Supplementary information for

Hydrogen adsorption in a nickel based coordination polymer with open metal sites in the cylindrical cavities of the desolvated framework

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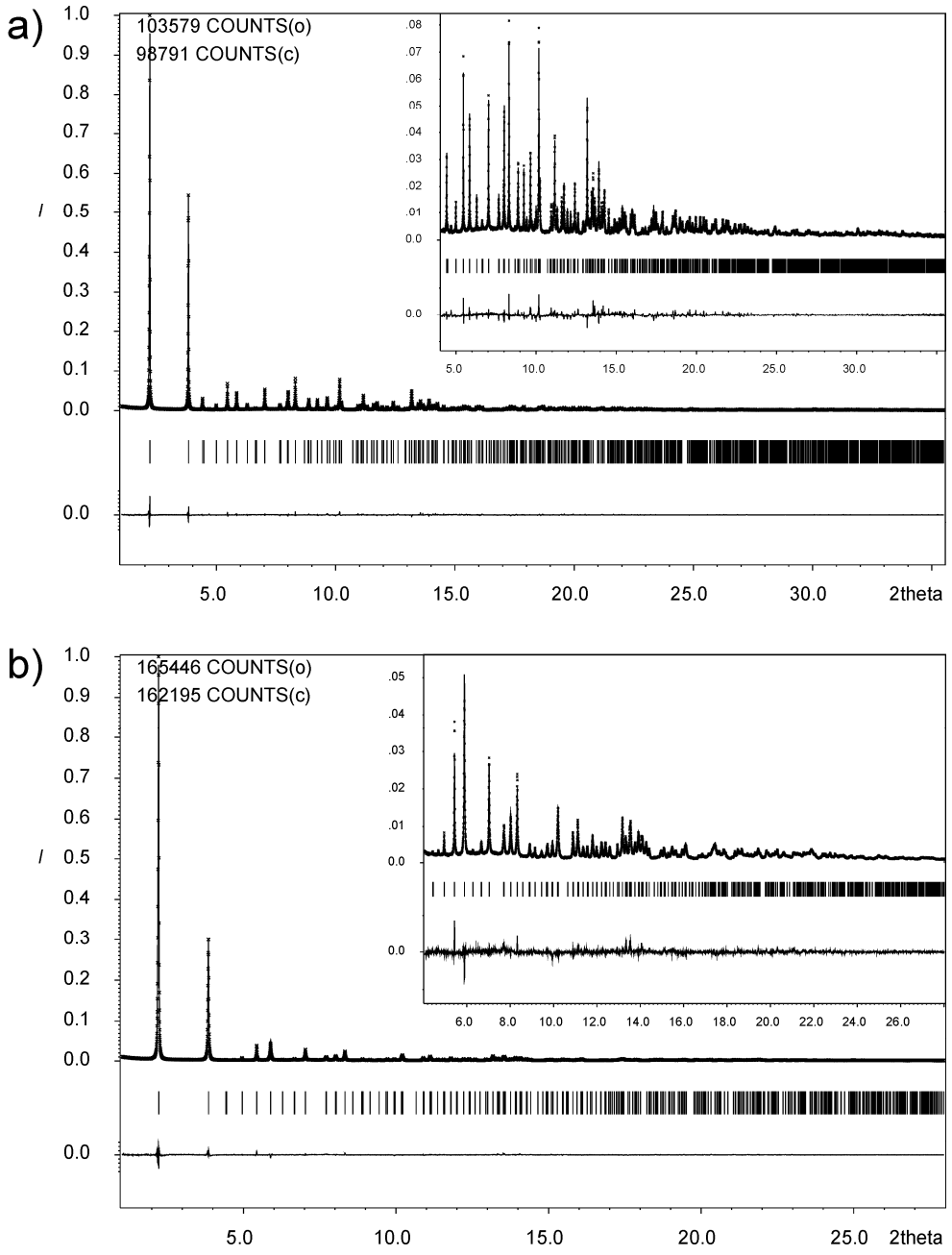
Structure determination of $Ni_2(dhtp)(H_2O)_2 \cdot 8H_2O$ **1** (hydrated and dehydrated form):

High-resolution Powder X-ray diffraction data was recorded at the Swiss-Norwegian beamline (SNBL/BM01) at the European Synchrotron radiation Source (ESRF), Grenoble, France. The synchrotron source operates with an average energy of 6 GeV and a current beam of typically 200 mA. The incident X-ray wavelength was 0.50134 Å. The SNBL receives its radiation from a bending magnet in the storage ring.
Both samples are from the same synthesis of **1**. They were filled into a capillary of 0.7 mm diameter. The dehydrated form was prepared by heating the filled capillary in a dynamic vacuum at 100ºC for 14 h, after which the capillary was flame sealed.
Data collection was performed over the angular range of 1-34.5º 2θ for hydrated **1** and 1-28º 2θ for dehydrated **1** with a step width of 0.004º at room temperature.
Indexation yielded the rhombohedral cells (hydrated **1**: $a = b = 25.9783(7)$ Å, $c = 6.6883(2)$ Å, $\alpha = \beta = 90º$, $\gamma = 120º$; dehydrated **1**: $a = b = 25.7856(12)$ Å, $c = 6.7701(10)$ Å, $\alpha = \beta = 90º$, $\gamma = 120º$) with high figures of merit. The space group was assumed to be $R\bar{3}$ in accordance with the structure of $Co_2(dhtp)(H_2O)_2 \cdot 8H_2O$ that has a very similar powder X-ray pattern. Systematic absences were consistent with this choice. There are, however, two very weak reflections at 4.69° and 9.085° that do not fit this indexation. The fact that their positions are identical in both samples already suggests that they can be safely regarded as impurity. This is proven by comparison with a measurement that was done on a different batch of **1** in our home lab prior to the beamtime at the Synchrotron which does not contain the two reflections.
A full profile Le Bail fit and Rietveld refinement were performed with the Jana2000 program. The structural models were taken from the single-crystal structure determinations of the corresponding hydrated and dehydrated cobalt compound. In both, the asymmetric unit contains only half the organic molecule. To achieve a regular geometry of the aromatic ring, the carbon and oxygen atoms were therefore split into the two possible positions making up one full molecule with a site occupation factor of 0.5 each. The second position was constrained to x(Atom 2) = 1 – x(Atom 1), y(Atom 2) = 1 – y(Atom 1), z(Atom 2) = 2 – z(Atom 1), and $U11$(Atom 2) = $U11$(Atom 1) to maintain the crystallographic equivalence of both atoms. The hydrogen atom on the aromatic ring was restrained in its distance and angles, and its isotropic displacement parameter was coupled to the carbon atom it is bonded to. For the dehydrated form, in addition, the distances, angles and torsion angles of the organic molecule were restrained, and the isotropic displacement parameters of the carbon atoms of the aromatic ring were restrained to identical values. The site occupation factors of the water molecules in the hydrated sample were set to 1.25 to account for the additional electrons that are contributed by the hydrogen atoms instead of trying to refine hydrogen positions. After maximal convergence of the refinement was achieved, a difference Fourier map was calculated. In both cases, no significant peaks that may represent atoms were found and

maximum and minimum values of the electron density are balanced (Rho max/min 0.38/-0.76 for hydrated **1**, 0.35/-0.39 for dehydrated **1**).
Final results for hydrated **1**: $C_4H_{11}NiO_8$, M = 229.8 g mol^{-1}, trigonal space group $R\bar{3}$, $a = b$ = 25.9783(7) Å, c = 6.6883(2) Å, $\alpha = \beta = 90°$, $\gamma = 120°$, Z = 18, λ = 0.50134 Å, T = 295 K, 2θ range 1.024-35.492º, step size 0.004º, R_p = 0.0576, R_{wp} = 0.0752, R_{exp} = 0.0409, R_{Bragg} = 0.0281, χ^2 = 3.38; Dehydrated **1**: C_4HNiO_3, M_r = 155.7 g mol^{-1}, trigonal space group $R\bar{3}$, , $a = b$ = 25.7856(12) Å, c = 6.7701(10) Å, $\alpha = \beta = 90°$, $\gamma = 120°$, Z = 18, λ = 0.50134 Å, T = 295 K, 2θ range 1.024-27.996º, step size 0.004º, R_p = 0.0629, R_{wp} = 0.0847, R_{exp} = 0.0357, R_{Bragg} = 0.0304, χ^2 = 5.63.



Rietveld refinement plots of the hydrated (a) and dehydrated (b) form of **1** (crosses: observed pattern, line: calculated pattern, bottom line: difference plot, all plotted on the same scale. Bragg peaks are indicated by tick marks. Insets: enlarged view of the high angle range).