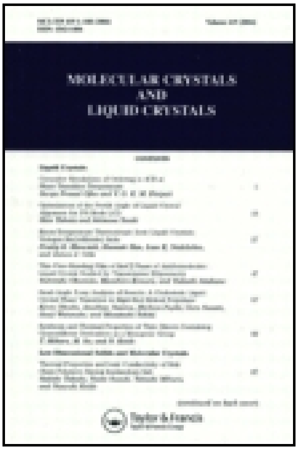

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Synthesis of High-Spin Molecular Species Using Nitroxide Organic Radicals and Transition Metal Ions

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SYNTHESIS OF HIGH-SPIN MOLECULAR SPECIES USING NITROXIDE ORGANIC RADICALS AND TRANSITION METAL IONS.

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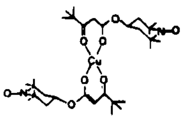
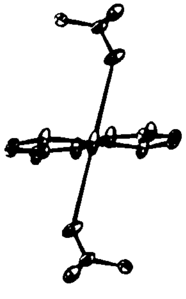
Abstract The coordination chemistry of bidentate nitroxides is reviewed. Practical indications for the synthesis of extended ferro- or ferrimagnetic chains with high-spin ground states consisting of alternating transition-metal ions and bidentate nitroxide radicals are reported.

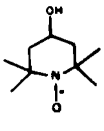
INTRODUCTION

Organic nitroxyl compounds are stable free radicals with weak Lewis base character. They can coordinate to metal ions, but stable adducts are formed only with acidic metal centers like hexafluoroacetylacetonates. The first fully characterized metal-nitroxyl adduct was $Cu(hfac)_2Tempo^{1,2}$ (hfac = hexafluoroacetylacetonato, Tempo = 2,2,6,6-tetramethylpiperidinyl-1-oxy) for which the room temperature diamagnetism indicated that the two S = 1/2 spins were antiferromagnetically coupled. The first examples for ferromagnetic coupling between nitroxides and copper(II) ions were the two adducts 1a and 1b.[3,4,5]

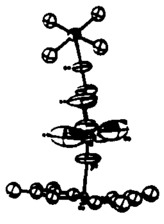


1a





1b

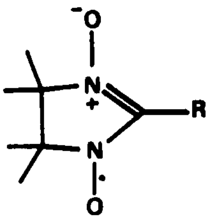


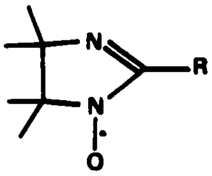
In these two examples, the nitroxides are axially bound to the metal ion and the two interacting orbitals are nearly orthogonal, whereas in Cu(hfac)$_2$ Tempo the equatorial bonding of the nitroxyl ligand leads to a large overlap between the copper $d_{x^2-y^2}$ orbital and the π^* orbital of the ligand. Therefore, the magneto-structural correlations for the copper(II) derivatives were readily established and have been rationalized through Hueckel calculations.[3,6] Similar work on the adducts of first row transition metals afforded a rather good understanding of the coupling mechanism between nitroxides and metal ions.[7]

The search for high-spin copper derivatives prompted us to examine in which case an axial bonding of the nitroxide to the metal is favored. In Cu(hfac)$_2$ Tempo, the large overlap between the orbitals containing the unpaired electrons is obtained because the Cu-O-N plane is perpendicular to the mean plane of the equatorially bound Tempo. This structural feature has been observed not only for all the equatorially bonded copper derivatives, but also for the other nitroxyl-metal adducts which exhibit antiferromagnetic coupling and an axial ligation.[7-9] It is quite obvious that this overlap plays a role in stabilizing the adduct; as a consequence, for copper, the equatorial bonding is favored over the axial one in the absence of other factors.

Careful examination of the crystal structures of **1a** and **1b** shows that the axial binding- with a Cu-O-N angle close to 180°- is mainly the consequence of remote interactions of another part of the nitroxide. Very illustrative is compound **1b** in which the free radical is a bidentate ligand leading to a chain structure as a consequence of the binding of both the hydroxyl and nitroxyl oxygen atoms to metal ions.

2a





2b

The nitronyl nitroxides[10] **2a** also are bidentate ligands which were expected to function as bridging ligands and for which an axial binding of the two coordination sites to the copper was anticipated, since each of them would experience a remote interaction for the other. Moreover, it was also expected that the full delocalization of the unpaired electron on the two sites would lead to ferromagnetically coupled chains of alternating nitroxyl and copper(II) spins. This has been achieved[11] as has been the synthesis of ferrimagnetic chains using cobalt(II), nickel(II) and manganese(II)[12] (see Gatteschi, D., Caneschi, A., Sessoli, R. Rey, P.; this journal).

However, many difficulties have been encontered. In synthetising these chain compounds, we often obtained clusters of finite sizes, and metal complexes of the reduced or the oxidized forms of the nitroxide. These results were not unexpected since an electronic transfer between the metal and the nitroxide is possible depending upon the redox potentials of the two species; also, as the R group of the nitroxide **2** can be changed, various degrees of steric hindrance and intermolecular interaction may be possible and some of these may favor a finite instead of an extended structure.

In summary, the synthesis of extended linear chains of nitroxyl-metal adducts is severely limited: first, because the metal center must be a strong electron acceptor; second, because steric hindrance associated to inter- or intramolecular interactions may cause the final product to be a finite cluster instead of an extended adduct.

We wish to give our present understanding of the different parameters which determine the formation of clusters versus chain compounds by studying a few examples, and to describe our present state of research in trying to obtain adducts of any metal center by using functionalized nitroxides.

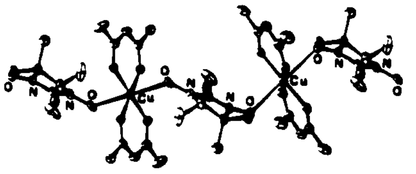
CHAINS VERSUS CLUSTERS

Since all the compounds that we will discuss are hexafluoroacetylacetonates, the only parameters of importance are the nature of the metal ion and the nature of the R group on the free radical (Figure 2).

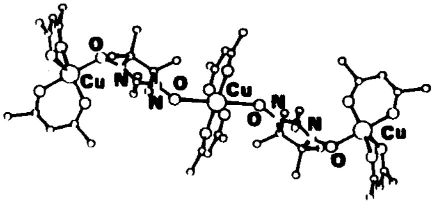
Concerning the metal ion, it is well known that the metal-oxygen bond length increases on going, for instance, from copper to manganese and, therefore, the coordination sphere will be less crowded for the later than for the former. Indeed, it has been observed, using NITPh,(2a, R=Phenyl), that chain compounds are obtained with Mn(II) and not with Cu(II). We will consider first copper(II) derivatives.

Copper(II) derivatives

Copper(II) is a particularly interesting case because very different coordination geometries - tetrahedral, square planar and pyramidal, bipyramidal trigonal and octahedral- are possible. Therefore, it is anticipated that adducts with different magnetic properties may be obtained. Indeed, adducts comprising the metal ion with all of these different geometrical environments and interesting ferromagnetic extended chains of alternating nitroxides and octahedral Cu(II) ions[12](3a) have been obtained using NITMe (2a, R= Me).[6,13] Surprisingly, the use of NITEt (2a,R=Et) leads, along with a similar chain compound, to a cluster comprising two nitroxides and three copper(II) ions (3b).[14]



3a



3b

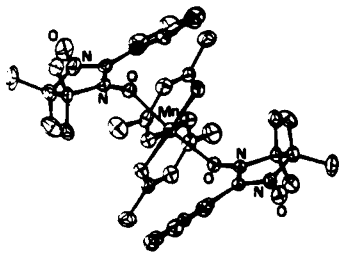
The magnetic behavior of this adduct is that of an isolated S = 1/2 spin from 300 to 5 K. This finding is easily interpreted assuming that each nitroxide experiences a strong antiferromagnetic interaction with one Cu(II) ion leaving an uncoupled isolated third copper center. The crystal structure brings strong support to this interpretation since the coordination geometry of the two terminal copper atoms is trigonal bipyramidal and the two nitroxides are axially bound to them. For such a binding geometry a large overlap is expected and a weak ferromagnetic interaction is anticipated for the octahedral third metal ion which is axially bonded to the nitroxides. Thus, the overall magnetic behavior is that of an isolated S = 1/2 spin.

As mentioned above, there is no doubt that a large overlap contributes to the stability of the adduct and thus most of the copper nitroxyl complexes must be antiferromagnetically coupled. Accordingly, an equatorial binding of a nitroxide to Cu(II) is more likely but will lead only to pentacoordinated complexes due to steric constraints. On the other hand, but for the same reason, an octahedral coordination, as required in high spin extended chains, is possible only with axially bound nitroxides but it will lead to less stable complexes. However, it must be remembered that intra- or intermolecular interactions may stabilize such structures, and we have been able to characterize some such examples. The structure of a particular adduct is given by a delicate balance between steric hindrance and electron pairing. In the example under consideration (3b), a compromise between these requirements is achieved since the two free radicals have both their NO groups coordinated and the maximum electron pairing compatible with the steric crowding is obtained. It is likely that the change of a methyl group for an ethyl group leads to more steric crowding which is released, at least around the terminal Cu(II) ions, which are only pentacoordinated. It is worth noting that in this case the difference of energy between the chain compound and the cluster is so small that both forms are obtained.

Manganese derivatives

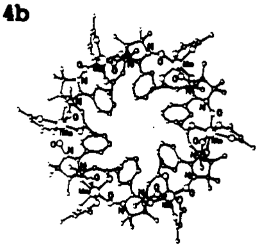
Manganese is the other metal ion which has been used extensively in the synthesis of metal-nitroxyl species.[7,8,12] Only antiferromagnetic interactions are possible with a d^5 metal but, due to the high spin S=5/2 state, ferrimagnetic chains may be designed.

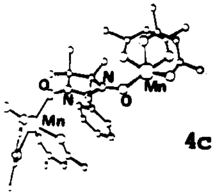
Compared to copper(II), the axial and equatorial ligation of the nitroxyl ligand are more equivalent since in both cases a large overlap is expected resulting in the same stabilization of the complex. Furthermore, the decompression of the coordination sphere will make the coordination geometry around the metal less sensitive to the bulkiness of the nitroxide. Thus, the coordination chemistry of Mn(II) with nitroxides seems to be more predictable than that of Cu(II). However, it has proven to be more versatile than we assumed at first. For instance, using NITPh (2a, R=Ph) and slightly different experimental procedures, four compounds were obtained.



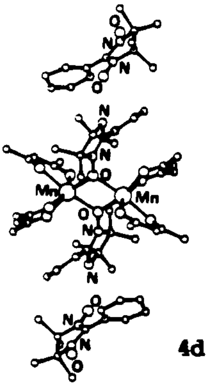
4a

4b





4c



4d

A discrete trans bisnitroxyl complex[7] (**4a**), analogous to that discribed with Tempo[8], is obtained working with the right proportions of reactants in dilute solutions at room temperature. It therefore seems that, like for Cu(II), the bulky phenyl group is better accommodated in a trans octahedral geometry. However, when the preparation is made at higher temperature (60 °C), an extended chain is obtained (no suitable crystals have been obtained for this compound) along with, if the solution is more dilute, a cyclic compound comprising six Mn(II) ions linked by six radicals[15] (**4b**). This hexamer has a S=12 ground state showing a strong Mn-radical antiferromagnetic coupling. More interestingly, one can note that each Mn ion is coordinated to two nitroxides in a cis geometry. This arrangement shows that the steric crowding of the coordination sphere is not a determining factor in this case. As shown in structure 4c, the plane of the phenyl groups of the nitroxides are nearly parallel to the mean plane of the hexafluoroacetylacetonato ligands, and we propose that at such a distance (3.5 A), some π-π interactions are responsible for the observed structure.

Finally, working at high temperature (100 °C), an unpredictable redox process takes place leading to a manganese complex of the reduced form of the nitroxide **2b** (R=Ph)[16]. In this complex, the manganese ions keep their oxidation state and the nitroxide is not only reduced to the hydroxylamine but is deoxygenated to the imino form. The mechanism of this process is not yet elucidated since no other Mn containing derivative has been characterized.

Conclusion

These few examples have been chosen because copper(II) and manganese(II) are the two metal ions which, with nitroxides, lead to the most interesting extended chains.

The synthesis of such high spin species is indeed possible but, in each case other molecular species may be obtained depending on the experimental conditions. Actually, in some cases the difference in energy between two possible structures is so small that it is difficult to define a precise procedure.

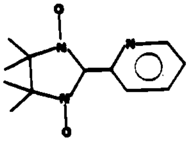
COMPLEXES OF FUNCTIONALIZED NITROXIDES

All the extended compounds prepared as yet exhibit three-dimensional order transitions with Curie temperatures $\lesssim 10$ K. One of the principal reasons for such low temperature transitions is the shielding of the chains in the solid state by the bulky hexafluoroacetylacetonate ligands. All our attempts to get extended compounds using manganese halides as less steric demanding metal moieties were unsuccesful with the free radicals **2**. Actually, only copper and cobalt halide[17-19] derivatives of nitroxides have been reported. With the aim of preparing ferrimagnetic chains of nitroxides and transition metal ions, we have developed the synthesis of functionalized free radicals.

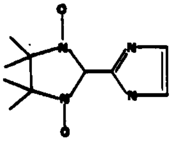
Indeed, if the free radical bears a strong donor group it could be anticipated that it would coordinate to any metal ion. In the two examples (**5a**,**5b**), this donor group is placed in such a position that it will enforce the coordination of the nitroxyl oxygen atom by a chelate effect.

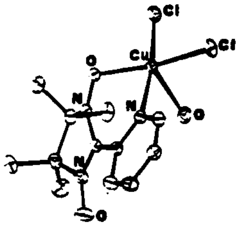
Compound **5a** (NITPy) has been designed to give discrete adducts since the study of such complexes is useful in the interpretation of the properties of the extended species. The only fully characterized complex of 5a is $CuCl_2NitPy,H_2O$ (5c) in wich, indeed, the nitroxyl oxygen atom is now included in a chelate ring.

5a



5b





5c

It is likely that the same chelate rings are found in the Co, Ni and Mn derivatives although the stoichiometry of these adducts is 2/1, and the metal ion probably in an octahedral environment. No interesting magnetic properties were expected for the complexes; all exhibit antiferromagnetic couplings.

The adducts obtained using the nitroxide 5b, also show only low spin ground states. Since no crystal struture has been obtained as yet for any of these complexes it is not possible to know if this antiferromagnetic behavior is due to the formation of discrete species or if strong interactions between the metal ions of different chains are predominant.

CONCLUSION

The coordination chemistry of the nitroxyl free radicals is fascinating. We have described only a few examples relevant to the syntheses of high-spin molecular species. However, one must keep in mind that each nitroxyl oxygen atom may function as a bridging atom; one nitroxide may be coordinated to as much as four metal ions. Very subtle intra- or intermolecular interactions may have a dramatic effect on the structure and the magnetic properties of the adducts. It is anticipated that this field, which is rapidily expanding, offers very promising strategies for the synthesis of molecular ferromagnets.

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