Electronic Supplementary Information:
Rearrangement of Van-der-Waals Stacking and Formation of a Singlet State at $T = 90$ K in a Cluster Magnet

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1 Synchrotron powder diffraction analysis

Table 1 is a summary of Rietveld refinement parameters to $T = 300$ K synchrotron X-ray powder diffraction data shown in main text Fig. 1(a). Low temperature synchrotron X-ray powder diffraction data near liquid nitrogen temperatures shows no signs of symmetry lowering distortions despite a temperature reading of approximately 80 K near the sample. Rietveld refinement of the HT ($P3m1$) structure to the data near liquid nitrogen temperatures is shown in Fig. S1 and is summarized in Table 2. 80 K is far below the first-order phase transition in Nb$_3$Cl$_8$ ($\approx 90$ K)—the absence of any Nb$_3$Cl$_8$ LT phase, therefore, is attributed to sample heating from the 30 KeV ($\lambda \approx 0.41$ Å) incident X-ray beam. As is the case with the $T = 300$ K data, fitting the low temperature data to lower symmetry models ($P3$, $P3m$, $P3$, and $C2/m$) results in no improvement of the fit, either quantitatively or qualitatively.

Table 1: Nb$_3$Cl$_8$ Rietveld refinement to synchrotron X-ray ($\lambda = 0.4132$ Å) powder diffraction data at $T = 300$ K, shown in main text Fig. 1(a). The spacegroup is $P3m1$ (164) with lattice parameters $a = 6.74566(3)$ Å, $c = 12.28056(7)$ Å, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$. All sites are fully occupied, cell volume was calculated to be $V = 483.947(6)$ Å$^3$, and atomic displacement parameters were freely refined for all atoms. The fit quality is given by $R_{wp} = 11.34\%$, $R_p = 9.03\%$, and $\chi^2 = 3.286$. Errors are computed statistical uncertainties.

| Atom | Wyckoff position | x       | y       | z       | $U_{iso}(\text{Å}^2)$ |
|------|-----------------|---------|---------|---------|----------------------|
| Nb   | 6i              | 0.52763(2) | 0.05525(5) | 0.24577(5) | 0.00473(6) |
| Cl-1 | 2d              | 2/3     | 1/3     | 0.0978(2) | 0.0045(4)  |
| Cl-2 | 2d              | 1/3     | 2/3     | 0.3555(2) | 0.0085(5)  |
| Cl-3 | 6i              | 0.6696(2) | -0.1652(1) | 0.1350(1) | 0.0069(3)  |
| Cl-4 | 6i              | 0.3374(2) | 0.1687(1) | 0.3835(1) | 0.0103(3)  |

Table 2: Nb$_3$Cl$_8$ Rietveld refinement to synchrotron X-ray ($\lambda = 0.4132$ Å) powder diffraction data at $T \approx 90$ K, shown in Fig. S1. The spacegroup is $P3m1$ (164) with lattice parameters $a = 6.73255(2)$ Å, $c = 12.22222(5)$ Å, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$. All sites are fully occupied, cell volume was calculated to be $V = 479.777(4)$ Å$^3$, and atomic displacement parameters were freely refined for all atoms. The fit quality is given by $R_{wp} = 9.31\%$, $R_p = 7.61\%$, and $\chi^2 = 2.141$. Errors are computed statistical uncertainties.

| Atom | Wyckoff position | x       | y       | z       | $U_{iso}(\text{Å}^2)$ |
|------|-----------------|---------|---------|---------|----------------------|
| Nb   | 6i              | 0.52746(2) | 0.05493(4) | 0.24622(4) | 0.00182(4) |
| Cl-1 | 2d              | 2/3     | 1/3     | 0.0981(2) | 0.0024(3)  |
| Cl-2 | 2d              | 1/3     | 2/3     | 0.3560(1) | 0.0041(3)  |
| Cl-3 | 6i              | 0.6709(1) | -0.16456(6) | 0.13528(7) | 0.0023(2)  |
| Cl-4 | 6i              | 0.3359(1) | 0.16793(6) | 0.38192(8) | 0.0051(2)  |

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Figure S1: Nb₃Cl₈ Rietveld analysis of synchrotron X-ray diffraction data at liquid nitrogen (LN) temperatures. Black dots are data, red line is the calculated fit, blue line is the difference, tick marks are Bragg reflections for Nb₃Cl₈ (black) and a minor impurity, NbOCl₂ (orange, 0.5(2) wt%). The higher Q data are multiplied ×20 (4 ≥ Q ≥ 8) and ×100 (8 ≥ Q ≥ 12) to highlight the quality of the fit.

2 DFT band structure calculations

Figure S2: Band structure calculations on HT-Nb₃Cl₈ with (a) no spin polarization (SP), spin-orbit coupling (SOC), or Hubbard U, (b) SP but no SOC/U (c) SP and SOC but no U, and (d) SP, SOC, and U = 4 eV. The red highlighted bands in (a) are the highest occupied a₁ orbitals, which are split at the Γ-point from the formation of a bonding/anti-bonding pair and are far in energy (~1 eV) from the degenerate e orbitals. In (b)-(d), the total splitting of the a₁ band (blue) is due to antiferromagnetic order. The spin polarized calculations are initiated with the application of an applied field to break spin degeneracy. This results in calculations (b)-(d) converging with antiferromagnetic order where Nb₃Cl₁₃ cluster spins are oriented in the crystallographic c-axis. In (d), the antiferromagnetic band splitting is exacerbated by the electronic interaction induced by the Hubbard U.

Calculations on the high temperature (HT) structure of Nb₃Cl₈ were performed without spin-polarization [Fig. S2 (a)], with spin-polarization [Fig. S2 (b)], with spin-orbit coupling [Fig. S2 (c)], and with a Hubbard U term [Fig. S2 (d)], all of which display the same qualitative highest occupied molecular orbital (HOMO) splitting at the Γ point as in Fig. S2 (a). The calculations in Fig. S2 (b)-(d) have an additional splitting of the HOMO bands over the entire Brillouin zone originating from the formation of antiferromagnetic order between ferromagnetic planes. The onset of antiferromagnetic order in Fig. S2 (b)-(d) stems from the initial application of a magnetic field to split spin degeneracy despite a reduction of the applied field with subsequent calculation iterations and a convergence with no applied field. The application of a Hubbard U, Fig. S2 (d), is required to fully open the gap and predict insulating behavior. The splitting observed in the a₁ derived bands in these calculations is allowed due to the unit cell symmetry and there being an
even number of electrons per unit cell [1]. The large cluster interaction energy indicated by the width of the $a_1$ band ($\approx 200\text{ meV}$) clearly plays a key role in the collective transition from a triangular lattice $S = 1/2$ antiferromagnet to a system of static singlets.

The special points of the Brillouin zone used in the HT phase calculations are for a trigonal unit cell in the hexagonal setting and are $\Gamma = (000)$, $K = (\frac{1}{3} \frac{2}{3} 0)$, $M = (0 \frac{1}{3} 0)$, $A = (00 \frac{1}{2})$, $L = (0 \frac{1}{2} \frac{1}{2})$, and $H = (\frac{1}{3} \frac{1}{3} \frac{1}{3})$. The special points of the Brillouin zone for a monoclinic unit cell in the $C2/m$ space group with unique axis $b$, cell choice 1 used in the LT calculations are $V = (\frac{1}{2} 1 0)$, $Z = (\frac{1}{2} \frac{1}{2} 1)$, $\Gamma = (000)$, $A = (00 \frac{1}{2})$, $M = (\frac{1}{2} \frac{1}{2} \frac{1}{2})$, $L = (\frac{1}{2} 0 \frac{1}{2})$.

3 Spin-Peierls analysis

The transition into a spin-Peierls (SP) state is marked by an exponential decay of the magnetic susceptibility as a function of temperature [2]. The SP transition temperature depends on the magnetic interaction strength and the spin excitation gap in the SP state. Nb$_3$Cl$_8$ does not have an exponential decay into the low-temperature (LT) state—the first-order nature of the transition results in remnant domains of the HT phase upon cooling. Instead, a plot of magnetic susceptibility collected upon warming, Fig. S3, of the $c || \mu_0 H$ data [reproduced from main text Fig. 2 (a)] must be used in modeling the behavior of the bulk LT state. As can be seen in Fig. S3, the susceptibility data is flat in temperature (with the exception of the Curie tail in $T \leq 50\text{ K}$) up to the transition at $T \approx 100\text{ K}$. To test that the magnetic susceptibility from a SP state ($\chi_{\text{SP}}$) is varying minimally with temperature, a Curie-Weiss fit to the LT data up to $T = 50\text{ K}$ and $T = 100\text{ K}$ was performed to extract a value of $\chi_0 \approx \chi_{\text{SP}}$ for the two temperature regions, a deconvolution of the Curie tail contribution. Values of $\chi_0 = 0.8$ and $0.7 \times 10^{-4}$ emu-Oe$^{-1}$-mol f.u.$^{-1}$ are extracted for fits up to $T = 100\text{ K}$ and $T = 50\text{ K}$ respectively.

![Figure S3: Nb$_3$Cl$_8$ magnetic susceptibility data (black dots) as a function of temperature upon warming. The data at LT is a convolution of a Curie tail and the intrinsic behavior of the LT magnetic state of Nb$_3$Cl$_8$. The colored lines are calculations of the exponential behavior expected of a spin-Peierls state. As can be seen, a gap of at least $2\Delta = 1000\text{ K}$ must exist in order to observe the magnetic behavior of a spin-Peierls state in Nb$_3$Cl$_8$.](image)

The magnetic behavior of a SP state can be approximated by the exponential [3]

$$\chi_m = C e^{(-2\Delta/k_bT)} + \chi_o$$

where $\chi_m$ is the molar susceptibility, $C$ is the Curie constant, $2\Delta$ is the gap to the first excited state, $k_B$ is Boltzmann’s constant, and $\chi_o$ is the temperature independent contribution to the susceptibility. It is important to note that the
transition temperature between HT and LT states in Nb$_3$Cl$_8$ is not necessarily the spin-Peierls transition—since the transition in Nb$_3$Cl$_8$ is first-order, the HT and LT magnetic behaviors need not be related in any way. Assuming the LT state in Nb$_3$Cl$_8$ is a SP state, then calculations for various magnitudes of the spin gap show that the gap must be at least $2\Delta = 1000$ K in order reproduce the observed behavior. These calculations assume the Curie constant is the value extracted from the HT fit for a $s = 1/2$ system, $C = 0.484$ emu · K · mol $^{-1}$ · Oe $^{-1}$, and the temperature independent contribution is $\chi_0 = 0.8 \times 10^{-4}$ emu · Oe $^{-1}$ · mol $^{-1}$.

The magnitude of the spin gap may also be estimated, assuming LT Nb$_3$Cl$_8$ is a spin-Peierls state and the transition temperature $T_c = 100$ K, by examining the ratio of the susceptibility above and below the transition as is done in other SP materials such as CuGeO$_3$ [4]. Approximating $\chi_{HT}/\chi_{LT} \approx R$, and rearranging $R = e^{-\Delta/k_B T_c}$ to $\Delta = T_c \cdot \ln(R)$ with $R \approx 30$ gives $\Delta = 1000$ K · ln(30) = 340 K. This is on the same order as to what may be expected of a SP system, where the gap $\Delta \approx 1.5 \cdot T_c$.

We can also make an approximation of the exchange constant $J$ in the Nb$_3$Cl$_8$ spin-Peierls system from the spin-phonon coupling constant given by Cross and Fisher [5]. Here, $T_c = 0.8 \cdot J \cdot \eta$, or $J = \frac{T_c \cdot 1.25}{\eta}$. Assuming the value of $\eta$ used for CuGeO$_3$, $\eta = 0.2$, is used for Nb$_3$Cl$_8$, the calculation yields a $J = \frac{1000 \cdot 1.25}{0.2} = 625$ K—much larger than the value extracted from the Curie-Weiss fit to the HT susceptibility data of $\theta = 51.2$ K. This discrepancy may be indicative of a strong enhancement of the exchange constants upon entering the LT state from the structural rearrangement, or that a spin-Peierls model fails to adequately explain the magnetic behavior of Nb$_3$Cl$_8$.

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