Supplementary information:

Electron paramagnetic resonance and electric characterization of [CH₃NH₂NH₂][Zn(HCOO)₃] perovskite metal formate framework

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Electric Polarization

Figure S1: Electric field dependence of the electric polarization of 1 obtained along the axis perpendicular to the (035) plane at 168 and 178 K.
Figure S2: Inverse temperature dependence of the mean relaxation time. The observed linear behavior indicates Arrhenius-type temperature dependence: \[ \tau = \tau_\infty e^{-E_a/k_B T} \], where the activation energy \( E_a = 0.33(2) \text{ eV} \) and the attempt relaxation time \( \tau_\infty = 3.9(9) \times 10^{-16} \text{ s} \).
Additional EPR Data

Figure S3: (a) Simulated Q-band spectrum using $g = 2.0002$, $A_{\text{iso}} = -262$ MHz, $D = 1.8$ GHz and $E = 100$ MHz. The experimental spectrum of 2 is presented for comparison. In (b) the central fs transition is enlarged indicating a clear mismatch of the hf lines in comparison with the experiment. A clear discrepancy between the simulated and experimental spectra indicates that such spin Hamiltonian parameters are unsuitable to describe the main Mn$^{2+}$ species in 2.
Figure S4: Normalized room temperature X-band CW EPR spectra of manganese doped MHyZnF compound kept under dry and afterwards under wet conditions. Note the much stronger intensity of impurity Mn$^{2+}$ species in the wet sample.

Figure S5: (a) Two-pulse echo-detected field-sweep pulse EPR spectrum of 2 recorded at 25 K. (b) The corresponding first derivative spectrum. The arrow in (a) marks position at which the ESEEM, ENDOR and relaxation time measurements were performed.
Figure S6: Normalized temperature dependent X-band spectra of 2. Emphasis on (a) central and (b) outer transitions. Simulation of the 324 K spectrum is also presented in (a).

Figure S7: Temperature dependence of the axial zfs parameter of the impurity Mn$^{2+}$ species of 2. The values of $D$ were estimated from the width of the fs. Error bars are smaller than data points.
Figure S8: The kinetics of the longitudinal magnetization recovery of Mn$^{2+}$ ions in 2. The recovery is two-exponential at (a) 67 K, while it is single exponential at (b) 127 K. In (b) and (d) the corresponding magnetization kinetics are scaled by $\sqrt{t}$.

Figure S9: (a) Time and (b) frequency domain patterns of the two-pulse and three-pulse ESEEM experiments of 2 obtained at 25 K and 325 mT. In (b) the proton Larmor frequency and its double value are indicated by the arrows.
IR and Raman data

Low-frequency temperature-dependent Raman spectra of 2 were measured using a Renishaw InVia Raman spectrometer equipped with a confocal DM 2500 Leica optical microscope, a thermoelectrically cooled CCD as a detector, Eclipse filter, a diode laser operating at 830 nm and a Linkam cryostat cell THMS600. Far-IR temperature-dependent IR spectra were measured using a Biorad 575C FT-IR spectrometer and a helium-flow Oxford cryostat. The spectral resolution of Raman and IR spectra was 2 cm$^{-1}$.

Temperature-dependent Raman and IR spectra of 2 are presented in Figures S10 and S11. Among the observed bands, only those observed near 440 and 270 cm$^{-1}$ can be attributed to internal modes, i.e., $\delta$(CNN) and $\tau$(CH3) modes. The remaining bands correspond to the lattice modes, that is, translations of MHy$^+$, HCOO$^-$ and Zn$^{2+}$/Mn$^{2+}$ cations as well as librational motions of MHy$^+$ and HCOO$^-$ cations. Lattice dynamic calculations performed for related [(CH$_3$)$_2$NH$_2$][Ni(HCOO)$_3$] framework compound showed that the lattice modes are strongly coupled.$^1$ Nevertheless, we propose assignment of the lattice modes of 2 based on some observations of Raman and IR spectra for related framework compounds.$^{2-4}$ Firstly, librational modes of the HCOO$^-$ ions give rise to strong Raman and weak IR bands whereas...
opposite behavior is observed for T'(HCOO−) modes. Secondly, librational and translational modes of protonated amines are observed as weak bands, usually below 200 cm\(^{-1}\). Thirdly, translations of divalent cations contribute significantly to the modes observed in the 200-400 cm\(^{-1}\) range.

Temperature-dependent spectra show three major features upon cooling. Firstly, Raman and IR bands remain broad down to 180 K but exhibit strong narrowing below 160 K. Secondly, many bands split at low temperature into a few components and some additional weak bands appear. Thirdly, all bands exhibit hardening with decrease of temperature in the 300-180 K range and softening as \(T_c\) is approached from below. The narrowing and splitting of bands confirms that 2 undergoes an order-disorder phase transition associated with significant decrease of symmetry. Lack of any pronounced softening upon cooling is also consistent with an order-disorder character of the phase transition.
Figure S11: (a) Temperature-dependent Raman spectra of 2 in the 30-300 cm$^{-1}$ range, (b) temperature dependence of selected Raman wavenumbers and (c) temperature dependence of FWHM for the 194 cm$^{-1}$ (blue), 159 cm$^{-1}$ (magenta), 140 cm$^{-1}$ (green) and 111 cm$^{-1}$ (red) Raman bands.
Figure S12: (a) Temperature-dependent IR spectra of 2 in the 100-475 cm\(^{-1}\) range, (b) temperature dependence of selected IR wavenumbers and (c) temperature dependence of FWHM for the 297 cm\(^{-1}\) (magenta), 201 cm\(^{-1}\) (green), 164 cm\(^{-1}\) (blue) and 143 cm\(^{-1}\) (red) bands.
References


