Structural and spectroscopic study of organic-inorganic transition metal based layered magnets

P. Rabu*, M. Drillon and C. Hornick

IPCMS, Groupe des Matériaux Inorganiques, UMR 7504, CNRS-ULP, 23, rue du Loess, 67037 Strasbourg, France

The layered transition metal hydroxide based compounds $M_2(OH)_{3-x}(A^{n-})_{x/n} \cdot zH_2O$, with M = Co, Cu, and A = organic anion, constitute a new class of organic – inorganic magnetic materials. Series of compounds are synthesized by anionic exchange reaction from transition metal hydroxide acetate or nitrate (A = OAc, NO_3). This reaction induces structural change of the exchanged compounds. The combination of powder X-ray diffraction, infrared and UV-visible spectroscopy analyses and the analogy with known parent compounds allow to discuss the correlation between the structure and the magnetic properties. It is shown how the size and nature of the organic anion A influence strongly the properties of the bulk material. The fact that the inserted anion A coordinates the metal centers in the inorganic hydroxide based sheets induces a great interaction between the organic and inorganic subnetworks.

Introduction

Recently, a novel trend of investigation has been the combination of both molecular and solid state chemistry to build hybrid organic-inorganic materials [1]. Clearly, the research on hybrid compounds is very appealing for the design of novel 3d networks in which the physical properties of both assemblies, that are normally found in distinct materials, are in close conjunction [2-5].

Smectite clay minerals (montmorillonite for instance), in which silicate layers are negatively charged by substituting divalent metal ions for trivalent ones, constitute versatile host layer structures for organic or inorganic species. A large number of such cation exchangeable layer compounds are known in which the intercalated species favor pillared structures.

Anion exchangeable layered compounds are less common, probably because the anions are usually strongly bound to the metal ions, and form the framework of the crystal. Exchange of interlamellar anions by organic species (dicarboxylic acid anions) was first reported by Miyata and Kumura [6]. Then, the interlayer arrangement of anionic surfactants has been extensively studied in layered double hydroxides (LDH's) $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}A^-_x$ consisting of positively charged hydroxide layers, separated by A^- anions counter-balancing the positive charge of the hydroxy layers [3,4,7,8]. In such compounds, the counterion A^- is located in between the hydroxy layers, and no real chemical bond exists usually between the guest and host sub-networks. The cohesion is basically due to electrostatic interactions, and when available to weak hydrogen bond couplings.

On the other hand, new hybrid magnetic materials have been prepared by anion exchange reaction, in which the exchangeable anion A^- is coordinated to the divalent metal ion. The layered compounds $M_2(OH)_3A$ (M = Co, Cu, and $A = NO_3^-$ or OAc^-) are shown to be well adapted for substitution reactions [9-12]. The exchange for large organic species (*i.e.* aliphatic chain anions) coordinating the metal ion enables to tune the basal spacing, and accordingly to modify drastically the magnetic properties [11,12]. Thus, n-alkyl chain molecules involving a single anionic function (carboxylate or sulfate anion), have been used to separate basic layers (Fig. 1a).

In that case, the organic spacers exhibit a saturated carbon chain, whose length is mediated by the number of carbon atoms, up to 40 Å [10]. The magnetic interaction within layers is highly dependent on the nature of the anionic function and the chain stacking, so that ferro-, ferri- or antiferromagnetic behavior may be stabilized. Clearly, the *n*-alkyl chains do not participate directly to interlayer interaction – they may be viewed as "neutral" pillars – but they modulate the distance between magnetic sheets, and as a result influence through-space magnetic interactions. We have shown that, due to dipolar coupling [13], ferromagnetic 3d order is stabilized when basal spacing becomes large enough (> 10 Å). The interaction mechanism between ferromagnetic layers is then mainly driven by the divergence of the in-plane spin-spin correlation length when temperature is decreased. Such systems appear to be good prototypes of monolayer magnets interacting through classical dipolar interactions. Similarly, radical-based anions have been grafted onto copper(II) and cobalt(II) hydroxide layers [14],
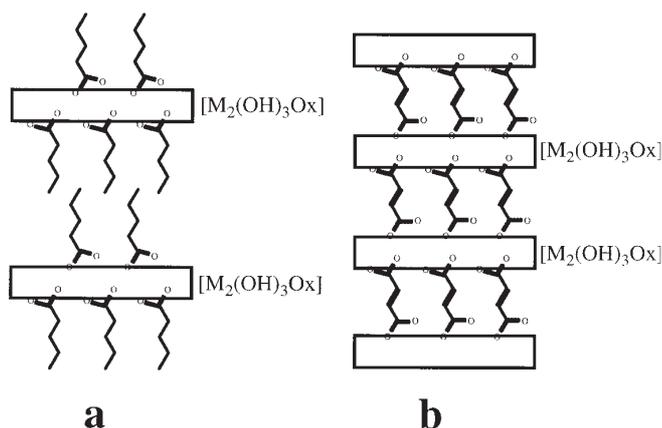
Figure 1. Structural model of layered exchanged compounds obtained by using a) *n*-alkyle monoanions or b) *n*-alkenedioates anions.

giving new hybrid multilayer ferromagnets, with a strong coupling between organic and inorganic networks.

Finally, it appears to be worthwhile to control the connection between magnetic layers, which determine the properties of the bulk material. For this purpose, we have focused on the design of dicarboxylate-based compounds, involving difunctional unsaturated bridging anions between magnetic layers (Fig. 1b). From the comparison of the hybrid systems with saturated and unsaturated aliphatic chains, new insights have been provided on the role of π electrons in the interlayer exchange mechanism. It is focused here on the structural and chemical characteristics of this family of copper(II) and cobalt(II) compounds and on their influence on the magnetic properties.

Organic-inorganic hydroxide-based compounds

Synthesis

A series of layered copper(II) compounds $Cu_2(OH)_{4-x}(A^{n-})_{x/n}$ · zH_2O ($A=C_nH_{2n+1}SO_4^-$, $C_nH_{2n+1}COO^-$, $CO_2(CH_2)_nCO_2^{2-}$) has been prepared by anion exchange reaction, starting from $Cu_2(OH)_3(OAc)$•H_2O [10,11,12]. The starting hydroxy-acetate is synthesized by titration of copper acetate by potassium hydroxide with the OH:Cu = 3:2 molar ratio [10]. The acetate ions are exchanged by organic anions after dispersion of $Cu_2(OH)_3(OAc)$•H_2O in aqueous solution of the relevant sodium salts at low temperature (25 °C), resulting in a green crystalline powder which is washed with alcohol, and then dried at 40 °C.

In the case of *n*-alkyl carboxylate anions, two series with the formulation $Cu_2(OH)_{4-x}(C_nH_{2n+1}CO_2)_x$•$zH_2O$, ($x = 1 \pm 0.1$)

may be isolated for n = 7, 9, 10, 12, by using low concentration of the substituting anion (0.2M) and a ratio r = A⁻/OAc⁻ = 5:1 [10,11]. The first phase (α–type) is obtained at the first stage of the exchange reaction. Upon going on the reaction 10-15 h, another phase (β–type) is observed. The stoichiometry of the latter differs essentially by its water content; the α–type derivatives are hydrated (z = 0.3-0.5), while the β-type derivatives are anhydrous (z = 0). Further, the β phases may exhibit a OH^-/$C_nH_{2n+1}CO_2^-$ ratio lower than 3 (down to 1.2), indicating that a part of the hydroxyl ions have been exchanged.

The change from α to β phase is followed by pH measurement. Indeed, during the substitution, the pH value shows a plateau (α-phase) and a characteristic increase corresponding to the stabilization of β-phase. Then a decrease of the pH is associated to slight dehydration of the products, decomposing into CuO, as evidenced by X-ray diffraction analysis. This investigation is useful for the improvement of the reaction conditions depending on the expected product (α or β). For short *n*-alkyl-carboxylate chains (n = 4, 5), only the α-type phase is observed. The two series of compounds exhibit a linear variation of the basal spacing with the chain length n (Fig. 2). The value obtained for the β series is much higher, suggesting a clear discrepancy with the α structure. The pH variation is in favor of a topotactic exchange during the first step of the reaction (α-phase) followed by a dissolution-crystallization process (β-phase). This assumption is supported by the powder X-ray diffraction study, which indicates a clear structural modification between α and β phases (see below).

Similarly, a series of copper(II) hydroxy-dicarboxylates has been prepared. Then, the acetate ions are exchanged for n-alkanedioate anions $CO_2XCO_2^{2-}$, with X = $(CH_2)_n$ and n = 1 to 8. Similar exchange reactions have been achieved
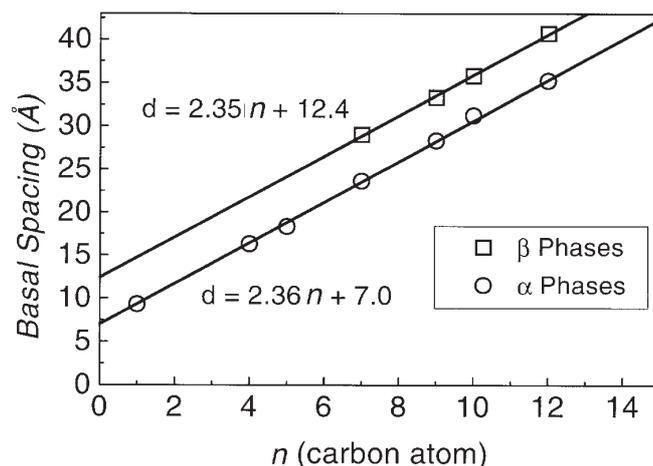

Figure 2. Variation of the stacking periodicity d$_{001}$ (basal spacing) as a function of the alkyl chain length in copper(II) alkyl-carboxylate hydroxide series $Cu2(OH)_3(C_nH_{2n+1}COO)$·$zH_2O$ (see text).

with unsaturated *n*-alkenedioate anions by using the fumaric ($X = C_2H_2$), transhexene-dioic ($X = C_4H_6$) and muconic ($X = C_4H_4$) acid salts. Following the usual procedure, $Cu_2(OH)_3(OAc) \cdot H_2O$ powder (1 mmol) is dispersed into 30 ml of an aqueous solution (0.25 M) of the corresponding sodium dicarboxylate ($XC_2O_4Na_2$), at room temperature. After 1 day, the exchange is completed by repeating once the treatment of the reaction product with a fresh dicarboxylate solution, for 2 days. The precipitate is isolated as a green crystalline powder. The general formulation of the compounds is $Cu_2(OH)_{4-x}(XC_2O_4)_{x/2} \cdot zH_2O$, with $1.0 < x < 2.4$ and $0.1 < z < 1.6$.

Series of layered cobalt(II) compounds $Co_5(OH)_8(C_nH_{2n+1}COO)_2 \cdot zH_2O$ ($n = 7$, 9, 10, 12), $Co_7(OH)_{12}(C_nH_{2n+1}SO_4)_2 \cdot zH_2O$ ($n = 6$, 9, 12) and $Co_7(OH)_{12}(CO_2XCO_2) \cdot zH_2O$ are also obtained by anion exchange. A suspension of pink hydroxy-nitrate $Co_2(OH)_3(NO_3)$ in aqueous solution is then used as starting material. The latter is obtained by slow hydrolysis of an aqueous solution (3.5 M) of $Co(NO_3)_2 \cdot H_2O$ by KOH (1 M), with OH:Co = 1.3, at 95 °C [15]. The exchange reactions are carried out at 45 °C, under argon flux. The pH is set to 7.5 by addition of NaOH at the beginning of the reaction. The bluish-green crystal powder is washed with alcohol and dried at 40 °C.

For all compounds, the acetate or nitrate anions are totally exchanged, and the stoichiometries in organic anion and water agree with C, H and H_2O chemical analysis within less than 0.3 mass percent. The Cu and Co amounts are determined from weight losses at 500 °C and 700 °C under air, respectively (final products, CuO and Co_3O_4).

Influence of organic spacers

All compounds exhibit a lamellar structure as evidenced by XRD patterns which show, in the low 2θ range, intense *00l* diffraction lines, up to at least the third order. This corresponds to the stacking periodicity of the hydroxide-based layers (basal spacing). During the exchange process, the completeness of the reaction is checked by the abrupt change in peak position, by comparison with the starting materials $Cu_2(OH)_3(OAc) \cdot H_2O$ ($d_{001} = 9.3$ Å) or $Co_2(OH)_3(NO_3)$ ($d_{001} = 6.93$ Å). The basal spacing is increased according to the size of the organic chains, as illustrated in figure 2. The other reflections (*hkl* with *h* and $k \neq 0$) are much smaller, and exhibit the usual line width increase for disordered pillared compounds [16]. Despite the poor quality of crystallographic data, the diffraction patterns may usually be analyzed by using hexagonal or pseudo-hexagonal unit cells [10]. The similarity of XRD patterns with those of $Cu_2(OH)_3(OAc) \cdot H_2O$ or $Co_2(OH)_3(NO_3)$ suggests that the local structure of the hydroxide-based layers remains more or less similar after exchange reaction. In turn, the color change of the cobalt(II) exchanged compound (bluish-green) points to the occurrence of tetrahedral sites for the metal ion, and accordingly a structural modification of the inorganic layers.

As might be anticipated, the interlayer spacing (*c* parameter) is closely related to the carbon chain length. According to the model used by Meyn *et al.* [7], the linear variation of the basal spacing with the number of carbon atoms *n* agrees with the relationship $d(Å) = d_0 + \eta(1.27n\cos\theta)$. In this expression, η is the number of layers of aliphatic chains in between the inorganic sheets ($\eta = 1$ or 2 for a mono or bilayer packing, respectively), *n* is the number of carbon atoms along the chains, and θ is the angle of the chains with respect to the normal to the layers. The distance d_0 represents the sum of d_1, the size of the bridging group (sulfate or carboxylate for instance), d_2, the van der Waals distance between terminal methyl groups and inorganic layers or between facing methyl groups, (for mono-anions, Fig. 1), and d_3, the thickness of the inorganic layer.

X-ray diffraction study

Experimentally, the $d = f(n)$ variations for the two copper(II) *n*-alkyl carboxylate analogues (Fig. 2) indicate a bilayer packing of the alkyl chains, with a tilt angle $\theta = 22°$ with respect to the normal to the layers. In contrast, the difference between d_0 values (about 5.4 Å) suggests different thicknesses of the inorganic layers. The thickness of the inorganic layers, d_4, deduced by subtracting from d_0 the d_1 (1.2 Å) and d_2 (3 Å) values is shown to be about 1.6 Å and 7 Å for the α and the β series, respectively. The value achieved for the former, involving the copper hydroxide acetate, agrees well with the structure of the parent compound $Cu_2(OH)_3NO_3$ ($d = 6.95$ Å), exhibiting a brucite–like structure [17]. The $d = f(n)$ variation is linear for *n* ranging from 1 to 12. So, a brucite-like inorganic layer may be assumed. The value obtained for the β series is much higher, suggesting a clear discrepancy with the brucite-like structure as regards the hydroxide based sheets.

The variation of d_{001} with the chain length for the copper(II) *n*-alkane dicarboxylates shows a step-like variation, in agreement with the *n* parity. This is related to the systematic change of orientation of the carboxylate groups in each bridging unit. Thus, for a given parity, a linear variation of d_{001} is observed, in agreement with the length of the exchanged anion, but the slopes are different for *n* odd or even, indicating a different tilt angle of the molecules (42.9° and 25.7° for odd and even *n* series, respectively). The d_0 value deduced from the extrapolation of *d* to $n = 0$ differs by ca. 2 Å between the odd (8.3 Å) and even (6.3 Å) series. The mean value (7.3 Å) suggests that the hydroxide-based layers in the exchanged compounds are identical to those of the copper(II) hydroxy-nitrate, showing a quasi-planar triangular array of copper(II) ions in octahedral surrounding. For unsaturated dicarboxylate anions, very close basal spacings are observed (0-0.2 Å step aside), compared to the corresponding saturated derivative.

Considering now the cobalt(II) *n*-alkyl carboxylate series, a single-layer packing is deduced, corresponding to a tilt angle of the chains with respect to the *c* axis, $\theta = 52°$. The distance $d_0 = 17.98$ Å is refined, and the inorganic layer

thickness is shown to be about 7.3 Å. For $Co_2(OH)_{3.2}(OAc)_{0.8}$, a structural model may be proposed on the basis of the X-ray diffraction results, and taking into account the van der Waals spheres for constitutive atoms. The acetate anion is coordinated to cobalt(II) ion by the oxygen atom, and occupies the interlayer spacing with a head to tail arrangement. Such a structural model for the inorganic layer is also found for the copper(II) hydroxy-acetate [11,18].

The cobalt(II) mono- and dicarboxylate compounds are characterized by a basal spacing larger than that of the copper(II) analog by about 3.2 Å. Such a difference is due to a larger thickness of the inorganic layer [11]. As noted above, the color change (from pink to bluish green) after anion-exchange points to the presence of cobalt(II) ions in tetrahedral surrounding. It can be predicted that the local structure of the metal-based layers is close to that of $Zn_5(OH)_8(NO_3)_2 \cdot zH_2O$ [19], $(Zn,Co)_5(OH)_8(Cl)_2 \cdot H_2O$ [20] or $Co_7(OH)_{12}(NO_3)_2 \cdot zH_2O$ [21]. In these compounds, the inorganic 2d network consists of a median layer of transition metals in Oh site, with metal vacancies at the apex of which lie two metal ions in Td symmetry. The latter are surrounded by three oxygen atoms of the median layer completed by an oxygen atom belonging to the nitrate, or a Cl atom. Owing to the chemical composition of the above compounds, which agrees with $Co_5(OH)_8(C_nH_{2n+1}COO)_2 \cdot zH_2O$ (z = 2.5 to 3.8), it can be assumed that the structure of the layers derives from the zinc analogues above. In the frame of this model structure for the cobalt(II) compound, the organic anions might be connected through carboxylate moieties to the Co(Td) metal ions, and occupy the space in between the layers with water molecules.

The n-alkyl sulfate series exhibits a somewhat different variation of the basal spacing with n. The linear dependence of d, given by $d = 14.02 + 0.88n$, agrees with a tilt angle $\theta = 46°$. In the same procedure as above, the thickness of the inorganic layer is shown to be 8.6 Å (without including water molecules), which may be compared to $Z_{n5}(OH)_8(NO_3)_2$ (7.3 Å). The difference between both values (1.3 Å) is likely due to the water molecules. For that series, chemical analysis gives a formulation $Co_7(OH)_{12}(C_nH_{2n+1}SO_4)_2 \cdot zH_2O$, showing that the packing of octahedral and tetrahedral sites in the layers differs from the zinc hydroxide nitrate. Here, 2/7 of cobalt(II) ions occupy tetrahedral sites instead of 2/5 in the zinc hydroxide nitrate.

Spectroscopy Analysis

Clearly, the lack of crystal structure resolution in these series is a limiting factor for any sound discussion of the structural changes. Some insight is given by Infrared (IR) spectroscopy, on the coordination of the metal cation by the organic ligand, the presence of water molecules, and the occurrence of hydrogen bonding for the cohesion of the stacking. In the particular case of the copper(II) monocarboxylate compounds, the spectra allow to differentiate the α and β phases, and to precise the mechanism involved during the anion exchange reaction (Fig. 3a).

For the hydrated compounds (α series), the broad absorption band in the range 3200-3600 cm^{-1} is the signature of lattice water. This band disappears with the α to β transformation, and a hydroxyl stretching mode appears at 3600 cm^{-1} [21]. For the anhydrous analogues, the absorption band at 3200 cm^{-1} may be attributed to quite strong hydrogen bonds. Further, more complex feature appears in the range 1400-1600 cm^{-1}. In the case of the hydroxide acetate $Cu_2(OH)_3(CH_3COO) \cdot H_2O$, the difference between the two bands related to the carboxylate doublet ($\Delta\nu$ = 140 cm^{-1}), suggests a bridging carboxylate [22], the two oxygen atoms of the carboxylate groups being involved, one with a
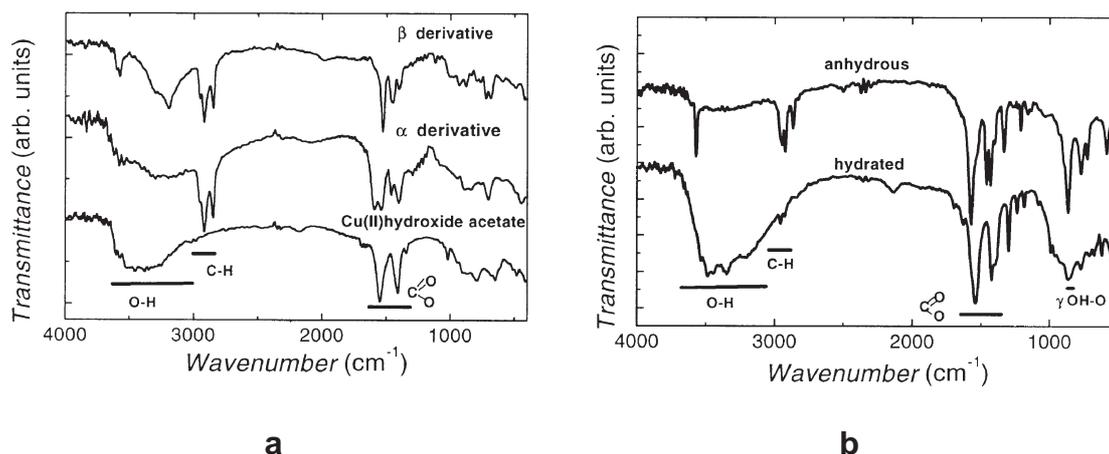

a

b

Figure 3. Characteristic infrared spectra of a) the copper(II) hydroxide monocarboxylate series, and b) the copper(II) hydroxide dicarboxylate series.

copper(II) ion, the other in a very strong hydrogen bond with neighbouring hydroxyl ion. For the exchanged compounds, this doublet is still present, and slightly shifted to 1535 cm^{-1} and 1400 cm^{-1}. Additional bands occur, in particular at 1600 cm^{-1}, in the case of the hydrated α–phases. The latter stretch vibration, together with the overlapping band at 1400 cm^{-1}, is attributed to the presence of unidentate COO groups. It is noted that the spectrum of the hydrated hydroxyacetate exhibits no band at 1600 cm^{-1}, indicating that the water contribution at this frequency is likely very weak. Thus, it is assumed that, in a first step (α–phase), two carboxylates doublets are superimposed, one with a unidentate character, the other with a bridging character. The former disappears completely at the final stage of the reaction (β–phase). The occurrence of significant structural changes is also supported by EXAFS investigations [12]. Indeed, the raw spectra shows an intense peak at 6.3 Å for the α-phase, related to the next nearest neighbor Cu-Cu distance. The magnitude of this peak is strongly decreased in the β-phase suggesting a displacement of the copper atoms from their initial linear arrangement.

In the case of the copper(II) dicarboxylate analogues, IR spectra exhibit a broad feature in the hydroxyl stretching region (3000-3600 cm^{-1}) which corresponds to lattice water, according to the water quantitative analysis. Set of super-imposed bands (Fig. 3b) is attributed to free CuO-H and CO-H hydrogen bonds. The spectra of the quasi anhydrous compounds presents only one intense free O-H band at 3560-3570 cm^{-1}. The presence of organic molecules is confirmed by several bands around 2750 cm^{-1} which are attributed to C-H vibrations. The carboxylate doublet is clearly identified at 1530-1580 cm^{-1} and 1400-1430 cm^{-1}. The first one corresponds to the C=O stretch. From the position of the band, it is likely that the carboxyl groups are bonded to copper(II). The doublet is unique, indicating that the two carboxylate functions are linked to the layers, according to the charge balance between the organic and inorganic sub-networks. Finally, a relatively strong band around 870 cm^{-1}, attributed to the out-of-plane γOH-O vibration [23], is recorded for five compounds, namely the succinic (864 cm^{-1}), adipic (864 cm^{-1}), trans-hexenedioic (873 cm^{-1}), muconic (884 cm^{-1}) and sebacic (895 cm^{-1}) acid derivatives.

On the other hand, for the cobalt(II) compounds, the presence of two coordination sites for cobalt(II) ion is pointed out from UV spectra (Fig. 4). The occurrence of intense transitions at 590 cm^{-1} ($^4T_{1g} \rightarrow {}^4A_{2g}$) and 650 cm^{-1} ($^4A_2 \rightarrow {}^4T_1(P)$) are characteristic of high spin cobalt(II) in both Oh and Td environment, respectively. The structural model proposed above by analogy with $Zn_5(OH)_8(Cl)_2 \cdot H_2O$ is thus confirmed. It consists of stacks of inorganic layers made up of cobalt(II) ions in octahedral and tetrahedral surroundings, the latter being located on each side of the median layers. The aliphatic chains are likely connected through the carboxylate moieties to the Co(Td) metal ions, and occupy the space between layers with a tilt angle with respect to the c axis.
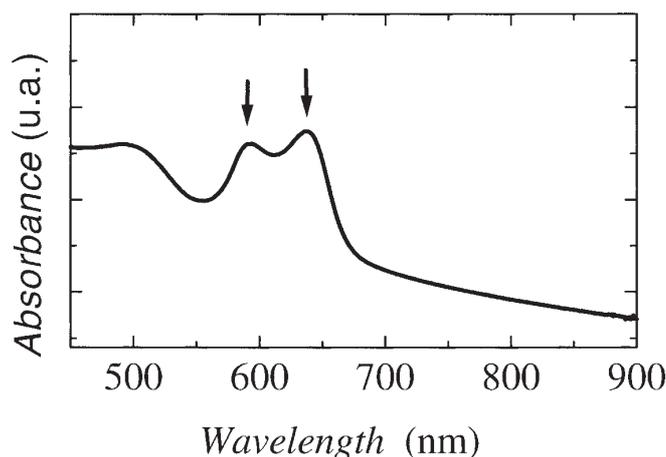

Figure 4. U. V. visible spectra of $Co_5(OH)_8(C_7H_{15}CO_2)_2 \cdot aq.$

Finally, most of these compounds exhibit a layered structure where hydroxide based sheets are interleaved by long carbon chain molecules, which are known to be more or less flexible. Then, noticeable structural modification might be expected under pressure depending on the compressibility of the carbon chain. In fact, it appears from XRD under iso-static pressure (up to 35 kbar) that the interlayer distance d_{001} is not significantly affected by the compression [24]. In turn, only the diffraction lines related to the in-plane periodicities are shifted towards smaller distances under pressure. Thus, the modification of the magnetic properties of these compounds observed under external pressure is likely mainly related to the variation of the in-plane exchange interactions, due to the modification of the exchange pathways between neighboring metal ions.

Conclusion

Molecular materials showing ferromagnetic properties have been extensively investigated during the last decade, with the aim of isolating high Tc ferromagnets with large spontaneous magnetization and hysteretic effects. These properties are shown to depend closely on the spin and lattice dimensionalities on the one hand, on the nature of the ligands favoring the exchange interactions between neighboring spin units on the other hand.

The influence of very large ligands, such as *n*-alkyl sulfate or carboxylate anions, has been studied in a series of copper(II) and cobalt(II) hybrid compounds. In such systems, the interlayer spacing is mediated by the length of the organic anion, and spectacular 3D magnetic orders may be observed for interlayer distances as large as 40 Å. The variation of the interlayer distance with *n* agrees with the stacking of *n*-alkyl chains in single (sulfate) or double
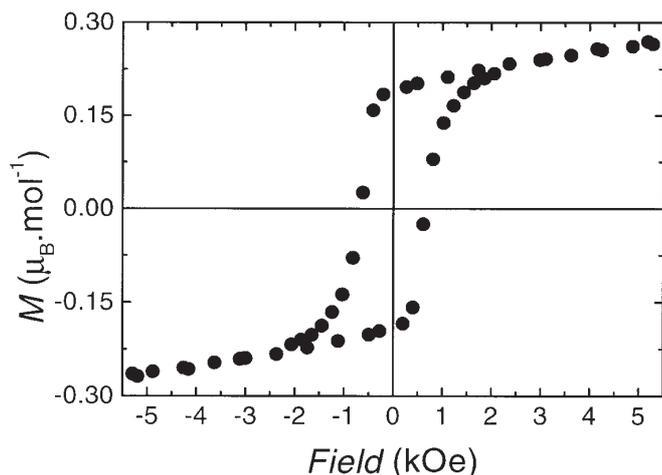
Figure 5. Magnetization versus field curve for Cu$_2$(OH)$_3$(C$_7$H$_{15}$COO) at 4 K.

(carboxylate) layers, and the tilt angle with respect to the layers. Owing to the nature of the ligands, the alkyl chains do not participate directly to the interlayer coupling but noticeable changes can occur on the magnitude of the in-plane interaction, in particular for copper(II) compounds whose behavior is closely related to structural features.

Further, it can be pointed out that, for ferromagnetic in-plane interactions, the situation depends to a large extent on the interlayer spacing. For small spacing (less than 10 Å), the interlayer interactions via hydrogen bond superexchange pathways stabilize a 3D AF order, and a metamagnetic transition is observed in low field. When the spacing is larger (large n values), the superexchange mechanisms can no longer be considered as efficient. Nevertheless, the compounds exhibit a spontaneous magnetization in zero field, with ordering temperatures ranging between 10 K (copper(II) systems) and 55 K (cobalt(II) systems), and a characteristic hysterisis cycle (Fig. 5). Such large ferromagnetic ordering temperatures and their weak dependence on the interlayer spacing can hardly be related to superexchange interactions. This behavior can only be explained by considering dipolar through-space interactions between layers. Indeed the strength of the electrostatic exchange and dipolar interaction energies between magnetic layers at a distance r apart, decrease crudely as r^{-10} and r^{-1}, respectively. Clearly, the electrostatic interaction is by far the more important contribution for small r values, but, in turn, it is negligible compared with the dipolar interaction for large distances. For interacting copper(II) ions, the turning distance given from a rough calculation is found to be $r\sim10$ Å. The influence of cooperativity for magnetic layers interacting through dipolar coupling only enables to explain the occurrence of the very long range ferromagnetism.

References

1. Burch, R. Ed. *Pillared Clays, Catalysis Today* **1988**, *2*, 1; Occelli, M.L. ; Robson, H. Eds, *Expanded Clays and Other Microporous Solids*; Van Nostrand Reinhold: New York, **1992**.
2. Watanabe, K.; Kondow, T.; Soma, M.; Onishi, T.; Tamaru, K. *Proc. Roy. Soc. London* **1973**, *A333*, 51.
3. Ouahab, L. *Chem. Mater.* **1997,** *9*, 1909.
4. Bénard, S.; Yu, P. ; Coradin, T.; Rivière, E.; Nakatani, K.; Clément, R. *Adv. Mater.* **1997,** *9*, 981.
5. Clement, R. *Science* **1993**, *263*, 658; Clément, R.; Lacroix, P.G.; O'Hare, D.; Evans, J. *Adv. Mater.* **1995**, *6*, 794.
6. Miyata, S. and Kumura, T. *Chem. Lett.* **1973**, 843.
7. Meyn, M.; Beneke, K.; Lagaly, G. *Inorg. Chem.* **1993**, *32*, 1209; Meyn, M.; Beneke, K.; Lagaly, G. *Inorg. Chem.* **1990**, *29*, 5201.
8. Prevot, V.; Forano, C.; Besse, J.P. *J. Mat. Chem.* **1999**, *9*, 155; Bujoli-Doeuff, M.; Force, L.; Gadet, V.; Verdaguer, M.; El Malki, K.; de Roy, A.; Besse, J.P.; Renard, J.P. *Mat. Res. Bull.* **1991**, *26*, 577.
9. Yamanaka, S.; Sako, T; Seki, K.; Hattori, M. *Solid State Ionics* **1992**, *53-56* , 127
10. Drillon, M.; Hornick, C.; Laget, V.; Rabu, P.; Romero, F.; Rouba, S.; Ulrich, G.; Ziessel, R. *Mol. Cryst. Liq. Cryst.* **1995**, *273*, 125; Rabu, P.; Rouba, S.; Laget, V.; Hornick, C.; Drillon, M. *J. Chem. Soc., Chem. Comm.* **1996**, 1107; Laget, V.; Rabu, P.; Hornick, C.; Romero, F.M.; Ziessel, R.; Turek, P.; Drillon, M. *Mol. Cryst. Liq. Cryst.* **1997**, *305*, 291.
11. Laget, V.; Hornick, C.; Rabu, P.; Drillon, M.; Ziessel R. *Coord. Chem. Rev.* **1998**, *178*, 1533; Laget, V.; Hornick, C.; Rabu, P.; Drillon, M. *J. Mat. Chem.* **1999**, *9*, 169.
12. Fujita, W.; Awaga, K. *Inorg. Chem.* **1996**, *35*, 1915; Fujita, W.; Awaga, K. *Inorg. Chem.* **1997**, *36*, 196.
13. Drillon, M. and Panissod, P. *J. Magn. Mat.* **1998**, *188*, 93.
14. Laget, V.; Hornick, C.; Rabu, P.; Drillon, M.; Turek, P.; Ziessel, R. *Adv. Mater.* **1998**, *10*, 1024
15. Rabu, P.; Angelov, S.; Legoll, P.; Belaïche, M.; Drillon, M. *Inorg. Chem.* **1993**, *32*, 2463.
16. Reynolds, R.C. in: Modern Powder Diffraction, Bish, R.C. ; Post, J.E. Eds., *Reviews in Mineralogy* **1989**, *20*.
17. Effenberger, H. *Z. Kristallogr.* **1983**, *165*, 127.
18. Masciocchi, N.; Corradi, E.; Sironi, A.; Moretti, G.; Minelli, G.; Porta, P. *J. Solid State Chem.* **1997**, *131*, 252.
19. Stählin, W. and Oswald, H.R. J. *Solid State Chem.* **1971**, *2*, 252.
20. Stählin, W. and Oswald, H.R. *Acta cryst.* **1970**, *B26*, 860 ; Allman, R. *Z. Kristallogr.* **1968**, *126*, 417 ; Stählin, W. and Oswald, H.R. *J. Solid State Chem.* **1971**, *3*, 256.
21. Markov, L.; Petrov, K.; Petkov V. *Thermochimica Acta* **1986**, *106*, 283.
22. Laget, V.; Drillon, M.; Hornick, C.; Rabu, P.; Romero, F.; Turek, P.; Ziessel, R. *J. Alloys and Compounds* **1997**, *262-263*, 423.
23. Nakamoto, K. in: *Infrared and Raman Spectra of inorganic and Coordination Compounds*; John Wiley & Sons: Chichester, **1986**.
24. Zotov, N.; Petrov, K.; Dimitrova–Pankova, M. *J. Phys. Chem. Solids* **1990**, *51*, 1199.
25. Levchenko, V.; Ksenofontov, V.; Dulnev, V.; Zubov, E.; Spiering, H.; Rabu, P.; Drillon, M.; Gütlich, P. in preparation.