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Valerie Laget [a], Pierre Rabu [a], Claudie Hornick [a], Francisco Romero [c], Raymond Ziessel [c], Philippe Turek [b] & Marc Drillon [a]

[a] Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 46 du CNRS, 23 rue du Loess, 67037, Strasbourg Cedex, France

[b] Institut Charles Sadron, Université Louis Pasteur, 6 rue Boussingault, 67083, Strasbourg cedex, France

[c] Laboratoire de Chimie, d'Electronique et de Photonique Moléculaires, ECPM, 1, rue Blaise Pascal, 67008, Cedex Strasbourg, France

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NEW LAYERED HYDROXIDE-BASED ORGANIC/INORGANIC FERROMAGNETS WITH BASAL SPACINGS UP TO 40 Å

VALERIE LAGET, PIERRE RABU, CLAUDIE HORNICK, FRANCISCO ROMERO[‡], RAYMOND ZIESSEL[‡], PHILIPPE TUREK[†], MARC DRILLON
Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 46 du CNRS, 23 rue du Loess, 67037 Strasbourg Cedex France; [†] Institut Charles Sadron, Université Louis Pasteur, 6 rue Boussingault, 67083 Strasbourg cedex France; [‡] Laboratoire de Chimie, d'Electronique et de Photonique Moléculaires, ECPM, 1, rue Blaise Pascal, 67008 Cedex Strasbourg France.

Abstract: We report the structure-magnetic property relationship of layered metal(II)-based carboxylate compounds, which are shown to be suitable inorganic host lattices for the insertion of organic anions. Unprecedented ferromagnetic interactions are evidenced for distances as far as 40 Å between metal layers. The properties of copper(II) n-alkyl carboxylates and cobalt(II)-iminonitroxide radical hybrid ferromagnets are discussed.

INTRODUCTION

Molecular compounds exhibiting ferromagnetic ordering transition are attracting increasing attention in recent years[1]. From a magnetic viewpoint, radical-based organic compounds offer clearly appealing prospects, though long range order occurs at very low temperature only. The strategy consists in assembling molecular building units in a controllable fashion, in order to promote ferromagnetic exchange interactions between nearest neighbors. As far as the spin carriers are close to each other, the exchange coupling is usually described by the symmetry of magnetic orbitals or spin polarization effects, and dipolar interactions are negligeable. The interaction mechanisms may in turn differ fundamentally when considering extended bridging ligands, as it will be evidenced in this paper.

Basically, the design of 3d architectures in molecular chemistry is difficult to realize, so that hybrid organic-inorganic compounds may be very promising for stabilizing high T_c ferromagnets. Anion-exchange reactions are well-known in smectite clays, and layered double hydroxides[2] (LDH's) $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}A_x^-$. The latter consist of organic as well as inorganic anions (A) located between the hydroxide layers, counter-balancing the positive charge due to the substitution of divalent by trivalent metal ions. Yamanaka et al.[3] have shown that layered copper(II) hydroxide acetate, $Cu_2(OH)_3(CH_3COO).H_2O$, is likewise a good candidate for exchange reactions. Unlike the LDH's, this compound and the nitrate analogs only involve single valence metal ion, so that the substitution of NO_3^- or OAc^- may occur instead of simple intercalation of anionic species in the interlayer space.

Recently, it was demonstrated that the layered compounds, $M_2(OH)_3X$ (with M=Co, Cu) in which the exchangeable species, $X=NO_3^-$ or OAc^-, is coordinated to the divalent metal ion, are well-adapted for the design of new hybrid organic-inorganic compounds with outstanding magnetic properties[4-7]. The structure may be viewed as a 2d triangular network of divalent metal atoms, made up of $[M_2(OH)_3]$ layers held together through hydrogen bonds involving the exchangeable-anion X (Figure 1). The in-plane metal-metal distances are very close for the different compounds (~3.15 Å) whereas the interlayer spacing (c parameter) varies from 6.9 Å (nitrate) to 9.3 Å (acetate).

From a magnetic viewpoint, the cobalt(II) compounds are good prototypes of ferromagnetic 2d systems, while the behavior for the copper(II) derivatives is closely dependent on the bridging ligand; it is 2d antiferromagnetic for the nitrate and 2d ferromagnetic for the acetate. At low temperature, all these compounds exhibit an antiferromagnetic ground-state, due to hydrogen bond interactions.

We have reported in previous works[4-6] the influence of large organic anions, such as n-alkyl-sulfate, on the magnetic properties of copper(II) and cobalt(II) compounds. In this paper, we focus on new hybrid compounds showing ferromagnetic properties, in:

(i) a series of copper(II) n-alkyl-carboxylates in which the interlayer spacing is mediated by the length (n) of the organic species,

(ii) a novel magnetic organic-inorganic compound made up of stacks of cobalt(II) hydroxide layers interleaved by an imino-nitroxide benzoic radical.

The occurrence of very long range ferromagnetic interactions is discussed on basis of dipolar and exchange interaction mechanisms.

ALKYL-CARBOXYLATE COPPER(II) COMPOUNDS

A series of layered copper(II) compounds in which the exchanged anion is n-alkyl-carboxylate was prepared according to the procedure reported in [6,7].

The copper hydroxide acetate, used as starting material, is prepared by titrating a 0.2 M copper acetate solution with 0.2 M NaOH, at 60 °C (Na:Cu=1.5). The $Cu_2(OH)_3(C_nH_{2n+1}COO).mH_2O$ compounds are obtained by exchange reaction, using the appropriate sodium salts (0.2 M). The above chemical formula corresponds to a complete exchange of acetate by the alkylcarboxylate anion, in agreement with elemental analysis. After one day, the precipitate is washed with ethanol and air dried, giving green colored powder which consists of platelet shape crystallites, as shown by scanning electron microscopy. The reaction is reproducible, but three days reaction for the long chain exchanged compounds gives different X-ray powder diffraction patterns, with the same stoichiometry except slight variation of the water content, without systematic rule.

In all cases, the $Cu_2(OH)_3(C_nH_{2n+1}COO).mH_2O$ products are characterized by the presence of intense (00l) diffraction lines, in agreement with the layered Botallackite-type structure. The copper(II) hydroxide acetate exhibits monoclinic symmetry, as indicated previously by Yamanaka et al.[3], while the lattice parameters for longer alkyl chain carboxylates are refined from monoclinic or hexagonal unit cells, depending on the degree of ordering of the exchanged anions. As might be anticipated, varying the alkyl chain length changes the interlayer spacing (c parameter), while the in-plane distances remain constant. Furthermore, depending on the reaction time (1 or 3 days), two different structural varieties are evidenced for the largest n values, characterized, from X-ray diffraction patterns, by different interlayer spacings. They are referred to as α (small c) and β (large c) varieties. For both series, the interlayer spacings vary linearly with the alkyl chain length (n), according to the relation $d(Å) = d_0+2.54n.\cos\theta$ proposed by Meyn et al.[2] for hydroxide double salts (Figure 2).

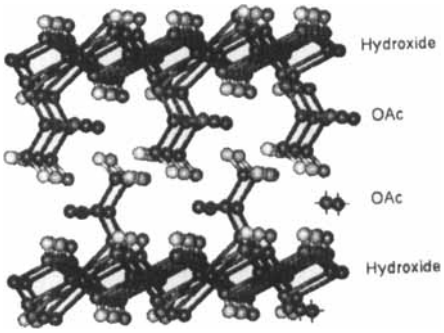


Figure 1 : Structural model for the layered compound $Cu_2(OH)_3(OAc).H_2O$

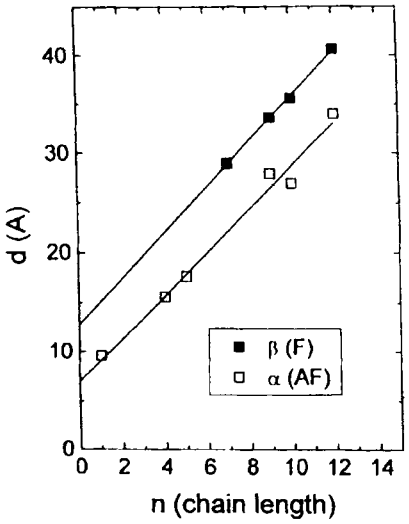


Figure 2 : Variation of the interlayer spacing as a function of n in $Cu_2(OH)_3(C_nH_{2n+1}COO).mH_2O$

The slopes of the two straight lines are very close while d_0 values are found to be 6.9 Å and 12.8 Å for the α and β compounds, respectively. This implies that (i) in both series, the alkyl chains are stacked head-to-tail in bilayers, with a tilt angle θ = 25-30° with respect to the c axis, (ii) the α and β polymorphs are characterized by different (inorganic) layer thickness, as indicated by the d_0 values. The additive term d_0 includes two contributions: the distance from the center of the layer to the carboxylate carbon atom and the distance between the methyl groups belonging to adjacent chains.

The structure of the hydroxide layers in the β compounds is difficult to predict. However, it is to be noted that two site symmetries have already been reported for the related cobalt(II) salt $Co_7(OH)_{12}(NO_3)_2.nH_2O$, inducing a double-layered structure[8].

The magnetic properties of the n-alkyl carboxylates have been investigated using a DSM8 magnetic equipment (Manics) and a SQUID magnetometer (Métronique). The magnetic behaviors of the series are illustrated in Figure 3, as the temperature dependence of the χT product for n=7 and 12. The Curie constants deduced from high temperature measurements agree with the expected value for two Cu(II) per molecular unit. The α

polymorphs exhibit a continuous decrease of the χT product down to 2 K, denoting the antiferromagnetic character of the exchange couplings. In turn, the behavior of the β polymorphs drastically differs. Upon cooling, a decrease of χT is first observed down to a minimum at 60 K whatever the n value, then a very sharp increase at lower temperature, pointing towards a ferrimagnetic or canted spin arrangement within the copper(II) layers. The very large value of χT_{max} is the signature of a net magnetic moment in the ground-state. Note that the decrease of χT at very low temperature is not significant, the magnetization variation being no longer linear with applied field.

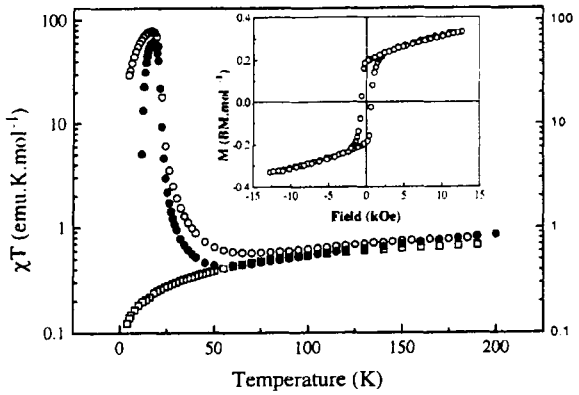


Figure 3 : Magnetic behaviors of α (square) and β (circle) $Cu_2(OH)_3(C_nH_{2n+1}COO).mH_2O$ for n = 7 and 12 (open and filled symbols, respectively).

The occurrence of long range ferromagnetic order is illustrated for n=7 by a characteristic hysteresis loop in the M(H) curve at T=4.2 K (inset of Figure 3). A similar behavior is observed for the different β compounds, even for very large interlayer spacings (up to 40 Å). The ordering temperatures (T_c), recorded from remanent magnetization curves, are found to lie between **20** and 15 K for n ranging from 7 to 12.

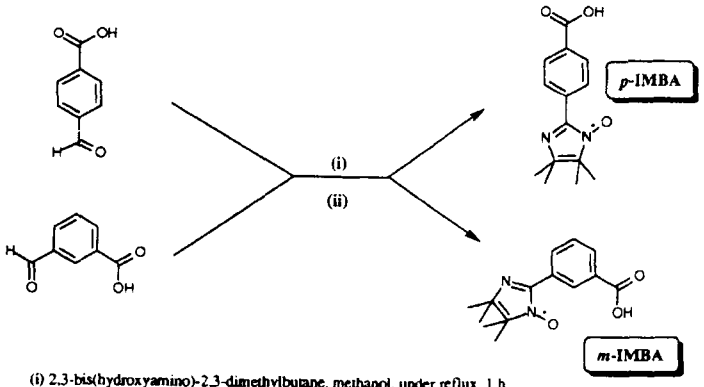
The magnetic study of this series of layered compounds shows that spectacular F or AF behaviors may be observed, depending on the structure of copper(II) layers. In the paramagnetic region, the behavior of β polymorphs is typical of low dimensional ferrimagnets, and so may be described by a model of uncompensated spin sublattices within copper(II) layers. At low temperature, the long range order may then be explained by a ferromagnetic alignment of the net moments through small interlayer interactions.

Clearly, these last cannot be understood in a simple way, by means of the concept of superexchange interaction. Moreover, the alkyl chains coordinated to copper(II) ions do not participate directly to the interlayer coupling, and their presence makes hydrogen bond effects negligible. A model of rigid ferromagnetic layers coupled by dipolar interactions only, may explain the stabilization of a ferromagnetic ground-state[4]. Indeed, if this coupling which varies as m^2/r^3 should be negligible for large r distances, the divergence of $m=g\langle S\rangle$ in the vicinity of T_c ($m=300\ \mu_B$ at 20 K for n=12) may explain that it most likely becomes the driving force in the present compounds.

In some extent, such systems may be considered as molecular magnets with giant magnetic moments interacting through space.

METAL-RADICAL HYBRID FERROMAGNET

A new benzoic acid-substituted imino-nitroxide (IMBA) free radical has been used for stabilizing hybrid materials. The free radicals **1** (*m*-IMBA) and **2** (*p*-IMBA) were prepared by sequence of reactions sketched below.



(i) 2,3-bis(hydroxyamino)-2,3-dimethylbutane, methanol, under reflux, 1 h.
(ii) $NaIO_4$, water/dichloromethane, RT, 3h.

Scheme 1

According to a general method reported previously[4,9] the formyl derivatives were allowed to react with 2,3-bis(hydroxyamino)-2,3-dimethylbutane. The resulting hydroxyimidazolidines were oxidized with $NaIO_4$ by phase transfer to afford the imino-nitroxide derivatives **1** and **2** in fair yields. The presence of an acid function within the

aldehyde precursor facilitates the formation of the dehydrated intermediate (hydroxyimidazolidine versus dihydroxyimidazolidine in the classical cases). Both orange-red IMBA radicals **1** and **2** are very stable and can be purified by chromatography on silica gel. The products have been characterized by classical chemical techniques and all the data (NMR, chemical analysis, IR) agree with the formulated compounds. Recrystallization from a dichloromethane/hexane solution gives red monocrystals of p-IMBA **2**. The molecular structure, to be published elsewhere, consists of a 3-dimensional network, in which each radical is connected to three neighbors via very strong hydrogen bonds (1.54 Å).

This imino nitroxide radical has been used, as its conjugated base, in the anion-exchange reaction with layered cobalt(II) hydroxynitrate, in the same conditions as above. In the present case, the MX_2 layers are not charged, so that the substitution of the nitrate groups may occur, instead of simple intercalation in the interlayer space, giving an hybrid compound (**rad2-Co**), with organic (radical **2** anion) and inorganic (Co(II)) spin carriers. The X-ray powder diffraction of the exchanged product shows that in-plane arrangement is unaltered, while the interlayer distance changes from 6.9 Å (nitrate derivative) to 20.2 Å (hybrid).

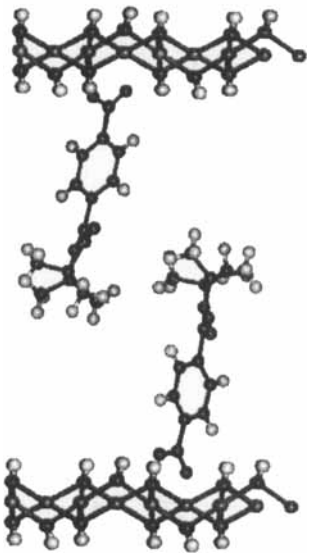


*Figure 4 : Schematic structural model for the hybrid layered compound **rad2-Co***

The increase of the interlayer spacing is in agreement with the expected layered arrangement shown in Figure 4. The magnetic behaviors of the cobalt(II) hydroxide nitrate, and hybrid **rad2-Co** compound are illustrated in Figure 5 as plots of $\chi T = f(T)$. $Co_2(OH)_3(NO_3)$ has already been described as a 2d ferromagnetic system, exhibiting at

low temperature (T<9.8 K) a metamagnetic behavior due to antiferromagnetic interlayer interaction[10]. The free radical has been characterized as a Curie paramagnet S=1/2.

Clearly, the exchange of nitrate anions by p-IMBA **2** induces a drastic change of the χT variation. At high temperature, the value of 5.4 emu.K/mol agrees with that expected for the sum of two isolated cobalt(II) and one free radical. Upon cooling, a constant increase of χT is observed down to about 6 K (χT_{max}=204 emu.K/mol). We note the absence of any minimum in the curve, in comparison to the compounds having non magnetic anions discussed earlier, suggesting all interactions are purely ferromagnetic.

Thus, it is shown that a strong ferromagnetic coupling between both sublattices, the cobalt(II) layer on one hand, the organic radicals on the other, takes place at low temperature. Below 8 K, the occurence of a long range ferromagnetic order is confirmed by magnetization measurements, showing a typical hysteresis loop with H_c= 380 Oe at 1.8 K (Figure 5).

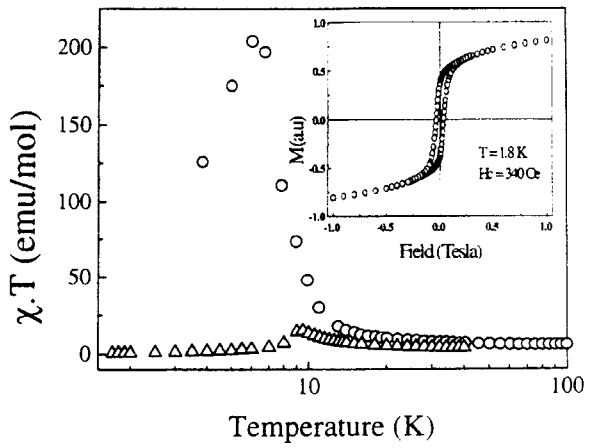


Figure 5 : Magnetic behaviors of $Co_2(OH)_3(NO_3)$ (triangle) and ***rad2-Co*** *(circle). The field dependent magnetization is shown for* ***rad2-Co*** *in the inset*

The EPR study of a powder of **rad2-Co** has been performed at X-band between 4 K and 300 K over a broad field sweep range (0-5 kG). Above 20 K, the EPR spectrum (Figure 6) consists of a narrow line at g=2.0065, superimposed to a broad line of width

c.a. 800 G. The peak-to-peak line width, ΔB_{pp}, of the narrow component increases continuously from 16 G at room temperature up to c.a. 50 G at 20 K. It is assumed that the narrow line corresponds to the signal of the organic radical, whereas the broad feature is assigned to the Co(II) ion resonance.

This line is single shaped, i.e. without a large g-tensor anisotropy, with an average g-factor close to 2, pointing to the signal of Co(II) ions within a tetrahedral environment[4]

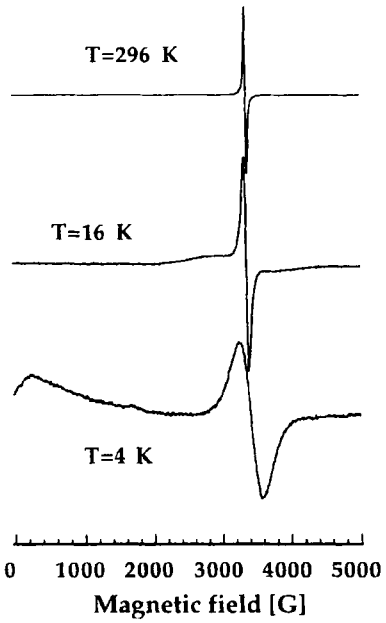


Figure 6 : X-band EPR spectra of ***rad2-Co*** *at room temperature, 16 K and 4 K.*

Besides the noticeable occurrence of two signals, one from the cobalt ion and the other from nitronyl nitroxide radical, the most striking features are observed below c.a. 20 K. The suceptibility plotted in Figure 7 corresponds to the peak-to-peak amplitude multiplied by the square of the line width. It is worth noting that the observed behavior is divergent below 10 K. The high temperature data may be fitted by a Curie-Weiss law with a θ value of 10 K (see inset in Figure 7). Interestingly, a weak signal is observed at half-field (g close to 4) at 4 K. It is marked as a small hump at 1650 G in Figure 6.

The experimental conditions allow to detect this signal up to about 25 K. With the lack of a detailed structural analysis, it is tentatively assigned to the radical spin pairing of neighbouring radicals sandwiched between the inorganic cobalt(II) sheets.

These results fully confirm the existence of ferromagnetic interactions between the organic and inorganic sublattices, as evidenced by the magnetic susceptibility experiments. A broad feature appears near 400 G at 10 K and is growing at lower

temperature. Its origin is not yet explained. Further experiments are in progress, dealing in particular with series of similar Co(II) derivatives.

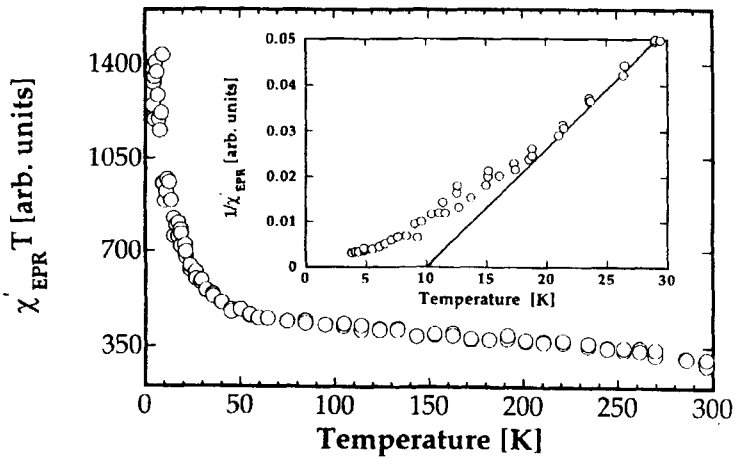


Figure 7: Temperature dependence of the EPR susceptibility for the ***rad2-Co*** *compound.*

CONCLUSION

We have demonstrated in this paper that self assembled stacks of two interpenetrating sublattices may favor very long range magnetic correlations. Thus, long range ferromagnetic order is observed between copper(II) layers as far as 40 Å, illustrating the important role of dipolar interactions. These are most likely also relevant in the metal-radical compound **(rad2-Co)**, even if the organic (radical) and inorganic (cobal(II)) spin carriers may be coupled through the π-system of the benzoic acid. The present result points to the fact that the divergence of the correlation length, and as a result of <S> within the ferromagnetic layers, is the important feature to promote the dipolar effects responsible for the 3d ordering.

In this respect, this family of layered hybrid systems differs from the classical radical-based molecular compounds (namely, radical complexed to metal ions), and appears very promising for the design of new kinds of ferromagnets.

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