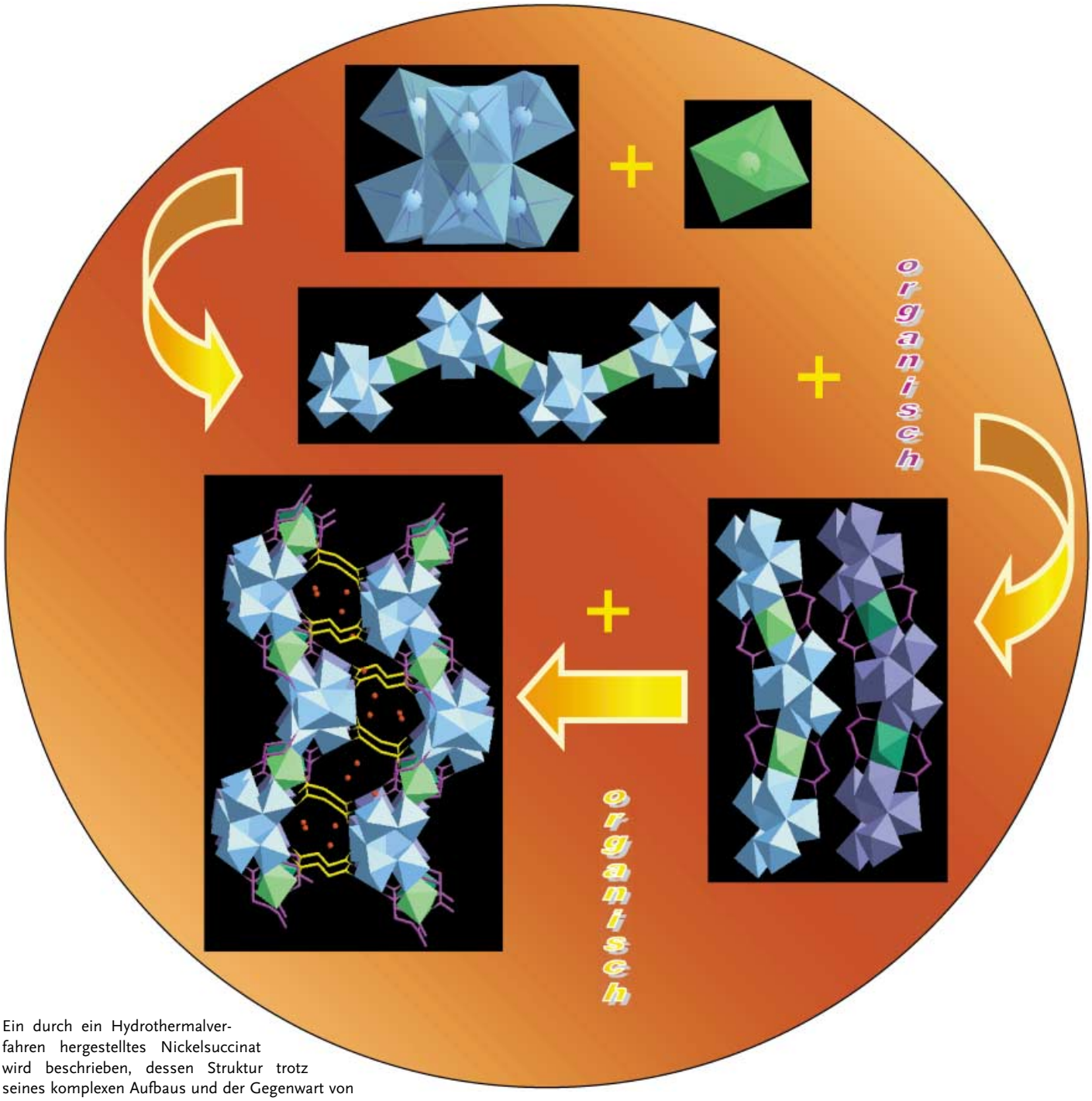
Zuschriften



Ein durch ein Hydrothermalverfahren hergestelltes Nickelsuccinat wird beschrieben, dessen Struktur trotz seines komplexen Aufbaus und der Gegenwart von 55 nichtäquivalenten Atomen aus Synchrotron-Pulverbeugungsdaten vollständig gelöst werden konnte. Mehr zu dieser Verbindung, die aus einer einzigartigen Hexanickel-Einheit mit interessanten magnetischen Wechselwirkungen aufgebaut und unterhalb 20 K ferrimagnetisch ist, erfahren Sie in der Zuschrift von N. Guillou et al. auf den folgenden Seiten.

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Microporous Nickel Succinate

A Layered Nickel Succinate with Unprecedented Hexanickel Units: Structure Elucidation from Powder-Diffraction Data, and Magnetic and Sorption Properties**

Nathalie Guillou, Carine Livage, Wouter van Beek, Marc Noguès, and Gérard Férey*

During the last decade, synthesis of hybrid organic–inorganic compounds based on transition metals has been actively investigated. It allows the wide-ranging functionality of transition metals (e.g., magnetic and optical properties, electrical conductivity, and ferroelectricity) to be associated with the ability of the organic moiety to modulate structural arrangements.[1] Moreover, the use of hydrothermal conditions can considerably enlarge the range of possible architectures that may arise from a metal and an organic molecule. It is even more efficient when the organic molecule is flexible, for example, the linear dicarboxylic acid succinic acid.[2] In general terms, coordination polymers obtained with divalent metal ions such as Mn^{II}, Fe^{II}, Co^{II}, Cu^{II}, and Zn^{II} often exhibit interesting architectures, but metal/oxide condensation is essentially "classical", with edge- and sometimes corner-sharing octahedra.[3] By contrast, with nickel, inorganic condensation is more diverse: Our first investigations on nickel phosphates showed that Ni could generate microporous materials with novel M–O–M connectivities in which polyhedra can share faces, edges, and/or corners.[4] This was followed by the first hydrothermally synthesized nickel succinate,[5] which forms a remarkable honeycomb nickel oxide network, and by two new nickel carboxylates with rigid linkers.[6] Here we describe the second nickel succinate, the structure of which, in spite of its complexity and the presence of 55 nonequivalent atoms, was completely solved ab initio from synchrotron powder-diffraction data. It forms a novel network with an unusual hexanuclear building block that confers peculiar ferrimagnetic properties on the material. To our knowledge this unit has never been observed, neither in solid-state chemistry nor in the rich domain of polyoxometalates.[7]

The nickel succinate was synthesized by classical hydrothermal reaction.[8] Synchrotron powder data were collected on the Swiss-Norwegian beamline at the ESRF.[9] A monoclinic solution ($a = 7.8597(1)$, $b = 18.8154(3)$, $c = 23.4377(4)$ Å, $\beta = 92.0288(9)°$, $V = 3463.9(4)$ Å^3) was consistent with the $P2_1/c$ space group. In the angular range $2\theta =$ 1–44°, 2921 integrated intensities were extracted for direct-methods calculations, and 252 phases were observed for $|E|$ values greater than 1.2 and refined by using 4213 unique triplets. By increasing the number of direct-methods attempts to 256, the most probable E map revealed all nickel atoms, most of the surrounding oxygen atoms and a few carbon atoms. Subsequent Rietveld refinement converged approximately to $R_B = 0.30$ and $R_F = 0.20$. Successive difference Fourier maps alternated with profile refinements then completed the inorganic framework. The use of soft distance and angular constraints gradually differentiated electron-density maps and allowed the location of the organic moieties and the free water molecules. At the final stage, the structural model contained 55 non-hydrogen atoms, and soft constraints were maintained for the organic molecules. The final Rietveld refinement ($2\theta = 2.5$–40°, 2266 reflections, 170 structural parameters; Figure 1) corresponds to satisfactory model indicators ($R_B = 0.063$ and $R_F = 0.066$) and profile factors ($R_P = 0.049$ and $R_{WP} = 0.062$).

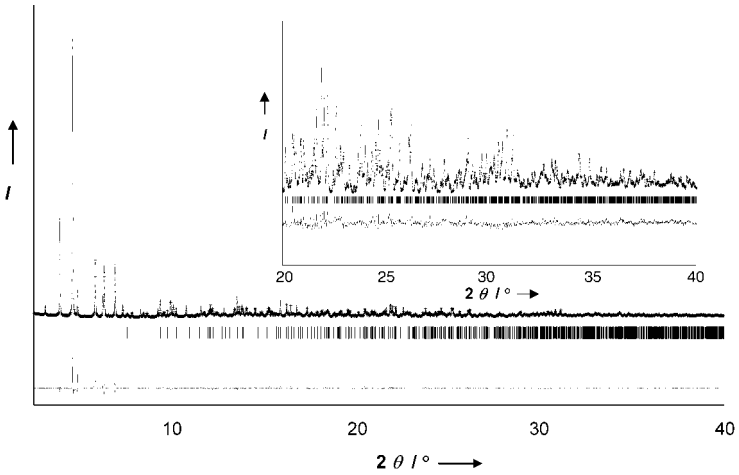

Figure 1. Final Rietveld plot of MIL-73. A zoom at high angles is shown as inset.

This new nickel succinate, denoted MIL-73, is built up from organic–inorganic (100) layers. Nickel oxide corrugated chains running along the b axis are connected by succinate ions along the c axis (Figure 2a). All carboxy groups of the four independent succinate anions are deprotonated. Half of the organic molecules decorate the chains, and the other half covalently connect them. Nickel atoms occupy seven independent crystallographic sites with octahedral geometry. The Ni atoms are cooordinated by two μ_4-, two μ_3-, and three μ_2-O atoms; two terminal water molecules; and O atoms of four succinate ions. Bond valence calculations give values very close to 1 for the two μ_4-O atoms, and values in the range 0.77(5)–0.61(3) for the three μ_2-O atoms.[10] This leads to assignment of the μ_4-O atoms to hydroxo groups, as were already observed in nickel(II) complexes,[11] and to the

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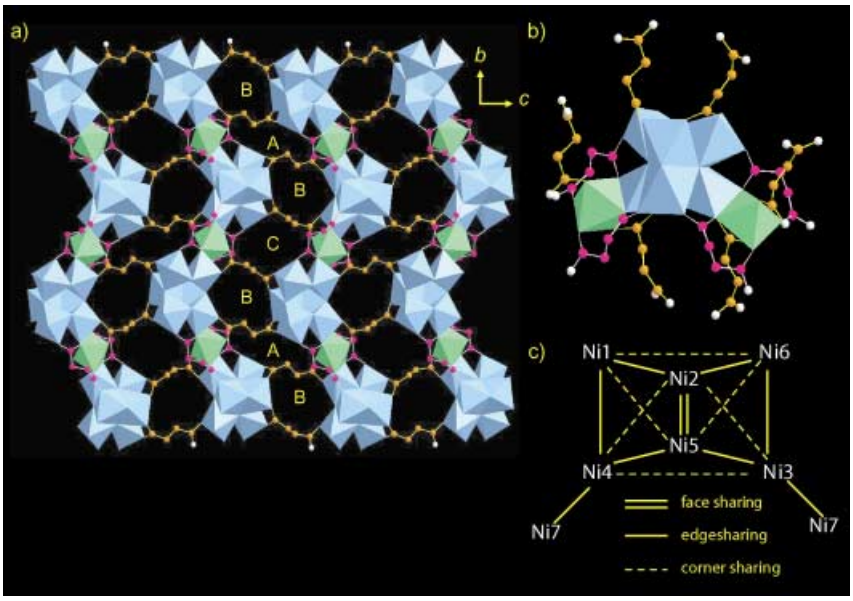

Figure 2. a) Projection of the structure along the *a* axis showing the three types of channels A–C. b) Polyhedral view of the hexanickel unit (blue) connected to two bridging Ni7 octahedra (green). Decorating succinate ions are represented in purple and bridging ones in orange. c) Schematic view of the connectivity of the Ni-centered octahedra.

assumption that the three μ_2 sites are statistically occupied by two hydroxo ligands and one water molecule. This corresponds to the chemical formula $[Ni_7(C_4H_4O_4)_4(OH)_6(H_2O)_3]\cdot 7H_2O$. Inorganic chains are built up from unusual hexanickel units connected by a seventh octahedron (Ni7, green in Figure 2). This polyhedron shares two *trans* edges with two neighboring Ni_6 units. In the Ni_6 unit a dimer of face-sharing octahedra is grafted onto a tetramer formed by two dimers of edge-sharing octahedra (Ni1, Ni4 and Ni6, Ni3) whose corners are connected via hydroxide ions. The face-sharing Ni atoms are connected to the tetramer by sharing edges with the two adjacent nickel octahedra, and corners with the opposite ones (Figure 2c). The cohesion of successive layers is ensured by strong hydrogen bonds involving one of the three μ_2-"hydroxo/water" and the two terminal water molecules (d (O···O) = 2.73(4), 2.88(4) Å). A pseudo-three-dimensional hybrid framework is thus formed in which three types of channels (A–C in Figure 2a) contain seven water molecules, connected to the framework by hydrogen bonds.

The thermal behavior of $[Ni_7(C_4H_4O_4)_4(OH)_6(H_2O)_3]\cdot 7H_2O$ was investigated by X-ray thermodiffraction (in air) and gravimetric analysis (under flowing nitrogen).[12] A gradual weight loss of 3.4% up to 45 °C corresponds to the loss of 2.4 adsorbed water molecules without any structural change. Then, the loss of the seven occluded water molecules (found: 9.9 wt%, calcd: 10.5 wt%) occurs with three successive crystallographic changes at 60, 110, and 180 °C (Figure 3). This dehydration is reversible, but rehydra-

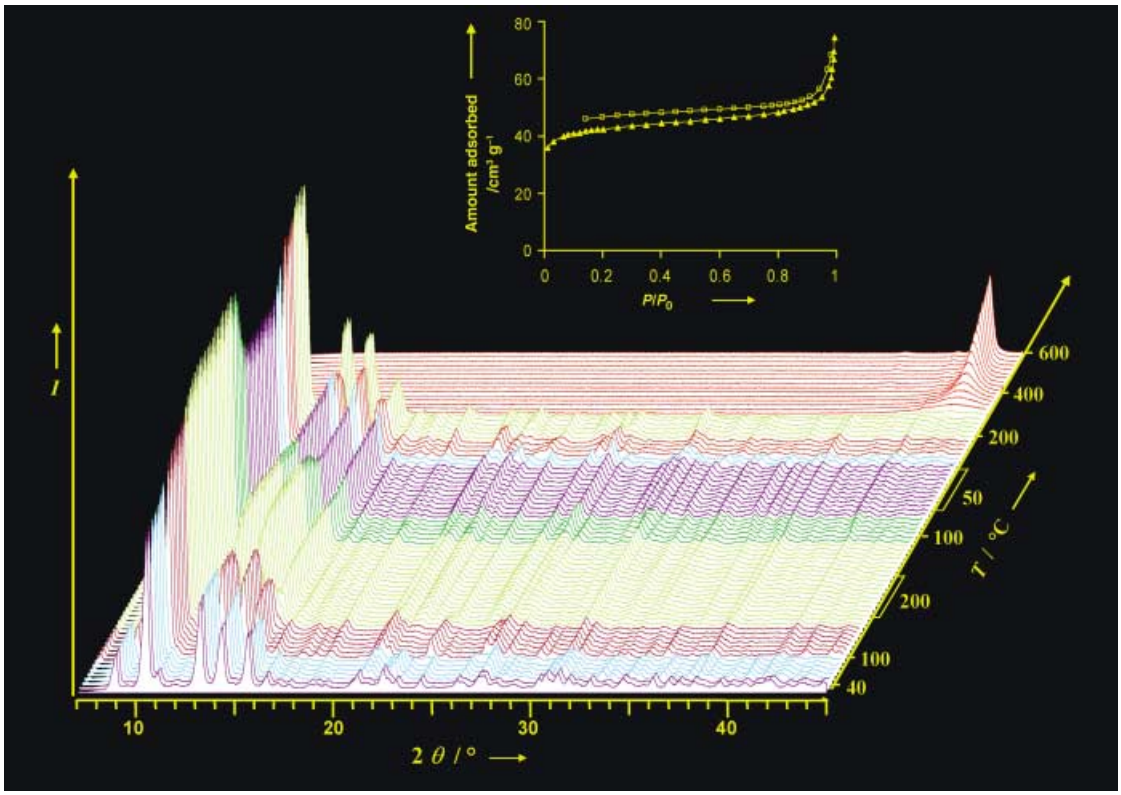

Figure 3. Thermal evolution of diffractograms during dehydration–rehydration (40–200–50 °C) and decomposition (up to 600 °C) of MIL-73. Adsorption (lower curve) and desorption (upper curve) isotherms for nitrogen at 77 K are shown in the inset. A = amount adsorbed.

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tion is characterized by progressive changes in the diffractogram between 120 and 60 °C, instead of successive steps. This behavior may indicate sorption properties. The weight loss between 225 and 300 °C was attributed to the three coordinated water molecules (found: 4.3 wt %, calcd: 4.5 wt %). The structure collapses at 280 °C in air with the loss of the hydroxo groups and combustion of the organic moieties. A sample activated at 170 °C under vacuum gave a typical type-1 N_2 adsoption isotherm (Figure 3, inset) and a surface area of 135(4) $m^2 g^{-1}$, which clearly indicates considerable porosity for this compound.[13]

$[Ni_7(C_4H_4O_4)_4(OH)_6(H_2O)_3]\cdot 7H_2O$ is ferrimagnetic below 20 K. The paramagnetic part of the $1/\chi(T)$ curve follows a Curie–Weiss law (150–300 K) with $C = 9.65$ K emu mol^{-1}, $\theta_p = -101$ K, and $\mu_{eff} = 3.3\ \mu_B$ per atom. The difference between zero-field and field-cooled (100 G) curves provides a good estimation of the magnetic ordering temperature of 20 K.[14] Magnetization data versus applied field H below T_N confirm this assessment and the extrapolated saturation magnetization was estimated to be 4.7 μ_B per formula unit. The high θ_p value relative to those currently obtained for Ni compounds indicates very strong antiferromagnetic interactions.[4–6] The complexity of the Ni-O-Ni connectivity, in which polyhedra can be linked by faces, edges, and corners, means that the compound is magnetically frustrated. Indeed, if only vertex connections with large angles, which favor antiferromagnetic superexchange, are taken into account, antiferomagnetic interactions are expected in the Ni1-Ni5-Ni6 and Ni4-Ni2-Ni3 triangles (Figure 2c), and hence spin frustration is inevitable. A saturation magnetization of 4.7 μ_B suggests the coexistence of two magnetic networks with five spin-up and two spin-down centers. This experimental value is, of course, lower than that calculated for cooperative ferrimagnetism ($M_s = 6\ \mu_B$ assuming $g = 2$) resulting from the strong spin frustration, which often decreases magnetic moments.[15]

In summary, a nickel succinate was synthesized by a hydrothermal technique. Its structure contains a unique hexanickel unit with interesting magnetic interactions: The compound is ferrimagnetic below 20 K. The novelty of the structure illustrates the flexibility of nickel oxide networks and confirms the versatility of nickel inorganic condensation under hydrothermal conditions.[5,6] Moreover, after removing the water of hydration, it also becomes porous (135(4) $m^2 g^{-1}$) and can reversibly reabsorb water molecules. Finally, the structure determination (55 atoms and 165 atomic coordinates) from synchrotron-powder diffraction data reaches the limits of "traditional" ab initio methods.[16] Above this limit and for larger cells, a new way of collecting data[17] or "direct-space" strategies in the case of organic materials,[18] must be used, as was shown recently.

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[1] a) G. Férey, *Chem. Mater.* **2001**, *13*, 3084 – 3098; b) S. Feng, R. Xu, *Acc. Chem. Res.* **2001**, *34*, 239 – 247; c) M. Eddaoudi, H. Li, O. M. Yaghi, *J. Am. Chem. Soc.* **2000**, *122*, 1391 – 1397.

[2] a) C. Livage, C. Egger, G. Férey, *Chem. Mater.* **2001**, *13*, 410 – 414; b) 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; c) F. Serpaggi, G. Férey, *J. Mater. Chem.* **1998**, *8*, 2737 – 2741.

[3] a) Y. Kim, E. Lee, D.-Y Jung, *Chem. Mater.* **2001**, *13*, 2684 – 2690; b) M. Riou-Cavellec, C. Albinet, J.-M. Grenèche, G. Férey, *J. Mater. Chem.* **2001**, *11*, 3166 – 3171; c) C. Livage, N. Guillou, J. Marrot, G. Férey, *Chem. Mater.* **2001**, *13*, 4387 – 4392; d) E. Lee, Y. Kim, D.-Y. Jung, *Inorg. Chem.* **2002**, *41*, 501 – 506; e) 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; f) S. S.-Y. Chui, S. M.-F. Los, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, *283*, 1148 – 1150; g) H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276 – 279.

[4] a) N. Guillou, Q. Gao, M. Noguès, R. E. Morris, M. Hervieu, G. Férey, A. K. Cheetham, *C. R. Acad. Sci. Ser. IIc* **1999**, *2*, 387 – 392; b) N. Guillou, Q. Gao, P. M. Forster, J.-S Chang, M. Noguès, S.-E. Park, G. Férey, A. K. Cheetham, *Angew. Chem.* **2001**, *113*, 2913 – 2916; *Angew. Chem. Int. Ed.* **2001**, *40*, 2831 – 2834.

[5] P. M. Forster, A. K. Cheetham, *Angew. Chem.* **2002**, *114*, 475 – 477; *Angew. Chem. Int. Ed.* **2002**, *41*, 457 – 459.

[6] a) H. Kumagai, Y. Oka, M. M. Akita-Tanaka, K Inoue, *Inorg. Chim. Acta* **2002**, *332*, 176 – 180; b) 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; c) N. Guillou, S. Pastre, C. Livage, G. Férey, *Chem. Commun.* **2002**, 2358 – 2359.

[7] J.-P. Jolivet, *Metal Oxide Chemistry and Synthesis*, J. Wiley, New York, **2000**.

[8] Reactions were carried out in a Teflon container (23 mL) at 180 °C for 2 d under autogenous pressure. The reaction mixture contained $NiCl_2\cdot 6H_2O$ (0.550 g), succinic acid (0.411 g), KOH (0.534 g), and H_2O (5 mL) in the molar ratio 1:1.5:4.1:120. After cooling (pH 6), the pale green powder was washed with distilled water. Elemental analysis (%): calcd: C 16.60, H 3.66, Ni 35.49; found: C 16.65, H 3.66, Ni 33.80.

[9] High-resolution synchrotron data were measured with a Debye–Scherrer diffractometer geometry and a Si(111) analyzer crystal ($\lambda = 0.7999$ Å). The powder was introduced in a 1.5 mm capillary and the pattern was scanned in the range $2\theta = 1$–60° with a step length of $2\theta = 0.0035°$ and a counting time of 1 s per step. To improve the counting statistics at high angles, the pattern was then divided in two 2θ regions (1–15 and 15–45°), with times per step of 1 and 3 s, respectively. Pattern indexing was carried out with DICVOL91 (A. Boultif, D. Louër, *J. Appl. Crystallogr.* **1991**, *24*, 987 – 993). Direct methods and Fourier difference calculations were performed with SHELXTL (G. M. Sheldrick, **1997**). Pattern matching and Rietveld refinements were performed by using FullProf (J. Rodriguez-Carvajal in *Collected Abstract of Powder Diffraction Meeting* (Toulouse), **1990**, p. 127) and integrated in WinPlotr (T. Roisnel, J. Rodriguez-Carvajal, *Mater. Sci. Forum* **2001**, *378–381*, 118 – 123). CCDC-194049 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 Center, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[10] N. Brese, M. O'Keeffe, *Acta Crystallogr. Sect. B* **1991**, *47*, 192 – 196.

[11] A. J. Edwards, B. F. Hoskins, E. H. Kachab, A. Markiewicz, K. S. Murray, R. Robson, *Inorg. Chem.* **1992**, *31*, 3585 – 3591.

[12] 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, $Co_{K\alpha}$ radiation) equipped with an M Braun linear position-sensitive detector (PSD). The dehydration–rehydration process was studied at 10 °C intervals (40–200–50 °C), and decomposition at 20 °C intervals up to 600 °C; temperature ramp of 0.1 °C s^{-1}; several hours at 200 and 50 °C. Thermogravimetric analysis was performed using a TA

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Instruments TGA-2050 apparatus (nitrogen flow 60 ml min^{-1}, 2 °C min^{-1}).
[13] The BET surface area of the sample activated at 170 °C under vacuum for 64 h was studied on a Micromeritics ASP200 porosimeter.
[14] Magnetization measurements were performed on a Quantum Design Squid magnetometer (MPMS-5).
[15] G. Férey, R. de Pape, M. Leblanc, J. Pannetier, *Rev. Chim. Miner.* **1986**, *23*, 474 – 484.
[16] a) R. E. Morris, J. J. Owen, J. K. Stalick, A. K. Cheetham, *J. Solid State Chem.* **1994**, *111*, 52 – 57; b) L. B. McCusker, R. W. Grosse-Kunstleve, C. Bearlocher, M. Yoshikawa, M. E. Davis, *Microporous Mater.* **1996**, *6*, 295 – 309; c) D. M. Poojary, A. Cabeza, M. A. G. Aranda, S. Bruque, A. Clearfield, *Inorg. Chem.* **1996**, *35*, 1468 – 1473; d) M. Louër, C. Le Roux, J. Dubac, *Chem. Mater.* **1997**, *9*, 3012 – 3016.
[17] T. Wessels, C. Baerlocher, L. B. McCusker, E. J. Creyghton, *J. Am. Chem. Soc.* **1999**, *121*, 6242 – 6247.
[18] a) K. D. M. Harris, M. Tremayne, B. M. Kariuki, *Angew. Chem.* **2001**, *113*, 1674 – 1700; *Angew. Chem. Int. Ed.* **2001**, *40*, 1626 – 1651; b) E. Tedesco, G. W. Turner, K. D. M. Harris, R. L. Johnston, B. M. Kariuki, *Angew. Chem.* **2000**, *112*, 4662 – 4665; *Angew. Chem. Int. Ed.* **2000**, *39*, 4488 – 4491; c) E. Y. Cheung, E. E. McCabe, K. D. M. Harris, R. L. Johnston, E. Tedesco, K. M. P. Raja, P. Balaram, *Angew. Chem.* **2002**, *114*, 512 – 514; *Angew. Chem. Int. Ed.* **2002**, *41*, 494 – 496; d) R. B. Von Dreele, P. W. Stephens, G. D. Smith, R. H. Blessing, *Acta Crystallogr. Sect. D* **2000**, *56*, 1549 – 1553.

Colorimetric Isomer Probes

Towards the Development of Colorimetric Probes to Discriminate between Isomeric Dicarboxylates**

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The development of new chemosensors based on supramolecular concepts is a field of current interest.[1] A significant amount of work has been devoted to obtain specific chemosensors that are able to change, upon complexation with the target guests, one or several macroscopic properties in response to the molecular coordination event. Changes in fluorescence[2] and in absorbance[3] are the output signals used in the development of optical chemosensors. Although a number of chromogenic receptors for the sensing of metal ions have been developed,[4] very few chromogenic receptors for anions have been described in the literature that are based on recognition approaches.[5] Most of the receptors have been developed for the colorimetric sensing of inorganic anions,[6] whereas very few have been designed for recognition of organic anions,[7] particularly in aqueous environments. Thus, the development of chromogenic reagents for such species remains a challenge. In this context, and as an advancement of this field, we wish now to report a chromogenic system for the colorimetric discrimination between certain organic isomers (*cis*/*trans* and *ortho*/*meta*/*para* dicarboxylates). Differentiation of isomers is, in general, a difficult task because of their rather similar chemical and physical properties. To the best of our knowledge, the examples we show here are the first supramolecular-based colorimetric probes for the detection of isomeric anions.

Most of the known colorimetric anion chemosensors are based on host molecules containing anion coordination sites coupled to chromogenic signaling units. In those receptors, coordination of the anion usually modifies the charge-transfer band of the chromogenic group resulting in "naked-eye" anion detection. A different approach involves the use of anion-induced reactions that can be either reversible or irreversible.[8] We have recently reported the use of one such anion-induced reversible reaction for the selective detection of ATP in water/organic solvent mixtures.[9] The system was based on the cyclization of yellow 1,3,5-triarylpent-2-en-1,5-diones to the magenta pyrylium cation. A family of 1,3,5-triarylpent-2-en-1,5-diones were synthesized by electrophilic aromatic substitution of the corresponding aniline derivative with 2,6-diphenylpyrylium perchlorate in DMF at 150 °C. Subsequent column chromatography on aluminum oxide afforded the receptors L^1–L^8 in approximately 35 % yield. The UV/Vis spectra of L^1–L^8 are very similar, with a band centered at around 370–380 nm, which is indicative of their brightly yellow color. The structures of the compounds L^1–L^8 are shown in Scheme 1.

Figure 1 shows a photograph of buffered dioxane/water (70:30 v/v) solutions of L^8 at approximately pH 6 (0.01 M HEPES buffer, HEPES = 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) containing an equimolar amount of certain carboxylate (acetate, benzoate) and dicarboxylate anions (terephthalate, $^-OOC–(CH_2)_n–COO^-$, $n = 0$ to 7, oxalate, malonate, succinate, glutarate, adipate, pimelate, suberate). The solution remains yellow upon addition of all the above mentioned species, except for the oxalate and malonate ions, whereby the solutions turn red-magenta. This remarkable color change is, as stated above, a result of the anion-induced selective cyclization of L^8 to give the colored 2,4,6-triphenylpyrylium cation (absorption maximum at approximately 550 nm). Figure 1 also shows the color variation observed upon addition of maleate or fumarate dicarboxylate ions to buffered solutions of L^5 (0.01 M HEPES buffer, approximately pH 6). The solution is yellow in the presence

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