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A molecular-based magnet incorporating the $[\text{Ru}(\text{bpy})_3]^{2+}$ chromophore (bpy = 2,2'-bipyridine)

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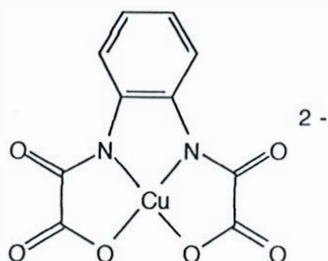
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Abstract. – The compound $[\text{Ru}(\text{bpy})_3]\text{Mn}_2[\text{Cu}(\text{opba})]_3 \cdot 13\text{H}_2\text{O}$ (bpy = 2,2'-bipyridine, opba = *ortho*-phenylenebis(oxamato)) in which the photophysically active chromophore $[\text{Ru}(\text{bpy})_3]^{2+}$ is located between anionic ferrimagnetic layers exhibits a spontaneous magnetization at $T_c = 12$ K.

The first molecular-based magnets were described in 1986^{1,2}. Since then, quite a few molecular materials exhibiting a spontaneous magnetization below a critical temperature T_c have been reported^{3,4}. Recently, it was suggested that one of the main issues in this field of research concerned the synergy between magnetic and optical properties⁵⁻⁷. Indeed, most of the molecular magnetic materials are weakly colored while classical magnets are usually opaque. Here we report on one of the very first molecular-based magnets incorporating the photophysically active $[\text{Ru}(\text{bpy})_3]^{2+}$ chromophore, with bpy = 2,2'-bipyridine. Its formula is $[\text{Ru}(\text{bpy})_3]\text{Mn}_2[\text{Cu}(\text{opba})]_3 \cdot 13\text{H}_2\text{O}$ ($1 \cdot 13\text{H}_2\text{O}$); $[\text{Cu}(\text{opba})]^{2-}$ stands for the Cu(II) precursor:



with opba = *ortho*-phenylenebis(oxamato). $1 \cdot 13\text{H}_2\text{O}$ is a new member of a family of $\text{Mn}(\text{II})_2\text{Cu}(\text{II})_3$ molecular-based magnets with T_c ranging from 12 to 22.5 K^{8,9}. The structure of one of these compounds has been solved⁹. It consists of a two-dimensional anionic skeleton with edge-sharing hexagons, and cations located between the layers. The corners of each hexagon are occupied by Mn(II) ions, and the middles of the edges by Cu(II) ions.

$1 \cdot 13\text{H}_2\text{O}$ was synthesized as follows: First, $[\text{Ru}(\text{bpy})_3]\text{I}_2 \cdot 6\text{H}_2\text{O}$ ¹⁰ and $\text{Na}_2[\text{Cu}(\text{opba})] \cdot 3\text{H}_2\text{O}$ ⁸ were prepared as described. The reaction of 2 $\text{Ag}(\text{NO}_3)$ and $\text{Na}_2[\text{Cu}(\text{opba})] \cdot 3\text{H}_2\text{O}$ in water afforded $\text{Ag}_2[\text{Cu}(\text{opba})]$ which precipitated (yield: 96%). Heating at reflux for ca. 20 min equimolar amounts of $[\text{Ru}(\text{bpy})_3]\text{I}_2 \cdot 6\text{H}_2\text{O}$ and solid $\text{Ag}_2[\text{Cu}(\text{opba})]$ in water resulted in a precipitate of AgI and a deep orange-brown solution which gave single crystals of $[\text{Ru}(\text{bpy})_3][\text{Cu}(\text{opba})] \cdot 9\text{H}_2\text{O}$ ($2 \cdot 9\text{H}_2\text{O}$) by slow evaporation in the dark (yield: 80%). Finally, $1 \cdot 13\text{H}_2\text{O}$ was obtained by mixing together two solutions in dimethylsulfoxide, one containing Mn(II) chloride, the other containing $2 \cdot 9\text{H}_2\text{O}$, with the molar ratio Cu/Mn = 1.6. $1 \cdot 13\text{H}_2\text{O}$ appeared as an orange-brown microcrystalline powder (yield: 76% with respect to Mn). Anal. calc. for $\text{C}_{60}\text{N}_{52}\text{N}_{12}\text{O}_{31}\text{Cu}_3\text{Mn}_2\text{Ru}$ ($1 \cdot 13\text{H}_2\text{O}$): C,

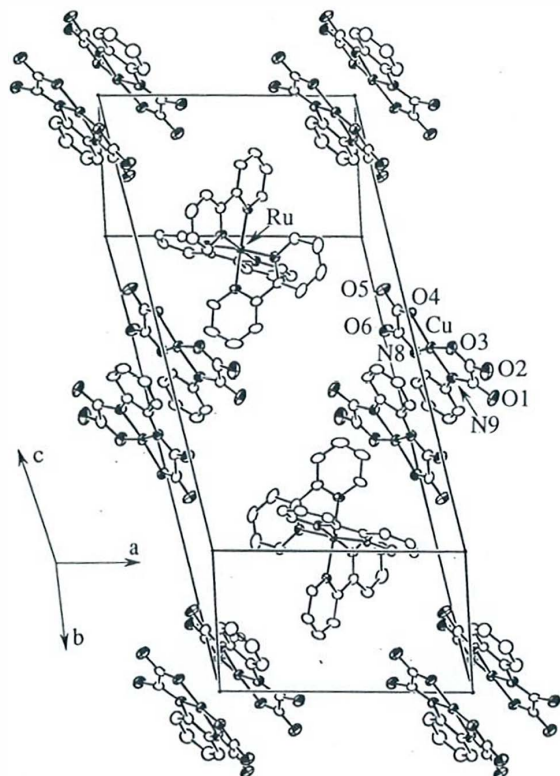


Figure 1. – Projection of the crystal structure of $[\text{Ru}(\text{bpy})_3][\text{Cu}(\text{opba})] \cdot 9\text{H}_2\text{O}$. For clarity the noncoordinated water molecules have been omitted.

38.97; H, 3.38; N, 9.09; Cu, 10.31; Mn, 5.94; Ru, 5.47. Found: C, 38.65; H, 3.38; N, 9.10; Cu, 9.93; Mn 5.62; Ru, 5.86.

The crystal structure of the precursor $2 \cdot 9\text{H}_2\text{O}$ has been solved¹¹. This structure is shown in Figure 1. As expected, $2 \cdot 9\text{H}_2\text{O}$ crystallizes in a centrosymmetrical space group, $P2_1/c$, so that the two enantiomeric forms of the chiral cation $[\text{Ru}(\text{bpy})_3]^{2+}$ are present. Interestingly, this structure is the first one showing a free bis(oxamato) $\text{Cu}(\text{II})$ dianion. The average value of the $\text{Cu}-\text{N}$ and $\text{Cu}-\text{O}$ bond lengths are equal to 1.89 and 1.85 Å, respectively, and the $\text{C}-\text{C}$ bond lengths within the oxamato group are typical of a single bond; their average value is 1.54 Å.

The magnetic properties of $1 \cdot 13\text{H}_2\text{O}$ are characteristic of ferrimagnetic layers exhibiting a long-range magnetic ordering at $T_c = 12$ K. The $\chi_M T$ versus T plot shown in Figure 2a (χ_M being the molar magnetic susceptibility and T the temperature) presents a rounded minimum around 110 K, and increases more and more rapidly as T is lowered further. The temperature dependence of the magnetization within a magnetic field of 1 Oe below 25 K is shown in Figure 2b. The field-cooled magnetization (FCM) shows a break around 12 K. The zero-field-cooled magnetization (ZFCM) at any temperature below T_c is much weaker than the FCM,

so that the remnant magnetization is close to the FCM. (One has approximately $\text{REM} = \text{FCM} - \text{ZFCM}$). At least ten out of the thirteen water molecules may be very easily removed under vacuum, or by a gentle warming. It is remarkable that the magnetic properties of $1 \cdot 3\text{H}_2\text{O}$ are strictly identical to those of the fully hydrated compound, which suggests that these labile water molecules are almost free between the anionic layers separated by the large $[\text{Ru}(\text{bpy})_3]^{2+}$ cations. It is also worth pointing out that T_c for $1 \cdot 13\text{H}_2\text{O}$ is much the same as for other members of the family incorporating less bulky cations⁷.

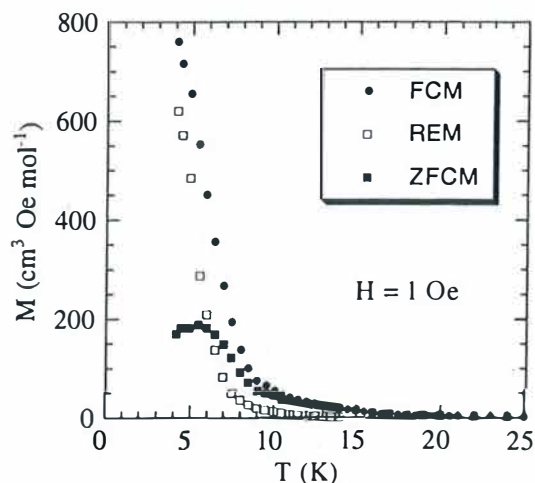
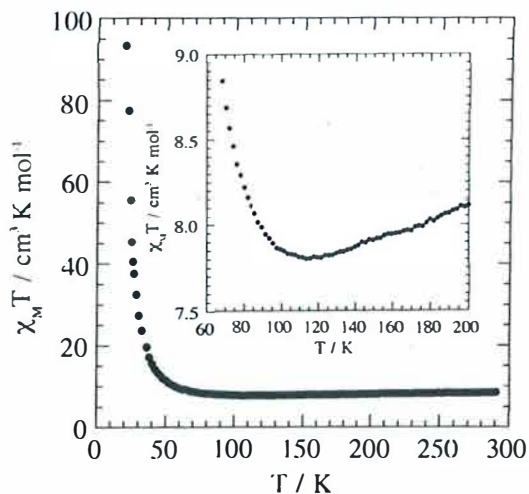


Figure 2. – (a) $\chi_M T$ versus T curve for $[\text{Ru}(\text{bpy})_3]\text{Mn}_2[\text{Cu}(\text{opba})]_3 \cdot 13\text{H}_2\text{O}$; the insert emphasizes the minimum of $\chi_M T$ around 110 K. (b) Temperature dependence of the magnetization for $[\text{Ru}(\text{bpy})_3]\text{Mn}_2[\text{Cu}(\text{opba})]_3 \cdot 13\text{H}_2\text{O}$ within a magnetic field of 1 Oe. FCM = field-cooled magnetization, ZFCM = zero-field-cooled magnetization, REM = remnant magnetization.

Preliminary photophysical results on an aqueous solution of **2** indicate that the luminescence of the $[\text{Ru}(\text{bpy})_3]^{2+}$ cation is quenched by the presence of the $[\text{Cu}(\text{opba})]^{2-}$

species, probably through an energy transfer process. The quenching rate constant has been found to be $4.3 \times 10^9 \text{ mol}^{-1} \text{ sec}^{-1}$. We hope to report on the luminescence of $1 \cdot 13\text{H}_2\text{O}$, or on the quenching mechanism in the rather near future.

Acknowledgement

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- ¹¹ *Crystal data*: $\text{Ru}(\text{C}_{10}\text{H}_8\text{N}_2)_3\text{Cu}(\text{C}_{10}\text{H}_4\text{O}_6\text{N}_2) \cdot 9\text{H}_2\text{O}$; $M_r = 1043.47$, Monoclinic, $P2_1/c$, $a = 13.365(5)$, $b = 13.861(6)$, $c = 26.678(9)$ Å, $\beta = 103.26(2)^\circ$, $V = 4450$ Å³, $Z = 4$, $d_{\text{calc}} = 1.557 \text{ gcm}^{-3}$, $\mu = 8.850 \text{ cm}^{-1}$, $\lambda(\text{MoK}\alpha) = 0.71073$ Å. The refinements by full matrix least squares for 587 variables gave final $R = 0.045$, $R_w = 0.062$ using 3644 absorption corrected data with $I \geq 4\sigma(I)$. A crystal was taken directly with its mother liquor, sealed in a Lindemann glass capillary, and mounted on a Enraf Nonius CAD4 diffractometer for data collection. Full structure solution data, atomic coordinates, bond lengths and angles, thermal parameters, and observed and calculated structure factor tables can be obtained on request from the authors.