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Multiple Quantum Coherences from Hyperfine Transitions in a Vanadium(IV) Complex

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Supporting Information

ABSTRACT: We report a vanadium complex in a nuclear-spin free ligand field that displays two key properties for an ideal candidate qubit system: long coherence times that persist at high temperature, T_2 = 1.2 μs at 80 K, and the observation of quantum coherences from multiple transitions. The electron paramagnetic resonance (EPR) spectrum of the complex $[V(C_8S_8)_3]^{2-}$ displays multiple transitions arising from a manifold of states produced by the hyperfine coupling of the $S = {}^1/_2$ electron spin and $I = {}^7/_2$ nuclear spin. Transient nutation experiments reveal Rabi oscillations for multiple transitions. These observations suggest that each pair of hyperfine levels hosted within $[V(C_8S_8)_3]^{2-}$ are candidate qubits. The realization of multiple quantum coherences within a transition metal complex illustrates an emerging method of developing scalability and addressability in electron spin qubits. This study presents a rare molecular demonstration of multiple Rabi oscillations originating from separate transitions. These results extend observations of multiple quantum coherences from prior reports in solid-state compounds to the new realm of highly modifiable coordination compounds.

Quantum information processing (QIP) has the potential to impact areas across science, including the simulation of quantum systems[1] and understanding protein folding.[2] There are numerous candidates for the smallest unit of a QIP system, the qubit. Of those candidates, electronic spin is appealing because electronic spin based qubits can be addressed by EPR spectroscopy and chemical synthesis can be employed to tune and scale these systems.[3] The viability of electronic spin based qubits has been well established in solid-state compounds[4] and molecular species.[3,5−7] Thus far, however, the vast majority of these compounds rely on either lanthanides or multinuclear species as the source of electronic spin. However, application of the method by which chemists can naturally approach the study of new qubits, synthetic fine-tuning, necessitates the development of alternative, more easily adaptable systems. In particular, mononuclear coordination complexes of transition metals allow the careful study and advancement of candidate qubits due to the relative simplicity of ligand field and structural adjustment.

Much of the research into electronic spin-based molecular qubit candidates is hampered by rapid collapse (decoherence) of electronic spin superpositions.[6] In one prior example, research on a mononuclear system[7c] revealed significantly longer coherence times at much high temperatures than multinuclear systems, further reinforcing their utility. The evolution of molecular systems appropriate for QIP requires not only increasing qubit coherence times, but also strategies to scale systems to include multiple qubits in a single molecular assembly. One approach to scaling may utilize the multitude of transitions that result from hyperfine interactions in complexes with $S = {}^1/_2$ paramagnetic ions and large nuclear spins I. Here, a large I produces a plethora of transitions, while the low electronic spin suppresses spin-related decoherence pathways.[8]

Proofs-of-concept for this approach were demonstrated in numerous investigations of coupled electronic and nuclear spins in solid-state compounds where faster operation times, relative to pure nuclear spin qubits, and longer coherence times, relative to pure electronic spin qubits, were observed.[4c−f] Of importance is the development of synthetically tunable, molecule-based hyperfine systems for QIP, as such systems will allow synthetic, structural fine-tuning and afford the fundamental insight required for the directed modification of qubits. Thus, our attention was drawn toward V^{4+} complexes with nuclear spin free (I = 0) ligands. Vanadium(IV) is an $S = {}^1/_2$ ion with a nearly 100% naturally abundant ^{51}V isotope ($I = {}^7/_2$), generating eight potential EPR transitions for investigation. Our preference for nuclear spin-free ligands arises from the knowledge that nuclear spins are potent causes of both decoherence and spectral broadening.[6,9] These two sources limit applicability of a hyperfine qubit; the former destabilizes superpositions, while the latter precludes manipulation of individual hyperfine qubits. Herein we report a pulsed EPR analysis of a V^{4+} complex $(Bu_4N)_2[V(C_8S_8)_3]$ (**1**)[10] (see Figure 1) that demonstrates both long coherence times and coherent spin control of multiple hyperfine transitions.

To realize the observation of quantum coherences from multiple hyperfine transitions, the separations generated by hyperfine coupling (A) with the vanadium nucleus need to be larger than the manipulation pulse bandwidth. Otherwise, spectral convolution may lead to loss of resolution for qubit control. Thus, the initial step in the evaluation of **1**'s potential for QIP was determination of A. An echo-detected, field-swept spectrum (EDFS) was recorded by monitoring the integrated electron spin echo intensity as a function of applied magnetic dc field (see Figure 2). A dilute concentration (1 mM) of **1** in

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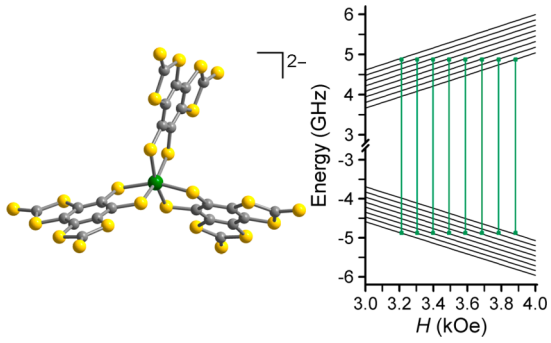

Figure 1. (Left) Molecular structure of $[V(C_8S_8)_3]^{2-}$ as determined in the crystal structure of the Ph_4P^+ salt.[10] Green, yellow, and gray spheres represent vanadium, sulfur, and carbon atoms, respectively. (Right) Energies of spin states with increasing applied dc field for $[V(C_8S_8)_3]^{2-}$ oriented with the molecular trigonal axis perpendicular to the applied field. Energies were calculated for an $S = {}^1/_2$ and $I = {}^7/_2$ spin with $g_\parallel = 1.992$, $g_\perp = 1.972$, $A_\parallel = 6$ MHz, $A_\perp = -258$ MHz. Capped green vertical lines indicate observed $\Delta M_S = 1$, $\Delta M_I = 0$ transitions potentially accessible for QIP.

butyronitrile was used to minimize interactions with other nearby vanadium complexes. Note that in contrast to standard continuous wave (cw) EPR, the spectrum has an absorptive line shape and not a derivative type. The spectrum reveals a very sharp absorption centered at 3492 Oe with seven broad, relatively weaker transitions at 3231, 3313, 3404, 3583, 3678, 3771, and 3860 Oe. The separations between peak maxima are relatively constant at an average of 90(4) Oe, a value larger than the expected maximum pulse bandwidth (30 Oe for a 10 ns pulse). Easyspin[11] was used to model the spectrum and quantitate the strength of A for the $S = {}^1/_2$ electronic and $I = {}^7/_2$ nuclear spins of the ^{51}V ion. The best simulation with the axial Hamiltonian $\hat{H} = g\mu_B \boldsymbol{HS} + \boldsymbol{IAS}$, where g is an axial g-tensor, μ_B is the Bohr magneton, $\boldsymbol{H}$ is the magnetic field, $\boldsymbol{S}$ is electronic spin, $\boldsymbol{I}$ is the nuclear spin of the ^{51}V nucleus, and $\boldsymbol{A}$ the axial hyperfine coupling tensor, produced $g_\parallel = 1.992$, $g_\perp = 1.972$, $A_\parallel = 6$ MHz, and $A_\perp = -258$ MHz for **1**. These g and A values are in line with expectations for a trigonal prismatic V^{4+} ion with the principal axes of g and A coincident to the pseudotrigonal molecular axis.[12,13] Further, though the magnitudes of the $g_\parallel$ and $g_\perp$ values compare favorably with other triligated V^{4+} species with bidentate S-donor ligands, the

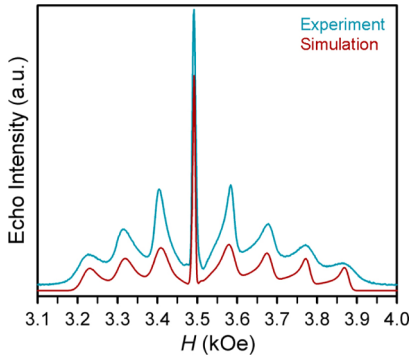

Figure 2. Echo-detected, field-swept, X-band spectrum of a 1 mM solution of **1** in butyronitrile at 20 K (blue line). The red line is a simulation produced using Easyspin for an $S = {}^1/_2$ spin and $I = {}^7/_2$ nuclear spin with $g_\parallel = 1.992$, $g_\perp = 1.972$, $A_\parallel = 6$ MHz, and $A_\perp = -258$ MHz.

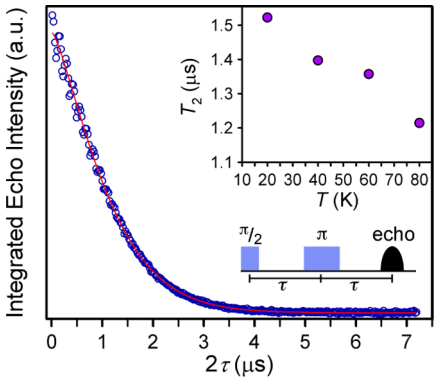

Figure 3. Integrated echo intensity as a function of delay time (τ) for **1** under an applied dc field of 3486 Oe at 80 K with graphical depiction of Hahn-echo pulse sequence. The red line is a best fit to a stretched exponential decay with $T_2 = 1.21(1)$ μs. Inset: Temperature dependence of T_2 for **1**.

isotropic hyperfine coupling, $A_{iso} = (A_\parallel + 2A_\perp)/3$, at 174 MHz ($58 \times 10^{-4}$ cm^{-1}) appears at the lower limit of expected values (175−197 MHz).[13] Note, this variability in the hyperfine coupling constant as a function of ligand highlights a potential route toward future transition fine-tuning in the trigonal pseudooctahedral vanadium(IV) platform. The results of the theoretical simulation indicate the $S = {}^1/_2$ levels of **1** are split into a manifold of $|M_S, M_I\rangle$ states as depicted in Figure 1. Thus, the transitions observed in Figure 2 are of the type $|-({}^1/_2), M_I\rangle \rightarrow |+({}^1/_2), M_I\rangle$, beginning with the $|-({}^1/_2), +({}^7/_2)\rangle \rightarrow |+({}^1/_2), +({}^7/_2)\rangle$ transition at 3231 Oe and $|-({}^1/_2), -({}^7/_2)\rangle \rightarrow |+({}^1/_2), -({}^7/_2)\rangle$ at 3860 Oe. The EDFS spectrum demonstrates that the hyperfine coupling in **1** provides eight separate transitions potentially available for QIP, despite the smallest possible nonzero electronic spin. The observation of an echo at each peak indicates that superposition formation occurs at each of the hyperfine transitions observed in the spectrum (see Figure 1). Thus, particularly rich coherent spin dynamics appear operational in **1**.

Determination of **1**'s suitability as a qubit necessitated establishing the longevity of its superposition state, commonly parametrized as the spin−spin relaxation time or coherence time, T_2.[14] For **1**, this was accomplished via measuring the decay rate of the magnetization echo induced by application of a Hahn-echo pulse sequence. These experiments were performed on a 1 mM solution of **1** in butyronitrile (see Figure 3, Supporting Information) at an applied field of 3486 Oe, the field of the largest intensity echo (see Figure 2). For **1** at 20 K, the spin−echo decays in intensity with increasing delay time 2τ, and was modeled with an exponential decay to extract $T_2 = 1.52(1)$ μs from the experimental data. The spectrum also exhibits a weak oscillation in intensity. This oscillation is from electron spin−echo envelope modulation (ESEEM) by protons of the surrounding environment (see Figure S2).[14] With increasing temperature, the value of T_2 decreases only slightly, from 1.40(1) μs at 40 K to 1.36(1) μs at 60 K and finally 1.21(1) μs at 80 K. These results are exceptional within the range of molecular paramagnetic species studied thus far for QIP. Mono- and multinuclear species often possess comparable T_2 values, yet such values are observed at low temperatures (<10 K) and typically drop significantly with increasing temperature.[3b,5a,6,7] Among similarly investigated electron spin-qubits of vanadium, we note that the T_2 values are longer than those detected for the $S = {}^1/_2$ $[V_{15}As_6O_{42}(H_2O)]^{6-}$ ($T_2 \approx$

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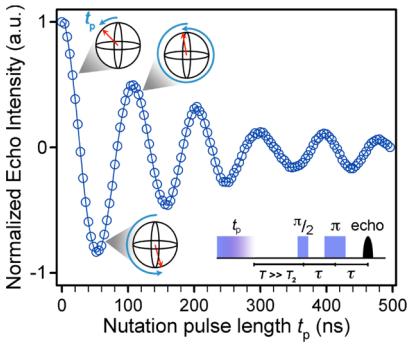

Figure 4. Echo intensity as a function of increasing nutation pulse length, t_p, collected on a 1 mM solution of **1** at 20 K, H_{dc} = 3486 Oe, and B_1 is attentuation of 11 dB. The orientations of the magnetization vector following specific t_p values are graphically depicted along with the employed pulse sequence.

0.2 μs at 2.4 K) despite the significantly higher temperature range of investigation here.[5b,g] We also note that at the temperature scale of the current measurements, the T_2 values are comparable to the best mononuclear candidate CuPc ($T_2 \approx$ 1 μs).[7c] Thus, the T_2 values for **1** suggest that it would be superior to those of many other paramagnetic transition metal complexes with regard to the future study of QIP.

An advantage of **1** as a hyperfine qubit for QIP is the multiple transitions for superposition formation within an easily accessible field and frequency window. Importantly, this benefit is only sustained if the other potential superpositions are as long-lived as the one corresponding to the primary echo of Figure 2. Application of Hahn-echo pulse sequences at 20 K and H_{dc} = 3400 and 3580 Oe (see Figure S2), the fields of the two next-strongest echoes observed in the EDFS, provided decay curves that were modeled to give T_2 values of 1.52(1) and 1.57(4) μs, values very close to that observed at 3486 Oe. Thus, superposition stability at 20 K does not appear to be extremely sensitive to these particular transitions in **1**. Of the spin states of **1**, the electronic parts of the states can be expected to perform a more active role in decoherence than the nuclear contributions, as electronic spins are generally more sensitive to the surrounding environment than are nuclear spins. Thus, decoherence pathways in **1** for the superpositions accessed at 3400, 3486, and 3580 Oe are likely nearly identical, which may enforce the similar T_2 values for these superpositions.

To be viable, a qubit requires, in addition to a long T_2, the ability to be placed into any arbitrary superposition. These properties in **1** were investigated by variable-power transient nutation experiments. In these experiments, a variable-length microwave nutation (tipping) pulse (t_p) is applied to the system, which places the spins into a particular superposition determined by the power and length of t_p. Subsequently, the existence of the superposition is verified by the observation of an echo following the application of a two-pulse Hahn-echo sequence (see pulse sequence depicted in Figure 4). As shown in Figures 4 and S3, a damped oscillation is observed at multiple powers for **1**. In the absence of ESEEM or cavity background signals, these oscillations signify that all arbitrary superpositions are indeed accessible for the primary transition of **1**. These nutations are known as Rabi oscillations. Exclusion of the aforementioned oscillation generators proceeded via analysis of dependence of the frequency of the cycling, the Rabi frequency (Ω_R), on the microwave power (B_1). If the oscillations are genuinely of the Rabi type, the frequency will vary with the magnitude of B_1. Fourier analysis of the nutation data at 3486 Oe yielded Ω_R values of 28.1, 17.6, and 10.2 MHz at B_1 attenuation of 3, 7, and 11 dB, respectively (see Figures S4 and S5). These values overlap closely with those of the $|M_S = -(^1/_2)\rangle$ to $|M_S = +(^1/_2)\rangle$ transition of a compound commonly employed as a standard for these measurements, 2,2-diphenyl-1-picrylhydrazyl radical (DPPH). Together, these results establish the observation of Rabi oscillations, signifying that **1** is able to reach any arbitrary superposition.

Investigation of the possibility of coherent spin manipulation of the other $\Delta M_S = 1$, $\Delta M_I = 0$ transitions proceeded via additional nutation experiments at H_{dc} = 3400 and 3580 Oe (see Figures S3–S5). At each of these fields, Rabi oscillations are also observed, with identical Ω_R values and B_1 dependence as seen at H_{dc} = 3486 Oe. The time span between a maximum in the oscillation and an adjacent minimum indicates the length of time required for the most rudimentary logic operation, a spin flip, for a transition at a given B_1. In principle, this operation time should be significantly shorter than the lifetime of the qubit for applicability. At 3400, 3486, and 3580 Oe, inspection of the maxima and minima reveal such time to be 20, 34, and 52 ns at 3, 7, and 11 dB attenuation of B_1, respectively. This similarity is likely because, as for the transition at 3486 Oe, the probed transitions are of $|M_S = -(^1/_2)\rangle$ to $|M_S = +(^1/_2)\rangle$ character. Nevertheless, the observed oscillations establish the $|-(^1/_2), +(^3/_2)\rangle \rightarrow |+(^1/_2), +(^3/_2)\rangle$ and $|-(^1/_2), -(^1/_2)\rangle \rightarrow |+(^1/_2), -(^1/_2)\rangle$ transitions in **1** as additional platforms for coherent spin control, with operating times 2 orders of magnitude faster than the corresponding superposition lifetimes.

The foregoing results underline the potential of molecular V(IV) complexes for the development and understanding of hyperfine qubits. The promising coexistence of long T_2 values and relatively short operation times across multiple hyperfine transitions in a molecular species is unprecedented. Indeed, these properties together suggest that a collection of interacting V(IV) ions may perform as a large register of hyperfine qubits. Moreover, we note that the tunability of the system, primarily through selection of alternative ligands or counterions, offers a potential route to a deeper understanding of factors that affect the utility of V(IV) spin centers for QIP. In light of the potential structural and electronic tunability of the VS_6 platform, future work will be directed toward probing the dependence of the coherent spin dynamics on structural and electronic changes to the coordination sphere of the V^{4+} ion.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full experimental and crystallographic details; additional spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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