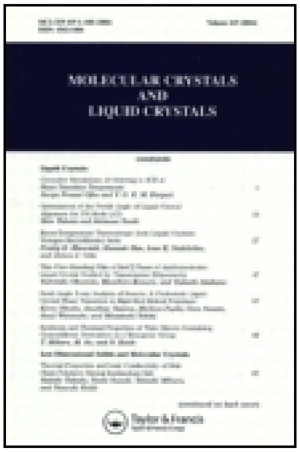

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New Nitroxide Based Molecular Magnetic Materials

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NEW NITROXIDE BASED MOLECULAR MAGNETIC MATERIALS

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Abstract Nitroxide free radicals are widely used as spin carriers for the design of Molecular Magnetic Materials. Indeed, they are among the only few purely organic materials ordering ferromagnetically and their coordination properties allow to built molecular structures where the nature of the interaction between individual spin carriers can be controlled.

In this contribution we describe new nitroxide ligands which have been designed for obtaining clusters and extended structures of exchange coupled species. In particular, are described copper(II) clusters which undergo a structural change with the temperature and exhibit a spin transition like behavior and complexes of new chelating nitroxides which allow the use of poorly acidic metal centers to design extended molecular structures.

INTRODUCTION

Since a decade, considerable attention has been devoted to nitroxide free radicals [1-5] and their metal complexes[6-9] which are now widely used as building blocks for the design of Magnetic Molecular Materials. Indeed, nitroxides are among the few purely organic magnetic materials and their complexes exhibit magnetic interactions spread over a large range of energy.[7,8] Coordination of a nitroxyl group to a metal ion by the spin density rich oxygen atom[10] insures strong interaction between the metal spin(s) and the organic spin. In addition, it has been shown that the nature of the interaction could be controlled at least when the metal ion is copper(II). High-spin molecules[11] and extended polymetallic derivatives ordering at low temperature[12-15] have been described.

The synthesis of nitroxide metal complexes is rather complicated since the free radical is such a poor Lewis base[16] that it only binds to metal centers carrying electron-withdrawing groups.[17] Thus, most of the reported metal-nitroxide complexes are derivatives of metal-hexafluoroacetylacetonates where the presence of the bulky fluorinated ligands is a strong limitation for designing extended structures which would exhibit bulk magnetic properties. Using nitronyl nitroxides however, infinite chains of alternating metal ions and free radicals have been obtained which order below 10 K.[8,14] Evidently, such low Curie temperatures are the consequence of the dimensionality of the compounds; interchain interactions are so weak that high ordering temperatures cannot be expected is these complexes.

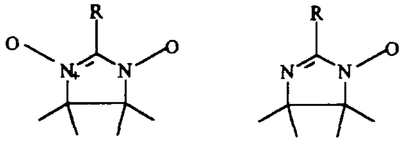


FIGURE 1. Chemical sketch of the nitronyl and imino nitroxides

An approach to higher dimensionality has been developed which involves functionalized nitroxide ligands. Donor atoms such as nitrogen can be included in the substituent (Figure 1)[18] and if the nitroxyl oxygen is placed in a chelating position, the presence of this donnor site will insure the coordination of the nitroxyl group. Several attempts along this line have shown that this strategy leads to complexes of weakly acidic metal centers.[19,20] However, a three dimensional structure can only be obtained if the nitroxide ligand is bridging. We have therefore developed the coordination chemistry of poly-chelating nitronyl nitroxides.

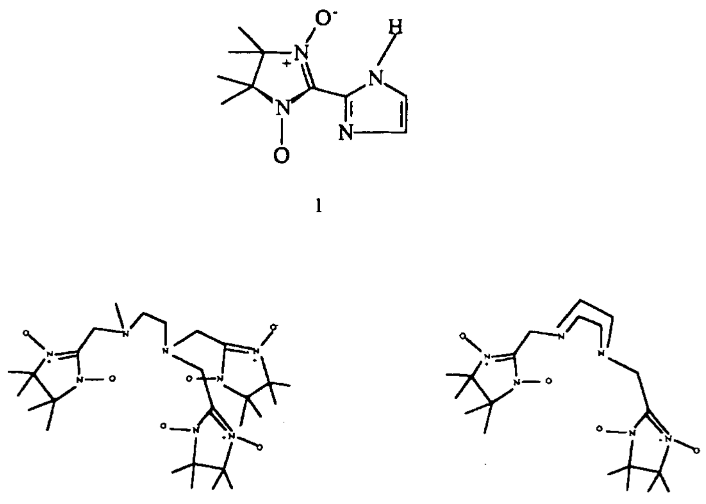
In this contribution we will also describe a few complexes of copper(II) with nitrogen-substituted nitroxides which are not chelating ligands. In this case coordination of the nitroxyl group is obtained using copper(II)-hexafluoroacetylacetonate. Most of these complexes have a cyclic structure comprising two types of copper ions. Coordination of the nitroxyl group to one of these copper ions is labile: it changes from axial to equatorial on decreasing the temperature.[21,22] The magnetic behavior of these complexes mimics that of the transition spin complexes. In addition, another complex illustrates the same change of geometry which depends on the presence of solvent molecules in the lattice.

These two types of nitroxide ligands illustrate the versatility of free radical coordination chemistry and new trends toward molecular magnetic materials.

CHELATING NITROXIDE LIGANDS

As mentioned before, coordination of the oxyl site of a nitroxide ligand to weakly acidic metal centers would only happen if "help" from a strong donor site is effective as, for example, in a chelating mode.

The synthesis of chelating ligands has been developed in our laboratory and a few of them are sketched in Figure 2.



1

2 3

FIGURE 2. Polychelating nitronyl nitroxide ligands.

In the case of the 2-imidazolyl substituted ligand , the ionizable imidazolyl group also offers the opportunity to reduce the number of counter-ions and to relax steric crowding around the metal ion. Using this ligand, a few complexes have been characterized which illustrates the possibility of obtaining metal derivatives where the coordination sphere comprises only nitroxide ligands. Particular attention has been payed to manganese(II) derivatives; in Figure3 is represented a one-dimensional complex where the coordination sphere of the metal ion is fully completed by nitroxide ligands.

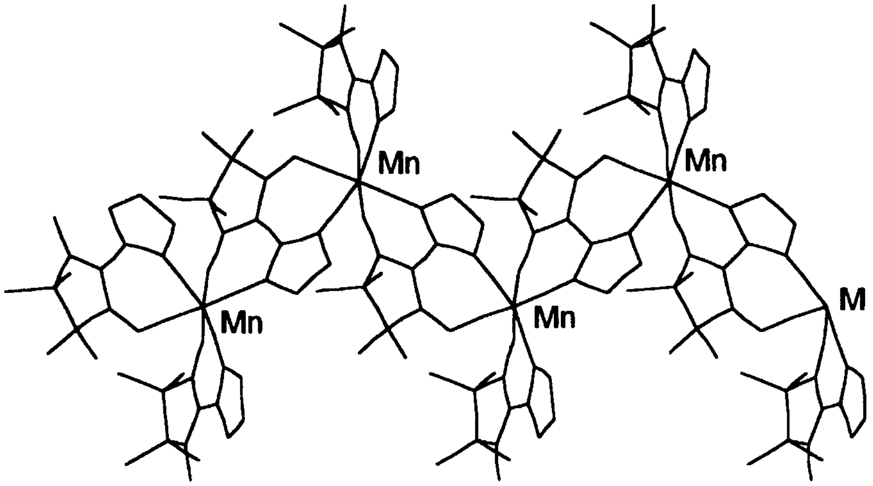


FIGURE 3. X-Ray structure of a manganese(II) complex of ligand 1.

Although these results bring strong support to this strategy, it is well known that a three dimensional structure would only be obtained if one is able to control the chirality of the structure.[23] Indeed, the octahedral geometry of the metal center exhibits Δ and Λ isomerism: a racemic formed by alternating octahedrons of opposite chirality would lead to planar structures while a three dimensional arrangement would result only if the octahedrons have the same chirality. Accordingly, we have developed the synthesis of chiral nitroxide free radicals (Figure 4). It is expected that the chirality of the complex and therefore its three-dimensionality, will be induced by the chirality of the ligand. Preliminary investigation of the different possible isomers does show that steric hindrance would drive the structure toward segregation of metal spheres of same chirality.

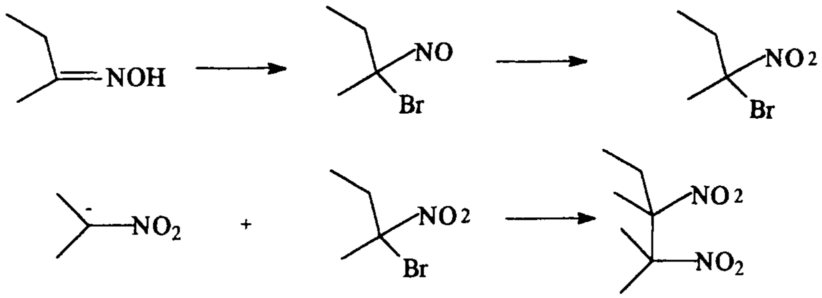


FIGURE 4. Synthetic scheme of precursors of chiral nitroxide ligands.

Important investment in organic chemistry is required for these studies but the same synthetic scheme would lead to perdeuterated complexes which are needed for neutron diffraction investigations.

Ligands 2 and 3 have been designed for more prospective studies. Since these ligands have four or five sites of coordination, the corresponding complexes will be coordinatively insaturated. Accordingly, these complexes are potential buiding blocks which can be used for with other plydentate ligands. Several complexes of these ligands have been prepared which exhibit interesting properties. A full account of these studies will be given in a near future.

NON-CHELATING LIGANDS

A series of pyridyl, pyrimidyl and pyrazinyl substituted nitronyl nitroxides have been prepared in which a pyridyl nitrogen site is not chelating but located in meta position with respect to the nitroxyl fragment (Figure 5). These syntheses were aimed at obtaining paramagnetic ligands able to bind several metal ions. Since the coordination of the two nitroxyl groups was desired, complexes of these ligands involve hexafluoroacetylacetonates.

Among complexes of several transition metal ions, copper(II) derivatives proved to exhibit unprecedented properties.

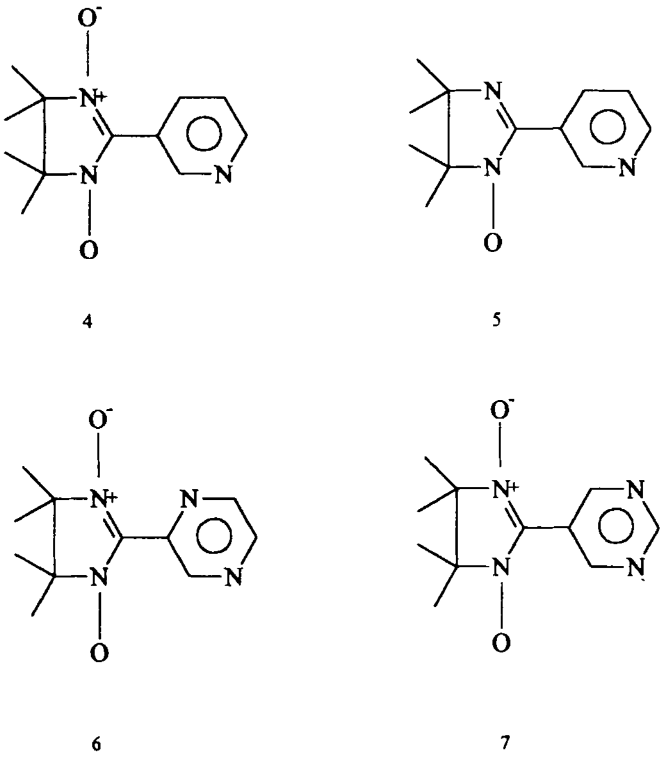


FIGURE 5. Pyridyl, pyrimidyl and pyrazinyl substituted nitroxide ligands.

Ligands 4 and 5 behave similarly leading to polynuclear structures where four copper(II) ions are bound by two ligands.[21, 22] These complexes are cyclic such that two octahedral metal centers are involved in the cycle while the two others are pentacoordinated and pending. Worth noting is the axial coordination of the nitroxide ligand to both the octahedral intracyclic and to the extracyclic pentacoordinated metal ions at room temperature. The two complexes differ essentially in the polyhedron of the external metal center which is a square pyramid for 4 and trigonal bipyramid for 5.

The magnetic behavior of these complexes is characterized by a decrease of the magnetic susceptibility as the temperature decreases (Figure 6); a Curie law behavior is observed at high and low temperature but the six spins are independent at 300 K while only two spins are active at 50 K.

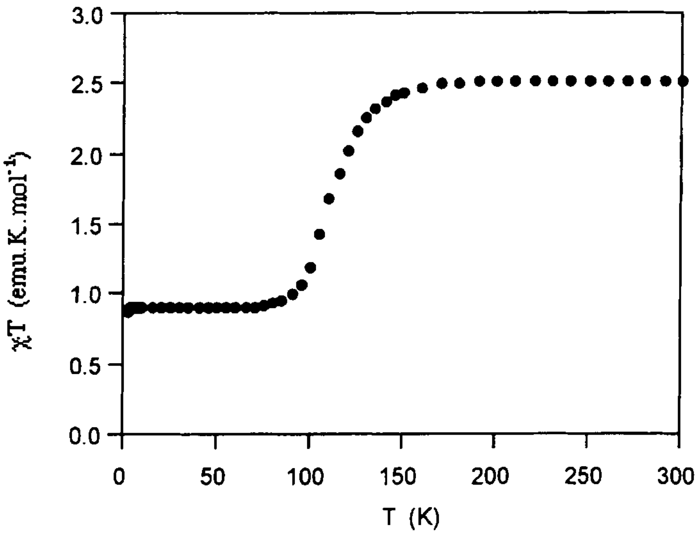


FIGURE 6. Magnetic behavior of the copper(II) complex of ligand 4.

A low temperature structural determination of one of these complexes afforded understanding of this phenomenon: at low temperature, the coordination of the nitroxyl oxygen atom to the intracyclic octahedral metal has switched from axial to equatorial. Concomitantly, the nitroxide-copper exchange interaction has switched from weakly ferromagnetic to strongly antiferromagnetic. Thus, at low temperature one observes only the two extracyclic pentacoordinated copper(II) centers. Therefore, this pseudo spin transition is the consequence of a geometry change around the copper ion.

Although the origin of the observed "transition" is different, these complexes exhibit many phenomenological features related to intermolecular interactions similar to those of the spin transition complexes. For example, the transition is smooth without hysteresis for the derivative of 4 while it is sharp and with hysteresis for that of 5. In addition, the derivative of 5 exhibits other features related to a geometry change around the extracyclic pentacoordinated metal center.

In order to get insight into the influence of the chemical structure of the ligand and of the presence of extra coordination sites on the magnetic transition we have studied the corresponding complexes of ligands 6 and 7 which both offer, compare to 4 and 5, an extra nitrogen coordination site. In ligand 6 this site is in a chelating position with one of the nitroxyl groups and is expected to afford an extracyclic metal center which would be octahedral. In ligand 7, the extra site is equivalent to that in 4 and a chain of cycles could be obtained.

Ligand 6 affords two complexes whith different stoichiometries. The first one, A (Figure 7) is a centrosymmetric five-spin system comprising three copper(II) ions bridged by two nitroxide ligands. As expected two of the metal centers are terminal and involved in a chelate structure while the third one is octahedral and bound in a trans fashion to two nitroxyl groups.

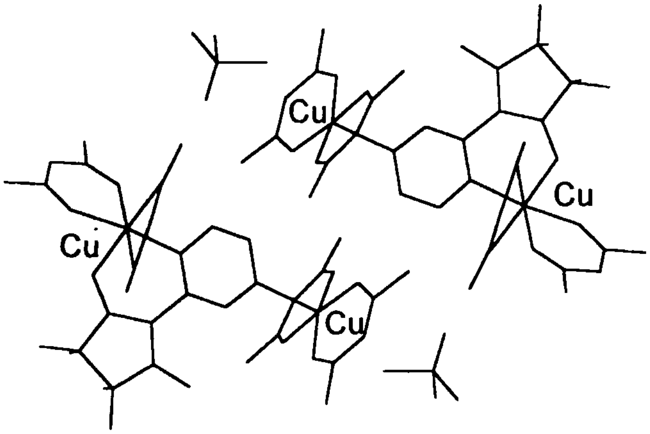


FIGURE 7. Molecular structure of the pyrazinic copper(II) complex and B.

The second one, B (Figure 7) is a three spin system where two copper ions are bridged by one pyrazinic nitroxide ligand; in addition, the cell comprises one molecule of chloroform from which the complex has been crystallized. One of the metal ion is octahedral and engaged in a chelate structure while the other one is pentacoordinated and bound to the free radical by the pyrazinic nitrogen atom. Although complex B could be considered as part of complex A, there are drastic structural differences. In particular, the coordination geometry of the nitroxide ligand to the chelated metal ion can be described as equatorial in A and axial in B.

Accordingly, and as expected, the magnetic behavior of these two complexes are strikingly different. In A, the decrease of the χ T product with the temperature agrees with a rather strong antiferromagnetic interaction; the low temperature limit value of 0.41 emu K mole^{-1} is in agreement with a five-spin system. This magnetic behavior was modeled using an antiferromagnetic interaction of -147 cm^{-1} ($J = -2JS_1S_2$). Contrastingly; for B one observes a Curie law behavior consistent with three independent spins down to 20 K; a small increase of χ T below this temperature agrees with a ferromagnetic coupling and an axial ligation of the nitroxyl group to the chelated copper center.

On standing one month at room temperature or two days under vacuum, complex B exhibits a magnetic behavior similar to that of A showing that two spins are now antiferromagnetically coupled with $J = -118$ cm^{-1}. In this new complex there is no more chloroform and the coordination binding of the nitroxyl group is equatorial.

These two examples afford the following expectations: i) When one of nitroxyl groups of the nitronyl nitroxide ligand is engaged in a chelating structure the second nitroxyl group is not coordinated. This is in line with our previous findings that the two NO groups of a nitronyl nitroxide are not able to bridge two octahedral copper(II) ions.[24] ii) The coordination geometry of the nitroxyl group is higly dependent on the crystal packing. In complex B, this geometry switches from axial to equatorial depending on the presence of the molecule of chloroform. Although these intermolecular interactions are difficult to control, these findings show the versatility of the magnetic properties of metal-nitroxide complexes.

Ligand 7 leads to a copper(II) complex whose structure is represented in Figure 8. In this case the cyclic arrangement which was observed for the pyridyl substituted ligands is found. In addition, the expectation of obtaining chains of cycles was met. However, this arrangement, which was believed to favor a transition behavior, is characterized by an equatorial ligation of the nitroxyl group to the intracyclic copper ion even at room temperature. Du to steric hindrance, the second nitroxyl group is not coordinated and the chains develop through the second nitrogen site of the substituant.

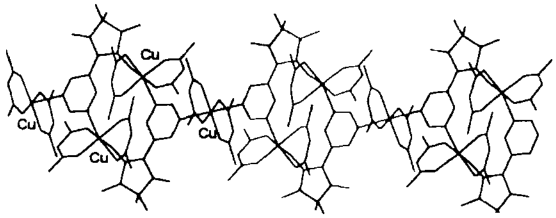


FIGURE 8. Molecular structure of the copper(II) complex derived from ligand 7

Attempts have been made to investigate the magnetic behavior at high temperature since it was thought that equatorial vs axial conversion could occur higher than room temperature. Only decomposition of the complex was observed in the 300-430 K temperature range.

CONCLUSION.

Nitroxide free radicals are among the most versatile spin carriers for designing molecular magnetic materials. As stated above they are among the few purely organic compounds ordering ferromagnetically. Although the ordering temperatures are low, the characterized materials open ways for studying exchange mechanisms between umpaired electron residing in p orbitals.

More interesting however, are the coordination derivatives of these free radicals. Coordination to metal ions occurs by the spin density rich nitroxyl oxygen leading to large exchange interactions. In addition these interactions depend on the geometry of the metal environment. Thus, using nitronyl and imino nitroxide it has been possible to characterize transition spin-like complexes in which the metal-radical exchange interaction switches from weakly ferromagnetic to strongly antiferromagnetic as the temperature decreases.

The most challenging problem of metal-nitroxide magnetochemistry however, is the design of three-dimensional structures ordering at high temperature. Since in the purely organic compounds the intermolecular interactions are difficult to control and their magnitude is weak, high Curie temperatures are not expected unless the different paramagnetic centers would be linked by organic fragment able to mediate large interactions. Contrastingly, metal complexes of nitroxides are more flexible. Although the nitroxyl group is a poor Lewis base, acid metal centers are able to give coordination compounds whose properties are among the most interesting reported so far. In addition, it is shown in this article that the use of chelating nitroxide ligands is one of the most promising strategy for buiding three dimensional structures of exchange coupled spin carriers.

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