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Progress and design challenges for high-spin molecules*

Martin T. Lemaire

Department of Chemistry, Brock University, 500 Glenridge Avenue, St. Catharines, ON, L2S 3A1, Canada

Abstract: In this short critical review, selected examples of current (within the past two years) synthetic efforts toward the construction of high-spin molecules are explored, including the use of metal complexes containing stable free radical ligands, lanthanide or actinide complexes, and other coordination clusters, or a completely different approach, taking advantage of non-Heisenberg exchange in fully delocalized mixed-valence complexes (spin-dependent delocalization, SDD, or double exchange). A description of reported work in this regard is followed by a brief general discussion that highlights what the future may hold for high-spin molecule design.

Keywords: double exchange; high-spin molecules; metal–radical complexes; molecule-based magnetic materials; single-molecule magnets.

INTRODUCTION

2011 is the International Year of Chemistry, therefore, it is a natural time to reflect on our science, acknowledge the progress that has been made, and also identify the important challenges with which we struggle today, including those new challenges that lie ahead. The field of molecule-based magnetic materials is relatively young, but has grown enormously over the past 20 years. With this short critical review article, my objective is to highlight examples of very recent progress made primarily over the past two years within one key area that is at the heart of the science of molecule-based magnetic materials—the preparation and study of high-spin molecules, with a focus on very recent reports featuring new approaches to the design and synthesis of paramagnetic complexes. Three key areas in this regard are described, including the metal–radical approach toward high-spin molecules, the utility of double exchange (spin-dependent delocalization, SDD) as a means to prepare high-spin molecules in mixed-valence complexes, and current reports of lanthanide-based single-molecule magnets (SMMs) with high magnetization reversal energy barriers. A general summary is provided including a discussion focused on the future of high-spin molecule design.

HIGH-SPIN MOLECULES

Nature prefers pairing up electrons into chemical bonds, which is why open-shell free radicals are typically so reactive and unstable. In polymetallic coordination complexes, the low-spin state of the complex is often favored by *antiferromagnetic* coupling between the metals, which can be thought of as the

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[‡]Corresponding author

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limit of very weak bond formation. High-spin molecules, defined as discrete compounds with at least two unpaired electrons of parallel spin direction (S = 1 or greater), are much more difficult to achieve. These materials are not only of theoretical interest, high-spin molecules are intensely sought as new SMMs [1], magnetic refrigerants [2], or as contrast agents for magnetic resonance imaging (MRI) [3] to name but a few applications. SMMs have been suggested as components in new hybrid molecular spintronic devices, and work in this regard is underway [4]. Some targeted synthetic approaches have been shown to produce high-spin molecules: In particular, the *metal–radical approach*, which relies on coordination of stable free radical ligands to transition-metal ions, takes advantage of strong direct metal–radical exchange coupling [5]. Non-Heisenberg spin exchange, including the *double exchange* mechanism, have also been shown to produce high-spin molecules in delocalized mixed-valence complexes (vida infra), but this is largely underexplored [6].

Metal-radical complexes

The *metal-radical approach* toward high-spin molecules is a well-established synthetic mechanism toward paramagnetic complexes which relies on coordination of stable free radical ligands to transitionmetal ions. The advantage offered by the use of radical ligands is simply that metal-radical magnetic exchange coupling is *direct* between the magnetic orbitals of the radical and metal ion. Because the magnetic coupling is direct, simple application of the Goodenough–Kanamoori [7] magnetic orbital symmetry rules often enables the prediction of the nature of the magnetic coupling in advance—for example, ferromagnetic exchange is often observed between rigidly chelated π -radicals and 6-coordinate transition-metal ions with d_{σ} magnetic orbitals and antiferromagnetic coupling is regularly generated with metal ions furnishing d_{π} magnetic orbitals [8]. Despite the fact that rationally targeting high-spin molecules via metal-radical synthetic methods seems like an ideal way to generate high-spin paramagnetic clusters, the majority of metal-radical coordination complexes are monometallic or extended 1-, 2-, or 3-dimensional coordination polymers, with the exception of a handful of reports of metal-radical clusters albeit generated serendipitously [9]. This disparity is probably due in part to the difficulty in the preparation of stable radical ligands with structures amenable to controlled cluster formation.

It is intriguing to envision the combination of metal–radical chemistry with the grid-type coordination architectures produced by Lehn [10], Thompson [11], and others. In this regard, Hicks reported the synthesis and properties of ditopic verdazyl biradicals with structures related to diamagnetic oligopyridine ligands reported by Lehn (Fig. 1) [12]. Unfortunately, there have been no reports of coordination complexes bearing these biradical ligands, and we can speculate that stability or steric issues are responsible for this disparity. In most structurally characterized metal–verdazyl coordination complexes [13], the metal–verdazyl coordinate bond is the longest and thus weakest, and it is interesting to imagine the magnetic implications for new metal–verdazyl complexes featuring stronger metal–verdazyl coordination. Also, magnetic coupling *between* the verdazyl rings through the intervening molecular orbitals of the ligand noted in Fig. 1 (left) is weak—while these structures would be expected to produce, *locally*, strong metal–verdazyl magnetic coupling in polynuclear complexes, *globally*, the



Fig. 1 Left: Ditopic verdazyl biradical reported by Hicks. Right: New chelating verdazyl ligand reported by Brook.

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magnetic coupling in the complex is likely to be weak. The challenge becomes the design of other radical ligands featuring enhanced stabilities or structures more amenable to adopt predictable coordination architectures with metal ions in which all magnetic interactions within the complex are strong.

Brook [14] and others [15] have described the synthesis and electronic properties of new verdazyl radicals with enhanced stability relative to traditional verdazyls bearing methyl substituents at the 1 and 5 ring positions by incorporating isopropyl substituents at these ring positions. In a brilliant design, Brook has very recently reported the preparation of a new tridentate chelating verdazyl radical in which the weakly basic verdazyl ring comprises the central ring of the ligand, flanked by 2-pyridyl substituents at the 3 and 5 positions of the verdazyl ring (Fig. 1, right) [16]. This ligand structure reduces the steric restraint to metal coordination from the 1 and 5 verdazyl ring substituents because one of those substituents is itself a coordinating pyridine ring, while the other N-isopropyl is on the opposite side of the metal binding site. This ligand was coordinated to nickel(II) and as anticipated, the nickel-verdazyl coordinate bond was found to be much shorter (1.98 Å) than in other reported nickel-verdazyl structures (2.19 and 2.23 Å). Variable-temperature magnetic properties are fascinating and indicate strong nickel-verdazyl ferromagnetic coupling. In fact, coupling between verdazyl rings through the metal center is also strongly ferromagnetic. Perturbation of the verdazyl electronic structure was indicated in the electronic spectrum of the nickel complex, suggesting that the verdazyl spin is delocalizing into nickel-based d_{π} orbitals and implicating the verdazyl ligand as potentially non-innocent. Hicks and co-workers have reported verdazyl ligand non-innocence in verdazyl-ruthenium complexes, offering another intriguing facet to metal-verdazyl chemistry to be explored [17].

The group of Preuss has developed the coordination chemistry of the thiazyl radical over the past six years [18]. The thiazyl heterocycle features a diverse set of properties including electrical conductivity [19], magnetic bistability [20], and even ferromagnetism [21]. A number of mono- and bimetallic metal bis(hexafluoroacetylacetonato) complexes of substituted thiazyl radicals have been reported by Preuss and co-workers, and these have been shown to exhibit interesting magnetic properties. Another recent report from the Preuss group has suggested a feasible *supramolecular* means to high-spin molecule production in which all local spin–spin interactions are *antiferromagnetic* [22]. In the solid state, a benzoxazole-substituted thiazyl complex with Mn(hfac)₂ was shown to form a spin dimer; intra- and intermolecular manganese–thiazyl interactions are all antiferromagnetic, resulting in ferri-magnetic alignment between the remaining manganese-based unpaired electrons, resulting in an S = 4 ground state. What is intriguing is the relatively strong intermolecular magnetic coupling between the spin density rich thiazyl S atom and O atom of the ancillary hfac ligand (–2.5 K). The propensity for dimer formation in thiazyl chemistry, therefore, may actually be viewed as a structural advantage as a means to produce magnetic clusters with high-spin ground states in a supramolecular fashion.

Our own group is attempting to produce ferromagnetically coupled metal-radical coordination clusters via spin polarization mediated magnetic coupling between triarylamminium radical cations and coordinated metal ions. Recently, we have reported an intramolecular ferromagnetic interaction between coordinated manganese(II) and a 2,2'-bipyridine-substituted triarylamminum radical cation (Fig. 2, right) [23]. Substitution of 2,2'-bipyridine at the 5 ring position with the amminium radical cation results in π spin density at the amminium N atom with the same sign as the spin density on the coordinated manganese ion via polarization of the intervening pyridine ring π spin density. Our efforts in this regard are currently focused on increasing the stability of the metal-triarylamminium radical cation complexes, the production of polymetallic complexes with metal ions bridged by polytopic triarylamminum radicals, and strengthening intramolecular magnetic exchange coupling in these complexes through the incorporation of substituents.

It is clear that metal-radical coordination complexes provide a terrific platform to construct highspin complexes. The polytopic verdazyl radicals discussed earlier offer potential as scaffolds to create high-spin and strongly coupled complexes, particularly the new structurally variant reported by Brook. The challenge in the use of metal-radical complexes to produce high-spin complexes is in large meas-



Fig, 2 Left: Benzoxazole-substituted thiazyl radical complex with Mn(hfac)₂ reported by Preuss. Right: 2,2-Bipyridine-substituted triarylamminium radical cation complexes reported by Lemaire.

ure related to the design and synthesis of new variants of stable radical amenable to the rational assembly of polynuclear complexes in which all magnetic interactions are predictably strong and ferromagnetic.

New approaches toward SMMs and other paramagnetic clusters

Recent approaches toward SMMs have made use of lanthanide ions (or actinide ions, to a lesser extent) in a wide variety of coordination complexes [24]. Two general strategies have been identified, which include a lanthanide (or actinide) only approach in mono- or more commonly polymetallic clusters, and another so-called 3d–4f approach, which also includes first-row transition-metal ions exchange coupled with other lanthanide ions in the cluster. In both cases, the large spin-orbit coupling of the lanthanide ion is responsible for the magnetoanisotropy, which results in zero-field splitting and SMM properties. For example, Murugesu and co-workers have reported bimetallic dysprosium(III) complexes containing bridging (2-hydroxy-3-methoxyphenyl)methylene (isonicotino)hydrazine ligands [25]. The arrangement of the structurally rigid bridging ligands provides a ferromagnetic interaction between the dysprosium ions, and very large energy barriers to magnetization relaxation of 56 and 71 K are observed. In another report, Murugesu and co-workers produced a tetrametallic dysprosium complex exhibiting the largest barrier to magnetization reorientation of any reported SMM (170 K), largely due to single ion anisotropy as magnetic interactions between ions were found to be weak [26].

The first ferromagnetic interaction and SMM behavior in a cluster containing iron(III) and dysprosium(III) ions in an unusual { Fe_4Dy_4 } ring structure were reported by Powell et al. [27]. A magnetization relaxation barrier of 30 K was reported. This is an interesting strategy to combine the strong paramagnetism of iron(III) ions with strongly anisotropic dysprosium(III) ions. Brechin et al. have also reported { $Mn^{III}_4Ln^{III}_4$ } clusters using calix[4]arene as a scaffold (Ln = Gd, Tb, Dy) [28]. Of note, the reported Gd complex has properties that make its application as a magnetic refrigerant in the place of expensive and rare ³He advantageous. Other interesting lanthanide-centered SMMs include mononuclear lanthanide polyoxometallate complexes [29]. These materials are of interest as a result of solution stability, magnetic isolation of the lanthanide ion, and the absence of nuclear spins, which are responsible for quantum decoherence. The application of polyoxometallate-based SMMs toward quantum computing represents a tantalizing feature of this chemistry. Long and Rinehart reported the first actinide-based SMM with a simple trigonal prismatic uranium(III) complex containing three diphenylbis(pyrazolylborate) ligands [30]. The increased spin-orbit coupling of actinide complexes relative to their lanthanide counterparts could represent another path toward enhanced magnetization relaxation barriers.

Cyanide is a well-known ambidentate ligand with a rich history in coordination chemistry. A wide variety of magnetic materials have been produced containing bridging cyanide ligands, which can mediate strong magnetic superexchange between bridged metal ions [31]. Dunbar and co-workers recently

published a { Mo_8Mn_{14} } cluster using [Mo(CN)₇]⁴⁻ in an effort to produce high-spin clusters with strong magnetoanistropy resulting from the heptacyanomolybdate fragment [32]. The resulting cluster features the highest-spin ground state of any cyanide-bridged complex (S = 31) and incorporates an unprecedented 22 paramagnetic centers. Other interesting cyanide-based clusters have been reported recently by Holmes [33], including an {Fe₂Co₂} square, which is optically and magnetically bistable as a result of thermal or photoinduced electron-transfer processes between metal ions through the cyanide bridge, and Long [34] has reported vanadium(II) "star-like" cyano-bridge clusters of the general formula [(Py5Me₂)₄V₄M(CN)₆]⁵⁺ (M = Cr, Mo) bearing strong exchange couplings and S = 9/2 ground states, well isolated from higher-energy spin excited states. An effort to increase magnetoanisotropy in these materials is currently focused on using other more anisotropic second-row transition-metal ions.

Lanthanide or actinide complexes of the type described above offer a wealth of basic research in magnetochemistry to explore. While investigation of these materials as SMMs is in a relatively early stage, tremendous strides have already been realized with respect to high-energy barriers to magnetization reversal. Given that the SMM with the highest magnetization reversal barrier reported to date features weak magnetic coupling between the dysprosium ions clearly indicates that strong magnetoanisotropy is the key component in the design of high anisotropy barrier lanthanide-only SMMs. This result is underscored by recent theoretical [35] and experimental [36] reports that highlight the importance of anistotropy over total spin. That being said, a high-spin ground state well isolated from spin excited states is one important condition for anisotropy barriers to be raised closer to room temperature. One proven way to achieve energetically isolated spin ground states is by the creation of paramagnetic complexes with strong exchange coupling between paramagnetic centers. Achieving this in lanthanideonly or lanthanide complexes with first-row transition-metal ions is difficult owing to poor overlap between magnetic orbitals (f-f or d-f) resulting in weak exchange coupling. An alternative approach could include enhancing magnetic coupling in polynuclear complexes containing anisotropy-rich second- or third-row transition-metal ions via coordination with stable radicals or via double exchange (vida infra) in mixed-valence complexes.

Spin-dependent delocalization (double exchange)

Typically, high-spin molecules are created by designing molecules in which the unpaired electrons interact via Heisenberg exchange coupling, and there are numerous accounts of molecules with high-spin ground states prepared in this manner. Another, but much less investigated paradigm for the synthesis of high-spin molecules relies on electron transfer in electronically mixed-valence systems to align unpaired electrons in a ferromagnetic fashion. In 1951, Zener ascribed the ferromagnetism in mixed-valence Mn^{III}/Mn^{IV} manganite conductors with a perovskite structure to what he referred to as a "double exchange" interaction between the manganese ions [37]. The term "double" indicates that the itinerant electron couples to both ions, simultaneously, and with a simple application of Hund's rule the remaining metal-based unpaired d-electrons must furnish the same spin direction and the ferromagnetically coupled state—the high-spin state—is energetically favored in these mixed-valence materials (Fig. 3): A relatively simple mechanism to achieve a high-spin ground state in a molecular complex from a synthetic design point of view: The necessary structural components include at least two paramagnetic centers featuring class III mixed-valency (complete delocalization). In fact, double exchange is observed in ubiquitous iron-sulfur proteins in biological inorganic chemistry, including mixed-valence ferredoxins [38].



Fig. 3 A double-exchange interaction in a bimetallic mixed-valence complex. M(A) or M(B) refer to the two metal ions electronically coupled in the mixed-valence complex. In this example, the ground state features an S = 9/2 spin state.

While a number of theoretical articles [6a,b,39] have described double-exchange stabilization in mixed-valence complexes, far fewer are the number of experimental reports of high-spin molecules with double-exchange stabilization of the high-spin state. Examples of purely "organic" double exchange or SDD are extremely rare. Of note, as early as 2001 Shultz and co-workers reported the preparation of a mixed-valence bis(semiquinone) biradical anion by one electron reduction of an *anti-ferromagnetically* coupled triradical (Fig. 4) [40]. Variable-temperature electron paramagnetic resonance (EPR) studies indicated a ferromagnetic interaction in the generated mixed-valence species, which was rationalized on the basis of spin delocalization. Shultz has more recently reported similar SDD stabilization of the S = 3/2 state in low-spin cobalt(III) metal complexes containing mixed-valence nitronyl nitroxide-semiquinone and nitronyl nitroxide-catecholate ligands [41]. The magnetic coupling mediated by the itinerant electron is so strong, in fact, that lone thermal population of the high-spin state is observed up to 300 K! These materials are actively under investigation for application in molecular spintronic devices.



Fig. 4 Mixed-valence bis(semiquinone) anion prepared by Shultz.

An elegantly simple new targeted approach toward ferromagnetic stabilization via double exchange was very recently reported by Long and co-workers [42]. A series of bimetallic vanadium(II) complexes were reported bearing a pentapyridine-based ancillary ligand leaving one free vanadium coordination site for binding to a bridging imidazolate ligand (one particular example containing the bridging ligand 4,5-dimethylbenzimidazolate is shown in Fig. 5). Imidazole is well known to electron-ically couple metal ions in a wide variety of mixed-valence ruthenium(II)/(III) complexes, and the choice of vanadium is ideal owing to the d_{π} unpaired electrons allowing for strong overlap with the imidazolate π system. Mixed-valence vanadium(II)/(III) bimetallic complexes were prepared by one-

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Fig. 5 Precursor to a mixed-valence bimetallic vanadium complex reported by Long ($R = CH_3$) generated by one-electron oxidation.

electron oxidation of the homovalent precursors with Cp_2FePF_6 . Variable-temperature magnetic susceptibility experiments on the mixed-valence materials clearly indicated high-spin ground states (S = 5/2) well separated from other spin-excited states.

The application of electron-transfer mediated exchange coupling toward the production of highspin molecules is underexplored and presents itself as a rich mine of research opportunity. The relatively simple structural requirements to observe double exchange, including at least two paramagnetic centers in differential oxidation states and electronically coupled in the class III sense, are fairly straightforward to achieve from a synthetic point of view. One key design element includes the choice of bridging ligand, and the imidazole heterocycle and derivatives thereof, are well-established electronic couplers in mixed-valence bimetallic ruthenium complexes. Therefore, the synthesis of polytopic imidazole-based bridging ligands for the production of mixed-valence polynuclear complexes should be actively pursued as a new avenue toward high-spin molecules. The examples noted above highlight the enormous potential offered by the double-exchange mechanism toward a range of high-spin species that are sought as new high-spin clusters in SMMs, or as components in molecular spintronic devices.

SUMMARY AND CONCLUSIONS

The future of high-spin molecule design?

From a theoretical perspective, the pursuit and study of high-spin molecules has always satisfied an intense curiosity because these molecules provide an exception to the tendency of Nature to pair up electrons. Over the past 30-40 years, researchers in this area have uncovered important design tools that can be applied toward the rational production of high-spin molecules. These design tools include the structures of spin coupling units (SCUs) and the nature and strength of magnetic coupling mediated by these linkers, and magnetic orbital interaction symmetry rules to describe magnetic interactions in polymetallic or metal-radical systems via super- or direct exchange pathways. Molecule-based magnet researchers have used these tools to create diverse families of high-spin molecules, including polymetallic clusters with small bridging ligands or metal complexes with stable free radical ligands. While the discovery of SMM properties in high-spin molecules may be described as serendipitous, rational and controlled synthetic approaches are becoming accessible, for example, the use of targeted structural distortion in Mn₆ clusters in an approach to increase magnetic coupling and anisotropy reported by Brechin [43]. An important challenge that remains is the ability to rationally synthesize polymetallic lanthanide complexes with predictive magnetic properties; however, Murugesu and Powell have demonstrated the fantastic potential that lanthanide complexes hold as SMMs and certainly will continue to forge ahead in this regard.

Metal-radical complexes continue to be pursued as new magnetic materials. The predictive nature and strength of metal-radical exchange coupling are principal advantages in this approach. Unfortunately, strong ferromagnetically coupled metal-radical clusters have not been well developed, due in part to difficulties in the synthesis of polytopic stable radicals amenable to metal coordination in which magnetic coupling between unpaired electrons within the ligand is also strong and ferromagnetic. To overcome this challenge, it is clear that new stable radical designs are necessary, and recent reports

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by Brook, which include new chelating verdazyl radicals, represent a step in the right direction. However, it is also important to think beyond the current stable radical structural paradigm in search of completely new stable open-shell molecules to enhance this chemistry in the same manner that thinking beyond Heisenberg spin exchange has led to new high-spin molecules via SDD. The design of new polytopic bridging ligands with the ability to electronically couple metal ions and produce class III mixed-valence polynuclear complexes represents a rich target for the production of complexes with double-exchange-stabilized high-spin ground states.

The design, synthesis, and study of high-spin molecules is at the heart of magnetic materials research, and without these materials, SMMs and MRI contrast agents, for example, would not exist. The study of high-spin molecules as components in new molecular spintronic materials underscores the need for continued research along this line. Certainly not every high-spin molecule will exhibit SMM properties, and there are plenty of examples of very high-spin molecules that do not. However, with every high-spin molecule produced we learn a little something new to help us with the future design of new molecules that do not conform to the natural tendency to pair up electrons.

REFERENCES

- (a) D. Gatteschi, R. Sessoli, J. Villain. *Molecular Nanomagnets*, Oxford University Press, Oxford (2006); (b) M. Murrie. *Chem. Soc. Rev.* **39**, 1986 (2010).
- 2. M. Evangelisti, E. K. Brechin. Dalton Trans. 39, 4672 (2010).
- B. Cage, S. E. Russek, R. Shoemaker, A. J. Barker, C. Stoldt, V. Ramachandaran, N. S. Dalal. Polyhedron 26, 2413 (2007).
- (a) L. Zhu, K. L. Yao, Z. L. Liu. Appl. Phys. Lett. 96, 082115 (2010); (b) L. Bogani, W. Wernsdorfer. Nat. Mater. 7, 179 (2008).
- 5. A. Caneschi, D. Gatteschi, R. Sessoli, P. Rey. Acc. Chem. Res. 22, 392 (1989).
- (a) J.-J. Girerd. J. Chem. Phys. 79, 1766 (1983); (b) M. Drillon, G. Pourroy, J. Darriet. Chem. Phys. 88, 27 (1984); (c) M. P. Shores, J. R. Long. J. Am. Chem. Soc. 124, 3512 (2002); (d) D. R. Gamelin, E. L. Bominaar, M. L. Kirk, K. Wieghardt, E. I. Solomon. J. Am. Chem. Soc. 118, 8085 (1996).
- (a) J. J. Kanamori. *Phys. Chem. Solids* 10, 87 (1959); (b) J. B. Goodenough. *J. Phys. Chem. Solids* 6, 287 (1958).
- 8. R. G. Hicks, M. T. Lemaire, L. K. Thompson, T. M. Barclay. J. Am. Chem. Soc. 122, 8077 (2000).
- 9. K. E. Vostrikova, D. Luneau, W. Wernsdorfer, P. Rey, M. Verdaguer. J. Am. Chem. Soc. 122, 718 (2000).
- M. Ruben, J. Rojo, F. J. Romero-Salguero, L. H. Uppadine, J.-M. Lehn. Angew. Chem., Int. Ed. 43, 3644 (2004).
- 11. L. N. Dawe, K. V. Shuvaev, L. K. Thompson. Inorg. Chem. 48, 3323 (2009).
- 12. R. G. Hicks, B. D. Koivisto, M. T. Lemaire. Org. Lett. 6, 1887 (2004).
- 13. B. D. Koivisto, R. G. Hicks. Coord. Chem. Rev. 249, 2612 (2005).
- 14. E. C. Paré, D. J. R. Brook, A. Brieger, M. Badik, M. Schinke. Org. Biomol. Chem. 3, 4258 (2005).
- J. B. Gilroy, S. D. J. McKinnon, P. Kennepohl, M. S. Zsombor, M. J. Ferguson, L. K. Thompson, R. G. Hicks. J. Org. Chem. 72, 8062 (2007).
- D. J. R. Brook, C. J. Richardson, B. C. Haller, M. Hundley, G. T. Yee. *Chem. Commun.* 46, 6590 (2010).
- 17. S. D. J. McKinnon, B. O. Patrick, A. B. P. Lever, R. G. Hicks. Chem. Commun. 46, 773 (2010).
- 18. K. E. Preuss. Dalton Trans. 23, 2357 (2007).
- 19. A. A. Leitch, X. Yu, S. M. Winter, R. A. Secco, P. A. Dube, R. T. Oakley. J. Am. Chem. Soc. 131, 7112 (2009).
- J. L. Brusso, O. P. Clements, R. C. Haddon, M. E. Itkis, A. A. Leitch, R. T. Oakley, R. W. Reed, J. F. Richardson. J. Am. Chem. Soc. 126, 8256 (2004).

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- C. M. Robertson, D. J. T. Myles, A. A. Leitch, R. W. Reed, B. M. Dooley, N. L. Frank, P. A. Dube, L. K. Thompson, R. T. Oakley. *J. Am. Chem. Soc.* **129**, 12688 (2007).
- 22. E. M. Fatila, J. Goodreid, R. Clérac, M. Jennings, J. Assoud, K. E. Preuss. *Chem. Commun.* 46, 6569 (2010).
- S. Adugna, K. Revunova, B. Djukic, S. I. Gorelsky, H. A. Jenkins, M. T. Lemaire. *Inorg. Chem.* 49, 10183 (2010).
- 24. R. Sessoli, A. K. Powell. Coord. Chem. Rev. 253, 2328 (2009).
- 25. P.-H. Lin, T. J. Burchell, R. Clérac, M. Murugesu. Angew. Chem., Int. Ed. 47, 8848 (2008).
- P.-H. Lin, T. J. Burchell, L. Ungur, L. F. Chibotaru, W. Wernsdorfer, M. Murugesu. Angew. Chem., Int. Ed. 48, 9489 (2009).
- D. Schray, G. Abbas, Y. Lan, V. Mereacre, A. Sundt, J. Dreiser, O. Waldmann, G. E. Kostakis, C. E. Anson, A. K. Powell. *Angew. Chem., Int. Ed.* 49, 5185 (2010).
- G. Karotsis, S. Kennedy, S. J. Teat, C. M. Beavers, D. A. Fowler, J. J. Morales, M. Evangelisti, S. J. Dalgarno, E. K. Brechin. J. Am. Chem. Soc. 132, 12983 (2010).
- (a) M. A. AlDamen, J. M. Clemente-Juan, E. Coronado, C. Martí-Gastaldo, A. Gaita-Ariño. J. Am. Chem. Soc. 130, 8874 (2008); (b) J.-D. Compain, P. Mialane, A. Dolbecq, I. M. Mbomekallé, J. Marrot, F. Sécheresse, E. Rivière, G. Rogez, W. Wernsdorfer. Angew. Chem., Int. Ed. 48, 3077 (2009).
- 30. J. D. Rinehart, J. R. Long. J. Am. Chem. Soc. 131, 12558 (2009).
- E. Pardo, R. Ruiz-Garcia, J. Cano, X. Ottenwaelder, R. Lescouezec, Y. Journaux, F. Lloret, M. Julve. *Dalton Trans.* 21, 2780 (2008).
- 32. X.-Y. Wang, A. V. Prosvirin, K. R. Dunbar. Angew. Chem., Int. Ed. 49, 5081 (2010).
- Y. Zhang, D. Li, R. Clérac, M. Kalisz, C. Mathonière, S. M. Holmes. *Angew. Chem., Int. Ed.* 49, 3752 (2010).
- 34. D. E. Freedman, D. M. Jenkins, J. R. Long. Chem. Commun. 4829 (2009).
- 35. O. Waldmann. Inorg. Chem. 46, 10035 (2007).
- 36. (a) D. E. Freedman, W. H. Harman, T. D. Harris, G. J. Long, C. J. Chang, J. R. Long. J. Am. Chem. Soc. 132, 1224 (2010); (b) A. M. Ako, V. Mereacre, R. Clérac, W. Wernsdorfer, I. J. Hewitt, C. E. Anson, A. K. Powell. Chem. Commun. 544 (2009).
- 37. C. Zener. Phys. Rev. 82, 403 (1951).
- 38. H. Beinert, R. H. Holm, E. Münck. Science 277, 653 (1997).
- (a) S. Franzen, D. A. Shultz. J. Phys. Chem. A 107, 4292 (2003); (b) J. Borras-Almenar, E. Coronado, S. M. Ostrovsky, A. V. Palii, B. S. Tsukerblat. Chem. Phys. 240, 149 (1999).
- 40. (a) D. A. Shultz, R. K. Kumar. J. Am. Chem. Soc. 123, 6431 (2001).
- M. L. Kirk, D. A. Shultz, R. D. Schmidt, D. Habel-Rodriguez, H. Lee, J. Lee. J. Am. Chem. Soc. 131, 18304 (2009).
- B. Bechlars, D. M. D'Alessandro, D. M. Jenkins, A. T. Iavarone, S. D. Glover, C. P. Kubiak, J. R. Long. *Nat. Chem.* 2, 362 (2010).
- C. J. Milios, A. Vinslava, P. A. Wood, S. Parsons, W. Wernsdorfer, G. Christou, S. P. Perlepes, E. K. Brechin. J. Am. Chem. Soc. 129, 8 (2007).