*Electronic Supplementary Information*

# Reversible Structural Switch in the Nano-Cavity of Crystalline Metallo-Macrocycle with Smooth Ligand Exchange by Non-Coordinating Guest Stimuli

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## General

Dipeptide ligand **1**·($CF_3CO_2H$) was synthesized according to the previously reported method.[S1] $Ni(NO_3)_2·6H_2O$ was purchased from Soekawa Chemical Co. MeOH (HPLC grade) was purchased from KANTO Chemical Co. All reagents and solvents were used without further purification. Differential scanning calorimetry (DSC) measurements were recorded on a Bruker DSC 3100SA under ambient pressure of $N_2$ gas at a scanning rate of 1 °C $min^{-1}$. Thermogravimetric measurements were recorded on a Bruker TG-DTA 2000SA under ambient pressure of $N_2$ gas at a scanning rate of 1 °C $min^{-1}$. Crystallographic data were collected on a Bruker APEXII CCD detector with Mo-$K\alpha$ radiation ($\lambda$ = 0.71075 Å). The structures were solved by direct methods using the program SHELXS. The refinement (on $F^2$) and graphical calculations were performed using the SHELIXL program suite.[S2, S3]

### Synthesis of $Ni_4$**1**$_4(NO_3)_8·14H_2O$

**1**·($CF_3CO_2H$)$_4$ (43.7 mg, 61.6 μmol) was neutralized by anion exchange resign (IRA-400) to obtain acid-free $\beta$-dipeptide **1** as a colorless syrup. To a solution of **1** in $H_2O$ (244 μL) was added $Ni(NO_3)_2·6H_2O$ (17.9 mg, 61.6 μmol) in $H_2O$ (244 μL). After filtration of the mixture, MeOH was added to the solution with a vapor diffusion method in incubator (20 °C). The purple prismatic crystals obtained after 2 weeks were collected and then washed with a mixture of $H_2O$ and MeOH ($v/v$ = 0.5) (0.15 mL × 2) and dried in air to afford $Ni^{II}$ complex (19.9 mg, 57%). (The yield was calculated based on estimated molecular weight from elementary analysis since the number of included water molecules was easily changed by external humidity and temperature.)

Mp = 236.3-237.3 °C (dec); IR 3318, 3272, 1660, 1578, 1316 $cm^{-1}$; Anal. Calc for $C_{48}H_{136}N_{36}Ni_4O_{50}$ ($Ni_4$**1**$_4(NO_3)_8(H_2O)_{14}$): C, 25.59; H, 6.09; N, 22.39. Found: C, 25.57; H, 6.24; N, 22.37.

**Crystal data for complex $Ni_4$1$_4(NO_3)_8$ at 93 K**: Specimen of $C_{48}H_{130}N_{36}Ni_4O_{47}$, approximate dimensions 0.100 mm × 0.140 mm × 0.160 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were collected at 93 K.

The total exposure time was 2.00 h. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data

using a tetragonal unit cell yielded a total of 17487 reflections to a maximum $\theta$ angle of 30.03° (0.71 Å resolution), of which 6693 were independent (average redundancy 2.613, completeness = 99.5%, $R_{int}$ = 1.89%, $R_{sigma}$ = 3.63%) and 6216 (92.87%) were greater than $2\sigma(F^2)$. The final cell constants of $a$ = 15.4881(7) Å, $b$ = 15.4881(7) Å, $c$ = 19.3281(9) Å, volume = 4636.5(4) Å$^3$, are based upon the refinement of the XYZ-centroids of 8660 reflections above 20 $\sigma(I)$ with 5.261° < $2\theta$ < 61.56°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.930. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8660 and 0.9144.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $I$-4, with $Z$ = 2 for the formula unit, $C_{48}H_{130}N_{36}Ni_4O_{47}$. The final anisotropic full-matrix least-squares refinement on $F^2$ with 345 variables converged at $R1$ = 5.07%, for the observed data and $wR2$ = 15.32% for all data. The goodness-of-fit was 1.060. The largest peak in the final difference electron density synthesis was 1.611 e$^-$/Å$^3$ and the largest hole was -0.662 e$^-$/Å$^3$ with an RMS deviation of 0.116 e$^-$/Å$^3$. On the basis of the final model, the calculated density was 1.575 g/cm$^3$ and $F$(000), 2316 e$^-$.

Refinement details: Because of disodered structure (especially $NO_3^-$ anion and included water molecules), Refinement was done by appling following restraints for $NO_3^-$ and included water molecules.

$NO_3^-$ anions were restrained by using SADI (restrained all O-N distance and O-O distance in nitrate), SIMU, ISOR for all $NO_3^-$ anions. FLAT restraint was also applied for disordered $NO_3^-$ anion ($NO_3$ (A) of water containing structure and $NO_3$(B) (consist of N(2MB), O(4MB), O(5MB), O(6MB)) and $NO_3$(C) of water-free structure). All included water molecules were refined without the addition of hydrogen atoms by using SIMU and ISOR restraint.

# Tables of Crystal data under various conditions

**Table S1** Crystal data and structure of $Ni_4\mathbf{1}_4(NO_3)_8$ under dry $N_2$ gas at various temperatures

| Temperature /°C | -180 | -150 | -100 | -50 | -40 | 0 |
|---|---|---|---|---|---|---|
| | $Ni_4\mathbf{1}_4(NO_3)_8\cdot 11H_2O$ | $Ni_4\mathbf{1}_4(NO_3)_8\cdot 11H_2O$ | $Ni_4\mathbf{1}_4(NO_3)_8\cdot 11H_2O$ | $Ni_4\mathbf{1}_4(NO_3)_8\cdot 11H_2O$ | $Ni_4\mathbf{1}_4(NO_3)_8$ | $Ni_4\mathbf{1}_4(NO_3)_8$ |
| Crystal size | 0.16 × 0.14 × 0.10 | 0.16 × 0.14 × 0.10 | 0.16 × 0.14 × 0.10 | 0.16 × 0.14 × 0.10 | 0.12 × 0.10 × 0.05 | 0.16 × 0.14 × 0.10 |
| Formula | $C_{48}H_{130}N_{36}Ni_4O_{47}$ | $C_{48}H_{130}N_{36}Ni_4O_{47}$ | $C_{48}H_{130}N_{36}Ni_4O_{47}$ | $C_{48}H_{130}N_{36}Ni_4O_{47}$ | $C_{48}H_{108}N_{36}Ni_4O_{36}$ | $C_{48}H_{108}N_{36}Ni_4O_{36}$ |
| $M$ | 2198.72 | 2198.72 | 2198.72 | 2198.72 | 2000.54 | 2000.54 |
| Crystal system | *Tetragonal* | *Tetragonal* | *Tetragonal* | *Tetragonal* | *Tetragonal* | *Tetragonal* |
| Space group | *I*-4 | *I*-4 | *I*-4 | *I*-4 | *I*-4 | *I*-4 |
| $a$ /Å | 15.4881(7) | 15.5024(7) | 15.5252(6) | 15.4928(7) | 14.619(2) | 14.6608(14) |
| $b$ /Å | 15.4881(7) | 15.5024(7) | 15.5252(6) | 15.4928(7) | 14.619(2) | 14.6608(14) |
| $c$ /Å | 19.3282(9) | 19.3585(9) | 19.3983(8) | 19.4045(18) | 18.944(5) | 18.9712 (19) |
| $\alpha$ /° | 90 | 90 | 90 | 90 | 90 | 90 |
| $\beta$ /° | 90 | 90 | 90 | 90 | 90 | 90 |
| $\gamma$ /° | 90 | 90 | 90 | 90 | 90 | 90 |
| $V$ /Å$^3$ | 4636.5(4) | 4652.3(4) | 4675.6(2) | 4657.6(7) | 4048.7(14) | 4077.7(7) |
| $Z$ | 2 | 2 | 2 | 2 | 2 | 2 |
| $\rho_{calcd}$ /g·cm$^{-1}$ | 1.575 | 1.570 | 1.562 | 1.568 | 1.641 | 1.629 |
| $F$(000) | 2316 | 2316 | 2316 | 2316 | 2096 | 2096 |
| $\mu$ /mm$^{-1}$ | 0.912 | 0.909 | 0.905 | 0.908 | 1.026 | 1.019 |
| $\theta$ range /° | 2.11-30.03 | 2.10-30.03 | 2.10-30.03 | 2.10-30.00 | 1.76-25.03 | 2.15-29.11 |
| GOF | 1.060 | 1.065 | 1.075 | 1.041 | 1.022 | 1.060 |
| Reflections collected | 17487 | 17533 | 17695 | 17519 | 10729 | 14209 |
| Independent reflections | 6693 | 6711 | 6755 | 6713 | 3585 | 5452 |
| Flack parameter | 0.097(15) | 0.088(15) | 0.089(14) | 0.096(15) | -0.03(2) | 0.056(13) |
| $R_{int}$ | 0.0189 | 0.0193 | 0.0186 | 0.0313 | 0.0685 | 0.0263 |
| $R_{sigma}$ | 0.0363 | 0.0360 | 0.0355 | 0.0453 | 0.0855 | 0.0445 |
| Final $R1$ ($I > 2\sigma(I)$ (all data)) | 0.0507(0.0546) | 0.0483(0.0531) | 0.0457(0.0493) | 0.0495(0.0557) | 0.0516(0.0839) | 0.0362(0.0575) |
| $wR2$ ($I > 2\sigma(I)$ (all data)) | 0.1476(0.1532) | 0.1349(0.1401) | 0.1297(0.1341) | 0.1386(0.1439) | 0.1090(0.1251) | 0.0897(0.1028) |
| CCDC No. | 856057 | 856058 | 856059 | 856060 | 856061 | 856062 |

**Table S1** (Continued). Crystal data and structure of $Ni_4$**1**$_4(NO_3)_8$ under dry $N_2$ gas at various temperatures

| Temperature /°C | 20 | 60 | -180[(a)] | -180[(b)] |
|---|---|---|---|---|
| | $Ni_4$**1**$_4(NO_3)_8$ | $Ni_4$**1**$_4(NO_3)_8$ | $Ni_4$**1**$_4(NO_3)_8$ | $Ni_4$**1**$_4(NO_3)_8 \cdot 11H_2O$ |
| Crystal size | 0.16 × 0.14 × 0.10 | 0.16 × 0.14 × 0.10 | 0.12 × 0.10 × 0.05 | 0.12 × 0.10 × 0.05 |
| Formula | $C_{48}H_{108}N_{36}Ni_4O_{36}$ | $C_{48}H_{108}N_{36}Ni_4O_{36}$ | $C_{48}H_{108}N_{36}Ni_4O_{36}$ | $C_{48}H_{130}N_{36}Ni_4O_{47}$ |
| *M* | 2000.54 | 2000.54 | 2000.54 | 2198.72 |
| Crystal system | *Tetragonal* | *Tetragonal* | *Tetragonal* | *Tetragonal* |
| Space group | *I*-4 | *I*-4 | *I*-4 | *I*-4 |
| *a* /Å | 14.6619(12) | 14.6824(8) | 14.567(7) | 15.488(7) |
| *b* /Å | 14.6619(12) | 14.6824(8) | 14.567(7) | 15.488(7) |
| *c* /Å | 18.9721(16) | 18.985(2) | 18.717(9) | 19.360(10) |
| $\alpha$ /° | 90 | 90 | 90 | 90 |
| $\beta$ /° | 90 | 90 | 90 | 90 |
| $\gamma$ /° | 90 | 90 | 90 | 90 |
| *V* /Å$^3$ | 4078.5(16) | 4092.6(6) | 3972(3) | 4644(4) |
| *Z* | 2 | 2 | 2 | 2 |
| $\rho_{calcd}$ /g·cm$^{-1}$ | 1.629 | 1.623 | 1.673 | 1.572 |
| *F*(000) | 2096 | 2096 | 2096 | 2316 |
| $\mu$ /mm$^{-1}$ | 1.019 | 1.015 | 1.046 | 0.910 |
| $\theta$ range /° | 2.15-29.09 | 2.15-28.59 | 1.77-25.01 | 1.68-24.95 |
| GOF | 1.061 | 1.083 | 1.037 | 0.998 |
| Reflections collected | 14097 | 13641 | 10416 | 5322 |
| Independent reflections | 5408 | 5179 | 3521 | 3871 |
| Flack parameter | 0.062(14) | 0.058(15) | 0.05(4) | 0.00(4) |
| $R_{int}$ | 0.0229 | 0.0222 | 0.1041 | 0.0622 |
| $R_{sigma}$ | 0.0393 | 0.0368 | 0.1248 | 0.1562 |
| Final *R*1 ($I > 2\sigma(I)$ (all data)) | 0.0372(0.0544) | 0.0382(0.0556) | 0.0816(0.1379) | 0.0771(0.1506) |
| *wR*2 ($I > 2\sigma(I)$ (all data)) | 0.0929(0.1057) | 0.0921(0.1053) | 0.1858(0.2161) | 0.1845(0.2304) |
| CCDC No. | 856063 | 856064 | 856065 | 856066 |

Condition (a): The sample was measured after setting at 60 °C. The sample was under dry $N_2$ gas at whole process of controlling temperature.
Condition (b): The sample was measured after setting at 60 °C as condition (a). Then, the sample once bring out from dry $N_2$ gas condition before measurement.

**Table S2** Crystal data and structure of $Ni_4\mathbf{1}_4(NO_3)_8$ in glass capillary with normal humidity (ca. 50% RH at room temperature) at various temperatures

| Temperature /°C | 0 | 20* | 40* | 60 | 40 (after 60 °C) * | 20 (after 60 °C) |
|---|---|---|---|---|---|---|
| Humidity /%RH | 52 (26 °C) | 44 (26 °C) | 52 (24 °C) | 59 (26 °C) | 48 (23 °C) | 59 (26 °C) |
| | $Ni_4\mathbf{1}_4(NO_3)_8{\cdot}11H_2O$ | $Ni_4\mathbf{1}_4(NO_3)_8{\cdot}11H_2O$ | $Ni_4\mathbf{1}_4(NO_3)_8{\cdot}4H_2O$ | $Ni_4\mathbf{1}_4(NO_3)_8$ | $Ni_4\mathbf{1}_4(NO_3)_8{\cdot}4H_2O$ | $Ni_4\mathbf{1}_4(NO_3)_8{\cdot}11H_2O$ |
| Crystal size | 0.14 × 0.14 × 0.10 | 0.09 × 0.07 × 0.05 | 0.10 × 0.07 × 0.05 | 0.14 × 0.14 × 0.10 | 0.09 × 0.07 × 0.05 | 0.14 × 0.14 × 0.10 |
| Formula | $C_{48}H_{130}N_{36}Ni_4O_{47}$ | $C_{48}H_{130}N_{36}Ni_4O_{47}$ | $C_{48}H_{116}N_{36}Ni_4O_{40}$ | $C_{48}H_{108}N_{36}Ni_4O_{36}$ | $C_{48}H_{116}N_{36}Ni_4O_{40}$ | $C_{48}H_{130}N_{36}Ni_4O_{47}$ |
| $M$ | 2198.72 | 2198.72 | 2072.61 | 2000.54 | 2072.61 | 2198.72 |
| Crystal system | *Tetragonal* | *Tetragonal* | *Tetragonal* | *Tetragonal* | *Tetragonal* | *Tetragonal* |
| Space group | *I*-4 | *I*-4 | *I*-4 | *I*-4 | *I*-4 | *I*-4 |
| $a$ /Å | 15.560(2) | 15.5400(16) | 15.476(3) | 14.694(4) | 15.470(3) | 15.535(6) |
| $b$ /Å | 15.560(2) | 15.5400(16) | 15.476(3) | 14.694(4) | 15.470(3) | 15.535(6) |
| $c$ /Å | 19.491(6) | 19.493(4) | 19.445(4) | 19.014(10) | 19.437(8) | 19.504(8) |
| $\alpha$ /° | 90 | 90 | 90 | 90 | 90 | 90 |
| $\beta$ /° | 90 | 90 | 90 | 90 | 90 | 90 |
| $\gamma$ /° | 90 | 90 | 90 | 90 | 90 | 90 |
| $V$ /Å$^3$ | 4719.1(18) | 4707.5(12) | 4657.2(17) | 4106(3) | 4652(2) | 4707(3) |
| $Z$ | 2 | 2 | 2 | 2 | 2 | 2 |
| $\rho_{calcd}$ /g·cm$^{-1}$ | 1.547 | 1.551 | 1.478 | 1.618 | 1.480 | 1.551 |
| $F$(000) | 2316 | 2316 | 2176 | 2096 | 2176 | 2316 |
| $\mu$ /mm$^{-1}$ | 0.896 | 0.898 | 0.898 | 1.012 | 0.899 | 0.898 |
| $\theta$ range /° | 1.67-29.31 | 1.68-29.16 | 2.09-27.10 | 1.75-25.07 | 2.10-25.17 | 1.68-25.13 |
| GOF | 0.957 | 0.997 | 0.994 | 0.941 | 0.954 | 0.957 |
| Reflections collected | 17365 | 17265 | 14767 | 10761 | 8909 | 12455 |
| Independent reflections | 6443 | 6295 | 5124 | 3641 | 4178 | 4239 |
| Flack parameter | 0.02(3) | 0.00(3) | 0.03(3) | 0.06(3) | 0.03(4) | 0.00(4) |
| $R_{int}$ | 0.1289 | 0.0773 | 0.0752 | 0.1715 | 0.1114 | 0.1400 |
| $R_{sigma}$ | 0.1917 | 0.1088 | 0.1005 | 0.2217 | 0.1734 | 0.1778 |
| Final $R1$ ($I > 2\sigma(I)$ (all data)) | 0.0788(0.1844) | 0.0675(0.1256) | 0.0756(0.1242) | 0.0628(0.1988) | 0.0789(0.1807) | 0.0760(0.1608) |
| $wR2$ ($I > 2\sigma(I)$ (all data)) | 0.1703(0.2163) | 0.1536(0.1819) | 0.1844(0.2129) | 0.0806(0.1108) | 0.1853(0.2342) | 0.1633(0.2008) |
| CCDC No. | 856067 | 856068 | 856069 | 856070 | 856071 | 856072 |

*To improve resolution at high angle region, these data were measured again using a different crystal after all data were once collected with the same crystal.

# Supplement to the crystal structures of $Ni^{II}$-macrocycles

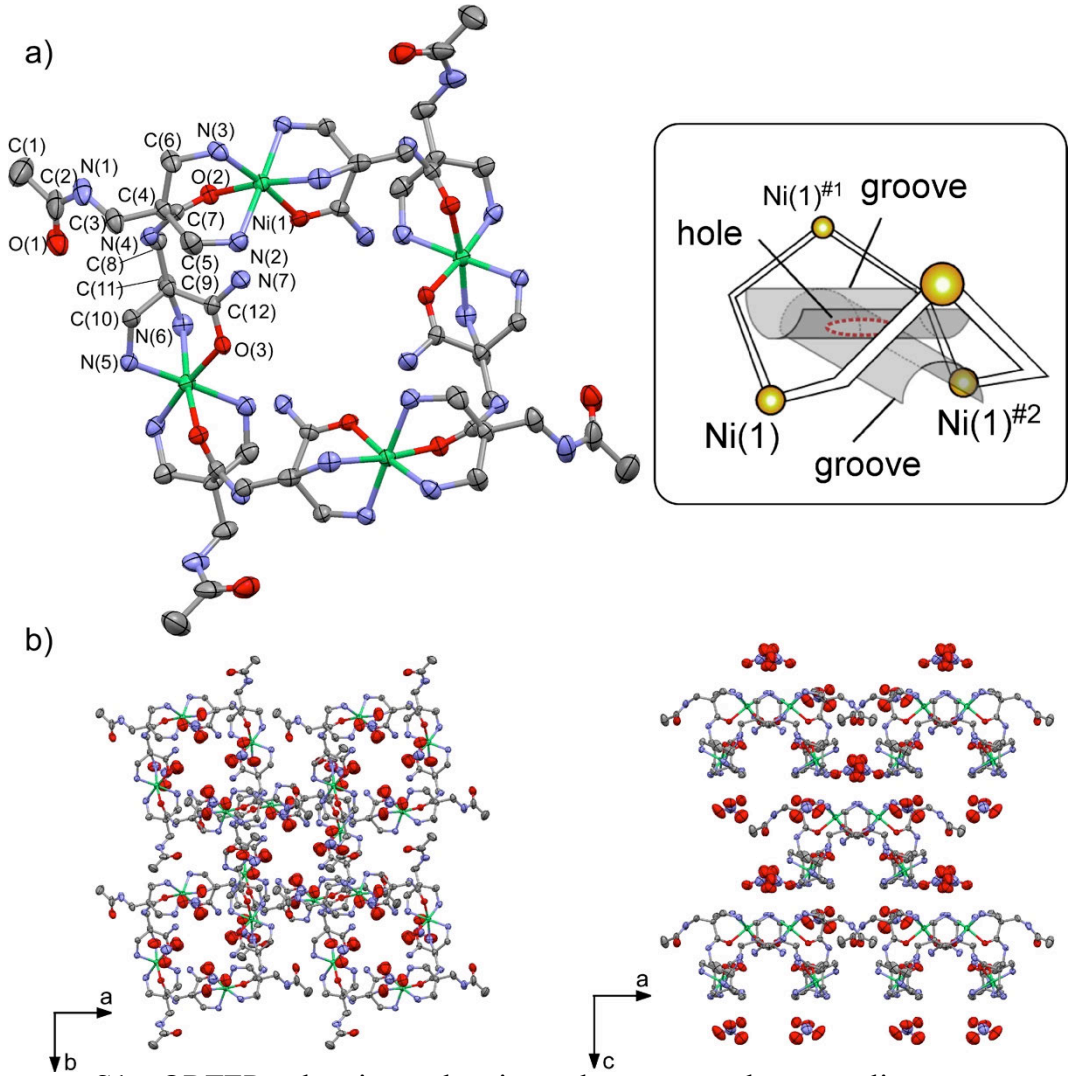


**Figure S1** ORTEP drawing showing the tetranuclear cyclic structure of $Ni_4$**1**$_4(NO_3)_8 \cdot 11H_2O$ at 20 °C: (a) a cyclic backbone with a schematic figure of "twisted boat structure" (inset of *a*) and (b) the packing structures from top view (left) and side view (right).

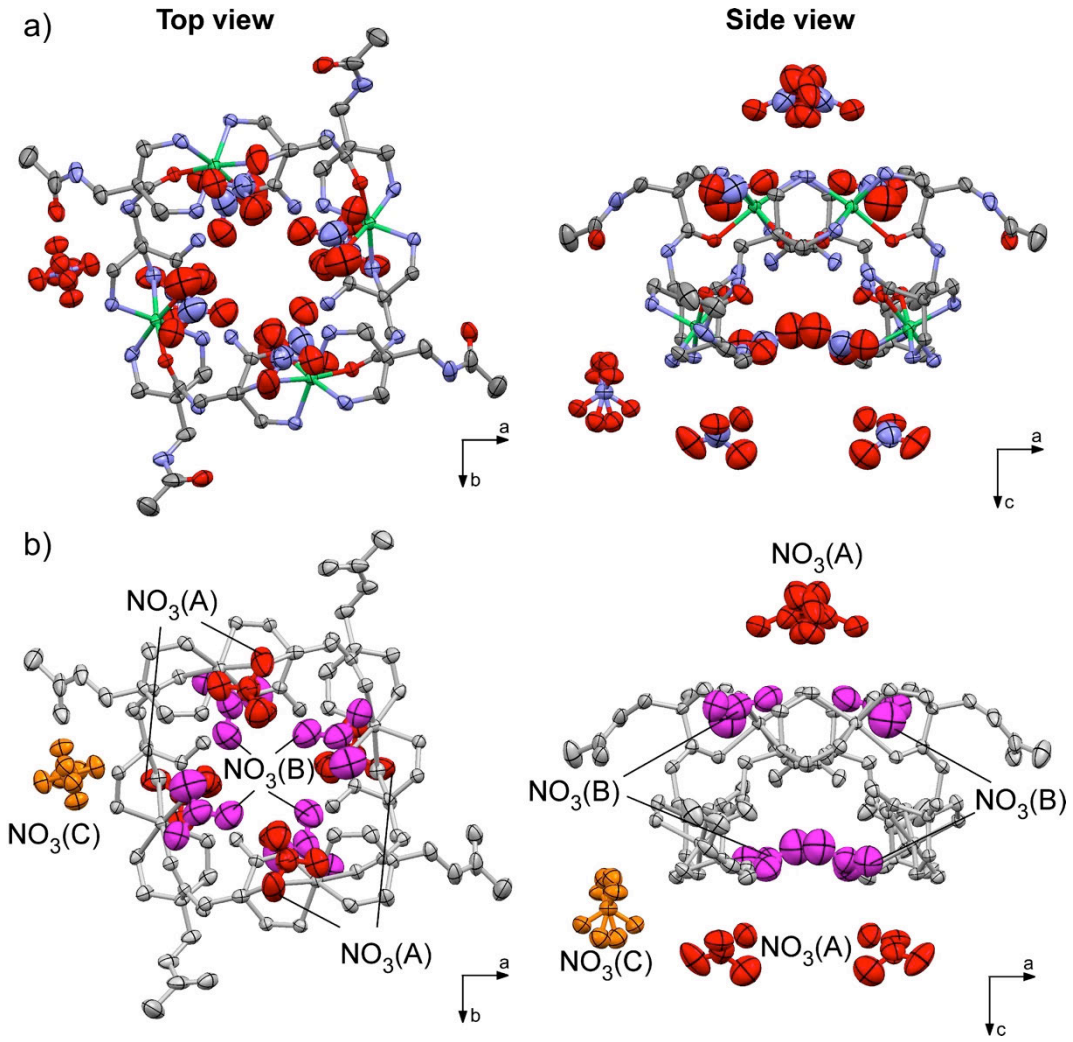


**Figure S2** ORTEP drawing showing the three identical positions of $NO_3^-$ ions in the crystal of $Ni_4\mathbf{1}_4(NO_3)_8 \cdot 11H_2O$ at 20 °C: (a) each atom is colored (C: grey, O: red, N: blue, Ni: green) and (b) each identical position was colored to be distinguished ($NO_3$(A): red, $NO_3$(B): pink, $NO_3$(C): orange)

**Additional information about $NO_3^-$ ions in the crystal structure**

$NO_3$(A) ions exist with full occupancy (*i.e.* 4 $NO_3$(A) ions per a complex). On the other hand, $NO_3$(B) ions exist with the occupancy of 0.75, suggesting that $NO_3^-$ ions actually exist only three of four positions as shown in Figure S2 (*i.e.* 3 $NO_3$(B) ions per a complex)). $NO_3$(B) ions are disordered above 40 °C. Finally, only one $NO_3$(C) ion exists in each complex.

$NO_3$ (A) and $NO_3$(C) ions are disordered at all measured temperatures and $NO_3$(B) ions are disordered above 40 °C.

$NO_3$(A):N(1M), O(1M), O(2M), O(3M)

$NO_3$(B):N(2M), O(4M), O(5M), O(6M)

$NO_3$(C):N(3M), O(7M), O(8M)

*Disordered atoms are distinguished by the addition of "A" or "B" at the end of atoms' names. (*i.e.* O(1MA) and O(1MB))

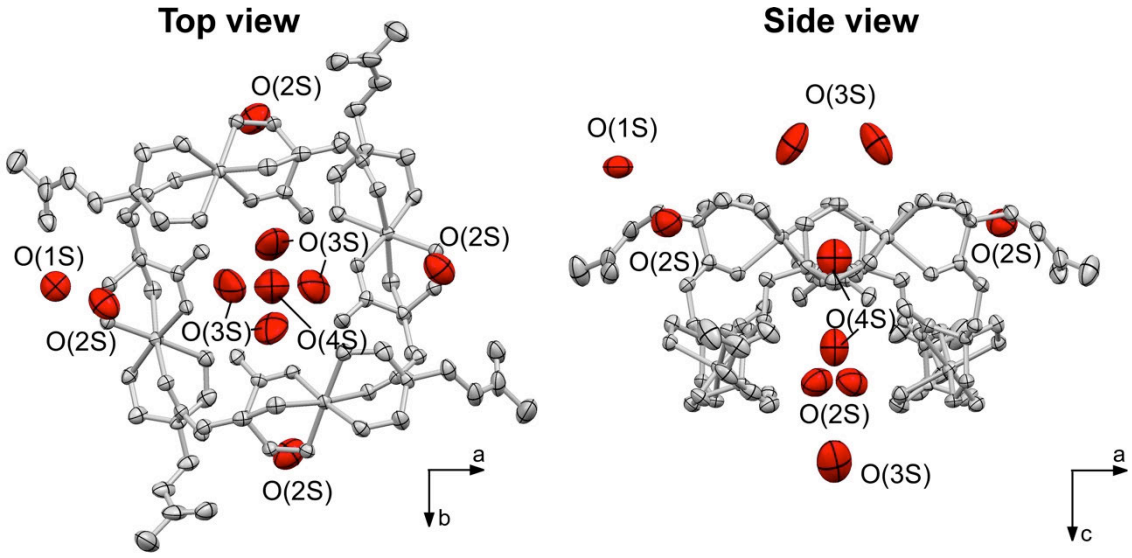


**Figure S3** ORTEP drawing showing the four identical water positions in the crystal of $Ni_4$**1**$_4(NO_3)_8 \cdot 11H_2O$ at 20 °C.

**Detailed study of structural changes in the crystal of $Ni_4I_4(NO_3)_8$**

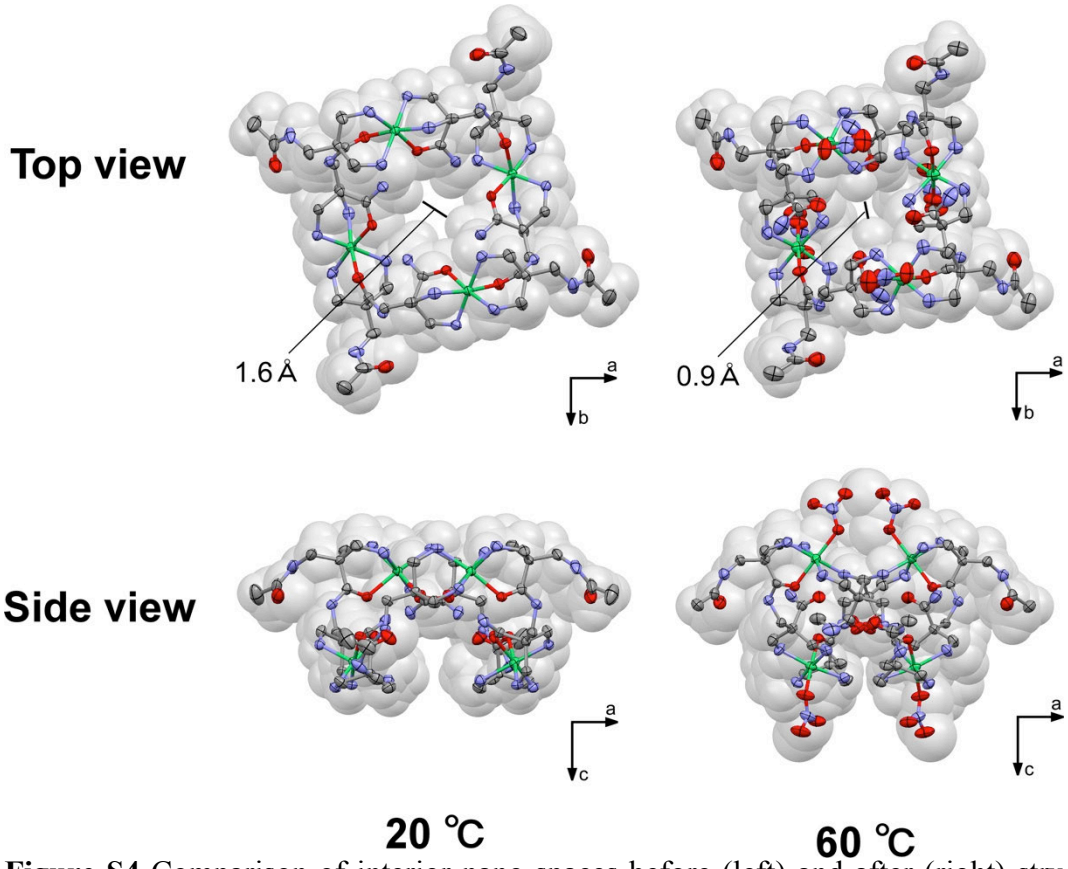


**Figure S4** Comparison of interior nano-spaces before (left) and after (right) structural changes: distances shown in the figure were calculated by (distances between atom centers) – (sum of van der Waals radius of the atoms).

**Table S3** Changes of Ni(II)-Ni(II) distances in the cyclic structure at various temperatures.

Measured under dry $N_2$ gas

| Temperature /°C | -180 | -150 | -100 | -50 |
|---|---|---|---|---|
| Ni(1)-Ni(1)#1 | 7.9721(5) | 7.9774(5) | 7.9882(5) | 7.9811(6) |
| Ni(1)-Ni(1)#2 | 9.0780(6) | 9.0877(6) | 9.1095(5) | 9.0931(6) |

| Temperature /°C | -40 | 0 | 20 | 60 |
|---|---|---|---|---|
| Ni(1)-Ni(1)#1 | 8.4704(17) | 8.4863(8) | 8.4852(7) | 8.4911(8) |
| Ni(1)-Ni(1)#2 | 8.1336(14) | 8.1483(9) | 8.1462(8) | 8.1549(7) |

Measured in capillary

| Temperature /°C | 0 | 20 | 40 | 60 |
|---|---|---|---|---|
| Ni(1)-Ni(1)#1 | 7.9923(17) | 7.9946(13) | 7.9763(15) | 8.497(3) |
| Ni(1)-Ni(1)#2 | 9.1382(17) | 9.1257(14) | 9.0838(18) | 8.164(2) |

| Temperature /°C | 40 °C after heating at 60 °C | 20 °C after heating at 60 °C |
|---|---|---|
| Ni(1)-Ni(1)#1 | 7.945(3) | 7.997(2) |
| Ni(1)-Ni(1)#2 | 9.079(4) | 9.121(4) |

#1 and #2: refer to an inset in Figure S1a.
Unit: Å

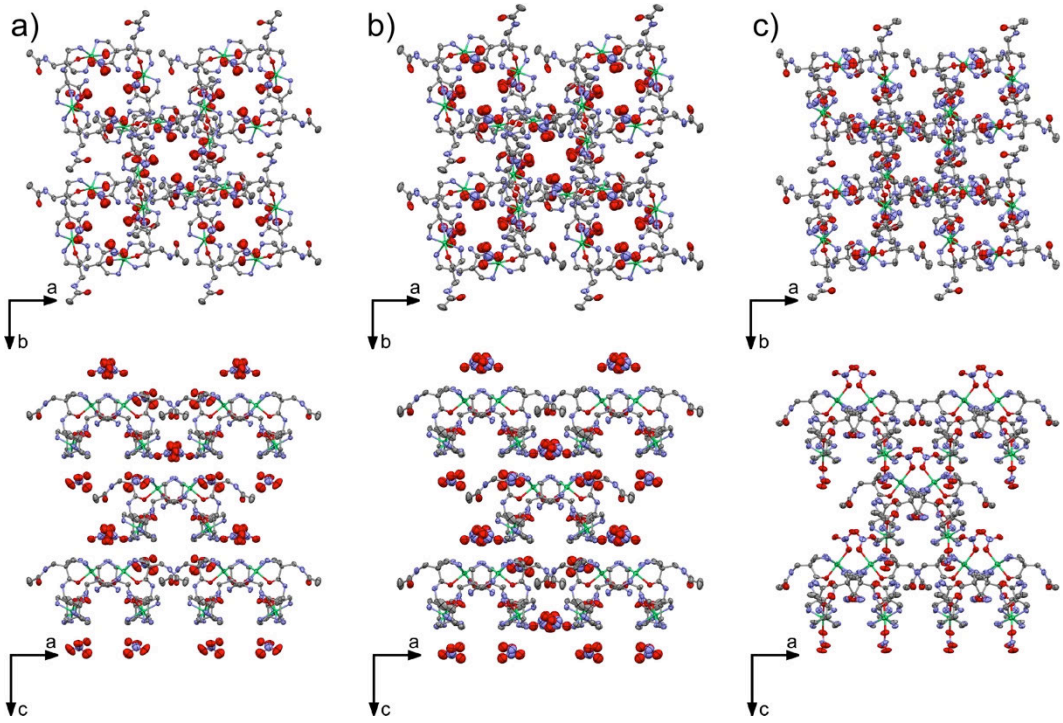


**Figure S5** ORTEP drawing showing crystal packing structure at 20 (a), 40 (b), and 60 (c) °C. Anions and water molecules except $NO_3$(A), coordinating to the Ni(II) center at the structural transition, are omitted for clarify.

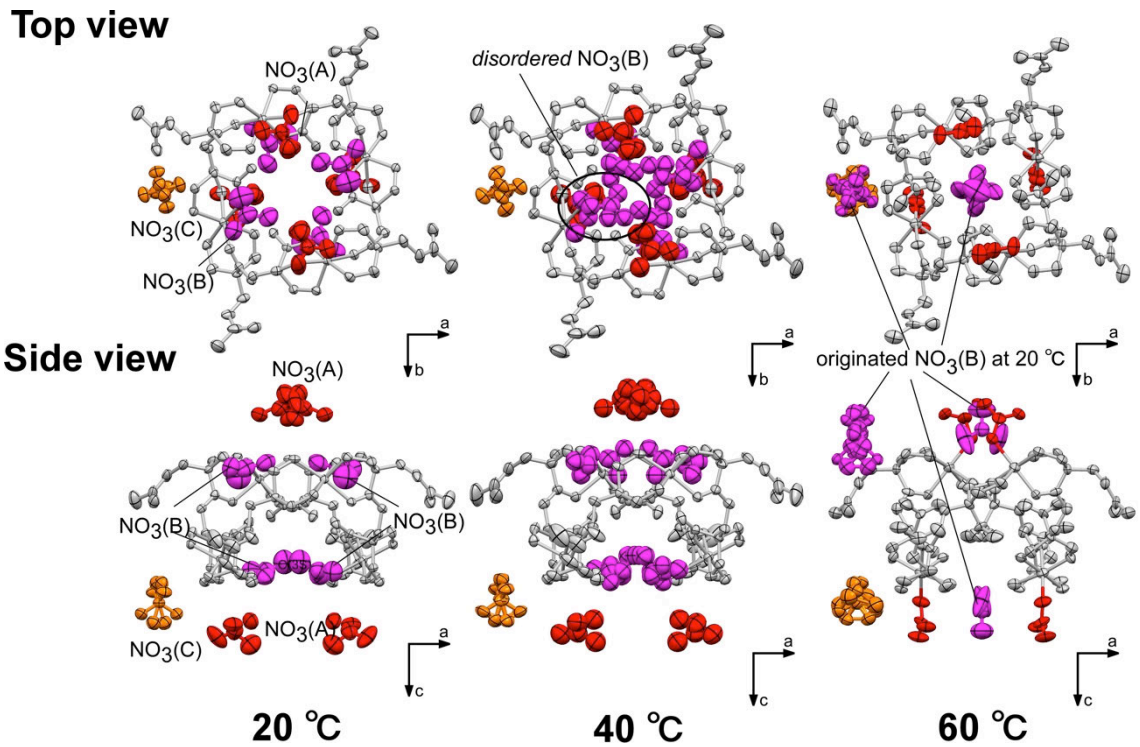


**Figure S6** Comparison of crystal structure of $Ni_4\mathbf{1}_4(NO_3)_8$ at 20, 40, and 60 °C with ORTEP drawings. Anions are colored to be distinguished for symmetry equivalence at 20 °C. ($NO_3$(A): red, $NO_3$(B): pink, $NO_3$(C): orange)

**Description about structural transition of $NO_3^-$ ions in the water content-dependent structural changes**

As described above, $NO_3$(B) ions exist at three of four positions as shown in Figure S6 at 20 °C. At 60 °C, one of them located outside the cyclic structure and two of them located between two metal-coordinated $NO_3^-$ ions (*i.e.* $NO_3$(A)). At 40 °C, $NO_3$(B) ions were found disordered at two different positions (Figure S6).

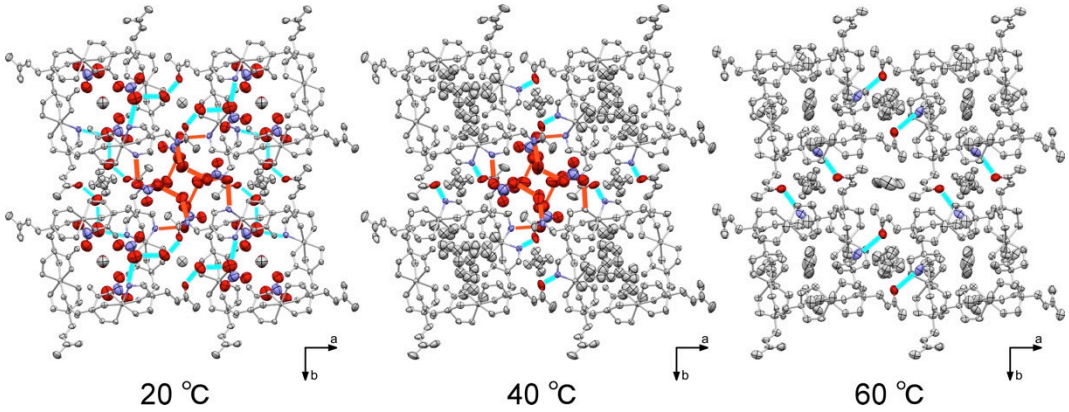


**Figure S7** Changes of intermolecular hydrogen-bond networks at 20, 40, and 60 °C. Sky blue lines and orange lines represent hydrogen-bonding interactions (see also Table S4). Atoms except hydrogen-bonded ones were colored grey.

**Table S4** Short contacts possibly providing intermolecular hydrogen bonds.

| 20 °C | | 40 °C | | 60 °C | |
|---|---|---|---|---|---|
| Drawn as blue lines in Figure S7 | | | | | |
| O(1)-O(2S) | 2.890(12) | N(5)-O(1) | 3.174(10) | N(7)-O(1) | 3.010(12) |
| O(2S)-O(6M) | 2.93(2) | | | | |
| N(2)-O(6M) | 2.990(17) | | | | |
| Drawn as orange lines in Figure S7 | | | | | |
| N(1)-O(3S) | 2.842(15) | N(1)-O(3SA) | 2.85(3) | | |
| | | N(1)-O(3SB) | 3.06(3) | | |
| O(3S)-O(2MB) | 2.763(20) | O(3SB)-O(2MB) | 2.93(3) | | |
| | | O(3SA)-O(2MA) | 2.82(5) | | |
| O(1M)-N(3) | 2.983(10) | N(3)-O(1M) | 2.917(11) | | |

Unit: Å

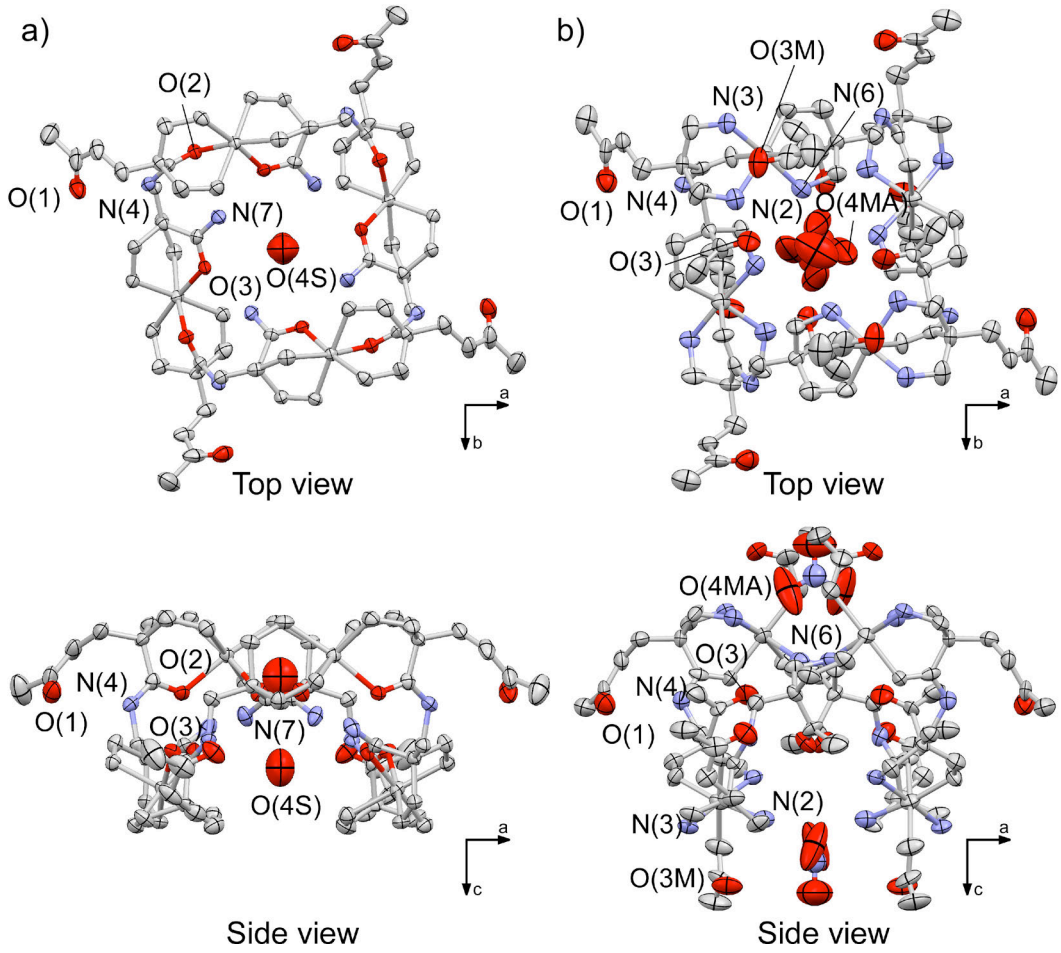


**Figure S8** Changes of intramolecular hydrogen-bond networks before (a: 20 °C) and after (b: 60 °C) structural transition. Atoms except hydrogen-bonded or contacted one were colored grey. Some anions and water molecules are omitted for clarify (see also Table S5).

**Table S5** Short contacts possibly providing hydrogen-bonds around the central hole.

| | 20 °C | 40 °C | 60 °C |
|---|---|---|---|
| N(4)-O(1) | 2.827(8) | 2.790(10) | 2.876(10) |
| N(7)-O(2) | 2.992(8) | 2.975(8) | (-) |
| N(7)-O(3) | 2.860(8) | 2.851(8) | (-) |
| N(7)-O(4S) | 3.152(10) | 3.063(12) | (-) |
| N(6)-O(3) | (-) | (-) | 3.084(11) |
| N(2)-O(4M) | (2.990(17)*1) | (3.053(16)*1) | 2.96314) |
| N(2)-O(3M) | (3.101(10)) | (3.073(11)) | 2.985(11) |
| N(3)-O(3M) | (3.256(10)) | (3.230(11)) | 2.916(11) |

*1: N(2)-O(6M) of $NO_3$(B)
Unit: Å

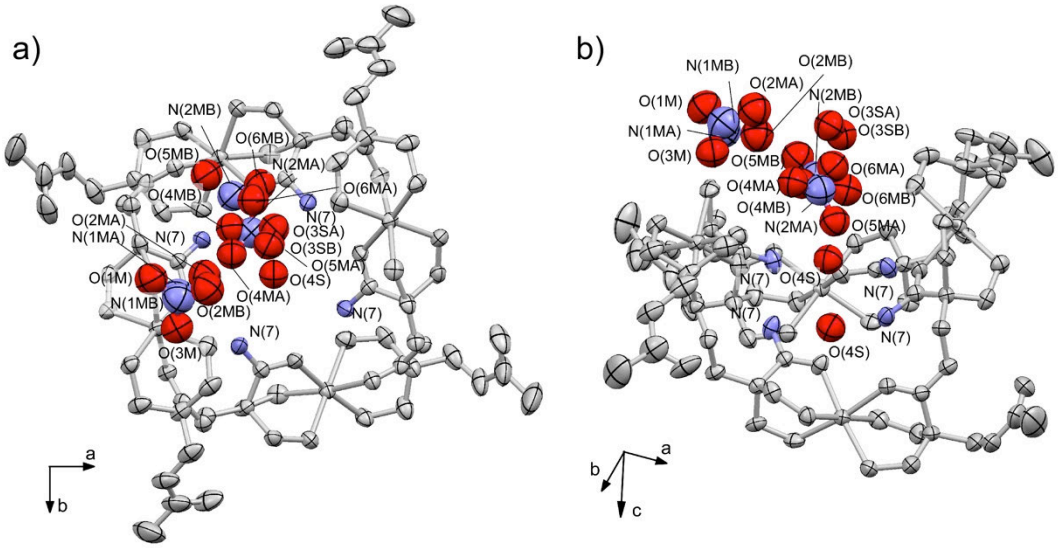


**Figure S9** ORTEP drawing showing the arrangement of $NO_3^-$ ions around O(3S) and O(4S) from top view (a) and side view (b) at 40 °C. Hydrogen atoms and some anions are omitted for clarify.

**Table S6** Short contacts possibly providing hydrogen-bond around O(3S) and O(4S) at 40 °C.

| around O(3S) | | around O(4S) | |
|---|---|---|---|
| contact with $NO_3$(A) | | contact with the cyclic complex | |
| O(3SA)-O(2MA)<br>O(3SB)-O(2MB) | 2.83(4)<br>2.93(3) | O(4S)-N(7) | 3.060(10) |
| contact with $NO_3$(B) | | contact with $NO_3$(B) | |
| O(3SA)-O(4MA)<br>O(3SB)-O(4MB) | 2.66(5)<br>2.68(3) | O(4S)-O(4MB) | 2.91(2) |

O(4S) does not exist with O(4MA), O(5MA), O(6MA), N(2MA).
Unit: Å

## Supplement to thermogravimetric study of $Ni_4\mathbf{1}_4(NO_3)_8$

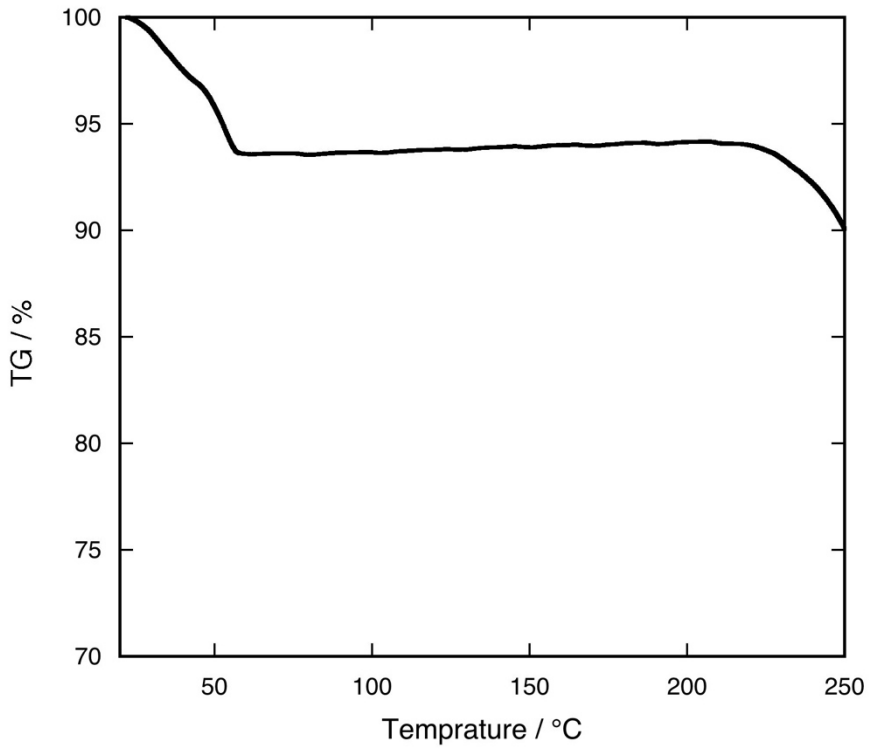


**Figure S10** TG curve of $Ni_4\mathbf{1}_4(NO_3)_8$ measured in $N_2$ gas (1 °C /min)

**Detailed discussion about the effects of water content on the structural transitions**

The water content in crystal structure is not well consistent with that observed in the thermal study (*i.e.* the total numbers of included waters at 20 °C: 11 and 7.6 molecules per a complex by X-ray structural analysis and TG measurement, respectively). However, focusing on the second step of water desorption, both results suggest that ca. 4 water molecules per a complex are removed in the process although it is not easy to determine water content accurately by single-crystal X-ray analysis because $NO_3^-$ ions are hardly disordered under this condition.

Thus, the difference of the total numbers of water molecules between the two measurements might be caused by the loss of water after grinding crystals for thermogravimetric measurements in light of the fact that water desorption rapidly occurs at room temperature.

## Supplement to differential scanning calorimetry (DSC) measurement of $Ni_4\mathbf{1}_4(NO_3)_8$

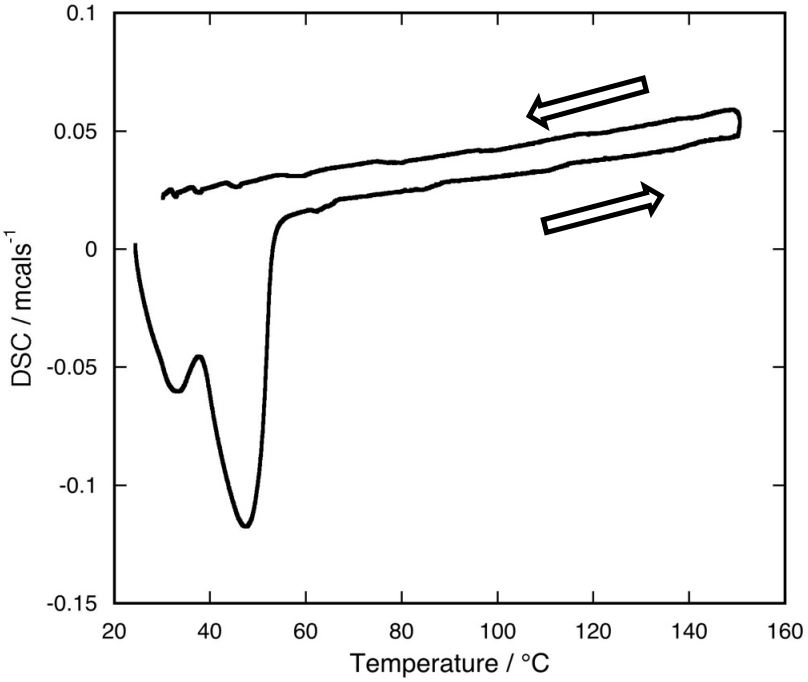


**Figure S11** DSC curve of $Ni_4\mathbf{1}_4(NO_3)_8$ measured in $N_2$ gas (1 °C /min)

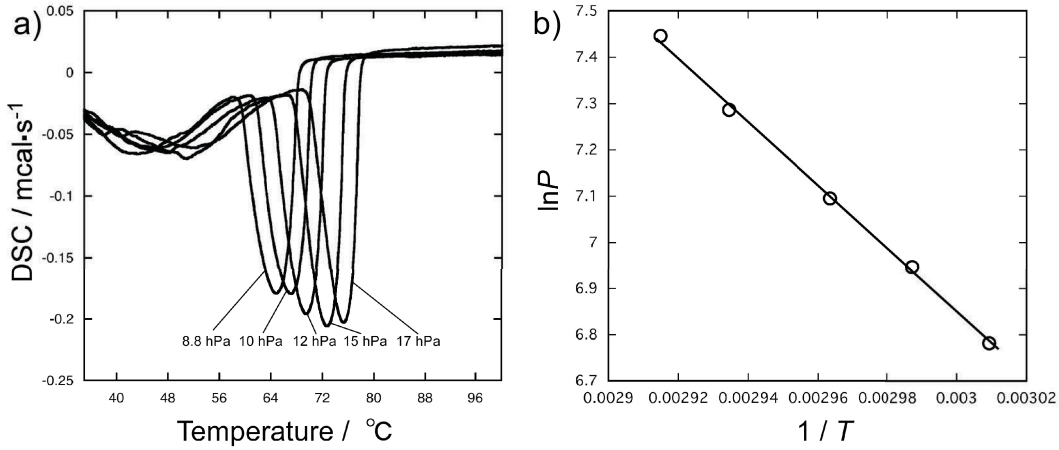


**Figure S12** DSC curves of $Ni_4\mathbf{1}_4(NO_3)_8$ measured in $N_2$ gas containing various water vapor pressure[a] (8.8 ~ 17 hPa) (a) and the plot of logarithim of vapor pressure as a function of absolute temperature of the second sharp endothermic peaks (b). The peak areas were almost same under various conditions.

a: Water vapor pressure in $N_2$ gas was monitored by using thermo-hydrometer and was controlled by varying the temperature of water in gas flow path (from 5 to 15 °C).
The adsorption enthalpy ($\Delta H$iso) was calculated by using the Calusius-Clapeyron equation ((d ln$P$) / (d 1/$T$) = $\Delta H$iso/R: $P$ = water vapor pressure, $\Delta H$iso = adsorption enthalpy, $R$ = gas constant, $T$ = absolute temperature of second endothermic peak).

## XRD pattern of $Ni_4\mathbf{1}_4(NO_3)_8$ after grinding for thermal measurement.

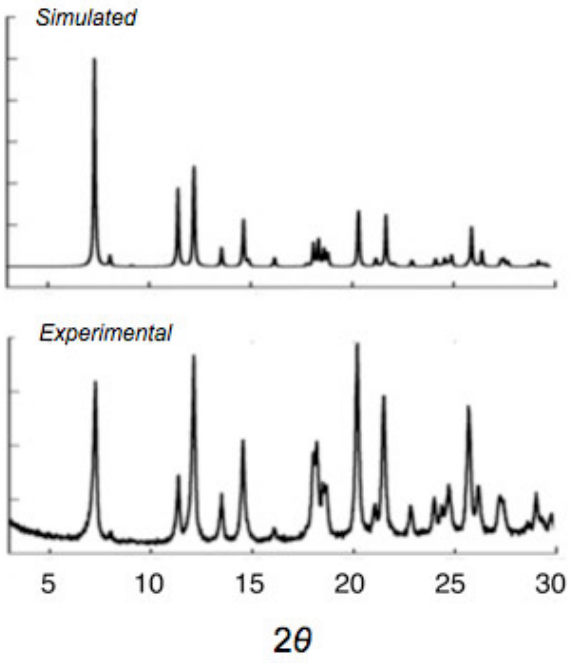


**Figure S13** X-ray powder diffraction pattern of $Ni_4\mathbf{1}_4(NO_3)_8$. A simulated diffraction pattern of the sample used for single-crystal X-ray analysis (a: at 20 °C) and a measured diffraction pattern of that used for thermal analysis (grinding sample) (b: at 25 °C).

**References**:

[S1] : R. Miyake; S. Tashiro; M. Shiro; K. Tanaka; M. Shionoya, *J. Am. Chem. Soc.* **2008**, *130*, 5646-5647.

[S2] : G. M. Sheldrick, SHELXL-97, Program for refinement of crystal structures, University of Göttingen (Germany), **1997**.

[S3] : G. M. Sheldrick, SADABS, Program for scaling and correction of area detector data, University of Göttingen (Germany), **1996**.