Ligand Radicals as Modular Organic Electron Spin Qubits


Abstract: The intrinsic redox activity of the dithiolene ligand is presented here as the novel spin host in the design of a prototype molecular electron spin qubit, where the traditional roles of the metal and ligand components in coordination complexes are inverted. A series of paramagnetic bis(dithiolene) complexes with group 10 metals—nickel, palladium, platinum—provides a backdrop to investigate the spin dynamics of the organic ligand radical using pulsed EPR spectroscopy. The temperature dependence of the phase memory time (T_M) is shown to be dependent on the identity of the diamagnetic metal ion, with the short times recorded for platinum a consequence of a diminishing spin-lattice (T_1) relaxation time driven by spin-orbit coupling. The utility of the radical ligand spin center is confirmed when it delivers one of the longest phase memory times ever recorded for a molecular two-qubit prototype.

Introduction

The seminal work of Leuenberger and Loss[1] who proposed encoding quantum information using the spin states of molecular magnets has spurred a flurry of activity in the development of molecule-based electron spin qubits.[2] The advantage of electrons resides in the ease of their initialization and a large gyromagnetic ratio that facilitates their manipulation to effect quantum algorithms.[3, 4] The drawback is they tend to have less favorable coherence lifetimes than their nuclear spin counterparts as expressed in terms of the spin-lattice relaxation (T_1) and the phase memory (T_M) times, where the latter represents the lifetime of the superposition state.[5] For spin qubits based on transition metal complexes, this handicap has been conquered by skillful tailoring of the chemical environment about the paramagnetic metal ion to remove components with deleterious effects on the performance. Tactics such as nuclear spin bath control and careful isolation of the paramagnetic center have catapulted the phase memory time of a paramagnetic metal ion to times, where the latter translates the ubiquitous dithiolene ligand, which is readily oxidized and linked by diamagnetic metal ions. The construct utilizing the ubiquitous dithiolene ligand, which is readily oxidized to create the S=1/2 center confined to its constituent, nuclear-spin-free (S_2C_2) core.[17, 18] These long coherence times lead to low error rates and high fidelities that are required for large-scale, fault-tolerant quantum computing.[9]

While these single-spin qubits are primed for such an undertaking, they do not lend themselves to meeting the equally important challenge of quantum gating and addressability that are requirements for universal quantum computation. To tackle this goal, a new design is needed to produce molecules with more than one spin center that can be selectively controlled to generate entanglement. These long coherence times lead to low error rates and high fidelities that are required for large-scale, fault-tolerant quantum computing.[9]

With the long phase memory times realized, considerable energy is now focused on dissecting the intricacies of spin dynamics essential to quantum information processing and related disciplines.[10–12] While these single-spin qubits are primed for such an undertaking, they do not lend themselves to meeting the equally important challenge of quantum gating and addressability that are requirements for universal quantum computation. To tackle this goal, a new design is needed to produce molecules with more than one spin center that can be selectively controlled to generate entanglement. These long coherence times lead to low error rates and high fidelities that are required for large-scale, fault-tolerant quantum computing.[9]

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Results and Discussion

Synthesis and characterization

Compounds 1–3 were synthesized in high yield via one-electron reduction of the parent neutral complexes using PPh₃BH₄. The integrity of the sample was conveniently tracked with electronic spectroscopy, as the prominent band is distinct both in energy and intensity when comparing the monoanionic and neutral members that constitute each electron transfer series (Figure S1 in Supporting Information). The characteristic absorption band is diagnostic of the electronic structure of these bis(dithiolene) species where the low-energy yet high intensity is defined as an intervalence charge transfer (IVCT) transition to the higher occupied molecular orbital (HOMO), which is the singly-occupied (SOMO) $b_{2g}$ MO in $D_{2h}$ symmetry, from the $b_{1u}$ HOMO-1, which are both ligand-based.[19]

The molecular structures of 1–3 have been characterized by X-ray diffractometry; a representative structure is shown in Figure 1. The central metal ion adopts a square planar geometry ($a =17.6\,\text{Å}$). This is a consequence of crystal packing as evidenced by the perfectly planar geometry ($a =0\,\text{Å}$) of the complex ion with a [NEt₄]⁺ counterion.[20] The anisyl substituents are rotated relative to the $\{\text{NiS}_4\}$ unit in 1 exhibiting the largest drift toward tetrahedral ($a =14.8\,\text{Å}$) across the series. Therefore via induction, the anisyl group is electron donating reflecting the softer, more polarizable sulfur atoms compared with aromatic dithiolenes or maleo-nitrile dithiolate, mnt.[21]

![Figure 1. The molecular structure of [Ni(adt)$_2$]$.\text{Ni}$, showing distance of ligand protons from the spin barycenter (top), and the Mulliken spin density population from ZORA-PBE0 DFT calculations (bottom). The spin density at the metal ion in 1–3 is listed. Spin density is plotted with an isovalue 0.004 au.](Image)

An important consideration for the forgoing examination of the spin dynamics of this molecular building block is the presence of protons on the periphery of the ligand. Despite the absorption of conjugation that confines the spin density to the ($\text{S}_2\text{C}_2$) core (Figure 1), the vocal nuclear spin of protons pres-ents an efficient decoherence pathway through dipolar coupling.[10, 22] The three types of proton in the ligand-two aromatic and one methyl-are on average 3.4 &., 5.5 &. and 7.5 &., re-spectively, away from the spin barycenter (Figure 1). The orbital parentage manifests in the intraligand bond distances for 1–3. The average C bond distance of ca. 1.74 &. and average C C distance of ca. 1.37 &. are shorter and longer, respectively, than the corresponding bond lengths in the dianionic dithio-late form of the ligand (Table S2). This is characteristic of an oxidized dithiolene, which due to the centrosymmetry of each complex, is distributed over both ligands. The electronic structure of 1–3 is defined as $[\text{M}^{\text{II}}(\text{L}_2^3)]^1$ ($L =\text{dithiolene}$), which is an abridged description derived from the limiting resonance forms $[\text{M}^{\text{II}}(\text{L}^2)](\text{L})^1$ $[\text{M}^{\text{II}}(\text{L})](\text{L}^2)^1$.[19]

Continuous-wave EPR spectroscopy

The cw X-band EPR spectra of 1–3 recorded in frozen CH₂Cl₂/ DMF solution at 130 K display signals typical of an $S =1/2$ system with rhombic g-values in agreement with those reported in the literature.[23] The profiles for all three spectra are similar with $g_1 > g_2 > g_3$ (Table 1). The spectrum of 2 exhibits weak shoulders about each $g$-value indicating the presence of hyperfine splitting from $^{195}$Pt ($I =5/2$, 22.2 % abundant), which are most pronounced on the low-field lines (Figure S7). Spectral simulation was achieved with A = (9.0, 5.9, 4.6) 0 10 $^6$ $^-1$ cm. A more prominent hyperfine interaction is observed in the spectrum of 3, where coupling to the $^{195}$Pt ($I =1/2$, 33.8 % abundant) isotope yielded A = (33, 106, 83) 0 10 $^6$ cm $^-1$ (Figure S9). The larger coupling in 3 is a direct consequence of the nuclear $g$-value of $^{195}$Pt (gN =1.219) which is roughly 5 times

| Table 1. Summary of experimental and calculated data[a] for 1–3. |
|---|---|---|
| M | Ni | Pd | Pt |
| $\mu_{\text{iso}}$ [cm$^{-1}$][b] | 700 | 1300 | 3400 |
| %MED | 25.2 | 12.8 | 18.9 |
| $\lambda_{\text{MM}}$ | 0.25 | 0.11 | 0.14 |
| $g_1$ | 2.1182 (2.0979) | 2.0508 (2.0521) | 2.1653 (2.1864) |
| $g_2$ | 2.0402 (2.0650) | 2.0419 (2.0487) | 2.0654 (2.1062) |
| $g_3$ | 1.9993 (2.0013) | 1.9628 (1.9671) | 1.8472 (1.8644) |
| $R_{\text{gH}}$ | 0.66 | 0.10 | 0.31 |
| $\Delta g_{\text{YY}}$ | 0.1189 | 0.0880 | 0.3181 |
| $B_0$ [mT] | 340.6 | 343.3 | 339.1 |
| $T_{\text{1,6}}$ [ms][d] | 6.31(3) | 4.99(1) | 1.64(2) |
| $T_{\text{M,5}}$ [ms][e] | 4.89(1) | 2.07(2) | 3.63(2) |
| T[n] [MHz][f] | 13.6 | 15.5 | 14.5 |

[a] From ZORA-PBE0 level of theory (calculated g-values in parenthesis).
[b] Values taken from ref. [26]. [c] Rhombicity, $R_0 = (g_1 \, g_2)/(g_1 \, g_3)$. [d] $g$-anisotropy, $D_g = g_1 \, g_2$. [e] $B_0 =344.5$ mT corresponding to the high field hyperfine line of $g_2$ (see Figure S16). [f] Relaxation time at 10 K (error given in parenthesis). [g] Rabi frequency from nutation experiment at 10 K and 6 dB microwave attenuation.
larger than that of $^{105}$Pd ($g_N = 0.256$). The more meaningful measure of metal content in the magnetic orbital is the rhombicity of the g-values which ranges from 0.10 for 2 to 0.66 for 1 (Table 1). The low rhombicity as well as the low isotropic part of the magnetic hyperfine coupling indicates that the metal contribution to the SOMO is smallest for 2. Conversely, 1 being the most rhombic has the largest metal contribution to its magnetic orbital. The anisotropy of the g-values stems from the spin-orbit coupling (SOC) constant of the metal center tempered by its contribution to the ground state. As SOC commutes as $Z^1$, the largest g-anisotropy is observed for 3 because of the greater SOC constant of platinum ($Z = 78$). The equivalent g-anisotropy for 1 and 2 reflects the smaller palladium content to the SOMO in the latter despite having the larger SOC constant. Interestingly, the metal content as assessed by g-anisotropy is also modulated by the dithiolene ligand, being larger for aromatic-type dithiolenes such that a more significant proportion of the spin resides on the alkyl dithiolene variant used here.$^{21, 25}$

Theoretical calculations

The geometry-optimized structures for the complex anions in 1–3 are in excellent agreement with the experimental data, with the metal-sulfur and intraligand bond distances and angles accurately reproduced (Table S2 in Supporting Information). Moreover the optimized structures are strictly planar demonstrating the modest tetrahedralization about the nickel ion in 1 as a consequence of crystal packing. Inspection of the frontier MOs reveals four metal d orbitals lower in energy than the ligand-based $b_{2g}$ and $b_{3g}$ ($D_{2h}$ point group) which undergo symmetry-allowed $p$-interactions with metal d orbitals.$^{19}$ The $b_{2g}$ symmetric SOMO is ligand-centered such that the electronic structure is best represented as $[M^1(L_2^3)]^1$. The unpaired spin is delocalized across both ligands as regulated by the metal ion, whose contribution trends Ni > Pt > Pd across the series (Table 1). As a consequence 2 has a low spin density of 0.11 at the Pd$^{II}$ ion indicating an almost negligible contribution from the Pd$^{III}$ configuration to the ground state. In contrast, the 0.25 spin density at nickel shows enhanced Ni$^{III}$ character in 1 that accounts for its EPR spectral profile. The electronic structure has been verified by very accurate calculation of the g-values for 1–3 (Table 1). This level of precision allows for meaningful insight that correlates composition and electronic structure factors on the spin dynamics of molecular qubits based on coordination complexes.

Pulsed EPR spectroscopy

The decoherence of the spin superposition as quantified by the phase memory time was investigated for 1–3 over the temperature range 5–120 K on 1 mm solutions in 2 % [D$_7$]DMF/CD$_2$Cl$_2$. The decay of the Hahn echo measured at the magnetic field corresponding to the absorption maxima ($g_2$) in the EPR spectrum follows a biexponential profile; the Hahn echo decay for 1–3 measured at 10 K are compared in Figure 2. The biexponential fit gives an estimate for the fast ($T_{M,f}$) and slow ($T_{M,s}$) relaxation processes, with the latter used as the qubit’s decoherence parameter. The slow component is longest for 1 at 4.89(1) ms, and shortest for 2 at 2.07(2) ms, with 3 residing between these times at 3.63(2) ms (Figure 3). These times are equal to or eclipse a swathe of S = 1/2 coordination complexes reported recently.$^{22}$ The few with phase memory times that surpass this have their composition and environment purged of nuclear spins.$^{6, 11, 25}$ The phase memory time displays no orientation dependence nor does it correlate with g-anisotropy as observed previously.$^{25, 27}$ The variation within the series of 1 >3 >2 is directly correlated to the spin density at the metal center (see above). The major contributor to spin decoherence is electron-nuclear spin interaction, which is the dominant factor at very low temperatures (<30 K). The nuclear spin bath comprises protons on the anisyl substituents of the dithiolene ligand, the protons and

Figure 2. Comparison of the Hahn echo data (open circles) and corresponding biexponential fit (solid lines) for 1–3 recorded in 2 % [D$_7$]DMF/CD$_2$Cl$_2$ at 10 K. Fit parameters are given in Tables S6–S8.

Figure 3. Comparison of the slow (top) and fast (bottom) contributions to phase memory time ($T_{M}$) for 1 (squares), 2 (circles) and 3 (triangles) over the temperature range 5–120 K. Error bars are based on the standard deviation of the fit (Tables S6–S8).
noteworthy that simultaneous hyperfine coherences within a manageable field range to build up a multi-electron and nuclear spin transition allowing access to quantum hyperfine component about \( g \).

As group 10 is descended (Figure 4). This is the same trend observed in complexes (Figure S1).

The significance of SOC has been previously shown to impact spin-lattice times when comparing first- and second-row metals in systems where the metal is the spin host. Here, with an unpaired electron predominantly on the ligand, the metal ion presents a heavy-atom effect, a phenomenon that has been exploited in a range of materials, most notably enhancing the performance of semiconductors in spintronic devices.

At the measurement temperature, a direct spin relaxation process is dominant, but as the temperature increases the Raman mechanism takes precedence and becomes more efficient with increasing SOC. While relaxation times cannot be directly computed, we have used the calculated electronic structure parameters to estimate \( T_{1,s} \) for 1 and 2 when compared to that for 3. This estimate uses the ratio of the SOC constant for Ni and Pd to that for Pt, and the parentage of the spin in the molecule that resides on the metal ion (Table 1). These estimates are compared to the experimental values in Figure 4, and the good agreement obtained highlights the intrinsic association between SOC and spin-lattice relaxation such that it is an important consideration in the makeup of any spintronic system. We have begun to explore using these molecules as an alternative to metal dichalcogenides in graphene-based heterostructures.

To demonstrate coherent spin control, echo-detected nutation experiments were performed by applying a microwave pulse of duration \( t_p \) to produce Rabi-like oscillations between two states that correspond to arbitrary superpositions of the electron spin (Figure 5 a). Confirmation that these are Rabi oscillations comes from the linear dependence of the oscillation frequency \( \omega_R \) with the applied microwave amplitude \( B_1 \), which was varied by selecting microwave attenuations of 6, 10 and 14 dB (Figure 5 b). Changes in the oscillations were observed at \( t_p \) >400 ns which were independent of the microwave attenuation and arise from the electron spin interacting with surrounding protons.
To expand the utility of the radical ligand as spin host, we have developed a series of heteroleptic metalldithiolene complexes as a platform for implementing two-qubit quantum gates.\(^{[17, 18, 38]}\) The central design strategy involves \(\{\text{MS}_2\text{P}_2\}\) building blocks where the metal is coordinated by a redox-active di-thiolene ligand on one side and a redox-inert diphosphine ligand on the other. The latter serves as the vector of propagation, and we have synthesized complexes with two metalldithiolene units linked via a tetraphosphine bridge,\(^{[17, 18]}\) which can be further elaborated into what can be considered multi-qubit polymers.\(^{[39]}\) The synthesis is highly modular, where metals and ligands are selectively installed and positioned in a way that infuses the system with an unprecedented degree of control that fosters single qubit addressability. We can demonstrate this potential with the compound \([\{\text{Ni(adt)}\}_2\text{m-tpbz}\}] (4).\) Essentially this is an expanded bis(dithiolene) complex, where the metal ion in the monometallic complexes 1–3 are now replaced by the \((\text{M(m-tpbz)}\text{M})\) spacer that separates the terminal dithiolene ligands by ca. 1 nm.\(^{[17]}\) Charge-neutral 4 is readily oxidized at very mild potential; the two-electron event produces the diradical \([4]^2+\) where each dithiolene now possess an unpaired spin giving a near degenerate singlet-triplet ground state. The optimized structure exhibits the same intraligand bond distances consistent with a coordinated diethynyl radical (Figure S32). Aside from the inherent air stability of this diradical, it is the first cationic molecular spin qubit whose electro-static field perturbs the interaction with decohering hydrogen atoms in the solvent shell compared with its anionic counter-parts.\(^{[2]}\) The importance of electrostatics and charge distribution on spin relaxation lifetimes has recently been investigated by Freedman and co-workers.\(^{[22]}\) The cw EPR spectrum is characterized with miniscule anisotropy (\(g = 2.010, 2.017, 2.007\)) and a vanishingly small zero-field splitting of the \(S = 1\) state of \(D = 0.0018\) cm \(^{-1}\) and negligible rhombicity (Figure S25).\(^{[17]}\) The fluid solution spectrum gives a partially resolved hyperfine structure that shows equivalent coupling from all four \(^{31}\text{P}\) nuclei revealing \(J_{\text{aa}} = \text{J}_{\text{bb}}\) such that the estimate provided by DFT calculations of 3.1 cm \(^{-1}\) is very reasonable and under-scores the near degenerate singlet-triplet ground state in \([4]^2+\) (Figure S34). The effect of the intramolecular spin coupling (\(J\) and \(D\)) on the phase memory time of this dicaticonic complex has been measured at 20 K on a 1 mm sample of the complex electrochemically generated in CH\(_2\)Cl\(_2\) solution containing 0.1 m \([\text{N(nBu)}\text{PF}_6]\) as electrolyte, that is, a fully protiated environment. The result is compared to the corresponding mono-spin species, \([\text{Ni(adt)(dppb)}]^+\), \([5]^+\), which represents the bi-partite system sans intramolecular spin coupling (Figure 6). A biexponential fit to the Hahn echo decay yielded \(T_{\text{M,aa}}\) of 3.39(4) ms for \([4]^2+\) \(S = 1\) and 5.16(6) ms for \([5]^+\) \(S = 1/2\) at 20 K, where the impact of intramolecular spin coupling in the former results in ca. 30 % reduction of the phase memory life-time. The longer time for \([5]^+\) compared with 1 is consequence of the miniscule spin density (6 %) on the nickel ion (Figure 6 inset).

**Conclusion**

This work represents the first study that utilizes the organic component of coordination complexes—the ligand—as the...
Synthesis: The compounds \([\text{M(adt)}]_2\) operated multi-qubit quantum gates. We developed this platform with the aim of executing electrically spin states and entanglement scenarios. We will continue to achieve this by altering the metal and ligand components of the two-qubit species at an equivalent temperature. The phase memory time for the prototype two-qubit complex \([\text{4}]\) surpasses lifetimes recorded for all other transition-metal-based two-qubit species at an equivalent temperature. The solvent was removed under reduced pressure. The value of \(a\), \(b\), and \(c\) were determined by solving \(F\) and \(\alpha\) using the WinGX software.

Moreover, this molecular system delivers sufficiently long relaxation times negating any need to optimize the surrounding environment. Key to the challenge of single qubit addressability, we demonstrate electrochemical activation of the spin qubit which is an effective handle to switch the qubit “on” and “off” by applying an appropriate potential, which occurs on a timescale orders of magnitude faster than the lifetime of the superposition state. The ability to electrically activate individual qubits is achieved by altering the metal and ligand components of the molecule, and therein lies the ability to switch between various spin states and entanglement scenarios. We will continue to develop this platform with the aim of executing electrically operated multi-qubit quantum gates.

**Experimental Section**

**Synthesis:** The compounds \([\text{M(adt)}]_2\) (\(\text{M} = \text{Ni}, \text{Pd}, \text{Pt}\)) were prepared following the procedure of Schrauzer and Mayweg.\(^{[43]}\) \([\text{PPPh}_3]_2\text{[BH}_4\text{]}\) was synthesized following the literature method.\(^{[44]}\) Solvents either were dried with a system of drying columns from the Glass Contour Company (CHCl\(_3\), hexanes) or freshly distilled according to standard procedures (CH\(_3\)OH).\(^{[45]}\) Dichloromethane-d\(_2\) and N,N-D\(_2\) DMF were degassed by six successive freeze-pump-thaw cycles and dried over 3 & molecular sieves prior to use. The positions of hydrogen atoms of \(\text{PPPh}_4^+\) were refined with anisotropic thermal parameters.

All non-hydrogen atoms were refined with anisotropic thermal parameters. Anisotropic thermal parameters for disordered CH\(_n\) and distribution of g- and A-values (strain) were employed to account for the linewidth variation (Tables S5).

Pulsed X-band EPR data were measured using a Bruker ELEXYS E580 spectrometer equipped with an Oxford Instruments CF35 continuous Helium flow cryostat. Samples were prepared by dissolving 1–3 in CD\(_2\)Cl\(_2\) to a concentration of 1 mm, loading into 3.8 mm o.d. quartz EPR tubes and adding 2 % (v/v) D\(_2\)DMF to aid glassing. The solution samples were degassed via three freeze-pump-thaw cycles, followed by flame sealing. Simulated EPR spectra were simulated following the spin Hamiltonian \(H = g\ \hat{n}\cdot\text{B}\cdot\text{S} + \alpha\cdot\text{S} + \beta\cdot\text{I}\cdot\text{A} + \gamma\cdot\text{I}\cdot\text{S}\cdot\text{A}\), where \(g\) is the Land g-factor, and \(\alpha\) is the hyperfine coupling constant for the spin-active \(\text{122}^\text{Pd}\) and \(\text{195}^\text{Pt}\) nuclei in 2 and 3, respectively; the other parameters have their usual meanings. Satisfactory fits were achieved using a Lorentzian lineshape with molecular tumbling accommodated by the isotropic liquids model given by \(K_{\text{1},\text{2}} = a\cdot\text{P}_\text{H} + c\cdot\text{M}_\text{H}^2\) (Table S4).\(^{[46]}\) Randomly oriented EPR spectra were simulated following the spin Hamiltonian \(H = w\cdot\text{g}\cdot\text{B}\cdot\text{S} + \text{S}\cdot\text{A}\cdot\text{I}\), where \(w\) and \(A\) are the 3 0 3 electron Zeeman and magnetic hyperfine interaction matrices, respectively. A Gaussian lineshape and distribution of g- and A-values (strain) were employed to account for the linewidth variation (Tables S5).

**SHELXS-97**\(^{[47]}\) and SHELXL-97\(^{[47]}\) using the WinGX\(^{[48]}\) software pack-age. Corrections for incident and diffracted beam absorption effects were applied using empirical absorption corrections.\(^{[49]}\) All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of hydrogen atoms of \(\text{PPPh}_4^+\) counterions and disordered CH\(_2\)Cl\(_2\) solvent content were calculated based on stereochemical considerations and refined isotropically. The disordered H\(_2\)O content was identified in the difference Fourier map and refined with isotropic thermal parameters. However, the hydron atom associated with the H\(_2\)O content were not possible to be located from the difference Fourier map and have been omitted from the refinement cycles. Final unit cell data and refinement statistics are collected in Table S1. CCDC 1851991–1851993 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

**EPR Spectroscopy:** Continuous wave X-band EPR spectra was recorded on a Bruker ELEXYS E500 spectrometer. Spectra were simulated using the simulation package XSOPE.\(^{[50]}\) Fluid solution spectra were simulated using a spin Hamiltonian of the form \(H = g\ \hat{n}\cdot\text{B}\cdot\text{S} + \alpha\cdot\text{S} + \gamma\cdot\text{I}\cdot\text{S}\cdot\text{A}\) and \(\text{122}^\text{Pd}\) and \(\text{195}^\text{Pt}\) nuclei in 2 and 3, respectively; the other parameters have their usual meanings. Satisfactory fits were achieved using a Lorentzian lineshape with molecular tumbling accommodated by the isotropic liquids model given by \(K_{\text{1},\text{2}} = a\cdot\text{P}_\text{H} + c\cdot\text{M}_\text{H}^2\) (Table S4). Randomly oriented EPR spectra were simulated following the spin Hamiltonian \(H = w\cdot\text{g}\cdot\text{B}\cdot\text{S} + \text{S}\cdot\text{A}\cdot\text{I}\), where \(w\) and \(A\) are the 3 0 3 electron Zeeman and magnetic hyperfine interaction matrices, respectively. A Gaussian lineshape and distribution of g- and A-values (strain) were employed to account for the linewidth variation (Tables S5).
ll(t) \equiv g + A_\text{r} \exp(-t/T_1) + A_\text{p} \exp(-t/T_{1,\text{s}}).\] Nutation measurements were performed at three different microwave powers with a nutation pulse of variable length (tipping) pulse followed by a Hahn echo sequence ($t_\text{p} - T_\text{p}/2 - t - T_\text{p}/2 - \text{echo}$). Data were collected employing 4-phase cycling, in which $p/2 = 16$ ns, $p = 32$ ns and $t = 400$ ns for nutation pulse lengths $T = 400$ ns and 1800 ns. The tipping pulse $t_\text{p}$ is augmented in 4 ns increments from a starting value of 4 ns. Nutation data was processed by subtracting a stretched exponential baseline from the echo decay, then zero-filling with 1024 or 2048 points, followed by a Fourier transform with a Hamming window.

Other physical methods: Cyclic voltammetry measurements were performed with a Metrohm Autolab P128 potentiostat. The electrode configuration consisted of a 2 mm glassy carbon working electrode, a platinum auxiliary electrode and a reference electrode consisting of Ag/AgNO$_3$ (0.01 m in MeCN) incorporated into a salt bridge containing supporting electrolyte (to minimize Ag$^+$ leak-age). Solutions of the complexes (1–2 mm) were prepared in dichloromethane containing 0.1 m [N{Bu$_3$}][PF$_6$] as electrolyte. All reduction potentials are referenced versus the ferrocenium/ferrocene (Fc/$^{15}$Fc) couple. Electronic absorption spectra were recorded on a Shimadzu UVA 3600 spectrophotometer (range 200–1600 nm). Electrospay ionization (ESI) mass spectra were obtained on a Bruker microOTOF-Q mass spectrometer.

Calculations: All calculations in this work were performed with the electronic structure program ORCA.$^[52]$ Geometry optimizations were carried out using the BP86 functional with dichloromethane as solvent.$^[53]$ A segmented all-electron relativistically contracted basis set of triple-$\alpha$ quality (def2-TZVPP) was used for all atoms.$^[54]$ A scalar relativistic correction was applied using the zeroth-order regular approximation (ZORA) method$^[55]$ as implemented by van Wüllen.$^[56]$ In the context of ZORA, a one center approximation has been shown to introduce only minor errors to the final geometries. Auxiliary basis sets for all complexes used to expand the electron density in the calculations were chosen to match the orbital basis. The conductor like screening model (COSMO) was used for all calculations.$^[57]$ The self-consistent field calculations were tightly converged ($1 \times 10^{-6} E_h$ in energy, $1 \times 10^{-7} E_h$ in the density change, and $1 \times 10^{-7}$ in the maximum element of the DILL$^[58]$ error vector). The geometry search for all complexes was carried out in redundant internal coordinates without imposing geometry constraints. The property calculations at the optimized geometries were done with the PBE0 hybrid functional$^[59]$ and the RUCCSX algorithm to expedite calculation of the Hartree–Fock exchange.$^[60]$ In this case the same basis sets were used but with enhanced integration accuracy (SPECIALGRIDTACC 10) for the metal and sulfur atoms. Calculation of the $\mathbf{g}$-matrix included a larger the integration grid (Grid5) and fully decontracted basis sets.$^[61]$ We used the broken symmetry (BS) approach to describe our computational result of $4f^2 + 6s^2.$$^[62]$ We adopt the following notation: the given system was divided into two fragments. The notation BS(m,n) refers then to a broken sym-metry state with m unpaired $\alpha$-spin electrons essentially on frag-ment 1 and n unpaired $\beta$-spin electrons localized on fragment 2. In most cases, fragments 1 and 2 correspond to the metal and the $\pi$-gands, respectively. In this notation the standard high-spin, open-shell solution is written as BS(m+n,0). The BS(m,n) notation refers to the initial guess to the wave function. The variational process does, however, have the freedom to converge to a solution of the form BS(m,n) in which effectively the $n$-$\beta$ spin electrons pair up with $m$-$\alpha$ spin electrons on the partner fragment. Such a solu-tion is then a standard $d_{\text{spin}}(m,n)/2$ spin-unrestricted Kohn–Sham solution. As explained elsewhere,$^[63]$ the nature of the solution is in-vestigated from the corresponding orbital transformation (COT) which, from the corresponding orbital overlaps, displays whether the system should be described as a spin-coupled or a closed-shell solution. The exchange coupling constant J was calculated on broken-symmetry geometries using Equation (1),$^[64]$ and assuming the spin-Hamiltonian Equation (2) is valid

\[ J \leq \frac{E_\text{HFS}}{\Delta S^2} \]

Corresponding$^[63]$ and canonical orbitals, and density plots were constructed using the program Molekel.$^[65]$

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Conflict of interest

The authors declare no conflict of interest.

Keywords: EPR spectroscopy · ligand radicals · metallothiolene complexes · quantum computing · spin-orbit coupling

Do your qubit: The redox-active dithiolene ligand is presented as a novel spin host in the design of prototype molecular electron spin qubits. The modularity of the metallodithiolene motif is demonstrated in the assemblage of a prototype two-qubit system with one of the longest reported phase memory times for a coordination complex (see Figure).