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Preparation and Properties of the Aqua Ions $[W_4S_4(H_2O)_{12}]^{n+}$ ($n = 5, 6$) and Crystal Structure of $(Me_2NH_2)_6[W_4S_4(NCS)_{12}]\cdot 0.5H_2O$[#]

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The [3 + 1] reaction of $[W_3S_4(H_2O)_9]^{4+}$ with $[W(CO)_6]$ in 2 M HCl under hydrothermal conditions (130 °C) gives the $[W_4S_4(H_2O)_{12}]^{6+}$ cuboidal cluster, reduction potential 35 mV vs NHE (6+/5+ couple). The reduced form is obtained by controlled potential electrolysis. X-ray crystal structure was determined for $(Me_2NH_2)_6[W_4S_4(NCS)_{12}]\cdot 0.5H_2O$. The W–W and W–S bond lengths are 2.840 and 2.379 Å, respectively.

Introduction

Cuboidal M_4Q_4 complexes have a dominant role to play in the chemistry of transition-metal chalcogenide clusters.[1] At present two metals (Fe and Mo) provide the vast majority of known compounds. This is in large part because suitable lead-in compounds are available for the assembly of Fe_4Q_4 and Mo_4Q_4 cluster complexes. This is particularly so for $Q = S$ with $[Fe_4S_4X_4]^{2-}$ ($X^- = Cl^-, Br^-, I^-$),[2] and with the availability of the aqua ion $[Mo_4S_4(H_2O)_{12}]^{5+}$.[3] For the latter the 4+ and 6+ states can also be accessed with 5+ the most stable.[4] The 5+ cuboidal complex $[Mo_4S_4(H_2O)_{12}]^{5+}$ can be obtained on a preparative scale by a number of methods: (i) reductive coupling of two core Mo^V_2 dimer units $Mo_2(O)_2(\mu\text{-}S)_2^{2+}$;[5] (ii) reduction of $[Mo_3S_4(H_2O)_9]^{4+}$ with H_3PO_2;[6] (iii) a [2 + 2] reaction involving the Mo^V_2 and Mo^{II}_2 dimers $[Mo_2(\mu\text{-}S)_2Cl_8]^{2-}$ and $K_4[Mo_2Cl_8]$, or [3 + 1] reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with $K_4[Mo_2Cl_8]$ (as source of Mo^{II});[6,7] and (iv) the reaction of $[Mo(CO)_6]$ with Na_2S in acetic anhydride.[8] Because W is more difficult to reduce, neither of the first two approaches can be used. Route (iii) is difficult because of possible W^{II} starting materials are difficult to access, and (iv) gives only the W^{IV} product $[W_3O_3S(H_2O)_9]^{4+}$.[9]

The $W_4S_4^{6+}$ core is, however, formed as $[W_4S_4(CN)_{12}]^{6-}$ by the high-temperature reaction of polymeric $\{W_3S_7Br_4\}_x$ with KCN.[10] It is also obtained by the self-assembly reaction of $[W(CO)_6]$, $Na_2[WO_4]$, with P_4S_{10} in EtOH, and in a process involving the comproportionation of W^0 and W^{VI} to give $[W_4S_4(\mu\text{-dtp})_2(dtp)_4]$ (dtp = $(EtO)_2PS_2$).[11] An isomeric form of the latter $[W_4S_4(\mu\text{-dtp})_3(dtp)_3]$ is obtained from the reaction of "$H_3W_2Cl_9$" with P_4S_{10} in ethanol.[11] Although these are the first authentic examples of $W_4S_4^{6+}$ cuboidal clusters,

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[#] Dedicated to Professor F. A. Kuznetsov on the occasion of his 70th birthday.

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the metal sites are blocked by ligands that are not readily substituted. Preparation of the aqua ion is a preferred strategy, but to obtain the latter an alternative synthetic route is required. We report here a [3 + 1] procedure using the readily available $[W_3S_4(H_2O)_9]^{4+}$ and $[W(CO)_6]$.

Experimental Section

Starting Materials. Polymeric $\{W_3S_7Br_4\}_n$ was obtained by heating W, S, and Br_2 together in a sealed quartz tube.[12] Preparation of $[W_3S_4(H_2O)_9]^{4+}$ involves heating the polymer (1 g) in a steam bath (90 °C) with excess H_3PO_2 (2 mL; 50% w/w in H_2O; Aldrich) in concentrated HCl (20 mL) for 15 h.[13] The product was diluted 2-fold, filtered, diluted to 0.2 M HCl, and loaded onto a Dowex 50W-X2 cation-exchange column. Final elution was with 2 M HCl. Commercially available tungsten hexacarbonyl $[W(CO)_6]$ was used.

Analytical Procedures. Tungsten and sulfur were determined for $[W_4S_4(H_2O)_{12}]^{6+}$ in 2 M HCl by gravimetric method as WO_3 and $BaSO_4$, respectively. Elemental analyses (Carlo Erba 1106) were performed in the Laboratory of Microanalysis of the Institute of Organic Chemistry, Novosibirsk.

Spectra. IR spectra were recorded on KBr disks using an IFS-85 spectrometer (Bruker). UV−vis spectra (300−900 nm) were recorded on a Shimadzu UV-1202 spectrophotometer.

Preparation of $[W_4S_4(H_2O)_{12}]^{6+}$. A mixture of $[W(CO)_6]$ (50 mg; 0.142 mmol) and a 2.5 mL portion of a 50 mM solution of $[W_3S_4(H_2O)_9]^{4+}$ (0.125 mmol) in 2 M HCl were sealed in a Pyrex tube (6 mL) and heated at 130 °C for 2 days. After cooling, the dark-brown reaction mixture was filtered, diluted with water (12 mL), and allowed to stand in air at room temperature for 12 h. The product was loaded onto a Dowex 50W-X2 column (1.5 cm × 10 cm) and washed with 1 M HCl (25 mL), and two bands eluted in 2 M HCl. The first purple band of unreacted $[W_3S_4(H_2O)_9]^{4+}$ (12%) was discarded. A second brown-red band was collected. Yield: 85%. Solution analyses gave satisfactory W:S ratios (found: W:S = 1.00:1.02). The UV−vis absorption spectrum of the $[W_4S_4(H_2O)_{12}]^{6+}$ product in 2 M HCl has peak positions λ/nm at 452 and 770. To replace HCl by *p*-toluenesulfonic acid (Hpts), $[W_4S_4(H_2O)_{12}]^{6+}$ in 2 M HCl was diluted 5-fold, loaded onto a short Dowex 50W-X2 column (1.5 cm × 2 cm), and washed with water (200 mL). Elution was with 4 M Hpts.

Preparation of $(Me_2NH_2)_6 \cdot [W_4S_4(NCS)_{12}] \cdot 0.5H_2O$ (1). Crystals of **1** were obtained by first adding solid KNCS (40 mg) to a solution of $[W_4S_4(H_2O)_{12}]^{6+}$ (5 mM; 4 mL) in 2 M HCl, followed by Me_2NH_2Cl (50 mg). After thorough mixing the solution was allowed to stand at room temperature for 2 days. During this time, dark-brown octahedral crystals of **1** suitable for crystallography formed. These were filtered off and dried in air. Yield: 0.029 g (78%). Anal. Calcd for $C_{24}H_{49}N_{18}O_{0.5}S_{16}W_4$: C, 15.61; H, 2.68; N, 13.66; S, 27.79. Found: C, 15.72; H, 2.72; N, 13.75; S, 27.85. IR (as KBr pellet): ν(CN) 2102 (vs), ν(CS) 810 (m), δ(NCS)/ν(WN) 472 (w), 455 (w), 414 (w) cm^{-1}.

Electrochemical Studies. These were carried out with an AMEL 5000 potentiostat−galvanostat system controlled by a Pentium PC. The electrochemical cell was a conventional one with three electrodes. The reference was a standard calomel electrode, the counter electrode was a platinum sheetwire (Radiometer), and a glassy carbon working electrode (Metrohm) was used. As supporting electrolyte, aqueous 2 M Hpts, deoxygenated by bubbling nitrogen through the solution, was used. The $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ couple in 0.1 KCl (410 mV vs NHE) was chosen as an internal reference. Reduction potentials ($E°$) defined as $(1/2)(E_a + E_c)$, where E_a and E_c are the anodic and cathodic peak potentials, were obtained from cyclic voltammetry experiments. From repeated check determinations the reproducibility was ±5 mV.

Table 1. Crystallographic Data for $(Me_2NH_2)_6[W_4S_4(NCS)_{12}] \cdot 0.5H_2O$ (**1**)

formula	$C_{24}H_{49}N_{18}O_{0.50}S_{16}W_4$
fw	1846.17
space group	$Pa\bar{3}$
Z	8
crystal system	cubic
a, Å	22.760(3)
V, Å^3	11 791(2)
D(calcd), g·cm^{-3}	2.080
temp, °C	−70
λ, Ag Kα	0.560 86 Å
μ, cm^{-1}	4.498
R1[a]	0.0768
wR2[b]	0.2206

[a] Conventional R on F_{hkl}: $\sum|F_o| - |F_c|/\sum|F_o|$. [b] Weighted R on $|F_{hkl}|^2$: $\{\sum w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Bulk electrolysis experiments of ~4 mM solutions of $[W_4S_4(H_2O)_{12}]^{6+}$ in 4 M Hpts were performed under N_2. These required ~2 h, with both counter and working electrodes made up of platinum wire spirals (10 cm length; 0.5 mm in diameter). Cathodic and anodic compartments were separated by a liquid junction, with the reference electrode in the cathodic compartment alongside the working electrode. In the cathodic compartment $[W_4S_4(H_2O)_{12}]^{6+}$ was completely reduced, and the UV−vis spectrum of $[W_4S_4(H_2O)_{12}]^{5+}$ in 4 M Hpts was recorded.

X-ray Crystallography. The crystallographic data and details of diffraction experiments are given in Table 1. A dark-brown crystal of **1** of 0.40 × 0.38 × 0.37 mm size was mounted on a one-cycle STOE Image Plat IPDS diffractometer (T = 213 K, radiation Ag Kα, λ = 0.560 86 Å, graphite monochromator). Diffraction data were measured by taking narrow frames. Absorption corrections were applied by the merging of symmetrically equivalent reflections. A total 33 011 reflections were measured up to $\theta_{max} = 21.62°$, of which 4614 are unique ($R_{int} = 0.2554$ because of absorption effects). The structure was solved by direct methods. Both independent cations show high thermal motion and possible disorder. The oxygen atoms of water molecules are disordered over six positions. The structure was refined by anisotropic methods for anion and solvent water molecules using a SHELX-97 program set.[14] Hydrogen atoms of cations were refined in rigid-body approximation. The final residuals are R1 = 0.0768, wR2 = 0.1924 for 3256 $F_o > 4\sigma(F_o)$, and R1 = 0.1026, wR2 = 0.2206, GOF = 1.013 for all unique data. The main bond distances and angles are given in Table 2.

Results and Discussion

The incomplete cubane-type cluster ion $[W_3S_4(H_2O)_9]^{4+}$ reacts in aqueous HCl solution with $[W(CO)_6]$ (1).

$$W_3S_4^{\ 4+} + W^0 - 2e^- \rightarrow W_4S_4^{\ 6+} \tag{1}$$

Since $[W(CO)_6]$ is rather inert and insoluble in aqueous media, a hydrothermal synthetic approach has to be used.

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Table 2. Selected Bond Distances (Å) and Angles (deg) in (**1**)[a]

Bond Distances			
W(1)−W(1)#1	2.8350(10)	W(1)−N(13)	2.165(14)
W(1)−W(1)#2	2.8351(10)	W(2)−S(1)	2.380(4)
W(1)−W(2)	2.8513(10)	W(2)−S(1)#2	2.380(4)
W(1)−S(1)#1	2.378(4)	W(2)−S(1)#1	2.380(4)
W(1)−S(1)	2.378(4)	W(2)−N(21)#2	2.145(14)
W(1)−S(2)	2.376(4)	W(2)−N(21)#1	2.145(14)
W(1)−N(11)	2.162(14)	W(2)−N(21)	2.145(14)
W(1)−N(12)	2.162(15)		

Bond Angles			
W(1)#1−W(1)−W(1)#2	60.0	S(1)−W(2)−S(1)#2	104.12(10)
W(1)#1−W(1)−W(2)	60.188(12)	S(1)−W(2)−S(1)#1	104.11(10)
W(1)#2−W(1)−W(2)	60.190(12)	S(1)#2−W(2)−S(1)#1	104.11(10)
S(1)#1−W(1)−S(1)	104.26(19)	N(21)#2−W(2)−S(1)	85.8(5)
S(2)−W(1)−S(1)#1	104.58(11)	N(21)#1−W(2)−S(1)	163.1(5)
S(2)−W(1)−S(1)	104.56(11)	N(21)−W(2)−S(1)	86.2(5)
N(11)−W(1)−S(1)#1	162.2(4)	N(21)#2−W(2)−S(1)#2	86.2(5)
N(11)−W(1)−S(1)	86.4(4)	N(21)#1−W(2)−S(1)#2	85.8(5)
N(11)−W(1)−S(2)	86.0(5)	N(21)−W(2)−S(1)#2	163.1(5)
N(11)−W(1)−N(12)	79.7(7)	N(21)#2−W(2)−S(1)#1	163.1(5)
N(12)−W(1)−S(1)#1	87.0(5)	N(21)#1−W(2)−S(1)#1	86.2(5)
N(12)−W(1)−S(1)	84.9(4)	N(21)−W(2)−S(1)#1	85.8(5)
N(12)−W(1)−S(2)	162.3(4)	N(21)#2−W(2)−N(21)#1	81.2(7)
N(13)−W(1)−S(1)#1	84.2(5)	N(21)#2−W(2)−N(21)	81.2(7)
N(13)−W(1)−S(1)	163.3(4)	N(21)#1−W(2)−N(21)	81.2(7)
N(13)−W(1)−S(2)	86.8(5)	W(1)#2−S(1)−W(1)	73.18(11)
N(13)−W(1)−N(11)	82.1(6)	W(1)#2−S(1)−W(2)	73.63(11)
N(13)−W(1)−N(12)	81.1(6)	W(1−)S(1)−W(2)	73.62(11)
W(1)#1−W(2)−W(1)	59.62(2)	W(1)−S(2)−W(1)#2	73.26(16)
W(1)#1−W(2)−W(1)#2	59.62(2)	W(1)−S(2)−W(1)#1	73.26(16)
W(1)−W(2)−W(1)#2	59.62(2)	W(1)#2−S(2)−W(1)#1	73.26(16)

[a] Symmetry transformations used to generate equivalent atoms: #1, *z*,*x*,*y*; #2, *y*,*z*,*x*.

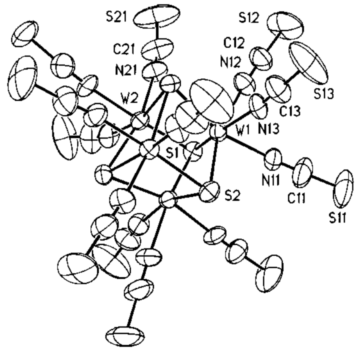

Figure 1. Drawing of $[W_4S_4(NCS)_{12}]^{6-}$ in **1**. Thermal ellipsoids are given with 50% probability. Tungsten−tungsten bonds are omitted for clarity. Only crystallographically independent atoms are labeled.

The title compound $(Me_2NH_2)_6\ [W_4S_4(NCS)_{12}]\cdot 0.5H_2O$ (**1**) could be isolated in high yield from 2 M aqueous solution in the presence of KNCS and Me_2NH_2Cl (2).

$$[W_4S_4(H_2O)_{12}]^{6+} + 12NCS^- \rightarrow [W_4S_4(NCS)_{12}]^{6-} + 12H_2O \quad (2)$$

X-ray Crystal Structure of 1. The X-ray crystal structure of $(Me_2NH_2)_6[W_4S_4(NCS)_{12}]\cdot 0.5H_2O$ (**1**) provided support for the W_4S_4 cuboidal cluster. The cluster anion is shown in Figure 1. It lies in a special position with site symmetry C_{3i} and possesses a normal cuboidal structure. The four tungsten atoms give a practically ideal tetrahedral shape interpenetrated by a larger tetrahedron of the four μ_3-S ligands. Each metal has three almost linear NCS ligands coordinated via the nitrogen. Compound **1** is isostructural with the previously determined structure of $(Me_2NH_2)_6\ [MoW_3S_4(NCS)_{12}]\cdot 0.5H_2O$.[15] The W−W and W−S bond lengths are 2.840 and 2.379 Å, respectively, and compare with corresponding values for $Mo_4S_4^{6+}$ cuboidal cluster in $[Mo_4S_4(edta)_2]^{2-}$ (2.810 and 2.355 Å) (edta = ethylenediaminetetraacetate)[16] and $[Mo_4S_4(CN)_{12}]^{6-}$ (2.845 and 2.395 Å).[10a] The volume of the W_4 tetrahedron (2.709 Å^3) is slightly greater than that of MoW_3 in $(Me_2NH)_6[MoW_3S_4(NCS)_{12}]\cdot 0.5H_2O$ (2.700 Å^3),[15] and it is very close to that found in $Cs_5K[W_4S_4(CN)_{12}]\cdot 2CH_3OH\cdot 2H_2O$ (2.710 Å^3).[10a] Average M−M distances are short in all cases and consistent with metal−metal bonding. The main bond lengths are summarized in Table 2.

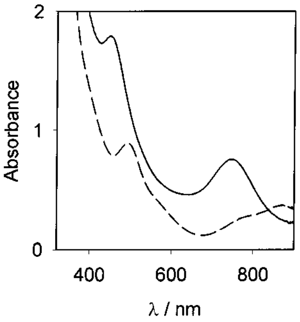

Figure 2. UV/vis spectra of $[W_4S_4(H_2O)_{12}]^{6+}$ (—) and $[W_4S_4(H_2O)_{12}]^{5+}$ (---) in 4 M Hpts.

UV/vis Spectrum and Stability. In 2 M HCl the $[W_4S_4(H_2O)_{12}]^{6+}$ cluster gives peak positions λ/nm (ϵ/M^{-1}cm^{-1}) at 452 (460), 770 (180), which suggest ligand-to-metal charge transfer (LMCT) transitions. Details of the spectrum in 4 M Hpts are indicated in Figure 2. Peak positions alongside those for $[Mo_4S_4(H_2O)_{12}]^{6+}$ are shifted to higher energy transitions.[3] Violet shifts in UV/vis peaks are also observed on replacing Mo with W in cyano complexes of cuboidal $M_3Q_4^{4+}$ and $M_4Q_4^{n+}$ (M = Mo, W; Q = S, Se, Te; n = 5, 6).[10,15,17−19] Details of the $[W_4S_4(H_2O)_{12}]^{5+}$ UV−vis spectrum (see next section) are included in Figure 2.

Electrochemistry. The $M_4Q_4^{n+}$ (M = Mo, W; Q = S, Se, Te) cuboidal clusters are capable of existing in three oxidation states ranging from the most oxidized (n = 6; 10 metal electrons) to the most reduced electron-precise 12-electron species with n = 4. Cyclic voltammetry experiments on $[W_4S_4(H_2O)_{12}]^{6+}$ in 4 M Hpts reveal the presence of only one well-defined and symmetrical redox couple prior to hydrogen evolution; see Figure 3. The equilibrium can be written as

$$[W_4S_4(H_2O)_{12}]^{6+} + e^- = [W_4S_4(H_2O)_{12}]^{5+} \quad (3)$$

with redox potential $E°' = 35$ mV very close to the predicted

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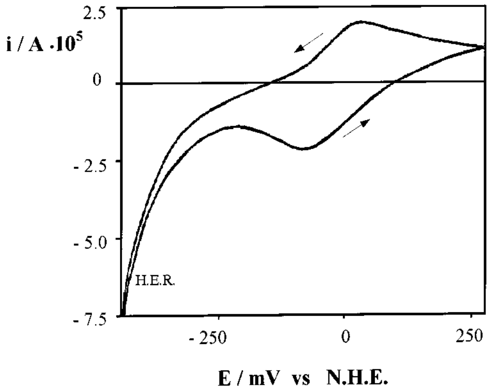

Figure 3. Cyclic voltammogram of $[W_4S_4(H_2O)_{12}]^{6+}$ in 2 M Hpts.

Table 3. Summary of CV Data (Potentials in mV Converted vs NHE; 25 °C) for $[Mo_{4-x}W_xS_4(H_2O)_{12}]^{n+}$ Complexes in 2 M Hpts

complex	$E°'_1$ (6+/5+ couple)	$E°'_2$ (5+/4+ couple)	ref
$[Mo_4S_4(H_2O)_{12}]^{n+}$	860	210	20
$[Mo_3WS_4(H_2O)_{12}]^{n+}$	673	6	15
$[Mo_2W_2S_4(H_2O)_{12}]^{n+}$	422	−248	15
$[MoW_3S_4(H_2O)_{12}]^{n+}$	258	−395	15
$[W_4S_4(H_2O)_{12}]^{n+}$	35	−627[a]	this work

[a] Predicted value.[15]

value of 39 mV.[15] Reduction potentials (vs NHE) for the 6+/5+ ($E°'_1$) and 5+/4+ ($E°'_2$) couples of the $[Mo_{4-x}W_xS_4(H_2O)_{12}]^{n+}$ cuboidal clusters are summarized in Table 3. These show a systematic trend to more negative values as more W atoms are incorporated. The shifts reflect the greater difficulty in generating the lower oxidation states of W. No evidence was obtained in this work for the formation of $[W_4S_4(H_2O)_{12}]^{4+}$. By extrapolating the data for Mo/W mixed clusters, the reduction potential for $[W_4S_4(H_2O)_{12}]^{5+/4+}$ is estimated to be −627 mV, which is 837 mV more negative than that for the $[Mo_4S_4\ (H_2O)_{12}]^{5+/4+}$ couple.[15,20]

Preparation of $[W_4S_4(H_2O)_{12}]^{5+}$. Controlled potential electrolysis of brown-red $[W_4S_4(H_2O)_{12}]^{6+}$ in 4 M Hpts gives the red-brown 5+ analogue as in (3). The lower energy peaks for $[W_4S_4(H_2O)_{12}]^{n+}$ (n = 5, 6) in the visible are dependent on the oxidation state; see Figure 2. Wavelength (λ/nm) shifts observed on reduction of $[W_4S_4(H_2O)_{12}]^{6+}$ and $[W_4S_4(H_2O)_{12}]^{5+}$, 453 → 493 and 766 → 830, indicate red shifts with the decreasing oxidation state. A solution of $[W_4S_4(H_2O)_{12}]^{5+}$ in 2 M Hpts undergoes 80% oxidation to $[W_4S_4(H_2O)_{12}]^{6+}$ in air after 7 h with some shaking. In contrast to $[Mo_4S_4(H_2O)_{12}]^{6+}$,[4a] the W analogue can be stored (under N_2, 4 °C) for several months without appreciable decay.

Table 4. Peak Positions λ/nm (ϵ/M^{-1} cm^{-1} per Cube) in the UV/vis/NIR Spectra of $[M_4S_4(H_2O)_{12}]^{5+}$, M = Mo, W Cuboidal Clusters in 2.0 M Hpts

	color	λ/nm (ϵ/M^{-1} cm^{-1})	ref
$[W_4S_4(H2O)12]^{5+\,a,b}$	red-brown	493 (~230), 830 (~90)	this work
$[MoW_3(H_2O)_{12}]^{5+}$	orange-brown	522 (660), 850 (200)	15
$[Mo_2W_2(H_2O)_{12}]^{5+}$	pink-gray	560 (534), 1020 (168)	15
$[Mo_3W(H_2O)_{12}]$	green (-blue)	611 (499), 1038 (188)	15
$[Mo_4S_4(H_2O)_{12}]^{5+}$	green	635 (435), 1100 (122)	15

[a] In 4.0 M Hpts. [b] Additional shoulders at ~570 and 770 nm.

Conclusions

To summarize, W_4S_4 cuboidal clusters are more difficult to access than those of Mo_4S_4. In this work the preparation and properties of $[W_4S_4(H_2O)_{12}]^{6+}$ and $[W_4S_4(H_2O)_{12}]^{5+}$ are described. The preparation of $[W_4S_4(H_2O)_{12}]^{5+}$ completes the series of 5+ W/Mo cuboidal clusters alongside $[MoW_3S_4(H_2O)_{12}]^{5+}$, $[Mo_2W_2S_4(H_2O)_{12}]^{5+}$, $[Mo_3WS_4(H_2O)_{12}]^{5+}$, and $[Mo_4S_4(H_2O)_{12}]^{5+}$.[15,20] The increase in reducing properties with W content is illustrated by the linear trend in reduction potentials $E°'_1$, which give an 825 mV variation; see Table 3.[15] An estimate of the 5+/4+ reduction potential $E°'_2$ of −627 mV[15] accounts for the difficulty in preparing the $[W_4S_4(H_2O)_{12}]^{4+}$ product. The increase in reducing properties is also illustrated by the shift in LMCT UV−vis−NIR peak positions to higher energies with increasing number of W atoms; see Table 4.

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Supporting Information Available: X-ray crystallographic files for **1** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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