

Redox Tuning the Weakley Sandwich POM Archetype for the Oxygen Evolution Reaction

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1) Instrumentation and Materials

Single Crystal X-Ray Diffraction: Single crystal datasets and unit cells were collected at 150(2) K on a Bruker Apex II Quasar diffractometer equipped with a graphite monochromator (λ (MoK α) = 0.71Å) at 150(2)K. Structure solution and refinement was carried out using SHELXS-97^[1] and SHELXL-97^[2] via WinGX^[3].

Thermogravimetric Analysis (TGA): Thermogravimetric analysis was performed on a TA Instruments Q 500 Thermogravimetric Analyzer under air flow at a typical heating rate of 10°C min⁻¹.

Fourier-transform infrared (FT-IR) spectroscopy: The FT-IR spectrum was collected in transmission mode using a JASCO FT-IR 4100 spectrometer. Wavenumbers (ν) are given in cm⁻¹.

ESI-MS (electrospray ionization mass spectrometry): Measurements were performed using a *Waters Synapt-G2* spectrometer. The instrument was operated in negative mode and with an electrospray source regularly calibrated using 2µg/L NaI solution in 1:1 2-propanol/H₂O from Waters Q-ToF Qualification Standard Kit. The sample was dissolved in 1:1 mixture of HPLC grade deionized water and HPLC grade acetonitrile and injected into the spectrometer at a flow rate of 5 µL·min⁻¹. The following parameters were used for acquisition of all spectra: ESI capillary voltage, 2.9 kV; sample cone voltage, 10.0 V; extraction cone voltage, 4.0 V; source temperature, 80 °C; desolvation temperature, 180 °C; cone gas (N₂) flow, 15 L/h; desolvation gas (N₂) flow, 750 L/h; source gas flow, 0.0 mL/min; trap gas flow, 2.0 mL/min; helium cell gas flow, 180 mL/min; IMS gas flow, 90.0 mL/min; IMS DC entrance, 25.0; helium cell DC, 35.0; helium exit, -5.0; IMS bias, 3.0; IMS DC exit, 0.0; IMS wave velocity, 1087 m/s; IMS wave height, 23.7 V. Data were acquired using MassLynx v4.1 and initially processed using *Waters DriftScope v2.2* software. IMS-MS spectra are displayed with a linear intensity scale using the color-coding shown in the accompanying key; no filtering is applied to limit signals/remove noise. Data analysis was performed on the *Waters Driftscope v 2.2* software.

ICP-OES (Inductively coupled plasma – optical emission spectroscopy): The sodium and potassium compounds were dissolved in HPLC grade water without digestion. The Compounds containing caesium were digested in 3 mL hydrogen peroxide and then dissolved in HPLC grade water. The instrument used was an Agilent 5100.

Electrochemistry: Measurements were made on a single channel Bio Logic SP150 potentiostat.

Oxygen evolution: Oxygen evolution was detected with an Ocean Optics NeoFOX oxygen sensing system equipped with a FOXY probe inserted into the gas space of the reactor, close to the anode.

2) Synthesis and Characterization

All chemicals were purchased from Sigma Aldrich Chemical Company Ltd. and used without further purification.

Synthesis of Compounds 1-3: 5.48 g (22 mmol) of $\text{Co}(\text{CH}_3\text{-COO})_2 \cdot 4\text{H}_2\text{O}$ was dissolved in 50 mL of degassed water. In 100 mL of degassed water 1.57 g (11.06 mmol) of Na_2HPO_4 , $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (*See Table S.1.) and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ * were dissolved. This solution was stirred and glacial acetic acid* was added dropwise to adjust the pH to 6.5. Both solutions were transferred into a 250mL two neck round bottom flasks, one neck was attached to a condenser and a glass pipette that was connected to a nitrogen line was attached in the other neck. The solution was refluxed for 2h. During this time nitrogen gas was bubbled into the solution. After that, the dark brown mixture was hot filtered and left to cool down to room temperature. Then it was filtered again and 3 g (30.62 mmol) of $\text{K}(\text{CH}_3\text{-COO})$ were added to the filtrate and stirred for 5 minutes, after that, the solution was filtered again and the liquor was left to crystallize in a fume hood. After one day big clear reddish-brown block crystals (Compounds **1a**, **2a** and **3a**) and small light brown-goldish rectangles (Compounds **1b**, **2b**, and **3b**) are obtained. Both types of crystals were separated by eye, considering that the darker blocks are heavier than the small rectangles.

Table S1. Reagents used in the reactions 1, 2 and 3.

Compounds	$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$	$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$
	(g)	(mmol)	(g)	(mmol)
1	19.79	60	9.68	40
2	16.49	50	12.10	50
3	13.19	40	14.52	60

Synthesis of 1a[C_s] (same procedure was applied to synthesize 1b[C_s], 2a[C_s], 2b[C_s], 3a[C_s] and 3b[C_s]): 0.5 g of **1a** were dissolved in 20mL of water (brown solution), then 1 M CsCl solution were added dropwise allowing the formation of a pale-brown precipitate when the solution turned colourless the addition of the CsCl solution is stopped (approx. 5mL). All was stirred for 20 minutes and the precipitate was collected by Büchner filtration. The powder was dried overnight in a desiccator and grinded the next day using a mortar and a pestle.

* For the synthesis of **3b[C_s]** the reaction was scaled by half due to the lack of starting material (**3b**)

Table S2. Yield table. Yields calculated based on W and starting material before Cs exchange.

CODE	Yield (weight)	Yield % (based on W)	Yield % (based on starting material)
1a	1.72 g	6.4%	N/A
1b	1.17 g	4.4%	N/A
1a[C_s]	0.55 g	N/A	97.0%
1b[C_s]	0.53 g	N/A	91.4%
2a	2.26 g	9.7%	N/A
2b	0.57 g	2.4%	N/A
2a[C_s]	0.55 g	N/A	94.0%
2b[C_s]	0.39 g	N/A	66.7%
3a	1.71 g	8.7%	N/A
3b	0.38 g	2.0%	N/A
3a[C_s]	0.51 g	N/A	89.8%
3b[C_s]	0.21 g	N/A	72.6%

Formula assignments for the compounds: Elemental analysis , ICP-OES for W, Mo, Co, Na, K, P and Cs and T.G.A.

Compound 1a: Proposed formula: $K_4Na_6Co_4(H_2O)_2(P_2Mo_7W_{11}O_{68}) \cdot 28H_2O$. Molecular weight: 4914.25 g·mol⁻¹. Expected: W: 41.15, Mo: 13.67, Co: 4.79, Na: 2.81 and K: 3.18. Found: W: 43.18, Mo: 14.23, Co: 4.98, Na: 3.38 and K: 3.24. TGA weight loss observed: 10.44%, calcd: 10.26%. IR bands (cm⁻¹): 3388.93 (br), 1614.42 (sh), 1031.92 (sh), 927.76 (sh), 866.04 (sh), 667.37 (br).

Compound 1b: Proposed formula: $K_3Na_7Co_4(H_2O)_2(P_2Mo_7W_{11}O_{68}) \cdot 22H_2O$. Molecular weight: 4790.05 g·mol⁻¹. Expected: W: 42.21, Mo: 14.02, Co: 4.92, Na: 3.35 and K: 2.45. Found: W: 44.05, Mo: 12.27, Co: 4.89, Na: 3.43 and K: 2.41. TGA weight loss observed: 8.26%, calcd: 8.27%. IR bands (cm⁻¹): 3406.29 (br), 1614.42 (sh), 1035.77 (sh), 935.48 (sh), 873.75 (sh), 692.44 (br).

Compound 1a[Cs]: Proposed formula: $Cs_{8.9}K_{0.7}Na_{0.4}Co_4(H_2O)_2(P_2Mo_7W_{11}O_{68}) \cdot 16H_2O$. Molecular weight: 5623.16 g·mol⁻¹. Expected: W: 35.96, Mo: 11.94, Co: 4.19, Cs: 21.03, Na: 0.16 and K: 0.49. Found: W: 35.28, Mo: 11.14, Co: 4.10, Cs: 20.79, Na: 0.22 and K: 0.60. TGA weight loss observed: 5.39%, calcd: 5.13%. IR bands (cm⁻¹): 3433.29 (br), 1620.21 (sh), 1031.92 (sh), 925.83 (sh), 866.04 (sh), 582.50(br).

Compound 1b[Cs]: Proposed formula: $Cs_9K_{0.5}Na_{0.5}Co_4(H_2O)_2(P_2Mo_7W_{11}O_{68}) \cdot 20H_2O$. Molecular weight: 5702.99 g·mol⁻¹. Expected: W: 35.45, Mo: 11.77, Co: 4.13, Cs: 20.97, Na: 0.20 and K: 0.34. Found: W: 36.90, Mo: 9.88, Co: 4.09, Cs: 22.21, Na: 0.21 and K: 0.47. TGA weight loss observed: 5.32%, calcd: 6.32%. IR bands (cm⁻¹): 3446.79 (br), 1637.56 (sh), 1031.92 (sh), 925.83 (sh), 866.04 (sh), 717.52 (br).

Compound 2a: Proposed formula: $K_4Na_6Co_4(H_2O)_2(P_2Mo_{7.6}W_{10.4}O_{68}) \cdot 27H_2O$. Molecular weight: 4843.49 g·mol⁻¹. Expected: W: 39.37, Mo: 15.31, Co: 4.85, Na: 2.83 and K: 3.20. Found: W: 38.27, Mo: 16.55, Co: 5.00, Na: 2.77 and K: 3.29. TGA weight loss observed: 9.91%, calcd: 10.05%. IR bands (cm⁻¹): 3408.22 (br), 1614.42 (sh), 1029.99 (sh), 923.90 (sh), 864.11 (sh), 657.73 (br).

Compound 2b: Proposed formula: $K_4Na_6Co_4(H_2O)_2(P_2Mo_{7.6}W_{10.4}O_{68}) \cdot 27H_2O$. Molecular weight: 4843.49 g·mol⁻¹. Expected: W: 39.47, Mo: 15.05, Co: 4.87, Na: 2.84 and K: 3.23. Found: W: 40.36, Mo: 15.42, Co: 4.73, Na: 2.64 and K: 2.8. TGA weight loss observed:

10.15%, calcd: 10.05%. IR bands (cm⁻¹): 3385.07 (br), 1622.13 (sh), 1031.92 (sh), 933.55 (sh), 867.97 (sh), 694.37 (br).

Compound 2a[Cs]: Proposed formula: Cs₉K_{0.7}Na_{0.3}Co₄(H₂O)₂(P₂Mo_{7.6}W_{10.4}O₆₈)·18H₂O. Molecular weight: 5617.44 g·mol⁻¹. Expected: W: 34.04, Mo: 12.98, Co: 4.20, Cs: 21.29, Na: 0.12 and K: 0.49. Found: W: 33.44, Mo: 12.57, Co: 4.15, Cs: 21.92 Na: 0.15 and K: 0.60. TGA weight loss observed: 5.72%, calcd: 5.78%. IR bands (cm⁻¹): 3433.29 (br), 1614.42 (sh), 1031.92 (sh), 923.90 (sh), 864.04 (sh), 705.95 (br).

Compound 2b[Cs]: Proposed formula: Cs_{9.4}K_{0.3}Na_{0.3}Co₄(H₂O)₂(P₂Mo_{7.6}W_{10.4}O₆₈)·18H₂O. Molecular weight: 5654.96 g·mol⁻¹. Expected: W: 33.81, Mo: 12.89, Co: 4.17, Cs: 22.09, Na: 0.12 and K: 0.21. Found: W: 31.93, Mo: 13.69, Co: 4.96, Cs: 21.09, Na: 0.15 and K: 0.23. TGA weight loss observed: 5.73%, calcd: 5.74%. IR bands (cm⁻¹): 3429.43 (br), 1620.21 (sh), 1029.99 (sh), 923.90 (sh), 866.04 (sh), 705.95 (br).

Compound 3a: Proposed formula: K₄Na₆Co₄(H₂O)₂(P₂Mo₈W₁₀O₆₈)·33H₂O. Molecular weight: 4916.42 g·mol⁻¹. Expected: W: 37.39, Mo: 15.61, Co: 4.79, Na: 2.80 and K: 3.18. Found: W: 36.24, Mo: 16.17, Co: 4.85, Na: 2.10 and K: 3.02. TGA weight loss observed: 12.08%, calcd: 12.09%. IR bands (cm⁻¹): 3379.29 (br), 1614.42 (sh), 1029.99 (sh), 923.90 (sh), 862.18 (sh), 684.73 (br).

Compound 3b: Proposed formula: K₂Na₈Co₄(H₂O)₂(P₂Mo₈W₁₀O₆₈)·27H₂O. Molecular weight: 4776.12 g·mol⁻¹. Expected: W: 38.49, Mo: 16.07, Co: 4.94, Na: 3.85 and K: 1.60. Found: W: 36.86, Mo: 17.29, Co: 5.05, Na: 4.04 and K: 1.00. TGA weight loss observed: 10.28%, calcd: 10.84%. IR bands (cm⁻¹): 3388.93 (br), 1614.42 (sh), 1029.99 (sh), 923.90 (sh), 864.11 (sh), 675.09 (br).

Compound 3a[Cs]: Proposed formula: Cs₉K_{0.7}Na_{0.3}Co₄(H₂O)₂(P₂Mo₈W₁₀O₆₈)·18H₂O. Molecular weight: 5582.28 g·mol⁻¹. Expected: W: 32.93, Mo: 13.74, Co: 4.22, Cs: 21.42, Na: 0.12 and K: 0.49. Found: W: 31.18, Mo: 14.08, Co: 4.19, Cs: 21.40, Na: 0.27 and K: 0.55. TGA weight loss observed: 5.79%, calcd: 5.81%. IR bands (cm⁻¹): 3446.79 (br), 1637.56 (sh), 1031.92 (sh), 925.83 (sh), 866.04 (sh), 717.52 (br).

Compound 3b[Cs]: Proposed formula: Cs_{9.4}K_{0.3}Na_{0.3}Co₄(H₂O)₂(P₂Mo₈W₁₀O₆₈)·20H₂O. Molecular weight: 5655.83 g·mol⁻¹. Expected: W: 32.50, Mo: 13.57, Co: 4.17, Cs: 22.09 Na: 0.12 and K: 0.21. Found: W: 30.17, Mo: 14.16, Co: 4.60, Cs: 23.62, Na: 0.15 and K: 0.28.

TGA weight loss observed: 6.37%, calcd: 6.37%. IR bands (cm⁻¹): 3423.65 (br), 1618.28 (sh), 1031.92 (sh), 923.90 (sh), 864.11 (sh), 700.16 (br).

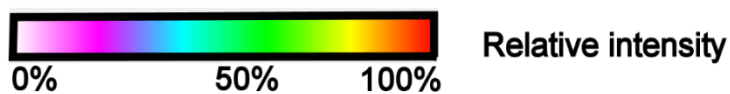
Table S3. Number of potassium, sodium, molybdenum and tungsten atoms per formula for compounds **1a**, **1b**, **2a**, **2b**, **3a** and **3b**. Crystallization water molecules are also included.

	Element				Crystallization
	K	Na	Mo	W	water
1a	4.0	6.0	7.0	11.0	28
1b	3.0	7.0	7.0	11.0	22
2a	4.0	6.0	7.6	10.4	27
2b	4.0	6.0	7.6	10.4	27
3a	4.0	6.0	8.0	10.0	33
3b	2.0	8.0	8.0	10.0	27

Table S4. Number of caesium, potassium, sodium, molybdenum and tungsten atoms per formula for non-crystalline compounds **1a**[Cs], **1b**[Cs], **2a**[Cs], **2b**[Cs], **3a**[Cs] and **3b**[Cs]. Hydration water molecules are also included.

	Element					Water
	Cs	K	Na	Mo	W	molecules associated
1a [Cs]	8.9	0.7	0.4	7.0	11.0	16
1b [Cs]	9.0	0.5	0.5	7.0	11.0	20
2a [Cs]	9.0	0.7	0.3	7.6	10.4	18
2b [Cs]	9.4	0.3	0.3	7.6	10.4	18
3a [Cs]	9.0	0.7	0.3	8.0	10.0	18
3b [Cs]	9.4	0.3	0.3	8.0	10.0	20

3) ESI-IM-MS (Electrospray ionization-ion mobility-mass spectrometry)



Compound 1a:

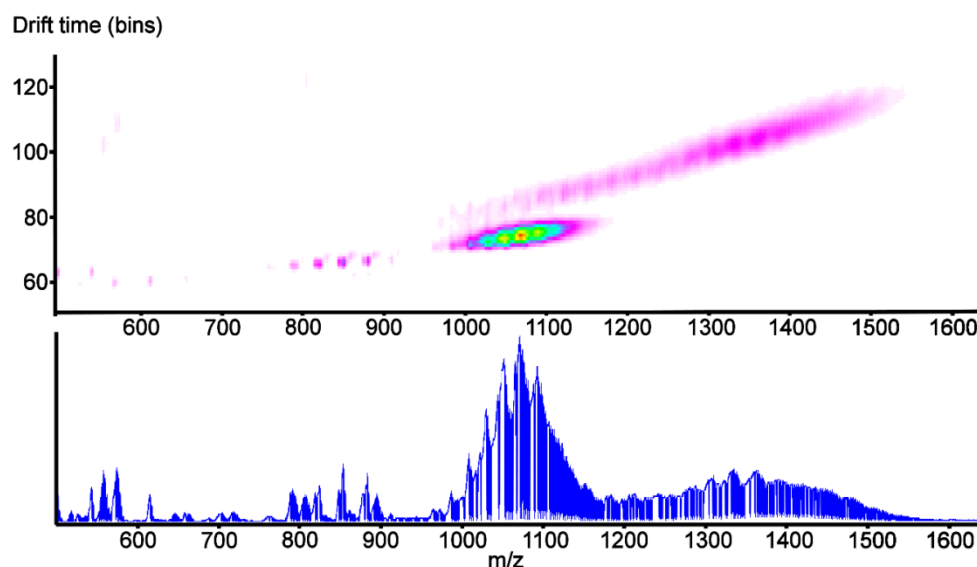
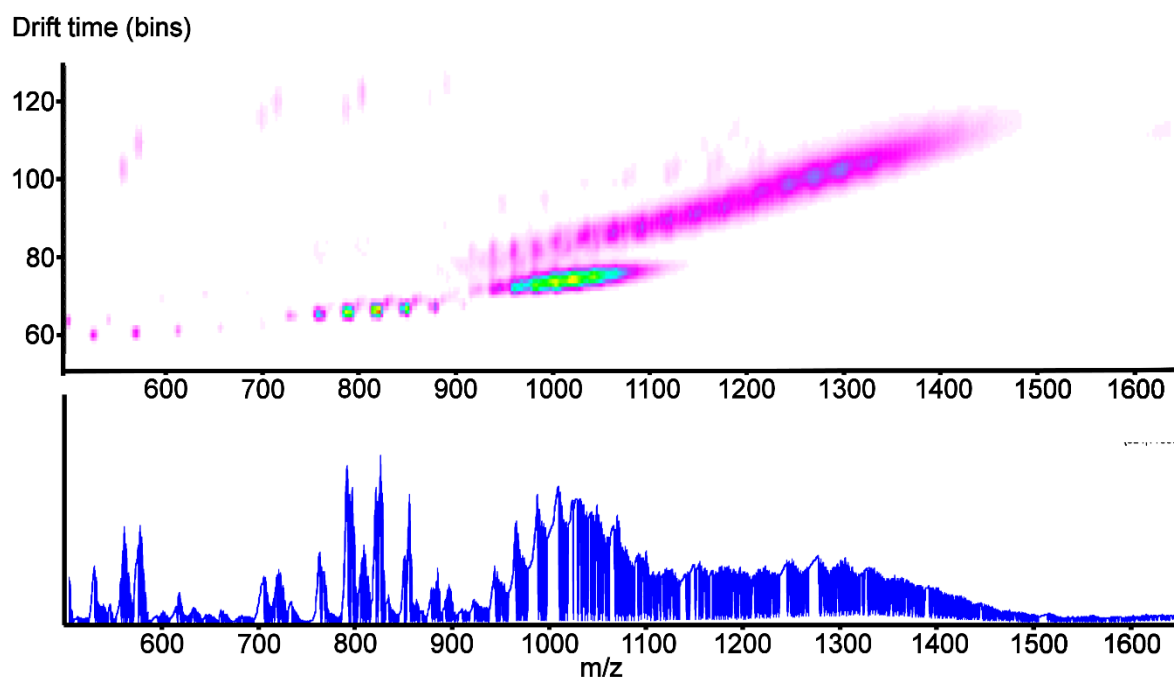


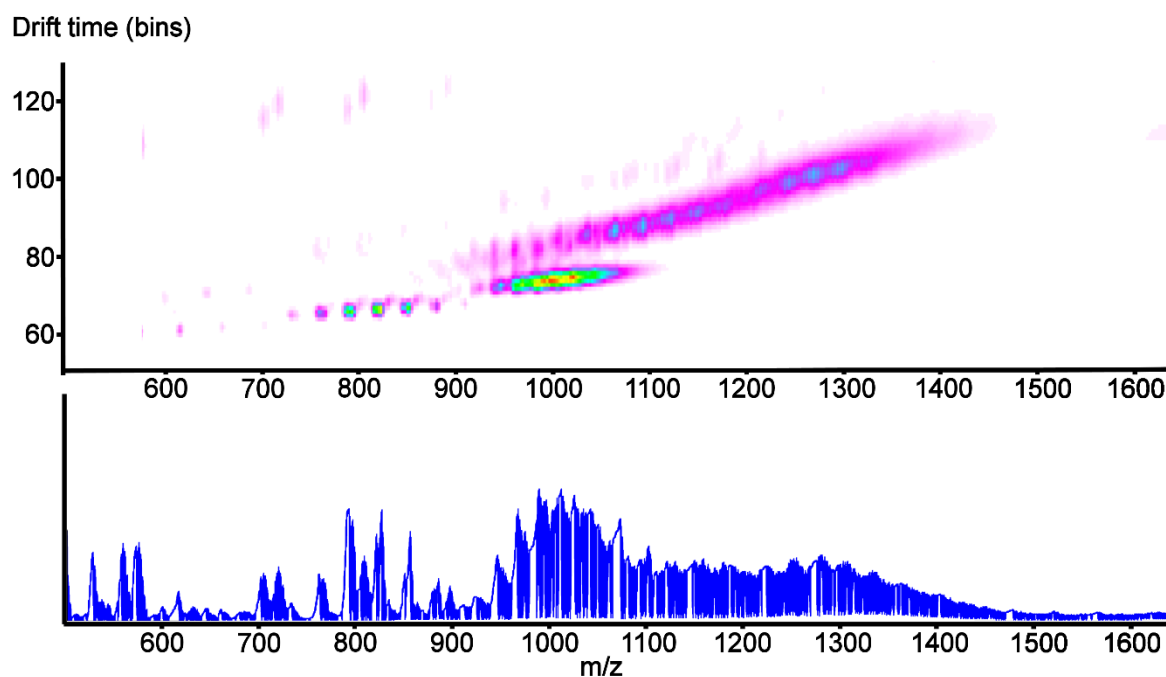
Figure S1. ESI-IM-MS of Compound 1a.

Table S5. Assignments corresponding to the molecular peaks of Compound 1a.

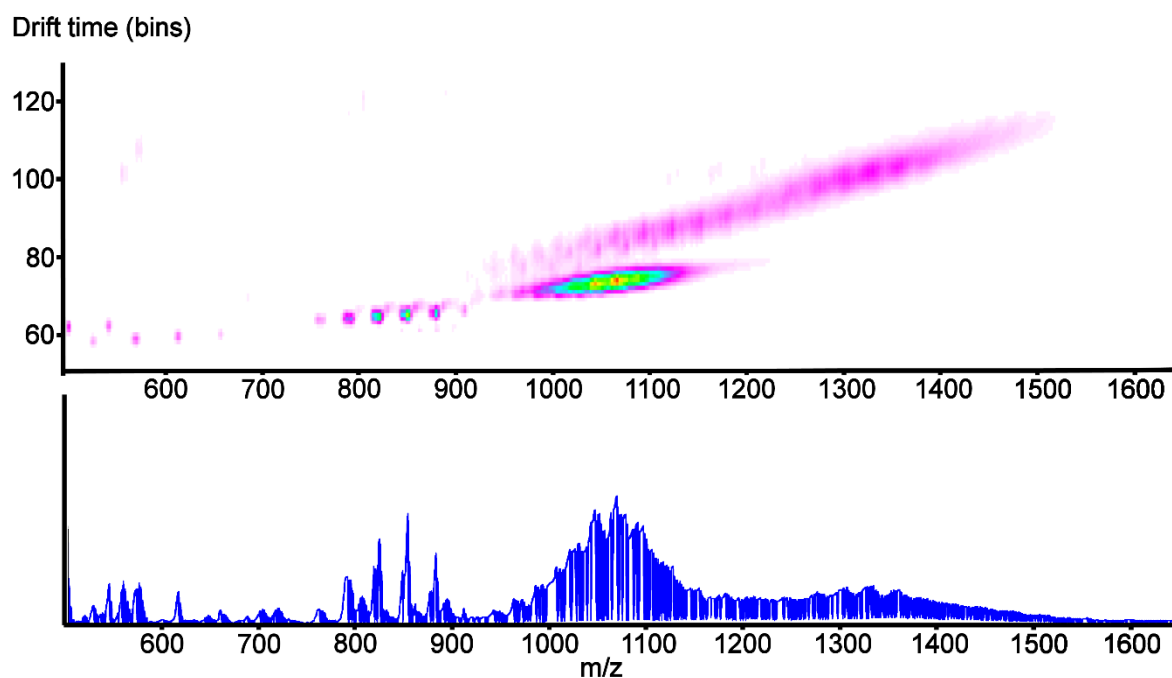
Charge	m/z (obs.)	m/z (calc.)	Proposed formula
-4	986.6	986.5	$\text{K}_3\text{Na}_2\text{HCO}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{11}\text{W}_7\text{O}_{68})(\text{H}_2\text{O})$
-4	1008.7	1008.9	$\text{K}_2\text{Na}_3\text{HCO}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{10}\text{W}_8\text{O}_{68})(\text{H}_2\text{O})_2$
-4	1030.9	1031.0	$\text{K}_2\text{Na}_3\text{HCO}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_9\text{W}_9\text{O}_{68})(\text{H}_2\text{O})_2$
-4	1053.9	1054.0	$\text{K}_2\text{Na}_4\text{CO}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_8\text{W}_{10}\text{O}_{68})(\text{H}_2\text{O})$
-4	1070.7	1070.5	$\text{K}_2\text{Na}_3\text{HCO}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_7\text{W}_{11}\text{O}_{68})(\text{H}_2\text{O})$
-4	1092.7	1092.5	$\text{K}_2\text{Na}_3\text{HCO}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_6\text{W}_{12}\text{O}_{68})(\text{H}_2\text{O})$
-3	1280.6	1280.6	$\text{K}_2\text{Na}_3\text{H}_3\text{CO}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{12}\text{W}_6\text{O}_{68})(\text{H}_2\text{O})$
-3	1309.6	1309.7	$\text{KNa}_3\text{H}_3\text{CO}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{11}\text{W}_7\text{O}_{68})(\text{H}_2\text{O})_3$
-3	1333.9	1334.0	$\text{KNa}_4\text{H}_2\text{CO}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{10}\text{W}_8\text{O}_{68})(\text{H}_2\text{O})$
-3	1363.9	1363.7	$\text{K}_1\text{Na}_4\text{H}_2\text{CO}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_9\text{W}_9\text{O}_{68})(\text{H}_2\text{O})$
-3	1389.2	1389.0	$\text{K}_3\text{H}_4\text{CO}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_8\text{W}_{10}\text{O}_{68})(\text{H}_2\text{O})$

Compound 2a:**Figure S2.** ESI-IM-MS of Compound **2a**.**Table S6.** Assignments corresponding to the molecular peaks of Compound **2a**.

Charge	m/z (obs.)	m/z (calc.)	Proposed formula
-4	943.4	943.2	$\text{K}_2\text{Na}_3\text{HCo}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{13}\text{W}_5\text{O}_{68})_1(\text{H}_2\text{O})_2$
-4	964.6	964.5	$\text{KNa}_3\text{H}_2\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{12}\text{W}_6\text{O}_{68})(\text{H}_2\text{O})_4$
-4	986.4	986.5	$\text{KNa}_3\text{H}_2\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{11}\text{W}_7\text{O}_{68})(\text{H}_2\text{O})_4$
-4	1008.6	1008.5	$\text{KNa}_3\text{H}_2\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{10}\text{W}_8\text{O}_{68})(\text{H}_2\text{O})_4$
-4	1026.2	1026.0	$\text{KNa}_3\text{H}_2\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_9\text{W}_9\text{O}_{68})(\text{H}_2\text{O})_3$
-4	1047.9	1048.0	$\text{KNa}_3\text{H}_2\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_8\text{W}_{10}\text{O}_{68})(\text{H}_2\text{O})_3$
-4	1069.9	1070.0	$\text{KNa}_3\text{H}_2\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_7\text{W}_{11}\text{O}_{68})(\text{H}_2\text{O})_3$
-3	1098.9	1099.2	$\text{Na}_4\text{H}_3\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{18}\text{O}_{68})(\text{H}_2\text{O})_3$
-3	1127.2	1127.2	$\text{Na}_3\text{H}_4\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{17}\text{W}_1\text{O}_{68})(\text{H}_2\text{O})_4$
-3	1155.7	1155.9	$\text{KNa}_2\text{H}_4\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{16}\text{W}_2\text{O}_{68})(\text{H}_2\text{O})_3$
-3	1185.2	1185.3	$\text{KNa}_2\text{H}_4\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{15}\text{W}_3\text{O}_{68})(\text{H}_2\text{O})_3$
-3	1220.6	1220.6	$\text{KNa}_2\text{H}_4\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{14}\text{W}_4\text{O}_{68})(\text{H}_2\text{O})_4$
-3	1249.9	1249.6	$\text{KNa}_2\text{H}_4\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{13}\text{W}_5\text{O}_{68})(\text{H}_2\text{O})_4$
-3	1278.9	1279.0	$\text{KNa}_2\text{H}_4\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{12}\text{W}_6\text{O}_{68})(\text{H}_2\text{O})_4$
-3	1308.2	1308.3	$\text{KNa}_2\text{H}_4\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{11}\text{W}_7\text{O}_{68})(\text{H}_2\text{O})_4$
-3	1337.9	1337.7	$\text{KNa}_2\text{H}_4\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{10}\text{W}_8\text{O}_{68})(\text{H}_2\text{O})_4$

Compound 3a:**Figure S3.** ESI-IM-MS of Compound 3a.**Table S7.** Assignments corresponding to the molecular peaks of Compound 3a.

Charge	m/z (obs.)	m/z (calc.)	Proposed formula
-4	950.3	950.5	Na ₃ H ₃ Co ₄ (H ₂ O) ₂ (P ₂ Mo ₁₂ W ₆ O ₆₈)(H ₂ O) ₃
-4	966.1	966.0	NaH ₅ Co ₄ (H ₂ O) ₂ (P ₂ Mo ₁₁ W ₇ O ₆₈)(H ₂ O) ₄
-4	972.0	972.0	KNa ₂ H ₃ Co ₄ (H ₂ O) ₂ (P ₂ Mo ₁₁ W ₇ O ₆₈)(H ₂ O) ₂
-4	1004.0	1004.0	KNa ₃ H ₂ Co ₄ (H ₂ O) ₂ (P ₂ Mo ₁₀ W ₈ O ₆₈)(H ₂ O) ₃
-4	1025.9	1026.0	KNa ₃ H ₂ Co ₄ (H ₂ O) ₂ (P ₂ Mo ₉ W ₉ O ₆₈)(H ₂ O) ₃
-4	1048.0	1048.2	KNa ₃ H ₂ Co ₄ (H ₂ O) ₂ (P ₂ Mo ₈ W ₁₀ O ₆₈)(H ₂ O) ₃
-4	1069.9	1069.9	KNa ₃ H ₂ Co ₄ (H ₂ O) ₂ (P ₂ Mo ₇ W ₁₁ O ₆₈)(H ₂ O) ₃
-3	1098.9	1099.2	Na ₄ H ₃ Co ₄ (H ₂ O) ₂ (P ₂ Mo ₁₈ O ₆₈)(H ₂ O) ₃
-3	1127.2	1127.2	Na ₃ H ₄ Co ₄ (H ₂ O) ₂ (P ₂ Mo ₁₇ W ₁ O ₆₈)(H ₂ O) ₄
-3	1155.7	1155.9	KNa ₂ H ₄ Co ₄ (H ₂ O) ₂ (P ₂ Mo ₁₆ W ₂ O ₆₈)(H ₂ O) ₃
-3	1187.3	1187.5	Na ₄ H ₃ Co ₄ (H ₂ O) ₂ (P ₂ Mo ₁₅ W ₃ O ₆₈)(H ₂ O) ₃
-3	1222.9	1222.6	K ₂ Na ₃ H ₂ Co ₄ (H ₂ O) ₂ (P ₂ Mo ₁₄ W ₄ O ₆₈)(H ₂ O)
-3	1252.5	1252.3	KNa ₄ H ₂ Co ₄ (H ₂ O) ₂ (P ₂ Mo ₁₃ W ₅ O ₆₈)(H ₂ O) ₂
-3	1277.8	1278.0	K ₂ NaH ₃ Co ₄ (H ₂ O) ₂ (P ₂ Mo ₁₂ W ₆ O ₆₈)(H ₂ O) ₃
-3	1303.5	1303.7	KNa ₃ H ₃ Co ₄ (H ₂ O) ₂ (P ₂ Mo ₁₁ W ₇ O ₆₈) ₁ (H ₂ O) ₂

Compound 1b:**Figure S4.** ESI-IM-MS of Compound **1b**.**Table S8.** Assignments corresponding to the molecular peaks of Compound **1b**.

Charge	m/z (obs.)	m/z (calc.)	Proposed formula
-4	994.8	995.0	$\text{K}_2\text{Na}_2\text{H}_2\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{11}\text{W}_7\text{O}_{68})(\text{H}_2\text{O})_5$
-4	1008.4	1008.5	$\text{K}_3\text{Na}_2\text{HC}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{10}\text{W}_8\text{O}_{68})(\text{H}_2\text{O})$
-4	1030.9	1031.0	$\text{K}_2\text{Na}_3\text{HC}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_9\text{W}_9\text{O}_{68})(\text{H}_2\text{O})_2$
-4	1051.7	1051.5	$\text{KNa}_2\text{H}_3\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_8\text{W}_{10}\text{O}_{68})(\text{H}_2\text{O})_5$
-4	1070.4	1070.5	$\text{K}_2\text{Na}_3\text{HC}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_7\text{W}_{11}\text{O}_{68})(\text{H}_2\text{O})$
-4	1092.4	1092.5	$\text{K}_2\text{Na}_3\text{HC}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_6\text{W}_{12}\text{O}_{68})(\text{H}_2\text{O})$
-3	1279.2	1279.0	$\text{K}_3\text{H}_4\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{12}\text{W}_6\text{O}_{68})(\text{H}_2\text{O})_2$
-3	1307.5	1307.7	$\text{K}_2\text{NaH}_4\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{11}\text{W}_7\text{O}_{68})(\text{H}_2\text{O})_3$
-3	1337.9	1337.7	$\text{KNa}_2\text{H}_4\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{10}\text{W}_8\text{O}_{68})(\text{H}_2\text{O})_4$
-3	1362.5	1362.3	$\text{KNa}_3\text{H}_3\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_9\text{W}_9\text{O}_{68})(\text{H}_2\text{O})_2$

Compound 2b:

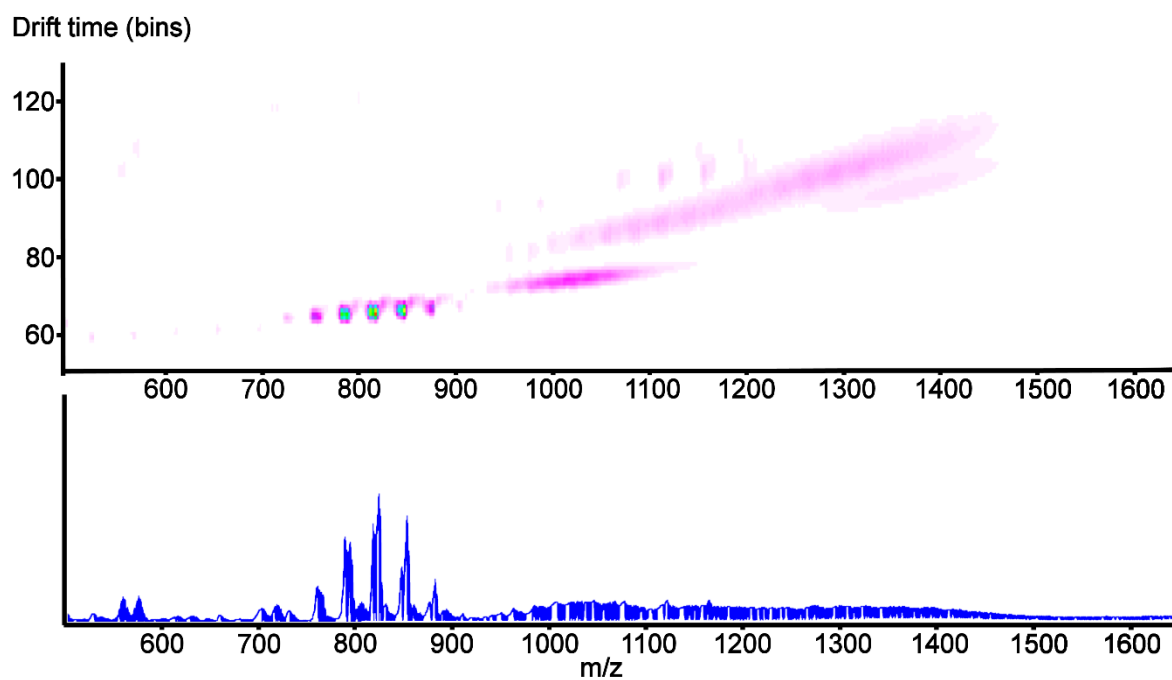
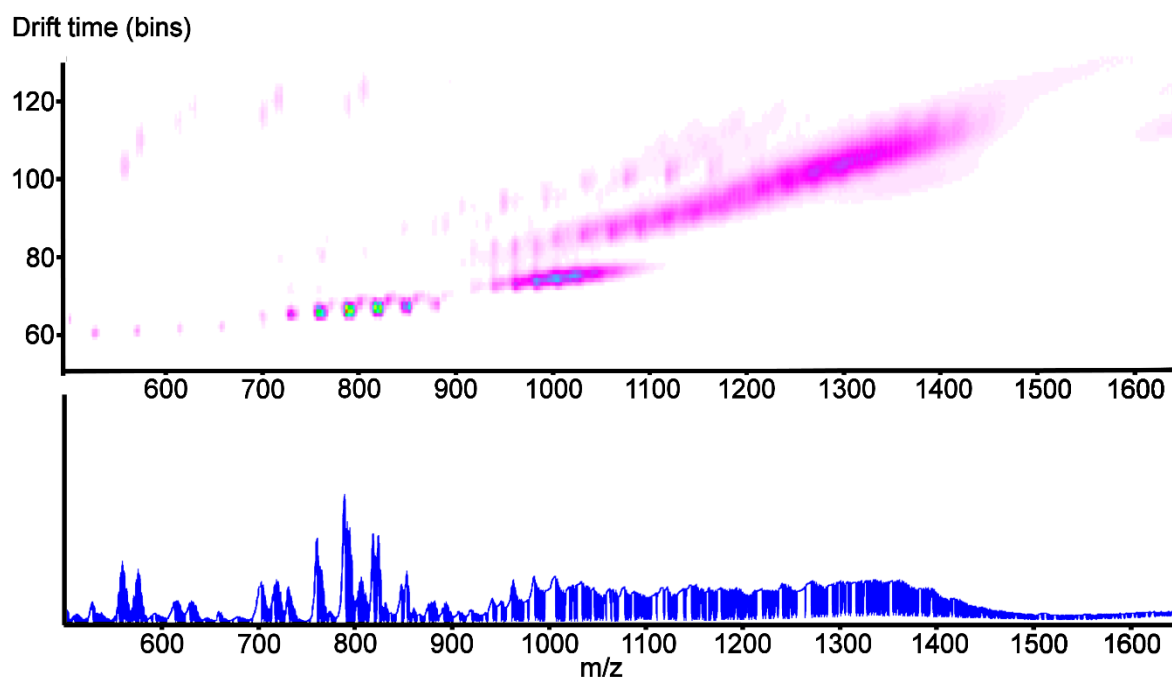


Figure S5. ESI-IM-MS of Compound **2b**.

Table S9. Assignments corresponding to the molecular peaks of Compound **2b**.

Charge	m/z (obs.)	m/z (calc.)	Proposed formula
-4	965.3	965.5	$\text{KH}_5\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{11}\text{W}_7\text{O}_{68})(\text{H}_2\text{O})_3$
-4	987.3	987.5	$\text{KH}_5\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{10}\text{W}_8\text{O}_{68})(\text{H}_2\text{O})_3$
-4	1026.5	1026.5	$\text{K}_2\text{Na}_3\text{HCo}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_9\text{W}_9\text{O}_{68})(\text{H}_2\text{O})$
-4	1048.8	1049.0	$\text{KNa}_4\text{HCo}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_8\text{W}_{10}\text{O}_{68})(\text{H}_2\text{O})_2$
-3	1256.2	1255.9	$\text{K}_3\text{NaH}_3\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{13}\text{W}_5\text{O}_{68})(\text{H}_2\text{O})_2$
-3	1279.2	1279.0	$\text{K}_3\text{H}_4\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{12}\text{W}_6\text{O}_{68})(\text{H}_2\text{O})_2$
-3	1306.2	1306.3	$\text{K}_2\text{H}_5\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{11}\text{W}_7\text{O}_{68})(\text{H}_2\text{O})_4$
-3	1332.3	1332.3	$\text{K}_2\text{Na}_2\text{H}_3\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{10}\text{W}_8\text{O}_{68})(\text{H}_2\text{O})$
-3	1422.9	1423.0	$\text{K}_3\text{Na}_3\text{HCo}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_8\text{W}_{10}\text{O}_{68})(\text{H}_2\text{O})_3$

Compound 3b:**Figure S6.** ESI-IM-MS of Compound **3b**.**Table S10.** Assignments corresponding to the molecular peaks of Compound **3b**.

Charge	m/z (obs.)	m/z (calc.)	Proposed formula
-4	964.6	964.5	$\text{KNa}_3\text{H}_2\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{12}\text{W}_6\text{O}_{68})(\text{H}_2\text{O})_4$
-4	986.6	986.5	$\text{KNa}_3\text{H}_2\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{11}\text{W}_7\text{O}_{68})(\text{H}_2\text{O})_4$
-4	1008.6	1008.5	$\text{K}_3\text{Na}_2\text{H}_1\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{10}\text{W}_8\text{O}_{68})(\text{H}_2\text{O})$
-4	1028.3	1028.5	$\text{Na}_6\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_9\text{W}_9\text{O}_{68})(\text{H}_2\text{O})_2$
-4	1048.4	1048.2	$\text{KNa}_3\text{H}_2\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_8\text{W}_{10}\text{O}_{68})(\text{H}_2\text{O})_3$
-3	1249.9	1249.6	$\text{KNa}_2\text{H}_4\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_{13}\text{W}_5\text{O}_{68})(\text{H}_2\text{O})_4$
-3	1367.8	1367.7	$\text{K}_2\text{Na}_2\text{H}_3\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_9\text{W}_9\text{O}_{68})(\text{H}_2\text{O})_2$
-3	1395.2	1395.0	$\text{K}_3\text{H}_4\text{Co}_4(\text{H}_2\text{O})_2(\text{P}_2\text{Mo}_8\text{W}_{10}\text{O}_{68})(\text{H}_2\text{O})_2$

4) Electrochemistry

Nafion ink – Carbon black electrode preparation: 10 mg of catalyst were mixed with 10 mg of Carbon Black. 1 mL of a 3:1 (H₂O:2propanol) solution was added, 80 μ L of Nafion binder were also added to the mixture which was sonicated for a minimum of 2 h before depositing on the surface of a glassy carbon electrode and drying in a 100°C oven for 5 minutes. For a glassy carbon of surface area 0.07 cm² 5.5 μ L of ink were used (Bulk electrolysis and cyclic voltammetry). For a glassy carbon of surface 0.196 cm² 15 μ L of ink were used (rotating disc electrode linear sweep voltammetry and Tafel data).

Carbon paste electrode (CPE) preparation (working electrode for chronopotentiometry, oxygen evolution reaction measurement): Carbon paste electrodes were prepared by mixing in an Agathe mortar carbon paste (ALS, Carbon Paste Oil) and the catalyst to be tested (compounds **3a**[Cs] and **3b**[Cs] in 20% percentage weight of catalyst to carbon paste). Surface area of electrode: 0.07 cm².

Reference and counter electrodes: in all experiments an Ag/AgCl electrode (KCl saturated, which is +0.197V vs NHE). The counter electrode used in the linear sweep voltammetry, cyclic voltammetry and bulk electrolysis was a platinum mesh. The counter electrode used for all experiments was a platinum mesh. For linear sweep voltammetry, cyclic voltammetry was performed using 25 mL of solution in a single cell. Bulk electrolysis and the chronopotentiometry for oxygen evolution data were performed in a single cell using 40 mL of solution.

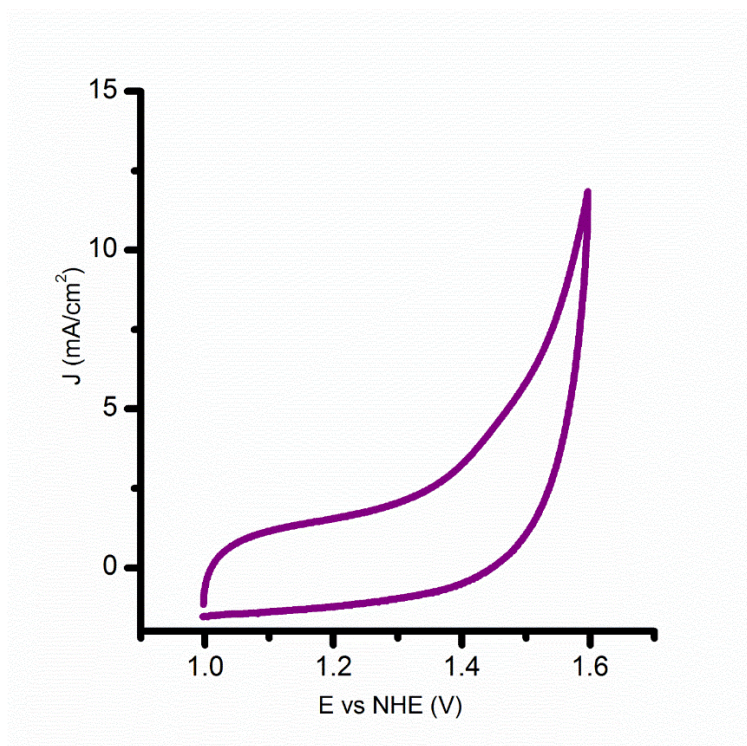


Figure S7. Cyclic voltammetry of compound **3a**[Cs] (10th cycle). Scan rate 100 mV/s. pH = 7.1, 50 mM KPi buffer, 1M KNO₃

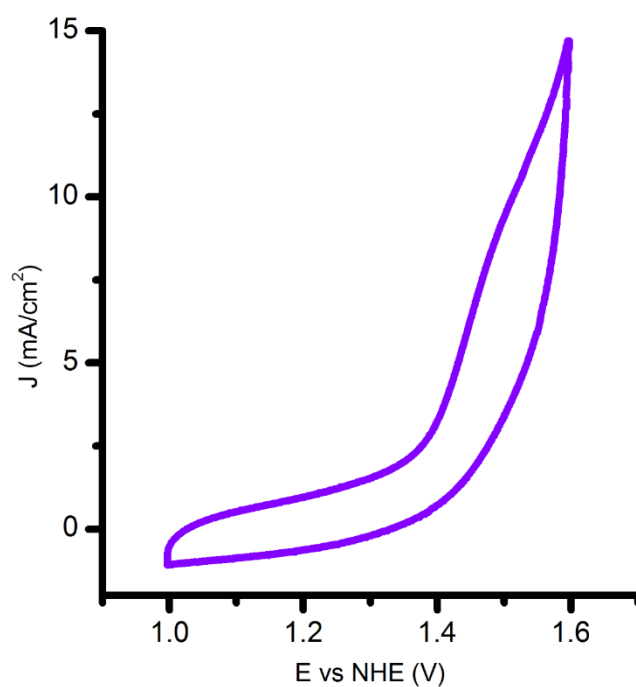


Figure S8. Cyclic voltammetry of compound **3b**[Cs] (10th cycle). Scan rate 100mV/s. pH = 7.1, 50mM KPi buffer, 1M KNO₃.

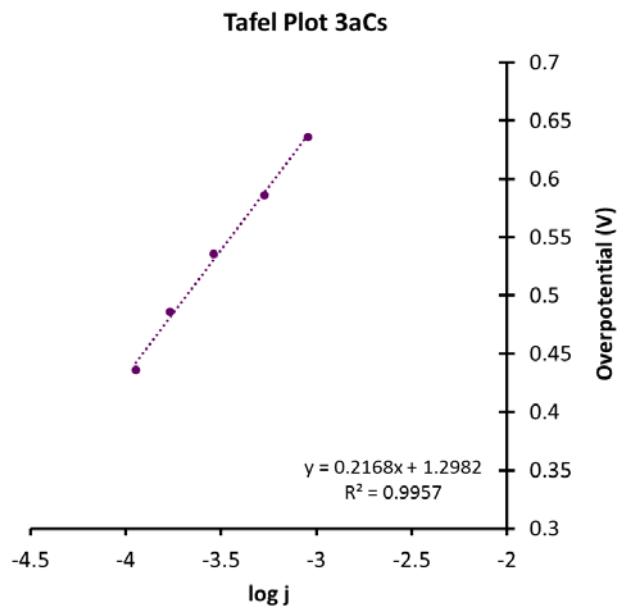


Figure S9. Tafel data extracted from doing 1 min bulk electrolysis per step scanning from 0.8 V to 1.4 V vs Ag/AgCl in 50 mV increments. pH = 7.1, 50 mM KPi buffer, 1M KNO₃. On the left axis the Overpotential is calculated vs NHE.

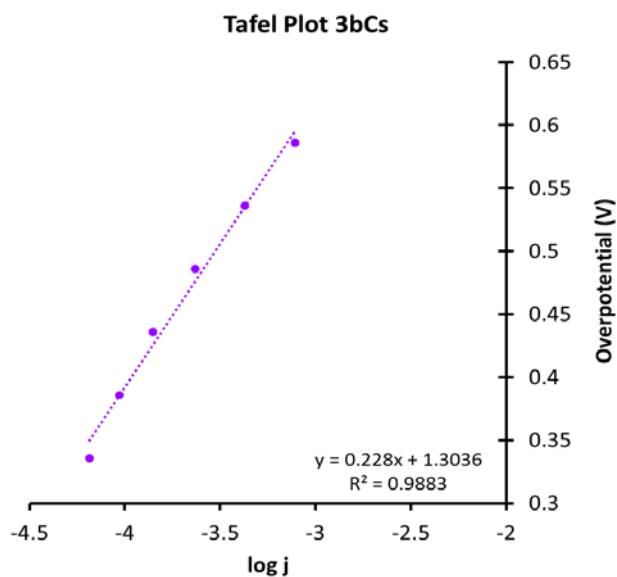


Figure S10. Tafel data extracted from doing 1 min bulk electrolysis per step scanning from 0.8 V to 1.4 V vs Ag/AgCl in 50 mV increments. pH = 7.1, 50 mM KPi buffer, 1M KNO₃. On the left axis the Overpotential is calculated vs NHE.

5) XRD data

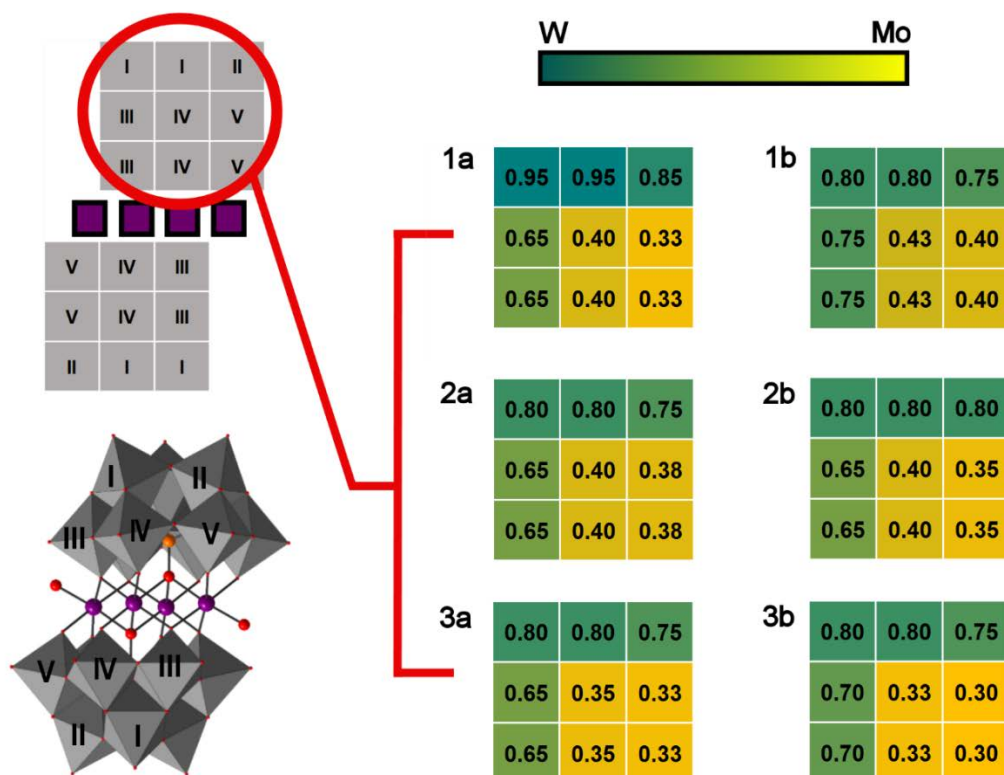


Figure S11. Left hand side: representation of the molybdenum doped Weakley Sandwich $\{Co_4Mo_xW_y\}$ showing the crystallographically identified unique positions in both polyhedral and simple 2D formats. Right hand side: Heat map representation of the tungsten occupancy across these five positions in one of the symmetrically linked halves of the Weakley sandwich.

Table S11. Table showing the occupancies for the addenda atoms in the mixed W/Mo {Co₄} cluster, the unique positions are coloured using the same colour scheme as figure S.11.

Compound	Unique Position	W	Mo
Compound 1a	I	0.95	0.05
	II	0.85	0.15
	III	0.65	0.35
	IV	0.40	0.60
	V	0.33	0.67
Compound 1b	I	0.80	0.20
	II	0.75	0.25
	III	0.75	0.25
	IV	0.43	0.57
	V	0.40	0.60
Compound 2a	I	0.80	0.20
	II	0.75	0.25
	III	0.65	0.35
	IV	0.40	0.60
	V	0.38	0.62
Compound 2b	I	0.80	0.20
	II	0.80	0.20
	III	0.65	0.35
	IV	0.40	0.60
	V	0.35	0.65
Compound 3a	I	0.80	0.20
	II	0.75	0.25
	III	0.65	0.35
	IV	0.35	0.65
	V	0.33	0.67
Compound 3b	I	0.80	0.20
	II	0.75	0.25
	III	0.70	0.30
	IV	0.33	0.67
	V	0.30	0.70

Compound 1a**Table S12.** Crystal data and structure refinement for **1a**

Identification code	1a	
Empirical formula	Co ₄ H ₆₈ K ₄ Mo ₇ Na ₆ O ₁₀₂ P ₂ W ₁₁	
Formula weight	4986.47	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 12.8215(9) Å	a = 90°.
	b = 16.4595(9) Å	b = 104.134(7)°.
	c = 21.4820(14) Å	g = 90°.
Volume	4396.2(5) Å ³	
Z	2	
Density (calculated)	3.767 Mg/m ³	
Absorption coefficient	16.410 mm ⁻¹	
F(000)	4544	
Crystal size	0.119 x 0.109 x 0.050 mm ³	
Theta range for data collection	2.968 to 25.999°.	
Index ranges	-13<=h<=15, -20<=k<=20, -26<=l<=24	
Reflections collected	35591	
Independent reflections	8584 [R(int) = 0.1197]	
Completeness to theta = 25.242°	99.4 %	
Absorption correction	Analytical	
Max. and min. transmission	0.560 and 0.268	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8584 / 102 / 526	
Goodness-of-fit on F ²	1.054	
Final R indices [I>2sigma(I)]	R1 = 0.0541, wR2 = 0.0896	
R indices (all data)	R1 = 0.1113, wR2 = 0.1126	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.94 and -1.83 e.Å ⁻³	

Table S13. Crystal data and structure refinement for **1b**

Identification code	1b	
Empirical formula	Co ₄ H ₇₂ K ₃ Mo ₇ Na ₇ O ₁₀₄ P ₂ W ₁₁	
Formula weight	5006.39	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.5498(4) Å b = 13.2384(5) Å c = 18.2069(7) Å	a = 70.714(3)°. b = 73.693(3)°. g = 73.331(3)°.
Volume	2463.35(17) Å ³	
Z	1	
Density (calculated)	3.375 Mg/m ³	
Absorption coefficient	14.608 mm ⁻¹	
F(000)	2284	
Crystal size	0.100 x 0.070 x 0.050 mm ³	
Theta range for data collection	2.744 to 25.998°.	
Index ranges	-14<=h<=14, -16<=k<=16, -22<=l<=22	
Reflections collected	37800	
Independent reflections	9661 [R(int) = 0.0843]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Analytical	
Max. and min. transmission	0.560 and 0.296	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9661 / 0 / 645	
Goodness-of-fit on F ²	1.047	
Final R indices [I>2sigma(I)]	R1 = 0.0509, wR2 = 0.1141	
R indices (all data)	R1 = 0.0803, wR2 = 0.1332	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.61 and -2.09 e.Å ⁻³	

Table S14. Crystal data and structure refinement for **2a**

Identification code	2a	
Empirical formula	Co ₄ H ₆₈ K ₄ Mo _{7.60} Na ₆ O ₁₀₂ P ₂ W _{10.40}	
Formula weight	4933.72	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 12.8186(7) Å	a = 90°.
	b = 16.4757(9) Å	b = 103.945(3)°.
	c = 21.4920(11) Å	g = 90°.
Volume	4405.2(4) Å ³	
Z	2	
Density (calculated)	3.720 Mg/m ³	
Absorption coefficient	15.679 mm ⁻¹	
F(000)	4506	
Crystal size	0.100 x 0.080 x 0.070 mm ³	
Theta range for data collection	2.436 to 26.000°.	
Index ranges	-15 ≤ h ≤ 15, -20 ≤ k ≤ 20, -26 ≤ l ≤ 26	
Reflections collected	63371	
Independent reflections	8644 [R(int) = 0.0565]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Empirical	
Max. and min. transmission	0.0446 and 0.0184	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8644 / 0 / 629	
Goodness-of-fit on F ²	1.035	
Final R indices [I > 2σ(I)]	R1 = 0.0275, wR2 = 0.0698	
R indices (all data)	R1 = 0.0313, wR2 = 0.0724	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.67 and -1.21 e.Å ⁻³	

Table S15. Crystal data and structure refinement for **2b**

Identification code	2b	
Empirical formula	Co ₄ H ₇₆ K ₄ Mo _{7.60} Na ₆ O ₁₀₆ P ₂ W _{10.40}	
Formula weight	5005.79	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.5555(6) Å	a = 70.706(3)°.
	b = 13.2545(7) Å	b = 73.748(3)°.
	c = 18.2029(10) Å	g = 73.586(2)°.
Volume	2470.0(2) Å ³	
Z	1	
Density (calculated)	3.365 Mg/m ³	
Absorption coefficient	13.987 mm ⁻¹	
F(000)	2293	
Crystal size	0.100 x 0.060 x 0.050 mm ³	
Theta range for data collection	1.877 to 25.999°.	
Index ranges	-14<=h<=11, -16<=k<=16, -22<=l<=22	
Reflections collected	27668	
Independent reflections	9688 [R(int) = 0.0601]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Empirical	
Max. and min. transmission	0.745 and 0.552	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9688 / 6 / 682	
Goodness-of-fit on F ²	1.088	
Final R indices [I>2sigma(I)]	R1 = 0.0388, wR2 = 0.0940	
R indices (all data)	R1 = 0.0467, wR2 = 0.0983	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.56 and -1.93 e.Å ⁻³	

Table S16. Crystal data and structure refinement for **3a**

Identification code	3a	
Empirical formula	Co ₄ H ₇₀ K ₄ Mo ₈ Na ₆ O ₁₀₃ P ₂ W ₁₀	
Formula weight	4916.58	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 12.8289(10) Å	a = 90°.
	b = 16.4982(8) Å	b = 104.001(7)°.
	c = 21.5069(12) Å	g = 90°.
Volume	4416.8(5) Å ³	
Z	2	
Density (calculated)	3.697 Mg/m ³	
Absorption coefficient	15.176 mm ⁻¹	
F(000)	4500	
Crystal size	0.108 x 0.103 x 0.044 mm ³	
Theta range for data collection	2.962 to 25.998°.	
Index ranges	-14<=h<=15, -19<=k<=20, -24<=l<=26	
Reflections collected	34900	
Independent reflections	8616 [R(int) = 0.1329]	
Completeness to theta = 25.242°	99.4 %	
Absorption correction	Analytical	
Max. and min. transmission	0.640 and 0.391	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8616 / 180 / 601	
Goodness-of-fit on F ²	1.046	
Final R indices [I>2sigma(I)]	R1 = 0.0576, wR2 = 0.0851	
R indices (all data)	R1 = 0.1247, wR2 = 0.1143	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.09 and -1.95 e.Å ⁻³	

Table S17. Crystal data and structure refinement for **3b**

Identification code	3b	
Empirical formula	Co ₄ H ₇₈ K ₂ Mo ₈ Na ₈ O ₁₀₇ P ₂ W ₁₀	
Formula weight	4956.42	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 12.3085(7) Å b = 13.3333(7) Å c = 16.1967(9) Å	a = 96.018(4)°. b = 100.985(4)°. g = 110.885(4)°.
Volume	2394.3(2) Å ³	
Z	1	
Density (calculated)	3.437 Mg/m ³	
Absorption coefficient	13.925 mm ⁻¹	
F(000)	2274	
Crystal size	0.100 x 0.070 x 0.050 mm ³	
Theta range for data collection	1.940 to 26.000°.	
Index ranges	-15<=h<=15, -16<=k<=16, -19<=l<=19	
Reflections collected	34268	
Independent reflections	9384 [R(int) = 0.0903]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Empirical	
Max. and min. transmission	0.745 and 0.424	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9384 / 0 / 624	
Goodness-of-fit on F ²	1.027	
Final R indices [I>2sigma(I)]	R1 = 0.0532, wR2 = 0.1267	
R indices (all data)	R1 = 0.0754, wR2 = 0.1408	
Extinction coefficient	n/a	
Largest diff. peak and hole	3.28 and -2.07 e.Å ⁻³	

6) ICP-OES

Table S18. Inductively coupled plasma optical emission spectrometry (ICP-OES) data for compounds **1a**, **1b**, **2a**, **2b**, **3a**, and **3b** note that we present two different batches of each compound.

Compound	Co %	K %	Mo %	Na %	W %
1a	4.99	3.24	14.23	3.38	43.18
1a	5.45	3.75	15.62	3.10	47.20
1b	4.89	2.41	12.27	3.43	44.00
1b	4.50	3.10	11.92	2.67	39.81
2a	5.00	3.29	16.55	2.77	38.27
2a	4.79	2.89	14.61	2.53	38.64
2b	5.11	3.88	16.16	3.13	34.68
2b	5.22	3.40	17.39	3.46	34.43
3a	4.85	3.02	16.17	2.11	36.24
3a	4.79	2.98	16.48	2.50	35.02
3b	5.59	3.90	20.67	4.46	28.13
3b	5.17	3.41	18.38	3.08	33.53

Table S19. Ratio of Na, K, Mo and W to Co, considering that there are 4 Co atoms per cluster.

Compound	Ratio (Relative to Cobalt)				
	Co	K	Mo	Na	W
1a	1.00	0.98	1.75	1.74	2.77
1a	1.00	1.04	1.76	1.46	2.78
1b	1.00	0.74	1.54	1.80	2.88
1b	1.00	1.04	1.63	1.52	2.84
2a	1.00	0.99	2.03	1.42	2.45
2a	1.00	0.91	1.87	1.35	2.59
2b	1.00	1.14	1.94	1.57	2.18
2b	1.00	0.98	2.05	1.70	2.11
3a	1.00	0.94	2.05	1.12	2.40
3a	1.00	0.94	2.11	1.34	2.34
3b	1.00	1.05	2.27	2.04	1.61
3b	1.00	0.99	2.18	1.53	2.08

7) References

- (1) Sheldrick, G. M. A short history of SHELX. *Acta. Crystallogr. Sect. A* **64**, 112–122 (2008).
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- (3) Farrugia, L. J. WinGX and ORTEP for Windows: an update. *J. Appl. Crystallogr.* **45**, 849–854 (2012).