Close Encounters of the Weak Kind: Investigations of Electron–Electron Interactions between Dissimilar Spins in Hybrid Rotaxanes

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Supporting Information

ABSTRACT: We report a family of hybrid [2]rotaxanes based on inorganic [Cr₇NiF₈(O₂CR)₁₆]− (“[CrNi]”) rings templated about organic threads that are terminated at one end with pyridyl groups. These rotaxanes can be coordinated to [Cu(hfac)]₃ where [hfac] = 1,1,1,5,5,5-hexafluoroacetylacetonato, to give 1:1 or 1:2 Cu:[Cr₇Ni] adducts: [Cu(hfac)]₃{[Cu(hfac)]₃{[py-CH₂NH₂CH₂CH₂Ph]-[Cr₇NiF₈(O₂C)₁₆]_{16}}}, [Cu(hfac)]₃{[py-CH₂NH₂CH₂CH₂]-[Cr₇NiF₈(O₂C)₁₆]_{16}}), [Cu(hfac)]₃{[py-CH₂NH₂CH₂CH₂]-[Cr₇NiF₈(O₂C)₁₆]_{16}}), {[Cu(hfac)]₃{[py-CH₂NH₂CH₂CH₂]-[Cr₇NiF₈(O₂C)₁₆]_{16}}), and {[Cu(hfac)]₃{[3-py-CH₂CH₃NH₂(CH₂)₄CH₃]-[Cr₇NiF₈(O₂C)₁₆]_{16}}}, the structures of which have been determined by X-ray diffraction. The {Cr₇Ni} rings and Cu种类 ions both have electronic spin S = 1/2, but with very different g-values. Continuous-wave EPR spectroscopy reveals the exchange interactions between these dissimilar spins, and hence the communication between the different molecular components that comprise these supramolecular systems. The interactions are weak such that we observe AX or AX₂ type spectra. The connectivity between the {[CrNi]} ring and thread is determined in such that the magnitude of the exchange interaction J can be tuned. The coupling is shown to be dominated by through-bond rather than through-space mechanisms.

INTRODUCTION

There is a growing literature on the design, synthesis, and study of molecular systems as potential qubits for quantum information science (QIS) using electron spins. The first such proposal was for a Mn₁₂ cluster, a single-molecule magnet, but most subsequent studies have focused on S = 1/2 systems that provide a simple two-level quantum system. Such molecules require sufficiently long phase memory (or decoherence) times (T_m) to allow spin manipulation without loss of quantum phase information to the environment, and many studies have focused on maximizing T_m. Systems studied include nitroxyls, fullerenes, lanthanide ions, V₄⁺ and Cu⁺ complexes. Such work has recently been extended to examine a molecular qudit which allows the implementation of the Grover algorithm in a TB₁₀ sandwich complex via manipulation of the metal hyperfine states.

The next challenge for molecular systems is to move beyond single qubit gates, requiring the introduction of controllable coupling between two or more qubits. In principle, such coupling between molecular spin qubits can be controlled very precisely via the chemistry. Attempts have been made toward this in systems including organic radicals, lanthanide dimers, vanadyl dimers, and fullerene dimers. For some QIS proposals it is a requirement to be able to address the individual spin qubits selectively. One approach is to couple two different spins such that the interaction (J) is much weaker than the difference in Zeeman energies (|J| ≪ ΔγμBB), defining a weakly coupled “AX” spin system. Takui has referred to this as “g-engineering.” We recently demonstrated that such an approach can be built into coordination cages exploiting supramolecular chemistry. This is based on systems of the general formula (cation)[Cr₇NiF₈(O₂CR)₁₆], which consist of a ring of seven Cr₃⁺ and one Ni²⁺ ion, with each edge bridged by one fluoride and two carboxylates; the cation is typically a protonated secondary amine. {Cr₇Ni} rings have a well-isolated S = 1/2 ground state, arising from strong antiferromagnetic nearest neighbor exchange, with coherence times at low temperatures that can be optimized by choice of carboxylate (R') and cation. The chemical robustness resulting from the Cr₃⁺ (d³) oxidation state enables a remarkable range of chemistry to be performed on these rings, for example, site-specific ligand substitutions, introducing functional groups that allow building into more complex structures. The largest we have characterized to date contains 24 {Cr₇Ni} rings centered on a Pd₁₂ cage.

In the (cation)[Cr₇NiF₈(O₂CR)₁₆] structures, the cation sits in the center of the {[CrNi]} ring. If suitable extended and sterically demanding R groups are chosen then [2]rotaxane structures are formed. If instead an extended diaminon
thread is used, for example [RNH₂(CH₂)_nNH₃]⁻⁻, then a {Cr₇Ni} ring can form on each ammonium group to form [3]rotaxanes which are {Cr₇Ni}₂ homodimers. We have previously shown that we can detect the very weak {Cr₇Ni}···{Cr₇Ni} interactions in a range of these [3]rotaxanes by pulsed EPR methods. More recently, we used a related approach to couple {Cr₇Ni} to a heterospin center. This involved introducing a pyridyl (py) headgroup to an extended amine py-CH₂NHCH₂CH₂Ph (thread A, Table 1) which can then form the [2]rotaxane {HA}[Cr-NiF₆(O₂CMe)₁₆] (1) where the head of the thread is now functionalized (Figure S1a). This can be reacted with Lewis acid metal species, for example, [Cu(hfac)]⁻⁻ (Hhfac = 1,1,1,5,5,5-hexafluoroacetylelacetonato), to form {[Cu(hfac)]⁻⁻[HA][Cr-NiF₆(O₂CMe)₁₆]} (2). We showed by continuous wave EPR that the S = 1/2 Cu²⁺ ion and the S = 1/2 {Cr₇Ni} ring (which have g-values of ca. 2.1 and 1.8, respectively), are weakly coupled (at Q-band magnetic fields) giving distinct resonances for the two components, each split by a J-coupling in a manner more commonly associated with NMR spectroscopy. Hence, we demonstrated that we had an AX electron spin system based on supramolecular chemistry principles. However, the mechanism for this interaction was unclear, being too strong and isotropic for through-space dipolar interactions, yet with no obvious exchange pathway other than through H-bonding between the ring F atoms and the ammonium groups.

In this work we systematically vary the thread that links the {Cr₇Ni} ring and Cu²⁺ site in order to probe the mechanism(s) of the spin–spin interaction. This introduces a number of changes including the through-space and through-bond distances, and the types of bonds (saturated or unsaturated) between the S = 1/2 centers.

### RESULTS

#### Synthesis and Structural Characterization

Four of the five threads used were prepared by Schiff-base condensations followed by reduction, adapting literature methods. The fifth thread (B) was commercially available. Thread A (Table 1) forms the [2]rotaxane {[HA][Cr-NiF₆(O₂CMe)₁₆]} (1) (Figure S1a) and subsequently its adduct {[Cu(hfac)]⁻⁻[HA]-[Cr-NiF₆(O₂CMe)₁₆]} (2) (Figure 1) via a 1:1 reaction with [Cu(hfac)]⁻⁻. Crystals of 2 can be grown from warm acetone, and crystallize in the orthorhombic Pnma space group. The pyridyl group of the thread binds to [Cu(hfac)]⁻⁻ at the apical site of a square-pyramidal geometry at the Cu²⁺ ion. The ammonium of HA lies at the {Cr₇Ni} centroid with a Nam–Cu distance of 9.09(2) Å [8.99(2) Å through-bond distance]. The average Cu–{Cr₇Ni} distance (average over individual metal ions) is 8.46(3) Å with an average N₄m–Cu–M angle (θ) of 31.38(15)° (Table 2).

In order to vary the Cu–{Cr₇Ni} separations, four more [2]rotaxanes were synthesized with varying threads (Figure S1b–e). Similar chemistry with thread B (Table 1) gives {[HB][Cr-NiF₆(O₂CMe)₁₆]} (3) (Figure S1b) then {[Cu(hfac)]⁻⁻[HB][Cr-NiF₆(O₂CMe)₁₆]} (4) (Figure 2). Threads A and B only differ by the end group at the far end of the chain from the pyridyl, with A terminated with a phenyl group, providing significant steric bulk to prevent slippage of the {Cr₇Ni} ring off the thread (as shown by EPR, see later). In HB the terminus is a methyl group: despite the smaller size presenting no obvious steric barrier to dissociation (hence making 3 and 4 “pseudorotaxanes”), again solution EPR proves the integrity of 4 in solution (see later). Presumably this is a result of the H-bonding between the fluorides of the {Cr₇Ni} ring and the ammonium protons. 4 crystallizes in the tetragonal P4/nnc space group, resulting in disorder of the pyridyl···[Cu(hfac)]⁻⁻ over four equivalent sites.

X-ray crystallography shows that, in contrast to 2, the thread pyridyl group does not bind at the apical site of the square pyramidal geometry at Cu. Instead, it binds in an equatorial site, with one of the Cu···O bonds now defining the apical site. Hence, the Cu coordination geometry is rotated by 90° with respect to the {Cr₇Ni} ring cf. 2 (at least in the solid state). Given the otherwise similar linkages there are minimal structural differences to 2, with through-bond and through-space N₄m···Cu distances of 9.09(2) and 7.14(3) Å, respectively. However, the average Cu–{Cr₇Ni} distance is 8.31(3) Å [average θ of 32.06(18)°], slightly shorter than in 2.

To extend the Cu–{Cr₇Ni} distance an extra CH₂ group was introduced between the pyridyl and amine groups in C (Table 1), which forms the [2]rotaxane {[HC]-...
In contrast to the systems based on A and B, rotaxane 5 reacts with [Cu(hfac)₂] to produce the 2:1 complex {[Cu(hfac)₂][{HC·[Cr₇NiF₈(O₂C₄tBu)₁₆]}₂]} (Figure S1c). 6 crystallizes in the monoclinic I2/a space group. The increased py···amine separation allows a second molecule of 5 to bind at the CuII site, giving trans-{(py)₂(hfac)₂} octahedral coordination at the CuII ion. The through-bond and through-space N am···Cu distances are 10.57(8) Å and 8.59(8) Å respectively, with an average Cu···{Cr₇Ni} distance of 9.69(3) Å (average θ of 27.35(14)°).

To further increase the Cu···{Cr₇Ni} distance, thread D was prepared, incorporating an p-C₆H₄ arene spacer between the pyridyl and amine (Table 1). Thread D gives the [2]rotaxane {[HD][Cr₇NiF₈(O₂C₄tBu)₁₆]} 7 (Figure S1d). Reaction of 7 with [Cu(hfac)₂] gives {[Cu(hfac)₂][{HD·[Cr₇NiF₈(O₂C₄tBu)₁₆]}₂]} 8 (Figure S1e). 8 crystallizes in the orthorhombic P2₁/c space group. As with 6, the greater separation of the [Cu(hfac)₂] and [Cr₇Ni] fragments enables formation of the 2:1 product. However, in contrast to 6, in 8 the two molecules of 7 bind in a cis fashion at the six-coordinate CuII ion. The through-bond and through-space N am···Cu distances are 14.76(4) Å and 11.44(4) Å, respectively, with an average Cu···{Cr₇Ni} distance of 12.30(4) Å (average θ of 20.95(15)°).

Finally, thread E was synthesized (Table 1), which has the same amine···py linkage as in C except the pyridyl group is now substituted in the 3-position. Thread E produces

\[
{[HC·[Cr₇NiF₈(O₂C₄tBu)₁₆]} \rightarrow \{[HE·[Cr₇NiF₈(O₂C₄tBu)₁₆]} \rightarrow \{[HE·[Cr₇NiF₈(O₂C₄tBu)₁₆]} \rightarrow \{[HE·[Cr₇NiF₈(O₂C₄tBu)₁₆]}
\]

(Figure 3). 9 crystallizes in the monoclinic space group C2/c. Again, in contrast to 6, the two molecules of 9 bind cis to one another at the six-coordinate CuII ion. This is accommodated by buckling of the two threads. The through-bond and through-space N am···{Cr₇Ni} distances are 9.47(4) Å and 7.79(4) Å, respectively, with an average Cu···{Cr₇Ni} distance of 9.49(4) Å (average θ = 27.64(14)°).

The synthetic work produces five new heterospin systems, which vary in the coordination number and geometry at the copper site, and in the relative orientation of the z-axis at the Cu site, and the unique axis of the ring, which is the direction

| Cu–N am dist. via space (Å) | 2  | 4  | 6  | 8  | 10 |
|---------------------------|----|----|----|----|----|
| Cu–N am dist. via bonds (Å) | 8.99 | 9.09 | 10.60 | 14.76 | 9.21 |
| avg. Cu–M dist. via space (Å) | 8.46 | 8.31 | 9.69 | 12.30 | 9.49 |
| avg. θ N am–Cu–M (deg)    | 31.38 | 32.06 | 27.35 | 20.95 | 27.64 |

Table 2. Structural Data for Compounds 2, 4, 6, 8, and 10

![Figure 2. Crystal structure of 4, the red arrows show the unique z axis for the CuII and {Cr₇Ni}. For 4 they are perpendicular to one another. Colors as for Figure 1.](image1.png)

![Figure 3. Crystal structure of 6. Colors as for Figure 1, with dull yellow (S).](image2.png)

![Figure 4. Crystal structure of 8. Colors as for Figure 1.](image3.png)

![Figure 5. Crystal structure of 10. Colors as for Figure 3.](image4.png)
normal to the plane defined by the eight metal sites. In 2 the Cu\(^{II}\) ion has a 5-coordinate square-based pyramidal environment with the local z axis pointing to the apex where the \([2\text{-}2\text{rotaxane}]\text{pyridine}\) is bound. Hence the unique axes of the ring and Cu are almost colinear. In 4, the \([2\text{-}2\text{rotaxane}]\text{pyridine}\) is bound in the equatorial plane of the Cu square-based pyramid; hence, the unique axes of the Cu and \{Cr-Ni\} are almost perpendicular. In 6, which has a \(\text{trans-\{Cr7Ni\}}\) six coordination at Cu, there is a marked elongation along one of the O\(\cdots\)Cu\(\cdots\)O axes (Cu\(\cdots\)O 2.20 Å), which defines the Cu z-axis, and this is orthogonal to the Cu\(\cdots\)N direction and to the unique axes of the \{Cr-Ni\} rings. In both 8 and 10, which have cis-\{Cr7Ni\} arrangements, there is a marked elongation along the sole \(\text{trans} \text{O}\cdots\text{Cu}\cdots\text{O}\) direction (2.215–2.280 Å); other Cu\(\cdots\)O and Cu\(\cdots\)N distances 1.980–2.069 Å); therefore, here the Cu z-axis is again orthogonal to the unique \{Cr-Ni\} axes.

**EPR Spectroscopy.** Continuous wave (CW) Q-Band EPR (ca. 34 GHz) spectroscopy measurements were performed on the supramolecular complexes 2, 4, 6, 8 and 10 as powders and as 3 mM solutions in dry (1:1) CH\(_2\)Cl\(_2\):toluene at 5 K. The solution spectra have significantly narrower line widths than those from powders (Figure S5). At 5 K the EPR spectra of the isolated (cation)\{Cr-Ni\} species are dominated by the S = 1/2 ground state of the \{Cr-Ni\} ring.18

We start by describing the simplest spectrum, which is observed for 8 (Figure 6). Complex 8 has the longest separation of the Cu and \{Cr-Ni\} components, and the CW EPR spectrum appears as a simple superposition of the independent spectra of the components. Simulation\(^{26}\) (with a 1:2 weighting of the Cu\{Cr-Ni\} components) gives g-values that are typical for these species: g\(_{Cu}\) = 2.041, 2.041, 2.287, and g\(_{Cr-Ni}\) = 1.778, 1.755, 1.714, where \(x, y, z\) refer to the local g-frames of the two components. The g\(_{Cu}\) values are consistent with tetragonal coordination with \(g_{\parallel}\) corresponding to the elongated O\(\cdots\)Cu\(\cdots\)O direction (see above). For isolated \{Cr-Ni\} rings, single crystal studies show that \(g_{\parallel}\) (the unique axis, approximating to axial symmetry) corresponds to the normal to the \{Cr-Ni\} plane.18 The spectra are very sharp, and there is good resolution of the \(^{63,65}\text{Cu}\) hyperfine (\(I = 3/2\)) interaction on the g\(_{\parallel}\)(Cu) component, giving a well-defined quartet with \(A_{\parallel} = 450\) MHz. Since there is no effect of any Cu\(\cdots\)\{Cr-Ni\} coupling in these CW spectra, simulations are independent of the relative orientation of g(Cu) and g(Cr-Ni).

Complexes 2 and 4, based on a very similar thread, have the shortest Cu\(\cdots\)\{Cr-Ni\} separations. The crystal structure of 4 gives the apical position of the Cu coordination sphere as perpendicular to the Cu\(\cdots\)py direction and hence, surprisingly, different to 2. However, this is complicated by disorder of the hfac groups in the structure. We have performed single crystal EPR measurements on 4 to test the orientation of g(Cu) with respect to the g\(_{\parallel}\)(Cr-Ni). An indexed crystal was aligned such that a plane of data could be measured where the applied magnetic field (B) could be rotated from perpendicular to the \{Cr-Ni\} ring to being in the \{Cr-Ni\} plane. The resulting angular variation (Figure S12) shows that the maxima in g(Cu) (i.e., lowest resonance fields) correspond the maxima in g(Cr-Ni). Because g\(_{\parallel}\)(Cu) > g\(_{\parallel}\)(Cr-Ni) and g\(_{\parallel}\)(Cr-Ni) < g\(_{\parallel}\)(Cr-Ni) this is consistent with the crystal structure model. However, there is no guarantee that this structure is retained in solution and EPR spectra of 2 and 4 in frozen solution are very similar (Figures 7 and 8, respectively). Each component of

![Figure 6](image6.png)

**Figure 6.** CW Q-Band (ca. 34 GHz) EPR spectrum of 8 in solution at 5 K (black) and simulation (blue).

![Figure 7](image7.png)

**Figure 7.** CW Q-Band (ca. 34 GHz) EPR spectra of 2 in solution at 5 K (black) and simulation (blue).
isotropic exchange interactions of normal, hence we have set the $g_{\text{Cu}} = 2.045, 2.327$; and $g_{\text{Cr7Ni}} = 1.782, 1.767, 1.712$; and $g_{\text{Cu}} = 2.065, 2.045, 2.327$; and $A_{\text{Cu}} = 450$ MHz. Excellent agreements with the experimental spectra of 2 and 4 are found with isotropic exchange interactions of $J = -0.015$ and $-0.013$ cm$^{-1}$ (450 and 390 MHz), respectively (Table 3). The calculated relative intensities within the exchange split doublets are sensitive to the sign of $J$, and we find better agreement with an antiferromagnetic interaction.

The observation of an exchange-split spectrum for the pseudorotaxane 4 is definitive proof that the thread and ring do not dissociate in solution (in this solvent system), despite the lack of a bulky stopper on the thread. This is an indication of the importance of the H-bonding interactions between the secondary ammonium protons of the thread with the bridging fluorides of the {Cr7Ni} ring. The very similar $J$-coupling for 2 and 4 also demonstrates that the relationship between the Cu and {Cr7Ni} are near identical in the two complexes. This either implies that they relax to the same geometry at Cu in solution, or that the exchange coupling is not very sensitive to the position of the pyridyl group binding site at Cu. The latter seems unlikely, given that the Cu magnetic orbital ($d_{z^2}$ in the local axis system) would either be orthogonal to or in the plane of the Cu⋯{Cr7Ni} interaction. Hence, the former explanation seems more likely, we can further speculate that the very slightly smaller $|J_f|$ in 4 than in 2 might reflect a minimal partial slippage, or greater flexibility, in 4 due to the lack of a bulky stopper. However, even if true, this is a very minor effect.

The simple form of the spectra for 2 and 4 arises because the difference in Zeeman energies of the two spins ($\Delta g_{\mu}B$) is much greater than the exchange interaction between them, and the latter acts as a perturbation on the former. Approximating to $g = 2.1$ and 1.8 for Cu and {Cr7Ni}, respectively, for an applied field of $B = 1.2$ T (roughly $g = 2.0$ for 34 GHz) $\Delta g_{\mu}B = 0.17$ cm$^{-1}$ (or 5 GHz), which is five to six times larger than $|J_f|$ Hence, 2 and 4 are well described as AX spin systems under these conditions.

Spectra of 6 (Figure 9) do not show the clear resolution of $J$ that is evident in 2 and 4. Hence the Cu⋯{Cr7Ni} interactions are significantly weaker than in 2 and 4, due to the additional CH$_3$ group between the ammonium and pyridyl groups in thread C. However, the spectrum is noticeably broadened compared to that of 2 and 4, and also to that of 8 (which is also a 1:2 Cu:{Cr7Ni} species). Given the latter (the strongest and weakest coupled systems studied here) it is safe to assume

All $g$-values (and hyperfine) were initially fixed using values from equivalent isolated Cu and {Cr7Ni} species, with $J$ adjusted as the only free variable; all parameters were then refined within narrow limits to produce the best agreement. For 2, the apical Cu–py direction is parallel to the {Cr7Ni} normal, hence we have set the $g_z$ components of the two spins to be coparallel. However, we find that the calculated spectra are insensitive to this relative orientation for the small (with respect to the difference in Zeeman energy) and isotropic $|J_f|$ values that we observe here. Introducing a slight $g$-rhombicity gives a better fit to the relative intensities. The final parameters are $g_{\text{Cu}}(\text{Cu}) = 2.065, 2.045, 2.327$; and $A_{\text{Cu}} = 450$ MHz. Excellent agreements with the experimental spectra of 2 and 4 are found with isotropic exchange interactions of $J = -0.015$ and $-0.013$ cm$^{-1}$ (450 and 390 MHz), respectively (Table 3). The calculated relative intensities within the exchange split doublets are sensitive to the sign of $J$, and we find better agreement with an antiferromagnetic interaction.

Table 3. EPR CW Q-Band Spectroscopy Data$^a$ for Compounds 2, 4, 6, 8 and 10

|     | 2       | 4       | 6       | 8       | 10      |
|-----|---------|---------|---------|---------|---------|
| $g_{\text{Cu}}(\text{Cu})$ | 1.780, 1.765, 1.710 | 1.782, 1.767, 1.712 | 1.772, 1.750, 1.717 | 1.778, 1.755, 1.714 | 1.772, 1.750, 1.698 |
| $g_{\text{Cu}}(\text{Cr7Ni})$ | 2.065, 2.045, 2.325 | 2.065, 2.045, 2.327 | 2.041, 2.030, 2.278 | 2.041, 2.041, 2.287 | 2.041, 2.030, 2.278 |
| $A_{\text{Cu}}$ (MHz) | 450 | 450 | 450 | 450 | 450 |
| $J$ (MHz) | $-450$ | $-390$ | $\pm 150$ | $< \pm 30$ | $\pm 90$ |

$^a$3 mM solutions in CH$_2$Cl$_2$:toluene at 5 K.

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that the broadening is a manifestation of the intramolecular Cu⋯(Cr-Ni) interactions (all species are studied at the same concentrations). The broadening arises because |J| is of a similar magnitude to the intrinsic line widths. [For example, the Cu hyperfine interaction is more poorly resolved for 6 in solution than in, for example, 2 and 8 in the solid state; Figure S5.] Hence, we have estimated |J| for 6 by simulations, with fixed line widths, where |J| is increased systematically from zero. The Hamiltonian is now:

\[ \hat{H} = \mu_B S^\text{Cu} \cdot \mathbf{g}_\text{Cu} \cdot \mathbf{B} + \sum_{i=1,2} \mu_B S^\text{Cr7Ni,i} \cdot \mathbf{g}_\text{Cr7Ni,i} \cdot \mathbf{B} + S^\text{Cu} \cdot A^\text{Cu} \cdot S^\text{Cu} - 2J \sum_{i,j=1,2} S^\text{Cu} \cdot S^\text{Cr7Ni,j} \]

The \( g_x^\text{Cu} \) and \( g_x^{\text{Cr7Ni}} \) orientations are assumed to be perpendicular, given that the elongated O–Cu–O axis is perpendicular to the unique \{Cr-Ni\} axis. However, as above, the calculated spectra are only sensitive to this for much larger |J| (>0.05 cm\(^{-1}\)), or 1.5 GHz, with our line widths). We find reasonable agreement with |J| = 0.005 cm\(^{-1}\) (150 MHz), although this is obviously less well-defined than in 2 and 4 (and is insensitive to the sign of \( J \), Figure S7). Note that 6 is behaving as an AX\(_2\) spin system, and in principle the Cu spectrum is now being split into 1:2:1 triplets by the weak J-coupling with the two equivalent \{Cr7Ni\} rings. We have previously reported spectra of \{Cu(NO\(_3\))\(_2\)(Me\(_2\)CO)\}\(_2\) \([\text{pyCH}_2\text{NH}_2\text{CH}_2\text{CH}_2\text{Et}]\)[Cr-NiF\(_8\)(O\(_2\)C\(_2\)Bu\(_{16}\))]\(_2\),

where |J| is bigger at –0.010 cm\(^{-1}\) (300 MHz) and the triplet structure is resolved more clearly. Finally, spectra of 10 (Figure 10), where the position of substitution at the pyridyl group is changed, have resolution for |J| in 8, and calculated spectra show that |J| must be <\( \approx 0.001 \text{ cm}^{-1}\) (30 MHz) for this complex.

**Relaxation Measurements by Pulsed EPR.** We have previously reported electron spin relaxation studies on compound 2, which has the shortest linker between the Cu and \{Cr7Ni\} groups and the largest |J| of the compounds studied here. In order to test if there is significant variation in relaxation behavior with |J| and/or linker we now report such measurements on compound 8 which has the longest linker and the weakest |J|.

The phase memory time \( T_m \) was determined by a standard Hahn echo decay sequence \( [\pi/2-\tau-\pi-\tau-\pi-\tau-\phi-\text{echo}] \) at Q-band for 8 in dry toluene:DCM (1:1) at 5 K for 3 mM solutions, and at 3 and 5 K for 0.2 mM solutions (Table 4). Measurements

![Figure 10. CW Q-Band (ca. 34 GHz) EPR spectrum of 10 in solution at 5 K (black) and simulation (blue).](image)

**Table 4. Relaxation Times for 8 from Q-Band Pulsed EPR**

| features                  | \( g_x^\text{Cu} \) | \( \text{Mid} g_x^\text{Cu}/g_y^\text{Cu} \) | \( g_x^\text{Cr7Ni} \) | \( T_m \) (ns) | \( T_1 \) (\( \mu_s \)) |
|---------------------------|----------------------|---------------------------------------------|------------------------|--------------|------------------|
| field position (mT)       |                      |                                             |                        |              |                  |
| 3 mM, 5 K                 | 1067                 | 1115                                        | 1162                   | 1353         |                  |
| 0.2 mM, 5 K               | 493(5)               | 503(5)                                      | 514(3)                 | 327(1)       |                  |
| 0.2 mM, 3 K               | 739(1)               | 822(1)                                      | 912(1)                 | 469(0.4)     |                  |
| 0.2 mM, 3, 5 K            | 345(7)               | 400(8)                                      | 281(4)                 | 126(1)       |                  |
| concentration, temperature|                      |                                             |                        |              |                  |
| 3 mM, 5 K                 | –                    | 273(15)                                     | 254(7)                 | 254(4)       |                  |
| 0.2 mM, 5 K               | 493(5)               | 503(5)                                      | 514(3)                 | 327(1)       |                  |
| 0.2 mM, 3 K               | 739(1)               | 822(1)                                      | 912(1)                 | 469(0.4)     |                  |

were taken at different static magnetic fields \( B_0 \). Here, we discuss those taken at the maxima in the echo detected field swept (EDFS) spectra (Figure S8) for both the Cu \( B_0 = 1162 \text{ mT} \) and \{Cr7Ni\} components \( B_0 = 1353 \text{ mT} \), corresponding to orientations in the local \( g_x \) plane for either component. We find \( T_m = 250 \text{ and } 254 \text{ ns for the Cu and } \{\text{Cr7Ni}\} \) components, respectively, for the 3 mM solution at 5 K: these extend to 514 and 327 ns, respectively, for the 0.2 mM solution at the same temperature, showing that \( T_m \) is still limited by intramolecular effects at the higher concentration. On cooling the 0.2 mM solution to 3 K, \( T_m \) increases to 912 and 469 ns for Cu and \{Cr7Ni\}, respectively (Figures S9, S10). Spin–lattice relaxation \( T_1 \) times were determined by inversion recovery measurements \( [\pi-T-\pi/2-\tau-\pi-\tau-\phi-\text{echo}] \) under the same conditions (Table 4, Figure S11), giving \( T_1 = 281 \text{ and } 126 \text{ ns for the Cu and } \{\text{Cr7Ni}\} \) components, respectively.

The \{Cr7Ni\} relaxation time constants \( T_1 \) and \( T_m \) are similar to those for isolated (cation)\{Cr-NiF\(_8\)(O\(_2\)C\(_2\)Bu\(_{16}\))\)\(_2\) rings \((T_m = 400-700 \text{ ns}, \text{ depending on the cation})^{20} \), \( T_1 \) of ca. 100 \( \mu_s \) for \{Me\(_2\)NH\(_2\)\}(Cr-NiF\(_8\)(O\(_2\)C\(_2\)Bu\(_{16}\))).\(^{19}\) Data for isolated square-pyramidal \{Cu(hfac)\(_2\)(py)\} or trans-[Cu-(hfac)\(_2\)(py)\(_2\)] complexes, equivalent to our Cu moieties in 2 and 8, have not been reported but a related monomeric six-coordinate complex \{Cu(hfac)\(_2\)(4,4’-Methyl-2,2’-bipy)\} has \( T_m \approx 3 \text{ ms and } T_1 \approx 1000 \text{ ms}^{27}\). These are substantially longer than \{Cr7Ni\}, as expected given than the latter are strongly exchange coupled clusters of high-spin ions (Cr\(_{III}\) and Ni\(_{III}\)). They are also longer than the Cu ions in 2 and 8, although we cannot compare directly given that structural factors can have significant effects on relaxation in Cu\(_{III}\) monomers.\(^{28}\) (We are unable to measure the Cu spin over a wide enough temperature range in order to fit \( T_1 \) to a mechanistic model; see below.) The important observation is that the slower relaxation of the monometallic Cu than the \{Cr-Ni\} ring is preserved in the supramolecular adducts.
The effect of a faster relaxing spin on a slower relaxing spin depends critically on the relative magnitude of the coupling and the difference in resonance frequency of the two spins. If the coupling is substantial in this regard then the $1/T_1$ relaxation rate of the slow relaxing system will be enhanced to match that of the fast relaxing spin. We do not observe this here, hence the relaxation behavior of these supramolecular adducts is also consistent with description as weakly coupled AX$_2$E spin systems. However, even when the interaction is weak it can still significantly enhance the relaxation of the slow spin (see the equations given in ref 27) and it is possible that this is the reason that the Cu components in 2 and 8 relax faster than in monomeric [Cu(hfac)$_2$](4,4′-Me$_2$-2,2′-bipy).

Given this, we performed complementary X-band relaxation measurements on 8 (Figures S13, S14): the lower resonance fields give a smaller difference in resonance frequency which should enhance the effect of the interaction on the slow relaxing Cu spin. At 3 K, we find $T_1$ for the Cu component (measured at the equivalent $B_0$) does indeed decrease, from 281 to 175 μs (Q- and X-band, respectively). However, surprisingly, we find that $T_1$ for the {Cr-Ni} component also decreases: there is clearly more than one contributing factor to the relaxation behavior, and this will be studied in depth in a future paper.

The transverse relaxation times of compound 8 are comparable to those of 2 which has $T_m$ ca. 1 μs and 600 ns for Cu and {Cr-Ni}, respectively, under similar conditions. (Note care needs to be taken in comparing the 1:1 adduct 8 with the 2:1 adduct 2 as this changes the local concentrations of spins which can affect relaxation.) This implies that both compounds are in the "slow exchange" regime where the 1/$T_1$ relaxation rate of the fast relaxing spins is slow compared to the interaction frequency. This is consistent with 1/$T_1$ for the {Cr-Ni} component also decreases: there is clearly more than one contributing factor to the relaxation behavior, and this will be studied in depth in a future paper.

The exception to this trend is compound 10 where $|J|$ is smaller than for 6 despite the shorter Cu–{Cr-Ni} distances (see later). This trend would be expected of both through-space (dipolar) or through-bond (exchange) interactions. We have calculated the dipolar interactions in 2, 4, 6, 8, and 10 based on the crystal structures, and using projection factors for the S = 1/2 ground state the same as the materials studied here the resolution is aided by the very different intrinsic g-values of the {Cr-Ni} ring and Cu$^2+$ ion. The weak coupling in all these systems is consistent with the electron spin relaxation behavior, being very similar between the strongest (2) and weakest (8) coupled materials, and the retention of the slower relaxation times of Cu in the presence of the faster relaxing {Cr-Ni} rings.

The magnitude of the Cu–{Cr-Ni} interaction $|J|$ varies inversely with the distance between the two components (Table 3). The exception to this trend is compound 10 where $|J|$ is smaller than for 6 despite the shorter Cu–{Cr-Ni} distances (see later). This trend would be expected of both through-space (dipolar) or through-bond (exchange) interactions. We have calculated the dipolar interactions in 2, 4, 6, 8, and 10 based on the crystal structures, and using projection factors for the S = 1/2 ground state the same as the materials studied here the resolution is aided by the very different intrinsic g-values of the {Cr-Ni} ring and Cu$^2+$ ion. The weak coupling in all these systems is consistent with the electron spin relaxation behavior, being very similar between the strongest (2) and weakest (8) coupled materials, and the retention of the slower relaxation times of Cu in the presence of the faster relaxing {Cr-Ni} rings.

A series of new hybrid [2]rotaxanes (1, 3, 5, 7, and 9) has been made, each comprising a {Cr-Ni} ring about an asymmetric, long-chain secondary ammonium thread functionalized with a pyridyl group at one end. Each of these [2]rotaxanes binds to [Cu(hfac)$_2$]$_2$ to form the extended [2]rotaxane adducts 2, 4, 6, 8, and 10, respectively. In these structures, the distance between the Cu$^{1+}$ ion and {Cr-Ni} (ring) is dictated by the spacing between the secondary ammonium site and the pyridyl group in the thread (Table 1). These separations also control the stoichiometry of the adducts. In 2 and 4, the spacer is a single CH$_2$ group, and the resulting proximity of the bulky {Cr-Ni} pivalates and the hfac-groups only allows a single [2]rotaxane to coordinate at Cu, forming 1:1 adducts. The resulting square pyramidal geometry at Cu has the hfac groups folded away from the {Cr-Ni}, preventing coordination of a further [2]rotaxane at Cu. [For 2 and 4, the square pyramidal geometries at Cu have different orientations (and apical ligands) in the solid state, but may relax to the same structure in solution.] In contrast, in 6, 8, and 10 the spacers in the threads are longer [(CH$_2$)$_3$CH$_2$] or (C$_6$H$_4$CH$_2$)]. This relieves the strain between {Cr-Ni} and Cu such that a second [2]rotaxane can coordinate at Cu to form 2:1 adducts, with pseudo-octahedral coordination at Cu. There is no obvious reason why, of the 2:1 adducts, 6 should favor trans and 8 and 10 should favor cis geometries at Cu. 

CW EPR gives the magnitude, or upper limit, of the exchange coupling between the heterospin (S = 1/2) Cu$^{1+}$ ion and {Cr-Ni} ring(s). These order as 2 $\approx$ 4 $> 6 > 10 > 8$, with the range spanning 12$J$/B = 0.030 to $< 0.002$ cm$^{-1}$ (900 to <60 MHz). Given that these interactions are much weaker than the difference in Zeeman energy (ca. 5 GHz at Q-band magnetic fields), these are well described as AX or AX$_2$ spin systems. Resolution of such spectra are actually rather rare in CW EPR because, in general, when these conditions are met the J-splitting tends to lie within the experimental line width.31 In the materials studied here the resolution is aided by the very different intrinsic g-values of the {Cr-Ni} ring and Cu$^2+$ ion. The weak coupling in all these systems is consistent with the electron spin relaxation behavior, being very similar between the strongest (2) and weakest (8) coupled materials, and the retention of the slower relaxation times of Cu in the presence of the faster relaxing {Cr-Ni} rings.

Even for 4, with the shortest Cu–{Cr-Ni} distances, the largest magnitude component of the dipolar matrix is $-0.0034$ cm$^{-1}$ (100 MHz) (Table S2), almost an order of magnitude smaller than the experimentally observed $|J|$. Calculated CW EPR spectra including only the dipolar interaction matrix are indistinguishable from the sum of the isolated spins for all compounds studied here (using a fixed line width of 12 mT). Hence, dipolar coupling is not dominating in these compounds. Moreover, for 2 and 4, where there is clear resolution of the exchange-splitting in both g$_{\alpha}$ and g$_{\beta,\gamma}$ components of the spectra, we can experimentally observe the isotropic nature of J: an isotropic interaction is not consistent with dipolar coupling. The separation of Cu and {Cr-Ni} is too far for direct orbital overlap, hence the exchange must be through-bond. These pathways involve hydrogen bonds (of two fluorides of the ring to the two ammonium protons on the thread), which must limit the magnitude of the exchange. In contrast, we have previously reported {Cr-Ni} rings bound to Cu$^{1+}$ via a functionalized $-\text{O}_2\text{C}-\text{py}$ carboxylate on the ring, providing a through-bond pathway entirely via covalent (or coordination) bonds. In that case, we observed strong coupling in the EPR spectra (i.e., 12$|J|$ $\approx \Delta g_{\alpha,\beta}$; with $|J|$ = $-0.44$ cm$^{-1}$ or 13 GHz).

The anomalous coupling in compound 10 is consistent with a through-bond mechanism. These two complexes have similar py-CH$_2$CH$_2$NH$_2$R connectivity between Cu and {Cr-Ni} other than the position of substitution of the pyridyl: this is para for 6 and meta for 10. It is well understood from studies of electronic coupling via conjugated pathways that stronger...
coupling is observed for para than meta linked centers.\textsuperscript{35,36} We have noted related effects in a family of covalently bound \{Cr-Ni\} dimers linked via di-immines coordinated directly to the Ni ions.\textsuperscript{37} For 8, which has the longest linker, we observe no evidence of coupling in the CW EPR spectra and this defines an upper limit to any possible interaction (|J| < 0.002 cm\(^{-1}\) or 60 MHz). The largest magnitude component of the calculated dipolar matrix for 8 is \(-0.0012 \text{ cm}^{-1}\) (40 MHz; Table S2), hence for this length of linker the dipolar interactions are likely to be dominant or at least significant with respect to \(J\).

Very weak interactions, exchange and/or dipolar, are potentially measurable by pulsed dipolar EPR spectroscopy. We have previously measured the interactions between two \{Cr-Ni\} rings in different dimeric structures using double electron–electron resonance (DEER) spectroscopy,\textsuperscript{23} with interaction frequencies in the range ca. 6–1 MHz \{(Cr-Ni)\}–\{Cr-Ni\} separations 16–31 Å. In the materials studied here, the spectral separation of the two components is too large for DEER methods. An alternative technique is relaxation induced dipolar modulation (RIDME) which measures the oscillations in the echo decay of a slow relaxing spin due to \(T_1\) flipping of a faster relaxing spin. We have previously used RIDME to measure the interaction in a [2]rotaxane containing a \{Cr-Ni\} ring about a tempo-terminated thread \((\text{Ph-}(\text{CH}_2)_2\text{NH}_2\text{CH}_2\text{(C}_6\text{H}_4)_2\text{-tempo})[\text{Cr}_7\text{NiF}_8(\text{O}_2\text{C})_2\text{ff}]\)\textsuperscript{38} This gave a dipole-dominated frequency of 9 MHz (0.0003 cm\(^{-1}\); tempo–{Cr-Ni} distance of 16.8 Å) with a vanishingly small exchange interaction.

We attempted Q-band RIDME measurements on 8, observing on the slower relaxing Cu spectrum (five-pulse \(\pi/2\) \(-\pi/2\) \(-\pi\) \(-\pi/2\) \(-\pi/2\) \(-\pi/2\)-refocused echo sequence; 0.2 mM in 1:1 CH\(_2\)Cl\(_2\):toluene at 3 K). However, we did not observe any oscillations. The strength of interaction that can be detected by such methods is limited by the excitation bandwidth of the pulses,\textsuperscript{39} but we observed no oscillations for pulses as short as 12 ns. Hence, we believe the Cu–{Cr-Ni} interaction for 8 lies in a “blind-spot” between being detectable by CW EPR line broadening and RIDME experiments with conventional microwave pulses. This blind-spot is more significant for these sorts of materials than in organic diradicals\textsuperscript{40} because of the smaller intrinsic line widths of the latter. It may be possible to overcome this by exploiting broad-band excitation methods enabled by pulse shaping technologies.\textsuperscript{11} We are also currently designing Cu–{Cr-Ni} rotaxanes with longer and more rigid linkers that should put the interaction energy in the range appropriate for RIDME experiments, and diamagnetic analogues\textsuperscript{41} that will allow such experiments on aligned single crystals.\textsuperscript{55}

\section*{CONCLUSION}

In conclusion, we have reported a family of hybrid inorganic–organic rotaxanes based on paramagnetic inorganic rings templated about organic threads. The rotaxanes can be coordinated to Cu\(^{II}\) complexes, via a pyridyl terminal group templated about organic threads. The rotaxanes can be further transformed, to provide dissimilar electron spin {Cr\(_7\)Ni} dimers linked via di-immines coordinated directly to the Ni ions.\textsuperscript{37} For 8, which has the longest linker, we observe no evidence of coupling in the CW EPR spectra and this defines an upper limit to any possible interaction (|J| < 0.002 cm\(^{-1}\) or 60 MHz). The largest magnitude component of the calculated dipolar matrix for 8 is \(-0.0012 \text{ cm}^{-1}\) (40 MHz; Table S2), hence for this length of linker the dipolar interactions are likely to be dominant or at least significant with respect to \(J\).

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