Crystal structure, ferromagnetic ordering and magnetic anisotropy for two cyano-bridged bimetallic compounds of formula $Mn_2(H_2O)_5Mo(CN)_7 \cdot nH_2O$

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Slow diffusion of aqueous solutions containing $K_4[Mo^{III}(CN)_7]\cdot 2H_2O$ and a Mn^{II} salt, respectively, affords well shaped single crystals of two cyano-bridged bimetallic phases ordering ferromagnetically with a pronounced magnetic anisotropy in the magnetically-ordered phase.

Bimetallic hexacyanometallate compounds involving 3d metal ions, of the Prussian Blue type, are interesting materials at the frontier between solid state and molecular chemistry.[1–6] As a matter of fact, all their magnetic characteristics (nature of the interaction between nearest neighbors, saturation magnetization, coercivity) are nicely in line with the theoretical models developed in molecular magnetism,[7,8] in particular as far as the symmetry rules involving the magnetic orbitals are concerned.[9] However, these compounds have some drawbacks. First, nobody, as yet, has succeeded in growing single crystals suitable for thorough physical measurements; secondly, their crystal structure as deduced from X-ray powder patterns is cubic, so that they exhibit no magnetic anisotropy. Here, we report on two new cyano-bridged bimetallic species obtained as well shaped single crystals, exhibiting long-range ferromagnetic ordering along with pronounced magnetic anisotropy.

Slow diffusion in a H-shaped tube under nitrogen of two deoxygenated aqueous solutions containing $K_4[Mo(CN)_7]\cdot 2H_2O$[10] and $Mn(NO_3)_2\cdot 6H_2O$, respectively, afforded two kinds of single crystals, with elongated plate (α phase) and prism (β phase) shapes, respectively. Both phases are air sensitive, and all the magnetic investigations were carried out with either single crystals protected by a grease envelop or powder samples placed in quartz tubes sealed under vacuum.

The crystal structures of both phases were solved.‡ The local environments of the metal sites are similar, but the three-dimensional organizations are different. There is one molybdenum and two manganese sites. The molybdenum atom is surrounded by seven C–N–Mn linkages. All the cyano groups are bridging. The coordination polyhedron may be viewed as a distorted pentagonal bipyramid.[11,12] The two manganese sites are in distorted octahedral surroundings. The manganese atom Mn1 is surrounded by four N–C–Mo linkages and two water

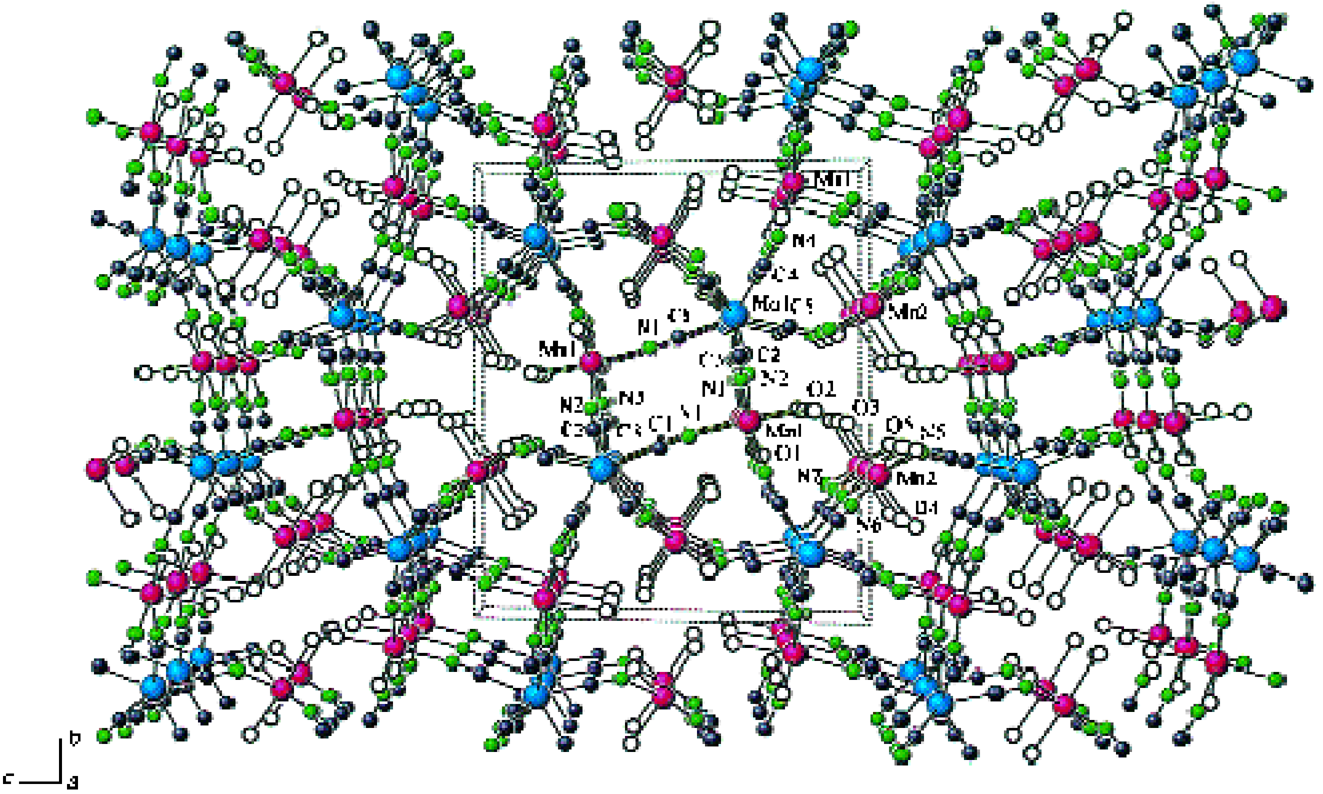

Fig. 1 Crystal structure of $Mn(H_2O)_5Mo(CN)_7{\cdot}4H_2O$ (α phase). The manganese atoms are in red, the molybdenum atoms in blue, the oxygen atoms in white, the nitrogen atoms in green, and the carbon atoms in black. The non-coordinated water molecules are omitted for clarity. The Mo–C bond lengths range from 2.127(4) to 2.174(4) Å, the Mn–N bond lengths from 2.181(4) to 2.242(3) Å and the Mn–O bond lengths from 2.195(4) to 2.308(4) Å.

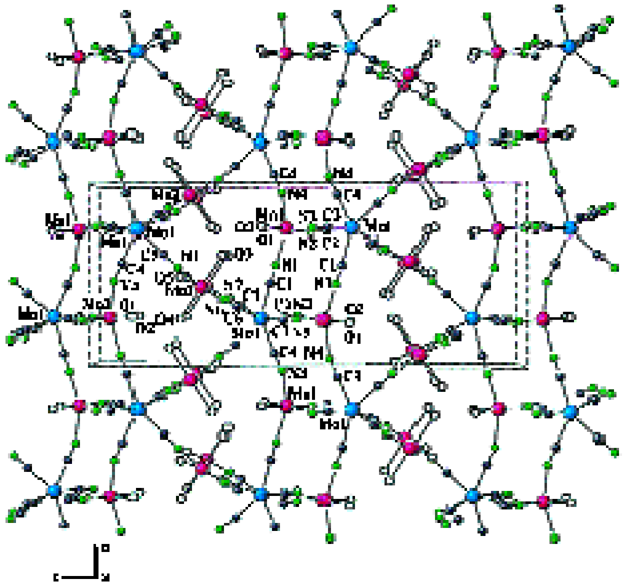

Fig. 2 Crystal structure of $Mn(H_2O)_5Mo(CN)_7{\cdot}4.75H_2O$ (β phase). The color codes are the same as in Fig. 1. The non-coordinated water molecules are omitted for clarity. The Mo–C bond lengths range from 2.110(7) to 2.191(7) Å, the Mn–N bond lengths from 2.158(5) to 2.190(6) Å and the Mn–O bond lengths from 2.223(6) to 2.350(5) Å.

molecules, and the manganese atom Mn2 is surrounded by three N–C–Mo linkages and three water molecules. The structural arrangements may be described as cyano-bridged $Mo1_2Mn1_2$ lozenge motifs linked to each other through two cyano bridges along the *a* axis direction to form a sort of accordion. The Mn2 atoms, located between the accordions, are linked to two molybdenum atoms of one of the accordions and one molybdenum atom of an adjacent accordion. In the α phase each lozenge is linked to four other lozenges through a cyano bridge in the *bc* plane along the [011] and [01$\bar{1}$] directions (Fig. 1). In the β phase each lozenge is linked to only two other lozenges through two cyano bridges in the *bc* plane along the [011] direction (Fig. 2).

Both phases exhibit a long-range magnetic ordering at T_c = 51 K. The field-cooled magnetization curves obtained in cooling a single crystal of the α phase within a magnetic field of 100 Oe aligned along the *a*, *b* and *c** axis directions, successively, are shown in Fig. 3. These curves display a characteristic break at T_c, then the magnetization remains constant as the temperature is lowered further. The strong magnetic anisotropy which is observed is probably of dipolar origin,[13] and reflects the low crystal symmetry which contrasts with the perovskite-like structure of the Prussian Blue phases. The field dependences of the magnetization below T_c reveal a saturation magnetization very close to 11 μ_B. This value corresponds to what is expected for a ferromagnetic state in which the S_{Mo} = 1/2 and S_{Mn} = 5/2 local spins are aligned along the field direction. The overall ferromagnetic nature of the interactions between the spin carriers is supported further by the profile of the $\chi_M T$ *vs.* T curves of polycrystalline samples, χ_M being the magnetic susceptibility per repeat unit and T the temperature. At room temperature, $\chi_M T$ is equal to 9.1(1) emu K mol^{-1} for both phases, which corresponds to what is expected for non-interacting Mo^{3+} and Mn^{2+} ions, and increases continuously and more and more rapidly as T is lowered.

Several factors confer a great interest on the compounds described in this paper, namely: (*i*) the beauty of the crystal structures; (*ii*) the possibility of growing rather large single crystals suitable for anisotropy measurements; (*iii*) the presence of high-spin 3d and low-spin 4d spin carriers;[14] (*iv*) finally, the originality of the physical properties in the magnetically ordered state. These properties will be detailed in a subsequent paper.

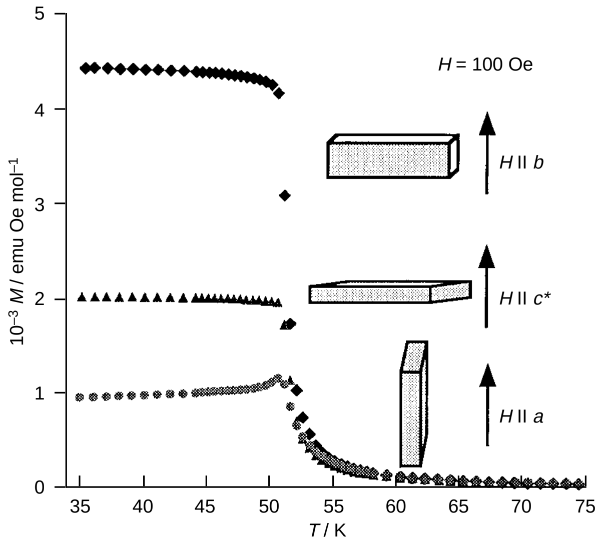

Fig 3 Field-cooled magnetization curves along the *a*, *b* and *c** axis directions of a single crystal of the α phase. The applied magnetic field is 100 Oe.

Notes and References

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‡ *Crystal data*: α phase: $C_7H_{18}N_7O_9Mn_2Mo$, M = 550.10, monoclinic, space group $P2_1/c$ (no. 14), a = 7.951(5), b = 16.819(3), c = 15.189(6) Å, β = 104.29(2)°, U = 1969(2) Å^3; Z = 4, D_c = 1.856, 3292 observations [$I \geqslant 2\sigma(I)$], 287 variables, R = 0.0351, wR_2 = 0.0690, GOF = 1.027.

β Phase: $C_7H_{19.5}N_7O_{9.75}Mn_2Mo$, M = 563.62, monoclinic, space group $P2_1/c$ (no. 14), a = 7.885(3), b = 10.406(7), c = 25.233(11) Å, β = 98.11(2)°, U = 2050(2) Å^3, Z = 4, D_c = 1.826, 2923 observations [$I \geqslant 2\sigma(I)$], 244 variables, R = 0.0475, wR_2 = 0.1025, GOF = 1.090. All data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer with use of Mo-Kα radiation. CCDC 182/823.

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Received in Cambridge, UK, 26th February 1998; 8/01644E