A large copper-niobate cluster with pagoda-shaped subunit $\{Nb_{20}O_{59}\}$

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Materials and measurement

All the reagents were readily available from commercial sources and used without further purification. The FT-IR spectra in KBr pellets were recorded in the range 400–4000 cm^{-1} with a Perkin-Elmer Spectrum Two spectrophotometer at room temperature. Elemental analyses for C, H, N were determined with a CHNS/O Vario EL cube elemental analyzer. The thermal behavior of compound was examined by Bruker Tensor-II thermal analyses (TG, Netzsch) for confirming the number of water molecules. The samples were heated to 700 °C with a heating rate of 10 °C /min, under a flowing N_2 atmosphere. The UV-vis spectra were recorded in the range 200–800 cm^{-1} with a UH 4150 spectrograph. ESI-MS were performed on an AB SCIEX Triple TOF 4600 spectrometer. The solution was infused at a flow rate of 5 μL/min and the data were collected in negative-mode. Cu, Nb, K, Na examined by a PerkinElmer Optima 2100 DV inductively coupled plasma optical-emission spectrometer. ESR spectra were recorded with a Bruker EMXPLUS X-band spectrometer at room temperature. The magnetic field was calibrated with a Quantum Design SQUID MPMS3 magnetometer. EDS spectrum was obtained on a JSM-7610F scanning electron microscope equipped with OXFORD x-act EDS.

Synthesis

A mixture of $K_7HNb_6O_{19}\cdot 13H_2O$ (0.60 g, 0.438 mmol),[S1] $NaHCO_3$ (0.18 g, 2.1 mmol), $Cu(CH_3COO)_2\cdot H_2O$ (0.105 g, 0.526 mmol), KCl (0.097 g, 0.13 mmol) was mixed in 8 mL

deionized water. After stirred 40 min, 0.1 mL en was added. Stirring for about 20 min, the resulting mixture was sealed in a Teflon-lined autoclave (23 mL) and heated at 160 °C for 5 days. After cooling to room temperature, brownish red solution was obtained and left to evaporate slowly. Red block crystals appeared after 1 week. Yield: 10 % (based on $K_7H[Nb_6O_{19}]\cdot 13H_2O$). Anal. Calcd (%) for $C_{16}H_{263}N_{16}Cu_8K_{20}Na_{19}Nb_{144}O_{487}$: C, 0.82; H, 1.12; N, 0.95; Cu, 2.16; Nb, 56.74; K, 3.32; Na, 1.85; found: C, 1.15; H, 1.22; N, 1.03; Cu, 2.23; Nb, 56.81; K, 3.50; Na, 1.94. IR (KBr): 3313, 1631, 1591, 1486, 1459, 1330, 1278, 1103, 1043, 913, 833, 763, 705, 607, 504, 477 cm^{-1}.

X-ray Crystallography

Good quality crystal was selected and placed on a Rigaku XtaLAB Pro diffractometer with Cu Kα radiation (λ = 1.54184 Å) at 200 K. Data collection and reduction were performed using the program CrysAlisPro.[S2] The intensities were corrected for absorption using empirical method implemented in SCALE3 ABSPACK scaling algorithm. The structures were solved with direct methods,[S3] and refined by full-matrix least squares on F^2 using OLEX2.[S4] Almost all the atoms except few lattice water molecules were refined anisotropically. The hydrogen atoms of the en groups were placed in calculated positions and then refined using a riding model (U_{iso} = 1.2 U_{eq}). In addition, only 68 water molecules were achieved with the X-ray structure analysis and the remaining crystallization water molecules were estimated by thermogravimetry and CHN elemental analysis, namely $K_{20}Na_{19}[H_{18.5}\{Cu(en)_2\}_2(H_4Cu_2Nb_{72}O_{205})]_2\cdot 77H_2O$. The crystal data and structure refinement results of the compound is summarized in Table S1.

Table S1. Crystal data and structural refinement for compound **1**.

	Compound **1**
Empirical Formula	$C_{16}H_{245}N_{16}Cu_8K_{20}Na_{19}Nb_{144}O_{478}$
Formula Weight	23416.60
Temperature/K	200
Crystal System	*Monoclinic*
Space Group	$P2_1/n$
a/Å	39.8703(2)

b/Å	28.15080(10)
c/Å	63.1542(3)
β/°	92.7110(10)
Volume/Å^3	70803.7(6)
Z	4
ρ_{calc} g/cm^3	2.180
μ/mm^{-1}	20.418
F(000)	43284.0
Crystal Size/mm^3	0.16 × 0.11 × 0.08
Radiation	Cu Kα (λ = 1.54178 Å)
2ϑ Range for Data Collection/°	4.438 to 147.344
Index Ranges	-49 ≤ *h* ≤ 39, -19 ≤ *k* ≤ 34, -70 ≤ *l* ≤ 78
Reflections Collected	286571
Independent Reflections	135419 [R_{int} = 0.0578, R_{sigma} = 0.0855]
Data/Restraints/Parameters	135419/67/6227
Goodness-of-fit on F^2	1.023
Final *R* Indexes [I>=2σ (I)]	R_1 = 0.0769, wR_2 = 0.1942
Final *R* Indexes [all data]	R_1 = 0.0958, wR_2 = 0.2077
Largest Diff. Peak/hole/e Å^{-3}	3.95/-2.24

Figures and tables

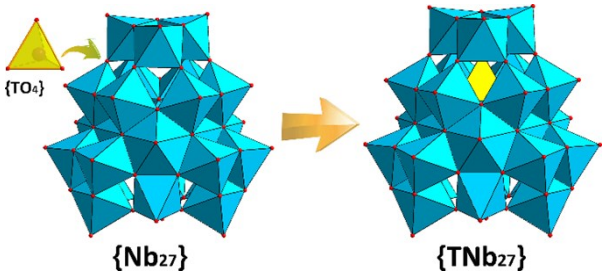


Fig. S1 Polyhedral representation of isopolyniobate {Nb_{27}} and heteropolyniobate {TNb_{27}}.

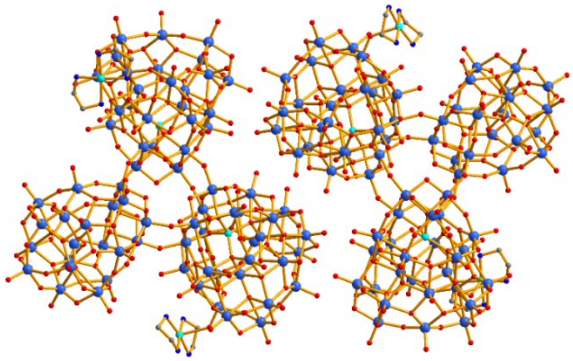


Fig. S2 Two polyoxoanions in compound **1** (Na, K atoms and H_2O molecules are omitted for clarity).

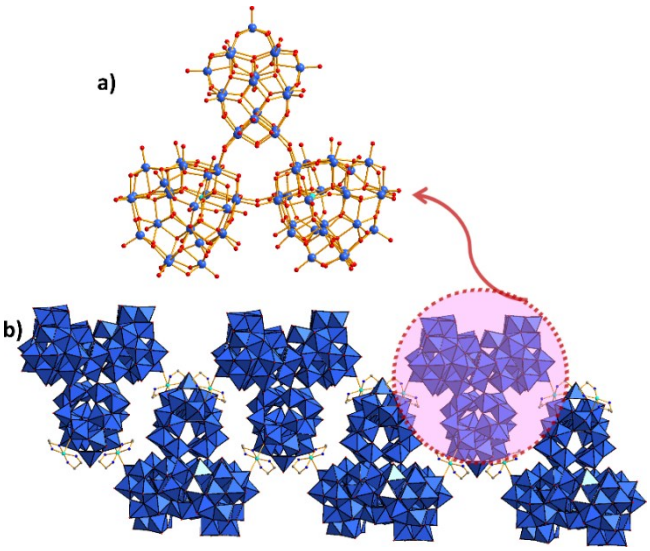


Fig. S3 a) Structural representation of polyoxoanion; b) one 1D chain structure of compound **1**.

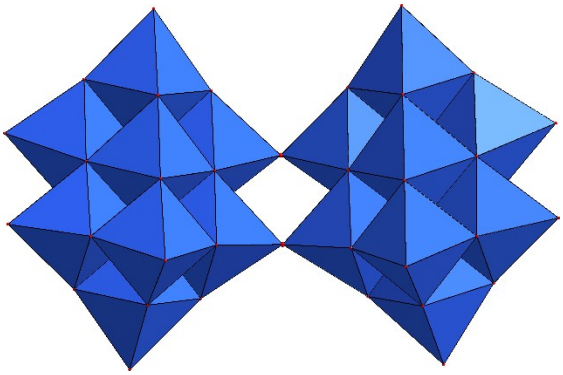


Fig. S4 Polyhedral representation of classical $[Nb_{20}O_{54}]^{8-}$.

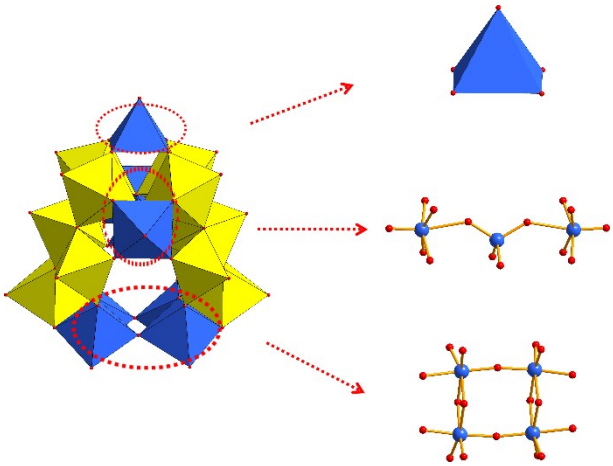


Fig. S5 Structural representations of $\{Nb_{20}O_{59}\}$ subunit and three linker between two $\{(NbO_7)Nb_5\}$ fragments.

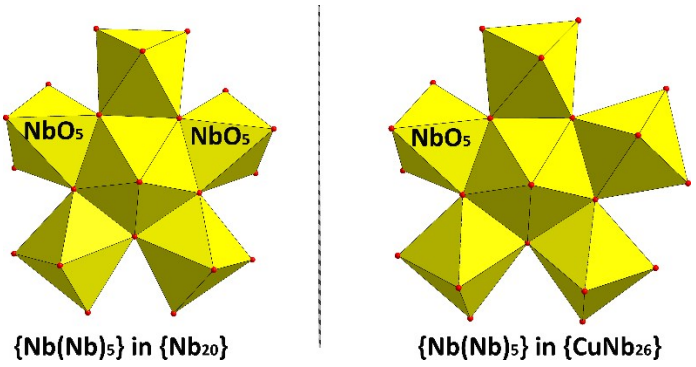


Fig. S6 $\{Nb(Nb)_5\}$ fragments in two subunits.

Table S2. The BVS of Nb atoms.

Atom	Value	Atom	Value	Atom	Value	Atom	Value
Nb1	4.91	Nb37	4.99	Nb73	5.05	Nb2E	4.74
Nb2	4.38	Nb38	4.77	Nb74	4.94	Nb3A	4.97
Nb3	4.82	Nb39	4.85	Nb75	4.56	Nb3B	4.94
Nb4	4.84	Nb40	5.02	Nb76	4.89	Nb3C	5.13
Nb5	4.96	Nb41	4.99	Nb77	5.04	Nb3D	4.97
Nb6	4.97	Nb42	5.04	Nb78	5.08	Nb3E	4.92
Nb7	5.05	Nb43	4.97	Nb79	4.93	Nb4A	4.96
Nb8	4.70	Nb44	4.94	Nb80	4.79	Nb4B	5.07
Nb9	5.02	Nb45	5.00	Nb81	5.02	Nb4C	4.93
Nb10	4.94	Nb46	4.99	Nb82	5.02	Nb4D	5.00
Nb11	4.97	Nb47	4.91	Nb83	5.12	Nb4E	5.04
Nb12	5.07	Nb48	4.96	Nb84	5.03	Nb5A	4.44
Nb13	4.99	Nb49	4.99	Nb85	5.01	Nb5B	5.07
Nb14	5.05	Nb50	4.83	Nb86	4.96	Nb5C	4.98
Nb15	4.91	Nb51	4.86	Nb87	5.06	Nb5D	5.04
Nb16	4.92	Nb52	4.91	Nb88	5.03	Nb5E	4.81
Nb17	4.65	Nb53	4.96	Nb89	4.83	Nb6A	4.98
Nb18	4.88	Nb54	4.84	Nb90	5.06	Nb6B	4.94
Nb19	4.99	Nb55	4.96	Nb91	4.89	Nb6C	4.46
Nb20	4.49	Nb56	5.14	Nb92	4.98	Nb6D	4.95
Nb21	4.87	Nb57	4.91	Nb93	4.96	Nb6E	4.90
Nb22	5.07	Nb58	4.94	Nb94	4.94	Nb7A	4.59
Nb23	4.63	Nb59	4.97	Nb95	4.89	Nb7B	4.98
Nb24	4.93	Nb60	4.94	Nb96	4.96	Nb7C	4.93
Nb25	5.09	Nb61	5.04	Nb97	4.97	Nb7D	4.98
Nb26	4.95	Nb62	4.93	Nb98	5.10	Nb7E	5.06
Nb27	4.65	Nb63	4.96	Nb99	5.02	Nb8A	4.67

Nb28	4.46	Nb64	4.97	Nb1A	5.04	Nb8B	4.51
Nb29	4.92	Nb65	4.98	Nb1B	4.57	Nb8C	5.02
Nb30	5.06	Nb66	5.04	Nb1C	4.99	Nb8D	4.99
Nb31	4.95	Nb67	4.99	Nb1D	4.90	Nb8E	5.03
Nb32	5.03	Nb68	5.02	Nb1E	5.07	Nb9A	5.20
Nb33	5.11	Nb69	4.98	Nb2A	4.50	Nb9B	4.99
Nb34	4.57	Nb70	4.72	Nb2B	4.86	Nb9C	4.84
Nb35	4.98	Nb71	4.94	Nb2C	4.93	Nb9D	4.94
Nb36	5.07	Nb72	4.99	Nb2D	5.00	Nb9E	5.02

Table S3. The BVS of oxygen atoms in polyoxoanion.

Atom	Value	Atom	Value	Atom	Value	Atom	Value
O1	1.53	O104	1.87	O207	1.49	O310	1.85
O2	1.52	O105	1.88	O208	1.69	O311	1.95
O3	1.80	O106	1.97	O209	1.56	O312	1.71
O4	1.64	O107	1.44	O210	1.60	O313	1.76
O5	1.48	O108	1.72	O211	1.52	O314	1.60
O6	1.45	O109	2.00	O212	1.60	O315	1.12
O7	1.50	O110	1.56	O213	1.74	O316	2.01
O8	1.69	O111	1.83	O214	1.60	O317	1.58
O9	1.58	O112	1.89	O215	1.91	O318	1.74
O10	1.52	O113	1.94	O216	1.64	O319	1.95
O11	1.50	O114	1.70	O217	1.59	O320	1.97
O12	1.54	O115	1.84	O218	1.79	O321	1.94
O13	1.50	O116	1.96	O219	1.76	O322	1.97
O14	1.65	O117	1.48	O220	1.50	O323	1.96
O15	1.69	O118	1.38	O221	1.77	O324	1.86
O16	1.84	O119	1.79	O222	1.61	O325	1.74
O17	1.80	O120	1.95	O223	1.48	O326	1.44
O18	1.96	O121	1.38	O224	1.84	O327	1.78
O19	1.83	O122	1.48	O225	1.59	O328	1.90
O20	1.92	O123	1.48	O226	1.63	O329	1.28
O21	1.97	O124	1.46	O227	1.45	O330	1.67
O22	1.69	O125	1.79	O228	1.53	O331	1.94
O23	1.71	O126	1.90	O229	1.86	O332	1.92
O24	1.72	O127	1.79	O230	1.60	O333	1.89
O25	1.54	O128	1.91	O231	1.81	O334	1.73
O26	1.46	O129	1.75	O232	1.62	O335	1.80
O27	1.57	O130	1.91	O233	2.44	O336	1.69

O28	1.60	O131	1.96	O234	1.55	O337	1.90
O29	1.69	O132	1.86	O235	1.89	O338	1.91
O30	1.86	O133	1.75	O236	1.82	O339	1.43
O31	1.92	O134	1.70	O237	1.86	O340	1.50
O32	1.52	O135	1.36	O238	1.72	O341	1.52
O33	1.79	O136	1.55	O239	1.68	O342	1.76
O34	1.40	O137	2.47	O240	1.66	O343	1.92
O35	1.48	O138	1.79	O241	1.82	O344	1.98
O36	1.59	O139	1.87	O242	1.79	O345	2.00
O37	1.59	O140	1.69	O243	1.93	O346	1.85
O38	1.82	O141	1.78	O244	1.83	O347	1.48
O39	1.87	O142	1.85	O245	1.90	O348	1.98
O40	1.86	O143	1.87	O246	1.97	O349	1.70
O41	1.83	O144	2.47	O247	1.91	O350	1.80
O42	1.86	O145	1.71	O248	1.96	O351	1.95
O43	1.79	O146	1.98	O249	1.83	O352	1.88
O44	1.88	O147	1.83	O250	1.50	O353	1.28
O45	1.47	O148	1.77	O251	1.49	O354	1.98
O46	1.86	O149	1.96	O252	1.47	O355	1.99
O47	1.72	O150	1.70	O253	1.81	O356	1.64
O48	1.56	O151	1.10	O254	1.53	O357	1.88
O49	1.84	O152	1.84	O255	1.69	O358	1.69
O50	1.44	O153	1.70	O256	1.98	O359	2.38
O51	1.40	O154	1.55	O257	1.50	O360	1.88
O52	1.75	O155	2.44	O258	1.59	O361	1.93
O53	1.95	O156	1.97	O259	1.89	O362	1.68
O54	1.58	O157	1.89	O260	1.90	O363	2.01
O55	1.44	O158	1.72	O261	1.74	O364	2.37
O56	1.83	O159	1.97	O262	1.61	O365	1.95
O57	1.65	O160	1.84	O263	1.76	O366	2.37
O58	1.79	O161	1.91	O264	1.84	O367	1.99
O59	1.96	O162	1.79	O265	1.27	O368	1.61
O60	1.87	O163	2.48	O266	1.89	O369	1.62
O61	1.50	O164	1.65	O267	1.45	O370	2.01
O62	1.93	O165	1.97	O268	1.89	O371	1.86
O63	1.91	O166	1.96	O269	1.97	O372	1.72
O64	1.86	O167	1.68	O270	1.93	O373	1.90
O65	1.65	O168	1.68	O271	1.41	O374	2.45
O66	1.72	O169	1.26	O272	1.81	O375	2.46
O67	1.91	O170	1.96	O273	1.55	O376	1.70
O68	1.44	O171	1.30	O274	1.51	O377	1.86

O69	1.66	O172	1.86	O275	1.64	O378	1.74
O70	1.79	O173	1.99	O276	1.43	O379	1.61
O71	1.50	O174	1.28	O277	1.71	O380	1.89
O72	1.22	O175	1.76	O278	1.45	O381	1.95
O73	1.90	O176	1.83	O279	1.85	O382	1.95
O74	1.48	O177	2.01	O280	1.75	O383	1.99
O75	1.55	O178	1.88	O281	1.87	O384	2.35
O76	1.89	O179	1.96	O282	1.92	O385	1.95
O77	1.82	O180	1.42	O283	1.70	O386	1.68
O78	1.56	O181	1.56	O284	1.91	O387	1.81
O79	1.89	O182	1.93	O285	2.43	O388	2.43
O80	1.49	O183	1.96	O286	1.52	O389	1.09
O81	1.58	O184	1.89	O287	1.46	O390	2.00
O82	1.83	O185	1.30	O288	1.81	O391	1.99
O83	1.70	O186	1.89	O289	1.56	O392	1.99
O84	1.83	O187	1.65	O290	1.65	O393	1.48
O85	1.51	O188	2.43	O291	1.99	O394	1.91
O86	1.66	O189	1.96	O292	1.72	O395	1.99
O87	1.72	O190	1.52	O293	1.98	O396	1.94
O88	1.97	O191	1.49	O294	1.97	O397	1.88
O89	1.70	O192	1.49	O295	1.49	O398	1.98
O90	1.54	O193	1.59	O296	1.88	O399	1.99
O91	1.43	O194	1.69	O297	1.52	O400	2.48
O92	2.00	O195	1.55	O298	1.66	O401	2.46
O93	1.59	O196	1.73	O299	1.92	O402	1.80
O94	1.90	O197	1.82	O300	2.02	O403	1.92
O95	1.95	O198	1.55	O301	2.01	O404	1.91
O96	1.76	O199	1.83	O302	1.07	O405	1.85
O97	1.87	O200	1.86	O303	1.73	O406	1.74
O98	1.64	O201	1.57	O304	1.93	O407	2.01
O99	1.92	O202	1.51	O305	1.69	O408	1.96
O100	1.67	O203	1.92	O306	1.69	O409	1.94
O101	1.69	O204	1.57	O307	1.42	O410	1.70
O102	1.99	O205	1.89	O308	1.78		
O103	1.89	O206	1.93	O309	1.75		

IR spectra

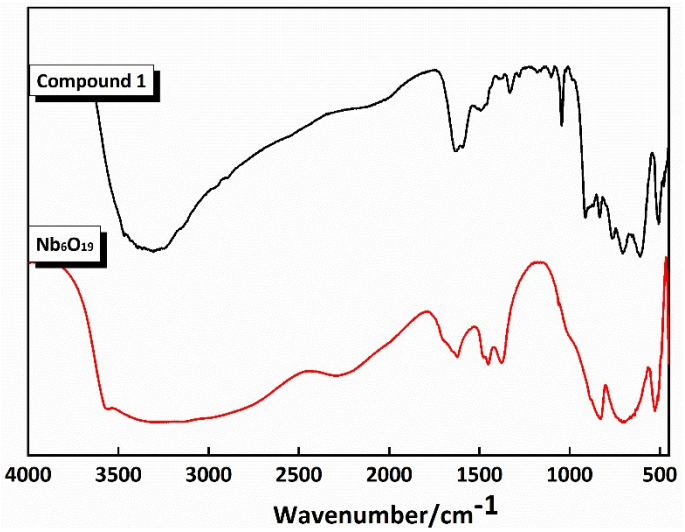


Fig. S7 IR spectra of compound **1** and {Nb_6O_{19}}.

TG analysis

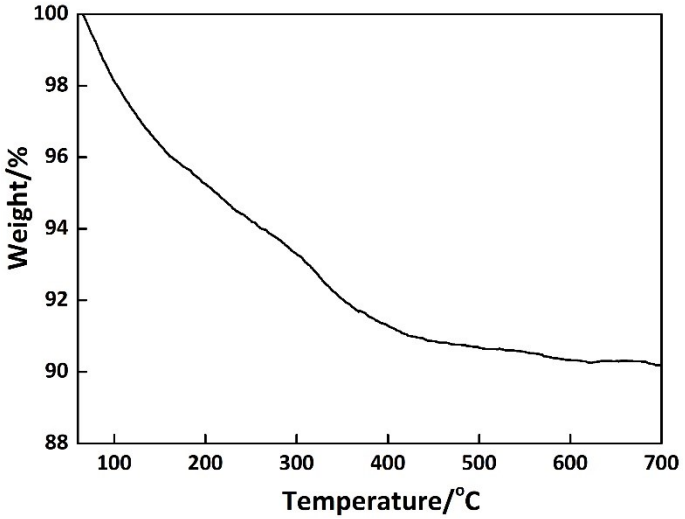


Fig. S8 TGA curve of compound **1**.

As shown in Fig. S8, the TG curve of compound **1** shows one step weight loss of 9.83 %, corresponding to the release of lattice water molecules, the dehydration of 45 protons and eight ethylenediamine molecules. Therefore, the number of lattice water molecule is 77, namely $K_{20}Na_{19}[H_{18.5}\{Cu(en)_2\}_2(H_4Cu_2Nb_{72}O_{205})]_2{\cdot}77H_2O$. The calculated value is 9.87 %.

UV spectrum

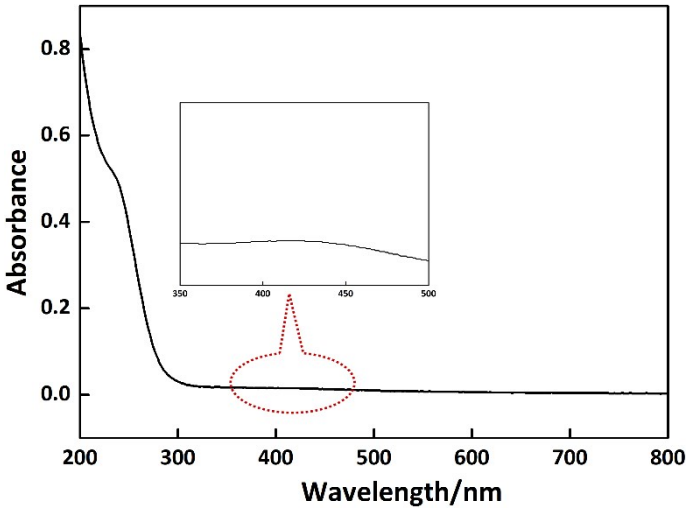


Fig. S9 UV spectrum of compound **1** (inset: a higher concentration of the compound).

EDS-TEM

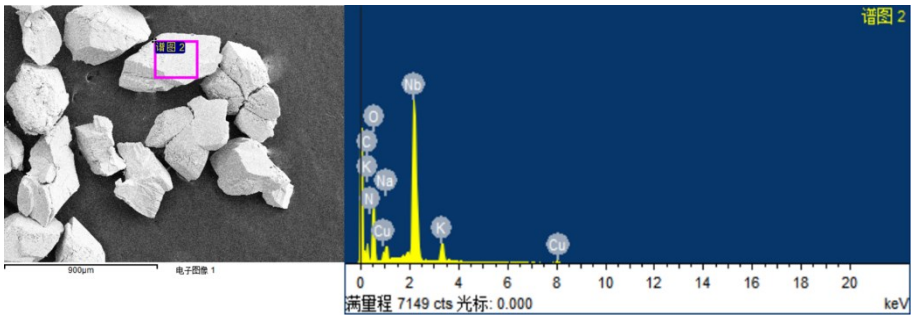


Fig. S10 The TEM of compound 1 and the EDS spectrum.

Table S4. The EDS results about the relative atomic number (based on the number of Cu) and the average value

Element	1	2	3	4	Average value
Cu	1.000	1.000	1.000	1.000	1.00
Nb	13.070	14.680	14.540	15.000	14.32
K	2.505	2.972	2.830	2.860	2.79
Na	1.866	3.000	2.610	1.930	2.35

ESI-MS analysis

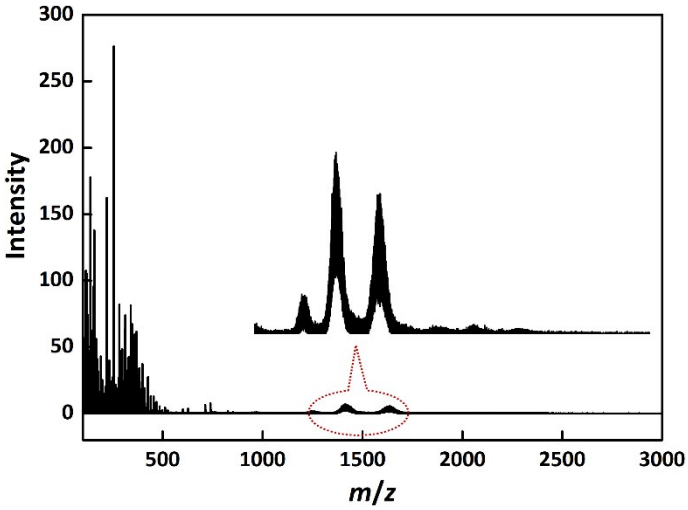


Fig. S11 ESI-MS spectra of compound **1** at *m*/*z* 100–3000.

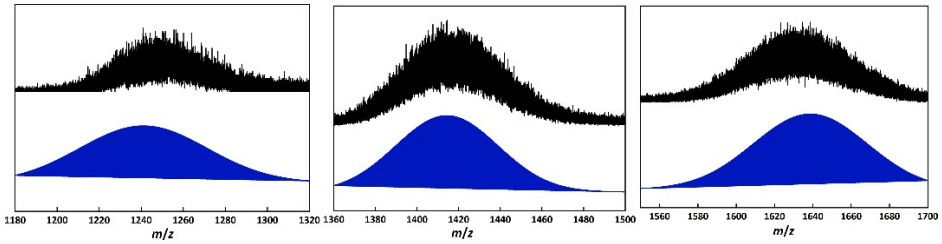


Fig. S12 Experimental (upper, black) and simulative (under, blue) peaks.

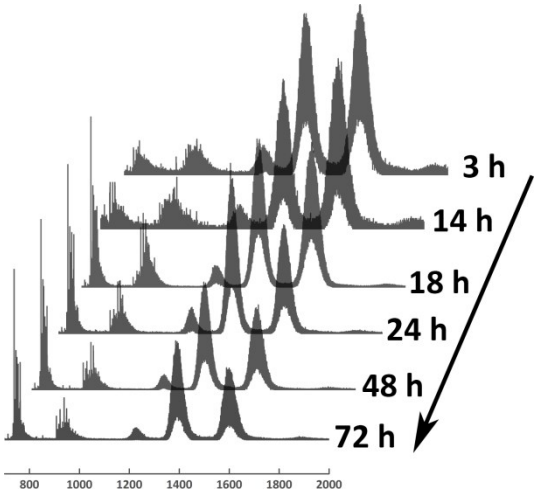
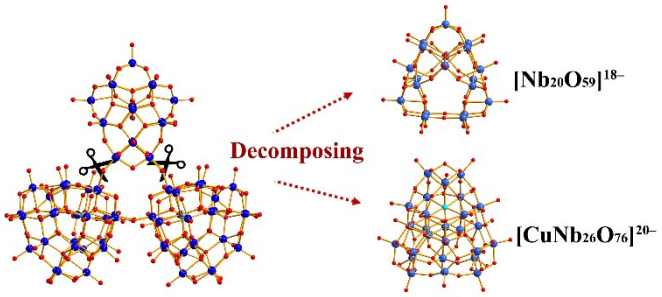


Fig. S13 Time-resolved stability of the solution of compound **1**.



$K_{20}Na_{19}[H_{18.5}\{Cu(en)_2\}_2(H_4Cu_2Nb_{72}O_{205})]_2 \cdot 77H_2O \longrightarrow$

$4[CuNb_{26}O_{76}]^{20-} + 2[Nb_{20}O_{59}]^{18-} + 20K^+ + 19Na^+ + 69H^+ + 4[Cu(en)_2(H_2O)_2]^{2+} + 57H_2O$

Fig. S14 The scheme and equation for showing the compositions of the fragmented parts.

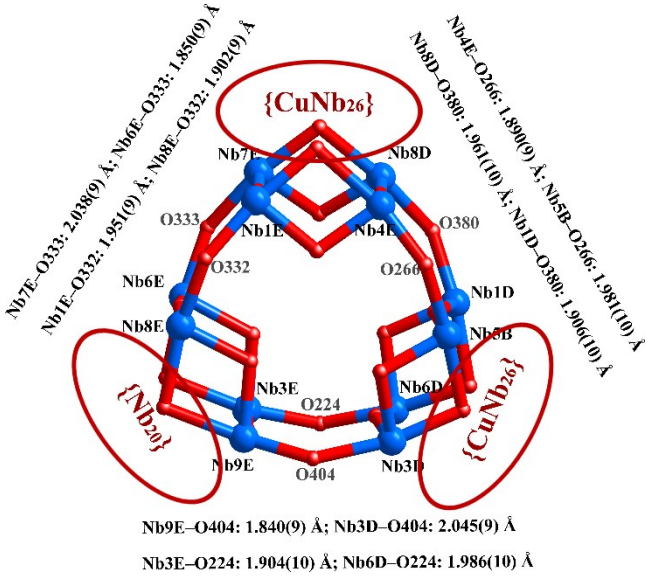


Fig. S15 The connection mode in $\{Nb_{12}\}$ cavity and the relevant Nb–O bond lengths.

Magnetic property

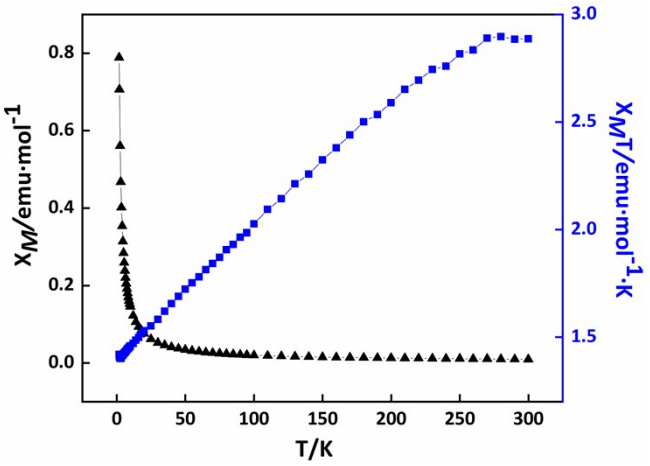


Fig. S16 Temperature dependence of χ_M and $\chi_M T$ of compound **1**.

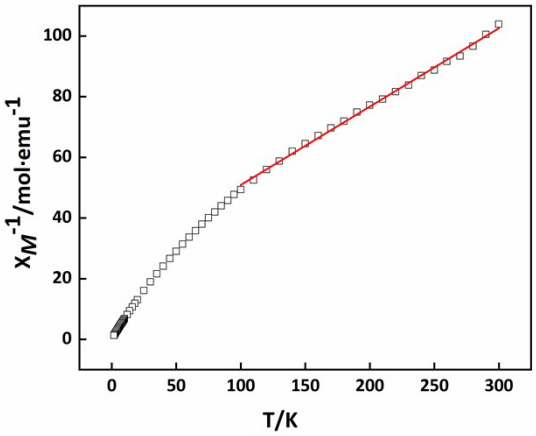


Fig. S17 Temperature dependence of $1/\chi_M$ of compound **1**.

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