Electronic Supplementary Material (ESI) for Dalton Transactions.

Grafting $\{Cp^*Rh\}^{2+}$ on the surface of Nb and Ta Lindqvist-type POM

P.A. Abramov[1,2], M.N. Sokolov[1,2], A.V. Virovets,[1] S. Floquet[3], M. Haouas[3], F. Taulelle[3], E. Cadot[3], C. Vicent[4], V.P. Fedin[1,2]

[1] *Nikolaev Institute of Inorganic chemistry SB RAS, Novosibirsk, Russia 630090*

[2] *Novosibirsk State University*, *Novosibirsk, Russia 630090*

[3] *Institut Lavoisier de Versailles, UMR 8180, University of Versailles Saint-Quention en Yvelines, 45 Avenue des Etats-Unis, 78035 Versailles, France*

[4] *Serveis Centrals d'Instrumentació Científica, Universitat Jaume I, Av. Sos Baynat s/n, 12071 Castelló, Spain*

Supporting information

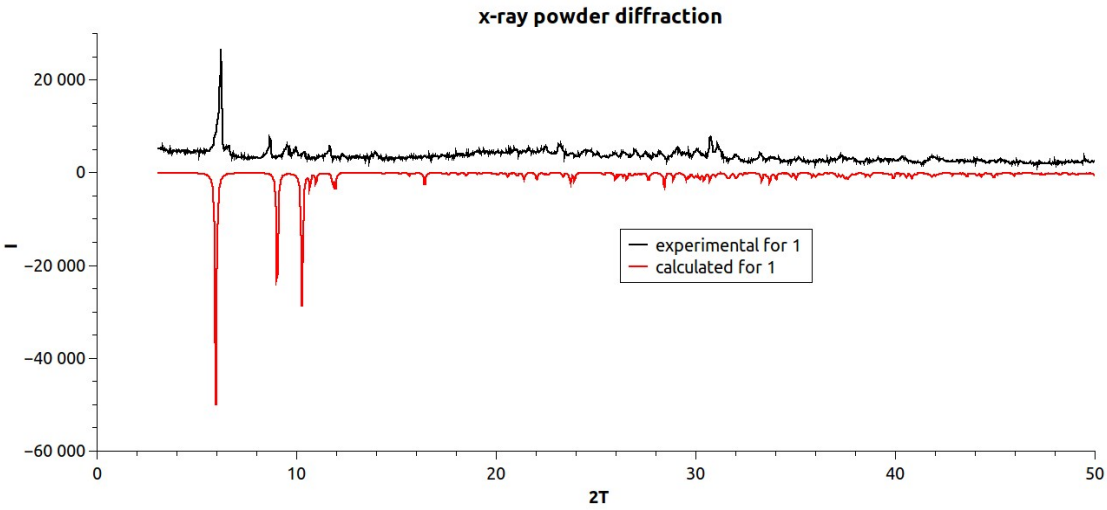

Fig. S1. X-ray powder pattern for complex **1**.

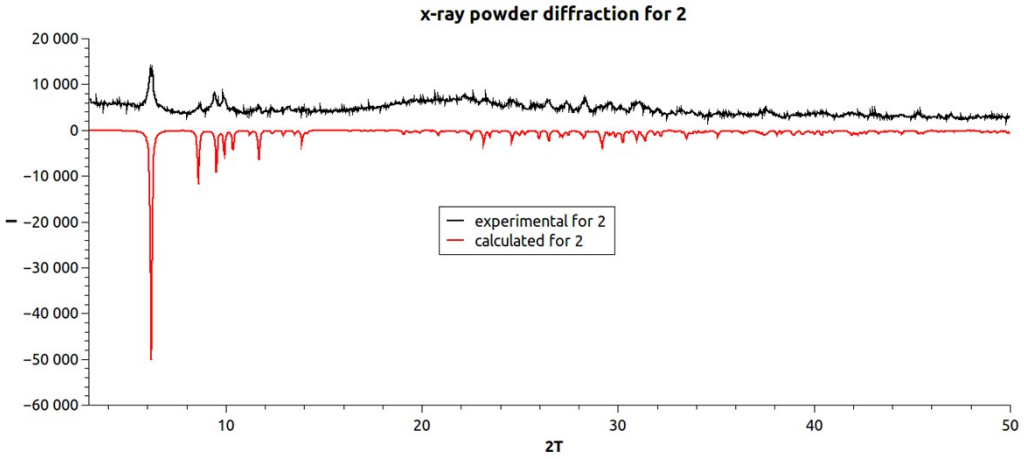

Fig. S2. X-ray powder pattern for complex **2**.

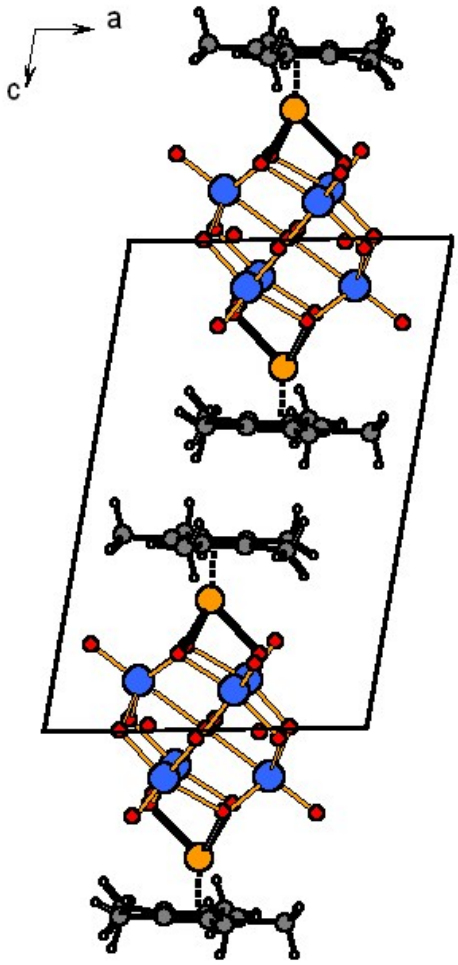

Fig. S3. Part of the layered crystal packing of **2**, formation of π-π interactions between layers. Tantalum is blue, Rh is orange, C is grey.

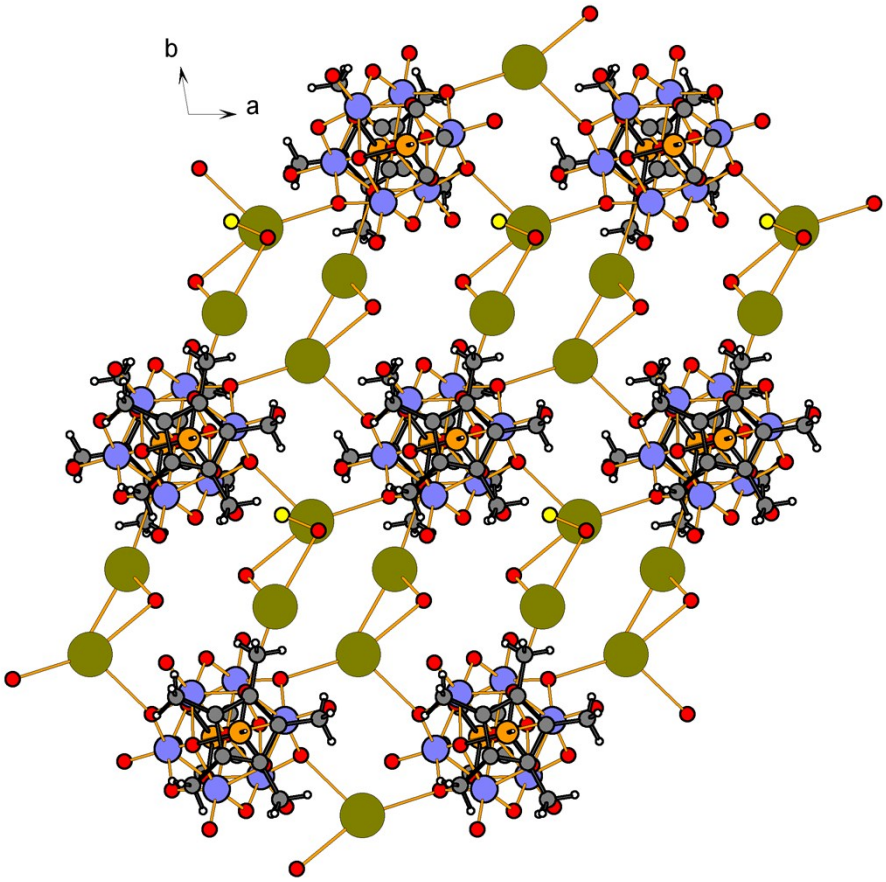

Fig. S4. Dimers of Cs+ (green-brown) cations inside the layer in the crystal packing of **2**. Tantalum is blue, rhodium is orange. Disordered positions of the water molecules are shown as red and yellow.

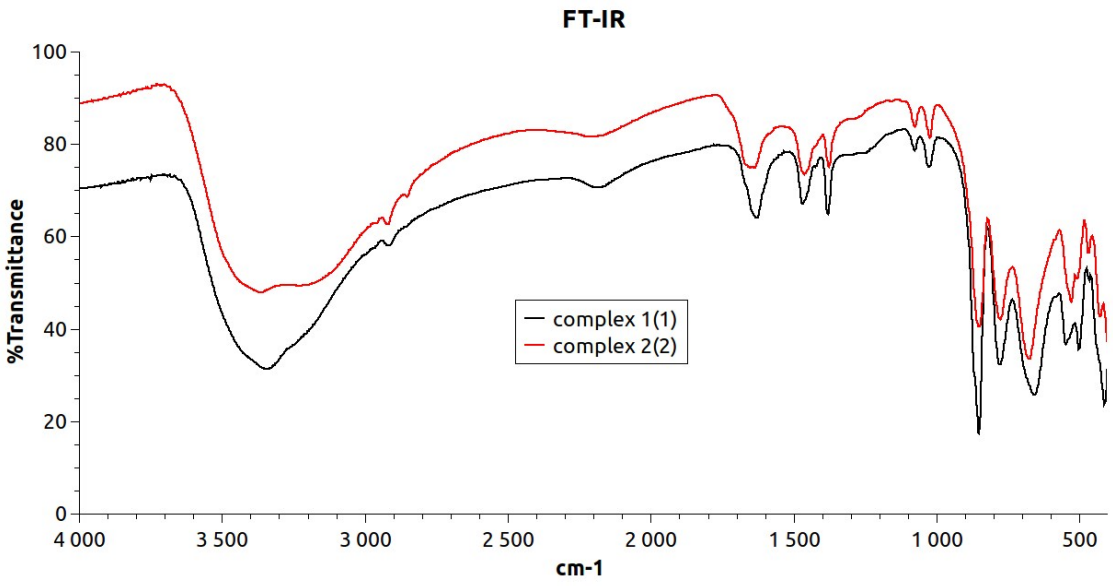

Figure S5. FT-IR spectra of 1 and 2.

The FT-IR spectra of 1 and 2 show characteristic vibration bands resulting from the Lindqvist hexaniobate structure, namely, the peak at 861 cm^{-1} attributed to terminal Nb–Ot characteristic vibration, as well as peaks at 772, 686, 532, and 437 cm^{-1} assigned to bridging Nb–Ob–Nb vibration [1]. IR bands from {Cp*Rh} fragments are 2952, 2875, 1465, 1374, 1150, 1063 cm^{-1}.

[1] A.V. Besserguenev, M.H. Dickman, M.T. Pope, Inorg. Chem. 2001, 40, 2582.

Table S1. Experimental details

	1	**2**
Chemical formula	$C_{20}H_{70}K_4Nb_6O_{39}Rh_2$	$C_{20}H_{66}Cs_4O_{37}Rh_2Ta_6$
M_r	1854.44	2721.89
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$
Temperature (K)	150	150
a, b, c (Å)	14.8711 (17), 9.5972 (11), 19.615 (2)	9.5851 (10), 10.5155 (11), 14.6458 (15)
α, β, γ (°)	90, 91.761 (3), 90	95.814 (3), 99.365 (3), 98.708 (3)
V (Å^3)	2798.1 (5)	1427.7 (3)
Z	2	1
F(000)	1828	1230
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	2.15	14.61
Crystal size (mm)	0.28 × 0.06 × 0.04	0.08 × 0.07 × 0.07
Diffractometer	Bruker Apex2 Duo	Bruker Apex2 Duo
Absorption correction	Empirical (using intensity measurements) based on intensities (*SADABS*, Bruker, 2005)	Empirical (using intensity measurements) based on intensities (*SADABS*, Bruker, 2005)
T_{min}, T_{max}	0.603, 0.746	0.596, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19444, 8599, 6081	8488, 6435, 4679
R_{int}	0.062	0.036
θ values (°)	$\theta_{max} = 30.7$, $\theta_{min} = 2.1$	$\theta_{max} = 27.5$, $\theta_{min} = 2.2$
Range of h, k, l	$-21 \le h \le 11$, $-13 \le k \le 13$, $l = -26 \le l \le 28$	$-12 \le h \le 11$, $-13 \le k \le 10$, $-18 \le l \le 19$

$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.066, 0.143, 1.10	0.048, 0.106, 1.03
No. of reflections, parameters, restraints	8599, 327, 6	6435, 327, 108
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0218P)^2 + 45.4204P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0387P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.94, -1.70	2.10, -3.68

Computer programs: Apex2 V.1.27 (Bruker, 2005), *SHELXS97* (Sheldrick, 1990), *SHELXL97* (Sheldrick, 1997), *SHELXTL* V6.22 (Bruker, 2000-2005), local programs.