive review article see [3]), and $\kappa$-(BEDT-TTF)$_2$X salts [4] (for review see [5, 6]), where BEDT–TTF = bis(ethylendithio)tetrathiafulvalene, and Z and X are monovalent cation and anion, respectively (scheme 1 shows their chemical structures). Characteristic behaviour of frustrated spins has been observed through the temperature dependence of magnetic susceptibility $\chi$ in several Z[Pd(dmit)$_2$]$_2$ salts [2]. In the temperature dependence of $\chi$, a round maximum appears, indicating the onset of antiferromagnetic correlation over the
lattice, as usual in the low-dimensional quantum spin antiferromagnets, but the temperature of the $\chi$ maximum is much lower than the Weiss temperature inferred from the high-temperature tail of $\chi$ as a measure of the mean-field interactions. This behaviour is explainable only by the effect of frustration, which efficiently suppresses the growth of antiferromagnetic correlation. Similar behaviour has been found in $\kappa$-(BEDT–TTF)$_2$Cu$_2$(CN)$_3$ [4] and a few other materials [7–9]. Most Z[Pd(dmit)$_2$]$_2$ salts exhibit antiferromagnetic ordering at lower temperatures [2], while no magnetic phase transition is detected in $\kappa$-(BEDT–TTF)$_2$Cu$_2$(CN)$_3$ down to very low temperatures, which is viewed as the first evidence for a gapless spin-liquid state realised in $\kappa$-(BEDT–TTF)$_2$Cu$_2$(CN)$_3$ [4].

In both cases, the dimers of the featuring molecules form 2D conduction layers in a nearly close-packed fashion. The conduction layers and the insulating layers comprising closed-shell counterions are alternatingly stacked in the crystals. Each dimer has one charge carrier, so as to form an effectively half-filled electron system. At ambient pressure, in fact, most Z[Pd(dmit)$_2$]$_2$ salts are Mott insulators having one $S = 1/2$ spin localised on each dimer. Under a suitable pressure [10] or a uniaxial strain [11, 12], they exhibit metallic conductivity, and superconductivity is found at low temperatures near the metal-insulator transition. The dimer [Pd(dmit)$_2$]$_2$ is a radical anion, while (BEDT–TTF)$_2^+$ is a cation. In addition to this apparent contrast, there are several significant differences between the two families. For example, the $\chi$ behaviour showing strong frustration effect is commonly observed in many Z[Pd(dmit)$_2$]$_2$ salts [2], whereas, among the $\kappa$-(BEDT–TTF)$_2$X salts, only the Cu$_2$(CN)$_3$ salt exhibits such behaviour [4], the other $\kappa$-salts being metals or paramagnetic insulators with significant antiferromagnetic correlation [5, 6]. In the Z[Pd(dmit)$_2$]$_2$ series, in contrast, a variety of unconventional valence bond states [13–17] appear around the spin-frustrated state depending on the cation and pressure. For this reason, the Z[Pd(dmit)$_2$]$_2$ series occupy a unique position in molecular materials.

Another significant point that provides the Z[Pd(dmit)$_2$]$_2$ series with novel physical behaviour is the extraordinarily strong dimerization in [Pd(dmit)$_2$]$_2$. It remarkably modifies the energy level structure of the dimer so as to give a unique quantum chemical effect, the HOMO–LUMO interchange depicted in figure 2. (HOMO and LUMO are the abbreviations of the highest occupied and lowest unoccupied molecular orbitals, respectively.) This effect was pointed out by 1990 [18–23], and has been marked as a unique character of the Z[Pd(dmit)$_2$]$_2$ series. More sophisticated calculations support this conclusion [24–26]. A novel phase transition is driven by this effect in some Z[Pd(dmit)$_2$]$_2$ salts [13–15]. Some of the observed phenomena [13–15] can never be expected for the single-level systems such as the conventional TTF-based conductors. From a quantum chemical viewpoint, the HOMO–LUMO interchange is based not only on the strong dimerization but also on the symmetries of HOMO and LUMO, which are characteristic of the metal-dithiolene complexes [3]. The material design inspired by these features has been developed; it leads to the single-component molecular metals based on Ni(tmdt)$_2$ (tmdt = trimethylethylenetetrathiiofulvalenedithiolate) [27]. In this case, the small HOMO–LUMO energy gap makes efficient HOMO–LUMO band crossing (hybridization) so as to form multiple Fermi surfaces stabilising metallic state [28–30]. On the other hand, in the dimer [Pd(dmit)$_2$]$_2$, the strong dimerization, owing to the Pd–Pd quasi-bonding, results in partial energetic transposition, rather than hybridization, of HOMO and LUMO. As a result, each dimer retains quantum degrees of freedom, whose potential role in the solid-state properties is an outstanding topic in the physics of Z[Pd(dmit)$_2$]$_2$.

In this paper, we begin with qualitative discussions on the molecular orbital characters of the Pd(dmit)$_2$ molecule and its dimer to explain the origin and evidence of the exotic HOMO–LUMO interplay effect in section 2. In the presence of the HOMO–LUMO interplay, the role of the MO characters is crucial even in the solid-state properties. Section 3 summarises the variation of the physical properties of the Z[Pd(dmit)$_2$]$_2$ series with Z. The effect of frustration on the metal-insulator boundary in the phase diagram is pointed out. In section 4, common magnetic behaviour of the triangular frustrated spin system based on Z[Pd(dmit)$_2$]$_2$ is outlined. A possible spin-liquid state in Z[Pd(dmit)$_2$]$_2$, evidenced by recent experiments, is also mentioned. Section 5 describes a novel charge separation phenomenon due to the HOMO–LUMO interplay. In order to explain the observed electron pairing, an idea of electron–hole composite system is introduced and applied to the dimer [Pd(dmit)$_2$]$_2$. Section 6 presents the discovery of spin-gapped ground state and pressure-induced superconductivity in a frustrated spin system of Z[Pd(dmit)$_2$]$_2$. In this article, only typical experimental data are explicitly referred to. The structural and electrical data for a wide range of related compounds can be found in the comprehensive review [3] and references therein.
Figure 1. (a) The HOMO–LUMO interchange caused by the strong dimerization. (b) A schematic display of the typical packing mode of the dimers in the β'-type crystals, showing the solid-crossing structure. The definition of the transfer integrals is also indicated.

2. Quantum chemical background: molecular characteristics of Pd(dmit)$_2$ and its dimer

Prior to the solid-state properties, let us take a brief look at the chemical characteristics of Pd(dmit)$_2$ and its dimer. Figure 1 schematically shows the chemical structure and orbitals of Pd(dmit)$_2$. The 4d$_{xz}$ orbital of Pd, which is asymmetric with respect to the $x$ and $z$ directions in terms of the assumed $D_{xy}$ symmetry, is relevant to the frontier levels. This leads to a significantly different role from that of the central C–C unit in formation of HOMO of a TTF-based molecule; HOMO is usually π bonding over the central C=C unit, i.e. symmetric with respect to $x$. The Pd(dmit)$_2$ molecule may be partitioned to the three units, the central Pd and the two wings, dmit π ligands. Therefore, three combinations are possible with respect to the Pd–S coordination: bonding, anti-bonding and non-bonding. As a result of the $\alpha$-axisymmetry of the Pd 4d$_{xz}$ orbital, the Pd–S bonding and anti-bonding orbitals are $\alpha$-symmetric, and the $\alpha$-symmetric orbital is non-bonding with little contribution of Pd 4d$_{xz}$. These are the common features of the planar metal-dithiolene complex molecules [3]. In contrast, the relevant molecular orbitals of a TTF-based molecule should be either bonding ($\alpha$-symmetric) or anti-bonding ($\alpha$-asymmetric) with respect to the central C=C unit. Therefore, HOMO of a TTF-based molecule (bonding molecular orbital) is energetically separated from LUMO at least by the C–C π bonding energy. No such restriction operates in the case of the metal-dithiolen complex; the metal-sulphur non-bonding molecular orbital is purely on ligands, and it can have energy close to that of one of the others [3, 28, 29]. This implies how to control the HOMO–LUMO gap using a symmetric three-unit molecule. In the case of Pd(dmit)$_2$, the Pd–S bonding orbital lies far below the Fermi level, and the Pd–S anti-bonding orbital (LUMO) is slightly higher than the non-bonding orbital (HOMO). These two molecular orbitals have similar characters within a ligand, but HOMO is $\alpha$-symmetric with little 4d contribution, while the $\pi-\pi$-hybridised LUMO is $\alpha$-asymmetric [3]. These peculiar features in principle originate from the symmetric ligand-metal-ligand (L–M–L) three-unit structure of the metal-complex molecule.

For an isolated M(dmit)$_2$ molecule ($M = Ni$, Pd), excess electrons are originally injected into LUMO. This assignment is retained even in the solid state of Ni(dmit)$_2$; the conduction band of Ni(dmit)$_2$ compounds comprises LUMO [3]. For a face-to-face columnar arrangement of Ni(dmit)$_2$ molecules, the asymmetric form of LUMO does not favour large intercolumnar overlapping, unlike the HOMO of BEDT–TTF. This appends quasi-one-dimensional (1D) conduction to each layer, although 2D character is built up by the alternating stacking of the conduction layers with different column directions (the solid-crossing structure) in the crystals (figure 1(b)). An exception is found in some cases, where only the face-to-face-like overlapping modes, including the spanning overlap, form a honeycomb-like 2D network with a non-columnar arrangement [3, 31, 32].

The situation is altered for negatively charged Pd(dmit)$_2$ in the solid state (figure 1(a)). The 4d orbital of Pd, which is larger than the Ni-3d orbital, promotes dimerization by Pd–Pd bond formation, as found in the x-ray structure analyses of most Pd(dmit)$_2$ compounds. The effect is so strong that the dimerization splitting exceeds the small HOMO–LUMO energy separation [3, 18–23]. Consequently, the bonding combination (with respect to the two molecules in the dimer) combination of LUMOs (b-LUMO) has lower energy than the anti-bonding combination of HOMOs, which is occupied by the excess electrons. In other words, the LUMO of the dimer [Pd(dmit)$_2$] is the anti-bonding combination of HOMOs (a-HOMO) of Pd(dmit)$_2$. In what follows, we use the labels HOMO and LUMO, irrespective to the dimerization or valence, to specify the orbitals formed from the HOMOs and LUMOs of the isolated neutral Pd(dmit)$_2$ molecules, respectively. The symmetry of the Pd(dmit)$_2$ HOMO yields considerable side-by-side (intercolumnar) transfers of carriers between the dimers formed in this way. Like in the BEDT–TTF salts, a 2D band structure based on Pd(dmit)$_2$ HOMO plays a significant role in the Z[Pd(dmit)$_2$]$_2$ series. The band calculations [3, 24–26] for them indicate 2D hole-type Fermi surfaces based on Pd(dmit)$_2$ HOMO, in spite of the negative charges of Pd(dmit)$_2$ in the compounds. This specific aspect is called HOMO–LUMO inversion or HOMO–LUMO interchange.

Experimentally, this peculiar electronic structure of the dimers can be easily observed in the infrared (IR) spectra of Z[Pd(dmit)$_2$]$_2$ [14, 21–23]. For the light polarization along the dimerization direction, Z[Pd(dmit)$_2$]$_2$ exhibits a
remarkable absorption peak in the near-IR range (ca. 1.2 eV). No such absorption is observed in other molecular conductors. This absorption is attributed to the bonding–anti-bonding excitation. In case of weak dimerization, only the LUMO electron can be excited, which cannot account for the peak intensity. The HOMO–LUMO interchange due to strong dimerization enables the three electrons (two in LUMO and one in HOMO) to be excited in the dimer, which consistently explains the observed spectral features, giving direct evidence for the HOMO–LUMO interchange in $Z[\text{Pd(dmit)}]_2$ [14, 21–23]. It is also noticeable that the bonding–anti-bonding splitting of HOMOs and LUMOs are nearly the same. This means that the intermolecular overlap in the dimer is determined mainly by the ligand $\pi$ orbitals, which are almost identical in the HOMO and LUMO. The spectral evidence for the HOMO–LUMO interchange scheme suggests that the unit dimer $[\text{Pd(dmit)}]_2^-$ is potentially a multi-carrier system having two electrons in b-LUMO and one hole in a-HOMO levels [13]. The situation is somewhat similar to that in the single-component molecular metal Ni(tmd)$_2$ having electron-like and hole-like Fermi surfaces [27–30], though the b-LUMO (filled band) electrons in $Z[\text{Pd(dmit)}]_2$ are completely paired in the dimer. In $Z[\text{Pd(dmit)}]_2$, only the a-HOMO hole band is partially filled. However, both levels are sensitive to dimerization strength, so that these charge carriers can couple to the structural deformation of the dimer [13]. This HOMO–LUMO interplay is never expected for the systems with weak dimerization (Ni(tmd)$_2$ salts) and for the HOMO band systems of the TTF-based $\pi$ donors. In the sense described here, the peculiar properties of the $Z[\text{Pd(dmit)}]_2$ series and the first single-component molecular metal Ni(tmd)$_2$ share the same quantum chemical origin. This provides a useful viewpoint in understanding the molecular mechanism of the phase transition as discussed in section 5.

For the $Z[\text{Pd(dmit)}]_2$ series, the average valence is $-1$ in terms of the dimer unit $[\text{Pd(dmit)}]_2^-$, which means the half-filling of the a-HOMO band. Therefore, the key factors in systematic understanding the physical states of such a strongly correlated electron system are the interdimer transfer integrals $t$ and the intradimer (on-site) electron repulsion energy $U_{\text{dimer}}$. The parameter $U_{\text{dimer}}$ is a function of the nearest-neighbour Coulomb repulsion $V_{\text{intra}}$ and transfer integral $t_A$ [33], as in the case of the dimeric BEDT–TTF salts [34]. As a result of the strong dimerization (large $V_{\text{intra}}$ and $t_A \gg t$), the $Z[\text{Pd(dmit)}]_2$ series is characterised by large $U_{\text{dimer}}$, which keeps the system near the Mott criticality (the metal-insulator boundary). A systematic change in the physical behaviour is driven by the control of the interdimer transfer integrals, as experimentally observed in the dependence on cation type, pressure or uniaxial strain. In the presence of the HOMO–LUMO interchange, $U_{\text{dimer}}$ can be drastically modified by an inhomogeneous distortion of the dimers [13]. This causes an effectively negative value of $U_{\text{dimer}}$, as observed in a spontaneous pairing of the electrons in a dimer with coupling to the lattice distortion [13].

3. Structural and magnetic classification of $Z[\text{Pd(dmit)}]_2$

Most $Z[\text{Pd(dmit)}]_2$ salts are isostructural. The common crystal structure is called the $\beta'$ structure (note that this is not the same convention as used for the BEDT–TTF salts) with the space group $C2/c$ [3]. The crystal is formed by alternating stacking of the Pd(dmit)– anion layers and the insulating cation layers. In a layer (the ab-plane), the dimers $[\text{Pd(dmit)}]_2$ are parallel and the structure is pseudo-columnar. In contrast, non-parallel packing of dimers is the main structural motif of the $\kappa'$(BEDT–TTF)$_2$X. Because of the considerable HOMO–HOMO overlapping between the columns, the system cannot be 1D, and a 2D triangular network is formed in the layer. Along the c-direction (perpendicular to the layers), the crystallographically equivalent layers related by the c-glide symmetry alternate with different orientations. This provides solid crossing of the pseudo-columns (figure 1(b)) [3]. The salts with $Z = \text{Et}, \text{Me}_2\text{As}, \text{Y}^+$ (Et = C$_2$H$_5$, Me = CH$_3$; $x = 0, 2$ for $Y = \text{P}$ and $x = 0, 1, 2$ for $Y = \text{As, Sb}$) belong to this class and are Mott insulators at ambient temperature and pressure. The Cs salt [35] also has the $\beta'$ structure. Unlike the others, this salt is metallic at ambient condition and exhibits a metal-insulator transition at 56.5 K [35].

The structures similar to, but not identical to, the $\beta'$ structure are found in the EtMe$_3$P salt [16, 17] and in the Me$_2$N salts [36, 37]. At least two polymorphs are found in the EtMe$_3$P salt. The one with the space group $P2_1/m$ has triangular layers similar to those in the $\beta'$ structure, but the layers are related by the mirror symmetry, so that the columns are orientated parallel in the whole crystal, and the solid-crossing is lost [16, 17]. The other polymorph has lowered symmetry (space group, $P 1$) and no solid-crossing too; it undergoes two structural phase transitions accompanied by doubled in-plane periodicity and charge disproportionation at low temperatures [38]. In spite of the structural similarity to the $\beta'$ type salts, it does not show magnetically frustrated behaviour specific to the 2D triangular systems, suggesting charge fluctuations enhanced due to larger in-plane anisotropy. The Me$_2$N salt exhibits polymorphs based on solid-crossing columns with subtle structural difference [36, 37]. The $\beta$-Me$_2$N salt shows magnetic behaviour similar to that of the $\beta'$-type salts [37, 39]. Another sub-family based on trialkylchalcogeneide cations has been found, in which supramolecular cation-anion interactions play a significant role in the crystal [3, 40, 41].

From now on, let us concentrate on the triangular systems (the $\beta'$ type salts, the $\beta$-Me$_2$N salt and the $P2_1/m$ EtMe$_3$P salt), where the geometrical spin frustration operates. Based on the $\chi$ behaviour and magnetic ground states, they can be classified into the following types (see table 1):

- **(I)** Antiferromagnetic ordering at ca. 40 K, (the Me$_4$P and Me$_4$As salts),
- **(II)** Antiferromagnetic ordering in the 10–25 K range (the Et$_2$Me$_2$P, Et$_2$Me$_2$As, EtMe$_3$As, Me$_5$Sb and $\beta$-Me$_2$N salts),
- **(III)** No magnetic ordering (the EtMe$_3$Sb salt),
A phase transition to a spin-singlet state with differently charged dimers (the Et₂Me₂Sb salt).

(V) A phase transition to a spin-singlet state with equivalent dimers (the P₂₁/₃ Me₄As salt).

Figure 2 shows typical temperature dependence of $\chi$. Above the magnetic transition temperatures, the salts are paramagnetic insulators showing temperature dependence of $\chi$ characteristic of a spin-1/2 Heisenberg antiferromagnet on a triangular lattice [2]. The antiferromagnetic order observed for types (I) and (II) is a 2D Néel-like collinear order, as that on a square lattice, with the easy axis perpendicular to the layer (see the next section). In addition, the Cs salt has the same ground state as the Et₂Me₂Sb salt below the metal-insulator transition temperature. Above that temperature, it exhibits Pauli-like constant $\chi$ consistent with the metallic behaviour. More details on types (I), (II) and (III) are described in section 4, and (IV) and (V) are treated in sections 5 and 6, respectively. The variety of spin ground states observed in the triangular Pd(dmit)$_2$ salts is summarised in figure 3.

This classification reflects in the conductivity behaviour. Type (I) salts are insulating at any pressure, but become metallic under specific uniaxial strain. Metallic behaviour appears in types (II) and (III) under hydrostatic pressure in the range 0.5–1 GPa, but those salts become insulating again at low temperatures under pressure above 1 GPa. X-ray analyses have shown that the high-pressure insulating phase has different anion layers with lowered symmetry [42]. Pressure-induced metallic phase is also found in types (IV) and (V). Bulk superconductivity appears around the insulator-metal boundary of type (V), while the spin-singlet insulator phase is predominant at low temperatures in type (IV) (see sections 5 and 6). Although superconductivity has often been observed near the antiferromagnetic insulator-metal boundary in type (II) by resistivity measurements, it is efficiently suppressed by large current density and only weak diamagnetic shielding could be detected in the Et₂Me₂P and Me₄Sb salts [43]. Therefore, it has been concluded that the superconductivity by the antiferromagnetic insulator phase is usually not a bulk phenomenon [43], but a surface or an edge effect, whose origin has not been clarified yet. On the other hand, it is recently found that the $\beta$-Me₂N salt exhibits diamagnetic response under pressure, indicating bulk superconductivity ($T_c \sim 5 \text{ K}$ at $P = 0.53 \text{ GPa}$) [44]. In the $\beta$-Me₂N salt, $t_{\text{d}}$ is the largest interdimer transfer, which is different from the other type (II) salts with the $\beta'$-structure, where $t_{\text{d}} \leq t_{\text{B}}$. (The indices A, B, s and r are denote the intermolecular relation defined in figures 2 and 4(a).) This structural difference

Table 1. Classification of magnetic properties of the triangular Z[Pd(dmit)$_2$].

<table>
<thead>
<tr>
<th>Type</th>
<th>Cation, Z</th>
<th>Ground states$^a$</th>
<th>Transition temperatures</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I)</td>
<td>Me$_4$P</td>
<td>AF LRO</td>
<td>$T_N = 40$ K</td>
<td>[53, 55]</td>
</tr>
<tr>
<td>(II)</td>
<td>Me$_4$As</td>
<td>AF LRO</td>
<td>$T_N = 25$ K</td>
<td>[53, 55]</td>
</tr>
<tr>
<td>(III)</td>
<td>Et$_2$Me$_2$P</td>
<td>AF LRO</td>
<td>$T_N = 14$ K</td>
<td>[54, 55, 57]</td>
</tr>
<tr>
<td>(IV)</td>
<td>Me$_4$Sb</td>
<td>AF LRO</td>
<td>$T_N = 18$ K</td>
<td>[2, 55]</td>
</tr>
<tr>
<td>(V)</td>
<td>Me$_4$N$^b$</td>
<td>AF LRO</td>
<td>$T_N = 12$ K</td>
<td>[36, 37, 55]</td>
</tr>
</tbody>
</table>

$^a$ AF LRO is antiferromagnetic long-range order.

$^b$ The $\beta$-phase.

$^c$ Metallic at room temperature (unfrustrated).

$^d$ Metal-insulator transition.
phase. In the most frustrated regime, the critical lines are closely spaced, around which the novel ground states appears as discussed below.

4. Frustrated paramagnetic state, antiferromagnetic order and a possible gapless spin liquid

As mentioned in the preceding sections, the common magnetic behaviour of the triangular $\text{Z[Pd(dmit)$_2$]}_2$ salts is the weakly temperature dependent $\chi$ with a broad maximum at the temperature $T_{\text{max}}$, which is much lower than $\theta = zJ/4k_B$ (the mean-field Weiss temperature) [2, 17, 37], where $z$ denotes the number of nearest-neighbour sites ($z = 6$ for the triangular lattice), and the exchange coupling $J$ is defined by the spin Hamiltonian $H = \sum_{\langle i,j \rangle} J_{ij} S_i \cdot S_j$. For an unfrustrated low-dimensional quantum antiferromagnet, $T_{\text{max}} \approx \theta$ is expected, with antiferromagnetic correlation growing over the lattice below $T_{\text{max}}$. In the present cases, however, we obtain $J/k_B = 240–280$ K and $T_{\text{max}} = 60–120$ K, where $k_B$ is the Boltzmann constant. This indicates that the frustration prevents the antiferromagnetic correlation from growing out of the repeating unit, and the system is paramagnetic over a wide temperature range. The temperature dependence was analysed in terms of the Padé approximant expression [2] on the basis of high-temperature series expansion of $\chi$ of the spin–1/2 Heisenberg model on the triangular lattice [47]. It has been shown that the temperature dependence is satisfactorily explained by this model near and above $T_{\text{max}}$, and the exchange parameters $J$ are thus obtained for the triangular $\text{Z[Pd(dmit)$_2$]}_2$ salts [2, 48].

As temperature is lowered below $T_{\text{max}}$, $\chi$ drops exponentially until it changes the slope at $T_N$ in the (I) and (II) cases. The drop of $\chi$ indicates that antiferromagnetic correlation rapidly spreads over the layer. As known for the square-lattice antiferromagnets [49], such features are characteristics of an unfrustrated 2D system just above $T_N$. This means that the frustration is released in this temperature range, which is a crossover from the high-temperature frustrated paramagnet to the antiferromagnetically correlated state [50, 51]. In other words, it is the interplay between the short-ranged physics of frustration and the long-range correlation, as found generally in quantum liquid systems. The spatial anisotropy $\Delta J = J - J'$, rather than $J$, should play a key role in this range. At higher temperatures, $T \gg \Delta J/k_B$, the effect of $\Delta J$ is negligible, so that the spins are frustrated. At low temperatures, $\Delta J$ operates to release the frustration by making the system like a square-lattice-like antiferromagnet with effective couplings of $\Delta J$.

Once the 2D antiferromagnetic correlation grows in this way, even very weak interlayer couplings can implement the bulk antiferromagnetic ordering at $T_N$. This is the reason for the steeply varying $\chi$ just above $T_N$. Similar change in $\chi(T)$ slope at $T_N$ is found in other 2D quantum antiferromagnetic systems [52], though it is dissimilar to that in the conventional 3D antiferromagnetic case. Below $T_N$, $\chi$ becomes anisotropic to show that the easy axis is perpendicular to the plain [16], as expected from the dipolar couplings in a 2D antiferromagnet. For the (I) and (II) types of the triangular $\text{Z[Pd(dmit)$_2$]}_2$ salts,
the rapid growth of antiferromagnetic correlation just above $T_N$ has been observed by the muon spin rotation/relaxation ($\mu$SR) technique, which probes slow dynamics of spins and the internal field. The changes in the $\mu$SR time-spectra and relaxation rate towards the antiferromagnetic ordering complete within a narrow temperature range (0.8 K) in the Me$_2$P salt (I) [53]. The change is not so acute in the Et$_2$Me$_2$P salt (II) [54], indicating that the latter is more frustrated, as expected. Electron spin resonance (ESR) and nuclear spin resonance (NMR) measurements have also been applied to characterise the antiferromagnetic ordering in the triangular Z[Pd(dmit)$_2$]$_2$ salts. An early ESR study [55] clarified the cation dependence of $T_N$ and pointed out the correlation between $T_N$ and strength of frustration that expected from the structural anisotropy of interdimer couplings. This magneto-structural correlation suggests the crucial role of frustration in the system. It should be emphasized here that $T_N$ is scaled by the anisotropy $\Delta J$, rather than by $J$, in the present frustrated systems, unlike in the ordinary antiferromagnets. The NMR studies [56, 57], probing the fast dynamics, have reported the critical behaviour of the relaxation rate $1/T_1$ of the Me$_2$P (I) and Et$_2$Me$_2$P (II) salts. The growth of antiferromagnetic correlation, as noted by the critical slowing down effect, is more evident in the Me$_2$P salt: $1/T_1$ starts to increase even at temperature twice as high as $T_N$. This does not contradict to the $\mu$SR experiments probing slow dynamics regime because both $\mu$SR and NMR results indicate larger antiferromagnetic correlation and less frustrated nature of the Me$_2$P salt. Pulsed ESR and antiferromagnetic resonance experiments using millimetre waves [58, 59] have been carried out for the Et$_2$Me$_2$P salt. The results are explainable by the antiferromagnetically ordered spin system having the easy axis perpendicular to the layer below $T_N$ [59].

NMR reveals that $T_N$ is raised by pressure. For the Me$_2$P salt, $T_N$ increases up to 50 K at 0.7 GPa, and application of 0.5 GPa enhances $T_N$ of the Et$_2$Me$_2$P salt up to 25 K [57]. This pressure effect on $T_N$ has been confirmed by the $\chi$ measurements under pressure [46]. Similar results were reported for the $\beta$-Me$_4$N salt [37, 39]. Taking account of the $P$--$T$ phase diagram inferred from the resistivity measurements, the insulating phase expands to higher pressures and temperatures by forming the antiferromagnetic order. The shape of the insulator-metal boundary is therefore prescribed by the stability of the insulating phase. Since the frustration diminishes the stability of the insulating phase, the correlation found between the transport and magnetic properties for the triangular Z[Pd(dmit)$_2$]$_2$ salts is understood from this viewpoint. For example, the stiffness of the insulating state of the Me$_2$P salt is related to the less frustrated nature, stronger antiferromagnetic correlation and higher $T_N$, which arise from the spatial anisotropy of the interdimer couplings. These experimental results point out that not only the strength of electron correlation but also the frustration is the controlling factor for the insulator-metal criticality [2, 3, 45, 46]. The highly frustrated spins, giving high entropy in the insulating state by breaking the antiferromagnetic long-range order, provide relative stability of the metallic state, in which entropy is released efficiently at low temperatures.

The $\chi$ of the EtMe$_2$Sb salt (III) exhibits no sign of magnetic ordering down to 10 K, and the temperature dependence is approximately explained by the spin-1/2 Heisenberg antiferromagnetic model on the triangular lattice with $J/k_B = 220$--250 K [60, 61]. NMR study of this salt [61] has shown that neither magnetic long-range order nor spin freezing occurs in this salt down to 1.37 K. Therefore, the ground state of this salt is assigned to a spin liquid
with zero gap or very small gap (<1% of J). In this case, the high-temperature frustrated paramagnetic state continues to the ground state, possible gapless spin-liquid state, without an apparent phase transition (or a symmetry breaking). The appearance of the gapless non-magnetic state has been predicted by the path-integral renormalization group calculations for the highly frustrated Hubbard model on an anisotropic triangular lattice [62]. The temperature dependence of the relaxation rate 1/T1 shows gradual growth of antiferromagnetic correlation below 200 K, but no critical enhancement down to 1.37 K. The NMR spectra show inhomogeneous broadening due to static internal field at low temperatures (<10 K). The origin of this inhomogeneous broadening has not been clarified yet. Recently, the absence of magnetic order down to 19.4 mK has been confirmed [63], and power-law temperature dependence of 1/T1 has been observed below 1 K [64]. Similar NMR features have been reported for another spin-liquid material, κ-(BEDT–TTF)2Cu2(CN)3 [4, 65]. In these cases, it is not easy to rule out the possible effect of the structural disorder [66]. Similar to the orientationally disordered CN− anions in κ-(BEDT–TTF)2Cu2(CN)3, the non-centrosymmetric cations EtMe3Sb+ are disordered in the present case. Further studies are still required to clarify the origin and nature of these puzzling spin-liquid states.

5. A novel charge separation in the Et2Me2Sb salt

Similar to the spin-liquid EtMe3Sb salt, the Et2Me2Sb salt (IV) and the P21/m EtMe2P salt (V) belong to the most frustrated class among the triangular Z[Pd(dmit)2]2 salts, judging from the structure and χ results. However, these two salts exhibit phase transitions to non-magnetic gaped ground states. (In our earlier study [2], it was argued that the Et2Me2Sb salt has no phase transition. It turned out later that this is due to the suppression of the phase transition by impurity [67].) Structural changes are involved in these transitions.

In a sufficiently pure sample of the Et2Me2Sb salt, a steep drop of χ appears at 70 K [67] (figure 5). This indicates a first-order phase transition to a diamagnetic phase. The diamagnetic nature is also found by μSR measurements [54], which show fast relaxation in the low-temperature phase. Correspondingly, resistivity is noticeably enhanced below this temperature. These changes are hysteric with a width of ca. 1 K. X-ray analyses [15] have revealed that the low-temperature phase has a doubled periodicity along the b-axis as a result of alternating arrangement of two types of dimers: contracting (strongly dimerised) and expanding (weakly dimerised) ones. The two Pd(dmit)2 molecules forming a dimer remain equivalent. These structural features suggest non-uniform charge distribution over the dimers.

Extended Hubbard model calculations [13] have been carried out of the unique electronic structure of the dimer [Pd(dmit)2]2− (see section 2). The dimer is modelled by a four-level system of b-HOMO, b-LUMO, a-HOMO and a-LUMO. Within the dimer, the intramolecular Coulomb repulsion U and intermolecular Coulomb repulsion V and intermolecular transfer integrals t are taken into account. The strength of dimerization is expressed by changing t and V; a stronger dimer corresponds to the larger t and V. The effective repulsion on a dimer Udimer is evaluated as the energy cost to cause charge disproportionation (separation) 2[Pd(dmit)2]2− → [Pd(dmit)2]0 + [Pd(dmit)2]2− for a two-dimer set. It has been shown that the two-dimer system with the uniform valence is unstable against this disproportionation when the non-equivalent distortions of the dimers are assumed [13]. A large energy gain stems from the bonding and resonating energies in the contracted neutral dimer [Pd(dmit)2]02−, in which all the electrons occupy the bonding levels (b-HOMO and b-LUMO), and the cost of V is cancelled because of zero net charge. The bond strengthening (contraction) and reduction of electron repulsion are cooperative in the neutral dimer. This efficiently compensates the energy cost arising from the pairing of a-HOMO electrons in [Pd(dmit)2]2−, so that the total cost can be negative at a certain condition. The electron pairing

![Figure 5](image-url)
(intradimer valence bond formation) and the inhomogeneous distortions of the dimers are thus coupled. The origin of the charge separation is thus assigned to the HOMO–LUMO interplay in the dimer [13]. The x-ray analyses report the bond lengths in the molecules. The changes in the bond lengths at the transition agree with the valence change assumed here [15]. The in-plane arrangement of the charged and neutral dimers coincides with one of the predicted patterns from Madelung calculations [67].

The calculations predict 1:2 splitting of the bonding-antibonding photo-excitation appearing in the near-IR region [14]. In fact, the reflectivity spectra exhibit the expected splitting of the near-IR peak at low temperatures [14]. All spectral features in the near-IR range are consistently explained by the above model, from which the energy levels of the dimers are evaluated (figure 5). A similar splitting was reported for the low-temperature phase of the Cs salt [21, 23, 35], which exhibits a second-order metal-insulator transition at 56.5 K. The x-ray analyses [15] have shown that the low-temperature phase has the structure identical to that of the Et₂Me₂Sb salt below 70 K. Therefore, the metal-insulator transition in the Cs salt has been concluded to have the same origin as based on the HOMO–LUMO interplay in the strongly dimerised structure, though it was previously considered to result from the nesting of quasi 2D Fermi surfaces [35]. Fast photo-response (relaxation within a few picoseconds) has been observed for the near-IR reflectivity spectra of the low-temperature phase of the Et₂Me₂Sb salt using the pump-probe technique, which showed photo-induced melting of the charge-separated state [68]. The pumping power dependence suggests the photo-excitation causes a cooperative phenomenon, i.e., a photo-induced phase transition to a state similar to the high-temperature phase [68].

The x-ray analyses suggest that the first-order nature of the transition in the Et₂Me₂Sb salt is due to the conformational change of the cations [15], which can accommodate and benefit the distortion in the Pd(dmit)₂ layers to latch the transition. The transition temperature of the Et₂Me₂Sb salt is significantly suppressed by cation impurities [45], which also suggests the role of the cation conformation. Simple Cs cation cannot act in such a way. According to the susceptibility [69] and specific heat [70] measurements for the Et₂Me₂Sb salt under pressure, the first-order nature of the transition is retained even at high pressures, where the high-temperature phase is metallic. Therefore, it is concluded that the difference in the high-temperature phases of the two salts, i.e., a frustrated paramagnetic insulator vs. metal, does not concern the order of the transition. Although it is not fully understood why the charge separation appears only in the two salts, the above results suggest that it is related to the dynamics of the lattice distortion such as the cation conformational change.

Since the low-temperature phase of the Et₂Me₂Sb salt is diamagnetic, the value of spin susceptibility just above the first-order transition temperature is easily found as a sharp rise of χ upon heating. This is useful, particularly in the pressure experiments, which often suffer from the magnetic background signals. The transition temperature and χ of the high-temperature phase along the phase boundary are thus measured as a function of pressure [69]. The transition temperature takes a maximum value ca. 100 K, which is consistent with the resistivity results. Along the phase boundary, χ continuously decreases with pressure until it becomes pressure independent for the high-temperature metallic state appearing above ca. 0.6 GPa [69]. This is consistent with the crossover nature of the Mott boundary at high temperatures above the critical point [46].

It is worth noting that, as well as b-LUMO electrons, hole injection into the a-HOMO level (removal of anti-bonding electrons) provides intermolecular bonding energy in the dimer. In this sense, it is convenient to treat the dimer at the average valence [Pd(dmit)₂]²⁺ as a system of one unpaired hole (a-HOMO) and an electron pair (b-LUMO) [13]. It follows naturally that the holes acting in the anionic background attract each other by cancelling the negative charges of the b-LUMO electrons. This results in the hole pairing (removal of a-HOMO electrons) to cause a neutral dimer having doubled intradimer valence bond corresponding to the hole and electron pairs. In this system with the HOMO–LUMO interchange, the neutral dimer is not an empty object but a composite of two electrons and two holes. Since the spin degree of freedom is held by a-HOMO and the net negative charge comes from b-LUMO at the average valence, a kind of spin-charge separation (opposite distributions of the spin and negative charge densities) is expected to favour less charged spin-singlet valence bond pairs. When this pairing completes within a dimer, the charge reduction processes to the limit of a neutral dimer (a complete charge separation). This two-level electron-hole composite scenario cannot be applied to the HOMO-based systems such as the BEDT–TTF salts. On the other hand, the molecular origin (the HOMO–LUMO interplay) is in close connection with the single-component metal Ni(tmdt)₂, in which electrons and holes coexist and hybridise with each other [28–30].

6. Valence bond ordering and pressure-induced superconductivity in the P2₁/₃EtMe₃P salt

The P2₁/₃EtMe₃P salt (type V) undergoes a second-order phase transition at 25 K, where χ shows a bend [16, 17] (figure 6). Above this temperature, χ shows typical temperature dependence of the frustrated paramagnet of the triangular Pd(dmit)₂ salts \((J/k_B = 250 \text{ K})\), while χ exponentially approaches zero as \(T\) is lowered from 25 K. NMR spectra indicate the absence of long-range magnetic order at low temperatures [61]. X-ray analyses show that all the dimers are still crystallographically equivalent in the low-temperature phase, but the intermolecular interactions are modulated along the column direction to give the doubled periodicity [17] (figure 6). Since the spin-1/2 unit is the dimers in this case, it is concluded that interdimer spin-singlet pairs (valence bonds) are formed along the column in the low-temperature phase. Note that this salt has parallel column structure [16], unlike the other triangular [Pd(dmit)₂]²⁺ salts...
having solid-crossing columns. The crystal slightly expands to the intercolumnar directions through the transition to the spin-gapped states [17]. The analysis of the temperature dependence of \( \chi \) [17] and ESR study [71] of this material consistently give the spin-gap value of ca. 35 K in the \( T = 0 \) limit.

These features are similar to those found in the spin-Peierls case. The spin-gapped ground states with the spontaneously broken translational symmetry of exchange couplings are commonly formed in both cases. However, the \( P2_1/m \) EtMe\(_3\)P salt is a 2D system, for which an occurrence of a spin-Peierls transition has not been reported so far. A Néel type antiferromagnetic ordering is more preferred in an ordinary 2D system. In the present case, the highly frustrated nature suppressed the antiferromagnetic ordering, so that the spin-gapped state can appear instead, in order to reduce the high entropy of the frustrated spins. The appearance of such a dimer order has been predicted by a theoretical study [72] of the spin-1/2 Heisenberg antiferromagnets on an anisotropic triangular lattice without symmetry breaking. The predicted columnar arrangement of valence bonds [72] is consistent with that found in the \( P2_1/m \) EtMe\(_3\)P salt. The spin-gapped phase discovered in the 2D triangular Pd(dmit)\(_2\) salts should be distinguished from the conventional spin-Peierls phase related originally to the one-dimensionality. Here, we call this new phenomenon valence bond order, to discriminate it from the valence bond solid used mainly to specify the spin-gapped state without translational symmetry breaking (e.g., the Haldane systems). For the appearance of the valence bond order, suppression of the antiferromagnetic order by frustration is required. The lattice structures—the parallel columns and the discrete counterion layers—can assist the valence bond ordering. In addition, the effective hole-hole attraction (a kind of spin-charge separation), operating in the HOMO–LUMO interchanging system as pointed out in the preceding section, can contribute to reduce the energy cost of the interdimer valence bond pairing by making inhomogeneous site charges in the dimer. Therefore, it would be worth examining how this mechanism contributes to the valence bond formation by experimental evaluation of the site charge distribution.

Pressure-induced superconductivity has been found in the \( P2_1/m \) EtMe\(_3\)P salt by resistivity measurements, which also show complicated insulator-metal phase boundary at low temperatures, as noted by re-entrant behaviour [16]. Static magnetization measurements have been carried out to examine the bulk properties under the in situ calibrated pressure. Bulk superconductivity appears around the insulator-metal critical pressure [73], with \( T_c = 4.8 \) K at 0.18 GPa, 5.5 K at 0.2 GPa, and 0.3 K at 0.44 GPa. It is the first report of bulk Meissner signals (figure 7) detected in the Z[Pd(dmit)\(_2\)] series. Taking account of the resistivity results [16, 74], the \( P-T \) phase diagram is inferred from the magnetic experiments [73] (figure 7). An outstanding point is that the superconducting phase adjoins the spin-gapped insulating phase. This suggests a close connection of the superconducting pairing and the valence bond pairing. These features remind us of the \( x-T \) phase diagram (\( x \) denotes hole concentration) for the high-\( T_c \) superconductors, in which the so-called pseudo-gap phase is contiguous to the superconducting phase in the under-doped regime. It is suggestive but not simple to relate these two systems because the Pd(dmit)\(_2\) salts can be examined only by pressure control, and the frustration, lattice distortion and symmetry breaking play more significant roles in the Pd(dmit)\(_2\) salts. Several theories have been proposed for the possible novel pairing symmetry in the superconductivity on the triangular lattice [1, 75–79]. In order to test the possibilities, microscopic and dynamical information on this pressure-induced superconductivity should be explored.

The valence bond ordering temperature gradually decreases with pressure [46, 73], as is expected from the volume expansion in the valence bond ordering. The expansion is presumably related to the columnar arrangement of the valence bond pairs. The valence-bond order disappears at about 0.2 GPa, where it is replaced by the metallic phase. Unlike the insulating phase stabilised by antiferromagnetic ordering in the (I) and (II) cases, the first-order phase boundary between the frustrated paramagnetic insulator (low-pressure phase) and the metal (high-pressure phase) has positive slope in the low-temperature part of the \( P-T \) phase diagram. This corresponds to the insulator-metal transition observed on cooling. The large entropy contained in the frustrated phase explains the positive slope. The system re-enters into the valence bond ordered state on further cooling at the pressures close to the boundary. This means that the stability of the insulating phase is attained by the spin-gap formation at lower temperatures. The stability is
diminished by application of high magnetic field as to break the valence bond pairs. The field-induced insulator–metal transition is in fact observed by the resistivity measurements in the 4–8 T range at the pressure just near the insulator-metal boundary [74]. As expected for the valence bond related superconductivity, the highest $T_c$ 5.5 K is attained at the insulator-metal boundary.

7. Conclusion

In the $Z[Pd(dmit)$_2$]_2$ system, the two unique characteristics are shown to lead particular physical properties, in addition to the Mott physics, which is common to the other strongly correlated molecular systems with half-filling. First, the frustration, stemming from the 2D triangular arrangement of the spin-1/2 units, affords suppressed antiferromagnetic ordering, for which a magneto-structural correlation specific to frustrated systems is found. Second, the HOMO–LUMO interchange operating in the dimer $[Pd(dmi)$_2$]_2$, as clearly indicated by the spectroscopic studies and the charge separation phenomena, provides an electron–hole composite picture, which is useful in understanding the valence bond related magnetic properties. The finding of the valence bond order and the pressure-induced superconductivity in this frustrated triangular system would contribute to the physics of strongly correlated electron systems.

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