Dc and ac magnetic properties of the two-dimensional molecular-based ferrimagnetic materials $A_2M_2[Cu(opba)]_3 \cdot n$solv [$A^+$ = cation, M^{II} = Mn^{II} or Co^{II}, opba = *ortho*-phenylenebis(oxamato) and solv = solvent molecule]

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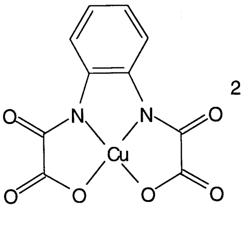
This paper is devoted to a thorough study of the magnetic properties, both in the dc and ac modes, of two-dimensional ferrimagnetic materials. The general formula of the compounds, abbreviated as $A_2M_2Cu_3$, is $A_2M_2[Cu(opba)]_3 \cdot n$solv where A^+ stands for a counter cation (radical cation, alkali-metal or tetraalkylammonium), opba is *ortho*-phenylenebis(oxamato), M^{II} is Mn^{II} or Co^{II}, and solv is a solvent molecule (Me_2SO or H_2O). The dc magnetic susceptibility data for all compounds down to *ca.* 50 K are characteristic of two-dimensional ferrimagnets. In the $A_2Mn_2Cu_3$ series, three classes of compounds have been distinguished. Class I has a unique representative, $AV_2Mn_2Cu_3$, where AV^+ is the radical cation 2-(1-methylpyridinium-4-yl)-4,4,5,5-tetramethylimadozolin-1-oxyl-3-oxide, the structure of which has already been solved. This compound is a magnet with T_c = 22.5 K. Class II corresponds to compounds with large cations (tetraethyl- and *n*-tetrabutylammonium). They also behave as magnets with T_c around 15 K. Class III corresponds to compounds with small cations (alkali-metal ions and tetramethylammonium). They behave as metamagnets with a long-range antiferromagnetic ordering in zero field around 15 K, and a field-induced ferromagnetic state. The critical fields are of the order of 0.15 kOe. All the $A_2Co_2Cu_3$ compounds are magnets with T_c around 30 K. Furthermore, the cobalt derivatives show a very strong coercivity, with coercive fields of several kOe at 5 K. They also display a pronounced magnetic after-effect in the ordered phase. In the course of this work several peculiar features have been observed. In particular, the $A_2Mn_2Cu_3$ compounds have been found to present weak but significant negative out-of-phase ac magnetic signals at temperatures just above T_c. All the observed phenomena are discussed and, in particular, a mechanism for the long-range ordering in these two-dimensional compounds has been proposed.

For more than a decade, one of our main fields of research has dealt with the design of molecular-based magnets and the study of their physical properties. The very first compounds of this kind were described in 1986 by Miller *et al.*,[1,2] and by our group.[3,4] Since these pioneering results, quite a few research groups have initiated some activity along this line, and a large number of molecular-based materials exhibiting a spontaneous magnetization below a certain critical temperature have been reported.[3–10] In many cases these compounds contain two kinds of spin carriers, either two different metal ions,[11–20] or a metal ion and an organic radical.[21–28] In at least two cases three spin carriers were involved.[29–31] Other very interesting magnetic compounds, at the frontier between molecular and solid-state chemistry, have also been reported.[32–34] Furthermore, several conferences have been devoted to this subject in recent years.[35–37]

The synthetic approach we have advocated to design molecular-based magnets is *via* heterobimetallic compounds. This approach consists of designing low-dimensional heterobimetallic species showing ferrimagnetic behaviour, and of assembling them within the crystal lattice in a ferromagnetic fashion. The ferrimagnetic behaviour arises from antiferromagnetic interactions between different spin carriers. We first focused on one-dimensional,[19,38,39] then on two-dimensional ferrimagnets.[12,20] The one-dimensional compounds are synthesized by reacting a dianionic copper(II) precursor such as $[Cu(opba)]^{2-}$:



where opba is *ortho*-phenylenebis(oxamato), with a divalent metal ion, M^{II}, in 1:1 stoichiometry. Two-dimensional compounds may be also obtained by reacting the dianionic precursor with a divalent metal ion, but in 2:3 stoichiometry and in the presence of two equivalents of a non-coordinating cation A^+. This affords compounds of formula $A_2M_2[Cu(opba)]_3 \cdot n$solv where solv is a solvent molecule. Many types of cations A^+ may be utilized, including alkali-metal, simple organic cations such as tetraalkylammonium, as well as radical cations. In one case, involving the radical cation 2-(1-methylpyridinium-4-yl)-4,4,5,5-tetramethylimidazolin-1-oxyl-3-oxide (AV^+), the crystal structure of the compound was solved.[29,30] This structure, shown in Fig. 1, consists of two perpendicular and fully interlocked networks of honeycomb-like layers. In this compound the interlocking arises from the bridging ability of the radical cation which bridges two Cu^{II} ions belonging to perpendicular layers. Since all the other A^+ cations used in this work lack any coordination ability, their structure is probably that of a single network of parallel honeycomb layers, with the A^+ cations situated between the layers.

In preceding papers we reported on the magnetic properties of some of these two-dimensional compounds, exclusively in the dc mode.[12,29–31] Here, we present a detailed investigation of the magnetic properties in both dc and ac modes. We will focus on two series of compounds, with M^{II} = Mn^{II} and Co^{II}, respectively. For convenience, all the compounds of formula $A_2M_2[Cu(opba)]_3 \cdot n$solv are abbreviated to $A_2M_2Cu_3$. The nature and the number of solvent molecules present in the structure, as deduced from chemical analyses, are specified in Tables 1 and 2.

Experimental

Syntheses

Solvents and reagents were obtained commercially, and were used without further purification. The ligand *ortho*-phenylene-

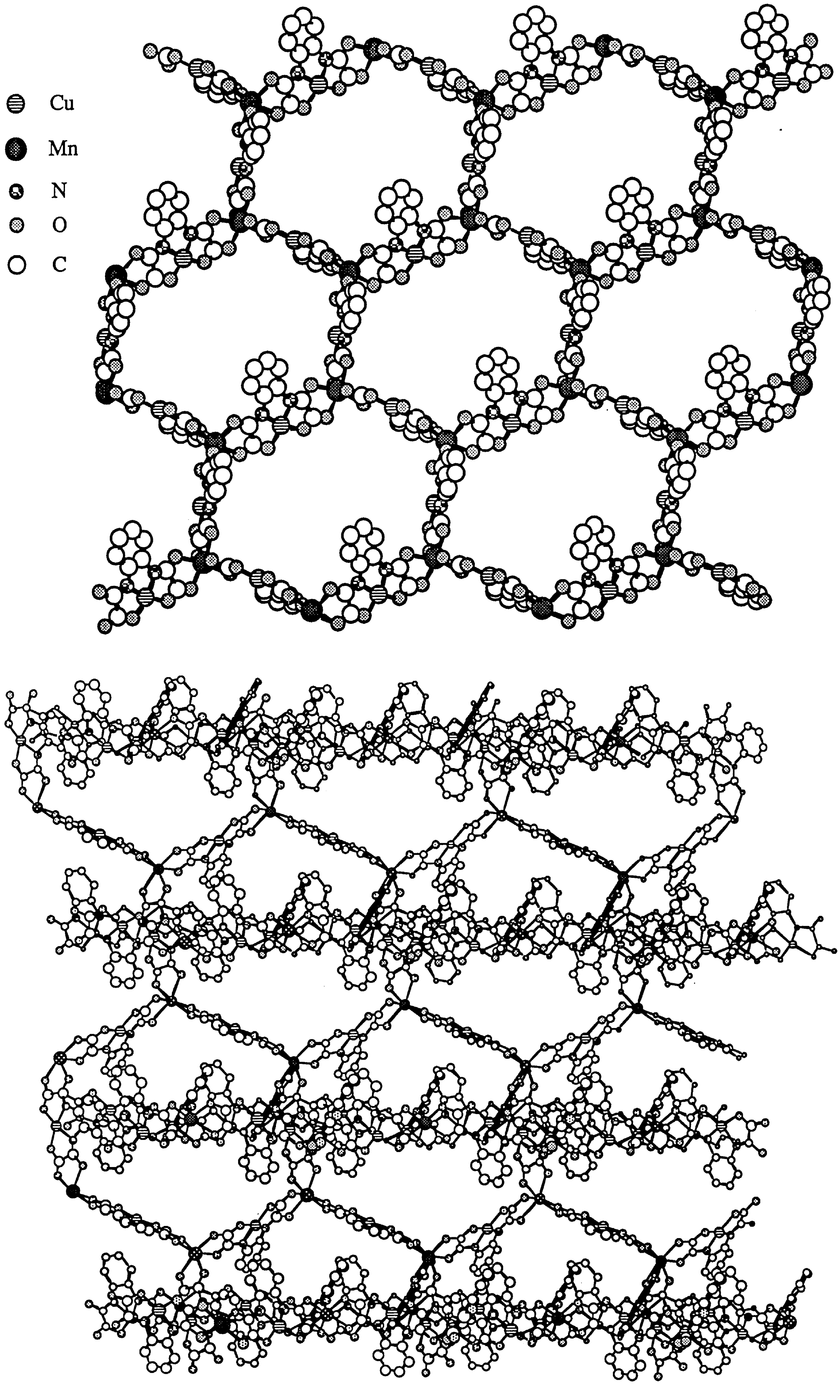


Fig. 1 Structure of $AV_2Mn_2Cu_3$. (Top) view of a honeycomb-like layer. (Bottom) view showing the interpenetration of the two perpendicular networks (reproduced with permission from ref. 29 and 30).

Table 1 Some characteristic temperatures (K) for the magnetic properties of the $A_2Mn_2Cu_3$ materials

	dc mode	ac mode	
	$\chi_M T^a$	$\chi'_M{}^b$	$\chi''_M{}^b$
class I			
$A^{\cdot}{}_2Mn_2[Cu(opba)]_3 \cdot 2Me_2SO \cdot 2H_2O$	115	23	22.5
class II			
$(NEt_4)Mn_2[Cu(opba)]_3 \cdot 4Me_2SO \cdot 2H_2O$	125	15.5	15.5
$(NBu_4)Mn_2[Cu(opba)]_3 \cdot 4Me_2SO \cdot 2H_2O$	125	15	15
class III			
$Na_2Mn_2[Cu(opba)]_3 \cdot 11Me_2SO \cdot 10H_2O$	125	15	
		5.5	5.5
$K_2Mn_2[Cu(opba)]_3 \cdot 11Me_2SO \cdot 10H_2O$	120	14	
		7.5	6
$(NMe_4)_2Mn_2[Cu(opba)]_3 \cdot 4Me_2SO \cdot 2H_2O$	125	14	
		8	

[a]Temperature for minimum of $\chi_M T$. [b]Temperature for maximum of χ'_M or χ''_M.

Table 2 Some characteristic temperatures (K) for the magnetic properties of the $A_2Co_2Cu_3$ materials

	dc mode	ac mode	
	$\chi_M T^a$	$\chi'_M{}^b$	$\chi''_M{}^b$
$Na_2Co_2[Cu(opba)]_3 \cdot 6Me_2SO \cdot 4H_2O$	—[c]	31	31
$K_2Co_2[Cu(opba)]_3 \cdot 12Me_2SO \cdot 3H_2O$	—[c]	32.5	32.5
$Cs_2Co_2[Cu(opba)]_3 \cdot 5Me_2SO \cdot 4H_2O$	—[c]	32.5	32.5
$(NMe_4)_2Co_2[Cu(opba)]_3 \cdot 7Me_2SO \cdot H_2O$	—[c]	33	32.5
$(NBu_4)_2Co_2[Cu(opba)]_3 \cdot 6Me_2SO \cdot H_2O$	95	29	28.5

[a]Temperature for minimum of $\chi_M T$. [b]Temperature for maximum of χ'_M or χ''_M. [c]The magnetic susceptibility data were not measured above 70 K.

bis(ethyloxamate), H_2Et_2opba, was synthesized as previously described.[12,39] The synthesis of $AV_2Cu(opba) \cdot H_2O$ and $AV_2Mn_2[Cu(opba)]_3 \cdot 2Me_2SO \cdot 2H_2O$ were also performed as previously described.[29,30] On the other hand, the syntheses of the other precursors $A_2Cu(opba) \cdot n$solv and ferrimagnetic materials $A_2M_2[Cu(opba)]_3 \cdot n$solv were slightly modified. A typical synthesis of a precursor, $(NBu_4)_2Cu(opba)$, is as follows: an aqueous solution of NBu_4OH (8.77 g, 40% m/m, 13.5 mmol) was added dropwise, with rapid stirring, to a solution of H_2Et_2opba (2.92 g, 3.25 mmol) and $CuCl_2 \cdot 2H_2O$ (0.55 g, 3.23 mmol) in methanol (100 ml). Initially, a green precipitate was formed, but upon continued addition of the base this redissolved to give a blue–violet solution. The reaction mixture was stirred for 5 min, filtered, and the solvent removed under reduced pressure to give the crude product as an oil, which slowly crystallized. Recrystallization from acetonitrile gave violet needles of $(NBu_4)_2Cu(opba)$, which were collected by filtration and dried under vacuum (1.95 g, 76%). The preparation of $A_2Cu(opba)$ precursors with other organic cations (NMe_4^+ and NEt_4^+) was the same but using the appropriate hydroxides. For the alkali-metal cations, Na^+, K^+ and Cs^+, water was added as a co-solvent to aid the solubility of the precursors (methanol–water, 80/20 v/v).

A typical example of the synthesis of a ferrimagnetic material, that of $(NBu_4)_2Mn_2[Cu(opba)] \cdot 4Me_2SO \cdot 2H_2O$, is as follows: $(NBu_4)_2Cu(opba)$ (0.2469 g, 0.449 mmol) was dissolved in Me_2SO (2 ml), which gives a violet solution to which was added $Mn(MeCO_2)_2 \cdot 4H_2O$ (0.059 g, 0.241 mmol). The resulting blue solution was filtered, and allowed to stand. After one day a microcrystalline product had formed. This was collected by filtration, washed with Me_2SO, dried under vacuum for 4 h, and stored at −18 °C. All the other derivatives were synthesized by a similar procedure. It is probably worth specifying here that for the $A_2Mn_2[Cu(opba)]_3 \cdot n$solv derivatives the effect of concentration upon the reaction is crucial. If the solution is too concentrated, Me_2SO solvated manganese(II) acetate appears in addition to the expected compound whereas if the solution is too dilute, no compound is obtained, Mn^{II} being slightly base sensitive, with decompositions before or during the crystallization, producing an insoluble brown impurity. For cobalt derivatives, the effect of concentration is not so crucial, although if the solution is too dilute precipitation will take longer.

Chemical analyses of all elements, except oxygen, were carried out and satisfactory results were obtained. In particular, the ratio Cu/M (M = Mn or Co) was found to be 1.5 ± 0.04 for all the compounds. On heating the solvent molecules are removed, which usually leads to an increase of the critical temperatures.[12] However, the resulting compounds seem to be poorly crystallized, so we discuss them no further.

Magnetic measurements

These were carried out with a Quantum Design MPMS-5S SQUID magnetometer, working in both dc and ac modes between 2 and 300 K, and from 0 to 50 kOe.

$A_2Mn_2[Cu(opba)]_3 \cdot n$solv compounds

We can distinguish three classes of $A_2Mn_2Cu_3$ compounds, namely: class I containing a unique representative with AV^+, class II where A^+ is a large cation (NEt_4^+ or NBu_4^+) and class III where A^+ is a small cation (Na^+, K^+ or NMe_4^+). Independently of their magnetic properties, it became evident over the course of this work that not all these materials had the same stability. While compounds of classes I and II were stable for over a year at room temperature compounds of class III were found to gradually decompose. At room temperature this decomposition is noticeable within a few hours of their removal from the mother-liquor, and was apparently complete within a matter of a day and was detected as a colour change from blue to purple. Storing the samples in the cold, however, extends their lifetime sufficiently for physical studies to be performed. The study of the magnetic properties of the compounds after decomposition very strongly suggests that a mixture of a chain compound $MnCu(opba) \cdot n$solv[12,39] and the isolated precursor $A_2Cu(opba)$ was obtained. It is sufficient to point out that compounds of class III seem to be thermodynamically unstable with respect to the breakdown of the planar structure into chains and residual non-coordinated copper precursors. The Rb^+ and Cs^+ compounds were found to be so unstable that they could not be studied.

Dc magnetic properties. Both the temperature and field dependences of the dc magnetic responses were investigated. The temperature dependences may be represented in the form of the $\chi_M T$ *vs.* T plots, where χ_M is the dc molar magnetic susceptibility and T the temperature. The $\chi_M T$ *vs.* T plot for $AV_2Mn_2Cu_3$ has already been investigated in detail.[29,30] All the other compounds behave in a similar way down to *ca.* 30 K. At room temperature, $\chi_M T$ is *ca.* 8.1 emu K mol^{-1}, which is slightly lower than expected for isolated spin carriers. Then $\chi_M T$ decreases smoothly as the temperature is lowered, reaches a rounded minimum around 120 K, then increases very abruptly at lower T to a very large maximum value around 15 K. This maximum value of $\chi_M T$ is roughly twice as large for compounds of class II than for compounds of class III. A typical example, that of $(NBu_4)_2Mn_2Cu_3$, is shown in Fig. 2. The minimum in the $\chi_M T$ *vs.* T plot reveals antiferromagnetic interactions between nearest-neighbour metal ions without correlation length, and the huge increase of $\chi_M T$ at low temperature is due to the increase of the correlation length with the S_{Mn} spins of Mn^{II} ions aligned along the field direction and the S_{Cu} spins of Cu^{II} ions aligned along the opposite direction.

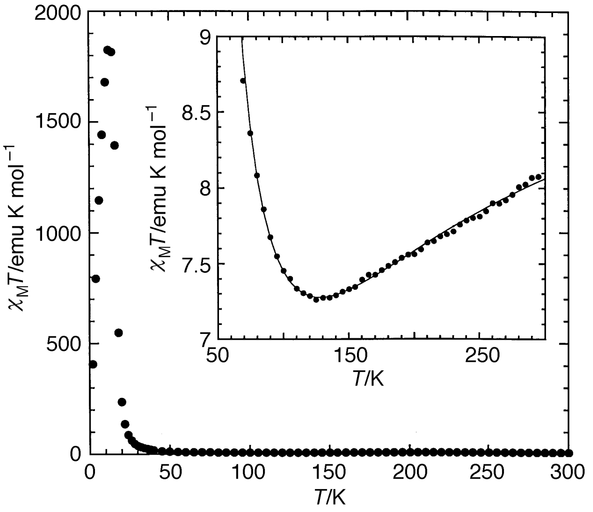


Fig. 2 $\chi_M T$ *vs.* T plot for $(NBu_4)_2Mn_2Cu_3$. Black dots represent the experimental data, and the full line represents the calculated curve in the 50–300 K temperature range, using the high-temperature expansion approach (see text). The insert emphasizes the minimum of $\chi_M T$ characterizing the ferrimagnetic behaviour.

Recently, we developed two theoretical approaches of the thermodynamical properties of $A_2Mn_2Cu_3$ two-dimensional compounds, the former based on a high-temperature expansion and the latter on a Monte Carlo simulation.[40] In both approaches $S_{Mn} = 5/2$ is treated as a classical spin and $S_{Cu} = 1/2$ is treated as a quantum spin. The high-temperature expansion was developed up to eleventh order in J/kT where J is the interaction parameter occurring in the spin-Hamiltonian of the form $-JS\boldsymbol{S}_{Mn}\cdot\boldsymbol{S}_{Cu}$, which led to the following expression:

$$\chi_M T = \frac{N\beta^2}{3k}\Big\{2g_{Mn}{}^2S^2 + \frac{9}{4}g_{Cu}{}^2 - 6g_{Mn}g_{Cu}SK + 2\left(g_{Mn}{}^2S^2 + g_{Cu}{}^2\right)K^2 - \frac{2}{3}g_{Mn}g_{Cu}SK^3 - \frac{3}{5}g_{Cu}{}^2K^4 - \frac{8}{45}g_{Mn}g_{Cu}SK^5 + \left(\frac{2}{25}g_{Mn}{}^2S^2 + \frac{533}{945}g_{Cu}{}^2\right)K^6 + \frac{2}{945}g_{Mn}g_{Cu}SK^7 - \left(\frac{4}{315}g_{Mn}{}^2S^2 + \frac{5683}{14175}g_{Cu}{}^2\right)K^8 - \frac{4}{525}g_{Mn}g_{Cu}SK^9 + \left(\frac{524}{99225}g_{Mn}{}^2S^2 + \frac{19912}{66825}g_{Cu}{}^2\right)K^{10} + \frac{7108}{5457375}g_{Mn}g_{Cu}SK^{11}\Big\}$$

with: $S = [S_{Mn}(S_{Mn}+1)]^{\frac{1}{2}}$ and $K = -JS/2kT$ where k is the Boltzmann constant and β the electron Bohr magneton. An excellent agreement, as shown in Fig. 2, was found between the experimental data down to 50 K and calculated data for $J = -33.1$ cm^{-1}, and the local Zeeman factors $g_{Mn} = 2.0$ and $g_{Cu} = 2.2$.

Below *ca.* 30 K the χ_M *vs.* T curves differ between classes I–III. $AV_2Mn_2Cu_3$ shows a break in the χ_M *vs.* T plot at $T_c = 22.5$ K, corresponding to a long-range ferromagnetic ordering. Compounds of class II behave qualitatively in a similar way, but with T_c around 15 K. On the other hand, the magnetic behaviour of class III compounds is more complex. At very low field χ_M shows a maximum around 15 K, suggesting that the long-range ordering is antiferro- rather than ferro-magnetic. This maximum of χ_M vanishes when applying a magnetic field above *ca.* 0.15 kOe, which is characteristic of metamagnetic behaviour (Fig. 3).

The field dependence of the magnetization, $M = f(H)$, at 2 K for $AV_2Mn_2Cu_3$ has already been reported.[29,30] The magnetization first increases very rapidly, as expected for a magnet, then instead of reaching a saturation value at low field, increases smoothly as H increases, and does not reach saturation even at 200 kOe. This peculiar behaviour was attributed to the progressive decoupling of the radical spin with respect to the $Mn_2[Cu(opba)]_3$ skeleton spin. For all the compounds of classes II and III the magnetization at 2 K first increases very rapidly, then reaches a saturation value of *ca.* 7 μ_B. This value corresponds well to that expected if all the S_{Mn} spins are oriented along the field direction, and all the S_{Cu} spins oriented along the opposite direction. An interesting feature is that $\partial M/\partial H$ is not at a maximum at exactly zero field, but at a field which depends on temperature. For instance, for $(NBu_4)_2Mn_2Cu_3$, the maximum of $\partial M/\partial H$ is observed at 60 and 100 Oe at 5 and 10 K, respectively. This behaviour implies that a small coercive field is required to orient the domains, and therefore that some anisotropy is present in the system.

For all the $A_2Mn_2Cu_3$ materials, the coercive fields are extremely weak being of the order of 10 Oe. These magnets do not exhibit significant hystereses, in striking contrast with the $A_2Co_2Cu_3$ derivatives.

Ac magnetic properties. The ac magnetic properties also reveal differences between the three classes of the $A_2Mn_2Cu_3$ compounds. In the following we define χ'_M and χ''_M as the in- and out-of-phase molar magnetic susceptibilities, respectively.

Let us first consider the unique class I compound, $AV_2Mn_2Cu_3$. Fig. 4 shows the in-phase, χ'_M, and out-of-phase, χ''_M, responses as a function of temperature at a frequency of 125 Hz and a drive amplitude of 3 Oe. χ'_M shows a sharp maximum at 23 K, which reveals a long-range magnetic ordering. χ''_M also shows a maximum near this temperature, at 22.5 K. The non-zero value of χ''_M reveals that in the magnetically ordered state the local momenta do not compensate. χ''_M reflects the magnetization lag with respect to the ac field, and depends on both the relaxation time and the drive frequency. Furthermore, χ'_M and χ''_M are strongly correlated and represent two components of the same quantity. Assuming that the relaxation time in the magnetically ordered phase does not vary dramatically with temperature and that the drive frequency is fixed results in similar temperature depen-

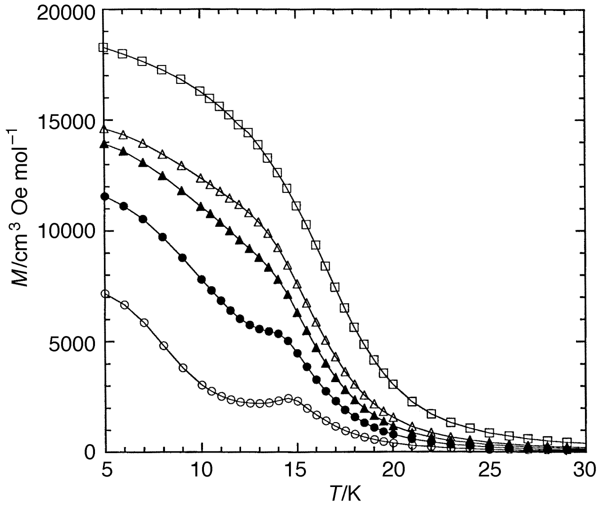


Fig. 3 χ_M *vs.* T plot for $Na_2Mn_2Cu_3$ at various fields. The full lines are guides for the eye. $H = 0.05$ (#), 0.10 ($), 0.15 (+), 0.20 ('), 0.40 kOe (%).

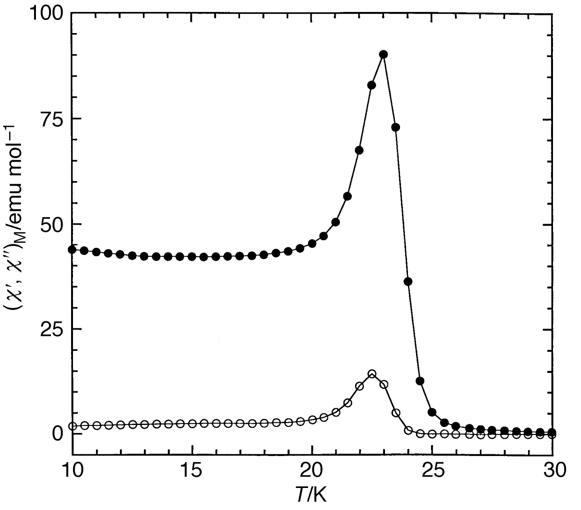


Fig. 4 In-phase, x'_M ($), and out-of-phase, x''_M (#), ac molar magnetic susceptibilities for $AV_2Mn_2Cu_3$

dences of x'_M and x''_M. The rapid decrease of both x'_M and x''_M below T_c may have two origins: (i) for microcrystalline powders the particles may form monodomains and Landau theory for second-order phase transitions predicts such behaviour;[41,42] (ii) measurements are carried out under a very weak ac field, and the hysteresis loop starts to open at temperatures lower than T_c. The very weak coercivity observed for the $A_2Mn_2Cu_3$ compounds of classes I and II might be sufficient to give rise to the observed behaviour.[41,43]

We can consider $(NBu_4)_2Mn_2Cu_3$ as a typical example of a compound belonging to class II. The temperature dependences of the x'_M and x''_M responses are shown in Fig. 5. x' shows a very sharp peak at 15 K, and x''_M an even sharper peak at the same temperature, which can be regarded as the critical temperature. In other respects, the high-temperature side of the x''_M curve reveals a weak but significant negative out-of-phase response. This behaviour was seen for different samples arising from different synthetic procedures, and may be considered as an intrinsic property. We note that negative out-of-phase responses have already been observed by several authors.[44,45]

Finally, the ac response for $Na_2Mn_2Cu_3$ as an archetype of class III compounds is examined (Fig. 6). The in-phase signal shows two peaks, a well pronounced one at 15 K and a rounded one around 5.5 K. The out-of-phase signal, on the other hand, shows a single peak at 5.5 K; compared to class I and II compounds, the x''_M signal remains very weak, even at 5.5 K. It follows that at 15 K the material exhibits a transition toward a magnetically ordered state without spontaneous magnetization. This transition is therefore antiferromagnetic. Another magnetic transition takes place around 5.5 K toward a magnetically ordered state, apparently with spontaneous magnetization. A weak negative x''_M signal is observed in the temperature range 9–20 K, with surprisingly a minimum value around 15 K. The metamagnetic behaviour of $Na_2Mn_2Cu_3$ is nicely demonstrated by the temperature dependences of x''_M under various dc fields. While x''_M is very slightly negative around 15 K in zero field, it shows a positive peak at 100 Oe.

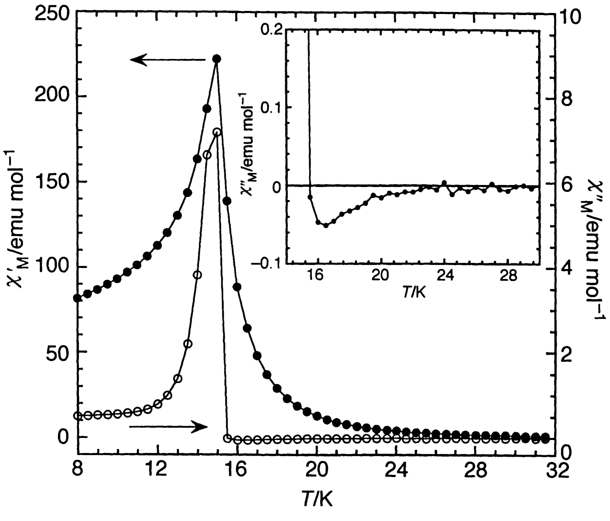


Fig. 5 In-phase, x'_M ($), and out-of-phase, x''_M (#), ac molar magnetic susceptibilities for $(NBu_4)_2Mn_2Cu_3$. The full line is a guide for the eye.

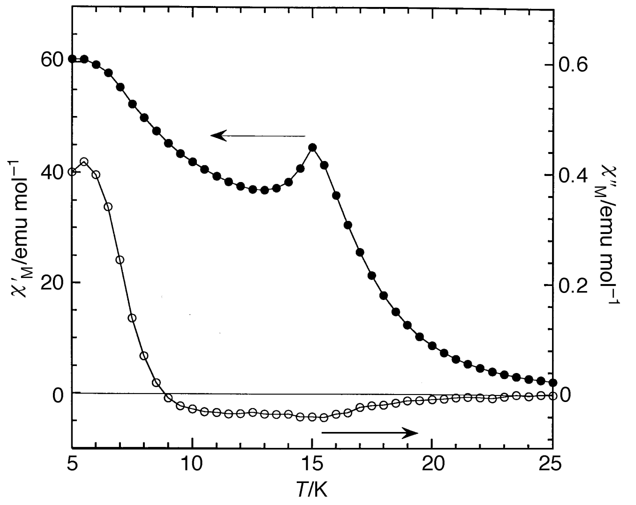


Fig. 6 In-phase, x'_M ($), and out-of-phase, x''_M (#), ac molar magnetic susceptibilities for $Na_2Mn_2Cu_3$. The full line is a guide for the eye.

$A_2Co_2[Cu(opba)]_3 \cdot n$solv compounds

All the cobalt derivatives present similar magnetic properties and are more stable than the manganese derivatives, those with large cations (NEt_4^+ and NBu_4^+) being perhaps slightly more stable than those with small cations (Na^+, K^+, Cs^+ and NMe_4^+).

Dc magnetic responses. Fig. 7 shows a typical example of a x_MT *vs.* T curve for an $A_2Co_2Cu_3$ material; *i.e.* of $(NBu_4)_2Co_2Cu_3$. At room temperature x_MT is *ca.* 7 emu K mol^{-1}, and decreases as the temperature is lowered, revealing again a ferrimagnetic behaviour. A minimum of x_MT is observed around 95 K. As the temperature is lowered further, x_MT increases dramatically, and reaches a maximum around 30 K. In the present case, there is no adequate theoretical model to interpret quantitatively the magnetic susceptibility data.

The field dependences of the magnetization are particularly interesting. First, the maximum of $\partial M/\partial H$ in the first magnetization curve is observed for a rather large field, and is temperature dependent. For $K_2Co_2Cu_3$ this maximum occurs at 2 kOe at 5 K, and 1 kOe at 25 K. This behaviour reveals a large magnetic anisotropy. Secondly, even at 50 kOe, saturation is not reached. The magnetization value for $K_2Co_2Cu_3$ at 50 kOe is 1.9 m_B while a saturation value >3 m_B may be anticipated. Most remarkably, the $A_2Co_2Cu_3$ compounds present extremely broad magnetic hysteresis loops, as shown in Fig. 8 for $K_2Co_2Cu_3$. The coercive field was 4.20 kOe at 5 K, 2.58 kOe at 15 K, and 0.58 kOe at 25 K. For the $A_2Co_2Cu_3$ materials the coercive field tends to decrease slightly as the size of A^+ increases. For instance, the coercive field for $(NBu_4)_2Co_2Cu_3$ is found to be 1.40 kOe at 5 K.

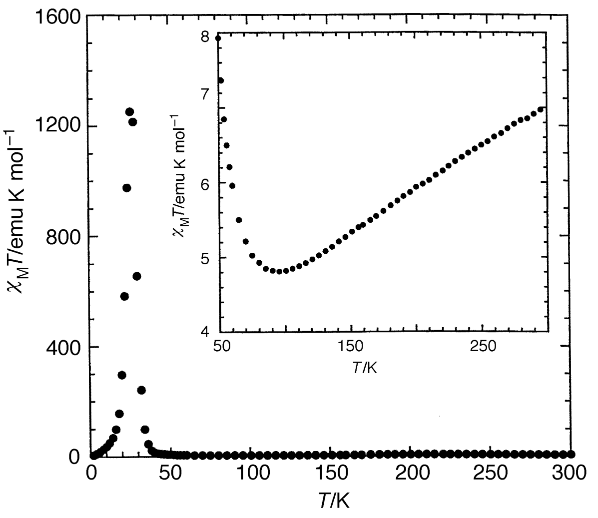


Fig. 7 $\chi_M T$ *vs.* T plot for $(NBu_4)_2Co_2Cu_3$. The insert emphasizes the minimum of $\chi_M T$ characterizing the ferrimagnetic behaviour.

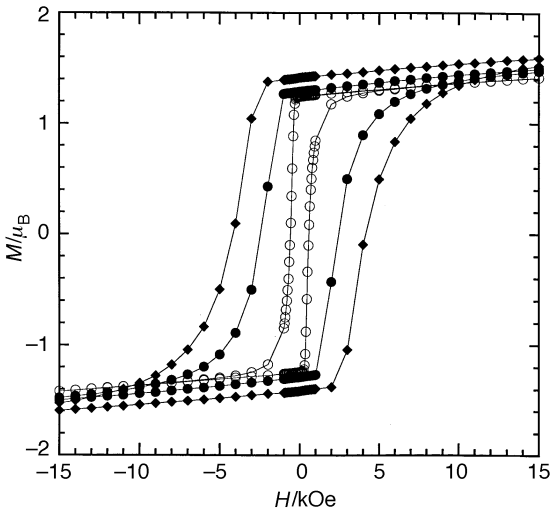


Fig. 8 Magnetic hysteresis loops for $K_2Co_2Cu_3$ at 5 (2), 15 ($) and 25 K (#). The full lines are guides for the eye.

In the course of this study we made an interesting observation concerning the magnetic relaxation in the ordered state as illustrated for $(NBu_4)_2Co_2Cu_3$. The sample was first cooled below the critical temperature $T_c = 29$ K in zero field, then a field of 50 Oe was applied and the time dependence of the magnetization was measured. Fig. 9 shows the results at three different temperatures, 5, 15 and 25 K. In order to compare the three curves, the magnetization was set at zero at $t = 0$. The magnetization exhibits an after-effect for >1 h. At the three temperatures the $M = f(t)$ curve was found to follow logarithmic behaviour, which suggests that the system presents a distribution of energy barriers.[46]

The temperature dependence of the relaxation demonstrates that the process is thermally activated. The magnetization increases faster as the system is closer to the critical temperature. This behaviour is similar to the temperature dependence of the $M = f(H)$ hysteresis loops. In all probability, the hysteresis loops for the $A_2Co_2Cu_3$ compounds are time dependent.

Ac magnetic responses. A typical example of an ac magnetic response is shown in Fig. 10 for $(NBu_4)_2Co_2Cu_3$. χ'_M displays a peak at 29 K, and χ''_M displays a peak at 28.5 K and this latter temperature is taken as the critical temperature. No negative out-of-phase signal was observed.

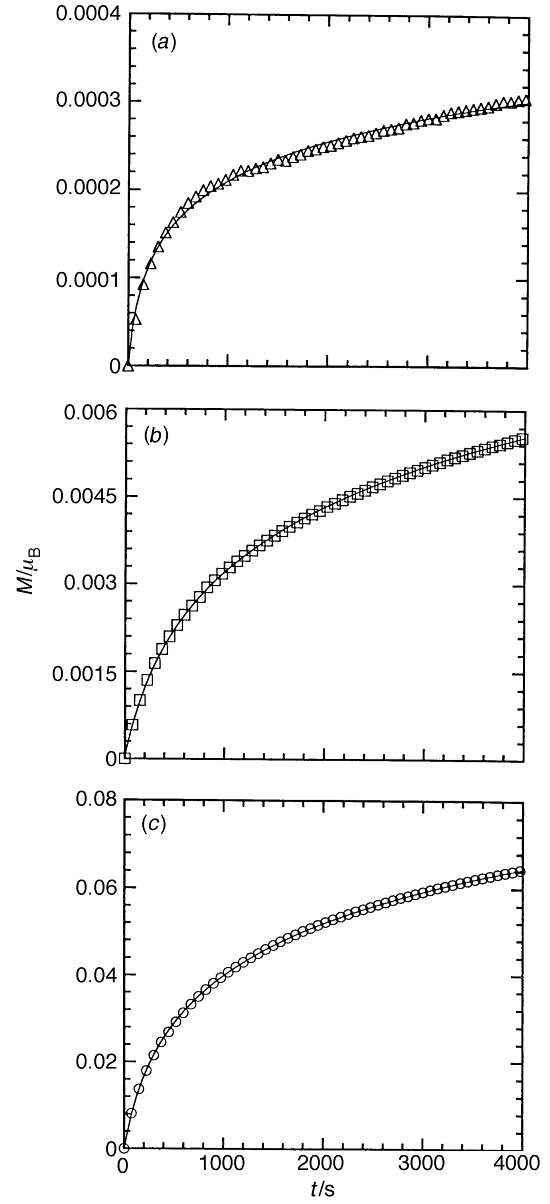


Fig. 9 Time dependences of the magnetization under 50 Oe for $(NBu_4)_2Co_2Cu_3$ at (*a*) $T = 5$ K, (*b*) $T = 15$ K, (*c*) $T = 25$ K. The full lines represent a fitting of the experimental data, using logarithmic laws.

In order to fully characterize the nature of the long-range magnetic ordering in the $A_2Co_2Cu_3$ materials, we checked that the maxima of both χ'_M and χ''_M did not depend on the frequency within experimental uncertainty between 10 and 1000 Hz and firmly excluded superparamagnetic behaviour.[47]

Discussion

In this section we discuss (i) the possible structures of the compounds, (ii) the differences between the magnetic properties of $A_2Mn_2Cu_3$ compounds belonging to class I and II on the one hand, and to class III on the other, (iii) the mechanism of the long-range magnetic ordering, and finally (iv) the origin of the huge coercivity observed for the $A_2Co_2Cu_3$ compounds.

Structures of the compounds

Only the crystal structure of $AV_2Mn_2Cu_3$ has been solved.[29,30] However, for all the $A_2Mn_2Cu_3$ compounds the dc magnetic

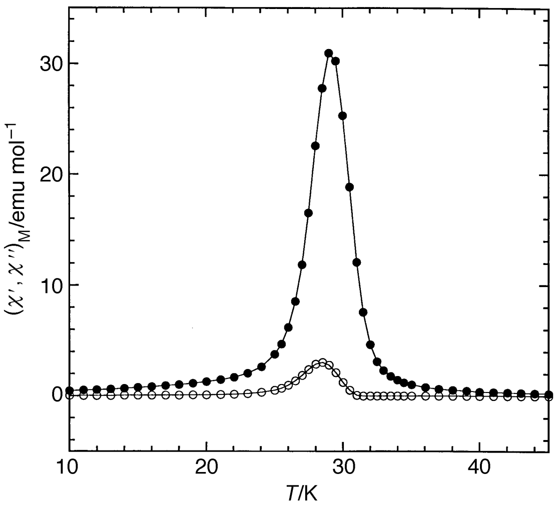


Fig. 10 In-phase, x'_M ($), and out-of-phase, x''_M (#), ac molar magnetic susceptibilities for $(NBu_4)_2Co_2Cu_3$. The full line is a guide for the eye.

susceptibility data above *ca.* 30 K are very similar. These data are very well described by a two-dimensional model of edge-sharing hexagons with Mn^{II} ions at the corners of the hexagons and Cu^{II} ions at the middles of the edges. It follows that it is quite reasonable to assume that these honeycomb like layers are present in all compounds. What, as yet, remains unknown is the relative position of the layers as well as the position of A^+ cations between the layers. The $A_2Co_2Cu_3$ compounds are obtained as microcrystalline powders with very small grains, and attempts to grow single crystals suitable for X-ray diffraction appear to be fruitless. On the other hand, the situation is not so severe for $A_2Mn_2Cu_3$ compounds. The gel technique affords hexagonal plate-shaped single crystals albeit too small. However, for $(NBu_4)_2Mn_2Cu_3$ we succeeded in obtaining the lattice parameters, $a = 9.65$ Å, $b = 34.54$ Å, $c = 15.21$ Å, b = 101.3°, $V = 4970$ Å^3 in a monoclinic crystal system. It is worth noting that the cell volume is roughly half that of $AV_2Mn_2Cu_3$, and that the lattice parameters would be compatible with a two-dimensional honeycomb like structures and a basal spacing of *ca.* 9.5 Å.

We have already pointed out the instability of the $A_2Mn_2Cu_3$ compounds belonging to class III. This instability might be due to the fact that the A^+ cations in class III materials are too small to fit properly the available space both inside the Mn_6Cu_6 hexagons and between the layers.

Class II *vs.* class III $A_2Mn_2Cu_3$ compounds

One of the striking results of this work concerns the differences between class II $A_2Mn_2Cu_3$ compounds with large A^+ cations and class III $A_2Mn_2Cu_3$ compounds with small A^+ cations. While the former behave as normal magnets with T_c around 15 K, the latter present a more complex magnetic behaviour, which can be analysed as follows: down to *ca.* 30 K they exhibit two-dimensional ferrimagnetic behaviour with a minimum of x_MT at the same temperature as for class II compounds, and a rapid increase of x_MT below this temperature. Around 15 K, x_M in low field and x'_M show a maximum, but not x''_M. This can be attributed to a long-range antiferromagnetic ordering. A magnetic field of *ca.* 0.15 kOe is sufficient to overcome the antiferromagnetic interlayer interactions. These class III compounds may be defined as metamagnets. What remains unclear is the nature of the transition revealed by the maximum of x''_M around 5.5 K. A possible hypothesis is the onset of a canted antiferromagnetism (or weak ferromagnetism) at that temperature.

The crucial point concerning the differences between the class II and III compounds is that the long-range magnetic ordering in zero field is ferromagnetic for the former and antiferromagnetic for the latter, which brings important insights on the mechanism of the long-range ordering in these compounds (see below).

Mechanism of long-range ordering

The long-range magnetic ordering in two-dimensional compounds may have two origins, namely in-plane magnetic anisotropy and/or interplane interactions. It is well established that there is no long-range ordering for a pure two-dimensional array of isotropic spins.[48] The fact that T_c is roughly twice as large for $A_2Co_2Cu_3$ than for $A_2Mn_2Cu_3$ compounds suggests that magnetic anisotropy plays a significant role. Even for the manganese derivatives some magnetic anisotropy is present as revealed by the fact that $\partial M/\partial H$ is at a maximum for a non-zero applied field. This weak anisotropy which is not sufficient to give a hysteresis loop might contribute to long-range ordering.

Let us now examine the role of the interlayer interactions. For $A_2Mn_2Cu_3$ we have seen that apparently the nature of these interactions depends on the size of A^+. Such a crossover between antiferro- (AF) and ferromagnetic (F) interactions might result from a competition between exchange (or orbital) effects favouring the AF interactions when the layers are close to each other and dipolar effects favouring F interactions when the layers are farther apart from each other. If so, then except for $A_2Mn_2Cu_3$ compounds of class III, dipolar effects would dominate. The dipolar interactions are expected to decrease as the interlayer distance becomes very large. This is observed when using very bulky cations such as $[Ru(bipy)_3]^{2+}$ or $[Ru(phen)_3]^{2+}$.[49,50]

To summarize, we can conclude that long-range ordering arises from the combined effect of in-plane anisotropy and interplane interactions. Those latter have both an exchange and dipolar origins.

Origin of the coercivity in $A_2Co_2Cu_3$ compounds

The $A_2Co_2Cu_3$ compounds to the best of our knowledge are molecular-based magnets exhibiting the strongest coercivity reported so far and we have already discussed the origin of this. The value of the coercive field at a given temperature for a polycrystalline magnet depends on both chemical and structural factors such as the size and the shape of the grains within the sample. As far as chemical factors are concerned, the key role is played by the magnetic anisotropy of the spin carriers which prevents the domains from rotating freely when applying the field.[31] For $A_2Co_2Cu_3$ compounds the large coercivity arises from the magnetic anisotropy of the Co^{II} ion in octahedral surroundings.

Conclusion

What is particularly appealing in the field of molecular materials is to observe physical properties which differ from those of classical materials which is usually a consequence of elaborate molecular structure. Here we have described the magnetic properties of a series of two-dimensional ferrimagnetic compounds, focusing on the long-range ordering. In all cases, the magnetic properties above *ca.* 50 K are characteristic of the ferrimagnetic regime. As the temperature is lowered, each layer acquires a very large magnetic momentum resulting from the non-compensation of the M^{II} (Mn^{II} or Co^{II}) spins on the one hand and the Cu^{II} spins on the other. The momenta of the ferrimagnetic layers can couple within the lattice either in an AF or in a F fashion. The former situation is encountered for the compounds $A_2Mn_2Cu_3$ of class III. The AF interlayer interactions, however, are very weak, and can be overcome by applying a magnetic field of 0.15 kOe. These compounds are therefore metamagnets. The latter situation is encountered for all the other compounds. The mechanism of the long-range ordering probably involves both in-plane anisotropy and interplane interaction (of both exchange and dipolar origin). The role of the magnetic anisotropy is further evidenced by the very strong coercivity of the Co^{II} containing materials. A puzzling result arises from this work, namely the negative out-of-phase signals observed for the $A_2Mn_2Cu_3$ compounds. So far, we have no convincing interpretation of this behaviour. In this connection some peculiarities concerning molecular-based ferrimagnets have already been reported.[17,51,52]

Molecular-based magnetic materials have already shown surprising behaviour from chemical, physical and even theoretical perspectives. We are convinced that further new phenomena, concerning magnetic as well as other physical properties, will be observed and we are pursuing our work along this line.

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