

Supplementary Information

Recent Studies on the Reaction of $[X_6O_{19}]^{8-}$ (X=Nb, Ta) Polyanions under Acidic Conditions

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Table S1. A summary of PONbs and POTas synthesized under acid conditions.

Molecular formula	Corresponding author	Article	Year
Lindqvist-type Mixed-PONb clusters			
Cs ₄ Na[Ta ₃ W ₃ O ₁₉]·6H ₂ O	M. Nyman	<i>Dalton Trans.</i> , 2015, 44, 15813.	2015
Cs ₅ [NbW ₉ O ₃₂]·7.5H ₂ O	M. Nyman	<i>Dalton Trans.</i> , 2015, 44, 15813.	2015
Cs ₅ [TaW ₉ O ₃₂]·6.5H ₂ O	M. Nyman	<i>Dalton Trans.</i> , 2015, 44, 15813.	2015
Cs ₆ [Ta ₂ W ₈ O ₃₂]·6H ₂ O	M. Nyman	<i>Dalton Trans.</i> , 2015, 44, 15813.	2015
Keggin-type Mixed-PONb clusters			
[(CH ₃) ₃ NH] ₇ [Si(NbO ₂) ₃ W ₉ O ₃₇]	Craig L. Hill	<i>J. Med. Chem.</i> , 1994, 37, 816.	1994
Cs ₇ [Si(NbO ₂) ₃ W ₉ O ₃₇]	Craig L. Hill	<i>J. Med. Chem.</i> , 1994, 37, 816.	1994
α-K ₅ [Si(NbO ₂)W ₁₁ O ₃₉]	Craig L. Hill	<i>J. Med. Chem.</i> , 1994, 37, 816.	1994
α-[(CH ₃) ₃ NH] ₅ [Si(NbO ₂)W ₁₁ O ₃₇]	Craig L. Hill	<i>J. Med. Chem.</i> , 1994, 37, 816.	1994
(<i>n</i> -Bu ₄ N) ₄ [PNbW ₁₁ O ₄₀]	ROBERT H. BEER	<i>Polyhedron</i> , 1995, 14, 2139.	1995
(<i>n</i> -Bu ₄ N) ₄ [PTaW ₁₁ O ₄₀]	ROBERT H. BEER	<i>Polyhedron</i> , 1995, 14, 2139.	1995
(TBA) ₄ H ₂ [(NbO ₂) ₃ PW ₉ O ₃₇]	Craig L. Hill	<i>Inorg. Chem.</i> , 1998, 37, 5550.	1998

(TBA) ₄ H ₂ [Nb ₃ PW ₉ O ₄₀]	Craig L. Hill	<i>Inorg. Chem.</i> , 1998, 37, 5550.	1998
(TBA ₃)H ₃ [Nb ₆ P ₂ W ₁₈ O ₇₇]	Craig L. Hill	<i>Inorg. Chem.</i> , 1998, 37, 5550.	1998
Cs ₂₀ [Nb ₄ O ₆ (α-Nb ₃ SiW ₉ O ₄₀) ₄]	Craig L. Hill	<i>Angew. Chem.</i> , 1999, 38, 3205.	1999
A-α-[Si ₂ Nb ₆ W ₁₈ O ₇₇] ⁸⁻	Craig L. Hill	<i>Chem. Commun.</i> , 1999, 1651.	1999
A-α-Cs ₆ H[Si(NbO ₂) ₃ W ₉ O ₃₇]·9H ₂ O	Gyu-Shik Kim	<i>Bull. Korean Chem. Soc.</i> , 2003, 24, 1005.	2003
Cs _{6.5} K _{0.5} [GeW ₉ (NbO ₂) ₃ O ₃₇]·6H ₂ O	Lin Xu, Shu-Xia Liu	<i>Chem. Eur. J.</i> , 2010, 16, 13435.	2010
Cs _{6.5} K _{0.5} [GeW ₉ Nb ₃ O ₄₀]·10H ₂ O	Lin Xu, Shu-Xia Liu	<i>Chem. Eur. J.</i> , 2010, 16, 13435.	2010
Cs ₅ [H ₁₅ Ge ₂ W ₁₈ Nb ₈ O ₈₈]·18H ₂ O	Lin Xu, Shu-Xia Liu	<i>Chem. Eur. J.</i> , 2010, 16, 13435.	2010
Cs ₈ K ₃ H ₉ [Ge ₄ W ₃₆ Nb ₁₆ O ₁₆₆]·27H ₂ O	Lin Xu, Shu-Xia Liu	<i>Chem. Eur. J.</i> , 2010, 16, 13435.	2010
Cs ₃ K ₄ [(Ge ₂ W ₁₈ Nb ₆ O ₇₈)Eu(H ₂ O) ₄]·23H ₂ O	Shu-Xia Liu	<i>CrystEngComm.</i> , 2012, 14, 1397.	2012
Cs ₈ K ₉ [(Ge ₄ W ₃₆ Nb ₁₂ O ₁₅₆)Eu(H ₂ O) ₃]·25H ₂ O	Shu-Xia Liu	<i>CrystEngComm.</i> , 2012, 14, 1397.	2012
Cs ₁₂ K ₂ [Cs(GeW ₉ Nb ₃ O ₄₀) ₄ (SO ₄)Eu ₅ (H ₂ O) ₃₆]·61H ₂ O	Shu-Xia Liu	<i>CrystEngComm.</i> , 2012, 14, 1397.	2012
Cs _{12.5} K _{1.5} [Cs ₂ (GeW ₉ Nb ₃ O ₄₀) ₄ Eu ₄ (H ₂ O) ₂₂]·28H ₂ O	Shu-Xia Liu	<i>CrystEngComm.</i> , 2012, 14, 1397.	2012
Cs _{11.5} [(GeW ₉ Nb ₃ O ₄₀) ₄ Eu _{5.5} (H ₂ O) ₂₆]·24H ₂ O	Shu-Xia Liu	<i>CrystEngComm.</i> , 2012, 14, 1397.	2012
CsK _{2.25} [GeW ₉ Nb ₃ O ₄₀ Eu _{1.25} (H ₂ O) ₁₂]·8H ₂ O	Shu-Xia Liu	<i>CrystEngComm.</i> , 2012, 14, 1397.	2012
Cs ₅ K[AsW ₉ (NbO ₂) ₃ O ₃₇]·7H ₂ O	Shu-Xia Liu	<i>Inorg. Chim. Acta.</i> , 2011, 376, 296.	2011
Cs _{5.5} Na _{0.5} [AsW ₉ Nb ₃ O ₄₀]·17H ₂ O	Shu-Xia Liu	<i>Inorg. Chim. Acta.</i> , 2011, 376, 296.	2011
Cs ₁₀ K ₃ H ₃ [As ₄ W ₃₆ Nb ₁₆ O ₁₆₆]·28H ₂ O	Shu-Xia Liu	<i>Inorg. Chim. Acta.</i> , 2011, 376, 296.	2011
Cs ₅ KH[(Si ₂ W ₁₈ Nb ₆ O ₇₈)Cr(H ₂ O) ₄]·11H ₂ O	Xin-Long Wang, Yan Xing, Zhong-Min Su	<i>ChemPlusChem.</i> , 2013, 78, 775.	2013
Cs ₄ [(Si ₂ W ₁₈ Nb ₆ O ₇₈)Cr ₂ (H ₂ O) ₈]·14H ₂ O	Xin-Long Wang, Yan Xing, Zhong-Min Su	<i>ChemPlusChem.</i> , 2013, 78, 775.	2013
Cs ₄ K ₄ H[(Si ₂ W ₁₈ Nb ₆ O ₇₈)FeCl ₂ (H ₂ O) ₂]·13.5H ₂ O	Xin-Long Wang, Yan Xing, Zhong-Min Su	<i>ChemPlusChem.</i> , 2013, 78, 775.	2013
Cs ₁₉ K ₂ [Nb ₄ O ₆ (SiW ₉ Nb ₃ O ₄₀) ₄]Cl·27H ₂ O	Liang Zhao, Zhong-Min Su	<i>Inorg. Chem. Commun.</i> , 2014, 44, 195.	2014
[H ₃ La ₈ (H ₂ O) ₃₂ (C ₆ H ₅ NO ₂) ₆][SiW ₉ Nb ₃ O ₄₀] ₃ ·8H ₂ O	Chao Qin, Zhong-Min Su	<i>New J. Chem.</i> , 2017, 41, 10532.	2017
[Cu ^I Cu ^{II} ₃ (μ ₃ -OH)(H ₂ O) ₆ (trz) ₃] ₂ (PW ₉ Nb ₃ O ₄₀)·13H ₂ O	Bin Yue, Heyong He	<i>Dalton Trans.</i> , 2018, 47, 233.	2018
[Cu ^I Cu ^{II} ₃ (μ ₃ -OH)(H ₂ O) ₄ (Htrz)(trz) ₃] ₂ (PW ₉ Nb ₃ O ₄₀)·13H ₂ O	Bin Yue, Heyong He	<i>Dalton Trans.</i> , 2018, 47, 233.	2018
K ₆ H ₃ [Nb ₂ K(H ₂ O) ₄ (A-α-SiW ₉ O ₃₄) ₂]·23H ₂ O	Jingyang Niu	<i>Inorg Chem Commun.</i> , 2012, 17, 75.	2012

$\text{Cs}_{10}\text{Na}_3[(\text{SiW}_9\text{Nb}_3\text{O}_{38})_3\text{MnO}_3(\text{H}_2\text{O})_3] \cdot 18\text{H}_2\text{O}$	Dongdi Zhang, Jingyang Niu	<i>Dalton Trans.</i> , 2016, 45, 15236.	2016
$\text{Cs}_{12}[(\text{SiW}_9\text{Nb}_3\text{O}_{38})_3\text{WO}_3(\text{OH})_3] \cdot 33\text{H}_2\text{O}$	Jingyang Niu, Dongdi Zhang	<i>RSC Adv.</i> , 2017, 7, 36416.	2017
Wells-Dawson-type Mixed-PONb clusters			
$\text{K}_6\text{Na}_4\text{H}_8[\text{Ln}_6(\text{H}_2\text{O})_{38}(\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62})_4] \cdot 45\text{H}_2\text{O}$ Ln=Eu, Ce	Shu-Xia Liu	<i>Eur. J. Inorg. Chem.</i> , 2012, 3229.	2012
$[(n\text{-C}_4\text{H}_9)_4\text{N}]_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$	Richard G. Finke	<i>Inorg. Chem.</i> , 2014, 53, 2666.	2014
$\text{Na}_{12}[\text{H}_{24}\{\text{Nb}_4\text{O}_6(\text{OH})_4\}\{\text{Nb}_6\text{P}_2\text{W}_{12}\text{O}_{61}\}_4] \cdot 24\text{H}_2\text{O}$	Jingping Wang, Jingyang Niu	<i>Inorg. Chem.</i> , 2014, 53, 9917.	2014
$\text{K}_7[\text{H}_{13}\{\text{Nb}_6(\text{O}_2)_4\text{P}_2\text{W}_{12}\text{O}_{57}\}_2] \cdot 31\text{H}_2\text{O}$	Jingping Wang, Jingyang Niu	<i>Inorg. Chem. Front.</i> , 2015, 2, 254.	2015
$(\text{NH}_4)_{16}[\text{H}_{14}\{\text{P}_2\text{W}_{12}\text{Nb}_7\text{O}_{63}(\text{H}_2\text{O})_2\}_4\{\text{Nb}_4\text{O}_4(\text{OH})_6\}_4] \cdot 16\text{H}_2\text{O}$	Jingping Wang, Jingyang Niu	<i>Inorg. Chem. Front.</i> , 2015, 2, 254.	2015
$\text{K}_{10}[\text{H}_{123}\text{Nb}_3\text{P}_{12}\text{W}_{72}\text{Mn}^{\text{III}}_{12}\text{Mn}^{\text{II}}_3\text{NaO}_{424}] \cdot 26\text{H}_2\text{O}$	Jingping Wang, Jingyang Niu	<i>Chem. Eur. J.</i> , 2015, 21, 17683.	2015
$(\text{TMA})_2\text{K}_5[\text{H}_5(\text{Nb}_6\text{P}_2\text{W}_{12})_2\text{Co}_3(\text{H}_2\text{O})_{11}\text{O}_{121}] \cdot 31\text{H}_2\text{O}$	Tianbo Liu, Jingyang Niu	<i>Inorg. Chem.</i> , 2020, 59, 6747.	2020
$\text{K}_4\text{Na}_4[\text{H}_6\text{P}_2\text{W}_{12}\text{Nb}_4\text{O}_{59}(\text{NbO}_2)_2] \cdot 48\text{H}_2\text{O}$	Bin Yue, Heyong He	<i>Inorg. Chem. Commun.</i> , 2014, 40, 108.	2014
$[\text{Ag}_{25}\{\text{C}\equiv\text{CC}(\text{CH}_3)_3\}_{16}(\text{CH}_3\text{CN})_4(\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62})]$	Tomoji Ozeki	<i>Inorg. Chem.</i> , 2015, 54, 1650.	2015
$\text{Cs}_5\text{K}_4\{\text{Cr}_3(\text{H}_2\text{O})_{12}[\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]_2\} \cdot 60\text{H}_2\text{O}$	Chao Qin, Chao Lai, Zhong-Min Su	<i>Dalton Trans.</i> , 2017, 46, 13345.	2017
$\text{Cs}_{13}\text{K}_5\text{NaH}_3\{\text{Cr}_4(\text{H}_2\text{O})_{12}[\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]_4\} \cdot 13\text{H}_2\text{O}$	Chao Qin, Chao Lai, Zhong-Min Su	<i>Dalton Trans.</i> , 2017, 46, 13345.	2017
$\text{Cs}_9[\text{P}_2\text{W}_{15}(\text{NbO}_2)_3\text{O}_{59}] \cdot 16\text{H}_2\text{O}$	Chao Qin, Chao Lai, Zhong-Min Su	<i>Dalton Trans.</i> , 2017, 46, 13345.	2017
$\text{H}_4\{\text{Er}_3[3\text{-PyB}(\text{OH})_3]_4(\text{H}_2\text{O})_{12}\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}\} \cdot 19\text{H}_2\text{O}$	Jie Zhang, Xuenian Chen	<i>Chem. Commun.</i> , 2019, 55, 2525.	2019
$\text{H}_3\{[\text{Er}_2[3\text{-PyB}(\text{OH})_2(\text{H}_2\text{O})_{11}][\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]] \cdot 25\text{H}_2\text{O}$	Jie Zhang, Xuenian Chen	<i>Chem. Commun.</i> , 2019, 55, 2525.	2019
$\text{H}_3\{[\text{Eu}_2[3\text{-PyB}(\text{OH})_2(\text{H}_2\text{O})_{11}][\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]] \cdot 11\text{H}_2\text{O}$	Jie Zhang, Xuenian Chen	<i>Chem. Commun.</i> , 2019, 55, 2525.	2019
$\text{K}_8\text{H}[\text{P}_2\text{W}_{15}(\text{NbO}_2)_3\text{O}_{59}] \cdot 12\text{H}_2\text{O}$	Lunyu Qu	<i>Polyhedron.</i> , 1996, 15, 2273.	1996
$\text{H}_{19}[\text{M}_4(\text{H}_2\text{O})_x(\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62})_3] \cdot m(\text{HCOOH}) \cdot n\text{H}_2\text{O}$ (M = Cu, Co, Mn, Zn)	Shujun Li, Xuenian Chen	<i>Dalton Trans.</i> , 2021, 50, 8690.	2021
$\text{Na}_4\text{H}_2[(3\text{-PyB})_4(\text{P}_2\text{W}_{15}\text{Ta}_3\text{O}_{62})_4] \cdot 7\text{C}_5\text{H}_5\text{N} \cdot 45\text{H}_2\text{O}$	Zhiping Zheng, Carsten Streb, Xuenian Chen	<i>Angew. Chem. Int. Ed.</i> , 2020, 59, 8537.	2020
$\text{Na}_2\text{H}_{26}[(3\text{-PyB})_4(\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62})_4] \cdot 2\text{C}_5\text{H}_5\text{N} \cdot 37\text{H}_2\text{O}$			
$\text{Eu}_3\text{Na}_{20.5}\text{K}_{2.5}\text{H}_{54}[\text{K}_4(\text{P}_2\text{W}_{15}\text{Ta}_3\text{O}_{62})_{12}(5\text{-PymB})_3(5\text{-PymBOH})_{12}] \cdot 94\text{H}_2\text{O}$	Zhiping Zheng, Carsten Streb, Xuenian Chen	<i>Angew. Chem. Int. Ed.</i> , 2020, 59, 8537.	2020
$\text{Na}_{15}\text{H}_{71}[\text{K}_4(\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62})_{12}(5\text{-PymB})_3(5\text{-PymBOH})_{12}] \cdot 99\text{H}_2\text{O}$			
$\text{NaH}_{15}\{\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}\}_2(4\text{PBA})_2((4\text{PBA})_2\text{O}) \cdot 53\text{H}_2\text{O}$	Shujun Li, Carsten Streb, Xuenian Chen	<i>Angew. Chem. Int. Ed.</i> , 2021, 60, 16953.	2021
$\text{H}_{27}[(4\text{PyB})_3\text{O}_2(\text{OH})_3][\text{Ln}_2(\text{H}_2\text{O})_{12}(\text{P}_2\text{Nb}_3\text{W}_{15}\text{O}_{62})_4(4\text{PyBOH})_4] \cdot x\text{H}_2\text{O}$	Shujun Li, Carsten Streb, Xuenian Chen	<i>Angew. Chem. Int. Ed.</i> , 2023, 62, e202314999.	2023

$K_2Na_2H_3[(Fe(H_2O)_4)_3(P_2W_{15}Nb_3O_{62})_2] \cdot 24H_2O$	Shujun Li, Bing Yu, Xuenian Chen	<i>Chinese Chem. Lett.</i> , 2022, 33, 4395.	2022
$K_2Na_3H_4[(Cr(H_2O)_4)_3(P_2W_{15}Nb_3O_{62})_2] \cdot 32H_2O$	Shujun Li, Bing Yu, Xuenian Chen	<i>Chinese Chem. Lett.</i> , 2022, 33, 4395.	2022
$K_4Na_8H_4\{[Nb_4O_6(H_2O)_4Na_4(H_2O)_8][LaP_2W_{12}Nb_6O_{61}(H_2O)_7]_4\} \cdot 60H_2O$	Bin Yue, Heyong He	<i>Polyhedron</i> , 2021, 195, 114974.	2021
$K_4Na_8H_4\{[Nb_4O_6(H_2O)_4Na_4(H_2O)_8][CeP_2W_{12}Nb_6O_{61}(H_2O)_7]_4\} \cdot 58H_2O$	Bin Yue, Heyong He	<i>Polyhedron</i> , 2021, 195, 114974.	2021
$K_4Na_8H_4\{[Nb_4O_6(H_2O)_4Na_4(H_2O)_8][PrP_2W_{12}Nb_6O_{61}(H_2O)_7]_4\} \cdot 78H_2O$	Bin Yue, Heyong He	<i>Polyhedron</i> , 2021, 195, 114974.	2021
$K_4Na_8H_4\{[Nb_4O_6(H_2O)_4Na_4(H_2O)_8][NdP_2W_{12}Nb_6O_{61}(H_2O)_7]_4\} \cdot 66H_2O$	Bin Yue, Heyong He	<i>Polyhedron</i> , 2021, 195, 114974.	2021
$H_{14}[(Co(H_2O)_3)_2(C_{10}H_8N_2)_4(P_4W_{30}Nb_6O_{123})] \cdot 4(C_{10}H_8N_2) \cdot 8H_2O$	Shujun Li, Bing Yu	<i>ACS Appl. Mater. Interfaces</i> , 2022, 14, 19278.	2022
Keggin-type Mixed-POTa clusters			
$Cs_3K_{3.5}H_{0.5}[SiW_9(TaO_2)_3O_{37}] \cdot 9H_2O$	Shuxia Liu	<i>J. Am. Chem. Soc.</i> , 2012, 134, 19716.	2012
$Cs_{10.5}K_4H_{5.5}[Ta_4O_6(SiW_9Ta_3O_{40})_4] \cdot 30H_2O$	Shuxia Liu	<i>J. Am. Chem. Soc.</i> , 2012, 134, 19716.	2012
$CsNa_2H[Cu(bpy)(H_2O)_3]_3\{[Cu(bpy)_2][Cu(bpy)(H_2O)_2]_3[Ta_4O_6(SiW_9Ta_3O_{40})_4]\} \cdot 17H_2O$ (bpy=2,2'-bipyridine)	Zhi-Ming Zhang, En-Bo Wang	<i>ChemPlusChem</i> , 2014, 79, 1153.	2014
$K_4Na_4H_4[Ta_4O_6(SiW_9Ta_3O_{40})_4][Cu(apy)(H_2O)_2]_4 \cdot 42H_2O$ (apy=3-aminopyridine)	Zhi-Ming Zhang, En-Bo Wang	<i>ChemPlusChem</i> , 2014, 79, 1153.	2014
$Cs_3K_2[(Si_2W_{18}Ta_6O_{78})Cr(H_2O)_4] \cdot 8H_2O$	Chao Qin, Zhong-Min Su	<i>CrystEngComm</i> , 2016, 18, 8722.	2016
$Cs_3K_4H_2[(Si_2W_{18}Ta_6O_{78})FeCl_2(H_2O)_2] \cdot 15H_2O$	Chao Qin, Zhong-Min Su	<i>CrystEngComm</i> , 2016, 18, 8722.	2016
$Cs_{12.5}K_{4.5}H[Ta_{12}Si_4W_{37}O_{158}] \cdot 25H_2O$	Chao Qin, Zhong-Min Su	<i>Dalton Trans.</i> , 2017, 46, 10177.	2017
$Cs_{12}K_3H_7[MnTa_{18}Si_6W_{54}O_{231}] \cdot 61H_2O$	Chao Qin, Peng Huang, Zhong-Min Su	<i>Chem. Commun.</i> , 2020, 56, 2403.	2020
Wells-Dawson-type Mixed-POTa clusters			
$K_5Na_4[P_2W_{15}O_{59}(TaO_2)_3] \cdot 17H_2O$	Shuxia Liu	<i>J. Am. Chem. Soc.</i> , 2012, 134, 19716.	2012
$K_8Na_8H_4[P_8W_{60}Ta_{12}(H_2O)_4(OH)_8O_{236}] \cdot 42H_2O$	Shuxia Liu	<i>J. Am. Chem. Soc.</i> , 2012, 134, 19716.	2012
$Cs_{16}K_{16}Na_4[Ta_{18}P_{12}W_{90}(OH)_6(H_2O)_2O_{360}] \cdot 24H_2O$	Chao Qin, Zhong-Min Su	<i>Chem. Commun.</i> , 2016, 52, 13787.	2016
$Cs_{26}K_2H_2[Yb_2Ta_{18}P_{12}W_{90}(OH)_6(H_2O)_{16}O_{360}] \cdot 52H_2O$	Chao Qin, Zhong-Min Su	<i>Chem. Commun.</i> , 2016, 52, 13787.	2016
$H_{20}[P_8W_{60}Ta_{12}(H_2O)_4(OH)_8O_{236}] \cdot 125H_2O$	Xuenian Chen, Fengji Ma, Jie Zhang	<i>J. Solid State Chem.</i> , 2016, 243, 1.	2016
$[Ln_3(H_2O)_{22}][P_2W_{15}Ta_3O_{62}] \cdot nH_2O$ (Ln = Y, La, Ce, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu)	Shuxia Liu, Zhiping Zheng, Xuenian Chen	<i>Inorg. Chem.</i> , 2018, 57, 6624.	2018

$\text{Cs}_3\text{K}_4\{\text{Cr}_3[\text{Ta}_3\text{P}_2\text{W}_{15}\text{O}_{62}]_2(\text{H}_2\text{O})_{12}\} \cdot 15\text{H}_2\text{O}$	Chao Qin, Zhong-Min Su	<i>J. Mater. Chem. A</i> , 2017, 5, 22970.	2017
$\text{Cs}_{8.5}\text{K}_8\text{Na}_2\text{H}_5.5\{\text{Cr}_4[\text{Ta}_3\text{P}_2\text{W}_{15}\text{O}_{62}]_4(\text{H}_2\text{O})_{12}\} \cdot 53\text{H}_2\text{O}$	Chao Qin, Zhong-Min Su	<i>J. Mater. Chem. A</i> , 2017, 5, 22970.	2017
$(\text{NH}_4)_{41}\text{H}_7[\text{K}_3(\text{H}_2\text{O})_3(\text{P}_2\text{W}_{15}\text{Ta}_3\text{O}_{62})_6(\text{Mo}_2\text{O}_4\text{CH}_3\text{CO}_2)_3(\text{MoO}_3)_2] \cdot 85\text{H}_2\text{O}$	Jiangwei Zhang, Xuenian Chen	<i>ACS Appl. Mater. Interfaces</i> , 2019, 11, 43287.	2019
hetero-peroxo-PONb clusters			
$\text{Cs}_{2.5}\text{Na}_2\{\text{As}_2\text{Nb}_4(\text{O}_2)_4\text{O}_{14}\text{H}_{1.5}\} \cdot 11\text{H}_2\text{O}$	Jingping Wang, Jingyang Niu	<i>Dalton Trans.</i> , 2014, 43, 9843.	2014
$\text{TMA}_3[\text{HNb}_4\text{P}_2\text{O}_{14}(\text{O}_2)_4] \cdot 9\text{H}_2\text{O}$	Jung-Ho Son	<i>Chem. Eur. J.</i> , 2015, 21, 6727.	2015
$\text{TMA}_3[\text{H}_7\text{Nb}_6\text{P}_4\text{O}_{24}(\text{O}_2)_6] \cdot 7\text{H}_2\text{O}$	Jung-Ho Son	<i>Chem. Eur. J.</i> , 2015, 21, 6727.	2015
$(\text{CN}_3\text{H}_6)_6\text{H}_4[\text{P}_4\text{Nb}_6(\text{O}_2)_6\text{O}_{24}] \cdot 4\text{H}_2\text{O}$	Jingyang Niu, Jingping Wang	<i>CrystEngComm</i> , 2017, 19, 2768.	2017
$(\text{CN}_3\text{H}_6)_4\text{H}_4[\{\text{Cd}(\text{H}_2\text{O})_4\}\{\text{P}_4\text{Nb}_6(\text{O}_2)_6\text{O}_{24}\}] \cdot 7\text{H}_2\text{O}$	Jingyang Niu, Jingping Wang	<i>CrystEngComm</i> , 2017, 19, 2768.	2017
$\text{Cs}_3\text{H}_3\{\text{[M}(\text{H}_2\text{O})_{4.5}\text{]}_2[\text{P}_4\text{Nb}_6(\text{O}_2)_6\text{O}_{24}]\} \cdot 5\text{H}_2\text{O}$ [M = Co, Ni, Zn]	Jingyang Niu, Jingping Wang	<i>CrystEngComm</i> , 2017, 19, 2768.	2017
$\text{Cs}_3\text{H}_3[\{\text{Cd}(\text{H}_2\text{O})_4\}_2\{\text{P}_4\text{Nb}_6(\text{O}_2)_6\text{O}_{24}\}] \cdot 12\text{H}_2\text{O}$	Jingyang Niu, Jingping Wang	<i>CrystEngComm</i> , 2017, 19, 2768.	2017
$[\text{Ln}^{\text{III}}(\text{H}_2\text{O})_6]_2[\text{H}_4(\text{NbO}_2)_6\text{P}_4\text{O}_{24}] \cdot n\text{H}_2\text{O}$ [Ln = Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb]	Jingyang Niu, Dongdi Zhang	<i>Sci. Rep.</i> , 2017, 7, 10653.	2017
$\text{Cs}_4\text{H}_4[\text{P}_2\text{Se}_2\text{Nb}_6(\text{O}_2)_6\text{O}_{22}] \cdot 10\text{H}_2\text{O}$	Jingyang Niu, Jingping Wang	<i>Dalton Trans.</i> , 2019, 48, 13135.	2019
$\text{Cs}_2\text{K}_3\{\text{[Ln}(\text{H}_2\text{O})_6\text{]}\text{[H}_{2.5}\text{P}_2\text{Se}_2\text{Nb}_6(\text{O}_2)_6\text{O}_{22}\text{]}\}_2 \cdot n\text{H}_2\text{O}$ [Ln = Dy, Tm, Yb, Lu]			
$\text{Cs}_2\{\text{[Ln}(\text{H}_2\text{O})_4\text{]}\text{[H}_4\text{P}_2\text{Se}_2\text{Nb}_6(\text{O}_2)_6\text{O}_{22}\text{]}\}_2 \cdot n\text{H}_2\text{O}$ [Ln = Ce, Pr, Sm, Eu, Gd]	Jingyang Niu, Jingping Wang	<i>Inorg. Chem.</i> , 2022, 61, 12181.	2022
$\text{Cs}_5\text{K}_2\text{H}_m\{\text{[Ln}(\text{H}_2\text{O})_6\text{]}\text{[P}_2\text{Se}_2\text{Nb}_6(\text{O}_2)_6\text{O}_{22}\text{]}\}_2\{\text{[Ln}_x(\text{H}_2\text{O})_y\text{]}\}_2\text{[P}_2\text{Se}_2\text{Nb}_6(\text{O}_2)_6\text{O}_{22}\text{]}\} \cdot n\text{H}_2\text{O}$ [Ln = Ho, Er, Tm, Yb, Lu]			
hetero-peroxo-POTa clusters			
$\text{Cs}_3[\text{H}_9\text{P}_4\text{Ta}_6(\text{O}_2)_6\text{O}_{25}] \cdot 9\text{H}_2\text{O}$	Jingyang Niu, Jingping Wang	<i>Inorg. Chem.</i> , 2017, 56, 5537.	2017
$(\text{CN}_3\text{H}_6)_6[\text{H}_4\text{P}_4\text{Ta}_6(\text{O}_2)_6\text{O}_{24}] \cdot 4\text{H}_2\text{O}$	Jingyang Niu, Jingping Wang	<i>Inorg. Chem.</i> , 2017, 56, 5537.	2017
$\text{Cs}_3\text{H}_3[\text{Ni}_2(\text{H}_2\text{O})_4\{\text{P}_4\text{Ta}_6(\text{O}_2)_6\text{O}_{24}\}] \cdot 7\text{H}_2\text{O}$	Jingping Wang, Jingyang Niu	<i>Chinese Chem. Lett.</i> , 2022, 33, 4675.	2021
$\text{Cs}_3\text{NaH}_4[\text{Zn}(\text{H}_2\text{O})_4\{\text{P}_4\text{Ta}_6(\text{O}_2)_6\text{O}_{24}\}] \cdot 13\text{H}_2\text{O}$			
$\text{Cs}_3\text{NaH}_4[\text{Cd}(\text{H}_2\text{O})_4\{\text{P}_4\text{Ta}_6(\text{O}_2)_6\text{O}_{24}\}] \cdot 8\text{H}_2\text{O}$	Jingping Wang, Jingyang Niu	<i>Chinese Chem. Lett.</i> , 2022, 33, 4675.	2021
$\text{Cs}_3[\text{Ln}(\text{H}_2\text{O})_6\{\text{H}_4(\text{TaO}_2)_6\text{As}_4\text{O}_{24}\}] \cdot 7\text{H}_2\text{O}$ (Ln = Sm, Eu, Tb, Dy, Er, Tm, Yb, Lu)	Jingping Wang, Jingyang Niu	<i>Inorg. Chem.</i> , 2019, 58, 13030.	2019
$\text{Cs}_2\text{KH}[(\text{TaO}_2)_6\text{Se}_4(\text{OH})_4\text{O}_{17}] \cdot 10\text{H}_2\text{O}$	Dongdi Zhang, Jingyang Niu	<i>Dalton Trans.</i> , 2020, 49, 4078.	2020
$\text{CsK}[\text{Ln}(\text{H}_2\text{O})_6(\text{TaO}_2)_6\text{Se}_4(\text{OH})_3\text{O}_{18}] \cdot 11\text{H}_2\text{O}$ [Ln = Tb, Dy, Ho, Er, Tm, Yb]	Dongdi Zhang, Jingyang Niu	<i>Dalton Trans.</i> , 2020, 49, 4078.	2020
$\text{CsK}[\text{Ln}(\text{H}_2\text{O})_6(\text{TaO}_2)_6\text{Se}_4(\text{OH})_3\text{O}_{18}] \cdot 11\text{H}_2\text{O}$ [Ln = Eu, Gd, Lu]	Guoping Yang, Dongdi Zhang	<i>Dalton Trans.</i> , 2022, 51, 9988.	2022

$\text{Cs}_2\text{K}_{1.5}\text{Na}_{1.5}[\text{Se}_4(\text{TaO}_2)_6(\text{OH})_3\text{O}_{18}] \cdot 17\text{H}_2\text{O}$	Ke Li, Dongdi Zhang	<i>Tungsten</i> , 2022, 4, 158.	2022
$\text{KNa}_2[\text{HSe}_2(\text{TaO}_2)_6(\text{OH})_4(\text{H}_2\text{O})_2\text{O}_{13}] \cdot 15\text{H}_2\text{O}$	Ke Li, Dongdi Zhang	<i>Tungsten</i> , 2022, 4, 158.	2022

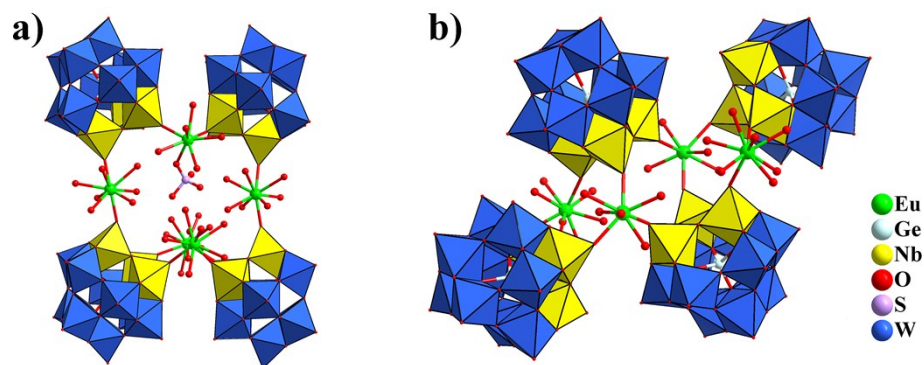


Fig. S1. Polyhedral representation of $[\text{Cs}(\text{GeW}_9\text{Nb}_3\text{O}_{40})_4(\text{SO}_4)\text{Eu}_5(\text{H}_2\text{O})_{36}]^{14-}$ and $[\text{Cs}_2(\text{GeW}_9\text{Nb}_3\text{O}_{40})_4\text{Eu}_4(\text{H}_2\text{O})_{22}]^{14-}$ polyanion.

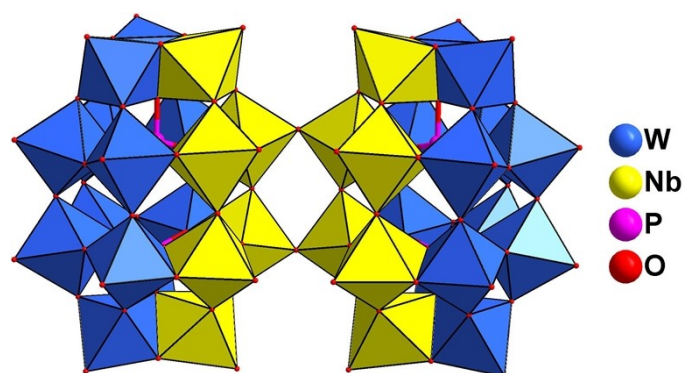


Fig. S2. Polyhedral representation of $\{\text{P}_4\text{W}_{24}\text{Nb}_{12}\text{O}_{122}\}$ dimeric sub-units in $[\text{H}_{24}\{\text{Nb}_4\text{O}_6(\text{OH})_4\}\{\text{Nb}_6\text{P}_2\text{W}_{12}\text{O}_{61}\}_4]^{12-}$ polyanion.

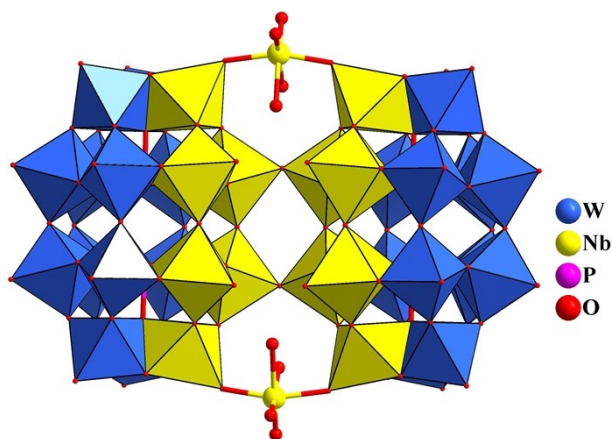


Fig. S3. Polyhedral representation of $\{\text{P}_4\text{W}_{24}\text{Nb}_{14}\text{O}_{126}\}$ sub-unit in $[\text{H}_{14}\{\text{P}_2\text{W}_{12}\text{Nb}_7\text{O}_{63}(\text{H}_2\text{O})_2\}_4\{\text{Nb}_4\text{O}_4(\text{OH})_6\}]^{16-}$ polyanion.

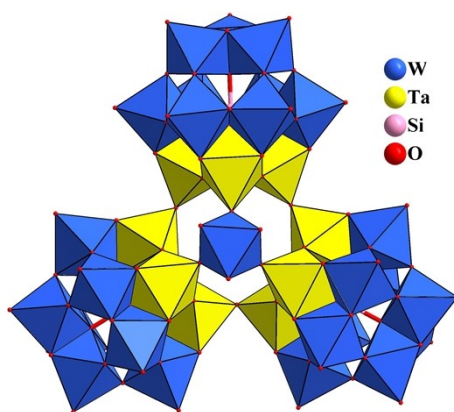


Fig. S4. Polyhedral representation of triangle $\{\text{Si}_3\text{Ta}_9\text{W}_{28}\text{O}_{120}\}$ unit in $[\text{Ta}_{12}\text{Si}_4\text{W}_{37}\text{O}_{158}]^{18-}$ polyanion.

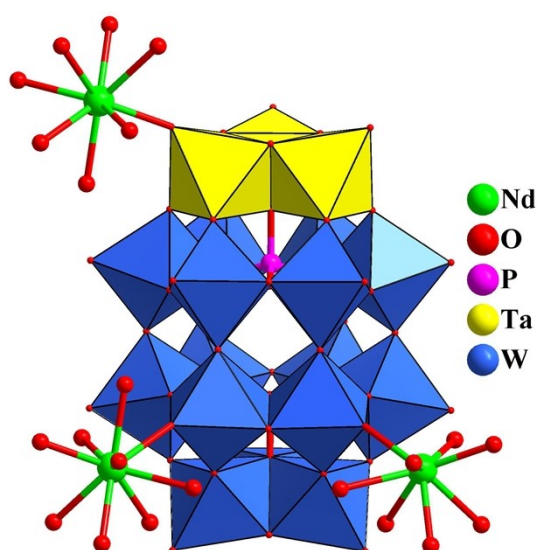


Fig. S5. The position of Ln^{III} cations in $[\text{Ln}_3(\text{H}_2\text{O})_{22}][\text{P}_2\text{W}_{15}\text{Ta}_3\text{O}_{62}] \cdot n\text{H}_2\text{O}$.

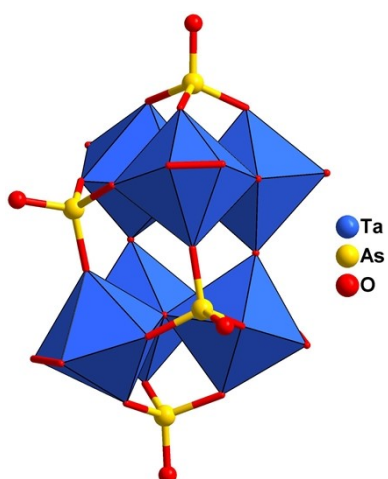


Fig. S6. Polyhedral representation of $\{(\text{TaO}_2)_6\text{As}_4\text{O}_{24}\}$ subunit in $\text{Cs}_3[\text{Ln}(\text{H}_2\text{O})_6\{\text{H}_4(\text{TaO}_2)_6\text{As}_4\text{O}_{24}\}] \cdot 7\text{H}_2\text{O}$.