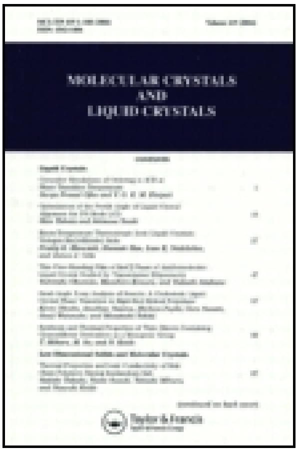

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Recent Experimental and Theoretical Studies of Molecular and Layered Metal-Radical Based Magnets

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RECENT EXPERIMENTAL AND THEORETICAL STUDIES OF MOLECULAR AND LAYERED METAL-RADICAL BASED MAGNETS

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Abstract: We report in this paper the preparation and magnetic properties of layered metal(II) hydroxynitrates and hydroxyacetates which display, according to the metal ion, either ferro (Co(II) and Ni(II)) or antiferromagnetic (Cu(II)) intralayer interactions. These compounds are shown to be suitable host lattices for organic species. 2,6- and 2,5- pyridine-based nitronyl-nitroxide biradicals have been synthesized and their magnetic properties investigated. They respectively display ferro- and antiferromagnetic behaviors. X-rays studies show an angle of 88° (in the 2,6 case) and 0° (in the 2,5 case) between both radicals. The synthesis of a new imino-nitroxide benzoic acid radical, characterized by classical methods and X-rays diffraction, and preliminary results of exchange reaction with copper(II) basic salts are also discussed.

INTRODUCTION

There is today a tremendous search for new three dimensional ferromagnets exhibiting a high temperature magnetic ordering, both in molecular and solid state chemistry[1]. Pure organic compounds were the main reason for excitement in the last few years, but now the interest in hybrid organic-inorganic compounds seems to prevail for stabilizing high

Tc ferromagnets. The chemistry of layered materials and that of intercalated organic species may thus offer fascinating compounds with outstanding properties.

Among layered compounds, the transition metal hydroxynitrates $M(OH)_{2-x}(NO_3)_x$, mH_2O (with M = Co, Ni, Cu) are well known for a long time. These compounds are still currently investigated, since they are good precursors for the synthesis of simple or mixed metal oxides with interesting catalytic and electric properties[2]. From a structural point of view, the hydroxynitrates derive from the CdI_2 type structure of $M(OH)_2$. They can be described as 2d triangular arrays of metal ions with large interplanar distances, and accordingly, they are good candidates for studying bidimensional magnetic systems.

On the other hand, molecular units exhibiting intramolecular ferromagnetic interactions are needed for the construction of molecular-based magnets[1]. They usually display low density and can easily be formulated as molecular films or monolayers, which in some cases, are partially transparent in the visible spectrum. Clearly, for molecular-based magnets, an appropriate molecular structure must be designed to avoid the natural tendency of the spins to be anti-aligned leading to antiferromagnetism. To stabilize molecular materials displaying a zero-field magnetization below some critical temperature, one must assemble paramagnetic subunits so that the interactions between local spin carriers result in a net magnetic moment at the bulk material scale.

As part of our interest in molecular based ferromagnetic materials, and in order to increase the critical temperatures, we are currently trying several approaches:

1) the use of more sophisticated ligand based spin carriers (e.g. chelate substituted mono- or biradicals[3]), which may cross-link infinite molecular chains, thus forming two or ideally three-dimensional structures,

2) the intercalation of organic free radicals into host solid matrices (e.g. layered double hydroxides or hydroxyacetate compounds). The electronic and magnetic properties of these metallo-radicalar systems can readily be tuned by a control of the spatial arrangement of free radicals into the inorganic host lattice.

LAYERED HYDROXYNITRATES $M_2(OH)_3(NO_3)$, WITH M = Co, Ni, Cu

Apart slight distortions, the structural arrangement of the layered hydroxynitrates $M_2(OH)_3(NO_3)$ derives from that of $M(OH)_2$ by substituting ¼ of hydroxyl groups by nitrate ions, thus inducing a large enhancement of the interplanar distance, from ~4.65 Å to ~6.9 Å (Figure 1). It can be noted that, in some cases, $M(OH)(NO_3)$, H_2O is stabilized, the structure of which is described as infinite double chains of octahedrally coordinated divalent metal[4].

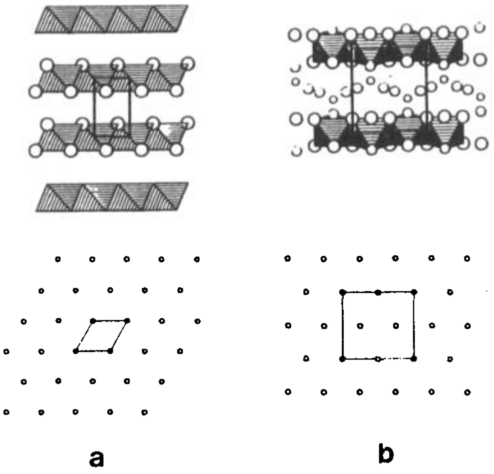


FIGURE 1. Structures of $Co(OH)_2$ (a) and $Co_2(OH)_3(NO_3)$ (b) showing the stacking of cobalt(II) layers along the c axis and the unit cell in the (a,b) plane.

The magnetic studies of layered cobalt(II) hydroxynitrate[5] have shown the ferromagnetic character of the planar triangular arrays (2d). In this section, we compare the properties of the two dimensional metal-based hydroxynitrates to the hydroxide parent compounds.

The cobalt(II) hydroxynitrate was obtained by following the method reported by Glibert and Markov[6]. The crystal structure agrees with monoclinic symmetry (space group $P2_1/m$) with unit cell parameters a = 5.531(2) Å, b = 6.2999(8) Å, c = 6.964(1) Å, ß = 93.18(3)°. No turbostratic disorder was observed. The average in-plane Co(II)-Co(II) distance, $d_{Co\text{-}Co}$=3.15 Å, is very close to the one reported for $Co(OH)_2$ ($d_{Co\text{-}Co}$=3.17 Å), but the interlayer distance differs very much ($c = 1.5c_0$). As a result, it can be claimed that $Co_2(OH)_3(NO_3)$ is a better example of two-dimensional system than $Co(OH)_2$.

The magnetic behaviors of both cobalt(II) compounds are plotted in Figure 2. For $Co_2(OH)_3(NO_3)$, the magnetic susceptibility exhibits a sharp maximum at Tc = 9.8 K (+/- 0.1 K) close to the value observed for $Co(OH)_2$ (Tc = 10 K). $\chi T = f(T)$ shows a constant value at high temperature (namely 3.6 $emu.mol^{-1}.K$), a strong increase for $T < 30$ K, and a drop to zero below Tc. Note that such a behavior is similar to that of the cobalt(II) hydroxide, with an enhancement of the magnetic moment close to Tc. It is characteristic of ferromagnetic in-plane interactions between cobalt(II) ions, as emphasized by Takada et al for $Co(OH)_2$[7].

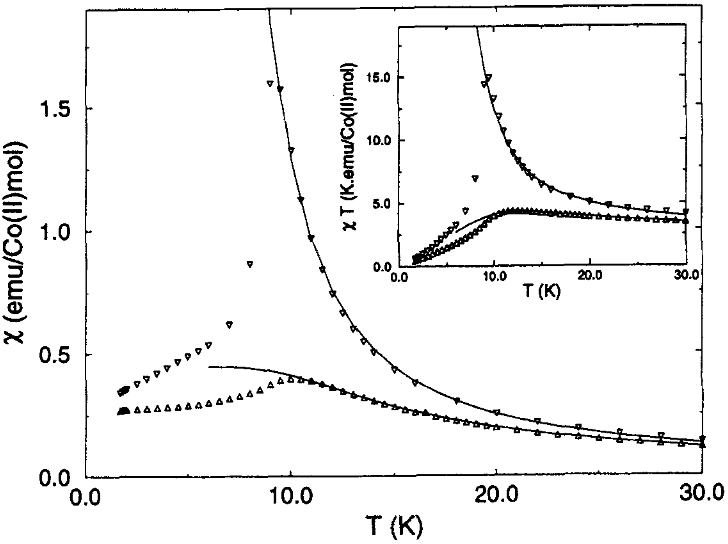


FIGURE 2. Magnetic susceptibility and χT product of $Co(OH)_2$ (Δ) and $Co_2(OH)_3(NO_3)$ (∇) ; Solid lines represent the best fits from the HTS expansion[9].

Clearly, the susceptibility results indicate for both compounds two regimes, corresponding to short-range ($T > Tc$) and long-range ($T < Tc$) magnetic correlations between cobalt(II) ions. At high temperature, ferromagnetic in-plane interactions dominate the magnetic properties, as evidenced by the sharp increase of χT when approaching the ordering temperature. Thus, these compounds may be viewed as good prototypes of 2d triangular ferromagnets, the properties of which closely depend on the spin dimensionality. At low temperature, a crucial problem concerns the lattice dimensionality, in other words, to what extent the thermodynamic properties of the cobalt(II) layers are affected by the weak interlayer interactions which are always present.

Cobalt(II) salts provide extensively studied examples of layered XY-type (planar anisotropy) systems. However, it should be noted that most of them show antiferromagnetic in-plane interactions[8]. In the case of cobalt(II) hydroxynitrate, it can be stated that the presence of NO_3^- groups breaks the trigonal symmetry, thus promoting a preferential axis within the easy XY plane. Accordingly, such a system may be viewed as a good example of in-plane Ising type anisotropy in a predominately XY-type system.

As a result of the combined action of crystal-field and spin-orbit coupling, the lowest multiplet of Co(II) is well approximated by an effective spin $S = 1/2$, with highly anisotropic properties. An analysis of the magnetic data, corresponding to the low dimensional behavior, has been performed for both Co(II) compounds on the basis of the S=1/2 2d Ising model.

TABLE 1. Values of the best fit parameters g, J and zj obtained using H.T.S. expansion[9].

Compound	dimensionality	g	J(K)	zj(K)
$Co(OH)_2$	2D	5.79	2.1	--
	2D/3D	5.09	9.2	-2.57
$Co_2(OH)_3(NO_3)$	2D	5.15	6.7	--
	2D/3D	5.11	7.4	-0.23

Two procedures were followed in the fitting process. In the first analysis, inter-plane exchange interactions were neglected, and the data were fitted from the expression derived by Van Dyke and Camp[9]. The results giving the best agreement between theory and experiment are listed in Table 1.

In the second analysis, we introduced the influence of interlayer interactions (zj) by use of the mean field approximation. Clearly, the interaction between adjacent layers depends on the interlayer distance, namely c parameter, so that it is expected to be more efficient for $Co(OH)_2$ than for $Co_2(OH)_3(NO_3)$. In this approximation, a very good description of the magnetic susceptibility was obtained from the parameters listed in Table 1.

From the above results, it appears that:

(i) the in-plane ferromagnetic coupling (J) cannot be determined unambiguously with a simple two-dimensional model.

(ii) the two-dimensional character is much more pronounced for $Co_2(OH)_3(NO_3)$ than for $Co(OH)_2$, as predicted from structural data.

This result agrees with the field dependent magnetization measurements which show a metamagnetic behavior for both compounds, with critical fields ranging from 0.17 T for the hydroxynitrate to 1.5 T for the hydroxide.

Finally, if interlayer interactions are needed for the occurrence of long range 3d ordering, the divergence of the in-plane correlation length ξ close to Tc appears to be the driving force, according to the relationship $kTc \sim \xi^2 jS^2$.

Unlike the cobalt(II) compound, the nickel(II) derivative is non stoichiometric and can be formulated as $Ni_2(OH)_{3+x}(NO_3)_{1-x}$.[10]. Accordingly, if the symmetry of the crystal is well hexagonal (D_{3d}), like for $Ni(OH)_2$, it is lowered to C_{2v} at the scale of the metal ion. As a result, a distribution of the single-ion anisotropy may be expected.

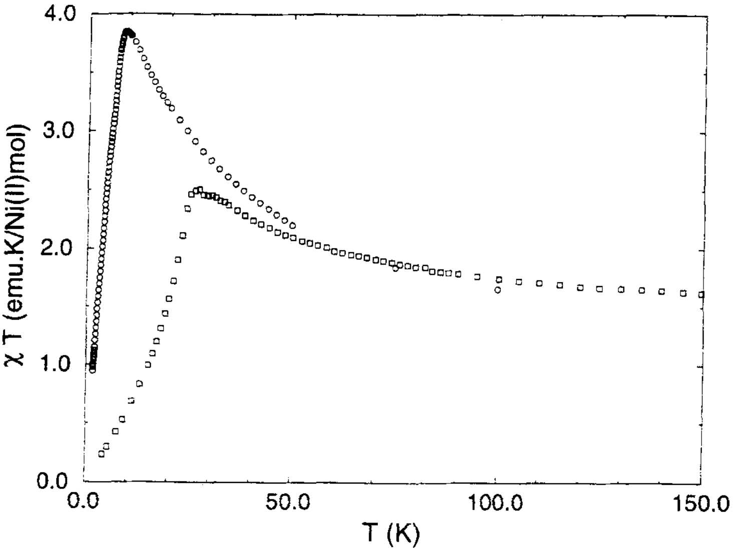


FIGURE 3. Magnetic susceptibility and χT product of $Ni(OH)_2$ (□) and $Ni_2(OH)_3(NO_3)$ (o).

The magnetic behaviors of the hydroxide and hydroxynitrate are displayed in Figure 3, as plots of $\chi T = f(T)$ (applied field H = 0.1 T). These results show the typical signature of a strong planar character, with in-plane ferromagnetic interactions, and a long range antiferromagnetic order at 10 K for the hydroxynitrate, and at 25 K for the hydroxide. It is to be noted that both cobalt(II) analogues exhibit Tc values close to 10 K. The decrease of the ordering temperature when substituting ¼ of hydroxyl groups by nitrate groups is likely related to the structural disorder of the metal environment, which induces a distribution of the single-ion anisotropies. Unfortunately, a model of triangular 2d lattice with S = 1 and single-ion anisotropy is not available to analyze the data properly.

The copper(II) hydroxynitrate is isostructural with the cobalt(II) derivative, i. e., a structural order is observed by X-rays diffraction between OH^- and NO_3^- anions. The structure is monoclinic (space group $P2_1/m$) with unit cell parameters a = 5.61 Å, b = 6.09 Å, c = 6.93 Å, β = 94.48°[11].

The temperature dependent susceptibility (Figure 4) shows a maximum at T_c = 12 K which may be related to the occurrence of a long range ordering. On the other hand, the decrease of χT upon cooling from 0.91 emu.mol^{-1}K at 150 K, down to 4.9x10^{-2}

emu.mol^{-1}.K at 1.7 K provides clearly evidence for antiferromagnetic in-plane interactions. Basically, such a system may be considered as a good prototype of frustrated Heisenberg 2d system, which from a theoretical point of view is still controversial as regards to the nature of the ground-state.

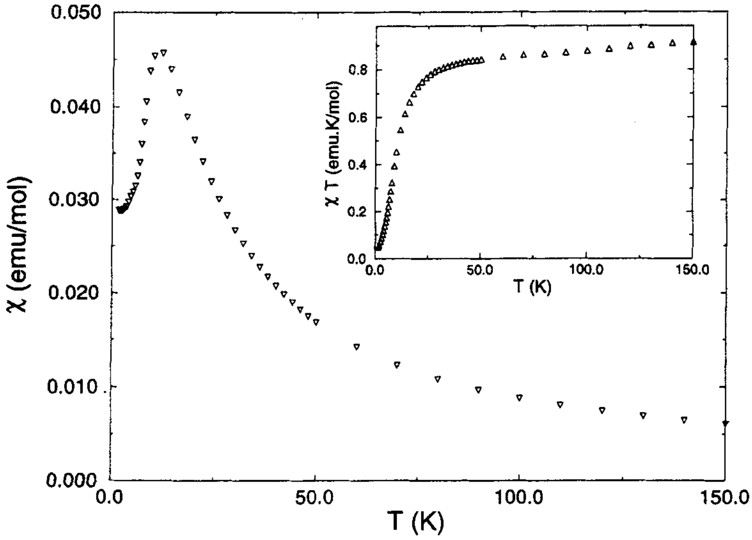


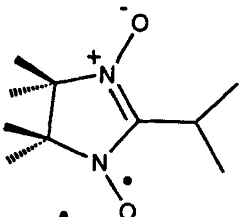
FIGURE 4. Magnetic susceptibility and χT product of $Cu_2(OH)_3(NO_3)$.

The low temperature variation of χ(T) seems to agree with a long range antiferromagnetic order below Tc. However, it must be noticed that such a magnetic order was not detected from neutron diffraction experiment on deuterated powder samples. As a result, it can be assumed that the maximum of susceptibility is related to short range antiferromagnetic interactions within copper(II) layers. An analysis of the data from the exact diagonalization study of finite clusters is in progress.

PYRIDINE-BASED BIRADICALS AND ANIONIC IMINO-NITROXIDE MONO-RADICAL

Many different low dimensional molecular materials have been studied and some of these exhibit ferromagnetism at low temperature[12]. One of the most interesting approaches is the use of metal complexes of stable organic free radicals (e.g. 2-isopropyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide, compound **A** in Figure 5). With one unpaired electron delocalized over two equivalent N-O groups, this free radical **A**, can form linear chains by bridging two individual metal complexes (e.g.

$[M(hfac)_2(A)]_n$ derives from $M(hfac)_2$, where M is Mn(II), Ni(II), or Cu(II) and hfac is hexafluoroacetylacetonate, Figure 5)[13].



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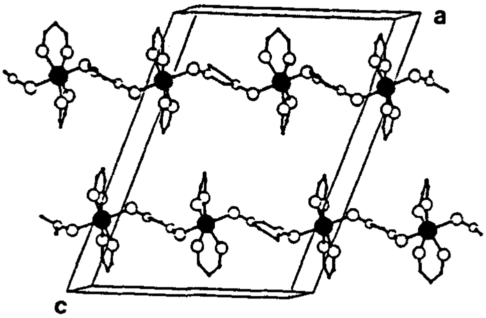
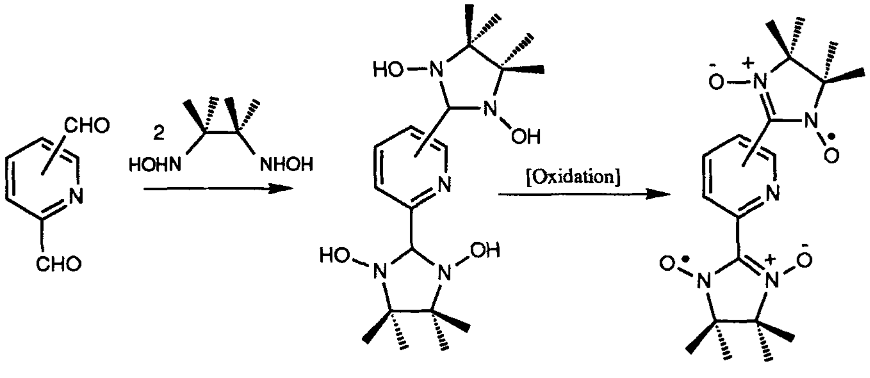


FIGURE 5. View of the unit cell of $[Mn(hfac)_2(A)]$. The CF_3 and CH_3 groups have been omitted for the sake of clarity[13].

The magnetic properties of these polymeric chains can be either ferromagnetic (as with copper) or ferrimagnetic (as with manganese or nickel). The free radical **A** not only acts as the bridging ligand for the chain structure but also provides the unmatched spins. A chain compound formed by copper(II) and a tridentate nitronyl nitroxide pyridine based monoradical has also been reported.[14] More recently, a pyrimidine based nitronyl nitroxide and its imino nitroxide analogue have been prepared and their magnetic properties studied[15].

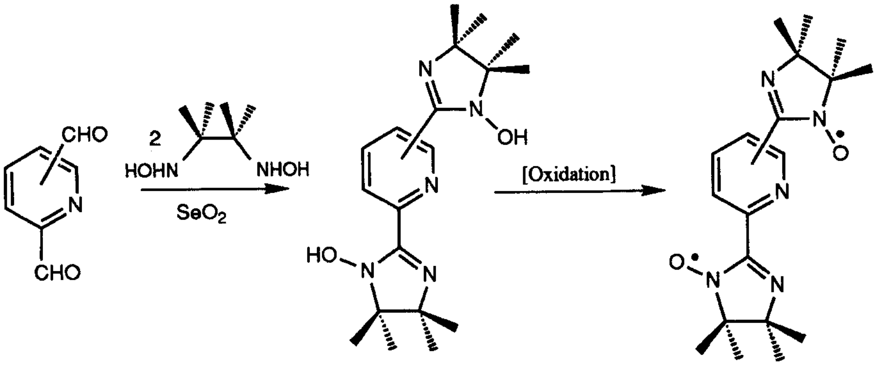
Despite the tremendous amount of work devoted to the synthesis and properties of free radicals[16], nitronyl nitroxide biradicals have only been scarcely studied[17,18].



1 in the 2,6 positions
2 in the 2,5 positions

SCHEME 1

Pyridine-based nitronyl nitroxide biradicals were prepared in good yield by multiple condensation of *N,N'*-dihydroxy-2,3-diamino-2,3-dimethylbutane with the corresponding dialdehydes (Scheme 1). Precipitation of the product from the reaction mixture, drives the reaction towards condensation. Mild oxidation of the *N,N'*-dihydroxyimidazolidines under phase transfer conditions (dichloromethane/water), using $NaIO_4$ or Ag_2O gave the corresponding pure deep-violet nitronyl-nitroxide biradicals **1** and **2** [3]. Selective preparation of the corresponding imino nitroxide biradicals **3** and **4** was achieved in the presence of selenium dioxide (5 mol%), which favors the dehydration of the N,N'-dihydroxyimidazolidine intermediate. Mild oxidation as described above, afforded the corresponding orange biradicals **3** and **4** (Scheme 2)[19]. All four biradicals were characterized by FT-IR, UV-Vis and FAB^+ mass spectroscopy. Magnetic properties displayed in Figure 6 show that both nitronyl nitroxide radicals **1** and **2** behaves differently.



3 in the 2,6 positions
4 in the 2,5 positions

SCHEME 2

For **1**, an increase of the χT product is observed down to 5 K (χT = 0.77 emu. mol^{-1}.K), which agrees with intramolecular ferromagnetic interaction between biradicals in 2,6 positions, then a drop at lower temperature due to weak antiferromagnetic intermolecular interactions. A model of spin-1/2 dimer, with a singlet-triplet splitting J, gives a good fit with experiment for the intra and intermolecular exchange couplings J = +13.6 K and zj = -1 K, respectively.

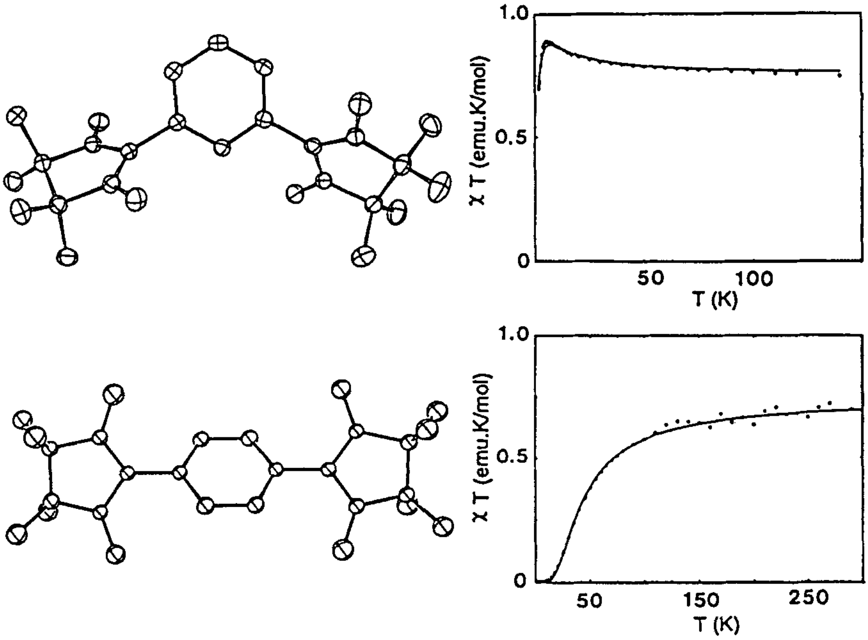
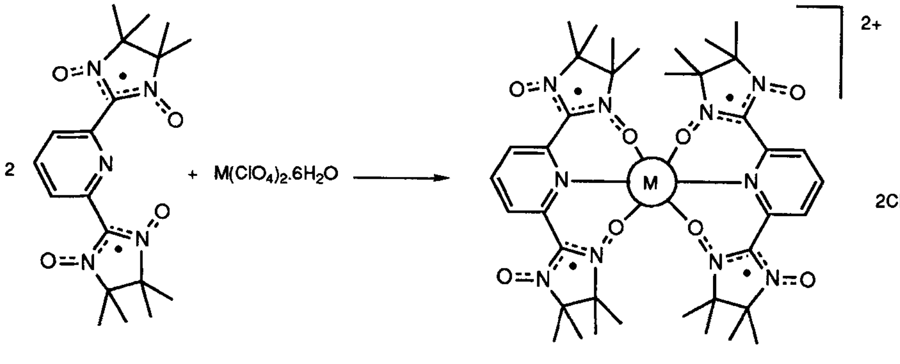


FIGURE 6. Top : molecular structure of biradical **1** and temperature dependence of χT. The solid line represents the fit of the experimental data ($\mathcal{H} = -JS_1S_2 - zjS_z\langle S\rangle$). Bottom : the same as precedent for biradical **2** (with zj = 0)

In case **2**, the χT product decreases from 0.75 emu.mol^{-1}.K at 300 K down to zero at very low temperature which is typical of antiferromagnetic interactions between nitronyl-nitroxide radicals in 2,5 positions. The best agreement with experimental data gives in that case J= -78.6 K. These results confirm the key role played by the spin polarization in the π conjugated systems, on the sign of the exchange coupling. The fact that for the 2,6 compound the two radicals are close to orthogonality (88.5° between both radicals) reinforces the ferromagnetic character of the interaction. An angle of 0 degree between both radicals and an angle of 38.7 degrees between the radical and the pyridine plane where found in the 2,5 compound. Complexation studies of ligand **1** with copper(II) and nickel(II) salts show the selective formation of a mononuclear complex with a 2/1 ligand/metal stoichiometry (Scheme 3). These complexes have been characterized by fast atom bombardment mass spectroscopy in positive mode FAB$^+$ (942/944 $[M+2e+2H-ClO_4]^+$, for **5** and 935/937 $[M-ClO_4]^+$ for **6**) and by elemental analysis. Nitronyl-nitroxide coordination to the metal is confirmed by a significant shift of the NO stretching frequency (16 and 25 cm^{-1} for the Cu(II) and

Ni(II) complexes respectively). A significant hyperchromic effect of the $n \rightarrow \pi^*$ electronic transition is also observed in both complexes.

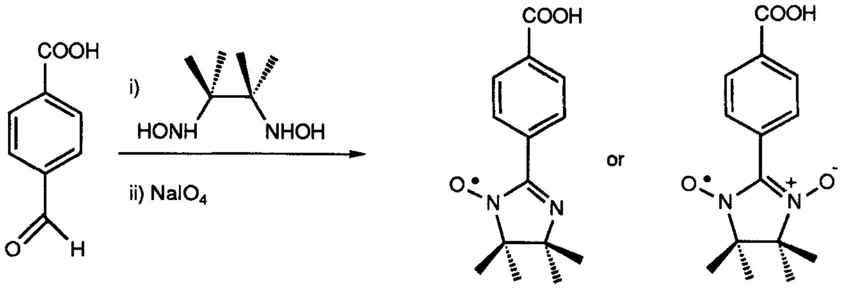


1

5 M = Cu(II)
6 M = Ni(II)

SCHEME 3

Acidic (or anionic) free radicals have previously been prepared and have mostly been used as spin probes and spin labels, exploiting their paramagnetic nature in order to obtain structural information of the protein environment[20]. We now describe here the synthesis, and characterization of a new benzoic acid (or benzoate)-substituted imino nitroxide free radical (7 in Scheme 4). This radical was prepared by a classical method (87% yield for 7)[16,17]. Due to the presence of an acid function on the skeleton, the use of SeO_2 was not longer needed to generate in good yield the imino nitroxide radical. The deep-blue nitronyl nitroxide radical **8** has previously been prepared[21]. However, in our conditions, we observe that the acidic form of **8** is not stable and must be stored as sodium salt[22]. The orange-red imino radical **7** is stable under standard conditions.



7 8

SCHEME 4

TABLE 2. Selected data for monoradical 7 $C_{14}H_{17}N_2O_3 \cdot H_2O$

IR[a)] (cm^{-1})	UV-vis[b)] λmax(nm), ($\varepsilon(M^{-1}\ cm^{-1})$)	FAB[+c)]	elemental analysis
			C, 59.71
1375	454 (390)	263.2	H, 6.77
1577	318 (4600)		N, 10.09

a) In KBr pellets, and correspond to $\nu_{N\text{-}O}$ and $\nu_{N=C}$ stretching vibrations
b) Measured in CH_2Cl_2, for characteristic UV-vis absorptions see ref. 16
c) Obtained using m-nitrobenzylalcohol as matrix, corresponds to $[M+2H^++e^-]^+$

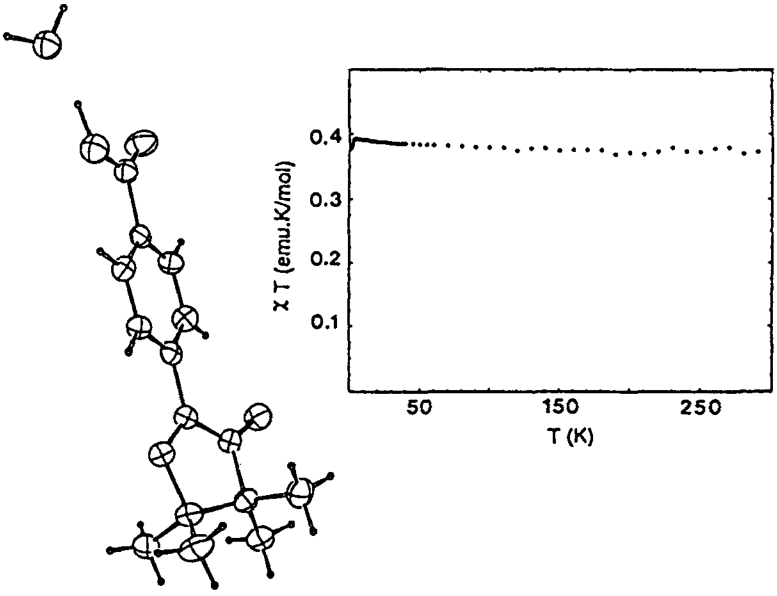


FIGURE 7. Molecular structure of monoradical 7 and temperature dependence of χT product.

This new radical 7 has been characterized by classical methods (IR, UV-vis, mass spectrometry, and elemental analysis, see Table 2) as well as by single crystal structure determination (Figure 7). A magnetic moment of 1.73 μ_B at room temperature was determined with a SQUID susceptometer (right hand side of Figure 7).

TOWARDS INTERCALATION IN HOST LAMELLAR MATERIALS.

This imino nitroxide benzoic acid radical 7 has been used in anion-exchange reactions with layered copper hydroxyacetate. Interlayer anion-exchange reactions have previously been observed in smectite clays[23] or pillared hydrotalcite materials[24]. Indeed, many layered double hydroxide salts (LDH's) do exchange anions and, in particular are very reactive towards organic anions and anion surfactants (such as fatty acid anion, alkyl sulfates and alkane sulfonates)[25,26]. The same works mention the good reactivity of some lamellar hydroxynitrates (see first part) towards such kind of organic anions. In this case, the MX_2 layers ($X = OH^-$, NO_3^-) are not charged like for the LDH's. Thus the substitution of the nitrate groups may occur, instead of simple intercalation in the interlayer space[26,27]. The in-plane arrangement is unchanged, while the interlayer distance may vary in a large amount (Figure 8). It follows that a large interaction between the metal ions and exchanged anions is expected.

Recent experimental results on the copper(II) based hybrid compounds $Cu_2(OH)_3(X)$ ($X = NO_3^-$, CH_3COO^-, $C_{12}H_{25}SO_4^-$) confirm the existence of covalent bond between the metal ion and the organic species. Figure 9 shows the dependency of the magnetic behavior of these 2d triangular systems for the different X ligands The two dimensional character of these compounds is well illustrated when comparing $Cu_2(OH)_3(NO_3)$ and $Cu_2(OH)_3(C_{12}H_{25}SO_4)$ which show the same behavior, though the interlayer distances are very different (6.9 Å and 26.5 Å, respectively).

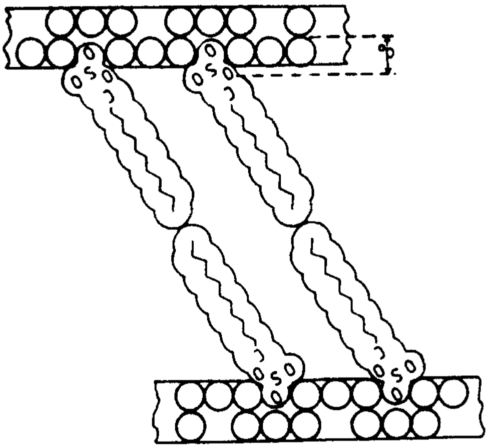


FIGURE 8. Structural model for hybrid layer compound after substitution of metal ligand by alkylsulfonate molecules (see reference 26)

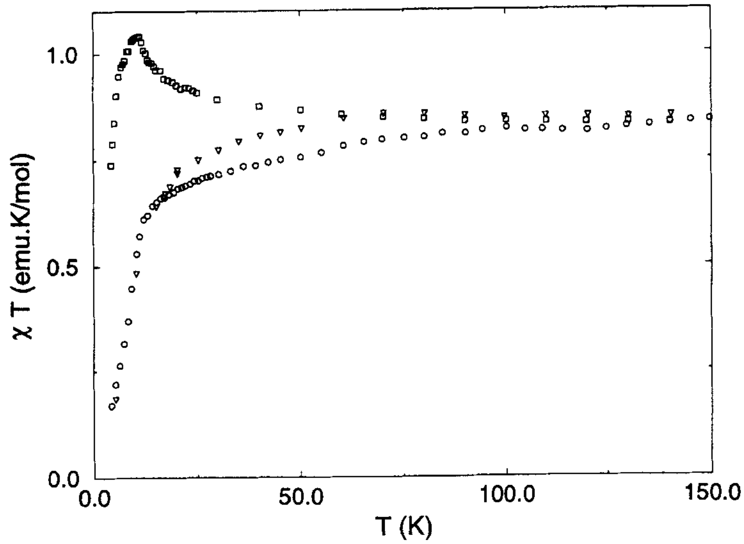


FIGURE 9. Temperature dependence of the χT product for basic copper salts $Cu_2(OH)_3(X)$, with X = NO_3^- (∇), CH_3COO^- (□), $C_{12}H_{25}SO_4^-$ (o).

On the other hand, the possibility of tuning the magnetic properties with the ligand is illustrated by the use of acetate ion, for which a ferromagnetic behavior appears, with an interlayer distance of 9.3 Å.

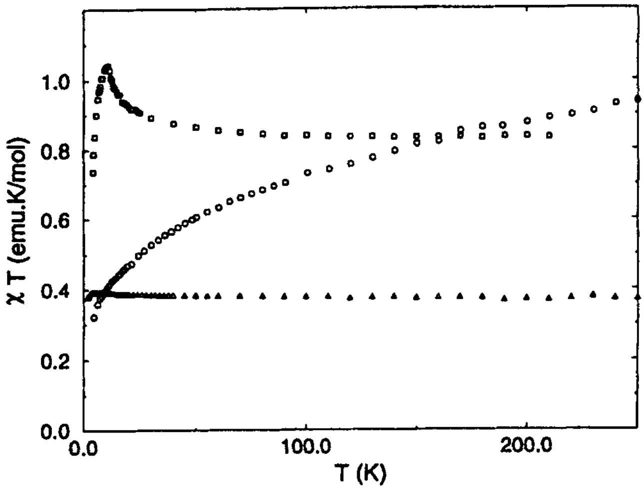


FIGURE 10. Temperature dependence of the χT product for basic copper salt obtained by exchange reaction of copper(II) hydroxyacetate with radical 7 (o). The magnetic behaviors of $Cu_2(OH)_3(CH_3COO)$ (□), and the isolated radical 7 (Δ) are displayed for comparison.

The use of radical anions for stabilizing new hybrid materials has been achieved for the first time. In particular, the radical 7 in Scheme 5 has been introduced into the layered copper(II) hydroxyacetate.

The magnetic behaviors of the free radical, copper(II) hydroxyacetate, and hybrid compound are compared in Figure 10. It appears clearly that for the latter a strong antiferromagnetic coupling between both sublattices, the copper(II) layer on one hand, the organic radicals on the other hand. Experiments with the cobalt(II) and nickel(II) layer compounds are in progress in order to stabilize 3d ferrimagnets. Finally, it can be noted that these materials differ from the classical radical-based molecular compounds (namely, radical complexed to metal cations), and thus appear very promising for the future.

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