Ferro/antiferromagnetism mediated by interlayer organic spacers in layered copper(II) compounds

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Spectacular and unexpected behaviours from long-range antiferromagnetic to ferromagnetic states are observed for a novel family of layered compounds, $Cu_2(OH)_3X{\cdot}mH_2O$ (X = *n*-alkylcarboxylate) depending on the layer spacing (up to *ca.* 28 Å); in contrast, the analogous *n*-alkylsulfate derivatives are predominantly three-dimensional antiferromagnets.

Transition-metal hydroxide nitrates, $M_2^{II}(OH)_3)(NO_3){\cdot}mH_2O$ (M = Co, Ni, Cu) have been known for a long time[1] but their magnetic properties have only recently been reported.[2,3] The parent compound, $M_2(OH)_4$, has the brucite structure, consisting of two-dimensional triangular arrays of M^{II} ions octahedrally coordinated by six hydroxo ligands. The hydroxide nitrate is obtained by substituting one of the OH^- by NO_3^-; this increases the interlayer spacing from *ca.* 4.6 to *ca.* 6.9 Å. Cobalt(II) and nickel(II) hydroxide nitrates display ferromagnetic interactions while the copper(II) derivative exhibits antiferromagnetic behaviour.[2–4]

Similar substitution with *n*-alkyl-carboxylate or -sulfate[†] results in a tunable magnetic system with well defined interlayer spacings. In this case, we were able to increase the spacing to as much as *ca.* 28 Å. We report here very unexpected behaviours in the copper(II) compounds $Cu_2(OH)_3X{\cdot}mH_2O$ (X = $C_nH_{2n+1}CO_2$), which exhibit long-range antiferro- to ferromagnetic orders for increasing *n*. In contrast, when X = $C_nH_{2n+1}SO_4^-$ the compounds are antiferromagnets. It is proposed that the mechanism of the exchange between layers of ferromagnetically coupled metal ions is basically dipolar, and that the organic spacers only serve to separate the magnetic layers.

The monoclinic symmetry and unit-cell parameters of the copper(II) hydroxide acetate agree with previous findings.[7] Following the model proposed for the packing of acetate ligand in the interlayer space[5,6] (Fig. 1), the ligand is bound to the copper atom through one of its oxygen atoms, and the methyl ends from adjacent layers are packed in a zip-like fashion. Longer alkyl-chain sulfate and carboxylate derivatives have hexagonal symmetry like the parent metal hydroxide, suggesting a statistical arrangement of X.

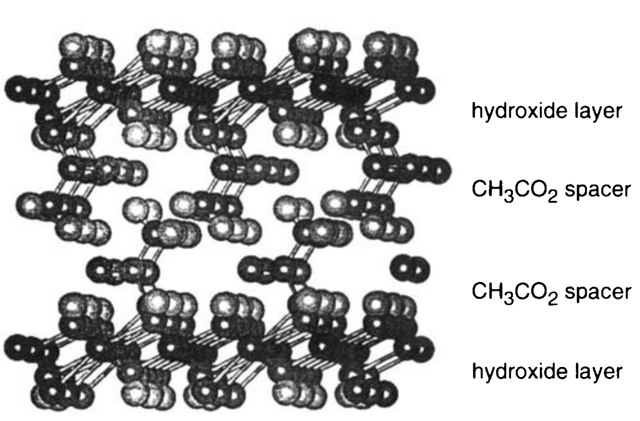

Fig. 1 Proposed structural model for $Cu_2(OH)_3(CH_3CO_2){\cdot}H_2O$ (water molecules are omitted)

For $Cu_2(OH)_3(C_nH_{2n+1}SO_4){\cdot}mH_2O$, the interlayer spacing increases linearly with the alkyl chain length (*n*), according to the relation $d(Å) = 1.27n + 12.01$. This implies that the alkyl chains are stacked in monolayers and most likely orientated normal to the layers.[5] In this configuration, the terminal methyl groups of the alkyl chains exhibit hydrophobic interactions with the hydrogen atoms of the hydroxide layers.

For $Cu_2(OH)_3(C_7H_{15}CO_2){\cdot}mH_2O$, two polymorphs, α and β, with different XRD patterns have been isolated. The difference in the interlayer spacing indicates that the alkyl chains are stacked in different ways. Using the model proposed for hydroxide double salts (HDSs)[5] strongly suggests that in the α polymorph the alkyl chains are arranged head-to-tail. On the

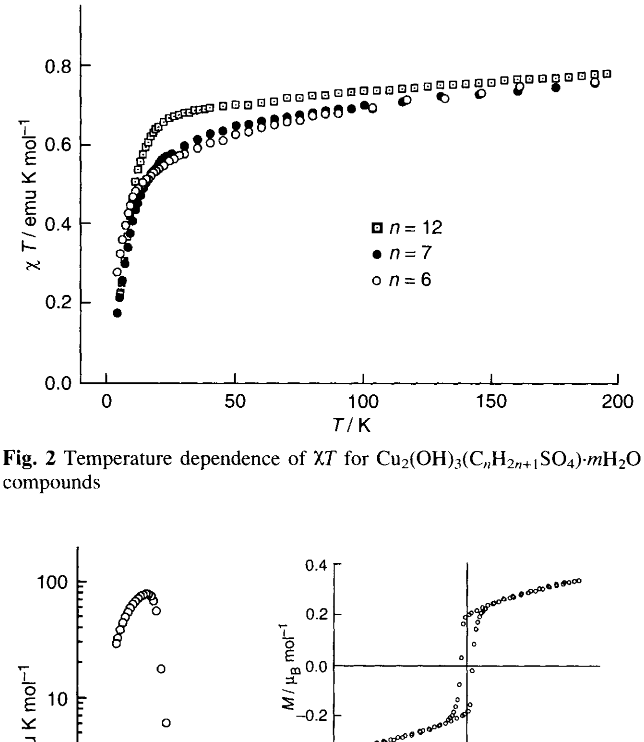

Fig. 2 Temperature dependence of χT for $Cu_2(OH)_3(C_nH_{2n+1}SO_4){\cdot}mH_2O$ compounds

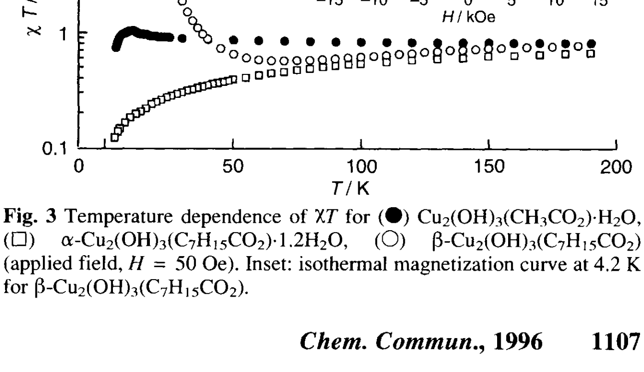

Fig. 3 Temperature dependence of χT for (●) $Cu_2(OH)_3(CH_3CO_2){\cdot}H_2O$, (□) α-$Cu_2(OH)_3(C_7H_{15}CO_2){\cdot}1.2H_2O$, (○) β-$Cu_2(OH)_3(C_7H_{15}CO_2)$ (applied field, H = 50 Oe). Inset: isothermal magnetization curve at 4.2 K for β-$Cu_2(OH)_3(C_7H_{15}CO_2)$.

Table 1 Refined crystallographic cell parameters for layered copper(II) compounds

Compound	a/Å	b/Å	c/Å	β/°	Ref.
$Cu_2(OH)_3(CH_3CO_2)\cdot H_2O$	5.289	6.131	9.305	94.1	6
$Cu_2(OH)_3(C_6H_{13}SO_4)\cdot 0.6H_2O$	5.389(2)	6.329(2)	19.214(9)	93.9(3)	This work
$Cu_2(OH)_3(C_7H_{15}SO_4)\cdot 0.7H_2O$	3.208(3)	3.208(3)	21.20(2)	Hexagonal	This work
$Cu_2(OH)_3(C_{12}H_{25}SO_4)$	3.215(3)	3.215(3)	27.42(4)	Hexagonal	This work
α-$Cu_2(OH)_3(C_7H_{15}CO_2)\cdot 1.2H_2O$	3.111(5)	3.111(5)	23.15(7)	Hexagonal	This work
β-$Cu_2(OH)_3(C_7H_{15}CO_2)$	5.102(4)	6.148(8)	28.83(4)	94.65(7)	This work

other hand, for the β polymorph the relationship given by Meyn *et al.*[5] for bilayer structures with tilted alkyl chains, $d(Å) = 2.54n\cdot\cos\alpha + 14.2$, agrees with the observed basal spacing for a tilt angle $\alpha \approx 35°$ with respect to the normal to the planes.

The magnetic properties were investigated with a Faraday-type instrument (Manics) and a SQUID magnetometer (Métronique). The temperature dependence of the susceptibility for copper(II) alkylsulfates (at 500 Oe), is plotted as χT *vs.* T in Fig. 2. At high temperatures, the observed value is that expected for two Cu^{II} (d^9, $S = 1/2$) per mole (*ca.* 0.8 emu K mol^{-1}). At low temperatures, the decrease of χT clearly indicates that an antiferromagnetic (AF) interaction dominates. Owing to the large separation between the magnetic layers, 19.2 Å ($n = 6$) to 27.4 Å ($n = 12$), two-dimensional intralayer correlation is responsible for the observed behaviour. The small difference between compounds with different alkyl chain lengths may be due to slight in-plane structural modifications and thus exchange interactions.

The temperature dependences of χT for the copper(II) alkylcarboxylate derivatives is shown in Fig. 3. Similarly to the alkylsulfates, the high temperature values are close to those expected. Upon cooling, the hydroxide acetate shows a constant value of χT, then a slight increase up to 1.0 emu K mol^{-1} at 10 K, suggesting a weak ferromagnetic (F) intralayer interaction. At lower temperatures, a drop of χT indicates that interlayer AF interactions result in a three-dimensional ordered state. The behaviours of the α and β long-chain polymorphs differ drastically. The former shows a continuous decrease of χT down to 4 K, indicating the predominance of short-range AF interactions. On the other hand, the β-form is characterized by a decrease of χT upon cooling, a minimum around 60 K and a very strong increase at lower temperatures. The very large value of χT_{max} ($T = 16$ K) is clear evidence that a net magnetic moment is stabilized at low temperature. At $T = 4.2$ K, the occurrence of a characteristic hysteresis loop in the $M = f(H)$ plot ($M_R = 0.19\ \mu_B\ mol^{-1}$, $H_C = 690$ Oe) indicates the existence of long-range ferromagnetic order between copper(II) layers (Fig. 3).

The magnetic study of this series of hybrid compounds shows that spectacular and unexpected behaviours are observed, depending on the basal spacing. When alkylsulfate groups are coordinated to copper(II) ions, the magnetic behaviour is always antiferromagnetic. On the other hand, alkylcarboxylate groups show either F or AF behaviour, depending on the exchangeable anion and the stacking mode in the interlayer space. It has been demonstrated for copper(II) exchange-coupled systems[8] that slight modifications of Cu^{II}–Cu^{II} oxo bridges is likely to be responsible for changes in intralayer couplings.

Concentrate now upon β-$Cu_2(OH)_3(C_7H_{15}CO_2)$ which exhibits the largest basal spacing ($d = 28.7$ Å). In the paramagnetic region, the variation of χT is characteristic of a low-dimensional ferrimagnet, 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. Clearly, the long-range interlayer interaction cannot be understood in a simple way, by means of the concept of orthogonality of the magnetic orbitals. Moreover, the alkyl chains coordinated to copper(II) ions do not participate directly in the interlayer interaction, and their presence makes hydrogen-bond effects negligible. Thus, a model of rigid ferromagnetic layers coupled by dipolar interactions only, may explain the stabilization of a ferromagnetic ground state.[4] In some ways, such a system is quite similar to Co/Ru or Co/Cu superlattices consisting of alternating magnetic and non-magnetic metal layers, even if the basic mechanism of the interactions differs. Such layered compounds with tunable basal spacing appear thus to be very promising for the design of new three-dimensional ferromagnets.[9,10] Further structural and magnetic investigations are in progress.

Footnote

† *Synthesis*: $Cu_2(OH)_3(CH_3CO_2)\cdot H_2O$ was prepared by slow titration of 50 ml of copper acetate (0.2 mol dm^{-3}) with 75 ml of NaOH (0.2 mol dm^{-3}) (OH:Cu = 1.5:1) at 60 °C.[5] The blue-green precipitate was filtered as soon as the mixture was cooled to room temp. and washed with ethanol and air-dried at 40 °C. Alkylsulfate derivatives were prepared by anion exchange from copper hydroxide acetate monohydrate[5] dispersed in a 0.1 mol dm^{-3} aqueous sodium alkylsulfate solution (Na:Cu = 1.5:1). After stirring for 2 d, the suspension was filtered and the procedure repeated. $Cu_2(OH)_3(C_nH_{2n+1}SO_4)\cdot mH_2O$ for $n = 6, 7, 12$, have been isolated. $Cu_2(OH)_3(C_7H_{15}CO_2)\cdot mH_2O$ was obtained similarly with 0.2 mol dm^{-3} sodium caprylate, $C_7H_{15}CO_2Na$, solution (Na:Cu = 2:1). Two compounds with distinct interlayer spacing were isolated after 1.5 and 4 d stirring, respectively. We refer to these as α and β, with c values of 23.15 and 28.83 Å, respectively. The chemical compositions of the samples, determined by elemental analyses, are given in Table 1. The purity of the samples and the absence of starting materials was verified by XRD.

Powder XRD patterns were collected at room temperature using a D500 Siemens diffractometer (Co-Kα_1 = 1.78897 Å). Strong and sharp (001) reflections for all the compounds confirm their layered structures.[5,6] The refined crystal cell parameters (Table 1) indicate that the interlayer spacing depends closely on the length of the alkyl group.

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