A Three-Dimensional Homometallic Molecular Ferrimagnet**

Sanjit Konar, Partha Sarathi Mukherjee,
Ennio Zangrando, Francesc Lloret,* and
Nirmalendu Ray Chaudhuri*

Multidimensional molecular-based magnets are the focus of considerable current research effort from both fundamental and device-related perspectives.[1] Two- or three-dimensional (2-D, 3-D) homometallic magnetic systems can behave as ferromagnetic, antiferromagnetic, or as metamagnetic materials depending on the nature of the spin coupling.[1b, 2] However, an example of a 3-D homometallic system with ferrimagnetic behavior has not yet been reported because the conditions for the noncompensation of the individual spin moments are difficult to achieve in these systems. In this communication we report the synthesis, crystal structure, and magnetic behavior of a 3-D homometallic ferrimagnet that orders magnetically at 6 K. To the best of our knowledge, this is the first 3-D homometallic molecular ferrimagnet.

Hydrothermal treatment of $Ni(NO_3)_2 \cdot 6\,H_2O$ with disodium fumarate ($Na_2(CO_2CH=CHCO_2)$; Na_2(fum)) in water at 170 °C leads to the formation of the complex $[Ni_3(fum)_2(\mu_3\text{-}OH)_2(H_2O)_4]_n \cdot (2\,H_2O)_n$ **1**. The X-ray analysis shows a 3-D structure[3] formed by chains of fused Ni^{II} octahedral units. These chains, in which all the metal atoms are coplanar, include two crystallographically independent ions: A symmetry related pair Ni(1) and Ni(1′) separated by 3.017(1) Å that alternates with Ni(2), located on a center of symmetry. The Ni(1)–Ni(2) and Ni(1′)–Ni(2) distances are 3.661(1) and 3.557(1) Å, thus forming a figure close to an isosceles triangle. The three metal atoms share an edge of their octahedron, being capped by the hydroxyl oxygen O(5), alternatively above and below the chain but slightly displaced by 0.55 Å (Figure 1). The fumarate carboxylate groups bridge the longest edges of the metal triangle, completing the coordination sphere of Ni(2), whereas the hexacoordination about Ni(1) is achieved through the oxygen atoms of two water molecules, Ow(1) and Ow(2). The Ni–O distances with fumarate oxygen atoms and hydroxo ligand are all comparable and range from 2.039(3) to 2.085(3) Å, while those involving the water molecules are slightly longer (Ni(1)–O(1w) 2.101(3) and Ni(1)–O(2w) 2.107(3) Å). The O-Ni-O *cis* angles lie in the range from 83.2(1) to 96.8(1)°, namely with a deviation of ±7° from the ideal 90° value required for a purely octahedral coordination geometry. The dicarboxylate anions, acting as a bridging bis-bidentate ligand, diverge from the chain and connect to metal centers of an adjacent chain, thereby leading to a 3-D framework where the shortest Ni–Ni interchain distance is 8.140 Å. Figure 2 shows a view of the 3D framework with channels occupied by crystallization

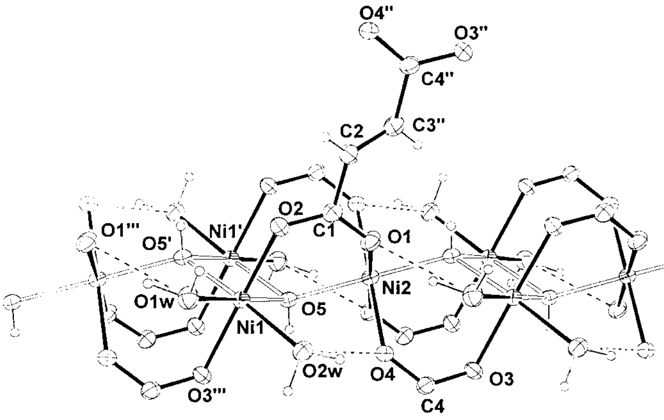

Figure 1. ORTEP plot (40 % thermal ellipsoids) of the metal chain and atomic numbering scheme for **1**. Open bonds indicate Ni–OH connections; only a single complete fumarate anion is shown for the sake of clarity. Coordination bond lengths and intermetallic distances [Å]: Ni(1)-Ni(1′) 3.017(1), Ni(1)-Ni(2) 3.661(1), Ni(1′)-Ni(2) 3.557(1), Ni(1)-O(1w) 2.101(3), Ni(1)-O(2w) 2.107(3), Ni(1)-O(2) 2.039(3), Ni(1)-O(3) 2.066(3), Ni(1)-O(5) 2.079(3), Ni(1)-O(5′) 2.038(3), Ni(2)-O(1) 2.085(3), Ni(2)-O(4) 2.074(3), Ni(2)-O(5) 2.068(3). Symmetry operations: $(x, y, z)' = (-x+1, -y+2, -z+1)$; $(x, y, z)'' = (x, -y+3/2, z+1/2)$; $(x, y, z)''' = (x+1, y, z)$.

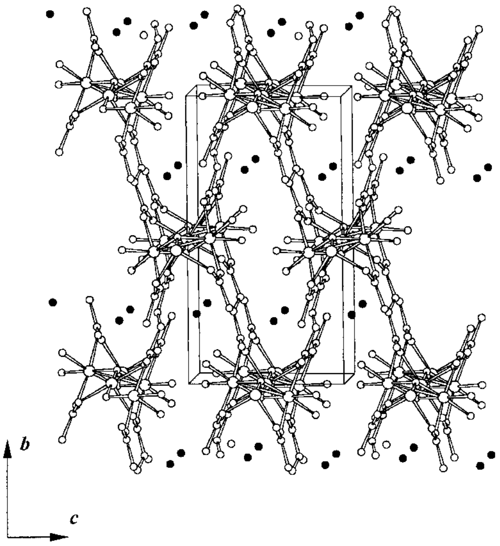

Figure 2. Packing view along axis *a* showing the 3-D structure with crystallization water molecules (oxygen atoms as shaded spheres) located in the framework.

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[*] Prof. N. R. Chaudhuri, S. Konar
Department of Inorganic Chemistry
Indian Association for the Cultivation of Science
Kolkata 700032 (India)
Fax: (+91) 33-473-2805
E-mail: icnrc@mahendra.iacs.res.in

Prof. F. Lloret
Department de Quimica Inorganica
Universitat de Valencia
46100 Burjassot (Spain)
Fax: (+34) 6-386-4322
E-mail: Francisco.Lloret@uv.es

P. S. Mukherjee
Department of Chemistry
Kalna College
Kalna 713409 (India)

Prof. E. Zangrando
Dipartimento di Scienze Chimiche
University of Trieste
34127 Trieste (Italy)

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water molecules. It is worthwhile to note that the coordinated water molecules make intrachain (O(1w)–O(1) 2.781, O(2w)–O(4) 2.810 Å; see Figure 1) and interchain hydrogen bonds (O(1w)–O(2w) 2.847 Å) that reinforce the overall structure. Finally, a solvent water molecule, O(3w), accommodated in the channels (Figure 2) is bound to the framework through O(2) (2.892 Å) and O(3) (2.712 Å). A few structurally characterized compounds containing Ni^{II} chains with di- and polyfunctional ligands have been reported so far. Metal chain complexes with oligopyridylamino ligands represent a remarkable example of a metal wire[4] with intermetallic distances in the range 2.20–2.38 Å. Structural features of the present metal chain seem more appropriately compared with a nickel chloride sequence,[5] formed by pentameric oligomers (Ni–Ni distances of about 3.0 Å) linked through di-μ-chloro bridges (Ni–Ni 3.4 Å), where the intermetallic distances are comparable to those reported here. However, the present structure, of infinite -$(Ni)_2$-Ni- units capped by a μ_3-hydroxo ligand and bridged by dicarboxylate fumarate anions, represents an unique example of a 3-D network.

The magnetic behavior[6] of the title complex **1** is shown in Figure 3 in the form of $\chi_M T$ versus T plot (χ_M is the magnetic susceptibility per three Ni^{II} ions). This curve shows that at room temperature the $\chi_M T$ value (3.5 $cm^3 mol^{-1} K$) corresponds to three magnetically isolated Ni^{II} ions and when the temperature decreases the $\chi_M T$ values decrease; a minimum (2.5 $cm^3 mol^{-1} K$) is observed at 17 K. Below this minimum, $\chi_M T$ rapidly increases and reaches a very high value before becoming strongly field dependent at around 6 K ($\chi_M T = 170\, cm^3 mol^{-1} K$ at 5.5 K for $H = 100$ G). This curve is characteristic of ferrimagnetic behavior. The inset of Figure 3 shows the field-cooled magnetization and reveals spontaneous magnetization at 6 K. This critical temperature is also confirmed by an ac-susceptibility measurement. Finally, the magnetization curve, which is shown in Figure 4, exhibits a saturation value about 2.2 BM and a hysteresis loop with a critical field of 65 G and remnant magnetization of 0.55 BM (see Figure 4 inset). All these data indicate that **1** behaves as a magnet with a spontaneous magnetization below 6 K.

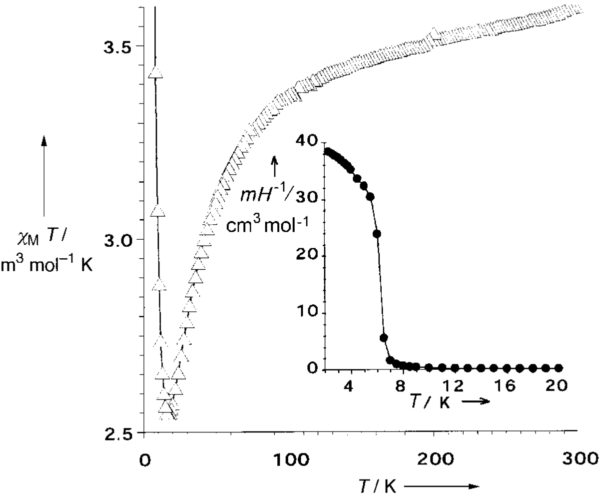

Figure 3. Plot of $\chi_M T$ versus T for **1**. Inset: Field-cooled magnetization curve (under an applied magnetic field $H = 100$ G) showing ferromagnetic order at 6 K.

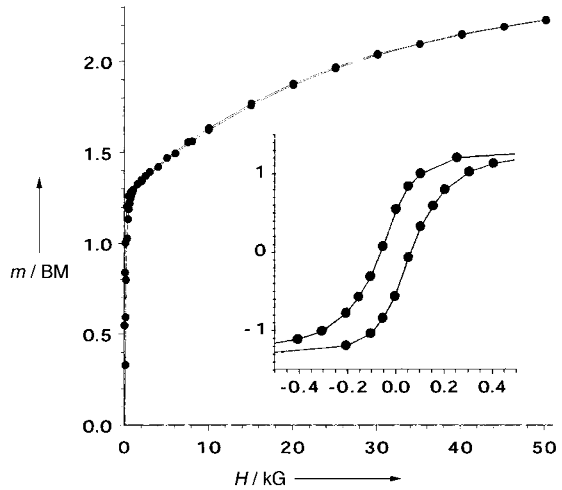

Figure 4. Magnetization curve for **1** at 2 K. Inset: Hysteresis loop at 2 K with decreasing H first.

In the structure we have a chain with hydroxo and carboxylato bridges. The hydroxo bridge has Ni-O(H)-Ni angles lying in a range for which ferromagnetic coupling between two Ni^{II} centers has been observed,[7] and a $S = 2$ ground spin state for this fragment is expected at a low temperature. The single hydroxo (open angle) and carboxylate bridges give antiferromagnetic interaction between the Ni(2) atom ($S = 1$) and the ferromagnetic fragment ($S = 2$), leading to a ferrimagnetic chain system with alternating $S = 2$ and $S = 1$ spin values (Figure 5). Individual ferrimagnetic chains interact with adjacent chains in a ferromagnetic fashion through the fumarate skeleton to yield a ferromagnetic compound below 6 K. The saturation value (2.2 BM) in

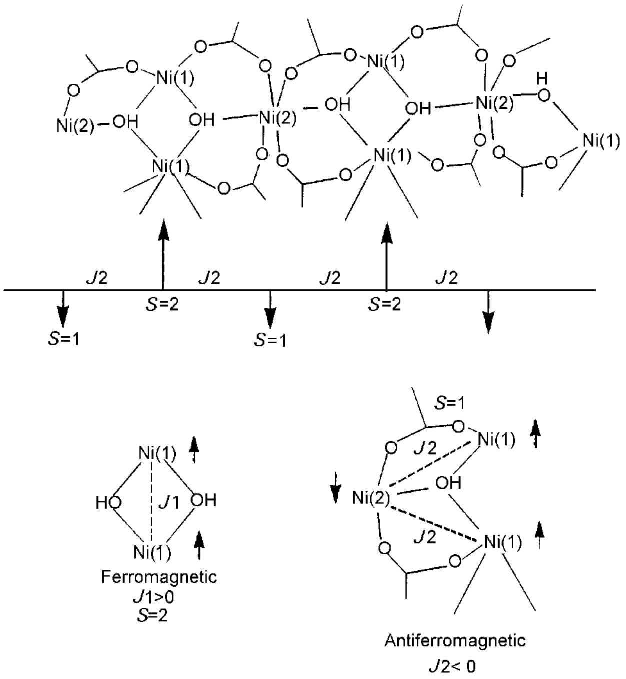

Figure 5. Spin states of the Ni^{II} chain in the ground state overlaid onto the molecular structure. The alternating spin states produce a ferrimagnetic chain system.

the magnetization curve (Figure 4) is in agreement with the magnetic coupling scheme proposed above, that is, antiferromagnetic coupling between $S=1$ and $S=2$ leads to a triplet ground spin state with $g=2.2$. These features rule out the possibility of magnetic ordering through spin canting or a helical ferromagnet. Further magnetic properties of this unique homometallic system are under investigation.

Experimental Section

1: In a typical synthesis, $Ni(NO_3)_2 \cdot 6H_2O$ (1 mmol) was heated with Na_2(fum) (1 mmol) in water (15 mL) at 170 °C for 24 h in a teflon-lined steel vessel. Overnight cooling of the vessel results in a microcrystalline green solid along with single crystals (65 % yield) suitable for X-ray diffraction. Elemental analysis (%): calcd (found): C 17.57 (17.66), H 3.29 (3.38).

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[3] Crystal data: $C_8H_{18}Ni_3O_{16}$ (**1**) $M_r=546.35$, monoclinic, space group $P2_1/c$, $a=6.558(3)$, $b=8.128(3)$, $c=15.506(4)$ Å, $\beta=96.36(3)^\circ$, $V=821.4(5)$ Å^3, $Z=2$, $\rho_{calcd}=2.209$ g cm^{-3}, $\mu=3.490$ mm^{-1} ($Mo_{K\alpha}$), $F(000)=556$. θ range for data collection 4.01–30.15°, final $R=0.0508$, $wR2=0.1383$, $S=1.141$ for 146 parameters and 3606 reflections, 2216 unique [R(int) = 0.0455], of which 1866 with $I>2\sigma(I)$, max. positive and negative peaks in ΔF map 0.906 and −0.926 e Å^{-3}. The data set was collected on a Nonius DIP-1030H system equipped with $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å) at room temperature. A total of 30 frames were collected, each with a rotation of 6° about φ and an exposure time of 12 min over a half of reciprocal space; the detector is 80 mm from the crystal. Data reduction and cell refinement was carried out using the program MOSFLM.[8] The structure was solved by Patterson and Fourier analyses and refined by the full-matrix least-squares method based on F^2 using SHELX 97[9] to SHELX 86. All the calculations were performed using the WinGX System (Ver. 1.64).[10] CCDC 171598 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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Arene–Perfluoroarene Interactions as Physical Cross-Links for Hydrogel Formation[**]

Andreas F. M. Kilbinger and Robert H. Grubbs[*]

In 1960 Patrick and Prosser discovered that hexafluorobenzene (HFB, m.p. = 5.0 °C) and benzene (m.p. = 5.4 °C), both liquids at room temperature, form a 1:1 solid complex with a melting point of 23.7 °C when mixed together.[1] Extensive X-ray crystallographic studies by Dahl showed that a wide variety of aromatics[2] form such 1:1 cocrystals with HFB, all showing alternating columnar face-to-face stacking. The packing behavior was explained theoretically to arise from electrostatic interactions between the two partners with the quadrupolar moment of HFB being complementary to that of benzene or its hydrocarbon derivatives.[3, 4] The binding energy between the two aromatic rings (benzene–HFB) was computed to be 3.7 kcal mol^{-1}.[5] Similar stacking motifs have been observed for several other cocrystals of perfluorinated aromatic compounds with their non-fluorinated analogues.[6–8] Crystal structures of 1:1 complexes between perfluoroarenes and arenes of mismatched geometry have also been reported.[9–14] Because the geometric arrangement in the solid state is to some extent predictable, fluorinated compounds have been prepared with the aim of engineering their geometric orientation in the crystal.[15–17]

We were particularly interested in using perfluoroarene–arene interactions to aggregate polymers in solution. While a number of noncovalent interactions are well investigated in polymeric systems,[18–20] no case has been reported where perfluoroarene–arene interactions were employed. Our idea was to modify either end of the polymer chain with aromatic groups in the hope that they would form alternating stacks in the presence of a perfluorinated additive in solution. Association by the end groups would increase the molecular weight, this could easily be shown by an increase of viscosity. Naphthalene as the aromatic group at the polymer chain end in combination with the perfluorinated additive octafluoronaphthalene (OFN) seemed a good candidate. The stacking behavior of naphthalene with OFN in the solid state is well known, the 1:1 complex between naphthalene and OFN shows an increased melting temperature of around 45–50 °C with respect to either stacking partner and many naphthalene derivatives are commercially available or synthetically accessible in few reaction steps.

Initial experiments with nonpolar polymers, such as poly(norbornene), poly(cyclooctadiene), and others prepared by ring-opening metathesis polymerization (ROMP), with naph-

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[*] Prof. Dr. R. H. Grubbs, Dr. A. F. M. Kilbinger
California Institute of Technology
Division of Chemistry and Chemical Engineering
Mail code 164-30, Pasadena, CA 91125 (USA)
Fax: (+1) 626-5649297
E-mail: rhg@caltech.edu

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