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Metamagnetic Behavior of the Novel Bimetallic Ferromagnetic Chain Compound $MnNi(NO_2)_4(en)_2$ (en = Ethylenediamine)

Olivier Kahn,*,† Evangelos Bakalbassis,†,‡ Corine Mathonière,† Masayuki Hagiwara,§ Koichi Katsumata,§ and Lahcène Ouahab‖

Laboratoire des Sciences Moléculaires, Institut de Chimie de la Matière Condensée de Bordeaux, UPR CNRS No. 9048,
33608 Pessac, France, The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-01, Japan, and Laboratoire
de Chimie du Solide et Inorganique Moléculaire, URA CNRS No. 1495, Université de Rennes I, 35042 Rennes, France

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The bimetallic chain compounds have played an important role in the field of molecular magnetism.[1−7] Some of them were found to exhibit a long-range magnetic ordering with the onset of a spontaneous magnetization at a critical temperature T_c. In most cases, the intrachain interaction is antiferromagnetic, so that the compound may be described as a one-dimensional ferrimagnet.[8] In one case, at least, an intrachain ferromagnetic interaction was reported. However, the structure of this compound of formula $Mn^{III}Cu^{II}(dmg)_2(H_2O)_2(CH_3CO_2)$, with dmg = dimethylglyoximato, has only been postulated from EXAFS and XANES data.[9]

In this communication, we report the synthesis, the crystal structure, and the preliminary physical properties of a bimetallic chain compound of a new type with intrachain ferromagnetic interaction. The formula of this compound is $MnNi(NO_2)_4(en)_2$, with en = ethylenediamine. It was synthesized by self-assembling of the neutral precursor $[Ni(NO_2)_2(en)_2]$, the Mn(II) cation, and two additional nitrite anions.

$[Ni(NO_2)_2(en)_2]$ was prepared as previously described.[10] $MnNi(NO_2)_4(en)_2$ was synthesized as follows: To a purple solution of 0.267 g (1 mmol) of $[Ni(NO_2)_2(en)_2]$ dissolved in 10 mL of methanol was added a solution of 0.234 g (1 mmol) of $MnCl_2{\cdot}6H_2O$ and 0.134 g (2 mmol) of $NaNO_2$ dissolved in 10 mL of methanol. The resulting mixture was stirred at room temperature for 30 min, after which it was filtered and reduced to 5 mL. Single crystals were obtained by slow evaporation. Anal. Calcd for $C_4H_{16}N_8O_8MnNi$: C, 11.50; H, 3.86; N, 26.82; Mn, 13.15; Ni, 14.05. Found: C, 11.68; H, 3.92; N, 26.59; Mn, 13.21; Ni, 14.42.

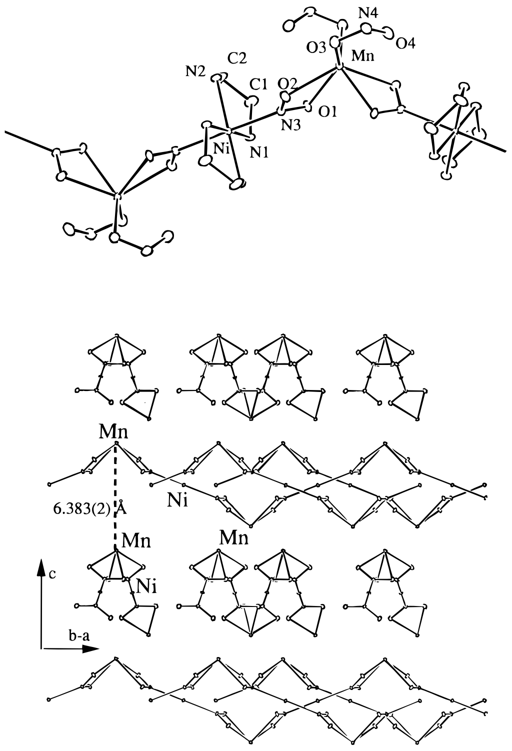

Figure 1. Top: Structure of the bimetallic chain in $MnNi(NO_2)_4(en)_2$. Bottom: Crystal packing for $MnNi(NO_2)_4(en)_2$.

The crystal structure of $MnNi(NO_2)_4(en)_2$ was determined at room temperature.[11] The structure consists of bimetallic chains running in a zigzag fashion, as shown in Figure 1. The Ni(II) ion is located on an inversion center. It is surrounded by six nitrogen atoms; four of them belong to two ethylenediamine ligands in *trans* positions, and two of them belong to NO_2^- briging ligands, also in *trans* positions. NO_2^- behaves as a nitro ligand with respect to the Ni atom. The NiN_6 core is very nearly a perfect octahedron, with Ni−N bond lengths ranging from 2.099(6) to 2.144(5) Å. The Mn(II) ion is located on a 2-fold symmetry axis. It is surrounded by four NO_2^- groups; two of them (N3O1O2 and the symmetry-related N3*O1*O2*) are bridging and are bound to Mn(II) in a bidentate nitrito fashion with Mn−O1 = 2.261(5) Å and Mn−O2 = 2.363(4) Å. The other two NO_2^- groups (N4O3O4 and the symmetry-related N4*O3*O4*) are terminal and may be viewed as monodentate nitrito ligands, with Mn−O3 = 2.178(6) Å. It should be stressed here, however, that the Mn−O4 separation involving the formally nonbonded oxygen atom is equal to only 2.474(5) Å. The manganese coordination polyhedron is, therefore, quite unusual with a 6 + 2 coordination. The values of the dihedral

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† Institut de Chimie de la Matière Condensée de Bordeaux.

‡ Permanent address: Laboratory of Applied Quantum Chemistry, Faculty of Chemistry, Aristotle University of Thessaloniki, 540 06, Thessaloniki, Greece.

§ The Institute of Physical and Chemical Research.

‖ Université de Rennes I.

(1) Gleizes, A.; Verdaguer, M. *J. Am. Chem. Soc.* **1984**, *106*, 3727.

(2) Pei, Y.; Verdaguer, M.; Kahn, O.; Sletten, J.; Renard, J. P. *Inorg. Chem.* **1987**, *26*, 138.

(3) Kahn, O.; Pei, Y.; Verdaguer, M.; Renard, J. P.; Sletten, J. *J. Am. Chem. Soc.* **1988**, *110*, 782.

(4) Coronado, E.; Drillon, M.; Fuertes, A.; Beltran, D.; Mosset, J.; Galy, J. *J. Am. Chem. Soc.* **1986**, *108*, 900.

(5) Coronado, E.; Drillon, M.; Nugteren, P. R.; de Jongh, L. J.; Beltran, D.; Georges, R. *J. Am. Chem. Soc.* **1989**, *111*, 3874.

(6) Kahn, O. Adv. *Inorg. Chem.* **1995**, *43*, 1789.

(7) Turner, S.; Kahn, O.; Rabardel, L. *J. Am. Chem. Soc.* **1996**, *118*, 6428.

(8) Kahn, O. *Molecular Magnetism*; VCH: New York, 1993.

(9) Lloret, F.; Ruiz, R.; Julve, M.; Faus, J.; Journaux, Y.; Castro, I.; Verdaguer, M. *Chem. Mater.* **1992**, *4*, 1150.

(10) *Jikken Kagaku Koza*; Inokuchi, Ed.; Maruzen Co.: Tokyo, 1991.

(11) Crystal data: formula = $C_4H_{16}N_8O_8MnNi$, fw = 417.87, orthorhombic, space group *Pccn* (No. 56), $a = 14.559(2)$ Å, $b = 7.898(2)$ Å, $c = 12.765(2)$ Å, $V = 1467.9(5)$ Å^3, $Z = 4$, $d_{cal} = 1.892$ g cm^{-3}. Single-crystal diffraction data were collected on an Enraf-Nonius CAD4 diffractometer using the $\theta-2\theta$ scan technique, with graphite-monochromated Mo Kα ($\lambda = 0.710\,73$ Å) radiation. A total of 1557 independent reflections were collected. The structure was solved using direct-method techniques. $R = 0.038$ and $R_w = 0.051$ for 708 reflections with $I \geq 4\sigma(I)$.

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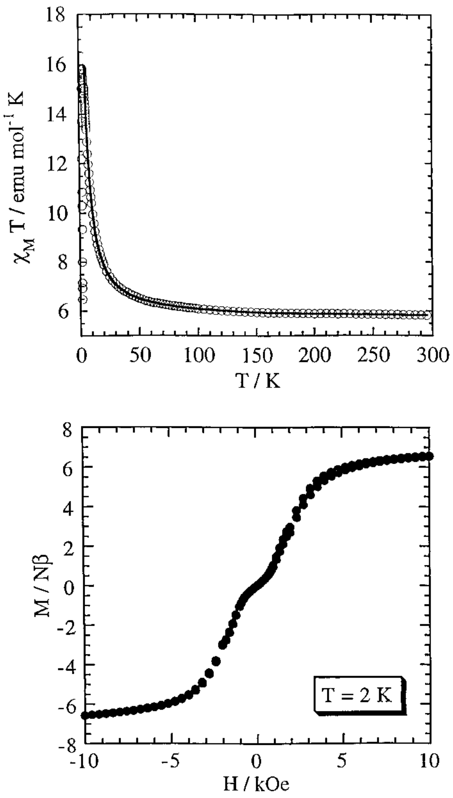

Figure 2. Top: Experimental (○) and calculated (—) $\chi_M T$ versus T curves for $MnNi(NO_2)_4(en)_2$. Bottom: Field dependence of the magnetization at 2 K for $MnNi(NO_2)_4(en)_2$.

angles around the Mn atom may also support a dodecahedral geometry. The intrachain Mn---Ni separation is equal to 4.817(5) Å.

Within the lattice, the chains form two sets of alternating layers, both perpendicular to the *c*-axis direction, as shown in Figure 1. In one of the sets, the chains run along the [110] direction; in the other set, they run along the [$\bar{1}$10] direction.

The magnetic susceptibility data are represented in Figure 2 in the form of the $\chi_M T$ versus T curve, χ_M being the molar magnetic susceptibility and T the temperature. At room temperature, $\chi_M T$ is equal to 5.7 emu K mol^{-1}, a value slightly above what would be expected for isolated Mn(II) and Ni(II) ions with local spins $S_{Mn} = {}^5/_2$ and $S_{Ni} = 1$, respectively. $\chi_M T$ increases more and more rapidly as T is lowered, then exhibits a very sharp maximum at 2.9 K with $\chi_M T = 16.0$ emu K mol^{-1}, and eventually decreases as T is lowered further. A maximum of χ_M is observed at $T_N = 2.35$ K. This behavior is characteristic of Mn(II)−Ni(II) intrachain ferromagnetic interactions, with a long-range antiferromagnetic ordering of the ferromagnetic chains occurring at T_N.

These magnetic susceptibility data can be quantitatively interpreted using a model in which S_{Mn} is treated as a classical spin and S_{Ni} as a quantum spin.[12] Assuming that the interaction Hamiltonian is $\mathbf{H} = -J\sum_i S_{Mn,i}\cdot\mathbf{S}_{Ni,i}$ results in a J value of 1.33(1) cm^{-1}, the local Zeeman factors being found as $g_{Mn} = 2.01(2)$ and $g_{Ni} = 2.24(1)$. The experimental data were fitted in the 12−300 K temperature range, where the influence of the interchain interactions is assumed to be negligible.

The variation of the magnetization M versus the applied magnetic field H at 2 K, i.e. below T_N, is also shown in Figure 2. The curve exhibits a change in sign of $\partial^2 M/\partial H^2$ at $H_c = 1.2$ kOe, which is typical of a metamagnetic behavior. The zero-field ground state below 2.35 K is an antiferromagnetic state. The field H_c is sufficient to overcome the weak antiferromagnetic interchain interactions and lead to a ferromagnetic-like state.[13] The saturation magnetization is found to be around 6.3 Nβ, which corresponds to what is expected for a Mn(II)−Ni(II) compound with all the local spins oriented along the field direction.

The work described in this communication presents several appealing aspects: (i) the self-assembling of the $[Ni(en)_2(NO_2)_2]$, Mn(II), and NO_2^- constituents; (ii) the unprecedented structure of the bimetallic chain; (iii) the ferromagnetic nature of the Mn(II)−Ni(II) interaction; (iv) finally, the metamagnetic behavior of the compound. We intend to explore further the physics of this compound, to analyze the mechanism of the Mn(II)−Ni(II) interaction and to synthesize new bimetallic compounds from the $[Ni(en)_2(NO_2)_2]$ precursor.

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Supporting Information Available: Listings of crystal and refinement data, positional parameters, general displacement parameter expressions, and bond lengths and bond angles (4 pages). Ordering information is given on any current masthead page.

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[12] Kahn, O.; Pei, Y.; Nakatani, K.; Journaux, Y. *New J. Chem.* **1992**, *16*, 269.

[13] Willett, R. D.; Gaura, R. M.; Landee, C. P. In *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum: New York, 1983; Vol. 3, p 143.