Electronic Supporting Information

DOI: 10.1039/c4cc05689b

Reversible capping/uncapping of phosphorous-centered Keggin-type polyoxoniobate clusters

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Synthesis of PSb₂Nb₁₂

Sb₂O₃ (0.73 g), 5 g of hydrous niobium oxide (80 % w/w), 6 g of TMAOH·5H₂O and 0.45 g of H₃PO₄ was weighed in a PTFE-lined autoclave (23 mL capacity), and hydrothermally reacted in an oven at 140 °C for 4 days. The product solution was washed repeatedly with isopropanol in a plastic centrifuge tube (50 mL) until viscous product remained. The product was extracted with ethanol. Solvent evaporation in air leaves polycrystalline material. Small amount of TMACI was added during the recrystallization in water to aid crystallization. Crystals suitable for single crystal X-ray crystallography was grown after a few months. The crystalline product was washed with small amount of ethanol on a frit. Yield=6.2 g (76 %). Elemental analysis Found: C 13.33, H 5.12, N 3.88, Nb 36.2, P 1.01, Sb 8.77. Calcd for $C_{36}H_{168}N_9Nb_{12}O_{70}PSb_2$: C 13.36, H 5.23, N 3.89, Nb 34.44, P 0.96, Sb 7.52.

Synthesis of PNb14

Hydrous niobium oxide (3 g, 80% w/w) was mixed with 5 g of TMAOH·5H₂O in a PTFE-lined autoclave. 1 g of H₃PO₄ was added and the mixture was hydrothermally reacted at 120 °C for 3 days. The waxy product was washed 2-3 times with isopropanol in a plastic centrifuge tube (50 mL). The product was extracted with ethanol (~200 mL). The ethanolic solution was evaported in a rotary evaporator. Small amount of ethanol (~10 mL) was added to separate out the crystalline material. The crystalline product was washed on a frit with ethanol. Single crystals suitable for X-ray diffraction were obtained during the slow evaporation of ethanolic extract in an oven. Yield=2.4 g (60 %). Elemental analysis Found: C 13.92, H 5.14, N 4.09, Nb 41.0, P 1.07. Calcd for $C_{36}H_{160}N_9Nb_{14}O_{68}P$: C 13.78, H 5.14, N 4.01, Nb 41.44, P 0.99.

Synthesis of PNb₁₂

From PNb_{14} : PNb_{14} (0.5 g) was weighed in a vial (20 mL) and 3 mL of TBAOH solution (40 %) was added. The open vial was placed in an oven at 85 °C overnight. Crystalline solid settled. The supernatant solution was removed and the remaining crystalline solid was soaked and washed with ethanol several times on a frit. Yield =0.18 g (37 %). Elemental analysis Found: C 15.59, H 5.94, N 4.42, Nb 35.7, P 1.06. Calcd for C₄₀H₁₈₇N₁₀Nb₁₂O₇₁P: C 15.55, H 6.10, N 4.53, Nb 36.08, P 1.00.

From PV_2Nb_{12} : PV_2Nb_{12} (0.9 g) was weighed in a vial (20 mL) and 3 mL of TBAOH solution (40 %) was added. The open vial was placed in an oven at 85°C overnight. Crystalline solid settled. The supernatant solution was removed and the crystalline solid was soaked in ethanol, washed with ethanol several times on a frit. Yield =0.38 g (40 %).

Conversion from PNb_{14} to PV_2Nb_{12} : In a PTFE-lined autoclave, PNb_{14} (0.5 g) was dissolved in 5 mL of H₂O and 33 mg of V₂O₅ was added. The mixture was hydrothermally reacted at 120 °C for 16 h. The yellow solution was washed with isopropanol and ethanol a few times in a plastic centrifuge tube (50 mL) until sticky yellow product formed. The product was extracted with methanol. Yield=0.43 g (92 %).

Conversion from PNb_{14} to PSb_2Nb_{12} : In a PTFE-lined autoclave, PNb_{14} (0.5 g) was dissolved in 5 mL of H₂O and 50 mg of Sb₂O₃ was added. The mixture was hydrothermally reacted at 120 °C for 2 days. The solution was washed with isopropanol and ethanol a few times in a plastic centrifuge tube (50 mL) until sticky product formed. The product was extracted with methanol. Yield=0.48 g (93 %).

Conversion from PNb_{12} to PV_2Nb_{12} : In a PTFE-lined autoclave, PNb_{12} (0.4 g) was dissolved in 5 mL of H₂O and 24 mg of V₂O₅ was added. The mixture was hydrothermally reacted at 120 °C for 16 h. The yellow solution was washed with isopropanol and ethanol a few times in a plastic centrifuge tube (50 mL) until sticky yellow product formed. The product was extracted with methanol. Yield=0.37 g (98 %).

Conversion from PNb_{12} to PSb_2Nb_{12} : In a PTFE-lined autoclave, PNb_{12} (0.4 g) was dissolved in 5 mL of H₂O and 39 mg of Sb_2O_3 was added. The mixture was hydrothermally reacted at 120 °C for 16 h. The solution was washed with isopropanol and ethanol a few times in a plastic centrifuge tube (50 mL) until sticky product formed. The product was extracted with methanol. Yield=0.28 g (67 %).

X-ray crystallography

The crystallographic data were collected by using Bruker APEX II diffractometer equipped with monochromatic Mo K α radiation (λ =0.71073Å). The diffraction data were reduced by SAINT software¹ and absorption correction was applied with SADABS software.² The crystal structures were solved with direct method by using SHELXTL package³ and refined with SHELXL 2013 program. Some of the disordered crystallization water and TMA ions were refined isotropically or with partial occupancy model to make the refinement converge. The H atoms in methyl groups in TMA ions were refined with riding model. Some H atoms in TMA ions causing refinement instability were omitted.

Crystal Data.

TMA₉[PSb₂Nb₁₂O₄₀]·28H₂O (CCDC 1014963). C₁₀₄H₂₆₄N₂₆Nb₃₆O₂₀₉P₃Sb₆, M = 9391.57, Triclinic, a = 13.5271(6), b = 15.3790(7), c = 38.1915(18) Å, a = 95.015(1), $\beta = 93.776(1)$, $\gamma = 93.571(1)^{\circ}$, U = 7879.0(6) Å³, T = 88(2) K, space group *P*-1 (no.2), Z = 1, 94959 reflections measured, 32166 unique ($R_{int} = 0.0217$) which were used in all calculations. The final $wR(F^2)$ was 0.1036 (all data).

TMA₉[PNb₁₄O₄₂]·26H₂O (CCDC 1014964). C₂₈H₈₄N₇Nb₁₄O₆₈P, M = 2938.73, Triclinic, a = 13.429(7), b = 14.943(8), c = 25.521(13) Å, a = 77.020(7), $\beta = 88.450(7)$, $\gamma = 82.922(7)^{\circ}$, U = 4953(4) Å³, T = 88(2) K, space group *P*-1 (no.2), Z = 2, 55628 reflections measured, 20237 unique ($R_{int} = 0.0503$) which were used in all calculations. The final $wR(F^2)$ was 0.2301 (all data).

TMA₁₀[H₅PNb₁₂O₄₀]·30.5H₂O (CCDC 1014965). C₄₀H₅₂N₁₀Nb₁₂O₇₀P, M = 2938.80, Triclinic, a = 13.479(2), b = 13.786(2), c = 16.904(2) Å, $\alpha = 70.1318(18)$, $\beta = 69.2539(18)$, $\gamma = 74.0995(18)^\circ$, U = 2720.1(7) Å³, T = 88(2) K, space group *P*-1 (no.2), Z = 1, 32376 reflections measured, 11113 unique ($R_{int} = 0.0195$) which were used in all calculations. The final $wR(F^2)$ was 0.2525 (all data).

Instrumental Detail

Electrospray mass spectrometry (ESI-MS) was conducted by using Agilent LC/MSD 1100 model (G1956b). The solution was directly injected at a rate of 0.1 mL/min with a cone voltage of 20 V. The 10 mM solutions of each compound were prepared to study the pH dependent stability. The solution was titrated with TMAOH solution (25%) or TMAOH·5H₂O in the basic titration and 1 M HCl solution for the acid titration to minimize the volume change of the solution. Small aliquot (5 μ L for PNb₁₂ and PSb₂Nb₁₂ or 20 μ L for PNb₁₄) of solution in each pH was diluted with 0.5 mL of water for injection to acquire pH dependent ESI-MS data. Elemental analyses of the compounds were performed in Galbraith Laboratory (Knoxville, TN). TGA analyses were conducted by using Netzsch STA 449 system under static air at a temperature ramping rate of 10 °C/min. FT-IR spectra were acquired by using Bruker Tensor 27 spectrometer by using KBr pellet where small amount of sample is dispersed.

The ³¹P MAS-NMR spectra were collected at the UCD Keck NMR facility on a Bruker Avance spectrometer based on an 11.7 Tesla magnet. The ³¹P resonance frequency on this spectrometer is 202.447 MHz. The ³¹P MAS-NMR spectra were collected using a 2 μ s pulse width with a spectral window of 250 kHz, 32 or 64 acquisitions and 30 s recycle delay. The sample was spun at 15 kHz. Solution-phase ³¹P NMR spectra were collected with a Bruker Avance spectrometer located at the UCD NMR facility. This spectrometer is based on an 11.7 T magnet (v₀=202.448 MHz for ³¹P) and is fitted with a 5-mm broadband probe. The ³¹P NMR spectra were taken at 298 K and referenced against an external aqueous 85 % H₃PO₄ solution.

¹ Bruker (2007). SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.

² Bruker (2001). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

³ G. M. Sheldrick, Acta Cryst. 2008, A64, 112-122.

Identification code	PSb_2Nb_{12}	PNb ₁₄	PNb ₁₂
Empirical formula	C104 H264 N26 Nb36 O209 P3 Sb6	C28 H84 N7 Nb14 O68 P	C40 H52 N10 Nb12 O70 P
Formula weight	9391.57	2938.73	2938.8
Temperature	88(2) K	88(2) K	88(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P -1	P -1	P -1
Unit cell dimensions	$a = 13.5271(6) \text{ Å} \alpha = 95.0150(10)^{\circ}$	$a= 13.429(7) \text{ Å} \alpha = 77.020(7)^{\circ}$	$a=13.479(2)$ Å $\alpha=70.1318(18)^{\circ}$
	$b=15.3790(7)$ Å $\beta=93.7760(10)^{\circ}$	$b=14.943(8)$ Å $\beta=88.450(7)^{\circ}$	$b=13.786(2)$ Å $\beta=69.2539(18)^{\circ}$
	$c = 38.1915(18) \text{ Å} \gamma = 93.5710(10)^{\circ}$	$c = 25.521(13) \text{ Å} \gamma = 82.922(7)^{\circ}$	$c= 16.904(2) \text{ Å} \gamma = 74.0995(18)^{\circ}$
Volume	7879.0(6) Å ³	4953(4) Å ³	2720.1(7) Å ³
Z	1	2	1
Density (calculated)	1.979 Mg/m ³	1.971 Mg/m ³	1.794 Mg/m^3
Absorption coefficient	1.877 mm ⁻¹	1.670 mm ⁻¹	1.328 mm ⁻¹
F(000)	4569	2868	1429
Crystal size	0.245 x 0.217 x 0.104 mm ³	0.417 x 0.131 x 0.112 mm ³	0.430 x 0.227 x 0.136 mm ³
Crystal color and habit	colourless plate	colourless block	colourless block
Diffractometer	Bruker APEX-II CCD	Bruker APEX-II CCD	Bruker APEX-II CCD
Theta range for data collection	1.946 to 26.372°.	2.239 to 26.372°.	2.343 to 26.372°.
Index ranges	-16<=h<=16, -19<=k<=19, -	-16<=h<=16, -18<=k<=18, -	-16<=h<=16, -17<=k<=17, -
-	47<=l<=47	31<=l<=31	21<=l<=21
Reflections collected	94959	55628	32376
Independent reflections	32166 [R(int) = 0.0217]	20237 [R(int) = 0.0503]	11113 [R(int) = 0.0195]
Observed reflections (I >	29918	14599	9520
2sigma(I))			
Completeness to theta = 25.242°	99.90%	99.70%	99.80%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6466	0.7455 and 0.5392	0.7456 and 0.6535
Solution method	SHELXS-97 (Sheldrick, 2008)	SHELXS-97 (Sheldrick 2008)	SHELXS-97 (Sheldrick 2008)
Refinement method	SHELXL-97 (Sheldrick, 2008)	SHELXL-2013 (Sheldrick 2013)	SHELXL-2013 (Sheldrick 2013)
Data / restraints / parameters	32166 / 0 / 1805	20237 / 0 / 1054	11113 / 0 / 606
Goodness-of-fit on F2	1.162	1.055	1.044
Final R indices [I>2sigma(I)]	$R_1 = 0.0461, wR_2 = 0.1020$	$R_1 = 0.0877, wR_2 = 0.2135$	$R_1 = 0.0966, wR_2 = 0.2440$
R indices (all data)	$R_1 = 0.0495, wR_2 = 0.1036$	$R_1 = 0.1169, wR_2 = 0.2301$	$R_1 = 0.1070, wR_2 = 0.2525$
Extinction coefficient	n/a	n/a	n/a
Largest diff. peak and hole	2.059 and -1.567 e.Å ⁻³	2.322 and -2.876 e.Å ⁻³	2.554 and -1.745 e.Å ⁻³



Fig. S1 ESI-MS of PNb12 (top), PSb2Nb12 (middle) and PNb14 (bottom) and the their peak assignments



Fig.S2 TGA data of PSb₂Nb₁₂, PNb₁₄ and PNb₁₂. The calculated amount of water and TMA are as below.

 $(N(CH_3)_4)_9PSb_2Nb_{12}O_{40}(H_2O)_{28} (f.w.=3198.6)$ $28H_2O=468.3(15.8\%) 9TMA=666.9(20.8\%)$ $(N(CH_3)_4)_9PNb_{14}O_{42}(H_2O)_{26} (f.w.=3138.6)$ $26H_2O=468.3(14.9\%) 9TMA=666.9(21.2\%)$ $(N(CH_3)_4)_{10}H_5PNb_{12}O_{40}(H_2O)_{30.5} (f.w=3081.0)$ $30.5H_2O=549.3(17.8\%) 10TMA=741.0(24.1\%)$



Fig.S3 Thermal ellipsoid model representation of PNb_{14}



Fig. S4 Top view of the pseudo-Keggin structures (magenta:O, light blue: Nb, purple: Sb) of PNb_{12} (left) and PSb_2Nb_{12} (right). The numbers indicate O···O distances in the capping site in Å unit.



Fig. S5 Top view of the Keggin structures (magenta:O, light blue: Nb, purple: Sb, yellow: V) of PSb_2Nb_{12} (top), PNb_{14} (bottom left) and PV_2Nb_{12} (bottom right). The numbers indicate O···O distances (Å unit) and O-O-O angles within the capping site.



Fig.S6 FT-IR spectra of PSb₂Nb₁₂, PNb₁₄ and PNb₁₂



Fig. S7 ESI-MS of PSb₂Nb₁₂ depending on pH



Fig. S8 ESI-MS of PNb_{14} depending on pH



Fig. S9 ESI-MS of PNb12 depending on pH



Fig.S10 ESI-MS monitored during the reaction of 50 mg of PNb₁₄ (top) or 50mg of PNb₁₂ (bottom) with 5 mg of Sb₂O₃ in 2 mL of water.



Fig.S11 ESI-MS monitored during the reaction of 50 mg of PNb₁₄ (top) or 50 mg of PNb₁₂ (bottom) with 5 mg of V₂O₅ in 2 mL of water.