

*Electronic Supplementary Information for:*

**Semi-vacant Wells-Dawson anions. Synthesis of tri-tungsten-vacant derivatives and crystallographic studies of  $[\alpha\beta\alpha\text{-}(\text{Cu}^{\text{II}}\text{OH}_2)_2(\text{Cu}^{\text{II}})_2(\text{AsW}_{15}(\text{OH}_2)_3\text{-}(\text{OH})\text{O}_{52})_2]^{12-}$**

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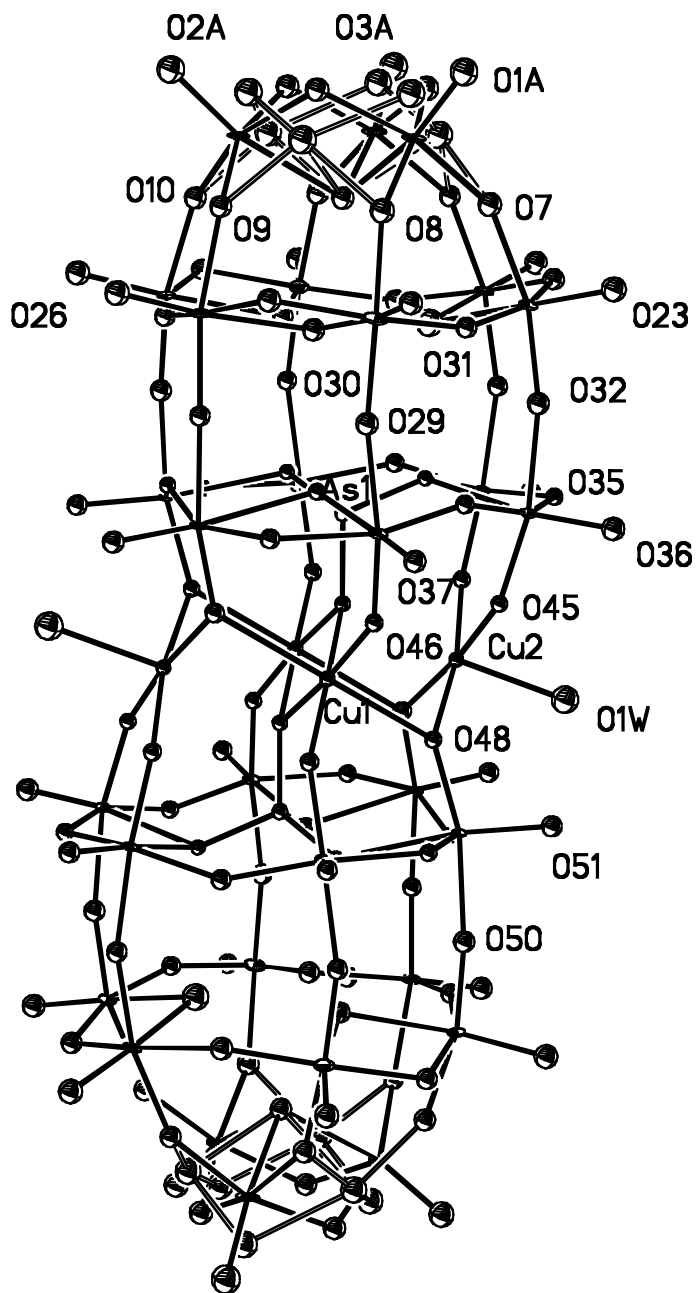
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**Figure S1.** Thermal ellipsoid plot of **2** (50% probability surfaces). The slight disorder (4%) in the  $\text{W}_3\text{O}_{13}$  "cap" units is shown (each cap is 96%  $\alpha$ -isomer and 4%  $\beta$ -isomer).

**Table S1.** W(VI)-based reduction potentials for **1**, **1Zn**, and **1Cu**.

Figure S1.



**Table S1.** W(VI)-based reduction potentials for **1**, **1Zn**, and **1Cu**.<sup>a</sup>

complex	$-E_{pc1}$ (V)	$-E_{pc2}$ (V)	$-E_{pc3}$ (V)
<b>1</b>	0.528	0.644	0.876
<b>1Zn</b>	0.576	0.736	0.924
<b>1Cu</b>	0.588 <sup>b</sup>	0.648	0.820

<sup>a</sup>Conditions: POM concentration:  $2 \times 10^{-4}$  M in 0.4 M  $\text{CH}_3\text{COOLi}/\text{CH}_3\text{COOH}$  (pH 5) solution; scan rate:  $10 \text{ mV s}^{-1}$ ; working electrode: glassy carbon; reference electrode: SCE; <sup>b</sup>This wave appears as a shoulder following a copper deposition wave with a cathodic peak potential  $E_{pc} = -0.320$  V and a characteristic desorptive oxidation peak potential located at  $E_{pa} = -0.10$  V.