Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supporting Information

A $\{Fe_3Nb_{25}\}$ cluster based on Fe-centred-Keggin unit

Zhijie Liang, Ke Wang, Dongdi Zhang, Pengtao Ma, Jingyang Niu,* and Jingping Wang*

Henan Key Laboratory of Polyoxometalate Chemistry, Institute of Molecular and Crystal Engineering,

College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, P. R. China

CONTENTS

1. Experimental Section

1.1 Materials and Methods

The IR spectra were recorded on Perkin Elmer Spectrum Two spectrometer (used KBr for solid sample palletized) in the range of 400−4000 cm^{-1}. Water contents were determined by TG analyses on a Mettler-Toledo TGA/SDTA 851^e thermal analyzer in a flowing nitrogen atmosphere with a heating rate of 10 °C min^{-1}. XRPD experiments were performed on a Bruker AXS D8 Advance diffractometer instrument with Cu Kα radiation ($\lambda = 1.54056$ Å) in the $2\vartheta = 5–45°$ range. Energy-dispersive X-ray spectroscopy (EDX) measurement was performed on an AXIS ULTRA scanning electron microscope. Elemental analyses of C, H, and N were performed with a PerkinElmer 2400-II CHNS/O analyzer. Elemental analyses (Na, K, Fe, Nb) were performed by using a PerkinEimer Optima 2100DV analyzer. ESI-MS measurements were performed on an AB SCIEX Triple TOF 4600 spectrometer operating in negative ion mode and data was analyzed using the Peakview 2.0 software provided. Variable-temperature magnetic susceptibility data were obtained on a SQUID magnetometer (Quantum Design, MPMS3) in the temperature range of 1.8-300 K.

1.2 Synthesis

Synthesis of **1**: A solution of $Fe(NO_3)_3·7H_2O$ (0.28 g, 0.70 mmol) in 1.03 mL H_2O added successively 0.11 mL en, 0.034 mL H_2O_2 and 0.73 mL HCl_{aq} (1 mol·L^{-1}) was added to a stirred solution of $K_7HNb_6O_{19}·13H_2O$ (0.65 g, 0.48mmol) in 10 mL H_2O. The pH of the resulting brick-red solution was adjusted to 10.9 with NaOH (2 mol·L^{-1}), then the solution was placed in a Teflon autoclave at 160 ° for 4 days. After slow cooling to room temperature, a brick-red solution was obtained, filtered and was transferred to a straight glass tube. Another isopropyl alcohol/water (1:3, volume ratio) solvent was carefully layered onto the resulting brick-red solution and isopropyl alcohol was carefully layered onto the mixed solvent. Diffusion between two phases produced orange-yellow block-like crystals after two weeks. Yield: (10 % based on $K_7HNb_6O_{19}·13H_2O$). Elemental analysis calcd (%) for $C_4H_{63}Fe_3K_3Na_2N_4Nb_{25}O_{93}$: C 1.11; H 1.47; N 1.30; K:Na:Fe:Nb = 3:2:3:25. Found: C 1.00; H 1.40; N 1.60; K:Na:Fe:Nb = 3.6:2.2:2.6:25. Selected characteristic FT-IR (powder) bands: 908, 856, 757, 674, 512 cm^{-1}.

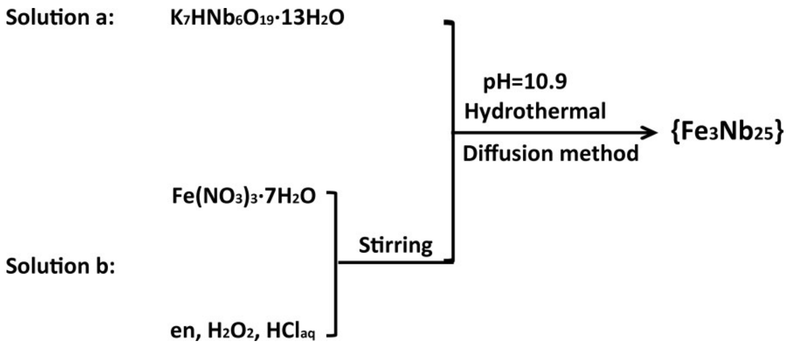


Fig. S1 The experimental process.

1.3 X-ray Crystallography

Table S1 Crystal data and structure refinement for **1.**

	1
Empirical formula	$C_4H_{63}Fe_3K_3Na_2N_4Nb_{25}O_{93}$
Formula weight	4308.98
T/K	296.15
Crystal system	Triclinic
Space group	*P-1*
λ/Å	0.71073
a/Å	16.251(3)
b/Å	16.270(5)
c/Å	26.665(5)
α/º	95.865(5)
β/º	98.824(3)
γ/º	119.937(3)
V/Å^3	5905(2)
Z	2
R_{int}	0.0533
Dc/g·cm^{-3}	2.418
Limiting indices	-19≤h≤19 -15≤k≤19 -24≤l≤31
F(000)	4062
Measured reflections	30414
Data/restraints/Parameters	20737/31/1099
μ/mm^{-1}	2.889
GOF on F^2	1.042
R_1,wR_2[$I>2\sigma(I)$]	$R1$ = 0.0998 $wR2$ = 0.2547
R_1,wR_2[all data]	$R1$ = 0.1429 $wR2$ = 0.2952

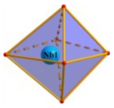
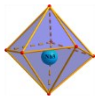
1.4 Bond Valence Sum (BVS) Calculations

Table S2 The BVS calculations of all the oxygen atoms in **1a.**

Atom	BVS	Atom	BVS	Atom	BVS	Atom	BVS
O1	1.49	O20	2.65	O39	1.82	O58	1.94
O2	1.83	O21	2.00	O40	1.98	O59	1.73
O3	1.93	O22	1.80	O41	1.53	O60	1.71
O4	1.94	O23	1.98	O42	1.44	O61	1.78
O5	1.94	O24	1.96	O43	1.60	O62	1.66
O6	1.64	O25	1.82	O44	1.83	O63	1.47
O7	1.96	O26	1.84	O45	1.78	O64	1.69
O8	1.91	O27	1.95	O46	1.91	O65	1.41
O9	1.99	O28	1.78	O47	1.82	O66	1.81
O10	1.92	O29	2.02	O48	1.74	O67	1.55
O11	1.93	O30	1.96	O49	1.50	O68	1.51
O12	1.93	O31	1.73	O50	1.76	O69	1.81
O13	1.99	O32	1.87	O51	1.75	O70	1.97
O14	1.95	O33	1.55	O52	1.99	O71	1.55
O15	1.98	O34	1.75	O53	1.50	O72	1.70
O16	1.33	O35	1.69	O54	1.42	O73	1.72
O17	1.94	O36	1.37	O55	1.53	O74	1.55
O18	1.93	O37	1.94	O56	1.85	O75	1.47
O19	1.52	O38	1.36	O57	1.45	O76	1.72
Fe1	2.93	Fe2	3.20	Fe3	3.24	Fe4	3.03

2. Additional Structural Table and Figures

Table S3 The geometry configuration of Nb and Fe atoms in **1a.**

Atom	Coordination number	Geometry configuration	Coordination configuration
Nb1	6	Octahedron	
Nb2	5	Tetragonal-pyramid	
Nb3	7	Pentagonal-bipyramid	

Fe1	4	Tetrahedron	

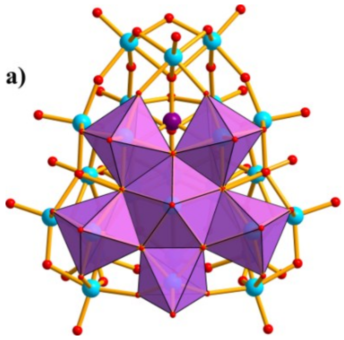


Fig. S2 One of the {Nb(Nb)$_5$} moieties and the distance of Nb···Nb.

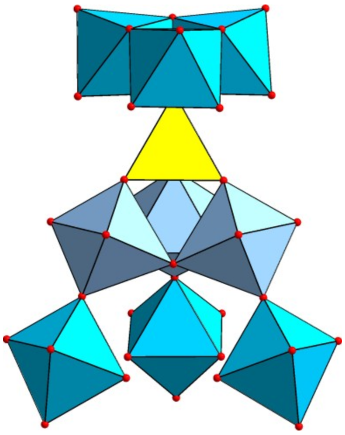


Fig. S3 The tripod formed by {Nb_3O_{13}} and three {$Fe_{0.67}Nb_{1.33}O_{11}$} as well as {FeO_4}.

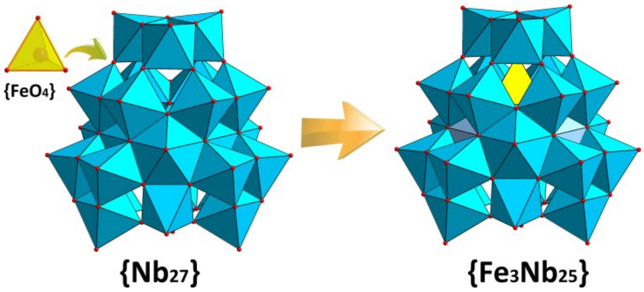


Fig. S4 Representation of {Nb_{27}} and {Fe_3Nb_{25}}.

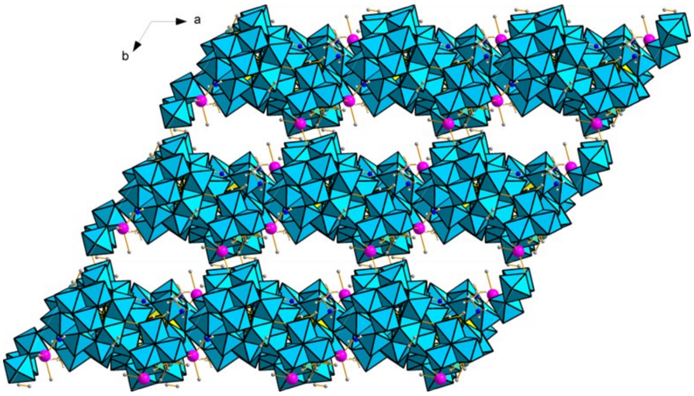


Fig. S5 Packing arrangement of **1**.

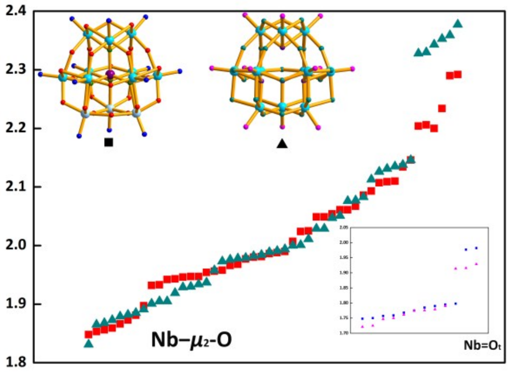


Fig. S6 The comparison of Nb–μ_3-O bond lengths in $\{Fe_3Nb_{10}\}$ (■) of **1a** and $\{Nb_{12}\}$ (▲) of $[HNb_{27}O_{76}]^{16-}$.

3. Additional Measurements

3.1 X-ray Powder Diffractograms

As shown in Fig. S7, the prominent diffraction peaks of experimental pattern match well with the simulated pattern indicating that the samples are pure. However, there are some differences in reflection intensities between them. It may be due to the scanning speed and the variation in preferred orientation.

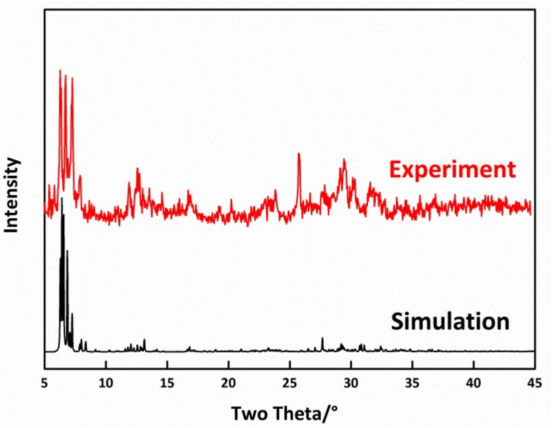


Fig. S7 The XRPD patterns for experiment (top) and simulation (bottom) of **1**.

3.2 IR Spectra

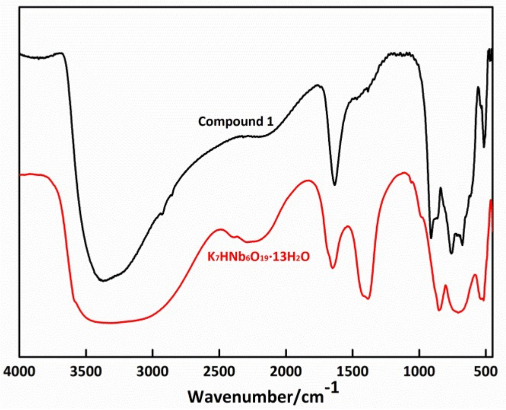


Fig. S8 The IR spectra of $K_7HNb_6O_{19}\cdot 13H_2O$ and compound **1**.

3.3 Thermogravimetric analysis

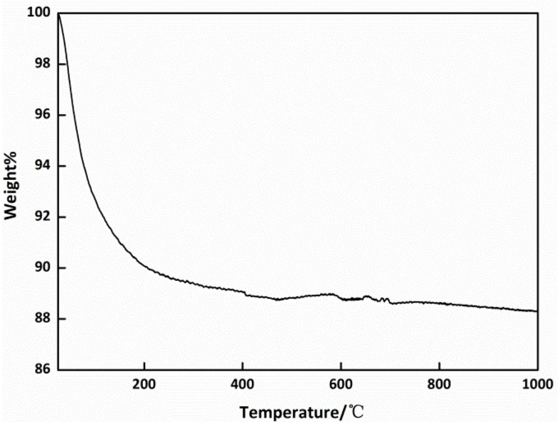


Fig. S9 Thermogravimetric curve of **1**.

3.4 SEM-EDX Spectrum

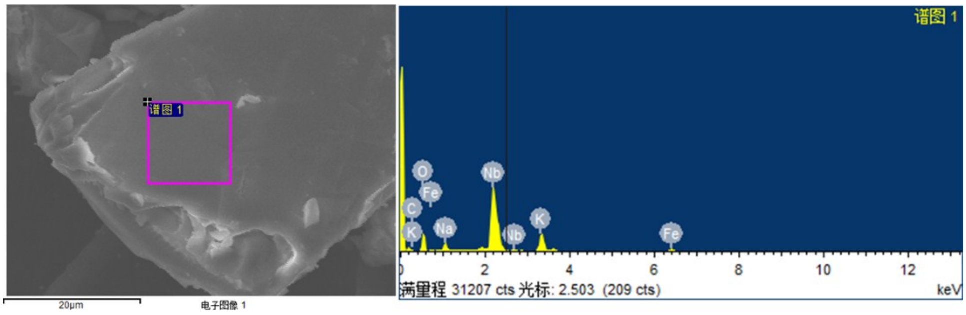


Fig. S10 SEM image and EDX spectrum of single crystal of **1.**

3.5 Magnetic Property

The temperature dependence of the magnetic susceptibility of **1** was measured from 1.8 to 300 K in an applied magnetic field of 1000 Oe. The plot of χ_M and $\chi_M T$ versus T is shown in Fig. S11. This further indicates the presence of the Fe ions.

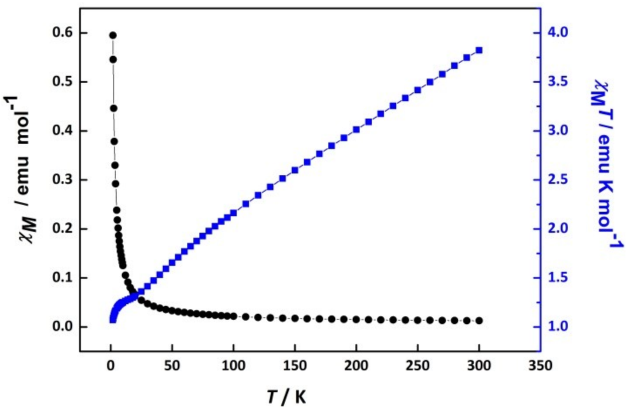


Fig. S11 Plots of temperature dependence of χ_M (●) and $\chi_M T$ (■) for **1** under 1000 Oe field between 1.8 and 300 K.

4. Mass Spectrometric Study of the Compound

These solutions were filtered and introduced to the spectrometer *via* direct injection at a flow rate of 5 μL min^{-1} using a syringe pump. Spectrometer settings were kept the same throughout and were as follows: ionspray voltage: -4500 V, curtain gas flow, 25 PSI; ion source gas 1, 15 PSI ; ion source gas 2, 15 PSI; ion energy 1, -1.1 V; pulser frequency, 11.332 KHz; pulse 1 duration, 3.902 us; declustering potential, -10 V; collision energy, -5.0 V.

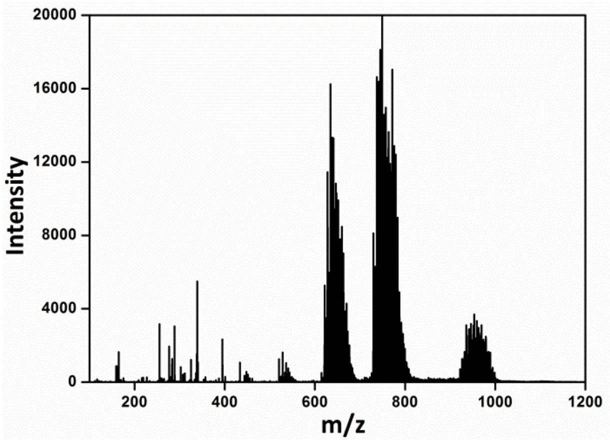


Fig. S12 The ESI-MS of **1** (the overall scale).

Table S4 The assignment of mass spectral data for compound **1.**

m/z (obs.)	Peaks Assignment	*m/z* (calc.)
528.62	$[H_{10}K_8Na_4Nb_{15}O_{51}(H_2O)]^{5-}$	528.48
634.73	$[H_{12}Fe_3Nb_{25}O_{76}(H_2O)_5]^{6-}$	634.72
757.25	$[H_{10}Na_3Fe_3Nb_{25}O_{76}]^{5-}$	757.04
953.55	$[H_{13}NaFe_3Nb_{25}O_{76}(H_2O)_4]^{4-}$	953.58