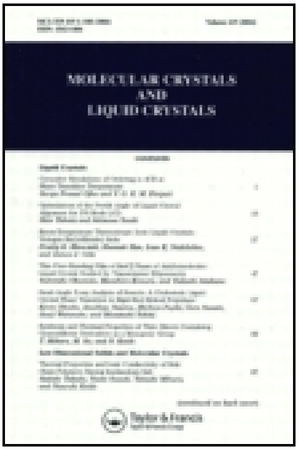

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Magnetic Materials Based on Nitronyl Nitroxide Radicals Complexes: From Mononuclear Building Blocks to One- and Two-Dimensional Compounds

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Magnetic Materials Based on Nitronyl Nitroxide Radicals Complexes: from Mononuclear Building Blocks to One- and Two-Dimensional Compounds

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Absract: In this paper is reported a series of Mn(II) complexes with nitronyl nitroxides specifically design to act as bis-chelating ligands. Starting with the mononuclear complexes used as molecular building blocks it is shown how they may polymerise to afford either one dimensional or two dimensional layered compounds exhibiting long-range magnetic ordering.

Keywords: Manganese(II) complexes; nitroxide free radicals

INTRODUCTION

Most of the actual interest devoted to nitroxide free radicals [1] and their metal complexes [2] comes from their potential use as building blocks for designing molecular magnetic materials. Indeed, nitroxides are among the few open-shell organic species stable *per se* and in the presence of metal ions. This latter property has stimulated the development of a sophisticated

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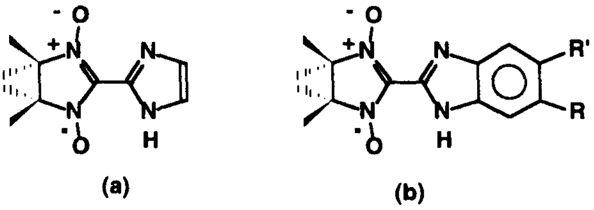
coordination chemistry which resulted in the characterization of exchange coupled heterospin systems.

One of the main drawbacks of nitroxides however, is the poor Lewis basicity of the NO group which can only coordinate to metal centers carrying electron withdrawing ligands such as hexafluoroacetonato. Because of the presence of these ancillary ligands the number of nitroxide radicals which can bind on a metal center is limited and extended structures possessing bulk properties are not obtained. This limitation has been overcome using high-spin polynitroxides able to bind several metal centers. This approach proved to be efficient and example of high Tc magnetic materials were reported [3].

A different approach relies on nitronyl nitroxide radicals where a strong donor group is located in the vicinity of the NO groups which enforce the coordination of the nitroxyl group to any metal center. Since electron withdrawing ligands are not needed, polydimensional structures resulting from the binding of several radical ligands may be obtained.



(a) (b)

FIGURE 1: Scheme of the nitronyl nitroxide radicals (a) NIT-ImH, (b) NIT-Bz(R,R')ImH (R=R'=H, CH_3, Cl or R=H and R'=H, CH_3, NO_2)

Accordingly, 2-imidazolyl- and 2-benzimidazolyl substituted nitronyl nitroxide radicals were synthesized in which two symmetrical chelating sites (Figure 1) allow the synthesis of extended compounds.

Manganese(II) mononuclear compounds:

Before deprotonation these ligands are mono-chelating and, as expected, lead to complexes of formula $[M^{II}(L)_3](ClO_4)_2$ (L = NIT-ImH and NIT-Bz(H,H)ImH and M= Mn, Co, Ni and Zn)) in which the coordination sphere of the metal center is fully occupied by only nitroxide ligands. (FIGURE 2).

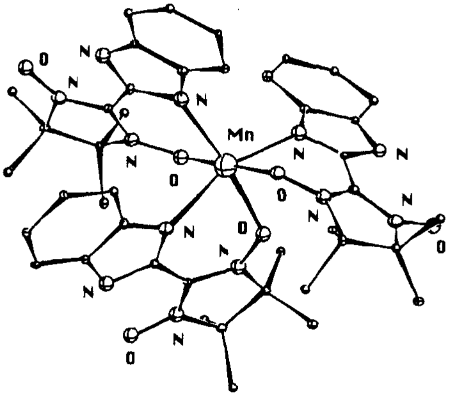


FIGURE 2 View of the $[Mn^{II}(NIT\text{-}Bz(H,H)ImH)\ ]^{2+}$ cation.

For sake of conciseness a particular attention will be paid to the magnetic properties of the manganese(II) complexes $Mn^{II}(NIT\text{-}ImH)_3](ClO_4)_2$ (**1**) and $[Mn^{II}(NIT\text{-}Bz(H,H')ImH)_3](ClO_4)_2$ (**2**).

At room temperature the product of the magnetic molar susceptibility with the temperature χT (2.91cm^3 K mol^{-1} (**1**) and 2.5 cm^3 K mol^{-1} (**2**)) is well below the expected ones for isolated spins (5.5cm^3 K mol^{-1}). When cooling χT rapidly decrease to reach a plateau whose χT value corresponds to a S=1 ground spin state (1 cm^3 K mol^{-1}). This magnetic behavior is consistent with a four-spin system where Mn(II)–nitroxide interactions are antiferromagnetic (J = -53(2)cm^{-1} (**1**) and -79(5)cm^{-1} (**2**), $H = -2SJ_{ij}S_iS_j$),

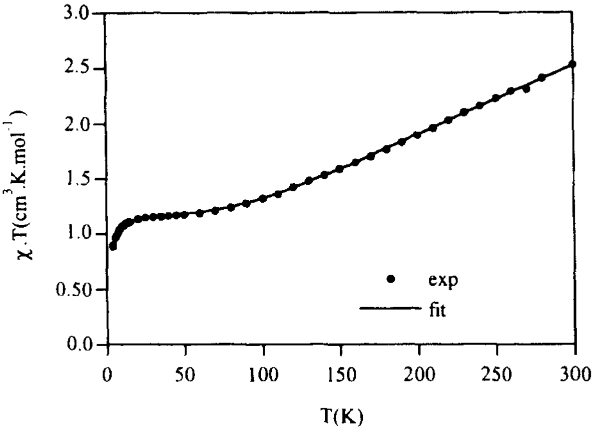


FIGURE 3 Plot of χT vs. T for $[Mn^{II}(NIT\text{-}Bz(H,H)ImH)_3](ClO_4)_2$.

and intermolecular interactions are weaker than 2 cm^{-1}. Despite a good agreement, this model does not take into account the possible inter and intramolecular interactions between the nitroxide radicals. Such interactions were considered in the interpretation of the magnetic behavior of the zinc(II) isostructural compound $[Zn^{II}(NIT\text{-}ImH)_3](ClO_4)_2$ (**3**) for which χT at room temperature (1.0 cm^3 K mol^{-1}) is well below the expected value for three uncoupled radicals and decreases rapidly to a zero value at low temperature. However for the Mn(II) complexes taking in account such interactions does not bring any improvement in fitting the data.

These mononuclear species are particularly interesting since they can be deprotonated to afford extended compounds.

Manganese(II) unidimensional compounds:

Depending on the counter anion and on the deprotonating agent, using NIT-ImH four 1D compounds $\{[Mn^{II}(NIT\text{-}Im)(H_2O)_2]\ OAc\}_n$ (**4**), $\{[Mn^{II}(NIT\text{-}Im)(DMSO)_2]\ BPh_4\}_n$ (**5**), $\{[Mn^{II}(NIT\text{-}Im)(ImH)(H_2O)]\ NO_3 . H_2O\}_n$ (**6**), $\{[Mn^{II}(NIT\text{-}Im)\ (NIT\text{-}ImH)]\ ClO_4\}_n$ (**7**) were obtained.

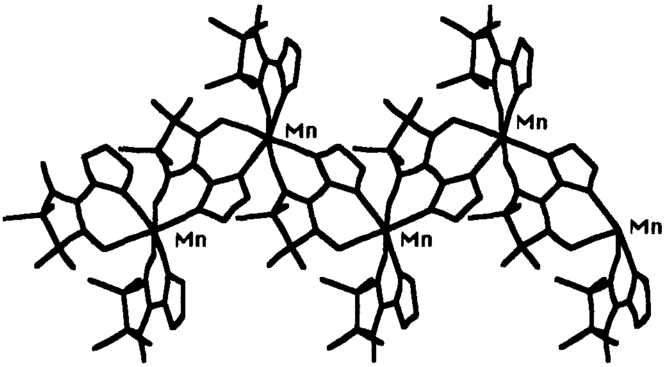


FIGURE 4 View of the chain structure $\{[Mn^{II}(NIT\text{-}Im)\ (NIT\text{-}ImH)]^+\}_n$ (7).

Among these compounds the deprotonated nitroxide radicals NIT-Im$^-$ acts as a bridging tetradentate ligands toward the manganese(II) ions resulting in infinite zigzag chains with S=1/2 and S=5/2 alternating spins. For **4-6** the coordination sphere of the manganese(II) ion is completed by diamagnetic molecules (H_2O, DMSO or Imidazole) while for **7** there is an additional but non-bridging radical ligand NIT-ImH (FIGURE 4).

In the range 2-400K the four compounds show similar magnetic behavior (FIGURE 5). At 400K χT values (4.4 (4)cm^3 K mol^{-1} for **4-6** and 3.3 cm^3 K mol^{-1} for **7**) are weaker than those expected for non interacting spins and are the signature of Mn(II)-nitroxide antiferromagnetic interactions as found for the mononuclear complexes *vide infra*. On cooling χT reaches a minimum and then increases to a maximum at 10-20K. The presence of the minimum is the signature of a ferrimagnetic 1D system.

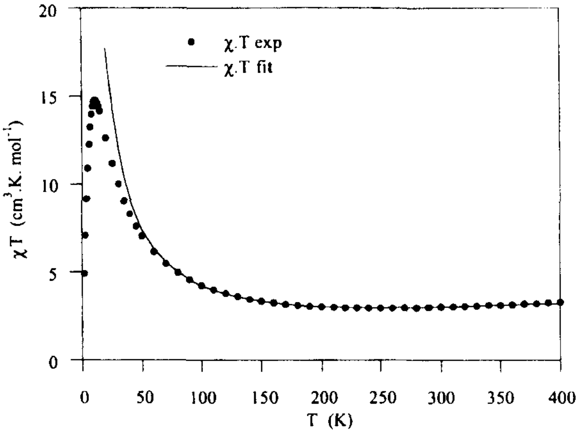


FIGURE 5 Plot of χT vs. T for $\{[Mn^{II}(NIT\text{-}Im)\ (NIT\text{-}ImH)]ClO_4\}_n$ (**7**).

The observed decrease of χT at low temperature is probably due to saturation effects. For compounds **4-6** the modeling of the temperature dependence of the molar magnetic susceptibility was carried out using reported equations for antiferromagnetically coupled S=1/2 and S=5/2 alternating spins. In the case of compound **7** a similar model taking in account the additional radical was developed. Mn(II)-nitroxide thus obtained are in agreement with those found for the mononuclear species.

For each compound the temperature dependence χ'' of the ac magnetic susceptibilities shows peaks below 4.5K indicating long-range magnetic ordering. This is confirmed by zero-field-cool magnetization (ZFCM) and field-cool-magnetization (FCM) measurements at low field (5G) which show remnent magnetization below 5K for **4**, **6**, **7** and 2K for **5** (FIGURE 6).

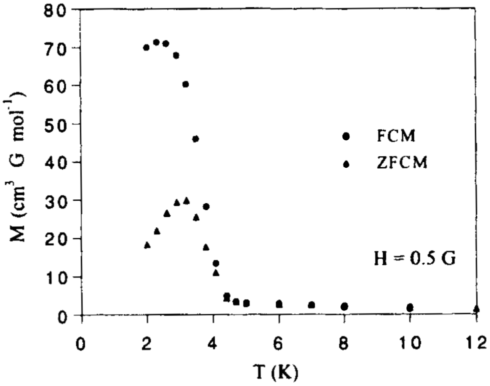


FIGURE 6 Magnetization vs. T for $\{[Mn^{II}(NIT\text{-}Im)(NIT\text{-}ImH)]ClO_4\}_n$ (**7**).

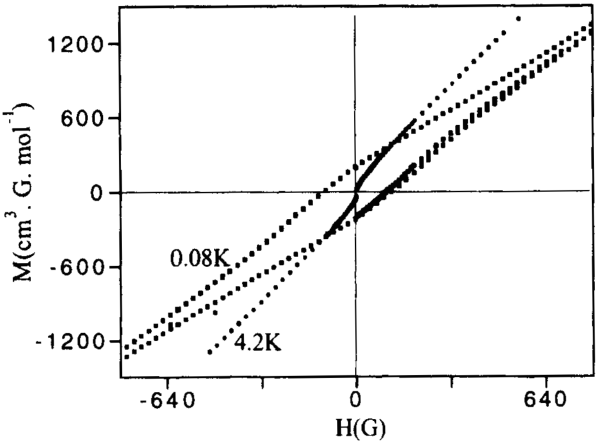


FIGURE 7 Magnetization vs. H for $\{[Mn^{II}(NIT\text{-}Im)(NIT\text{-}ImH)]ClO_4\}_n$ (**7**).

The field dependence of the magnetization below 4K show hysteresis loops with saturating values corresponding to a small fraction of the expected total magnetization (FIGURE 7). This feature which is observed at low temperature for all the 1D compounds is the signature of the onset of weak ferromagnetism and is ascribed to the canting of the Mn(II) ions within the chains due to a low-symmetry environment.

These compounds are the first 1D examples involving nitroxide radicals and transition metal ions where the coordination sphere is free from ancillary electron-withdrawing ligands

Manganese(II) bidimensional compounds

Two-dimensional compounds of general formula $\{[Mn^{II}_2(L)_3]\ X\}_n$ (L=NIT-ImH or NIT-Bz(R,R')ImH) were synthesized in methanol when reacting the radical ligands (L) with $Mn^{II}(OAc)_2.4H_2O$ followed by addition of a counter anion (X). Using NIT-ImH and X = ClO_4, BPh_4 or PF_6 , 2D compounds are obtained while the chain compound **4** is characterized when X=Cl, NO_3, SO_4, Triflate. However, NIT-Bz(R,R')ImH affords 2D compounds independently of the nature of the counter anions.

The crystal structure of $\{[Mn^{II}_2(NIT\text{-}Im)_3]\ ClO_4\}_n$ **8** determined by X-ray diffractometry brings evidence for a lamellar structure [5]. The perchlorate anions are intercalated between $\{[Mn^{II}_2(NIT\text{-}Im)_3]\}$ sheets separated by 10.32(1)Å (FIGURE 8).

Within the $\{[Mn^{II}_2(NIT\text{-}Im)_3]\}$ sheets each radical bridges two Mn(II) ions of opposite Δ and Λ chirality. This arrangement results in a 2D distorted honeycomb structure in agreement with previous findings.

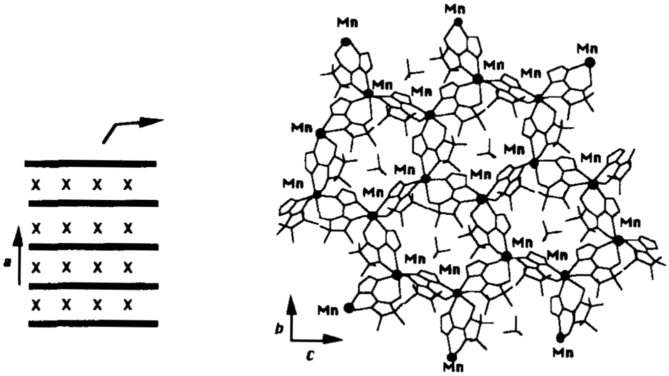


FIGURE 8 View of the 2D structure $\{[Mn^{II}_2(NIT\text{-}Im)_3]\ ClO_4\}_n$ **8.**

It is indeed known that building blocks of formula $[M^{m+}(L^{n-})_3]^{m-3n}$, where L is a bis-chelating ligand, may lead to 2D structures when Δ and Λ metal centers alternate or 3D species when the chirality is identical within the molecular framework [6].

As found for 0D and 1D compounds, the magnetic behavior agrees with Mn(II)-nitroxide antiferromagnetic interactions (FIGURE 9). On cooling, χT increases to a maximum at 300.2K (8.45 cm^3 K mol^{-1}) where an abrupt drop is observed to reache a minimum at 260K (6.44 cm^3 K mol^{-1}). On cooling further χT increases again up to a maximum at 10K whose value is field dependent. Measurements performed on cooling or heating as well are identical and show no hysteresis effect of the transition at 300.2K.

Since the inter sheet distance is large, one can assume that the high temperature behavior reflects mainly the magnetic properties of isolated layers.

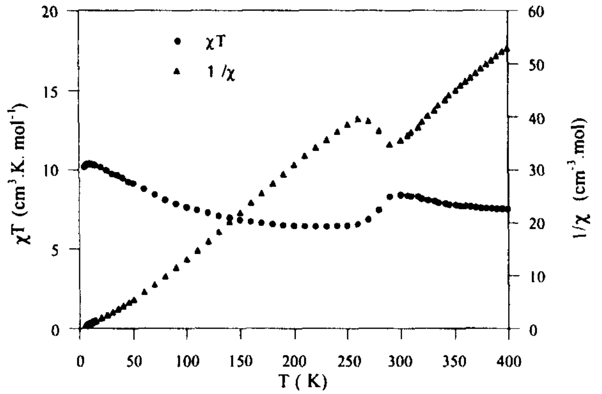


FIGURE 9 Magnetic behavior of $\{[Mn^{II}_2(NIT\text{-}Im)_3]\ ClO_4\}_n$ **8**.

Thus, the decrease of χT at 300.2 K is likely the consequence of a weakening of the intra layer interactions. However crystal structure determinations at 313K and 193K do not bring a clear understanding of this. Among the 2D compounds only $\{[Mn^{II}_2(NIT\text{-}Im)_3]\ ClO_4\}_n$ (**8**) and $\{[Mn^{II}_2(NIT\text{-}Im)_3]\ PF_6\}_n$ (**9**) exhibit such behavior. The other compounds in the series exhibit a continuous increasing of χT down to a maximum at low temperature.

Examination of the ZFCM and FCM curves show the onset of long-range magnetic ordering below 1.4K in **8** which is confirmed by the presence of an hysteresis loops in the field dependence of the magnetization below 1.4K. A similar behavior is observed when the counter anion is PF_6.

Mn(II) derivatives of NIT-Bz(R,R')ImH display higher ordering temperature whatever the counter anions (X=Cl, NO3, SO4, Triflate). For example, {[Mn$^{II}_2$(NIT-Bz(H,H)ImH)$_3$] ClO$_4$}$_n$ **10** orders at 40K.

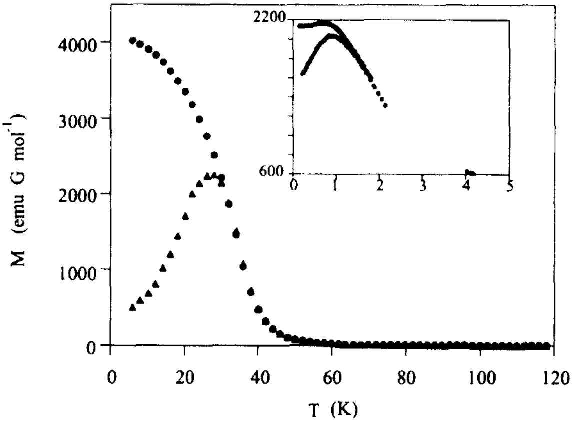


FIGURE 9 Magnetic behavior of {[Mn$^{II}_2$(NIT-Im)$_3$] ClO$_4$}$_n$ **8** (insert) and {[Mn$^{II}_2$(NIT-Bz(H,H)ImH)$_3$] ClO$_4$}$_n$ **10**.

CONCLUSION

The results described herein provide strong support to the metal-radical approach based on the use of chelating nitronyl nitroxide ligands and represent an important progress in the design of extended compounds exhibiting magnetic ordering.

Although two-dimensional systems with honeycomb layered structure have already been described those reported here are unique because exchange coupling within the sheets are large. They bring a new and original contribution to the field of intercalation compounds. Indeed, much remains to be done to understand the relation of the magnetic properties both with the chemical nature of the substituant on the radicals or with the crystal packing. These results also show that it should be possible to generate the corresponding 3D networks which are chemically and locally identical. This will be possible if control of the chirality of the metal centers is achieved. Work in this direction is in progress.

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