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Supporting information for article:

An ordering phase transition, short hydrogen bonds and high *Z´* in the structure of Ni(Hpydc)2·3H2O

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Supporting Information

S1. History of the structure reports of $Ni(Hpydc)_2•3H_2O$ at room temperature

The earliest report of $Ni(Hpydc)_2•3H_2O$ resulted from crystallization of an aqueous solution of $Ni(NO_3)_2$ and pyridine-2,6-dicarboxylic acid or the "freshly precipitated hydroxide" (PYDCNI, Gaw *et al*., 1971). The crystal data was obtained by Weissenberg methods and the structure refined block-diagonally. They observe, "…the uncoordinated carboxyl oxygen atoms are bridged by hydrogen-bonding water molecules. We have no evidence at the present time for the presence of hydronium ions in the hydrogen-bonding network." A second determination, with crystals from slow evaporation of an aqueous solution made up by Ni^{2+} ions and dipicolinic acid in ratio 1:2 using an "on-line" single crystal automated diffractometer for data collection (PYDCNI01, Villa *et al*., 1972) and block-diagonal refinement, stated that the third hydrate molecule was disordered into two parts at 60:40 occupancy: "As indicated…the O(11) water molecule is statistically distributed in two positions, one of them (O(11B)), is inconsistent with the packing contacts through the center of symmetry at ½, ½, 0. This situation indicates that the center of symmetry arises as a consequence of the statistical distribution of this molecule, all the remaining part of the structure being centrosymmetrical." The same year (PYDCNI02, Quaglieri *et al*., 1972), using a crystal grown from the metal perchlorate and dipicolinic acid in a ratio of 1:2, with slow evaporation from an aqueous solution, Weissenberg photography, and block-diagonal refinement also displayed disorder, it was written that the thermal motion on water oxygen O11 made the location of its hydrogens impossible. For the other two waters, they looked for and refined positions that were between the non-bonded carboxylic acid oxygen and the water oxygens. These O···O distances were short. A four-circle diffractometer was used in an extensive study of seven different complexes using the $Hpydc^-$ ligand (PYDCNI03, Nathan & Mai, 2000). Synthesis was carried out using a hydrated metal acetate refluxed in aqueous solution with Et_4NOH and H_2pydc in a 1:2:2 mole ratio. Crystals were obtained by reducing the volume of water then cooling, leading to recrystallization from water. Hydrogen positions were idealized—not refined. One water molecule is disordered (hydrogens were not assigned to it). In the presence of pyridine-2,6-diamine (PYDCNI04, Moghimi *et al*., 2002), crystals of $Ni(Hpydc)_2•3H_2O$ formed from $NiCl_2•6H_2O$, H_2pydc and water in 1 h at 60 °C whereas crystals of $[(Hpyda)_2][Ni(pydc)_2]•H_2O$ formed after 2 weeks at room temperature. No coordinates were published. Hydrothermal synthesis at 393 K with $Ni(NO_3)_2•6HO$, H_2pydc, and NaOH in a ratio of 1.5: 1:2 with additional H_2O was reported in 2012 (PYDCNI05, Sanotra, *et al*.). A CCD area detector was employed. No mention is made of disordered H_2O, but it shows up in the published coordinates. The structure is described as supramolecular and porous due to the extensive hydrogen bonding. The publication reporting the 7th determination (PYDCNI06, Zhong *et al*., 2004) could not be

retrieved but does contain a "?" in the deposited coordinates for the third water molecule. The same year a structure with four, instead of three solvate waters was published (QAKYUX, Wang *et al*., 2004). It was formulated as $(H_3O)_2$[Ni(pydc] •$2H_2O$. Even though the solution of $NiCl_2$•$6H_2O$ and H_2pydc was acidified to pH 4.5 by the addition of dilute HCl, based on the unit cell and coordinates, evidently this is the same structure as given here. Most recently, the structure was described as $[Ni(Hpydc)_2]$•(H_3O)•$2H_2O$ in the paper by Mirzaei, et al. (PYDCNI07, 2014). However, this formula cannot be correct because it is not charge balanced. In addition to the 2-aminopyrazine that was used in the synthesis reported here, pyrazine (Gharamaleki, 2009) and 2-methylimidazole (Ghadermazi, 2010) have been employed in the reaction and yield the same products.

Table S1. Selected hydrogen-bond parameters for 298 K $[(H_3O)][Ni(Hpydc)(pydc)]$•$2H_2O$

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
O6—H6···O10	0.99 (4)	1.49 (4)	2.469 (2)	169 (4)
O9—H9A···O8^{i}	0.91 (4)	1.70 (4)	2.610 (2)	176 (3)
O9—H9C···O3	1.16 (4)	1.30 (4)	2.456 (2)	178 (4)
O10—H10A···O2^{ii}	0.93 (3)	1.86 (3)	2.676 (2)	145 (3)
O10—H10B···O2^{iii}	0.89 (2)	1.90 (3)	2.745 (2)	159 (3)

Symmetry code(s): (i) *x*, −*y*+1/2, *z*−1/2; (ii) −*x*, *y*+1/2, −*z*+1/2; (iii) *x*, −*y*+3/2, *z*−1/2.

S2. Transformations

If one considers the intermediate space group to be *Cc*, the progress of the transformation from room temperature to 90 K can be seen as, first, a loss of the inversion center and screw axis of $P2_1/c$, a doubling of **a** and **b**, and a change from Z′ = 1 to Z′ = 4. In the progress from *Cc* to $P\bar{1}$ the glide plane is lost but the inversion center is restored. The new cell axes **b** and **c** correspond to the two centering vectors of -1/2 + **b**/2 and –**a**/2 - **b**/2 in *Cc*. The net change is from one molecule in the asymmetric unit to four molecules in the asymmetric unit.

At room temperature, the **α** polymorph exists as monoclinic $P2_1/c$. Upon cooling, the polymorph transforms to the **β** polymorph in $P\bar{1}$. The matrix for transformation of the unit cell, written as a column vector, from **α** to **β** is given by:

$$\begin{pmatrix} 0 & 0 & 1 \\ -1 & 1 & 0 \\ -1 & -1 & 0 \end{pmatrix}$$

The inverse transformation is given by:

$$\begin{pmatrix} 0 & -\frac{1}{2} & -\frac{1}{2} \\ 0 & \frac{1}{2} & -\frac{1}{2} \\ 1 & 0 & 0 \end{pmatrix}$$

The transformation from the intermediate *Cc* to $P2_1/c$ is given by:

$$\begin{pmatrix} \frac{1}{2} & 0 & 0 \\ 0 & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Table S2. Selected hydrogen-bond parameters for 90 K

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
O15—H15···O7W	1.13 (3)	1.37 (3)	2.4609 (15)	161 (3)
O19—H19A···O8W	1.03 (3)	1.44 (3)	2.4581 (16)	171 (3)
O26—H26A···O6W	1.00 (2)	1.52 (2)	2.5224 (16)	176 (2)
O31—H31A···O4W	1.20 (3)	1.23 (3)	2.4339 (16)	177 (3)
O1W—H1A···O10W	0.85 (3)	1.76 (3)	2.5852 (17)	162 (2)
O1W—H1B···O28	1.10 (3)	1.47 (3)	2.5475 (15)	167 (3)
O1W—H1C···O23	1.18 (3)	1.29 (3)	2.4590 (15)	170 (3)
O2W—H2A···O11	0.852 (19)	1.84 (2)	2.6575 (15)	160.1 (17)
O2W—H2B···O22	0.85 (3)	1.74 (3)	2.5772 (15)	170 (3)
O2W—H2C···O2	1.16 (3)	1.27 (3)	2.4275 (15)	174 (2)
O3W—H3A···O11W^{i}	0.94 (3)	1.62 (3)	2.5317 (18)	163 (2)
O3W—H3B···O4	0.96 (2)	1.61 (2)	2.5679 (16)	175 (2)
O3W—H3C···O10^{i}	0.96 (3)	1.55 (3)	2.5076 (16)	172 (3)
O4W—H4A···O17^{ii}	0.85 (2)	1.81 (2)	2.6507 (16)	171.4 (19)

O4W—H4B···O12W	0.85 (3)	1.78 (3)	2.5983 (19)	160 (3)
O5W—H5A···O13^{iii}	0.77 (3)	1.80 (3)	2.5628 (16)	170 (3)
O5W—H5B···O9W	0.91 (3)	1.79 (3)	2.6242 (17)	151 (2)
O5W—H5C···O7	1.19 (3)	1.27 (3)	2.4499 (15)	176 (3)
O6W—H6A···O11^{iv}	0.76 (2)	2.00 (2)	2.7459 (15)	164 (2)
O6W—H6B···O22^{iv}	0.86 (2)	1.99 (2)	2.7856 (15)	154 (2)
O7W—H7A···O30^{v}	0.85 (2)	1.82 (2)	2.6560 (15)	166 (2)
O7W—H7B···O30^{vi}	0.87 (2)	1.93 (2)	2.7408 (16)	155 (2)
O8W—H8A···O6^{ii}	0.88 (2)	1.81 (2)	2.6509 (15)	161 (2)
O8W—H8B···O6^{iii}	0.77 (2)	2.01 (2)	2.7405 (16)	159 (2)
O9W—H9A···O18^{vii}	0.85 (3)	1.84 (3)	2.6846 (16)	170 (3)
O9W—H9B···O8	0.86 (2)	2.00 (2)	2.8250 (16)	162 (2)
O10W—H10A···O27^{viii}	0.78 (3)	1.90 (3)	2.6842 (16)	176 (2)
O10W—H10B···O24	0.82 (3)	2.07 (3)	2.8293 (16)	155 (3)
O11W—H11A···O3^{ix}	0.83 (4)	1.89 (4)	2.7037 (17)	166 (3)
O11W—H11B···O9	0.89 (2)	1.89 (3)	2.7406 (16)	159 (2)
O12W—H12A···O14^{x}	0.90 (4)	1.81 (4)	2.6912 (17)	166 (3)
O12W—H12B···O18^{ii}	0.99 (4)	1.98 (4)	2.8633 (18)	148 (3)

Symmetry code(s): (i) −*x*, −*y*+1, −*z*; (ii) *x*+1, *y*, *z*; (iii) −*x*+1, −*y*+1, −*z*; (iv) −*x*+2, −*y*, −*z*+1; (v) −*x*+1, −*y*, −*z*+1; (vi) *x*−1, *y*, *z*; (vii) −*x*+1, −*y*+1, −*z*+1; (viii) −*x*+2, −*y*+1, −*z*+1; (ix) *x*, *y*−1, *z*; (x) *x*+1, *y*, *z*+1.

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