Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary Information

Noncovalently Connected Metal−Organic Framework Assembled from Ni(III)-supported Polyoxometalate−Imidazolate Hybrid

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1. Materials and Measurements

All the chemicals were obtained from commercial sources, and were used without further purification. Elemental analyses (C, N, and H) were measured on a Perkin-Elmer 2400 CHN elemental analyzer; Si, Ni and W were determined with a Plasma-SPEC(I) ICP atomic emission spectrometer. Diffuse reflectivity was measured from 200 to 800 nm using barium sulfate ($BaSO_4$) as a standard with 100% reflectance on a Varian Cary 500 UV-Vis spectrophotometer. Single-crystal X-ray diffraction data were recorded on a Bruker D8 Venture single crystal X-ray diffractometer with Mo Kα (λ = 0.71073 Å) under low temperature 173 K. Powder X-ray diffraction measurement was recorded radiation ranging from 5º to 50º at room temperature on a Siemens D5005 diffractometer with Cu-Kα (λ = 1.5418 Å). Thermogravimetric analysis (TGA) of the samples was performed using a Perkin-Elmer TG-7 analyzer heated from room temperature to 600 ºC under nitrogen at the heating rate of 10 °C·min^{-1}. X-ray photoelectron spectroscopy analyses were performed on a VG ESCALABMKII spectrometer with an Al-Kα (1486.6 eV) achromatic X-ray source. The vacuum inside the analysis chamber was maintained at 6.2×10^{-6} Pa during the analysis.

2. Crystallographic data for 1

The suitable single crystal of compound **1** was glued on a glass fiber. Data collection was performed on a Bruker D8 Venture single crystal X-ray diffractometer with Mo Kα (λ = 0.71073 Å) under low temperature 173 K. A multiscan correction was applied. The structure was solved by the direct method and refined by full matrix least-squares on F^2 using the SHELXL program.[S1] During the refinement of these crystal structures, all non-hydrogen atoms were refined anisotropically. The H atoms on their mother carbon and nitrogen atoms were located in calculated positions and were included in the refinement riding on their respective parent atoms. The hydrogen atoms for the solvent water molecules in the crystal structure could not be located through Fourier electron density map, although they were included in the molecular formula and molecular mass. The SQUEEZE program[S2] was used to remove the contributions of disordered water solvate from the structure factor file used in the final refinement. The crystal structure of **1** contains large solvent accessible voids that are large enough to contain disordered solvent molecules. Based on charge-balance consideration,

elemental analyses, and TGA, three water molecules were included in the molecular formula directly, although the SQUEEZE data suggested that the formula unit could perhaps have contained a further 42 water molecules. Relevant crystal data and structure refinements of compound **1** are summarized in Table S1. Selected bond lengths (Å) and angles (˚) for **1** are listed in the Tables S2. Crystallographic data for **1** have been deposited in the Cambridge Crystallographic Data Center with CCDC reference number 1028317.

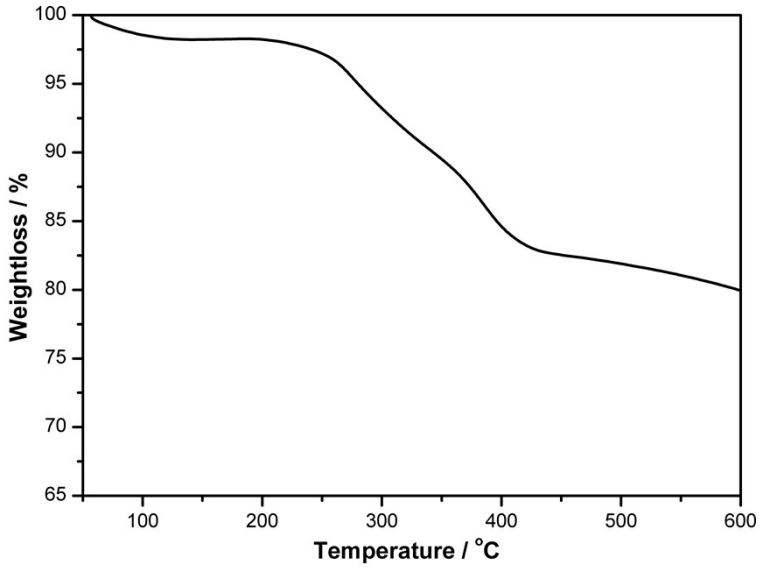

Fig. S1 The TG curve of compound **1**.

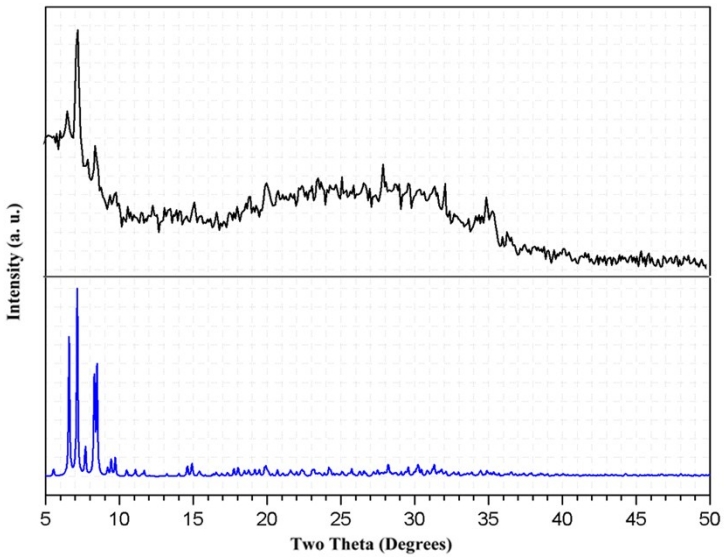

Fig. S2 The XRD pattern of the as-synthesized (blue line) and simulated pattern (black line) of **1**.

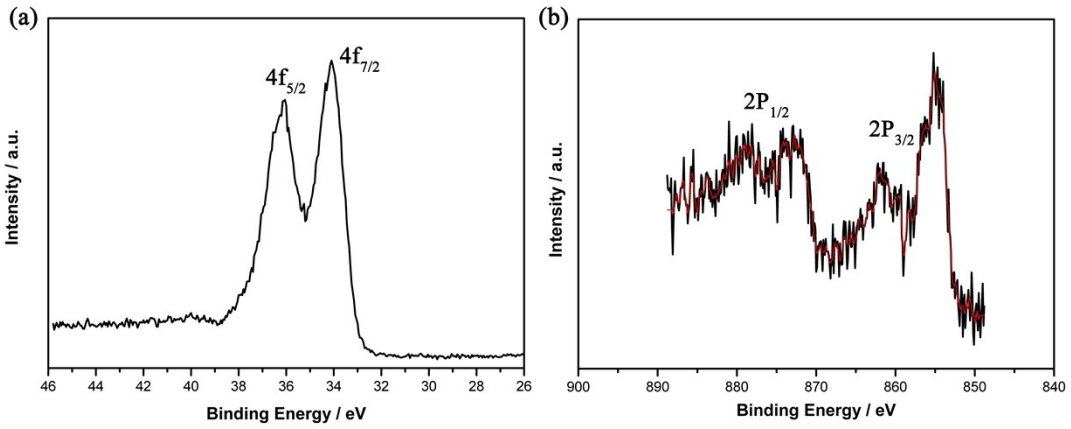

Fig. S3 XPS spectrum of compound **1**, (a) for W and (b) for Ni.

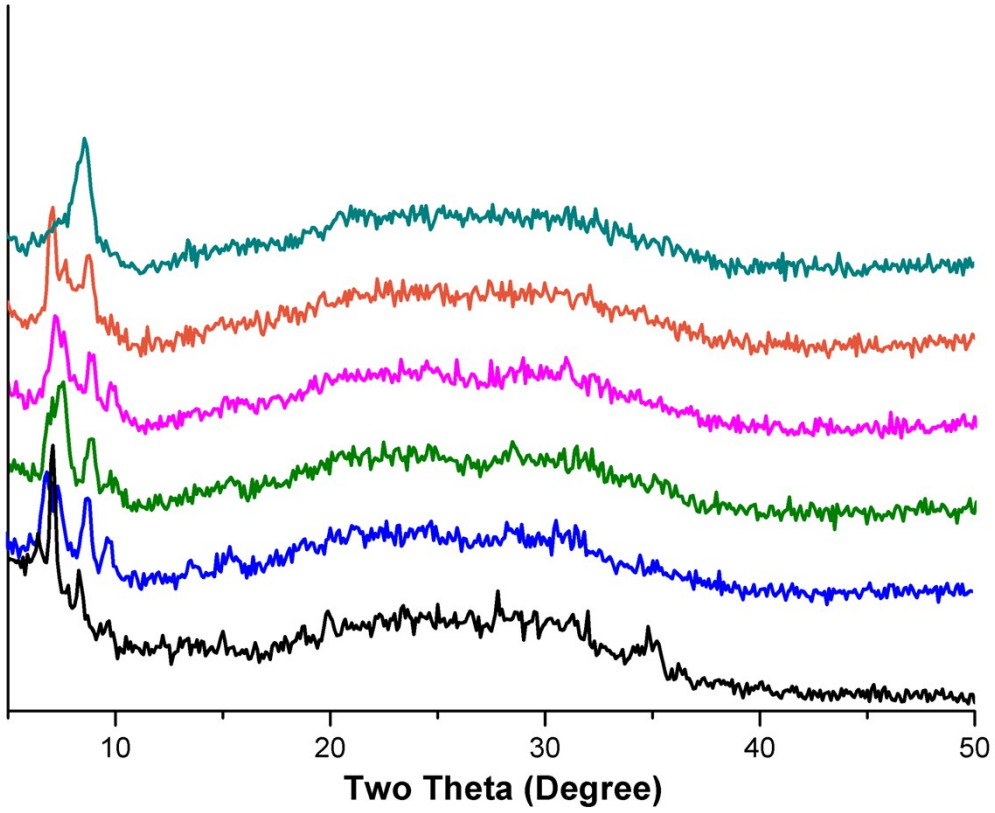

Fig. S4 The Thermodiffractograms of the as-synthesized sample (black), 100 °C (blue), 150 °C (olive), 200 °C (magenta), 250 °C (orange), 300 °C (dark cyan).

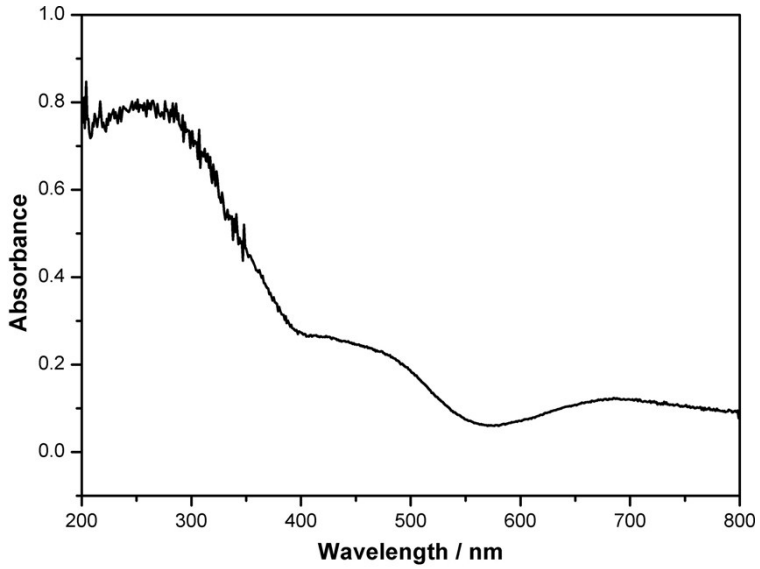

Fig. S5 UV-vis-NIR absorption spectrum of **1**.

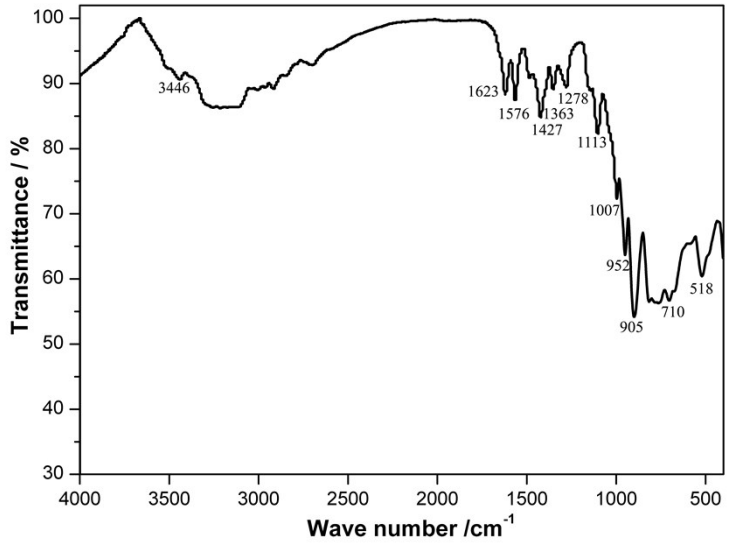

Fig. S6 IR spectrum for compound **1**.

Table S1. Crystal Data and Structural Refinement Parameters for Compound 1

	1
empirical formula	$C_{24}H_{45}N_{12}Ni_2O_{42}SiW_{11}$
Formula weight	3341.38

Crystal system	Trigonal
Space group	*R*-3
***a* (Å)**	49.6795(9)
***b* (Å)**	49.6795(9)
***c* (Å)**	23.7404(8)
***α* (º)**	90
***β* (º)**	90
***γ* (º)**	120
***V* (Å^3)**	50743(3)
Z	18
D_{calc} (mg m^{-3})	1.945
***μ* (mm^{-1})**	11.560
***T* (K)**	173 K
Reflections collected/ unique	126387/21441
GOF	1.005
R_1/wR_2 [I > 2σ(I)]	0.038/0.108

Table S2 Selected bond distances (Å) and angles (˚) for compound 1

1			
W1-O1	1.767(6)	W2-O2	1.926(6)
W1-O2	1.895(6)	W2-O25	1.965(6)
W1-O3	1.723(7)	W2-O29	2.054(6)
W1-O4	1.969(7)	W2-O30	1.732(7)
W1-O7	2.045(6)	W2-O31	1.754(6)
W1-O13	2.339(6)	W2-O32	2.334(5)
W3-O15	1.719(6)	W4-O10	1.920(6)
W3-O20	1.937(6)	W4-O18	1.721(6)
W3-O22	1.882(6)	W4-O26	1.890(6)
W3-O25	1.891(6)	W4-O28	1.916(6)
W3-O26	1.952(5)	W4-O29	1.864(6)
W3-O32	2.340(5)	W4-O32	2.380(5)
W5-O7	1.876(7)	W6-O11	1.917(7)
W5-O8	1.925(7)	W6-O17	1.717(6)
W5-O9	1.710(6)	W6-O19	1.886(6)
W5-O10	1.895(6)	W6-O28	1.900(6)
W5-O11	1.924(7)	W6-O34	2.351(5)
W5-O13	2.369(5)	W6-O38	1.916(7)
W7-O16	1.728(7)	W8-O12	1.932(7)
W7-O19	1.960(6)	W8-O27	1.922(7)
W7-O20	1.900(6)	W8-O34	2.338(6)
W7-O21	1.827(6)	W8-O36	1.832(6)
W7-O27	1.955(6)	W8-O37	1.725(8)
W7-O34	2.349(6)	W8-O38	1.972(6)
W9-O4	1.912(7)	W10-O5	1.964(7)
W9-O5	1.858(6)	W10-O24	1.929(6)
W9-O6	1.722(7)	W10-O33	2.311(5)
W9-O8	1.947(6)	W10-O35	1.734(7)
W9-O12	1.903(7)	W10-O36	2.040(6)

W9-O13	2.325(6)	W10-O39	1.773(7)
W11-O14	1.723(6)	Ni1-O1	2.007(7)
W11-O21	2.024(6)	Ni1-O23	2.042(6)
W11-O22	1.934(6)	Ni1-O31	1.992(6)
W11-O23	1.775(6)	Ni1-O33	2.208(6)
W11-O24	1.937(6)	Ni1-O39	2.049(7)
W11-O33	2.340(5)	Ni1-N1	2.005(9)
Si1-O13	1.639(6)	Ni2-N4	1.890(7)
Si1-O32	1.626(6)	Ni2-N6	1.910(8)
Si1-O33	1.621(5)	Ni2-N8	1.905(7)
Si1-O34	1.631(6)	Ni2-N10	1.906(8)
O1-W1-O2	92.7(3)	O2-W1-O13	84.5(2)
O1-W1-O4	92.0(3)	O3-W1-O1	103.8(3)
O1-W1-O7	160.7(3)	O3-W1-O2	102.1(3)
O1-W1-O13	88.2(2)	O3-W1-O4	99.3(3)
O2-W1-O4	156.2(3)	O3-W1-O7	95.5(3)
O2-W1-O7	84.2(3)	O3-W1-O13	165.8(3)
O4-W1-O7	83.7(3)	O25-W2-O29	82.7(2)
O4-W1-O13	72.4(2)	O25-W2-O32	73.3(2)
O7-W1-O13	72.5(2)	O29-W2-O32	72.2(2)
O2-W2-O25	156.2(2)	O30-W2-O2	102.2(3)
O2-W2-O29	84.5(2)	O30-W2-O25	98.9(3)
O2-W2-O32	83.7(2)	O30-W2-O29	95.0(3)
O30-W2-O31	104.9(3)	O15-W3-O20	100.7(3)
O30-W2-O32	165.5(3)	O15-W3-O22	102.4(3)
O31-W2-O2	93.1(3)	O15-W3-O25	99.1(3)
O31-W2-O25	92.1(3)	O15-W3-O26	99.1(3)
O31-W2-O29	160.0(3)	O15-W3-O32	170.6(2)
O31-W2-O32	87.8(2)	O20-W3-O26	84.7(2)
O20-W3-O32	85.4(2)	O25-W3-O26	87.7(2)

O22-W3-O20	86.7(2)	O25-W3-O32	74.4(2)
O22-W3-O25	93.6(2)	O26-W3-O32	74.2(2)
O22-W3-O26	158.0(2)	O10-W4-O32	84.3(2)
O22-W3-O32	85.0(2)	O18-W4-O10	101.6(3)
O25-W3-O20	159.7(2)	O18-W4-O26	100.3(3)
O18-W4-O28	101.3(3)	O28-W4-O10	83.9(3)
O18-W4-O29	101.0(3)	O28-W4-O32	83.7(2)
O18-W4-O32	172.5(2)	O29-W4-O10	89.6(3)
O26-W4-O10	157.7(3)	O29-W4-O26	90.5(2)
O26-W4-O28	87.6(2)	O29-W4-O28	157.6(2)
O26-W4-O32	74.3(2)	O29-W4-O32	74.2(2)
O7-W5-O8	89.2(3)	O9-W5-O8	100.0(3)
O7-W5-O10	90.5(3)	O9-W5-O10	101.4(3)
O7-W5-O11	158.7(3)	O9-W5-O11	101.5(3)
O7-W5-O13	74.6(2)	O9-W5-O13	170.9(2)
O8-W5-O13	73.0(2)	O10-W5-O8	158.3(3)
O9-W5-O7	99.7(3)	O10-W5-O11	86.6(3)
O10-W5-O13	86.0(2)	O17-W6-O28	103.3(3)
O11-W5-O8	85.9(3)	O17-W6-O34	170.4(3)
O11-W5-O13	84.2(2)	O17-W6-O38	98.5(3)
O11-W5-O14	84.4(2)	O19-W6-O11	158.1(2)
O17-W6-O11	101.7(3)	O19-W6-O28	89.9(3)
O17-W6-O19	100.1(3)	O19-W6-O34	73.8(2)
O19-W6-O38	89.4(3)	O16-W7-O19	99.4(3)
O28-W6-O11	85.9(3)	O16-W7-O20	102.2(3)
O28-W6-O34	84.4(2)	O16-W7-O21	103.4(3)
O28-W6-O38	158.0(2)	O16-W7-O27	98.9(3)
O38-W6-O11	86.7(3)	O16-W7-O34	169.1(3)
O38-W6-O34	74.3(2)	O19-W7-O34	72.6(2)
O20-W7-O19	86.8(2)	O21-W7-O34	84.7(2)

O20-W7-O27	158.3(3)	O27-W7-O19	84.9(3)
O20-W7-O34	85.1(2)	O27-W7-O34	73.3(2)
O21-W7-O19	157.2(3)	O12-W8-O34	84.6(3)
O21-W7-O20	89.0(3)	O12-W8-O38	84.7(3)
O21-W7-O27	91.0(3)	O27-W8-O12	158.5(3)
O27-W8-O34	74.1(2)	O37-W8-O12	101.7(4)
O27-W8-O38	87.0(3)	O37-W8-O27	99.2(3)
O36-W8-O12	88.9(3)	O37-W8-O34	170.5(3)
O36-W8-O27	91.3(3)	O37-W8-O36	102.4(3)
O36-W8-O34	84.6(2)	O37-W8-O38	99.7(3)
O36-W8-O38	157.8(3)	O38-W8-O34	73.7(2)
O4-W9-O8	86.8(3)	O6-W9-O4	98.7(3)
O4-W9-O13	73.7(2)	O6-W9-O5	101.3(3)
O5-W9-O4	91.7(3)	O6-W9-O8	99.6(3)
O5-W9-O8	159.0(3)	O6-W9-O12	101.8(3)
O5-W9-O12	88.4(3)	O6-W9-O13	169.9(3)
O5-W9-O13	85.8(2)	O8-W9-O13	73.7(2)
O12-W9-O4	159.1(3)	O24-W10-O33	74.5(2)
O12-W9-O8	85.8(3)	O24-W10-O36	83.8(3)
O12-W9-O13	85.5(2)	O35-W10-O5	99.7(3)
O5-W10-O33	85.5(2)	O35-W10-O24	100.0(3)
O5-W10-O36	81.2(3)	O35-W10-O33	174.4(3)
O24-W10-O5	156.4(2)	O35-W10-O36	96.7(3)
O35-W10-O39	101.8(3)	O14-W11-O21	96.4(3)
O36-W10-O33	82.0(2)	O14-W11-O22	102.2(3)
O39-W10-O5	94.1(3)	O14-W11-O23	103.4(3)
O39-W10-O24	94.5(3)	O14-W11-O24	99.9(3)
O39-W10-O33	79.8(2)	O14-W11-O33	173.4(3)
O39-W10-O36	161.4(3)	O21-W11-O33	82.1(2)
O22-W11-O21	80.4(2)	O23-W11-O33	78.6(2)

O22-W11-O24	154.8(2)	O24-W11-O21	85.2(2)
O22-W11-O33	83.9(2)	O24-W11-O33	73.6(2)
O23-W11-O21	159.9(3)	O1-Ni1-O23	167.3(2)
O23-W11-O22	91.9(3)	O1-Ni1-O33	90.7(2)
O23-W11-O24	94.7(3)	O1-Ni1-O39	91.5(3)
O23-Ni1-O33	76.8(2)	O31-Ni1-N1	93.6(3)
O23-Ni1-O39	88.2(3)	O39-Ni1-O33	76.9(2)
O31-Ni1-O1	86.2(3)	N1-Ni1-O1	93.1(3)
O31-Ni1-O23	91.4(2)	N1-Ni1-O23	99.5(3)
O31-Ni1-O33	91.0(2)	N1-Ni1-O33	174.2(4)
O31-Ni1-O39	167.7(2)	N1-Ni1-O39	98.6(3)
N4-Ni2-N6	92.9(3)	N8-Ni2-N6	88.9(3)
N4-Ni2-N8	173.9(3)	N8-Ni2-N10	90.4(3)
N4-Ni2-N10	87.9(3)	N10-Ni2-N6	178.7(4)

Table S3 Hydrogen bonding geometry (Å, °) for compound **1**

D–H···A	[ARU]	D–H	H···A	D···A	D–H···A
N(2)–H(2)···O(1)	[4666]	0.88	2.25	3.045(12)	151
N(3)–H(3A)···O(23)		0.88	2.08	2.883(13)	151
N(3)–H(3A)···O(31)		0.88	2.48	3.074(10)	126
N(5)–H(5)···O(4)	[4666]	0.88	1.94	2.804(11)	166
N(7)–H(7)···O(20)	[14554]	0.88	2.32	3.190(9)	172
N(9)–H(9)···O(8)	[17456]	0.88	1.97	2.811(14)	161
N(11)–H(11)···O(11)	[1555]	0.88	2.48	3.228(13)	144
N(11)–H(11)···O(12)	[1555]	0.88	2.44	3.146(10)	137
N(12)–H(12)···O(18)	[4667]	0.88	2.02	2.841(9)	155

Translation of ARU-Code to CIF and Equivalent Position Code

[4666] = 1-x, 1-y, 1-z

[4667] = 1-x, 1-y, 2-z

[14554] = 2/3-y, 1/3+x-y, -2/3+z

[17456] = -1/3+y, 1/3-x+y, 4/3-z

Table S4. The BVS calculation result of all the oxygen atoms in **1**

Oxygen Code	Bond Valence	Oxygen Code	Bond Valence	Oxygen Code	Bond Valence
O1	1.881	**O14**	1.687	**O27**	1.886
O2	2.034	**O15**	1.789	**O28**	2.046
O3	1.686	**O16**	1.663	**O29**	1.841
O4	1.952	**O17**	1.714	**O30**	1.646
O5	2.05	**O18**	1.696	**O31**	1.951
O6	1.691	**O19**	1.975	**O32**	1.965
O7	1.821	**O20**	1.991	**O33**	1.936
O8	1.898	**O21**	2.021	**O34**	1.963
O9	1.747	**O22**	2.051	**O35**	1.637
O10	2.05	**O23**	1.815	**O36**	1.972
O11	1.977	**O24**	1.913	**O37**	1.677
O12	1.995	**O25**	1.948	**O38**	1.861
O13	1.945	**O26**	1.983	**O39**	1.816

Table S5. The BVS calculation result of W, Ni and Si atoms in **1**

Code	Bond Valence	Code	Bond Valence
W1	6.208	**W7**	6.082
W2	6.061	**W8**	6.056
W3	6.046	**W9**	6.163
W4	6.119	**W10**	6.016
W5	6.172	**W11**	6.118
W6	6.153	**Si1**	4.112

Ni1	2.191	**Ni2**	2.682

References

[S1] G. M. Sheldrick, Acta Cryst., 2015, C71, 3-8.

[S2] A. L. Spek, Acta Cryst., 2015, C71, 9–18.