Thermodynamics of the quantum spin liquid state of the single-component dimer Mott system κ-H_3(Cat-EDT-TTF)$_2$

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Thermodynamic properties of the proton-mediated single component dimer-Mott insulator of κ-H_3(Cat-EDT-TTF)$_2$, which has a two-dimensional triangle lattice structure of $S = 1/2$ spins, are reported. The extraordinary large electronic heat capacity coefficient $\gamma = 58.8$ mJ K^{-2} mol^{-1} observed by the low-temperature heat capacity measurements up to 6 T suggests the formation of the gapless spin liquid ground state. Although the magnetic interaction J/k_B is quite different from those of other dimer-Mott spin liquids, the thermodynamic feature scales well with the Wilson ratio of 1.4–1.6. The heat capacity measurements also detected that the deuteration of the proton-linkage changes the ground state to the nonmagnetic one with almost vanishing γ. Using the data of the deuterated compound, the accurate temperature dependence of the magnetic heat capacity reflecting on the low-energy excitations from the gapless spin liquids ground state is discussed.

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The realization of the quantum spin liquid ground state in the two dimer-Mott insulating compounds of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ and EtMe$_3$Sb[Pd(dmit)$_2$]$_2$, where BEDT-TTF (ET) is bis(ethylenedithio)tetrathiafulvalene and dmit is 1,3-dithiole-2-thione-4,5-dithiolate, respectively, has stimulated various researches of frustration physics in strongly correlated molecular systems [1–8]. Electron spins with $S = 1/2$ are localized on each donor/acceptor dimer unit due to the on-dimer Coulomb repulsion in effectively half-filled electronic bands in them. Although the antiferromagnetic interaction between neighboring dimers is in an order of $|J/k_B| \sim 10^2$ K, they do not show any magnetic ordering nor glassy freezing down to extremely low temperatures owing to frustration of the triangle system [4,7–9]. The rather large spin entropy near $T = 0$ K gives realistic possibilities of the theoretical predictions such as the long-range RVB state, formation of spinon Fermi surface, etc. [10–14].

Recently, a novel-type layered molecular compound of κ-H_3(Cat-EDT-TTF)$_2$, with dimer-based triangle structure, was synthesized and it was reported as a promising candidate for the quantum spin liquid system [15–17]. It forms a κ-type dimer-triangle lattice of Cat-EDT-TTF molecules in the same layer. Each molecule in a dimer unit is linked to different Cat-EDT-TTF molecules in the up/down layer through hydrogen bonding. The positive charge of Cat-EDT-TTF is compensated by (O-H-O)$^-$ bonding that exists as a mediation linker part. Absence of thick counterion layers and a tunable electronic state through hydrogen bonding can give quite unique aspects as a proton-spin coupled system among organic charge transfer complexes [15,16]. The intradimer transfer due to the overlap of π electrons in HOMOs is rather strong, similar to the case of κ-(BEDT-TTF)$_2$X compounds where X denotes monovalent counteranions and therefore the electronic state would be a dimer-Mott triangle system. In order to study the low-energy feature of the organic spin liquids and to get information related to the spin excitations, we performed heat capacity measurements under magnetic fields. We discuss peculiar characters of a gapless spin liquid from the temperature and magnetic fields dependence of the heat capacities. Universal discussion with other dimer-Mott spin liquids and comparison with a deuterated compound are given based on the thermodynamic parameters.

The samples of κ-H_3(Cat-EDT-TTF)$_2$ were synthesized with the procedure reported previously [15,16]. The crystals are obtained as tiny single crystals with a typical size of 0.5 mm × 0.2 mm × 0.05 mm and we measured the heat capacity by the relaxation calorimetry technique for a small amount of sample [18]. The total mass of the sample was 242.3 μg and this batch contains nearly 30 pieces of crystal (crystal sample). We confirmed that the temperature dependence of the magnetic susceptibility reproduces well the reported temperature dependence by Isono *et al.* [17] as is shown in the inset of Fig. 1. We also measured a compacted-pellet sample made from fine powder with total mass of 748.1 μg (pellet sample) to confirm reproducibility of thermodynamic data. A deuterated sample κ-D_3(Cat-EDT-TTF)$_2$, where the OH protons in the crystals are all replaced by deuterons [19], was measured, of which the sample mass is 292.8 μg.

The temperature dependencies of the heat capacity of κ-H_3(Cat-EDT-TTF)$_2$ are shown in Fig. 1. To discuss the overall dependence, we show the data in a logarithmic scale. There is no significant difference between the crystal and the pellet samples except for the slight discrepancy at the lowest temperature region. The absolute values of C_p are 8.18×10^{-2} J K^{-1} mol^{-1} at 1.0 K and 1.03 J K^{-1} mol^{-1} at 10 K. The abrupt increase of the absolute value from 1.0 to 10 K is a common feature in such molecular crystals which have relatively soft lattice as compared with intermetallic compounds. However, the rather large heat capacity values of about 10^2 mJ K^{-1} mol^{-1} around 1.0 K is a peculiar feature for the present Mott insulating compound, meaning that spins on each dimer site are fluctuating in such a low energy region. The spin entropy is retained without any long-range order down to the low temperature region and the continuous excitations exist owing to the large degeneracy of quantum spin states. In the figure, the temperature dependencies of heat capacity of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ and EtMe$_3$Sb[Pd(dmit)$_2$]$_2$ are also

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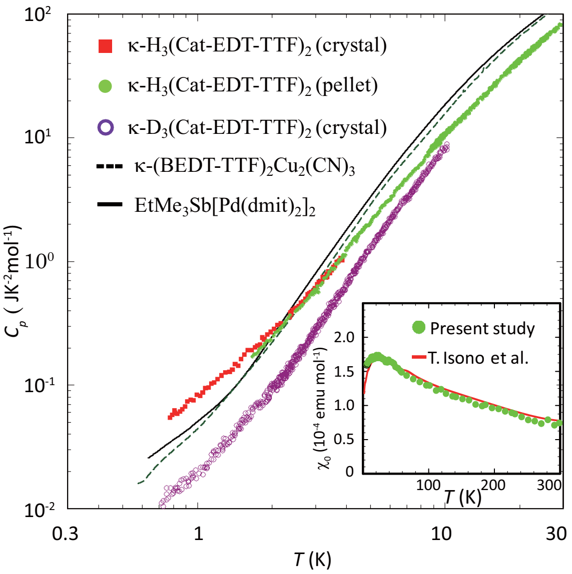

FIG. 1. The temperature dependencies of the heat capacity of the κ-H$_3$(Cat-EDT-TTF)$_2$ in logarithm plot. The data obtained by multipieces crystal sample (crystal) and those obtained by pellet sample (pellet) are indicated by red square and green circles, respectively. The data of κ-D$_3$(Cat-EDT-TTF)$_2$ and two other dimer Mott spin liquid compounds (κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ and EtMe$_3$Sb[Pd(dmit)$_2$]$_2$) are also indicated by purple open circle, green line, and ocher line, respectively. The inset shows the temperature dependence of the magnetic susceptibility of the κ-H$_3$(Cat-EDT-TTF)$_2$.

shown for comparison [1,2]. Although the latter two salts with thick counterion layers have the similar temperature dependencies of C_p, that of κ-H$_3$(Cat-EDT-TTF)$_2$ is different in all temperature ranges. The difference of this temperature dependence may be attributed to the absence of counterion layers. It is noticeable that the C_p values of κ-H$_3$(Cat-EDT-TTF)$_2$ below 1.0 K are much larger than the values of these compounds.

In Fig. 2(a) we show C_pT^{-1} vs T^2 plot of the low temperature heat capacity below 3.2 K obtained for the crystal sample. We also show the data under magnetic fields in the same figure. The absence of any magnetic field dependence up to a rather strong field of 6 T, as is shown in the figure, excludes the possibility of nonequilibrium freezing like spin-glass formation. The spins are not ordered and show a liquidlike feature with quantum mechanical fluctuations in this temperature region. Even in such a low temperature region, the C_pT^{-1} does not have a linear relation against T^2 and shows moderate rounding with decreasing temperature. The extrapolation of this dependence down to $T = 0$ K in this plot gives an unexpectedly large γ value of $58.8 \pm 5.0\,\mathrm{mJ\,K^{-2}\,mol^{-1}}$. The rather large electronic density of states due to the spinon excitations in the gapless spin liquid is suggested in this compound. The γ value is nearly three times larger than that of EtMe$_3$Sb[Pd(dmit)$_2$]$_2$ [2] and this is qualitatively consistent with the smaller $J/k_\mathrm{B} = -80$ K reported by Isono *et al.* [17]. The low temperature magnetic susceptibility evaluated from the SQUID and the torque measurements down to the dilution temperature region in Ref. [17] claimed that the susceptibility below 1 K becomes almost constant with $\chi_0 = 1.2 \times 10^{-3}$ emu/mol. This value is again about three times larger than that of EtMe$_3$Sb[Pd(dmit)$_2$]$_2$ with $J/k_\mathrm{B} = -220$ to 250 K [8,9]. We also compare the crystal sample and pellet sample in Fig. 2(b). The value of heat capacity of the pellet sample was slightly smaller than crystal sample but the slope of C_pT^{-1} vs T^2 is almost the same. The γ value of the pellet sample was estimated to be 45–$55\,\mathrm{mJ\,K^{-2}\,mol^{-1}}$. It is considered that the structural disorders induced in this proton-mediated system may work to form a local singlet spin state in the dimer, since the structural disorder may affect the position of the protons in hydrogen linkage and produces a nonmagnetic dimer. The lower γ in the pellet samples may be explained by the formation of such nonmagnetic dimers due to the break of the network linkage of protons. However, it still gives much larger values compared with other spin liquid compounds.

The relation between magnetic parameter and the thermodynamic ones of three compounds are compared in Fig. 3. The vertical axis is the γ and the horizontal axis shows

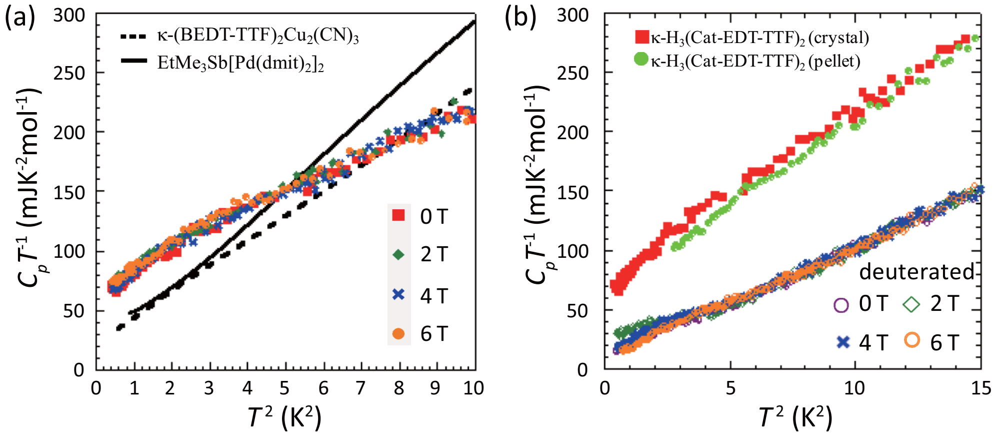

FIG. 2. (a) The C_pT^{-1} vs T^2 plot of the heat capacity of κ-H$_3$(Cat-EDT-TTF)$_2$ at a low temperature region. The field dependencies up to 6 T are also plotted. The dashed lines show the data of other two spin liquid compounds of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ and EtMe$_3$Sb[Pd(dmit)$_2$]$_2$. (b) Comparison of C_pT^{-1} vs T^2 plots of multipieces crystal sample and pellet sample of κ-H$_3$(Cat-EDT-TTF)$_2$. The data of κ-D$_3$(Cat-EDT-TTF)$_2$ obtained under fields up to 6 T are also plotted.

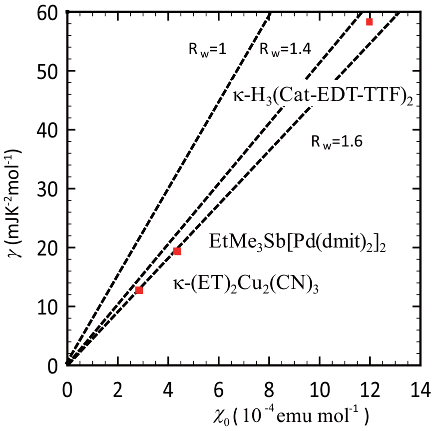

FIG. 3. Relation between the electronic heat capacity coefficient γ and magnetic susceptibility extrapolated down to zero χ_0. The dashed line indicate the relation of the value in the case of $R_w = 1$, 1.4, and 1.6, where R_w denotes the Wilson ratio.

the χ_0 evaluated by magnetic susceptibility extrapolated down to $T = 0$ K. In the cases of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ and EtMe$_3$Sb[Pd(dmit)$_2$]$_2$, it was reported that the magnetic susceptibility gives almost constant values at a low temperature region below about 5 K similar to the case of the present κ-H$_3$(Cat-EDT-TTF)$_2$. The χ_0 value of them is reported as 2.9 and 4.4 emu mol^{-1}, respectively [7,9]. The broken lines in the figure demonstrate the relation explained by the Wilson ration $R_w = 1.0$, 1.4, and 1.6. The data of the three compounds are explained by the $R_w = 1.4-1.6$ and this result implies that the magnetic susceptibility and the heat capacity scales well using a kind of density of states probably related to the spinons. This result gives an evidence that the ground state of κ-H$_3$(Cat-EDT-TTF)$_2$ is certainly a spin liquid and has similar aspects as those of EtMe$_3$Sb[Pd(dmit)$_2$]$_2$ and κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$. The higher γ value of this compound can be explained by the difference of interdimer magnetic interactions J/k_B which scales the inverse of density of states of spin excitations.

Since the Cat-EDT-TTF molecule forms a hydrogen-bonding network between another molecule in an up or down layer by keeping a dimerized structure in each layer, it has a unique character as a proton-electron linked charge transfer system. The electronic state of the dimer changes drastically depending on the position of protons in the linkage [19]. According to the theoretical calculation, the potential profile of the proton and the deuteron between two Cat-EDT-TTFs are quite delicate [20,21]. In the case of κ-H$_3$(Cat-EDT-TTF)$_2$, protons stay at the intermediate position between two layers and consequently all Cat-EDT-TTF molecules have a common valence of +0.5 [19,22]. On the other hand, the deuterated compound of κ-D$_3$(Cat-EDT-TTF)$_2$ reveals a transition from the paramagnetic state to the nonmagnetic state at about 180 K where a kind of ordering of the deuteron position occurs. A drastic charge ordering between a charge-rich molecule with +0.94 and a charge-poor one with +0.06 occurs concomitantly at this temperature and this charge disproportionation separates a charge-poor dimer pair and a charge-rich dimer pair which finally forms single states located alternatively in the 2D structure as is discussed in detail in Refs. [19,22]. The nonmagnetic ground state, therefore, is realized due to the simultaneous ordering of this charge order and spin singlet formation in the charge-rich dimers. These structural features should be reflected in the low energy phonon structure. Therefore, we compare the heat capacity of the spin liquid compound of κ-H$_3$(Cat-EDT-TTF)$_2$ and that of the nonmagnetic compound of κ-D$_3$(Cat-EDT-TTF)$_2$. The data of the deuterated compound are also plotted in Figs. 1 and 2(b). In contrast to the proton compound, the heat capacity of the deuterated compound has smaller values in the whole temperature range studied because of the absence of spin contribution. It also obeys a linear relation in the C_pT^{-1} vs T^2 plot, except for the lowest temperature region. The fitting of the data between 2.6 and 4 K to the $C_pT^{-1} = AT^{-3} + \gamma + \beta T^2$ gives $A = 4.86$ mJ K^3 mol^{-1}, $\gamma = 2.90$ mJ K^{-2} mol^{-1}, and $\beta = 9.84$ mJ K^{-4} mol^{-1}. The first term is a kind of Schottky heat capacity probably due to the paramagnetic spins produced by disorder, since there might be some hydrogen bonding parts produced by deuterium-hydrogen exchange owing to atmospheric H$_2$O [19]. The small value of A means that less than 1% of the paramagnetic impurities are included in the κ-H$_3$(Cat-EDT-TTF)$_2$ sample which is also supported by the x-ray analysis in Ref. [19]. The much smaller value of γ corresponding to 4.8% of that in pristine κ-H$_3$(Cat-EDT-TTF)$_2$ demonstrates that the nonmagnetic states are certainly realized and the feature observed here may well be attributed to the lattice heat capacity. The anomalous contribution at the lowest temperature below 2.6 K is not so simple and its magnetic fields dependence should be analyzed with the model with proton spin dynamics. However, the entropy contribution of this residual structure in C_pT^{-1} vs T^2 is only 0.5%–1.0% of Rln2 and this value is quantitatively consistent with the replacing rate discussed above [19].

The Debye-like feature of the deuterated compound shown in Fig. 2(b) indicates that the lattice heat capacity of this single component compound does not have specific libration phonon modes at a low energy region. This is in fine contrast with the heat capacity of numerous 2:1 salts of TMTSF, BEDT-TTF, BETS, etc., in which the donor molecules form segregate stacking from counteranions. In the latter, the planar symmetric donors may have libration phonon modes and give an additional contribution expressed by the Einstein type model [23–25]. It is inferred that the linkage by proton or deuteron makes the interlayer connection rigid and leads the lattice vibration to have more three-dimensional character, although the lattice itself retains flexible features as is inferred from the absolute value of the β.

It is reasonable to consider that the discrepancy between the data of the proton compound and the deuteron compound reflects the accurate spin contribution. Figure 4(a) shows the temperature dependence of the discrepancy between two salts plotted in ΔC_pT^{-1} vs T plot. An almost linear increase of ΔC_pT^{-1} means that the thermal excitations can be expressed by the T-linear term and the quadratic term. These low energy excitations also have similar features as the magnetic heat capacity of the spin liquid in κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, as was discussed in Ref. [1]. The spin entropy evaluated from this discrepancy is shown in the inset of Fig. 4(a). The entropy at 10 K reaches to about 1.50 J mol^{-1} K^{-1} which is about 26% of Rln2 corresponding to the full entropy of

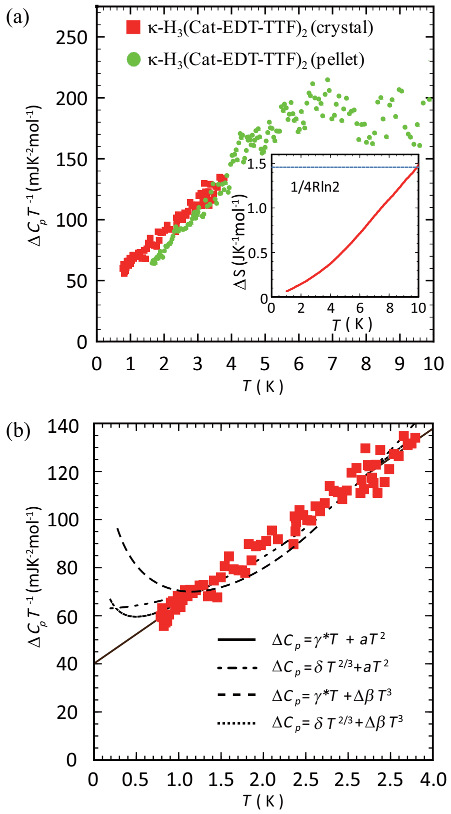

FIG. 4. (a) The temperature dependencies ΔC_pT^{-1} of κ-H$_3$(Cat-EDT-TTF)$_2$. The ΔC_pT^{-1} was evaluated as a discrepancy of proton compound and deuteron compound. The inset shows the temperature dependence of magnetic entropy of κ-H$_3$(Cat-EDT-TTF)$_2$. (b) The fitting of the electronic heat capacity of crystalline sample using the formula of $\Delta C_p = \gamma^*T + aT^2$, $\Delta C_p = \delta T^{2/3} + aT^2$, $\Delta C_p = \gamma^*T + \Delta\beta T^3$, and $\Delta C_p = \delta T^{2/3} + \Delta\beta T^3$. The latter fitting of the latter two models are not successful. The obtained parameters for the former two are $\gamma^* = 39.7\,\mathrm{mJ\,K^{-2}\,mol^{-1}}$, $a = 24.4\,\mathrm{mJ\,K^{-4}\,mol^{-1}}$ and $\delta = 35.4\,\mathrm{mJ\,K^{-5/3}\,mol^{-1}}$, $29.9\,\mathrm{mJ\,K^{-4}\,mol^{-1}}$, respectively.

the $S = 1/2$ system. As is expected for spin liquids, the large contribution of spin entropy is retained in the low energy region as compared with the characteristic hump in magnetic susceptibility explained by the 2D Heisenberg model. The dashed line in the figure shows 1/4*R*ln2 predicted for the spin liquid by the rhombus approximation [26]. The existence of a $T^{2/3}$ term instead of the T-linear term cannot be excluded, since the fitting curves of the heat capacity C_p using $\gamma^*T + aT^2$, and $\delta T^{2/3} + aT^2$, shown in Fig. 4(b), do not give so large a discrepancy in the analyses of heat capacity in the present temperature region as was suggested in Ref. [27] in the κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$. However, the inclusion of the quadratic term was found to be inevitable to fit the experimental data. The two fitting models give almost the similar values of $a = 24.4\,\mathrm{mJ\,K^{-3}\,mol^{-1}}$ for the former and $a = 29.4\,\mathrm{mJ\,K^{-3}\,mol^{-1}}$ for the latter, which also supports the importance of this term to describe spin excitations. The subtraction of lattice heat capacity based on the nonmagnetic deuterated compound may contain some ambiguities, since the deuteration sometimes induces changes in low energy phonon structures. In order to examine this point, we also fitted the electronic heat capacity data in Fig. 4(a) by including a $\Delta\beta T^3$ term. The fittings results also shown in Fig. 4(b) cannot reproduce the experimental data which explains that the power lower than the cubic term is intrinsic for the spin excitations. It is also indicated that in the case of BEDT-TTF based compounds including κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, the deuteration do not induce a large difference in the lattice heat capacity [28]. The discrepancy occurring by the deuteration in the βT^3 is usually less than a few percent in BEDT-TTF salts which do not affect the entropic discussion of spin excitations [29,30].

The broad hump structure in ΔC_pT^{-1} vs T plot in Fig. 4(a) appears around 6–7 K corresponding to the $0.075-0.09\,J/k_\mathrm{B}$. This feature means that a moderate crossover from Heisenberg-like state to liquid state with large magnetic entropy may takes place around these temperatures. The similar humps are reported in κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ and EtMe$_3$Sb[Pd(dmit)$_2$]$_2$ around 5.7 and 3.7 K, respectively, by heat capacity measurements [1,2]. In the case of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, the charge disproportionation due to intradimer and interdimer Coulomb repulsion produces a kind of dipole moment which shows relaxerlike frequency dependencies of dielectric properties. A broad hump structure in heat capacity is related to charge and lattice degrees of freedom [1,31]. The coupling with low-energy phonons through charge disproportionation gives the large β values in the lattice heat capacity in the liquid states. This is also considered as a typical feature of spin liquid phase [1,2]. Similar coupling of the spin degrees of freedom with the charge and lattice may be expected in this case, since the electronic state of this material is synchronized with the position of the protons in this compound. The lattice dynamics accompanied with charge disproportionation may well be induced in the proton compound. The pressure dependence and effects and application of electronic fields may be necessary to further examine the thermodynamic properties.

In conclusion, we performed systematic heat capacity measurements at low temperatures and under magnetic fields for novel κ-type organic triangle system κ-H$_3$(Cat-EDT-TTF)$_2$. The large magnetic heat capacity was observed at a low temperature region. The extrapolation of C_pT^{-1} down to $T = 0$ K gives a γ value of $58.8 \pm 5.0\,\mathrm{mJ\,K^{-2}\,mol^{-1}}$. The universal scaling through the Wilson ratio of $R_\mathrm{w} = 1.4-1.6$ was found to be held in the present compound with other organic spin liquids of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ and EtMe$_3$Sb[Pd(dmit)$_2$]$_2$, though the transfer energy and intradimer interactions which determine J/k_B are quite different between these compounds. The deuteration of the compound certainly produces the nonmagnetic ground states. The results by thermodynamic measurements demonstrate that κ-H$_3$(Cat-EDT-TTF)$_2$ is a good candidate for studying low energy thermodynamics of organic spin liquid compounds.

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