![ESRF logo] ESRF	**Experiment title:** *Ab initio* structure determination from powder diffraction of two new Nickel microporous oxides	**Experiment number:** CH-938
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Report:

The preparation of open frameworks based on transition metals is currently one of the most important aims of research due to their practical application as catalysts, hosts in intercalation compounds and their potential electronic properties. Two of our last results concern nickel-phosphate compounds, which present 24-membered ring channels [Guillou *et al. C.R. Acad. Sci. Paris*, 1999, **2**, 387; Guillou *et al. Angew. Chem. Int. Ed*, 2001, **40**, 2831]. We recently introduced a new way for obtaining microporous materials in which an organic partner (carboxylate) is part of the open framework. Our first results concern the synthesis of two new cobalt-succinates that present infinite networks of Co-O-Co with open windows [Livage *et al. J. Mater. Chem.*, 1998, **8**, 2743; Livage *et al. Chem. Mater.*, 1999, **6**, 1546]. We are now interested in nickel compounds and we recently synthesised two new compounds. They were prepared as green powders from hydrothermal reactions at 180°C and their powder diffraction data collected on a Siemens D-5000 diffractometer could be indexed with satisfactory figures of merit. The unit cell parameters and the supposed space group were the following:

(1) $a = 7.871(2)$ Å $b = 18.837(5)$ Å $c = 23.448(7)$ Å $b = 92.00(3)°$ $V = 3475$ Å^3; S.G: $P2_1/c$.

(2) $a = 16.417(6)$ Å $b = 10.515(4)$ Å $c = 19.514(7)$ Å $b = 119.73(3)°$ $V = 2925.1$ Å^3; S.G. $P2/c$ or Pc

The aim of the experiment was the *ab initio* structural resolution of **(1)** and **(2)** from synchrotron powder diffraction data. High-resolution synchrotron powder data of the nickel-succinates were then collected on the diffractometer of BM01B line of ESRF. Measurements were made with a Debye-Scherrer diffractometer geometry and a Si 111 analyser crystal to select a monochromatic wavelength of 0.7999 Å. The very fine powder was introduced in capillaries ($\phi = 1$ and 1.5 mm) and patterns were scanned in the range 1-45°($2q$) with a step length of 0.0035°($2q$) and a counting time of 1s step^{-1}. To improve the counting statistics at high $2q$ angles, patterns were divided in two $2q$ regions (1-15° and 15-45°) with times per step of 1 and 3s, respectively. The data from the four detectors were normalised by using the monitor counts and *ab initio* structural determinations were undertaken.

Compound (1): A structureless whole pattern profile refinement by Le Bail method (program FullProf available in the WinPLOTR software package) confirmed the monoclinic unit cell previously found, and the $P2_1/c$ space group. 2921 integrated intensities were extracted in the angular range 1-44° ($2q$), and were used in SHELXTL for direct methods calculations. By increasing the number of direct methods attempts to 256, the most probable E-map revealed the location of the 7 independent nickel atoms with 17 surrounding oxygens and few carbons. These corresponding atomic coordinates were used as a starting model in the Rietveld refinement, which converged approximately to $R_B = 0.30$ and $R_F = 0.20$, confirming the validity of the initial hypothesis. Successive difference Fourier maps alternated with profile refinements in the Rietveld method allowed to complete the inorganic framework. At this stage, the use of soft distance and angular constraints, to stabilise the oxide framework, gave gradually clearer difference electron density maps and allowed to complete the organic moieties and the location of the free water molecules. At the final stage, the structural model contains 55 non-hydrogen atoms. The final fit obtained between calculated and observed patterns corresponds to satisfactory crystal structure model indicators ($R_B = 0.067$ and $R_F = 0.070$) and profile factors ($Rp = 0.051$ and $Rwp = 0.063$) as shown on Figure 1.
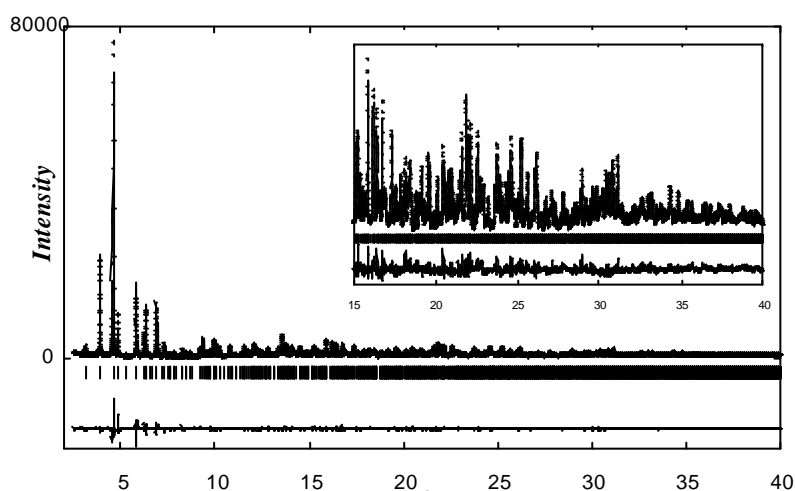

Figure 1: *Final Rietveld plot of (1), or $Ni_7(O_2C$-$(CH_2)_2$-$CO_2)_4O_2(OH)_2(H_2O)_5.7H_2O$*
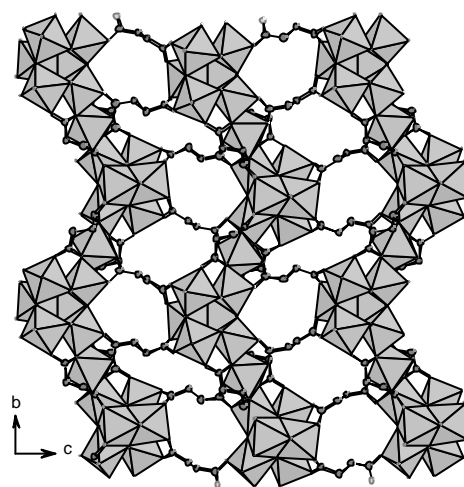

Figure 2: *Projection of the structure of (1) along a*

The structure of **(1)** or $Ni_7(O_2C$-$(CH_2)_2$-$CO_2)_4O_2(OH)_2(H_2O)_5.7H_2O$, can be described from hybrid organic-inorganic layers in the *bc* plane (see Figure 2). These layers are constructed from nickel oxide corrugated chains running along the *b* axis. These chains are built from NiO_6 hexameric units where octahedra are connected by sharing a face, edges and corners. In a chain, hexamers are connected *via* a seventh octahedron, which shares two edges in *trans* position with two neighbouring hexamers. All acidic groups are deprotonated. Half of the succinates decorates the chains, then the other half connects them along the *c* axis. No covalent bond links adjacent layers and the three dimensional arrangement is ensured by hydrogen bonds, directly between two adjacent layers and *via* free water molecules. These results will be presented at EPDIC-8 conference and will be soon published.

Compound (2): All attempts to solve the structure in the monoclinic space groups failed. A check for possible higher metrical symmetry of the lattice using the Lepage code led to a rhombohedral unit cell ($a = 21.049(2)$, $c = 45.83(1)$ Å and $V = 17585(6)Å^3$; S.G. R-$3c$). Unfortunately, Forster and Cheetham solved, at the same time, the structure of **(2)** or $Ni_7(O_2C$-$(CH_2)_2$-$CO_2)_6 (OH)_2(H_2O)_2.2H_2O$, from single crystal [Forster and Cheetham *Angew. Chem. Int. Ed*, 2002, **41**, 457].

Synchrotron powder patterns of $Ga(P_2O_7)F.[H_3N$-$(CH_2)_3$-$NH_3].3H_2O$ **(3)** and of $CoCl_4[NH_3$-$(CH_2)_2$-$NH_3]$ **(4)** could also be measured during the experiment time. Synchrotron data of **(3)** compared with conventional X-ray source data, clearly show a split of some lines. Unfortunately, all of them could not be indexed with satisfactory figures of merit, showing that the compound was probably not a pure phase. The structure of **(4)** could be solved *ab initio* and the final Rietveld refinement converged to very good structural model indicators ($R_B = 0.039$ and $R_F = 0.044$) and profile factors ($R_{wp} = 0.043$ and $R_p = 0.035$). The quality of the data is really impressing and most of H-atoms could be deduced from the last difference Fourier map.