Ferro- and Ferri-magnetism in Oximato-bridged $M^{III}Cu^{II}$ Chains (M = Mn and Fe). A Molecular Based Ferromagnet with T_c = 9 K: [$Mn^{III}Cu^{II}$-bis(1,2-cyclohexanedioneoximato)(acetato)$(H_2O)_2$]

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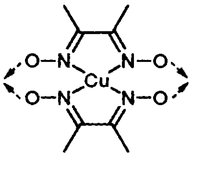
The study of the magnetic properties of the compounds $[M^{III}Cu^{II}(L)_2(MeCO_2)(H_2O)_2]$, M = Mn and L = dimethylglyoximato (dmg) **1** or 1,2-cyclohexanedioneoximato (chd) **2** and M = Fe and L = dmg **3**, shows that **1** is a metamagnetic compound, **2** is a bulk ferromagnet with T_c = 9 K and **3** orders antiferromagnetically at 7.5 K.

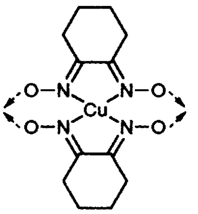
The search for molecular-based magnets is a field of increasing activity and interest.[1,2]. Recently, we reported the structural and magnetic properties of $[Mn^{III}Cu^{II}(dmg)_2(MeCO_2)(H_2O_2]$ **1** (dmg^{2-} = dianion of dimethylglyoxime).[3] Its structure is made of oximato-bridged $Mn^{III}Cu^{II}$ infinite chains which are linked through carboxylato bridges that connect the Mn^{III} ions. Its magnetic behaviour revealed a strong intrachain ferromagnetic coupling between Cu^{II} and Mn^{III} (J_{intra} = +52 cm^{-1}) and a very weak antiferromagnetic interaction between Mn^{III} ions through the carboxylato bridge (J_{inter} *ca.* 0.08 cm^{-1}). A complementary study as a function of the applied field showed that **1** is a metamagnetic system with T_N (Néel temperature) and H_c (critical field) 12 K and 4500 G, respectively.

Since recent studies on the magnetic properties of polynuclear compounds of Mn^{III} involving carboxylato bridges, have revealed the occurrence of weak couplings either ferro- or antiferro-magnetic depending on small structural changes,[4] we introduced slight modifications in the Mn^{III} environment of the compound **1** by replacing the $Cu(dmg)_2{}^{2-}$ precursor by its parent $Cu(chd)_2{}^{2-}$ (chd^{2-} = dianion of 1,2-cyclohexanedioneoxime). Substitution of Mn^{III} in **1** by Fe^{III} was also carried out. In the present communication we report the synthesis, the structural characterization and the magnetic properties of $[Mn^{III}Cu^{II}(chd)_2(MeCO_2)(H_2O)_2]$ **2** and $[Fe^{III}Cu^{II}(dmg)_2(MeCO_2)(H_2O)_2]$ **3**.

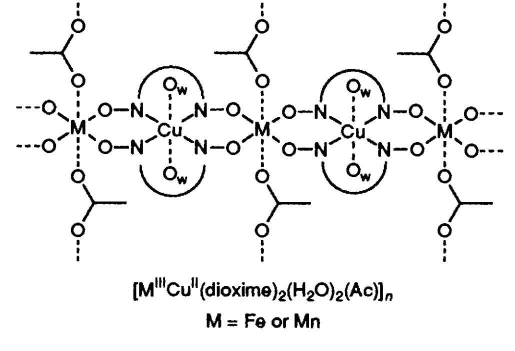
Compounds **2** and **3** were synthesised by air oxidation of methanolic solutions of manganese(II) or iron(II) acetate in the presence of $Cu(chd)_2{}^{2-}$ or $Cu(dmg)_2{}^{2-}$, respectively. In the absence of single crystals suitable for X-ray diffraction, X-ray absorption was used for their structural characterization. The metal ions in this series exhibit elongated octahedral surroundings: $Cu[N_4O_2]$ [four short Cu–N(oxime) at 1.99 Å and two longer Cu–O(water) in the range 2.12–2.35 Å] and $M[O_6]$ [four short M–O(oxime) at 1.95 (Mn) and 2.00 Å (Fe), and two longer M–O (carboxylate) at 2.17 (Mn) and 2.10 Å (Fe)]. Mn^{III} exhibits a more pronounced axial distortion than Fe^{III}, as expected from the Jahn–Teller effect in the former. Two manganese (**1** and **2**) or two iron (**3**) atoms were found at *ca.* 3.3 Å from each copper atom in all three complexes, in agreement with the formation of oximato bridged bimetallic chains. The carboxylato groups which are bound to either Mn^{III} or Fe^{III} should act as bridges between Mn^{III} or Fe^{III} from different chains. In this respect, the EXAFS data at the copper K-edge show the presence of metal ions at *ca.* 4 Å, supporting this hypothesis. Moreover, the structures of **1**–**3** are likely to have a close resemblance (X-ray powder diffraction), the proposed structure is shown below.



$[Cu(dmg)_2]^{2-}$



$[Cu(chd)_2]^{2-}$



$[M^{III}Cu^{II}(dioxime)_2(H_2O)_2(Ac)]_n$
M = Fe or Mn

The thermal dependence† of χ_MT for **2** is shown in Fig. 1(*a*). χ_MT is equal to 4.9 cm^3 mol^{-1} K at 290 K (μ_{eff} = 6.26 μB), a value which is higher than the spin-only value (μ_{eff} = 5.20 μB) of a magnetically non-interacting Mn^{III}–Cu^{II} pair, and very close to that expected for a sextuplet state (μ_{eff} = 5.92 μB). When cooling, χ_MT increases slowly and a linear plot of χ^{-1} *vs* *T* is observed for $T > 50$ K with a positive Weiss constant, θ *ca.* +50 K, indicating that ferromagnetic interactions dominate. An abrupt increase in χ_MT occurs when the sample is cooled to below 20 K, and its magnetization becomes satured for $T < 9$ K: χ_M is roughly constant, and χ_MT decreases linearly with *T*. This behaviour is indicative of a relatively strong ferromagnetic coupling and suggests the approach to a possible ferromagnetic phase transition. This phase transition is confirmed by AC susceptibility measurements in the temperature range 4–20 K. They show an out-of-phase signal around 9 K [Fig. 1(*a*)]. The field dependence of the magnetization at 2 K is characteristic of a polycrystalline three-dimensional ferromagnet. The magnetization climbs steeply to a value of 14000 cm^3 G mol^{-1} by 1000 G at 1.8 K, and then gradually increases to a maximum of 22200 cm^3 G mol^{-1} at the highest field employed, 22000 G. The theoretical saturation magnetization, M_S per MnCu unit, for a spin $S = S_{Mn} + S_{Cu} = 5/2$ and $g = 2$ is 27900 cm^3 G mol^{-1}. These results show that **2** is indeed a ferromagnet, not a ferrimagnet, which would display a much smaller saturation magnetization (M_S = 16700 cm^3 G mol^{-1}). The zero-field susceptibility is very large but not infinite, and M is not constant for $H > 1000$ G. These deviations from an ideal ferromagnet can be attributed to demagnetization effects and to the fact that the susceptibility is averaged over all orientations of the polycrystalline compound (including both soft and hard magnetization axes).

The magnetic behaviour of **3** is shown in Fig. 1(*b*). At room temperature the χ_MT value is 4.10 cm^3 K mol^{-1} (μ_{eff} = 5.72 μB), a value which is smaller than that expected for two uncoupled Fe^{III} and Cu^{II} ions (μ_{eff} = 6.16 μB). χ_MT decreases as *T* is lowered, reaches a large minimum around 200 K (χ_MT = 3.92 cm^3 mol^{-1} K), and then increases again, as *T* is lowered, up to 21.5 cm^3 K mol^{-1} at 8.5 K. Below 8.5 K, χ_MT decreases rapidly and a maximum of χ_M is observed at 7.5 K in

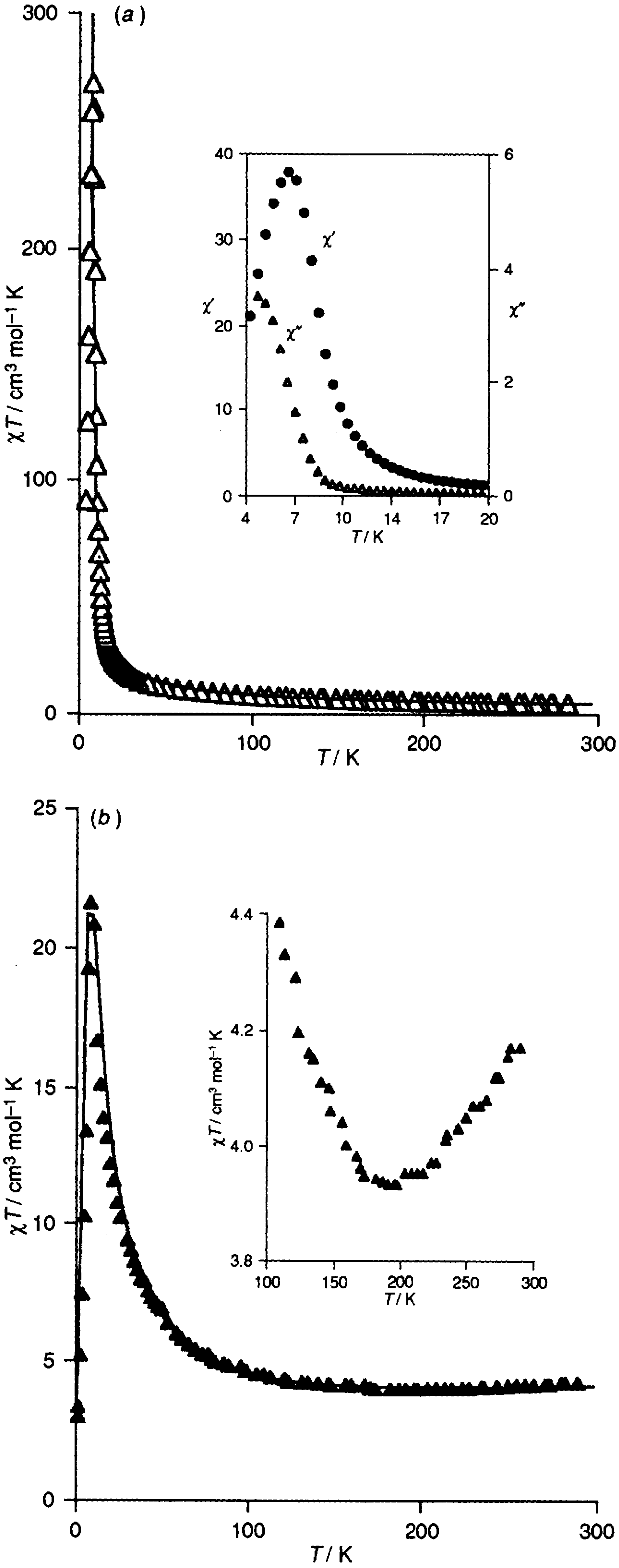


Fig. 1 Thermal dependence of the product of the molar magnetic susceptibility with temperature (H = 50 G) for **2**(*a*) and **3**(*b*). Experimental points are shown as triangles and the theoretical curves were calculated as discussed in the text. The inserts show the thermal variation of both the in-phase, χ', and the out-of-phase, χ'', components of the AC susceptibility for **2**(*a*) and expanded region of the minimum of $\chi_M T$ curve for **3**(*b*).

an applied field of 50 G. This behaviour is characteristic of a ferrimagnetic chain with an antiferromagnetic coupling between Cu^{II} and Fe^{III} ions. AC susceptibility measurements in the temperature range 4–20 K show no out-of-phase signal.

The $\chi_M T$ data down to *ca.* 30 K for **2** and **3** can be fitted with the appropriate expressions for one-dimensional alternating spin chains[5] with $S_1 = 2$ and $S_2 = 1/2$ **2** and $S_1 = 5/2$ and $S_2 = 1/2$ **3**. The best fit parameters are $g_{Mn} = 2.0$, $g_{Cu} = 2.28$ and $J_{intra} = +51$ cm^{-1} for **2** and $g_{Fe} = 1.99$, $g_{Cu} = 2.17$ and $J_{intra} = -48$ cm^{-1} for **3** (the Hamiltonian in the form $\mathbf{H} = -JS_1S_2$). Below 30 K the experimental values of $\chi_M T$ for **2** increase much more quickly than the corresponding theoretical ones, while they increase more slowly in **3**. Indeed, the χ_M data for **3** present a maximum. These features indicate that ferromagnetic **2** and antiferromagnetic **3** interchain coupling occurs. As in **1**, we suggest that this magnetic interchain coupling is due to the acetate bridging between the Mn^{III} ions. According to such a structural arrangement, the compounds **2** and **3** would be two-dimensional, with a large intrachain magnetic interaction and a weak interchain one as in **1**. Consequently, we can treat these two-dimensional compounds as a 'chain of chains'[3] (in the case of **2** only for $T > T_c$). The best fits for **2** and **3** give $J_{inter} = +0.07$ and -0.06 cm^{-1}, respectively. These values agree with a very weak interchain coupling.

The observed $J_{intra} = +51$ cm^{-1} for **2** is very close to that of **1** (52 cm^{-1}). This ferromagnetic interaction between Mn^{III} (d^4) and Cu^{II} (d^9) ions can be understood as follows: owing to the Jahn–Teller effect, which is operative in both metal ions, it is possible to achieve strict orthogonality between the magnetic orbitals d_{xy}, d_{xz} and d_{z^2} of Mn^{III} ($d_{x^2-y^2}$ orbital is empty) and the one of Cu^{II}, $d_{x^2-y^2}$, if both metal ions are located in the xy-plane. The occurrence of an electron in the $d_{x^2-y^2}$ orbital of Fe^{III} (d^5) provides an antiferromagnetic pathway between Fe^{III} and Cu^{II}, responsible for the ferrimagnetism observed in **3**. The value of $J_{intra} = -48$ cm^{-1} for **3** is very similar to that reported for [Mn^{II}(phen)$_2$Cu^{II}(pdmg)](ClO$_4$)$_2$·2.5H$_2$O ($J_{Mn-Cu} = -50$ cm^{-1}).[6]

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† The magnetic properties have been studied in the 1.8–300 K temperature range under different external fields (0–22000 G) with a SQUID (Métronique Ingénierie) magnetometer and a pendulum-type apparatus. Low-field measurements were also performed on an AC susceptometer measuring both the real and imaginary component of the molar susceptibility, χ_M.

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