

**Octacyanomethylate qubit candidates**

Journal:	<i>Dalton Transactions</i>
Manuscript ID	DT-COM-06-2018-002312.R1
Article Type:	Communication
Date Submitted by the Author:	03-Jul-2018
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Octacyanometallate qubit candidates †

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Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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We report the temperature dependence of the spin dynamics of the octacyanometallates [Mo(CN)₈]³⁻ and [W(CN)₈]³⁻. At 5 K, these complexes display remarkably long spin-lattice relaxation times of 1.05 s, and 0.63 s, respectively. We probe the contributing factors to the spin relaxation and demonstrate the impact of spin-orbit coupling as a handle to tune vibrationally mediated spin-lattice relaxation.

Quantum information processing (QIP) promises to fundamentally transform our approach to computation, enabling advances in fields ranging from biochemistry to physics to cryptography.^{1,2} Creation of viable quantum bits, or qubits necessitates the development of systems wherein long-lived superpositions of quantum states are possible. Electron spins, both in molecules and solid-state systems, offer considerable advantages as candidate qubits, including their facility of manipulation with pulsed microwaves.³⁻¹² Magnetic molecules are extremely promising species with which to study the variables that influence coherence time, T_2 , as synthetic chemistry offers a means to tune factors contributing to decoherence. Indeed, through such experimentation, our laboratory and others have developed design principles for increasing coherence times and have implemented them to achieve millisecond coherence times.¹³⁻¹⁶ These and other related advances have allowed the demonstration of gate operations, the proof of concept implementation of Grover's quantum search algorithm, and a theoretical demonstration of adiabatic quantum computation using electron spin qubits.¹⁷⁻²¹

To further enhance our understanding of spin dynamics in coordination compounds and to propel the field past single- or few-qubit systems, it is vital to understand the factors contributing to spin-lattice relaxation, T_1 , which represents the maximum information storage time as well as the upper limit to T_2 . Indeed, the study of T_1 has recently seen renewed interest for these reasons.^{22,23} By understanding the impact of chemical properties on the specific relaxation mechanisms operative in these compounds, we can implement new design principles to create the next generation of molecular qubits and larger multi-qubit architectures.

Homoleptic cyanometallate complexes and cyanometallate frameworks provide a convenient platform upon which to study fundamental spin relaxation processes. Cyanometallate complexes have been foundational in the development of modern transition metal chemistry; the study of cyanometallates dates back hundreds of years with the discovery of Prussian Blue.^{24,25} Over the past several decades, the study of magnetism using cyanometallate chemistry has flourished, with emphasis on the structurally predictable networks generated from cyanometallate building units.²⁶⁻³⁰ Such networks allow for the convenient construction of spatially well-defined arrays of paramagnetic metal ions, a highly appealing prospect for qubits.^{31,32} Indeed, if cyanometallate complexes can be established as viable candidate qubits, they would offer significant promise for the creation of spatially controlled qubit arrays.

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† Dedicated to Prof. Kim R. Dunbar in honour of her 60th birthday.

Electronic Supplementary Information (ESI) available: Synthetic and experimental details from EPR experiments, fitting parameters and discussion, additional figures and fits. See DOI: 10.1039/x0xx00000x

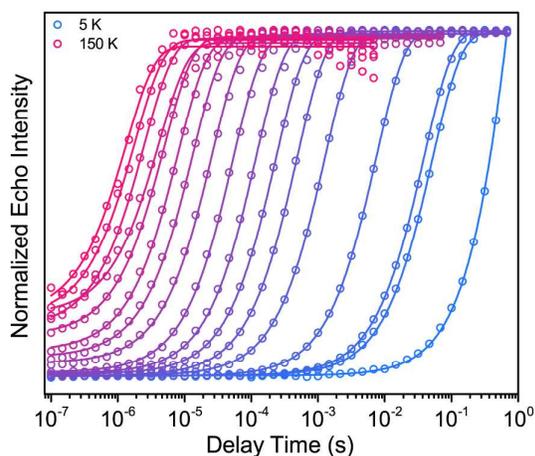


Figure 1: Saturation recovery curves as observed upon application of the described saturation recovery pulse sequence (see ESI for detail) on a 0.5 mM solution of **1** in a butyronitrile glass. The solid lines are fits to the data utilizing a monoexponential function.

To initiate our studies of cyanometallates, we probed the coherence properties of two structurally analogous homoleptic cyanometallate complexes, $[\text{Mo}(\text{CN})_8][\text{HNBu}_3]_3$ and $[\text{W}(\text{CN})_8][\text{HNBu}_3]_3$.³³ These two species feature within many reported frameworks,^{34–40} yet their coherence properties remain unknown. $[\text{Mo}(\text{CN})_8][\text{HNBu}_3]_3$ (**1**) and $[\text{W}(\text{CN})_8][\text{HNBu}_3]_3$ (**2**) offer two primary advantages which led to their selection for this study. First, since both complexes are $S = \frac{1}{2}$, their transitions are easily addressable, owing to the absence of zero-field splitting, which could disrupt electron paramagnetic resonance (EPR) addressability and thereby convolute the analysis of observed relaxation rates. Second, these eight-coordinate compounds are isostructural in solution.^{41,42} This structural similarity allows us to directly compare the influence of spin-orbit coupling on the processes that contribute to the spin-lattice relaxation time, T_1 .

To investigate the viability of these two complexes as candidate qubits, we acquired pulsed electron paramagnetic resonance (EPR) data for each complex in both a butyronitrile glass and a 40 vol % dimethylformamide/toluene glass over a wide temperature range. We observed a spin echo up to 150 K for **1** and 90 K for **2**. This overall relaxation behaviour largely persisted across samples and in different solvent conditions. Here, we were interested in two parameters: T_1 , the spin-lattice relaxation time, and T_2 , the coherence time. Understanding these variables is crucial to evaluating qubit performance, as T_2 represents the operational time of the qubit, and T_1 is both the upper bound to T_2 and is the maximum information storage time.⁴³

We initiated our experiments by determining T_1 through a saturation recovery experiment. In this experiment, a train of picket fence pulses saturates the transition. The return of the peak is then monitored as a function of time after the saturation pulse train with a Hahn-echo detection sequence. The echo intensity is then plotted as a function of the delay time between the end of the picket fence pulse train and the

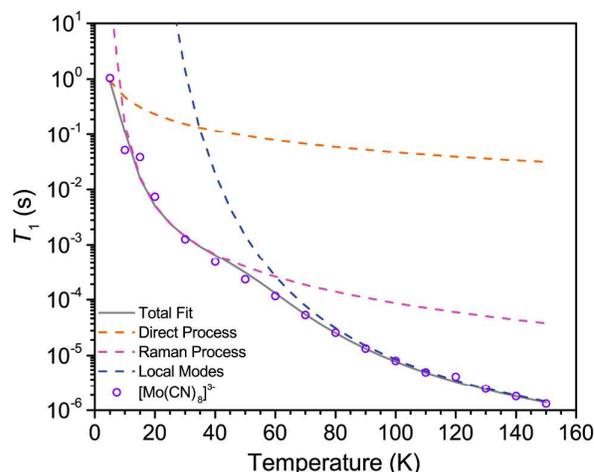


Figure 2: Plot of the spin-lattice relaxation time, T_1 vs. temperature from 5 K to 150 K in a 0.5 mM solution of **1** in a butyronitrile glass. The solid line is a fit to the data using the model given in the main text incorporating the direct process, the Raman process, and contributions from local modes (shown as dashed lines).

detection sequence. We extracted T_1 values by fitting the resulting saturation recovery curves (Figure 1) to a monoexponential function. The full details of the data fitting can be found in the ESI.

To determine which processes mediate the spin lattice relaxation of these compounds, we fit the temperature dependence of T_1 to the model

$$\frac{1}{T_1} = A_{\text{dir}}T + A_{\text{ram}}\left(\frac{T}{\theta_D}\right)^9 J_8\left(\frac{\theta_D}{T}\right) + A_{\text{loc}}\frac{e^{\Delta_{\text{loc}}/T}}{(e^{\Delta_{\text{loc}}/T} - 1)^2}$$

wherein we accounted for the influence of three different relaxation processes: the direct process, the Raman process and local modes. In the model above, A_{dir} , A_{ram} , and A_{loc} are the direct, Raman, and local mode coefficients respectively, θ_D is the Debye temperature, J_8 is the transport integral

$$J_8\left(\frac{\theta_D}{T}\right) = \int_0^{\theta_D/T} x^8 \frac{e^x}{(e^x - 1)^2} dx$$

and Δ_{loc} is the energy of the local mode vibrations.⁴⁴ Understanding each of these processes is vital to understanding the manifestation of chemical principles operative in the temperature dependence of the spin-lattice relaxation. At temperatures below 10 K, the direct process, wherein the excited state relaxes through a single phonon-induced spin flip, is frequently significant.⁴⁵ Given that this is formally a spin-forbidden process requiring the breaking of time reversal symmetry, the influence of a hyperfine field typically mediates this process.⁴⁶ In the intermediate temperature regime (20 – 60 K), the Raman process is most prominent. This process is a two-phonon event analogous to Raman scattering of photons. Above 60 K, the Raman process gives way to local mode relaxation, in which more localised vibrational modes dominate relaxation, in contrast to the long-range phonons contributing to relaxation *via* the Raman

process. These localised vibrational modes have become a subject of much interest in QIP, and scientists have recently

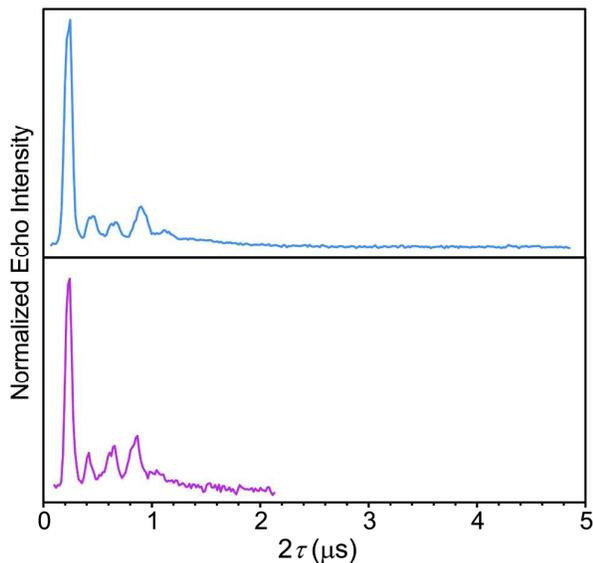


Figure 3: Two-pulse Hahn-echo decay curves of a 0.5 mM solution of **1** (top) and a 0.5 mM solution of **2** (bottom) collected at 40 K in butyronitrile. These curves are representative of the data across all temperatures sampled for both **1** and **2**. The extremely deep ESEEM modulation was composed of three frequencies, a result of the ^{14}N nuclei of the cyanide ions experiencing exact cancellation, resulting in a splitting of the nuclear sublevels.

achieved computational insight into them.^{47,48}

Notably, at 5 K, we observe unusually large values of T_1 for both **1** and **2** of 1.05 s, and 0.63 s in butyronitrile respectively. These values offer significant promise for the use of compounds such as **1** and **2** as qubits. We attribute the marked increase in T_1 relative to other coordination compounds to the relatively small contribution of the direct process to the relaxation in these systems. A fit to the data yielded a direct constant (A_{dir}) of less than $1.0 \text{ K}^{-1}\text{s}^{-1}$ for both compounds, which falls significantly outside of the range of $A_{\text{dir}} = 10 - 50 \text{ K}^{-1}\text{s}^{-1}$ found for most transition metal complexes.⁴⁰ We hypothesise that the small contribution of the direct process arises from the low natural abundance of spin-active nuclei with which the spin is directly interacting ($^{95}\text{Mo} = 15.92\%$, $^{97}\text{Mo} = 9.55\%$, $^{183}\text{W} = 14.31\%$).⁴⁶ More in-depth discussion of this phenomenon can be found in the ESI.

With increasing temperature, the Raman process begins to dominate, and the T_1 values of **1** and **2** diverge, consistent with the difference in spin-orbit coupling between the two complexes ($\zeta = 900 \text{ cm}^{-1}$ and $\zeta = 2700 \text{ cm}^{-1}$ for Mo^{5+} and W^{5+} respectively).⁴⁹ As spin-orbit coupling of the complex increases, the interaction between the spin and the phonon bath strengthens. Therefore, we expect ions containing heavier metals to display more rapid spin-lattice relaxation.⁵⁰ We find that **2** displays an order of magnitude larger Raman coefficient (A_{ram}) (0.86 MHz vs. 0.053 MHz) and slightly larger local mode coefficient (A_{loc}) (90 MHz vs. 20 MHz) than **1**. In addition to a smaller local mode coefficient, we observe lower

characteristic local mode energies for **2** than for **1** (416.1 K for **2** and 514.0 for **1**). We suggest that the strong interaction

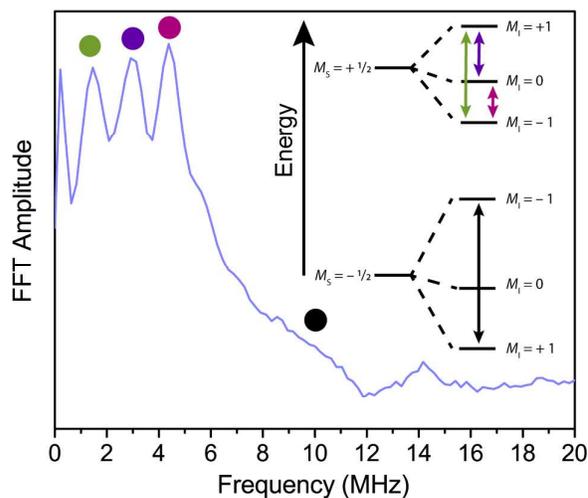


Figure 4: Fourier transform of the ESEEM modulation of a 0.5 mM solution of **1** at 40 K in butyronitrile. The three frequencies arise from nullification of the external field at the ^{14}N nuclei, which results in the splitting of the M_I states shown in the inset. The ^{14}N frequencies are marked with a colour corresponding to the transition to which they correspond.

between the spin and the electronic energy levels resulting from spin-orbit coupling in **2** increases the susceptibility of this complex to relax as a result of vibrational distortions to its ligand sphere. This, in turn, lowers the energy at which vibrational relaxation processes become operative in **2**.⁴⁵ The increase in the contributions of these vibrational relaxation processes leads to the loss of a measurable spin echo by 90 K in **2**, in contrast to the persistence of the echo in **1** until 150 K. In this case, the influence of specific local modes on the relaxation of these complexes cannot be deconvoluted from the spin-orbit contribution which powerfully impacts T_1 . Future studies on other cyanometallate series will probe this effect.

The second key figure of merit for a qubit is T_2 , which we investigated by performing two-pulse Hahn echo experiments. Intriguingly, upon inspection of the T_2 data, we observed deep electron spin echo envelope modulation (ESEEM) within the decay curves of both **1** and **2** (Figure 3). A Fourier transform of the data reveals that three distinct frequencies and a broad unresolved feature comprise the ESEEM (Figure 4). We attribute the unusually strong ESEEM in this case to a coincidental, but well preceded exact cancellation condition, wherein $A_{\text{iso}} = 2\nu_I$, where A_{iso} is the isotropic hyperfine parameter and ν_I is the nuclear Larmor frequency.⁵¹ This condition is met when the hyperfine field cancels out the external field, leaving the nuclear spin sublevels to split from the influence of the electric quadrupole interaction. As illustrated in Figure 4, we observe the diagnostic three-line pattern (green, purple, and red dots) followed by a broad higher frequency feature (black dot) in the Fourier transform of the data.

To interpret our T_2 data and extract information regarding the temperature dependence of T_2 for **1** and **2** without overparameterization, we normalised the data collected at each temperature to the 5 K data and subsequently fit the resulting curve to the exponential function:

$$N(\tau) = Ae^{-2\tau/T_R}$$

where N is the curve resulting from the division of a higher temperature curve by the 5 K curve, A is a y-axis scalar term, and T_R in this case is the ratio of the T_2 at the higher temperature to the T_2 at 5 K. This approach enabled us to obtain the temperature dependence of T_2 relative to the T_2 value at 5 K. We have included further details of this fitting in the ESI. For both compounds, we observe a decrease in T_2 as temperature increases – likely influenced by a decrease in T_1 and by fluctuations of methyl groups in the solvent molecules.^{45,52} This behaviour is expected, as in other studies, we and others have observed that T_2 generally remains constant as a function of temperature until approximately 30 K, and then decreases resulting from environmental interference.^{53–55} These data demonstrate, however, that we can measure T_2 out to the same temperature we can measure T_1 , thus indicating that these complexes are likely T_1 limited, meaning that the spin-lattice relaxation process indeed serves as the limiting factor to coherence. Future measurements at higher field will enable exact determination of T_2 values as we will have moved away from the exact cancellation condition.

Conclusions

We demonstrate that two cyanometallate complexes are viable qubit candidates, and indeed comprise two of the paucity of examples of second and third row transition metal complexes. At 5 K, these compounds exhibit exceptionally long spin-lattice relaxation times of approximately 1 s. We attribute this observation to the relatively small contribution from the direct process to spin-lattice relaxation resulting from the weak hyperfine field exerted by the transition metal nucleus on the electron spin. In accordance with the smaller spin-orbit coupling constant of **1**, we observe a smaller change in relaxation time with increasing temperature relative to **2**, implicating the stronger influence of spin-orbit coupling in the higher temperature vibrational relaxation processes than in the direct process. This reflects that changes in spin-orbit coupling can be used as a handle to control spin-lattice relaxation by tuning the Raman and local mode contributions but that the direct process is more strongly influenced by other factors.

We propose that these compounds and similar cyanometallates will continue to be valuable platforms upon which to perform these well-controlled studies into fundamental relaxation behaviours – particularly local mode relaxation processes, given the relative simplicity of the ligand field. We also suggest that cyanide frameworks incorporating these ions are worthy of study as potential solid-state qubit

arrays given the exceptionally long spin-lattice relaxation times of their constituent parts.

Conflicts of interest

There are no conflicts to declare.

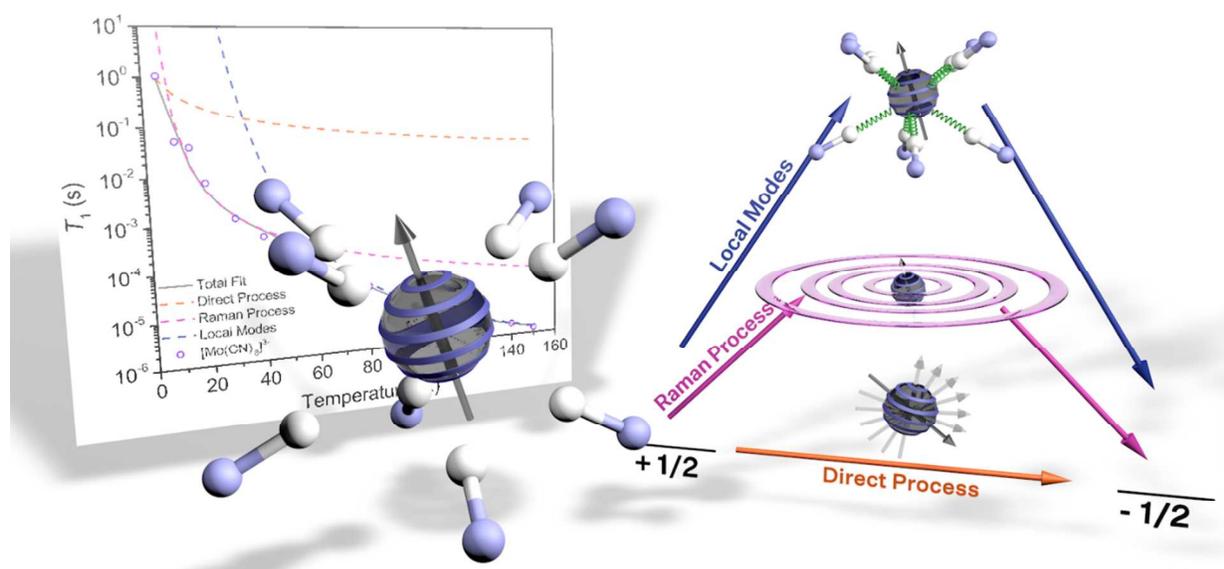
Notes and references

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§ We thank C.J. Yu for experimental assistance and helpful discussions. We further acknowledge assistance from M.S. Fataftah for insightful discussions into relaxation processes and for editing. This research was conducted with the support of the National Science Foundation for CAREER award CHE-1455017 (D.W.L. and D.E.F.), and the Presidential Early Career Award for Scientists and Engineers (FA9550-17-1-0247) (D.E.F.). This work was also supported by the National Science Foundation under grant no. CHE-1565925 (M.R.W.). T.J.P. recognises the support of an NSF Graduate Research Fellowship (DGE-1324585).

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Cyanometallates are excellent building blocks for networks, we demonstrate counterintuitively long spin-lattice relaxation times in two heavy octacyanometalltes.