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Quantum spin coherence in halogen-modified Cr_7Ni molecular nanomagnets

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Among the factors determining the quantum coherence of the spin in molecular magnets are the presence and the nature of nuclear spins in the molecule. We have explored modifying the nuclear-spin environment in Cr_7Ni-based molecular nanomagnets by replacing hydrogen atoms with deuterium or the halogen atoms, fluorine or chlorine. We find that the spin coherence, studied at low temperatures by pulsed electron-spin resonance, is modified by a range of factors, including nuclear spin and magnetic moment, changes in dynamics owing to nuclear mass, and molecular morphology changes.

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Since the proposal that they may be used to host elementary quantum algorithms [1,2], research in the area of molecular magnets has increased rapidly. Such magnets offer a range of properties useful for the components of a quantum computer [3]: flexible and tuneable electron-spin structures [4]; high spins permitting dense quantum memory [1]; the ability to self-assemble by chemical means into multiple molecular magnet "superstructures" [5–7]; and possible formation of a dilute oriented ensemble, which allows manipulation of anisotropic spin multiplets [8]. In particular, antiferromagnetically coupled rings can form well-defined spin ground states, which inherit the long coherence times of their constituent components and offer the advantage that perturbations can be applied on the molecular rather than atomic length scale [9,10].

In order to be useful in a quantum computer, the phase memory time (T_m) of a qubit must exceed significantly the duration of single-qubit manipulations. At low enough temperature, we found this to be true of a Cr_7Ni molecular magnet, whose paramagnetic ions can be treated as an effective electron-spin-1/2 system [11]. By varying key structural components, the main phase decoherence mechanisms were revealed to be nuclear-spin diffusion and spectral diffusion, in particular involving low-mass highly magnetic protons, both on the molecule and in the solvent. As in previous studies, methyl groups were found to be particularly effective in driving dephasing owing to the possibility of significant librational motion, and rotational tunneling motions, even at liquid helium temperatures. By optimizing the structure to reduce librational motion and replacing hydrogen with deuterium, which has an approximately six times lower magnetic moment than hydrogen, we were able to extend phase memory significantly. In a compound with all protons removed, we found $T_m > 15\ \mu s$ at 1.5 K [12].

The aim of the present investigation is to determine the effects on phase memory time in Cr_7Ni of substituting halogens for hydrogen in the constituents of the ring. This was motivated by the chemically similar, but physically distinct, properties of these atoms (Table I). Fluorine has very similar magnetic properties to hydrogen but has a mass that is 19 times greater, enabling us to explore motional effects. In particular, trifluoromethyl (CF_3) groups cannot tunnel through rotational barriers whereas the three protons of conventional methyl (CH_3) groups are able to do so. Furthermore, the chlorine atom has a much smaller magnetic moment than hydrogen and is relatively bulky so it could, for example, replace an entire methyl group, allowing construction of bulky ligands containing fewer magnetic nuclei [13].

All structures were derived from the parent compound $Cr_8F_8Piv_{16}$, which has a diamagnetic ground state. It consists of a ring of octahedrally coordinated trivalent chromium ions, each bridged to its neighbor by one fluoride and two bulky pivalate (2,2-dimethylpropanoate) carboxylate bridging ligands. Coupling between the eight Cr^{3+} ($s = 3/2$) ions is antiferromagnetic, leading to a ground-state total spin, $S = 0$. By substituting one Cr^{3+} with a divalent Ni^{2+} ($s = 1$) and introducing a suitable central templating cation to balance the negative charge of the ring, we form a paramagnetic ground state of total spin, $S = 1/2$. This total spin can be controlled by alternative choice of divalent metal ion [14,15], but all compounds investigated here are based on the Cr_7Ni ring. We explore the effect of several classes of modification: substituting the pivalate in the bridging ligand with a group in which we replace H with D, F, or Cl; templating around different cations; and solvent deuteration. Figure 1 shows the structures that we were motivated to study by the possibility of modifying the phase memory time of the Cr_7Ni spin.

Cr_7Ni rings assemble readily around a wide range of cations [12]. Here, we chose to study rings templated around either a caesium cation (Cs^+), which we have earlier found to support long phase coherence times, or a large dipropyl ammonium ($Pr_2NH_2^+$) cation, offering an alternative synthetic target. These cations are shown in blue in Fig. 1(b). We identified acetates (Ac), and benzoates (Ben), shown in red in Fig. 1(b), as carboxylate ligands in which hydrogens may readily be exchanged for halogens.

We found that not all combinations of cations and ligands in Fig. 1 formed stable compounds. It was possible to synthesize fully Cl-substituted Ac rings around the $Pr_2NH_2^+$ template, but this was not stable in solution, so it was not possible to study pulsed electron-spin resonance (ESR) in this structure. The analogous Cs^+ structure is expected to be even less

TABLE I. Nuclear spins and magnetic moments of nuclei used in this study.

Element	Nuclear spin	Magnetic moment relative to ^{1}H
^{1}H	1/2	1
^{2}H (D)	1	0.307
^{19}F	1/2	0.941
^{35}Cl	3/2	0.294
^{37}Cl	3/2	0.245

stable and we did not attempt to synthesize it. Hydrogenated-, deuterated-, and fluorinated-Ben ligand structures formed successfully around the $Pr_2NH_2^+$ cation. While it was possible to synthesize the chlorinated Ben, it was not soluble in the solvents used for pulsed ESR spectroscopy. We were able to synthesize hydrogenated-Ben and deuterated-Ben rings around Cs^+, but the synthesis of fluorinated-Ben generated many byproducts, and we did not obtain a sample of the pure fully substituted ring. Details of the synthesis are given in [16].

Given that fluorine is much more electronegative than hydrogen (3.98 on the Pauling scale, compared with 2.20 for hydrogen), we considered the possibility that fluorine substitution might distort the structure sufficiently to modify the exchange couplings within the Cr_7Ni ring. To check this, we performed dc magnetic susceptibility measurements, using a standard Quantum Design Magnetic Property Measurement System (MPMS) 7-T superconducting quantum interference device, on powder samples of the *h*-Ben, *d*-Ben, and *f*-Ben samples templated around the $Pr_2NH_2^+$ cation, across the temperature range 1.8 to 300 K, with an applied magnetic field intensity of 0.1 Am^{-1}. The susceptibility data are in agreement with previously reported values for Cr_7Ni [17], and features in the susceptibility can be identified with magnetic excitations in the ring, permitting the extraction of the magnitude of the exchange constants [18]. As shown in Fig. 2, the magnetic susceptibilities of all three compounds are almost identical, with turning points, indicative of exchange coupling strength, occurring at the same temperatures. We conclude that there is little variation in the strength of the exchange interactions in the metal ring for the compounds that we have studied here.

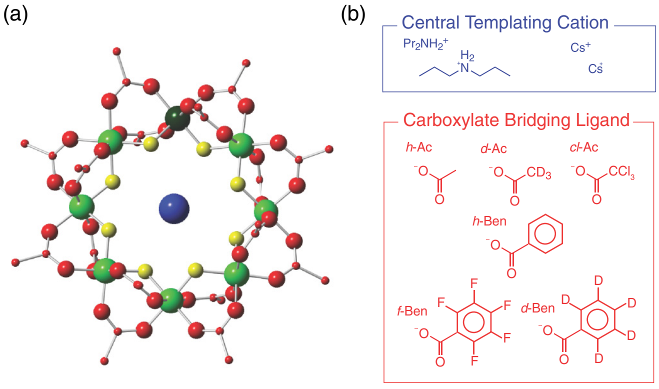

FIG. 1. (Color online) Structures of the Cr_7Ni molecules. (a) Structure of $Cs[Cr_7NiF_8Ac_{16}]$. The colored balls represent either different atom types—Cr (light green), Ni (dark green), and F (yellow)—or different interchangeable substituents—a central templating cation (blue) and carboxylate bridging ligand (red). Hydrogen atoms have been omitted for clarity. (b) Appropriately color coded chemical structures of some possible variants with abbreviated names.

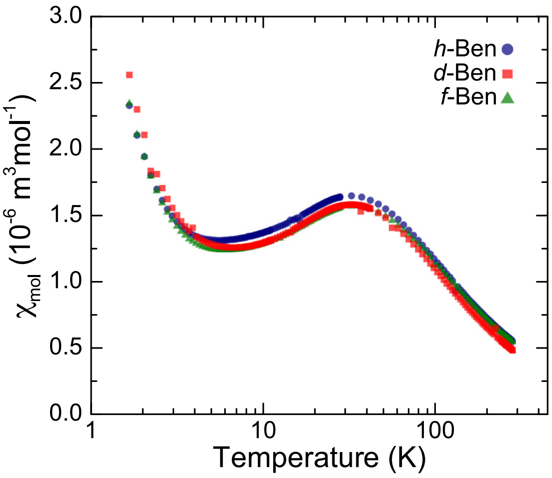

FIG. 2. (Color online) Magnetic susceptibility χ_m as a function of temperature T for compounds templated around a $Pr_2NH_2^+$ cation.

We measured phase memory times of all fully substituted, stable compounds using *X*-band (≈9.5 GHz) pulsed ESR spectroscopy over the temperature range 3 to 5 K, applying the standard Hahn echo sequence, $\pi/2 - \tau - \pi - \tau -$ echo, where τ is incremented, with a two-step phase cycle [19]. We dissolved the compounds in dry hydrogenated or deuterated toluene (*h*-tol and *d*-tol, respectively) and diluted such that intermolecular dipolar interactions could be neglected ($\lesssim 10^{-4}$M). We degassed all samples via a freeze-pump-thaw method and subsequently flame sealed the sample tubes. We flash froze the samples before inserting them in the spectrometer to ensure that the solvent formed a glass.

Example spectra and fits are shown in Fig. 3. In the top panel of Fig. 3, there is a strong electron-spin echo envelope modulation (ESEEM) at the deuterium nuclear Larmor frequency. This arises due to the excitation and subsequent interference of forbidden transitions involving a nuclear-spin transition [19]. The magnetic moments of hydrogen and fluorine nuclei are sufficiently large that the bandwidth of a 128-ns π pulse is not wide enough to excite their ESEEM. Using lengthened pulses, reducing the excitation bandwidth, we were able to reduce but not to remove entirely ESEEM due to the deuterium nucleus, which has a lower magnetic moment ($\gamma_H/\gamma_D \approx 6.5$). Spectra not exhibiting ESEEM fitted well to a stretched exponential function [Eq. (1)] where τ is the time delay between pulses, $Y(0)$ is the extrapolated echo intensity at $\tau = 0$, and c accounts for a small constant baseline offset of instrumental origin. T_m and x are phenomenological parameters known as the phase memory time and stretch parameter, respectively. Their values depend on both the dominant mechanism of decoherence and its rate [13,20,21]. In the cases in which ESEEM was present, the first term of Eq. (1) was multiplied by a modulation function accounting for both the fundamental frequency and first harmonic of the ESEEM [16]:

$$Y(2\tau) = Y(0)\exp[-(2\tau/T_m)^x] + c. \qquad (1)$$

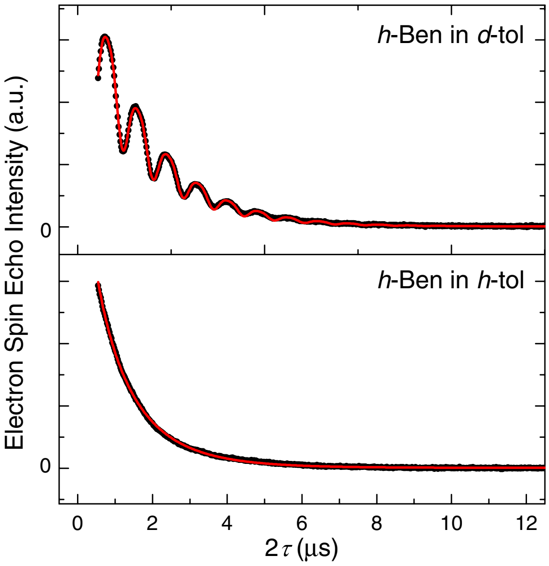

FIG. 3. (Color online) Echo decay curves (black points) with the relevant fits (red line), for the *h*-Ben compound templated around a $Pr_2NH_2^+$ cation, at temperature $T = 4$ K.

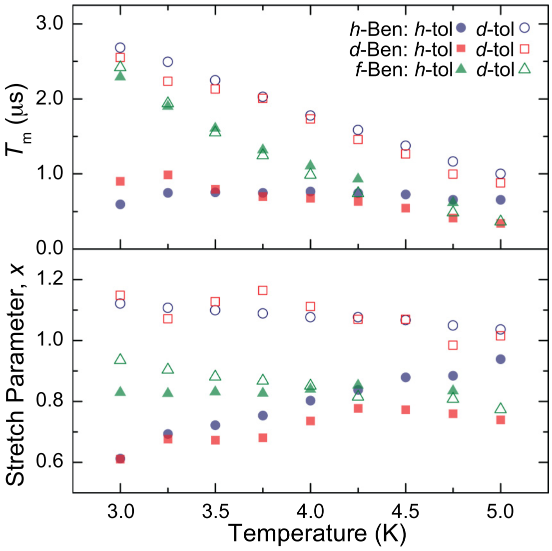

FIG. 4. (Color online) Phase memory time T_m and stretch parameter x for compounds templated around a $Pr_2NH_2^+$ cation. Error bars from the fit are omitted as these were on the order of the marker size.

Phase decoherence that is not refocused in an echo experiment results from magnetic field fluctuations at the site of the excited electron spin. In the dilute rigid limit, we expect the primary cause to be nuclear-spin flip-flop processes. Although conserving net magnetization, these cause local magnetic field fluctuations at the site of the electron spin. The flip-flop rate of any individual nucleus is low (typically ≈10 kHz), but the efficiency of the decoherence process can be enhanced by a large bath of available spins, for example, in the solvent. We refer to this process as nuclear-spin diffusion and it gives rise theoretically to a stretch parameter of $2 \leqslant x \leqslant 3$, depending on the exact model [13,20,21]. Moving away from the rigid limit, decoherence can additionally be caused by motion of magnetic nuclei with respect to the electron spin. At the temperatures investigated, we expect bond vibration to be frozen out. However rotations and librations are still possible, particularly of light atoms. We refer to decoherence resulting from these motions as spectral diffusion and this tends to give rise to a lower stretch parameter, reaching 0.5 if the motional correlation time is on the order of the pulse delay [13].

Figure 4 shows the T_m and x values for compounds templated around the ammonium cation. There is a marked increase in T_m at low temperatures for the fluorinated compound. As fluorine and hydrogen are magnetically similar, and we confirmed through magnetization experiments that the intramolecular exchange interactions are similar, we conclude that this difference arises from structural effects. As with other 2,6-substituted benzoic acids, in the pentafluorobenzoate the aromatic ring of the benzoate ligands is rotated out of the plane of the carboxyl group [22]. This significantly alters the local environment of the central templating cation, with rotation and libration of the methyl groups significantly more hindered in the fluorinated compound. The temperature dependence of the phase memory time indicates that this motion is frozen out at lower temperatures for the fluorinated compound but continues to dominate phase decoherence through spectral diffusion for the protonated and deuterated compounds. Despite variation in the efficiency of dephasing by spectral diffusion both between compounds and with temperature, in all cases the stretch parameter remains low ($x < 1.2$) across the given temperature range. This indicates that spectral diffusion rather than nuclear-spin diffusion is the limiting phase decoherence pathway in the regime investigated.

We also note that the phase memory times for the *h*-Ben and *d*-Ben ligands are very similar and in *h*-tol remain roughly constant with temperature. This is in contrast to previously investigated ligands such as pivalate, for which deuteration has a significant effect [12]. The insensitivity to ligand deuteration (which is not expected to affect structure) shows that in these compounds the protons of the ligand are not involved in the limiting phase decoherence pathway. The likely reason for this is that the relatively unhindered rotation of the methyl groups of the ammonium cation is much more effective at driving phase decoherence, aided both by the possibility of quantum tunneling transitions and a shallow rotational potential well arising from the shielding of the cation from the solvent environment by the axial benzoate ligands.

The T_m and x values for *h*-Ben and *d*-Ben compounds templated around the Cs^+ cation are presented in Fig. 5. As in our previous study [12], we do not observe caesium ESEEM, and we conclude that the caesium nucleus does not directly affect the phase coherence. Although caesium substitution of the fluorinated compound was not possible we may note that the phase memory time now increases with decreasing temperature for protonated and deuterated benzoate ligands, exceeding those in the respective ammonium templated compounds in *h*-tol. This supports the hypothesis that, when coupled to a large proton spin bath, the protons of the ammonium cation limit phase coherence. The low stretch parameter ($x < 1.2$) again indicates spectral diffusion to be the dominant decoherence mechanism in these caesium templated compounds.

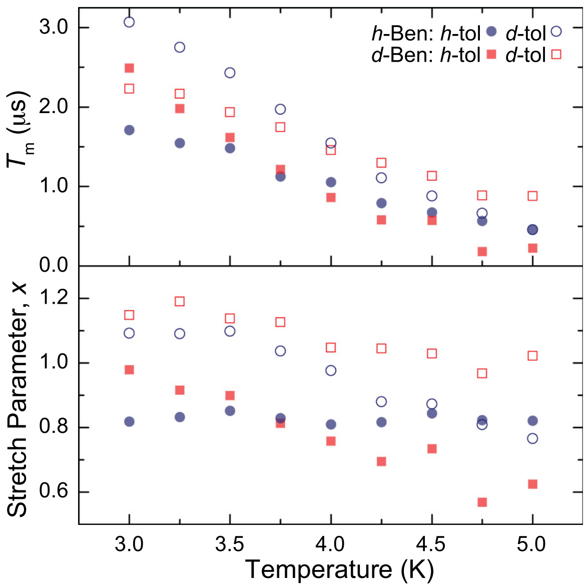

FIG. 5. (Color online) Phase memory time T_m and stretch parameter x for compounds templated around a Cs^+ cation. Error bars from the fit are omitted as these were on the order of the marker size.

In all of the cases studied except the fluorinated compound it is found that solvent deuteration increases phase memory times. This is not unexpected, given that the solvent nuclei provide a large spin network that can be very effective in dephasing the electron spin directly, as well as acting as a spin bath for nuclear-spin flip flops with other nuclei in the system, including those of the carboxylate ligand and central templating cation.

To conclude, in order to further elucidate the decoherence mechanisms at work in Cr_7Ni based molecular magnets, we have explored the synthesis of a group of compounds in which hydrogen is replaced by deuterium, fluorine, or chlorine. Phase memory times have been measured via pulsed ESR over the temperature range 3–5 K, and we find that structural changes associated with inclusion of fluorine atoms provide the dominant effect modifying phase decoherence pathways.

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