

Origin of Magnetic Ordering in a Structurally Perfect Quantum Kagome Antiferromagnet

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The ground state of the simple Heisenberg nearest-neighbor quantum kagome antiferromagnetic model is a magnetically disordered spin liquid, yet various perturbations may lead to fundamentally different states. Here we disclose the origin of magnetic ordering in the structurally perfect kagome material $\text{YCu}_3(\text{OH})_6\text{Cl}_3$, which is free of the widespread impurity problem. *Ab initio* calculations and modeling of its magnetic susceptibility reveal that, similar to the archetypal case of herbertsmithite, the nearest-neighbor exchange is by far the dominant isotropic interaction. Dzyaloshinskii-Moriya (DM) anisotropy deduced from electron spin resonance, susceptibility, and specific-heat data is, however, significantly larger than in herbertsmithite. By enhancing spin correlations within kagome planes, this anisotropy is essential for magnetic ordering. Our study isolates the effect of DM anisotropy from other perturbations and unambiguously confirms the predicted phase diagram.

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Quantum spin liquids are magnetically disordered, yet highly entangled states, promoted by quantum fluctuations on some geometrically frustrated spin lattices [1]. A paradigm predicting such a state even at zero temperature is the two-dimensional (2D) nearest-neighbor quantum kagome antiferromagnetic model (KAFM) [2–4] represented by Heisenberg, i.e., isotropic J_1 exchange bonds between spin-1/2 sites in Fig. 1. Yet, even small perturbations to this simple model can stabilize fundamentally different ground states, as their influence is strongly amplified by frustration. Various factors, including further-neighbor exchange interactions [5–11], magnetic anisotropy [9–14], defects [14–16], and structural distortions [17] have been the focus of theoretical investigations in recent years. One of the seminal predictions that still calls for a clear experimental validation is a quantum critical point induced by Dzyaloshinskii-Moriya (DM) magnetic anisotropy, separating a spin liquid from a magnetically ordered ground state of KAFM [12]. Here we elucidate the role of the DM interaction in promoting correlations that lead to magnetic ordering in a material that closely realizes the KAFM.

Actual KAFM realizations are as a rule plagued by several perturbations, making the assessment of the individual roles of these perturbations challenging. A direct consequence of many effects being intertwined is that even the existence of a spin gap in the spin-liquid ground state of the KAFM remains unsettled. In fact, for the hitherto most

intensively studied KAFM material herbertsmithite [24], indications of a finite gap [25] have been recently superseded by the conclusion that the gap is absent [26]. However, the effects of particular perturbations present in this material on its low-energy magnetism remain unknown. Relevant imperfections include sizable intersite ion mixing [27–29], large DM anisotropy [30], and subtle structural distortion away from perfect kagome symmetry [31,32]. On the contrary, in the recently synthesized KAFM material $\text{YCu}_3(\text{OH})_6\text{Cl}_3$ [33] no structure-related perturbations are present; there is no Cu-Y intersite disorder [33] and the initially reported small Y-site disorder [33] is absent in high-resolution neutron diffraction of high-quality powder samples [34]. Therefore, the recent discoveries of static internal magnetic fields below $T_N = 12$ K [34,35] and magnetic Bragg peaks at low temperatures [36] are rather surprising. Initially, a broad maximum in specific heat at a notably higher temperature of $T_{\text{max}} = 16$ K was also assigned to 3D ordering [35], causing a discrepancy with T_N where static internal fields appear. Experiments have further established that the average ordered Cu^{2+} magnetic moment of an otherwise regular 120° magnetic structure is strongly reduced [36] and is accompanied by persisting spin fluctuations even at the lowest temperatures [35]. The origin of such exotic magnetism is unknown, but even more fundamentally, the basic question of the magnetic-ordering mechanism present in this material remains unexplained. Since $\text{YCu}_3(\text{OH})_6\text{Cl}_3$ is a unique KAFM material with a

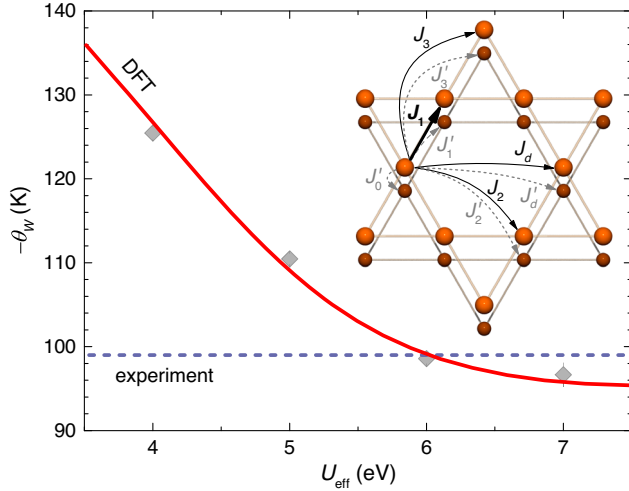


FIG. 1. Weiss temperature θ_W of $\text{YCu}_3(\text{OH})_6\text{Cl}_3$ determined from DFT + U calculations for different values of the effective on-site Hubbard repulsion U_{eff} (points). The dashed line shows the experimental value $\theta_W = -99$ K, while the solid line serves as a guide to the eye. The inset depicts two neighboring kagome layers of Cu^{2+} spin-1/2 ions with in-plane Heisenberg exchange interactions J_i (solid arrows) and interplane interactions J'_i (dashed arrows). The nearest-neighbor coupling J_1 is by far the dominant one [18].

very limited number of possible perturbations, determining the ordering mechanism would be very important for assessing the impact of these perturbations on the spin-liquid ground state of KAFM.

Here we show a combination of density functional theory (DFT), finite-temperature Lanczos method (FTLM), and electron spin resonance (ESR) results, which allows us to address the origin of the unexpected magnetic ordering in $\text{YCu}_3(\text{OH})_6\text{Cl}_3$. DFT calculations together with modeling of the magnetic susceptibility show that the nearest-neighbor Heisenberg exchange $J_1 = 82(2)$ K is by far the dominant isotropic interaction. Almost perfect agreement between numerical modeling and complementary ESR measurements, magnetic susceptibility, and specific heat data reveals an additional sizable out-of-plane DM anisotropy $D_z/J_1 = 0.25(1)$ that places the investigated compound in the magnetically ordered region of the KAFM phase diagram [12]. Moreover, FTLM modeling provides a novel insightful view into the role of DM interaction in KAFM and allows the precise determination of D_z , which is responsible for the maximum in specific heat at $T_{\text{max}} = 16$ K related to the enhancement of 2D chiral spin correlations. 3D order is established via a small interlayer exchange below $T_N = 12$ K, where static internal magnetic fields appear [35].

To understand the magnetism of $\text{YCu}_3(\text{OH})_6\text{Cl}_3$, the first task is to determine its dominant isotropic exchange interactions. As in other kagome compounds [37–40], we tackle this problem using total-energy (broken-symmetry) DFT + U calculations [41] (for details see Ref. [18]). We

assume that each site is coupled with sites up to the third nearest neighbor in the kagome layer and with equivalent sites in the neighboring two kagome layers (Fig. 1). Our calculated exchange constants and the corresponding Weiss temperature $\theta_W = -\sum_i z_i J_i/4$, where z_i is the number of neighbors coupled to a particular site with J_i [42], depend on the effective on-site Hubbard repulsion U_{eff} [18]. θ_W is compared with its experimental value of $-99(1)$ K, which is obtained from a Curie-Weiss fit to the susceptibility data (inset in Fig. 2). The experiment is well reproduced for $U_{\text{eff}} = 6$ eV (Fig. 1), a value consistent with previous studies on similar materials [37–40]. We find that the exchange interaction between nearest neighbors $J_1 = 84.2(4)$ K by far exceeds all other Heisenberg interactions, as all of them are below 5% of J_1 , irrespective of the chosen value of U_{eff} [18].

Next, we focus on the temperature dependence of the magnetic susceptibility to verify that the calculated exchange constants are consistent with experiment. We first compare the experimental susceptibility [35] to a high temperature series expansion (HTSE) calculation for a simplified J_1 - J_2 - J_d model [43] in Fig. 2. The HTSE curve fitted in the temperature range between 100 and 300 K matches the experiment very well and yields the exchange constants $J_1 = 79.5(1)$, $J_2 = 2.8(27)$, and $J_d = 4.3(54)$ K. Furthermore, we can compare the experiment to FTLM calculations for a pure nearest-neighbor KAFM on a $N = 42$ spin cluster [44]. Good agreement is

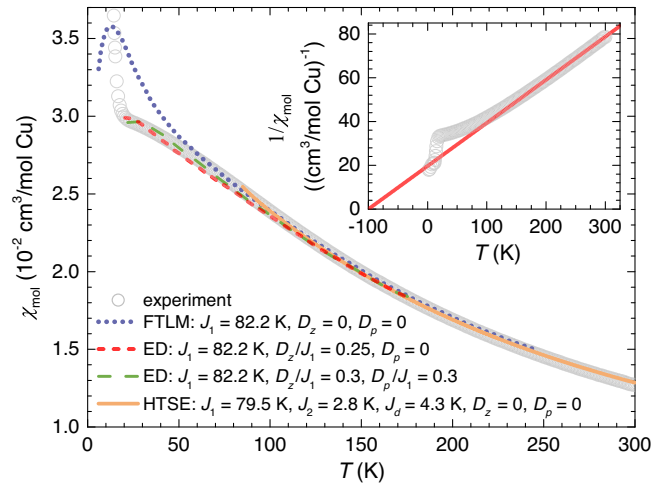


FIG. 2. Molar susceptibility χ_{mol} of $\text{YCu}_3(\text{OH})_6\text{Cl}_3$ in a field of 0.1 T [35], with its sharp increase at low temperatures indicating magnetic ordering. The solid line is a fit with the HTSE J_1 - J_2 - J_d model [43]. The dotted line shows FTLM calculations for isotropic KAFM on $N = 42$ sites [44]. The dashed lines are ED calculations with additional out-of-plane DM component D_z and in-plane component D_p for $N = 15$ sites [45], which are accurate to within 4% down to T_N [18]. The inset shows a Curie-Weiss analysis, $1/\chi_{\text{mol}} = (T - \theta_W)/C$, with the Weiss temperature $\theta_W = -99$ K and g factor $g = 2.077$.

obtained for temperatures down to $0.6J_1 \sim 50$ K with $J_1 = 82.2(1)$ K being the only free parameter (Fig. 2).

The fact that all three independent approaches yield very similar predictions, namely, a dominant Heisenberg exchange interaction $J_1 = 82(2)$ K, gives strong credibility to these results. As isotropic exchange interactions beyond the nearest neighbors are limited to at most 5% of J_1 , $\text{YCu}_3(\text{OH})_6\text{Cl}_3$ can be placed alongside herbertsmithite [38] as one of the best realizations of the nearest-neighbor KAFM. In all other well-studied examples, like kapellasite [37,39,43], haydeeite [37,39,46], volborthite [47], and vesignieite [48], further-neighbor interactions are much larger. As interactions $|J_2|, |J_3|, |J_d| \gtrsim 0.2J_1$ [5–7,9] or $|J'| \gtrsim 0.15J_1$ [8] are needed to induce magnetic ordering in the KAFM, these are evidently too small in $\text{YCu}_3(\text{OH})_6\text{Cl}_3$. The only remaining perturbation that can account for its ordered ground state is magnetic anisotropy. Since there are no symmetry restrictions [49], both the antisymmetric DM and the symmetric anisotropic exchange (AE) interaction are allowed. However, DM anisotropy is generally dominant in Cu^{2+} -based magnets because it is a one order lower correction to the isotropic exchange [49], so that the AE term is smaller by a factor $\Delta g/g \sim 0.2$ [50]. Here Δg is the shift of the g factor from the free electron value. Furthermore, as the easy-plane AE interaction that would be compatible with the observed planar magnetic order [36] does not lead to ordering of the KAFM [13,51], we expect the DM interaction to play a dominant role.

The next task is, therefore, to determine the DM interaction $\mathbf{D} \cdot (\mathbf{S}_i \times \mathbf{S}_j)$ between the nearest neighbors. First, we note that further-neighbor isotropic exchange interactions are too small to account for the large discrepancy between the experimental magnetic susceptibility and the nearest-neighbor FTLM calculations already at temperatures as high as $0.6J_1 \sim 50$ K (Fig. 2). On the contrary, a sizable DM interaction can explain this deviation. Indeed, according to exact-diagonalization (ED) calculations [45], the out-of-plane component D_z suppresses susceptibility compared to the isotropic KAFM, while the in-plane component D_p enhances it [18]. The experimental suppression is well reproduced for $D_z/J_1 = 0.25(1)$ all the way down to the ordering temperature if $D_p = 0$ (Fig. 2). For $D_p > 0$ a larger D_z is required [18], e.g., for $D_p/J_1 = 0.30$ one finds $D_z/J_1 = 0.30(1)$ (Fig. 2).

We can place further constraints on the magnitude of both DM components based on ESR results (for details see Ref. [18]), as magnetic anisotropy directly broadens the ESR spectra [52]. The measured spectra [18] are broader than in other Cu-based kagome compounds like herbertsmithite [30], vesignieite [53], and kapellasite [54] by almost an order of magnitude. Above 200 K the ESR linewidth is constant at $\Delta B = 6.8(5)$ T (inset in Fig. 3), which is consistent with the high-temperature paramagnetic regime and allows for the application of Kubo-Tomita (KT)

theory [55]. The well-established expression for the ESR linewidth on the kagome lattice [30,53] allows us to derive the $D_z(D_p)$ solution [18] shown in Fig. 3. Contrary to the case of susceptibility, which is affected oppositely by the two DM components, they both broaden the ESR linewidth. The total magnitude of the DM vector is therefore approximately limited by $D/J_1 \approx [2g\mu_B\Delta B/(\sqrt{\pi}k_B J_1)]^{1/2} = 0.36$, where k_B is the Boltzmann constant and μ_B is the Bohr magneton. The joint ESR and susceptibility analysis yields the limits $0.25 < D_z/J_1 < 0.29$ and $D_p/J_1 < 0.15$ (Fig. 3). We note, though, that in accordance with recent ED calculations demonstrating that the KT approach might somewhat overestimate the DM anisotropy on the kagome lattice [56], the true DM components should be closer to the lower limits, $D_z/J_1 = 0.25$ and $D_p/J_1 \approx 0$.

An independent check of the above estimates is provided by modeling previously published zero-field specific heat (c) data [35]. FTLM calculations [57,58] of the magnetic contribution to the specific heat c_m , which were performed on spin clusters with up to $N = 30$ spins for various D_z/J_1 and D_p/J_1 ratios (for details see Ref. [18]), reveal two well-resolved maxima in c_m for $D_z/J_1 \gtrsim 0.08$ [Fig. 4(a)], as previously also observed in ED calculations on smaller clusters [45]. A broad high-temperature maximum is, similarly to the spin-1/2 square lattice [59], found around $0.67J_1$ and does not shift with the DM interaction. Therefore, it is associated with the enhancement of nearest-neighbor spin correlations [60,61]. On the contrary, a much narrower low-temperature maximum shifts almost linearly with the out-of-plane DM component and is found

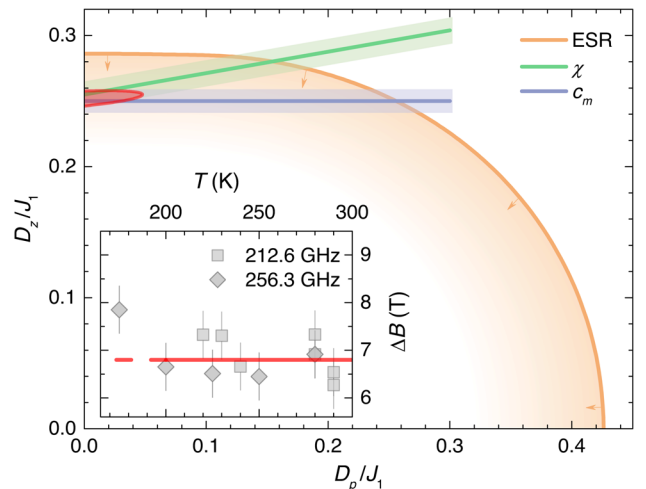


FIG. 3. The interdependence of both DM components in $\text{YCu}_3(\text{OH})_6\text{Cl}_3$ based on the analysis of the ESR linewidth (shown in the inset), magnetic susceptibility, and specific heat. Shaded regions show experimental uncertainty, while the arrows imply that ESR only gives an upper bound. The red area is the region with globally acceptable parameters, where the solid red line indicates the 1-sigma boundary.

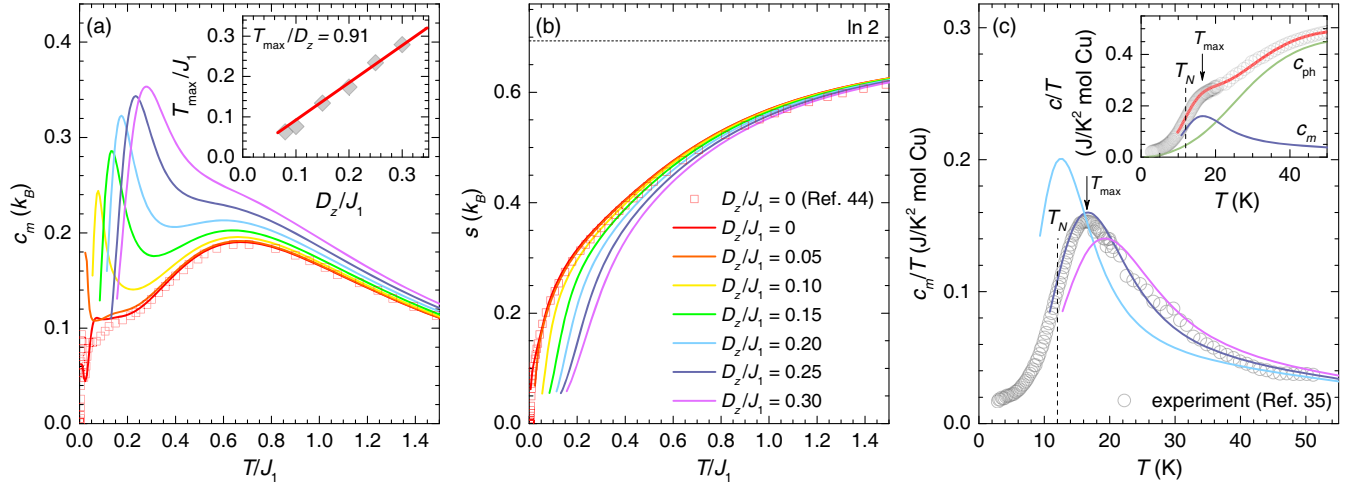


FIG. 4. The temperature dependence of (a) the magnetic specific heat c_m and (b) the entropy per site s in zero magnetic field obtained from the FTLM calculations on $N = 30$ spin clusters for various D_z values (lines). The data are shown only for temperatures where $s \geq 0.07k_B$ [18]. The results from Ref. [44] obtained on $N = 42$ spin clusters for $D_z/J_1 = 0$ are shown for comparison (symbols). The inset in (a) shows the variation of the low-temperature c_m maximum position T_{\max} with D_z/J_1 . (c) Selected FTLM calculations of c_m/T compared to the experimental data (circles). The inset shows the total specific heat of $\text{YCu}_3(\text{OH})_6\text{Cl}_3$ (circles; data taken from Ref. [35]) and the fit (red line) composed of the magnetic contribution for $D_z/J_1 = 0.25$ (blue line) and a phonon contribution (green line) [18]. The arrow indicates $T_{\max} = 16$ and the dashed line $T_N = 12$ K.

at $T_{\max} \simeq 0.91D_z$ [inset in Fig. 4(a)]. In sharp contrast, c_m is almost insensitive to the in-plane DM component at least up to $D_p/J_1 \leq 0.3$ [18,45]. As the D_z term linearly shifts the energy of the 120° spin structure of basic kagome triangles [36] while D_p does not, we attribute the low-temperature maximum to growing chiral spin correlations within the kagome planes. This makes specific heat a unique probe of the DM component D_z on the kagome lattice, which is much more sensitive [Fig. 4(c)] than magnetic susceptibility [18].

For $D_z/J_1 = 0.25$, the predicted magnetic specific heat nicely matches the experiment [Fig. 4(c)]. Indeed, we can fit the c/T data very well with the model $c = c_m + c_{\text{ph}}$ that includes a phonon contribution c_{ph} . The fit is already good for a simple Debye phonon model with the Debye temperature $\theta_D = 224(5)$ K and is further improved by including an additional Einstein phonon contribution [inset in Fig. 4(c)] [18], corresponding to a Raman active mode at 123 cm^{-1} , as found in structurally similar herbertsmithite [62]. The obtained $D_z/J_1 = 0.25(1)$ is in excellent agreement with the lower-bound estimate based on ESR and susceptibility modeling (Fig. 3) and thus provides further evidence that the in-plane DM component is much smaller, i.e., $D_p/J_1 < 0.05$. Although the DM anisotropy in $\text{YCu}_3(\text{OH})_6\text{Cl}_3$ is larger than in some other Cu^{2+} -based KAFM materials [30,53], its size is compatible with the order-of-magnitude estimate [49] $D_z/J_1 \sim \Delta g/g \sim 0.2$ for the Cu^{2+} ions [50].

Having established the main terms in the spin Hamiltonian of $\text{YCu}_3(\text{OH})_6\text{Cl}_3$, we are now in position to discuss the origin of its magnetic ordering. It is

theoretically well established that the out-of-plane DM interaction leads to a $q = 0$ long-range order of KAFM at zero temperature if its strength exceeds the critical value $D_z^c = 0.10(2)J_1$ [9,10,12,14] separating the spin liquid and the ordered phase. Contrary to the paradigmatic KAFM material herbertsmithite, which appears to be on the verge of criticality [30], we find that $\text{YCu}_3(\text{OH})_6\text{Cl}_3$ lies well inside the ordered phase. Nevertheless, the average ordered moment should be strongly suppressed due to quantum fluctuations. Indeed, the predicted moment of $0.35 \mu_B$ for $D_z/J_1 = 0.25$ [12] matches reasonably well with the experimental value of $0.42(2) \mu_B$ [36].

Finally, let us comment on the compatibility of our results with the celebrated Mermin-Wagner theorem [63], which precludes long-range order in the considered 2D model at nonzero temperatures due to continuous in-plane symmetry. As revealed by FTLM calculations, 2D short-range chiral order is established below $T_{\max} = 16$ K, while 3D order is only established below $T_N = 12$ K [Fig. 4(c)], where static internal magnetic fields appear, the longitudinal muon spin relaxation rate suddenly starts increasing and bulk susceptibility exhibits a clear cusp (see Fig. 6 in Ref. [18]). Finite T_N requires additional interlayer interactions J' and is determined by the growth of the in-plane correlation length ξ to the extent that the thermal energy drops below the interaction energy of short-range ordered 2D regions on neighboring kagome planes, when $T_N \approx [\xi(T_N)/d]^2 J' S(S+1)$, with d being the nearest-neighbor distance [60,61]. As ξ should only marginally depend on the interlayer interaction for $J'/J_1 \ll 1$ and thus T_N should only logarithmically depend on J' [59,61,64],

T_N is dominantly determined by D_z in $\text{YCu}_3(\text{OH})_6\text{Cl}_3$. This anisotropy promotes building up of 2D chiral spin correlations, which corresponds to effectively shifting a large release of the system's entropy to temperatures around $T_{\max} \approx D_z$ [Fig. 4(b)]. As a result, for $J'/J_1 \ll 1$ yielding $T_N < T_{\max}$ most of the entropy is already released around T_{\max} and the effective number of degrees of freedom involved in 3D ordering is significantly reduced, making the cusp in c_m at T_N unobservable [59]. Thus, 2D physics essentially prevails down to T_N and justifies the absence of any cluster-size dependence of the c_m curves in FTLM calculations [18].

In conclusion, $\text{YCu}_3(\text{OH})_6\text{Cl}_3$ turns out to be an extremely rare structurally perfect KAFM material, with the nearest-neighbor isotropic exchange interaction $J_1 = 82(2)$ K dominating all other isotropic interactions, while by far the most relevant perturbation is the out-of-plane DM anisotropy $D_z/J_1 = 0.25(1)$. This is determined from a perfect coincidence of the experiments and numerical calculations for the two most common bulk magnetic characterization techniques as well as ESR, which is unique in the field of frustrated magnetism. Such D_z/J places the system in the magnetically ordered part of the predicted phase diagram [12]. This provides an unambiguous experimental confirmation of the key role of the DM interaction in inducing magnetic order on the kagome lattice. Furthermore, now that this role is well understood, a sister compound $\text{Y}_3\text{Cu}_9(\text{OH})_{18}\text{OCl}_8$ with a slightly distorted kagome lattice and apparently a spin-liquid ground state [34] provides an ideal opportunity to study the effects of further perturbations. Since in this compound very similar exchange interactions and magnetic anisotropy as in $\text{YCu}_3(\text{OH})_6\text{Cl}_3$ are expected, the reasoning for its lack of magnetic ordering should be searched in deviations from perfect kagome symmetry.

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