



Review The Rise of Single-Ion Magnets as Spin Qubits

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Abstract: Recent studies revealed that magnetic molecules with single spin centers showed exciting phenomena related to quantum information processing, such as long quantum coherence times and Rabi oscillations. In this review, we go over these phenomena according to the essential metal ions, from which we can see the development of single-ion magnets as spin qubits is booming, especially quantum coherence times have been significantly enhanced from nanoseconds to hundreds of microseconds in a short period. Hence, the correlations between the molecular structures and quantum coherence are becoming clearer. In this regard, some chemical approaches to designing better spin qubits have been discussed.

Keywords: single-ion magnet; spin qubit; quantum coherence; quantum information processing

1. Introduction

Single-ion magnets (SIMs) are a kind of molecular magnets that contain only one spin center surrounded by organic ligands [1–5], and show potential applications for high-density information storage, molecular spintronic devices and quantum information processing (QIP) units [6–9]. In this review, we will focus on the topic of SIMs for QIP applications.

For classical computation, the data are encoded in binary digits (bits), each of which is a well-defined state (0 or 1). In contrast, qubits take the advantage of superposition of quantum microstates. The basic set for qubits is $|\psi\rangle = \alpha |0\rangle + \beta |1\rangle$. Hence, a qubit can be either $|1\rangle$ or $|0\rangle$, or any arbitrary superposition of these two states [10–12]. The key point for being a good qubit is to have long transverse relaxation time T_2 . Moreover, the spin-lattice relaxation time T_1 , which describes transitions from, say, $|1\rangle$ to $|0\rangle$, is also very important because to observe the Rabi oscillations both T_1 and T_2 must be long enough. Because the period of coherent Rabi oscillations $1/\Omega_R$, induced by an external stimulus (usually microwaves) between different qubit states, is actually used to evaluate the quality of a quantum system, the coherence time divided by half of the Rabi period, which is defined as $Q_M = 2\Omega_R T_2$ (Q_M is the qubit figure of merit) and represented by the number of coherent single-qubit operations, is useful to evaluate the performance of spin qubit. Only when the Q_M is large enough, can the material then be used for QIP [13]. Other than the long coherence times, the possibility of building quantum logical gates is also very important [14].

Up to date, suitable physical carriers for qubits are found in ion traps [15,16], photons [17], nuclear spins [18], superconducting circuits [19,20], spin-based systems [21], atomic impurities in solids [22,23] and coordination molecules [12,24–27]. Among those candidates, the coordination molecules are extremely exciting due to the ready chemical design and detailed magneto-structural correlations. Specifically, the primary factors influencing the quantum decoherence such as the magnitude of spins, spin-orbit coupling effects and nuclear spin bath, and other peripheral factors such as the donor atoms of the coordinating ligands and solvent molecules can be systematically clarified, which can

in turn guide the design of better molecular qubits [28–34]. Previously, such examples were only demonstrated by molecules with multi-metal centers [12,34]. More recently, new systems based on single-ion magnetic molecules were identified with even better performance owing to the well isolated environment. More excitingly, quantum logic gates such as the Controlled-NOT (CNOT) gate based on multiqubit can be readily achieved by chemical linkage of molecules [35–38] and quantum state can be read out by a single nuclear spin in TbPc₂ [39,40]. Here below, we discussed these exciting topics according to the comprising metal centers, highlighting their advantages for QIP applications.

2. Single-Ion Magnetic Molecules with Transition Metal Centers

As the valence electrons for 3d transition metals locate in outer d orbits, the ligands coordinating to the transition metals have great impact on the electronic structure of the central cations, which then significantly influence the property of quantum coherence. The story starts from the simplest spin-1/2 systems such as V(IV) and Cu(II) ions with only two-level states, spin-up and spin-down.

2.1. V(IV) Based Spin Qubits

Pioneering work searching for potential spin qubits started from the V(IV) ion with small spin-1/2 state and large nuclear spin I = 7/2 (see Table 1). The first example is the complex $(Bu_4N)_2[V(C_8S_8)_3]$ 1 [41], in which the V(IV) ion is coordinated to six S ions, providing a nuclear spin free peripheral environment (Figure 1a). The hyperfine coupling of the electron spin and nuclear spin produces multiple states detected by electron paramagnetic resonance (EPR) spectrum (Figure 1b). Eight separate transitions were found to be potentially available for quantum information processing. The coherence time T_2 is 1.2 µs at 80 K (performed on a 1 mM solution of **1** in butyronitrile). Rabi oscillations are observed by transient nutation experiments (Figure 1d), and the Rabi frequencies yielded from the nutation data at 3486 Oe at corresponding microwave power (B_1) attenuations, namely are 28.1 MHz, 17.6 MHz, and 10.2 MHz for 3 dB, 7 dB, and 11 dB.



Figure 1. (a) Molecular structure of $[V(C_8S_8)_3]^{2-}$ in 1 (Green, V; yellow, S; gray, C) and energies of spin states with increasing applied dc field for 1 oriented; (b) Echo-detected, field-swept, X-band spectrum of a 1 mM solution of 1 in butyronitrile at 20 K (blue line); (c) 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. Inset: Temperature dependence of T_2 for 1; (d) Rabi oscillations collected on a 1 mM solution of 1 at 20 K, H_{dc} = 3486 Oe, and 11 dB attenuation of B_1 (adapted with permission from [41]).

Subsequently, a series of V(IV) complexes $(Ph_4P)_2[V(C_8S_8)_3]$ **2**, $(Ph_4P)_2[V(\beta-C_3S_5)_3]$ **3**, $(Ph_4P)_2[V(\alpha-C_3S_5)_3]$ **4**, and $(Ph_4P)_2[V(C_3S_4O)_3]$ **5**, based on carbonsulfides (Figure 2a–d), were prepared to test the electronic donating ability on the quantum coherence times [42]. The similar S₆ coordination environment is maintained. Interestingly, the longest T_2 was found for **2** of 4 µs at 80 K, indicating the weaker donating ability is better since the donating ability sequence is $C_8S_8^{2-} < \beta-C_3S_5^{2-} < \alpha-C_3S_5^{2-} < C_3S_4O^{2-}$. In addition, the solvent effect on quantum coherence was investigated. Several solvents including some deuterated ones such as PrCN, PrCN/DMF, DMF/Tol, d_7 -DMF/ d_8 -Tol and CS₂ were chosen and found they have little effect on T_1 . In contrast, T_2 is significantly affected, e.g., T_2 for complex **2** in CS₂ is 1.18 µs (120 K), which is about 10 times longer than that in PrCN (0.108 µs, 120 K). Moreover, T_2 is temperature-dependent. At 10 K T_2 of **2** in CS₂ solution is enhanced to 675(7) µs, even longer than some prominent solid-state qubits [43,44]. Remarkably, Rabi oscillations were observed for all four complexes (Figure 2e), and Q_M for **2** was found to be 36,000, which is very high among molecule-based spin qubits. Hence, this series of V(IV) complexes indicates the spin qubits are significantly affected by nuclear spin bath.



Figure 2. Molecular structures of 2–5 (a–d) (Green, V; yellow, S; gray, C; red, O; Ph₄P groups are omitted for clarity); (e) Rabi oscillations for 2–5 that verify quantum control in each member of the series. Data were recorded in 1:1 DMF/Tol at 20 K, and 14 dB attenuation of B_1 . The spin-flip operation time of 52 ns is highlighted (adapted with permission from [42]).

The second class of mononuclear V(IV) based spin qubits contains the VO²⁺ unit with distinct short V=O double bond (about 1.6 Å), which is much shorter than other coordination bonds bound to the central V(IV) ions in a typical square pyramidal geometry. Such strong bond is believed to be responsible for a special d-orbital splitting which leaves the d_{xy} orbital being in the lowest place in energy levels and well separated from the other orbitals. This is evident in the complex VO(dpm)₂ 6 (dpm⁻ = dipivaloylmethanate) (Figure 3a) [45] whose V=O bond length is 1.59 Å, while other V–O single bonds averages at 1.96 Å. AC magnetic susceptibility study gives out-of-phase signals up to 80 K for frequencies lower than 10 kHz, which is the highest one among all reported molecular magnets. The relaxation time T_1 at 80 K reached 13.42 µs (Figure 3d). By pulsed EPR spectroscopy, the coherence time was detected. When complex 6 was dissolved in CH_2Cl_2 -toluene (1 mM), T_2 reaches 2.1 μ s at 80 K, and with 1:10 dispersion of diamagnetic TiO(dpm)₂, this T₂ can be further preserved up to 220 K. T1 was also determined by pulsed EPR spectroscopy, which gave the consistent results for AC magnetic susceptibility study, conforming that the two techniques are actually probing the same process. Complexes $VO(acac)_2$ 7 and $VO(dbm)_2$ 8) ($acac^- = acetylacetonate$, and $dbm^- =$ dibenzoylmethanate) (Figure 3b,c) share a similar coordination environment to 6 [46]. The V=O bond distances are 1.585 Å and 1.578 Å for 7 and 8, respectively. Both of 7 and 8 show out-of-phase AC signals under a static magnetic field of 0.2 T up to 40 K, which is associated with a giant spin-phonon bottleneck effect. Moreover, a pronounced crystal size dependence of the relaxation time was observed in complexes 6-8.



Figure 3. (**a**–**c**) Molecular structures of **6**–**8** (Green, V; gray, C; red, O; hydrogen atoms are omitted for clarity); (**d**) Frequency dependence of the imaginary component of the AC susceptibility of bulk **6** in $B_{dc} = 0.2$ T multiplied by temperature to be readable in the whole 2–80 K temperature range; (**e**) Pulsed EPR Hahn echo decay traces for a frozen 1 mM CH₂Cl₂-toluene solution of **6** at indicated temperatures recorded at 343 mT. In the Inset the employed pulse sequence; (**f**) Rabi oscillations for a frozen 1 mM CH₂Cl₂-toluene solution of **6** recorded at 4.3 K at 10 dB microwave attenuation (adapted with permission from [45]).

Complex	$T_1/\mu s$	$T_2/\mu s^a$	$T_2/\mu s^{b}$	T _R /K ^c	Ref.
$(Bu_4N)_2[V(C_8S_8)_3]$ (1)	-	1.2 (80 K)	1.52 (20 K)	20	[41]
$(Ph_4P)_2[V(C_8S_8)_3]$ (2)	4.90 (120 K)	1.18 (120 K)	675(7) (10 K)	20	[42]
$(Ph_4P)_{2[}V(\beta-C_3S_5)_{3]}$ (3)	2.24 (120 K)	0.86 (120 K)	6.13 (10 K)	20	[42]
$(Ph_4P)_2[V(\alpha - C_3S_5)_3](4)$	0.71 (150 K)	0.19 (150 K)	6.01 (10 K)	60	[42,47]
$(Ph_4P)_2[V(C_3S_4O)_3]$ (5)	3.16 (120 K)	0.96 (120 K)	2.79 (10 K)	20	[42]
VO(dpm) ₂ (6)	6 (110 K)	0.1 (220 K)	2.5 (10 K)	4.3	[45]
$VO(acac)_2$ (7)	$\approx 10^{2} (40 \text{ K})$	-	-	-	[46]
VO(dbm) ₂ (8)	$\approx 10^{2} (40 \text{ K})$	-	-	-	[46]
VOPc (9)	$2.4 imes10^{6}$ (7 K)	22 (10 K)	-	-	[31]
VOPc (9)	1.1 (300 K)	0.83 (300 K)	-	300	[48]
$[(Ph)_4P]_2[VO(\alpha-C_3S_5)_2]$ (10)	3.37 (293 K)	1.04 (293 K)	-	293	[47]

Table 1. V(IV) based single-ion spin qubits.

^a Reported T₂ values at the highest temperatures; ^b Best T₂ values; ^c Reported temperatures for Rabi oscillations.

Another mononuclear V(IV) based spin qubit with short V=O bond (1.58 Å) is the complex VOPc **9** (Pc = Phthalocyanine) (Figure 4a) [31,48]. Together with its d¹ electron configuration, this molecule makes a perfect two level system for spin qubit. Moreover, the out-of-phase signals of AC magnetic susceptibility for the frequency of 10 kHz can be observed up to 40 K under an applied static magnetic field of 0.2 T. An extraordinarily long T_1 (2.4 s at 7 K) was obtained by Q-band EPR measurements in 0.5 mM D₂SO₄-solution, and T_2 is 20 µs at 20 K under the same condition [31]. When VOPc is mixed with the isostructural diamagnetic host TiOPc in molar ratio of 1:1000, quantum coherence could be detected up to room temperature. T_1 of 1.1 µs at 300 K was obtained by inversion recovery experiments and by echo decay experiments, echo decay traces (Figure 4b) were detected up to room temperature with T_2 of 0.83 µs. Hence, for the first time, Rabi oscillation at room temperatures was detected in a solid state molecular system (Figure 4c). Besides, the quantum states of this electron spins based system can be efficiently initialized with high thermal stability, representing a promising qubit.



Figure 4. (a) Molecular structures of **9** (Green, V; gray, C; red, O; blue, N; hydrogen atoms are omitted for clarity); (b) Echo decay traces for **9** at indicated temperatures performed at 345 mT. Solid lines are the best fits; (c) Rabi oscillations recorded for **9** at 300 K for different microwave attenuations performed at 345 mT (adapted with permission from [48]).

More recently, a new mononuclear V(IV) complex $(Ph_4P)_2[VO(\alpha-C_3S_5)_2]$ **10** was reported, which enhances the quantum coherence by strong V=O double bond [47]. As shown in Figure 5a, the structure of **10** is similar to **4** except for the apical O atom. For comparison, the dynamic magnetism of both complexes was studied. Under a static magnetic field of 0.2 T, complex **4** displays slow magnetic relaxations below 10 K; while for complex **10**, the temperature is raised up to 40 K. Their quantum coherences were detected by continuous-wave and pulsed EPR measurements on diluted samples. For **4**, it was dispersed by $[(Ph)_4P]_2[Ti(\alpha-C_3S_5)_3]$ in a molar ratio of 1:19, which gives T_1 of 0.71 µs and T_2 of 0.19 µs at 150 K (Figure 5c). Complex **10** was mixed with $[(Ph)_4P]_2[MoO(\alpha-C_3S_5)_2]$ in a molar ratio of 1:19 for pulsed EPR measurements. At room temperature (293 K), both T_1 and T_2 of **10** remain high, namely 3.37 µs and 1.04 µs (Figure 5b). Rabi oscillations are also clearly observed at 293 K for diluted **10** and at 60 K for diluted **4**, indicating the enhancement of O substitution.



Figure 5. (a) Molecular structure of **10** (Green, V; yellow, S; gray, C; Ph₄P groups are omitted for clarity); (b) Echo decay traces for diluted **10** at indicated temperatures performed at X-band; (c) Echo decay traces for diluted **4** at indicated temperatures performed at X-band. Solid lines are the best fits (adapted with permission from [47]).

2.2. Cu(II) Based Single-Ion Spin Qubits

Except for V(IV), Cu(II) is another ion with spin-1/2 state. Several examples of mononuclear Cu(II) complexes have been reported as potential single-ion spin qubits (Table 2). The first one is CuPc **11** (Figure 6a) [31,49]. By organic-molecular-beam deposition, complex **11** and free phthalocyanine are able to assemble a monoatomic layer onto the layer of perylene-3,4,9,20-tetracarboxylic dianhydride. With the Hahn echo sequence, T_2 for **11** was determined to be 1 µs at 80 K. Moreover, Rabi oscillations of a 0.1% CuPc:H₂Pc were clearly observed at 5 K (Figure 6c) [49]. The impact of solvent deuteration on electron spin relaxation has been investigated by dissolving **11** in H₂SO₄ and D₂SO₄ [31]. For D₂SO₄, T_2 is about 41 µs at 7 K, which is five times longer than those in H₂SO₄ (Figure 6b). The ligand effect on the quantum coherence times was also investigated using complexes CuPc^{Cl} **12** and CuPc^F **13**. All the three complexes share a similar T_2 value of 40 µs at 7 K, indicating the ligand field effect is little in this series [31].

Table 2. Cu(II) based single-ion spin qubits.

Complex	$T_1/\mu s$	$T_2/\mu s^{a}$	$T_2/\mu s b$	T _R /K ^c	Ref.
CuPc (11)	10 ⁵ (7 K)	1.0 (80 K)	41 (7 K)	5	[31,49]
CuPcCl (12)	10 ⁵ (7 K)	40 (7 K)	-	-	[31]
CuPcF (13)	$6 imes 10^4$ (7 K)	40 (7 K)	-	-	[31]
$(PPh_4)_2[Cu(mnt)_2]$ (14)	0.48 (294 K)	0.6 (294 K)	68 (7 K)	15	[50]

^a Reported T₂ values at the highest temperatures; ^b Best T₂ values; ^c Reported temperatures for Rabi oscillations.



Figure 6. (a) Structures of complexes **11–13**; (b) Inversion recovery experiment (up) and Hahn echo experiment (down) for relaxation data of **11** in H₂SO₄ (red triangles) and D₂SO₄ (blue circles) at Q-band and 7 K (adapted with permission from [31]); (c) Rabi oscillations of a 0.1% CuPc:H₂Pc film recorded at 5 K and 330.5 mT for different microwave powers (adapted with permission from [49]).

 $(PPh_4)_2[Cu(mnt)_2]$ **14** $(mnt^{2-} =$ maleonitriledithiolate or 1,2-dicyanoethylene-1,2-dithiolate) is another high-performance single-ion spin qubit that displays long quantum coherence times at room temperature [50]. The Cu(II) ion in **14** is coordinated to four S ions in a square planner geometry (Figure 7a). The H atoms in this complex can be fully replaced by deuterium and its Ni analogy is diamagnetic, allowing a magnetic dilution study. At 294 K, electron spin echo-detected EPR measurements of the highly diluted sample (0.0001% of **14** in (PPh₄)₂[Ni(mnt)₂]) gave T_1 of 0.48 µs and T_2 of 0.6 µs (Figure 7b). Towards lower temperatures with 0.01% deuterated **14** in deuterated (PPh₄)₂[Ni(mnt)₂], T_2 is prolonged to 68 µs at 7 K. Moreover, Rabi-like oscillations of the echo intensities were clearly observed by nutation measurements of the same sample at 15 K with a merit $Q_M \approx 3400$.



Figure 7. (a) Molecular structure of **14** (Aqua, Cu; yellow, S; blue, N; black, P; gray, C; hydrogen atoms are omitted for clarity); (b) Temperature-dependent Hahn echo decay curves for **14**Cu_{0.001%}. Solid lines are the best fits (adapted with permission from [50]).

2.3. Other Transition Metals

Only two Cr(III) (spin-3/2) based single-spin qubits have been reported so far (Table 3). The first one is $(Ph_4P)_3[Cr(C_3S_5)_3]$ **15**, in which the Cr(III) ion is coordinated to six S atoms with a first-circle nuclear spin free coordination environment (Figure 8a) [51]. By magnetometer and continuous-wave EPR spectroscopy, D = +0.326(8) cm⁻¹ and E = -0.107(5) cm⁻¹ were determined, which gave a rhombicity |E/D| of 0.31. The high rhombicity would afford highly mixed M_S levels at low magnetic fields, producing significant intensity of forbidden EPR transitions with multiple M_S pairs for quantum studies. Pulsed X-band EPR spectroscopy measurement was carried out on deuterated **15** in $(d^{20}-Ph_4P)_3[Ga(C_3S_5)_3]$ (1%) (Figure 8b). T_1 sharply drops from 29(3) ms at 5 K to 875(5) µs at 30 K, while T_2 drops from 1.81(3) µs to 0.82(2) µs upon the same temperature change. Moreover, Rabi oscillations were clearly observed at 5 K with linear Ω_R against B_1 , indicating the provenance of the nutations (Figure 8c,d).

The other Cr(III) based single-ion spin qubit is $K_3[Cr(C_2O_4)_3]$ **16** (Figure 9a) [33]. The |D| value of **16** is about 0.7 cm⁻¹ and the *E* value is about 0.06 cm⁻¹ [52]. The inherent scalability and tunability engendered by zero-field splitting are illustrated in Figure 9b. The transitions between the multiple M_S pairs can be used as qubits, which is in accordance with the study of complex **15** [51]. T_2 for **16** is about 1.27 µs at 22 K, obtained by two-pulse Hahn echo sequence on 1 mM solutions of **16** in 1:1 (v/v) H₂O/glycerol (Figure 9c) [33].





Figure 8. (a) Molecular structure of $[Cr(C_3S_5)_3]^{3-}$ in **15** (Pink, Cr; yellow, S; gray, C, Ph₄P groups are omitted for clarity) and calculated splitting of the M_S energy levels with $H_{dc} = 2000$ G aligned along the *z*-axis of the molecule (arrows illustrate the allowed (green) and forbidden (purple) transitions within the s = 3/2 manifold); (b) Hahn-echo decay curves for 1% of deuterated **15** in $(d^{20}-Ph_4P)_3[Ga(C_3S_5)_3]$ at 5 K. Lines are best fits; (c) Rabi oscillations at $H_{dc} = 3500$ and 1000 G and Rabi frequency dependence on B_1 ; (d) Rabi frequency plotted as a function of increasing B_1 for 1% of deuterated **15** in $(d^{20}-Ph_4P)_3[Ga(C_3S_5)_3]$ and BDPA (1,3-bisdiphenylene-2-phenylallyl radical) at 5 K (adapted with permission from [51]).



Figure 9. (a) Molecular structure of $[Cr(C_2O_4)_3]^{3-}$ in **16** (Light blue, Cr; red, O; gray, C; cations are omitted for clarity); (b) Calculated splitting of the M_S energy levels with $H_{dc} = 1000$ G aligned along the z-axis of the molecule. Blue arrows indicate the six potential qubits; (c) T_2 decay curves for **16** at indicated temperatures. Lines are best fits (adapted with permission from [33]).

A series of analogous complexes $K_3[Fe(C_2O_4)_3]$ 17, $(Ph_4P)_3[Fe(CN)_6]$ 18, $K_3[Ru(C_2O_4)_3]$ 19, (Ph₄P)₃[Ru(CN)₆] **20**, (Ph₄P)₃[Os(CN)₆] **21** and **16** were used to study the influence of spin-spin and spin-orbit couplings on quantum coherence [33]. Complexes 19, 16 and 17 possess spin states of s = 1/2, 3/2, and 5/2 with the same coordination environment, which gives an opportunity to understand the impact of spin magnitude on quantum coherence (Figure 10a). At low temperature, T_2 value for **19** is the longest one ($3.44 \,\mu s$ at 5 K and $2.01 \,\mu s$ at 14 K), followed by **16** ($2.79 \,\mu s$ at 5 K and 1.86µs at 14 K) and then 17 (1.83 µs at 5 K and 0.81 µs at 14 K). This result indicates a larger spin increases the intermolecular dipolar interaction and hence enhances the decoherence rate [53–55]. However, at a higher temperature (22 K), T_2 for 16 becomes the longest, reaching 1.27 µs, which may also indicate spin magnitude can be varied without significantly compromising T_2 in certain conditions as long as it is appropriate for signal detection. As the spin states for complexes 18, 20, 21 are all 1/2, and the free ion SOC effects on T_2 can be compared. T_2 for those three complexes are in the order Fe(III) < Ru(III) < Os(III), which is coincident with the increase of SOC constants, namely 464 cm⁻¹, 880 cm⁻¹, and 3100 cm⁻¹ for **18**, **20** and **21** (Figure 10a and Table 3) [56–58]. Rabi oscillations and pulse sequence for a solution of **19** at 5 K, H_{dc} = 2812 G, and relative B_1 of 2.0 was observed (Figure 10b). Note that **21** is the only Os complex regarded as potential qubit.

Table 3. Other transition metals based single-ion spin qubits.

Complex	$T_1/\mu s$	$T_2/\mu s^{a}$	$T_2/\mu s^{b}$	T _R /K ^c	Ref.
$(Ph_4P)_3[Cr(C_3S_5)_3]$ (15)	875 (30 K)	0.82 (30 K)	1.81 (5 K)	5 K	[51]
$K_3[Cr(C_2O_4)_3]$ (16)	-	1.27 (22 K)	2.79 (5 K)	-	[33]
$K_3[Fe(C_2O_4)_3]$ (17)	-	0.45 (22 K)	1.83 (5 K)	-	[33]
$(Ph_4P)_3[Fe(CN)_6]$ (18)	-	0.60 (22 K)	2.38 (5 K)	-	[33]
$K_3[Ru(C_2O_4)_3]$ (19)	-	0.41 (22 K)	3.44 (5 K)	5	[33]
$(Ph_4P)_3[Ru(CN)_6]$ (20)	-	1.29 (22 K)	2.55 (5 K)	-	[33]
$(Ph_4P)_3[Os(CN)_6]$ (21)	-	1.04 (22 K)	4.12 (5 K)	-	[33]
$(Ph_4P)_3[Fe(C_5O_5)_3]$ (22)	1.18 (15K)	0.498 (40 K)	1.63 (5 K)	10	[59]
MnPc (23)	690 (7 K)	14 (7 K)	-	-	[31]
CoPc (24)	$1.11 imes10^4$ (7 K)	9.44 (7 K)	-	-	[31]

^a Reported *T*₂ values at the highest temperatures; ^b Best *T*₂ values; ^c Reported temperatures for Rabi oscillations.



Figure 10. (a) Depictions of the molecular structures of **16**, **17** and **19** (left) and **18**, **20** and **21** (right) (cations are omitted for clarity); (b) Rabi oscillations and pulse sequence for a solution of **19** at 5 K (adapted with permission from [33]).

Another Fe(III) based single-ion spin qubit is the complex $(Ph_4P)_3[Fe(C_5O_5)_3]$ **22** (Figure 11a) [59,60]. Variable-frequency CW EPR measurements at low temperatures (5 K) and high frequencies (208 GHz) on this trigonally distorted six-coordinate iron(III) complexes with O₆ coordination environments reveal a sharp resonance near g = 2.00 and negative *D* value of -0.30 cm⁻¹. To evaluate the spin

qubit viability of **22**, its diamagnetic analogy (Ph₄P)₃[Ga(C₅O₅)₃] was used for preparations of diluted samples, (Ph₄P)₃[Fe_{0.002}Ga_{0.998}(C₅O₅)₃] **22**a and the deuterated (Ph₄P-d²⁰)₃[Fe_{0.002}Ga_{0.998}(C₅O₅)₃] **22**b for pulsed EPR studies. At 5 K, T_1 are 11.3 µs and 8.0 µs for **22**a and **22**b, respectively. These values drop dramatically as increasing temperatures, which eventually went down to 1.18 µs and 0.82(1) µs, respectively, at 15 K. T_2 values for **22**a and **22**b at 5 K are 0.74 µs and 1.60 µs, respectively, highlighting the enhancement of T_2 with deuteration. Similar to T_1 , T_2 also decay rapidly upon warming, ultimately down to 0.34 µs for **22**a at 15 K. Moreover, clear Rabi oscillations were observed for both **22**a and **22**b at 10 K (Figure 11c,d) with liner dependence of Ω_R against B_1 , proving the qubit characteristic [59]. By multi-frequency pulsed EPR spectroscopic measurements, a high to low degree of M_S mixing in the high-spin qubit was discovered in **22**, which highlights the possibility of long T_1 and T_2 parameters in high-spin species through control of M_S level mixing [60].



Figure 11. (a) Molecular structure of $[Fe(C_5O_5)_3]^{3-}$ in **22** (Brown, Fe; red, O; gray, C; the Ph₄P groups are omitted for clarity); (b) Magnetic field dependence of the M_S levels of the s = 5/2 state in **22** for a magnetic field aligned perpendicular to the molecular z-axis (adapted with permission from [60]); (c) Rabi oscillations at $H_{dc} = 1608$ G with indicated B_1 for **22** at 10 K(adapted with permission from [59]; (d) Rabi oscillations at $H_{dc} = 1608$ G with indicated B_1 for **22** b at 10 K (adapted with permission from [60].

As far as we know, few mononuclear Mn and Co complexes were reported as potential spin qubits. The only investigation of these two ions was found in complexes MnPc (23) and CoPc (24), which were used to reveal the influences of central ion on quantum coherence behavior of complexes 9, 11–13 [31]. Pulsed Q-band EPR spectroscopy was measured on 0.5 mM D₂SO₄ solution of complexes 9, 11, 23 and 24 because they have the same ligand Pc. T_1 for those complexes were found to be in the order of 23 (0.69 ms) < 24 (11.1 ms) < 11 (103 ms) < 9 (2.4 s) at 7 K, which is in accord with the conclusion that smaller SOC effects generate longer spin-lattice relaxation times [33,61]. The T_2 values at 7 K are 22 µs, 41 µs, 14 µs and 9.44 µs for 9, 11, 23 and 24, respectively.

3. Single-Ion Magnetic Molecules with Single 4f Spins

Lanthanide-based SIMs have been intensively investigated for more than 10 years and have achieved significant progress in information storage and spintronic aspects, such as, (i) high magnetic hysteresis temperature (30 K) [62]; (ii) high magnetic anisotropic energy barrier (1000 K) [63]; and (iii) surface deposition of molecular magnets without changing the original magnetism [64–67]. In contrast, the attempts of using lanthanide-based SIMs as spin qubits have just begun [8,9,68,69]. Examples we will discuss include some lanthanide polyoxometalates [70–73], the famous TbPc₂ [39,40,74,75] and one Yb complex [76], see also Table 4.

Complex	$T_1/\mu s$	$T_2/\mu s^a$	$T_2/\mu s^{b}$	T _R /K ^c	Ref
$[Gd(P_5W_{30}O_{110})] K_{14}nH_2O$ (25)	1.6 (6 K)	0.41 (6 K)	-	5	[70,71]
$[Ho(W_5O_{18}P)_2]^{9-}$ (26)	20 (5 K)	-	8.4 (5 K)	-	[73]
TbPc ₂ (27)	-	-	64 (40 mK)	0.04	[40]
$Yb(trensal)_3$ (28)	0.2 (20 K)	0.17 (15 K)	0.53 (2.7 K)	5	[76]

Table 4. 4f based single-ion spin qubits.

^a Reported T_2 values at the highest temperatures; ^b Best T_2 values; ^c Reported temperatures for Rabi oscillations.

3.1. Single-Lanthanide Polyoxometalates as Spin Qubits

Though the magnetism of free Gd(III) ion is very isotropic, Gd(III) complexes with special coordination environments can behave as single-molecule magnets at very low temperatures [70,77]. The tungsten-based polyoxometalates are such ligand beds for Gd(III) ions. Compounds $[Gd(P_5W_{30}O_{110})]^{12-}$ (25) and $[Gd(W_5O_{18}P)_2]^{9-}$ (GdW₁₀) (Figure 12) show slow magnetic relaxation behaviors below 300 mK. The relaxation times for GdW₁₀ follow the activated behavior with an energy barrier of 2.2 K. However, for 25, relaxation times depend weakly on temperature and show a strong deviation from the expected thermally activated behavior. Qualitative fitting of their EPR data proves that the magnetic anisotropy is raised by mixing ground and excited states, resulting in easy-axial magnetic anisotropy for GdW₁₀ and an easy-plane magnetic anisotropy for 25. This difference further influences their application as spin qubits. Pulsed X-band EPR experiments give coherence figure of merit $Q_M > 50$ for 25 with observation of Rabi oscillations at 5 K, proving the possibility of spin qubits [71].

Another single-lanthanide polyoxometalate for spin qubit is the complex $[Ho(W_5O_{18}P)_2]^{9-}$ (26) [72,73], an analogy of GdW₁₀ with a different lanthanide center. The Ho(III) ion is encapsulated between two W₅O₁₈ POM units that provide a square-antiprismatic coordination geometry with D_{4d} symmetry (Figure 13a). By high-frequency and X-band EPR measurements, the hyperfine-split $m_j = \pm 4$ ground states can be observed (Figure 13b). The tunneling gap is about 9 GHz, which make 26 suitable for spin qubits [72]. The dilution study of 26 was carried out on Na₉[Ho_xY_(1-x)(W₅O₁₈)₂]·*n*H₂O, where *x* ranges from 0.001 to 0.25 [73]. For *x* = 0.001, a long T_2 of 8.4 µs was detected together with T_1 of 20 µs at 5 K (Figure 13c). Interestingly, T_2 remains at higher concentrations for a long period (about 8.0 µs for *x* = 0.01 and 0.7 µs for *x* = 0.1) at 5 K. The main contribution to those narrow resonances is found to be a Gaussian distribution in the B_4^4 parameter. Thus, by exploiting optimal operating points or atomic clock transitions between hyperfine states, quantum coherence times could be significantly protected regardless of spin concentrations [73].





Figure 12. (a) Molecular structures of GdW_{10} and 25; energy levels of GdW_{10} and 25 for $H_{dc} = 10$ mT; (b) Ac magnetic susceptibility measured at indicated temperatures and the relaxation times for GdW_{10} and 25 (adapted with permission from [70]); (c) Rabi oscillations for 25 at indicated microwave (adapted with permission from [71].



Figure 13. (a) Polyhedral representation, molecular structures and separate view along the axial z-direction of **26** (adapted with permission from [72]); (b) Zeeman diagrams corresponding to the hyperfine-split $m_J = \pm 4$ ground states (adapted with permission from [72]); (c) Field-swept T_2 recorded at 5.0 K at indicated frequencies and fields for Na₉[Ho_xY_(1-x)(W₅O₁₈)₂]·*n*H₂O (*x* = 0.001) (adapted with permission from [73]).

3.2. Tb(III) Based Nuclear-Spin Qubits

TbPc₂ **27**, one of the high-performance SIMs, has also been identified as one promising qubit for several reasons [39,40,74,75]. (I) The synthesis of this complex is facile and controllable with various

functional groups [78]; (II) The magnetic properties are robust, which can be retained after sublimation at 820 K on a copper surface [64]; (III) The two Pc ligands have a conjugated p system, which can easily conduct electrons; while the valence state for Tb(III) is very stable, so that the current flow does not damage the complex [39]; (IV) The flat Pc ligands help graft the complexes on various surfaces, including gold, carbon nanotube, graphite, etc. With all these characteristics, it is possible to make 27 a spintronic devices (Figure 14a). Magnetic studies of 27 reveal a strong uniaxial magnetic anisotropy with ground J = 6 state separated from the excited states by an energy gap of more than 400 cm⁻¹ [1,79]. With the nuclear spin I = 3/2, strong hyperfine coupling between the ground state and the nuclear spin makes the ground states split into four sub-states (Figure 14b), which can be functionalized as quantum microstates. The coherence time T_2 for 27 is about 64.0 µs with isotope-dependent relaxation times, while T_1 is more than 10 s. Moreover, Rabi oscillations are observed (Figure 14c,d) [40].



Figure 14. (a) Artist's view of a nuclear spin qubit transistor based on a single **27** molecule. The four anisotropic nuclear spin states of the Tb³⁺ (colored circles) can be manipulated by an electric field pulse (adapted with permission from [40]); (b) The two ground states are each split into four different sub-states owing to the hyperfine coupling with the nuclear spin (I = 3/2). Colored lines denote the I_z components: purple, -3/2; blue, -1/2; green, 1/2; and red, 3/2. Two processes are responsible for the magnetization reversal (adapted with permission from [39]); (c) Ramsey interference fringes obtained by repeating time-dependent external magnetic field and pulse sequence for 100 times at 40 mK (adapted with permission from [40]); (d) Rabi oscillations obtained by repeating the above sequence in (c) for 100 times at 40 mK (adapted with permission from [40]).

3.3. Yb(III) Based Spin Qubits

For Yb(III) ions, the ground state is a Kramers doublet with J = 7/2, which can be approximated as an effective spin-1/2 system at low temperatures [76]. Its isotopes include I = 1/2 (¹⁷¹Yb), I = 5/2 (¹⁷³Yb) and 0 for the others. To detect the quantum coherence of Yb(trensal) **28** (H₃trensal = 2,2',2"-tris(salicylideneimino)triethylamine), sample of 7% **28** in diamagnetic Lu(trensal) was prepared for EPR measurements (Figure 15a) [76]. Fitting the echo-detected field-swept (EDFS) X-band pulsed EPR spectrum gave both spin-lattice relaxation times T_1 and quantum coherence times T_2 (Figure 15c). The T_1 values are in accord with ac susceptibility studies on bulk **28**, which exhibits strong temperature dependence behavior and can be described by a power law [80]. On the contrary, T_2 is weakly temperature dependent and reaches 0.5 µs at 3 K. Clear oscillatory behavior was observed at 5 K (Figure 15d). The peak widths show little difference for all isotopes, but for the damping, the oscillations at "I = 0 lines" are much stronger than other isotopes. Besides, more than 70 Rabi oscillations can be observed extending to 4 µs. Together with the coherence figure of merit Q_M of about 40, complex **28** is an excellent candidate for QIP.



Figure 15. (a) Molecular structure of Yb(trensal) in **28** (Pink, Yb; red, O; blue, N; gray, C, hydrogen atoms are omitted for clarity); (b) Zeeman diagram of the I = 5/2 isotope; (c) Temperature dependence of T_1 and T_2 determined by pulsed EPR for 7% **28** in Lu(trensal); (d) Echo intensity, proportional to the expectation value $\langle S_z \rangle$, as a function of the length of the nutation pulse (t_p) at selected field positions at T = 5 K (microwave attenuation = 3 dB) and its corresponding Fourier transforms (adapted with permission from [76]).

3.4. Lanthanide-Doped Spin Qubits

By doping lanthanide ions into some inorganic crystals, many solid-state qubits were found, despite that it is hard to control the environment of lanthanide ions [13,81–86]. Typical examples include doping Er(III) ions into CaWO₄, which gives Er(III):CaWO₄ with T₂ of 50 μ s at 2.5 K and Q_M of 1400 [13] and Pr(III):Y₂SiO₅ with long phase memory time of 82 ms [82]. Other lanthanide elements using a similar doping method include Nd(III) [84] and Eu(III) [86].

4. Conclusions and Perspectives

From the above analyses, we can see the practice of SIMs for spin qubits is still in its infancy, especially for lanthanide based SIMs, yet many exciting results have been achieved in the field. These

include: (i) long quantum coherence times (e.g., complex 2 exhibits $T_2 = 657 \mu s$ at 7 K; complex 10 exhibits $T_2 = 1 \mu s$ for at room-temperature; while T_1 reaches 10 s for TbPc₂ at low temperatures); (ii) Rabi oscillations are well observed in many well isolated molecules; (iii) electrically read-out of a single nuclear spin using a molecular spintronic device was achieved; (iv) chemical linkage for CNOT gate operations was demonstrated. Last but not least, the decoherence-structural correlation of SIMs is becoming clearer, which is extremely encouraging for chemists who are working on this field because this knowledge may help to design better spin qubits. The key points can be summarized as follows. Firstly, the quantum states must exist, which may arise from hyperfine coupling of the electron spin and nuclear spin or the spin orbital coupling with a proper energy gap (reasonably between 2 and 20 GHz). Secondly, the ligands, especially the atoms directly coordinated to the metal center, would significantly influence the electronic structure of the center ions. Nuclear spin free atoms are often favorable in this area, such as C and S. Besides, if there is an H atom in the ligands, deuteration often helps to protect the quantum coherence. Finally, the concentration, which is often adjusted by solvents or diamagnetic analogy, is also crucial. Nuclear spin free solvents (e.g., CS₂) can effectively enhance the coherence time. Since all these factors are chemically controllable, it is very encouraging for chemists to design high performance single spin qubits based on the toolbox of synthetic chemistry. Only if the quantum coherence time is long enough at room temperature can the realization of QIP for daily usage be expected.

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