Supporting Information (SI)

Modulating structural and electronic properties of rare Archimedean and Johnson-type Mn cages

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Experimental Procedures

All chemicals mentioned were used as obtained from standard commercial sources. All manipulations were performed under aerobic conditions.

Synthesis of $[Mn^{II}_{12}(\mu_3\text{-}OH)_4(PhPO_3)_4(^tBuCO_2)_{12}(DMSO)_6]\cdot$solvent; (1·solvent)

$Mn(MeCO_2)_2\cdot 4H_2O$ (0.025 g, 0.10 mmol), $KMnO_4$ (0.063 g, 0.40 mmol) and pivalic acid (0.408 g, 4.00 mmol) were combined in MeCN (20 mL). After refluxing this solution for 30 minutes, phenylphosphonic acid (0.032 g, 0.20 mmol) was added. Reflux was continued for *ca.* 10 minutes before L(-)-proline (0.022 g, 0.20 mmol) was added. The resultant reaction mixture was refluxed further for additional 15 minutes before the light colored solution was filtered and DMSO (10 mL) was added to the filtrate. Following, the solvent quantity was reduced to 1/3rd of its original volume through evaporation under reduced pressure. The final reaction mixture was then filtered and the filtrate was allowed to evaporate slowly. Pale colored crystals were obtained within one week. The crystals were isolated by filtration, washed with DMSO and dried in air. Yield: *ca.* 20 % (based on Mn).

Note in relation to the crystallographic assignment: The electron density associated with solvent accessible void volume was rather diffuse and was removed using the SQUEEZE subroutine as implemented in PLATON software package.[1] This electron density (14357 electrons per formula unit) which derives from DMSO, H_2O and MeCN molecules.

Synthesis of $[Mn_{15}(\mu_3\text{-}O)_4(^tBuCO_2)_{7.15}(MeCO_2)_{4.85}(PhPO_3)_6(\mu\text{-}OMe)_6(\mu_3\text{-}OMe)_2(MeOH)_5]\cdot$solvent (2·solvent)

$Mn(MeCO_2)_2\cdot 4H_2O$ (0.125 g, 0.50 mmol), $KMnO_4$ (0.016 g, 0.10 mmol), pivalic acid (0.204 g, 2.00 mmol) and glacial acetic acid (0.060 g, 1 mmol) were combined in MeCN (15 mL). After refluxing this solution for 2 minutes, phenylphosphonic acid (0.040 g, 0.25 mmol) was added. The solution was then refluxed again for 2 minutes and 2,6-pyridinemethanol (0.014 g, 0.10 mmol) was added. The resultant solution was refluxed again for 2 minutes after which MeOH (20 mL) was added to the solution and the solution was then refluxed for 2.5 hours. The dark brown/red solution was then filtered hot and the filtrate was allowed to evaporate slowly at room temperature. Dark rod-shaped crystals were obtained during the time period of one week. The crystals were isolated by filtration, washed with a MeCN/MeOH (15/20 mL) mixture and dried in air. Yield: *ca.* 40 % (based on Mn).

Note in relation to the crystallographic assignment: The electron density associated with solvent accessible void volume was rather diffuse and was removed using the SQUEEZE subroutine as implemented in PLATON software package.[1] This electron density (172 electrons per formula unit) which derives from MeCN, H_2O and MeOH molecules.

<u>Elemental Analysis</u>

Elemental (C, H, N) analysis was performed on dried samples of **1** and **2** using an Exeter Analytical CE 440 at the microanalytical laboratory at the School of Chemistry and Chemical Biology of University College Dublin, Belfield, Dublin, Ireland.

Elemental analysis for **1**: $C_{96}H_{168}Mn_{12}O_{46}P_4S_6$ – Calculated (%) – C 38.01, H 5.58, N 0.00, S 6.34; found (%) – C 37.49, H 5.43, N 0.00, S 6.54.
Elemental analysis for **2**: $C_{94.45}H_{152.9}Mn_{15}O_{59}P_6$ – Calculated (%) – C 34.99, H 4.75, N 0.00; found (%) – C 34.46, H 4.45, N 0.00.

Single-Crystal X-Ray Diffraction

A suitable crystal was selected and immersed in oil, mounted in a mitiGen loop on a Bruker APEX-II CCD diffractometer. The crystal was kept at 100(2) K during data collection using an Oxford Cryostream low-temperature device. The diffraction frames were integrated and processed using the Bruker SAINT software package. The data were corrected for absorption effects using the multi-scan method (SADABS).[2] Using Olex2,[3] the structure was solved using intrinsic phasing as implemented in ShelXT[4] and refined using Least Squares minimization on F^2 with ShelXL.[5]

Powder X-Ray Diffraction (PXRD)

Powder XRD patterns for **1** and **2** were collected on a Bruker D2 Phaser diffractometer using Cu-Kα radiation at 30 kV and 10 mA, with a step size of 0.02° (2θ) between 5 and 40° (2θ), and data were collected at 25 ˚C. The samples were grounded and loaded on a low-background silicon sample holder.

Thermogravimetric Analysis

Thermogravimetric analysis was performed using a Perkin Elmer Pyris-1 thermogravimetric analyzer under a continuous flow of N_2. The measurements were carried out using dried samples. The sample was held at 30 ˚C for 2 minutes. This was followed by heating up to 700 ˚C at 3 ˚C /minutes.

FTIR Analysis

Infrared spectroscopy measurements were performed on a PerkinElmer Spectrum one FT-IR spectrometer using a universal ATR sampling accessory. Data was collected and processed using the Spectrum v5.0.1 (2002 PerkinElmer Instrument LLV) software. For the measurement, 8 scans were collated in the range of 4000 – 300 cm^{-1}.

SQUID Measurements

Magnetic susceptibility measurement was carried out on a 5 T MPMS SQUID from Quantum Design using 14.3 mg of **1** and 9.6 mg of **2**. Temperature dependence of magnetic susceptibility was measured in the temperature range of 4-300 K in an applied magnetic field of 0.1 T.

Electrochemistry

Electrochemical measurements were performed using a Biologic VSP potentiostat. The Ohmic drop was measured prior to each experiment and compensated using the positive feedback compensation as implemented in the instrument. The typical three-electrode set-up used for all the experiments, was composed of a Ag/AgCl (KCl 3M) reference electrode, a carbon paste (**CP**) working electrodes (surface area = 0.07 cm^2), and a Pt mesh. All the measurements in aqueous media were carried out in a 50 mM potassium phosphate (KP_i) buffer solution with KNO_3 (1 M) as electrolyte at pH 7.2. The **CP** blends were prepared by mixing **CP** and the desired amount of catalyst in an agate mortar. Following, the mixtures were inserted into the **CP** electrode pocket. The linear sweep voltammetry (LSV) measurements were conducted using an ALS RRDE-3A set-up with a **CP** rotating disc electrode (surface area = 0.07 cm^2) at 1,600 r.p.m.,

and at a scan rate of 1 mV s^{-1}. Bulk water electrolysis was performed using the same conditions as stated for the LSV measurements.

All the applied potentials (E_{app}) were converted to the normal hydrogen electrode (NHE) reference scale using:

$$E_{NHE} = E_{Ag/AgCl} + 0.210(V).$$

The overpotentials were calculated by subtracting the thermodynamic water oxidation potential ($E^0_{H_2O/O_2}$) to E_{app} as:

$$\eta = E_{app} - E^0_{H_2O/O_2}$$

where $E^0_{H_2O/O_2}$ was corrected by the pH value employing the Nernst equation:

$$E^0_{H_2O/O_2} = 1.229 - (0.059 \times pH) \text{ (V) vs NHE at 25 °C}$$

The onset potentials were estimated from the intersection point between the tangent lines of the Faradaic current at 0.5 mA cm^{-2} and the non-Faradic current. The geometrical area of the CP electrode was used to calculate the current densities.

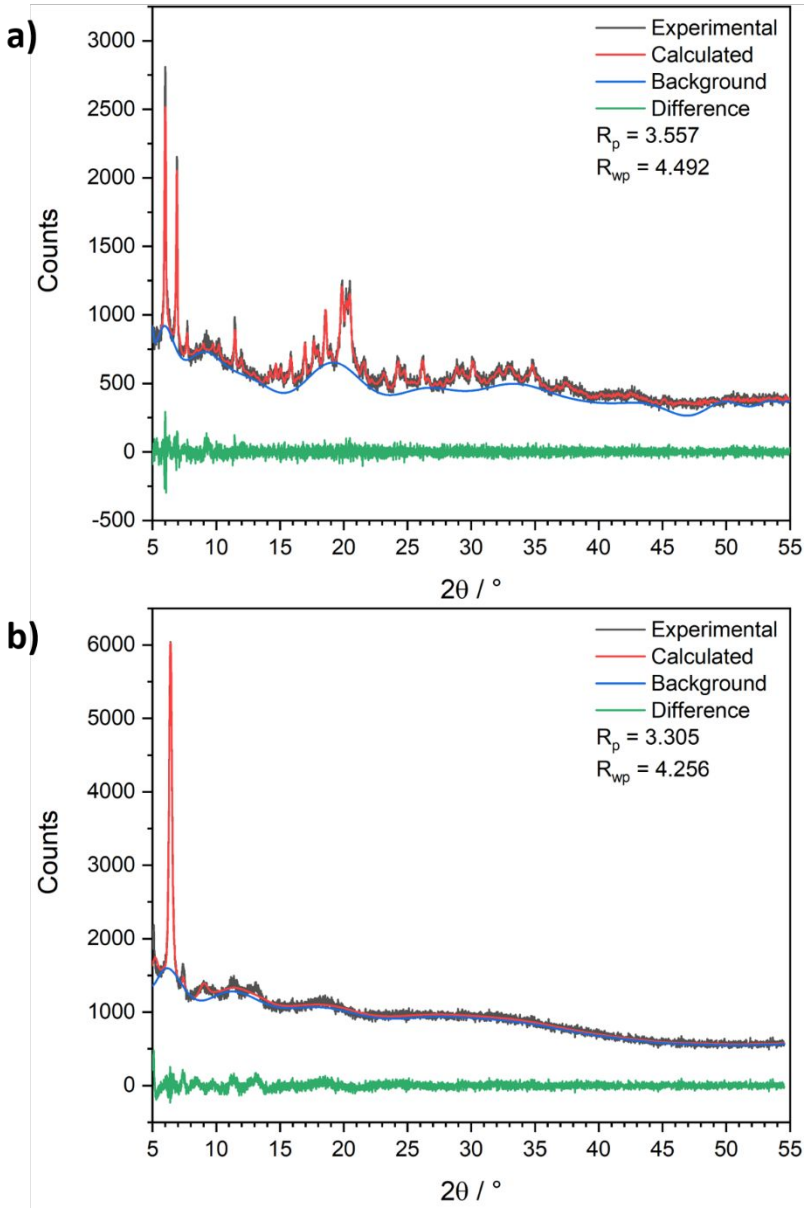

Figure S1. PXRD patterns of **a) 1** and **b) 2** (black). Simulated patterns (red) based on the single-crystal X-ray diffraction data (using CCDC-Mercury software package[6]) are overlaid for comparison. The fit between experimental and calculated patterns confirms the phase-purity of the samples and validates the provided structural models.

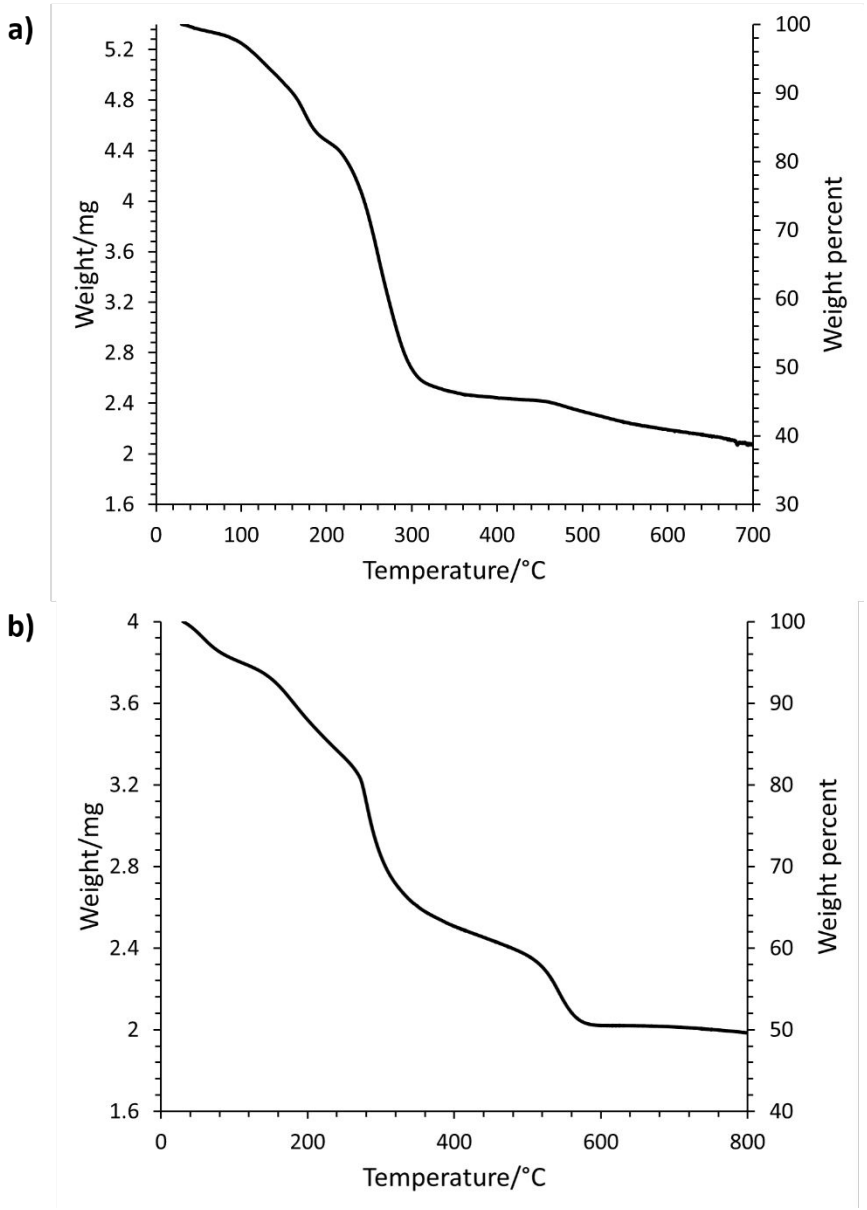

Figure S2. TGA analysis of dried **a) 1** and **b) 2** that were stored at room temperature. For **1**, the initial weight loss represents the loss of lattice solvent molecules followed by the loss of coordinating DMSO molecules. The pronounced weight loss observed between 200 and 315 °C corresponds to the loss of pivalate moieties form the structure. Further heating leads to partial decomposition of the phenyl phosphonate ligands which is most likely associated with the formation of phosphates. For **2**, the initial weight loss up to ~85 °C which results from the removal of constitutional solvent molecules trapped in the lattice. The following thermogravimetric step results from the loss of coordinating methanol molecules. Following, thermal decomposition of acetate and pivalate moieties occurs up to ~500 °C. This event is succeeded by the partial decomposition of the phosphonate ligands at temperatures up to ~600 °C. The gradual weight loss at higher temperatures most likely corresponds to the formation of Mn phosphate and oxide materials.

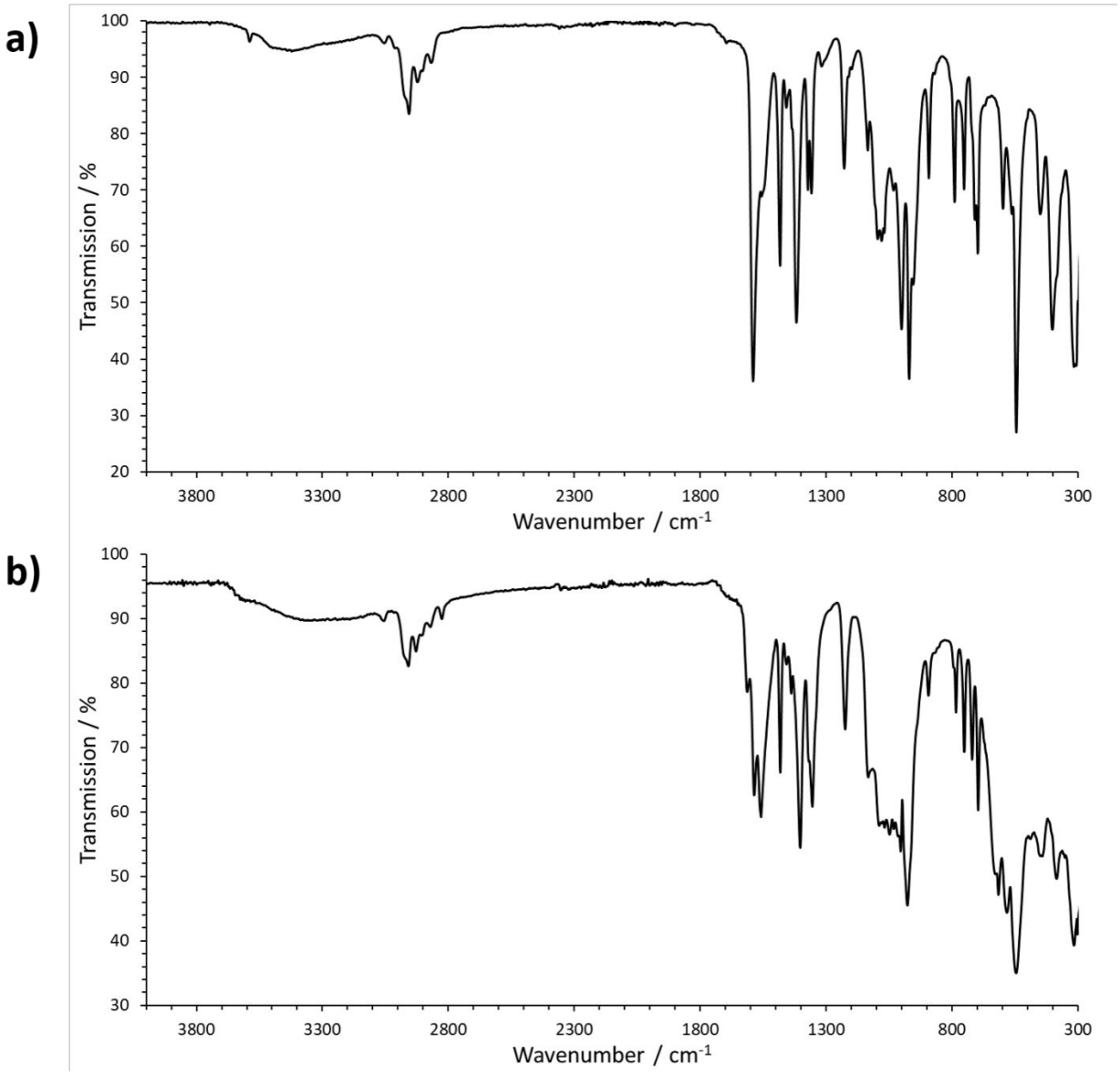

Figure S3. IR spectra of **a) 1** and **b) 2**.

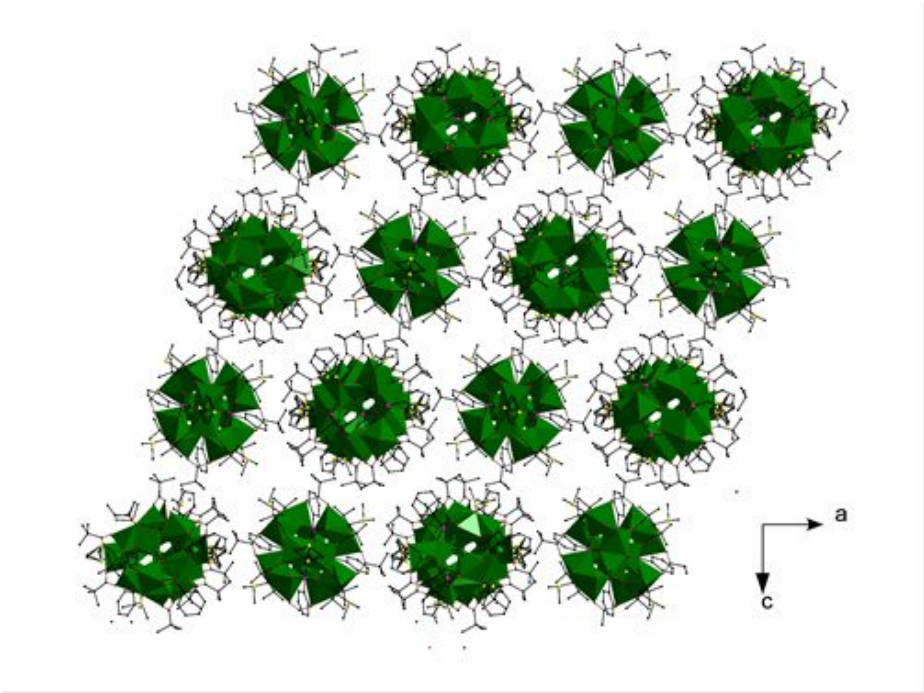

Figure S4. Packing the coordination clusters **1** in the crystal structure; view in the direction of the crystallographic *b*-axis (H-atoms neglected for clarity).

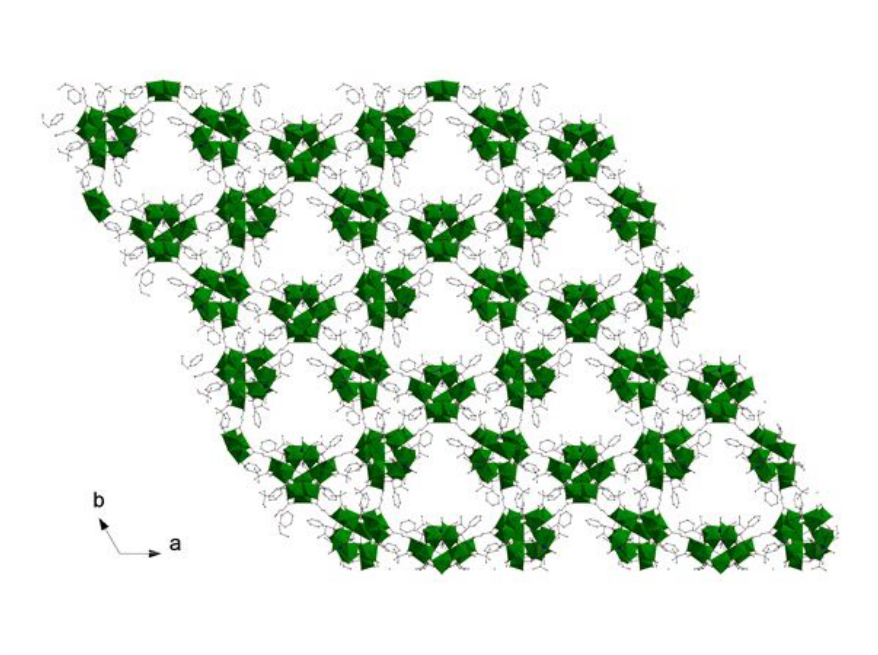

Figure S5. Packing the coordination clusters **2** in the crystal structure; view in the direction of the crystallographic *c*-axis (H-atoms neglected for clarity).

Table S1. Crystallographic information for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{96}H_{168}Mn_{12}O_{46}P_4S_6$	$C_{94.45}H_{152.9}Mn_{15}O_{59}P_6$
Formula weight	3033.81	3242.38
Temperature/K	100(2)	100(2)
Crystal system	trigonal	trigonal
Space group	$R\bar{3}c$	$R3$
a/Å	35.9770(10)	48.387(3)
b/Å	35.9770(10)	48.387(3)
c/Å	88.049(3)	17.8264(10)
α/°	90	90
β/°	90	90
γ/°	120	120
Volume/Å^3	98697(6)	36146(4)
Z	18	9
ρ_{calc}g/cm^3	0.919	1.341
μ/mm^{-1}	6.625	1.266
F(000)	28224.0	14909.0
Crystal size/mm^3	0.264 × 0.162 × 0.109	0.43 × 0.09 × 0.08
Radiation	CuKα (λ = 1.54178)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.762 to 122.374	5.052 to 52.344
Index ranges	-40 ≤ h ≤ 34, -38 ≤ k ≤ 33, -99 ≤ l ≤ 95	-59 ≤ h ≤ 59, -60 ≤ k ≤ 57, -22 ≤ l ≤ 22
Reflections collected	99748	152549
Independent reflections	16601 [R_{int} = 0.1161, R_{sigma} = 0.0972]	31014 [R_{int} = 0.1254, R_{sigma} = 0.1012]
Data/restraints/parameters	16601/181/845	31014/2460/2187
Goodness-of-fit on F^2	0.912	0.970
Final R indexes [I>=2σ (I)]	R_1 = 0.0630, wR_2 = 0.1763	R_1 = 0.0609, wR_2 = 0.1418
Final R indexes [all data]	$C_{96}H_{168}Mn_{12}O_{46}P_4S_6$	R_1 = 0.1112, wR_2 = 0.1683
Largest diff. peak/hole / e Å^{-3}	3033.81	0.76/-0.73
CCDC entry	**2025590**	**2025591**

Table S2. Bond valance sum (BVS) analysis for **1**.

Atom	Bond Valance Sum	Assigned Oxidation State
Mn1	2.194	+II
Mn2	2.136	+II
Mn3	2.203	+II
Mn4	2.190	+II
Mn5	2.200	+II
Mn6	2.148	+II

Table S3. Bond valance sum (BVS) analysis for O atoms and their assigned protonation state in **1**.

Atom	Bond Valance Sum	Assigned Oxidation State
O7	1.365	OH^-
O23	1.367	OH^-

Table S4. Bond valance sum (BVS) analysis for **2**.

Atom	Bond Valance Sum	Assigned Oxidation State
Mn1	2.191	+II
Mn2	1.974	+II
Mn3	3.203	+III
Mn4	3.139	+III
Mn5	3.290	+III
Mn6	3.275	+III
Mn7	2.967	+III
Mn8	3.291	+III
Mn9	3.095	+III
Mn10	2.095	+II
Mn11	2.097	+II
Mn12	1.991	+II
Mn13	3.134	+III
Mn14	3.154	+III
Mn15	3.160	+III

Table S5. Bond valance sum (BVS) analysis for O atoms and their assigned protonation state in **2**.

Atom	Bond Valance Sum	Assigned Oxidation State
O1	1.995	O^{2-}
O10	2.018	O^{2-}
O12	2.331	O^{2-}
O54	2.191	O^{2-}

Table S6. The onset overpotentials for water oxidation using **1/CP** and **2/CP** electrodes at different catalyst loadings.

Loading	Onset overpotential (mV)
1 (20%)	413
1 (40%)	251
2 (20%)	516
2 (40%)	521

References

(1) Spek, A. PLATON SQUEEZE: a tool for the calculation of the disordered solvent contribution to the calculated structure factors. *Acta Crystallograph. C* **2015,** 71 (1), 9-18.
(2) Bruker, S., Bruker AXS Inc., Madison, Wisconsin, USA. SADABS, Bruker AXS Inc., Madison, Wisconsin, USA. **2001**.
(3) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009,** 42, 339-341.
(4) Sheldrick, G. M. SHELXT - Integrated space-group and crystal-structure determination. *Acta Crystallogr. A* **2015,** 71, 3-8.
(5) Sheldrick, G. M. A short history of SHELX. *Acta Crystallogr. A* **2008,** 64, 112-122.
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