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### A convenient solution method for conversion of a W(II) octahedral cluster to W(IV) triangular cluster: synthesis and characterization of $\text{Cs}_3\text{Na}_2[\text{W}_3\text{Se}_4(\text{CN})_9] \cdot 0.5\text{Et}_4\text{NBr} \cdot 5\text{H}_2\text{O}$

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## A convenient solution method for conversion of a W(II) octahedral cluster to W(IV) triangular cluster: synthesis and characterization of $\text{Cs}_3\text{Na}_2[\text{W}_3\text{Se}_4(\text{CN})_9] \cdot 0.5\text{Et}_4\text{NBr} \cdot 5\text{H}_2\text{O}$

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A new solution method for the preparation of a triangular W(IV) cluster starting from an octahedral W(II) cluster is reported. The product  $\text{Cs}_3\text{Na}_2[\text{W}_3\text{Se}_4(\text{CN})_9] \cdot 0.5\text{Et}_4\text{NBr} \cdot 5\text{H}_2\text{O}$  (**1**) has been synthesized by boiling  $\text{W}_6\text{Br}_{12}$  in an aqueous solution of  $\text{Na}_2\text{Se}_x$ , followed by filtering off the dark solid which was then heated with an aqueous solution of NaCN and crystallized by the addition of CsBr and  $\text{Et}_4\text{NBr}$ . The compound was characterized by IR, UV-Vis, elemental analysis, and single crystal X-ray diffraction. The described W(II)-to-W(IV) conversion in solution is reported for the first time.

*Keywords:* Tungsten; Triangular clusters; Chalcocyanides; Crystal structure

### 1. Introduction

Most typical of Mo and W, cluster complexes containing the core unit  $\text{M}_3\text{Q}_4$  ( $\text{Q} = \text{S}, \text{Se}, \text{Te}$ ) continue to attract significant attention since the discovery of  $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$  and  $[\text{W}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$  [1, 2]. This incomplete cuboidal cluster core, whose full formula is  $\text{M}_3(\mu_3\text{-Q})(\mu_2\text{-Q})_3$ , consists of a triangular metal cluster  $\text{M}_3^{\text{IV}}$  coordinated by four chalcogenide bridging ligands, one  $\mu_3$  and three  $\mu_2$ . Each metal center can be coordinated up to three  $\text{H}_2\text{O}$ ,  $\text{Hal}^-$ ,  $\text{CN}^-$ , or  $\text{NCS}^-$  ligands as well as various organic groups and molecules (including chelating), and their combinations give rise to numerous compounds constituting a growing family of  $\text{M}_3\text{Q}_4$  derivatives [3]. Interest in these compounds (along with their heterometallic cubane derivatives) arises from their properties as promising non-linear optical materials [4–6], attractive candidates for the development of X-ray contrast agents [7] and biological activity in different enzymes. The  $\text{W}_3\text{S}_4$  derivatives are significantly less toxic than water-soluble tungsten heteropolyanions.

Among  $\text{M}_3\text{Q}_4$  derivatives, cyanide species  $[\text{M}_3\text{Q}_4(\text{CN})_9]^{5-}$  have a special place because of their relatively easy synthetic availability. The most direct methods for their preparation are based on treating of polymeric materials  $\{\text{M}_3\text{Q}_7\text{Br}_4\}_x$  with KCN in an

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aqueous solution (for M = Mo, W, Q = Se) [8] or with KCNSe in the melt at 180°C (for M = W, Q = S, Se) [9]. In the first case, the  $[M_3Q_4(CN)_9]^{5-}$  ions are usually isolated as  $Cs_5[M_3Se_4(CN)_9] \cdot CsCl \cdot 4H_2O$  salts (with yields up to ~45%), and in the latter case as  $K_5[W_3Q_4(CN)_9]$  salts (with modest yields of ~20%). The starting  $\{M_3Q_7Br_4\}_x$  polymers can be obtained from the combination of the elements [10] or molybdenum, from its halogenides and chalcogens in corresponding ratios at 400°C [11, 12]. No approach has been reported for trinuclear  $M_3Q_4$  clusters starting from other nuclearity tungsten or molybdenum cluster compounds.

In this article we report a new solution method for good-yield conversion of octahedral W(II) cluster to triangular W(IV) cluster with the  $[W_3Se_4(CN)_9]^{5-}$  resulting anion isolated as  $Cs_3Na_2[W_3Se_4(CN)_9] \cdot 0.5Et_4NBr \cdot 5H_2O$  (**1**).

## 2. Experimental

### 2.1. Materials and instruments

The starting polymeric  $W_6Br_{12}$  was prepared as described [13]. All other reagents were used as purchased without purification. Elemental analysis was carried out with a Euro Vector EA 3000 CHNS-analyzer. Energy dispersion spectroscopy (EDS) was performed on a scanning electron microscope (SEM) JEOL 6400. Infrared spectrum in KBr pellet was recorded using a Bruker Scimitar FTS 2000 spectrometer from 4000 to 375  $cm^{-1}$ . UV-Vis spectrum from 200 to 1100 nm was recorded on an Ultrospec 3300 pro spectrometer.

### 2.2. Synthesis and characterization

$W_6Br_{12}$  (0.40 g, 0.194 mmol) was boiled for 3 h in an aqueous solution of  $Na_2Se_x$  (generated *in situ* by the reaction of Se (0.612 g, 7.75 mmol) and  $NaBH_4$  (0.585 g, 15.5 mmol) in 25 mL of water [14]). The resulting dark solid formed during the reaction was filtered off and then heated with NaCN (0.10 g, 2.0 mmol) in 30 mL of water to dissolve the solid to a dark green solution. After filtration, CsBr (0.42 g, 2.0 mmol) and  $Et_4NBr$  (0.42 g, 2.0 mmol) were added sequentially to the solution ( $Et_4NBr$  was added after several unsuccessful attempts to crystallize pure Cs/Na salt, but its role appeared to be crucial – introduced into the structure, it gave large enough, quality crystals of **1**). Slow evaporation in air gave dark green crystals of **1**, which were collected and dried on filter paper. Yield 0.30 g, 45%. Anal. Calcd for  $C_{13}H_{20}Br_{0.5}Cs_3N_{9.5}Na_2O_5Se_4W_3$  (%): C, 9.0; H, 1.2; N, 7.6. Found (%): C, 8.7; H, 1.2; N, 7.3%. FT-IR ( $cm^{-1}$ )  $\nu_{CN}$ : 2118(s), 2069(sh). EDS shows the Cs:Na:W ratio: 3.2:1.7:3. UV-Vis spectrum in water;  $\lambda$  (nm) ( $\epsilon$ (mol L<sup>-1</sup>)<sup>-1</sup> cm<sup>-1</sup>): 321 (9600), 386 (6800), 621 (890).

### 2.3. Crystal structure determination

A needle-shaped crystal of **1** was selected under a microscope and then mounted to the tip of the thin glass fiber with an epoxy resin. X-ray intensity data were collected on a Bruker X8 Apex CCD diffractometer at 150(2) K using graphite monochromated

Table 1. Crystal data, data collection and refinement parameters for **1**.

Chemical formula	Cs <sub>3</sub> Na <sub>2</sub> [W <sub>3</sub> Se <sub>4</sub> (CN) <sub>6</sub> ] · 0.5Et <sub>4</sub> NBr · 5H <sub>2</sub> O
Molecular formula	C <sub>13</sub> H <sub>20</sub> Br <sub>0.5</sub> Cs <sub>3</sub> N <sub>9.5</sub> Na <sub>2</sub> O <sub>5</sub> Se <sub>4</sub> W <sub>3</sub>
Formula weight	1741.44
Temperature (K)	150(2)
Crystal size (mm <sup>3</sup> )	0.14 × 0.06 × 0.04
Crystal system	Monoclinic
Space group	C2/c
Z	8
Unit cell dimensions (Å, °)	
<i>a</i>	19.1917(6)
<i>b</i>	26.7091(7)
<i>c</i>	16.1270(8)
$\beta$	122.3500(10)
Volume (Å <sup>3</sup> ), Z	6983.6(4), 8
Calculated density (g cm <sup>-3</sup> )	3.313
Absorption coefficient (mm <sup>-1</sup> )	17.747
$\theta$ range for data collection (°)	1.54–30.09
Reflections collected	31,889
Unique reflections	10,235 ( $R_{\text{int}} = 0.048$ )
Observed reflections	7967 [ $I > 2\sigma(I)$ ]
Parameters refined	400
Final <i>R</i> indices [ $F^2 > 2\sigma(F^2)$ ]	$R_1 = 0.032$ , $wR_2 = 0.061$
$R(F^2)$ (all data)	$R_1 = 0.051$ , $wR_2 = 0.071$
Goodness-of-fit on $F^2$	1.025
Largest difference peak and hole (e Å <sup>-3</sup> )	2.30 and -2.78

Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The standard technique ( $\varphi$ -scan of narrow frames) was used. Data reduction and multi-scan absorption were carried out using SADABS [15]. The structure was solved by direct methods and refined by full-matrix least-squares on  $F^2$  using the SHELXTL software package [15]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of Et<sub>4</sub>N<sup>+</sup> were placed in geometrically idealized positions and refined as riding with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}_{\text{methylene}})$  or  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$ ; hydrogen atoms of H<sub>2</sub>O were not located. The residual electron density was between -2.78 and 2.30 e Å<sup>-3</sup>. Crystallographic data together with selected refinement details are given in table 1.

### 3. Results and discussion

#### 3.1. Synthesis

The method described gives the triangular W<sub>3</sub>Se<sub>4</sub><sup>4+</sup> cluster core-based compounds starting from W<sub>6</sub>Br<sub>12</sub>. The remarkable conversion arises from the W(II) cluster core W<sub>6</sub>Br<sub>8</sub><sup>4+</sup> readily transforming into the W(IV) core W<sub>3</sub>Se<sub>4</sub><sup>4+</sup>. Although the substitution of  $\mu_3$ -halide by  $\mu_3$ -chalcogenide is well known in cluster chemistry and, in our case, was expected to produce a W<sub>6</sub>Se<sub>*x*</sub>Br<sub>*8-x*</sub><sup>4-x</sup> octahedral core, the transition from W<sub>6</sub> octahedron to W<sub>3</sub> triangle has been reported for the first time. The process requires the formal oxidation of W(II) to W(IV) that is quite surprising, taking into account that the reaction medium saturated with polyselenide ions should possess the reducing activity. Considering the system to be free of oxidizing agents other than oxygen dissolved in water, the latter may be supposed as the most likely oxidant in the reaction.

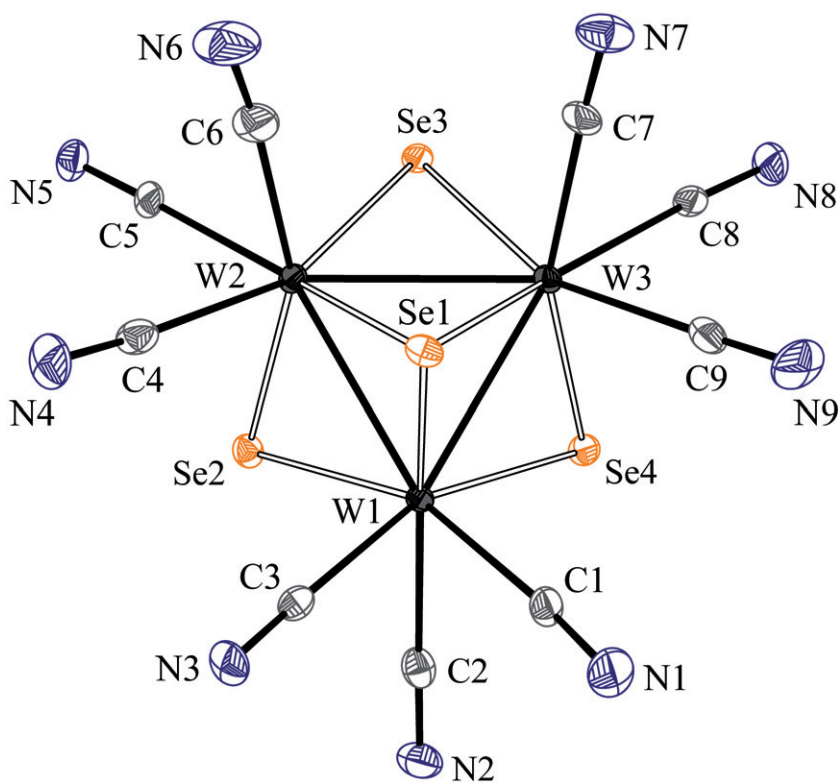


Figure 1. Displacement ellipsoid plot (at the 50% probability level) for  $[W_3Se_4(CN)_9]^{5-}$  with the atom labeling scheme.

It is reasonable to assume that, similar to peroxides, solutions of polysulfides (polyselenides) may have both reducing and oxidizing properties (indeed used in some organic syntheses). In our case, we can anticipate the half reaction:  $Se_x^{2-} + 2(x-1)e^- \rightarrow xSe^{2-}$  that might explain the oxidation of W(II) to W(IV). However, at the present stage we avoid speculations on the detailed mechanism as the question of the structure and composition of the amorphous intermediate (i.e., the “dark solid” which was heated with NaCN) is still open.

Summarizing, the behavior of molybdenum clusters  $Mo_6Hal_{12}$  (Hal = Cl, Br) in reactions with alkali metal polychalcogenides is completely different. According to previous studies, reactions with excess of  $S_x^{2-}$  led to the formation of the tetrahedral molybdenum polysulfide  $Cs_6[Mo_4S_{23.6}]$  [16], while reactions with  $Se_x^{2-}$  do not affect cluster core nuclearity and lead only to the replacement of  $\mu_3$ -ligands, affording the  $Mo_6Se_8$  core [17]. The different behavior of  $Mo_6$  and  $W_6$  species induced us to examine it in more detail. Compared to  $Mo_6$  complexes,  $W_6$  analogues show lower stability; even the synthetic approaches to these two cluster classes are often different. Unlike the  $Mo_6$  chalcogenides,  $W_6$  analogues cannot be prepared at high temperatures. In spite of this, there are a few examples when the hexanuclear tungsten derivatives were reported to react without changing of the core nuclearity. For instance,  $W_6Q_8$  (Q = S, Se, Te) complexes with various organic terminal ligands were synthesized starting from  $W_6S_8(PEt_3)_6$  and  $W_6S_8(4-tBuPy)_6$  [18] or directly from  $W_6Cl_{12}$  using reactions with

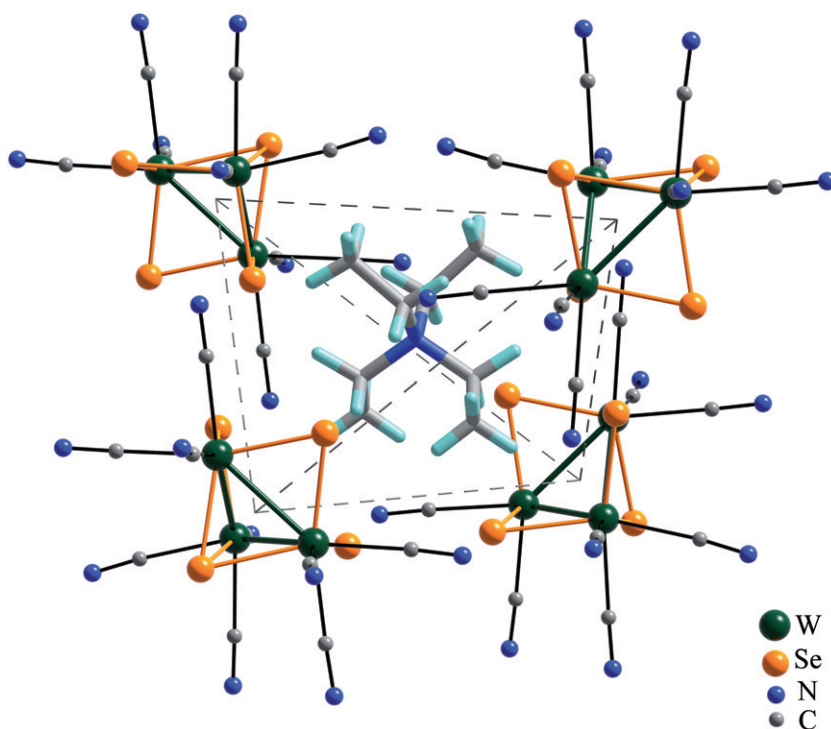


Figure 2. Fragment of the structure of **1** showing a distorted tetrahedral arrangement (indicated by dashed lines) of  $[\text{W}_3\text{Se}_4(\text{CN})_9]^{5-}$  surrounding the  $\text{Et}_4\text{N}^+$ . All other ions and water molecules have been omitted for clarity.

$\text{NaSH}$  or  $\text{Na}_2\text{Q}$  ( $\text{Q} = \text{Se}, \text{Te}$ ) [19, 20]. In all cases, organic solvents and dry atmosphere were needed. In this work, we used an aqueous solution and the similar reaction with polyselenide yielded the triangular  $\text{W}_3\text{Se}_4$ . This may implicitly argue for a role of water dissolved oxygen in the process.

### 3.2. Crystal structure

According to the single crystal X-ray structure determination, **1** contains one crystallographically independent  $[\text{W}_3\text{Se}_4(\text{CN})_9]^{5-}$  with all atoms occupying general positions (figure 1).  $\text{W}-\text{W}$  bond lengths are 2.8201(3), 2.8205(4), and 2.8275(4) Å (av. 2.823(4) Å).  $\text{W}-\mu_2\text{-Se}$ ,  $\text{W}-\mu_3\text{-Se}$ ,  $\text{W}-\text{C}$ , and  $\text{C}-\text{N}$  bond lengths fall into the ranges 2.4374(6)–2.4589(7) (av. 2.448(8) Å), 2.4915(7)–2.4945(7) (av. 2.493(2) Å), 2.151(7)–2.205(7) (av. 2.18(2) Å), and 1.131(9)–1.152(8) Å (av. 1.142(9) Å), respectively. Thus, the overall geometry of the anion is in agreement with that reported previously for  $\text{Cs}_5[\text{W}_3\text{Se}_4(\text{CN})_9] \cdot \text{CsCl} \cdot 4\text{H}_2\text{O}$  [8]. However, the crystal structure of **1** is largely driven by the presence of hydrophobic  $\text{Et}_4\text{N}^+$  making the packing of the  $[\text{W}_3\text{Se}_4(\text{CN})_9]^{5-}$  cluster anions rather different and less dense than  $\text{Cs}_5[\text{W}_3\text{Se}_4(\text{CN})_9] \cdot \text{CsCl} \cdot 4\text{H}_2\text{O}$ . Particularly, in the case of cesium salt, a weak dimerization of the anions through  $\text{Se} \cdots \text{Se}$  interactions of 3.4 and 3.7 Å (that are shorter than the intramolecular  $\text{Se} \cdots \text{Se}$

distances) can be supposed, while in **1** the shortest Se···Se separation of 3.8 Å is close to the sum of van der Waals radii, indicating almost no chalcogenide bonding. In the crystal, each Et<sub>4</sub>N<sup>+</sup> lies on a two-fold axis and is trapped in the distorted tetrahedral “cage” formed by four surrounding [W<sub>3</sub>Se<sub>4</sub>(CN)<sub>9</sub>]<sup>5-</sup> anions (figure 2). The anions themselves are interconnected through extensive coordination of their Se atoms and CN groups to the alkali metal cations.

#### 4. Conclusions

A new solution method for the preparation of [W<sub>3</sub>Se<sub>4</sub>(CN)<sub>9</sub>]<sup>5-</sup>-containing compounds has been reported. The product was isolated as Cs<sub>3</sub>Na<sub>2</sub>[W<sub>3</sub>Se<sub>4</sub>(CN)<sub>9</sub>]·0.5Et<sub>4</sub>NBr·5H<sub>2</sub>O and fully characterized. Unlike known synthetic approaches, the method uses the W<sub>6</sub>Br<sub>12</sub> octahedral polymer as a starting material and gives comparable or higher yield of the target product. The process occurs through the oxidation of W(II) to W(IV) under the possible action of oxygen dissolved in water, substitution of μ<sub>3</sub>- and terminal ligands, and crystallization of the triangular cluster complex. Results obtained from this study provide an alternate way to W<sub>3</sub>Se<sub>4</sub> core compounds and may increase the general knowledge on the chemistry of tungsten.

#### Supplementary material

CCDC 873773 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)

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