Supplemental information

Slowing magnetic relaxation

with open-shell diluents

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Supplemental Experimental Procedures

General considerations

All synthetic methods were carried out under an inert N₂ atmosphere inside of a VigorTech brand glovebox. Anhydrous metal(II) chloride salts were prepared following literature procedure.¹ Acetonitrile (CH₃CN) was dried using a commercial solvent system and stored in the glovebox over dried 4 Å molecular sieves for 48 h prior to use. Molecular sieves were activated by heating to 285 °C under reduced pressure overnight before being stored in the glovebox. Tetraphenylphosphonium bromide was recrystallized from acetone and dried under reduced pressure at 70 °C overnight before being pumped into the glovebox for storage. Benzene thiophenol (HSPh) and potassium tert-butoxide (KO-tBu) were purchased from Sigma Aldrich and used as received.

Synthetic Methods.

Preparation of (Ph₄P)₂[M(SPh)₄] (where M = Co, Ni, Fe, Mn, and Zn) was performed according to previous literature methods for the synthesis of Co by substituting the appropriate MCl₂ salt.² Subsequent dilutions were prepared similarly, starting with the desired mixed stoichiometry of MCl₂ and CoCl₂ salts. Successful co-crystallization of the dilution samples was confirmed via Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and comparison of powder x-ray diffraction patterns to the pure 1 (see Fig S22). Of note, it was found that initial stoichiometry of MCl₂ salt frequently did not directly correlate to final stoichiometry of the crystalline samples. For example, the 2:1 Ni:Co dilution was prepared beginning with a 1:1 Ni:Co solution, while the 9:1 Ni:Co dilution was prepared beginning with a 10:1 Ni:Co stoichiometry. Throughout the course of dilution synthesis, it was observed that more accurate final dilution concentrations were obtained when the CoCl₂ to be added was taken from a stock solution of CoCl₂ in acetonitrile, and the solutions were kept at an elevated temperature (48 °C) for the first hour after adding (Ph₄P)₂[SPh] to the MCl₂ solution. Although some of the inaccuracy may be the result of small fluctuations caused by static build up in the solutions, the inconsistency of incorporation for all diluents suggests that to some extent co-crystallization does not occur at the same rate between different species of the metal thiophenol complexes, and thus ICP-OES must be used to determine the actual extent of incorporation prior to analysis.

(Ph₄P)₂[Co₁.0Ni₂.1(SPh)₄] (1:2 Co:Ni): To 1 mL of a 0.06 mM solution of anhydrous CoCl₂ in acetonitrile was added 7.78 mg (0.06 mmol) of anhydrous NiCl₂ and then diluted with acetonitrile to a final volume of 2 mL. This solution was stirred and heated at 45 °C to increase solubility of NiCl₂. KSPh (0.88 mmol) was generated through the stoichiometric reaction of 98.7 mg KO-tBu and 90.36 µL of HSPh in 2 mL of MeCN to yield a white slurry. 371.0 mg (0.87 mmol) of (Ph₄P)Br was heated with stirring in 2 mL acetonitrile to give a colorless solution. The solution of (Ph₄P)Br was added to the KSPh slurry and an immediate color change to yellow was observed and a fine white precipitate formed. The solution was filtered over Celite to remove the white solid and the resulting yellow solution of (Ph₄P)₂[SPh] was then added to the hot solution of chloride salts with stirring. The reaction immediately turned a deep green and slowly became a dark reddish-brown over the course of several minutes. Once all remaining NiCl₂ was seen to have been dissolved into solution (~1 hr) the vial was removed from heat and allowed to sit undisturbed overnight in the glovebox. Upon decanting, a single gigantic crystal (2 cm x 1 cm) formed in the bottom of the vial. The single crystal was rinsed with Et₂O (2 x 2 mL) and dried under vacuum. ICP-OES: Ni: 67.4% Co: 32.6%. Powder X-ray diffraction data indicate the same crystal structure as for pure (Ph₄P)₂[Co(SPh)₄] (Fig. S3).

(Ph₄P)₂[Co₁.0Ni₁.9(SPh)₄] (1:9 Co:Ni): Same procedure as for above except the starting stoichiometry for NiCl₂ and CoCl₂ was 14.1 mg (0.109 mmol) to 1.41 mg (0.0109 mmol) respectively. Block-like, red/brown crystals grew overnight. ICP-OES: Ni: 90.1%, Co: 9.9%. Powder X-ray diffraction data indicate the same crystal structure as for pure (Ph₄P)₂[Co(SPh)₄] (Fig S3).

(Ph₄P)₂[Co₁.0Ni₃.8(SPh)₄] (1:34 Co:Ni): Same procedure as above except CoCl₂ was massed out as a solid before being dissolved in acetonitrile with NiCl₂. The starting stoichiometry for NiCl₂ and CoCl₂ was 14.1 mg (0.109 mmol) and 3.04 mg (0.023 mmol) respectively. Small, block-like red/brown crystals grew overnight. ICP-OES: Ni: 97.1% Co: 2.9%. Powder X-ray diffraction data indicate the same crystal structure as for pure (Ph₄P)₂[Co(SPh)₄] (Fig S3).
In the process of fitting, we tried various methods for parameterizing the magnetic susceptibility fits and comparing the results. Values were generally considered to be high due to the unaccounted contributions of the diluents, but the values were generally in agreement with previously published magnetic data for pure compounds. The susceptibility measurements were collected using a Quantum Design MPMS SQUID magnetometer. Samples were prepared by placing finely ground, microcrystalline samples into a gelatin capsule, restraining the powder with molten eicosane and finally wrapping the capsule in Teflon tape. Direct-current (dc) measurements were obtained with a 1000 G applied field and temperatures ranging from 1.8 K to 300 K. All DC measurements were corrected for the diamagnetic contribution of the sample holder, as well as the restraining material and ligand framework (calculated using Pascal’s constants). Alternating-current (ac) susceptibility measurements were collected at the parameters described in the main paper as well as the figures presented below. For AC susceptibility measurements of dilutions, all values of $\chi_M^{'''}$ and $\chi_M^{''''}$ are given per moles Co$^{2+}$, as determined by ICP analyses. $\chi_M^{'''}$ values calculated utilizing this dilution factor would appear artificially high because of the unaccounted contributions of the diluents, but $\chi_M^{'''}$ values were, generally, in agreement with previously published magnetic data for pure Co and Zn(SPh)$_4$-dilutions. Thus, in Figs. S9-S13, values of $\chi_M^{'''}$ and $\chi_M^{''''}$ are reported as those of the contained Co for best comparison. For DC susceptibility of pure compounds this strategy was not necessary, and good fits were found considering the total number of moles present in each sample. $\chi_M^{TT}$ fits were calculated using the PHI software suite and associated spin Hamiltonian by parameterizing the anisotropic gyromagnetic ratios ($g_r$, $g_v$, and $g_d$), the zero field splitting ($D$) and the transverse anisotropy ($E$). Fits for $\chi_M^{''''}$ were generated through the Origin software suite fitting package by using the following Cole-Cole equation (1.1) and parameterizing $\tau$, $\alpha$, $\chi_T$ and $\chi_S$. Initial guess values were estimated from the $\chi_M^{TT}$ graphs.

$$\chi''(\omega) = (\chi_T - \chi_S) \frac{(\omega \tau)^{1-a} \cos \frac{\pi a}{2}}{1 + 2(\omega \tau)^{1-a} \sin \frac{\pi a}{2} + (\omega \tau)^{2-2a}}$$

(1.1)

Details of Magnetic Susceptibility Fitting. $\chi_M^{TT}$ fits were performed using the PHI software suite and the following spin Hamiltonian:

$$\hat{H} = \mu_B B [g] S + D \left( S_z^2 - \frac{1}{3} S(S+1) \right) + E \left( S_x^2 - S_y^2 \right)$$

In the process of fitting, we tried numerous models as we balanced the desire to obtain new fits with not overparameterizing the models. Hence, we tested isotropic and anisotropic gyromagnetic ratios ($g_r$, $g_v$, and $g_d$), the zero field splitting ($D$) and the transverse anisotropy ($E$). Fits for $\chi_M^{''''}$ were generated through the Origin software suite fitting package by using the following Cole-Cole equation (1.1) and parameterizing $\tau$, $\alpha$, $\chi_T$ and $\chi_S$. Initial guess values were estimated from the $\chi_M^{TT}$ graphs.
inclusion of the quartic term with $g_z$, positive/negative values of zero field splitting $(D)$ and positive/negative values of the transverse anisotropy $(E)$.

In the case of Ni, it was found that fitting with an isotropic $g$ gave a reasonable quality fit without having to invoke anisotropy in $g$. For Co, Fe, and Mn, attempts to fit with an isotropic $g$ were attempted, but anisotropic $g$ values gave much better fits.

**Details of Temperature-Dependent Magnetic Relaxation Time Fitting.** Relaxation time data ($\tau$) were fit with equation (1.2) in Origin:

$$1/\tau = AT^n + 1/\tau_{\text{QTM}}$$  \hspace{1cm} (1.2)

Here, $A$ is a weighting factor for the contribution of the Raman process in magnetic relaxation at a given temperature, $n$ is the Raman exponent, and $\tau_{\text{QTM}}$ is the time of the quantum tunneling of the magnetization. Selection of these two relaxation processes for fitting followed the elimination of the other alternatives. The direct process, for which $1/\tau \propto B^{-4}$, was omitted because the complexes are being analyzed at 0 G DC magnetic field, and the rate of the process would hence be too slow to contribute.\(^5\) The Orbach process\(^6\) was omitted because there is no clear linear region in the Arrhenius plots (see Fig. 3). Importantly, previous attempts to fit the variable-temperature $\tau$ data for 1 using the Orbach process extracted “$U_{\text{eff}}$” $\approx$ 20 cm$^{-1}$, though that value falls far lower than 2D for the complex (the minimum value of $U$ possible and $> 100$ cm$^{-1}$), indicating that the process is likely not actually dominant at these temperatures.\(^7\) Other relaxation mechanisms, e.g. from local vibrational modes,\(^8\) or other thermally activated processes\(^9\) were omitted because these mechanisms are typically active only at $T > 100$ K. The best fit parameters are summarized in Table S2. Fitting the equation to the data produced better fits when ln($\tau$) was used for computing residuals as opposed to $\tau$.

**Electron Paramagnetic Resonance Measurements and Fitting Details.** High-frequency EPR spectra on (Ph$\downarrow$P)$_2$[Fe(SPh)$_4$] and (Ph$\downarrow$P)$_2$[Ni(SPh)$_4$] were recorded with a home-built spectrometer at the EMR facility of NHMFL. The instrument is a transmission-type device in which waves are propagated in cylindrical light-pipes. The microwaves were generated by a phase-locked oscillator (Virginia Diodes) operating at a frequency of 8-20 GHz and generating its harmonics, of which the 4th, 8th, 12th, 16th, 24th and 32nd were available. A superconducting magnet (Oxford Instruments) capable of reaching a field of 17 T was employed.\(^10\) Samples of (Ph$\downarrow$P)$_2$[Fe(SPh)$_4$] were ground to a fine powder in a glovebox prior to use for sample prep. This grinding was implemented as the “grass pattern” of peaks observed in some of the HF-EPR spectra (Fig. S3).

Samples of (Ph$\downarrow$P)$_2$[Mn(SPh)$_4$] used for EPR analyses were ground into a fine powder inside of an inert atmosphere glovebox and loaded into a quartz EPR tube (Wilmad 707-SQ-250M) and sealed with a septum. The EPR tubes were then quickly transported to a high vacuum schlenk line and sealed under dynamic vacuum (~100 mTorr). Room temperature EPR spectra were recorded on a Bruker ESR-300 spectrometer (Bruker Biospin, Rheinstetten, Germany) at 9.838 GHz with fields ranging from 0-600 mT.

HF-EPR spectra for Fe were fit using the program SPIN locally developed at the National High Magnetic Field Laboratory. A standard spin Hamiltonian for $S = 2$ was used:

$$\hat{H} = \mu_B \mathbf{B}[g]S + D \left\{ S_z^2 - \frac{1}{3} S(S + 1) \right\} + E \left\{ S_x^2 - S_y^2 \right\} + B^0_z O_z^0 + B^4_z O_4^z$$

To determine the parameters, multiple spectra were recorded at various microwave frequencies and the positions of the canonical resonances were fitted (Fig. S3). Powder spectra were subsequently simulated showing very good agreement with the experiment. The fitting procedures resulted in $g_x = 2.051(1)$, $g_y = 2.095(1)$, $g_z = 2.010(1)$, $D = +5.684(1)$ cm$^{-1}$, $E = +1.428(1)$ cm$^{-1}$, $B^0_z = -7.8(4) \times 10^{-4}$ cm$^{-1}$. Inclusion of the quartic term with $B^4_z$ significantly improved the fit, while no improvement resulted from taking $B^0_z$ into account. It was thus assumed to be zero.

Fitting of the 381 GHz and X-Band spectra for Mn was performed with the EasySpin\(^11\) program in MatLab\(^12\) with the pepper function for solid-state EPR. The following spin Hamiltonian was used:

$$\hat{H} = \mu_B \mathbf{B}[g]S + D \left\{ S_z^2 - \frac{1}{3} S(S + 1) \right\} + E \left\{ S_x^2 - S_y^2 \right\} + \text{IAS}$$
The following parameters were used to fit the experimental data $g_x, g_y, g_z, D, E$, and isotropic line broadening. HF-EPR spectra of Mn were simulated holding the $A$ value isotropic ($A_{iso} = 252$ MHz) and approximately the same magnitude as is generally observed for Mn$^{2+}$ ions.$^{13}$ Note that although peak intensities in the simulation are not in perfect agreement, this is likely due to mismatch in the precise broadening mechanism. At these high fields/frequencies, the field positions of the peaks are, however, robust. The field positions (not the intensities) are what ultimately give the $g, D$, and $E$ parameters utilized in our interpretation. Thus, the spin Hamiltonian parameters determined from the simulation are highly accurate, even if the simulated intensities are off. The simulated spectra for Fe were calculated by full diagonalization of the electronic Hamiltonian using the ‘matrix’ method in pepper. In contrast, the Mn spectra were computed by full diagonalization of the electronic Hamiltonian and first-order perturbation of the nuclear spins. This method offers significant reduction in computational time and generated identical spectra to the full diagonalization for this complex.

**Powder X-Ray Diffraction.** Powder X-Ray Diffraction patterns were obtained using a Bruker D8 Discover Series II diffractometer utilizing the LYNXEYE detector and a CuKα radiation source at 1600W (40 kV, 40mA). Samples were prepared in an inert atmosphere glovebox by loading 0.6mm diameter quartz capillaries with uniformly powdered sample and sealed using capillary wax before being centered on the goniometer. All patterns were collected from $2\theta = 5-50^\circ$, with a 0.02° increment, and a 1 sec exposure time.

**Other Physical Methods.** ICP-OES was carried out using a PerkinElmer Optima 7300 DV and the TOPM standards program in the Plant and Soil Science Laboratory at Colorado State University. All samples and reference standards were prepared by digesting in HNO$_3$ and diluting to 10% HNO$_3$ by volume with HPLC grade H$_2$O (filtered through 0.2 µm filter) and subsequent filtering of the digested sample through a glass fiber filter. Scanning electron microscopy (SEM) analysis was performed on a JEOL JSM-6500F field emission electron microscope at a working voltage of 15.5 kV and with an Oxford X-Max 80 mm$^2$ EDS detector. Samples were prepared on aluminum pucks inside of an inert atmosphere glovebox by placing finely ground polycrystalline samples on a small piece of carbon tape and subsequently removing any non-adhered crystallites. Once prepared, samples were transported to the SEM stage under a blanket of N$_2$ before being quickly loaded into the reduced pressure sample chamber. Minimal degradation has been observed on this timescale (based on PXRD patterns). Due to the polycrystalline nature of the samples, care was taken to only analyze crystallites which presented flat surfaces. EDS mapping of imperfectly aligned crystallites produced unreliable measurements.
Note S1: Additional Discussion of Sample Homogeneity. Sample homogeneity in the analyzed materials was arrived at from the aggregate of multiple structural techniques. First, PXRD data demonstrate that the cocrys tallizations do not produce new crystalline phases of materials. However, the overlap of the diffraction patterns means that the technique can not differentiate between mixtures of pure crystals versus crystals that contain mixtures of metals within their habits. The former possibility, in particular, is likely not the case on the basis of sample color. Dilutions of Co (green crystals) in Zn (white/colorless crystals) do not produce separate green and white crystals, but rather a homogeneous (by eye) collection of lighter-green crystals than the starting Co. Similarly, the other dilutions produce crystals that are colored as a mix of the two pure materials. Furthermore, our preliminary EDS analyses show that there is distribution of Co in the diluent crystals. Although EDS analysis of polycrystalline samples cannot provide excellent accuracy due to sample orientation, our initial analysis suggests reasonable homogeneity on µm length scales from crystallite to crystallite. Finally, the magnetic analyses suggest effective dilution: In the fitting of the individual variable-frequency scans, the parameter from the Cole-Cole equation describes the distribution in relaxation times for the sample, but practically correlates to the width of the $\chi''$ peak (in frequency space). For pure Co, $\alpha$ increases from 0.025 at 6.5 K to 0.276 at 2 K, indicating that upon transition to the tunneling regime, there are more potential relaxation times available to $[\text{Co(SPh)}_4]^2^-$. Upon dilution in Ni, $\alpha$ increases with increasing concentration of $[\text{Ni(SPh)}_4]^2-$: 0.384, 0.56, and 0.58 for 1:2, 1:9 and 1:34 dilutions of Co in Ni, respectively. This increase in $\alpha$ mirrors what typically happens when Co is dissolved in Mn, Fe, and Zn (Table S4). This increase is likely due to a measure of inhomogeneity at the nanometer scale in the solid solution phases of the dilutions, as varying local concentrations of open-shell bath molecules in the immediate environment would then impart varying impacts on $\tau_{QTM}$, and hence, a spread in the relaxation times.

Additional Discussion of Chemical Pressure Effects. Upon dilution of $[\text{Co(SPh)}_4]^2-$ in the various (Ph₃P)₃[M(SPh)]₄ matrices, the surrounding matrix can be expected to impart a "chemical pressure" on the Co coordination environment to make it resemble that of the host $[\text{M(SPh)}_3]^2-$ structure. The potential features of the Co ion that could change in response to this pressure are Co–S bond distances, S–Co–S angles (of the "pinched tetrahedron") and the dihedral angles between the two pinched CoS₂ planes of the tetrahedron. These proposed structural changes from chemical pressure are likely slight, owing to the similarity between the structures of the $[\text{M(SPh)}_3]^2-$ (M = Mn, Fe, Co, Ni, and Zn) complexes.

Importantly, although changes in chemical pressure may lead to some variance in the coordination environment, these effects do not appear to contribute significantly to the relaxation of $[\text{Co(SPh)}_4]$ diluted in its isostructural analogues. For the changes in the bond and dihedral angles, prior computations demonstrate that the rhombicity is insensitive to the possible 2-to-3° variation in S–Co–S bond angles and 1° variation in dihedral angles driven by chemical pressure. Hence, changes in angles are likely not the cause of the effective changes in the tunneling relaxation rate via rhombicity modification.

Furthermore, the trends in relaxation times are inconsistent with expected outcomes of changes in bond distances, suggesting that chemical pressure effects on bond distances are also not responsible for the relaxation effects. For example, the M–S bond distances of $[\text{M(SPh)}_3]^2-$ are longer than $[\text{Co(SPh)}_4]^2-$ (2.43(1) Å vs 2.33(1) Å, respectively). Thus, if chemical pressure were operative, the magnitude of the zero-field splitting for $[\text{Co(SPh)}_4]^2-$ should increase with weaker ligand field splitting (as is the general trend), thus enabling slower relaxation for $[\text{Co(SPh)}_4]^2-$ embedded in the $[\text{Mn(SPh)}_3]^2-$ diluent. This expectation is the opposite of what we observe from magnetic measurements. A similar argument can be made for the Ni diluent, the Ni–S distances of $[\text{Ni(SPh)}_4]^2-$ are shorter than the Co–S distances of $[\text{Co(SPh)}_4]^2-$, suggesting that, if chemical pressure effects were important, that Co would have a stronger ligand field when embedded in $[\text{Ni(SPh)}_4]^2-$ and thus, weaker zero-field splitting and faster relaxation. For both of these cases, the effects of chemical pressure on the magnetic relaxation processes are opposite of what we observed, suggesting a different mechanism is responsible for the observed changes.

Note S2: Additional NMR Analyses.

As an alternative hypothesis to the $S_{\text{eff}} = 0$ interpretation in the text, we tested whether the true operative effect of the bath could be less dependent on spin magnitude than the timescale of the fluctuations of the $[\text{M(SPh)}_3]^2-$ bath spins. Ample literature evidence demonstrates that half-filled shell ions like Mn⁶⁺ and Gd²⁺
tend to have orders of magnitude longer magnetic relaxation times than integer spin systems.\textsuperscript{20} Hence, the Mn bath spins may exhibit slow enough relaxation to enable interaction with Co and facilitate tunneling. In contrast, the integer-spin Fe and Ni bath spins, which could have significantly faster relaxation, are decoupled from Co and ineffective at modulating the tunneling process. Preliminary solid-state magic angle spinning \( ^1\text{H} \) nuclear magnetic resonance spectra on Mn, Fe, Ni, and Zn (see below, Figs. S19 and S20) suggest that this is not the case, but further investigations at low temperature are warranted.

**Solid-State Nuclear Magnetic Resonance Measurements and Fitting Details.** Solid-state \( ^1\text{H} \) NMR spectra were obtained using a CMX-Infinity (Chemagnetics, Fort Collins, CO USA) spectrometer operating at 8.5 T (360 MHz for \( ^1\text{H} \)) employing a single-resonance probe, using a 4.0 mm (rotor diameter) MAS module with a spinning speed of 15 kHz and using a rotating-frame RF intensity of 62.5 kHz (4.0 \( \mu \)s \( \pi/2 \) pulse). As the probe exhibits a significant \( ^1\text{H} \) background (relative to the signal obtained from the samples studied here), it was necessary to experimentally suppress the background. This was accomplished with the so-called DEPTH method\textsuperscript{21} that utilizes a number of \( \pi \) pulses with systematically varied rotating-frame phases to preserve the sample’s legitimate signal (which arises in the more intense rotating-frame RF field in the center of the sample coil) and suppresses the background signal (which arises in the less intense rotating-frame RF field surrounding the sample coil). Saturation recovery data were collected by first saturating all \( ^1\text{H} \) magnetization using ten \( \pi/2 \) pulses of constant phase, each spaced out at roughly \( 1/4 \) of the MAS rotation period (16.6 \( \mu \)s), followed by a systematically varied interval to permit re-establishment of the Boltzmann magnetization, and lastly followed by a DEPTH-3 sequence (one \( \pi/2 \) and two \( \pi \) pulses) to observe the then-recovered magnetization with background suppression.\textsuperscript{21}

Magnetization recovery time plots were fit by employing the single exponential rise equation [1.3]

\[
m(t) = m(\infty) \times (1 - \eta e^{-t/T_1})
\]

Here \( m(t) \) is the magnetization intensity at time \( t \), \( m(\infty) \) is the predicted magnetization intensity at infinity, \( \eta \) is the efficiency of magnetization saturation, and \( T_1 \) is the spin lattice relaxation. The magnetization \( m(t) \) was taken from recorded spectra and both \( m(\infty) \) and \( T_1 \) were parametrized and extracted from the best fit line to the recorded data. In the case of Co and Ni the magnetization recovery appears to have two relaxation regimes which were fit independently using equation [1.3]. Reported \( T_1 \) values for these complexes are the average of the two extracted \( T_1 \)s. The relaxation of Fe does not appear to follow an easily interpretable monoeponential behavior, highlighted in Fig. S15. Hence, it is difficult to directly quantitate \( T_1 \) for comparison between the molecules in this study, and deeper analyses will ultimately be pursued to enable understanding.

Our initial rationale was that a faster \( ^1\text{H} \) relaxation rate would evidence a more dynamic electron spin bath and potentially correlate to impact on relaxation in Co.\textsuperscript{22} Each species shows a single, broad peak (Fig. S19) in the \( ^1\text{H} \) spectrum centered around 6.5 ppm (\( ^1\text{H} \) chemical shift relative to TMS). Preliminary saturation recovery experiments performed on this peak (see SI and Fig. S20) reveal a range of \( ^1\text{H} \) relaxation rates. Here, 90\% of the \( ^1\text{H} \) magnetization is recovered by 0.5, 2.5, 6.0, and 9.0 s for Ni, Mn, Co, and Fe, respectively. The \( ^1\text{H} \) nuclei in Zn did not recover fully in our measurement, and 90\% recovery can be extrapolated to occur by ca. 20 s. These preliminary data suggest that differing rates of electron spin dynamics in Ni, Mn, and Fe are not the principal factor in controlling the relaxation times of Co. If they were, the \( ^1\text{H} \) relaxation rates of Ni and Fe would be expected to be nearly the same timescale to reflect similar bath electron spin relaxation times. Furthermore, the rate for Mn would be expected to be distinct from Ni, Fe, Co, and Zn, since dilution in Mn exclusively hastens the relaxation time of [Co(SPh)\( _4 \)]\textsuperscript{2-} faster than the bath of pure Co. Yet, the \( ^1\text{H} \) relaxation rate in Mn lands squarely in the middle of the studied complexes. Previous literature shows that temperature and field can have a profound impact on the nuclear relaxation spectra for magnetic molecules.\textsuperscript{23} In addition to the difference in field strength between the NMR and magnetometric analyses, the recorded NMR spectra are taken at near room temperature (~298 K), far different than the 2 K of the magnetometer. The active relaxation pathways are likely different from those active in the low-T regime observed for our magnetic susceptibility data. As discussed in the main body of the paper, we propose another explanation, not directly related to relaxation times, to rationalize the observed behavior of the paramagnetic diluents.
In addition to $T_1$, another potential probe for reporting the electron spin bath dynamics would be the $T_2^*$ of the protons. In principle, if one can assign the peaks and the peakshape is simple and symmetric, the peak linewidth can yield this parameter. However, peak assignment cannot be made with the data, due to the paramagnetism of the samples and peak width from the detailed experimental conditions. We do note that the similarity in peak shifts is surprising considering the paramagnetic nature of the compounds (Fig. S14), which is metal dependent. In general, we would expect to see less influence from the paramagnetic ion for resonant frequencies of the counterion (Ph$_4$P+), so the identified peak might stem primarily from counterion protons, but further studies would be necessary to conclusively assign them. Together, this inability to clearly assign the peak and the non-symmetric peak shapes preclude the extraction of any useful $T_2^*$ data for our analysis.

Note S3: Dipolar Field Model and Calculation Details

The details are partitioned into four subsections. In the first two subsections, we briefly define the out of phase magnetic susceptibility and its relationship to a relaxation rate, then we discuss relaxation rate in the context of an $S = \frac{1}{2}$ ion induced by a dipolar magnetic field. In the last two sections, we justify treatment of the embedded Co(II) ions of [Co(SPh)$_6$]$^{2-}$ as effective $S = \frac{1}{2}$ species, then describe how we calculated the expectation values of the dipolar field components $c_n^m = \langle h_n h_m \rangle (n = x, y, z)$ depicted and analyzed in the main manuscript. A visual depiction of the easy-axis vectors and transformed axis is given below (See Fig. S24).

Out-of-phase magnetic susceptibility description used for model:

First, we describe the relationship between the out-of-phase susceptibility and spin relaxation rate, which yielded the $\chi''$ versus frequency plots depicted in the main manuscript and here in the SI (Figs. 3, S8-S18). The AC magnetic field ($H$) used to measure the relaxation behavior has a simple sinusoidal, linearly polarized form, where $\omega$ is the frequency of the applied field:

$$H(t) = H \sin(\omega t)$$

the power absorbed by the spin system at a given frequency, $P(\omega)$, is:

$$P(\omega) = - \frac{1}{T} \int_0^T M^i(t) dH^j(t) = \frac{\omega}{2} H^i H^j \chi''^i(\omega)$$

where $M^i$ is the $i$-th component of the magnetization, $T$ is the period, and $\chi''$ is the imaginary part of the magnetic susceptibility tensor:

$$\chi(\omega) \equiv \chi'(\omega) + i\chi''(\omega).$$

Below we take the independent spin approximation and consider the $\chi$ due to a single spin for simplicity. It is useful to relate $\chi$ to the time-correlation function or relaxation function defined as

$$\Phi^{ij}(t) \equiv \frac{1}{2} \langle S^i(t) S^j(t) \rangle - \langle S^i(t) \rangle \langle S^j(t) \rangle$$

where $S^i$ is the $i$-th component of the spin operator. The symmetrization is to ensure that $\Phi^{ij}(t)$ is real. Below we assume $\langle S \rangle = 0$ in the absence of external magnetic fields. The fluctuation-dissipation theorem dictates that

$$\gamma^2 \Phi^{ij}(\omega) = \frac{2\hbar}{1 - e^{-\beta\omega}} (\chi'')^{ij}(\omega)$$

where $\gamma = g\mu_B/\hbar$ is the gyromagnetic ratio and $g$ is the Landé $g$-factor for the electronic spin. Since our interest is in $\chi''^{ij}$, it is sufficient to consider only the time correlation function, $\Phi$. In the case that $\Phi(t)$ is described by a simple exponential decay, $\Phi(t) = \Phi_0 e^{-\gamma t}$, where $\gamma$ is the decay rate ($\gamma > 0$), we have:
\[
\Phi(\omega) = \frac{2\Gamma}{\omega^2 + \Gamma^2} \Phi_0
\]

In the present experiments the frequency \( \omega (\leq 1000 \text{ Hz}) \) is much smaller than \( k_B T / \hbar \sim 10^{11} \text{ Hz} \). So \( e^{-\beta\hbar\omega} \approx 1 - \beta\hbar\omega \), and we can obtain \( \chi'' \):

\[
\chi''(\omega) \approx \frac{\omega \Gamma}{k_B T \omega^2 + \Gamma^2} \Phi_0
\]

which is non-monotonic with \( \omega \) and takes its maximum at \( \omega = \Gamma \). Thus, the position of the low-frequency peak of \( \chi''(\omega) \) corresponds to the decay rate. If more complex fitting functions (e.g., the Cole-Cole function) of the experimental \( \chi''(\omega) \) are needed, the decay behavior is likely to be more complicated than the simple exponential form.

**Relaxation of an \( S = \frac{1}{2} \) spin:**

In this subsection we give a general discussion on the relaxation of an \( S = \frac{1}{2} \) spin in the presence of a DC magnetic field and explain the difficulty in modeling it when the DC field vanishes. The consideration of \( S = \frac{1}{2} \) is also motivated by the fact that the low-frequency behavior of the \( \chi''(\omega) \) for Co spins is governed by the low-energy Kramers doublet behaving as a spin-\( 1/2 \).

We assume that the DC magnetic field is along \( z \), and the spin is also subject to a fluctuating magnetic field \( (\mathbf{h}) \) which is assumed to be much weaker than the DC field \( (h_0) \). The Hamiltonian is:

\[
\mathbf{H} = -h_0\mathbf{\sigma}_z - \mathbf{h}(t) \cdot \mathbf{\sigma}
\]

where \( \mathbf{\sigma} \) is the Pauli matrix vector and all numerical factors are absorbed into \( h_0 \) and \( \mathbf{h}(t) \). We also assume that \( \mathbf{h}(t) \) has a zero time-average. For simplicity we consider the time correlation function \( \Phi^{ii} \) only, i.e.

\[
\Phi^{ii}(t) = \langle \sigma^i(t)\sigma^i \rangle - \langle \sigma^i \rangle^2
\]

When \( |\mathbf{h}| \ll h_0 \), \( \Phi^{ii} \) can be calculated from time-dependent perturbation theory. Denoting \( H_0 = -h_0\mathbf{\sigma}_z \) and \( H(t) = -\mathbf{h}(t) \cdot \mathbf{\sigma} \), up to 2nd order of \( h \) one can find:

\[
\sigma^i(t) \approx \sigma^i_0(t) - \frac{1}{\hbar^2} \int_0^t dt_1 \int_0^{t_1} dt_2 \left[ \left[ \sigma^i_0(\mathbf{h}^k(t_2)T_0(t_2)h_0(t_1)h_0(t)h^k(t_1)h \right)
\]

where \( \langle \mathbf{h}^k(t_2)h_0(t_1)h_0(t)h^k(t_1)h \rangle \) is the stochastic average over \( \mathbf{h}(t) \), and \( U_0(t) = \exp(-iH_0t) \). We assume \( \mathbf{h}(t) \) to be described by a Gauss-Markov process with the autocorrelation

\[
\langle \mathbf{h}^k(t_2)h_0(t_1)h_0(t)h^k(t_1)h \rangle = c_h \delta^{jk} e^{-\Gamma_h|t_1-t_2|}
\]

Here, \( c_h \) is the variance of the dipolar fields at \( \Delta t = 0 \), \( \delta^{ij} \) is the Kronecker delta, and \( \Gamma_h \) is the phenomenological decay rate. The integrals in Eq. 10 can be done explicitly, leading to:

\[
\begin{align*}
\sigma^+(t) &= \sigma^+_0(t) \left[ 1 - \frac{c_h}{\hbar^2} \left( \frac{|t|}{\Gamma_h} + \frac{e^{-\Gamma_h|t|}}{\Gamma_h^2} \right) - \frac{|t|}{2i\omega - \Gamma_h} + \frac{e^{2i\omega|t|}}{(2i\omega - \Gamma_h)^2} - \frac{1}{(2i\omega - \Gamma_h)^2} \right] \\
\sigma^-(t) &= \sigma^-_0(t) \left[ 1 - \frac{c_h}{\hbar^2} \left( \frac{|t|}{\Gamma_h} + \frac{e^{-\Gamma_h|t|}}{\Gamma_h^2} \right) + \frac{|t|}{2i\omega + \Gamma_h} + \frac{e^{-2i\omega|t|}}{(2i\omega + \Gamma_h)^2} - \frac{1}{(2i\omega + \Gamma_h)^2} \right] \\
\sigma^z(t) &= \sigma^z_0(t) \left[ 1 - \frac{c_h}{\hbar^2} \left( \frac{2|t|\Gamma_h}{4\omega_0^2 + \Gamma_h^2} + \frac{e^{2i\omega_0|t|}}{(2i\omega_0 - \Gamma_h)^2} + \frac{e^{-2i\omega_0|t|}}{(2i\omega_0 + \Gamma_h)^2} - \frac{1}{(2i\omega_0 + \Gamma_h)^2} \right) \right]
\end{align*}
\]
where \( \omega_0 \equiv \hbar \omega / h \). Therefore, all components have a common form:

\[
\sigma^i(t) = \sigma_0^i(t)[1 - f(t)] \approx \sigma_0^i(t)e^{-f(t)}
\]

(13)

A more complete discussion on the approximation involved in the last step can be found in Ref.\(^{25}\). The decay behavior of \( \sigma(t) \) is thus due to the linear in \( t \) terms in Eq. 12. These can also be obtained by taking the long-time limit (\( |t| \to \infty \)), which gives:

\[
\begin{align*}
\sigma^+(t) & \approx \sigma_0^+(t) \exp \left[ -\frac{c_h}{\hbar^2} \left( \frac{|t|}{\Gamma_h} - \frac{|t|}{2i\omega_0 - \Gamma_h} \right) \right] \\
\sigma^-(t) & \approx \sigma_0^-(t) \exp \left[ -\frac{c_h}{\hbar^2} \left( \frac{|t|}{\Gamma_h} + \frac{|t|}{2i\omega_0 + \Gamma_h} \right) \right] \\
\sigma^z(t) & \approx \sigma^z(t) \exp \left[ -\frac{c_h}{\hbar^2} \left( 2\frac{|t|}{\Gamma_h} + \frac{4}{4\omega_0^2 + \Gamma_h^2} \right) \right]
\end{align*}
\]

(14)

In the \( \omega_0 \to 0 \) limit relevant to the AC susceptibility measurements, one cannot truncate the perturbation series at 2\(^{nd} \) order (to be discussed further below). However, in the following regime:

\[
\sqrt{c_h} / h \ll \omega_0 \ll \Gamma_h
\]

(15)

the 2\(^{nd} \) order perturbation result should still be valid, which gives:

\[
\Gamma^\pm = \Gamma^z = \frac{2c_h}{\hbar^2 \Gamma_h}
\]

(16)

Where \( \Gamma^z \) is the axial component of the relaxation rate. Although Eq. 15 may not be satisfied in the present experiments, the relaxation rate in Eq. 16 is still a useful reference for making qualitative estimates. For example, when [Co(SPh)\(_4\)]\(^2–\) is diluted by Ni or Zn which does not contribute to the fluctuating dipolar fields at low temperatures, the dipolar field felt by each [Co(SPh)\(_4\)]\(^2–\) is only due to the other Co ions, felt at long range. Then it is natural to expect that \( \Gamma_h \sim \Gamma \), and Eq. 16 suggests that:

\[
\Gamma \sim \Gamma_h \sim \sqrt{2c_h / h}
\]

(17)

We will see below that in the other limit \( \Gamma_h \ll \sqrt{c_h} / h \), \( \Gamma \) is of the same order as \( \Gamma_h \) and is independent of \( c_h \). Therefore Eq. 17 is expected to hold approximately when \( \Gamma_h \) is not too small compared to \( \sqrt{c_h} / h \).

A nonperturbative treatment of zero-field spin relaxation was first developed by Kubo and Toyabe,\(^{26}\) by treating \( h(t) \) as a random vector that can be described as a Gauss-Markov process. Analytic results can be obtained using this approach in the static limit (\( \Gamma_h = 0 \)) and isotropic \( c_h^R = c_h \). The result is the Kubo-Toyabe relaxation function:

\[
\Phi^{xx}(t) = \frac{1}{3} + \frac{2}{3} \left( 1 - \frac{c_h t^2}{\hbar^2} \right) e^{-\frac{c_h t^2}{2\hbar^2}},
\]

(18)

which approaches a constant as \( t \to \infty \). When \( \Gamma_h \) is finite the \( \frac{1}{3} \) will be replaced by a complex time-dependent function and only numerical results can be obtained in general. Therefore, the long-time decay
behave necessarily comes from finite $\Gamma_h$. In the present case, since $\Gamma_h$ itself is implicitly dependent on $c_h$ (as the bath spins are coupled together through the dipolar interaction), such a calculation is not necessarily useful. Instead, we may consider the other limit $\Gamma_h \ll \frac{\sqrt{c_h}}{\hbar}$ that was not able to be addressed using the perturbation method. For isotropic $c_h$, Ref. [6] showed analytically that in this limit the long-time behavior of $\Phi^{\text{xx}}$ is described by an infinite sum of exponentially decaying functions with different decay rates:

$$
\Gamma_n = \left( \frac{-1 + \sqrt{17}}{2} + 2n \right) \Gamma_h, n = 0, 1, 2, \ldots
$$

The long-time decay is then governed by $\Gamma_0 \approx 1.56 \Gamma_h$. Therefore, qualitatively we expect that the decay rate is of the same order of magnitude as $\Gamma_h$ in the limit of $\Gamma_h \ll \frac{\sqrt{c_h}}{\hbar}$ as well, and $\frac{\sqrt{c_h}}{\hbar}$ serves as an upper bound of $\Gamma$. The main problem with this approach is, however, that $\Gamma_h$ depends on the microscopic details of the bath, some of which are experimentally unknown here and therefore its value cannot be given by this theory.

**Relaxation of an effective $S = \frac{1}{2}$ pseudospin of a single Co ion**

The cobalt complex of the report is an $S = \frac{3}{2}$ molecule with large zero-field splitting. The local Hamiltonian of an isolated Co ion is governed by the crystal electric field (CEF) contribution. By keeping terms up to 2nd order in spin operators we have the following simplified CEF Hamiltonian:

$$
H_{\text{CEF}} = DS^2_x + E (S^2_y - S^2_z),
$$

where $D$ and $E$ are input from fits of experimental data. For $S = \frac{3}{2}$, the spin operators take the following form in the $S_z$ eigenstate basis $\{|m = -\frac{3}{2}\rangle, |m = -\frac{1}{2}\rangle, |m = \frac{1}{2}\rangle, |m = \frac{3}{2}\rangle\}$:

$$
S_x = \begin{pmatrix}
0 & \frac{\sqrt{3}}{2} & 0 & 0 \\
\frac{\sqrt{3}}{2} & 0 & 1 & 0 \\
0 & 1 & 0 & \frac{\sqrt{3}}{2} \\
0 & 0 & \frac{\sqrt{3}}{2} & 0
\end{pmatrix},
S_y = \begin{pmatrix}
0 & \frac{\sqrt{3}}{2} i & 0 & 0 \\
\frac{\sqrt{3}}{2} i & 0 & i & 0 \\
0 & -i & 0 & \frac{\sqrt{3}}{2} i \\
0 & 0 & -\frac{\sqrt{3}}{2} i & 0
\end{pmatrix},
S_z = \begin{pmatrix}
-\frac{3}{2} & 0 & 0 & 0 \\
0 & -\frac{1}{2} & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & \frac{3}{2}
\end{pmatrix}
$$

where we have set $\hbar = 1$. For the case of (PnP)$_2$[Co(SPh)$_4$], $D < 0$ and $|D| > |E|$, the two low-energy eigenstates mainly consist of the states with $m = \pm \frac{1}{2}$. At the lowest temperatures (below 10 K, where the $\chi''$ measurements were performed) the size of the $D$ ensures near complete population of these levels and negligible population of the higher lying $m = \pm \frac{3}{2}$ levels. Thus, we define them as up and down eigenstates of a pseudospin $S = \frac{1}{2}$ as follows (assuming $E > 0$):

$$
|\uparrow\rangle = u|m = 3/2\rangle - \sqrt{1 - u^2}|m = -1/2\rangle
$$
$$
|\downarrow\rangle = v|m = -3/2\rangle - \sqrt{1 - v^2}|m = 1/2\rangle
$$

where
\[
\begin{align*}
\nu &= \frac{\sqrt{D^2 + 3E^2 - D}}{\sqrt{3E^2 + (\sqrt{D^2 + 3E^2} - D)^2}}, \\
\Gamma &= \sqrt{\frac{D^2 + 3E^2}{\sqrt{3E^2 + (\sqrt{D^2 + 3E^2} - D)^2}}}
\end{align*}
\]

and \( u, \nu \) approach 1 as \(|E/D| \to 0\). One can then define the pseudospin operators \( \vec{\sigma} \) as the usual Pauli matrices but in the \(|\uparrow\rangle, |\downarrow\rangle \) basis. Moreover, the original \( S = \frac{3}{2} \) operators projected to the pseudospin space and rotated to the \(|\uparrow\rangle, |\downarrow\rangle \) basis have the following form

\[
(S_x, S_y, S_z) = (g_x \hat{\sigma}_x, g_y \hat{\sigma}_y, g_z \hat{\sigma}_z),
\]

\[
(g_x, g_y, g_z) = \left( \frac{D - 3E}{2\sqrt{D^2 + 3E^2}} + \frac{1}{2}, -\frac{D + 3E}{2\sqrt{D^2 + 3E^2}}, -\frac{D}{2\sqrt{D^2 + 3E^2}} + \frac{1}{2} \right) \approx \frac{3}{2} \left( \frac{E}{D}, \frac{E}{D}, 1 \right)
\]

Since \(|E/D| \ll 1\), magnetic fields predominantly couple to the z component of the pseudospin only. Thus, if one calculates \( \chi'' \) and \( \Phi \) using the \( S = \frac{3}{2} \) results in the previous subsections, the power absorption is dominated by \( \chi'' \) since the other contributions will be suppressed by \( E^2/D^2 \). On the other hand, in the expression of \( \sigma_z \) (or rather \( \hat{\sigma}_z \)) one would just need to do the following replacement:

\[
c_h \to \frac{9E^2\gamma_{Co}^2h^2}{8D^2} (c_h^x + c_h^y)
\]

if different components of the fluctuating magnetic fields are allowed to have different variances. We have also recovered the gyromagnetic ratio of Co (\( \gamma_{Co} = g_{Co}\mu_B/h \)) and \( h \). A crude estimate of the relaxation rate based on Eq. 16 is then

\[
\Gamma^z = \frac{9E^2\gamma_{Co}^2}{4D^2\Gamma_h} (c_h^x + c_h^y)
\]

or, if \( \Gamma^z \sim \Gamma_h \)

\[
\Gamma^z \sim \frac{3|E\gamma_{Co}|}{2|D|} \sqrt{c_h^x + c_h^y}
\]

From this result, we see that the relaxation rate is directly driven by magnetic dipolar field components in the xy plane relative to the embedded spin. We also see that the rate is dependent on the \( E \) of the embedded ion. As \( E \) is extremely small\(^{17} \) and likely consistent in the different environments owing to the strong structural similarities of the MS\(_{4}\) coordination shells,\(^{27} \) the rate changes as a function of bath are more likely to be impacted by changes in \( c_n^x \) and \( c_n^y \), which are diluent dependent.

**Estimation of \( c_n \)**

In this subsection we provide estimates of the \( c_n \) in the present experimental system. The dipolar magnetic field generated at the position of a Co ion in [Co(SPh)\(_2\)]\(^{2-} \) (assumed to be the origin) by another spin (\( S_i' \)) is:

\[
\mathbf{h}_i = \frac{\mu_0\gamma_y}{4\pi r_i^3} [3\hat{\mathbf{r}}_i (S_i'^z \cdot \hat{\mathbf{r}}_i) - S_i'^z],
\]

where \( \gamma_y \) is the gyromagnetic ratio of bath spins, \( \hat{\mathbf{r}}_i \) is the distance separating the two spins, and \( \mu_0 \) is the vacuum permeability. The total dipolar field at origin is:

\[
\mathbf{h}_d = \sum_i \mathbf{h}_i
\]

\[12\]
For the convenience of studying the temperature dependence of the bath spins, we introduce a basis \( \{ \hat{e}_i^\alpha \} = \{ \hat{x}, \hat{y}, \hat{z} \} \) consistent with the local coordinates of a bath spin \( S_i^\alpha \) (according to which its \( D \) and \( E \) are defined). Similarly, the local axis for the Co ion at the origin is defined as \( \{ \hat{e}_i^\alpha \} = \{ \hat{x}', \hat{y}', \hat{z}' \} \). Both \( \{ \hat{e}_i^\alpha \} \) and \( \{ \hat{e}_i'^\alpha \} \) are obtained by diagonalizing the electric quadrupole moment tensor due to the nonmagnetic ions surrounding a particular magnetic ion. As a first approximation, we assume the bath spins do not have correlation with each other. Then, taking \( \langle h_i^{x}(t) h_i^{x}(0) \rangle \) as an example,

\[
\langle h_i^{x}(t) h_i^{x}(0) \rangle = \sum_{ij} \langle h_i^{x}(t) h_j^{x}(0) \rangle = \sum_{i} \langle h_i^{x}(t) h_i^{x}(0) \rangle 
\]

\[
= \sum_{i} \left( \frac{\mu_0 \gamma_B^2}{4\pi r_i^3} \right)^2 [9 (\hat{\mathbf{r}}_i \cdot \hat{\mathbf{z}})^2 ((S_i^y(t) \cdot \hat{\mathbf{r}}_i)(S_i^y(0) \cdot \hat{\mathbf{r}}_i)) \\
- 3 (\hat{\mathbf{r}}_i \cdot \hat{\mathbf{z}})^2 ((S_i^y(t) \cdot \hat{\mathbf{r}}_i)(S_i^x(0) \cdot \hat{\mathbf{r}}_i)) + ((S_i^y(t) \cdot \hat{\mathbf{r}}_i)(S_i^y(0) \cdot \hat{\mathbf{r}}_i)) \\
+ ((S_i^x(t) \cdot \hat{\mathbf{r}}_i)(S_i^x(0) \cdot \hat{\mathbf{r}}_i))] 
\]

Therefore the calculation of \( \langle h_i^{x}(t) h_i^{x}(0) \rangle \) reduces to that of the relaxation function \( \Phi^{ij}(t) \) of the bath spins. If we take the form of \( \langle h_i^{x}(t) h_i^{x}(0) \rangle \) in Eq. 11, its Fourier transform will be,

\[
\langle h_i^{x}(\omega) \rangle = c_h \int_{-\infty}^{\infty} dt e^{i\omega t} e^{-\gamma B t} = \frac{2c_h \Gamma_h}{\omega^2 + \Gamma_h^2}. 
\]

Therefore

\[
c_h = \frac{\Gamma_h}{2} \langle h_i^{x}(\omega) \rangle_{\omega = 0}. 
\]

\( c_h \) can then be calculated from Eq. 30, with the time-correlation functions replaced by their Fourier transform evaluated at \( \omega = 0 \), multiplied by a prefactor of \( \Gamma_h/2 \). \( \Phi^{jk}(\omega = 0) \) for independent spins in thermal equilibrium is given by,

\[
\Phi^{jk}(\omega = 0) = \frac{\Gamma_h}{2} \sum_{pq} S_{pq}^j S_{pq}^k \frac{e^{-\beta E_p}}{\omega_{pq}^2 + \Gamma_h^2} + \frac{\gamma_h}{\omega_{pq}^2 + \Gamma_h^2} 
\]

where \( \omega_{pq} = (E_p - E_q)/\hbar \). When \( \hbar \Gamma_h \) is much smaller than \( D \) and \( E \) of the bath spins, the factor \( \gamma_h \) is effectively zero unless \( \omega_{pq} = 0 \), when it is 1, and hence behaves as a projection operator. In other words, we can write Eq. 33 as

\[
\Phi^{jk}(\omega = 0) = \frac{\Gamma_h}{2} \sum_{pq} S_{pq}^j S_{pq}^k e^{-\beta E_p}, 
\]

where \( (pq) \) means the summation only includes terms with \( E_{pq} = 0 \). The absence of inter-level matrix elements is the origin of the inactive dipolar field of integer spin baths with a singlet ground state.

The \( \Gamma_h \) in the above results in general increases with increasing temperature. At higher temperatures when the phonon-induced spin relaxation mechanism is active\(^{28} \) \( \Gamma_h \) will be approximately described by Arrhenius law, with the high-temperature limit determined by the ratio between the zero-field splitting of the spins and the Debye energy of the crystal and is usually several orders of magnitude smaller than \( |D| \). Therefore, it is a good approximation to project out the inter-level matrix elements as in Eq. 34 for all temperatures.

Another consequence of the projection is that \( \Phi^{jk}(\omega = 0) \) (and hence \( c_h^i \)) will not be isotropic even at temperatures much greater than \( |D| \). This is not contradictory with the isotropic static susceptibility in the high-temperature limit, since the latter is the real part of the susceptibility while \( \Phi^{jk}(\omega) \) is related to the imaginary part through the fluctuation-dissipation theorem, Eq. 5.

Due to the independent spin assumption, samples of different dopant concentrations can be considered simply by making:

\[
\langle h_i^{x}(t) h_i^{x}(0) \rangle = f_{Ni} \langle h_i^{x}(t) h_i^{x}(0) \rangle_{Ni} + f_{Co} \langle h_i^{x}(t) h_i^{x}(0) \rangle_{Co} 
\]

where \( f_\alpha \) is the concentration of species \( \alpha \), and \( \langle h_i^{x}(t) h_i^{x}(0) \rangle \) is the correlation calculated with all bath spins being species \( \alpha \). It is important to note that in calculating \( \langle h_i^{x}(t) h_i^{x}(0) \rangle \), one must use the correct spin Hamiltonians, i.e., \( S = \frac{3}{2} \) for \( Co \), and \( S = 1 \) for \( Ni \). The other parameter values used in our calculations are listed in Tables S6. Typical results for \( c_h \) are shown in Figures S22, S23, and Table S7. We did not include the results for \( Fe \) in
these figures, mainly because our theory may not work well for the case of $|E| \sim |D|$ at elevated temperatures.

Table S7 indicates that the typical size of the fluctuating dipolar magnetic field, when the bath spins have dipole moments, is $\sim 10^{-3}$ T. This can be converted to a frequency by doing the substitution in Eq. 25. Since $\frac{g\mu_B E}{D} \times 10^7 \sim 10^{-9}$ eV, the fluctuating dipolar field corresponds to an energy scale of $\sim 10^{-11} - 10^{-12}$ eV, or $10^3 - 10^4$ Hz. This is much larger than the $\frac{1}{\tau} < 10^2$ Hz measured experimentally. The experimental system is therefore in the limit of $\Gamma_h \ll \frac{\sqrt{\Gamma_h}}{\hbar}$. Thus, the slowing down of Co relaxation as the concentration of Ni increases is due to the decreasing $\Gamma_h$. Although qualitatively it is reasonable to expect that $\Gamma_h$ should decrease with decreasing $c_h$, their precise relationship can only be established by understanding the dynamics of the correlated bath spins, which is beyond the theory presented here and will be left for future study. Nonetheless, the qualitative trend is in agreement with the zero-field splitting and spin relaxation processes that are well-documented for mononuclear single molecule magnets like $[\text{Co(SPh)}_4]^2-$.28
Table S1: Summary of spin Hamiltonian parameters obtained from susceptibility and EPR analyses of Co, Ni, Fe, and Mn.

|       | Co     | Ni     | Fe     | Mn     |
|-------|--------|--------|--------|--------|
|       | $\chi_M T$ | EPR\(^a\) | $\chi_M T$ | EPR\(^a\) | $\chi_M T$ | HF-EPR\(^b\) | $\chi_M T$ | HF-EPR |
| $g_x$ | 2.076  | -      | -      | -      | 2.02    | 2.051(1)    | 1.895  | 2.000 |
| $g_y$ | 2.075  | -      | -      | -      | 2.08    | 2.095(1)    | 2.001  | 2.000 |
| $g_z$ | 2.576  | -      | -      | -      | 1.95    | 2.010(1)    | 2.124  | 2.004 |
| $g_{iso}^b$ | 2.24    | -      | 5.105\(^c\) | -      | 2.02    | 2.052    | 2.007   | - |
| $D$ (cm\(^{-1}\)) | -61.40  | -      | 67.59  | -      | 5.89    | 5.848(1)   | 0.354  | -0.12 |
| $E$ (cm\(^{-1}\))\(^d\) | 0.011   | -      | -0.25  | -      | 1.45    | 1.428(1)   | 0.00   | -0.04 |
| $A_{iso}$ (MHz)\(^f\) |                           |        |        |        |        |                      |        | 252   |

\(^a\)EPR silent on the instruments for this study. \(^b\)Generally computed. \(^c\)Extracted from fitting, as an isotropic $g$ enabled the best simulation of the $\chi_M T$ data. \(^d\)For $\chi_M T$, these values are best interpreted as $|E|$. \(^f\)Computed – but for HF-EPR, $A_{iso}$ set to that from the X-band analyses. \(^g\)Values (and uncertainties) extracted from the Florida map (Fig. S3).
Table S2: Summary of extracted relaxation parameters from fitting variable-temperature ac magnetic susceptibility data on 1 and dilutions in 2.

|                | Pure Co | 1:2 Co:Ni | 1:9 Co:Ni | 1:34 Co:Ni |
|----------------|---------|-----------|-----------|------------|
| $n^a$          | 5.6(1)  | 6.2(2)    | 6.09(8)   | 7.96(9)    |
| $A$ (K$^{-ns^{-1}}$) | 0.029(7) | 0.09(2)   | 0.07(1)   | 0.0026(3)  |
| $\tau_{QTM}$ (s) | 0.0066(4) | 0.039(3) | $^b$      | $^b$       |

$^a$Values of $n$ with uncertainties were obtained from fits, values without uncertainties were restrained to that value. $^b$No QTM was extracted from the fitting process for these samples.

Table S3: Relaxation rates determined from fits of the zero-field ac susceptibility measurements for dilutions of Co in Ni, Fe, Mn, and Zn (All data were recorded at 2.0 K)

| Ni Dilution | Pure Co | 73% Co | 58% Co | 25% Co | 9% Co | 3% Co |
|-------------|---------|--------|--------|--------|-------|-------|
| 1/$\tau$ (s$^{-1}$) | 177.3   | 96.2   | 62.7   | 32.9   | 5.9   | 0.7   |

| Fe Dilution | 84% Co | 57% Co | 24% Co | 16% Co | 6% Co |
|-------------|--------|--------|--------|--------|-------|
| 1/$\tau$ (s$^{-1}$) | 147.9  | 101.2  | 53.7   | 42.0   | 16.9  |

| Mn Dilution | 81% Co | 43% Co |
|-------------|--------|-------|
| 1/$\tau$ (s$^{-1}$) | 632.9  | 8222.6|

| Zn Dilution | 29% Co | 2.5% Co |
|-------------|--------|--------|
| 1/$\tau$ (s$^{-1}$) | 22.2   | 1.6    |
Table S4: Extracted $\alpha$ parameters from AC susceptibility fitting for various dilutions of Co in Ni. All parameters are taken from zero-field data.

| Sample     | Temperature (K) | $\alpha$ |
|------------|-----------------|----------|
| Pure Co    | 2               | 0.276    |
| 1:2 Co:Ni  | 2               | 0.384    |
| 1:9 Co:Ni  | 2               | 0.562    |
| 1:34 Co:Ni | 2               | 0.579    |

Table S5: Extracted $\alpha$ parameters from AC susceptibility fitting for various dilutions of Co into Ni, Fe, and Mn at 2 K. All values are taken from zero-field data.

| Sample     | Temperature (K) | $\alpha$ |
|------------|-----------------|----------|
| Co         | 2               | 0.276    |
| 1:2 Co:Ni  | 2               | 0.384    |
| 1:9 Co:Ni  | 2               | 0.522    |
| 1:34 Co:Ni | 2               | 0.579    |
| 1:17 Co:Fe | 2               | 0.389    |
| 1:14.5 Co:Mn | 2.3          | 0.276    |
| 1:1.27 Co:Mn | 2             | 0.352    |
Table S6: Parameter values used in the calculations of $c_h$ for Ni, Co and Mn bath spins.

| Parameter | Unit          | Value           |
|-----------|---------------|-----------------|
| $\hbar$   | [eV][sec]     | $6.582 \times 10^{-16}$ |
| $\hbar$   | [Joule][sec]  | $1.05 \times 10^{-34}$ |
| $\mu_B$   | [Joule][Tesla] | $9.27 \times 10^{-24}$ |
| $\mu_0$   | [Henry][Tesla] | $4\pi \times 10^{-7}$ |
| $c$       | [cm][sec]     | $2.998 \times 10^{10}$ |
| $g_{Ni}$  | -             | 5.105           |
| $g_{Co}$  | -             | 2.24            |
| $g_{Mn}$  | -             | 2.126           |

$\gamma = \frac{g \mu_B}{\hbar} = \frac{[\text{eV}]}{[\text{Tesla}][\text{eV}][\text{sec}]} = g \times 5.788 \times 10^{-5} \times \frac{1}{6.582 \times 10^{-16}}$

| $D_{Ni}$  | [eV]          | $+67.54 \text{ cm}^{-1} \times \hbar[\text{eV sec}] \times c[\text{cm/sec}]$ |
| $E_{Ni}$  | [eV]          | $-0.25 \text{ cm}^{-1} \times \hbar[\text{eV sec}] \times c[\text{cm/sec}]$ |
| $D_{Co}$  | [eV]          | $-61.4 \text{ cm}^{-1} \times \hbar[\text{eV sec}] \times c[\text{cm/sec}]$ |
| $E_{Co}$  | [eV]          | $+0.0011 \text{ cm}^{-1} \times \hbar[\text{eV sec}] \times c[\text{cm/sec}]$ |
| $D_{Mn}$  | [eV]          | $-0.097 \text{ cm}^{-1} \times \hbar[\text{eV sec}] \times c[\text{cm/sec}]$ |
| $E_{Mn}$  | [eV]          | $+0.008 \text{ cm}^{-1} \times \hbar[\text{eV sec}] \times c[\text{cm/sec}]$ |

Table S7: Calculated values of $c_h$ for Ni, Co and Mn as bath spins in units of $\text{T}^2$ at 2 K.

|            | Ni (no projection) | Ni (projection) | Co | Mn   |
|------------|---------------------|-----------------|----|------|
| $c_h^x$    | $5.1 \times 10^{-5}$ | $2.7 \times 10^{-7}$ | $6.7 \times 10^{-5}$ | $9.66 \times 10^{-5}$ |
| $c_h^y$    | $1.1 \times 10^{-4}$ | $4.8 \times 10^{-8}$ | $2.8 \times 10^{-5}$ | $7.14 \times 10^{-5}$ |
| $c_h^z$    | $1.6 \times 10^{-4}$ | $8.0 \times 10^{-8}$ | $4.1 \times 10^{-5}$ | $1.02 \times 10^{-4}$ |
Figure S1: PXRD patterns for pure (Ph₄P)₂[M(SPh)₄] samples and paramagnetic dilutions – dilution stoichiometries are indicated on the graph.
Table S7: EDS elemental mapping analysis for Fig. S2. Apparent concentrations have been normalized to Co.

| Sample Point | Fe Apparent Conc. | Co Apparent Conc. | % Co  |
|--------------|-------------------|-------------------|-------|
| Area 1       | 5.48              | 1                 | 15.4  |
| Point A      | 5.12              | 1                 | 16.3  |
| Point B      | 5.5               | 1                 | 15.4  |
| Area 2       | 6.04              | 1                 | 14.2  |
| Point C      | 5.76              | 1                 | 14.8  |
| Point D      | 6.19              | 1                 | 13.9  |
Figure S3: Variable temperature dc susceptibility ($\chi_M T$) data under an applied dc magnetic field of 1000 G for pure, polycrystalline samples of Co, Ni, Fe, and Mn. Fit lines were generated using PHI and the spin Hamiltonian parameters $g_z$, $D$, and $E$ as outlined in the main paper.
Figure S4: Top: HF EPR spectra of Fe recorded at 20 K with microwave frequencies indicated. Blue: experimental; red: simulated. Labels “a” through “j” refer to branches in map below. Bottom: Frequency dependencies of the resonance fields observed for Fe(SPh)_4. Circles: experimental points. The green, blue and red lines were calculated for the X, Y and Z directions, respectively.
Figure S5: Variable-temperature high field, high frequency EPR spectra for Fe, collected at 20 and 5 K, and 419 GHz. Spectra are normalized to the highest intensity peak to clearly illustrate the identity of the ground state transitions.
Figure S6: High-field, high-frequency EPR simulation comparison for positive (top) and negative (bottom) signs for $D$ and $E$ parameters for Fe at 7 K and 211.2 GHz.
Figure S7: 381 GHz, 50 K EPR spectra for a crushed, crystalline sample of Mn. The simulated spectra were generated using the Easyspin package in MATLAB as outlined in the SI experimental section. Parameters for these best simulations can be found in Table S1.
Figure S8: Variable temperature ac susceptibility data under zero applied field from (2.0 – 6.5 K) for a pure, polycrystalline sample of Co.
Figure S9: Variable-frequency ac susceptibility data under zero applied field at 3.0 K for pure, polycrystalline samples of Ni, Fe, and Mn.
Figure S10: Variable-field, variable-frequency ac susceptibility data collected at 3.0 K on a polycrystalline sample of Mn restrained in eicosane.
Figure S11: Variable temperature ac susceptibility data under zero applied field for a pure, polycrystalline sample of \(1:2\) Co:Ni. Top: In-phase susceptibility, and Bottom: Out-of-phase susceptibility. Fit lines for bottom were generated using equation (1.1) as described in the SI. All ac susceptibility measurements were adjusted for moles of Co in the sample, as determined by ICP-OES.
Figure S12: Variable temperature ac susceptibility data under zero applied field for a pure, polycrystalline sample of 1:9 Co:Ni. Top: In-phase susceptibility, and Bottom: Out-of-phase susceptibility. Fit lines for bottom were generated using equation (1.1) as described in the SI. All ac susceptibility measurements were adjusted for moles of Co in the sample, as determined by ICP-OES.
Figure S13: Variable temperature ac susceptibility data under zero applied field for a pure, polycrystalline sample of 1:34 Co:Ni. Top: In-phase susceptibility, and Bottom: Out-of-phase susceptibility. Fit lines for bottom were generated using equation (1.1) as described in the SI. All ac susceptibility measurements were adjusted for moles of Co in the sample, as determined by ICP-OES.
Figure S14: Variable temperature relaxation time for pure Co (black squares) and deconvoluted fit. See experimental section and Table S2 for fitting details. The parameters yielding these simulations are $A = 0.029(7) \text{ K}^{-n}\text{s}^{-1}$, $n = 5.6(1)$, and $\tau_{\text{QTM}} = 0.0066(4) \text{ s}$. 
Figure S15: Select in- and out-of-phase ac susceptibility data ($\chi_M'$ and $\chi_M''$, respectively) for Co:Ni dilutions at 2 K. Magnitudes of $\chi_M'$ and $\chi_M''$ are normalized to the values for pure Co at 2 K. Solid lines are guides for the eye.
**Figure S16**: Select in- and out-of-phase ac susceptibility data ($\chi'_M$ and $\chi''_M$, respectively) for Co:Fe dilutions at 2 K. Magnitudes of $\chi'_M$ and $\chi''_M$ are normalized to the values for pure Co at 2 K. Solid lines are guides for the eye.
Figure S17: Select in- and out-of-phase ac susceptibility data (χ'_M and χ''_M, respectively) for Co:Zn dilutions at 2 K. Magnitudes of χ'_M and χ''_M are normalized to the values for pure Co at 2 K. Solid lines are guides for the eye.
Figure S18: Select in- and out-of-phase ac susceptibility data ($\chi_M'$ and $\chi_M''$, respectively) for Co:Mn dilutions at 2 K. Magnitudes of $\chi_M'$ and $\chi_M''$ are normalized to the values for pure Co at 2 K. Solid lines are guides for the eye.
Figure S19: Arrhenius plot comparison of dilutions of Co in Fe, Ni, and Zn\textsuperscript{[7]} to the Arrhenius plot of pure Co. All relaxation rates were extracted from variable frequency ac susceptibility with zero applied magnetic field.
Figure S20: Solid-state NMR spectra for pure compounds (Co, Ni, Fe, Mn, and Zn) collected at room temperature at 15 kHz MAS. Spectra shown are from the longest recorded τ scan (see SI experimental) for each compound.
Figure S21: Magnetization recovery data obtained from the room temperature, solid state NMR spectra of the pure compounds. $M(\infty)$ and $T_1$ were extracted from exponential fits to the data (See SI). Top: Comparison of anomalous Fe recovery to the recovery of Zn ($\tau$ represents time after saturating pulses). Bottom: Magnetization recovery data plotted on a log scale. Black lines are fits to extract $T_1$ (The black line for Fe data is simply a guide for the eye, as no simple relaxation behavior is observed).
Figure S22: Variable temperature, orientation dependence of the dipolar fields calculated for crystalline matrices of Co (top), Ni (middle), and Mn (bottom) in mT$^2$. (note: $<h_{i}d_{i}>$ is synonymous with $c_{ii}^n$)
Figure S23: Variable temperature, concentration dependence of the dipolar fields calculated for crystalline matrices of Co in Zn, Ni, and Mn in mT². (note: $<h_i h_n>$ is synonymous with $c_n^i$)
**Figure S24:** Visual depiction of the easy-axis vector orientation and axis transformation used to calculate dipolar fields.
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