Reactions of $K_2[Ru(NO)Cl_5$ with pseudotrilacunary $\{XW_9O_{33}\}^{9-}$ (X = As^{III}, Sb^{III}) anions

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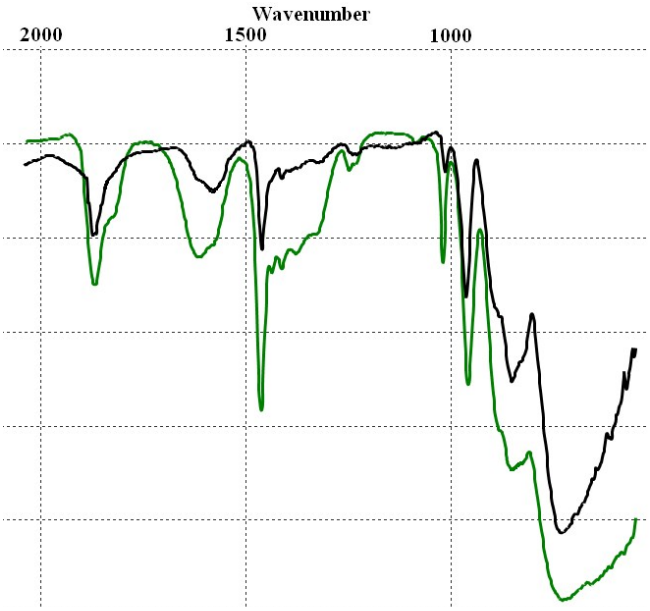
Supporting Information

Fig. S1. The FT-IR of IR of $((CH_3)_2NH_2)_7[As_2W_{17}\{Ru(NO)\}O_{61}]\cdot 4.5H_2O$ and **$(Bu_4N)_4H_3[\alpha_2\text{-}As_2W_{17}\{Ru(NO)\}O_{61}]$**



DMAH$^+$ salt: IR (ATR, cm^{-1}): 1868 (m), 1825 (sh), 1612 (m), 1580 (sh), 1463 (vs), 1437 (m), 1412 (m), 1378 (m), 1330 (m), 1248 (w), 1233 (w), 1085 (w), 1019 (m), 958 (s), 884 (sh), 853 (vs), 830 (sh), 728 (vs).
TBA$^+$ salt: IR (ATR, cm^{-1}): 1870 (m), 1580 (w), 1463 (m), 1412 (w), 1330 (w), 1235 (w), 1015 (w), 960 (m), 884 (sh), 852 (vs), 826 (sh), 728 (vs).

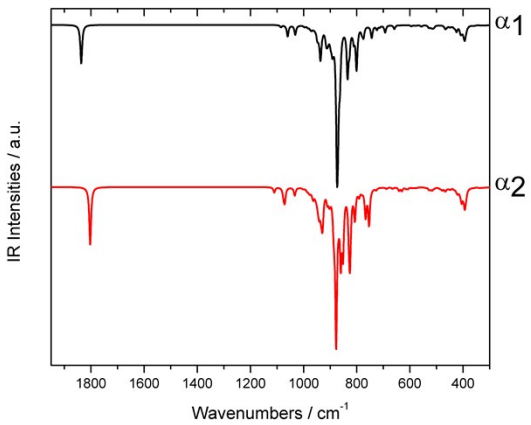
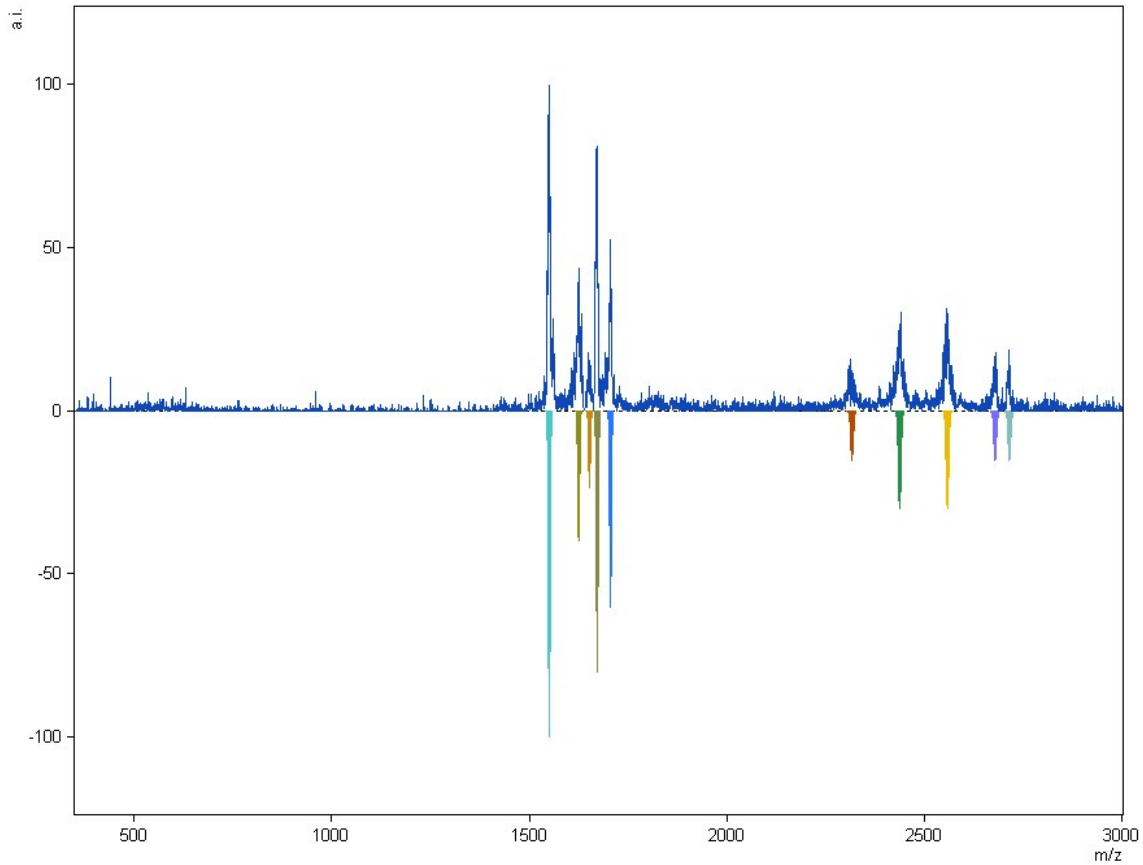


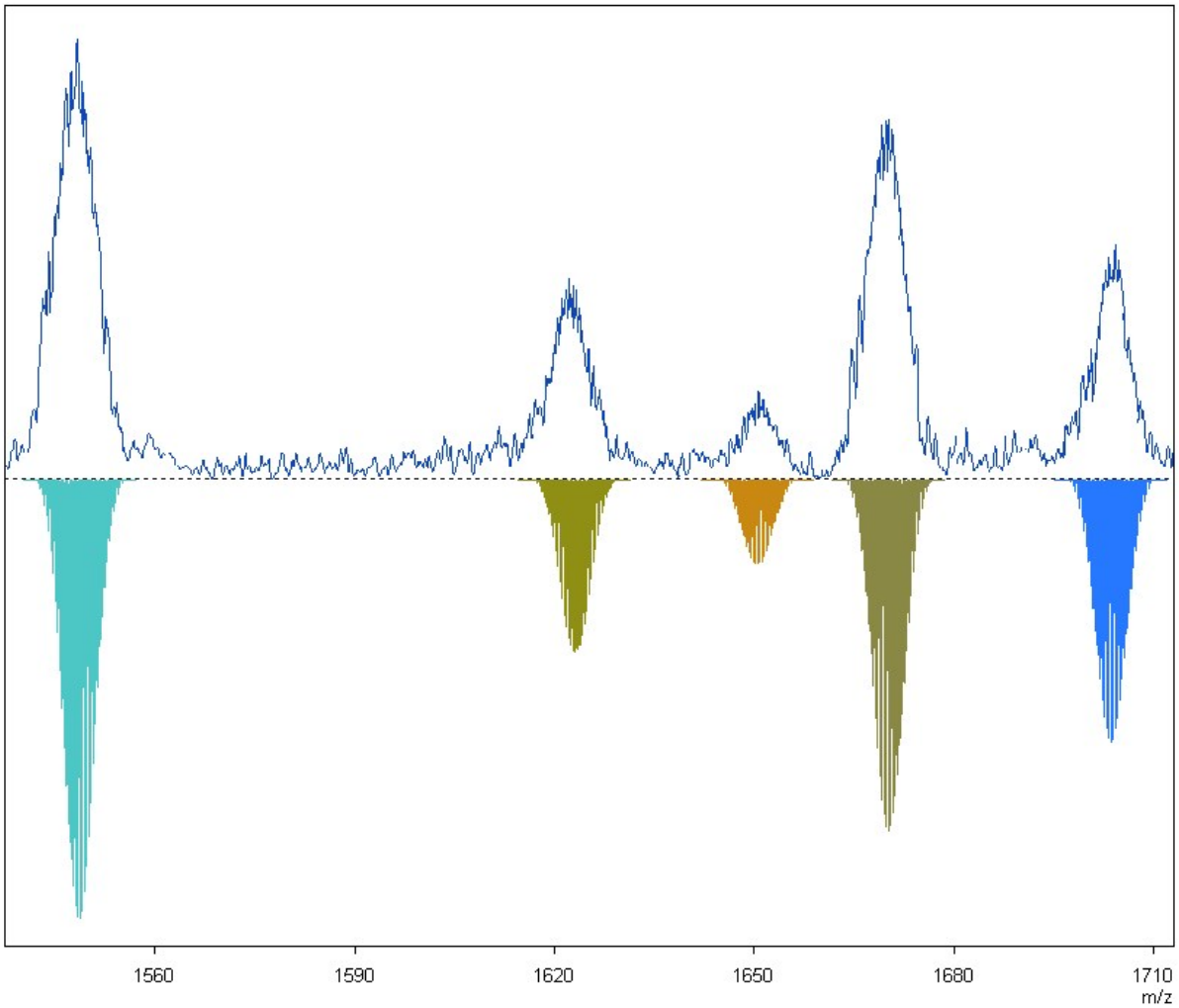
Fig. S1a. IR spectra of $[As_2W_{17}\{Ru(NO)\}O_{61}]^{7-}$ as computed at DFT M06-2X level (for the basis set, see Computational Details) in harmonic approximation. Comparison of the α_1 (black solid line) and α_2 phase (red solid line). No scale factor applied.

Fig. S2. ESI-MS spectrum of $(Bu_4N)_4H_3[As_2W_{17}\{Ru(NO)\}O_{61}]$ in CH_3CN

a) Full spectrum (calculated patterns have negative intensities).



b) Zoomed 1500-1710 m/z region (calculated patterns have negative intensities).



c) Zoomed 2250 - 2750 m/z region (calculated patterns have negative intensities).

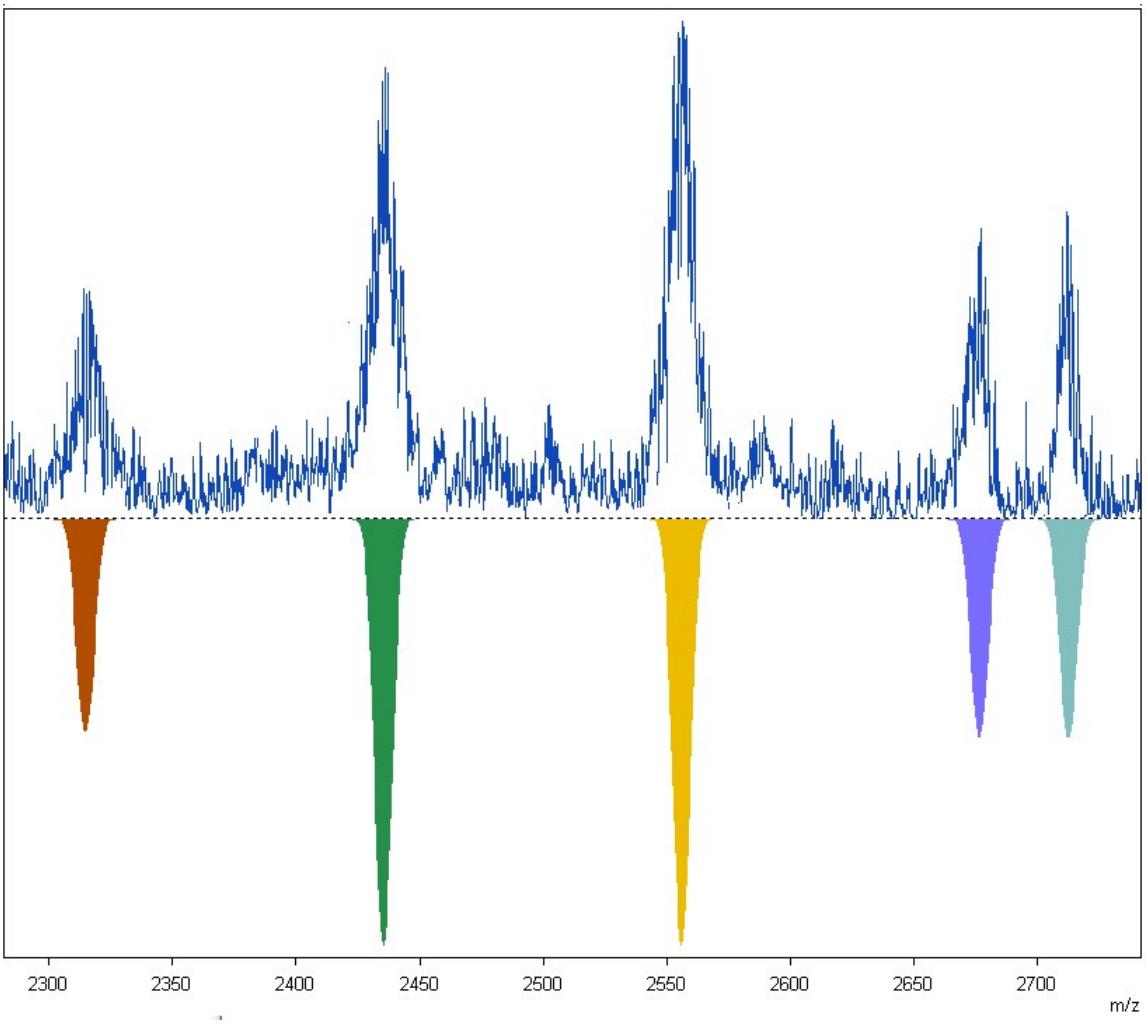


Table S1. Peak assignment for ESI-MS of $(Bu_4N)_4H_3[As_2W_{17}\{Ru(NO)\}O_{61}]$ in CH_3CN

anion	calc	exp
$\{(Bu_4N)H_3Ru(NO)As_2W_{17}O_{61}(H_2O)\}^{3-}$	1548.6	1548.6
$\{(Bu_4N)_2H_2Ru(NO)As_2W_{17}O_{61}\}^{3-}$	1623.1	1623.1
$\{(Bu_4N)_2H_2Ru(NO)As_2W_{17}O_{61}(CH_3CN)_2\}^{3-}$	1650.4	1650.4
$\{(Bu_4N)_2H_2Ru(NO)As_2W_{17}O_{61}(CH_3CN)_3(H_2O)\}^{3-}$	1670.1	1670.1
$\{(Bu_4N)_3HRu(NO)As_2W_{17}O_{61}\}^{3-}$	1703.5	1703.6
$\{(Bu_4N)H_4Ru(NO)As_2W_{17}O_{61}\}^{2-}$	2314.5	2314.4
$\{(Bu_4N)_2H_3Ru(NO)As_2W_{17}O_{61}\}^{2-}$	2435.1	2435.1
$\{(Bu_4N)_3H_2Ru(NO)As_2W_{17}O_{61}\}^{2-}$	2555.7	2555.7
$\{(Bu_4N)_4HRu(NO)As_2W_{17}O_{61}\}^{2-}$	2676.4	2676.5
$\{(Bu_4N)_4HRu(NO)As_2W_{17}O_{61}(H_2O)_4\}^{2-}$	2712.4	2712.4

Table S2. Atomic ratios W/Ru, W/Sb calculated from HPLC-ICP-AES-data.

Anion	W/Ru (theory)	W/Ru (found)	W/Sb (theory)	W/Sb (found)
$[SbW_{18}O_{60}]^{9-}$	-	-	18.0	16.6±1.7
$[SbW_{17}\{Ru(NO)\}O_{59}]^{10-}$	17.0	16.5±1.5	17.0	16.4±1.5
$[SbW_{15}\{Ru(NO)\}_3O_{57}]^{12-}$	5.0	5.4±0.5	15.0	16.0±1.5
$[As_2W_{17}\{Ru(NO)\}O_{61}]^{7-}$	17.0	17.3±1.6	-	-

Fig. S3. XRPD of **CsKNa-2** (calculated pattern has negative intensity)**.**

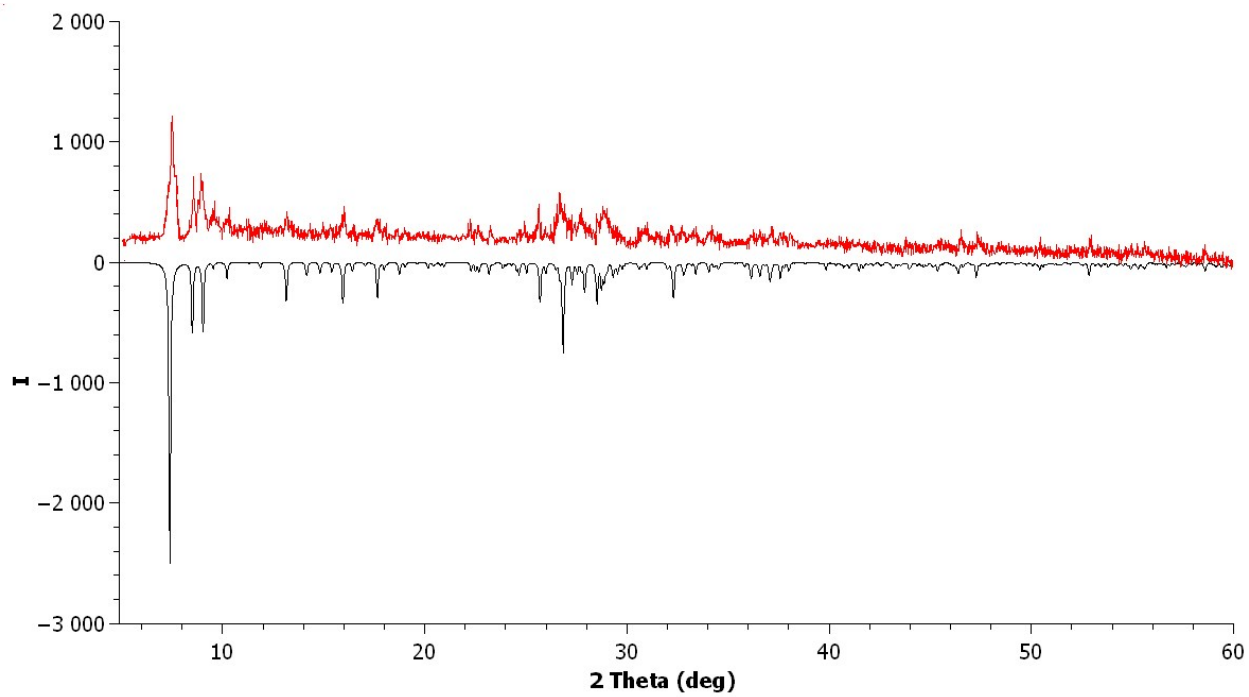
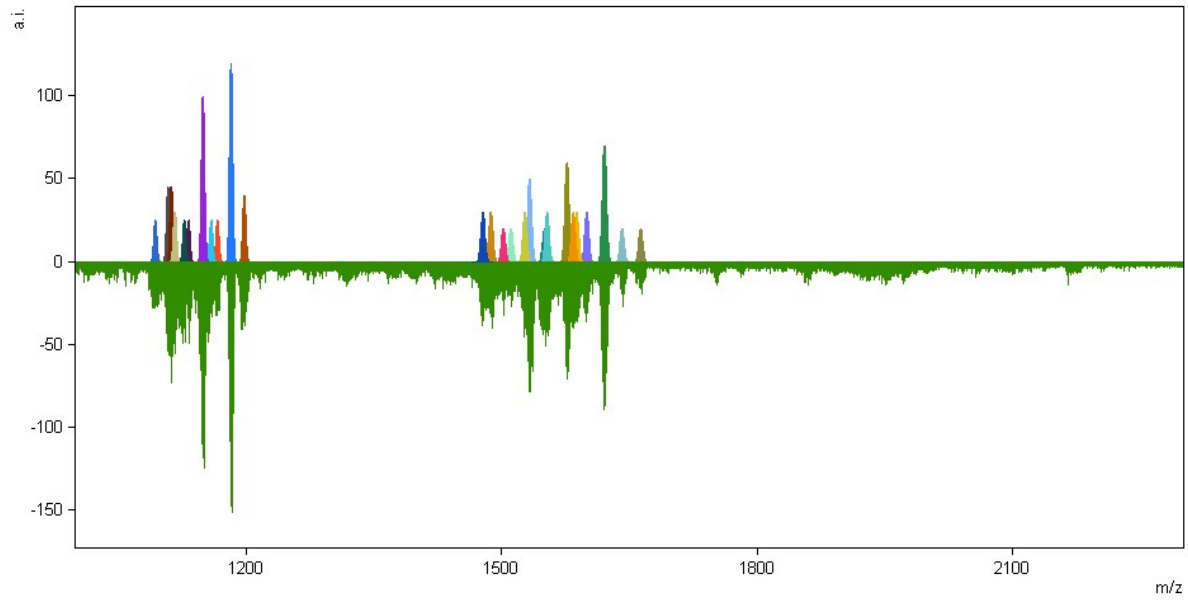


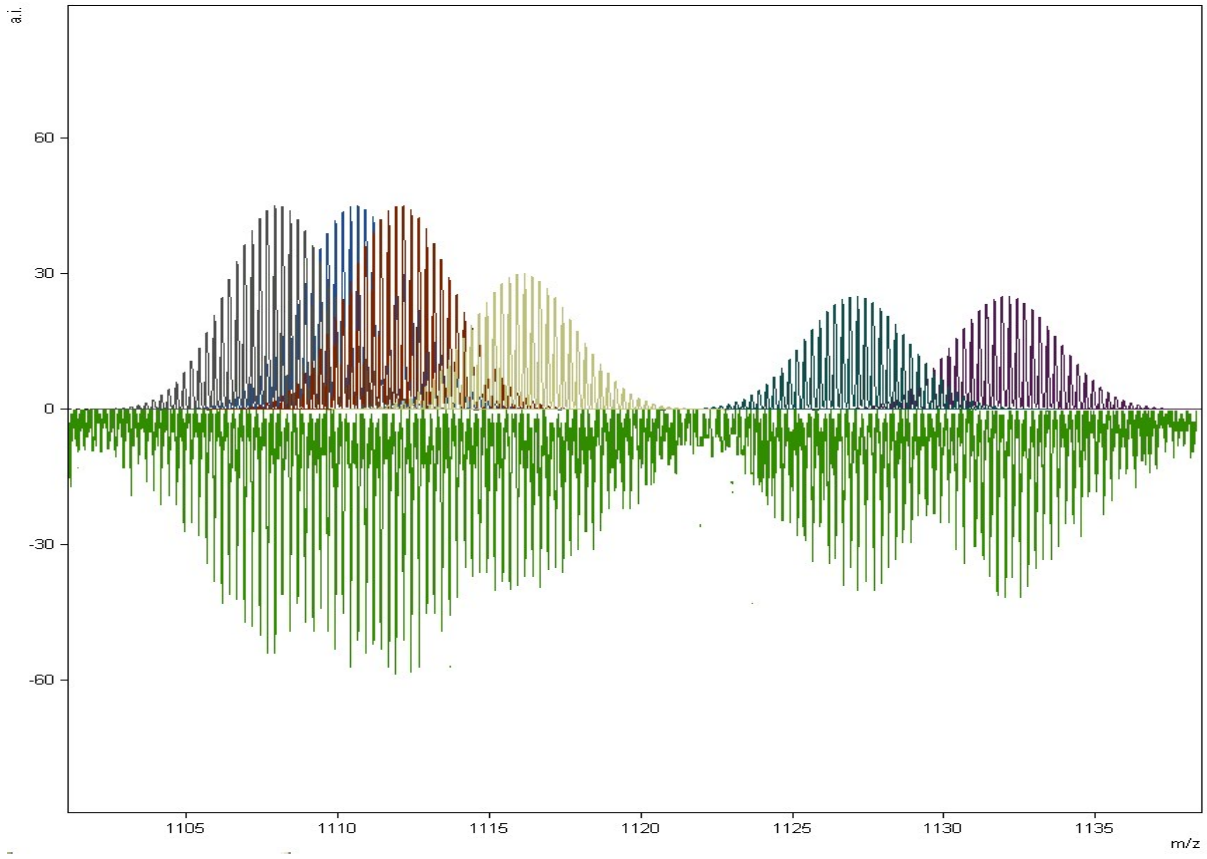
Fig. S4. HR-ESI-MS of **CsKNa-2** in aqueous solution (experimental spectrum at negative intensity).

a) Full spectrum (calculated patterns have positive intensities).

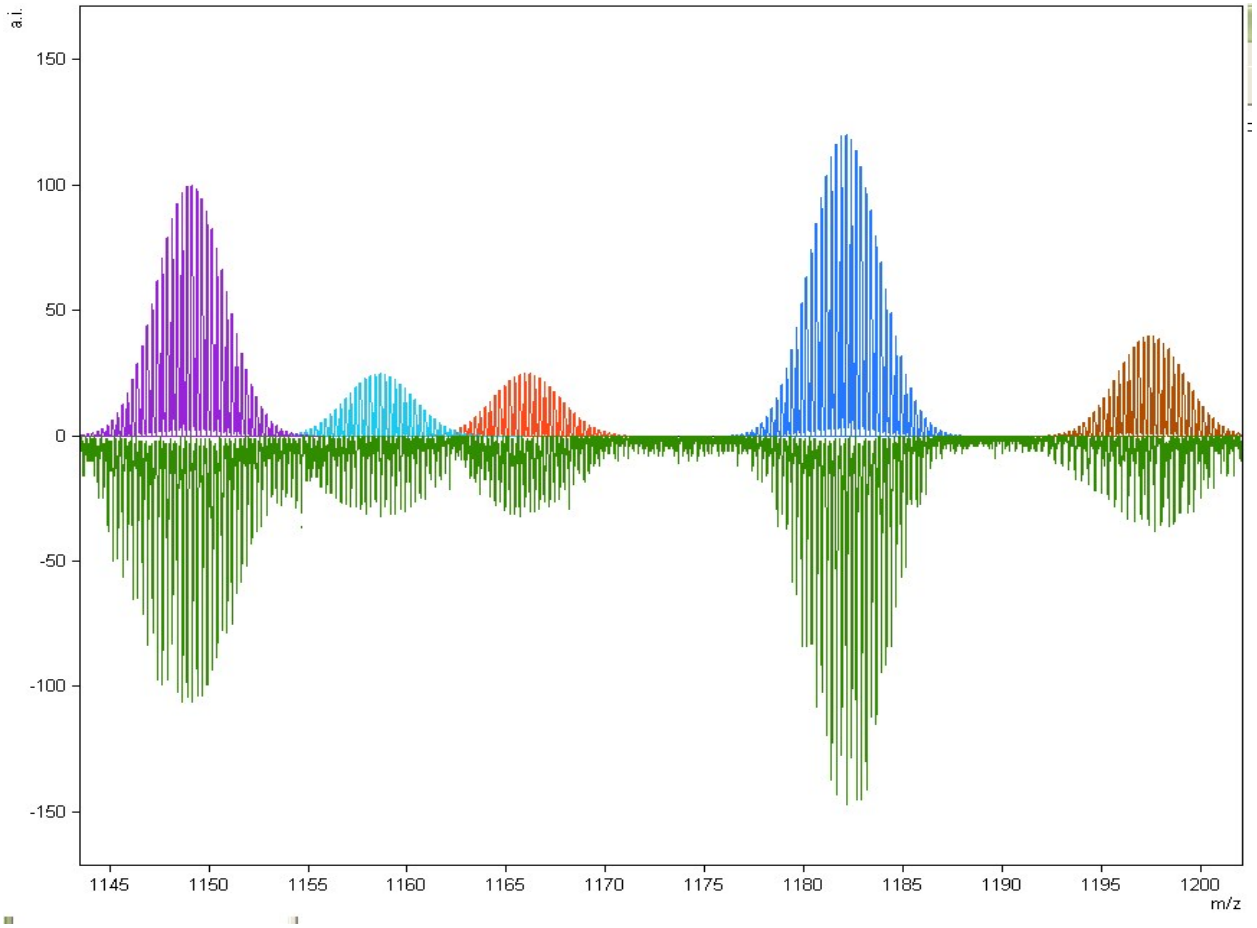


Comparison of observed and theoretical patterns

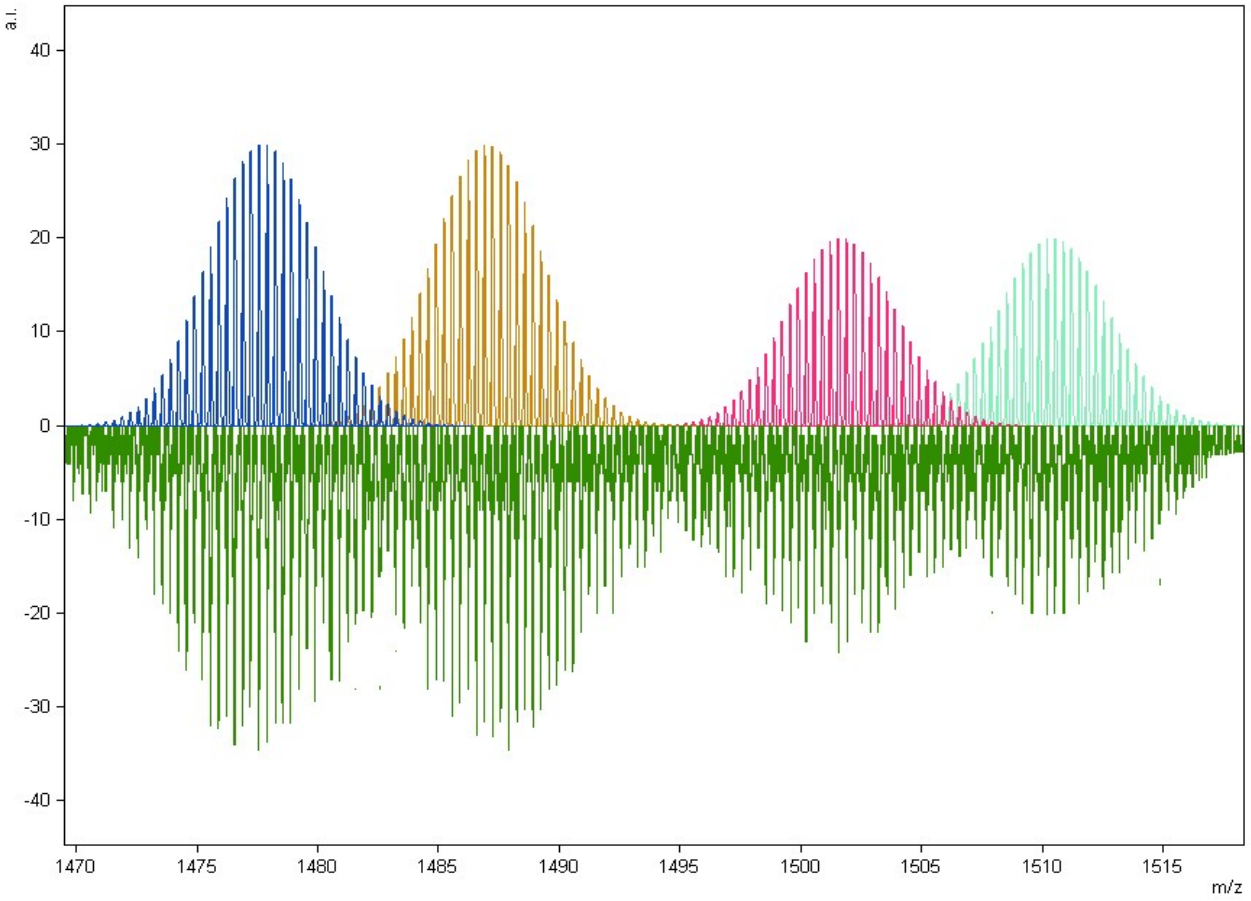
b) Zoomed 1100-1140 m/z area (calculated patterns have positive intensities).



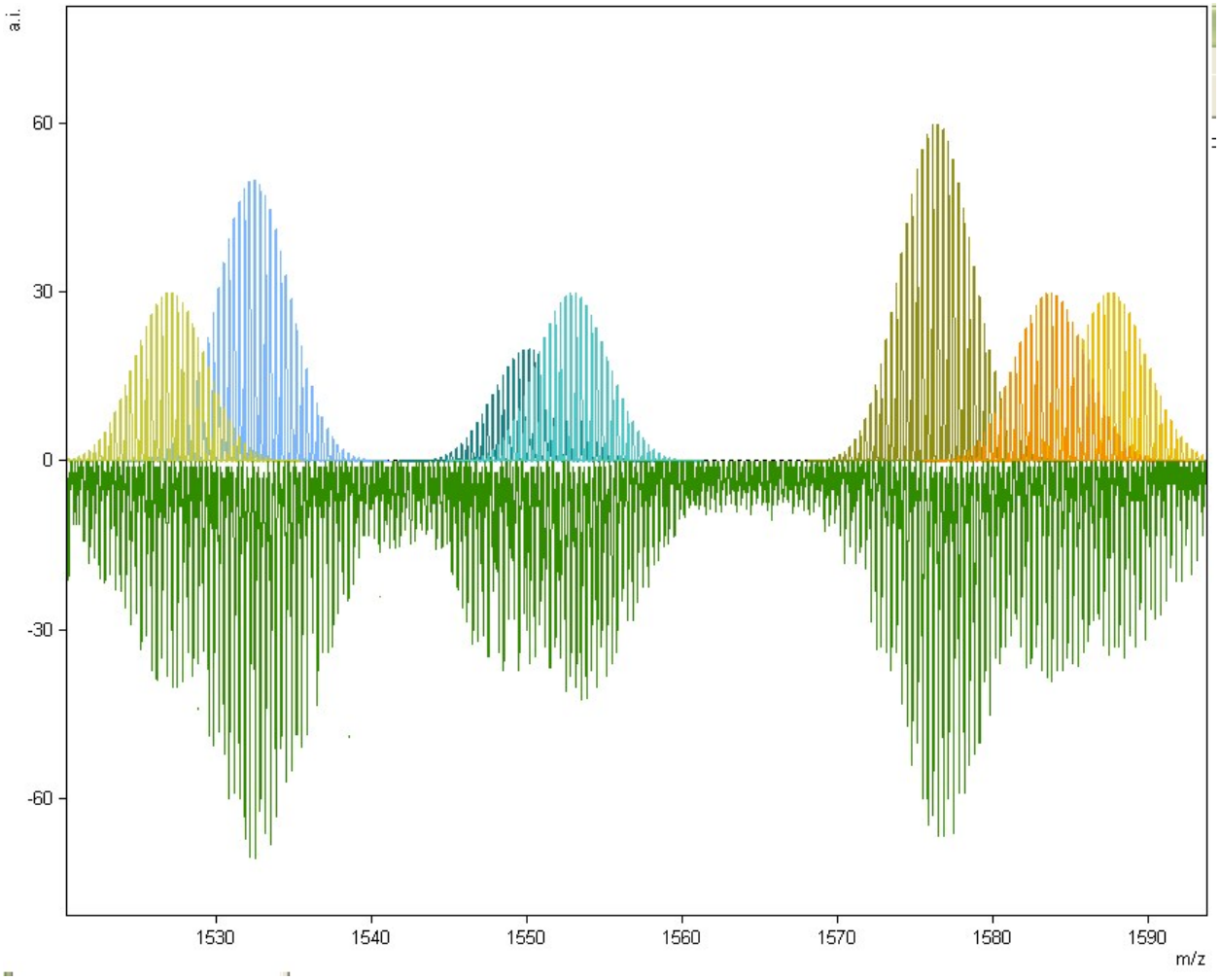
c) Zoomed 1140-1205 m/z area (calculated patterns have positive intensities).



d) Zoomed 1470-1520 m/z area (calculated patterns have positive intensities).



e) Zoomed 1520-1595 m/z area (calculated patterns have positive intensities).



f) Zoomed 1590-1670 m/z area (calculated patterns have positive intensities).

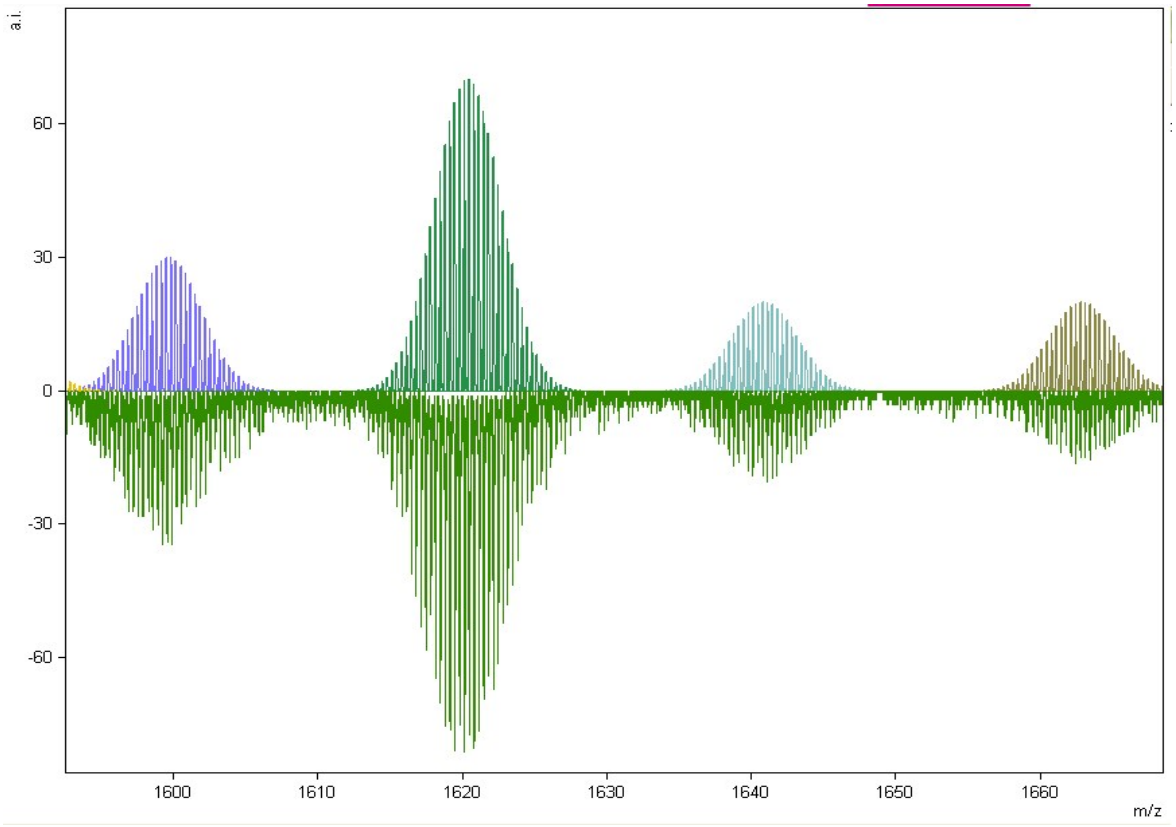


Table S3. Peak assignment for HR-ESI-MS of **CsKNa-2** in aqueous solution.

anion	calc	exp
$\{Na_2H_4SbW_{17}Ru(NO)O_{59}\}^{4-}$	1092.9	1092.9
$\{KNa_3H_2SbW_{17}RuNO)O_{59}\}^{4-}$	1107.9	1107.9
$\{K_3H_3SbW_{17}Ru(NO)O_{59}\}^{4-}$	1110.6	1110.6
$\{K_2Na_2H_2SbW_{17}Ru(NO)O_{59}\}^{4-}$	1112.1	1112.1
$\{K_3NaH_2SbW_{17}Ru(NO)O_{59}\}^{4-}$	1116.1	1116.1
$\{K_3Na_3SbW_{17}Ru(NO)O_{59}\}^{4-}$	1127.1	1127.1
$\{K_2Na_4SbW_{17}Ru(NO)O_{59}(H_2O)_2\}^{4-}$	1132.1	1132.1
$\{CsK_3NaHSbW_{17}Ru(NO)O_{59}\}^{4-}$	1149.1	1149.1
$\{CsK_4NaSbW_{17}Ru(NO)O_{59}\}^{4-}$	1158.6	1158.6
$\{Cs_2H_4SbW_{17}Ru(NO)O_{59}(H_2O)_4\}^{4-}$	1165.9	1165.8
$\{Cs_2NaK_3SbW_{17}Ru(NO)O_{59}\}^{4-}$	1182.1	1182.1
$\{Cs_3Na_3SbW_{17}Ru(NO)O_{59}\}^{4-}$	1197.3	1197.3
$\{KNa_3H_3SbW_{17}Ru(NO)O_{59}\}^{3-}$	1477.5	1477.5
$\{CsH_6SbW_{17}Ru(NO)O_{59}\}^{3-}$	1486.9	1486.9
$\{CsNa_2H_4SbW_{17}Ru(NO)O_{59}\}^{3-}$	1501.5	1501.5
$\{K_3Na_4SbW_{17}Ru(NO)O_{59}\}^{3-}$	1510.5	1510.5
$\{CsK_2Na_2H_2SbW_{17}Ru(NO)O_{59}\}^{3-}$	1527.2	1527.2
$\{CsK_3NaH_2SbW_{17}Ru(NO)O_{59}\}^{3-}$	1532.5	1532.5
$\{CsK_5HSbW_{17}Ru(NO)O_{59}\}^{3-}$	1550.1	1550.1
$\{Cs_2Na_3H_2SbW_{17}Ru(NO)O_{59}\}^{3-}$	1552.8	1552.8
$\{Cs_2NaK_3HSbW_{17}Ru(NO)O_{59}\}^{3-}$	1576.5	1576.5
$\{Cs_2K_3Na_2SbW_{17}Ru(NO)O_{59}\}^{3-}$	1583.8	1583.8
$\{Cs_3KH_3SbW_{17}Ru(NO)O_{59}\}^{3-}$	1587.5	1587.5
$\{Cs_3KH_3SbW_{17}Ru(NO)O_{59}(H_2O)_2\}^{3-}$	1599.5	1599.4
$\{Cs_3K_3NaSbW_{17}Ru(NO)O_{59}\}^{3-}$	1620.4	1620.4
$\{Cs_4Na_3SbW_{17}Ru(NO)O_{59}\}^{3-}$	1640.8	1640.9
$\{Cs_5H_2SbW_{17}Ru(NO)O_{59}\}^{3-}$	1662.7	1662.7

Fig. S5. HPLC-UV (left) and HPLC-ICP-AES (right) for aqueous solution of **CsKNa-2.**

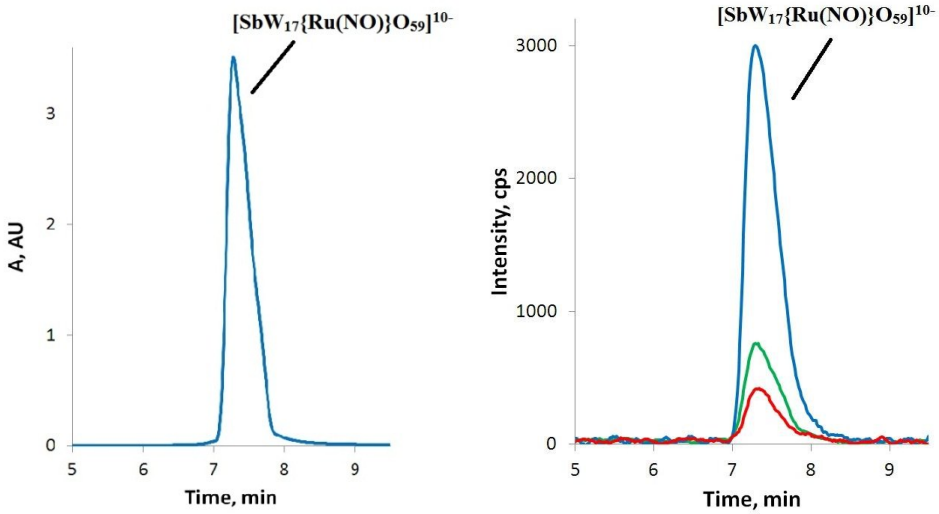
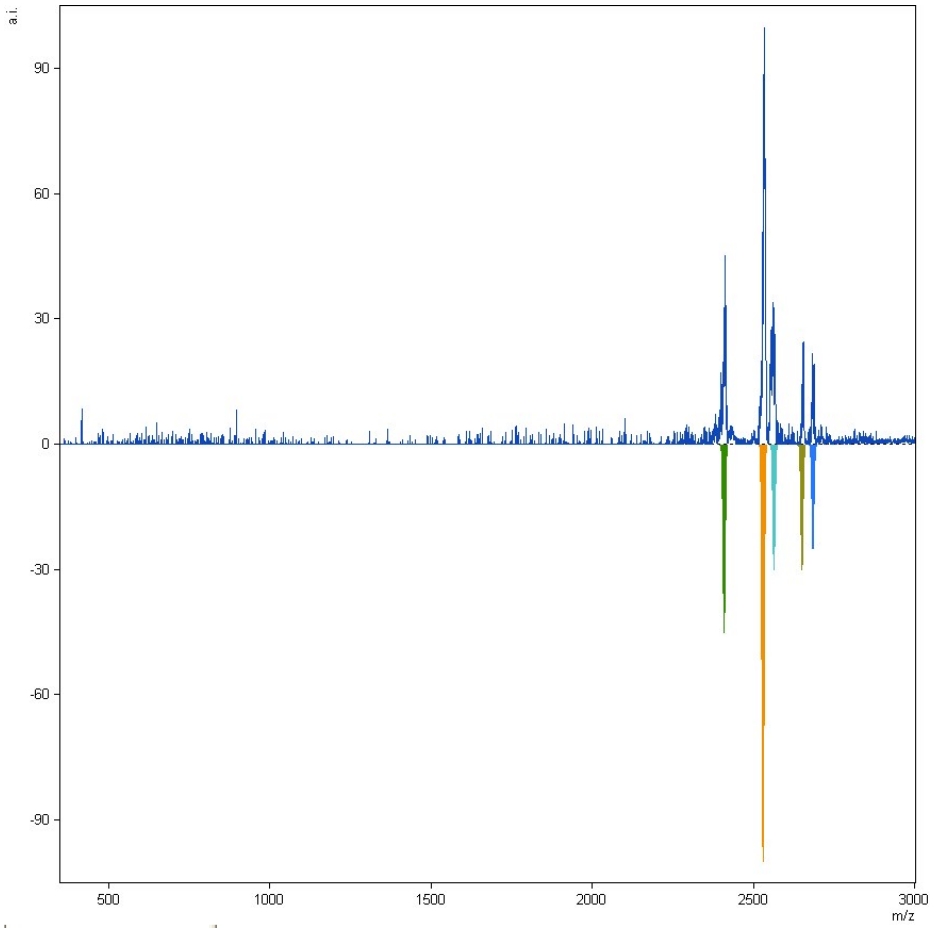


Fig. S7. ESI-MS spectrum of $[SbW_{17}\{Ru(NO)\}O_{59}]^{10-}$ and $[SbW_{18}O_{60}]^{9-}$ mixture in CH_3CN.

a) Full spectrum (calculated patterns have negative intensities).



b) Zoomed 2390-2700 m/z area (calculated patterns have negative intensities).

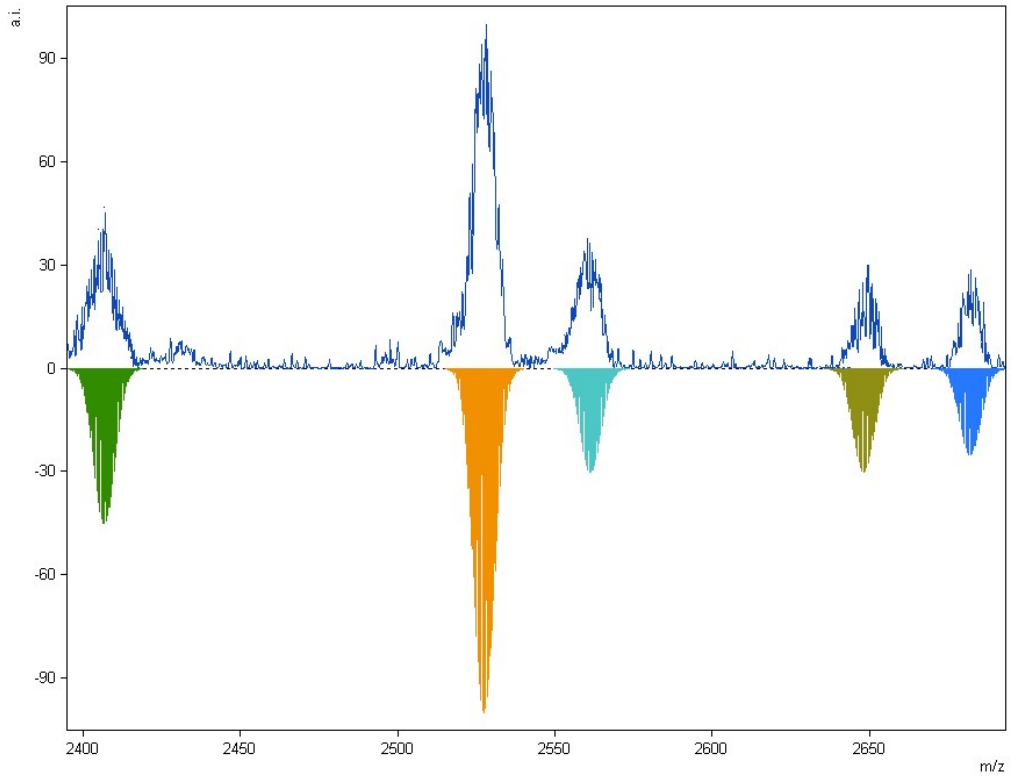
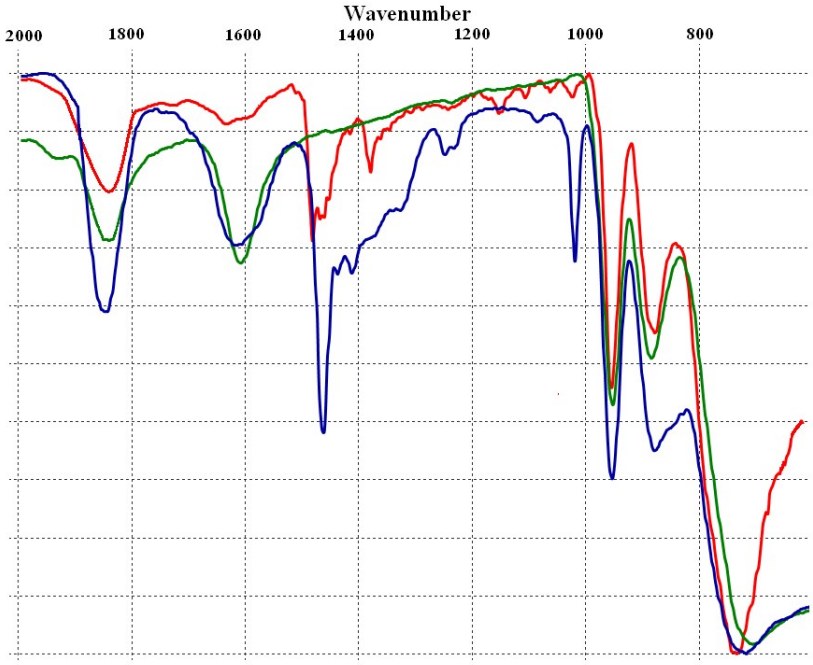


Table S4. Peak assignment for Fig. S7.

anion	calc	exp
$\{(Bu_4N)_2H_6RuNOSbW_{17}O_{59}\}^{2-}$	2406.6	2406.6
$\{(Bu_4N)_3H_5RuNOSbW_{17}O_{59}\}^{2-}$	2527.3	2527.4
$\{(Bu_4N)_3H_4SbW_{18}O_{60}\}^{2-}$	2561.3	2561.3
$\{(Bu_4N)_4H_4RuNOSbW_{17}O_{59}\}^{2-}$	2647.9	2647.9
$\{(Bu_4N)_4H_3SbW_{18}O_{60}\}^{2-}$	2681.9	2681.9

Fig. S8. Experimental FT-IR for DMA-2, TBA-2 and Cs_6KNa_3-2**.**



$DMAH^+$ salt: IR (ATR, cm^{-1}): 1842 (s), 1618 (s), 1462 (vs), 1438 (m), 1412 (m), 1326 (sh), 1248 (w), 1232(w), 1085 (w), 1019 (m), 954 (vs), 879 (s), 718 (vs).

TBA^+ salt: IR (ATR, cm^{-1}): 1837 (m), 1630 (w), 1481 (m), 1466(m), 1379 (m), 1153 (w), 955 (s), 878 (s), 733 (vs).

Cs^+ salt: IR (ATR, cm^{-1}): 1840 (m), 1608 (m), 952 (s), 882 (s), 718 (vs).

Fig. S9. Calculated IR spectra for $[SbW_{17}\{Ru(NO)\}O_{59}]^{10-}$ isomers.

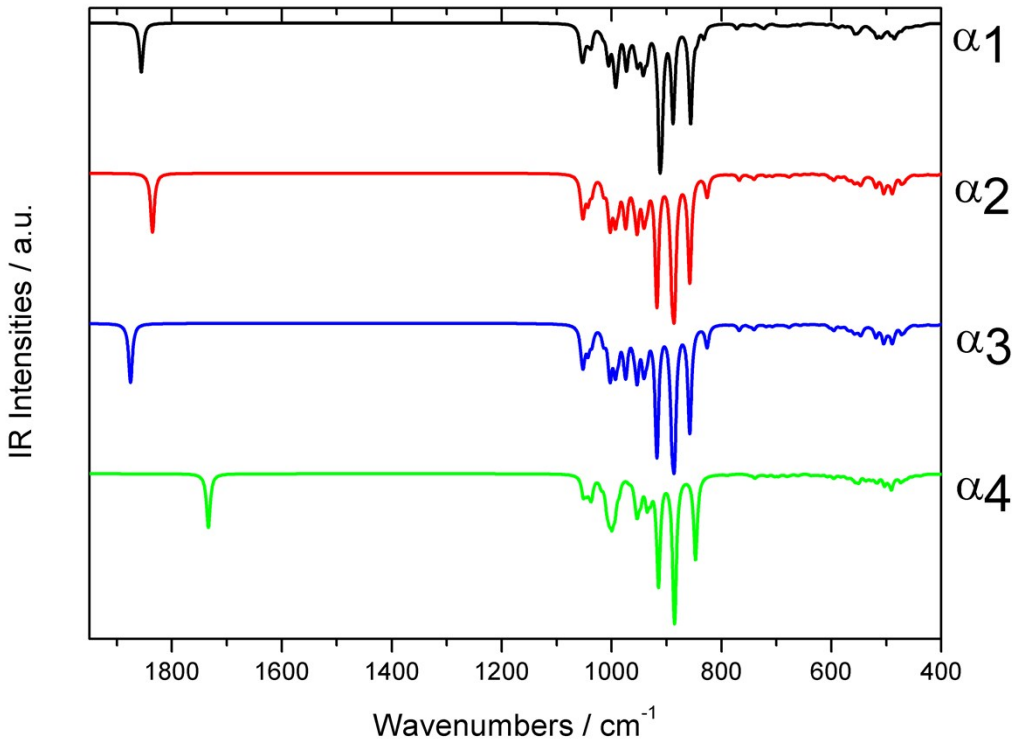


Fig. S10. The cyclic voltammogram of **Bu_4N-2** in CH_3CN at potential scan rate of 0.1 V/s.

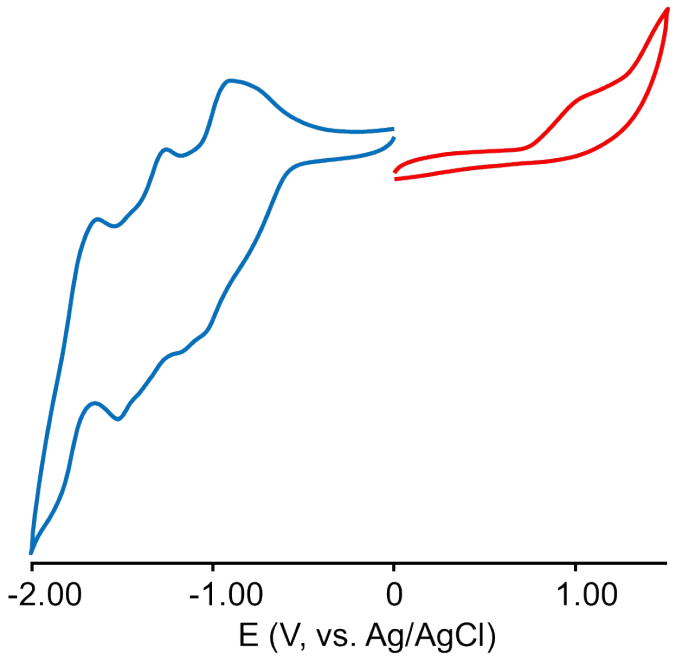
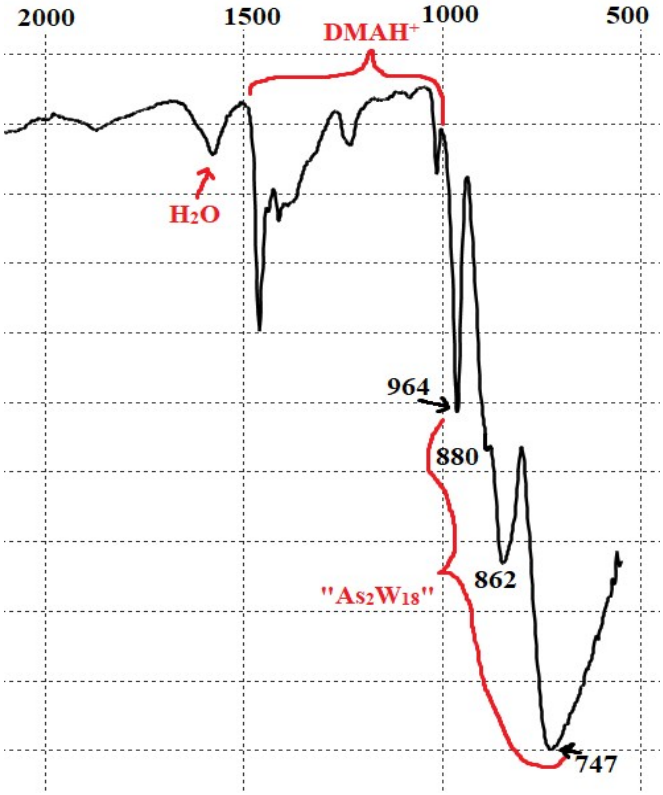


Table S5. Experimental details

	DMA-1	DMA-2	CsNaK-2
Chemical formula	$C_{10.40}H_{40.80}As_2N_{5.20}O_{66}Ru_0W_{18}$	$C_8H_{24}N_4O_{62}Ru_{1.02}SbW_{16.98}$	$Cs_{5.37}O_{65.60}RuSbW_{17}$
M_r	4754.02	4514.94	5111.88
Crystal system, space group	Monoclinic, $P2_1/n$	Trigonal, $R\bar{3}m$	Orthorhombic, *Pnnm*
a, *b*, *c* (Å)	22.9019 (4), 13.94647 (19), 24.2943 (4)	21.1706 (14), 21.1706 (14), 15.680 (2)	12.5497 (4), 18.5385 (7), 15.6808 (5)
a, β, γ (°)	90, 113.566 (2), 90	90, 90, 120	90, 90, 90
V (Å^3)	7112.4 (2)	6086.0 (11)	3648.2 (2)
Z	4	3	2
μ (mm^{-1})	30.01	24.56	29.98
Crystal size (mm)	0.22 × 0.15 × 0.07	0.27 × 0.23 × 0.16	0.33 × 0.13 × 0.10
T_{min}, T_{max}	0.966, 0.988	0.965, 0.974	0.955, 0.986
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	39135, 13888, 10986	5031, 1353, 1079	13707, 3553, 2920
R_{int}	0.043	0.032	0.047
θ values (°)	θ_{max} = 26.0, θ_{min} = 1.9	θ_{max} = 25.7, θ_{min} = 2.6	θ_{max} = 25.7, θ_{min} = 2.0
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.617	0.609	0.610
Range of *h*, *k*, *l*	-18 ≤ *h* ≤ 28, -16 ≤ *k* ≤ 17, -29 ≤ *l* ≤ 24	-12 ≤ *h* ≤ 25, -22 ≤ *k* ≤ 21, -19 ≤ *l* ≤ 15	-12 ≤ *h* ≤ 15, -22 ≤ *k* ≤ 17, -17 ≤ *l* ≤ 19
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.042, 0.100, 1.05	0.042, 0.110, 1.10	0.055, 0.164, 1.07
No. of reflections, parameters, restraints	13888, 829,19	1353, 92, 0	3553, 233,6
H-atom treatment	H-atom parameters not defined	H-atom parameters constrained	H-atom parameters not defined
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.044P)^2 + 40.0442P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0415P)^2 + 364.224P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.099P)^2 + 106.1746P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	3.79, -3.27	1.68, -2.41	4.45, -2.61

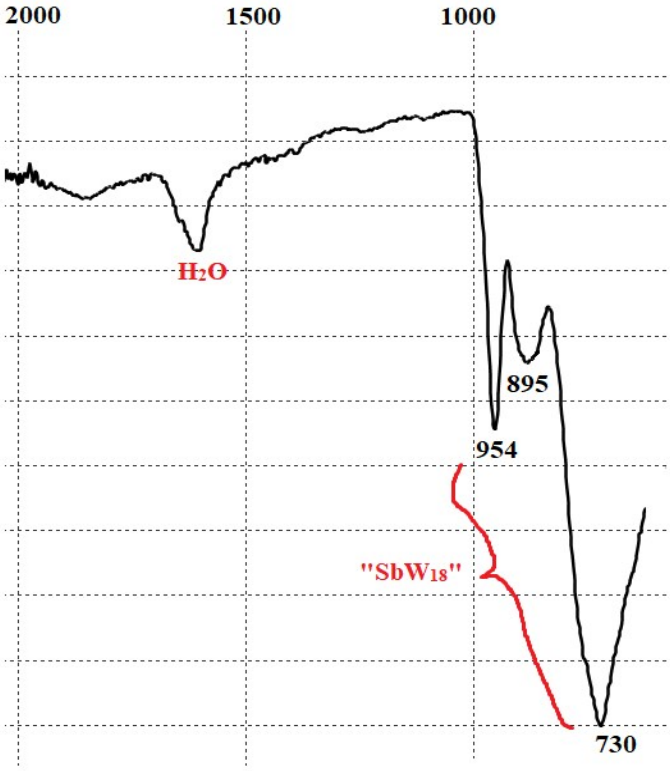
Computer programs: *CrysAlis PRO* 1.171.38.41 (Rigaku OD, 2015), *SHELXS2014* (Sheldrick, 2014), *SHELXL2014* (Sheldrick, 2014), ShelXle (Hübschle, 2011), CIFTAB-2014 (Sheldrick, 2014).

Fig. S11. FT-IR for $DMAH^+$ salt of $[As_2W_{18}O_{62}]^{6-}$.



Experimental: IR (ATR, cm^{-1}): 1580 (w), 1461 (m), 1439 (m), 1412 (m), 1390 (m), 1330 (sh), 1231 (w), 1014 (w), 964 (s), 880 (s), 862 (vs), 747 (vs).
Literature data (doi:10.1016/j.molstruc.2007.04.009**) for $H_6As_2W_{18}O_{62}$ (cm^{-1}):** 970, 872, 865, 767.

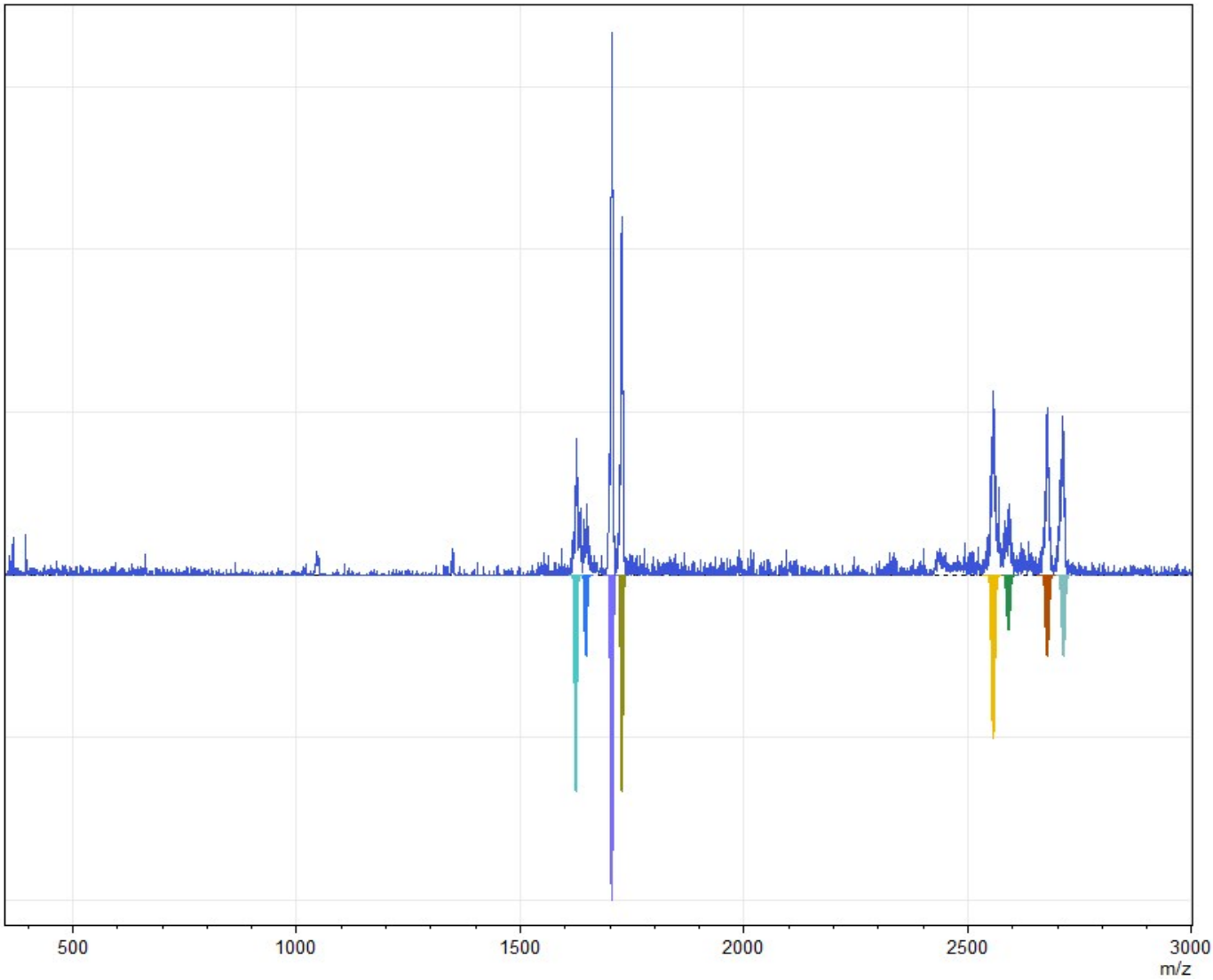
Fig. S11a. FT-IR for Cs^+ salt of $[SbW_{18}O_{62}]^{6-}$, which was precipitated from reaction mixture.



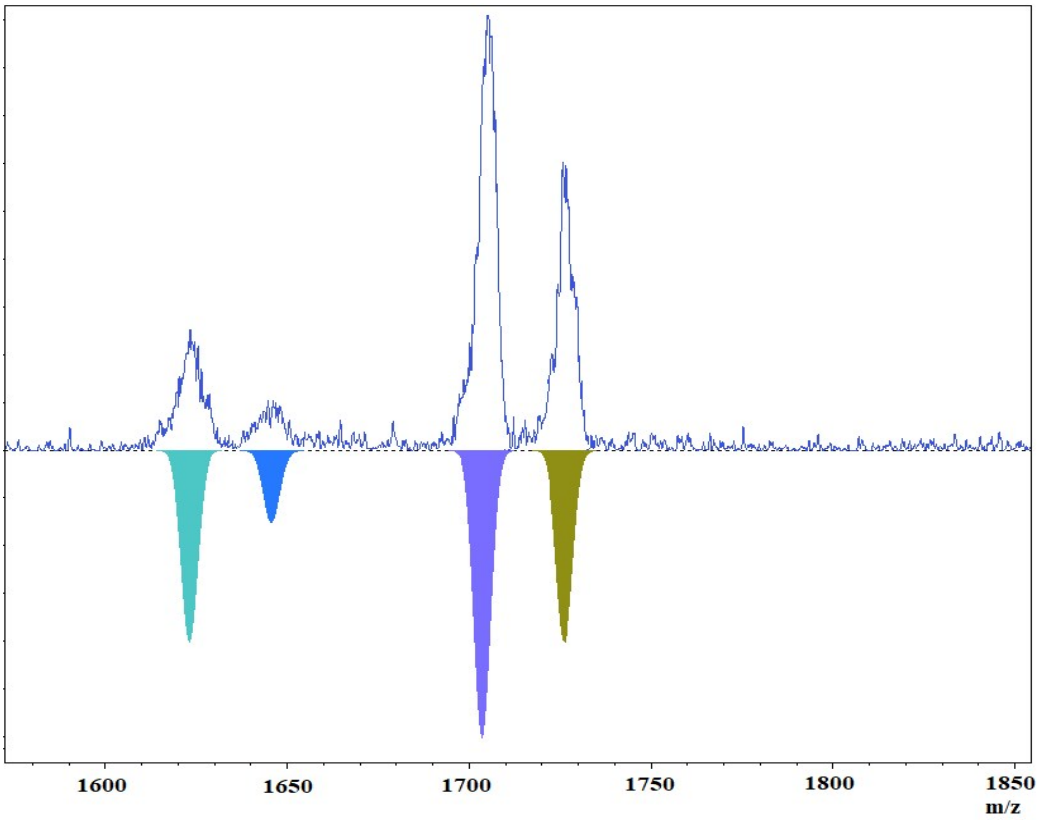
Experimental: IR (ATR, cm^{-1})**:** 1607 (w), 954 (s), 895 (m), 730 (vs).
According to literature data (https://doi.org/10.1016/j.molstruc.2010.01.023) characteristic vibrations of $[SbW_{18}O_{60}]^{9-}$ are 961, 892, 747 cm^{-1}.

Fig. S12. ESI-MS of $[As_2W_{17}\{Ru(NO)\}O_{61}]^{7-}$ and $[As_2W_{18}O_{62}]^{6-}$ mixture in CH_3CN prepared by precipitation with TBABr from reaction solution. This spectrum was recorded before chromatography.

a) Full spectrum (calculated patterns have negative intensities).



b) Zoomed 1570-1850 m/z region (calculated patterns have negative intensities).



c) Zoomed 2430 - 2830 m/z region (calculated patterns have negative intensities).

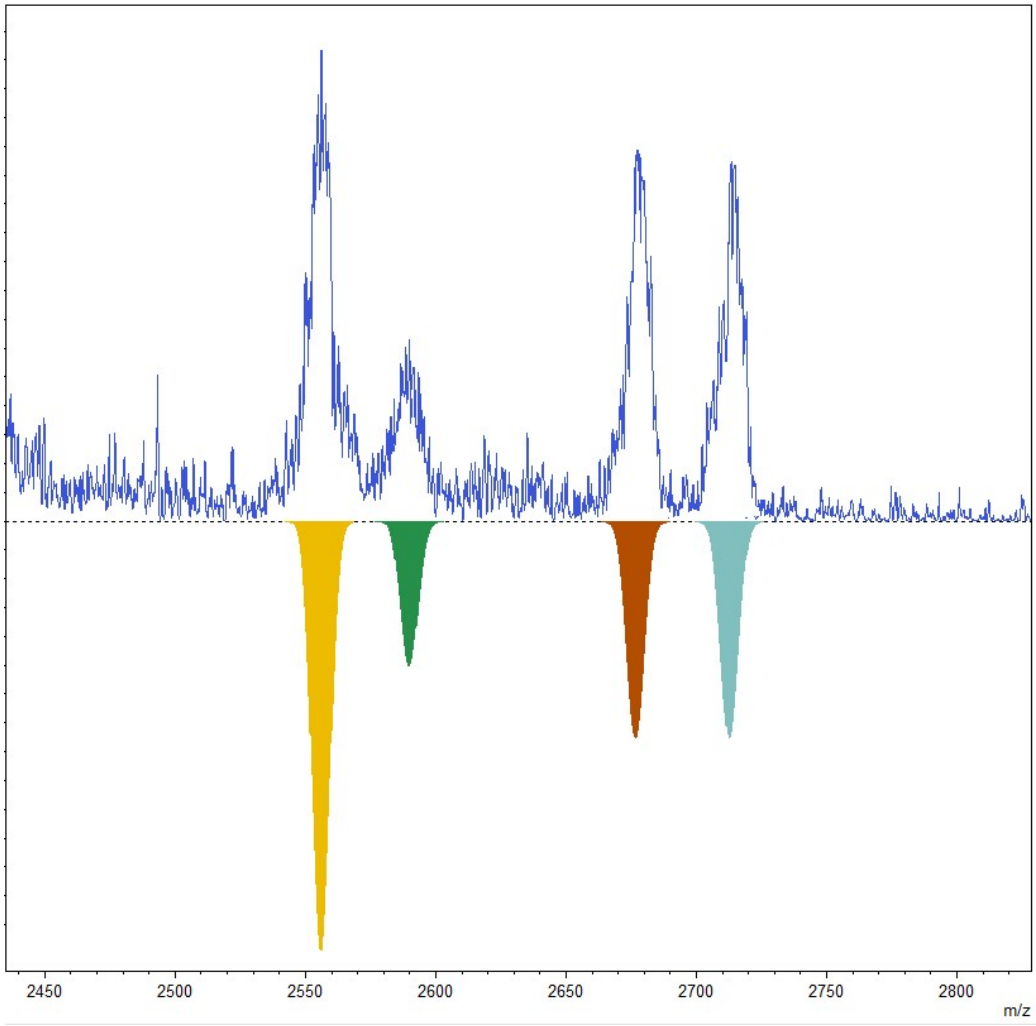


Table S6. Peak assignment for ESI-MS of $[As_2W_{17}\{Ru(NO)\}O_{61}]^{7-}$ and $[As_2W_{18}O_{62}]^{6-}$ mixture in CH_3CN.

anion	calc	exp
$\{(Bu_4N)_2H_2Ru(NO)As_2W_{17}O_{61}\}^{3-}$	1623.1	1623.2
$\{(Bu_4N)_2HAs_2W_{18}O_{62}\}^{3-}$	1645.6	1645.6
$\{(Bu_4N)_3HRu(NO)As_2W_{17}O_{61}\}^{3-}$	1703.5	1703.6
$\{(Bu_4N)_3As_2W_{18}O_{62}\}^{3-}$	1726.1	1726.0
$\{(Bu_4N)_3H_2Ru(NO)As_2W_{17}O_{61}\}^{2-}$	2555.7	2555.8
$\{(Bu_4N)_3HAs_2W_{18}O_{62}\}^{2-}$	2589.7	2589.7
$\{(Bu_4N)_4HRu(NO)As_2W_{17}O_{61}\}^{2-}$	2676.4	2676.5
$\{(Bu_4N)_4HRu(NO)As_2W_{17}O_{61}(H_2O)_4\}^{2-}$	2712.5	2712.4