Microporous Materials

The Chirality, Porosity, and Ferromagnetism of a 3D Nickel Glutarate with Intersecting 20-Membered Ring Channels

Nathalie Guillou, Carine Livage, Marc Drillon, and Gérard Férey*

Hybrid edifices based on transition metals are currently one of the most productive areas of chemical research. Indeed, the ability of the organic moiety to diversify structural arrangements associated with the wide-ranging properties of transition metals (e.g. magnetic and optical properties, electronic conductivity and ferroelectricity) is very attractive as soon as the inorganic subnetwork is at least one-dimensional.[1] Whereas synthesis at room temperature leads only to coordination polymers, it is now well known that hydrothermal conditions considerably increase the dimensionality of the inorganic part and therefore the stability of the compounds.[2] In these conditions, divalent cations, such as Mn,[3] Fe,[4] Co,[5] Cu,[6] and Zn[7] generally lead to 1- and 2D inorganic subnetworks. The important feature is that the extent of the metal-oxide condensation seems to strongly depend on the electronic structure of the cation. For example, condensation becomes important with Mn species, which sometimes give pseudo 3D inorganic skeletons.[3b] With nickel, the inorganic condensation is even more diverse and first investigations on carboxylates showed that Ni could generate microporous materials with novel M-O-M connectivities in which polyhedra can share faces, edges, and/or corners.[8] Indeed, $[Ni_7(C_4H_4O_4)_6(OH)_2(H_2O)_2]\cdot 2H_2O$ presents a remarkable honeycomb nickel oxide network,[8a] while $[Ni_7(C_4H_4O_4)_4(OH)_6(H_2O)_3]\cdot 7H_2O$ or MIL-73 has a layered structure constructed from nickel oxide chains containing unprecedented hexanickel building blocks.[8e]

Herein we describe a ferromagnetic, porous, nickel glutarate which has a complex framework of helical octahedral chains and very large intersecting 20-membered ring tunnels.

The compound was synthesized by classical hydrothermal reaction. Its structure was solved by ab initio structure determination from laboratory data. A cubic solution ($a =$ 16.5812(7) Å; $V = 4558.8(6)$ Å^3) was consistent with the two chiral $P4_332$ and $P4_132$ space groups. Since it is impossible to

[*] Dr. N. Guillou, Dr. C. Livage, Prof. G. Férey
Institut Lavoisier, UMR CNRS 8637
Université de Versailles Saint-Quentin-en-Yvelines
45 avenue des Etats-Unis, 78035 Versailles Cedex (France)
Fax: (+33) 1-3925-4358
E-mail: guillou@chimie.uvsq.fr
Dr. M. Drillon
Institut de physique et de Chimie
des Matériaux de Strasbourg
23 rue du Loess, 67037 Strasbourg (France)

Supporting information for this article (selected analytical data and structural data) is available on the WWW under http://www.angewandte.org or from the author.

  DOI: 10.1002/ange.200352520

determine an absolute structure from powder diffraction, $P4_332$ was arbitrarily chosen to solve the structure. Nevertheless, because the starting materials are nonchiral, the final compound is probably a mixture of microcrystals of the two enantiomeric forms. At the final stage, the structural model contained 16 non-hydrogen atoms, and soft constraints were maintained for the organic molecules. The final Rietveld refinement (angular range 5–90° (2θ); 416 reflections; 42 structural parameters; Figure 1) corresponds to satisfactory model indicators ($R_B = 0.033$ and $R_F = 0.030$) and profile factors ($R_P = 0.069$ and $R_{WP} = 0.095$).

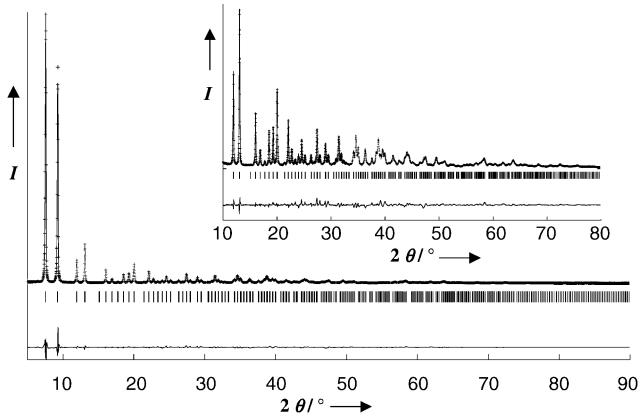

Figure 1. Final Rietveld plot of MIL-77. Inset: an expansion at high angles.

Views of the structure (Figure 2) show that this new nickel glutarate, denoted MIL-77, presents an open 3D network of edge-sharing nickel octahedra. This complex framework is generated by two independent nickel atoms: Ni1 located on the threefold axis and Ni2 on the twofold one. The two independent nickel atoms have octahedral coordination with bond lengths ranging from 1.97(1) to 2.17(2) Å. Each Ni1 octahedron shares three edges with three Ni2 octahedra, each Ni2 octahedron shares two of its *trans* edges with two neighboring Ni1 octahedra. This complicated oxide network can be simply described from helixes running along the *a* axis, where Ni1 and Ni2 polyhedra alternate (Figure 2a). Each helix is connected to four out-of-phase parallel neighboring ones (above and below, and in front and behind), through a third Ni2 octahedron, which generates corrugated twenty-membered rings (Figure 2b). That also induces the formation of perpendicular helixes in this chiral structure. Topologically, a few analogies could be found with the (10–3)a network observed for nickel coordination polymers.[9] The oxide framework is decorated by two independent, deprotonated, glutarate anions (Figure 2b). One is located on the twofold axis and has two multidendate carboxylate groups which each coordinate to three nickel atoms, in an μ_2 and a terminal fashion. This type of carboxylate connectivity is common and has been observed for numerous linear manganese, cobalt, and nickel dicarboxylates[3b,5a,5c,8a,8e] For the carboxylate groups of the second glutarate ion, one of the oxygen atoms coordinates through an μ_2 manner and the other is non-coordinating. This type of carboxylate connectivity seems to be more specific to nickel compounds.[8a,f] In the case of dicarboxylates, it has been observed, to date, only for one of the carboxylate groups.[8a] Since this glutarate ion is located on a threefold axis, it is disordered with statistic occupancy of 2/3. To complete octahedral environment of the nickel centers, 1/3 of the Ni site filled by carboxylate oxygen atom is also occupied by a bridging water molecule. This situation corresponds to the chemical formula, $[Ni_{20}\{(C_5H_6O_4)_{20}(H_2O)_8\}]\cdot 40\,H_2O$.

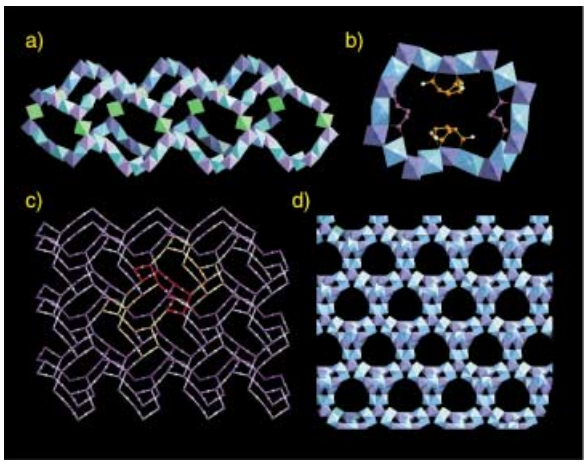

Figure 2. a) View of four helixes with alternating Ni1 (mauve) and Ni2 (pale blue) connected by Ni2 octahedra (green), b) polyhedral view of a corrugated twenty-membered ring with the two independent glutarate ions; the orange one is disordered with statistic occupancy of 2/3, c) view of the nickel network showing interconnected rings, d) view of the nickel oxide tunnels down [111].

The twenty-membered rings intersect each other (Figure 2c) to generate crossing tunnels in the [111] direction (Figure 2d). The shortest opposite O···O distance in the corrugated ring is 9.1 Å and the longest one is 15.8 Å. The pores are partially obstructed by glutarate ions, mostly by the disordered one with a C–C distance of about 4 Å between central atoms of two glutarate molecules.

The thermal behavior of $[Ni_{20}\{(C_5H_6O_4)_{20}(H_2O)_8\}]\cdot 40\,H_2O$ was characterized by thermogravimetric analysis (TGA; flowing oxygen) and X-ray thermodiffraction (air). A gradual weight loss observed until 150 °C corresponds to the presence of the 40 occluded water molecules (found: 15.8 wt %, calcd: 15.5 wt %) without significant structural change. Then, the loss of the eight coordinated water molecules (found: 2.7 wt %, calcd: 3.1 wt %) occurs between 255 and 275 °C on the TGA curve and is combined to a crystallographic change observed at 240 °C. The anhydrous compound rehydrates very slowly (several days) under air at room temperature, even if no structural change is observed on thermodiffractometry from 250 °C to 50 °C. Its total rehydration can be obtained under water-saturated air in less than one day. This behavior may indicate sorption properties. Between 330 and 360 °C the structure collapses with the combustion of the organic moieties (found: 48.8 wt %, calcd: 49.2 wt %).

A sample activated at 200 °C under vacuum gives a typical Type-1 isotherm and a surface area of 346(10) m^2g^{-1} which clearly indicates notable porosity for this compound. Curious-

ly, when the sample is activated under vacuum at 250 °C, the surface area decreases to 50(1) $m^2 g^{-1}$, which may indicate that important structural changes occur during the loss of the bridging water molecules. It is probably due to some motion of the organic molecules, which come to fill up the pores.

The magnetic properties of the compound, measured in a 3.5 Oe ac field, are displayed in Figure 3. Upon cooling from 9 to 4 K, χT remains quite small, and then increases sharply at lower temperature, up to 1750 emu K mol^{-1}, followed by a moderate decay. The presence of an out-of-phase signal (χ'')

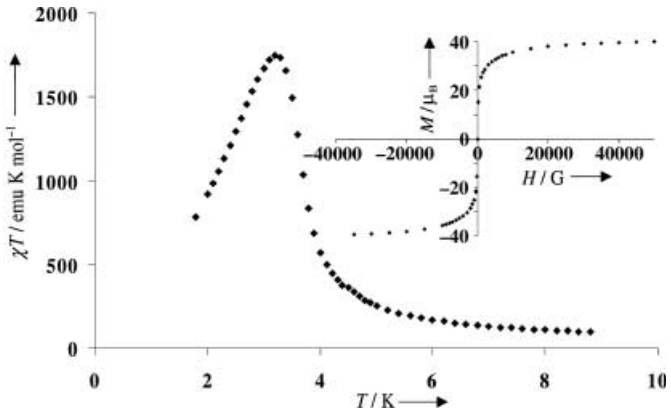

Figure 3. Thermal dependence of the χT product. The inset shows the magnetization versus the applied magnetic field at 2 K.

at the same temperature points to the stabilization of a magnetized state at low temperature. A plot of the field dependent magnetization at 2 K confirms these results (Figure 3). The saturation magnetization of 40 μ_B mol^{-1} for $H = 60\,000$ G, demonstrates that this compound is a pure cooperative ferromagnet ($Ms = 40\ \mu_B$ expected for $g = 2$), without any spin frustration. Such a behavior is characteristic of ferromagnetic exchange interactions, which are expected for edge sharing nickel(II) octahedra (Ni1-O1-Ni2 99.9(4)° and Ni1-O3-Ni2 97.1(4)° with Ni1-Ni2 3.097(5) Å).[10] The low T_c value is explained by the weakness of the ferromagnetic interaction for a bridge angle significantly larger than 90°.

In Summary, this nickel glutarate presents a chiral structure with very large crossing channels. For the first time, it has been possible to obtain a nickel carboxylate with a 3D network of pores, which is a pure ferromagnet at 4 K. Moreover, it becomes porous (346(10) $m^2 g^{-1}$) at 200 °C, after removing the water of hydration and can slowly reabsorb water molecules. A drastic decrease of the porosity, observed after activation of the sample at 250 °C, may correspond to a structural rearrangement. Some studies are in progress to explain this phenomenon. Once again, the originality of the structure illustrates the versatility of nickel-oxide networks and confirms the plasticity of nickel inorganic condensation under hydrothermal conditions.[5]

Experimental Section

Reactions were carried out in a teflon container (23 mL) at 180 °C for two days under autogenous pressure. The reaction mixture contained $NiCl_2 \cdot 6H_2O$ (1.102 g), glutaric acid (0.916 g), KOH (0.518 g), and H_2O/ethanol (50/50 vol, 5 mL) in the molar ratio 1:1.5:2:60. After cooling (pH 5), the pale green powder was washed with distilled water. Elemental analysis (%): calcd: C 25.88, H 4.69, Ni 25.29; found: C 25.32, H 4.36, Ni 24.92.

The X-ray powder diffraction data were collected on a Siemens D5000 diffractometer by using CuK_α radiation ($\lambda = 1.5418$ Å). The powder diffraction pattern was scanned over an angular range 5–90°(2θ) with a step length of 0.02°(2θ). To improve the counting statistics at high angles, the pattern was divided in two 2θ regions (1–35.98° and 36–90°), with times per step of 32 and 64 s, respectively. Pattern indexing was carried out with DICVOL91.[11] Structure solution was initialized with the EXPO package, integrating EXTRA, for extracting integrated intensities, and SIR97 for direct methods structure solution.[12] A list of 101 reflections was extracted in the angular range 7–70° (2θ) and nickel atoms with their environments were found unambiguously from the E-map with the highest figure of merit. This partial structure was then used as fragment to complete the structural model. The corresponding atomic coordinates were used as starting model for Rietveld refinement, using FullProf integrated in WinPlotr.[13] Successive Fourier difference calculations were then performed with SHELXL to finalize the structural model.[14]

X-ray thermodiffractometry was performed under static air in an Anton Parr HTK16 high-temperature device of a Siemens D-5000 diffractometer (θ–θ mode, CoK_α radiation) equipped with a M Braun linear position sensitive detector (PSD). The dehydration–rehydration processes have been studied at 10 °C intervals (40–250–50 °C) and decomposition at 20 °C intervals up to 600 °C; temperature ramp of 0.05 °C.s^{-1}; several hours at 250 and 50 °C. Thermogravimetric analysis was performed using a TA-Instruments TGA-2050 apparatus (oxygen flow 60 ml min^{-1}, 5 °C min^{-1}).

The BET surface area of samples activated under vacuum at 200 °C for 36 h and at 250 °C for 12 h was studied on a Micromeritics ASP200 porosimeter.

Magnetization measurements were performed on a Quantum Design Squid magnetometer (MPMS-5).

Received: July 30, 2003 [Z52520]
Published Online: October 20, 2003

Keywords: chirality · ferromagnetism · microporous materials · nickel · O ligands

[1] a) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705–714; b) G. Férey, *Chem. Mater.* **2001**, *13*, 3084–3098; c) S. Feng, R. Xu, *Acc. Chem. Res.* **2001**, *34*, 239–247; d) M. Eddaoudi, H. Li, O. M. Yaghi, *J. Am. Chem. Soc.* **2000**, *122*, 1391–1397.

[2] C. Livage, C. Egger, G. Férey, *Chem. Mater.* **2001**, *13*, 410–414.

[3] a) Y. Kim, E. Lee, D.-Y Jung, *Chem. Mater.* **2001**, *13*, 2684–2690; b) R. Vaidhyanathan, S. Natarajan, C. N. R. Rao, *J. Chem. Soc. Dalton Trans*, **2003**, 1459–1464; c) Y.-Q. Zheng, D. Sun, *J. Solid State Chem.* **2003**, *172*, 288–295.

[4] M. Sanselme, J. M. Grenèche, M. Riou-Cavellec, G. Férey, *Chem. Commun.* **2002**, 18, 2172–2173.

[5] a) C. Livage, C. Egger, G. Férey, *Chem. Mater.* **1999**, *11*, 1546–1550; b) Z.-L. Huang, M. Drillon, N. Masciocchi, A. Sironi, J.-T Zhao, P. Rabu, P. Panissod, *Chem. Mater.* **2000**, *12*, 2805–2812; c) L.-S. Long, X.-M. Chen, M.-L. Tong, Z.-G. Sun, Y.-P. Ren, R.-B. Huang, L.-S. Zheng, *J. Chem. Soc. Dalton trans.* **2001**, *19*, 2888–2890; d) M. Kurmoo, H. Kumagai, M. A. Green, B. W. Lovett, S. J. Blundell, A. Ardavan, J. Singleton, *J. Solid State Chem.* **2001**, *159*, 343–351.

[6] S. S.-Y. Chui, S. M.-F. Los, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, *283*, 1148–1150.

[7] a) H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276 – 279; b) T. A. Bowden, H. L. Milton, A. M. Z. Slawin, P. Lightfoot, *J. Chem. Soc. Dalton trans.* **2003**, *5*, 936 – 939.
[8] a) P. M. Forster, A. K. Cheetham, *Angew. Chem.* **2002**, *114*, 475 – 477; *Angew. Chem. Int. Ed.* **2002**, *41*, 457 – 459; b) H. Kumagai, Y. Oka, M. M. Akita-Tanaka, K. Inoue, *Inorg. Chim. Acta* **2002**, *332*, 176 – 180; c) S. Konar, P. S. Mukherjee, E. Zangrando, F. Lloret, N. R. Chaudhuri, *Angew. Chem.* **2002**, *114*, 1631 – 1633; *Angew. Chem. Int. Ed.* **2002**, *41*, 1561 – 1563; d) N. Guillou, S. Pastre, C. Livage, G. Férey, *Chem. Commun.* **2002**, 2358 – 2359; e) N. Guillou, C. Livage, W. van Beek, M. Noguès, G. Férey, *Angew. Chem.* **2003**, *115*, 643 – 647; *Angew. Chem. Int. Ed.* **2003**, *42*, 457 – 459; f) P. M. Forster, Z. Yang, A. K. Cheetham, *Solid State Sci.* **2003**, *5*, 635 – 642.
[9] a) C. J. Kepert, M. J. Rosseinsky, *Chem. Commun.* **1998**, 31 – 32; b) C. J. Kepert, T. J. Prior, M. J. Rosseinsky, *J. Am. Chem. Soc.* **2000**, *122*, 5158 – 5168; c) T. J. Prior, M. J. Rosseinsky, *Inorg. Chem.* **2003**, *42*, 1564 – 1575.
[10] J. B. Goodenough *Magnetism and the Chemical Bond*, Wiley, New York, **1963**.
[11] A. Boultif, D. Louër, *J. Appl. Crystallogr.* **1991**, *24*, 987 – 993.
[12] a) A. Altomare, M. C. Burla, M. Camalli, B. Carozzini, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Rizzi, *J. Appl. Crystallogr.* **1999**, *32*, 339 – 340; b) A. Altomare, M. C. Burla, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, *J. Appl. Crystallogr.* **1995**, *28*, 842 – 846; c) A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115 – 119.
[13] a) J. Rodriguez-Carvajal, *Collected Abstract of Powder Diffraction Meeting* (Toulouse) **1990**, p. 127; b) T. Roisnel, J. Rodriguez-Carvajal, *Mater. Sci. Forum* **2001** *378–381*, 118 – 123.
[14] G. M. Sheldrick, SHELXL-97, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany), **1997**. CCDC 216165 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).

