# Quantum spin liquid in the spin-1/2 triangular antiferromagnet $EtMe_3Sb[Pd(dmit)_2]_2$

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The family of layered organic salts $X[Pd(dmit)_2]_2$ are Mott insulators and form scalene-triangular spin-1/2 systems. Among them, $EtMe_3Sb[Pd(dmit)_2]_2$ has a nearly regular-triangular lattice. We have investigated the spin state of this salt by $^{13}$C-NMR and static susceptibility measurements. The temperature dependence of the susceptibility is described as that of a regular-triangular antiferromagnetic spin-1/2 system with an exchange interaction $J=220-250$ K. The $^{13}$C-NMR measurements reveal that there is no indication of either spin ordering/freezing or an appreciable spin gap down to 1.37 K, which is lower than 1% of $J$. This result strongly suggests that this system is in the quantum spin-liquid state with no appreciable spin gap, which has been long sought after.

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The magnetism of the quantum spin-1/2 system with antiferromagnetic Heisenberg interactions has been one of the central issue in condensed-matter physics because this system shows rich unconventional physical phenomena due to the strongest quantum fluctuations. Quantum fluctuations destabilize the magnetically long-range ordered (MLRO) state, which is inevitably realized in the ground state of a classical antiferromagnetic system. In some cases, the quantum fluctuations completely destroy the MLRO states, giving rise to quantum disordered states. A widely observed example is a fully spin-gapped state accompanied by spin dimerization such as the spin-Peierls state. This spin-gapped state is the "valence bond solid" (VBS) state in the broad sense, where the dominant term of the wave function is described by a localized array of singlet pairs. By contrast, on a symmetric lattice without dimerization, where there are various singlet-pair configurations of the same energy, they may resonate and the so-called "resonating valence bond" (RVB) state may emerge. This kind of quantum spin states without either magnetic ordering or lattice symmetry breaking are generally named the quantum spin-liquid states and have been intensively studied for a long time. However, on normal unfrustrated lattices without dimerization in two or three dimensions, it has been revealed that the effect of quantum fluctuations is too weak to destroy the MLRO state and, thus, the spin-liquid state cannot appear.[1–4] It is, therefore, generally believed that strong geometrical frustration which works significantly against the MLRO state is needed to realize the spin-liquid state, if it exists.

For this reason, spin-1/2 systems on frustrated lattices such as triangular lattices have attracted attention of many researchers, and much theoretical work has been conducted. However, real model materials of such systems are limited and only a few candidate materials for the spin liquid are known[5–7] despite the long concerted experimental effort. One of the candidates is the recently discovered organic salt with an isosceles-triangular lattice, $\kappa$-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$.[7] Inspired by this discovery, various theories from different viewpoints have been proposed in order to explain the origin of this spin liquid, which is still controversial.[8–12] Under such circumstances, to facilitate understanding of spin-liquid states on a triangular lattice, another example of the spin-liquid system is intensely desired. Discovery of such a material evidently provides useful information for elucidation of the key factors in the spin-liquid physics.

In this paper, we report the magnetic properties of a layered organic salt $EtMe_3Sb[Pd(dmit)_2]_2$, which forms a scalene but nearly regular-triangular spin system (dmit =1,3-dithiole-2-thione-4,5-dithiolate, Me=$CH_3$, Et=$C_2H_5$). We have reported preliminary results of $^{13}$C-NMR study on this system in a previous report, where we estimated the hyperfine coupling constant of the $^{13}$C site and suggested the possibility of the spin-liquid ground state in this system.[13] In the present paper, we report more convincing evidence for the spin liquid obtained by further NMR measurements and analyses. We also discuss the appearance of inhomogeneous broadening, which is considered to be common nature of the spin liquid with no spin gap.

The series of layered organic salts $X[Pd(dmit)_2]_2$, where $X$ is a nonmagnetic monovalent countercation such as $Me_4P$, $Me_4As$, $Me_4Sb$, $Et_2Me_2P$, $Et_2Me_2As$, $Et_2Me_2Sb$, $EtMe_3P$, or $EtMe_3Sb$, has a scalene-triangular lattice of $[Pd(dmit)_2]_2$ dimers as shown in Fig. 1. They are Mott insulators at ambient pressure and, thus, have a localized 1/2 spin on each dimer with antiferromagnetic interactions.[14] The orbital wave function on which the spin exists is composed of the $Pd(dmit)_2$ highest occupied molecular orbital, whose density lies only on the dmit ligands with little contribution of Pd 4$d$ orbitals.[14] Because the wave function spreads only on light elements, the spin-orbit interaction is sufficiently weak and, as a result, the spin-spin exchange interactions of this system are expected to be spherically symmetric. The strength of the frustration in the triangular lattice in $X[Pd(dmit)_2]_2$ can be controlled by the choice of $X$. In most of $X[Pd(dmit)_2]_2$, there is a small but significant difference between exchange interactions on the three sides of the triangle and, as a result, they undergo antiferromagnetic ordering owing to the less frustrated nature.[14–16]

On the other hand, $Et_2Me_2Sb[Pd(dmit)_2]_2$,[17–20] $EtMe_3P[Pd(dmit)_2]_2$ (space group $P2_1/m$),[21–23] and $EtMe_3Sb[Pd(dmit)_2]_2$ (space group $C2/c$) are considered to have nearly regular-triangular networks of transfer integrals.

 

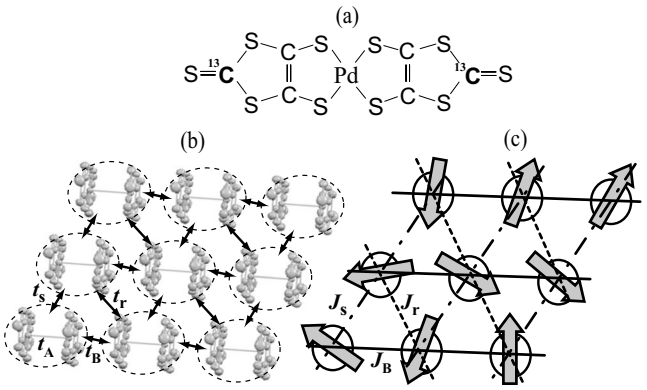


FIG. 1. (a) $Pd(dmit)_2$ molecule with selective substitution of $^{13}C$ isotope. The carbon atoms at both ends of the molecule are enriched. (b) Crystal structure of a $Pd(dmit)_2$ layer viewed along the long axis of the $Pd(dmit)_2$ molecule. Arrows ($t_B$, $t_s$, and $t_r$) indicate the transfer integral network between the $[Pd(dmit)_2]_2$ dimers. For $EtMe_3Sb[Pd(dmit)_2]_2$, $t_B$, $t_s$, and $t_r$ are calculated using the extended Hückel method as 28.3, 27.7, and 25.8 meV, respectively, while the intradimer transfer integral, $t_A$, is calculated as 453.5 meV. (c) Schematic of the spin system of $X[Pd(dmit)_2]_2$, where circles represent $[Pd(dmit)_2]_2$ dimers on which localized 1/2 spins exist. Three exchange interactions ($J_B$, $J_s$, and $J_r$) are nonequivalent but close to each other, reflecting the values of $t_B$, $t_s$, and $t_r$.

[We have estimated the interdimer transfer integrals along the three directions for the $EtMe_3Sb$ salt, as shown in the caption of Fig. 1(b).] Among them, the $Et_2Me_2Sb$ salt is exceptionally not mapped to a Mott insulator at low temperatures, unlike any other $X[Pd(dmit)_2]_2$ systems. It has turned out that this salt undergoes a first-order valence transition at 70 K to a gapped ground state with fully separated charges,[17–20] although early susceptibility measurements[16] had implied the possibility of a gapless spin-liquid ground state.

The remaining two salts, the $EtMe_3P$ and $EtMe_3Sb$ salts, are Mott insulators and, thus, have nearly regular-triangular spin systems, which are expected to exhibit a strong frustration effect. These two salts behave differently at low temperatures, which is likely due to the difference in the crystal structures.[22] In the $EtMe_3P$ salt, the VBS state accompanied by spin dimerization is realized below 25 K and, consequently, static susceptibility shows a rapid decrease with a full spin gap of about 40 K.[22] Superconductivity appears as the VBS state is suppressed by pressure.[23] Contrastingly, the $EtMe_3Sb$ salt shows no such rapid decrease indicating a phase transition, as will be described later. Thus, $EtMe_3Sb[Pd(dmit)_2]_2$ is expected to keep the nearly regular-triangular exchange network without spin dimerization down to low temperature, unlike the $EtMe_3P$ salts. This system is, therefore, one of the few model materials of the nearly regular-triangular spin-1/2 system.

Fine single crystals of $EtMe_3Sb[Pd(dmit)_2]_2$ were prepared by an aerial oxidation method. For the $^{13}C$-NMR measurement, we prepared enriched molecules as shown in Fig. 1(a). We performed the static uniform susceptibility and $^{13}C$-NMR measurements for a large number of the single crystals without any particular orientation. The susceptibility $\chi$ was measured in the temperature range from 300 to 4.5 K under a field of 5 T. The NMR measurements were performed from 299 to 1.37 K under 7.65 T. The spectra were obtained by the Fourier transformation of spin echo signals following the $(\pi/2)_x$-$(\pi)_x$ pulse sequence. The spin-lattice relaxation rate, $T_1^{-1}$, was obtained from the recovery curve of the integrated spin-echo intensity. Since the recovery curve becomes nonsingle exponential at low temperatures, we define $T_1$ as the time when the recovery curve reaches $1/e$.

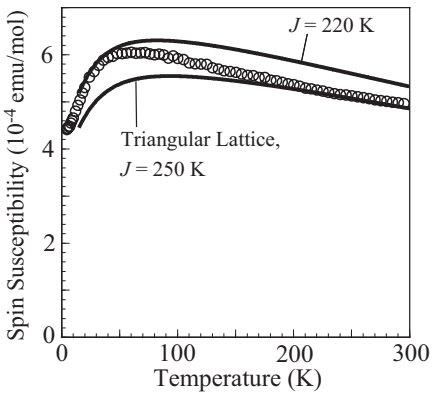


FIG. 2. Temperature dependence of the spin susceptibility of randomly oriented samples of $EtMe_3Sb[Pd(dmit)_2]_2$. Solid curves show the result of the [7/7] Padé approximants for the high-temperature expansion of the regular-triangular antiferromagnetic spin-1/2 system with $J$=220 and 250 K.

The temperature dependence of $\chi$ of $EtMe_3Sb[Pd(dmit)_2]_2$ is shown in Fig. 2, where the contributions of the core diamagnetism and of the impurity free spins have already been subtracted. The core diamagnetisms are estimated by using the reported value[24] for $Pd(dmit)_2$ and Pascal's law for $EtMe_3Sb$. The diamagnetic correction leaves an uncertainty of $0.3\times10^{-4}$ emu/mol, typically.[24] The subtracted free-spin contribution corresponds to one $S=1/2$ spin per $7\times10^2$ f.u.

As temperature is decreased from 300 K, $\chi$ gradually increases. Around 50 K, it exhibits a broad peak denoting significant development of the antiferromagnetic correlations. The solid lines in the figure show the theoretical curves[16] extrapolated using the [7/7] Padé approximants for the high-temperature expansion[25] of the regular-triangular spin-1/2 system with Heisenberg antiferromagnetic interactions, $J$ =220 and 250 K. In this calculation, we used a value of $g$ =2.038 for $[Pd(dmit)_2]_2^-$, which is based on electron spin resonance measurements.[26] Since these curves reproduce the observed $\chi$ behavior well, it is concluded that a nearly regular-triangular spin-1/2 system with $J$=220–250 K is realized in this compound. In detailed comparison, the observed $\chi$ has a slightly steeper temperature dependence above its peak temperature than the calculated $\chi$. This implies slight deviation from the regular triangle and/or existence of extra higher-order exchange interactions discussed later. In fact, a theoretical study reported that deviation from the regular triangle causes steeper temperature dependence of $\chi$.[27]

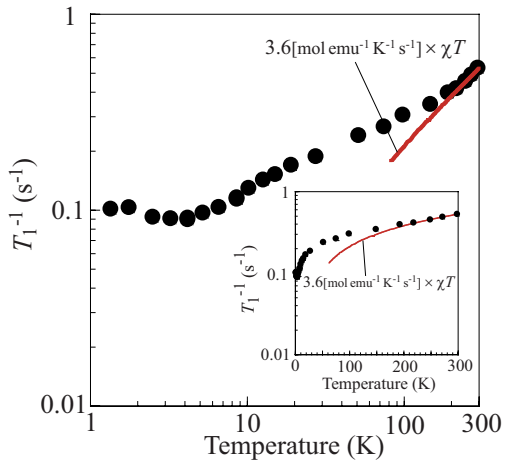


FIG. 3. (Color online) Temperature dependence of $^{13}$C nuclear spin-lattice relaxation rate of $EtMe_3Sb[Pd(dmit)_2]_2$. The transverse axis in the inset is linear so that data at high temperatures can be clearly illustrated, while it is logarithmic in the main figure. The solid curves show values calculated using 3.6 (mol emu$^{-1}$ K$^{-1}$ s$^{-1}$) $\times \chi T$, where $\chi$ and $T$ represent the spin susceptibility and the temperature, respectively.

The static spin susceptibility is usually related to the shift of NMR frequency. However, in the present case, the shift is as small as a few kilohertz, because of the small hyperfine coupling constant (about 900 kHz/$\mu_B$ as will be mentioned later). Therefore, it is difficult to obtain decisive results from the shift. On the other hand, the temperature dependence of the NMR relaxation rate $T_1^{-1}$ can be used as a sensitive probe of the spin fluctuations in the system, even in such a case.

Figure 3 shows $T_1^{-1}$ of $EtMe_3Sb[Pd(dmit)_2]_2$ as a function of temperature. The value of $T_1^{-1}$ gradually decreases as temperature decreases, showing no remarkable enhancement due to critical fluctuations. It is observed that $T_1^{-1}$ stops decreasing and retains a finite value below around 5 K.

First, we focus on spin fluctuations in a high-temperature region. We can evaluate the antiferromagnetic spin correlations by comparing $T_1^{-1}$ with the static spin susceptibility $\chi$. For the high-temperature paramagnetic states where the spin autocorrelation function decays exponentially with time, standard relaxation theory[28] generally yields

$$T_1^{-1} \propto \lim_{\omega \to 0} T \sum_q \frac{\chi''(q,\omega)}{\omega} \propto T \sum_q \frac{\chi'(q,\omega=0)}{\Gamma_q}, \qquad (1)$$

where $\chi(q,\omega)=\chi'(q,\omega)+i\chi''(q,\omega)$ is the dynamic spin susceptibility and $\Gamma_q$ is the characteristic decay rate of the autocorrelation function (in other words, the characteristic frequency of the spin dynamics). At sufficiently high temperatures ($T>J$) where the $q$-dependent antiferromagnetic correlations are negligible, all $\Gamma_q$ are equal to the temperature-independent exchange frequency,[29] and $\chi'(q,\omega=0)$ is also $q$ independent, i.e., $\chi'(q,\omega=0)=\chi$. In this case, $T_1^{-1}$ is proportional to $\chi T$. An enhancement from this behavior is a measure of the growth of the antiferromagnetic correlations, because it indicates an enhancement of $\chi'(q,\omega=0)/\chi'(q=0,\omega=0)$ and slowing down of $\Gamma_q$ at a specific $q$.

This enhancement comes to be recognizable below around 200 K in our data. As shown in the inset of Fig. 3, $T_1^{-1}$ is almost proportional to $\chi T$ around room temperature. The uncertainty of $\chi$ caused by the diamagnetic correction does not alter this observation. Thus, antiferromagnetic correlations are almost absent around room temperature. The proportionality coefficient, 3.6 mol emu$^{-1}$ K$^{-1}$ s$^{-1}$, gives the hyperfine coupling constant to be $9\times10^2$ kHz/$\mu_B$ by assuming Gaussian fluctuations[29] and by using an exchange frequency $\omega_{ex}=5\times10^{13}$ rad/s, which is calculated from the values $J=220-250$ K and the coordination number $z=6$. This hyperfine value is consistent with our previous estimations,[13] which were calculated on spectral-width analysis and on comparison of $T_1^{-1}$ between this system and the $\kappa$-$(BEDT\text{-}TTF)_2X$ family. This consistency supports our interpretation and analysis of the present behavior of $T_1^{-1}$ at high temperatures.

As temperature is decreased below 200 K, which corresponds to the energy scale of $J$, $T_1^{-1}$ starts to deviate from the $\chi T$ line, which means the growth of antiferromagnetic correlations. It is noted that the deviation, or the growth of the antiferromagnetic correlations, is quite gradual as shown in the inset. Actually, the peak in $\chi$, which indicates significant development of the antiferromagnetic correlations, is observed at a temperature much lower than 200 K. This unusually gradual growth of the antiferromagnetic correlations evidently shows the frustration effect.

Recently, $T_1^{-1}$ under antiferromagnetic fluctuations for the $\kappa$-$(BEDT\text{-}TTF)_2X$ family was discussed in a theoretical paper by Yusuf *et al.*,[30] where the phenomenological form for $\chi(q,\omega)$ based on the self-consistent renormalization (SCR) theory[31] is assumed. Although the calculation in the paper seems to reproduce also our data at high temperatures by tuning several parameters, it is open to question and needs to be studied further whether or not the phenomenological form of the SCR theory is applicable to the present frustrated Mott insulating phase.

As found in Fig. 3, $T_1^{-1}$ shows no critical enhancement and, thus, suggests the absence of spin ordering at least down to 1.37 K. This is markedly contrasting with the behavior of $T_1^{-1}$ for $Me_4P[Pd(dmit)_2]_2$, which shows critical enhancement around a MLRO temperature of 42 K.[15] Furthermore, $T_1^{-1}$ in the present system seems to retain a finite value at low temperatures. The recovery curve for $T_1^{-1}$ becomes nonsingle exponential at low temperatures, yielding some uncertainty in the estimation of the value of $T_1^{-1}$. However, it is clear that this system does not have an appreciable spin gap more than 1 K either with nodes or without nodes, because the estimated $T_1^{-1}$ does not show any sign of decreasing. It is surprising that the paramagnetic state remains down to 1.37 K despite the growth of the antiferromagnetic correlations from much higher temperatures around 200 K.

The absence of spin ordering is confirmed by the spectra of $EtMe_3Sb[Pd(dmit)_2]_2$ displayed in Fig. 4(a). As temperature is decreased, we observe no critical broadening of the spectrum characteristic of spin ordering. Instead, it gradually broadens at low temperatures. Despite the broadening, the spin-spin relaxation rate $T_2^{-1}$ remains almost constant over the entire temperature region and is approximately 1

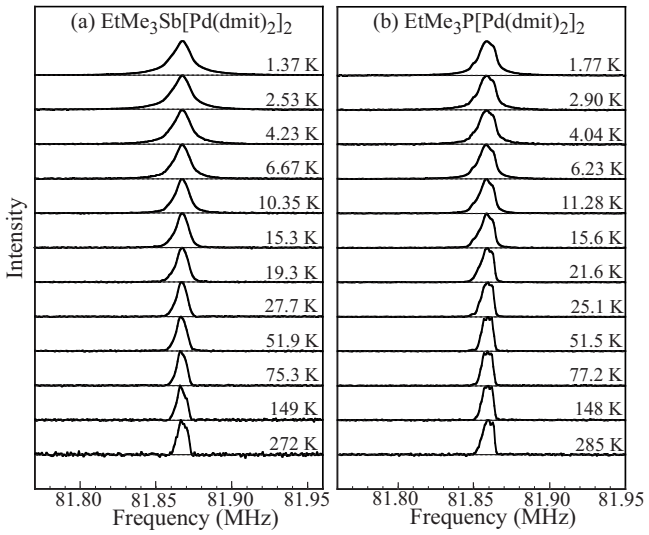


FIG. 4. (a) $^{13}$C-NMR spectra for randomly oriented samples of $EtMe_3Sb[Pd(dmit)_2]_2$. (b) Those of $EtMe_3P[Pd(dmit)_2]_2$ for comparison.

$\times 10^3$ $s^{-1}$. Thus, this is an inhomogeneous broadening due to static local fields. The observed local static fields are too small for this system to be understood as a MLRO or spin-glass state. The spectral tail is at most within $\pm 50$ kHz, which corresponds to a $[Pd(dmit)_2]_2$ moment of $\sim 0.05\mu_B$ judging from the hyperfine coupling constant mentioned before. Furthermore, the tail is composed of the minor fraction of the spectrum, while the dominant fraction stays at the center with little shift. This means that the small local moment exists only on a minority of the $[Pd(dmit)_2]_2$ dimers. We also measured $^{13}$C-NMR spectra of $EtMe_3P[Pd(dmit)_2]_2$ for comparison as shown in Fig. 4(b). The gradual inhomogeneous broadening at low temperatures is also observed even in $EtMe_3P[Pd(dmit)_2]_2$, which enters a nonmagnetic state below 25 K with a full spin gap. Therefore, the broadening observed in the two salts is not due to bulk magnetism, but most probably due to the impurity Curie spins caused by slight crystal imperfections. As a consequence, our analysis of the spectra also concludes that $EtMe_3Sb[Pd(dmit)_2]_2$ does not undergo either spin ordering or freezing at least down to 1.37 K.

The observed broadening is larger in $EtMe_3Sb[Pd(dmit)_2]_2$ than in $EtMe_3P[Pd(dmit)_2]_2$. The magnetization nucleated around locally symmetry-broken sites generally extends for a distance characterized by a spatial spin correlation length. In the ground state, the correlation length is roughly estimated to be $\sim J/\Delta$, where $\Delta$ is the spin gap of the system; if $\Delta$ is zero, the correlation length diverges and, as a result, a power-law decay of the spatial correlation function is expected. $EtMe_3P[Pd(dmit)_2]_2$ has a short correlation length because of the existence of the significant spin gap, while $EtMe_3Sb[Pd(dmit)_2]_2$ has a comparatively long correlation length or a power-law decay of the correlation function because of the absence of an appreciable spin gap. This is likely the reason why the broadening of $EtMe_3Sb[Pd(dmit)_2]_2$ is larger. It was reported that the $^{13}$C-NMR spectra of $\kappa$-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$, which does not have an appreciable spin gap either, also show a similar inhomogeneous broadening at low temperatures.[32] To take this and our results into consideration, the significant inhomogeneous broadening is considered to be a universal nature of the spin liquid with no appreciable spin gap because this state is quite sensitive to slight crystal imperfections due to the quasi-long-range correlation.

As described above, the spectra and $T_1^{-1}$ of $EtMe_3Sb[Pd(dmit)_2]_2$ do not show any features of the spin ordering or freezing at least down to 1.37 K, in spite of the growth of antiferromagnetic correlations from much higher temperature around 200 K. Since 1.37 K is lower than 1% of $J$, thermal fluctuations are so small as to be negligible in this temperature region. Thus, the absence of spin ordering or freezing is attributed not to thermal fluctuations but to quantum fluctuations. Considering the absence of an appreciable spin gap, which is concluded by the fact that $T_1^{-1}$ retains a finite value down to 1.37 K, this state is clearly distinct from the VBS state accompanied by spin dimerization. This state is, therefore, regarded as the quantum spin-liquid state, where the RVB scenario can be brought to realization.

A number of theoretical studies have been conducted on the regular-triangular Heisenberg spin-1/2 system, and there is a general consensus that the 120° spiral MLRO state is realized in the ground state,[25,33–35] in contrast to our experimental result.

Several theoretical studies on isosceles-triangular Heisenberg systems have suggested that slight deviation from the regular triangle can destroy the spiral MLRO state and realize the spin-liquid state.[12,36–41] Our result may be rationalized from such standpoints. It is desired to study whether or not the deviation from the regular triangle leads to the spin-liquid state even on a scalene-triangular lattice, because our system has a scalene structure rather than an isosceles one.

Another possible mechanism of the observed spin liquid is explained in light of the proximity of the Mott transition. Although $EtMe_3Sb[Pd(dmit)_2]_2$ is a Mott insulator, its insulating nature is easily destroyed by a pressure of a few kilobars.[42] This means that its transfer integrals, whose perturbing effect yields exchange interactions, are not much smaller than the electron correlation energy. Therefore, not only the second-order Heisenberg terms, but also the higher-order ones are expected to emerge as the ring exchange and long-range Heisenberg interactions. While the nearest-neighbor Heisenberg interactions seem to be predominant as the temperature dependence of the susceptibility shows, it is possible that such extra higher-order interactions are not negligible and play a significant role in the realization of the present spin liquid. In fact, some theories based on the spin Hamiltonian including the ring exchange,[8] and the Hubbard Hamiltonian with moderate on-site Coulomb repulsion,[9,10] successfully predict the gapless quantum spin-liquid state.

In conclusion, we have found a spin-liquid system on a triangular lattice, $EtMe_3Sb[Pd(dmit)_2]_2$. We have revealed by our $^{13}$C NMR study that this material has neither spin ordering/freezing nor an appreciable spin gap down to 1.37 K, which is lower than 1% of $J$. Inhomogeneous broadening appears at low temperature, similar to the other spin liquid system $\kappa$-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$. This is consistent with the quasi-long-range spin correlation characterizing the gapless nature.

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