Electronic Supplementary Material (ESI) for Chemical Communications.

Platinum polyoxoniobates

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Supporting information

Experimental part

General information. $[Pt(OH)_4(H_2O)_2]$ [1] and $K_7H[Nb_6O_{19}]\cdot 13H_2O$ [2] were prepared according to the literature. Commerical CsOH (Sigma Algrich) was used as purchased.

IR spectra (4000 – 400 cm^{-1}) were recorded on an IFS-85 Bruker spectrometer.

Elemental analyses were carried out by the analytical service of the Institute of Inorganic Chemistry (Novosibirsk).

NMR. ^{195}Pt NMR data was collected at Bruker Avance 500 spectrometer with inner references at room temperature. Reaction mixtures analyzed by addition of a small amount of D_2O, pure crystalline samples were dissolved in a mixed H_2O+D_2O solutions.

Synthesis of $Cs_2K_{10}[Nb_6O_{19}\{Pt(OH)_2\}]_2\cdot 13.4H_2O$ (Cs_2K_{10}-1): 0.100 g (0.07 mmol) of $K_7H[Nb_6O_{19}]\cdot 13H_2O$ was dissolved in 8 ml of water upon stirring and heating at 100 °C. To the resulting clear solution (pH = 12) 0.023 g of $[Pt(OH)_4(H_2O)_2]$ (0.07 mmol) was added. In order to accelerate the dissolution of platinum hydroxide and keeph the pH high to stabilize hexaniobate, 100 μl of 2M CsOH was added, final pH 12.

Then the solution was placed in a Teflon-lined Parr autoclave and kept for 10 hours at 150 °C (at lower temperature no reaction takes place). After cooling down and opening the container the solution was transferred into a small vial and left in air for crystallization. Yellow needle-like X-ray quality crystals of **Cs_2K_{10}-1** were isolated during slow evaporation in air after a few days. Yield 90%

IR (KBr, cm^{-1}): 3400 (s), 1649(s), 1630(s), 1402(m), 1370(m), 1007(m), 981(m), 943(m), 865(s), 834(s), 769(s), 702(s), 597(m), 534(s), 393(s).

EDX: Calc. Cs:K:Nb:Pt 2:10:12:2; Found 1.8:10.5:11.8:2.2

^{195}Pt NMR (D_2O, r.t.): $\delta = 3189$ ppm.

TGA: found 7.8%, calculated 7.6% ($13.4H_2O$)

$Na_2K_{10}[Pt(Nb_6O_{19})_2]\cdot 18H_2O$ (**Na_2K_{10}-2**) 0.20 g (0. 14 mmol) of $K_7H[Nb_6O_{19}]\cdot 13H_2O$ was dissolved in 8 ml of distilled water upon stirring and heating at 100 °C, after that 0.023 g of $[Pt(OH)_4(H_2O)_2]$ (0.07 mmol) was added, followed by addition of 100 µl of 2M CsOH (final pH 12). Then the solution was placed into a Teflon-lined Parr autoclave and kept for 10 hours at 170 °C. After cooling and opening the reactor the solution was transferred into an open beaker. Light-yellow single crystals of **Na_2K_{10}-2** in the shape of polyhedra were isolated. Yield 20%.

IR (KBr, cm^{-1}): 3342 (s), 1650 (s), 1402 (s), 1370 (s), 1007 (m), 981 (m), 863 (s), 833 (s), 763 (s), 702 (s), 667 (s), 535 (s).

EDX: Calc. Na:K:Nb:Pt 2:10:12:1; Found 1.9:11.0:11.7:1.1

^{195}Pt NMR of **Na_2K_{10}-2** (D_2O, r.t.): $\delta = 3422$ ppm.

TGA: found 9%, calculated 12% ($18H_2O$)

Crystallography. Crystallographic data and refinement details are given in Table S1 . The diffraction data were collected on a Bruker Apex Duo diffractometer with MoKα radiation ($\lambda = 0.71073$ Å) by doing φ and ω scans of narrow (0.5°) frames. Structures of **Cs_2K_{10}-1** and **Na_2K_{10}-2** were solved by direct methods and refined with full-matrix least-squares treatment against $|F|^2$ in anisotropic approximation with SHELXTL programs set [3].

Crystals of **Cs_2K_{10}-1** were always twinned due to combination of thin plates into the needles. Integration of experimental data with the Bruker program set did not result in full completeness. Crystal packing of this complex consists of dimeric $[Nb_6O_{19}\{Pt(OH)_2\}]_2^{12-}$ polyoxoanions, which form infinite columns along crystallographic axes *a* connecting through a dimers of potassium cations (Fig. S1).

The absorption corrections were applied empirically with SADABS program [4]. Hydrogen atoms of water molecules were not located. Further details may be obtained from the on quoting the depository number CSD 428355. Copies of this information may be obtained from ICSD (Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de)

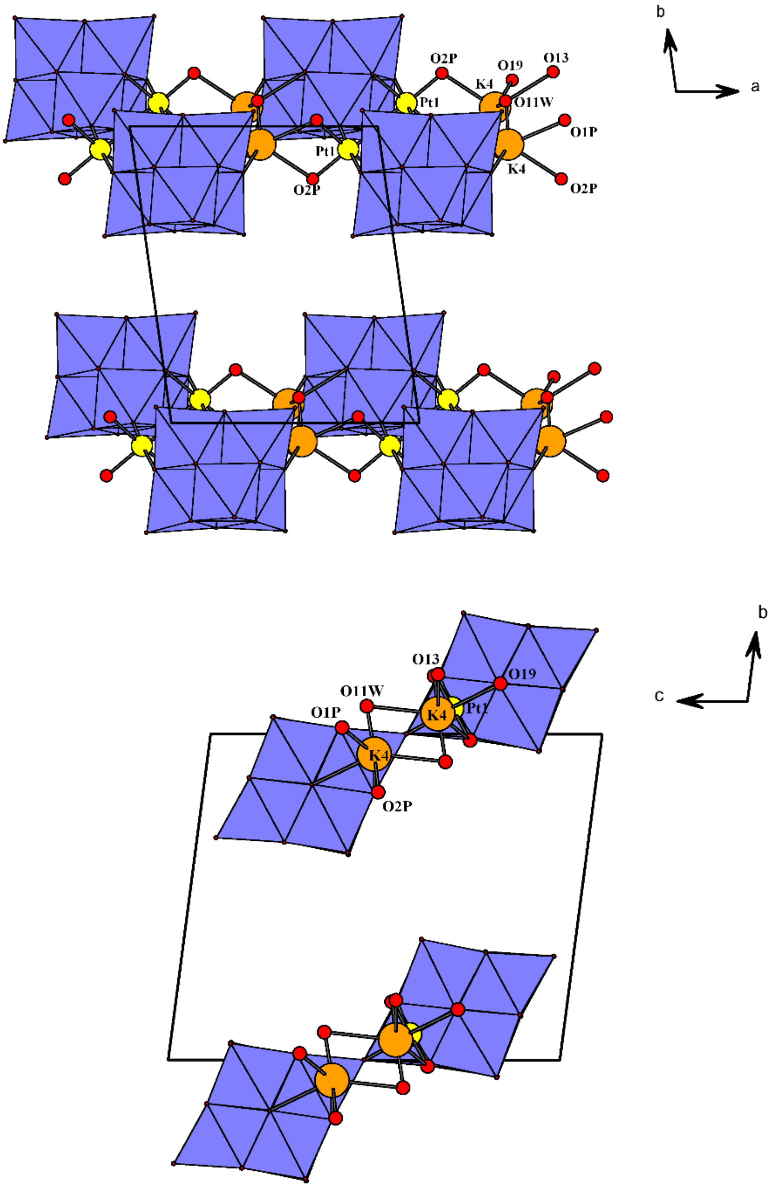

Fig. S1. Crystal packing of **Cs$_2$K$_{10}$-1**. along crystallographic axes *c* (up) and *a* (down)

Table S1. Experimental details

Experiments were carried out at 150 K with Mo *K*α radiation. Absorption was corrected for by multi-scan methods, *SADABS* (Bruker-AXS, 2004). H-atom parameters were not defined.

	$\mathbf{Cs_2K_{10}}$**-1**	$\mathbf{Na_2K_{10}}$**-2**
Chemical formula	$H_{30.80}Cs_2K_{10}Nb_{12}O_{65.40}Pt_2$	$H_{36}K_{10}Na_2Nb_{12}O_{56}Pt$
M_r	3239.36	2679.28
Crystal system, space group	Triclinic, $P\bar{1}$	Cubic, $Pa\bar{3}$
a, b, c (Å)	10.5213 (16), 12.6202 (19), 15.122 (2)	18.1811 (6), 18.1811 (6), 18.1811 (6)
α, β, γ (°)	96.136 (4), 98.791 (4), 96.912 (5)	90, 90, 90
V (Å^3)	1953.7 (5)	6009.8 (6)
Z	1	4
μ (mm^{-1})	6.81	5.33
Crystal size (mm)	0.35 × 0.07 × 0.05	0.10 × 0.08 × 0.08
Diffractometer	Bruker Apex Duo	Bruker Nonius X8Apex CCD
T_{min}, T_{max}	0.199, 0.727	0.618, 0.675
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13586, 7405, 5926	81602, 2311, 2004
R_{int}	0.043	0.057
Θ values (°)	$\Theta_{max} = 26.6$, $\Theta_{min} = 1.6$	$\Theta_{max} = 27.5$, $\Theta_{min} = 1.9$
Range of h, k, l	$-7 \leq h \leq 13$, $-15 \leq k \leq 15$, $-19 \leq l \leq 18$	$-23 \leq h \leq 23$, $-21 \leq k \leq 21$, $-23 \leq l \leq 23$
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.082, 0.230, 1.13	0.039, 0.143, 1.07
No. of reflections, parameters	7405, 415	2311, 144
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0652P)^2 + 179.1834P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.086P)^2 + 62.0731P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	4.30, -2.97	3.17, -0.96

Computer programs: *APEX2* (Bruker-AXS, 2004), *SAINT* (Bruker-AXS, 2004), *SHELXS2013*, *SHELXL2013*, *SHELXTL* (Bruker-AXS, 2004), CIFTAB-97 (Sheldrick, 1998).

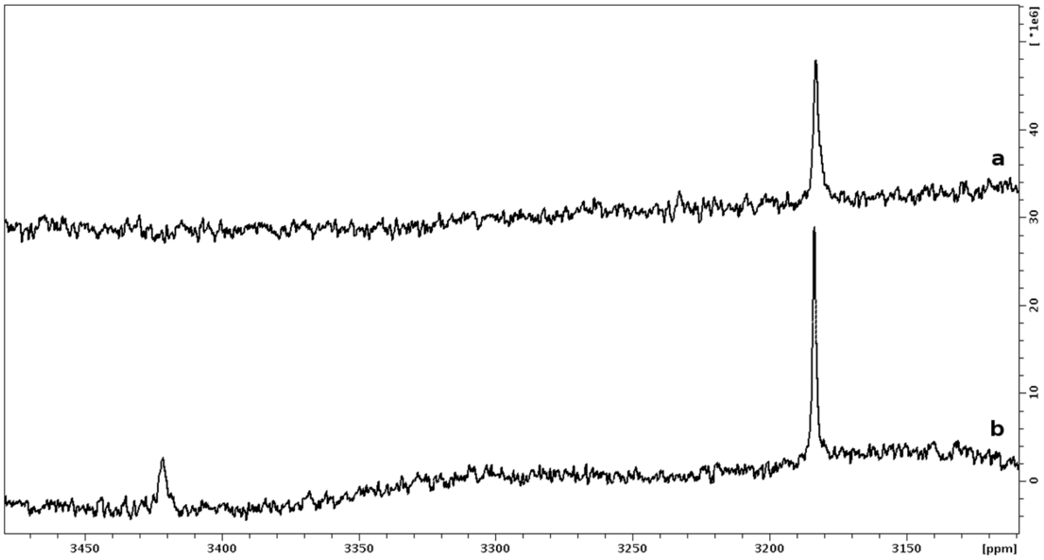

Fig. S2. ^{195}Pt NMR spectra of **1** (a) and a reaction mixture of **1** and **2** (b).

Electrospray Ionization Mass Spectrometry.

A Q-TOF Premier mass spectrometer with an orthogonal Z-spray electrospray source (Waters, Manchester, U.K.) was used. The temperature of the source block was set to 100 °C and the desolvation temperature to 120 °C. A capillary voltage of 3.3 kV was used in the negative scan mode, and the cone voltage was set to 5 V to control the extent of fragmentation of the identified species. TOF mass spectra were acquired in the W-mode operating at a resolution of ca. 15000 (fwhm). Mass calibration was performed using a solution of sodium iodide in isopropanol/water (50:50) from m/z 50 to 3000. Aqueous sample solutions were infused via syringe pump directly connected to the ESI source at a flow rate of 10 µL/min. Identification of each species we based on m/z determinations and comparison of the observed isotopic pattern of each compound with the theoretical isotope pattern calculated from their elemental composition using the MassLynx 4.1program. Because of the high charge of the identified Nb/O/Pt polyanions, extensive adduct formation with different cations (H+, K+ or Cs+) is observed that ultimately results in very crowded ESI mass spectra. For example, figure S3 (see below) displays the ESI mass spectrum of pure **Cs_2K_{10}-1** where the complete series of ions, namely $[(Nb_6O_{19}Pt(OH)_2)_2 + cat_8]^{4-}$ and $[(Nb_6O_{19}Pt(OH)_2)_2 + cat_9]^{3-}$ is observed. In this sense, the detection of the whole series of cation addcucts was also used as additional identification criterion. This is particularly useful for those samples where several species coexist and consequently the ESI mass spectrum is even more complicated. For example, in figure S3 ESI-MS spectra of clear fresh solution of **Cs_2K_{10}-1** is presented. Figures S4-S6 show the expanded regions of the ESI mass spectrum of adged (one week) aqueous solution of $[(Nb_6O_{19}Pt(OH)_2)_2]^{12-}$, where species $[(Nb_6O_{19}Pt(OH)_2)_2]^{12-}$, $[(Nb_6O_{19})_2Pt]^{12-}$, $[Nb_6O_{19}]^{8-}$ and $[Nb_6O_{19}Pt(OH)_3]^{7-}$ coexist. In this particular case, partial overlapping was observed and the observation of the whole series of identified polyanions as different cat+ adducts was useful as additional identification criterion.

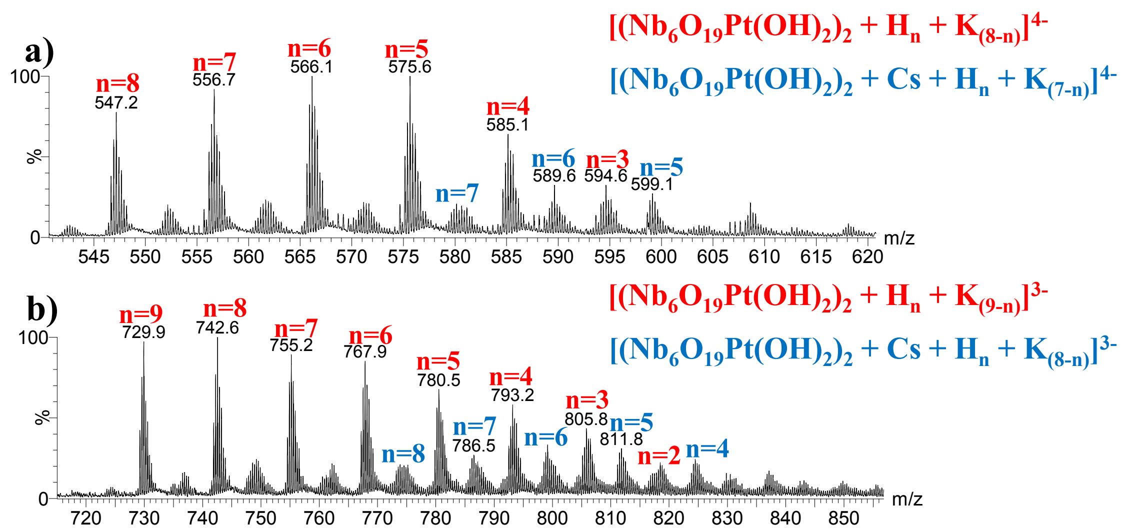

Figure S3. Different expanded regions of the ESI mass spectrum of aqueous solutions of **Cs_2K_{10}-1** a) in the m/z 540-620 range displaying complete peak assignment of species of general formula $[(Nb_6O_{19}Pt(OH)_2)_2 + cat_8]^{4-}$ and b) in the m/z 715-855 range displaying complete peak assignment of species of general formula $[(Nb_6O_{19}Pt(OH)_2)_2 + cat_9]^{3-}$ (cat stands for H^+, K^+ and Cs^+).

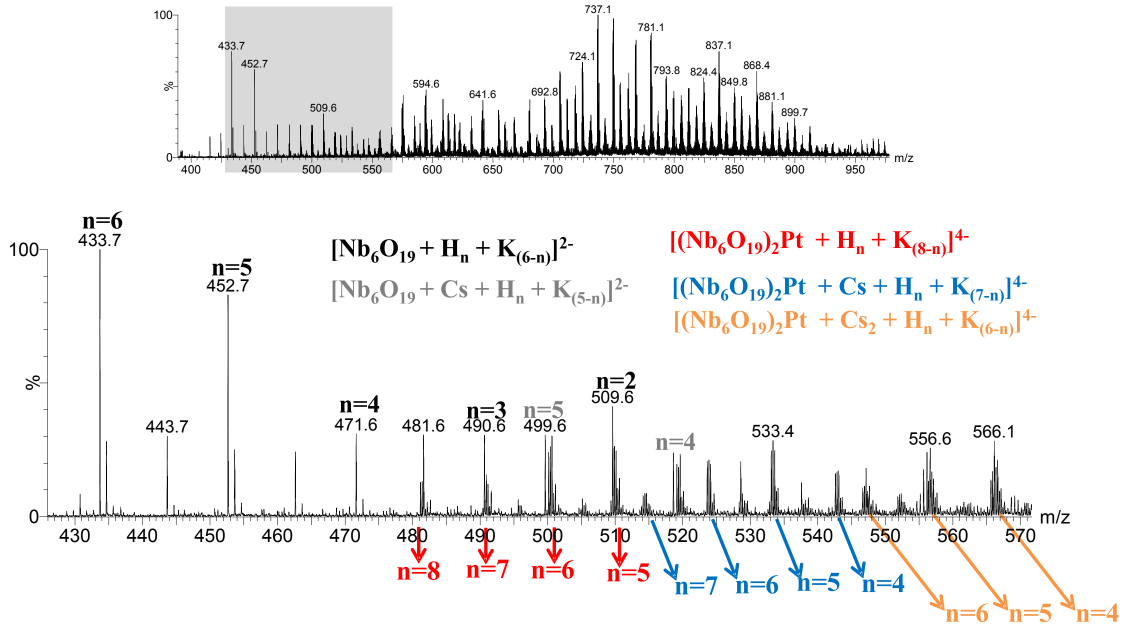

Figure S4. Full range ESI mass spectrum of aged aqueous solutions of **Cs_2K_{10}-1** (top). The grey background defines the expanded m/z region showed below. A series of peaks as different cation addcuts are observed consistent with the presence of $[Nb_6O_{19}]^{8-}$ and $[(Nb_6O_{19})_2Pt]^{12-}$.

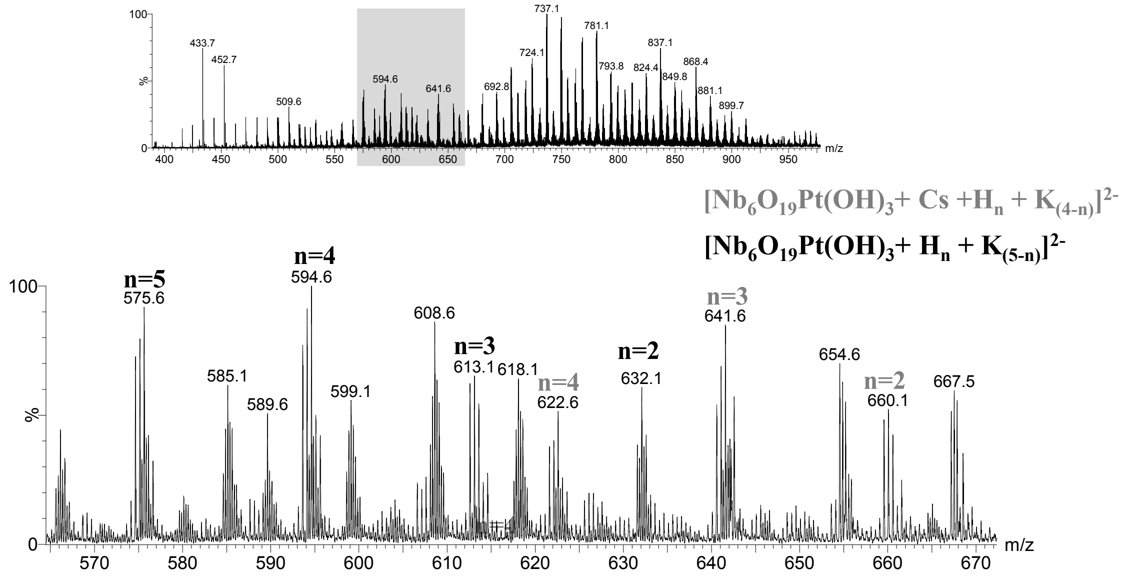

Figure S5. Full range ESI mass spectrum of aged aqueous solutions of **Cs_2K_{10}-1** (top). The grey background defines the expanded m/z region showed below. A series of peaks as different cation addcuts are observed consistent with the presence of $[Nb_6O_{19}Pt(OH)_3]^{7-}$.

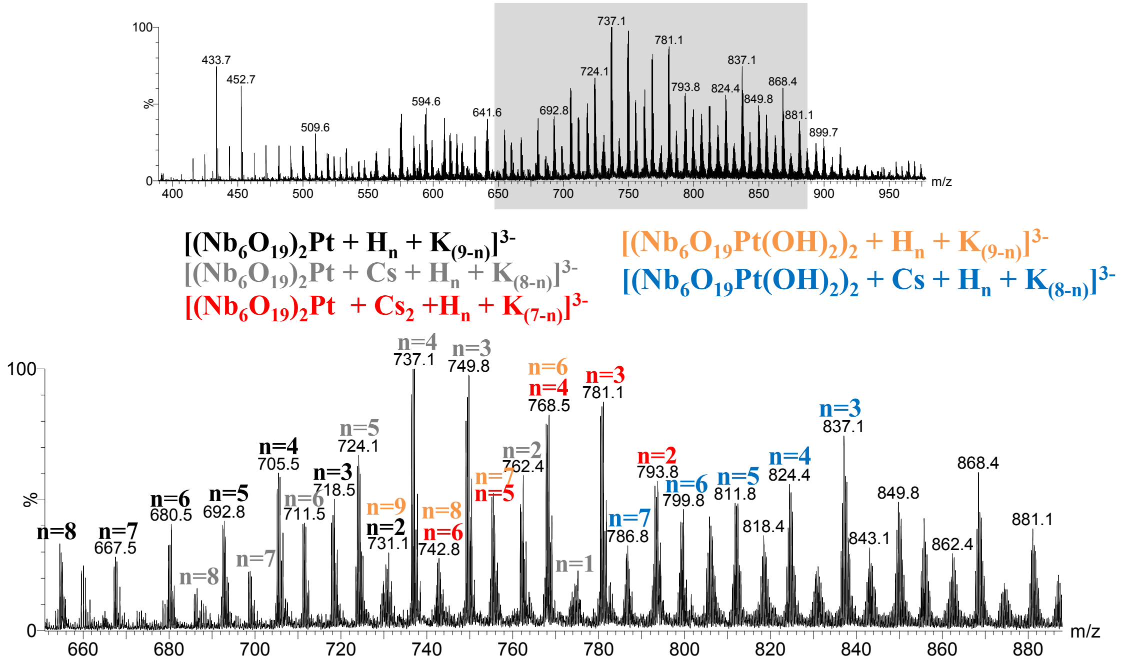

Figure S6. Full range ESI mass spectrum of aged aqueous solutions of **Cs_2K_{10}-1** (top). The grey background defines the expanded m/z region showed below. A series of peaks as different cation addcuts are observed consistent with the presence of $[(Nb_6O_{19})_2Pt]^{12-}$ and $[Nb_6O_{19}\{Pt(OH)_2\}]_2^{12-}$.

We can thus envision the following hydrolysis reactions depicted in equations 1 and 2 to explain the formation of $[Nb_6O_{19}Pt(OH)_3]^{7-}$ and $[Nb_6O_{19}]^{8-}$. Noticeably, these reactions also account for the interconversion between $[(Nb_6O_{19})_2Pt]^{12-}$ polyanion and $[Nb_6O_{19}\{Pt(OH)_2\}]_2^{12-}$ via common intermediate $[Nb_6O_{19}Pt(OH)_3]^{7-}$, the latter being formed both according to equation 1 and equation 2:

$$[(Nb_6O_{19})_2Pt]^{12-} + 3OH^- \rightarrow [Nb_6O_{19}\{Pt(OH)_3\}]^{7-} + [Nb_6O_{19}]^{8-} \ (1)$$

$$[Nb_6O_{19}\{Pt(OH)_2\}]_2^{12-} + 2OH^- \rightarrow 2[Nb_6O_{19}\{Pt(OH)_3\}]^{7-} (2)$$

No products other than **Cs_2K_{10}-1** and **Na_2K_{10}-2** were detected when more than 2 eq. of $[Pt(OH)_4(H_2O)_2]$ were used for reaction with hexaniobate.

[1] D. Vasilchenko, S. Tkachev, I. Baidina, S. Korenev, *Inorg. Chem.*, 2013, 52 (18), pp 10532–10541

[2] C. M. Flynn, G. D. Stucky, Inorg. Chem., 1969, 8, 178.

[3] *SHELXTL (Version 6.12)*, Bruker Advanced X-ray Solutions, Bruker AXS Inc., Madison, Wisconsin, USA, **2004**.

[4] *APEX2 (Version 1.08), SAINT (Version 7.03), and SADABS (Version 2.11)*, Bruker Advanced X-ray Solutions, Bruker AXS Inc., Madison, Wisconsin, USA, **2004**.

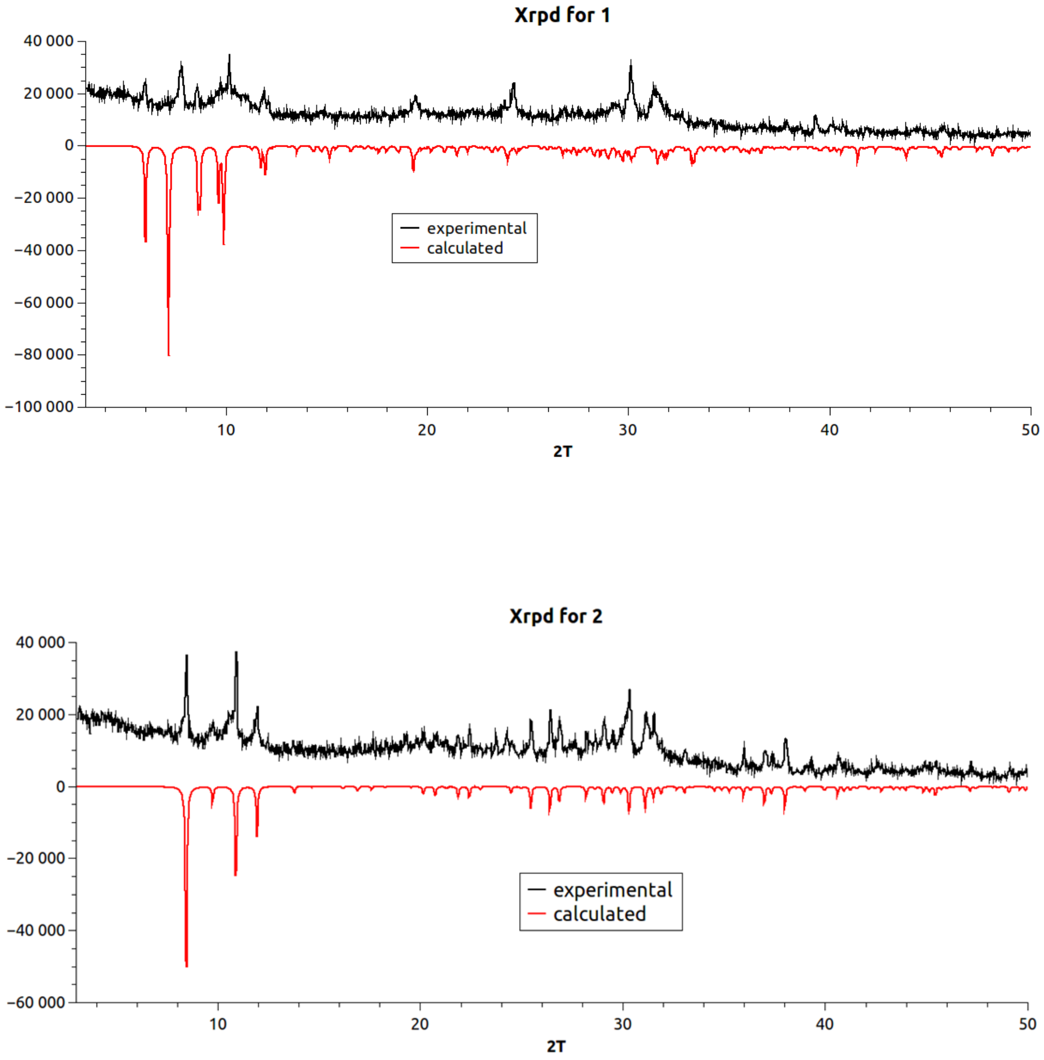

Figure. S7. X-ray powder patterns

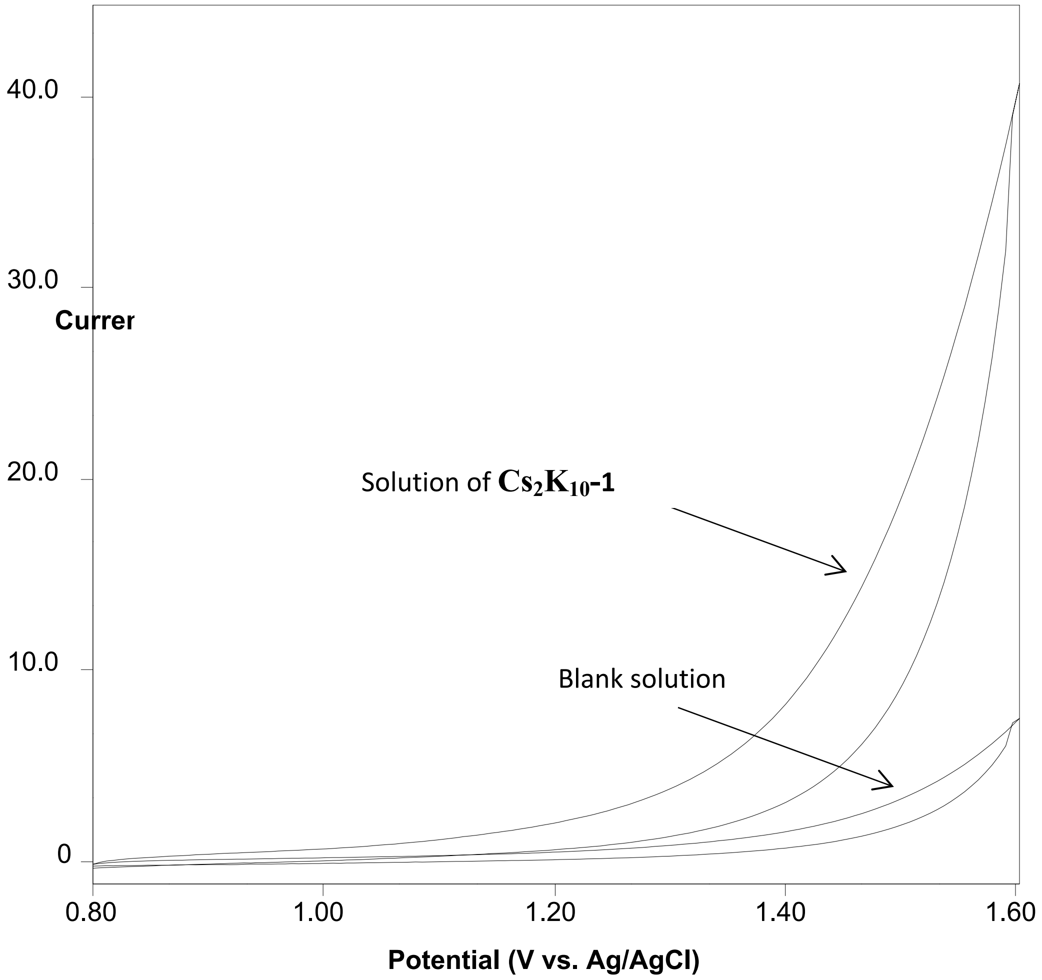

Figure S8. The cyclic voltammogram of **Cs_2K_{10}-1** in 0.1 M Na_2SO_4 at the glassy carbon electrode. Scan rate: 0.8 ↔ 1.6 V. Scan rate: 0.1 V s^{-1}.

Cyclic voltammetry was performed on a 797 VA Computrace electrochemical analyser (Metrohm, Switzerland). All measurements were carried out with a conventional three-electrode configuration consisting of glassy carbon working and platinum wire counter electrodes and a Ag/AgCl reference electrode containing aqueous 3 M KCl. The supporting electrolyte was 0.1 M Na_2SO_4 in water.