Supramolecular Chemistry

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A Three-Dimensional Metal–Organic Framework with an Unprecedented Octahedral Building Unit**

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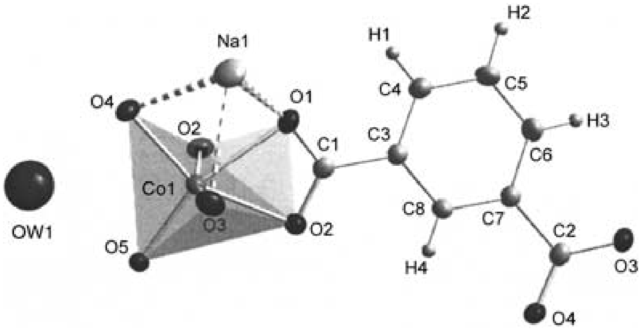
Among the numerous works devoted to porous hybrid solids, those on structures built up from a chosen inorganic unit reticulated with rigid organic linkers are very topical. The major goal is to control the "design" of the architectures to obtain materials with required properties.[1–5] Interesting architectures have been obtained with tetrameric ZnO_4 units,[6] cuboid zinc silicate cores,[7] and triangular oxo-centered building units with vanadium,[8] zinc,[4] and iron.[9] Recently, a crystalline metal–organic framework (MOF), MIL-100, with a giant cell and a large sorption capacity ($3100\ m^2 g^{-1}$) was constructed from this type of triangular unit containing chromium and trimesate ions.[10]

Depending on their architecture, compounds based on polynuclear metallic units offer potential for catalysis, gas storage, or separation. In the search for inorganic "seeds" to grow original 3D networks, we describe here a new hexacobalt octahedral building block.[11,12] This type of metal cage could also be useful for magnetic materials with potential applications as molecular magnets.[13,14] The synthetic challenge in this area is to increase and control the degree of nuclearity of the inorganic "clusters" that are responsible for the physical properties. Oligomerization is induced by heating either in solution or in the solid state.[15–17] The title compound, $Na_3[Co_6O(OH)(C_8H_4O_4)_6]\cdot H_2O$ (MIL-104), was synthesized by a classical solvothermal reaction. The hexamers are formed in situ by self-assembly and linked into an original three-dimensional network by the isophthalate dianions.

The structure of MIL-104 is generated by a cobalt atom and a carboxylate on general positions and a sodium ion, water molecule, and oxo-hydroxo oxygen on symmetry elements (Table 1). The metal is octahedrally coordinated to five oxygen atoms of four isophthalate ligands and a μ_3-O ion. The geometry is highly distorted, with a narrow O-Co-O angle (60.20(6)°) *trans* to a large one (105.32(7)°), and a short O—O distance (2.188(2) Å) opposite to a long one (3.165(2) Å). This peculiar geometry is always encountered when a carboxylate group binds the metal center in a chelating fashion (Figure 1).[18] The "bite" of the rigid group (ca. 2.1–2.2 Å) is too short for a regular octahedral symmetry. Six octahedra are associated to form a polynuclear "cluster". This

Table 1: Selected bond lengths [Å] and angles [°] as well as the atom-labeling scheme for $Na_3[Co_6O(OH)(C_8H_4O_4)_6]\cdot H_2O$ (MIL-104) with displacement ellipsoids drawn at the 50% probability level.[a]



Co1—O5	1.9465(6)	Co1—O2	2.171(2)
Co1—O4	2.033(2)	Co1—O1	2.192(2)
Co1—O3^A	2.129(2)	Co1—O2^B	2.258(2)
Na1—O1	2.256(2)	Na1—O4	2.523(2)
Na1—O3^A	2.592(2)		
O5-Co1-O4	105.32(7)	O4-Co1-O1	95.79(6)
O5-Co1-O3^A	100.81(7)	O4-Co1-O3^A	86.83(7)
O5-Co1-O2	98.41(8)	O4-Co1-O2	155.28(7)
O5-Co1-O1	158.58(8)	O3^A-Co1-O2	95.51(7)
O5-Co1-O2^B	91.17(6)	O3^A-Co1-O1	83.63(6)
O2-Co1-O1	60.20(6)		

[a] Symmetry code: A: $-x+y-1, -x+1, z$; B: $x-y+1, x+1, -z$.

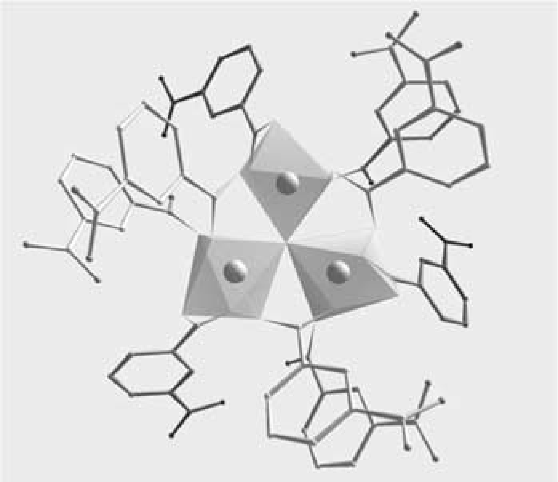


Figure 1. View of the octahedral triangular unit connected by nine isophthalate ions showing the cobalt environment. The 1,3-benzenedicarboxylate ligands adopt two modes of bonding, namely bridging and chelating. The cobalt octahedron presents an important distortion that is attributed to the chelating connection of the organic molecule.

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hexameric core is located on an inversion threefold axis and may be easily viewed as the association of two trimers (Figure 2). Each triangle, on a threefold axis, is composed of octahedra sharing a central μ_3-oxygen (Co-μ_3-O-Co 116.33(5)°). At variance to what is usually observed for oxo-centered trimers, the metal atoms are not coplanar with the central oxygen.[8,9] The cobalt "cluster" constructed by the connection through the vertices (six μ_2-O) of two trimers forms an unusual $\{Co_6(\mu_3\text{-}O)_2(\mu_2\text{-}O)_6(\mu_1\text{-}O)_{18}\}$ super-octahedron (Figure 2).[19,20] Bond valence calculations give a value of 1.5 for the μ_3-O atom.[21] This value, as well as the neutrality of the compound, leads to the statistical half occupancy of the μ_3 site by oxo and hydroxo anions. To the best of our knowledge, this unusual hexanuclear unit has never been observed either in the solid state or in coordination chemistry. This structure can be described as a classical MOF organization, with each hexamer joined by twelve bridging isophthalate ions to six neighboring units, with each metal unit serving as the octahedral node of a cuboid net (Figure 3a). The connection between two "clusters" is ensured by two nearly parallel bridging isophthalates with weak π–π interactions. In this description, the sodium ions occupy small cavities left free by the hexamers' packing. The alkali-metal cation has a distorted octahedral geometry formed by oxygen atoms of six carboxylate groups, with O-Na-O angles ranging from 68.02(2)° to 132.8(1)° and bond lengths ranging from 2.256(2) to 2.592(2) Å. Taking into account the sodium polyhedron, MIL-104 can also be considered as a 3D inorganic framework with sodium octahedra linking the hexameric units through face-sharing in a pseudo-cubic net (Figure 3b). In fact, each cobalt polyhedron is linked to a sodium ion to form a larger "super octahedron" around the hexamer. The topology here is the same as that found for ReO_3, with $\{Na_6Co_6O_{26}\}$ units as giant octahedra (Figure 3c). Thus MIL-104 provides a new example of scale chemistry.[22]

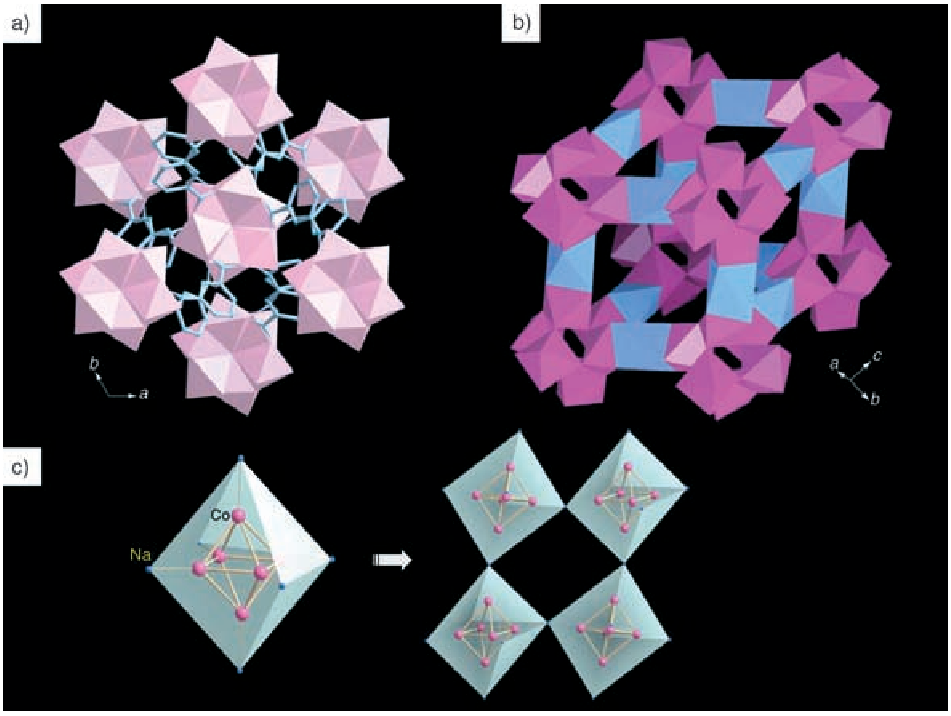

Figure 3. a) Projection of the structure showing one hexameric unit connecting six crystallographically equivalent "clusters" that lie at the corners of an octahedron. Each unit serves as a 6-connecting node of an infinite 3D network. b) View of the inorganic pseudo-cubic network including the sodium cation octahedra. c) Schematic representation of the $\{Na_6Co_6O_{26}\}$ "super octahedron" highlighting the relationship between the inorganic network and the ReO_3 structure.

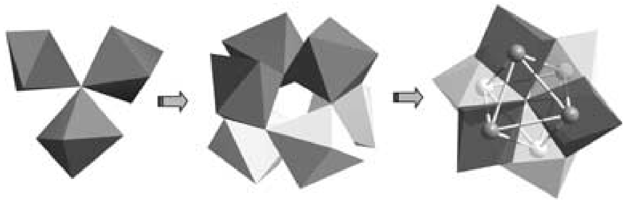

Figure 2. Schematic representation of the $\{Co_6(\mu_3\text{-}O)_2(\mu_2\text{-}O)_6(\mu_1\text{-}O)_{18}\}$ unit showing its octahedral geometry.

The temperature variation of the magnetic susceptibility measured in a 500 Oe field is shown in Figure 4.[23] Paramagnetic behavior is observed down to 50 K. A "plateau" is then observed in the χ versus T curve at 0.12 cm^{3}mol^{-1} in the range 30–14 K, followed by an increase up to 1.98 cm^{3}mol^{-1} at 1.8 K. The fit of the χ^{-1} versus T curve in the high temperature region gives a Weiss temperature, θ, of -118.5 K and a Curie constant of 2.92 K cm^3 per cobalt atom, which agrees well with that expected for high-spin Co^{II} in an octahedral site.[24] The negative sign of θ and the decrease of χT, which tends to zero at 1.8 K, point to the existence of antiferromagnetic exchange interactions. Spin–orbit coupling most certainly also contrib-

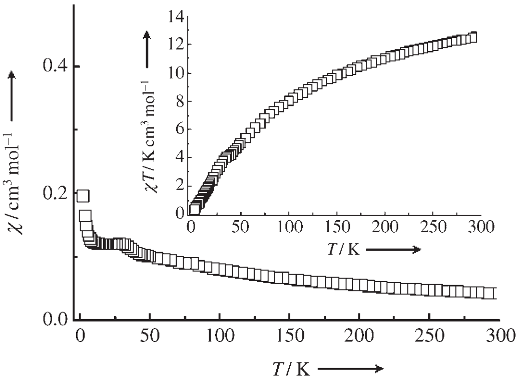

Figure 4. Temperature dependence of the magnetic susceptibility of compound MIL-104 recorded in a field of 550 Oe. The inset shows the corresponding variation of the χT product.

utes to this decay.[24–26] The hexamers are interconnected by large isophthalate bridges and are quite well isolated. Thus, the magnetic behavior is interpreted as being due to antiferromagnetic intrahexamer coupling. Moreover, the presence of a "plateau" in the susceptibility and of a Curie-like tail at low temperature indicate the existence of a residual moment, which might be due to the stabilization of an uncompensated moment by a frustration effect in the triangular cobalt motifs.[26]

In summary, a cobalt isophthalate constructed from a unique $\{Co_6O_{26}\}$ cage with octahedral geometry has been prepared. The novelty of the hexanuclear unit illustrates the influence of rigid organic partners upon metal oxide condensation. The great challenge in building-block chemistry is to establish reliable synthetic routes to stabilize desired inorganic motifs.[9,27] Complex inorganic units frequently appear as isolated compounds, and the relationship between "clusters" and synthetic conditions is often unpredictable.[28] For the formation of the title hexamer the crucial point seems to be the distortion of the trimer, which is characterized by an asymmetric linkage of the carboxylate groups: three bridging ones on one side and six nonbridging (intratrimer) ones on the opposite side (Figure 1). Therefore, no steric obstruction limits the condensation increment. On the contrary, with symmetrical triangles (three bridging groups on both side), the association of two trimers through vertices is topologically impossible. However, although it is understandable that chelating carboxylic groups help to induce the formation of the hexamer, the link between synthetic conditions and this type of coordination is far from being understood.[18]

Experimental Section

Preparation of $Na_3[Co_6O(OH)(C_8H_4O_4)_6]\cdot H_2O$ (MIL-104):[29] The reactions were carried out in a Teflon-lined autoclave at 180 °C for three days under autogenous pressure. The reaction mixture contained $CoSO_4\cdot 7H_2O$ (1.16×10^{-3} mol), isophthalic acid (HO_2C-(C_6H_4)-CO_2H; 1.73×10^{-3} mol), NaOH (3.46×10^{-3} mol), and H_2O/ethanol (25/75 v/v, 7.5 mL) in a ratio of 1:1.5:3:90. After the mixture was cooled (pH 6), the resulting violet crystals were washed with distilled water. IR (KBr pellet): $\tilde{\nu}=3580$ (w) and $3445\,cm^{-1}$ (s) (oxygen–hydrogen stretch of the water molecules and hydroxy group); 1613 (s), 1559 (s), 1539 (s), 1485 (s), 1457 (s), and $1395\,cm^{-1}$ (s) (symmetric and asymmetric stretching bands of the deprotonated carboxylic functions). Elemental analysis calcd (%) C 39.5, H 1.8, Co 24.3, Na 4.7; found: C 37.8, H 1.8, Co 22.5, Na 5.6. A single crystal was selected for structure determination by X-ray diffraction. Calculated density: $1.973\,g\,cm^{-3}$; measured: $1.961(2)\,g\,cm^{-3}$. The thermal behavior of $Na_3[Co_6O(OH)(C_8H_4O_4)_6]\cdot H_2O$ was studied by thermogravimetric analysis under nitrogen. It decomposes through two major processes, namely the loss of water molecules and the combustion of the organic moiety. The first loss appears at around 80 °C with the loss of the free water molecules (theoretical loss: 1.2%; observed loss: 1.6%). The structure of MIL-104 is preserved upon dehydration, as proved by X-ray thermodiffraction in air, up to 250 °C, which shows only tiny variations of the peak intensities. It reabsorbs water molecules upon cooling. The second weight loss occurs between 450 and 550 °C and is characteristic of the combustion of the organic moiety (theoretical weight loss: 59.0%; observed loss: 58.5%).

A violet crystal ($1.08\times0.34\times0.30\,mm^3$) was glued to a glass fiber. Intensity data were collected at room temperature with a Siemens SMART diffractometer equipped with a CCD two-dimensional detector ($\lambda(Mo_{K\alpha1})=0.71073$ Å).[30] The structure was solved and refined by full-matrix least-squares techniques, based on F^2, using the SHELX-TL software package.[31] Cobalt, sodium, and oxygen atoms were located by direct methods, and all remaining atoms, including hydrogen atoms, were found by successive difference Fourier maps. All atoms were refined anisotropically, except for hydrogen atoms. The refinement converged to $R_1=0.0339$ and $wR_2=0.0916$ for 2177 unique reflections and 146 parameters.[32]

The Supporting Information contains the atomic coordinates, the atom-labelling scheme, the TGA graph, the X-ray thermodiffraction study, and the magnetization versus field cycle.

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[1] G. Férey, *Chem. Mater.* **2001**, *13*, 3084–3098.
[2] B. Moulton, J. Lu, R. Hajndl, S. Hariharan, M. J. Zaworotko, *Angew. Chem.* **2002**, *114*, 2945–2948; *Angew. Chem. Int. Ed.* **2002**, *41*, 2821–2824.
[3] N. L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2005**, *127*, 1504–1518.
[4] J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon, K. Kim, *Nature* **2000**, *404*, 982–986.
[5] G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, *Acc. Chem. Res.* **2005**, *38*, 217–225.
[6] O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705–714.
[7] S. Y. Yang, L. S. Long, Y. B. Jiang, R. B. Huang, L. S. Zheng, *Chem. Mater.* **2002**, *14*, 3229–3231.
[8] K. Barthelet, D. Riou, G. Ferey, *Chem. Commun.* **2002**, 1492–1493.
[9] C. Serre, F. Millange, S. Surblé, G. Férey, *Angew. Chem.* **2004**, *116*, 6445–6449; *Angew. Chem. Int. Ed.* **2004**, *43*, 6285–6289.
[10] G. Férey, C. Serre, C. Mellot-Draznieks, F. Millange, S. Surblé, J. Dutour, I. Margiolaki, *Angew. Chem.* **2004**, *116*, 6456–6461; *Angew. Chem. Int. Ed.* **2004**, *43*, 6296–6301.
[11] D. S. Kim, P. M. Forster, R. Le Toquin, A. K. Cheetham, *Chem. Commun.* **2002**, 2148–2149.
[12] H. Kumagai, M. Ohba, H. Okawa, Y. Oka, K. Inoue, S. Kawata, M. Kurmoo, *Polyhedron* **2003**, *22*, 1917–1920.
[13] R. Sessoli, D. Gatteschi, H.-L. Tsai, D. N. Hendrickson, A. R. Schake, S. Wang, J. B. Vincent, G. Christou, K. Folting, *J. Am. Chem. Soc.* **1993**, *115*, 1804–1816.
[14] E. K. Brechin, R. A. Coxall, A. Parkin, S. Parsons, P. A. Tasker, R. E. P. Winpenny, *Angew. Chem.* **2001**, *113*, 2772–2775; *Angew. Chem. Int. Ed.* **2001**, *40*, 2700–2703.
[15] C. Livage, C. Egger, G. Férey, *Chem. Mater.* **2001**, *13*, 410–414.
[16] P. M. Forster, A. R. Burbank, A. K. Cheetham, C. Livage, G. Férey, *Chem. Commun.* **2004**, *10*, 368–369.
[17] R. A. Coxall, A. Parkin, S. Parsons, A. A. Smith, G. A. Timco, R. E. P. Winpenny, *J. Solid State Chem.* **2001**, *159*, 321–327.
[18] C. Livage, N. Guillou, J. Marrot, G. Férey, *Chem. Mater.* **2001**, *13*, 4387–4392.
[19] J.-P. Jolivet, *Metal Oxide Chemistry and Synthesis*, Wiley, Chichester, **2000**.
[20] G. Aromí, P. Christian, M. Helliwell, A. A. Smith, R. E. P. Winpenny, A. S. Batsanov, A. Parkin, S. Parsons, G. A. Timco, *Chem. Eur. J.* **2003**, *9*, 5142–5161.
[21] N. E. Brese, M. O'Keeffe, *Acta Crystallogr. Sect. B* **1991**, *47*, 192–197.
[22] G. Férey, *J. Solid State Chem.* **2000**, *152*, 37–48.
[23] The magnetic properties of the compound were investigated on powder samples with a Quantum Design MPMS-XL SQUID

magnetometer. All the magnetic data were corrected for the diamagnetism of the sample and of the holder.

[24] R. L. Carlin, *Magnetochemistry*, Springer, Berlin, **1986**.

[25] F. E. Mabbs, D. J. Machin, *Magnetism and Transition Metal Complexes*, Chapman and Hall, London, **1973**.

[26] E. Coronado, M. Drillon, P. R. Nugteren, L. J. De Jongh, D. Beltran, *J. Am. Chem. Soc.* **1988**, *110*, 3907–3913.

[27] a) S. Kitagawa, M. Kondo, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1739–1753; b) S. Noro, S. Kitagawa, M. Kondo, K. Seki, *Angew. Chem.* **2000**, *112*, 2161–2164; *Angew. Chem. Int. Ed.* **2000**, *39*, 2081–2084.

[28] N. Guillou, C. Livage, W. van Beek, M. Noguès, G. Férey, *Angew. Chem.* **2003**, *115*, 667–671; *Angew. Chem. Int. Ed.* **2003**, *42*, 643–647.

[29] FT-IR spectra were recorded on a Nicolet Magna-IR 550 spectrometer. Thermogravimetric analyses were performed with a TA-Instruments TGA-2050 apparatus (oxygen flow $60\,\mathrm{mL\,min^{-1}}$, $5\,^{\circ}\mathrm{C\,min^{-1}}$). Density experiments were performed with a Micromeritics multipycnometer operating under He flow. All the reagents were purchased from Aldrich Chemicals and used as supplied.

[30] Crystallographic data: $C_{48}H_{27}Co_6Na_3O_{27}$, trigonal, space group $R\bar{3}c$, $a = 14.100(1)$, $c = 42.727(5)$ Å, $V = 7356(1)$ Å^3, $Z = 6$, $\rho_{\mathrm{calcd}} = 1.973\,\mathrm{g\,cm^{-3}}$. Intensity data were collected in 1271 frames with ω scans (width of 0.30° and exposure time 30 s per frame). Data reduction was performed with the SAINT software and absorption corrections with SADABS (G. M. Sheldrick, SADABS: Program for Scaling and Correction of Area Detector Data, University of Göttingen, Göttingen, Germany, **1997**). $\mu(\mathrm{Mo}_{K\alpha}) = 2.109\,\mathrm{mm^{-1}}$, $F(000) = 4347$, $2\theta_{\max} = 59.9°$; 7477 reflections collected of which 2177 unique ($R_{\mathrm{int}} = 0.0244$). Final R indices (2177 observed reflections, ($I > 2\sigma(I)$)): $R_1 = 0.0339$, $wR_2 = 0.0916$. Highest residual electron density $0.55\,\mathrm{e\,Å^{-3}}$.

[31] G. M. Sheldrick, SHELXS97 and SHELXL97: Software package for Crystal Structure Determination, University of Göttingen, Germany, **1997**.

[32] CCDC-273335 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.