In the field of molecular magnetism, the determination of spin density maps provides crucial information about phenomena such as spin delocalization and spin polarization that play a role in magnetic interactions between metallic ions through organic bridges. The compound MnNi(NO$_2$)$_4$(en)$_2$ (with « en » = ethylenediamine) constitutes the first bimetallic ferromagnetic chain compound to be fully characterized, both magnetically and structurally. The chains present a zig-zag structure formed by alternating Mn(II) and Ni(II) ions bridged by a bidendate NO$_2^-$ group, as shown by Figure 1. The two oxygen atoms of the bridging nitro group are linked to Manganese and the nitrogen atom is bonded to Nickel.

The Nickel ion is located on an inversion center, in a nearly perfect octahedral environment. It is surrounded by four nitrogen atoms coming from the two ethylenediamine groups and by two NO$_2^-$ bridging nitrogen atoms. The Manganese ion resides on a twofold symmetry axis and presents an unusual coordination sphere consisting of eight oxygen atoms, with two non-bonding oxygen atoms at a slightly larger distance than the six others. The intrachain Mn ... Ni distance is equal to 4.817Å.

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The structure can be described as a superimposition of ABAB layers perpendicular to the [001] direction: in the A layer the chains are parallel to [110] while in the B layer they are directed along the [-110] direction. Magnetic susceptibility measurements give evidence for a weak intrachain ferromagnetic coupling $J = 1.33$ cm$^{-1}$. A long range antiferromagnetic ordering between the chains occurs at $T_N = 2.35$K. The behaviour of the magnetization versus magnetic field is characteristic of a metamagnetic compound with a threshold field of 1.2 K0e.

Figure 2 shows the induced spin density map, in projection perpendicular to the N1-Ni-N3 plane. The spin density is positive over all the map including on the NO$_2^-$ bridge. This map was obtained by a multipole model refinement on a set of 127 independent magnetic structure factors measured on the polarized neutron diffractometer 5C1 of the L.L.B. In this model the spin density is assumed to be the sum of atomic spin densities centered on the metal ions and on their first neighbours.. Spherical atomic spin densities were assumed for all atoms except Nickel, for which a 3d-type spin density was refined. The refined spin populations are normalized to 7 μB for each MnNi unit which corresponds to a system of local spins $S_{Mn^{2+}} = + 5/2$ and $S_{Ni^{2+}} = + 1$. 
The Mn$^{2+}$ and Ni$^{2+}$ spin populations are respectively equal to 4.48(4) and 1.62(3) $\mu B$. The unpaired spin on Ni$^{2+}$ is found to be essentially located in the $d_{xy}$ and $d_x^2$ orbitals. For Mn$^{2+}$, equal populations of the five 3d orbitals were assumed. The quantity of spin transferred from Mn$^{2+}$ to its neighbours only amounts to 8 per cent of the moment associated to the manganese region while the spin delocalization from Ni$^{2+}$ represents 24 per cent of the total moment on the nickel site, reflecting the stronger covalent character of the nickel than that of the manganese ion. The delocalization from the nickel ion towards the bridging N3 atom of the nitro group (0.01(3)$\mu B$) is clearly weaker than towards the atoms of the ethylenediamine groups N1 (0.16(3)$\mu B$) and N2 (0.09(3)$\mu B$). Similarly the spin transfer from Mn$^{2+}$ is smaller on both oxygen atoms of the bridge O1 (0.04(3)$\mu B$) and O2 (0.01(2)$\mu B$) than on the O3 atom (0.08(2)$\mu B$) of the non-bridging NO$_2^-$ groups. The weak spin population on the oxygen atom O4 (0.05(2)$\mu B$) may be explained by the larger Mn-O4 distance.

The apparently negligible spin transfer from both metallic ions towards the atoms of the NO$_2^-$ bridging group, compared to the significant spin transfer towards the external ligands is quite paradoxical. The interpretation that we propose is a balance between two phenomena which act in opposite ways: spin delocalization responsible for $\sigma$ type positive spin density on the neighbours of the metallic ions and spin polarization responsible for negative spin density of $\pi$ type on the second neighbours. On the spin density map, the positive spin actually delocalized from each metallic ion towards its first neighbours belonging to the bridge would then be compensated for by a negative contribution due to the presence of the other metallic ion.

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