

Copper hydroxide based organic/inorganic ferromagnets

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Abstract

Layered metal(II)-based carboxylate compounds are shown to be suitable for the design and preparation of new hybrid materials. The structure–magnetic property relationship of these kind of copper derivatives is discussed. Two series of copper(II) *n*-alkyl carboxylates are compared; one exhibits unprecedented ferromagnetic interactions for distances as far as 40 Å between the metal layers. Their properties are linked to a structural transformation of the inorganic layers from Brucite-like to Cu(OH)₂ type arrangement. © 1997 Elsevier Science S.A.

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1. Introduction

Basically, the design of 3d architectures in molecular chemistry is difficult to achieve, so that hybrid organic–inorganic compounds may be very promising for stabilizing new molecular materials such as high T_c ferromagnets. Among the layered structures, the layered transition metal hydroxide nitrates have been shown to be good examples of planar triangular magnetic systems, with basal spacing of approx. 6.9 Å [1,2]. From a magnetic point of view, 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, a metamagnetic behavior is observed, mainly driven by the inter-layer exchange interaction.

On the other hand, the layered compounds, $M_2(OH)_3X$ (with $M = Co, Cu$) in which the exchange-

able anion, $X = NO_3^-$ or OAc^- , is coordinated to the divalent metal ion through an oxygen atom O_X , are shown to be good candidates for substitution reactions [3]. The structure may be viewed as a 2d triangular network of divalent metal, made up of $[M_2(OH)_3O_X]$ layers held together through hydrogen bonds and involving the exchangeable-anion X . The in-plane metal–metal distances are very close for the different compounds (~ 3.15 Å) whereas the basal spacing (c parameter) differs according to the size of X , i.e. 6.9 Å (nitrate) and 9.3 Å (acetate). Thus, the use of large organic anions (alkylsulfates, alkylcarboxylates) for the substitution of X , enables us to tune the basal spacing from 10 Å to 40 Å and accordingly to control the magnetic dimensionality [4,5]. It has been shown recently that for large inter-plane spacing, long-range ferromagnetism is stabilized [6–8], with an unexpected hysteresis cycle, due to the leading effect of dipolar interactions [8,9].

Finally, an anionic exchange reaction has been carried out with organic radical anions, leading to the new hybrid ferromagnet $Co_2(OH)_3(p-IMB).1.6H_2O$ ($p-IMB$ = imino-nitroxide substituted benzoate

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anion), made of inorganic magnetic layers interleaved with magnetic organic species [9].

In this paper, we focus on the series of copper(II) *n*-alkyl-carboxylates. The occurrence of very long-range ferromagnetic interactions is discussed on the basis of structural findings deduced from powder X-ray diffraction and infrared spectroscopy.

2. Results and discussion

Two series of layered copper(II) compounds $\text{Cu}_2(\text{OH})_3(\text{C}_n\text{H}_{2n+1}\text{COO}) \cdot m\text{H}_2\text{O}$ were prepared according to the procedures reported elsewhere [5–9], which consist of an exchange reaction from copper hydroxide acetate powder, using the appropriate sodium salts in water. An hydrated series (noted α) and an anhydrous series (noted β) characterized by the same $\text{Cu}/\text{OH}/\text{C}_n\text{H}_{2n+1}\text{COO}$ stoichiometry have been isolated, respectively, after 1 day and 3 days of reaction.

In all cases, the $\text{Cu}_2(\text{OH})_3(\text{C}_n\text{H}_{2n+1}\text{COO}) \cdot m\text{H}_2\text{O}$ compounds exhibit intense (001) X-ray diffraction lines, in agreement with the layered-type structure of the materials (Fig. 1). As previously indicated, the copper(II) hydroxide acetate exhibits monoclinic symmetry, while the lattice parameters for longer alkyl carboxylate chains 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 inter-layer spacing (*c* parameter), while the in-plane parameters remain quasi-constant. The two different structural varieties, α and β , are observed for the

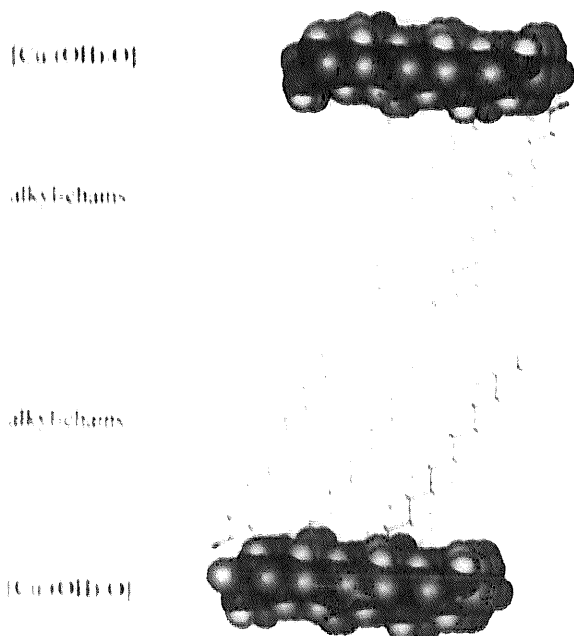


Fig. 1. Structural model for the layered copper(II) hydroxide-*n*-alkyl-carboxylates.

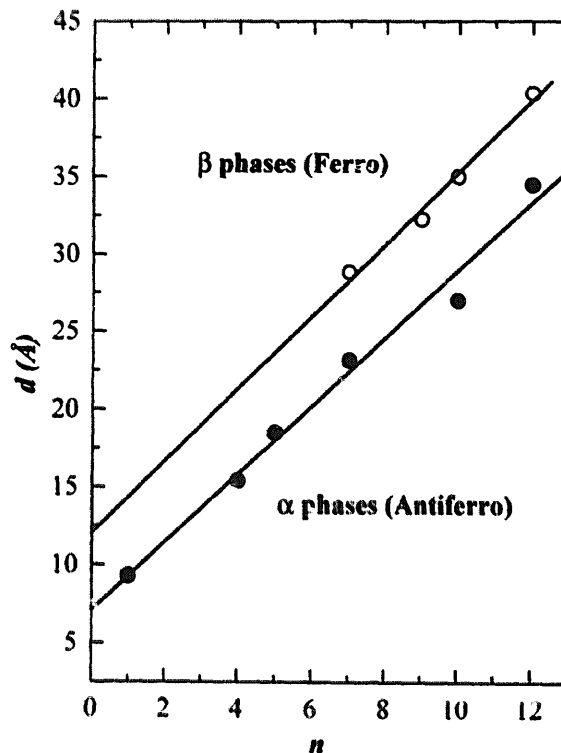


Fig. 2. Variation of the interlayer spacing as a function of *n* in $\text{Cu}_2(\text{OH})_3(\text{C}_n\text{H}_{2n+1}\text{COO}) \cdot m\text{H}_2\text{O}$.

largest *n* values. For both series, the inter-layer spacing varies linearly with the alkyl chain length (*n*), according to the relation $d(\text{\AA}) = d_0 + 2.54n \cdot \cos \alpha$ proposed by Meyn et al. [4] for hydroxide double salts (Fig. 2).

The temperature dependence of the χT product is illustrated in Fig. 3 for *n* = 7, which is representative of all the compounds. Whatever the *n* value is, the α compounds show a decrease of χT down to 2 K, denoting the antiferromagnetic character of the exchange couplings. In turn, the behavior of the β series differs drastically. Upon cooling, a decrease of χT is first observed down to a minimum at 60 K 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.

The occurrence of long-range ferromagnetic order is illustrated by a characteristic hysteresis loop in the *M*(*H*) curve at *T* = 4.2 K (inset of Fig. 3). Similar behavior is observed for the different β compounds, even for very large inter-layer spacing (e.g. up to 40 Å for *n* = 12). The ordering temperatures (*T_C*), are found to lie between 20 K and 15 K for *n* ranging from 7 to 12.

Structural investigation was completed with infrared spectroscopy measurements. The spectra obtained from samples corresponding to three stages

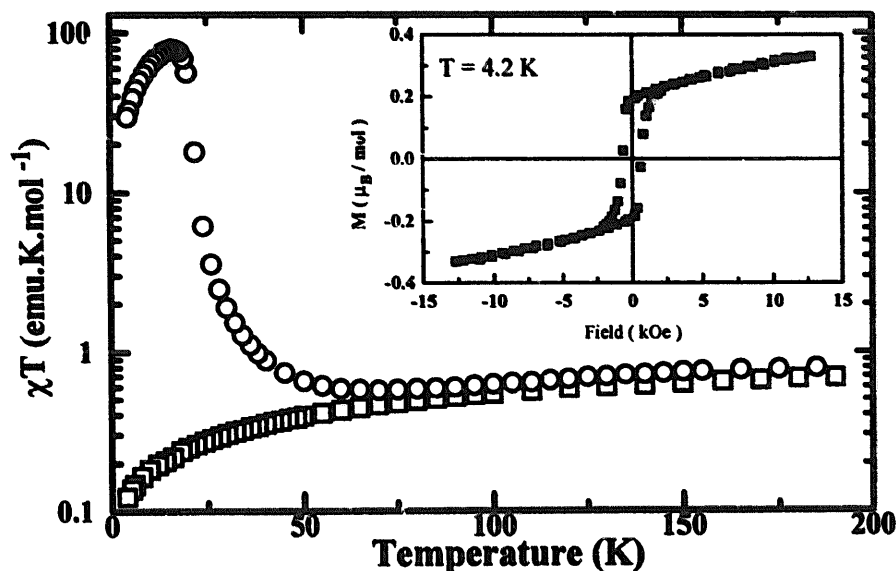


Fig. 3. Magnetic behavior of α (square) and β (circle) $\text{Cu}_2(\text{OH})_3(\text{C}_7\text{H}_{15}\text{COO}).m\text{H}_2\text{O}$.

during the exchange reaction are plotted in Fig. 4 and compared to that of the starting material.

For the hydroxide acetate and the other hydrated phases (α series), the broad absorption band in the range $3600\text{--}3200\text{ cm}^{-1}$ is the signature of lattice water. This band disappears with the dehydration process and a hydroxyl stretching mode [10] appears at 3570 cm^{-1} . For the anhydrous products, the absorption band at 3200 cm^{-1} may be attributed to quite strong hydrogen bonding as previously mentioned for copper hydroxide $\text{Cu}(\text{OH})_2$ [11a,11b,11c]. Furthermore normal modes for C–H are seen in the range $3000\text{--}2800\text{ cm}^{-1}$ for all the n -alkyl derivatives ($n > 1$). Finally, the most complex feature appears in

the range $1600\text{--}1400\text{ cm}^{-1}$. Let us first focus on the hydroxide acetate $\text{Cu}_2(\text{OH})_3(\text{CH}_3\text{COO}).\text{H}_2\text{O}$. The characteristic doublet due to the carboxylate group is measured at 1550 cm^{-1} (C=O) and 1410 cm^{-1} (C–O). Surprisingly, the difference between these two bands ($\Delta\nu = 130\text{ cm}^{-1}$) suggests a bridging carboxylate [10], each oxygen atom being linked to a different metal. In fact, such a situation could be ruled out here, since it necessitates a charge compensation and consequently a variation of the molecular weight which has never been obtained. It remains that the band positions suggest substantial electron delocalization on the two C=O bonds. An explanation could be that the two oxygen atoms of the carboxylate groups are en-

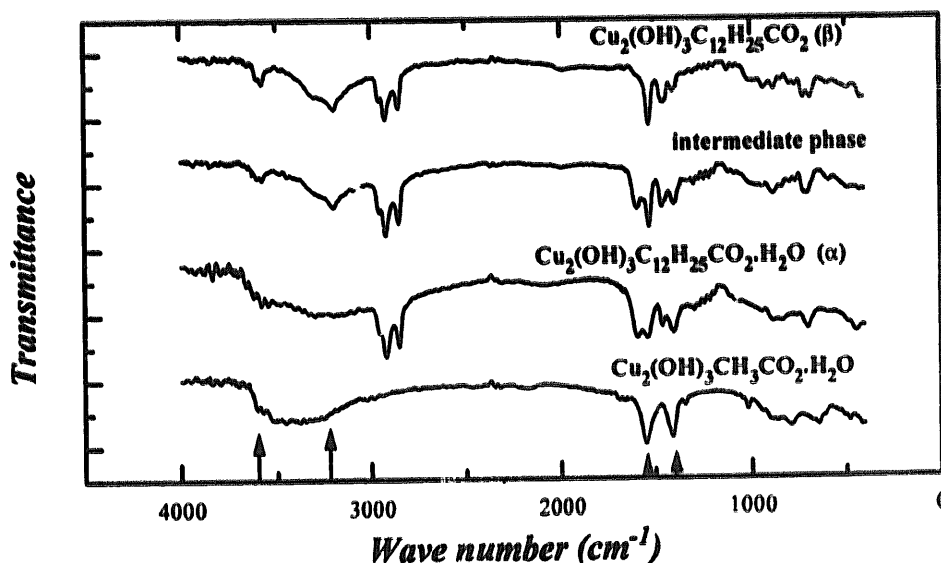


Fig. 4. Infrared spectra of α , intermediate and β phases ($n = 12$) compared to $\text{Cu}_2(\text{OH})_3(\text{CH}_3\text{COO}).\text{H}_2\text{O}$.

gaged, one with a copper(II) ion, the other in a very strong hydrogen bond with neighbouring hydroxyl ion. Clearly, it is difficult to draw a conclusion, in the absence of a crystal structure. It is well established, however, that in almost all copper hydroxy-salts, the OH^- ions are likely to be involved in strong hydrogen bond [11a,11b,11c]. When examining the results obtained for the exchanged compounds, this doublet is still present and slightly shifted at 1535 cm^{-1} and 1400 cm^{-1} . Additional bands occur, at 1465 cm^{-1} , assigned to δCH_2 scissoring and δCH_3 antisymmetric bending modes [12], and at 1600 cm^{-1} in the case of the hydrated phases (α). The latter stretch vibration, together with the overlapping band at 1410 cm^{-1} , may be attributed to the presence of unidentate COO groups. Thus it can be assumed that, in a first step (α), 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).

Note that polymorphism is very common in copper(II) salts [11a,11b,11c]. Moreover, while the starting material $\text{Cu}_2(\text{OH})_2(\text{CH}_3\text{COO})\cdot\text{H}_2\text{O}$ exhibits a quasi-Brucite arrangement of the layers [3,7,8] $\text{Cu}(\text{OH})_2$ shows a strong corrugation of the layers, mainly due to the Jahn–Teller effect [11a,11b,11c]. In addition to the IR band at 3200 cm^{-1} , another comparison with copper hydroxide can be made from the variation of inter-planar distance with n .

The slopes of the two straight lines (Fig. 2) are very close while d_0 values are found to be 7 \AA and 12.1 \AA 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 $\alpha = 25\text{--}30^\circ$ with respect to the c axis, (ii) the main difference between the two series is the (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 value $d_0 = 7\text{ \AA}$ obtained for the α series ($n = 0$, $\text{X} = \text{HCOO}^-$) is very similar to that found for $\text{Cu}_2(\text{OH})_2(\text{NO}_3)$ (6.93 \AA), whose structure consists of Brucite-like layers separated by nitrate groups [13]. The layer thickness is linked to the stacking parameter of cobalt(II) or nickel(II) hydroxides, i.e. around 4.65 \AA . In comparison, the stacking parameter in $\text{Cu}(\text{OH})_2$ is 10.59 \AA , namely approx. 5.9 \AA larger, which shed light on the difference between d_0 values deduced for α and β series (5.1 \AA).

These considerations are also relevant in explaining the observed magnetic behavior of the two series. Indeed, a structural modification of the hydroxide-based sheet 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 (ferromagnetic or antiferromagnetic) of the interaction [14]. Moreover, the existence of different coordination sites, as already mentioned for other copper(II) hydroxy-salt, [13,15] may promote a canting of magnetic sublattices, likely to be responsible of the behavior 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 \AA), this coupling is understood by using a model of rigid ferromagnetic layers coupled only by dipole interactions. In 2d ferromagnets, the spins align within correlation domains, whose size diverges in the vicinity of T_C . Thus, it stabilizes giant magnetic moments $g\langle S \rangle$ and the dipole interactions are shown to become the leading interaction mechanism between adjacent layers, even at very large distances.

3. Conclusion

The magnetic study of this series of hybrid organic–inorganic layered compounds shows that spectacular ferromagnetic or antiferromagnetic behavior may be observed, depending on the structure of copper(II) layers. The different structural and magnetic features have been related to a structural modification of the inorganic magnetic sheets, presumably due to a Jahn–Teller effect. Further experiments with model compounds are in progress in order to specify the nature of the carboxylate bond. Particular attention is being paid to the formation of a suitable product for crystal structure resolution.

Finally, it appears that self-assembled stacks of interpenetrating sublattices may favor very long-range magnetic correlations. Thus, long-range ferromagnetic order has been observed between copper(II) layers up to 40 \AA apart, illustrating the key role of the dipole interactions. In this respect, this kind of layered hybrid systems appears very promising for the design of new molecular multilayer magnets.

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