

Figure S1. χT vs. T and $1/\chi$ vs T plots for $[\text{Ni}(\text{HF}_2)(\text{pyz})_2]\text{PF}_6$ (**1**). The green line is a fit of the reciprocal magnetic susceptibility data to a Curie-Weiss law [$g = 2.043(1)$ and $\theta = -12.5(1)$ K].

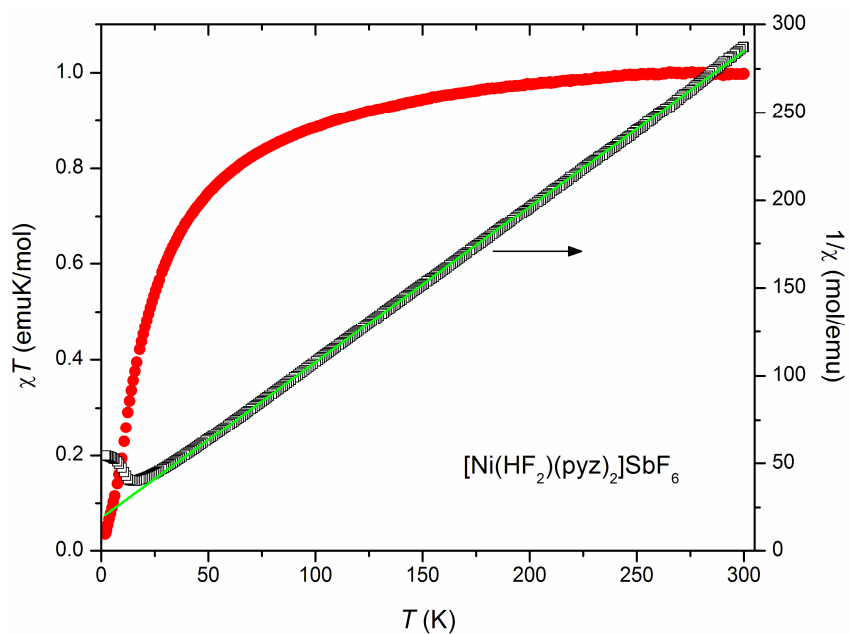


Figure S2. χT vs. T and $1/\chi$ vs T plots for $[\text{Ni}(\text{HF}_2)(\text{pyz})_2]\text{SbF}_6$ (**2**). The green line is a fit of the reciprocal magnetic susceptibility data to a Curie-Weiss law [$g = 2.081(1)$ and $\theta = -21.42(2)$ K].

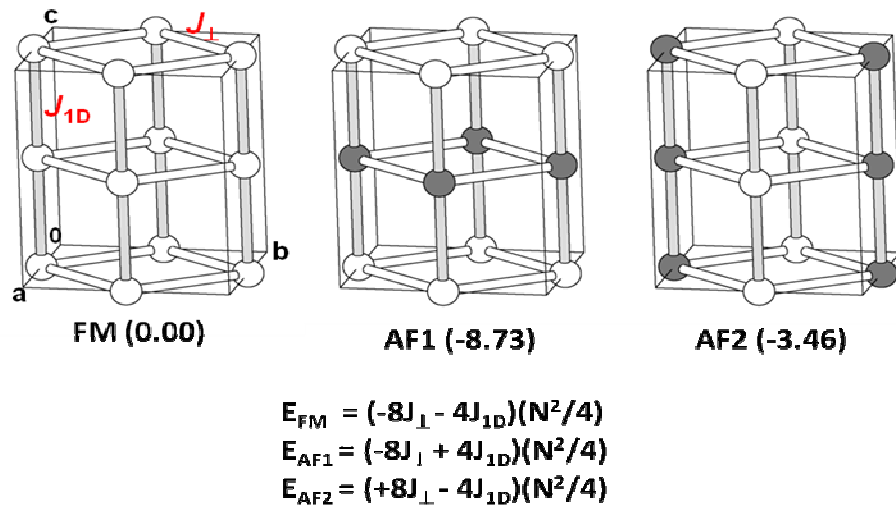
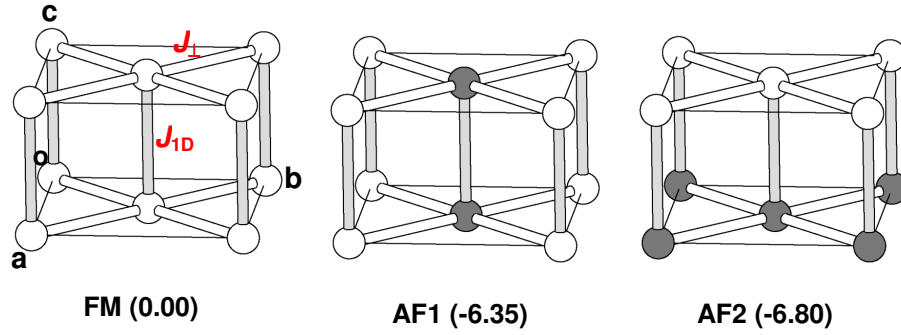


Figure S3. Three ordered spin states of $[\text{Ni}(\text{HF}_2)(\text{pyz})_2]\text{PF}_6$ (**1**) used to extract the two spin exchanges J_{\perp} and $J_{1\text{D}}$ considered, where the up-spin and down-spin Ni^{2+} sites are indicated by white and grey circles, respectively. The number in each parenthesis refers to the relative energies (in meV per 4 formula units) obtained from the GGA+U calculations with $U = 4$ eV. The total spin exchange energies (per 4 formula units) of the three ordered spin states, expressed in terms of J_{\perp} and $J_{1\text{D}}$, are also given.



$$E_{\text{FM}} = (-4J_{\perp} - 2J_{1\text{D}})N^2/4$$

$$E_{\text{AF1}} = (+4J_{\perp} - 2J_{1\text{D}})N^2/4$$

$$E_{\text{AF2}} = (-4J_{\perp} + 2J_{1\text{D}})N^2/4$$

Figure S4. Three ordered spin states of $[\text{Ni}(\text{HF}_2)(\text{pyz})_2]\text{SbF}_6$ (**2**) used to extract the two spin exchanges J_{\perp} and $J_{1\text{D}}$ considered, where the up-spin and down-spin Ni^{2+} sites are indicated by white and grey circles, respectively. The number in each parenthesis refers to the relative energies (in meV per 2 formula units) obtained from the GGA+U calculations with $U = 4$ eV. The total spin exchange energies (per 2 formula units) of the three ordered spin states, expressed in terms of J_{\perp} and $J_{1\text{D}}$, are also given.