

## A Novel Molecular Based Ferromagnet Ordering at 14 K

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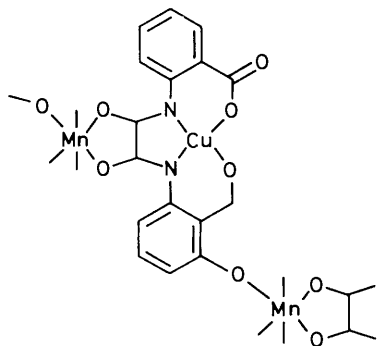
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The compound  $\text{MnCu}(\text{obbz})\cdot\text{H}_2\text{O}$  [obbz = oxamido bis(benzoato)], obtained by reaction of the  $\text{Mn}^{2+}$  ion with the copper(II) 'brick'  $[\text{Cu}(\text{obbz})]^{2-}$ , orders ferromagnetically at  $T_c = 14$  K; below  $T_c$  it exhibits a hysteresis loop characteristic of a soft ferromagnet.

The first molecular based ferromagnets have been reported only in the last few years.<sup>1,2</sup> Recently, three of us have described the compound  $\text{MnCu}(\text{pbaOH})(\text{H}_2\text{O})_3$  [pbaOH = 2-hydroxy-1,3-propylenebis(oxamato)], which orders ferromagnetically at  $T_c = 4.6$  K,<sup>3</sup> our basic strategy consisting of assembling  $\text{Mn}^{2+}\text{Cu}^{2+}$  ferrimagnetic chains within the crystal lattice in a ferromagnetic fashion. Here, we report a new compound of the same type, ordering at 14 K, *i.e.*, about 9 K higher:  $\text{MnCu}(\text{obbz})\cdot\text{H}_2\text{O}$  [(1) $\cdot\text{H}_2\text{O}$ ] where obbz = oxamido bis(benzoato).

Compound (1) $\cdot\text{H}_2\text{O}$  was synthesized in four steps. First,  $\text{H}_4(\text{obbz})$  (2) was obtained by adding dropwise oxalyl chloride ( $10^{-2}$  mol) to anthranilic acid ( $2.2 \times 10^{-2}$  mol) in tetrahydrofuran (THF) ( $50 \text{ cm}^3$ ). The acid (2)<sup>†</sup> precipitated as a white solid. The copper(II) brick,  $\text{Na}_2[\text{Cu}(\text{obbz})]\cdot 4\text{H}_2\text{O}$  (3), was then prepared from (2) ( $4 \times 10^{-3}$  mol) and NaOH ( $1.6 \times 10^{-2}$  mol) dissolved in  $250 \text{ cm}^3$  of water into which copper(II) nitrate ( $4 \times 10^{-3}$  mol) dissolved in  $25 \text{ cm}^3$  of water was added dropwise. Compound (3)<sup>†</sup> was obtained from the mixture as a purple polycrystalline powder by slow evaporation. (1) $\cdot 5\text{H}_2\text{O}$ <sup>†</sup> precipitated as a pale green polycrystalline powder when an aqueous solution of manganese(II) perchlorate ( $10^{-3}$  mol) was added to an equimolar aqueous solution of (3). (1) $\cdot 5\text{H}_2\text{O}$  was easily dehydrated *in vacuo* at room temperature or under ambient pressure at  $50^\circ\text{C}$ , to give (1) $\cdot\text{H}_2\text{O}$ .<sup>†</sup>

The magnetic properties of (1) $\cdot 5\text{H}_2\text{O}$  down to 10 K are identical (within experimental errors) to those of  $\text{MnCu}(\text{obp})(\text{H}_2\text{O})_3\cdot\text{H}_2\text{O}$  [obp = oxamido bis(propionato)],<sup>4</sup> with the characteristic minimum of the  $\chi_{\text{M}}T$  vs.  $T$  plot<sup>5,6</sup> ( $\chi_{\text{M}}$ : molar magnetic susceptibility) at *ca.* 40 K. This strongly suggests that, as in  $\text{MnCu}(\text{obp})(\text{H}_2\text{O})_3\cdot\text{H}_2\text{O}$ , the basic structure of (1) $\cdot 5\text{H}_2\text{O}$  is that of an alternating bimetallic chain in which the Mn and Cu atoms are bridged by an oxamido group on the one hand and by a carboxylato group on the other (see Figure 1).

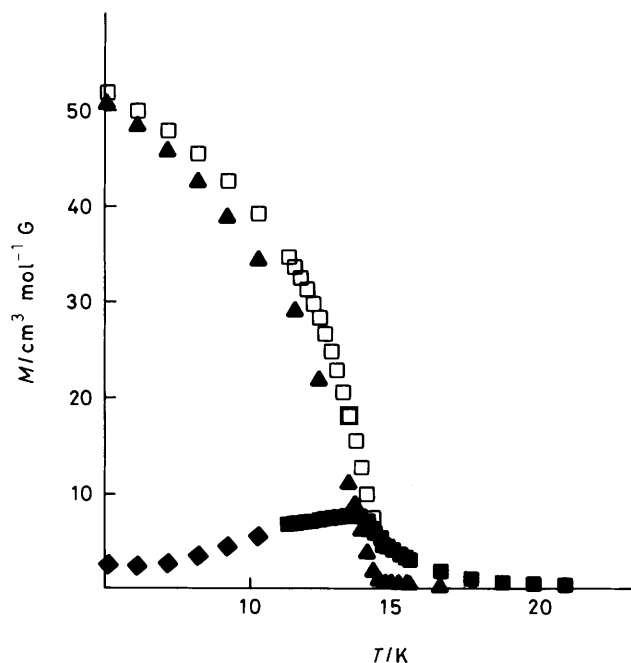


**Figure 1.** Schematic chain structure of  $\text{MnCu}(\text{obbz})\cdot 5\text{H}_2\text{O}$  [(1) $\cdot 5\text{H}_2\text{O}$ ].

<sup>†</sup> Satisfactory chemical analyses were obtained for  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_7\text{CuMn}$  [(1) $\cdot\text{H}_2\text{O}$ ],  $\text{C}_{16}\text{H}_{22}\text{N}_2\text{O}_{11}\text{CuMn}$  [(1) $\cdot 5\text{H}_2\text{O}$ ],  $\text{C}_6\text{H}_{12}\text{N}_2\text{O}_6$  (2), and  $\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}_{10}\text{CuNa}_2$  (3).

The weakly co-ordinated water molecules probably complete the six-co-ordination around  $\text{Mn}^{2+}$  and magnetically isolate the  $\text{Mn}^{2+}\text{Cu}^{2+}$  chains within the crystal lattice. In the dehydrated form (1) $\cdot\text{H}_2\text{O}$ , six-co-ordination around  $\text{Mn}^{2+}$  could be achieved through the packing of the chains involving the oxygen atoms of the carboxylato and/or oxamido groups, which would provide efficient interchain interaction pathways.

Upon cooling down to 14 K,  $\chi_{\text{M}}T$  for (1) $\cdot\text{H}_2\text{O}$  diverges, suggesting that a ferromagnetic transition occurs. This is confirmed when investigating the magnetization curve  $M = f(T)$  in the temperature range 5–20 K with a SQUID magnetometer, the applied magnetic field being 0.1 G (see Figure 2). The field cooled magnetization (FCM), obtained by cooling within the field, shows the typical feature of a ferromagnetic transition, *i.e.* a break in the curve around  $T_c = 14$  K. When the field was switched off, a remnant magnetization was observed which vanished at  $T_c$  upon warming. Finally, the zero-field-cooled magnetization (ZFCM), obtained in cooling in zero field and warming within the field, shows a maximum at  $T_c$ , as expected for a polycrystalline ferromagnet.<sup>3</sup> We also investigated the magnetization vs. field curve at 4.2 K, which showed a hysteresis loop characteristic of a soft ferromagnet with a coercive field of about 60 G ( $\text{G} = 10^{-4} \text{ T}$ ) and a remnant magnetization of  $6.3 \times 10^3 \text{ cm}^3 \text{ mol}^{-1} \text{ G}$  (see Figure 3).



**Figure 2.** Temperature dependence of the magnetization  $M$  of (1) $\cdot\text{H}_2\text{O}$  in the temperature range 5–20 K and a magnetic field of 0.1 G. □: field cooled magnetization; ▲: remnant magnetization; ◆: zero field cooled magnetization.

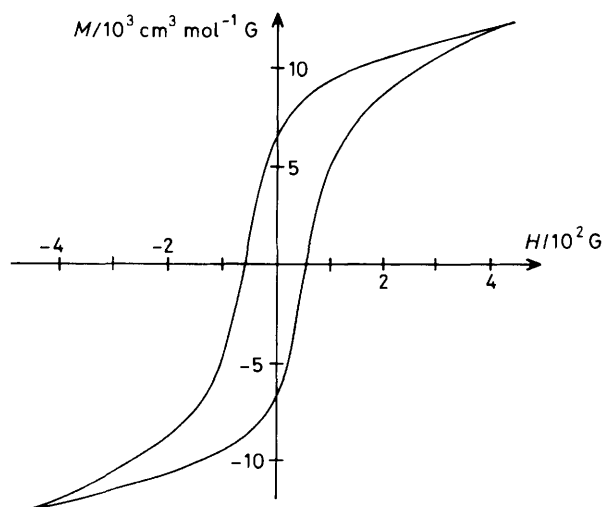


Figure 3. Hysteresis loop  $M = f(H)$  for a polycrystalline sample of  $(1) \cdot \text{H}_2\text{O}$  at 4.2 K.

In conclusion,  $\text{MnCu}(\text{obbz}) \cdot \text{H}_2\text{O}$  is a molecular based ferromagnet, with a well defined and reproducible chemical analysis, exhibiting the highest ordering temperature reported to date.

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