Supplementary Materials

Heteropolyniobates from the group IIIA Elements

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General Methods and Materials.

Alkali salts of the Lindqvist ion, $Cs_8[Nb_6O_{19}]\cdot 14H_2O$, $Rb_8[Nb_6O_{19}]\cdot 14H_2O$, and $K_8[Nb_6O_{19}]\cdot 16H_2O$ were obtained by methods reported prior, and purity was confirmed by infrared spectroscopy, X-ray powder diffraction and thermogravimetry. $Ga(NO_3)_3\cdot XH_2O$ was purchased from Strem Chemicals. $Al(NO_3)_3\cdot 9H_2O$ was purchased from Fisher Scientific company. Thermal analysis was performed with a TA Instruments SDT 2960 for simultaneous thermogravimetric and differential thermal analysis (TGA-DTA) under air flow with a heating rate of 10 °C/min. Powder X-ray powder diffraction data was performed on a Bruker D8 Advance with Cu-Kα radiation. Infrared spectra (400-4000 cm^{-1}) were recorded on a Thermo Nicolet 380 Ft-IR equipped with a Smart Orbit (Diamond) ATR accessory. Solution ^{27}Al NMR in D_2O was performed on Bruker Ultrashield Plus 500 MHz. Solution ^{71}Ga NMR in D_2O was performed on Bruker Avance III 600 MHz. Chemical shifts are referenced to pure $Al(NO_3)_3$ and $Ga(NO_3)_3$ as an external reference. Elemental composition was confirmed via energy dispersive spectroscopy (EDS) and referenced to known standards. ESI-MS spectrometry experiments have been carried out on an Aglient Technologies 6224 TOF MS instrument. The 1.0×10^{-6} $M\cdot L^{-1}$ solutions of POMs were infused using a syringe pump (300 μl min^{-1}). Mass spectra were recorded in the negative ion detection mode. The spectrometer was previously calibrated with the standard tune mix to give a precision of about 2 ppm in the region of 50–3200 m/z. Spectra were taken with the following instrumental parameters: nebulizer gas pressure, 30 psi; dry gas flow rate, 5 l/min; dry gas temperature, 325 °C; capillary voltage and current, 3500 V, 0.029 μA; fragmentor voltage, 100V.

Table S1. Crystal data and structure refinement for **K1**, **Rb1**, **Cs1**, and **K2**

	K1	**Rb1**	**Cs1**	**K2**
Empirical Formula	$H_{62}GaK_{14}NaNb_{18}O_{85}$	$H_{70}GaNb_{18}O_{89}Rb_{15}$	$H_{24}Cs_{13}GaNa_2Nb_{18}O_{66}$	$H_{63}AlK_{14}Nb_{18}O_{85}$
Fw (g·mol^{-1})	3734.99	4518.71	4596.10	3670.26
T(K)	193(2)	293(2)	193(2)	193(2)
Radiation (λ, Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	orthorhombic	triclinic	tetragonal	orthorhombic
Space group	$P2_12_12_1$	$P\bar{1}$	$P4_2/ncm$	$P2_12_12_1$
a (Å)	18.6023(18)	15.0863(1)	16.8515(13)	18.582(3)
b (Å)	18.6225(18)	17.94(12)	16.8515(13)	18.646(3)
c (Å)	24.567(2)	19.1713(13)	28.919(3)	24.646(4)
α (°)	90	63.539(1)	90	90
β (°)	90	82.135(1)	90	90
γ (°)	90	79.927(1)	90	90
V (Å^3)	8510.7(14)	4563.3(5)	8212.1(12)	8539(2)
Z	4	2	4	4
d_{calcd}, Mg·m^{-3}	2.915	3.289	3.717	2.855
μ, mm^{-1}	3.448	10.526	8.518	3.132
GOF	1.102	1.014	1.041	1.088
Final R indices [R>2σ(I)]	$R_1{}^a$ = 0.0253 w$R_2{}^b$ = 0.0621	$R_1{}^a$ = 0.0321 w$R_2{}^b$ = 0.0744	$R_1{}^a$ = 0.0531 w$R_2{}^b$ = 0.1553	$R_1{}^a$ = 0.0414 w$R_2{}^b$ = 0.1019
R indices (all data)	$R_1{}^a$ = 0.0271 w$R_2{}^b$ = 0.0632	$R_1{}^a$ = 0.0433 w$R_2{}^b$ = 0.0791	$R_1{}^a$ = 0.0594 w$R_2{}^b$ = 0.1624	$R_1{}^a$ = 0.0460 w$R_2{}^b$ = 0.1050

[a] $R_1 = \Sigma||F_0| - |F_c|| / \Sigma|F_0|$;
[b] $wR_2 = \Sigma[w(F_0^2 - F_c^2)^2]/ \Sigma[w(F_0^2)^2]^{1/2}$

Table S2. The bond length (Å) range in compounds **K1**, **K2**, **Rb1**, and **Cs1.**

Bond	**K1**	**K2**	**Rb1**	**Cs1**
Ga(Al)-O	1.807-1.851	1.747-1.788	1.809-1.852	1.812-1.849
Nb-O_t	1.733-1.781	1.726-1.781	1.739-1.797	1.734-1.789
Nb-O_{b1}	1.820-2.117	1.801-2.109	1.814-2.116	1.823-2.045
Nb-O_{b2}	2.079-2.139	2.080-2.133	2.072-2.125	2.089-2.115
Nb-O_{c1}	2.250-2.524	2.243-2.522	2.246-2.510	2.265-2.492
Nb-O_{c2}	2.079-2.106	2.092-2.128	2.082-2.099	2.092-2.092
Nb-O_{c3}	2.260-2.309	2.289-2.333	2.256-2.307	2.274-2.293

Nb-O_t	t=terminal or yl oxygen, bonded to one Nb
Nb-O_{b1}	b=bridging oxygen, bonded to two Nb atoms
Nb-O_{b2}	b=bridging oxygen, bonded to three Nb atoms
Nb-O_{c1}	c=central oxygen, bonded to six Nb atoms
Nb-O_{c2}	c=central oxygen, bonded to two Nb atoms and one Ga(Al) atom
Nb-O_{c3}	c=central oxygen, bonded to three Nb atoms and one Ga(Al) atom

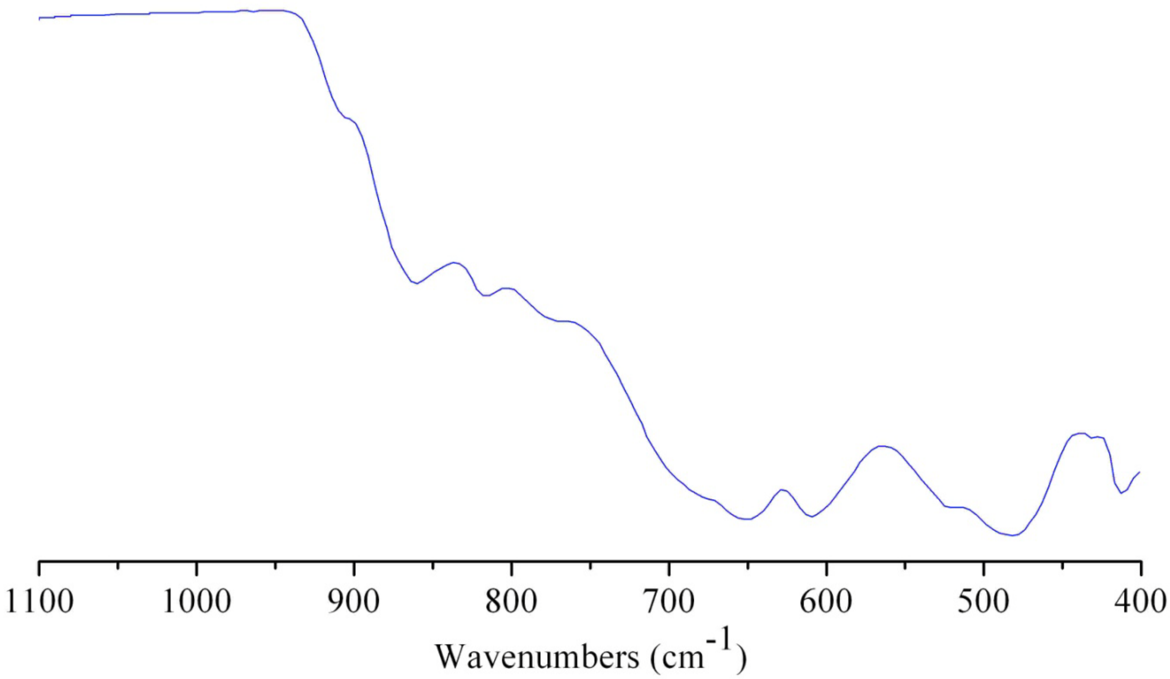

Fig. S1. IR spectra of **K1**.

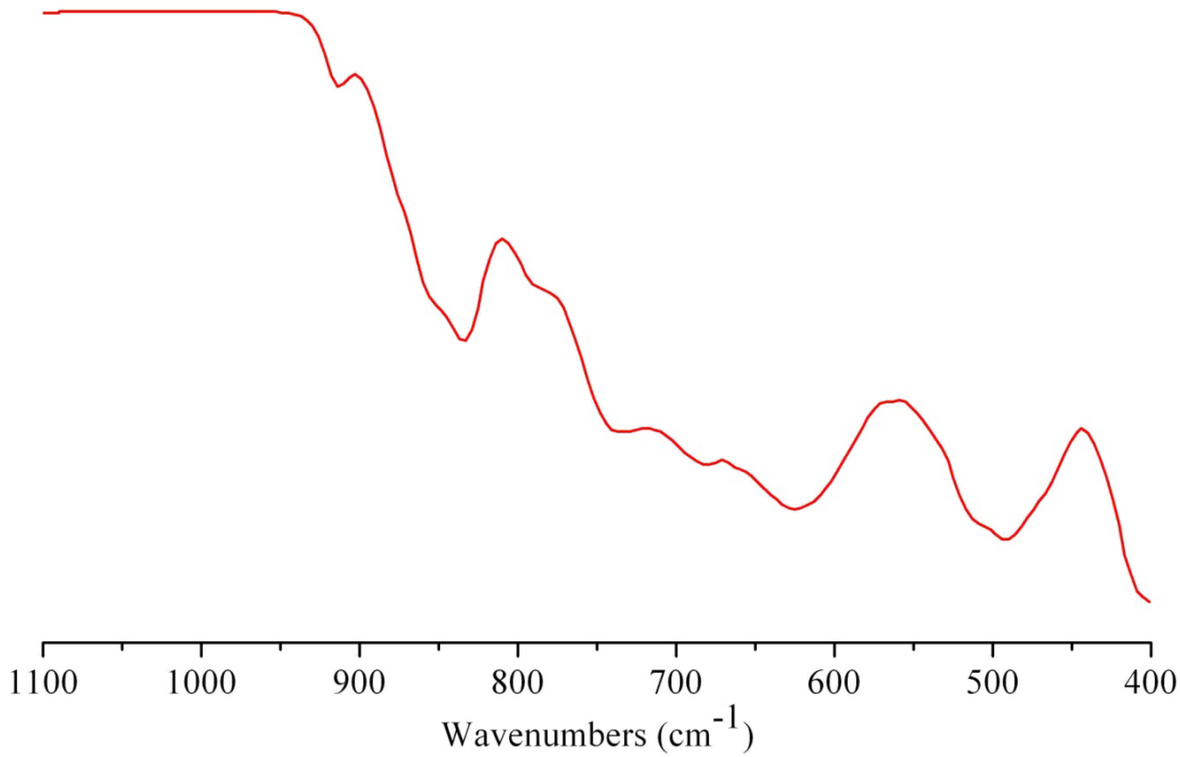

Fig. S2. IR spectra of **K2**.

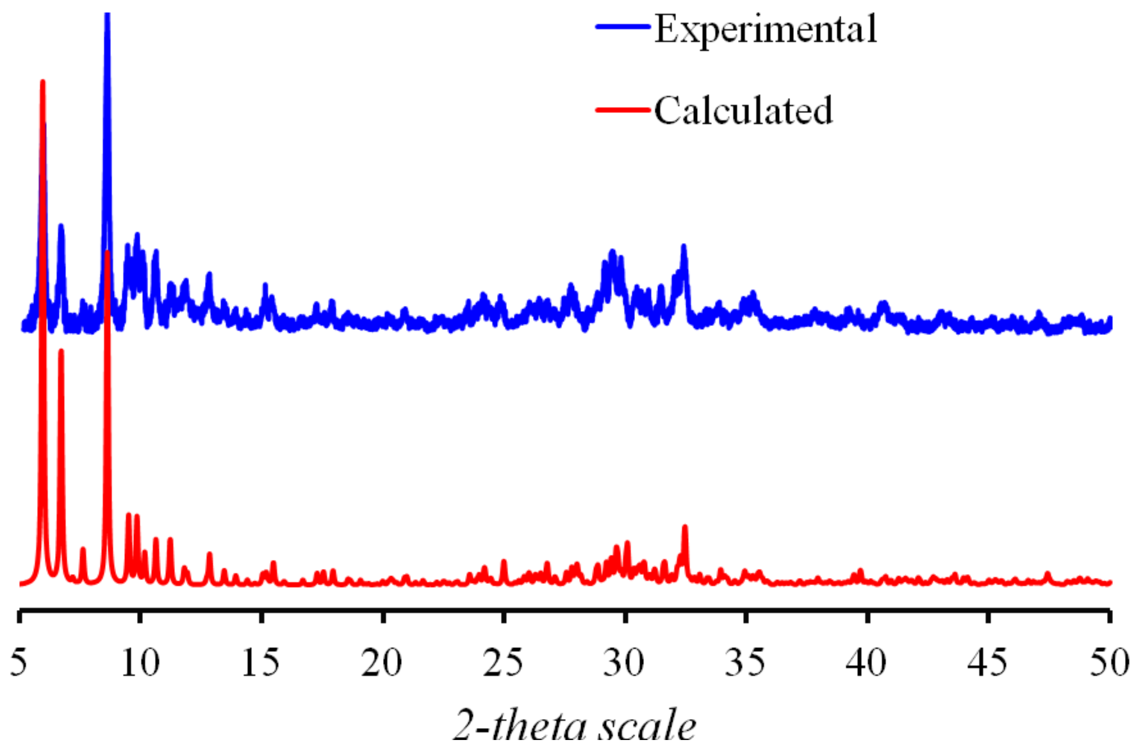

Fig. S3. X-ray powder diffraction of observed and calculated plots for **K1**.

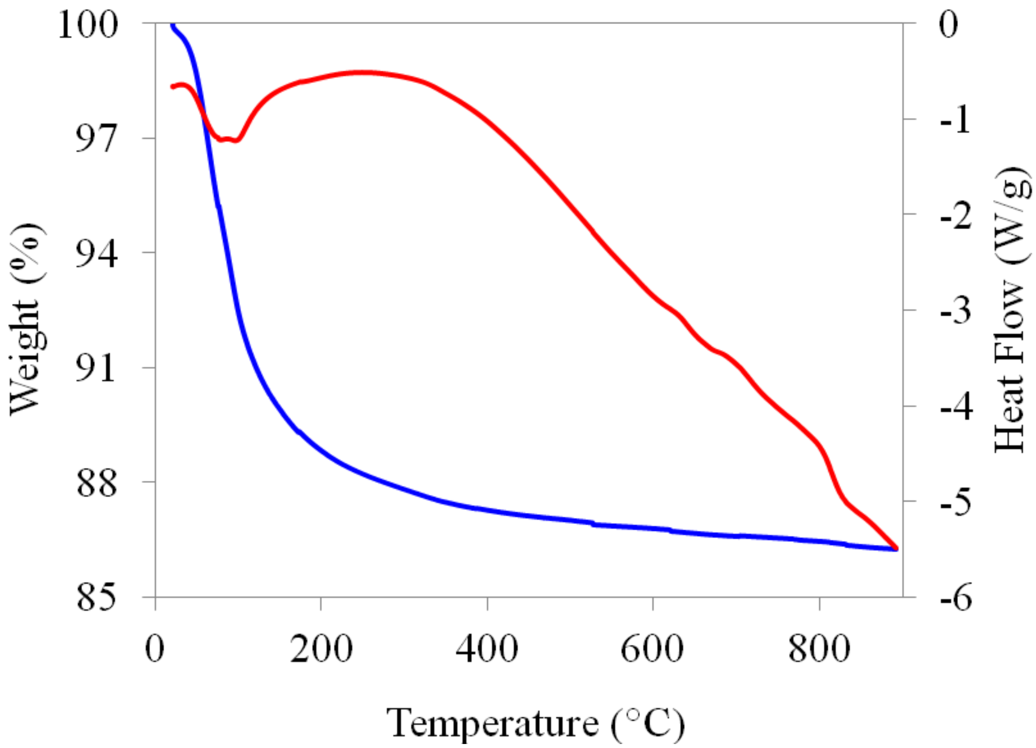

Fig. S5. Thermogravimetric (blue) differential thermal analysis (red) of **K1**.

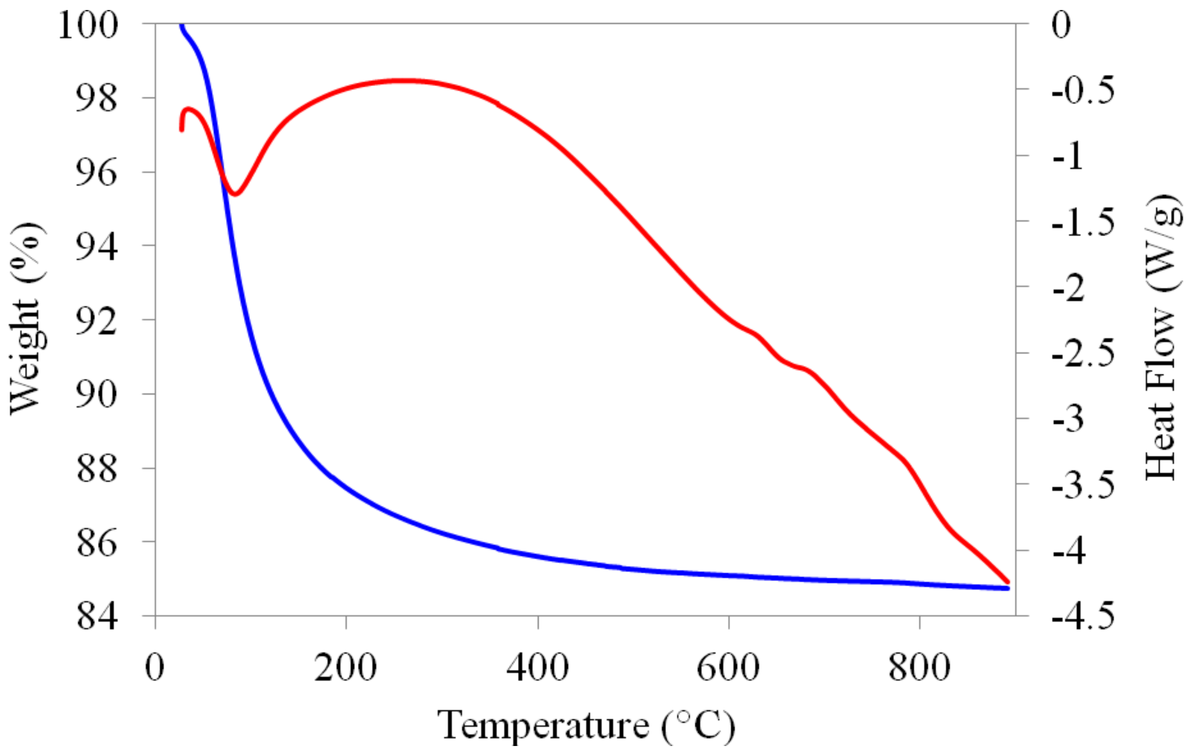

Fig. S6. Thermogravimetric (blue) differential thermal analysis (red) of **K2**.

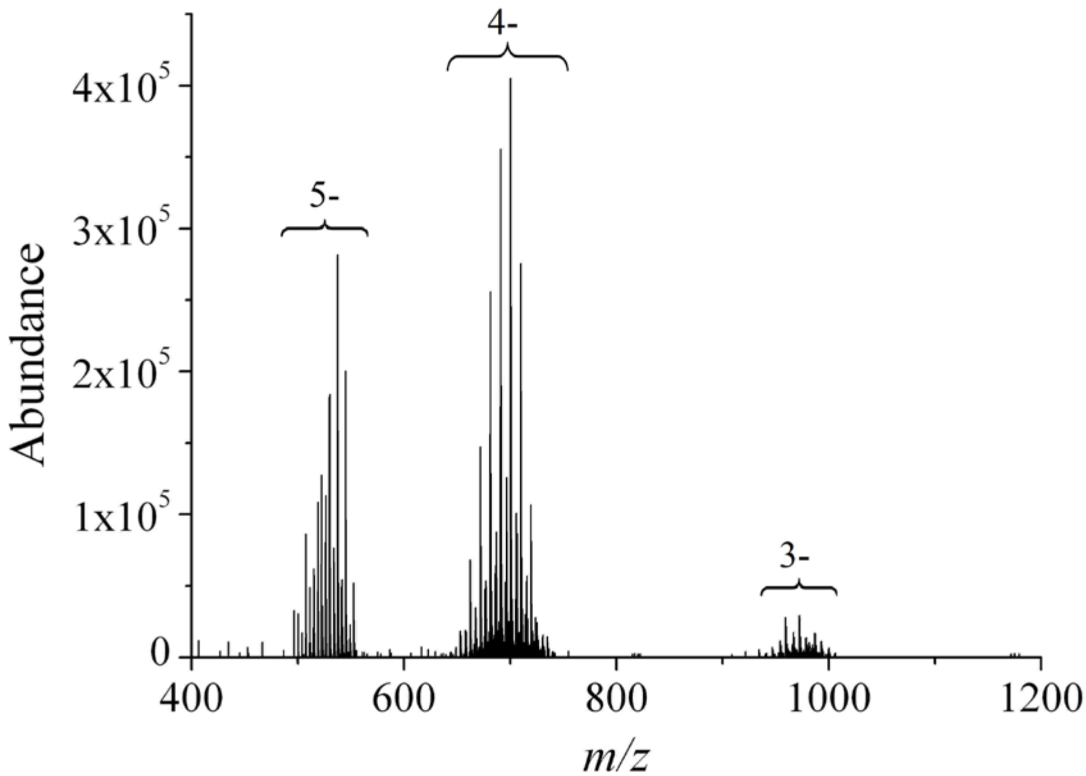

Fig. S7. ESI-MS for **K2**.

Table S3. Detailed assignment of mass spectral data for compound **K1**.

m/z observed	polyanion	Mass calculated	m/z calculated
	4-		
741.42	$[K_5Na_5H_2GaNb_{18}O_{57}]^{4-}$	2964.73	741.18
737.43	$[K_8H_2GaNb_{18}O_{56}]^{4-}$	2950.68	737.67
730.43	$[K_5Na_3H_4GaNb_{18}O_{57}]^{4-}$	2920.77	730.19
726.44	$[K_4Na_4H_4GaNb_{18}O_{57}]^{4-}$	2904.80	726.20
720.84	$[K_4Na_3H_5GaNb_{18}O_{57}]^{4-}$	2882.81	720.70
716.95	$[K_3Na_4H_5GaNb_{18}O_{57}]^{4-}$	2866.84	716.71
711.45	$[K_3Na_3H_6GaNb_{18}O_{57}]^{4-}$	2844.86	711.21
707.45	$[K_3Na_4HGaNb_{18}O_{55}]^{4-}$	2830.82	707.70
701.70	$[K_4Na_2GaNb_{18}O_{54}]^{4-}$	2806.80	701.70
697.96	$[KNa_4H_7GaNb_{18}O_{57}]^{4-}$	2790.92	697.73
697.71	$[K_3Na_3GaNb_{18}O_{54}]^{4-}$	2790.83	697.71
692.47	$[KNa_3H_8GaNb_{18}O_{57}]^{4-}$	2768.95	692.24
692.22	$[K_3Na_2HGaNb_{18}O_{57}]^{4-}$	2768.84	692.21
687.97	$[K_2Na_3HGaNb_{18}O_{54}]^{4-}$	2752.87	688.22
687.72	$[K_6H_5GaNb_{17}O_{54}]^{4-}$	2750.88	687.72
682.72	$[K_2Na_2H_2GaNb_{18}O_{54}]^{4-}$	2730.89	682.72
678.48	$[KNa_3H_2GaNb_{18}O_{54}]^{4-}$	2714.91	678.73
678.23	$[K_2Na_2GaNb_{18}O_{53}]^{4-}$	2712.88	678.22
673.49	$[Na_3H_5GaNb_{18}O_{55}]^{4-}$	2694.97	673.74
673.23	$[KNa_2H_3GaNb_{18}O_{54}]^{4-}$	2692.93	673.23
669.22	$[K_5H_2GaNb_{17}O_{52}]^{4-}$	2676.90	669.23
668.99	$[K_5H_2GaNb_{17}O_{52}]^{4-}$	2676.90	669.23
663.99	$[Na_2H_4GaNb_{18}O_{54}]^{4-}$	2654.98	663.74
659.50	$[K_4H_3GaNb_{17}O_{52}]^{4-}$	2638.95	659.74
654.51	$[K_3H_6GaNb_{17}O_{53}]^{4-}$	2619.00	654.76
650.51	$[K_3H_4GaNb_{17}O_{52}]^{4-}$	2600.99	650.25
	3-		
948.93	$[K_3Na_3H_7GaNb_{18}O_{57}]^{3-}$	2845.87	948.62
956.26	$[K_3Na_4H_6GaNb_{18}O_{57}]^{3-}$	2867.85	955.95
961.58	$[K_4Na_3H_6GaNb_{18}O_{57}]^{3-}$	2883.82	961.27
968.91	$[K_4Na_4H_5GaNb_{18}O_{57}]^{3-}$	2905.80	968.60
974.24	$[K_5Na_3H_5GaNb_{18}O_{57}]^{3-}$	2921.78	973.93
975.24	$[K_5Na_4H_2GaNb_{18}O_{56}]^{3-}$	2925.75	975.25
981.56	$[K_5Na_4H_4GaNb_{18}O_{57}]^{3-}$	2943.76	981.25
981.90	$[K_4Na_5H_6GaNb_{18}O_{58}]^{3-}$	2945.80	981.93
986.89	$[K_6Na_3H_4GaNb_{18}O_{57}]^{3-}$	2959.73	986.58
988.23	$[K_6Na_4HGaNb_{18}O_{56}]^{3-}$	2963.70	987.90
987.56	$[K_5Na_4H_6GaNb_{18}O_{58}]^{3-}$	2961.77	987.26
987.89	$[K_6Na_4HGaNb_{18}O_{56}]^{3-}$	2963.71	987.90
996.23	$[K_9H_2GaNb_{18}O_{56}]^{3-}$	2989.64	996.55
	5-		
561.37	$[K_8GaNb_{17}O_{53}]^{5-}$	2807.77	561.56
557.77	$[K_7H_3GaNb_{17}O_{54}]^{5-}$	2787.83	557.57
553.77	$[K_7HGaNb_{17}O_{53}]^{5-}$	2769.82	553.97
550.18	$[K_2Na_3GaNb_{18}O_{54}]^{5-}$	2751.86	550.37
546.18	$[K_6H_2GaNb_{17}O_{53}]^{5-}$	2731.86	546.37
542.58	$[K_6GaNb_{17}O_{52}]^{5-}$	2713.85	542.77
538.59	$[K_5H_3GaNb_{17}O_{53}]^{5-}$	2693.91	538.78
534.99	$[K_5HGaNb_{17}O_{52}]^{5-}$	2675.90	535.18
530.99	$[K_4H_4GaNb_{17}O_{53}]^{5-}$	2655.95	531.19
527.39	$[K_4H_2GaNb_{17}O_{52}]^{5-}$	2637.94	527.59
523.79	$[K_4GaNb_{17}O_{51}]^{5-}$	2619.93	523.99
519.80	$[K_3H_3GaNb_{17}O_{52}]^{5-}$	2599.98	519.99
516.20	$[K_3HGaNb_{17}O_{51}]^{5-}$	2581.97	516.40
512.20	$[K_2H_4GaNb_{17}O_{52}]^{5-}$	2562.03	512.41
508.60	$[K_2H_2GaNb_{17}O_{51}]^{5-}$	2544.02	508.80

Table S4. Detailed assignment of mass spectral data for compound **K2**.

m/z observed	polyanion	Mass calculated	m/z calculated
	4-		
653.02	$[KNaH_2AlNb_{18}O_{53}]^{4-}$	2611.00	652.75
662.51	$[KNa_2H_3AlNb_{18}O_{54}]^{4-}$	2650.99	662.75
667.50	$[K_2Na_2AlNb_{18}O_{53}]^{4-}$	2670.93	667.73
681.49	$[K_3Na_2HAlNb_{18}O_{54}]^{4-}$	2726.90	681.73
672.00	$[K_2Na_2H_2AlNb_{18}O_{54}]^{4-}$	2688.94	672.24
676.99	$[K_2Na_2H_4AlNb_{18}O_{55}]^{4-}$	2706.95	676.74
686.98	$[K_3N_{a3}AlNb_{18}O_{54}]^{4-}$	2748.88	687.22
690.98	$[K_4Na_2AlNb_{18}O_{54}]^{4-}$	2764.86	691.21
696.47	$[K_3Na_3H_4AlNb_{18}O_{56}]^{4-}$	2784.90	696.23
700.47	$[K_4Na_2H_4AlNb_{18}O_{56}]^{4-}$	2800.88	700.22
705.96	$[K_4Na_3H_3AlNb_{18}O_{56}]^{4-}$	2822.86	705.72
709.96	$[K_5Na_2H_3AlNb_{18}O_{56}]^{4-}$	2838.83	709.71
715.96	$[K_4Na_4H_4AlNb_{18}O_{57}]^{4-}$	2862.85	715.71
719.45	$[K_6Na_2H_2AlNb_{18}O_{56}]^{4-}$	2876.79	719.20
	5-		
507.81	$[K_3HAlNb_{17}O_{51}]^{5-}$	2540.03	508.01
511.41	$[K_3H_3AlNb_{17}O_{52}]^{5-}$	2558.04	511.61
515.01	$[K_3H_5AlNb_{17}O_{53}]^{5-}$	2576.05	515.21
519.00	$[K_4H_2AlNb_{17}O_{52}]^{5-}$	2596.00	519.20
522.61	$[K4H_4AlNb_{17}O_{53}]^{5-}$	2614.01	522.80
526.60	$[K_5HAlNb_{17}O_{52}]^{5-}$	2633.95	526.79
530.20	$[K_5H_3AlNb_{17}O_{53}]^{5-}$	2651.96	530.39
533.80	$[K_5H_5AlNb_{17}O_{54}]^{5-}$	2669.97	534.00
537.40	$[K_2Na_2HAlNb_{18}O_{54}]^{5-}$	2687.94	537.59
541.79	$[K_2Na_3AlNb_{18}O_{54}]^{5-}$	2709.92	541.98
544.99	$[K_3Na_2AlNb_{18}O_{54}]^{5-}$	2725.89	545.18
549.39	$[K_2Na_3H_4AlNb_{18}O_{56}]^{5-}$	2745.94	549.19
552.58	$[K_3Na_2H_4AlNb_{18}O_{56}]^{5-}$	2761.91	552.38
	3-		
921.64	$[K_4Na_2HAlNb_{18}O_{54}]^{3-}$	2765.86	921.96
934.29	$[K_5Na_2AlNb_{18}O_{54}]^{3-}$	2803.82	934.61
946.94	$[K_5Na_2H_4AlNb_{18}O_{56}]^{3-}$	2839.84	946.61
954.27	$[K_5Na_3H_3AlNb_{18}O_{56}]^{3-}$	2861.82	953.94
959.60	$[K_6Na_2H_3AlNb_{18}O_{56}]^{3-}$	2877.80	959.27
966.92	$[K_6Na_3H_2AlNb_{18}O_{56}]^{3-}$	2899.78	966.59
972.25	$[K_7Na_2H_2AlNb_{18}O_{56}]^{3-}$	2915.75	971.92
981.59	$[K_6Na_5AlNb_{18}O_{56}]^{3-}$	2943.74	981.25
984.91	$[K_8Na_2HAlNb_{18}O_{56}]^{3-}$	2953.77	984.59
986.91	$[K_7Na_4AlNb_{18}O_{56}]^{3-}$	2959.72	986.57
992.91	$[K_7Na_4H_2AlNb_{18}O_{57}]^{3-}$	2977.73	992.58

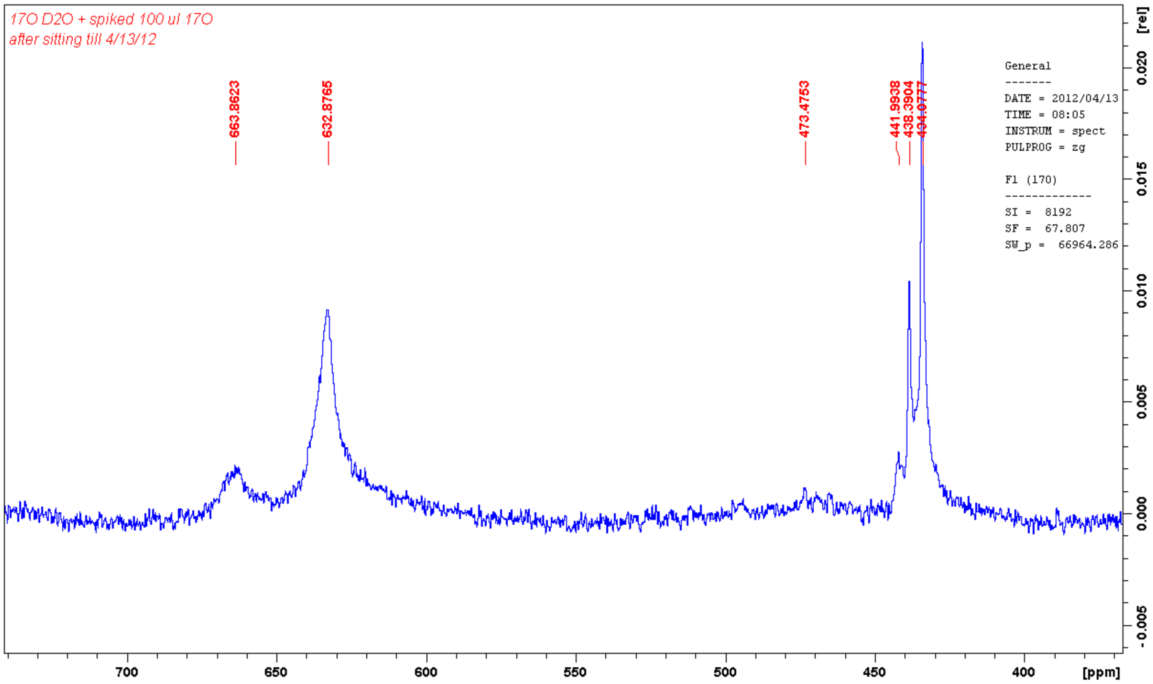

Figure S8. ^{17}O NMR spectrum of K-salt of $[GaNb_{18}O_{54}]^{15-}$ dissolved in 1 ml D_2O with 50 microliters $17OH_2$ (28%) added. Sharp peaks between 430 to 442 ppm are bridging μ_2-oxo ligands of the polyniobate. Broader peaks between 630 to 670 ppm are the terminal Nb=O resonances of the polyniobate. The Ga-bound aqua ligands were not observable, like due to broadening and masking by the large peak of free water.