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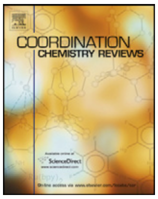

Review

Organic radicals, a promising route towards original molecule-based magnetic materials

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ABSTRACT

We describe our activities on radical-based compounds developed within the 6-year priority program of the DFG Schwerpunktprogramm "Molekularer Magnetismus". During this period, two families of radicals, based on nitroxide and verdazyl unpaired electron containing moieties, were used to build up purely organic compounds as well as coordination compounds. The versatility of their chemistry together with the variety and strength of the intra- and inter-molecular exchange interactions emphasised by calculation on model systems confirm the role of radicals as major building blocks for molecule-based magnetic materials.

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1. Introduction

Because they bear one or more unpaired electrons in their π-system arising from the overlap between 2p atomic orbitals, radicals have rapidly become recognised as interesting building blocks for molecule-based magnetic materials. As such, many reviews have been devoted along the years to the various families of radical containing compounds [1–8]. We therefore do not attempt to present an exhaustive description of the field. Though comparison with literature will be undertaken, we will focus on our work on nitroxide- and verdazyl-based compounds during the last years where related publications are considered. The perspectives we forecast to develop will also be presented.

In order to use radicals as building blocks for magnetic materials, these organic species should be stable under ambient conditions. This mere condition considerably reduces the number of available molecules [9,10]. The principal family is undoubtedly based on the nitroxide moiety especially the nitronyl- and imino-nitroxides (NIT, IN, respectively) while an emerging family takes advantage of the stability of the verdazyl (Vz) radicals. The first part of this paper will be devoted to the presentation and the comparison between these two families of stable radicals in terms of synthetic accessibility, structure, chemical and magnetic properties. A second part will deal with the synthesis of purely organic materials. The two last sections will describe the compounds obtained by exploiting the coordinating properties of both types of radicals.

2. Description and stability of the organic radicals

Two important families of radicals are described in the following report. The "historical" one is based on the nitroxide moiety

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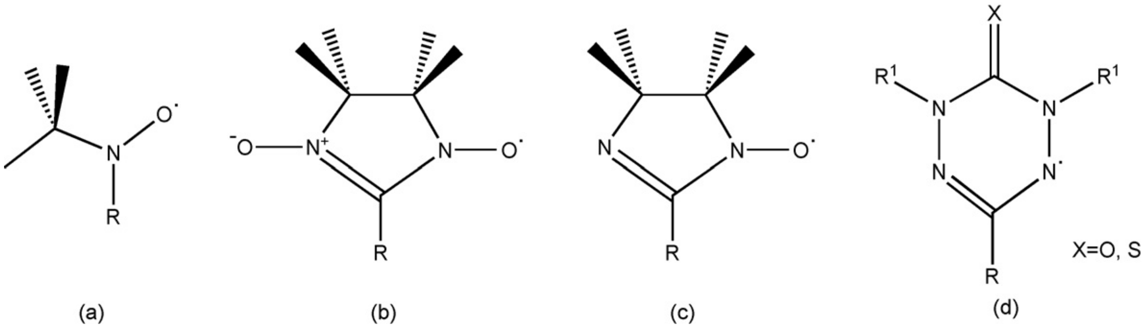


Scheme 1. Structure of tertiobutylnitroxide (a), nitronyl-nitroxide (NIT) (b), imino-nitroxide (IN) (c) and verdazyl (Vz) (d) radicals.

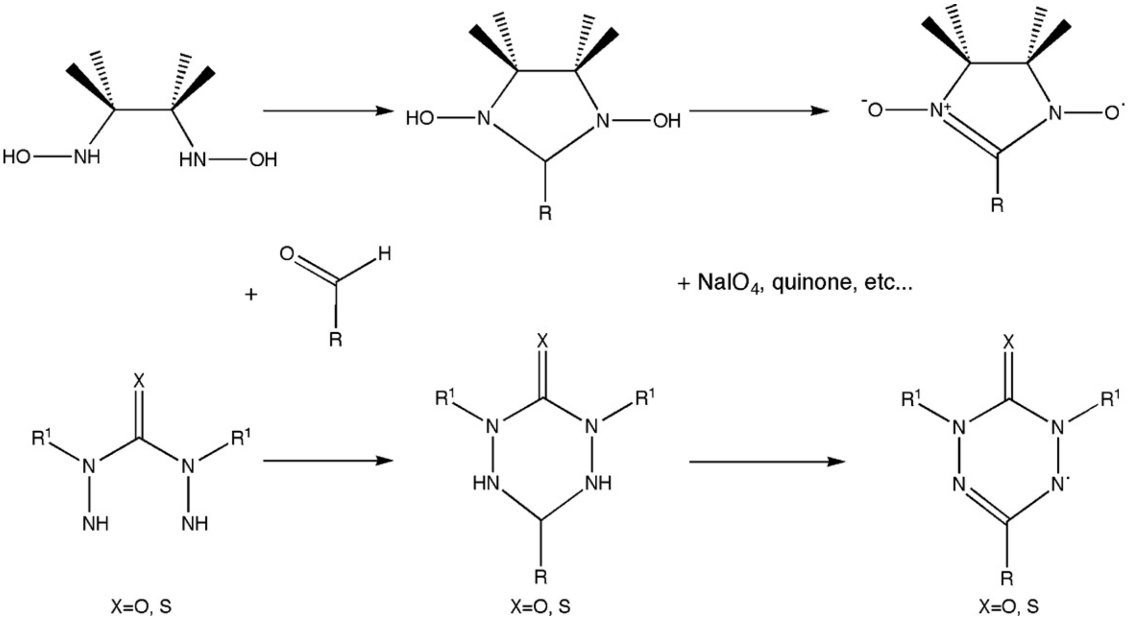
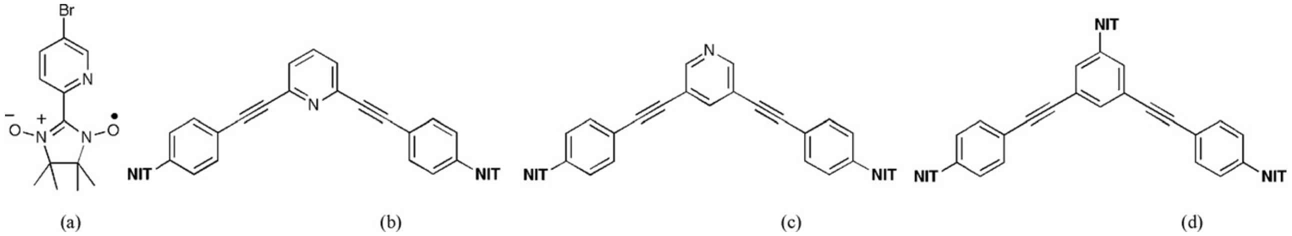


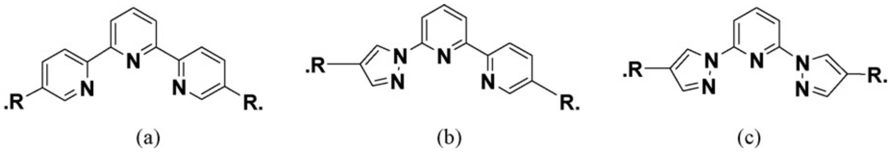
Fig. 1. Comparative syntheses of nitronyl-nitroxide (upper panel) and chalcogenoverdazyl (lower panel) radicals.

excluding the unsaturated linked spin labels as Tempo or Tempol [11–19]. The second family of radicals is an emerging one, based on the verdazyl moiety. In both cases, the unpaired electron is located in an antibonding π^*-orbital. The delocalisation of the electron in several p-orbitals stabilises the π^*-orbital (SOMO) and thereby enhances the stability of the radical. In the field of molecular magnetism, the most studied nitroxide-based radicals are tertbutylnitroxides (Scheme 1(a)) [20–24], nitronyl- and imino-nitroxides. In the last two radicals, the unpaired electron is delocalised on a nitronyl (Scheme 1(b)) or an imine function (Scheme 1(c)), respectively. In the verdazyl family, the radical is stabilised by delocalisation over the four nitrogen atoms of a six-membered heterocycle (Scheme 1(d)).

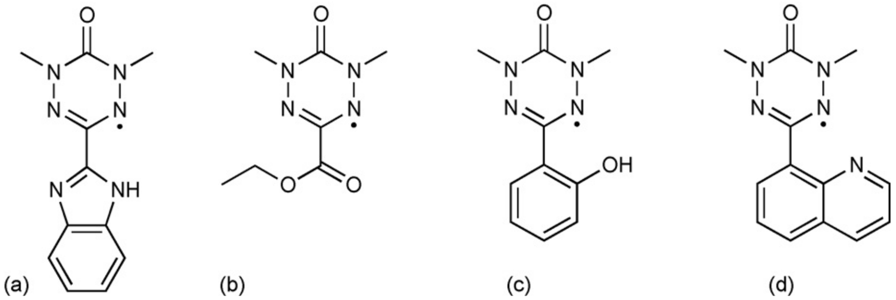
To obtain magnetic materials by using these radicals, one can rely on a wide variety of bond type, from strong covalent ones to weak intermolecular ones. Moreover, the heteroatoms of the radicals can be used as ligation sites towards metal ions leading to coordination compounds with organic and inorganic spin bearers and strong exchange interaction between the radical and the metal ion. In the case of Vz, the coordination ability of the nitrogen atom of the radical strongly depends on the choice of the R substituent. The possibility of intermolecular interactions between the π-orbitals of the radicals influences the packing of the molecules in the solid state and, hence, the magnetic properties of the materials. Finally, the functions brought by the R group can introduce complementary bonding pathways.



Scheme 2. NIT-containing heterofunctionalised mono- (a), di- (b and c) and tri- (d) radicals.



Scheme 3. Multifunctional biradicals with triplet ground state ($S = 1$), R = NIT and IN.



Scheme 4. Verdazyl-containing ligands with various coordinating pockets.

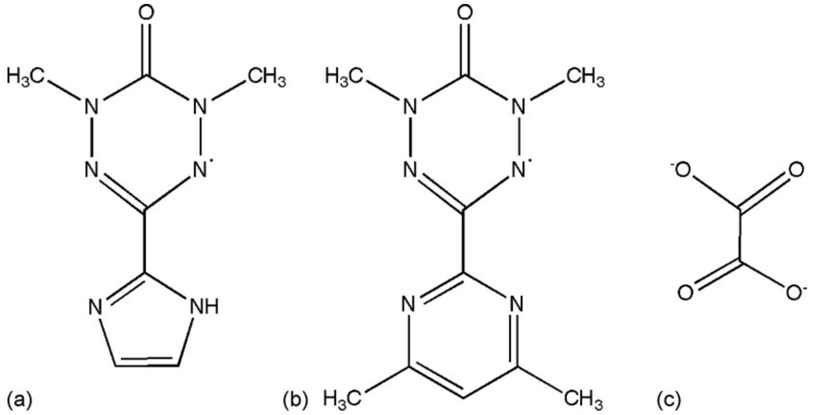
3. Synthesis of the organic radicals

The synthesis of these organic radicals follows a multi-step protocol where the key step in both pathways is the condensation with an aldehyde leading to ring closure (Fig. 1). This is well documented for both nitronyl-nitroxides [25–33] and verdazyl [34–41] derivatives. The first steps involve the synthesis of bis(hydroxylamino)-2,3-dimethylbutane and the bis(hydrazide)carbonic acid derivatives, respectively. As shown in Fig. 1, the two last steps are common to both types of radicals. The first reaction is the condensation with the aldehyde bearing a R substituent while the second step is the oxidation of the resulting molecule. The first step shown in Fig. 1 allows one to introduce any kind of R moiety. This easy synthetic access enabled the versatility of these two chemistries and justified the impressive literature published at least on the nitronyl-nitroxide derivatives [1,3]. The second step in Fig. 1 is the synthesis of the radical itself, carried out by using a wide variety of oxidising agents, either organic or inorganic [1,3,36,42,43]. In the former case, the formation of adducts may increase the stability of the radical [42]. Finally the solvent itself or dissolved dioxygen can be used for *in situ* oxidation [41,44–46]. This strategy can be useful to favour crystallisation upon precipitation. Nevertheless, it can lead to complicated situations related to the simultaneous presence of the radical and its reduced form in solution during the crystallisation process [46].

Although many radicals were developed in the late-1960s [26,28,29,34], they underwent a huge revival in molecular magnetism after the discovery of solid, crystalline, purely organic, magnets for both the NIT derivatives ($T_C = 0.6$ K [47] and 1.48 K [48]) and the dithiadiazolyl derivatives ($T_C = 36$ K) [49]. Since then hundreds of NIT, IN and Vz derivatives have been synthesised and tested for their solid state properties and suitability as ligands for metal coordination.

The NIT- and Vz-containing radicals whose properties are described hereafter are presented in Schemes 2–5. Their variety illustrates the versatility of the synthetic protocol described in Fig. 1. The three last radicals presented in Scheme 2 have been designed and synthesised to develop high spin ground state entities for supramolecular order, with the hope to further extend and strengthen such order. In this vein, we synthesised numerous bi- and tri-radicals. Starting from our first nitronylnitroxide triradical (Scheme 2(d)), we changed the central phenylNIT to a pyridine unit as a possible ligation site as shown in Scheme 2((b) and (c)) [50]. Although the exchange interaction between the two radical units decreases due to the extended bridge, they do possess high spin ground state.

In order to shorten the distance and enhance the intramolecular exchange interaction, a number of new heterocyclic diradicals were designed (Scheme 3) [51–54]. While the heterocycles can easily be addressed as a ligation site, another advantage of their use



Scheme 5. The imidazole (a) and 4,6-dimethylpyrimidine (b) 3-substituted 1,5-dimethyl-6-oxoverdazyl radicals and the oxalate ligand (c).

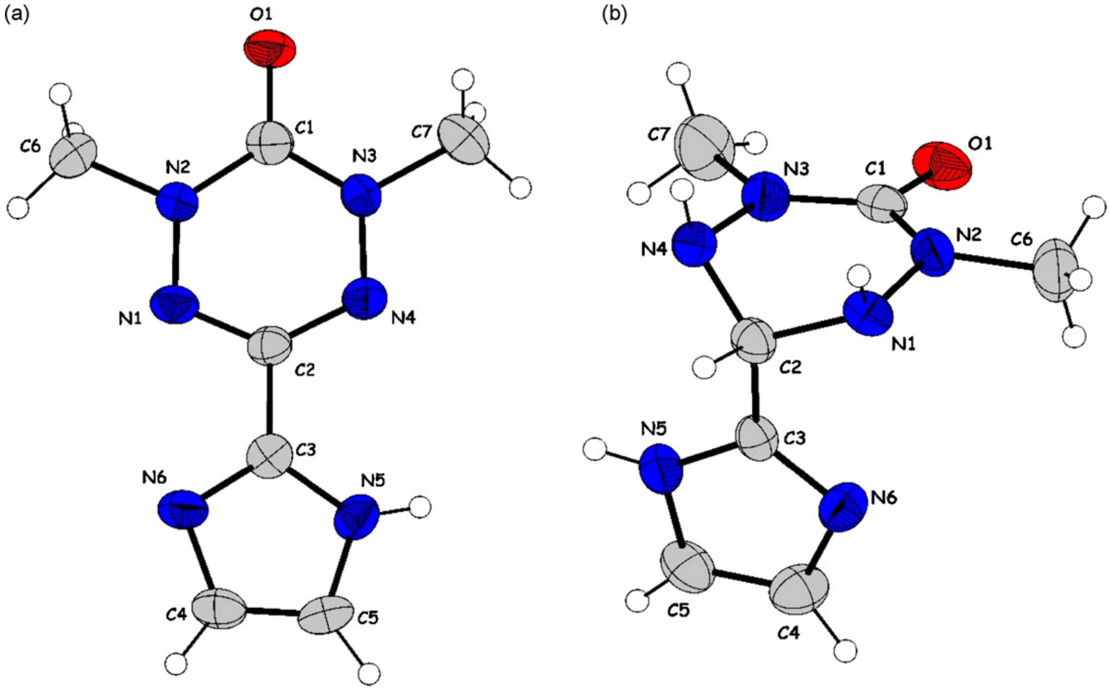


Fig. 2. Comparison between the structure of a verdazyl radical (a) with the structure of its tetrazane reduced form (b) (adapted from Ref. [44]).

compared to the benzene analogues was their lowered geometric demands, making the bridging cores nearly planar.

Thus the terpyridine-bridged NIT (Scheme 3(a)), has the same magnitude of the exchange interaction as for a *m*-triphenylene bridging unit with NO as radical unit [22], whereas the NO is usually thought to be the stronger radical coupling unit. It was intriguing to find out that even upon reducing the distance between the radical units going from pyridine (Scheme 3(a)) to pyrazole (Scheme 3((b) and (c)), leading to enhanced dipolar coupling, the exchange coupling is reduced. This could be explained by the five-members rings opening two different pathways of opposite spin polarisation pattern because of the implication of an even versus odd numbers of atoms [55], in contrast to the six-membered pyridine ring.

Unlike the NIT derivatives which can bind through their oxygen atoms, to date, there has been no coordination compound where the Vz radical behaves as a monodentate ligand through the nitrogen atoms bearing the unpaired electron. To bind the radical to a metal ion, it is essential to introduce a coordinating site on the R substituent to obtain chelating ligands. Our syntheses of N heterocycle or oxygen Lewis base substituted ligands are depicted in Scheme 4. Although some slight modifications [46] of standard protocols [34,38] are needed to obtain radicals a, b and c, the synthetic versatility towards verdazyl-based molecules is exemplified with this series of ligands with variable coordinating pockets.

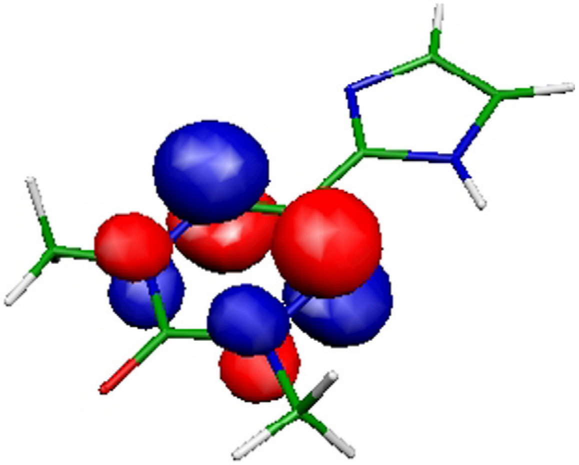


Fig. 3. Electron density in the SOMO of the imidazole-substituted oxoverdazyl radical (adapted from Ref. [63]).

We describe here the compounds obtained by using imidazole and 4,6-dimethylpyrimidine 3-substituted 1,5-dimethyl-6-oxoverdazyl radicals (Schemes 4 and 5). One motivation is to mimic the coordination behaviour of the oxalate ligand (Scheme 5(c)) to combine the capability of the latter to build multifunctional magnets [56–62] and the strong exchange interaction and, hence, ordering temperatures, brought about by the radical nature of the ligand.

4. Structure, electronic structure and spin density

Comparison of the crystallographic structures of the radical and of its reduced form can inform us about the reactivity of these molecules as ligands. This can be illustrated in the case of the imidazole substituted oxoverdazyl (imvz—Scheme 5(a)) [45]. Upon oxidation, the C2 carbon atom (Fig. 2) loses its hydrogen atom and goes from a tetrahedral to a trigonal environment. A similar, though less pronounced change of the environment of the N1 and N4 nitrogen atoms leads to a complete flattening of the molecule upon oxidation. Thus, provided that the imidazole moiety is deprotonated [7], the radical can behave as a bidentate bridging ligand like oxalate (Scheme 5(c)). Similar behaviour for the tetrazane precursor requires an important modification of the conformation of the molecule that has indeed been observed experimentally for the (2,4)dimethylpyridine derivative [63].

In a simple scheme, this flattening is closely related to electron delocalisation over the whole molecule. Nevertheless, to understand the reactivity of the radical towards a metal ion and the magnetic properties of mixed metal-radical architecture, it is

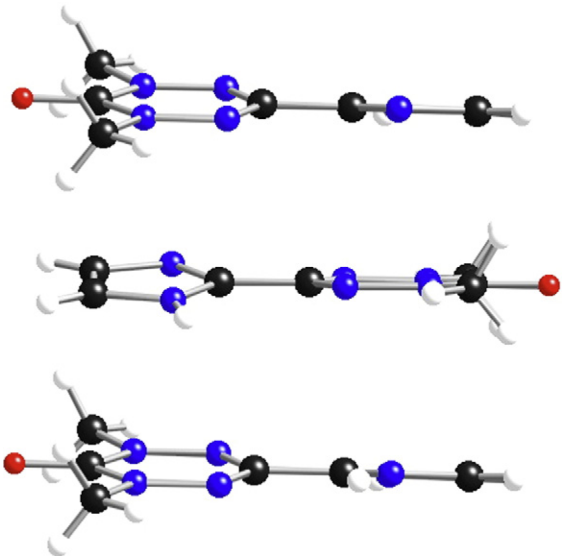


Fig. 4. Head-to-tail arrangement of the imvz radical in the solid state (adapted from Ref. [44]).

important to examine the frontier orbitals of the radical. In the case of the imidazole substituted oxoverdazyl (Scheme 5(a)), the calculation by *ab initio* methods [64] reveals that the electron density on the SOMO is almost exclusively localised on the four nitrogen atoms of the verdazyl ring (Fig. 3). Because the SOMO orbital bears the unpaired electron, this means that the spin density is essentially borne by the verdazyl moiety of the molecule. The localisation of the spin density contrasts with the spin density calculated by density functional theory (DFT) on the pyridine substituted radical [65], where a finite spin density is observed on the pyridine ring. The difference can be ascribed to the inherent influence of the substituent which will modify both the reactivity of the radicals and the magnetic properties of the radical-containing compounds. In contrast to the SOMO, the electron density in the SOMO−1 and SOMO+1 are of comparable magnitude on the N1 and N4 nitrogen atoms of the verdazyl and on the non-protonated nitrogen atom of the imidazole ring. As all three orbitals are of π-symmetry, these observations imply the existence of complex electronic interactions with the t_{2g} orbitals of the transition metal ion that may be attached to the radical.

5. Radicals as purely organic materials

The simplest compounds that can be obtained with these radicals is obtained by crystallising the radical alone. These materials are of fundamental interest because, in the solid state, mere radicals can behave as ordered magnets with temperature as high as 36 K [49]. Nevertheless, as exemplified by the decreases of the T_C from 36 K [49] to 1.3 K [66] upon substitution of the cyano by a nitro group in XC_6F_4CNSSN ($X = CN, NO_2$) radical, the magnetic properties of these compounds are highly sensitive to the intermolecular interactions between the radicals and, hence, to the organisation of the radicals in the solid state. It is therefore important to analyse the crystallographic structures of such compounds in order to determine the parameters governing the organisation of the molecules in the solid state.

A general trend is related to the flat structure of the oxidised molecule. This feature allows the molecules to stack in the solid state (Fig. 4) leading to a stabilisation of the overall structure thanks to π–π interactions between the radicals. Moreover, as exemplified in the case of imvz (Fig. 4) [45], the optimisation of both the dipolar interaction and the π-stacking of the radicals [67], leads to a head-to-tail arrangement of the molecules in the solid state.

This arrangement strongly influences the magnetic behaviour of the materials. The thermal variation of the susceptibility indicates an antiferromagnetic coupling between the radicals. The magnetic data for the structure shown in Fig. 4 can indeed be fitted using a 1D chain model leading to an exchange interaction parameter J of $-50\,\mathrm{cm}^{-1}$ ($H = -2J\Sigma S_i S_{i+1}$). As demonstrated by Jornet et al. for pyridine substituted derivatives, this exchange interaction can be described as a through space interaction governed by direct overlap of the orbitals of the neighbouring radicals [65].

In the case of imvz, the nitrogen atoms of the imidazole moiety are linked to crystallisation water molecules through hydrogen bonds, resulting in isolated columns of radicals separated by water molecules. This arrangement contrasts with the intriguing and complex supramolecular organisation in the solid state shown by 5-bromopyridyl-NIT (Fig. 5(a)). As in the case of imvz (Fig. 4), this radical undergoes π-stacking (Fig. 5(b)) and hydrogen bonding (Fig. 5(c)) involving crystallisation water molecules [54]. The pyridine rings actually form π-stacks in a columnar fashion such that positions of opposite spin polarisation are located on top of each other, which, according to McConnell mechanisms [55], should favour a ferromagnetic exchange interaction. In contrast with the case of imvz, the hydrogen bonds form squares connecting four columns of radicals (Fig. 5(c)). The magnetisation measurements showed a decrease below 50 K indicating noticeable antiferromagnetic interactions between the radicals.

While the alignment and magnetic properties of the monoradicals are not easily predicted since a small change of substituent can have a dramatic effect, as exemplified in the aforementioned case of the substitution of the cyano by a nitro group in XC_6F_4CNSSN ($X = CN, NO_2$) [49,66], our focus in this respect was directed towards new functional, high spin ground state entities (Schemes 2 and 3) which could be used as building blocks for higher dimensional solids with a better control over the supramolecular self-assembly.

Astonishingly the 5,5″-diNIT-2,2′:6′,2″-terpyridine diradical (Scheme 3(a)) undergoes π-stacking alignment as seen from the X-ray picture (Fig. 6(a)) [51,53]. Because of this alignment, the compound can be understood as a 1D chain of ferromagnetically

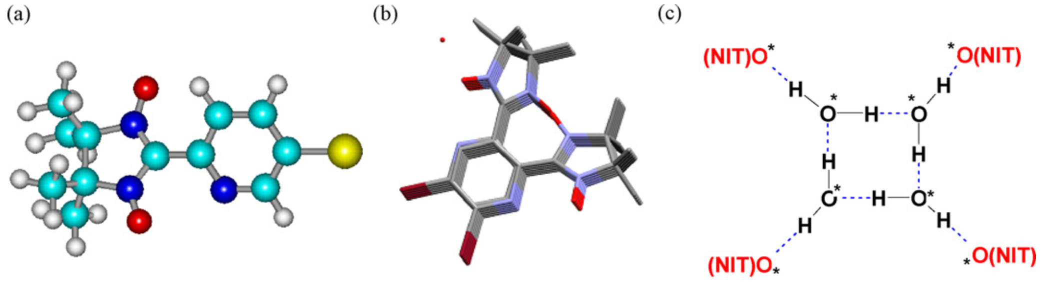


Fig. 5. *p*-Br-pyridineNIT radicals (a) undergo π-stacking (b), and H-bonded network (c).

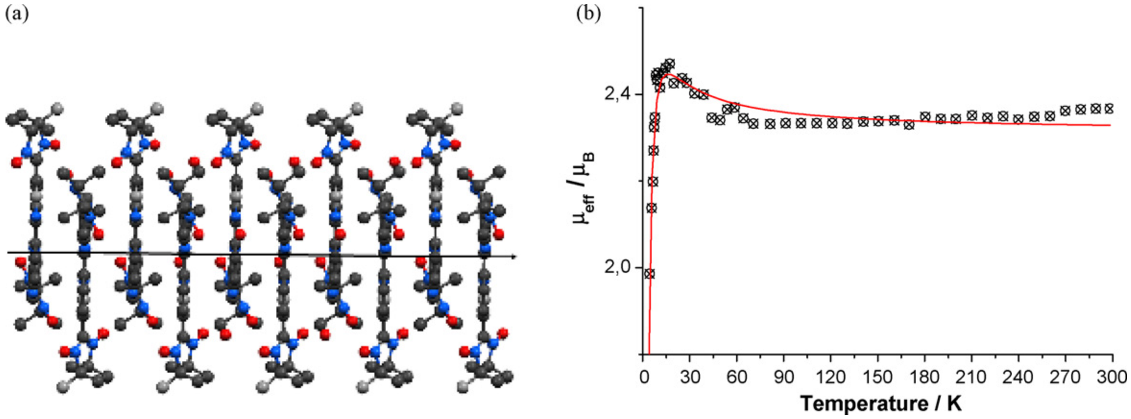


Fig. 6. 5,5″-diNIT-2,2′:6′,2″-Terpyridine diradical stacks (a) and thermal variation of the effective magnetic moment for the pure organic stack (b).

coupled biradicals ($S = 1$ ground state) where no further control of higher order is implemented. Although the effective moment μ_{eff} value increases upon lowering the temperature indicating some magnetic ordering, a maximum at 15 K is reached, then it drops sharply (Fig. 6(b)).

To exert good control over the supramolecular organisation and the magnetic properties, the synthesis of purely organic materials cannot be limited to the crystallisation of the radicals themselves. Nevertheless, until now, most studies have considered self-assembly and/or supramolecular ordering via π-stacking and hydrogen bonding of well-defined mono- and oligo-radicals. Some polymers containing radical units in the main or in the side chain have been presented [68–70]. By insisting on the control of the exchange interaction in such compounds, this could be an important route towards purely organic materials with a strong interaction exchange. The introduction of metal complexation with the richness of its bonding opportunities and magnetic properties has been better explored and some results are described below.

6. Synthesis of hybrid coordination compounds

The interest in building coordination compounds comprised of radical ligands is related to the strong exchange that can occur between the metal ions coupled via spin active organic spacers as well as to the versatility of the chemistry of the radicals.

In IN and NIT, independently of the nature of the R substituent (Fig. 1), there are already two ligation sites available for metal coordination. Thus with these radicals linear metal radical chains can be formed. Higher dimensionality is observed if these radicals carry another ligation site via their substituents or if they are used as the nitroxides for bi- and tri-radical formation before metalation. This possibility has been exploited for more than 20 years

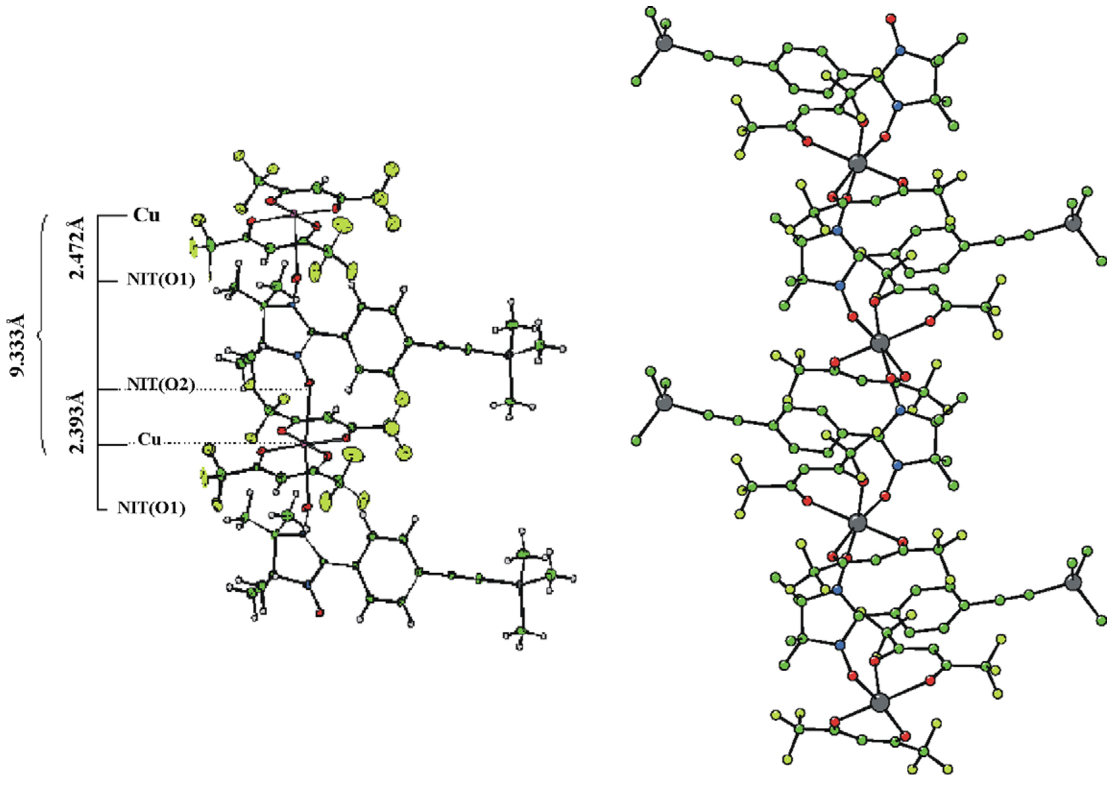


Fig. 7. Linear chains of NIT with (a) [Cu(hfac)$_2$] in *trans*-fashion and (b) with [Mn(hfac)$_2$] in *cis*-fashion.

to introduce radicals between metal ions [1,71–78]. A large variety of heterospin 1D, 2D and 3D structures have been observed. According to the weak basicity of the radical compared to regular diamagnetic ligands, strongly acidic partners are proposed for ligation to the radical. A simple way to enhance the acidity of the metal ions is to bind them with electron-attracting ligands. Among these ligands the most studied are the fluorinated diketonates and especially perfluorinated (1,1,1,5,5,5)hexafluoroacetylacetonate (hfac). Given the numerous compounds obtained from bis((1,1,1,5,5,5)hexafluoroacetylacetonate)metal(II) with nitronylnitroxide radicals [1,79,80], reacting the radicals with this building block is a test of the reactivity of the radicals.

Our contribution to this end follows this strategy. We first tried to synthesise linear chains by reacting trimethylsilyl end capped phenylacetylene NIT with $[Cu(hfac)_2]$ and $[Mn(hfac)_2]$ shown in Fig. 7 [81]. With copper(II) a *trans*-coordinated chain was formed with nearly orthogonal alignment between the copper and NO radical moieties (MB3(a)) leading to ferromagnetic interactions between the copper and the radical. The manganese(II) analog underwent *cis*-coordination (Fig. 7(b)). Since Mn(II) exhibits a $S = 5/2$ spin value, the antiferromagnetic exchange interaction between the Mn(II) and the NIT led to a ferrimagnetically coupled chain with $S = 2$ repeating units.

Using a linear chain model fit, the best parameter obtained from the fit for the copper(II)–NIT chain was $J = 6\,\mathrm{cm}^{-1}$ ($H = -2J\Sigma S_1 S_2$), while for the ferrimagnetic manganese(II)–NIT chain, a J-value of $-95\,\mathrm{cm}^{-1}$ was derived.

These promising results led us to consider biradicals for extended "double chain" formation. When starting from the biradical (Scheme 3(c)) coordinating with $[Cu(hfac)_2]$, a complex heterospin network was derived [82]. Within the network, 7 $[Cu(hfac)_2]$ units connect 2 biradicals in an ended two-way fashion (Fig. 8). In total, there are four different copper environments in each repeating unit, namely two octahedral (Oh) copper ions for Cu(1) and Cu(3) and two square pyramidal (SP) geometries with fivefold coordination for Cu(2) and Cu(4), all with different Cu–O and Cu–N bond lengths.

The spin network is thus composed of two tri-spin moieties and a central five spin unit.

While the magnetic measurement showed nearly paramagnetic behaviour with a minimum at 14 K and steep increase thereafter, an understanding of the subtle magnetic interactions took a long time to achieve, resulting in a complete survey of all the "hidden" magnetic interactions [83]. This quantum chemical approach using the broken symmetry density functional theory (PBE and PBE0) considering all spin subsystems led to a meaningful fit of the magnetic data. Otherwise, solutions assuming many-interactions could have been used for a fit but without sense for this spin system.

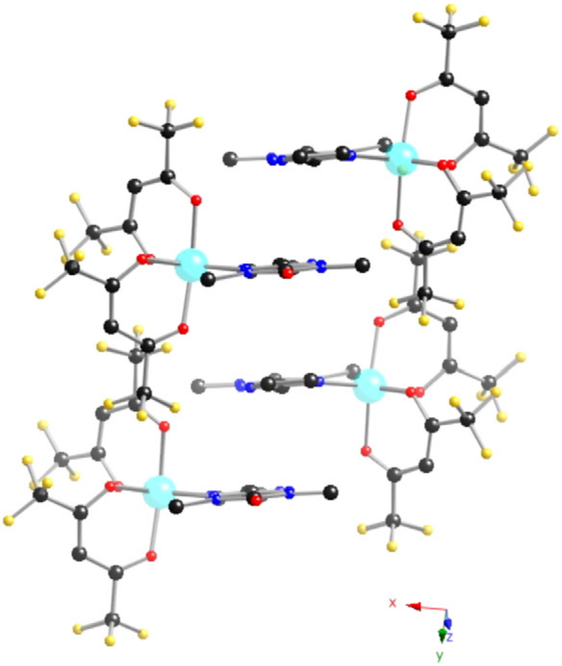


Fig. 9. $[M(hfac)_2(imvz)]$ (M = Mn, Ni) 1D structural chains (adapted from Ref. [44]).

Compared to nitroxides, the coordination chemistry of the verdazyl radicals is in its infancy. The first coordination bond implying a verdazyl radical has indeed be described by Brook et al. in 1997 [37]. The possible methodology to explore this virgin field closely follows the one developed for the nitroxides-based radicals over the years [84]. Thus, by reacting imvz (Scheme 4(b)) with $[M(hfac)_2]$ (M = Mn, Ni), we obtained two isostructural $[M(hfac)_2(imvz)]$ complexes (Fig. 9) [45]. In these complexes, the radical behaves as a bidentate ligand; in contrast with the dimethylpyrimidine

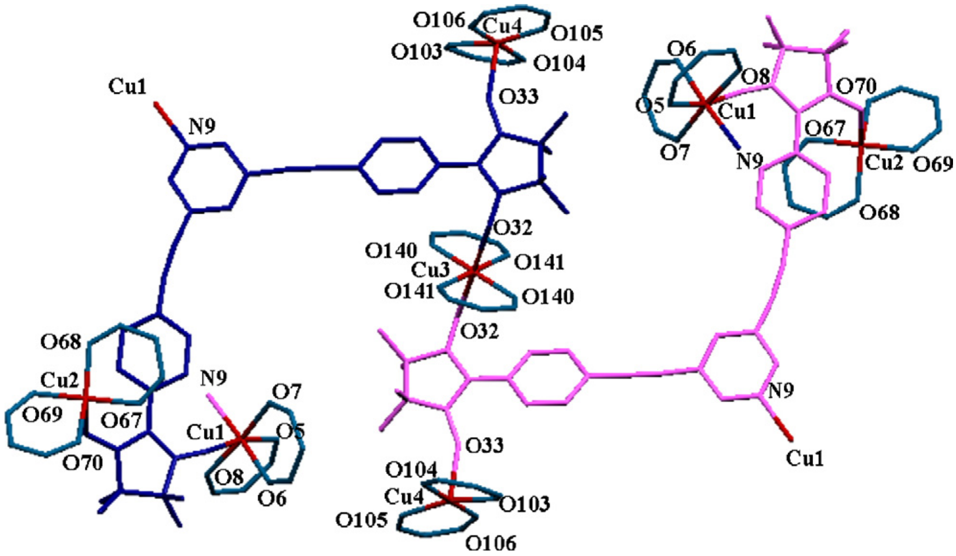


Fig. 8. Network obtained from $[Cu(hfac)_2]$ and the biradical shown in Scheme 2(c).

substituted derivatives [84], the radical does not act as a bridge because the imidazole group remains protonated.

The crystal packing is governed by the segregation of the perfluorinated moieties on one hand and the π-rich moieties on the other. A closer look at the π-stacking indicates that there is an alternation between verdazyl-imidazole and imidazole-imidazole interactions [45]. This observation is of crucial importance to propose an adapted model to fit the magnetic data. At first glance, one could propose a 1D model. Nevertheless, we know from the analysis of the magnetic behaviour of the radical alone that π–π interactions can mediate through-space antiferromagnetic exchange interactions; they are very strong for verdazyl-verdazyl stacking [85], moderate if the verdazyl interacts with the substituent bound to the verdazyl and negligible if the verdazyl moiety is not involved [65]. Following this statement, the magneto-structural analysis indicates that the magnetic data must be fitted by using a four spin model to take into account the metal-radical exchange interaction J_M (M = Mn, Ni) through the coordination bonds and the radical–radical exchange interaction J'_M through the verdazyl-imidazole π–π interactions [45]. Though it can appear surprising at first sight, the loss of the periodicity makes the fitting of the magnetic data more difficult to handle than for a “mere” 1D compound. The fitting procedure leads to $J_{Mn} = -63\,cm^{-1}$, $J_{Ni} = 193\,cm^{-1}$, $J'_{Mn} = -12.6\,cm^{-1}$ and $J'_{Ni} = -4.3\,cm^{-1}$ ($H = -JS_1S_2$).

In the model proposed by Kahn and Briat [86–89], the nature of the intramolecular exchange interaction between the radical and the metal ion can be understood by considering the different exchange pathways between the magnetic orbitals of the two spin bearers. Nevertheless, to go beyond this qualitative interpretation of the exchange interaction, we have performed *ab initio* calculations using the difference dedicated configuration interaction (DDCI) method to finely analyse the origin of the exchange magnetic interaction in these well-characterised model compounds [64]. Apart from a deeper understanding of the magnetic properties, these calculations bring fruitful information about the chemical bonding between the metal ion and the radical. In the quantum chemical approach, the starting point is to consider that the ground *electronic state* (GES) of the molecule is the standard “M^{2+}–vz” *electronic configuration* where the Vz bears one electron in its SOMO. Then, the GES is further stabilised by the participation of supplementary electronic configurations. The simplest ones are “M^{+}–vz^{+}” and “M^{3+}–vz^{-}”. The former formally corresponds to an electron transfer from the radical to the metal ion and, by analogy with the spectroscopic terminology, is referred to as a ligand-to-metal charge transfer (LMCT) while the latter is the reverse transfer and is referred to as a metal-to-ligand charge transfer (MLCT). In the case of [M(hfac)$_2$imvd] (M = Mn, Ni) complexes, the reading of the wavefunction in the GES indicates that MLCT does not participate to the GES in either complex while LMCT is rather strong in the manganese complex and symmetry forbidden in the nickel complex. These features can be related to the antibonding character of the SOMO of the radical which favours the electron transfer from the radical to the metal rather than the reverse process, that is to say LMCT upon MLCT.

The verdazyl moiety of the molecule thus behaves as a σ-donor, π-donor ligand while the imidazole moiety has its standard behaviour. Concerning the exchange interaction itself, it appears that the valence-only description of the exchange interaction, which roughly corresponds to Kahn's model [86–89], allows one to retrieve the expected tendency for the exchange interaction: with nickel(II), the two unpaired electrons of the metal ion are located in orbitals perpendicular to the SOMO π-orbital of the radical and, hence, the exchange interaction is ferromagnetic; with manganese(II), there exist overlapping magnetic orbitals and, hence, the exchange interaction is antiferromagnetic. Nevertheless in both cases, this description fails to give the correct absolute values of the exchange interaction; other mechanisms must be considered. In the nickel(II) complex, spin polarisation effects provide 1/4 of the exchange interaction. In the manganese(II) derivatives, dynamical correlation effects related to the LMCT account to up to 2/3 of the exchange interaction. These results emphasises the interest of such calculation in order to finely understand the microscopic origins of the exchange interaction between two spin bearers.

The experimental and theoretical study of these model compounds confirms the interest of verdazyl as ligand in molecular magnetism [6]. To take advantage of the strong exchange interaction between the radical and the metal ions to develop more sophisticated hybrid architectures, it is necessary to increase the connectivity of either partner in order to synthesise magnetic clusters of higher nuclearity or extended structures.

To obtain a 1D compound, the imidazole moiety of the verdazyl radical was replaced by a 4,6-dimethylpyrimidine substituent (Scheme 5(b)) leading to a bis(bidentate) bridging radical ligand. The [M(hfac)$_2$] building block was replaced by the perchlorate [90] salt of silver(I). The reaction between the two reactants indeed leads to the formation of a 1D coordination compound (Fig. 10) [63]. The counter ion was chosen to be as weakly coordinating as possible to avoid competition with the radical ligand for ligation to the metal ion. The importance of this last choice clearly appears when recognising the only other reported one-dimensional (1D) structure involving a verdazyl-based radical [37]. In this case, the use of chloride salts led to an alternation of verdazyl and chloride bridges between the metal ions. Because the chloride ion poorly mediates the exchange interaction, this alternation prevents the exploitation of the strong exchange coupling ability of the verdazyl radical to generate compounds with interesting magnetic properties. In the case of [Ag(pmvd°)]ClO$_4$CH$_3$CN, the diamagnetic silver(I) cation mediates an antiferromagnetic interaction between the radicals. The compound behaves as an assembly of isolated antiferromagnetically coupled 1D chains with an exchange coupling of

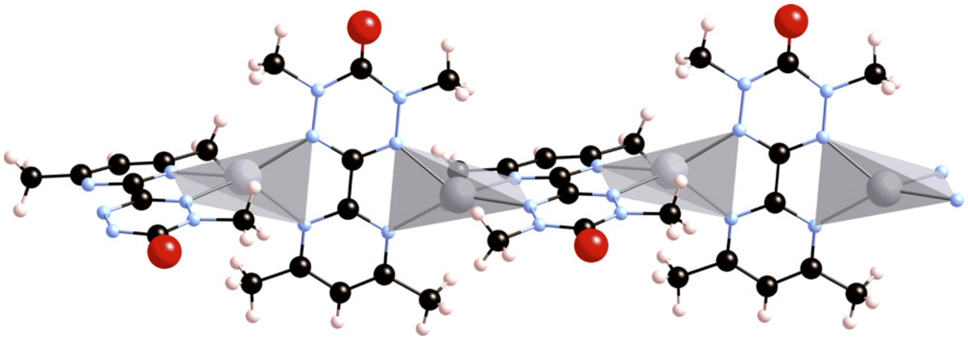


Fig. 10. One-dimensional structure in [Ag(pmvd°)]ClO$_4$.

$-7.5\,\mathrm{cm}^{-1}$. At this stage, it is difficult to draw simple conclusions from the magneto-structural correlations. In the chains, it appears that two radicals connected to one silver(I) are nearly perpendicular, the dihedral angle between them being equal to 95°. In a simple scheme, a perfect orthogonality would favour ferromagnetic exchange coupling [89]. Nevertheless, the theoretical study undertaken on the [M(hfac)$_2$(imvz)] has shown that several mechanisms must be considered to fully understand the exchange interaction in this family of compound [64].

7. Concluding remarks

Through the description of complementary approaches of radical-based magnetic materials, we have shown the richness of this field. This richness is based on the versatility of the chemistry. A wide variety of radicals can be obtained and, hence, the possibility of intra- and inter-molecular interactions rapidly increases.

For nitroxide-containing radicals, much work has already been done and the current trend orients the field towards the synthesis of more complex molecules. Increase of the complexity of the molecule leads to a multiplication of the possible interactions. This makes the control over supramolecular self-assembly more difficult. However, by accumulating data on such compounds, some construction rules are derived and provide help in the rational synthesis of the next generation of radical-based materials.

In the field of verdazyl-based chemistry, a comparable trend exists [6]. In order to better exploit the coordination properties of verdazyl-based ligands and to synthesise strongly coupled extended structures, two main directions could be developed. The first route is the extension of the use of hfac activated metal centres to paramagnetic lanthanide(III) ions. Due to the high coordination numbers of these cations, it is well known from NIT chemistry [72,91,92] that it is still possible to end up with 1D compounds despite the presence of three electron-attracting bidentate blocking ligands. The second strategy is the application to paramagnetic transition metal ions of the synthetic pathway that led to the silver(I) 1D compounds [63]. Given the higher coordination numbers of these metal ions, the dimensionalities obtained could be higher than one [7,93].

Because of the absence of spin-orbit coupling, radical-based systems are often considered as simple to model. Nevertheless, the complexity of the spin structures and/or the delocalisation of the unpaired electron over an important number of atoms lead to a wide variety of topologies and mechanisms governing the interaction exchange mechanisms in both nitroxide- and verdazyl-based hybrid organic–inorganic assemblies. Quantum chemical approaches appear as essential tools to fit the magnetic data in a meaningful manner as well as to finely analyse the interaction between the spin bearers. Following this statement, we plan to perform a careful theoretical inspection of the magnetic properties of the synthesised compounds in order to understand fully the different microscopic mechanisms governing both the chemical bonding and the exchange interaction in these systems. Such a theoretical approach is of particular importance for lanthanide-containing compounds because, in this case: (i) the phenomenological approaches are often questionable and (ii) the valence-only description is not adapted to describe systems where orbit and spin contributions cannot be decoupled [94–98].

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