Open-Framework Nickel Succinate, $[Ni_7(C_4H_4O_4)_6(OH)_2(H_2O)_2]\cdot 2H_2O$: A New Hybrid Material with Three-Dimensional Ni–O–Ni Connectivity**

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Hybrid inorganic–organic compounds are attracting interest as a class of materials that are well suited for the incorporation of transition metals into porous frameworks.[1, 2] In such materials, functionality can be introduced from either the inorganic species or the organic linker molecules. Transition metals are well known to confer redox character to zeolitic hosts, and may impart interesting magnetic and spectroscopic properties to porous materials. Organic species, on the other hand, can be used to adjust the channel size, alter the surface of pores, and impart chemical reactivity or chirality.

Much of the current effort on hybrid materials is directed towards synthesizing very open frameworks using rigid organic building blocks. This strategy, as demonstrated by the groups of Robson,[3] Yaghi,[4] and others, begins with metal atoms or clusters of known geometry and connects them using rigid organic linkages into the desired structure, yielding extended, open networks that often resemble classical high-symmetry inorganic structures. The success of this approach is evidenced by the synthesis of materials with unprecedented porosity[5] and large channels containing accessible metal sites.[6] However, this approach yields compounds with zero-dimensional metal–oxygen connectivity, which inhibits many of the cooperative effects well known in transition metal oxides.

By contrast, we have explored the synthesis of new hybrid materials containing multidimensional M–O–M frameworks (where M = metal center). Much of the previous work in this area has focused on transition metal vanadate hybrid materials.[7, 8] For transition metal carboxylates, several examples of multidimensional metal–oxygen connectivity occur for materials made with linear dicarboxylic acids. Kim and Jung prepared a series of Mn^{II} dicarboxylates (glutaric-1,12 dodecanedicarboxylic acid), all of which exhibit essentially the same structure with one-dimensional (1D) MnO_6 ribbons.[9] An isostructural Fe^{II} adipate[10] and a dense, two-dimensional (2D) Fe^{II} succinate[11] have also been reported. Férey and coworkers synthesized several cobalt succinates[12] based on 2D sheets of edge-sharing CoO_6 octahedra joined by succinate linkages to form a three-dimensional (3D) framework. One of these materials, MIL-16,[13] exhibits good thermal stability (300 °C) and reversible dehydration/rehydration, which are considered important indications of porosity. These few examples demonstrate that unbranched linear dicarboxylates support the formation of extended M–O–M structures with organic molecules filling at least part of the void space.

We have focused on nickel-containing compounds following our previous successes at synthesizing nickel phosphates with 3D Ni–O–Ni connectivity and good thermal stability.[14, 15] In the present work, we describe the synthesis of a nickel succinate. While synthesis of this phase using standard hydrothermal conditions was straightforward, we were unable to obtain single crystals for structural characterization. After many unsuccessful attempts, we adopted a biphasic approach in which succinic acid was dissolved in an organic solvent (cyclohexanol) that is not miscible with water, and water was used to dissolve the nickel source.[16] This approach led to single crystals on our first attempt, although it was later recognized that single crystals can only be obtained in a narrow range of synthetic conditions.

The honeycomb structure of nickel succinate is illustrated in Figure 1. To our knowledge, it is the first metal carboxylate with fully 3D M–O–M connectivity. Figure 2 presents one unit cell viewed down the *a* axis, and shows that the compound contains layers of edge-sharing NiO_6 octahedra connected by isolated corner-sharing NiO_6 octahedra. The layers, shown in Figure 3, consist of 15- and 12-rings of edge-sharing octahedra in a 2:1 ratio. The most prominent feature of the nickel succinate structure is the presence of unidimensional pores running parallel to the *c* axis. The pores are lined almost entirely by the methylene groups of the dicarboxylate, which creates an exceptionally hydrophobic surface. The pores have wide and narrow regions, which can be visualized as two 15-rings capped by narrow 12-ring apertures. There is approximately 4.0 Å between H atoms at these narrow apertures, which implies that the pores are actually a series of open cavities partially blocked every 23 Å. At its widest point, the cavity is 8.0 Å wide (atom to atom). Similar pores

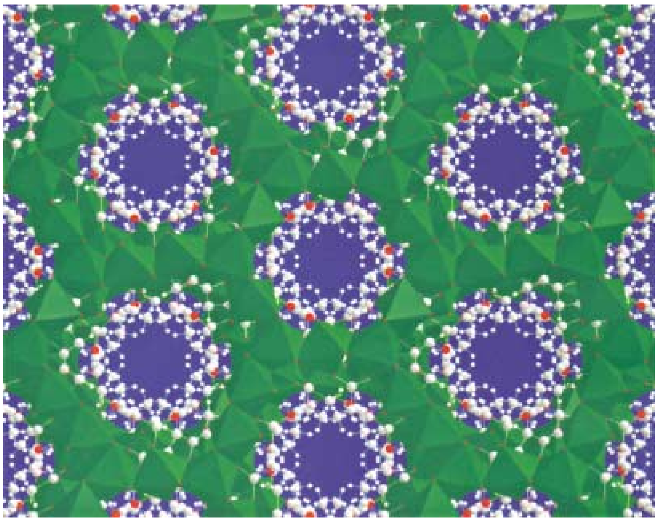

Figure 1. View of the nickel succinate structure down the *c* axis.

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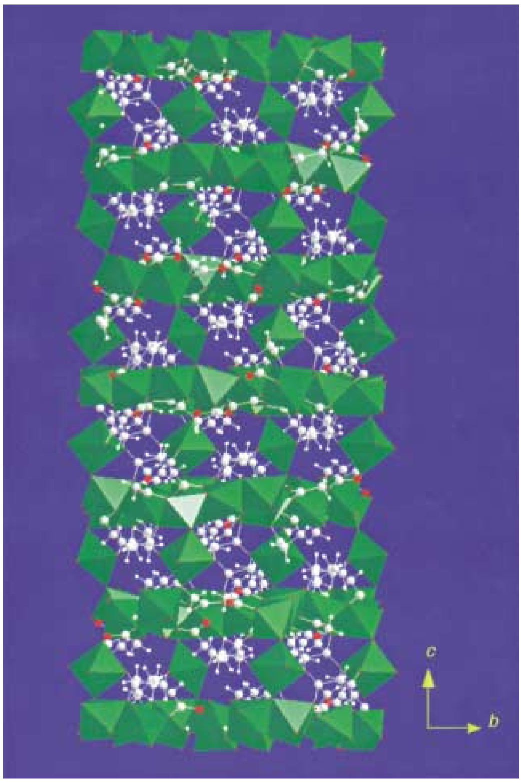

Figure 2. A single unit cell viewed down the *a* axis, with layers containing nickel-oxygen sheets (see Figure 3) apparent. Green: NiO_6 octahedra; red: oxygen.

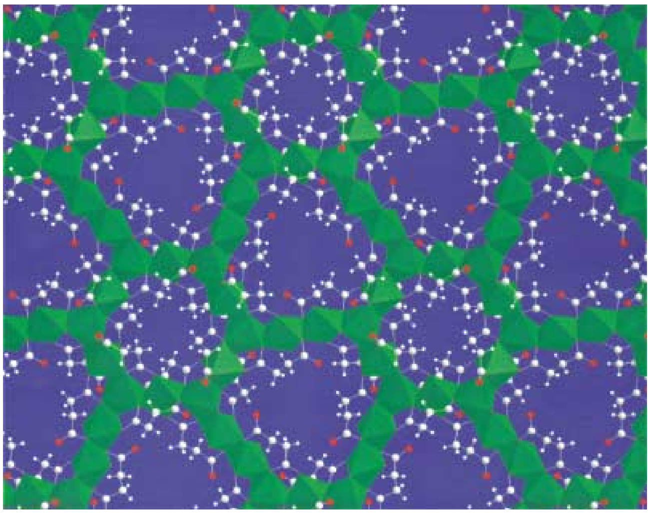

Figure 3. View of a single nickel-oxygen sheet from the *c* axis.

are seen in β-aluminum methylphosphonate.[17] We were unable to locate any water of hydration in the pores.

All four crystallographically independent Ni atoms are octahedrally coordinated to oxygen atoms with bond lengths between 2.006 and 2.110 Å and O-Ni-O angles ranging from 78.7 to 102.6°. The three Ni atoms within the layers (Ni(1), Ni(2), and Ni(4), not shown, see the Experimental Section for Cambridge Crystallographic Data Centre supplementary publication number) are coordinated by a combination of carboxylate oxygen atoms, hydroxide ions, and water molecules. For Ni(1), five of the oxygen atoms are associated with carboxylate groups and the sixth is a hydroxide ion shared between Ni(1), Ni(4), and the nickel between the layers (Ni(3)). In the case of Ni(2), all of the oxygen atoms are from carboxylate groups. For Ni(4), four of the coordination sites are occupied by carboxylate oxygen atoms, while the fifth and sixth sites, which are *trans* to each other, are occupied by the hydroxide anion and a coordinated water molecule directed into the cavity. Ni(3) has *trans* hydroxo ligands, which are shared with nickel atoms in the layers (see above), plus four carboxylate oxygen atoms. There are six carboxylate groups on the three succinate molecules in the asymmetric unit. Five of these groups coordinate to three Ni atoms, while the sixth coordinates with two nickel atoms and has one terminal oxygen atom.

Thermogravimetric analysis (TGA), performed under flowing N_2, shows a gradual weight loss of 6.0 wt %, which corresponds to the loss of four water molecules per formula unit between 200 and 240 °C. A change from blue-green to light green accompanies the water loss. We attribute this change to the loss of the coordinated water molecule (calcd 3.1 wt %), plus approximately six water molecules per cavity (calcd 3.1 wt %). A sample rehydrated by leaving it in air for several days shows a weight loss in the same region, but with a percentage that corresponds closely to the loss of only coordinated water (observed 2.5 wt %, calcd 3.1 wt %). This weight loss demonstrates that hydration is reversible, which indicates porosity. A weight loss of 50.3 % (calcd 50.8 %) between 380 and 400 °C corresponds to the pyrolysis of the organic component. The single-crystal structure, C,H,N analysis (see Experimental Section), and TGA results exclude the possibility of adsorbed cyclohexanol in the pores and are consistent with the chemical composition: $[Ni_7(C_4H_4O_4)_6(OH)_2(H_2O)_2]\cdot 2H_2O$.

Thermodiffractometry, performed under vacuum, shows only small losses in crystallinity through 400 °C, with some peaks remaining until 425 °C. The difference between the TGA and the XRD temperatures may be a result of the differing sample environments. To our knowledge, the decomposition temperature is the highest for any open-framework metal carboxylate. We attribute this exceptional stability to the 3D Ni-O-Ni framework[18] of the nickel succinate and to the strong coordination of d^8 Ni centers. The persistence of the parent phase past removal of coordinated water implies the formation of unsaturated metal sites in the dehydrated material. We are currently investigating the nature of these sites.

In spite of the extended Ni–O–Ni connectivity, magnetic susceptibility measurements reveal paramagnetic behavior down to about 5 K, with a magnetic moment of 2.78 μ_B and a Curie–Weiss temperature θ of 4.3 K. Clearly, there is a possibility that the system is magnetically frustrated.

Nickel succinate presents a remarkable 3D Ni–O–Ni framework with porosity and high thermal stability, demonstrating our expectation that multidimensional M–O–M frameworks offer advantages in several respects compared to metal–organic compounds based on isolated metal atoms or clusters. We are continuing to study this interesting phase and have also prepared a related material using glutaric acid,[19] details of which will be reported elsewhere.

Experimental Section

Single crystals: Succinic acid (0.20 g; Aldrich) was dissolved in cyclohexanol (4.0 g; Acros) and carefully layered above water (5.0 g) containing Ni(acetate)$_2 \cdot 6H_2O$ (0.20 g; Alfa Aesar) inside a Teflon autoclave liner (23 mL). The autoclave was heated under autogenous pressure to 150 °C for 3 days and the product, pale blue-green hexagonal platelets, was separated by filtration. Powder samples for physical characterization were prepared in a similar manner by combining Ni(acetate)$_2 \cdot 6H_2O$ (Alfa Aesar), succinic acid (Aldrich), and water in a 1:2:50 molar ratio. In situ X-ray powder diffraction data were collected every 25 °C on a Phillips X-Pert powder diffractometer using $Cu_{K\alpha}$ radiation. Elemental analysis (%) calcd: C 24.5, H 2.6; found: C 23.7, H 2.4; the calculation assumes 0.6 surface water molecules per formula unit, as measured by TGA.

Crystal data for $[Ni_7(C_4H_4O_4)_6(OH)_2(H_2O)_2] \cdot 2H_2O$, rhombohedral, $R\bar{3}c$, $a = 21.040(1)$, $c = 45.860(4)$ Å, $V = 17581(2)$ Å^3, $Z = 18$, $\rho = 1.995$ Mg m^{-3}, $R_1 = 0.0444$ for 3290 reflections, $I > 4\sigma I$ for 267 least-squares parameters. Single-crystal diffraction data were collected to 0.75 Å on a clear, hexagonal crystal (0.12 × 0.12 × 0.08 mm) using a Bruker SMART CCD system with $Mo_{K\alpha}$ radiation (0.71073 Å). An absorption correction was made using SADABS.[20] Lorentz and polarization corrections were made, the structure was solved using direct methods, and the data were refined against $|F^2|$ using the SHELXTL suite.[21] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions with isotropic U values 20% higher than the atom to which they were bound. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-169140. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[1] A. K. Cheetham, G. Férey, T. Loiseau, *Angew. Chem.* **1999**, *111*, 3466; *Angew. Chem. Int. Ed.* **1999**, *38*, 3269.

[2] T. J. Barton, L. M. Bull, W. G. Klemperer, D. A. Loy, B. McEnaney, M. Misono, P. A. Monson, G. Pez, G. W. Scherer, J. C. Vartuli, O. M. Yaghi, *Chem. Mater.* **1999**, *11*, 2633.

[3] R. Robson, *J. Chem. Soc. Dalton Trans.* **2000**, 3735.

[4] M. Eddaoudi, D. B. Moler, H. L. Li, B. L. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319.

[5] H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276.

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

[7] L. M. Zheng, X. Q. Wang, Y. S. Wang, A. J. Jacobson, *J. Mater. Chem.* **2001**, *11*, 1100.

[8] J. Do, A. J. Jacobson, *Inorg. Chem.* **2001**, *40*, 2468.

[9] Y. Kim, E. W. Lee, D. P. Jung, *Chem. Mater.* **2001**, in press.

[10] Y. Kim, D. Y. Jung, *Bull. Korean Chem. Soc.* **2000**, *21*, 656.

[11] Y. J. Kim, D. Y. Jung, *Bull. Korean Chem. Soc.* **1999**, *20*, 827.

[12] C. Livage, C. Egger, G. Férey, *Chem. Mater.* **2001**, *13*, 410.

[13] C. Livage, C. Egger, G. Férey, *Chem. Mater.* **1999**, *11*, 1546.

[14] N. Guillou, Q. M. Gao, M. Nogues, R. E. Morris, M. Hervieu, G. Férey, A. K. Cheetham, *C. R. Acad. Sci. Ser. IIc* **1999**, *2*, 387.

[15] N. Guillou, Q. M. Gao, P. M. Forster, J. S. Chang, S. E. Park, G. Férey, A. K. Cheetham, *Angew. Chem.* **2001**, *113*, 2913; *Angew. Chem. Int. Ed.* **2001**, *40*, 2831.

[16] P. M. Forster, P. M. Thomas, A. K. Cheetham, *Chem. Mater.* **2002**, in press.

[17] K. Maeda, Y. Kiyozumi, F. Mizukami, *Angew. Chem.* **1994**, *106*, 2429; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2335.

[18] L. M. Zheng, T. Whitfield, X. Wang, A. J. Jacobson, *Angew. Chem.* **2000**, *112*, 4702; Angew. *Chem. Int. Ed.* **2000**, *39*, 4528.

[19] Unit cell: $I4_1/a$, $a = 24.0585$, $c = 16.6154$ Å.

[20] SADABS: Area-Detector Absorption Correction, Siemens Industrial Automation, Inc., Madison, WI, **1996**.

[21] SHELXTL v5.1, Bruker-AXS, Inc., Madison, WI, **1988**.

Icosahedral Virus Particles as Addressable Nanoscale Building Blocks[**]

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Dedicated to Professor K. Barry Sharpless

Nanochemistry is the synthesis and study of well-defined structures with dimensions of 1–100 nanometers (nm), and thus spans the size range between molecules and materials.[1] While supramolecular chemistry (making small molecules bigger) and microfabrication techniques (making big structures smaller) attack from the flanks, biology employs many constructs of this size. Examples include the photosynthetic reaction center, the ribosome, and membrane-bound receptor-signaling complexes, all notable because of their sophisticated yet modular function. The burgeoning field of nanotechnology[2] seeks to mimic the information-handling, materials-building, and responsive sensing capabilities of biological systems at the nanometer scale. The special requirements of this enterprise would be well served by building blocks of the proper size with predictable and programmable chemistry.

Cowpea mosaic virus (CPMV) particles are 30 nm-diameter icosahedra, formed by 60 copies of two different types of protein subunits (Figure 1 a).[3] The physical, biological, and genetic properties of CPMV have been well characterized.[4] Approximately one gram of virus is easily and routinely obtained from a kilogram of infected leaves of the black-eye pea plant. The structure of CPMV has been characterized at 2.8 Å resolution by X-ray crystallography and an atomic model of the particle has been constructed.[5] The virion displays icosahedral symmetry to the resolution of the crystal structure and an infectious clone of the virus allows site-directed and insertional mutagenesis to be performed in a straightforward and rapid manner.[6] The particles are remarkably stable; they maintain their integrity at 60 °C (pH 7) for at least one hour and at pH values from 3.5 to 9 indefinitely at room temperature. Different crystal forms of the virus can be readily produced under well-defined conditions (Figure 1 d).[7, 8] Here we report on the selective

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