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Review

High-spin molecules based on metal complexes of organic free radicals

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Contents

Abstract

This review presents a survey of the literature dedicated to the design of metal complexes of stable free radical ligands that have a ground spin state of high multiplicity but excluding extended species. Most stable free radicals have a sophisticated chemistry allowing the design of multi-site coordination ligands whose metal complexes are oligonuclear with a fairly high ground spin state. The versatile magnetic behavior of these species associated with the direct bonding of metal and organic spin carriers is described. The advantages of using organic free radical ligands for building up single-molecule magnets (SMM) is discussed.

Keywords: Free radicals; Metal complexes; Single-molecule magnets; Paramagnetic ligands

1. Introduction

Magneto-chemistry, 30 years ago, was a technique investigating magnetic properties in order to obtain structural information, such as the nature of a metal ion and its chemical environment [1]. Studies devoted to metallo-proteins and metallo-enzymes are representative of this concern [2]. However, it has become a mature field of chemistry in recent years because interest has moved to the synthesis and the study of new molecular materials having new properties [3]. In this respect, magneto-chemistry is attracting much interest from the scientific community.

The design of molecular materials exhibiting magnetic properties relies on open shell fragments, transition metal ions or/and organic free radicals that must be associated in such a way that the nature of the magnetic interactions is controlled to produce a desired bulk material property. Therefore, the chemistry involved in the synthesis of molecular magnetic materials has to take into account the organization of all space; it is a difficult problem requiring chemical skill and intuition.

The main challenge was to synthesize molecule-based systems having spontaneous magnetization below a critical temperature using reliable synthetic strategies. Pioneering investigation in this field reported extended structures where transition metal ions magnetically interacted through bridging diamagnetic organic fragments. Since most ligands mediate antiferromagnetic (spin paired) interactions, efforts were directed

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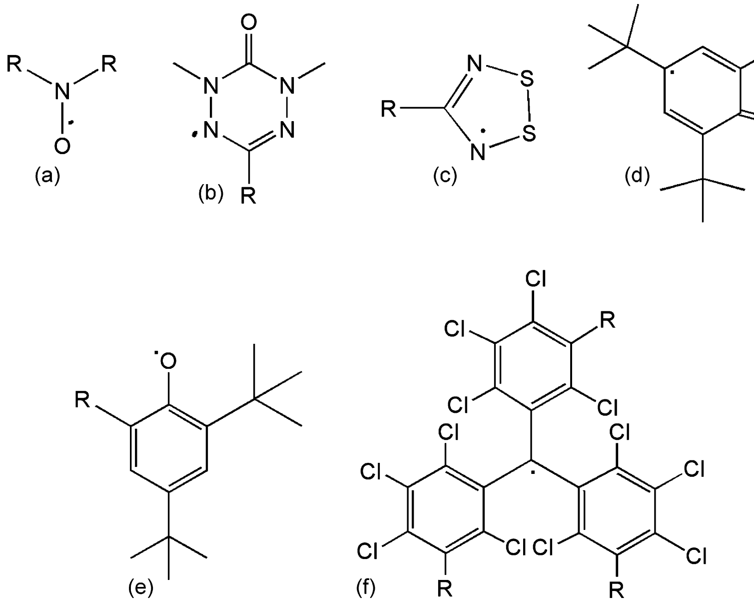

Fig. 1. Main families of stable free radicals relevant to the synthesis of high-spin molecules: (a) nitroxides, (b) verdazyls, (c) dithiadiazolyl, (d) semiquinones, (e) phenoxyls and (f) perchlorotriphenylmethyl.

toward the synthesis of organic fragments able to link alternating different metal centers with the aim of obtaining ferrimagnetic structures [4]. Indeed, if the metal ions have different spins and are regularly arranged along a 1D (or any higher dimension) structure, the resulting magnetic moment should never cancel out whatever the nature (ferro- or antiferromagnetic) of the interaction. However, this strategy suffers from an important synthetic drawback: the design of organic fragments able to organize multidimensional structures where different metal ions are selectively and regularly arranged into two inter-penetrating sublattices.

This difficulty is easily overcome if the bridging organic fragment itself carries one of the magnetic moments. Indeed, alternation of spin carriers is then a consequence of coordination and ferrimagnetism naturally follows from the presence of different organic ($S = 1/2$) and metallic ($S > 1/2$) magnetic centers. Such a strategy led to the first molecular complex ordering in the bulk where the organic spin carrier is tetracyanoethylenide; [5]. It was developed as the “metal–radical approach” in the 80s using stable nitroxide free radicals as building blocks in the design of molecular magnetic materials [6].

This overview focuses on progress aimed at using stable organic spin carriers in the synthesis of high-spin molecules. Only metal derivatives of stable free radicals are considered and extended structures ordering in the bulk are excluded. Extension to single-molecule magnets (SMMs) is discussed in the last section.

These free radicals are stable in the sense that compared with most organic compounds, they do not exhibit enhanced reactivity [7]. Considering nitroxides for example, whose chemistry is well developed, the N-oxyl group should be considered as a functional group which has its own reactivity. “Stable free radicals” react in specified conditions and give diamagnetic species with reducing agents but the radical center is retained in most other situations [8]. In coordination chemistry studies aimed at synthesizing magnetic materials, free radicals must not undergo metal–radical electron transfer which would result in diamagnetic compounds. This condition is generally fulfilled by control of redox potential through adequately chosen substituents.

Obviously, the different types of free radicals sketched in Fig. 1 do not show the same stability. Surprisingly however, phenoxyls (e), are more stable when coordinated than as isolated species; metal complexes are often obtained by oxidation of the phenolato metal complex [9]. In class (f) the radical center ($C^{\bullet}$) is never coordinated and complexes are known for compounds carrying carboxylic groups that are not high-spin molecules [10].

In the following, only the four (a–d) classes are considered since for the two other classes no metal-containing high-spin species have been characterized.

2. Nitroxide free radicals

There are several classes of nitroxides which all include at least one oxyl group [8,11].

Piperidinyl and pyrrolidinyl (not represented in Fig. 2) brought the first insight into metal–radical magneto-chemistry through the study of very simple species [12]. However, since magnetism is a bulk property (or at least the property of a finite collection of spin carriers), bridging ligands, such as nitronyl- (2a) and imino- (2b) nitroxides, [13] and polynitroxides, where nitroxyl groups are *m*-substituents of a phenyl ring (2e) are particularly attractive [14]. They all possess several oxyl groups and unsaturated structures allowing correlation of the unpaired spin density over the different coordination sites. They are the cornerstones of the metal–radical approach toward molecular magnets [6].

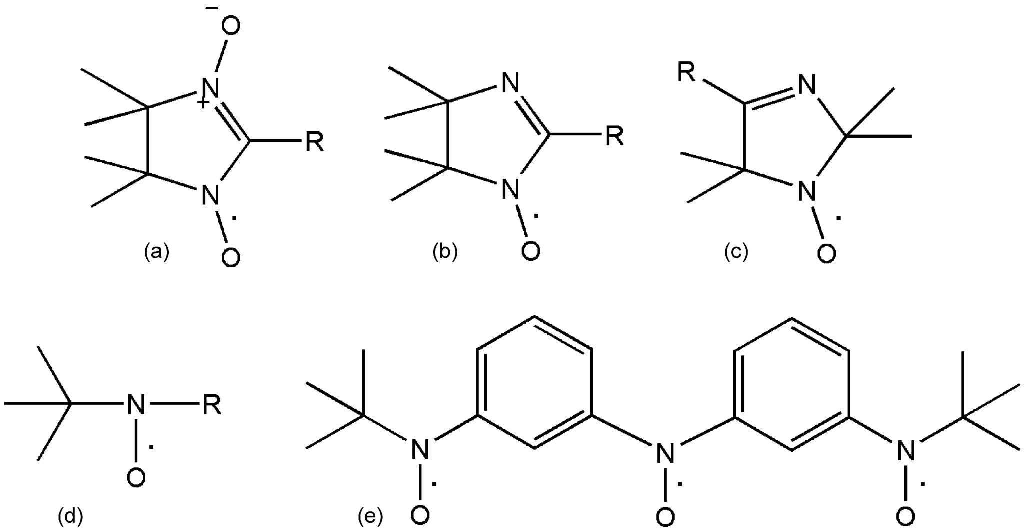

Fig. 2. Examples of nitroxide ligands: (a) nitronyl-, (b) imino-, (c) 3-imidazolinyl nitroxides, (d) aminoxyls and (e) aromatic polyaminoxyls.

2.1. Nitronyl and aminoxyl nitroxides

Nitronyl and aminoxyl nitroxides bind to metal ions only by oxygen atoms and, except for a few cases, [12b,15] spin pairing is the most usual situation [16].

Due to their bridging properties and well-established antiferromagnetic coupling, most nitronyl nitroxide–metal complexes exhibit ferromagnetic-alternating chains as described elsewhere [17]. Recently however, although infinite, a Co(II) containing chain has been shown to behave as a single chain magnet [18].

Discrete high-spin molecules are obtained as ferrimagnetic rings, for example, the discrete $[\mathrm{Mn(II)(hfac)_2NITPh}]_6$ ring shown in Fig. 3 [19]. Instead of developing as an infinite structure, π–π interactions between the phenyl ring of the 2-phenyl-substituted nitroxide and the ring of an *hfac* group favor a cyclic structure. Magnetic measurements (χT *versus* T) are typical of a ferrimagnetic ring with χT reaching a plateau at low temperature $\chi T = 75.5\,\mathrm{cm^3\,K\,mol^{-1}}$ close to the value ($\chi T = 78\,\mathrm{cm^3\,K\,mol^{-1}}$) expected for a $S = 12$ ground spin state which was confirmed by magnetization measurements.

In addition, an estimate of the manganese-radical exchange interaction ($J_{\text{Mn-Rad}} \approx -200\,\mathrm{cm^{-1}}$) was obtained [16b]. Note that free radicals, thanks to direct coordination of spin density rich donor atoms to metal ions, are well suited for giving large exchange interactions and very robust high-spin ground states. Despite the large S value, the compound behaves as a paramagnet throughout the temperature range.

The synthesis of high-spin rings has also been achieved using nitroxide substituted by nitrogen containing fragments (Fig. 4).

These free radicals react with metal-bis-(hexafluoroacetyl-acetonato) (Mn(II), Ni(II), Co(II)) to give rings including two metal ions and two ligands [20]. As an example, the manganese derivative of (4d) is displayed in Fig. 5.

Although the ligand is tridentate, only one oxyl oxygen atom and the *m*-pyridyl nitrogen are coordinated in a *cis*-fashion to a distorted octahedral metal ion. Note that such a cyclic structure is obtained only for *p*-pyridyl nitronyl nitroxides while it is observed for both *m*- and *p*-pyridyl-aminoyl derivatives.

From the magnetic point of view, as sketched in Fig. 6, the properties of the complexes depend on the position of the donor nitrogen atom. Indeed, the sign of the spin density on the pyridyl nitrogen atom is opposite in nitronyl and aminoxyl radicals giving rise to metal–ligand interactions of opposite natures. As can be inferred from Fig. 5, ferrimagnetic rings are obtained either with *m*-pyridyl nitronyl nitroxides or with *p*-pyridyl aminoxyls.

Considering the manganese complex described in Fig. 5, the metal–radical interaction through the NO group is antiferromagnetic and large; the increase of χT at low temperature is also modeled with a small negative interaction through the pyridyl fragment ($H = -2JS_1S_2$, $J = -4\,\mathrm{cm^{-1}}$) in agreement with a fer-

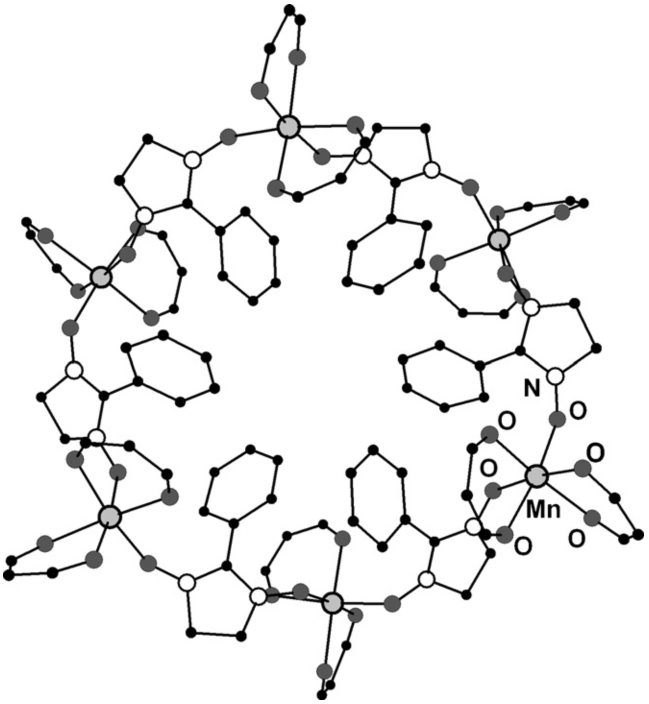

Fig. 3. Molecular structure of the cyclic $[\mathrm{Mn(II)(hfac)_2NITPh}]_6$ complex [19]. Hydrogen and fluorine atoms, and methyl groups are not represented.

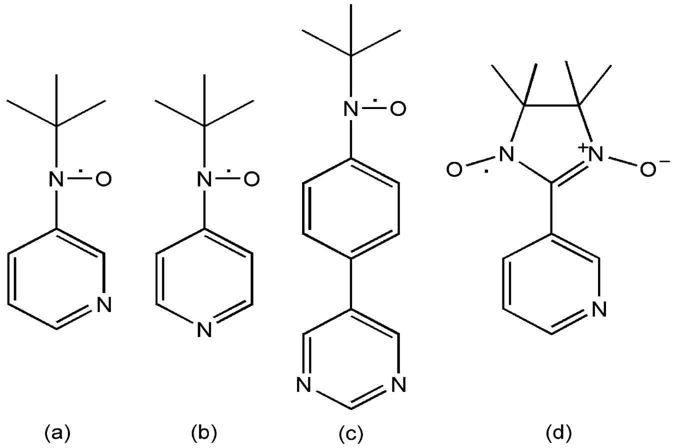

Fig. 4. Substituted nitroxides: (a) *m*-pyridyl aminoxyl, (b) *p*-pyridyl aminoxyl, (c) 4-(5-pyrimidyl)-phenyl aminoxyl, (d) *m*-pyridyl nitronyl nitroxide.

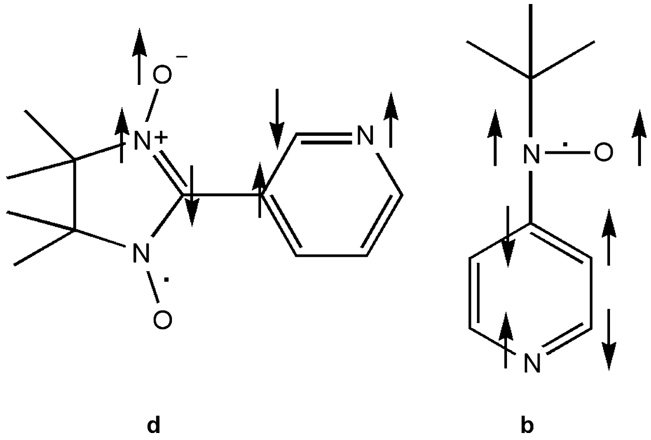

Fig. 6. Sketch of the spin distribution in pyridyl-substituted nitronyl- (d) and aminoxyl (b) radicals.

rimagnetic ring [20a]. Although the ground spin state is $S=4$, the weakness of this coupling constant and the presence of intermolecular interactions preclude the appearance of SMM properties. However, derivatives of aminoxyls are better suited for this purpose because the spin density on the pyridyl nitrogen atom is much larger and the absence of uncoordinated NO groups diminishes the chance of mediating intermolecular interactions as is observed in complexes of nitronyl nitroxides.

The design of ring complexes is an attractive way for controlling the dimensionality of metal complexes using multidentate free radicals. This strategy toward high-spin molecules is promissing because the clusters are generally well separated, a condition for such species to behave as a SMM. It would be, therefore, interesting to prepare analogous species including anisotropic metal ions such as Ni(II) or Co(II).

Another way to take advantage of both the bridging property and large metal–radical interactions would be to link already formed high-spin metal clusters on which a free coordination position is available. Although this possibility has been explored giving interesting chains of clusters, the design of discrete anisotropic species has still to be examined [21].

2.2. Imino nitroxides

Imino nitroxides are close cousins of nitronyl nitroxides since both have one unpaired electron delocalized on two coordination sites. However, their coordination properties are dramatically different. Coordination through the oxyl fragment leads, as observed for nitronyl nitroxides, to antiferromagnetic interactions – except with some rare-earth ions and for axial coordination to Cu(II) – while nitrogen coordination results in large ferromagnetic coupling (up to +200 cm^{-1}) with selected metal ions (Cu, Ni and Co) [22]. In contrast, it is strongly antiferromagnetic in Mn(II) derivatives. This behavior seems to be

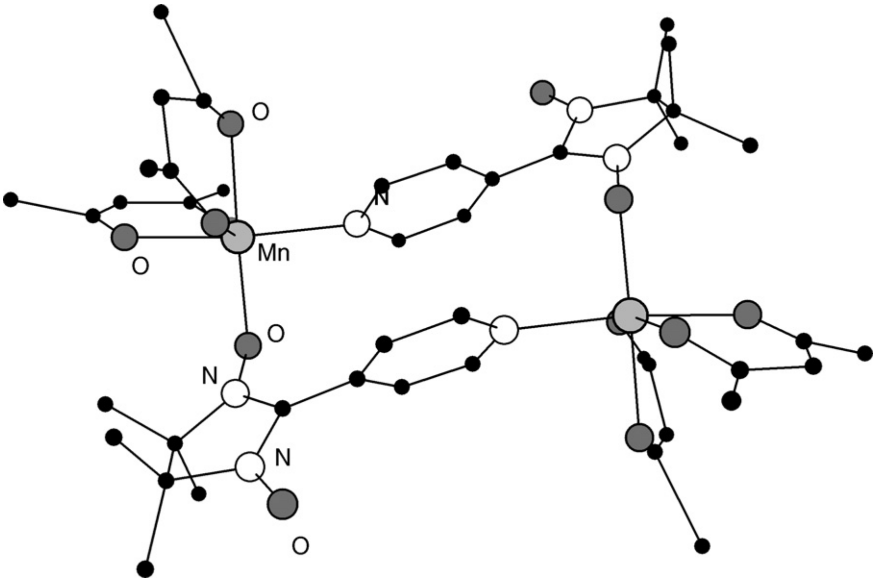

Fig. 5. Molecular structure of [4d(Mn(hfac)$_2$]$_2$ [20][20d]. Hydrogen and fluorine atoms are not represented.

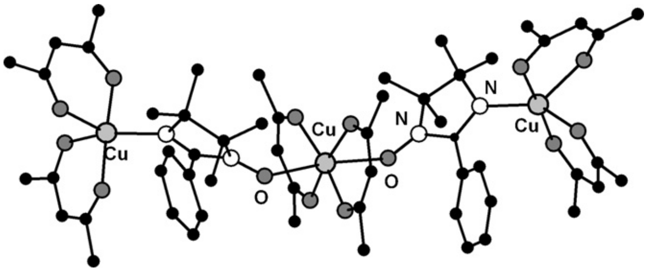

Fig. 7. Molecular structure of a five $S = 1/2$ spins involving Cu(II) and imino nitroxides ferromagnetically coupled [22a]. Hydrogen and fluorine atoms are not represented.

a common feature of all nitrogen containing free radicals like verdazyls or dithiadiazolyls.

Depending on N and/or O ligation, complex coupling patterns would be anticipated if imino nitroxides were bridging ligands. Fortunately, they are not bridging – except when involved in derivatives of penta-coordinated Cu(II) – so that discrete species can be designed.

The first reported high-spin molecule ($S = 5/2$) including imino nitroxides is a copper complex shown in Fig. 7.

This complex is important because it showed, for the first time, that copper–imino nitroxide interactions were ferromagnetic and large. Coupling of the two terminal metal ions through the imino nitrogen of the free radical is large ($J > +200\,\mathrm{cm}^{-1}$) while the central ion is also ferromagnetically coupled but weakly ($J = +10\,\mathrm{cm}^{-1}$). Worthy of note, in this case the radical ligand is bridging because the two terminal metal ions are penta-coordinated and steric crowding is released. Although the ground spin state of this complex is $S = 5/2$, this state is not strongly stabilized because one interaction is weak. However, it illustrates how imino nitroxides might be used for designing high-spin species.

Also ferromagnetic and large are Ni(II)- (and probably Co(II)) imino nitroxide interactions [22b]. However no example is known in which the ligand is bridging. This feature is well adapted for designing limited structures and to increase the ground state multiplicity of a preformed cluster using a chelating imino nitroxide (Fig. 8).

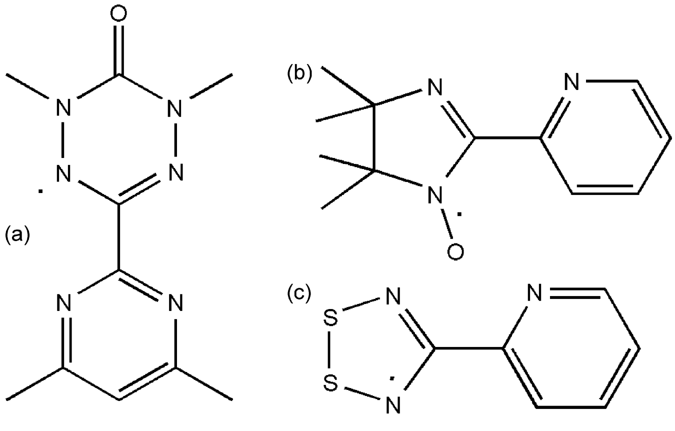

Fig. 8. Chelating (a) verdazyls-, (b) imino nitroxide- and (c) dithiadiazolyl free radicals used in the design of high-spin molecules.

For example, ferromagnetic interactions between paramagnetic centers in μ-cyano bimetallic complexes are well understood in discrete pentanuclear complexes including two Fe(III) and three Ni(II) ions where the magnetic orbitals are orthogonal [23]. In such complexes, the spin was increased from $S = 4$ to $S = 7$ replacing the diamagnetic ligands by chelating imino nitroxides [24].

The structure consists of two $[\mathrm{Fe(CN)_6}]$ octahedral fragments connected via three CN–Ni(IM-2Py)$_2$–NC bridges in a *fac* arrangement (Fig. 9). It is a unique molecular arrangement involving three shells of different spin carriers all coupled ferromagnetically [24]. The field-dependent magnetization curve saturates at 14 μ_B in agreement with a $S = 7$ ground spin state. Investigation of the low temperature behavior of single crystals in the 5–0.5 K temperature range by use of a home made microSQUID machine showed that an hysteresis loop opened below 1.2 K. The time dependence of the relaxation below 1.2 K was not exponential (logarithmic for $t > 50$ s) and more importantly, the relaxation process was temperature dependent down to 0.05 K. This behavior is in contradiction with the presence of quantum effects and confirms the absence of single-molecule properties.

This example was the most promising attempt to prepare a high-spin molecule including organic spin carriers and having SMM properties. Indeed, Ni(II) and low-spin Fe(III) are anisotropic and the spin ($S = 7$) is rather large. In this compound however, as shown by the opening of a small hysteresis loop, intermolecular interactions are too large for the compound to behave as a magnetically isolated cluster.

3. Verdazyl free radicals

Verdazyls are potentially bridging through two nitrogen atoms carrying large spin densities [25]. In that respect, they

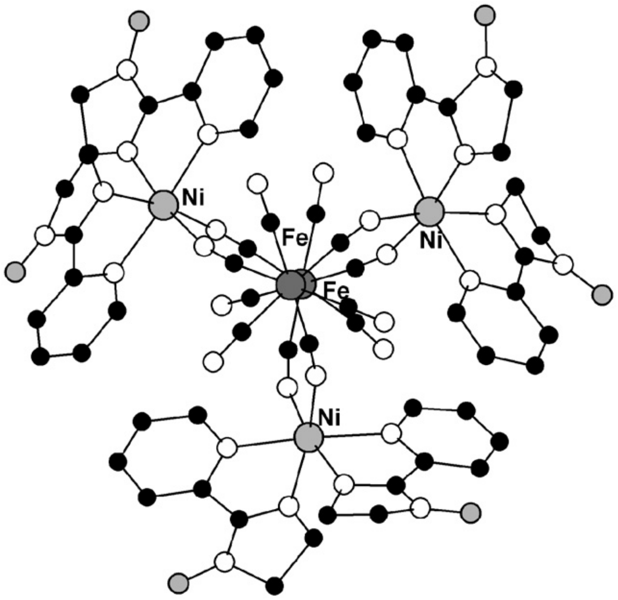

Fig. 9. Molecular structure of $[\mathrm{Fe_2(CN)_{12}Ni_3(IM\text{-}2Py)_6}]\cdot 4\mathrm{H_2O}$. Magnetic interactions are as follows: $J_{\mathrm{Ni\text{-}rad}} > +100\,\mathrm{cm}^{-1}$, $J_{\mathrm{Fe\text{-}Ni}} = +7\,\mathrm{cm}^{-1}$ [24]. Hydrogen atoms and methyl groups are not represented.

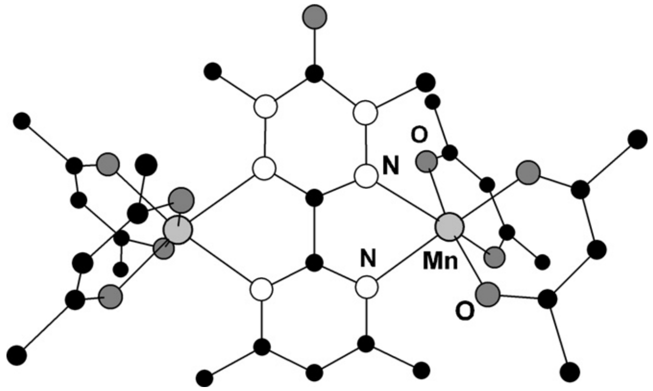

Fig. 10. Molecular structure of $[Mn(hfac)_2\text{-}(5\text{-}(4,6\text{-dimethylpyrimidine})\ \text{verdazyl}]$ [26a]. Fluorine and hydrogen atoms are not represented.

resemble imino nitroxides because, depending on the metal ion, magnetic interactions are large and ferromagnetic (Cu(II), Ni(II), Co(II)) or antiferromagnetic (Mn(II)) [26]. Therefore, high-spin molecules have been designed relying on both ferro- and antiferromagnetic strategies.

This pyrimidyl-substituted bis-chelating verdazyl free radical (Fig. 10) reacts with $Mn(hfac)_2$ to give a three-spin system where the metal–ligand interaction is $J_{\text{Mn–rad}} = -48\ \text{cm}^{-1}$. Therefore, the ground spin state of the complex may be sketched as two parallel Mn ($S = 5/2$) spin and one antiparallel radical ($S = 1/2$) spin, leading to $S_{\text{comp}} = 9/2$.

The same bis-chelating verdazyl ligand also functions as a bridging ligand toward Ni(II) leading to a complex whose structure is similar to that of the Mn(II) species (Fig. 10) [26b]. As expected, the metal–radical interaction is ferromagnetic and large and the ground spin state is $S = 5/2$.

In both complexes (Mn and Ni) the ligand is bridging but since hexafluoroacetylacetonato ancillary ligands were used, the complexes are discrete. Although the ground state of this Ni(II) complex is rather low, it illustrates a general synthetic approach where the choice of ancillary ligands is important. It might be anticipated that careful control of the connectivity would lead to oligomeric species whose spin is much higher and anisotropy is included thanks to the metal ions.

4. Dithiadiazolyl free radicals

Their coordination chemistry is much less developed than that of nitroxides and verdazyls but, having only nitrogen coordination sites, they should behave similarly as verdazyls. This expectation was confirmed by the few reported metal complexes of these free radicals and, importantly, a ferromagnetic interaction with Co(II) has been characterized Fig. 11 [27].

In this complex ($S = 2$), the metal–radical interaction has been estimated as $J = +80\ \text{cm}^{-1}$.

Dithiadiazolyl radicals could be chemically modified in order to be bis-chelating and bridging. In this respect they should offer the same potentialities as bridging verdazyls for designing high-spin molecules.

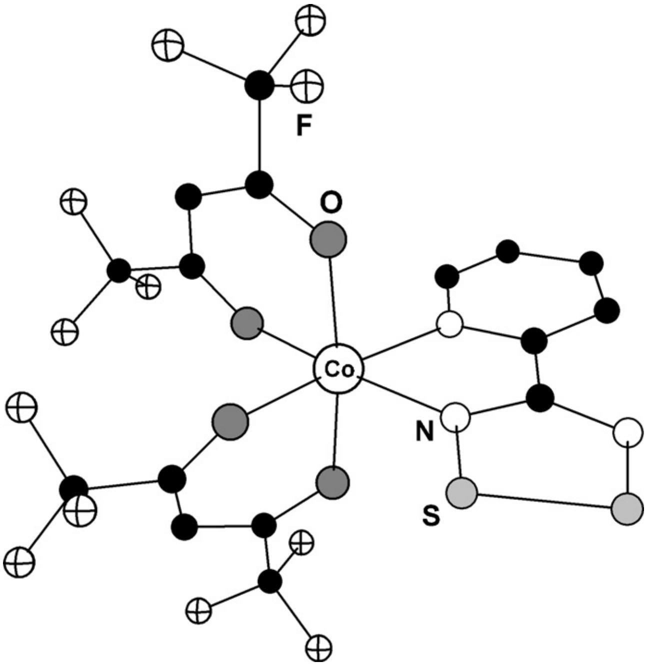

Fig. 11. Molecular structure of 4-(2-pyridyl)-substituted dithiadiazolyl radical with $Co(hfac)_2$ [27]. Hydrogen atoms are not represented.

5. *o*-Semiquinone free radicals

O-Semiquinones (*o*-SQ) are observed by EPR and are not very stable. However, as anionic species, they give rather stable metal complexes so that their contribution to the field of molecular magnetism is fairly important [28].

Although *o*-SQ are *O*,*O*-chelating ligands, the magnetic behavior of their metal complexes is intermediate between *O*-coordinated (nitroxides) and *N*-coordinated (imino nitroxides, verdazyls, dithiadiazolyls) free radicals. Thus, most Cu(II) and octahedral complexes of Ni(II) are high-spin species while, as observed for all organic free radicals, Mn(II) derivatives have low-spin multiplicity [29]. This behavior comes from the chelate ring, which has high aromatic character and brings the metal and radical magnetic orbitals into an orthogonal arrangement when the metal singly occupied orbitals have σ symmetry. However, distortion from this ideal geometry strongly depends on steric hindrance and thus depends on the presence of substituents on the semiquinone fragment, and on the bulkiness of ancillary ligands [30]. Except for a few cases, ferromagnetic also is the behavior of Gd(III) complexes [31].

Although they have two sites of coordination, being chelating ligands, semiquinones are not bridging. Therefore, even in the favorable cases where the metal–radical interaction is ferromagnetic the resulting complexes have rather small spin values. Synthesizing mixed species involving nitronyl nitroxides, [32] and semiquinones or bis- or tris-semiquinones or has elegantly solved this problem [34,33].

5.1. Heterospin ligands

Hetero-biradicals displayed in Fig. 12 were isolated and fully characterized as their Zn complexes [32]. In both compounds,

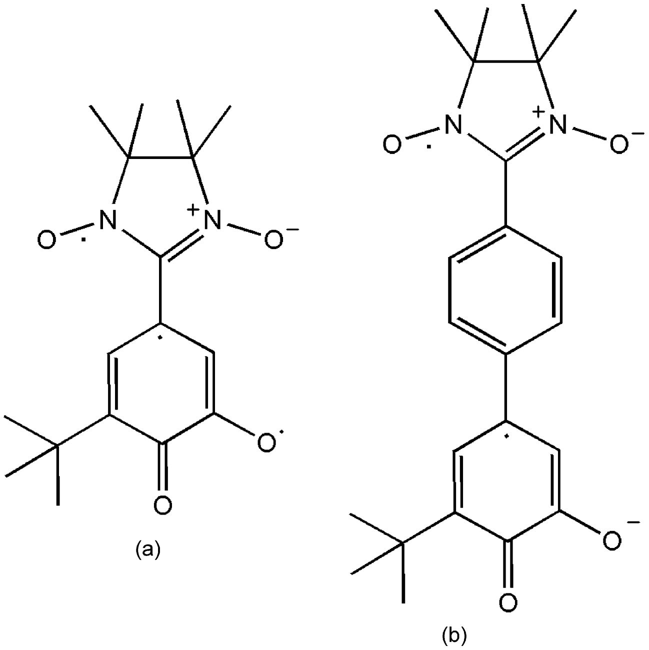

Fig. 12. Nitronyl nitroxide-*o*-semiquinone biradicals (NNSQ).

the two unpaired electrons are strongly coupled giving triplet ground states.

Ferromagnetic coupling is assured by covalently linking an SQ atom having positive spin density to a NN atom carrying negative spin density. $J_{\text{SQ–NN}}$ interactions have been estimated as $> +300\,\text{cm}^{-1}$ in (a) and $> +100\,\text{cm}^{-1}$ in (b).

A few metal complexes (Fig. 13) of biradical (a) in which penta-coordinated metal ions are bound only to the *o*-semiquinone fragment have been characterized [32a,c]. As expected, coupling with Mn(II), Ni(II) and Co(II) is fairly large and antiferromagnetic ($J_{\text{Mn}} = -40\,\text{cm}^{-1}$, $J_{\text{Ni}} = -70\,\text{cm}^{-1}$, $J_{\text{Co}} < 0\,\text{cm}^{-1}$) while interaction with Cu(II) is ferromagnetic ($J_{\text{Cu}} = +75\,\text{cm}^{-1}$). Interestingly, when involved in an octahedral Ni(II) complex, the radical is ferromagnetically coupled ($+80\,\text{cm}^{-1}$).

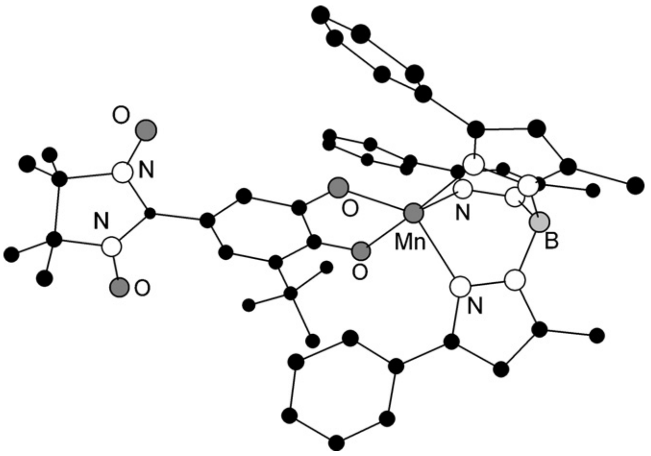

Fig. 13. Molecular structure of Mn(II) $\text{Tp}^{\text{Cum,Me}}$–NNSQ complex [32]. Hydrogen atoms and *i*-propyl groups are not represented.

Compare to metal complexes of 3,5-di-*t*-butyl-*o*-semiquinone, this ligand increases the total spin by 1/2 but, also, the large intra-ligand ferromagnetic interaction plays a decisive role in stabilizing the ground state from the first excited state. The total spin is not only higher but it is more robust [32c].

The potentialities of these ligands have not been explored thoroughly. Indeed, in these complexes bulky ancillary ligands have been used ($\text{Tp}^{\text{Cum,Me}}$ = tris-[3-(4′-cumenyl)-5-methylpyrazolyl]borate) which stabilize the complexes and prevent the formation of extended species. Unfortunately, no attempt has been made to take advantage of the nitroxide coordination sites to design polynuclear species.

5.2. Homo-spin ligands

Poly-*o*-semiquinone radicals bring opportunities to design high-spin polynuclear complexes. Following well-established rules, these polyradicals were designed in such a way as to obtain triplet or quartet ground states [33,34]. Examples of such ligands are displayed in Fig. 14; biradical (a) and triradical (c) are *m*-phenylene derivatives while biradicals (b) are derivatives of trimethylenemethane. In both cases, the coupler as the right structure for the SOMOs, in the polyradicals, to be “non-disjoint” [33c].

A thorough study has shown that intramolecular coupling in the Zn complexes is modulated by substituent effects (in a) and correlated, as expected, to the angle between the semiquinone rings [33c]. However, large ferromagnetic interactions ($> +30\,\text{cm}^{-1}$) are observed for angles as large as 50 °. In addition, it was shown that energy matching of coupler and SQ orbitals as well as coupler-modulated delocalization within mixed-valent states contribute also to magnetic exchange coupling.

Coordination chemistry of these ligands may be complicated by bonding requirements, which would lead to large angles between the SQ rings and intra-ligand antiferromagnetic coupling. Such complications were indeed observed in Co(III) and Fe(III) complexes where the intra-ligand magnetic interaction becomes antiferromagnetic upon coordination.

Nevertheless, high-spin molecules have been characterized (but no structures are available) using these polyradicals, mostly metal complexes of (a) (X = *t*-Bu) and (c). which afford binuclear and trinuclear species, respectively thanks to the use of blocking ancillary ligands, $\text{Tp}^{\text{Cum,Me}}$ or CTH (D,L-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane).

Note that depending on the ancillary ligand, penta- or hexa-coordinated species are obtained for $\text{Tp}^{\text{Cum,Me}}$ and CTH, respectively. In Mn(II) complexes, both geometries lead to antiferromagnetic behavior while for Ni(II) complexes they give antiferro- and ferromagnetic coupling, respectively.

From Table 1 it can be seen that molecules having a spin as large as 6 can be obtained. As usual, large metal–radical interactions are observed in the range $-200 < J < +200\,\text{cm}^{-1}$. However, in contrast to heterospin systems, the ground state is not well stabilized because the SQ–SQ interaction is rather weak.

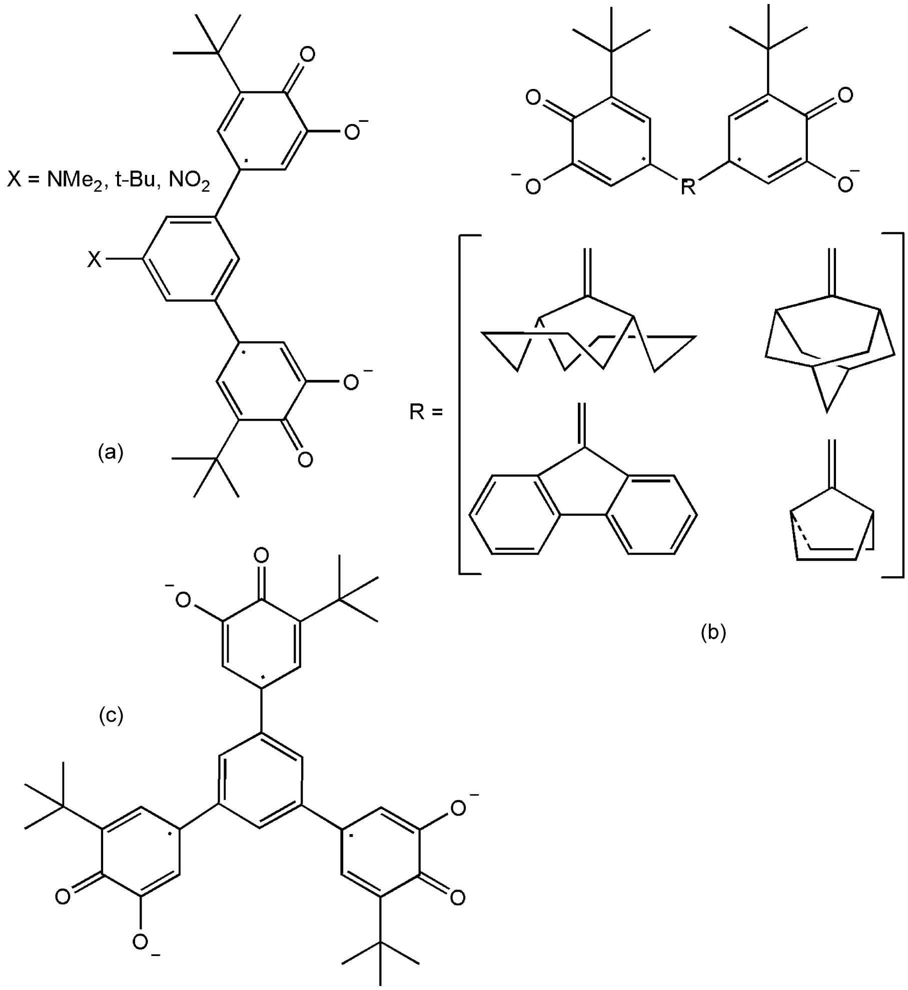

Fig. 14. Examples of bis- and tris-*o*-semiquinone radicals having a high ground spin state.

6. Conclusion and perspectives

Most of the coordination chemistry of organic free radicals was devoted to the design of extended species related to molecular magnets. According to a ferrimagnetic strategy, Mn(II) was the ideal metal ion because the metal–radical interaction is very large and the resulting spin is also large. Another frequently used metal ion is Cu(II) which brings opportunities to design ferro- or antiferromagnetic species depending on the coordination sphere.

Table 1
Ground spin state, metal–semiquinone (J_{M-SQ}) and semiquinone–semiquinone (J_{SQ-SQ}) coupling constants ($H = -2JS_1S_2$) for some metal complexes of bis- (a) and tris-*o*-semiquinones (c).

M	S	J_{M-SQ} (cm^{-1})	J_{SQ-SQ} (cm^{-1})	Reference
Bis-SQ				
Ni(II)	3	>+200	+13	[34b]
Cu(II)	2	+17	+3	[34b]
Cr(III)	3	<−200	+16	[34b]
Tris-SQ				
Mn(II)	6	<−180	+20	[34a]
Ni(II)	9/2	+85	+13	[34a]

As described before high-spin molecules were characterized and some of them have a rather high-spin ground state ($S = 12$). Moreover, owing to large metal–radical interactions, the ground state is generally strongly stabilized.

These features are related to recently reported new magnetic molecular objects: single-molecule magnets (SMMs). This new field became a challenge for chemists when the dodecanuclear mixed-valence manganese-oxo cluster with acetate ligands, $Mn_{12}(OAc)_{16}$, demonstrated experimental evidence for a single-molecule magnet behavior below 4 K and quantum phenomena such as thermally assisted tunnelling [35]. Search for other examples of such behavior resulted in the octanuclear iron(III)-oxo-hydroxo cluster, Fe_8, which exhibits ground state tunnelling and quantum phase interference [36]. In these polynuclear clusters, one observes fairly large intramolecular interactions between the metallic centers, very weak intermolecular interactions and electronic and structural anisotropy [37].

Most SMM's are polynuclear complexes where anisotropic metal ions are bridged by diamagnetic ligands [38]. The barrier between the two potential wells is high enough for controlling the thermally assisted magnetization relaxation. For example, in $Mn_{12}Ac$ the barrier should lead to a blocking temperature of 70 K but the actual blocking temperature however, is only

3 K because tunnelling is very effective [39]. Indeed, relaxation from the first excited state ($S = 9$) is 10^8 more effective than for the ground state ($S = 10$). Therefore, one has to control the energy gaps between the different spin states, which are highly dependent on the magnitude of the interactions between the spin carriers.

This challenge of Molecular Magnetism, the design of SMMs, is too recent for being a mature field for organic free radicals to be extensively involved. Most high-spin molecules based on organic free radicals metal complexes that have been described so far are not the result of a deliberate strategy and have been obtained according to a thorough screening of the coordination properties of organic spin carriers. Organic free radicals are highly isotropic. In addition, most of their complexes are derivatives of copper(II) and manganese(II) whose magnetic properties are simple to analyze. [6]. Therefore, none of the high-spin molecules characterized so far are SMMs. However, they offer opportunities to design valuable high-spin anisotropic molecules in two different ways: (i) they have demonstrated their bridging capabilities toward anisotropic metal ions, when adequately substituted. In that case, a ground spin state of high multiplicity would result from a *ferrimagnetic* structure. Such a strategy is the same as that described in the preceding sections except that the goal is to control the growth of the structure, (ii) they might play the role of terminal ligands in a preformed structure and increase the multiplicity of the ground state if they interact *ferromagnetically* with other spin carriers of the molecule. The latter strategy is virtually applicable to every existing system whose structure includes an anisotropic core.

Although organic spin carriers are highly isotropic, a "radical-based" strategy toward SMM's is promising. Metal–radical interactions may be large if the free radical carries coordination sites where a large spin density is delocalized and they may be strongly anisotropic if the metal ion is orbitally degenerate.

For designing free radical based SMMs, a few directions seem to be promising:

1. The coordination chemistry of free radicals should include anisotropic metal ions. Although attention has been paid to Ni(II) and Co(II), there are more attractive anisotropic metal ions such as rare-earth and 4d or 5d metal ions. Interesting results have been recently reported for the former compounds, however, the weakness of magnetic interactions in complexes involving rare-earth is a serious drawback [40,41]. In contrast, for low-spin 4d and 5d metal ions whose ground state is degenerate, anisotropy is expected to be as large as in rare-earth and the magnetic orbitals being diffuse, magnetic interactions should be large [42].

For example, low-spin Re(IV) heptacyanato or Os(III)-hexacyanato anions where the paramagnetic metal center ground state is degenerate, have very large spin-orbit coupling (>2500 cm^{-1}) might be used for designing clusters analogous to that described on Fig. 9 [37].

The structure of such complexes is difficult to predict because it will depend on steric demand but, even if only three Ni(IM-2Py) fragments (see Fig. 9) were coordinated to the anisotropic central metal ion, the resulting spin would be >11/2 whatever the nature of the magnetic interaction. These fairly high-spin and large M–Ni(II) interaction, and the large anisotropy of the metal ion should lead to blocking temperatures one order of magnitude higher that those reported so far.

2. Attention should be paid to the design of specific free radical ligands. Since in these 4d or 5d metal ions the magnetic orbitals are more diffuse than in 3d analogues, direct ligation of the free radical to the metal is expected to result in very large interactions and in a large energetic separation of the spin state levels, thus diminishing tunnelling relaxation. Ligands including soft coordination centers (N, P) in a chelating structure should be preferred. In addition, attention should be paid to the choice of ancillary ligand for controlling the redox potential and the number of free-coordinating positions at the metal ion.

Finally, when the coordination behavior of these free radicals toward 4d or 5d ions will be well understood, efforts toward the design of related clusters will probably bring attractive possibilities to obtain species exhibiting the right features warranting applications in spintronics.

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