JOURNAL OF
Materials
CHEMISTRY

# Hybrid organic–inorganic layered compounds prepared by anion exchange reaction: correlation between structure and magnetic properties†

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***Received 29th April 1998, Accepted 27th July 1998***

The synthesis, structure and magnetic properties of a series of hybrid organic–inorganic copper(II) compounds are reported. Anion exchange reactions were used to prepare layered materials made of copper(II)-based inorganic layers separated by long chain anions (*n*-alkyl sulfates or *n*-alkyl carboxylates). Contrary to classical intercalated compounds, the exchanged anion is coordinated to the metal ion. Different packing modes of the *n*-alkyl chains (mono- or bi-layers) are evidenced, depending on the bridging functions. The magnetic properties have been related to the nature of the anionic spacer and the basal spacing. When ferromagnetic in-plane interactions dominate, 3D ferromagnetic ordering is usually observed for large spacing, due to a dipolar coupling effect. For unsaturated aliphatic chains, π electrons are shown to reinforce the interlayer exchange coupling, giving a ferromagnetic ground-state.

## Introduction

Synthetic efforts to construct new microporous architectures with outstanding electronic or catalytic properties are of current interest in solid state chemistry.[1] A variety of layered host structures, such as clays, layered double hydroxides (LDH) or graphite,[2–4] has been investigated to stabilise pillared structures with metal oxide sol particles. Recently, a novel trend of investigation has been the combination of both molecular and solid state chemistry to construct hybrid organic–inorganic materials.[5] 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. Thus, striking results have been achieved in photo-induced magnetic and conducting materials[6,7] and in systems combining two basic properties, conductivity and magnetism or optics and magnetism, for instance.[8,9]

Smectite clay minerals (*e.g.* montmorillonite), in which silicate layers are negatively charged by the substitution of trivalent by divalent cations, constitute versatile host layered compounds for organic or inorganic species. A large number of such cation exchangeable layer compounds are known in which the intercalated species favour pillared structures, but it can be emphasized that no real chemical bond exists between the guest and host sub-networks. The cohesion is basically due to electrostatic interactions, and, when available, to weak hydrogen bond coupling. In contrast, anion exchangeable layered compounds are very rare, 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.[10] 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.[11,12] In such compounds, (i) the non-coordinated counter ion $A^-$ is located in between the hydroxy layers, and is easily exchanged with various anions, (ii) the stabilisation of two valence states for the metal ion induces a statistic disorder in the inorganic layers. In this way, the chemistry of simple hydroxides with botallackite-type structures appear to be more adapted for the design of hybrid materials with outstanding magnetic properties.[13–18] Recently, Yamanaka *et al.*[19] have investigated exchange reactions in the layered copper(II) compound $Cu_2(OH)_3(CH_3CO_2)\cdot H_2O$ in order to prepare highly active oxidation catalysts. It was demonstrated that the acetate anion located in the interlayer space may easily be substituted by halides, $NO_3^-$, $ClO_4^-$ or $MnO_4^-$ anions. The resulting compounds exhibit, like the parent β-$M(OH)_2$ hydroxides (M = Fe, Co, Ni), a 2D triangular array of the metal ions, with a distance between $[M(OH)_2]$ layers which is closely related to the size of the exchanged anion. Thus, the substitution of a quarter of the hydroxy ions by acetate groups induces a significant enhancement of the basal spacing from 4.65 Å for the hydroxide to 9.3 Å for the hydroxide acetate (Fig. 1). In turn, the lattice dimensions in the *a*-*b* plane remain unchanged.

Basically, the layered compounds $M_2(OH)_3X$, with M = Co, Cu and X = $NO_3^-$ or $OAc^-$ are shown to be well adapted for exchange reactions.[11,19,20] The use of large organic species (*n*-alkyl sulfates, mono- or di-carboxylates) for the substitution of X, enables one to tune the basal spacing, and accordingly

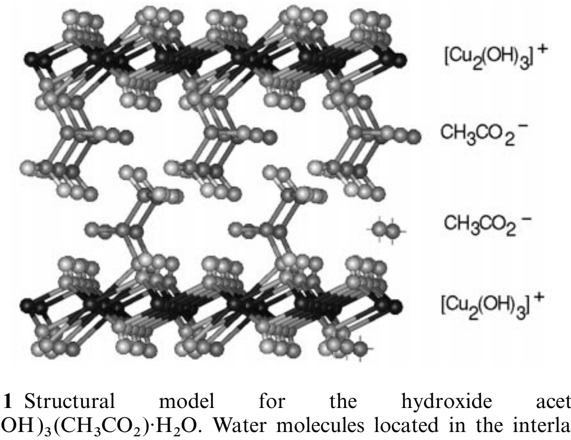

**Fig. 1** Structural model for the hydroxide acetate $M_2(OH)_3(CH_3CO_2)\cdot H_2O$. Water molecules located in the interlayer space are not represented.

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†Basis of the presentation given at Materials Chemistry Discussion No. 1, 24–26 September 1998, ICMCB, University of Bordeaux, France.

to control the magnetic dimensionality. Focus here is on the influence of large coordinating species upon the structure and magnetic properties of copper(II) basic salts. The correlations between structure and properties are detailed for the $Cu_2(OH)_3X$ series, where X is an organic (*i.e.* aliphatic chain) anionic spacer coordinating the divalent metal ion. For large interlayer spacing, it is evidenced that long range ferromagnetism is stabilised although interlayer throughbond interactions are negligible.[21] Similar results have been obtained for the cobalt(II) derivatives.[16]

## Experimental

A series of layered copper(II) compounds $Cu_2(OH)_3(X)\cdot zH_2O$ [$X = C_nH_{2n+1}SO_4^-$, $C_nH_{2n+1}CO_2^-$, $O_2C(CH_2)_nCO_2^{2-}$] has been prepared by anion exchange reactions, starting from copper hydroxide acetate. The copper hydroxide acetate $Cu_2(OH)_3(CH_3CO_2)\cdot H_2O$ is synthesised as a blue-green powder by titration of 0.1 M solution of copper(II) acetate with 0.1 M solution of NaOH for a molar ratio OH/Cu = 3 : 2, eqn. (1).

$$2\ Cu(CH_3CO_2)_2\cdot H_2O + 3\ NaOH \rightarrow Cu_2(OH)_3(CH_3CO_2)\cdot H_2O + 3\ Na^+(CH_3CO_2^-) \qquad (1)$$

The acetate ions are exchanged by aliphatic chain anions after dispersion in aqueous solution of the corresponding sodium salts at low temperature (25 °C), eqn. (2).

$$Cu_2(OH)_3(CH_3CO_2)\cdot H_2O + X^- \rightarrow Cu_2(OH)_3(X)\cdot zH_2O + CH_3CO_2^- \qquad (2)$$

The basal spacing is increased according to the size of the *n*-alkyl chains. The acetate anions are totally exchanged after a few hours, giving X-ray diffraction patterns which exhibit intense (00*l*) reflections, in agreement with layered structures. The number of (*hkl*) reflections with non-zero *h* or *k* is limited, due likely to a weak cohesion between inorganic layers favouring a turbostratic disorder. As the interplanar spacing changes discretely as the exchange reaction takes place, the disappearance of the starting materials to the benefit of the exchanged product is easily checked by powder XRD analysis. The compositions of the exchanged products were determined by elemental chemical analysis, involving the water content (Karl–Fisher method). These analyses were confirmed by thermogravimetric analysis (TGA). The comparison of the infrared (IR) spectra for the different compounds in the range 3000–3600 $cm^{-1}$ indicates a good agreement with the variation of the amount of water *z*.

By exchange with *n*-alkyl sulfate anions, two series of hybrid compounds are isolated with the general formulation $Cu_2(OH)_{4-x}(C_nH_{2n+1}SO_4)_x\cdot zH_2O$, ($x = 1 \pm 0.1$, $z = 0$ or 1). The variation of the basal spacing, plotted in Fig. 2, increases linearly with the aliphatic chain length, for both the hydrated and anhydrous series. In the case of *n*-alkyl carboxylate anions, several compounds reported in the literature[18–20] were obtained by using quite large concentrations of substituting anion (1 M). This procedure gives, in some cases, mixtures of phases as evidenced by extra reflections in the X-ray diffraction patterns. In fact, we have shown that two series may be isolated for $n = 7$, 9, 10, 12, by using lower concentrations of the substituting anion (0.2 M) and a ratio $r = X^-/OAc^- = 5:1$.[17,21] The first phase (α-type) is obtained after *ca.* 24 h exchange reaction. For additional reaction periods of 10–15 h, another phase (β-type) is observed characterized by a larger basal spacing. The stoichiometry of the latter differs essentially by its water content; the α-type phases are hydrated with the formulation $Cu_2(OH)_{4-x}(C_nH_{2n+1}CO_2)_x\cdot zH_2O$, ($x = 1 \pm 0.1$, $z = 0.3$–$0.5$), while the β-type phases are anhydrous. Further, the β phases may exhibit a $OH^-/C_nH_{2n+1}CO_2^-$ ratio lower than 3 : 1 (down to 2.8 : 1.2), indicating that after the substitution of acetate, some of the hydroxy ions have been exchanged.

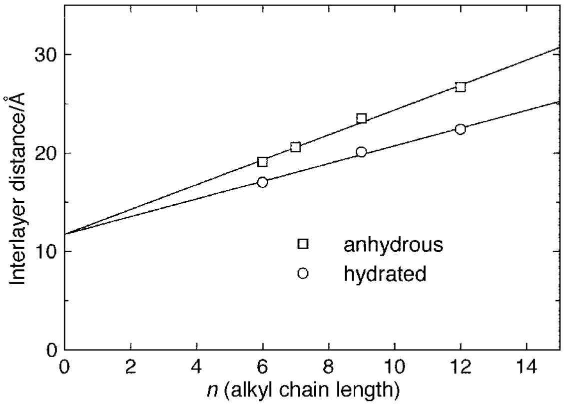

**Fig. 2** Variation of the basal spacing as a function of *n* in copper(II) *n*-alkyl sulfate compounds for the hydrated (circles) and anhydrous (squares) phases.

During the exchange process, the pH measurement appears to be particularly instructive in following the α- to β-type change (Fig. 3). Indeed, during the substitution, the pH shows a characteristic increase after *ca.* 24 h, corresponding to the stabilization of the β phase. This variation may be explained by the increase of $OH^-$ content in solution, according to the composition of the β phases. Then the decrease observed after 40 h is associated to slight dehydration of the products, decomposing into CuO, as evidenced by X-ray analysis. The α to β transformation is delayed when the ratio *r* is low, but a high value of *r* is necessary for a complete exchange and a good stability of the product in water. The best value is found to be $r = 5$ ($c = 0.2$ M) to isolate α phases and $r = 20$–$30$ for the synthesis of β phases. For short *n*-alkyl carboxylate chains ($n = 4$, 5), only the α-type phase is observed. As for the alkyl sulfate analogues, the two series of compounds exhibit a linear variation of the basal spacing with the chain length *n* (Fig. 4). Finally, the exchange reactions with *n*-alkyl dicarboxylates, $[(CH_2)_n(CO_2)_2]^{2-}$, have been investigated for $n = 1$ to 8, with a view to favouring the interaction between adjacent magnetic layers through the carboxylate functions. The variation of the basal spacing with *n* is reported in Fig. 5.

## Results and discussion

### Structure

According to the model used by Meyn *et al.*,[11] the linear variation of the basal spacing with the number of carbon

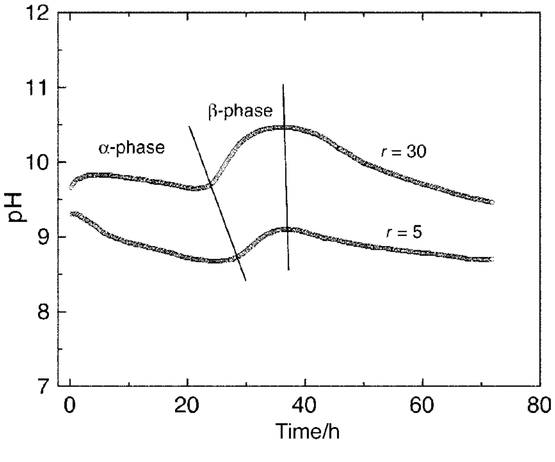

**Fig. 3** Variation of pH during the synthesis of copper(II) *n*-alkyl carboxylates, for ratios $r = X^-/OAc^- = 5$ and 30.

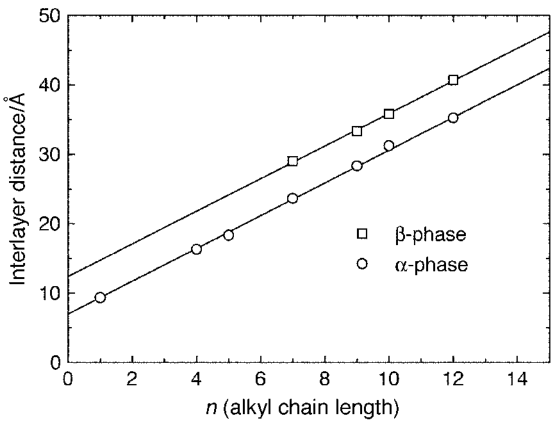

**Fig. 4** Variation of the basal spacing as a function of *n* in copper(II) *n*-alkyl carboxylates for the α and β phases.

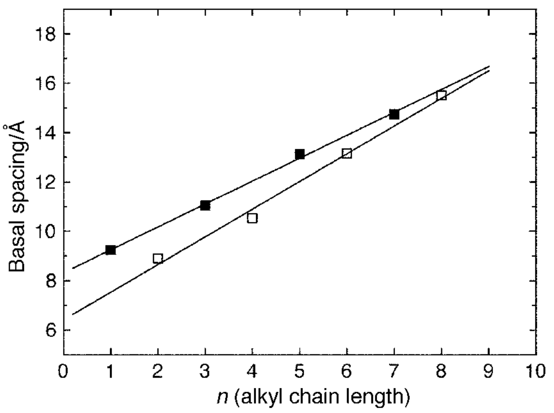

**Fig. 5** Variation of the basal spacing as a function of *n* in copper(II) *n*-alkyl dicarboxylates. Linear variations are observed for odd and even series.

atoms *n* agrees with the relationship $d(\text{Å}) = d_0 + \eta(1.27n\cos\theta)$. In this expression, $\eta$ is the number of layers of aliphatic chains in between the inorganic sheets ($\eta = 1$ or 2 for mono- or bi-layer packing, respectively), *n* is the number of carbon atoms along the chains, and $\theta$ is the angle of the chains with respect to the normal to the layers. The distance $d_0$ represents the sum of $d_2$, the size of the bridging group (sulfate for instance), $d_3$, the van der Waals distance between terminal methyl groups and inorganic layers or facing methyl groups, and $d_4$, the thickness of the inorganic layer (Fig. 6). In such a model, a *trans* conformation of the carbon atoms along the chains is assumed. Another description is based on the occurrence of a kink in the aliphatic backbone due to a *gauche* conformation in the chains. Such a situation has already been reported for long chain systems such as alkyl ammonium clays or *n*-alkylcopper(II) carboxylates.[22] For the latter, the occurrence of a *gauche* conformation for one part of the chains coordinated to the copper atoms is due to a steric effect, the all-*trans* conformation remaining the most stable. In the case of a *gauche* conformation, the variation of *d* with *n* for long chain systems (usually $n>4$) would still be linear, the tilt angle $\theta$ being eventually different from that corresponding to short chain ones. Thus, when available, the variation of *d* with *n* for a complete series would give two lines with different slopes for the short ($n<4$) and long ($n>4$) chains, in relation to the tilt angle. Further, for the long chains, an additional contribution to $d_0$ must be considered related to the chain length for $n=4$. Note however that for a homogeneous series, the molecular area of the chains has to be kept the same whatever the value of *n*. Thus a variation of $d_0$ or $\theta$ likely suggests a structural change within the inorganic layer.

Experimentally, the variation of $d=f(n)$ is well described by a monolayer packing of the chains for both alkyl sulfate series. The two straight lines (Fig. 2) converge towards $d_0 = 11.7$ Å, indicating identical thickness of the inorganic layers. For the anhydrous series, the slope of $d=f(n)$ (1.3) agrees with a perpendicular arrangement of the chains in the interlayer space, whereas the tilt angle is shown to be $\theta = 45°$ for the hydrated phases [Fig. 7(a)]. This structural modification may be explained by the presence of water molecules, as already reported for hydrated $\text{Zn}^{\text{II}}/\text{Cr}^{\text{III}}$ layered double hydroxides,[23] and related to the position of water molecules close to the inorganic layers. The variation of *d* for the hydrated phase

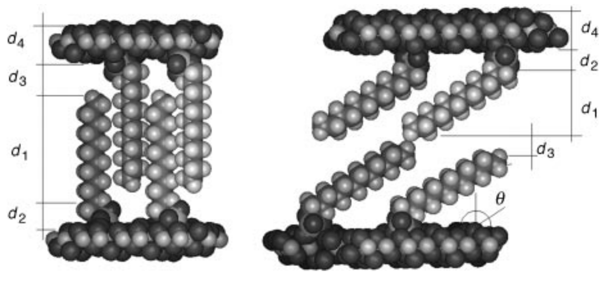

**Fig. 6** Structural model for layered *n*-alkyl compounds with mono- and bi-layer packing of the *n*-alkyl chains.

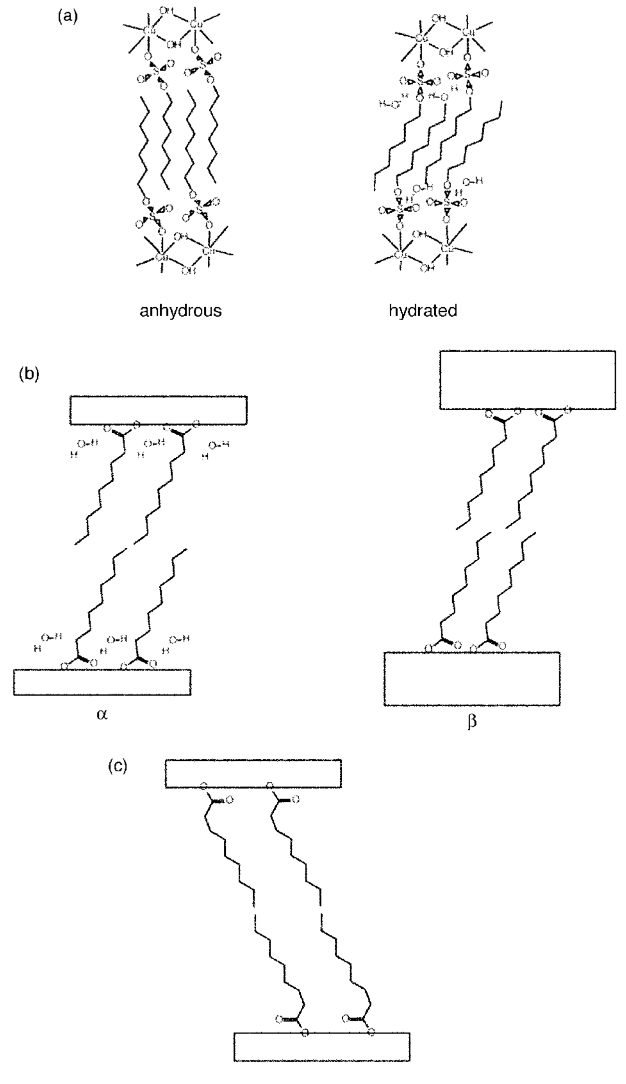

**Fig. 7** Structural model for the packing of alkyl chains in the hybrid copper(II) compounds: (a) *n*-alkyl sulfates, (b) *n*-alkyl carboxylates, (c) *gauche* conformation in *n*-alkyl carboxylates.

could be explained in the frame of a *gauche* conformation of the chains, allowing one to explain the apparent inorganic layer thickness. However, the fact that the anhydrous and hydrated series give the same $d_0$ value, and the high packing density of the aliphatic chains make the event very unlikely.

The $d = f(n)$ variations for the two alkyl carboxylate analogues (Fig. 4) indicate the same bilayer packing of the alkyl chains, with a tilt angle $\theta = 22°$. In contrast, for the all-*trans* model, the difference between $d_0$ values (about 5.4 Å) suggests different thicknesses of the inorganic layers [Fig. 7(b)]. The values of $d_4$ deduced by subtracting from $d_0$ the $d_2$ (1.2 Å) and $d_3$ (3 Å) values, are shown to be about 1.6 and 7 Å for the α and the β series, respectively. The value achieved for the former, involving copper hydroxide acetate, agrees well with the structure of copper(II) hydroxide nitrate.[24] The $d = f(n)$ variation is linear for $n$ ranging from 1 to 12, which is consistent with an all-*trans* conformation. So, a brucite-like inorganic layer may be assumed. The value obtained for the β series is much higher, in the same order as that deduced for the alkyl sulfate analogues, suggesting a clear discrepancy with the brucite-like structure. Together with the pH variation, these considerations are in favour of a topotactic exchange during the first step of the reaction (α phase) followed by a dissolution–crystallisation process (β phase). Note that the *gauche* conformation model may also give a satisfactory description of the stacking. Indeed, a bend beyond the 4th carbon atom is consistent with the experimental increase of $d_0$ compared to the α series [Fig. 7(c)]. Both series exhibit the same tilt angle $\theta$, and it can be assumed that the second part of the aliphatic chains ($n > 4$) has the same angle as the chains in the α phase. This hypothesis would also explain why the β phase occurs only for the longest chain compounds. The possible variation of the molecular area of the chains could be related to a structural transformation, in relation with the variation of the water amount.

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 IR spectroscopy on the two *n*-alkyl carboxylate series. The results, identical for all $n$ values, are detailed for $n = 7$.[25] The spectra, obtained from samples corresponding to α and β phases, are plotted in Fig. 8, and compared to that of the starting compound ($n = 1$). For the hydrated compounds (α series), the broad absorption band in the range 3200–3600 $\mathrm{cm^{-1}}$ is the signature of lattice water. This band disappears with the α to β transformation, and a hydroxy stretching mode appears at 3600 $\mathrm{cm^{-1}}$.[26] For the anhydrous analogues, the absorption band at 3200 $\mathrm{cm^{-1}}$ may be attributed to quite strong hydrogen bonds.

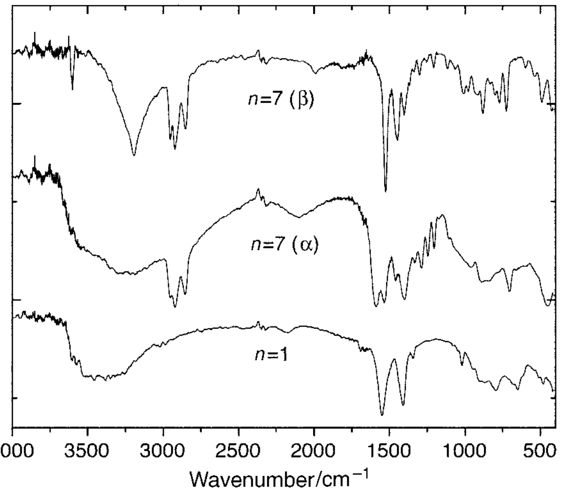

**Fig. 8** IR spectra of α- and β-phases ($n = 7$) compared to $Cu_2(OH)_3(CH_3CO_2)\cdot H_2O$.

Further, a complex feature appears in the range 1400–1600 $\mathrm{cm^{-1}}$. In the case of the hydroxide acetate $Cu_2(OH)_3(CH_3CO_2)\cdot H_2O$, the difference between the two bands related to the carboxylate doublet ($\Delta\nu = 140\ \mathrm{cm^{-1}}$), suggests a bridging carboxylate.[26] In fact, such a situation where each oxygen atom is linked to a different metal can be ruled out here, since it necessitates a charge compensation. Most likely, the two oxygen atoms of the carboxylate groups are involved, one with a copper(II) ion, the other in a very strong hydrogen bond with a neighboring hydroxy ion. For the exchanged compounds, this doublet is still present, and slightly shifted to 1535 and 1400 $\mathrm{cm^{-1}}$. Additional bands occur, in particular at 1600 $\mathrm{cm^{-1}}$, in the case of the hydrated α phases. The latter stretching vibration, together with the overlapping band at 1400 $\mathrm{cm^{-1}}$, is attributed to the presence of unidentate $CO_2$ groups. Thus, it is assumed that, in a first step (α phase), two carboxylate 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). Such structural variations are very common in copper(II) salts. Thus, while the starting compound $Cu_2(OH)_3(CH_3CO_2)\cdot H_2O$ shows a brucite-like packing of the layers, the hydroxide, $Cu(OH)_2$, exhibits a strong corrugation of the layers, mainly due to the Jahn–Teller effect. The occurrence of significant structural change is also supported by EXAFS investigations.[27] Indeed, the raw spectra show an intense peak at 6.3 Å for the α phase, related to the next nearest neighbour Cu–Cu distance. The magnitude of this peak is strongly decreased in the β phases suggesting a displacement of the copper atoms from their initial linear arrangement.

For the dicarboxylate compounds, the experimental basal spacings reported in Fig. 5 show a step-like variation corresponding to a change of $n$ parity. This effect may be related to the systematic change of the mutual orientation of the carboxylate groups. In turn, a given parity of $n$ corresponds to a linear variation of $d$. The slopes of the two straight lines are different, indicating a different tilt angle of the molecules with respect to the normal to the layers. The tilt angles are 42.9 and 25.7° for odd and even $n$, respectively. The extrapolated values of $d$ to $n = 0$ show a difference of 2 Å between the layer thickness for the odd (8.3 Å) and even (6.3 Å) series. The mean value is close to that observed for the monocarboxylate α compounds (7.0 Å).

## Magnetic properties

The magnetic properties of materials involving copper(II) ions are known to be very sensitive to any structural modification, as may be introduced by sulfate or carboxylate bridging species. As a result, great variations should be observed in the magnetic behaviour of the exchanged compounds.

The temperature dependent susceptibility for copper(II) *n*-alkyl sulfates is plotted as $\chi T$ *vs.* $T$ in Fig. 9. At high temperature, the observed value is that expected for two copper(II) ions per mole ($\approx 0.8\ \mathrm{cm^3\ K\ mol^{-1}}$). At low temperature, the decrease of $\chi T$ indicates that AF interactions dominate. Owing to the large separation between magnetic layers, 19.1 Å ($n = 6$) to 26.7 Å ($n = 12$), it can be stated that 2D short range correlations are responsible for the observed behaviours. Slight structural modifications of the layers likely explain the difference between $\chi T = f(T)$ variations. The temperature dependence of $\chi T$ for the copper(II) *n*-alkyl carboxylates is illustrated in Fig. 10 for $n = 1$ (acetate) and $n = 7$, which is representative of long chain compounds.[25] Upon cooling, the hydroxide acetate shows a constant value of $\chi T$, then a slight increase up to 1.0 $\mathrm{cm^3\ K\ mol^{-1}}$ at 10 K, suggesting weak ferromagnetic (F) intralayer interactions. At lower temperature, the drop of $\chi T$ indicates that interlayer AF interactions promote a 3D-ordered state.

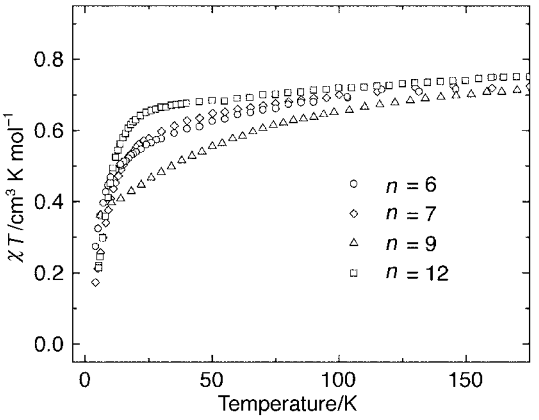

**Fig. 9** Temperature dependence of the $\chi T$ product for copper(II) *n*-alkyl sulfate compounds with increasing *n* values.

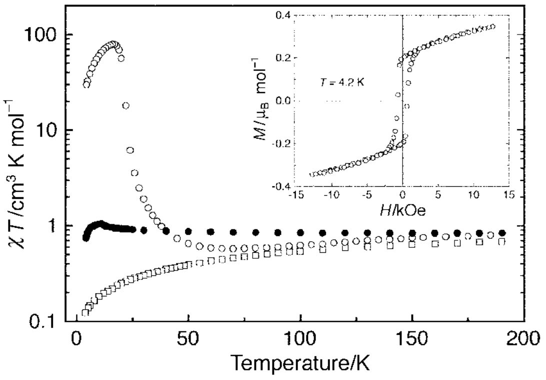

**Fig. 10** Temperature dependence of $\chi T$ for copper(II) *n*-alkyl carboxylates with $n=1$ (●), $n=7$ α (□) and $n=7$ β (○). Isothermal magnetization for the β phase is given in the inset.

Different behaviours are observed for the long chain polymorphs α and β. Whatever the *n* value, the α compounds show a decrease of $\chi T$ down to 2 K, indicating that the interactions are antiferromagnetic. In turn, the behaviour of the β series differs drastically. Upon cooling, a decrease of $\chi T$ is first observed down to a minimum at 60 K, then a very sharp increase at lower temperature, pointing towards a ferrimagnetic spin arrangement within the copper(II) layers. The very large value of $\chi T_{\max}$ is the signature of a net magnetic moment in the ground state.[17,18] The occurrence of long range ferromagnetic order is illustrated by a characteristic hysteretic effect in the $M/H$ curve at $T=4.2$ K (inset of Fig. 10). Similar behaviours are observed for the different β compounds, even for very large basal spacing (*e.g.* up to 40 Å for $n=12$). Finally, the ordering temperatures, determined with a SQUID magnetometer in an applied field of 0.5 Oe, range from 21.2 K for $n=7$ to 19 K for $n=12$, without clear relationship with the chain length.

The above structural considerations are also relevant for explaining the discrepancy in the magnetic behaviour of the two series α and β. Indeed, a structural modification of the hydroxide-based layer can induce significant changes in the distances and angle along the Cu–O–Cu bridges, and consequently in the exchange pathways, giving a change of sign (F or AF) of the interaction.[28] Moreover, the existence of different coordination sites, as already mentioned for other copper(II) hydroxy-salts,[29] may promote an uncompensated magnetic ground state, likely to be responsible for the behaviour for the β phases. At low temperature, the long range order is explained by a ferromagnetic alignment of the in-plane net moments through small inter-layer interactions. In view of the very large inter-plane distances (up to 40 Å), this coupling is understood by using a model of rigid ferromagnetic layers coupled by only dipolar interactions. In 2D ferromagnets, the spins align within correlation domains, whose size diverges exponentially in the vicinity of $T_C$. This promotes giant magnetic moments $g<S>$, and the dipolar couplings are shown to become the driving interaction mechanism between adjacent layers, even for very large distances.[30]

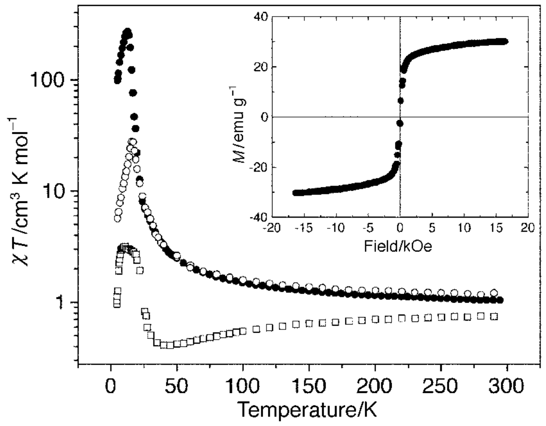

**Fig. 11** Temperature dependence of the $\chi T$ product for copper(II) saturated dicarboxylate compounds with $n=4$ (○) and $n=8$ (□), and $n=4$ unsaturated dicarboxylate (●). The field dependent magnetization of the unsaturated compound (at 4 K) is plotted in the inset.

The magnetic behaviour of the *n*-alkyl dicarboxylate compounds depends strongly on the *n* value. Among the investigated compounds, only those corresponding to $n=2$, 4 and 8 give intralayer ferro-or ferri-magnetic behaviours. The plots of the $\chi T$ product are illustrated in Fig. 11 for $n=4$ and 8. At low temperature, the short chain compound ($n=4$) exhibits an antiferromagnetic interlayer ordering (metamagnet), while the long chain compound ($n=8$) orders ferrimagnetically for $T<17$ K, as evidenced in the paramagnetic regime by the minimum of $\chi T$ at *ca.* 40 K. On the same figure, a comparison is made between the saturated (adipic acid) and unsaturated (*trans*-hexenedioic acid) $n=4$ compounds which have very close interlayer distances (10.4 and 10.2 Å, respectively). Both show a strong increase of $\chi T$, characteristic of in-plane ferromagnetic interactions, but contrary to the saturated compound, the latter exhibits a much larger divergence (factor 10), and a ferromagnetic long range ordering below 12.8 K. This one is evidenced by the variation of $M/H$ (inset of Fig. 11), exhibiting a small hysteresis effect at 4 K. This suggests that π electrons of the unsaturated chain could contribute to the interlayer exchange mechanism, in addition to through space dipolar interaction.

Finally, the magnetic study of these series of hybrid compounds shows that spectacular, and unexpected behaviours may be observed, depending on the basal spacing. When alkyl sulfate groups are coordinated to copper(II) ions, the magnetic behaviour is always antiferromagnetic. Alkyl carboxylate groups favour in turn either F or AF behaviours. The different structural and magnetic features are related to a structural modification of the inorganic magnetic layers, presumably due to Jahn–Teller effects. The influence of the solvent on this structural transformation has also been emphasized by Fujita *et al.* for $Cu_2(OH)_3L$ (L = 8-[*p*-(phenylazo)phenyl]oxyoctanoate).[31] This copper(II) exchanged salt exhibits a monolayer to bilayer transition of the organic sheets activated by soaking in acetonitrile and hot methanol. This transition is reversible and results in a magnetic transition (para- to ferro-magnet). It shows the possibility of using such organic–inorganic hybrid compounds as chemical sensors.

## Conclusion

Copper(II)-based organic–inorganic compounds have been prepared by exchange reaction, using the hydroxide acetate as starting material. It is shown that the exchangeable anion $CH_3CO_2^-$ may be substituted by large organic species (alkyl chain anions) at room temperature, through a mechanism of swelling of the inorganic network. The isolated hybrids differ from classical intercalated layered compounds, which consist of negatively (or positively) charged inorganic layers separated by counter ions. In the present compounds, the exchanged ions are coordinated to the metal(II) atom so that both subnetworks are in close interaction.

Owing to the nature of the ligands, the saturated alkyl chains do not participate directly to the interlayer coupling (contrary to unsaturated chains) but noticeable change can result in the magnitude of the in-plane interaction.

It can be pointed out that: (i) antiferromagnetic in-plane correlations promote, for large basal spacing, an AF 2D short-range order, (ii) 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 stabilise a 3D AF order, and a metamagnetic transition is observed in low field. When the spacing is made larger (large *n* values), the superexchange mechanisms can no longer be considered as efficient. Nevertheless, the compounds exhibit a spontaneous magnetization and a characteristic hysteresis cycle. The large ferromagnetic ordering temperatures and their weak dependence on the basal spacing can hardly be related to superexchange interactions. In turn, they can be explained by considering dipolar through-space interactions between layers.

Finally, this result demonstrates that the design of molecular ferromagnets may involve complementary strategies. The choice of suitable bridging ligands to optimize the overlap between magnetic orbitals and accordingly the exchange interaction is clearly the pertinent way. However, the self-assembling of magnetic layers may also promote long range magnetic correlations and, as a result, 3D ordering. To some extent, such systems are quite similar to Co/Ru or Co/Cu superlattices made of alternating magnetic and non-magnetic metal layers, even if the basic mechanism of the interactions differs. These hybrid layered compounds with tunable basal spacing thus appears promising for the design of new 3D ferromagnets.[32]

## Acknowledgements

The authors are particularly grateful to Dr. A. Skoulios for his help in discussions.

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*Paper 8/05870I*