Supporting information

Self-assembly of polyoxotungstate with tetrarhodium-oxo core: Synthesis, structure and ^{183}W NMR studies

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^{183}W NMR details

The ^{183}W NMR (20.8 MHz) spectra were recorded at 20º C from a 0.03 M solution on a Bruker AC-500 Spectrometer in 10 mm tubes. Chemical shifts were referenced to an external 2M Na_2WO_4 solution in alkaline D_2O.

X-ray diffractometry

Table S1 Experimental details

Crystal data	
Chemical formula	$H_{84}Na_{12}O_{108}Rh_4W_{18}$
M_r	5809.22
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	150
a, *b*, *c* (Å)	12.4410 (3), 13.7995 (4), 14.6207 (4)
α, β, γ (°)	98.835 (1), 104.179 (1), 103.041 (1)
V (Å^3)	2312.15 (11)
Z	1
F(000)	2593
Radiation type	Mo $K\alpha$
μ (mm^{-1})	23.17
Crystal size (mm)	0.18 × 0.14 × 0.05
Data collection	
Diffractometer	Bruker Nonius X8Apex CCD diffractometer
Absorption correction	Multi-scan *SADABS* (Bruker-AXS, 2004)
T_{min}, T_{max}	0.103, 0.390
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	25729, 13913, 12287
R_{int}	0.033
θ values (°)	$\theta_{max} = 30.6$, $\theta_{min} = 1.5$
Range of *h*, *k*, *l*	$-16 \geq h \geq 17$, $-19 \geq k \geq 18$, $-13 \geq l \geq 20$
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$	0.034, 0.107
GooF on F^2	1.168
No. of reflections, parameters, restraints	13913, 721, 0

H-atom treatment	H-atom parameters not refined
Weighting scheme	$w = 1/[\sigma^2(F_0^2) + (0.0537P)^2 + 2.4583P]$ where $P = (F_0^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e E^{-3})	2.86, -4.04

Computer programs: *APEX2* (Bruker-AXS, 2004), *SAINT* (Bruker-AXS, 2004), *SHELXS97* (Sheldrick, 1998), *SHELXL97* (Sheldrick, 1998), *SHELXTL* (Bruker-AXS, 2004), CIFTAB-97 (Sheldrick, 1998).

Table S2. Selected geometric parameters (Å)

Rh1—O14^{i}	2.045 (6)	W4—O10	1.749 (6)
Rh1—O16	2.014 (6)	W4—O11	1.901 (6)
Rh1—O18	1.996 (5)	W4—O12	1.867 (6)
Rh1—O19	2.097 (6)	W4—O13	1.936 (6)
Rh1—O24	1.995 (5)	W4—O21	1.952 (6)
Rh1—O32^{i}	2.046 (5)	W5—O4	2.055 (6)
Rh2—O6^{i}	2.013 (6)	W5—O5	2.126 (6)
Rh2—O14^{i}	2.043 (5)	W5—O7	1.748 (6)
Rh2—O18	2.010 (6)	W5—O12	2.062 (6)
Rh2—O18^{i}	2.018 (5)	W5—O30	1.886 (6)
Rh2—O32	2.045 (5)	W5—O35	1.784 (5)
Rh2—O35	2.022 (5)	W6—O9	2.240 (6)
O6—Rh2^{i}	2.013 (6)	W6—O16	1.808 (5)
O14—Rh1^{i}	2.045 (6)	W6—O22	1.991 (6)
O14—Rh2^{i}	2.043 (5)	W6—O25	1.962 (6)
O18—Rh2^{i}	2.018 (5)	W6—O28	1.742 (6)
O32—Rh1^{i}	2.046 (5)	W6—O29	1.924 (5)
W1—O1	2.272 (6)	W7—O1	2.283 (6)
W1—O6	1.808 (6)	W7—O2	1.912 (6)
W1—O20	1.999 (5)	W7—O15	1.951 (6)
W1—O27	2.003 (5)	W7—O20	1.891 (6)
W1—O29	1.913 (5)	W7—O21	1.882 (6)
W1—O31	1.737 (6)	W7—O23	1.722 (6)
W2—O1	2.235 (5)	W8—O2	1.921 (6)
W2—O14	1.917 (5)	W8—O3	1.721 (6)
W2—O15	1.955 (6)	W8—O9	2.305 (6)
W2—O27	1.915 (6)	W8—O11	1.919 (6)
W2—O33	1.897 (6)	W8—O17	1.901 (6)
W2—O34	1.740 (6)	W8—O22	1.895 (6)
W3—O4	1.889 (6)	W9—O9	2.223 (5)
W3—O5	2.146 (6)	W9—O17	2.003 (6)
W3—O8	1.733 (6)	W9—O24	1.818 (5)
W3—O13	1.960 (6)	W9—O25	1.957 (6)
W3—O32	1.912 (5)	W9—O26	1.755 (6)
W3—O33	1.974 (6)	W9—O30	1.943 (6)
W4—O5	2.194 (5)		

Symmetry code(s): (i) -*x*, -*y*, -*z*.

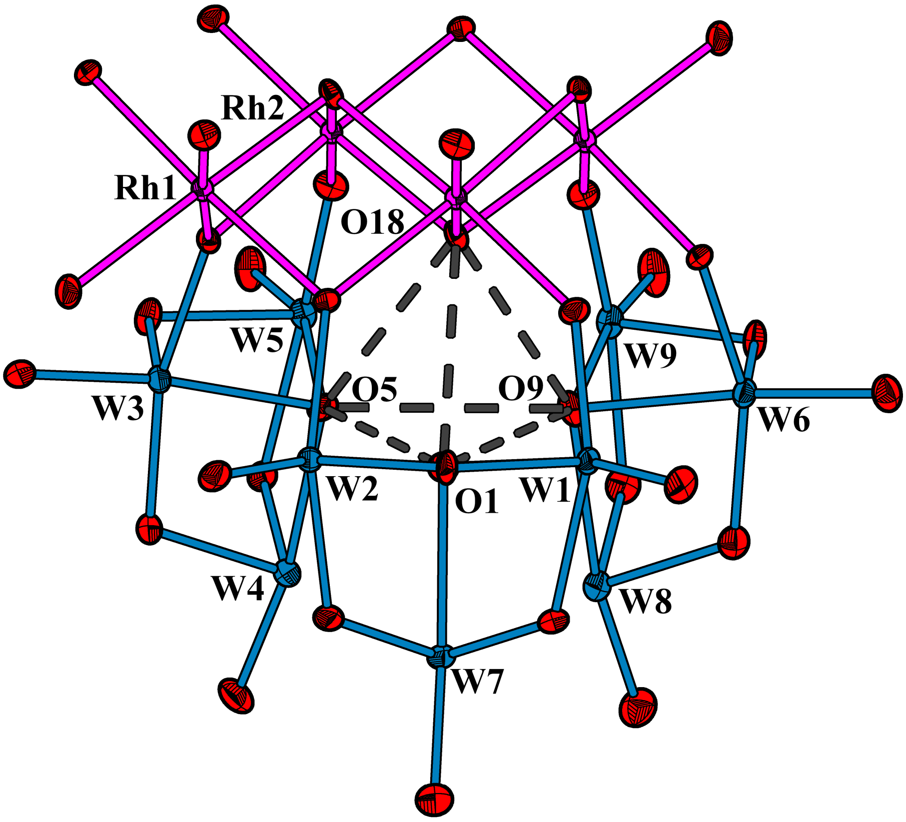


Fig. 1S. Tetrahedral cavity formed with O18, O1, O5, O9. Atoms are shown in 50% probability. μ_2-O ligands between W atoms are not shown for clarity.

Electrochemistry. The cyclic voltammetric measurements were carried out using an electrochemical analyzer 797 VA Computrace (Metrohom, Switzerland). A conventional three-electrode glass cell of 10 ml capacity was used. A 2 mm diameter glassy carbon disk electrode (Metrohm, Switzerland) was used as working electrode (GCE). A platinum wire served as the counter electrode. All solutions were deoxygenated using high-purity argon gas for 10-15 min prior to electrochemical experiments. Measurements were carried out at ambient temperature (20 ± 2 °C). All reagents were of analytical grade or higher and purchased from Sigma-Aldrich. 0.1 M Na_2SO_4 electrolyte was prepared using twice distilled water. Repeated cycling (Fig 2S shows 1st, 3rd, 5th and 6th cycles) shows that polarization route does not affect CVA behaviour. ΔE_p calculated as 0.715 V – 0.651 V = 0.064 V) is characteristic for one-electron processes. Increase in scan rate from 0.01 to 0.05 $B \cdot c^{-1}$ causes positive anodic and negative cathodic shifts and can be described by following regression equations: $E_p^a = 0.059 \log \upsilon + 0.83$ and $E_p^c = 0.057 \log \upsilon + 0.54$ for anodic and cathodic signals, respectively.[1] $dE_p/d\log v$ values correspond to the theoretical value of 0.059/n, where n is the number of transferred electrons. Increase in the scan rate decrease the reversibility of the electrochemical process and breaks symmetry between anodic and cathodic response signals. Linear dependence of i_a and i_p on the square root of the scan rate indicate that electron transfer is determined by the rate of diffusion of $[\{Rh_4(\mu_3\text{-}O\text{-})_2(H_2O)_2\}(H_2W_9O_{33})_2]^{12-}$ (Fig 3S, 4S). [2]

1. Kh. Z. Brainina, *Stripping Voltammetry in Chemical Analysis*, Haisted Press, New York, **1974**, p. 222.

2. A.J. Bard, L.R. Faulkner, *Electrochemical methods: fundamentals and application,* Wiley, New York, **1980.**

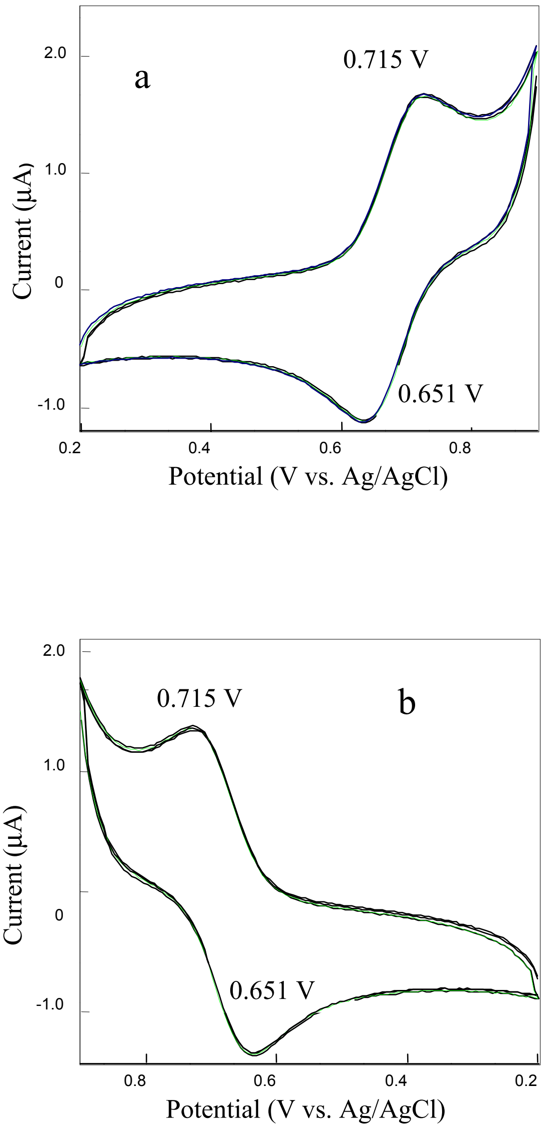


Fig. 2S. Cyclic cathodic-anodic (a) and anodic-cathodic (b) waves for CVA of 0.05 M of **1** in 0.1 M Na_2SO_4 between 0.2 ↔0.9 V at 0.01 V·s-1 scan rate.

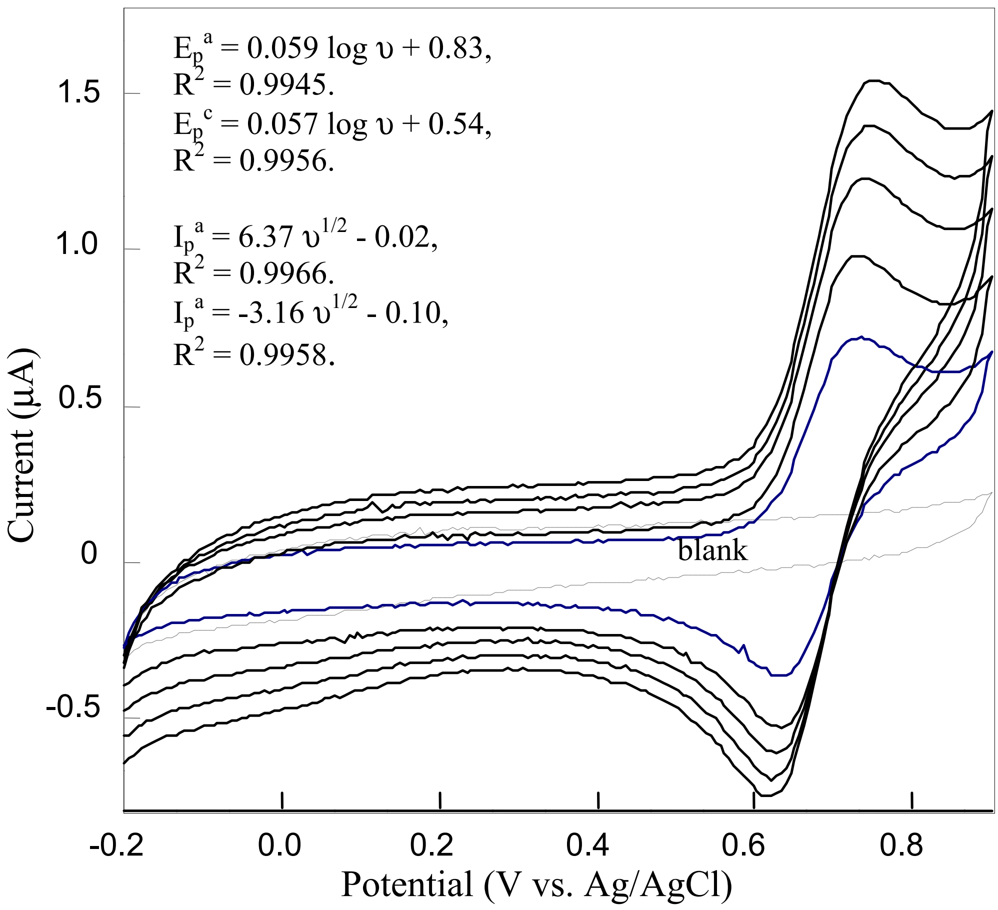


Fig. 3S. The cyclic voltammetric responses for 0.05 mM solution of **1** on the glassy carbon electrode in a 0.1 M Na_2SO_4 with a scan rate of 0.01, 0.02, 0.03, 0.04 and 0.05 V s^{-1}. Scan route: –0.2 ↔0.9 V.

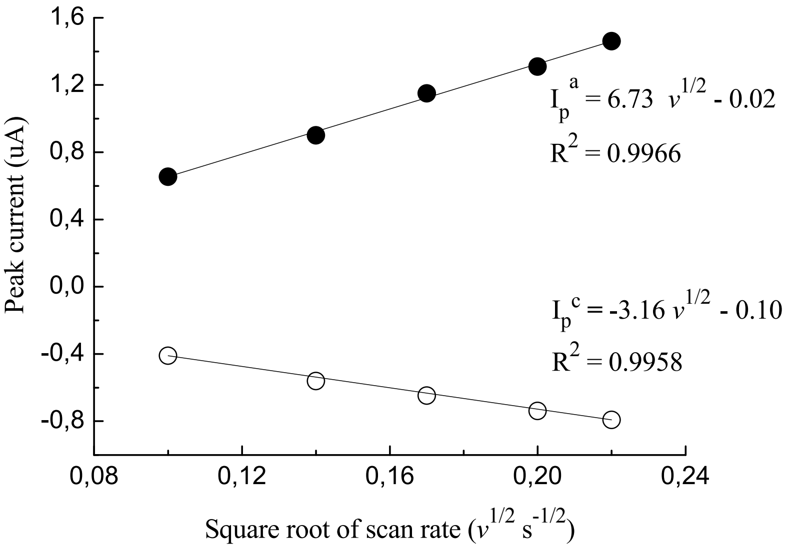


Fig. 4S. The plot of peak current (I_p) on square root of scan rate.

NMR treatment. According to symmetry considerations, there can be proposed four possible assigmnets (Fig 5S)

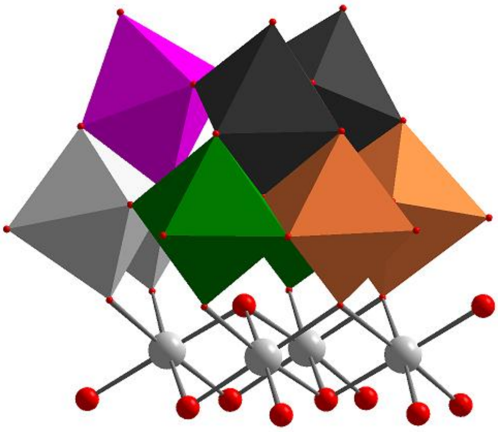
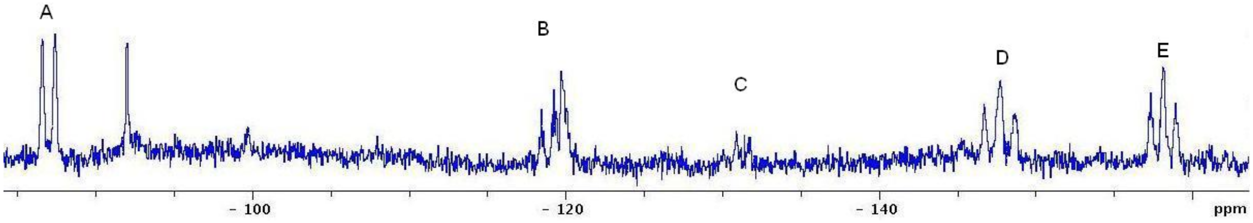


Figure 5S. Non-equivalent W atoms of $\{W_9O_{33}\}$ fragment; orange = 1, green = 2, grey = 3, black = 4, purple = 5.



Assuming that: $J_{4\text{-}5} = J_{1\text{-}4} = J_{1\text{-}2} = J_{2\text{-}4} \neq J_{3\text{-}5}$ and $J_{2\text{-}3} = J_{3\text{-}5}$

or $J_{1\text{-}2} = J_{1\text{-}4} = J_{2\text{-}4} = J_{3\text{-}5} = J_{2\text{-}3} \neq J_{4\text{-}5}$ yields: A = 2 or 4; B = 2 or 4; C = 5; D = 1 or 3; E = 1 or 3.