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SUPPORTING INFORMATION

Anionic or neutral? The charge of Ni_8 cubes in metal-organic framework compounds.

Ralph Freund,[a] Andreas Kalytta-Mewes,[a] Maryana Kraft,[a] and Dirk Volkmer*[a]

[a] Chair of Solid State and Materials Chemistry, University of Augsburg, Institute of Physics, Universitaetsstrasse1, 86159 Augsburg, Germany. Email: dirk.volkmer@physik.uni-augsburg.de

Table of Contents

1. Experimental Section

Materials. Chemicals and reagents were purchased from commercial suppliers and used as received.

Physical Measurements. Temperature-dependent diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was carried out using a Bruker Equinox 55 FT-IR spectrometer equipped with a Harrick Praying Mantis™ chamber for diffuse reflection spectroscopy in the range 4000 to 400 cm^{-1}. Samples were all mortared and dispersed with the addition of KBr to obtain sufficient dilution. All samples were carefully activated under vacuum beforehand. KBr was activated at 300 °C under vacuum.

X-ray powder diffraction (PXRD) data were collected in the 4–40° 2θ range using a Seifert XRD 3003 TT–powder diffractometer with a Meteor1D detector operating at room temperature using Cu $K\alpha_1$ radiation (λ=1.54187).

Single crystal X-ray diffraction measurements were conducted by mounting a single crystal on a MiTeGen MicroMount and collecting the X-ray reflection data set using a Bruker D8 Venture diffractometer. Intensity measurements were carried out using monochromatic (doubly curved silicon crystal) Mo Kα radiation (0.71073 Å) emitted from a sealed microfocus tube with generator setting of 50 kV and 1 mA. Integrated intensities and unit cell refinements were performed using the Bruker SAINT software package. The structures were solved by direct methods and refined using the SHELXL 2018/3 program.[1]

Argon sorption isotherms were measured with a Quantachrome Autosorb-1C instrument at 77 K up to p/p0=1. High purity gas was used for the adsorption experiments (argon 99.999 %). Prior to measurements, the samples were heated at 200 °C overnight in a vacuum.

Temperature programmed mass spectroscopy was performed using a BelCat-B catalyst analyzer (Bel Japan, Inc.) equipped with a thermal-conductivity detector and a coupled mass spectrometer (OmniStar GSD 320, Pfeiffer Vacuum). The gas flow rates were set to 30 mL min^{-1}. Each sample (5-10 mg each) was placed between two plugs of quartz wool in a quartz glass reactor and heated first to 100 °C and then to 250 °C and the reaction products were analyzed by mass spectrometry.

Energy-dispersive X-ray spectroscopy (EDX) measurements were made using a Zeiss Crossbeam 550 scanning electron microscope equipped with an EDAX SiLi detector with an operating voltage of 20 kV.

Synthesis of $[Ni_8X_6(bdp)_6]$ (1a, X=OH^-/H_2O) single crystals: 1,4-Benzenedipyrozole (1,4-H_2bdp, 0.1 mmol, 21.0 mg) and $Ni(NO_3)_2 \cdot 6H_2O$ (0.2 mmol, 59.0 mg) were ultrasonically dissolved in 5.4 mL mixed solvent of DMAc/H_2O (v:v = 5:4) and sealed in a 20 mL teflon lined stainless steel reactor. The reaction system was heated at 160 °C for 3 d in an oven. After cooling to RT, the resulting turquoise octahedral crystals of $[Ni_8X_6(bdp)_6]$ (X=OH^-/H_2O) were harvested by filtration and washed with 5 mL each of DMAc, H_2O, and EtOH and then dried in air (Yield 83% based on 1,4-H_2BDP).

Bulk synthesis of $[Ni_8X_6(bdp)_6]$ (1b, X=OH^-/H_2O): 1,4-Benzenedipyrozole (1,4-H_2bdp, 0.1 mmol, 21.0 mg) and $Ni(AcO)_2 \cdot 4H_2O$ (0.133 mmol, 33.0 mg) were ultrasonically dissolved in 5.4 mL mixed solvent of DMAc/H_2O (v:v = 5:4) and sealed in a 20 mL teflon lined stainless steel reactor. The reaction system was heated at 160 °C overnight in an oven. After cooling to RT, the resulting light blue powder of $[Ni_8X_6(bdp)_6]$ (X=OH^-/H_2O) were harvested by filtration and washed with 5 mL each of DMAc, H_2O, and EtOH and then dried in air (Yield 81% based on 1,4-H_2BDP).

Bulk synthesis of $[Ni_8X_6(bdp)_6]$ (1c, X=OH^-/H_2O): 1,4-Benzenedipyrozole (1,4-H_2bdp, 0.1 mmol, 21.0 mg) and $Ni(NO_3)_2 \cdot 6H_2O$ (0.133 mmol, 38.7 mg) were ultrasonically dissolved in 5.4 mL mixed solvent of DMAc/H_2O (v:v = 5:4) and sealed in a 20 mL teflon lined stainless steel reactor. The reaction system was heated at 160 °C overnight in an oven. After cooling to RT, the resulting light blue powder of $[Ni_8X_6(bdp)_6]$ (X=OH^-/H_2O) were harvested by filtration and washed with 5 mL each of DMAc, H_2O, and EtOH and then dried in air (Yield 67% based on 1,4-H_2BDP).

Synthesis of $Cs_2[Ni_8(OH)_6(bdp)_6]$ derivates: The different products of **1** were each suspended in 0.05 M solutions of CsCl in EtOH/H_2O (v:v = 1:1) and CsOH in EtOH/H_2O (v:v = 1:1), respectively. This was done over a period of 24 h while exchanging the metal salt solutions 5 times. The products were harvested by filtration, washed with 5 mL each of H_2O and EtOH, and then dried in air (Yield 100%).

2. EDX Analysis

EDX analysis was performed with samples on which Cs exchange was performed by suspension in metal salt solutions of CsCl and CsOH, respectively. The former exchange was done because Cl could be detected next to Cs in the sample if the network is neutral. Further, due to the extremely low basicity, Cl^- should also not cause deprotonation of the water ligands in a potentially neutral network. Exclusive Cs detection should not be possible in the neutral case. However, in all samples in which the exchange was carried out using CsCl, only Cs could be detected in EDX measurements, but no Cl at all, which clearly speaks for the anionic case of the network.

Thereafter, the exchange was always carried out with CsOH, since better results could be obtained with this approach.

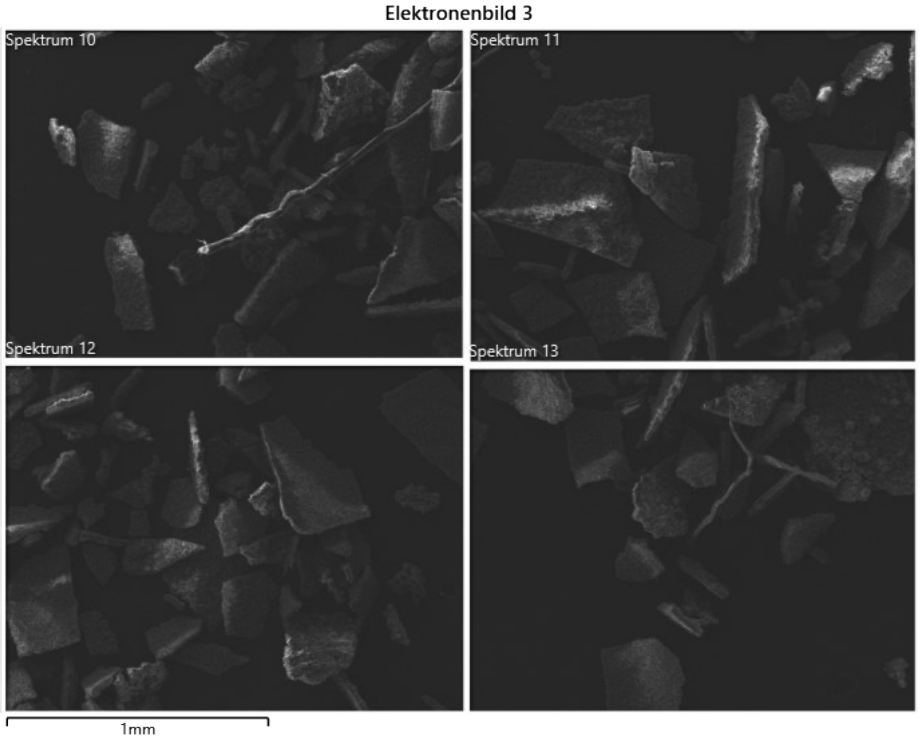

Figure S1: Electron image of the respective areas examined by EDX.

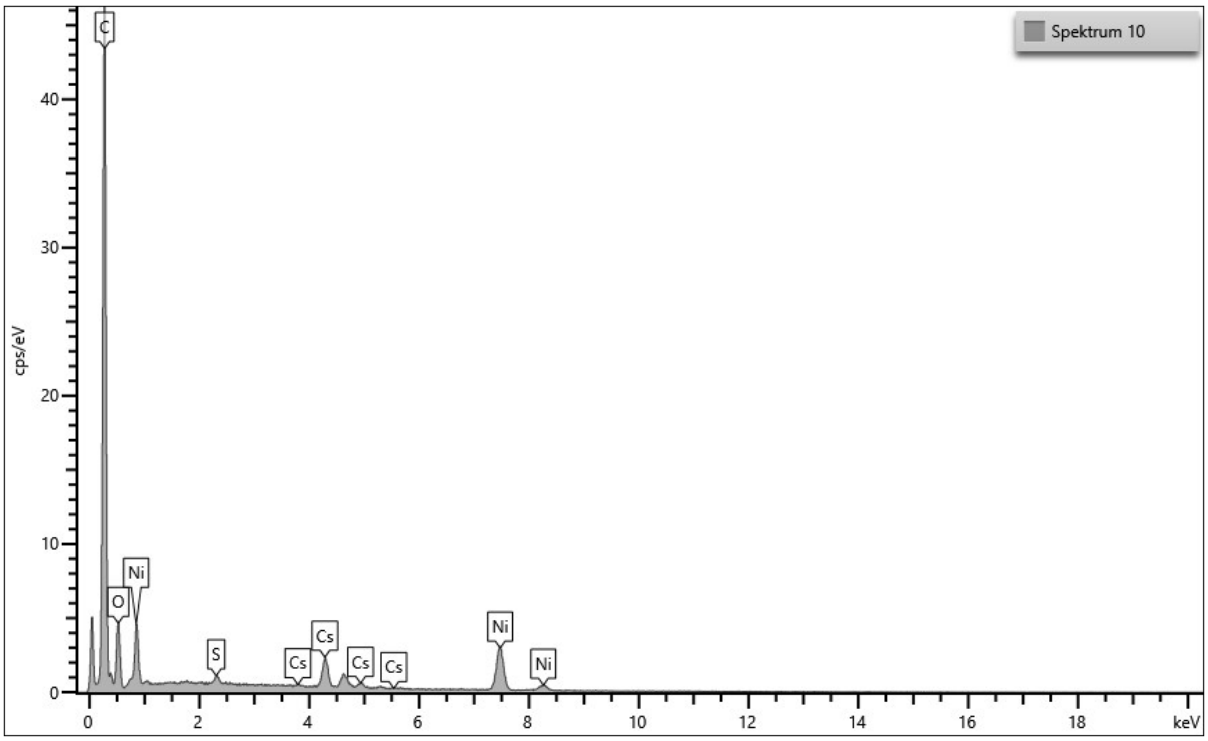

Figure S2: EDX spectrum of area 10.

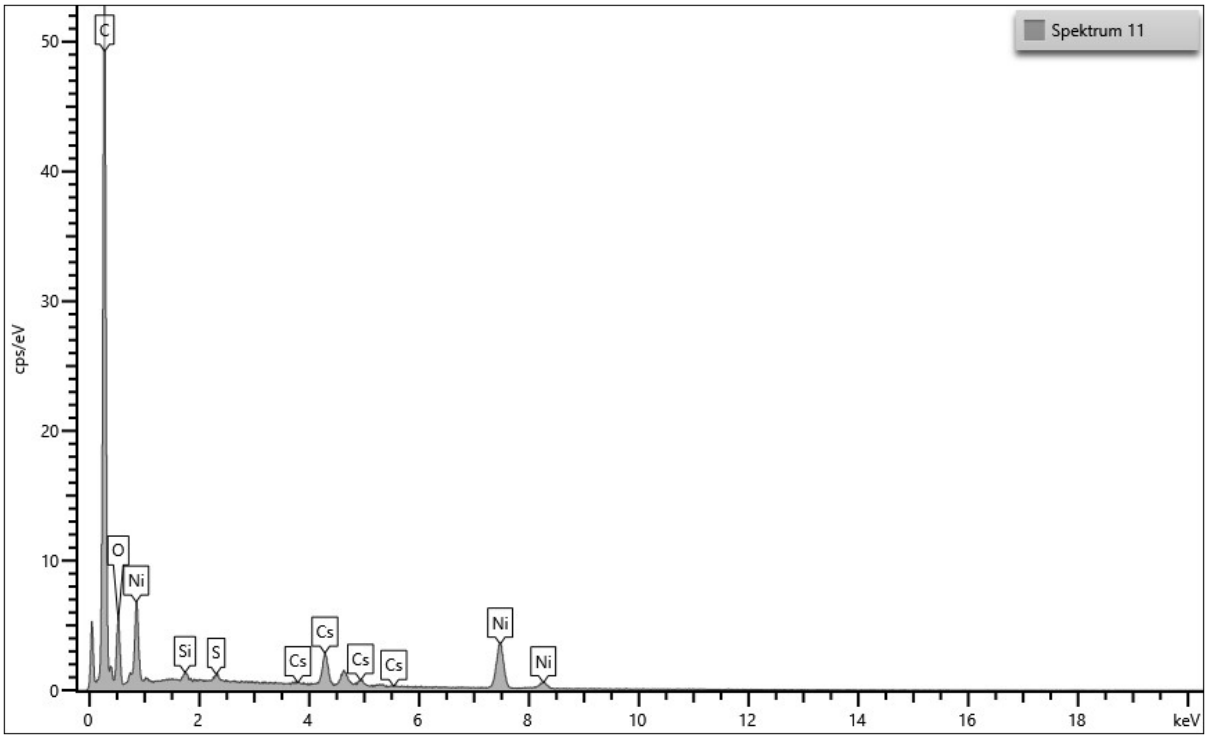

Figure S3: EDX spectrum of area 11.

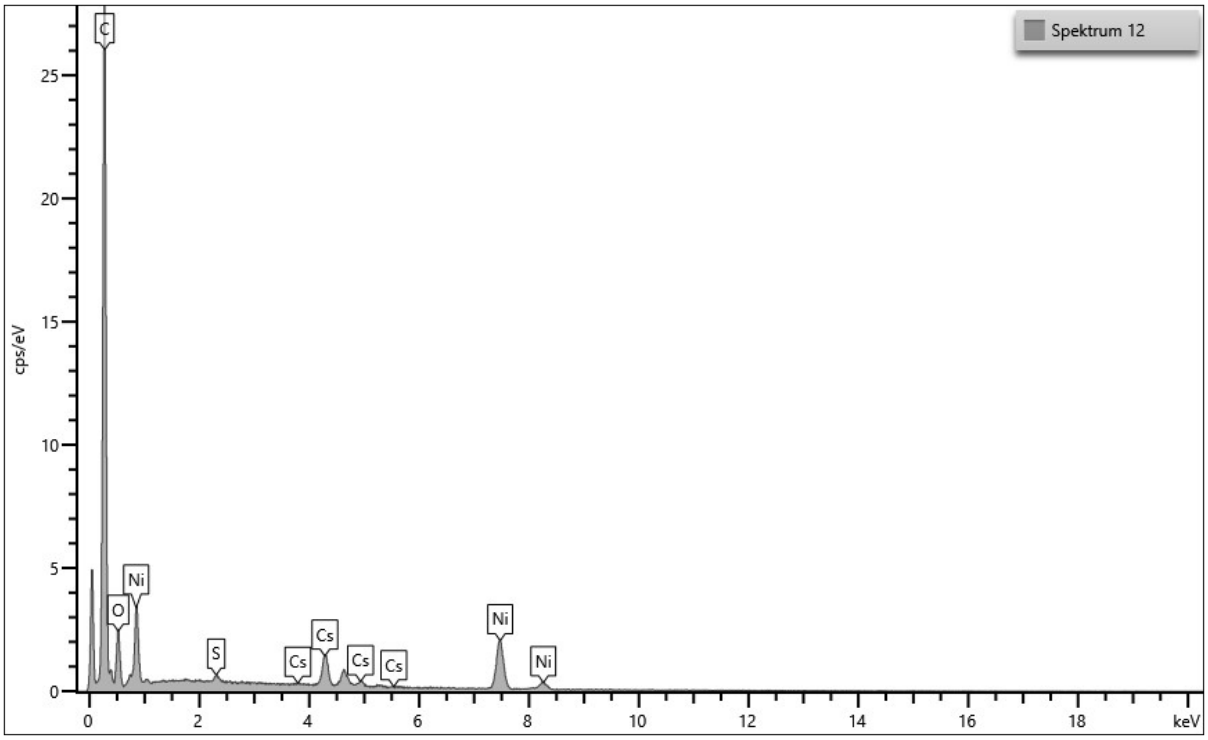

Figure S4: EDX spectrum of area 12.

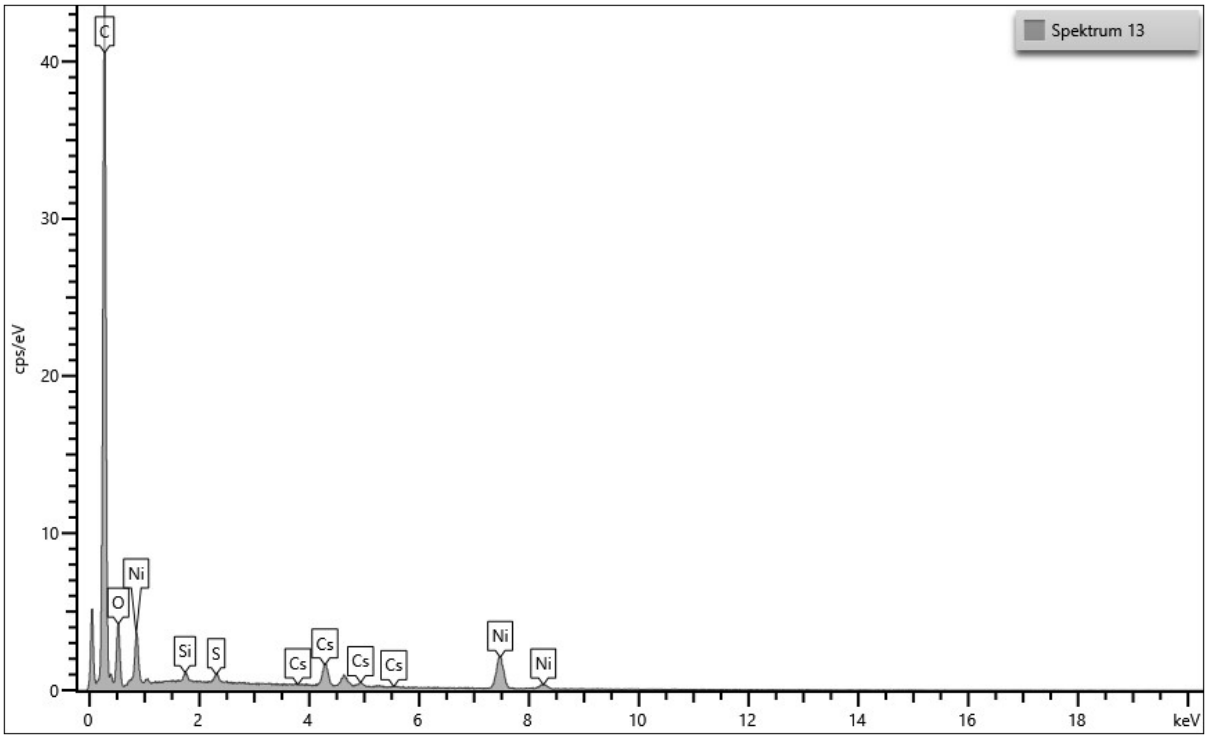

Figure S5: EDX spectrum of area 13.

Table S1: Overview of the atomic percent ratios of the different EDX measurements.

	Spectrum 10	Spectrum 11	Spectrum 12	Spectrum 13
Ni	79.45	78.87	80.10	79.13
Cs	20.55	21.13	19.90	20.87
Total	100.00	100.00	100.00	100.00

Table S2: Statistics of the different EDX measurements.

Statistics	Ni	Cs
Max	80.10	21.13
Min	78.87	19.90
Average	79.39	20.61
Standard deviation	0.53	0.53

3. PXRD Analysis

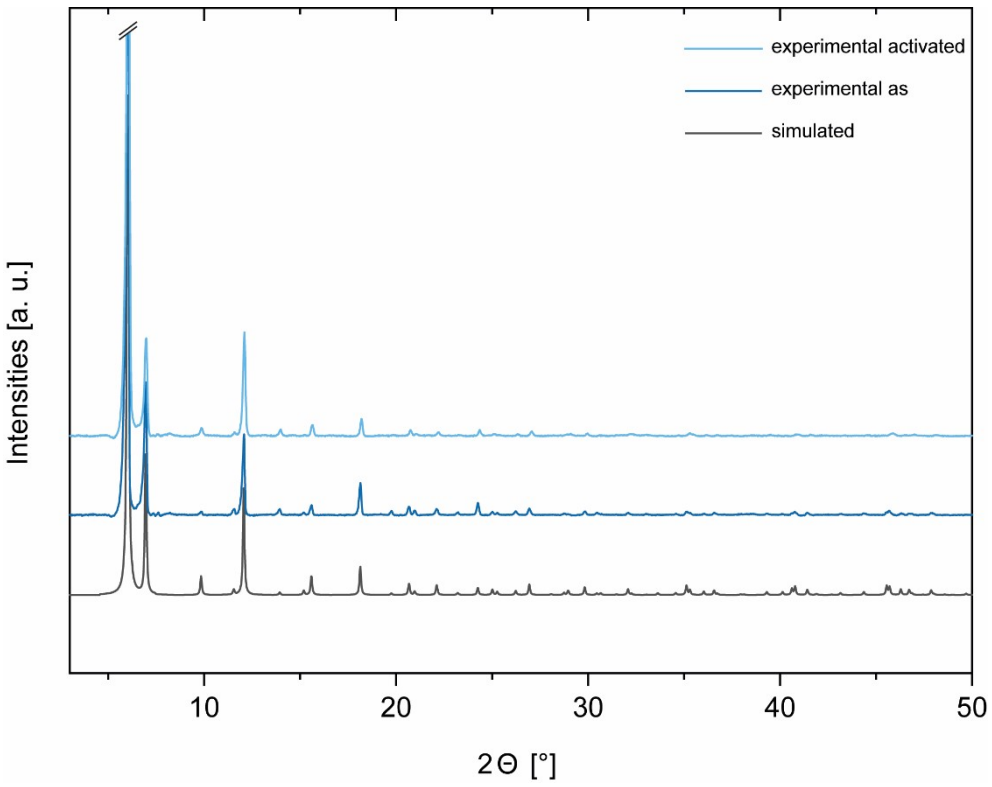

*Figure S6: PXRD of **1a**.*

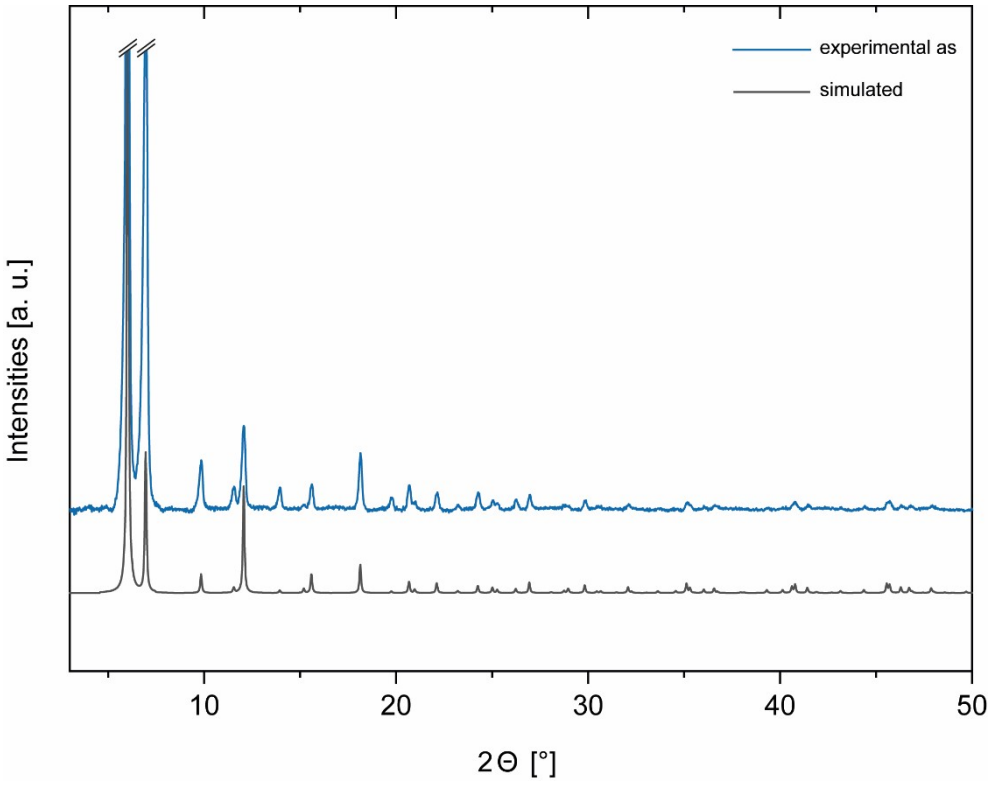

*Figure S7: PXRD of **1b**.*

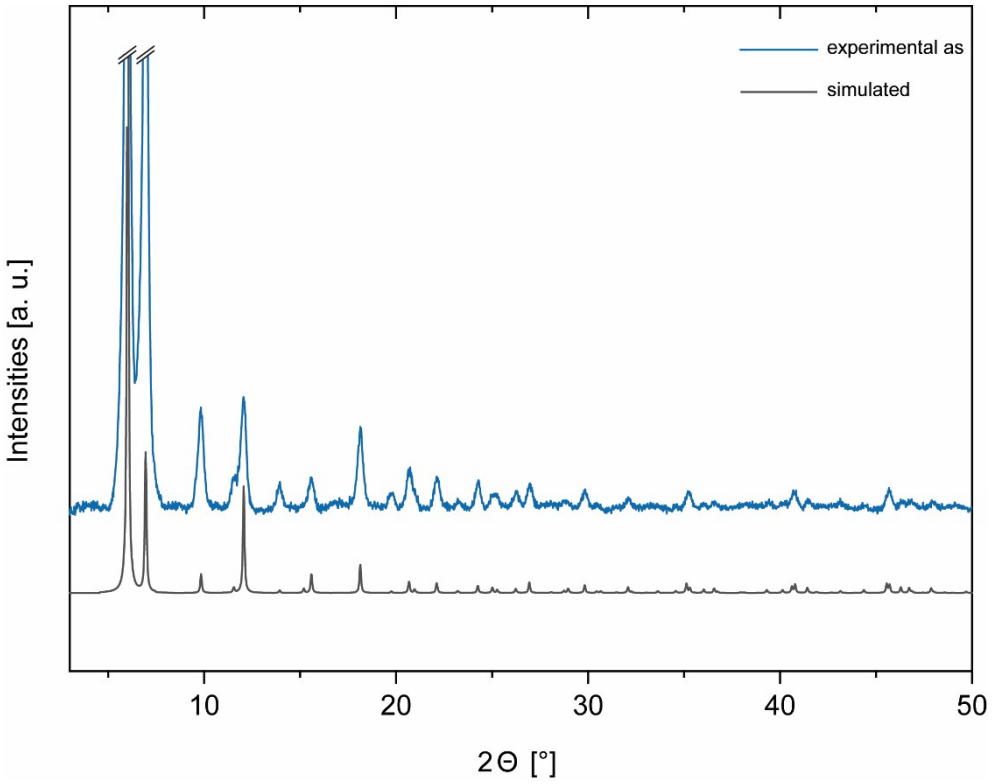

*Figure S8: PXRD of **1c**.*

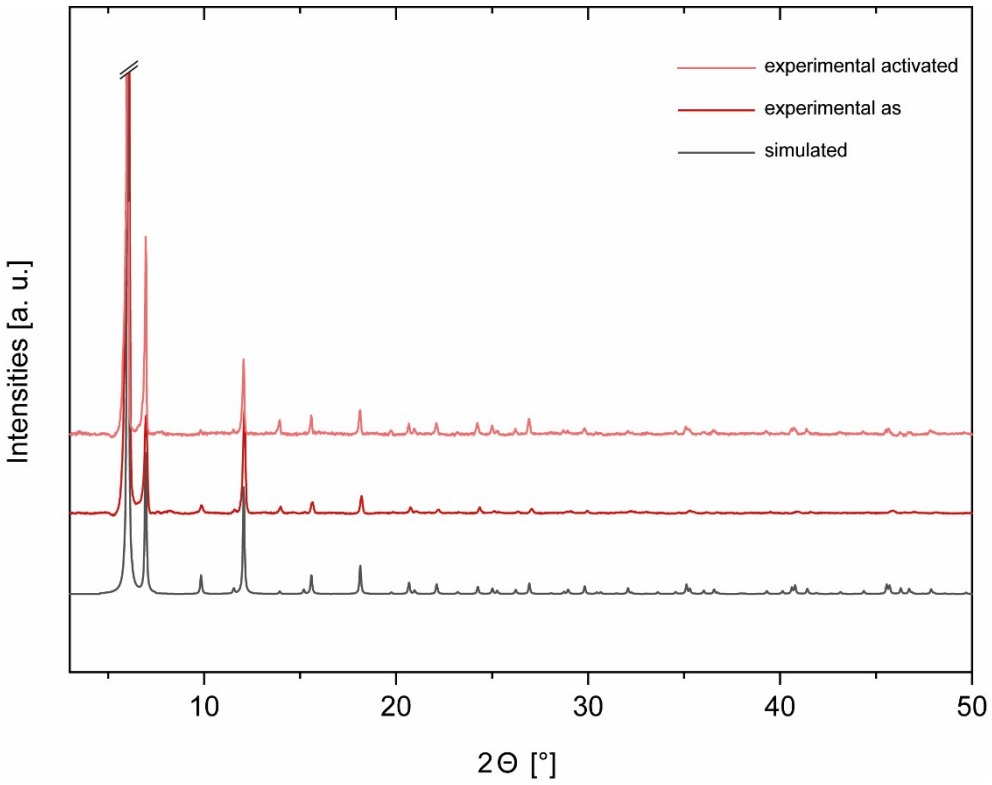

*Figure S9: PXRD of **2a**.*

4. BET Analysis

For the Cs free samples $[Ni_8(OH)_4(H_2O)_2(bdp)_6]$, a surface area of 2148 $m^2\,g^{-1}$ with a correlation coefficient of r=0.999986 and C=1.568E^3 for 5 selected data points in a pressure range of 0.002 – 0.02 P/P_O, and for the Cs-containing samples $Cs_2[Ni_8(OH)_6(bdp)_6]$, a surface area of 1949 $m^2\,g^{-1}$ with a correlation coefficient of r=0.999960 and C=1.549E^3 for 5 selected data points in a pressure range 0.007 – 0.03 P/P_O could be determined. In comparison, theoretical calculations determined a BET surface area of 2185 $m^2\,g^{-1}$ (Poreblazer), or 2291 $m^2\,g^{-1}$ (iRASPA) for $[Ni_8(OH)_4(H_2O)_2(bdp)_6]$ and 1916 $m^2\,g^{-1}$ (Poreblazer), or 1946 $m^2\,g^{-1}$ (iRASPA) for $Cs_2[Ni_8(OH)_6(bdp)_6]$.

By putting the molar masses of the Cs-free structure and the Cs-containing structure with maximum Cs content in relation to each other, the following ratio is obtained:

$$\frac{M\,[Ni_8(OH)_4(H_2O)_2(bdp)_6]}{M\,Cs_2[Ni_8(OH)_6(bdp)_6]} = \frac{1822.92\ g\ mol^{-1}}{2086.71\ g\ mol^{-1}} = 0.874$$

If we do the same with the obtained surfaces of the argon sorption measurements, we get the following value:

$$\frac{S\,Cs_2[Ni_8(OH)_6(bdp)_6]}{S\,[Ni_8(OH)_4(H_2O)_2(bdp)_6]} = \frac{1949\ cm^3\ g}{2148\ cm^3 g} = 0.907$$

If we put the two values in relation, we get the following value:

$$\frac{0.874}{0.907} = 0.964$$

Which, considering only the mass difference and the expected difference in surface area, is very consistent.

5. IR Analysis

The DRIFTS analysis described in the main text was purely for bulk samples. The same measurements were also performed with the single crystal samples, where synthesis-related impurities of $Ni(OH)_2$ could be detected, which could not be observed in PXRD measurements. Nevertheless, the same trends could be observed as for the bulk samples. A more detailed discussion of the various DRIFTS measurements is given below.

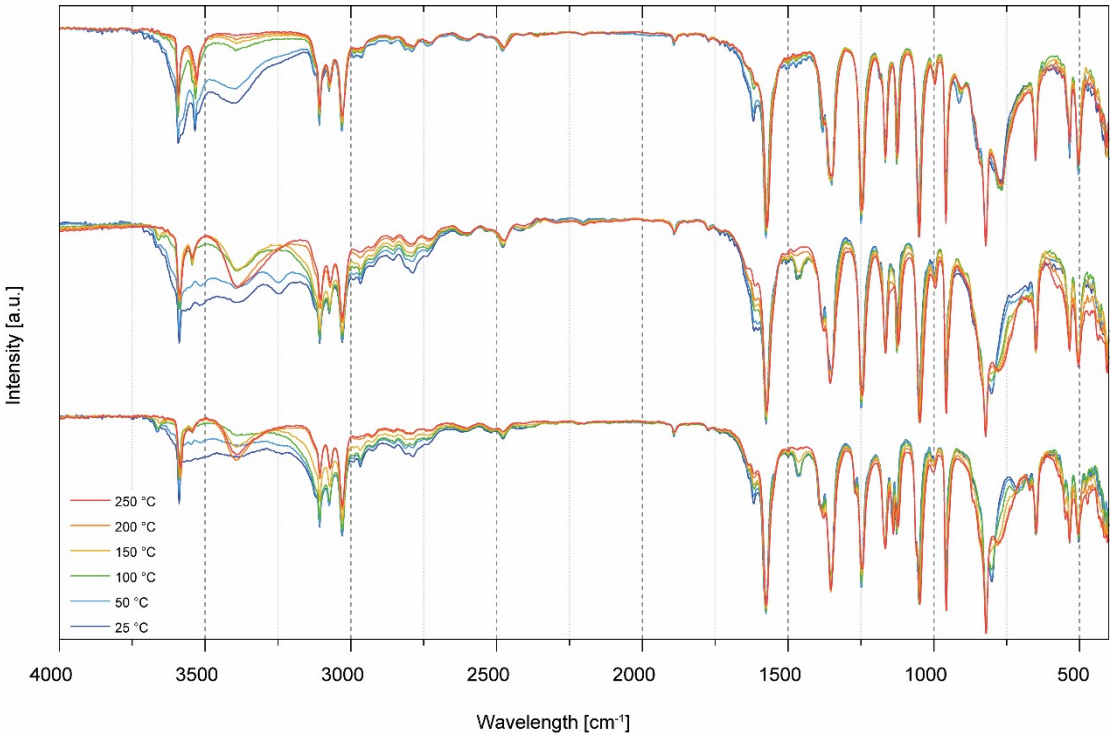

*Figure S10: DRIFTS measurement for bulk samples between 4000 and 400 cm^{-1}. Top $Cs_2[Ni_8(OH)_6(bdp)_6]$ (**2a**), middle $(DMA^+)_x[Ni_8(OH)_4(H_2O)_{2-x}(bpz)_6]$ (**1b**), bottom $(DMA^+)_2[Ni_8(OH)_6(bdp)_6]$ (**1c**).*

Fig. S10 shows the total wavenumber range examined for the DRIFTS measurements of the different bulk samples discussed in the main text. Here, the focus is on the areas that were not addressed in the main text. First, in the range between about 2600 and 3000 cm^{-1} for samples **1b** and **1c**, one can observe a background that decreases with increasing temperature. Further, one can note the decrease of two bands: on the one hand, a gradual decrease of the band at approximately 1617 cm^{-1}, and a sudden decrease of a band at 1463 cm^{-1} at temperatures between 150 and 200 °C. The first event of the band decrease can be attributed to the gradual release of dimethylacetamide, whereas the second event and the decrease of the background between 2600 and 3000 cm^{-1} can be attributed to the release of dimethylamine after successful proton transfer to the SBU with neutralization of the SBU (compare Fig. S11 for the IR data of dimethylacetamide and dimethylamine hydrochloride). Accordingly, only the first event can be observed in the DRIFTS of **2a** in Fig. S10, after Cs^+ forms the cation. Further, another vibration can be observed at about 3546 cm^{-1} for the two Cs-free structures (Fig. S10 middle and lower spectra), which is at similar energies to the additional OH stretching vibration caused by cesium (3530 cm^{-1}). This is attributed to the interaction of the OH groups with other elemental impurity cations, which cannot be excluded due to synthetic reasons (impurities in the metal salt, residues on vessel walls, etc.). This same vibration can also be found weakly pronounced in the IR studies of Masciocchi *et al*.[3]

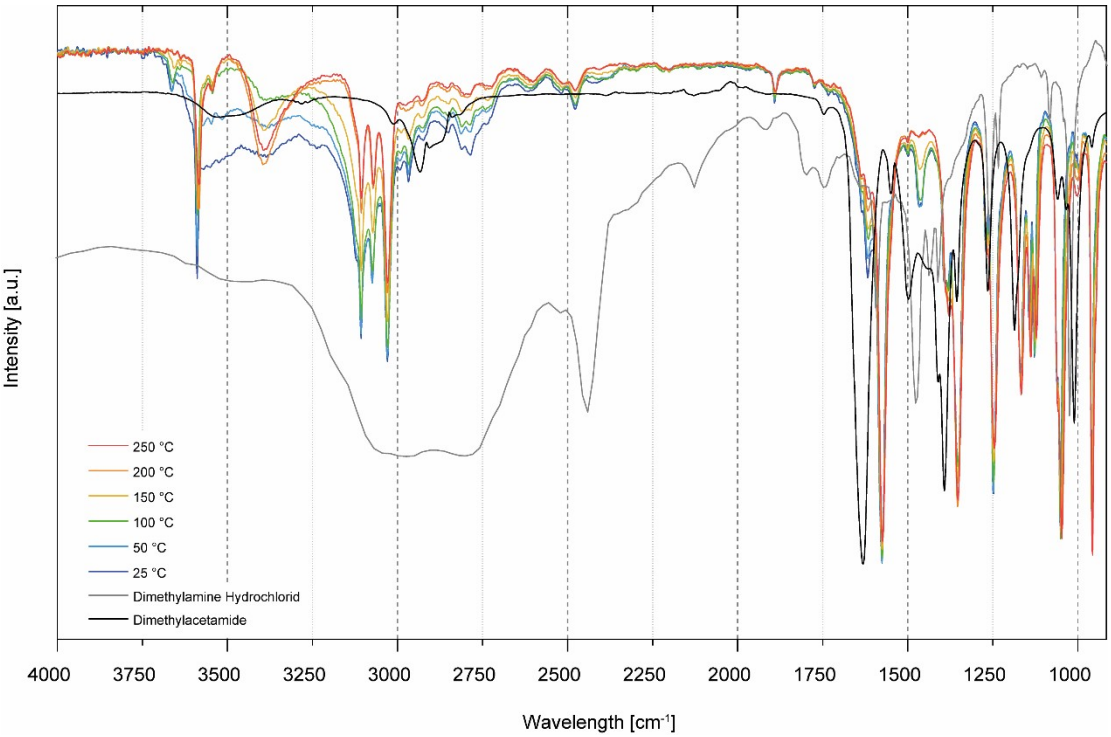

*Figure S11: DRIFTS measurement for $(DMA^+)_2[Ni_8(OH)_6(bdp)_6]$ (**1b**) and comparison with IR spectra of dimethylamine hydrochloride[2] and dimethylacetamide.*

For the DRIFTS measurements of the single crystalline samples (Fig. S12) the same trend as for the bulk samples can be observed. However, another OH stretching vibration band can be observed at 3644 cm^{-1}, which can be assigned to $Ni(OH)_2$, as well as a band at about 1705 cm^{-1}, which can be assigned to adsorbed water, which disappears above temperatures of 100 °C.

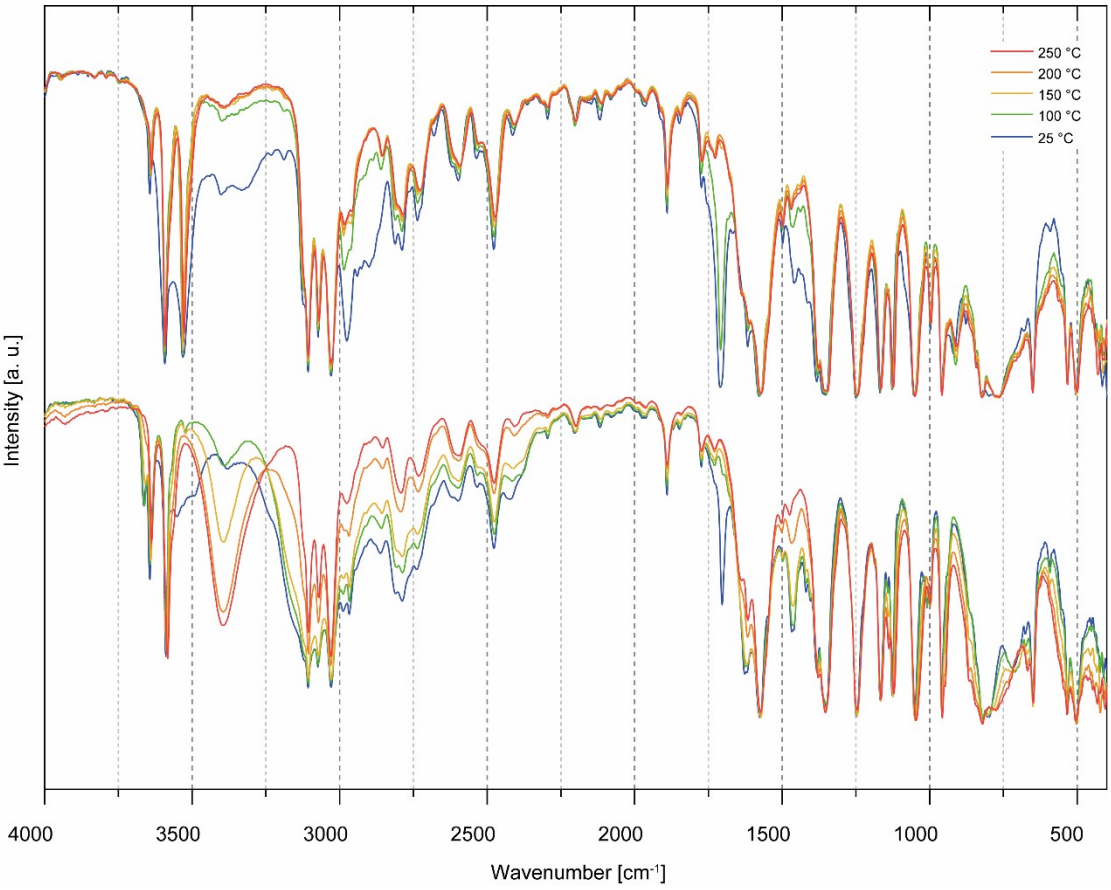

Figure S12: DRIFTS measurement for single crystal samples of $(DMA^+)_2[Ni_8(OH)_6(bdp)_6] \cdot (Ni(OH)_2)_x$ (bottom) and $Cs_2[Ni_8(OH)_6(bdp)_6] \cdot (Ni(OH)_2)_x$ (top).

6. MS Analysis

Temperature-dependent mass spectroscopy measurements were performed for (a) **1c** and (b) **1c** after activation at 200 °C (see Fig. S13). All elemental masses were detected, which can be expected for dimethylamine, dimethylacetamide, and decomposition products thereof. A detailed evaluation was hindered due to the strong mixing of the mass signals and its fragments. However, all signals expected for dimethylamine could be detected. Also the expectation that after a single release (a) no further release occurs after activation (b) could be observed.

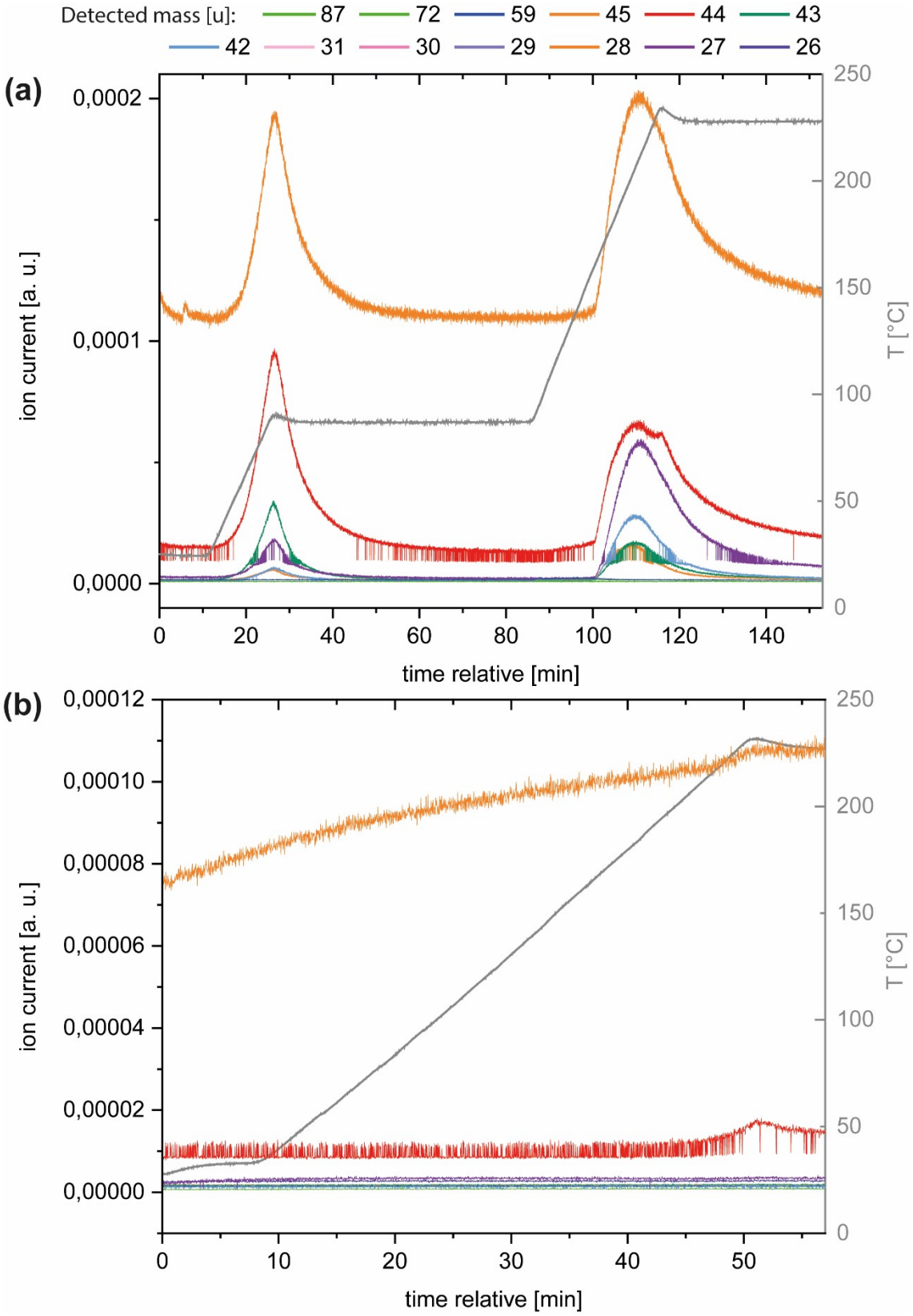

*Figure S13: Temperature-dependent mass spectroscopy measurement for (a) **1c** and (b) **1c** after activation at 200 °C.*

7. Theoretical Calculations

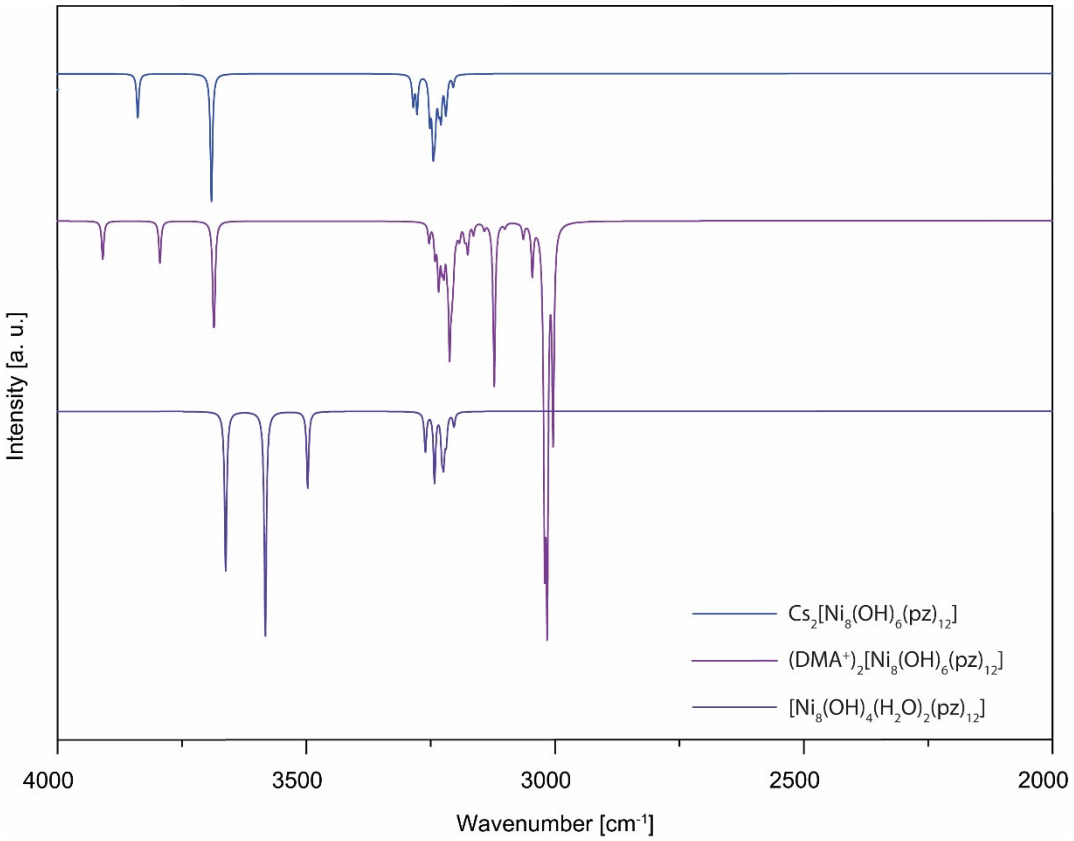

Figure S14: Theoretical calculation of expected IR vibrations using SBU cluster models.

Fig. S14 shows an overview of the expected IR active vibrations for the two anionic clusters $Cs_2[Ni_8(OH)_6(pz)_{12}]$ and $(DMA^+)_2[Ni_8(OH)_6(pz)_{12}]$, as well as the neutral cluster $[Ni_8(OH)_4(H_2O)_2(pz)_{12}]$, which were performed using theoretical calculations on SBU cluster models. It should be noted that these were performed for the assignment of the observed vibrations, but not to obtain statements regarding the expected wavenumbers. The symmetric and asymmetric stretching vibrations of the water ligands are represented as individually resolved vibrations in the theoretical calculations. In the experiments, only one broadened band can be detected for them, which results from superposition due to similar energies.

Ab inito DFT-D calculations were performed on different cluster variants representing different charge/protonation states of the $[Ni_8(OH)_6(pz)_{12}]$ SBU as explained in the main manuscript file. All calculations were performed with the DMOL3 DFT code (as part of the 2022 release of BIOVIA Materials Studio, Dassault Systemes).[4,5] Spin-polarized DFT calculations were performed employing DFT semi-core pseudopotentials and Double Numerical plus polarization (DNP) numerical basis sets for all atoms. In all DFT calculations the PBE gradient-corrected functional was used.[6] To account for noncovalent forces, such as hydrogen bonding and van der Waals (vdW) interactions, an atom-

pairwise dispersion correction as suggested by Tkatchenko and Scheffler (2009) was employed.[7] Geometry optimizations were performed under symmetry constraints, refining the atomic positions of cluster models retaining the highest possible point group symmetry, taking both structural parameters as well as spin polarization into account. Initial spin configurations of the d^8-Ni(II) centers were arranged such that complete antiferromagnetic exchange was enabled, leading to a total Spin=0 (= diamagnetic ground state) of the cluster models. Converged point group symmetries were as follows:

a) $(DMA^+)_2[Ni_8(OH)_6(pz)_{12}]$: point group Cs

b) $Cs_2[Ni_8(OH)_6(pz)_{12}]$: point group Cs

c) $[Ni_8(OH)_4(H_2O)_2(pz)_{12}]$: point group C2v

Mulliken population analyses revealed that the initial spin configuration was retained in the optimized structure models in all cases. Hessian elements were computed for all cluster compounds by displacing each atom in the model and computing a gradient vector, thus building a complete second derivative matrix. Harmonic vibrational frequencies were then obtained from this matrix of Cartesian second derivatives, infrared intensities were obtained from the atomic polar tensors, the latter being calculated as second derivative of the total energy with respect to the Cartesian coordinates and dipole moments.

Animation of the vibrations for $Cs_2[Ni_8(OH)_6(pz)_{12}]$:

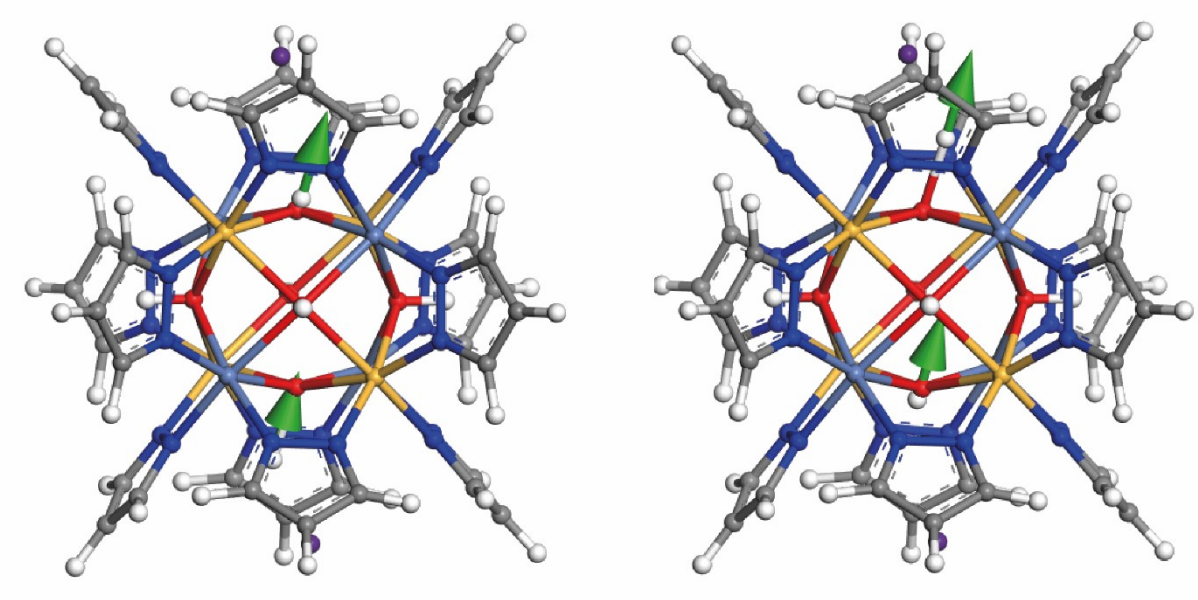

Figure S15: OH vibrations at 3838 cm^{-1} for $Cs_2[Ni_8(OH)_6(pz)_{12}]$.

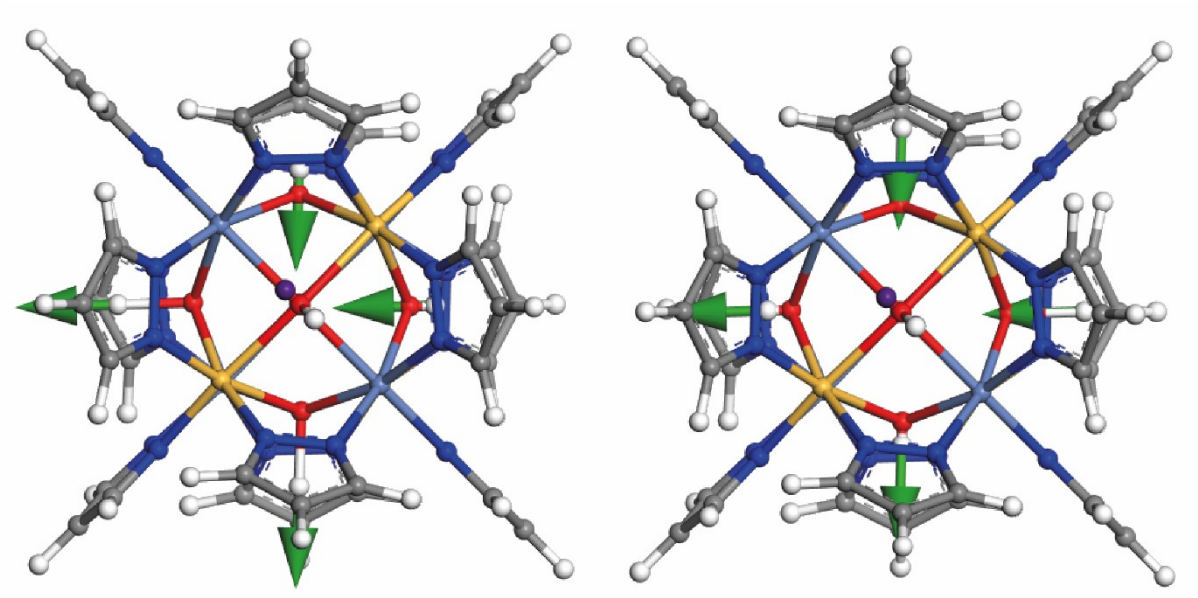

Figure S16: OH vibrations at 3691 cm^{-1} for $Cs_2[Ni_8(OH)_6(pz)_{12}]$.

Animation of the vibrations for $(DMA^+)_2[Ni_8(OH)_6(pz)_{12}]$:

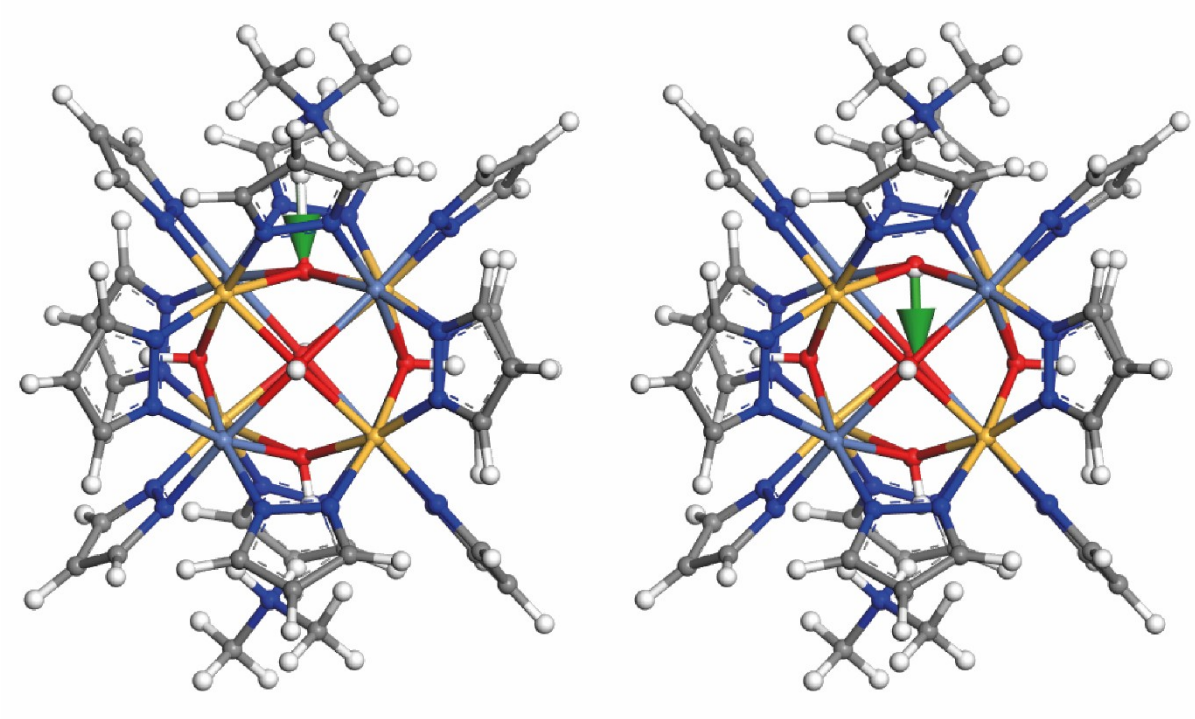

Figure S17: OH vibrations at 3909 cm^{-1} for $(DMA^+)_2[Ni_8(OH)_6(pz)_{12}]$.

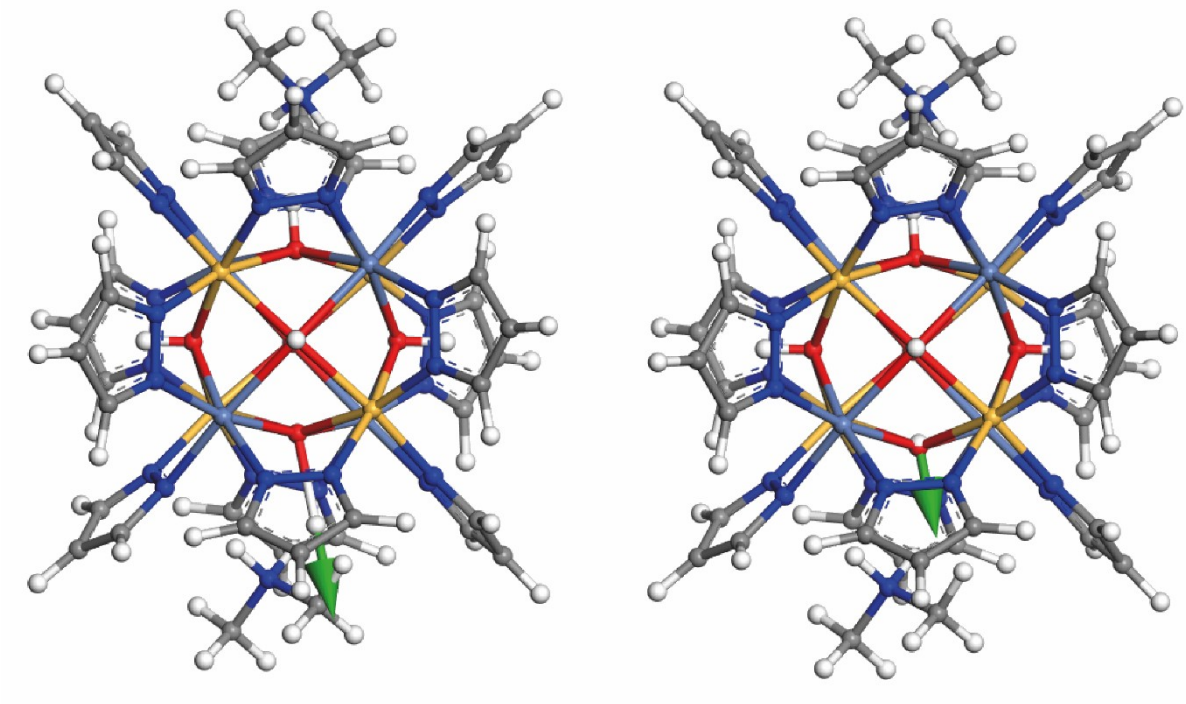

Figure S18: OH vibrations at 3794 cm^{-1} for $(DMA^+)_2[Ni_8(OH)_6(pz)_{12}]$.

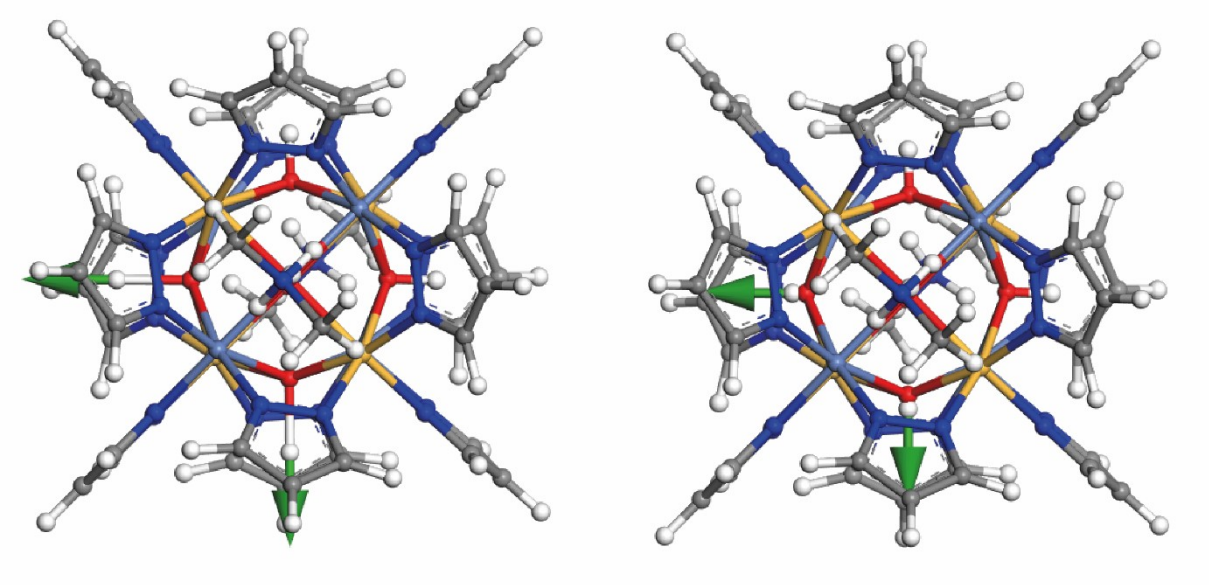

Figure S19: OH vibrations at 3687 cm^{-1} for $(DMA^+)_2[Ni_8(OH)_6(pz)_{12}]$.

Animation of the vibrations for $[Ni_8(OH)_4(H_2O)_2(pz)_{12}]$:

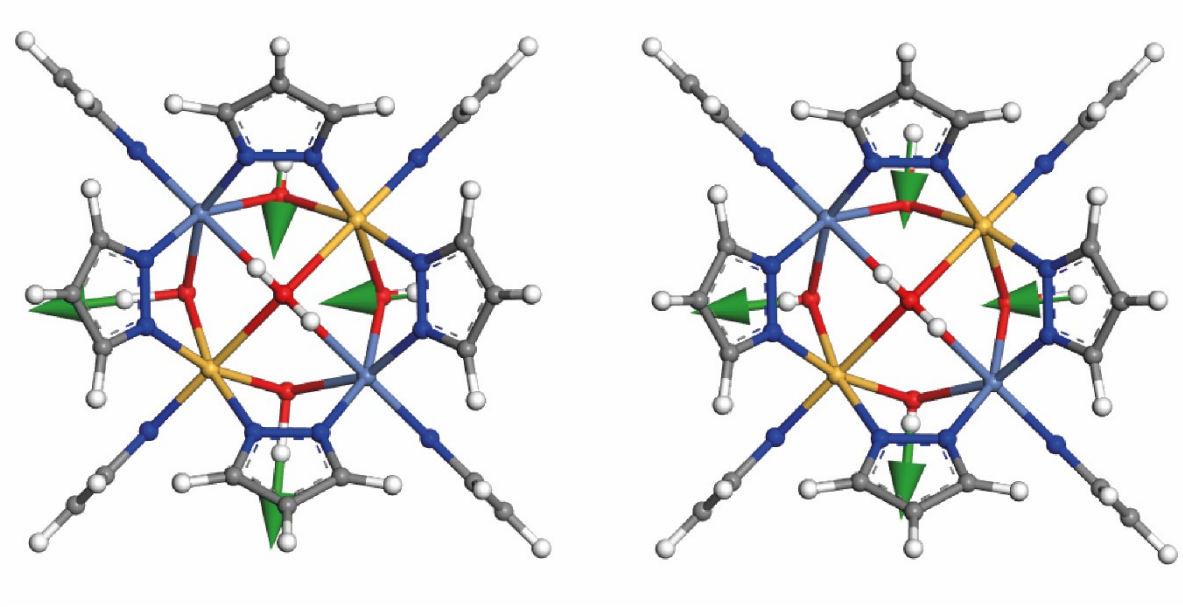

Figure S20: OH vibrations at 3662 cm^{-1} for $[Ni_8(OH)_4(H_2O)_2(pz)_{12}]$.

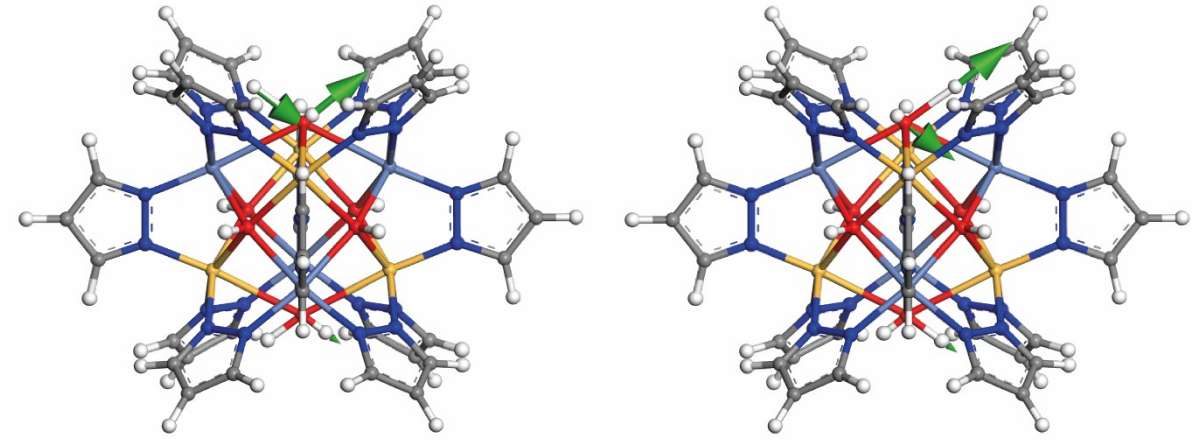

Figure S21: Asymmetric HOH vibrations at 3583 cm^{-1} for $[Ni_8(OH)_4(H_2O)_2(pz)_{12}]$.

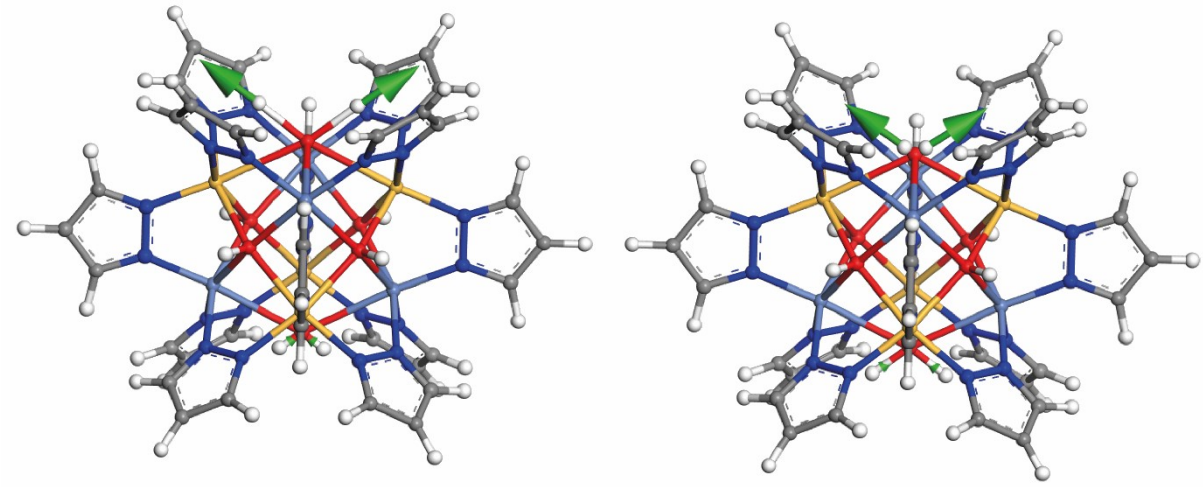

Figure S22: Symmetric HOH vibrations at 3496 cm^{-1} for $[Ni_8(OH)_4(H_2O)_2(pz)_{12}]$.

8. SC-XRD Analysis

*Table S3: Crystal data and structure refinement for **1a**.*

Identification code	mo_vk255_2_0m_a_sq	
Empirical formula	C72 H54 N24 Ni8 O6	
Formula weight	1821.07	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Cubic	
Space group	Fm-3m	
Unit cell dimensions	a = 25.4003(3) Å	α= 90°.
	b = 25.4003(3) Å	β= 90°.
	c = 25.4003(3) Å	γ = 90°.
Volume	16387.6(6) $Å^3$	
Z	4	
Density (calculated)	0.738 Mg/m^3	
Absorption coefficient	0.930 mm^{-1}	
F(000)	3704	
Crystal size	0.08 x 0.08 x 0.075 mm^3	
Theta range for data collection	2.268 to 29.971°.	
Index ranges	-35<=h<=31, -35<=k<=23, -12<=l<=35	
Reflections collected	13546	
Independent reflections	1249 [R(int) = 0.0271]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7483 and 0.6428	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1249 / 2 / 44	
Goodness-of-fit on F^2	1.060	
Final R indices [I>2sigma(I)]	R1 = 0.0215, wR2 = 0.0582	
R indices (all data)	R1 = 0.0269, wR2 = 0.0616	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.338 and -0.199 $e.Å^{-3}$	

*Table S4: Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for **1a**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.*

	x	y	z	U(eq)
Ni(1)	4413(1)	4413(1)	4413(1)	9(1)
C(1)	2567(1)	2819(1)	5429(1)	47(1)
O(1)	5000	4211(1)	5000	10(1)
N(1)	3899(1)	3899(1)	4734(1)	17(1)
C(2)	3545(1)	3545(1)	4570(1)	25(1)
C(3)	3303(1)	3303(1)	5000	26(1)
C(4)	2895(1)	2895(1)	5000	32(1)

*Table S5: Bond lengths [Å] and angles [°] for **1a**.*

Ni(1)-N(1)	2.0161(9)
Ni(1)-N(1)#1	2.0162(9)
Ni(1)-N(1)#2	2.0162(9)
Ni(1)-O(1)#2	2.1707(4)
Ni(1)-O(1)#1	2.1707(4)
Ni(1)-O(1)	2.1707(4)
Ni(1)-Ni(1)#3	2.9828(2)
Ni(1)-Ni(1)#4	2.9828(2)
Ni(1)-Ni(1)#5	2.9828(2)
C(1)-C(4)	1.386(2)
C(1)-H(3)	0.946(17)
O(1)-H(1)	0.789(18)
N(1)-C(2)	1.3409(14)
N(1)-N(1)#3	1.3537(18)
C(2)-C(3)	1.3963(15)
C(2)-H(2)	0.939(17)
C(3)-C(4)	1.465(2)
N(1)-Ni(1)-N(1)#1	95.98(3)
N(1)-Ni(1)-N(1)#2	95.98(3)
N(1)#1-Ni(1)-N(1)#2	95.98(3)
N(1)-Ni(1)-O(1)#2	90.80(3)
N(1)#1-Ni(1)-O(1)#2	169.85(4)
N(1)#2-Ni(1)-O(1)#2	90.80(3)

N(1)-Ni(1)-O(1)#1	169.84(4)
N(1)#1-Ni(1)-O(1)#1	90.80(3)
N(1)#2-Ni(1)-O(1)#1	90.80(3)
O(1)#2-Ni(1)-O(1)#1	81.53(5)
N(1)-Ni(1)-O(1)	90.80(3)
N(1)#1-Ni(1)-O(1)	90.80(3)
N(1)#2-Ni(1)-O(1)	169.85(4)
O(1)#2-Ni(1)-O(1)	81.54(5)
O(1)#1-Ni(1)-O(1)	81.54(5)
N(1)-Ni(1)-Ni(1)#3	66.17(3)
N(1)#1-Ni(1)-Ni(1)#3	130.304(10)
N(1)#2-Ni(1)-Ni(1)#3	130.304(10)
O(1)#2-Ni(1)-Ni(1)#3	46.601(8)
O(1)#1-Ni(1)-Ni(1)#3	103.67(4)
O(1)-Ni(1)-Ni(1)#3	46.602(8)
N(1)-Ni(1)-Ni(1)#4	130.303(10)
N(1)#1-Ni(1)-Ni(1)#4	130.304(10)
N(1)#2-Ni(1)-Ni(1)#4	66.17(3)
O(1)#2-Ni(1)-Ni(1)#4	46.601(8)
O(1)#1-Ni(1)-Ni(1)#4	46.601(8)
O(1)-Ni(1)-Ni(1)#4	103.68(4)
Ni(1)#3-Ni(1)-Ni(1)#4	90.0
N(1)-Ni(1)-Ni(1)#5	130.303(10)
N(1)#1-Ni(1)-Ni(1)#5	66.17(3)
N(1)#2-Ni(1)-Ni(1)#5	130.304(10)
O(1)#2-Ni(1)-Ni(1)#5	103.67(4)
O(1)#1-Ni(1)-Ni(1)#5	46.601(8)
O(1)-Ni(1)-Ni(1)#5	46.602(8)
Ni(1)#3-Ni(1)-Ni(1)#5	90.0
Ni(1)#4-Ni(1)-Ni(1)#5	90.0
C(4)-C(1)-H(3)	118.5(18)
Ni(1)#6-O(1)-Ni(1)#5	86.795(16)
Ni(1)#6-O(1)-Ni(1)#3	86.795(16)
Ni(1)#5-O(1)-Ni(1)#3	152.65(7)
Ni(1)#6-O(1)-Ni(1)	152.65(7)
Ni(1)#5-O(1)-Ni(1)	86.795(16)
Ni(1)#3-O(1)-Ni(1)	86.795(16)
Ni(1)#6-O(1)-H(1)	103.68(4)
Ni(1)#5-O(1)-H(1)	103.68(4)

Ni(1)#3-O(1)-H(1)	103.68(3)
Ni(1)-O(1)-H(1)	103.68(4)
C(2)-N(1)-N(1)#3	108.09(7)
C(2)-N(1)-Ni(1)	138.07(8)
N(1)#3-N(1)-Ni(1)	113.84(3)
N(1)-C(2)-C(3)	110.35(11)
N(1)-C(2)-H(2)	119.9(10)
C(3)-C(2)-H(2)	129.8(9)
C(2)-C(3)-C(2)#3	103.09(14)
C(2)-C(3)-C(4)	128.45(7)
C(2)#3-C(3)-C(4)	128.46(7)
C(1)-C(4)-C(3)	121.59(9)

Symmetry transformations used to generate equivalent atoms:

#1 z,x,y #2 y,z,x #3 x,y,-z+1 #4 x,-y+1,z

#5 -x+1,y,z #6 -x+1,y,-z+1

*Table S6: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$*

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	9(1)	9(1)	9(1)	-1(1)	-1(1)	-1(1)
C(1)	57(2)	54(1)	31(1)	-19(1)	16(1)	-46(1)
O(1)	10(1)	8(1)	10(1)	0	0	0
N(1)	18(1)	18(1)	15(1)	0(1)	0(1)	-7(1)
C(2)	28(1)	28(1)	19(1)	-1(1)	-1(1)	-18(1)
C(3)	27(1)	27(1)	22(1)	0	0	-17(1)
C(4)	35(1)	35(1)	26(1)	0	0	-25(1)

*Table S7: Hydrogen coordinates (x 104) and isotropic displacement parameters (Å2x 10 3) for **1a**.*

	x	y	z	U(eq)
H(3)	2634(11)	3013(10)	5740(8)	68(9)
H(1)	5000	3900(7)	5000	40(11)

H(2)	3491(4)	3491(4)	4208(7)	30

*Table S8: Crystal data and structure refinement for **1a activated**.*

Identification code	mo_vk262_act_cubic_0m_a_sq	
Empirical formula	C72 H54 N24 Ni8 O6	
Formula weight	1821.07	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Cubic	
Space group	Fm-3m	
Unit cell dimensions	a = 25.3036(11) Å	α= 90°.
	b = 25.3036(11) Å	β= 90°.
	c = 25.3036(11) Å	γ = 90°.
Volume	16201(2) $Å^3$	
Z	4	
Density (calculated)	0.747 Mg/m^3	
Absorption coefficient	0.940 mm^{-1}	
F(000)	3704	
Crystal size	0.08 x 0.08 x 0.075 mm^3	
Theta range for data collection	2.277 to 27.486°.	
Index ranges	-32<=h<=32, -32<=k<=32, -32<=l<=32	
Reflections collected	125932	
Independent reflections	993 [R(int) = 0.0483]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7355 and 0.6726	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	993 / 2 / 42	
Goodness-of-fit on F^2	1.122	
Final R indices [I>2sigma(I)]	R1 = 0.0214, wR2 = 0.0551	
R indices (all data)	R1 = 0.0308, wR2 = 0.0629	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.493 and -0.232 $e.Å^{-3}$	

*Table S9: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **1a activated**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.*

	x	y	z	U(eq)
Ni(1)	4417(1)	4417(1)	4417(1)	14(1)
C(1)	5419(2)	2548(2)	2837(1)	75(2)
N(1)	4740(1)	3904(1)	3904(1)	35(1)
O(1)	4208(1)	5000	5000	12(1)
C(2)	4571(1)	3546(1)	3546(1)	47(1)
C(3)	5000	3304(1)	3304(1)	48(1)
C(4)	5000	2893(1)	2893(1)	56(1)

*Table S10: Bond lengths [Å] and angles [°] for **1a activated**.*

Ni(1)-N(1)	2.0094(14)
Ni(1)-N(1)#1	2.0095(14)
Ni(1)-N(1)#2	2.0095(14)
Ni(1)-O(1)	2.1527(5)
Ni(1)-O(1)#2	2.1527(5)
Ni(1)-O(1)#1	2.1527(5)
Ni(1)-Ni(1)#3	2.9510(3)
Ni(1)-Ni(1)#4	2.9510(3)
Ni(1)-Ni(1)#5	2.9510(3)
C(1)-C(4)	1.380(4)
N(1)-N(1)#5	1.317(3)
N(1)-C(2)	1.349(2)
C(2)-C(3)	1.388(3)
C(3)-C(4)	1.472(4)

N(1)-Ni(1)-N(1)#1	96.19(6)
N(1)-Ni(1)-N(1)#2	96.19(6)
N(1)#1-Ni(1)-N(1)#2	96.19(6)
N(1)-Ni(1)-O(1)	170.23(6)
N(1)#1-Ni(1)-O(1)	90.32(5)
N(1)#2-Ni(1)-O(1)	90.32(5)
N(1)-Ni(1)-O(1)#2	90.32(5)
N(1)#1-Ni(1)-O(1)#2	90.32(5)
N(1)#2-Ni(1)-O(1)#2	170.23(6)

O(1)-Ni(1)-O(1)#2	82.35(7)
N(1)-Ni(1)-O(1)#1	90.32(5)
N(1)#1-Ni(1)-O(1)#1	170.23(6)
N(1)#2-Ni(1)-O(1)#1	90.32(5)
O(1)-Ni(1)-O(1)#1	82.35(7)
O(1)#2-Ni(1)-O(1)#1	82.35(7)
N(1)-Ni(1)-Ni(1)#3	130.245(16)
N(1)#1-Ni(1)-Ni(1)#3	66.02(4)
N(1)#2-Ni(1)-Ni(1)#3	130.245(16)
O(1)-Ni(1)-Ni(1)#3	46.728(11)
O(1)#2-Ni(1)-Ni(1)#3	46.729(11)
O(1)#1-Ni(1)-Ni(1)#3	104.22(5)
N(1)-Ni(1)-Ni(1)#4	130.245(16)
N(1)#1-Ni(1)-Ni(1)#4	130.245(16)
N(1)#2-Ni(1)-Ni(1)#4	66.02(4)
O(1)-Ni(1)-Ni(1)#4	46.728(11)
O(1)#2-Ni(1)-Ni(1)#4	104.22(5)
O(1)#1-Ni(1)-Ni(1)#4	46.729(11)
Ni(1)#3-Ni(1)-Ni(1)#4	90.0
N(1)-Ni(1)-Ni(1)#5	66.02(4)
N(1)#1-Ni(1)-Ni(1)#5	130.245(16)
N(1)#2-Ni(1)-Ni(1)#5	130.245(16)
O(1)-Ni(1)-Ni(1)#5	104.22(5)
O(1)#2-Ni(1)-Ni(1)#5	46.729(11)
O(1)#1-Ni(1)-Ni(1)#5	46.729(11)
Ni(1)#3-Ni(1)-Ni(1)#5	90.0
Ni(1)#4-Ni(1)-Ni(1)#5	90.0
N(1)#5-N(1)-C(2)	108.44(11)
N(1)#5-N(1)-Ni(1)	113.99(4)
C(2)-N(1)-Ni(1)	137.57(14)
Ni(1)#6-O(1)-Ni(1)#4	86.54(2)
Ni(1)#6-O(1)-Ni(1)#3	86.54(2)
Ni(1)#4-O(1)-Ni(1)#3	151.56(9)
Ni(1)#6-O(1)-Ni(1)	151.56(9)
Ni(1)#4-O(1)-Ni(1)	86.54(2)
Ni(1)#3-O(1)-Ni(1)	86.54(2)
N(1)-C(2)-C(3)	110.13(19)
C(2)#5-C(3)-C(2)	102.9(2)
C(2)#5-C(3)-C(4)	128.57(12)

C(2)-C(3)-C(4)	128.57(12)
C(1)-C(4)-C(3)	121.29(16)

Symmetry transformations used to generate equivalent atoms:

#1 y,z,x #2 z,x,y #3 x,y,-z+1 #4 x,-y+1,z

#5 -x+1,y,z #6 x,-y+1,-z+1

*Table S11: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1a activated**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2\ a^{*2}U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}]$*

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	14(1)	14(1)	14(1)	-2(1)	-2(1)	-2(1)
C(1)	73(2)	78(3)	75(3)	-58(2)	-31(2)	28(2)
N(1)	41(1)	31(1)	31(1)	-16(1)	-1(1)	-1(1)
O(1)	7(1)	15(1)	15(1)	0	0	0
C(2)	46(1)	48(1)	48(1)	-28(1)	-4(1)	-4(1)
C(3)	54(2)	46(1)	46(1)	-30(1)	0	0
C(4)	64(2)	51(1)	51(1)	-38(2)	0	0

*Table S12: Hydrogen coordinates (x 104) and isotropic displacement parameters (Å2x 10 3) for **1a activated**.*

	x	y	z	U(eq)
H(3)	5749(10)	2567(17)	3023(13)	100(15)
H(1)	3898(7)	5000	5000	15
H(2)	4211	3471	3471	57

*Table S13: Crystal data and structure refinement for **2a**.*

Identification code	mo_vk262_cs_0m_a_sq	
Empirical formula	C72 H54 Cs1.76 N24 Ni8 O6	
Formula weight	2054.50	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Cubic	
Space group	Fm-3m	
Unit cell dimensions	a = 25.3948(5) Å	α= 90°.
	b = 25.3948(5) Å	β= 90°.
	c = 25.3948(5) Å	γ = 90°.
Volume	16377.0(10) $Å^3$	
Z	4	
Density (calculated)	0.833 Mg/m^3	
Absorption coefficient	1.315 mm^{-1}	
F(000)	4090	
Crystal size	0.1 x 0.1 x 0.095 mm^3	
Theta range for data collection	2.268 to 27.489°.	
Index ranges	-32<=h<=26, -25<=k<=32, -32<=l<=24	
Reflections collected	16345	
Independent reflections	999 [R(int) = 0.0673]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7473 and 0.6264	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	999 / 3 / 53	
Goodness-of-fit on F^2	1.072	
Final R indices [I>2sigma(I)]	R1 = 0.0457, wR2 = 0.1342	
R indices (all data)	R1 = 0.0601, wR2 = 0.1428	
Extinction coefficient	0.00070(13)	
Largest diff. peak and hole	0.791 and -0.795 e.$Å^{-3}$	

*Table S14: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.*

	x	y	z	U(eq)
Ni(1)	4413(1)	5587(1)	5587(1)	12(1)
O(1)	4206(2)	5000	5000	12(1)
Cs(1)	4512(2)	7266(3)	5488(2)	114(4)
N(1)	4733(1)	6101(1)	6101(1)	19(1)
C(1)	4572(1)	6457(1)	6457(1)	30(1)
C(2)	5000	6697(1)	6697(1)	28(1)
C(3)	5000	7107(1)	7107(1)	34(1)
C(4)	5434(2)	7190(2)	7428(2)	50(2)

*Table S15: Bond lengths [Å] and angles [°] for **2a**.*

Ni(1)-N(1)	2.017(2)
Ni(1)-N(1)#1	2.018(2)
Ni(1)-N(1)#2	2.018(2)
Ni(1)-O(1)#3	2.1721(10)
Ni(1)-O(1)#4	2.1721(10)
Ni(1)-O(1)	2.1722(10)
Ni(1)-Ni(1)#5	2.9806(7)
Ni(1)-Ni(1)#6	2.9806(7)
Ni(1)-Ni(1)#7	2.9806(7)
Ni(1)-Cs(1)	4.278(8)
Ni(1)-Cs(1)#1	4.278(8)
Ni(1)-Cs(1)#2	4.278(8)
O(1)-H(1)	0.83(2)
Cs(1)-Cs(1)#5	2.480(11)
Cs(1)-Cs(1)#7	2.480(11)
Cs(1)-C(1)#1	3.208(5)
Cs(1)-C(1)	3.208(5)
Cs(1)-N(1)#1	3.389(7)
Cs(1)-N(1)	3.389(7)
Cs(1)-Cs(1)#8	3.508(15)
Cs(1)-C(2)	3.612(4)
Cs(1)-C(2)#1	3.612(4)

Cs(1)-H(2)	3.331(9)
N(1)-C(1)	1.341(4)
N(1)-N(1)#5	1.355(5)
C(1)-C(2)	1.389(4)
C(1)-H(2)	0.943(19)
C(2)-C(3)	1.470(6)
C(3)-C(4)	1.386(6)
C(4)-H(4)	0.925(19)

N(1)-Ni(1)-N(1)#1	95.90(10)
N(1)-Ni(1)-N(1)#2	95.90(10)
N(1)#1-Ni(1)-N(1)#2	95.90(10)
N(1)-Ni(1)-O(1)#3	90.62(9)
N(1)#1-Ni(1)-O(1)#3	170.24(12)
N(1)#2-Ni(1)-O(1)#3	90.63(9)
N(1)-Ni(1)-O(1)#4	90.62(9)
N(1)#1-Ni(1)-O(1)#4	90.63(9)
N(1)#2-Ni(1)-O(1)#4	170.24(12)
O(1)#3-Ni(1)-O(1)#4	82.03(15)
N(1)-Ni(1)-O(1)	170.24(12)
N(1)#1-Ni(1)-O(1)	90.63(9)
N(1)#2-Ni(1)-O(1)	90.63(9)
O(1)#3-Ni(1)-O(1)	82.03(15)
O(1)#4-Ni(1)-O(1)	82.03(15)
N(1)-Ni(1)-Ni(1)#5	66.23(7)
N(1)#1-Ni(1)-Ni(1)#5	130.33(3)
N(1)#2-Ni(1)-Ni(1)#5	130.33(3)
O(1)#3-Ni(1)-Ni(1)#5	46.68(2)
O(1)#4-Ni(1)-Ni(1)#5	46.68(2)
O(1)-Ni(1)-Ni(1)#5	104.01(10)
N(1)-Ni(1)-Ni(1)#6	130.33(3)
N(1)#1-Ni(1)-Ni(1)#6	130.33(3)
N(1)#2-Ni(1)-Ni(1)#6	66.24(7)
O(1)#3-Ni(1)-Ni(1)#6	46.68(2)
O(1)#4-Ni(1)-Ni(1)#6	104.01(10)
O(1)-Ni(1)-Ni(1)#6	46.68(2)
Ni(1)#5-Ni(1)-Ni(1)#6	90.0
N(1)-Ni(1)-Ni(1)#7	130.33(3)
N(1)#1-Ni(1)-Ni(1)#7	66.24(7)

N(1)#2-Ni(1)-Ni(1)#7	130.33(3)
O(1)#3-Ni(1)-Ni(1)#7	104.01(10)
O(1)#4-Ni(1)-Ni(1)#7	46.68(2)
O(1)-Ni(1)-Ni(1)#7	46.68(2)
Ni(1)#5-Ni(1)-Ni(1)#7	90.0
Ni(1)#6-Ni(1)-Ni(1)#7	90.0
N(1)-Ni(1)-Cs(1)	50.90(4)
N(1)#1-Ni(1)-Cs(1)	50.90(4)
N(1)#2-Ni(1)-Cs(1)	118.50(13)
O(1)#3-Ni(1)-Cs(1)	131.13(5)
O(1)#4-Ni(1)-Cs(1)	71.25(14)
O(1)-Ni(1)-Cs(1)	131.13(5)
Ni(1)#5-Ni(1)-Cs(1)	86.65(8)
Ni(1)#6-Ni(1)-Cs(1)	175.26(11)
Ni(1)#7-Ni(1)-Cs(1)	86.65(8)
N(1)-Ni(1)-Cs(1)#1	118.51(13)
N(1)#1-Ni(1)-Cs(1)#1	50.90(4)
N(1)#2-Ni(1)-Cs(1)#1	50.90(4)
O(1)#3-Ni(1)-Cs(1)#1	131.13(5)
O(1)#4-Ni(1)-Cs(1)#1	131.13(5)
O(1)-Ni(1)-Cs(1)#1	71.25(15)
Ni(1)#5-Ni(1)-Cs(1)#1	175.26(11)
Ni(1)#6-Ni(1)-Cs(1)#1	86.65(8)
Ni(1)#7-Ni(1)-Cs(1)#1	86.65(8)
Cs(1)-Ni(1)-Cs(1)#1	96.49(14)
N(1)-Ni(1)-Cs(1)#2	50.90(4)
N(1)#1-Ni(1)-Cs(1)#2	118.50(13)
N(1)#2-Ni(1)-Cs(1)#2	50.90(4)
O(1)#3-Ni(1)-Cs(1)#2	71.25(14)
O(1)#4-Ni(1)-Cs(1)#2	131.13(5)
O(1)-Ni(1)-Cs(1)#2	131.13(5)
Ni(1)#5-Ni(1)-Cs(1)#2	86.65(8)
Ni(1)#6-Ni(1)-Cs(1)#2	86.65(8)
Ni(1)#7-Ni(1)-Cs(1)#2	175.26(11)
Cs(1)-Ni(1)-Cs(1)#2	96.49(14)
Cs(1)#1-Ni(1)-Cs(1)#2	96.49(14)
Ni(1)-O(1)-Ni(1)#9	152.0(2)
Ni(1)-O(1)-Ni(1)#7	86.64(5)
Ni(1)#9-O(1)-Ni(1)#7	86.64(5)

Ni(1)-O(1)-Ni(1)#6	86.64(5)
Ni(1)#9-O(1)-Ni(1)#6	86.64(5)
Ni(1)#7-O(1)-Ni(1)#6	152.0(2)
Ni(1)-O(1)-H(1)	104.01(10)
Ni(1)#9-O(1)-H(1)	104.01(10)
Ni(1)#7-O(1)-H(1)	104.01(10)
Ni(1)#6-O(1)-H(1)	104.01(10)
Cs(1)#5-Cs(1)-Cs(1)#7	90.001(2)
Cs(1)#5-Cs(1)-C(1)#1	140.04(17)
Cs(1)#7-Cs(1)-C(1)#1	87.26(12)
Cs(1)#5-Cs(1)-C(1)	87.26(12)
Cs(1)#7-Cs(1)-C(1)	140.04(17)
C(1)#1-Cs(1)-C(1)	70.30(19)
Cs(1)#5-Cs(1)-N(1)#1	117.33(13)
Cs(1)#7-Cs(1)-N(1)#1	80.44(10)
C(1)#1-Cs(1)-N(1)#1	23.25(8)
C(1)-Cs(1)-N(1)#1	65.81(16)
Cs(1)#5-Cs(1)-N(1)	80.44(10)
Cs(1)#7-Cs(1)-N(1)	117.33(14)
C(1)#1-Cs(1)-N(1)	65.81(16)
C(1)-Cs(1)-N(1)	23.25(8)
N(1)#1-Cs(1)-N(1)	52.47(14)
Cs(1)#5-Cs(1)-Cs(1)#8	45.001(1)
Cs(1)#7-Cs(1)-Cs(1)#8	45.001(2)
C(1)#1-Cs(1)-Cs(1)#8	120.54(17)
C(1)-Cs(1)-Cs(1)#8	120.55(17)
N(1)#1-Cs(1)-Cs(1)#8	101.96(15)
N(1)-Cs(1)-Cs(1)#8	101.96(15)
Cs(1)#5-Cs(1)-C(2)	69.92(10)
Cs(1)#7-Cs(1)-C(2)	148.21(16)
C(1)#1-Cs(1)-C(2)	92.74(17)
C(1)-Cs(1)-C(2)	22.51(7)
N(1)#1-Cs(1)-C(2)	87.13(17)
N(1)-Cs(1)-C(2)	37.26(9)
Cs(1)#8-Cs(1)-C(2)	110.99(13)
Cs(1)#5-Cs(1)-C(2)#1	148.21(16)
Cs(1)#7-Cs(1)-C(2)#1	69.92(10)
C(1)#1-Cs(1)-C(2)#1	22.51(7)
C(1)-Cs(1)-C(2)#1	92.74(17)

N(1)#1-Cs(1)-C(2)#1	37.26(9)
N(1)-Cs(1)-C(2)#1	87.14(17)
Cs(1)#8-Cs(1)-C(2)#1	110.99(13)
C(2)-Cs(1)-C(2)#1	115.09(18)
Cs(1)#5-Cs(1)-Ni(1)	93.35(7)
Cs(1)#7-Cs(1)-Ni(1)	93.35(8)
C(1)#1-Cs(1)-Ni(1)	47.13(12)
C(1)-Cs(1)-Ni(1)	47.13(12)
N(1)#1-Cs(1)-Ni(1)	27.52(8)
N(1)-Cs(1)-Ni(1)	27.51(8)
Cs(1)#8-Cs(1)-Ni(1)	94.74(11)
C(2)-Cs(1)-Ni(1)	64.67(13)
C(2)#1-Cs(1)-Ni(1)	64.67(13)
Cs(1)#5-Cs(1)-H(2)	102.7(5)
Cs(1)#7-Cs(1)-H(2)	143.7(9)
C(1)#1-Cs(1)-H(2)	61.2(8)
C(1)-Cs(1)-H(2)	16.4(3)
N(1)#1-Cs(1)-H(2)	63.5(9)
N(1)-Cs(1)-H(2)	35.6(5)
Cs(1)#8-Cs(1)-H(2)	136.5(4)
C(2)-Cs(1)-H(2)	34.0(6)
C(2)#1-Cs(1)-H(2)	82.6(8)
Ni(1)-Cs(1)-H(2)	52.6(8)
C(1)-N(1)-N(1)#5	107.78(19)
C(1)-N(1)-Ni(1)	138.5(2)
N(1)#5-N(1)-Ni(1)	113.77(7)
C(1)-N(1)-Cs(1)	70.77(14)
N(1)#5-N(1)-Cs(1)	99.56(10)
Ni(1)-N(1)-Cs(1)	101.58(10)
C(1)-N(1)-Cs(1)#2	70.77(14)
N(1)#5-N(1)-Cs(1)#2	99.56(10)
Ni(1)-N(1)-Cs(1)#2	101.59(10)
Cs(1)-N(1)-Cs(1)#2	140.7(3)
N(1)-C(1)-C(2)	110.7(3)
N(1)-C(1)-Cs(1)	85.97(18)
C(2)-C(1)-Cs(1)	95.33(10)
N(1)-C(1)-Cs(1)#2	85.97(18)
C(2)-C(1)-Cs(1)#2	95.33(10)
Cs(1)-C(1)-Cs(1)#2	168.4(2)

N(1)-C(1)-H(2)	128(3)
C(2)-C(1)-H(2)	122(3)
Cs(1)-C(1)-H(2)	89.2(4)
Cs(1)#2-C(1)-H(2)	89.2(4)
C(1)-C(2)-C(1)#5	103.0(4)
C(1)-C(2)-C(3)	128.5(2)
C(1)#5-C(2)-C(3)	128.5(2)
C(1)-C(2)-Cs(1)	62.16(10)
C(1)#5-C(2)-Cs(1)	94.04(19)
C(3)-C(2)-Cs(1)	108.57(16)
C(1)-C(2)-Cs(1)#2	62.16(10)
C(1)#5-C(2)-Cs(1)#2	94.04(19)
C(3)-C(2)-Cs(1)#2	108.57(16)
Cs(1)-C(2)-Cs(1)#2	124.2(2)
C(1)-C(2)-Cs(1)#5	94.04(19)
C(1)#5-C(2)-Cs(1)#5	62.16(10)
C(3)-C(2)-Cs(1)#5	108.57(16)
Cs(1)-C(2)-Cs(1)#5	40.2(2)
Cs(1)#2-C(2)-Cs(1)#5	142.9(3)
C(1)-C(2)-Cs(1)#10	94.04(19)
C(1)#5-C(2)-Cs(1)#10	62.16(10)
C(3)-C(2)-Cs(1)#10	108.57(16)
Cs(1)-C(2)-Cs(1)#10	142.9(3)
Cs(1)#2-C(2)-Cs(1)#10	40.2(2)
Cs(1)#5-C(2)-Cs(1)#10	124.2(2)
C(4)-C(3)-C(2)	121.6(3)
C(3)-C(4)-H(4)	123(3)

Symmetry transformations used to generate equivalent atoms:

#1 -y+1,z,-x+1 #2 -z+1,-x+1,y #3 -y+1,-z+1,-x+1

#4 -z+1,-x+1,-y+1 #5 -x+1,y,z #6 x,-y+1,z

#7 x,y,-z+1 #8 -x+1,y,-z+1 #9 x,-y+1,-z+1

#10 z,-x+1,y

*Table S16: Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **2a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$*

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	12(1)	12(1)	12(1)	-1(1)	1(1)	1(1)
O(1)	12(2)	11(1)	11(1)	0	0	0
Cs(1)	114(5)	114(6)	114(5)	31(3)	16(4)	-31(3)
N(1)	18(1)	20(1)	20(1)	-7(1)	1(1)	1(1)
C(1)	25(2)	32(1)	32(1)	-19(2)	3(1)	3(1)
C(2)	27(2)	29(2)	29(2)	-16(2)	0	0
C(3)	33(3)	35(2)	35(2)	-22(2)	0	0
C(4)	36(3)	56(4)	58(4)	-40(4)	-14(2)	19(2)

*Table S17: Hydrogen coordinates (x 104) and isotropic displacement parameters (Å2x 10 3) for **2a**.*

	x	y	z	U(eq)
H(1)	3881(8)	5000	5000	260(130)
H(2)	4223(10)	6546(14)	6546(14)	69(15)
H(4)	5750(12)	7015(18)	7390(20)	37(15)

The following crystal data refers to the „**2a** 2“ mentioned in table 1 in the main text, a crystal taken from another batch with identical conditions as for **2a**.

*Table S18: Crystal data and structure refinement for **2a** 2.*

Identification code	mo_vk256_cs_0m_a_sq	
Empirical formula	C72 H54 Cs1.27 N24 Ni8 O6	
Formula weight	1990.00	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Cubic	
Space group	Fm-3m	
Unit cell dimensions	a = 25.4123(5) Å	α= 90°.
	b = 25.4123(5) Å	β= 90°.
	c = 25.4123(5) Å	γ = 90°.
Volume	16410.9(10) $Å^3$	
Z	4	
Density (calculated)	0.805 Mg/m^3	
Absorption coefficient	1.207 mm^{-1}	
F(000)	3984	
Crystal size	0.08 x 0.08 x 0.075 mm^3	
Theta range for data collection	2.267 to 29.956°.	
Index ranges	-35<=h<=25, -28<=k<=35, -27<=l<=35	
Reflections collected	25161	
Independent reflections	1249 [R(int) = 0.0337]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7478 and 0.6476	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1249 / 8 / 52	
Goodness-of-fit on F^2	1.105	
Final R indices [I>2sigma(I)]	R1 = 0.0388, wR2 = 0.1272	
R indices (all data)	R1 = 0.0425, wR2 = 0.1306	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.603 and -0.815 $e.Å^{-3}$	

*Table S19: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2a** 2. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.*

	x	y	z	U(eq)
Ni(1)	4413(1)	5587(1)	5587(1)	7(1)
O(1)	4208(1)	5000	5000	7(1)
N(1)	4734(1)	6101(1)	6101(1)	15(1)
C(1)	4571(1)	6456(1)	6456(1)	24(1)
Cs(1)	4524(2)	7248(3)	4524(2)	77(3)
C(2)	5000	6697(1)	6697(1)	23(1)
C(3)	5000	7106(1)	7106(1)	30(1)
C(4)	5431(2)	7180(1)	7432(1)	36(1)

*Table S20: Bond lengths [Å] and angles [°] for **2a** 2.*

Ni(1)-N(1)	2.0203(16)
Ni(1)-N(1)#1	2.0203(16)
Ni(1)-N(1)#2	2.0203(16)
Ni(1)-O(1)	2.1732(6)
Ni(1)-O(1)#3	2.1733(6)
Ni(1)-O(1)#4	2.1733(6)
Ni(1)-Ni(1)#5	2.9842(4)
Ni(1)-Ni(1)#6	2.9842(4)
Ni(1)-Ni(1)#7	2.9842(4)
Ni(1)-Cs(1)#3	4.239(6)
Ni(1)-Cs(1)#7	4.239(6)
Ni(1)-Cs(1)#8	4.239(6)
O(1)-H(1)	0.83(2)
N(1)-C(1)	1.341(2)
N(1)-N(1)#6	1.352(3)
N(1)-Cs(1)#7	3.361(5)
N(1)-Cs(1)#8	3.361(5)
N(1)-Cs(1)#9	3.817(5)
N(1)-Cs(1)#2	3.817(5)
C(1)-C(2)	1.393(3)
C(1)-Cs(1)#8	3.204(4)
C(1)-Cs(1)#7	3.204(4)
C(1)-H(2)	0.95(4)

Cs(1)-Cs(1)#6	2.419(10)
Cs(1)-Cs(1)#7	2.419(10)
Cs(1)-Cs(1)#9	3.422(14)
Cs(1)-C(2)#1	3.612(3)
Cs(1)-C(2)#7	3.612(3)
C(2)-C(3)	1.470(4)
C(3)-C(4)	1.386(4)
C(4)-H(3)	0.93(2)

N(1)-Ni(1)-N(1)#1	95.98(6)
N(1)-Ni(1)-N(1)#2	95.98(6)
N(1)#1-Ni(1)-N(1)#2	95.98(6)
N(1)-Ni(1)-O(1)	170.02(8)
N(1)#1-Ni(1)-O(1)	90.68(5)
N(1)#2-Ni(1)-O(1)	90.68(5)
N(1)-Ni(1)-O(1)#3	90.68(5)
N(1)#1-Ni(1)-O(1)#3	170.02(8)
N(1)#2-Ni(1)-O(1)#3	90.68(5)
O(1)-Ni(1)-O(1)#3	81.79(9)
N(1)-Ni(1)-O(1)#4	90.68(5)
N(1)#1-Ni(1)-O(1)#4	90.68(5)
N(1)#2-Ni(1)-O(1)#4	170.02(8)
O(1)-Ni(1)-O(1)#4	81.79(9)
O(1)#3-Ni(1)-O(1)#4	81.80(9)
N(1)-Ni(1)-Ni(1)#5	130.302(17)
N(1)#1-Ni(1)-Ni(1)#5	130.303(17)
N(1)#2-Ni(1)-Ni(1)#5	66.17(5)
O(1)-Ni(1)-Ni(1)#5	46.642(14)
O(1)#3-Ni(1)-Ni(1)#5	46.643(15)
O(1)#4-Ni(1)-Ni(1)#5	103.85(6)
N(1)-Ni(1)-Ni(1)#6	66.17(5)
N(1)#1-Ni(1)-Ni(1)#6	130.303(17)
N(1)#2-Ni(1)-Ni(1)#6	130.303(17)
O(1)-Ni(1)-Ni(1)#6	103.85(6)
O(1)#3-Ni(1)-Ni(1)#6	46.643(15)
O(1)#4-Ni(1)-Ni(1)#6	46.643(14)
Ni(1)#5-Ni(1)-Ni(1)#6	90.0
N(1)-Ni(1)-Ni(1)#7	130.302(17)
N(1)#1-Ni(1)-Ni(1)#7	66.17(5)

N(1)#2-Ni(1)-Ni(1)#7	130.303(17)
O(1)-Ni(1)-Ni(1)#7	46.642(14)
O(1)#3-Ni(1)-Ni(1)#7	103.85(6)
O(1)#4-Ni(1)-Ni(1)#7	46.643(15)
Ni(1)#5-Ni(1)-Ni(1)#7	90.0
Ni(1)#6-Ni(1)-Ni(1)#7	90.0
N(1)-Ni(1)-Cs(1)#3	119.24(11)
N(1)#1-Ni(1)-Cs(1)#3	51.11(3)
N(1)#2-Ni(1)-Cs(1)#3	51.11(3)
O(1)-Ni(1)-Cs(1)#3	70.75(11)
O(1)#3-Ni(1)-Cs(1)#3	130.82(5)
O(1)#4-Ni(1)-Cs(1)#3	130.82(5)
Ni(1)#5-Ni(1)-Cs(1)#3	86.18(7)
Ni(1)#6-Ni(1)-Cs(1)#3	174.60(10)
Ni(1)#7-Ni(1)-Cs(1)#3	86.18(7)
N(1)-Ni(1)-Cs(1)#7	51.11(3)
N(1)#1-Ni(1)-Cs(1)#7	51.11(3)
N(1)#2-Ni(1)-Cs(1)#7	119.23(11)
O(1)-Ni(1)-Cs(1)#7	130.82(5)
O(1)#3-Ni(1)-Cs(1)#7	130.82(5)
O(1)#4-Ni(1)-Cs(1)#7	70.75(11)
Ni(1)#5-Ni(1)-Cs(1)#7	174.60(10)
Ni(1)#6-Ni(1)-Cs(1)#7	86.18(7)
Ni(1)#7-Ni(1)-Cs(1)#7	86.18(7)
Cs(1)#3-Ni(1)-Cs(1)#7	97.37(12)
N(1)-Ni(1)-Cs(1)#8	51.11(3)
N(1)#1-Ni(1)-Cs(1)#8	119.23(11)
N(1)#2-Ni(1)-Cs(1)#8	51.11(3)
O(1)-Ni(1)-Cs(1)#8	130.82(5)
O(1)#3-Ni(1)-Cs(1)#8	70.75(11)
O(1)#4-Ni(1)-Cs(1)#8	130.82(5)
Ni(1)#5-Ni(1)-Cs(1)#8	86.18(7)
Ni(1)#6-Ni(1)-Cs(1)#8	86.18(7)
Ni(1)#7-Ni(1)-Cs(1)#8	174.60(10)
Cs(1)#3-Ni(1)-Cs(1)#8	97.37(12)
Cs(1)#7-Ni(1)-Cs(1)#8	97.37(12)
Ni(1)-O(1)-Ni(1)#10	152.31(12)
Ni(1)-O(1)-Ni(1)#7	86.72(3)
Ni(1)#10-O(1)-Ni(1)#7	86.72(3)

Ni(1)-O(1)-Ni(1)#5	86.72(3)
Ni(1)#10-O(1)-Ni(1)#5	86.72(3)
Ni(1)#7-O(1)-Ni(1)#5	152.31(12)
Ni(1)-O(1)-H(1)	103.85(6)
Ni(1)#10-O(1)-H(1)	103.85(6)
Ni(1)#7-O(1)-H(1)	103.85(6)
Ni(1)#5-O(1)-H(1)	103.85(6)
C(1)-N(1)-N(1)#6	108.05(12)
C(1)-N(1)-Ni(1)	138.12(15)
N(1)#6-N(1)-Ni(1)	113.83(5)
C(1)-N(1)-Cs(1)#7	71.70(12)
N(1)#6-N(1)-Cs(1)#7	99.14(9)
Ni(1)-N(1)-Cs(1)#7	100.99(7)
C(1)-N(1)-Cs(1)#8	71.70(12)
N(1)#6-N(1)-Cs(1)#8	99.14(9)
Ni(1)-N(1)-Cs(1)#8	100.99(7)
Cs(1)#7-N(1)-Cs(1)#8	142.6(3)
C(1)-N(1)-Cs(1)#9	85.40(10)
N(1)#6-N(1)-Cs(1)#9	60.40(8)
Ni(1)-N(1)-Cs(1)#9	115.09(10)
Cs(1)#7-N(1)-Cs(1)#9	38.74(16)
Cs(1)#8-N(1)-Cs(1)#9	143.15(15)
C(1)-N(1)-Cs(1)#2	85.40(10)
N(1)#6-N(1)-Cs(1)#2	60.40(8)
Ni(1)-N(1)-Cs(1)#2	115.09(10)
Cs(1)#7-N(1)-Cs(1)#2	143.15(15)
Cs(1)#8-N(1)-Cs(1)#2	38.74(16)
Cs(1)#9-N(1)-Cs(1)#2	113.1(2)
N(1)-C(1)-C(2)	110.4(2)
N(1)-C(1)-Cs(1)#8	84.89(14)
C(2)-C(1)-Cs(1)#8	95.43(7)
N(1)-C(1)-Cs(1)#7	84.89(14)
C(2)-C(1)-Cs(1)#7	95.43(7)
Cs(1)#8-C(1)-Cs(1)#7	167.1(2)
N(1)-C(1)-H(2)	123(2)
C(2)-C(1)-H(2)	127(2)
Cs(1)#8-C(1)-H(2)	89.5(3)
Cs(1)#7-C(1)-H(2)	89.5(3)
Cs(1)#6-Cs(1)-Cs(1)#7	89.997(1)

Cs(1)#6-Cs(1)-C(1)#11	141.02(13)
Cs(1)#7-Cs(1)-C(1)#11	87.88(10)
Cs(1)#6-Cs(1)-C(1)#7	87.88(10)
Cs(1)#7-Cs(1)-C(1)#7	141.02(13)
C(1)#11-Cs(1)-C(1)#7	70.32(14)
Cs(1)#6-Cs(1)-N(1)#7	80.86(9)
Cs(1)#7-Cs(1)-N(1)#7	118.22(11)
C(1)#11-Cs(1)-N(1)#7	66.21(11)
C(1)#7-Cs(1)-N(1)#7	23.41(5)
Cs(1)#6-Cs(1)-N(1)#11	118.22(11)
Cs(1)#7-Cs(1)-N(1)#11	80.86(9)
C(1)#11-Cs(1)-N(1)#11	23.41(5)
C(1)#7-Cs(1)-N(1)#11	66.21(11)
N(1)#7-Cs(1)-N(1)#11	53.06(10)
Cs(1)#6-Cs(1)-Cs(1)#9	45.0
Cs(1)#7-Cs(1)-Cs(1)#9	44.998(1)
C(1)#11-Cs(1)-Cs(1)#9	121.57(13)
C(1)#7-Cs(1)-Cs(1)#9	121.57(13)
N(1)#7-Cs(1)-Cs(1)#9	102.83(13)
N(1)#11-Cs(1)-Cs(1)#9	102.83(13)
Cs(1)#6-Cs(1)-C(2)#1	149.19(13)
Cs(1)#7-Cs(1)-C(2)#1	70.44(9)
C(1)#11-Cs(1)-C(2)#1	22.57(5)
C(1)#7-Cs(1)-C(2)#1	92.79(13)
N(1)#7-Cs(1)-C(2)#1	87.64(13)
N(1)#11-Cs(1)-C(2)#1	37.33(6)
Cs(1)#9-Cs(1)-C(2)#1	111.75(11)
Cs(1)#6-Cs(1)-C(2)#7	70.44(9)
Cs(1)#7-Cs(1)-C(2)#7	149.19(13)
C(1)#11-Cs(1)-C(2)#7	92.79(13)
C(1)#7-Cs(1)-C(2)#7	22.57(5)
N(1)#7-Cs(1)-C(2)#7	37.33(6)
N(1)#11-Cs(1)-C(2)#7	87.64(13)
Cs(1)#9-Cs(1)-C(2)#7	111.75(11)
C(2)#1-Cs(1)-C(2)#7	115.15(15)
Cs(1)#6-Cs(1)-N(1)#1	114.60(10)
Cs(1)#7-Cs(1)-N(1)#1	60.40(8)
C(1)#11-Cs(1)-N(1)#1	34.79(7)
C(1)#7-Cs(1)-N(1)#1	85.42(13)

N(1)#7-Cs(1)-N(1)#1	68.78(12)
N(1)#11-Cs(1)-N(1)#1	20.47(6)
Cs(1)#9-Cs(1)-N(1)#1	86.85(10)
C(2)#1-Cs(1)-N(1)#1	35.03(6)
C(2)#7-Cs(1)-N(1)#1	105.54(15)
Cs(1)#6-Cs(1)-N(1)#9	60.40(8)
Cs(1)#7-Cs(1)-N(1)#9	114.60(10)
C(1)#11-Cs(1)-N(1)#9	85.42(13)
C(1)#7-Cs(1)-N(1)#9	34.79(7)
N(1)#7-Cs(1)-N(1)#9	20.47(6)
N(1)#11-Cs(1)-N(1)#9	68.78(12)
Cs(1)#9-Cs(1)-N(1)#9	86.85(10)
C(2)#1-Cs(1)-N(1)#9	105.54(15)
C(2)#7-Cs(1)-N(1)#9	35.03(6)
N(1)#1-Cs(1)-N(1)#9	80.14(14)
Cs(1)#6-Cs(1)-Ni(1)#7	93.82(7)
Cs(1)#7-Cs(1)-Ni(1)#7	93.82(7)
C(1)#11-Cs(1)-Ni(1)#7	47.59(9)
C(1)#7-Cs(1)-Ni(1)#7	47.59(9)
N(1)#7-Cs(1)-Ni(1)#7	27.90(6)
N(1)#11-Cs(1)-Ni(1)#7	27.90(6)
Cs(1)#9-Cs(1)-Ni(1)#7	95.41(9)
C(2)#1-Cs(1)-Ni(1)#7	65.12(9)
C(2)#7-Cs(1)-Ni(1)#7	65.12(9)
N(1)#1-Cs(1)-Ni(1)#7	41.00(7)
N(1)#9-Cs(1)-Ni(1)#7	41.00(7)
C(1)#6-C(2)-C(1)	103.2(2)
C(1)#6-C(2)-C(3)	128.41(13)
C(1)-C(2)-C(3)	128.41(13)
C(1)#6-C(2)-Cs(1)#8	93.17(14)
C(1)-C(2)-Cs(1)#8	62.00(8)
C(3)-C(2)-Cs(1)#8	109.47(12)
C(1)#6-C(2)-Cs(1)#7	93.17(14)
C(1)-C(2)-Cs(1)#7	62.00(8)
C(3)-C(2)-Cs(1)#7	109.47(12)
Cs(1)#8-C(2)-Cs(1)#7	123.62(16)
C(1)#6-C(2)-Cs(1)#9	62.00(8)
C(1)-C(2)-Cs(1)#9	93.17(14)
C(3)-C(2)-Cs(1)#9	109.47(12)

Cs(1)#8-C(2)-Cs(1)#9	141.1(2)
Cs(1)#7-C(2)-Cs(1)#9	39.13(18)
C(1)#6-C(2)-Cs(1)#2	62.00(8)
C(1)-C(2)-Cs(1)#2	93.17(14)
C(3)-C(2)-Cs(1)#2	109.47(12)
Cs(1)#8-C(2)-Cs(1)#2	39.13(18)
Cs(1)#7-C(2)-Cs(1)#2	141.1(2)
Cs(1)#9-C(2)-Cs(1)#2	123.62(16)
C(4)-C(3)-C(2)	121.19(17)
C(3)-C(4)-H(3)	125(4)

Symmetry transformations used to generate equivalent atoms:

#1 -y+1,z,-x+1 #2 -z+1,-x+1,y #3 -y+1,-z+1,-x+1

#4 -z+1,-x+1,-y+1 #5 x,-y+1,z #6 -x+1,y,z

#7 x,y,-z+1 #8 z,-x+1,y #9 -x+1,y,-z+1 #10 x,-y+1,-z+1

#11 -y+1,z,x

*Table S21: Anisotropic displacement parameters ($Å^2x\ 10^3$) for **2a** 2. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$*

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	7(1)	7(1)	7(1)	-1(1)	1(1)	1(1)
O(1)	6(1)	8(1)	8(1)	0	0	0
N(1)	14(1)	16(1)	16(1)	-9(1)	1(1)	1(1)
C(1)	21(1)	26(1)	26(1)	-18(1)	2(1)	2(1)
Cs(1)	83(3)	65(4)	83(3)	-20(2)	-8(3)	-20(2)
C(2)	23(1)	24(1)	24(1)	-16(1)	0	0
C(3)	30(2)	30(1)	30(1)	-24(1)	0	0
C(4)	34(1)	37(1)	38(2)	-27(1)	-7(1)	11(1)

*Table S22: Hydrogen coordinates (x 104) and isotropic displacement parameters (Å2x 10 3) for **2a** 2.*

	x	y	z	U(eq)
H(1)	3882(8)	5000	5000	29(17)
H(2)	4209(14)	6523(9)	6523(9)	35(8)
H(3)	5758(12)	7020(20)	7390(20)	70(19)

Notes and references

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