Electronic Supplementary Material (ESI) for RSC Advances.

A Ni-containing Decaniobate Incorporating Organic Ligands: Synthesis, Structure, and Catalytic for Allylic Alcohol Epoxidation

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CONTENTS

1. Bond valence sum calculations of O and Ni

Table S1 The bond valence sum calculations of all the oxygen atoms on polyanion **1**

Atom	Bond valence	Atom	Bond valence
O(1)	1.48	O(2)	1.45
O(3)	1.45	O(4)	1.45
O(5)	1.77	O(6)	1.46
O(7)	1.83	O(8)	1.80
O(9)	1.74	O(10)	1.72
O(11)	1.95	O(12)	1.69
O(13)	1.75	O(14)	1.81
O(15)	1.87	O(16)	1.88

Table S2 The bond valence sum calculations of all the Ni atoms in polyanion **1**

Bond	Bond length	Bond Valence	Valence Sum
Ni(1)–O(13)	2.012	0.380	Σ(Ni1)=1.961
Ni(1)–O(13^1)	2.012	0.380	
Ni(1)–O(15)	2.092	0.306	
Ni(1)–O(15^1)	2.091	0.307	
Ni(1)–O(16)	2.107	0.294	
Ni(1)–O(16^1)	2.107	0.294	
Ni(2)–O(11^1)	2.031	0.361	Σ(Ni2)=2.103
Ni(2)–O(14)	2.039	0.353	
Ni(2)–O(15)	2.132	0.274	
Ni(2)–O(16)	2.136	0.272	
Ni(2)–N(1)	2.061	0.431	
Ni(2)–N(2)	2.078	0.412	

2. Additional Structural Figures

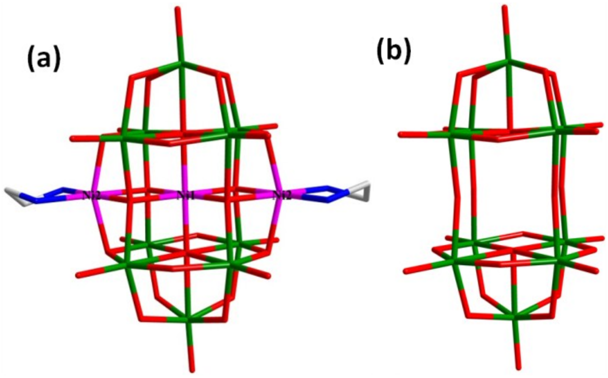


Fig. S1 (a) the structure of polyanion **1; (b)** the structure of polyanion $\{Nb_{10}\}$ or $\{W_{10}\}$

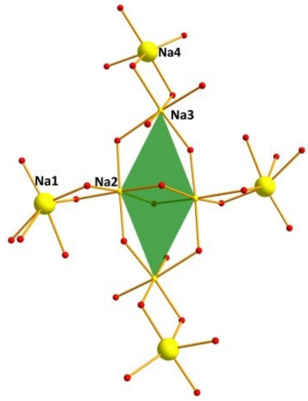


Fig. S2 Ball-and-stick representation of the $\{Na_8\}$ unit, Colour code: Na (yellow) and O (red).

3. Additional measurements

3.1 XRD

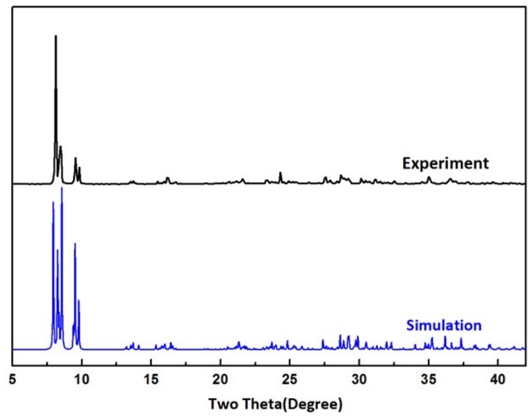


Fig. S3 Comparison of the simulated and experimental XRPD patterns

3.2 IR spectra

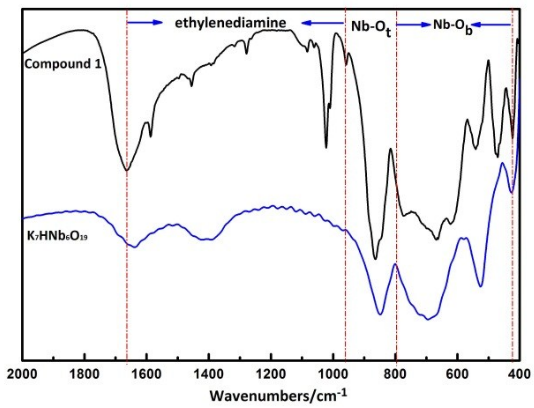


Fig. S4 The comparison of IR curves (**black**: compound **1**; **blue**: $K_7HNb_6O_{19}{\cdot}13H_2O$)

3.3 UV-vis spectra

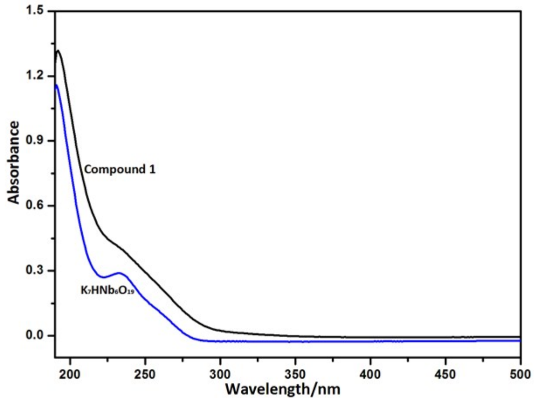


Fig. S5 The comparison of UV-vis curves (**black**: compound **1**; **blue**: $K_7HNb_6O_{19}\cdot 13H_2O$)

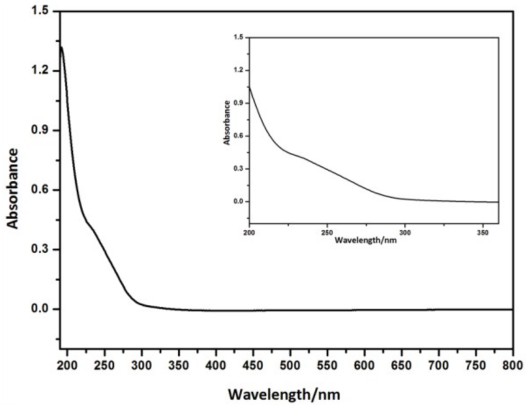


Fig. S6 The UV-vis spectra of compound **1** in the different range (**outside**: in the range of 190 to 800 nm; **inside**: in the range of 200 to 360nm.)

4. Mass spectrometric study of compound 1

Herein, ESI-MS date was obtained on AB SCIEX Triple TOF 4600 equipped with a syringe pump for direct source injection, with a Collision Energy (V) of −5, Declustering Potential (V) of −10 and an injection rate of 10 µL /min.

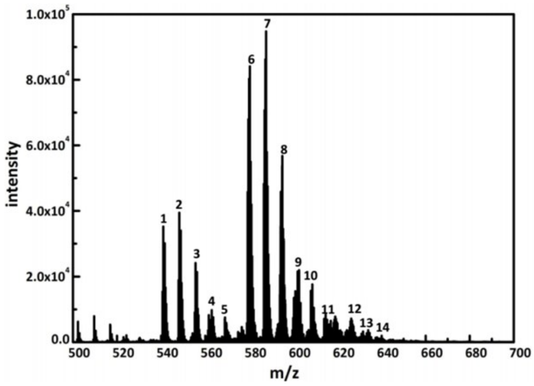


Fig. S7 The ESI mass spectrum of $\{Ni[Ni(en)]_2Nb_{10}O_{32}\}$ around *m*/*z* 587.95. Number correspond to peaks in table S3.

Table S3 Detailed assignment of mass spectral data around *m/z* 587.95

Formula	*m/z* (calcd)	*m/z* (found)	Peak Number
$[Ni_3Nb_{10}O_{32}H_5]^{3-}$	540.72	540.95	1
$[Ni_3Nb_{10}O_{32}\ NaH_4]^{3-}$	548.05	548.28	2
$[Ni_3Nb_{10}O_{32}Na_2H_3]^{3-}$	555.38	555.61	3
$[Ni_3Nb_{10}O_{32}Na_3H_2]^{3-}$	562.70	562.94	4
$[Ni_3Nb_{10}O_{32}Na_4H]^{3-}$	570.03	570.28	5
$\{Ni[Ni(en)]_2Nb_{10}O_{32}H_5\}^{3-}$	580.96	580.79	6
$\{Ni[Ni(en)]_2Nb_{10}O_{32}NaH_4\}^{3-}$	587.95	588.11	7
$\{Ni[Ni(en)]_2Nb_{10}O_{32}Na_2H_3\}^{3-}$	595.61	595.44	8
$\{Ni[Ni(en)]_2Nb_{10}O_{32}Na_3H_2\}^{3-}$	602.61	602.77	9
$\{Ni[Ni(en)]_2Nb_{10}O_{32}Na_4H\}^{3-}$	610.10	609.94	10
$\{Ni[Ni(en)]_2Nb_{10}O_{32}Na_5\}^{3-}$	617.42	617.30	11
$\{Ni[Ni(en)]_2Nb_{10}O_{32}Na_5(H_2O)\}^{3-}$	623.43	623.63	12
$\{Ni[Ni(en)]_2Nb_{10}O_{32}Na_5(H_2O)_2\}^{3}$	629.43	629.63	13
$\{Ni[Ni(en)]_2Nb_{10}O_{32}Na_5(H_2O)_3\}^{3}$	635.44	635.28	14

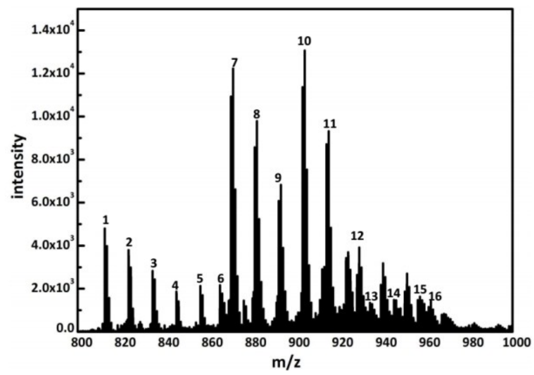


Fig. S8 The ESI mass spectrum of $\{Ni[Ni(en)]_2Nb_{10}O_{32}\}$ around *m/z* 904.45.Number correspond to peaks in table S4.

Table S4 Detailed assignment of mass spectral data around *m/z* 904.45

Formula	*m/z* (calcd)	*m/z* (found)	Peak Number
$[Ni_3Nb_{10}O_{32}H_6]^{2-}$	811.59	811.97	1
$[Ni_3Nb_{10}O_{32}NaH_5]^{2-}$	822.58	822.97	2
$[Ni_3Nb_{10}O_{32}Na_2H_4]^{2-}$	833.57	833.95	3
$[Ni_3Nb_{10}O_{32}Na_3H_3]^{2-}$	844.56	844.95	4
$[Ni_3Nb_{10}O_{32}Na_4H_2]^{2-}$	855.55	855.95	5
$[Ni_3Nb_{10}O_{32}Na_5H]^{2-}$	866.54	866.45	6
$\{Ni[Ni(en)]_2Nb_{10}O_{32}H_6\}^{2-}$	871.47	871.68	7
$\{Ni[Ni(en)]_2Nb_{10}O_{32}NaH_5\}^{2-}$	882.46	882.68	8
$\{Ni[Ni(en)]_2Nb_{10}O_{32}Na_2H_4\}^{2-}$	893.45	893.67	9
$\{Ni[Ni(en)]_2Nb_{10}O_{32}Na_3H_3\}^{2-}$	904.45	904.66	10
$\{Ni[Ni(en)]_2Nb_{10}O_{32}Na_4H_2\}^{2-}$	915.44	915.65	11
$\{Ni[Ni(en)]_2Nb_{10}O_{32}Na_5H\}^{2-}$	926.64	926.44	12
$\{Ni[Ni(en)]_2Nb_{10}O_{32}Na_6\}^{2-}$	937.63	937.43	13
$\{Ni[Ni(en)]_2Nb_{10}O_{32}Na_6(H_2O)\}^{2-}$	946.64	946.44	14
$\{Ni[Ni(en)]_2Nb_{10}O_{32}Na_6(H_2O)_2\}^{2-}$	955.65	955.96	15
$\{Ni[Ni(en)]_2Nb_{10}O_{32}Na_6(H_2O)_3\}^{2-}$	964.66	964.44	16

5. Magnetic Properties of compound 1

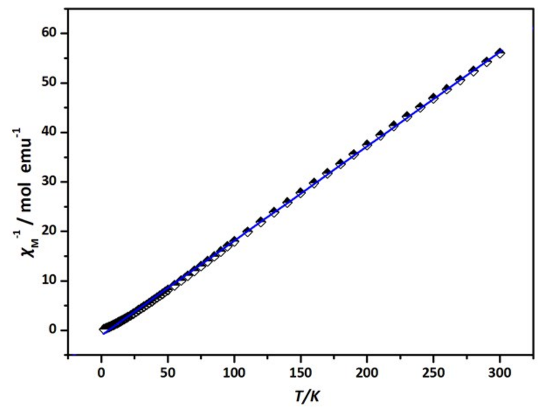
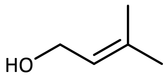
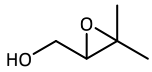
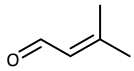
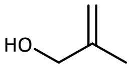
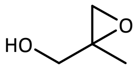
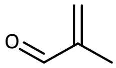
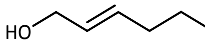
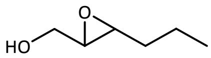
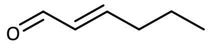
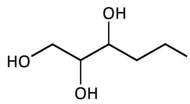
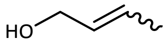
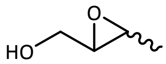
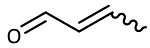
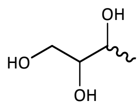


Fig. S9 The plots of χ_M^{-1} versus T in the range of 1.8–300 K.

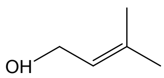
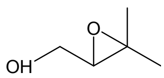
6. Catalytic properties

Table S5 Epoxidation of allylic alcohols with Catalyst **1**

Entry	Substrate	Product[c]	by-product	
1[a]				
2[b]				
3				
4				

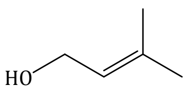
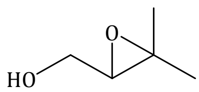
[a]Reaction conditions for the entry 1: catalyst (12 μmol), substrate (5 mmol) and H_2O (3 mL) at 25 °C. [b]Reaction conditions for the entries 2 to 4: catalyst (12 μmol), substrate (5 mmol) and H_2O (3 mL) at 35 °C. [c]The products and by-products were identified by GC-MS with dodecane as an internal standard.

Table S6 Epoxidation of 3-Methyl-2-buten-1-ol with different catalysts[a]

Entry	Catalyst	Substrate	Product	Con.[c](%)	Sel.(%)
1[b]	/			5	60
2	$Ni(NO_3)_2$			8	56
3	$K_7HNb_6O_{19}$			95	91
4	Compound **1**			98	94

[a]Reaction conditions for the entries 1 to 4: catalyst (12 μmol), substrate (5 mmol) and H_2O (3 mL) at 25 °C. [b]Blank experiment. The reaction was carried out without catalyst. [c]Conversion determined by using GC with dodecane as an internal standard. The products were identified by GC-MS.

Table S7 The conversion and selectivity of epoxidation of 3-Methyl-2-buten-1-ol carried out with the recovered catalyst and the solution at the end of the first run

Entry	Substrate	Product	Con.[d]（%）	Sel.(%)
1[a]			98	94
2[b]			8	73
3[c]			89	92

[a]Reaction conditions : catalyst (12 μmol), substrate (5 mmol), 30%H_2O_2 (8 mmol) and H_2O (3 mL) at 25 °C, 5 minutes. [b]Recovered catalyst. [c]Solution at the end of the first run. [d]Conversion determined by using GC with dodecane as an internal standard. The products were identified by GC-MS.

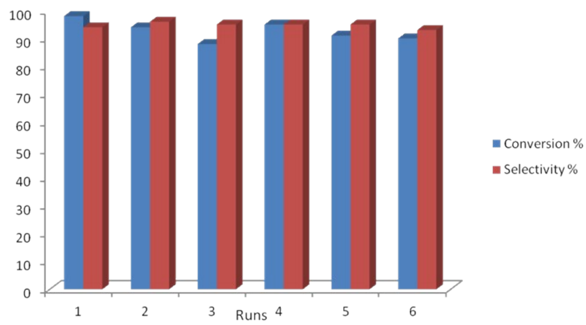


Fig. S10 Recycling of compound **1** catalytic system for the epoxidation of 3-Methyl-2-buten-1-ol.

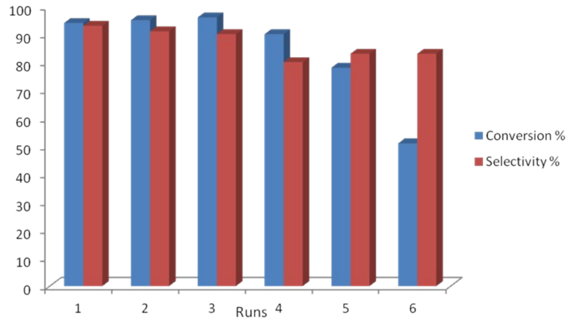
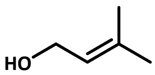
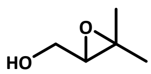
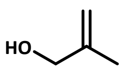
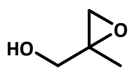
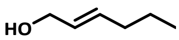
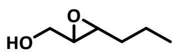
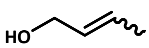
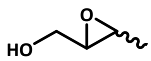


Fig. S11 Recycling of $K_7HNb_6O_{19}{\cdot}13H_2O$ catalytic system for the epoxidation of 3-Methyl-2-buten-1-ol.

Table S8 Epoxidation of various allylic alcohols with H_2O_2 in water catalyzed by $K_7HNb_6O_{19}{\cdot}13H_2O$

Entry	Substrate	Product	30%H_2O_2 (mmol)	Time (min)	Con.[b] (%)	Sel. (%)
1[a]			8	5	95	91
2			8	60	52	91
3			8	60	64	96
4			8	60	97	96

[a] Reaction conditions for the entries 1 to 4: catalyst (12 μmol), substrate (5 mmol), 30%H_2O_2 (8 mmol)and H_2O (3 mL) at 25 °C.[b] Conversion determined by using GC with dodecane as an internal standard. The products were identified by GC-MS

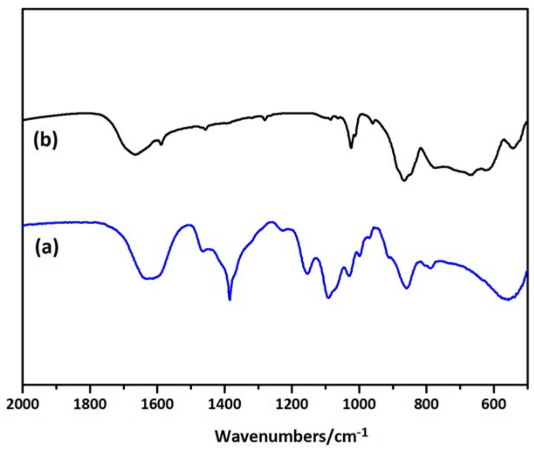
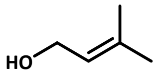
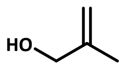
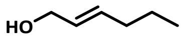
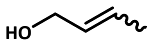


Fig. S12 IR spectra of the catalyst before and after the reaction: (a) the used catalyst; (b) the fresh catalyst.

Table S9 The efficiency of hydrogen peroxide

Reaction	Substrate	H_2O_2 efficiency [c] of Compound **1** (%)	H_2O_2 efficiency of $K_7HNb_6O_{19}·13H_2O$ (%)
1[a]		89	87
2[b]		42	55
3		51	77.3
4		69	90

[a] Reaction conditions for the entry 1: catalyst (12 μmol), substrate (5 mmol), 30% H_2O_2 (8 mmol) and H_2O (3 mL) at 25 °C, 5 min. [b] Reaction conditions for the entries 2 to 4: catalyst (12 μmol), substrate (5 mmol), 30% H_2O_2 (8 mmol)and H_2O (3 mL) at 35 °C, 60 min. [c] Residual H_2O_2 after the reaction was estimated by means of the iodometric method. H_2O_2 efficiency (%) = products (mol) /consumed H_2O_2 (mol) × 100.