Supplementary Information for

A two-fold 3D interpenetrating cyanido-bridged network based on the octa-coordinated $[Mo(CN)_8]^{4-}$ building block

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Table S1. Continuous Shape Measure parameters for octa-coordinated molybdenum (Mo1) centers in the structures of **1**, **2** and **3**; SAPR-8 = square antiprism, TDD-8 = triangular dodecahedron, BTPR-8 = biaugmented trigonal prism, JSD-8 = snub disphenoid.

shape	**1**	**2**	**3**
SAPR-8	2.872	**0.385**	2.796
TDD-8	**0.106**	1.909	**0.358**
BTPR-8	2.657	1.289	2.058
JSD-8	2.469	4.410	2.653

Table S2. Continuous Shape Measure parameters for hexa-coordinated nickel centers in the structures of **1**, **2**, and **3**; OC-6 = octahedron.

shape	**1** (Ni1)	**2** (Ni1)	**2** (Ni2)	**3** (Ni1)	**3** (Ni2)	**3** (Ni3)
OC-6	0.122	0.133	0.166	0.167	0.125	0.195

Table S3. Continuous Shape Measure parameters for tetra-coordinated nickel (Ni4) center in the structure of **3** and lithium (Li1) cations in the structure of **2**; SP-4 = square, T-4 = tetrahedron, SS-4 = *cis*-divacant octahedron, vTBPY-4 = axially vacant trigonal bipyramid.

shape	**2** (Li1)	**3** (Ni4)
SP-4	29.157	**0.197**
T-4	**0.402**	33.464
SS-4	7.531	19.118
vTBPY-4	3.488	34.961

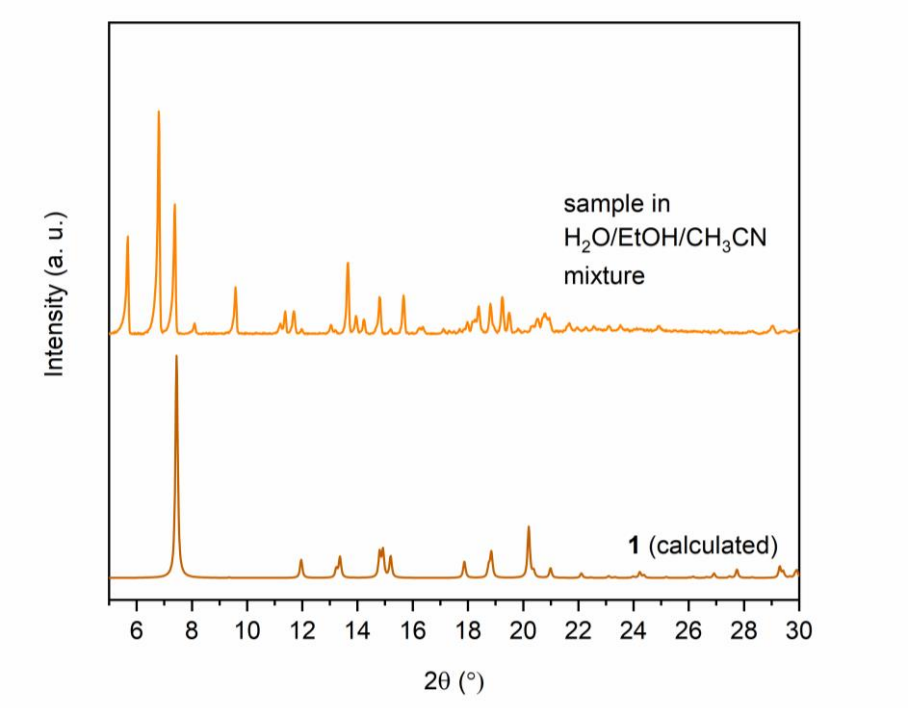

Figure S1. PXRD pattern of the contaminated product **1** under mother liquor in comparison to the pattern calculated for **1** from single crystal data.

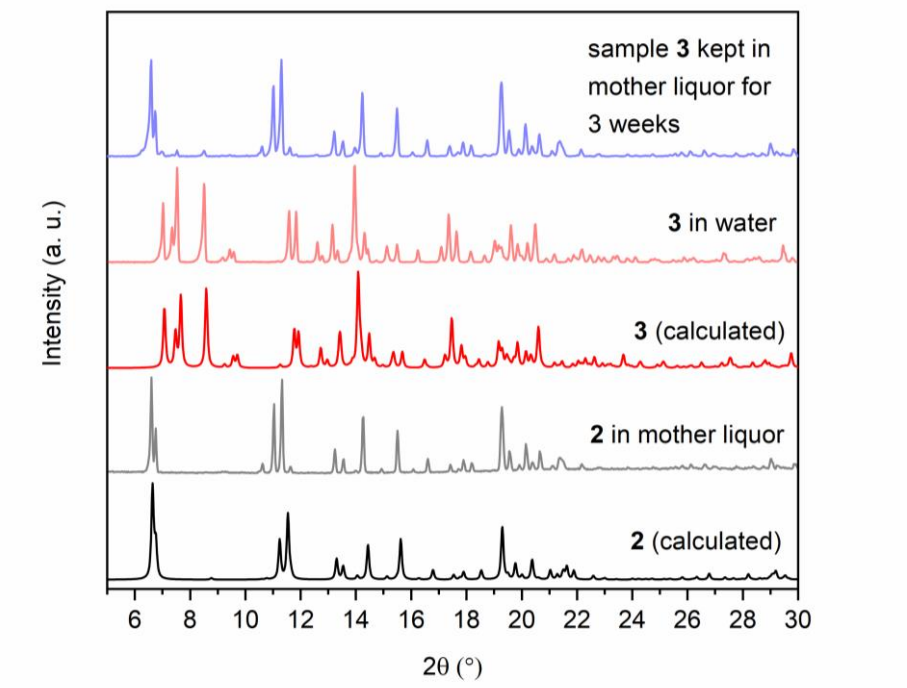

Figure S2. PXRD patterns for compound **2** in mother liquor and compound **3** in water and in mother liquor in comparison to the patterns generated from single-crystal data.

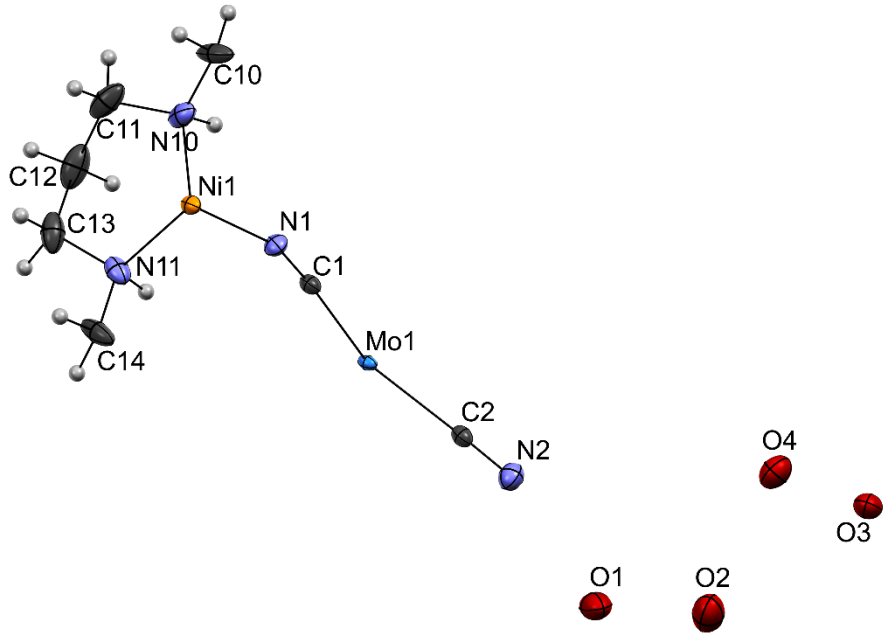

Figure S3. The asymmetric unit of compound **1**; thermal ellipsoids at 50% probability; hydrogen atoms omitted for clarity.

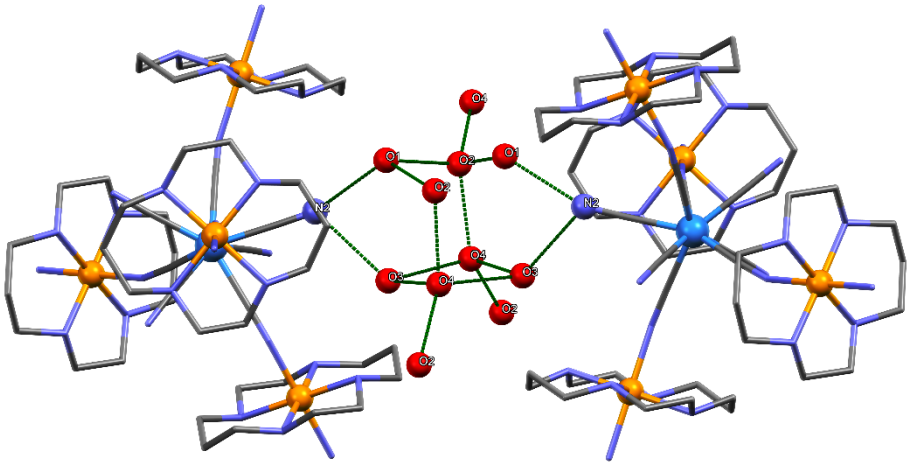

Figure S4. Hydrogen bonds in the structure of **1**.

Table S4. Hydrogen bonds in the structure of **1**.

D···A labels	D···A distance (Å)	Symmetry operations
N2-O1	2.856	x, y, z
N2-O3	3.028	-x, 1-y, z
O1-O2	2.702	x, y, z
O2-O4	2.850	x, y, z
O3-O4	2.800	x, y, z

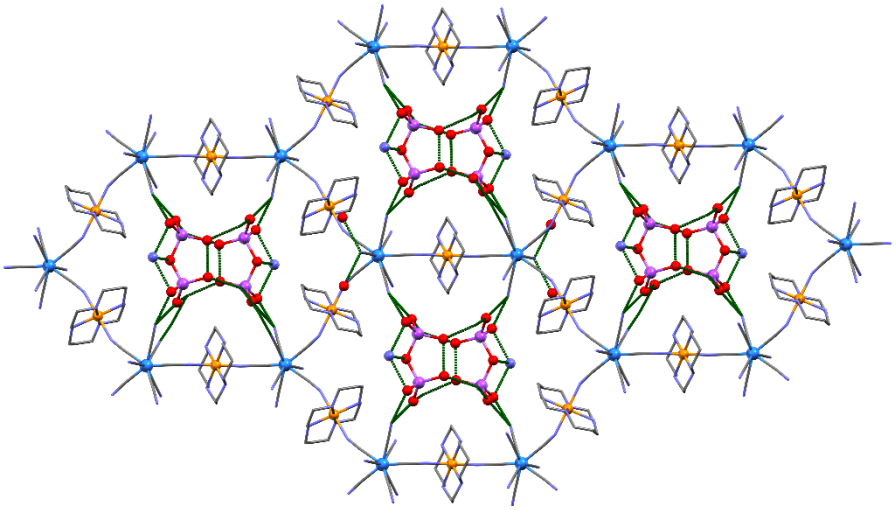

Figure S5. Hydrogen bonds in the structure of **2**.

Table S5. Hydrogen bonds in the structure of **2**.

D···A labels	D···A distance (Å)	Symmetry operations
N3-O1	2.899	x, y, z
N3-O2	2.747	x, y, z
N4-O1	2.786	1-x, 1-y, 1-z
N4-O3	3.051	1-x, 1-y, 1-z
N5-O7	2.807	x, y, z
O4-O4	2.735	x, y, z
O4-O6	2.736	x, y, z
O3-O6	2.769	x, y, z
O6-O7	2.724	x, y, z

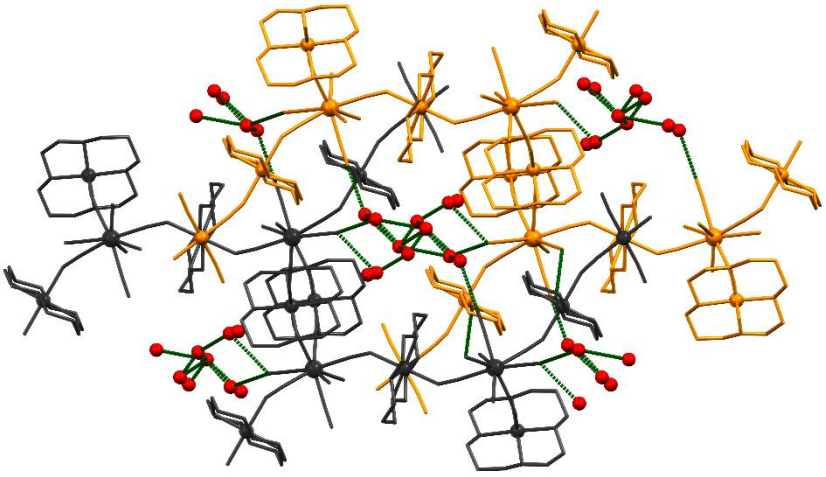

Figure S6. Hydrogen bonds in the structure of **3**.

Table S6. Hydrogen bonds in the structure of **3**.

D···A labels	D···A distance (Å)	Symmetry operations
N5-N30	3.074	x, y, z
N7-O1	3.065	1-x, 1-y, 2-z
N7-O2	2.963	1-x, 1-y, 2-z
N6-O3	2.892	x, y, z
O1-O5	3.022	x, y, z
O2-O3	2.811	x, y, z
O2-O5	2.623	x, y, z
O2-O6	3.001	x, y, z
O3-O6	2.619	x, y, z
O5-O6	1.825	x, y, z
O6-O6	2.841	x, y, z

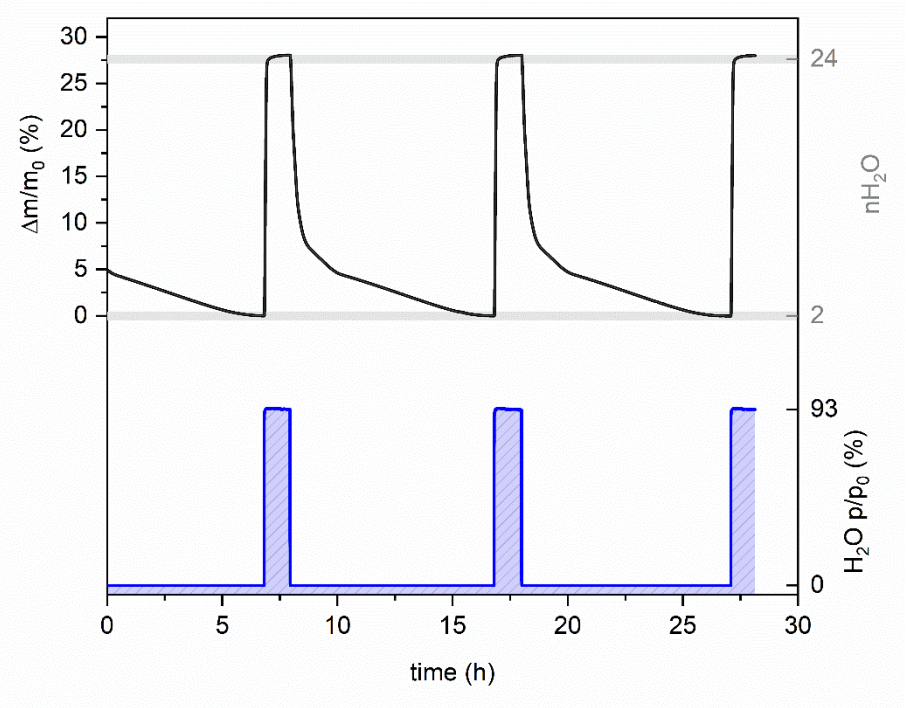

Figure S7. Relative mass change in time during sorption/desorption cycles for compound **2**.

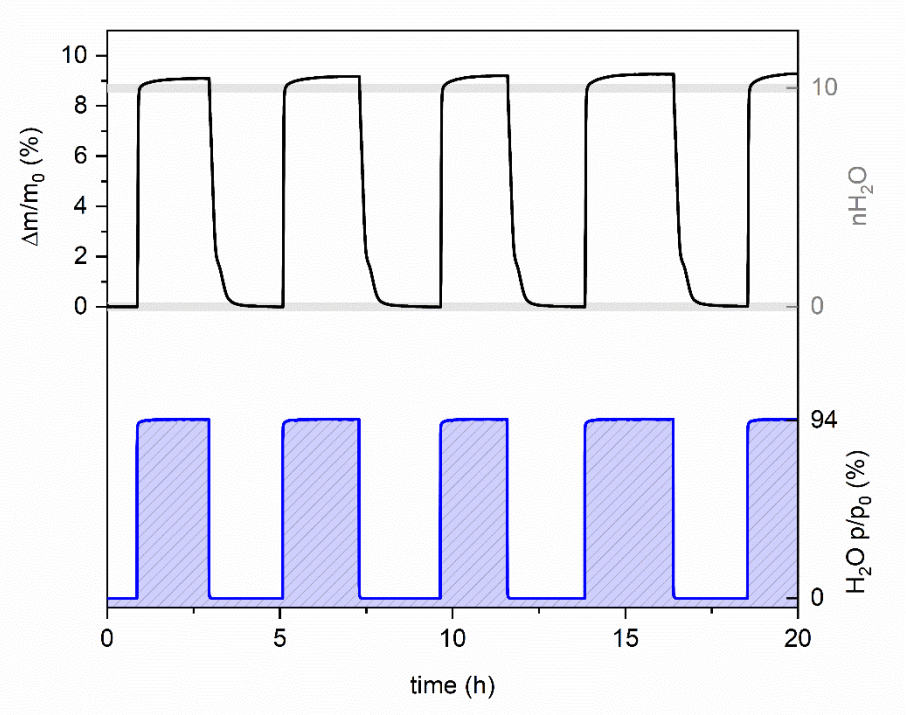

Figure S8. Relative mass change in time during sorption/desorption cycles for compound **3**.

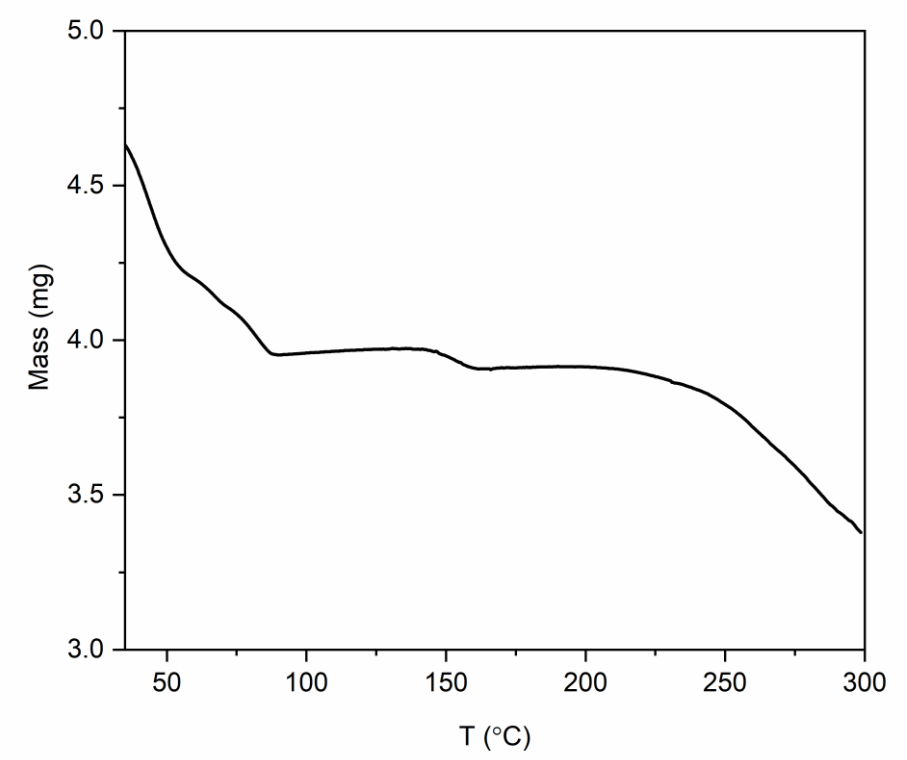

Figure S9. Thermogravimetric analysis for compound **2**.

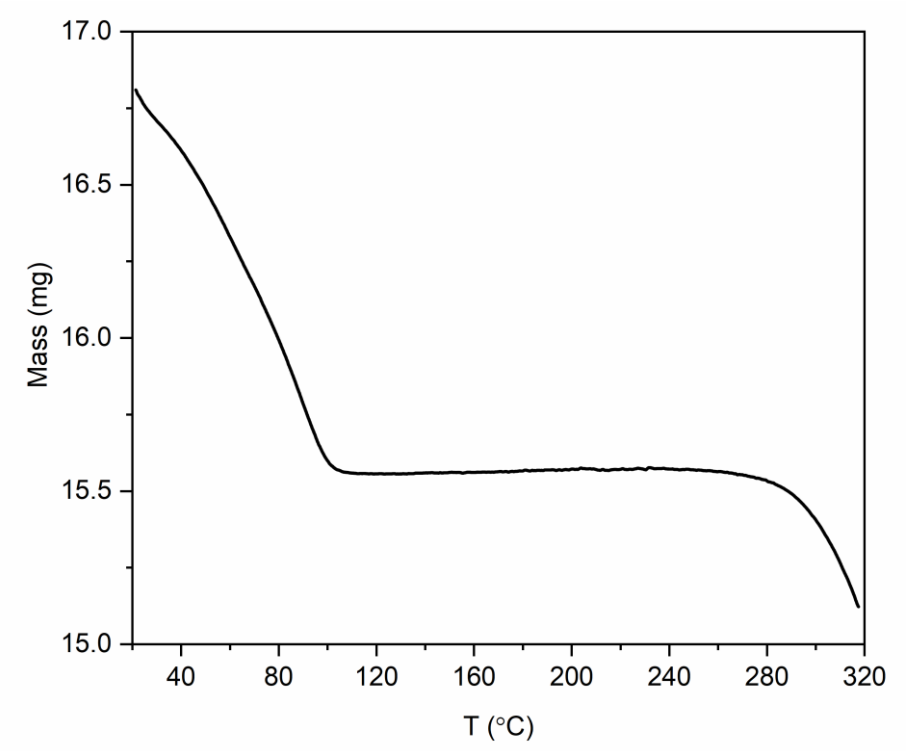

Figure S10. Thermogravimetric analysis for compound **3**.