

Selenium-capped trimolybdenum and tritungsten carbonyl clusters $[\text{Se}_2\text{M}_3(\text{CO})_{10}]^{2-}$ (M = Mo, W)

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Abstract

A facile synthesis of the novel selenium-capped trimolybdenum and tritungsten ring carbonyl clusters $[\text{Se}_2\text{M}_3(\text{CO})_{10}]^{2-}$ (M = Mo, **1**; W, **4**) have been achieved. The selenium-capped trimolybdenum cluster compound $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{Mo}_3(\text{CO})_{10}]$ ($[\text{Et}_4\text{N}]_2[\mathbf{1}]$) can be obtained from the reaction of the trichromium cluster compound $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{Cr}_3(\text{CO})_{10}]$ with 4 equiv. of $\text{Mo}(\text{CO})_6$ in refluxing acetone. On the other hand, when $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{Cr}_3(\text{CO})_{10}]$ reacted with 4 equiv. of $\text{W}(\text{CO})_6$ in refluxing acetone, the planar cluster compound $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{W}_4(\text{CO})_{18}]$ ($[\text{Et}_4\text{N}]_2[\mathbf{3}]$) was isolated, which could further transform to the tritungsten cluster compound $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{W}_3(\text{CO})_{10}]$ ($[\text{Et}_4\text{N}]_2[\mathbf{4}]$) in good yield. Alternatively, clusters **1** and **4** could be formed from the reactions of the monosubstituted products $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{Cr}_2\text{M}(\text{CO})_{10}]$ (M = Mo; W, $[\text{Et}_4\text{N}]_2[\mathbf{2}]$) with 3 equiv. of $\text{M}(\text{CO})_6$ in acetone, respectively. Complexes **1–4** are fully characterized by IR, ^{77}Se NMR spectroscopy, and single-crystal X-ray analysis. Clusters **1**, **2**, and **4** are isostructural and each display a trigonal bipyramidal structure with a homometallic M_3 ring (M = Mo, **1**; W, **4**) or a heterometallic Cr_2W ring that is further capped above and below by μ_3 -Se atoms. Further, the intermediate planar complex **3** exhibits a Se_2W_2 square with each Se atom externally coordinated to one $\text{W}(\text{CO})_5$ group. This paper describes a systematic route to a series of selenium-capped trimetallic carbonyl clusters and the formation and the structural features of the resultant clusters are discussed.

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Keywords: Selenium; Molybdenum; Tungsten; Carbonyl; Cluster

1. Introduction

Main group-containing transition metal clusters have attracted much attention due to their versatile structural features and reactivities as well as potential usages in both material and nanotechnology [1,2]. Contrary to the large number of chalcogen-bridged iron carbonyl clusters, chalcogen-stabilized group 6 metal carbonyl clusters were much fewer mainly due to the lack of rational synthetic routes [1–6]. Similar to the paucity of trichromium carbonyl clusters, the homonuclear molybdenum or tungsten carbonyl clusters with the Mo_3 or

W_3 ring are also limited, especially for those stabilized by heavier main group elements [4a,7,8]. Although the Se-capped trichromium carbonyl *closo*-cluster $[\text{Se}_2\text{Cr}_3(\text{CO})_{10}]^{2-}$ was obtained from the direct reaction of SeO_2 with $\text{Cr}(\text{CO})_6$ in basic methanol solution [5], the trimolybdenum and tritungsten congeners have never been achieved by similar methodologies. In this study, we will describe the facile metal–metal exchange reactions for the synthesis of the first selenium-capped trimolybdenum and tritungsten carbonyl clusters, in which an intermediate species is isolated to provide some valuable mechanistic information. In addition, the formation and structural features of the resultant homonuclear or the related heteronuclear clusters are discussed in terms of the effect of group 6 metals.

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2. Results and discussion

2.1. Synthesis of $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{Mo}_3(\text{CO})_{10}]$ ($[\text{Et}_4\text{N}]_2[\mathbf{1}]$) and the related reactions

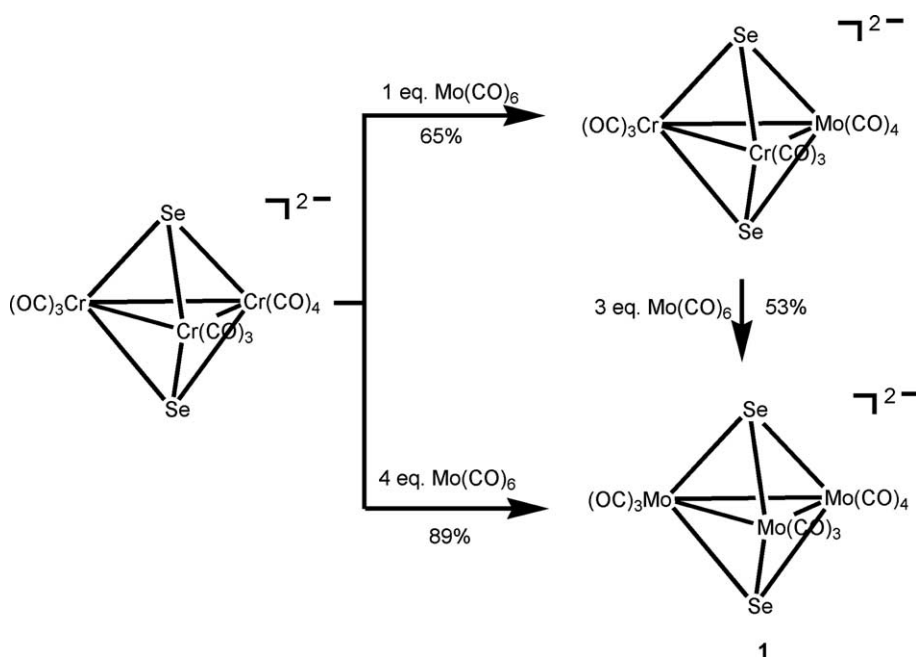
Although several monosulfur-bridged homonuclear group 6 ring carbonyl clusters were reported [4], similar types of clusters capped by the heavier selenium atom remained unknown before our study. We have recently communicated the first example of the selenium-capped trichromium carbonyl cluster $[\text{Se}_2\text{Cr}_3(\text{CO})_{10}]^{2-}$ from the treatment of SeO_2 and $\text{Cr}(\text{CO})_6$ in NaOH/MeOH solution [5]. The methodology was straightforward, however, similar strategies to the trimolybdenum and the tritungsten clusters were never successful. The trichromium cluster $[\text{Se}_2\text{Cr}_3(\text{CO})_{10}]^{2-}$ was shown to react slowly with $\text{Mo}(\text{CO})_6$ in acetone to give the monomolybdenum-substituted Cr–Mo cluster $[\text{Se}_2\text{Cr}_2\text{Mo}(\text{CO})_{10}]^{2-}$ [5]. To rationalize the formation of the Mo-substituted derivatives, we have examined the reactions of $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{Cr}_3(\text{CO})_{10}]$ with $\text{Mo}(\text{CO})_6$ in various ratios. In addition to the expected monomolybdenum-substituted cluster $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{Cr}_2\text{Mo}(\text{CO})_{10}]$, the new trimolybdenum-substituted Mo_3 cluster $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{Mo}_3(\text{CO})_{10}]$ ($[\text{Et}_4\text{N}]_2[\mathbf{1}]$) can be obtained, and the related cluster transformation in this system is also established (Scheme 1).

By the use of $[\text{Se}_2\text{Cr}_3(\text{CO})_{10}]^{2-}$ with 1 equiv. of $\text{Mo}(\text{CO})_6$ in acetone at refluxing temperature, the Mo-substituted cluster $[\text{Se}_2\text{Cr}_2\text{Mo}(\text{CO})_{10}]^{2-}$ was easily produced. $[\text{Se}_2\text{Cr}_2\text{Mo}(\text{CO})_{10}]^{2-}$ is structurally similar to $[\text{Se}_2\text{Cr}_3(\text{CO})_{10}]^{2-}$ with the exception that $\text{Cr}(\text{CO})_4$ is replaced by $\text{Mo}(\text{CO})_4$ [5]. The ease of the replacement of $\text{Cr}(\text{CO})_4$ rather than $\text{Cr}(\text{CO})_3$ with the incoming $\text{Mo}(\text{CO})_x$ group is ascribed to the weaker Se– $\text{Cr}(\text{CO})_4$ vs. Se– $\text{Cr}(\text{CO})_3$ bond

(Table 1). The ^{77}Se NMR spectrum of $[\text{Se}_2\text{Cr}_2\text{Mo}(\text{CO})_{10}]^{2-}$ was further taken to give one absorption at -108.6 ppm, consistent with its solid-state structure.

It was noted that similar reaction of $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{Cr}_3(\text{CO})_{10}]$ with 2 equiv. of $\text{Mo}(\text{CO})_6$ only led to a mixture of products, which was difficult to separate. The mixture was then subjected to ^{77}Se NMR spectroscopy to contain the monosubstituted product $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{Cr}_2\text{Mo}(\text{CO})_{10}]$ ($\delta -108.6$), an intermediate species ($\delta -201.9$), and the trisubstituted compound $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{Mo}_3(\text{CO})_{10}]$ ($[\text{Et}_4\text{N}]_2[\mathbf{1}]$) ($\delta 642.6$). Attempted isolation of the intermediate species failed due to its reactive nature to form $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{Cr}_2\text{Mo}(\text{CO})_{10}]$ and $[\text{Et}_4\text{N}]_2[\mathbf{1}]$ in solution. The subsequent substitution of $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{Cr}_2\text{Mo}(\text{CO})_{10}]$ with 1 equiv. of $\text{Mo}(\text{CO})_6$ could not solve the problem and gave similar mixture products. This intermediate species is proposed to be the dimolybdenum-substituted product $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{CrMo}_2(\text{CO})_{10}]$ based on its IR pattern similar to those in this series. The instability of $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{CrMo}_2(\text{CO})_{10}]$ is surprising and probably due to the poor metal–metal bonding in the ring.

When $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{Cr}_3(\text{CO})_{10}]$ was treated with 4 equiv. of $\text{Mo}(\text{CO})_6$ in acetone at elevated temperatures, the trimolybdenum compound $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{Mo}_3(\text{CO})_{10}]$ ($[\text{Et}_4\text{N}]_2[\mathbf{1}]$) could be formed cleanly. $[\text{Et}_4\text{N}]_2[\mathbf{1}]$ was fully characterized by spectroscopic methods and single-crystal X-ray analysis. X-ray analysis reveals that anion $\mathbf{1}$ exhibits a Se_2Mo_3 trigonal bipyramidal core geometry with a highly strained Mo_3 ring that is stabilized by carbonyl ligands and two selenium atoms. The ^{77}Se NMR spectrum of $[\text{Et}_4\text{N}]_2[\mathbf{1}]$ was taken to give one absorption at 642.6 ppm. Alternatively, $[\text{Et}_4\text{N}]_2[\mathbf{1}]$ could also be obtained from the treatment of the Mo-substituted cluster $[\text{Se}_2\text{Cr}_2\text{Mo}(\text{CO})_{10}]^{2-}$ with 3 equiv. of $\text{Mo}(\text{CO})_6$.



Scheme 1.

Table 1
Selected bond distances (Å) for $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{M}_3(\text{CO})_{10}]$ ($\text{M} = \text{group 6 metals}$)

Complex	E–M ^a	E–M ^b	M ^a –M ^a	M ^a –M ^b	Ref.
$[\text{Et}_4\text{N}]_2[\text{Se}_2\text{Cr}_3(\text{CO})_{10}]$	2.387(1)	2.575(2)	2.926(3)	2.849(2)	[5]
$[\text{Et}_4\text{N}]_2[\text{Se}_2\text{Mo}_3(\text{CO})_{10}]$ ($[\text{Et}_4\text{N}]_2[\mathbf{1}]$)	2.480(1)	2.716(1)	3.020(2)	3.014(1)	This work
$[\text{Et}_4\text{N}]_2[\text{Se}_2\text{W}_3(\text{CO})_{10}]$ ($[\text{Et}_4\text{N}]_2[\mathbf{4}]$)	2.533(1)	2.725(2)	3.072(1)	3.053(1)	This work
$[\text{Et}_4\text{N}]_2[\text{Se}_2\text{Cr}_2\text{Mo}(\text{CO})_{10}]$	2.416(4)	2.674(1)	2.947(2)	2.951(1)	[5]
$[\text{Et}_4\text{N}]_2[\text{Se}_2\text{Cr}_2\text{W}(\text{CO})_{10}]$ ($[\text{Et}_4\text{N}]_2[\mathbf{2}]$)	2.418(2)	2.676(2)	2.955(4)	2.971(2)	This work

^a The metal bonded to three carbonyls.

^b The metal bonded to four carbonyls.

2.2. Synthesis of $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{W}_3(\text{CO})_{10}]$ ($[\text{Et}_4\text{N}]_2[\mathbf{4}]$) and the related reactions

The substitution of $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{Cr}_3(\text{CO})_{10}]$ with $\text{W}(\text{CO})_6$ was also carried out due to the differing reactivity of $\text{W}(\text{CO})_6$ compared to $\text{Mo}(\text{CO})_6$ (Scheme 2).

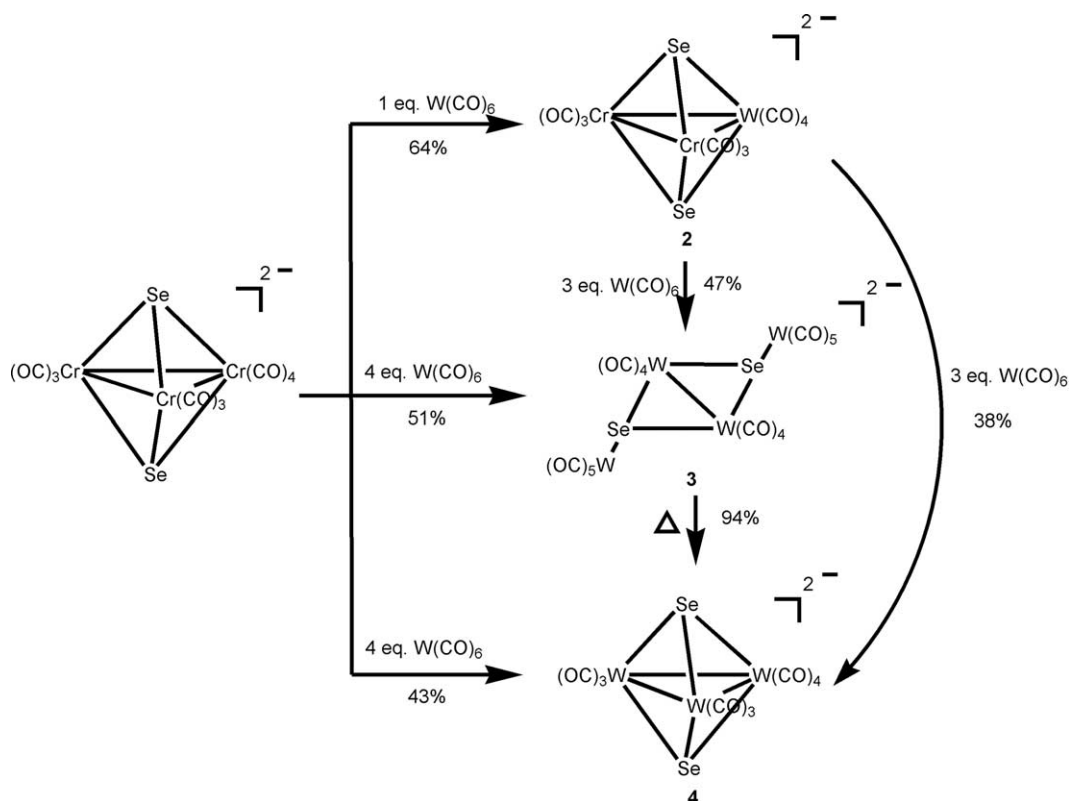
Similar to that in the Cr–Mo system, the reaction of $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{Cr}_3(\text{CO})_{10}]$ and 1 equiv. of $\text{W}(\text{CO})_6$ in refluxing acetone formed the monotungsten-substituted Cr–W compound $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{Cr}_2\text{W}(\text{CO})_{10}]$ ($[\text{Et}_4\text{N}]_2[\mathbf{2}]$). This result is again in agreement with the weaker bonding of Se–Cr(CO)₄ vs. Se–Cr(CO)₃. It was also found that the subsequent substitution $[\text{Et}_4\text{N}]_2[\mathbf{2}]$ with 1 equiv. of $\text{W}(\text{CO})_6$ failed to produce the ditungsten-substituted product due to its reactive nature.

In contrast to the Cr–Mo system, when $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{Cr}_3(\text{CO})_{10}]$ was treated with 4 equiv. of $\text{W}(\text{CO})_6$ in acetone at refluxing temperature, an intermediate species $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{W}_4(\text{CO})_{18}]$ ($[\text{Et}_4\text{N}]_2[\mathbf{3}]$) was isolated as the major

product. X-ray analysis shows that complex **3** exhibits a Se_2W_2 parallelogram with each Se atom externally coordinated with one $\text{W}(\text{CO})_5$ group. Only after the prolonged refluxing could this reaction lead to the formation of the W_3 cluster compound $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{W}_3(\text{CO})_{10}]$ ($[\text{Et}_4\text{N}]_2[\mathbf{4}]$), which resulted from ring closure processes of the *arachno*-complex **3** by the loss of the external $\text{W}(\text{CO})_5$ group and carbonyls. An independent experiment was also carried out to confirm the conversion of complex **3** to cluster **4** in acetone. Besides, the monotungsten-substituted cluster **2** was found to react with 3 equiv. of $\text{W}(\text{CO})_6$ to give the planar intermediate complex **3** and subsequently to form the W_3 cluster **4**.

2.3. Formation of $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{M}_3(\text{CO})_{10}]$ ($\text{M} = \text{Mo}$, $[\text{Et}_4\text{N}]_2[\mathbf{1}]$; W , $[\text{Et}_4\text{N}]_2[\mathbf{4}]$)

Metal–metal exchange reactions are well documented in many sulfur-capped metal cluster complexes, and some



Scheme 2.

intermediates are isolated to reveal the mechanistic information [1a,1b,1c,1e]. The bridging sulfido ligand has been shown to coordinate to the incoming metal group to facilitate metal–metal exchange reactions [1a,1b,1c,1e,9]. To the best of our knowledge, metal–metal exchange reactions in the selenium-capped metal clusters are particularly rare [1a,1b,1c,1e,10]. Our study here provides some valuable information regarding the metal–metal substitution in the selenium-capped trimetallic case.

As shown in Scheme 1, $[\text{Se}_2\text{Mo}_3(\text{CO})_{10}]^{2-}$ (**1**) can be obtained directly from the reaction of $[\text{Se}_2\text{Cr}_3(\text{CO})_{10}]^{2-}$ with 4 equiv. of $\text{Mo}(\text{CO})_6$ or from the stepwise substitution via the monosubstituted Cr–Mo cluster $[\text{Se}_2\text{Cr}_2\text{Mo}(\text{CO})_{10}]^{2-}$. The yield (89%) for the direct substitution is significantly higher than that (34%) for the stepwise substitution, suggestive of different reaction pathways for these two routes. Although the formation of cluster **1** from the reaction of $[\text{Se}_2\text{Cr}_3(\text{CO})_{10}]^{2-}$ with 4 equiv. of $\text{Mo}(\text{CO})_6$ was unclear, the analogous reaction with $\text{W}(\text{CO})_6$ allowed for the isolation of an intermediate planar complex $[\text{Se}_2\text{W}_4(\text{CO})_{18}]^{2-}$ (**3**) due to the milder reactivity of $\text{W}(\text{CO})_6$ vs. $\text{Mo}(\text{CO})_6$. The structure of *arachno*-complex **3** shows that each selenium atom is bonded to three W carbonyl groups, apparently resulting from ring opening processes, indicative of the stronger interaction of Se atom with incoming W carbonyls. The planar complex **3** can undergo ring reformation processes via the W–W and Se–W bond formation with the elimination of CO ligands and loss of one external metal fragment $\text{W}(\text{CO})_5$ to give the *closo*-cluster **4**.

2.4. Structural features of $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{M}_3(\text{CO})_{10}]$ ($M = \text{Mo}$, $[\text{Et}_4\text{N}]_2[\mathbf{1}]$; W , $[\text{Et}_4\text{N}]_2[\mathbf{4}]$), $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{Cr}_2\text{W}(\text{CO})_{10}]$ ($[\text{Et}_4\text{N}]_2[\mathbf{2}]$), and $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{W}_4(\text{CO})_{18}]$ ($[\text{Et}_4\text{N}]_2[\mathbf{3}]$)

Complexes $[\text{Et}_4\text{N}]_2[\mathbf{1}]$ – $[\text{Et}_4\text{N}]_2[\mathbf{4}]$ are structurally characterized by single-crystal X-ray analysis. Anionic clusters **1**, **2**, and **4** are isostructural and **2** and **4** are isomorphous species. Each of them displays a Se_2M_3 trigonal bipyramidal structure with a M_3 ring, in which two M atoms are coordinated with three carbonyls and one M atom with four carbonyls and each Se atom acts as a 4e donor, consistent with the Wade's rule for a five-vertex *closo*-structure containing six skeletal electron pairs (Figs. 1, 2, and 4). As known, chalcogen-capped homonuclear group 6 trimetallic carbonyl complexes are rare [4–6], and **1** and **4** present the first selenium-capped trimolybdenum and tritungsten carbonyl clusters. According to Curtis' suggestion [11], clusters **1**, **2**, and **4** each possesses two semibridging carbonyls for the metal coordinated with four CO ligands, which are evidenced by the shorter distances for $\text{Mo}(2)\cdots\text{C}(2)$, $\text{Cr}(1)\cdots\text{C}(1)$, and $\text{W}(1)\cdots\text{C}(3)$ (2.91(1), 2.85(2), and 2.93(2) Å) and the slightly bending of the carbonyls ($\text{Mo}(1)\text{--C}(2)\text{--O}(2)$ 169.5(8)°; $\text{W}(1)\text{--C}(1)\text{--O}(1)$ 166(2)°; and $\text{W}(2)\text{--C}(3)\text{--O}(3)$ 169(1)°).

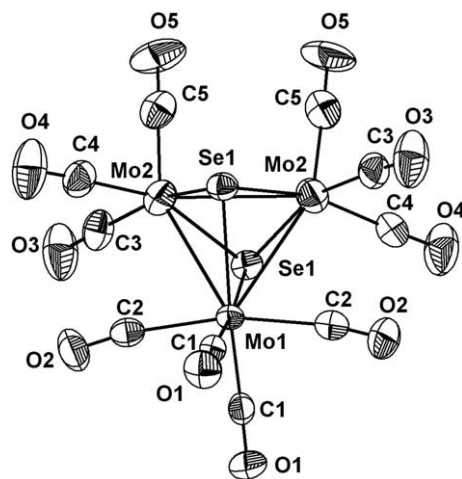


Fig. 1. ORTEP diagram showing the structure and atom labeling for the dianion **1**.

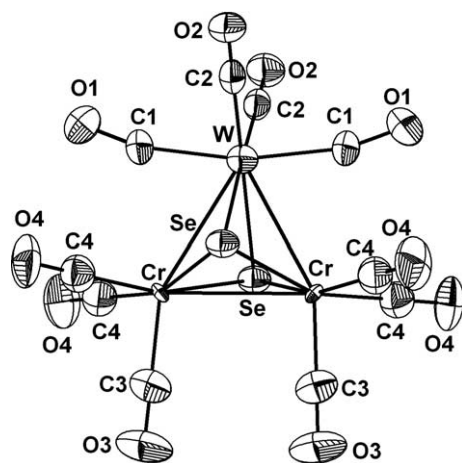


Fig. 2. ORTEP diagram showing the structure and atom labeling for the dianion **2**.

For comparison, the selected bond distances for the isostructural clusters $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{M}_3(\text{CO})_{10}]$ ($M = \text{group 6 metals}$) are listed in Table 1. As shown, the metal–metal and selenium–metal distances in **1** and **4** are longer than the corresponding lengths in $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{Cr}_3(\text{CO})_{10}]$ because of the increased size of Mo and W, and those distances in the heteronuclear analogs $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{Cr}_2\text{M}(\text{CO})_{10}]$ ($M = \text{Mo}$; **2**) are close due to the similar size of Mo and W. In the homonuclear clusters, it is of interest that the Se– $\text{M}(\text{CO})_3$ bond is significantly shorter than the Se– $\text{M}(\text{CO})_4$ bond, indicative of the weaker Se– $\text{M}(\text{CO})_4$ bonds caused by the higher coordination number of the M atom bonded with four carbonyls. Further, it is noted that the metal–metal bonds of the homonuclear rings are varied but comparable. The Mo–Mo lengths of **1** are 3.014(1) and 3.020(2) Å, which fall within the Mo–Mo bonding range in other related Mo_3 ring carbonyl compounds such as $[\text{PPN}]_2[\text{SMo}_3(\text{CO})_{12}]$ (average 3.027 Å) [4a] and $[\text{SMo}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})_6]^+$ (average 3.085 Å) [7d]. The W–W lengths of **4** are 3.0530(8) and 3.072(1) Å, which

are close to those in the few known W_3 ring carbonyl compounds, $[(\mu-\eta^5:\eta^5-C_{10}H_8)(\eta^5-C_5H_5)W_3(CO)_6(\mu_3-Sb)] \cdot 0.5(\text{toluene})$ (average 3.091 Å) [7c], $[Et_4N]_2[(OC)_5WSbW_3(CO)_9(\mu_3-OMe)_2(\mu_3-O)WO_2(OR)]$ (R = Me, H) (average 3.069 and 3.054 Å) [8a], $PW_4(\eta^5-C_5H_5)_3(CO)_{11}$ (average 3.093 Å) [7g], $CoW_3(CO)_9(\eta^5-C_5H_4Me)_3$ (average 2.956 Å) [12], and $W_3(\eta^5-C_5H_5)_3(CO)_6(\mu_3-PS)$ (average 3.128 Å) [8b].

The structure of the four-membered ring of complex **3** is a parallelogram, in which the $W(1)-Se(1)-W(1a)$ and $Se(1)-W(1)-Se(1a)$ angles are $70.40(2)^\circ$ and $109.60(2)^\circ$ (Fig. 3). The similar ring type of group 6 complexes was only observed in the Te-containing cases such as $[Te_2Cr_4(CO)_{18}]^{2-}$ [3b], $[Te_2W_4(CO)_{18}]^{2-}$ [3b], and $[Te_2-Cr_2M_2(CO)_{18}]^{2-}$ (M = Mo, W) [6]. Cluster **3** represents the first example of the selenium-containing group 6 metal complexes of this type. The W–W distance of the ring plane in **3** is 3.0196(5) Å, which is compared to the reported W–W lengths mentioned above. The Se–W lengths of **3** are 2.6224(7) and 2.6163(7) Å, which are close to those in $[W(CO)_2(As_3Se_3)_2]^{2-}$ (average 2.584 Å) [13] and $[CpW(CO)_3]_2Se_4$ (average 2.642 Å) [14].

2.5. Electrochemistry of $[Et_4N]_2[Se_2M_3(CO)_{10}]$ (M = Cr; Mo, $[Et_4N]_2[1]$; W, $[Et_4N]_2[4]$), and $[Et_4N]_2[Se_2Cr_2M(CO)_{10}]$ (M = Mo; W, $[Et_4N]_2[2]$)

As listed in Table 2, the electrochemical behavior of $[Et_4N]_2[Se_2M_3(CO)_{10}]$ (M = Cr; Mo, $[Et_4N]_2[1]$; W, $[Et_4N]_2[4]$) and $[Et_4N]_2[Se_2Cr_2M(CO)_{10}]$ (M = Mo; W, $[Et_4N]_2[2]$) has been studied by the cyclic voltammetry in acetonitrile solution using a platinum disk working electrode in the potential range ± 2.0 V vs. Ag/Ag^+ . In the homonuclear system, $[Et_4N]_2[Se_2Cr_3(CO)_{10}]$ displays one irreversible reduction and two irreversible oxidation processes, $[Et_4N]_2[1]$ shows one reversible reduction at +197.1 mV along with one irreversible reduction and four irreversible oxidation peaks, and $[Et_4N]_2[4]$ manifests four irreversible oxidation peaks. These results indicate that the Mo_3 cluster **1** possesses more diverse redox states than

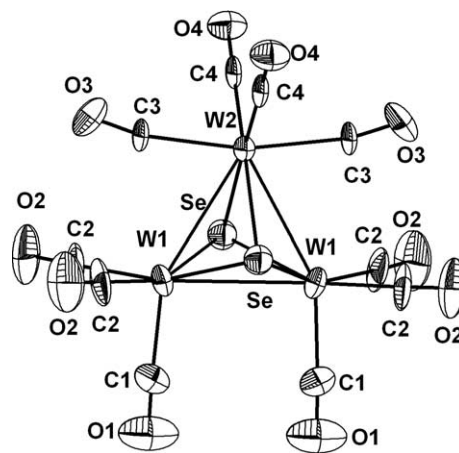


Fig. 4. ORTEP diagram showing the structure and atom labeling for the dianion **4**.

Table 2
Cyclic voltammetric data for $[Et_4N]_2[Se_2M_3(CO)_{10}]$ (M = group 6 metals)

Complex	E_{pa} (mV)	E_{pc} (mV)	ΔE (mV)	$E_{1/2}$ (mV)
$[Et_4N]_2[Se_2Cr_3(CO)_{10}]$ [5]	−113.0			
	+399.0			
$[Et_4N]_2[Se_2Mo_3(CO)_{10}]$ ($[Et_4N]_2[1]$)	−548.1			
	−395.8			
$[Et_4N]_2[Se_2W_3(CO)_{10}]$ ($[Et_4N]_2[4]$)	−211.5			
	+21.8			
$[Et_4N]_2[Se_2Cr_2Mo(CO)_{10}]$ [5]	+277.2	+197.1	80.1	+237.2
	+629.8			
$[Et_4N]_2[Se_2Cr_2W(CO)_{10}]$ ($[Et_4N]_2[2]$)	−492.0			
	−123.4			
$[Et_4N]_2[Se_2Cr_2Mo(CO)_{10}]$ [5]	+165.1			
	+293.3			
$[Et_4N]_2[Se_2Cr_2W(CO)_{10}]$ ($[Et_4N]_2[2]$)	−125.8			
	+436.7	+370.9	65.8	+403.8
$[Et_4N]_2[Se_2Cr_2W(CO)_{10}]$ ($[Et_4N]_2[2]$)	+692.4			
	−113.0			
	+377.4			
		+514.4		

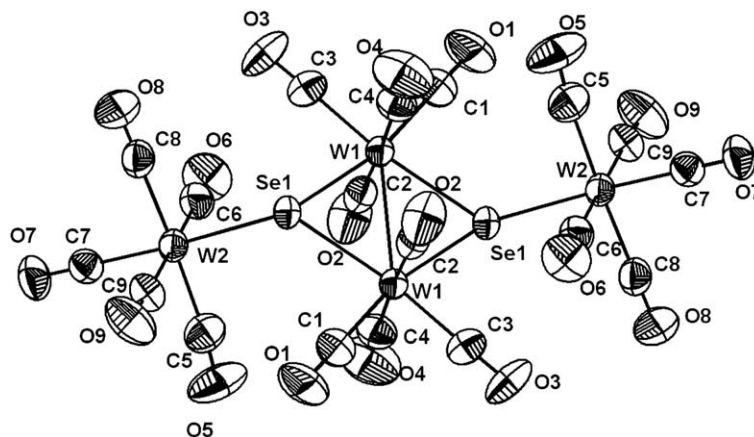


Fig. 3. ORTEP diagram showing the structure and atom labeling for the dianion **3**.

its analogous Cr₃ cluster [Se₂Cr₃(CO)₁₀]²⁻ and the W₃ cluster **4**. Besides, cluster **4** cannot be reduced electrochemically. The similar observation could be found in the Mo₃Se₄ core of [Mo₃Se₄(acac)₃(py)₃]⁺ which is easier to be reduced than its W analogue [15]. In the heteronuclear system, [Et₄N]₂[Se₂Cr₂Mo(CO)₁₀] exhibits one reversible reduction at +370.9 mV and two irreversible oxidation peaks, and the Cr₂W compound [Et₄N]₂[**2**] displays one irreversible reduction and two irreversible oxidation processes. Based on the oxidation potentials, [Et₄N]₂[**2**] is more easily oxidized compared to [Et₄N]₂[Se₂Cr₂Mo(CO)₁₀] probably owing to the larger number of electrons in W vs. Mo.

3. Conclusion

The novel selenium-capped trimolybdenum and tungsten carbonyl clusters [Se₂M₃(CO)₁₀]²⁻ (M = Mo, W) have been isolated from the metal substitutions of the trichromium cluster [Se₂Cr₃(CO)₁₀]²⁻, in which an intermediate planar complex is isolated to provide some useful clue to their formation. Further, the effect of group 6 metals on metal–metal exchange processes and the structural features of the resultant selenium-capped group 6 trimetallic clusters are systematically compared.

4. Experimental

4.1. General methods

All reactions were performed under an atmosphere of pure nitrogen using standard Schlenk techniques [16]. Solvents were purified, dried, and distilled under nitrogen prior to use. Mo(CO)₆ and W(CO)₆ (Strem) were used as received. [Et₄N]₂[Se₂Cr₃(CO)₁₀] was prepared according to the published method [5]. Infrared spectra were recorded on a Perkin–Elmer Paragon 500 IR spectrometer as solutions in CaF₂ cells. The ⁷⁷Se NMR spectra were taken on a JEOL 400 instrument at 76.31 MHz. Elemental analyses of C, H, and N were performed on a Perkin–Elmer 2400 analyzer at the NSC Regional Instrumental Center at National Taiwan University, Taipei, Taiwan. Electrochemical measurements were performed at the room temperature under the nitrogen atmosphere and recorded using a BAS-100W electrochemical potentiostat. A platinum disk working electrode, a platinum wire auxiliary electrode, and a non-aqueous Ag/Ag⁺ electrode were used in a three-electrode configuration. Tetra-*n*-butylammonium perchlorate (TBAP) was used as the supporting electrolyte, and the solute concentration was ~10⁻³ M. The redox potentials were calibrated with a ferrocenium/ferrocene (Fc⁺/Fc) couple in the working solution.

4.2. Improved synthesis of [Et₄N]₂[Se₂Cr₂Mo(CO)₁₀]

Acetone (40 mL) was added to a mixture of [Et₄N]₂[Se₂Cr₃(CO)₁₀] (0.68 g, 0.80 mmol) and Mo(CO)₆ (0.21 g,

0.80 mmol). The mixture was stirred and heated to reflux for 16 h to give a reddish-brown solution, which was filtered, and solvent was removed under vacuum. The residue was washed with Et₂O and CH₂Cl₂ which contained Cr(CO)₆ confirmed by IR spectroscopy. The residue was then extracted with MeCN to give a purplish-red sample of the previously known [Et₄N]₂[Se₂Cr₂Mo(CO)₁₀] [**5**] (0.47 g, 65%). ⁷⁷Se NMR (76 MHz, DMSO-*d*₆, 300 K): δ -108.6.

4.3. Synthesis of [Et₄N]₂[Se₂Mo₃(CO)₁₀] ([Et₄N]₂[**1**])

Acetone (30 mL) was added to a mixture of [Et₄N]₂[Se₂Cr₃(CO)₁₀] (0.31 g, 0.36 mmol) and Mo(CO)₆ (0.38 g, 1.45 mmol). The mixture was stirred and heated to reflux for 20 h to give a yellowish-brown solution, which was filtered, and solvent was removed under vacuum. The residue was washed with Et₂O and CH₂Cl₂ and extracted with MeCN to give an orange sample of [Et₄N]₂[Se₂Mo₃(CO)₁₀] ([Et₄N]₂[**1**]) (0.32 g, 89%). IR (ν_{CO}, MeCN): 2065 (w), 2048 (w), 2040 (w), 2008 (m), 1939 (vs), 1871 (s) cm⁻¹. Anal. Calc. for C₂₆H₄₀Mo₃N₂O₁₀Se₂: C, 31.66; H, 4.09; N, 2.84. Found: C, 31.36; H, 4.31; N, 2.78%. ⁷⁷Se NMR (76 MHz, DMSO-*d*₆, 300 K): δ 642.6. Compound [Et₄N]₂[**1**] is soluble in MeCN and acetone. Crystals of [Et₄N]₂[**1**] suitable for X-ray analysis were grown from MeCN–ether solution at -20 °C.

4.4. Reaction of [Et₄N]₂[Se₂Cr₂Mo(CO)₁₀] with Mo(CO)₆ (1:3)

Acetone (30 mL) was added to a mixture of [Et₄N]₂[Se₂Cr₂Mo(CO)₁₀] (0.27 g, 0.30 mmol) and Mo(CO)₆ (0.24 g, 0.90 mmol). The reaction solution was stirred and heated to reflux for 20 h. The resultant solution was filtered, solvent was removed under vacuum, and the residue was washed with CH₂Cl₂ and extracted with MeCN to give [Et₄N]₂[Se₂Mo₃(CO)₁₀] ([Et₄N]₂[**1**]) (0.16 g, 53%).

4.5. Synthesis of [Et₄N]₂[Se₂Cr₂W(CO)₁₀] ([Et₄N]₂[**2**])

Acetone (30 mL) was added to a mixture of [Et₄N]₂[Se₂Cr₃(CO)₁₀] (0.60 g, 0.70 mmol) and W(CO)₆ (0.25 g, 0.70 mmol). The mixture was stirred and heated to reflux for 2 days to give a reddish-brown solution, which was filtered, and solvent was removed under vacuum. The residue was washed with Et₂O and CH₂Cl₂ which contained Cr(CO)₆ confirmed by IR spectroscopy. The residue was then extracted with MeCN to give a purplish-red sample of [Et₄N]₂[Se₂Cr₂W(CO)₁₀] ([Et₄N]₂[**2**]) (0.44 g, 64%). IR (ν_{CO}, MeCN): 2000 (w), 1915 (vs), 1869 (s) cm⁻¹. Anal. Calc. for C₂₆H₄₀Cr₂WN₂O₁₀Se₂: C, 31.66; H, 4.09; N, 2.84. Found: C, 31.41; H, 4.03; N, 2.78%. ⁷⁷Se NMR (76 MHz, DMSO-*d*₆, 300 K): δ -172.5. Compound [Et₄N]₂[**2**] is soluble in MeCN and acetone. Crystals of [Et₄N]₂[**2**] suitable for X-ray analysis were grown from MeCN–ether solution at -20 °C.

4.6. Synthesis of $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{W}_4(\text{CO})_{18}]$ ($[\text{Et}_4\text{N}]_2[\mathbf{3}]$)

A mixture of $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{Cr}_3(\text{CO})_{10}]$ (0.77 g, 0.90 mmol) and $\text{W}(\text{CO})_6$ (1.27 g, 3.60 mmol) in the ratio of 1:4 was stirred and heated to reflux in acetone for 2 days to give a reddish-brown solution, which was filtered, and solvent was removed under vacuum. The residue was washed with Et_2O and CH_2Cl_2 and extracted with MeCN to give a reddish-brown sample of $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{W}_4(\text{CO})_{18}]$ ($[\text{Et}_4\text{N}]_2[\mathbf{3}]$) (0.76 g, 51%). IR (ν_{CO} , MeCN): 2054 (m), 2005 (s), 1950 (vs), 1931 (s), 1862 (m) cm^{-1} . Anal. Calc. for $\text{C}_{34}\text{H}_{40}\text{W}_4\text{N}_2\text{O}_{18}\text{Se}_2$: C, 24.63; H, 2.43; N, 1.69. Found: C, 24.81; H, 2.54; N, 1.97%. ^{77}Se NMR (76 MHz, DMSO- d_6 , 300 K): δ 158.9. Compound $[\text{Et}_4\text{N}]_2[\mathbf{3}]$ is soluble in MeCN and acetone. Crystals of $[\text{Et}_4\text{N}]_2[\mathbf{3}]$ suitable for X-ray analysis were grown from MeCN–ether solution at -20°C .

4.7. Synthesis of $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{W}_3(\text{CO})_{10}]$ ($[\text{Et}_4\text{N}]_2[\mathbf{4}]$)

A mixture of $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{Cr}_3(\text{CO})_{10}]$ (1.05 g, 1.23 mmol) and $\text{W}(\text{CO})_6$ (1.73 g, 4.92 mmol) in the ratio of 1:4 was stirred and heated to reflux in acetone for 4 days to give a reddish-brown solution, which was filtered, and solvent was removed under vacuum. The residue was washed with Et_2O and CH_2Cl_2 and extracted with MeCN to give a reddish-brown sample of $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{W}_3(\text{CO})_{10}]$ ($[\text{Et}_4\text{N}]_2[\mathbf{4}]$) (0.66 g, 43%). IR (ν_{CO} , MeCN): 2003 (m), 1937 (s), 1920 (vs), 1868 (s), 1825 (m) cm^{-1} . Anal. Calc. for $\text{C}_{26}\text{H}_{40}\text{W}_3\text{N}_2\text{O}_{10}\text{Se}_2$: C, 24.92; H, 3.22; N, 2.24. Found: C, 24.75; H, 3.02; N, 2.21%. ^{77}Se NMR (76 MHz, DMSO- d_6 , 300 K): δ 676.1. Compound $[\text{Et}_4\text{N}]_2[\mathbf{4}]$ is soluble

in MeCN and acetone. Crystals of $[\text{Et}_4\text{N}]_2[\mathbf{4}]$ suitable for X-ray analysis were grown from MeCN–ether solution at -20°C .

4.8. Conversion of $[\text{Et}_4\text{N}]_2[\mathbf{3}]$ to $[\text{Et}_4\text{N}]_2[\mathbf{4}]$

A sample of $[\text{Et}_4\text{N}]_2[\mathbf{3}]$ (0.52 g, 0.31 mmol) was stirred and heated to reflux in acetone for 2 days to give a reddish-brown solution, which was filtered, and solvent was removed under vacuum. The residue was washed with Et_2O and CH_2Cl_2 which contained $\text{W}(\text{CO})_6$ confirmed by IR spectroscopy. The residue was further extracted with MeCN to give a reddish-brown sample of $[\text{Et}_4\text{N}]_2[\mathbf{4}]$ (0.36 g, 94%).

4.9. Reaction of $[\text{Et}_4\text{N}]_2[\mathbf{2}]$ with $\text{W}(\text{CO})_6$ (1:3) (58 h)

Acetone (40 mL) was added to a mixture of $[\text{Et}_4\text{N}]_2[\mathbf{2}]$ (0.44 g, 0.45 mmol) and $\text{W}(\text{CO})_6$ (0.47 g, 1.34 mmol). The mixture was stirred and heated to reflux for 58 h to give a reddish-brown solution, which was filtered, and solvent was removed under vacuum. The residue was washed with CH_2Cl_2 and extracted with MeCN to give a reddish-brown sample of $[\text{Et}_4\text{N}]_2[\mathbf{3}]$ (0.35 g, 47%).

4.10. Reaction of $[\text{Et}_4\text{N}]_2[\mathbf{2}]$ with $\text{W}(\text{CO})_6$ (1:3) (4 days)

Acetone (30 mL) was added to a mixture of $[\text{Et}_4\text{N}]_2[\mathbf{2}]$ (0.29 g, 0.29 mmol) and $\text{W}(\text{CO})_6$ (0.31 g, 0.88 mmol). The mixture was stirred and heated to reflux for 4 days to give a reddish-brown solution, which was filtered, and solvent was removed under vacuum. The residue was washed with

Table 3

Crystallographic data for $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{Mo}_3(\text{CO})_{10}]$ ($[\text{Et}_4\text{N}]_2[\mathbf{1}]$), $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{Cr}_2\text{W}(\text{CO})_{10}]$ ($[\text{Et}_4\text{N}]_2[\mathbf{2}]$), $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{W}_4(\text{CO})_{18}]$ ($[\text{Et}_4\text{N}]_2[\mathbf{3}]$), and $[\text{Et}_4\text{N}]_2[\text{Se}_2\text{W}_3(\text{CO})_{10}]$ ($[\text{Et}_4\text{N}]_2[\mathbf{4}]$)

	$[\text{Et}_4\text{N}]_2[\mathbf{1}]$	$[\text{Et}_4\text{N}]_2[\mathbf{2}]$	$[\text{Et}_4\text{N}]_2[\mathbf{3}]$	$[\text{Et}_4\text{N}]_2[\mathbf{4}]$
Empirical formula	$\text{C}_{26}\text{H}_{40}\text{Mo}_3\text{N}_2\text{O}_{10}\text{Se}_2$	$\text{C}_{26}\text{H}_{40}\text{Cr}_2\text{WN}_2\text{O}_{10}\text{Se}_2$	$\text{C}_{34}\text{H}_{40}\text{W}_4\text{N}_2\text{O}_{18}\text{Se}_2$	$\text{C}_{26}\text{H}_{40}\text{W}_3\text{N}_2\text{O}_{10}\text{Se}_2$
Formula weight	986.34	986.37	1658.01	1250.08
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic
Space group	<i>Pbnn</i>	<i>Cmcm</i>	<i>P2₁/c</i>	<i>Cmcm</i>
Crystal dimensions (mm)	$0.35 \times 0.20 \times 0.10$	$0.50 \times 0.20 \times 0.15$	$0.30 \times 0.20 \times 0.10$	$0.35 \times 0.20 \times 0.15$
<i>a</i> (Å)	8.568(5)	8.586(4)	14.216(3)	8.484(2)
<i>b</i> (Å)	24.950(3)	24.794(4)	11.7390(2)	25.093(3)
<i>c</i> (Å)	16.196(2)	16.063(3)	14.7105(3)	16.348(3)
β (°)			105.9932(9)	
<i>V</i> (Å ³)	3462(2)	3420(2)	2359.88(8)	3480(1)
<i>Z</i>	4	4	2	4
<i>D_c</i> (g cm ⁻³)	1.892	1.916	2.330	2.386
μ (mm ⁻¹)	3.22	6.16	11.33	12.03
Diffractometer	Nonius (CAD4)	Nonius (CAD4)	Nonius (Kappa CCD)	Nonius (CAD4)
λ (Mo K α) (Å)	0.71073	0.71073	0.71073	0.71073
<i>T</i> (K)	293	293	293	293
θ Range for data collection (°)	1.63–24.96	1.64–26.88	4.19–27.55	1.62–25.90
<i>T_{min}</i> / <i>T_{max}</i>	0.50/0.72	0.26/0.40	0.02/0.05	0.05/0.16
Number of independent reflections	3047	2056	5356	1896
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^a (<i>I</i> > 2 σ (<i>I</i>))	0.056, 0.181	0.075, 0.237	0.037, 0.099	0.046, 0.123
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^a (all data)	0.104, 0.217	0.090, 0.251	0.045, 0.112	0.067, 0.151

^a $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ and $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$.

Table 4

Selected bond distances (Å) and bond angles (°) for [Et₄N]₂[Se₂Mo₃(CO)₁₀] ([Et₄N]₂[1]), [Et₄N]₂[Se₂Cr₂W(CO)₁₀] ([Et₄N]₂[2]), [Et₄N]₂[Se₂W₄(CO)₁₈] ([Et₄N]₂[3]), and [Et₄N]₂[Se₂W₃(CO)₁₀] ([Et₄N]₂[4])

<i>[Et₄N]₂[1]</i>			
Se(1)–Mo(1)	2.716(1)	Se(1)–Mo(2)	2.479(2)
Mo(1)–Mo(2)	3.014(1)	Mo(2)–Mo(2a)	3.020(2)
Mo(1)–C(2)	2.06(1)	Mo(1)–C(av)	2.00(5)
Mo(2)–C(av)	1.91(3)	Mo(2)···C(2)	2.91(1)
Se(1)–Mo(1)–Se(1a)	86.61(6)	Se(1)–Mo(2)–Se(1a)	97.37(5)
Se(1)–Mo(1)–Mo(2)	50.94(3)	Se(1)–Mo(2)–Mo(2a)	52.52(3)
Mo(1)–Se(1)–Mo(2)	70.78(4)	Mo(2)–Se(1)–Mo(2a)	75.02(5)
Mo(1)–Mo(2)–Mo(2a)	59.94(2)	Mo(2)–Mo(1)–Mo(2a)	60.12(4)
Mo(1)–C(2)–O(2)	169.5(8)		
<i>[Et₄N]₂[2]</i>			
Se(1)–W(1)	2.676(2)	Se(1)–Cr(1)	2.418(2)
Cr(1)–W(1)	2.971(2)	Cr(1)–Cr(1a)	2.955(4)
W(1)–C(1)	1.99(2)	W(1)–C(av)	1.96(3)
Cr(1)–C(av)	1.83(3)	Cr(1)···C(1)	2.85(2)
Se(1)–W(1)–Se(1a)	85.35(8)	Se(1)–Cr(1)–Se(1a)	97.21(9)
Se(1)–W(1)–Cr(1)	50.37(4)	Se(1)–Cr(1)–Cr(1a)	52.32(4)
W(1)–Se(1)–Cr(1)	71.15(6)	Cr(1)–Se(1)–Cr(1a)	75.35(9)
W(1)–Cr(1)–Cr(1a)	60.17(4)	Cr(1)–W(1)–Cr(1a)	59.66(8)
W(1)–C(1)–O(1)	166(2)		
<i>[Et₄N]₂[3]</i>			
Se(1)–W(1)	2.6224(7)	Se(1)–W(1a)	2.6163(7)
Se(1)–W(2)	2.7104(7)	W(1)–W(1a)	3.0196(5)
Se(1)–W(1)–Se(1a)	109.60(2)	Se(1)–W(1)–W(1a)	54.71(2)
Se(1a)–W(1)–W(1a)	54.90(2)	W(1)–Se(1)–W(1a)	70.40(2)
W(1)–Se(1)–W(2)	120.93(3)	W(1a)–Se(1)–W(2)	124.46(3)
<i>[Et₄N]₂[4]</i>			
Se(1)–W(1)	2.533(1)	Se(1)–W(2)	2.725(2)
W(1)–W(2)	3.0530(8)	W(1)–W(1a)	3.072(1)
W(2)–C(3)	2.05(1)	W(1)–C(av)	1.97(4)
W(2)–C(av)	2.00(6)	W(1)···C(3)	2.93(2)
Se(1)–W(2)–Se(1a)	88.12(6)	Se(1)–W(1)–Se(1a)	96.89(5)
Se(1)–W(2)–W(1)	51.61(3)	Se(1)–W(1)–W(1a)	52.66(2)
W(1)–Se(1)–W(2)	70.89(4)	W(1)–Se(1)–W(1a)	74.68(5)
W(1a)–W(1)–W(2)	59.79(1)	W(1)–W(2)–W(1a)	60.42(2)
W(2)–C(3)–O(3)	169(1)		

CH₂Cl₂ and extracted with MeCN to give a reddish-brown sample of [Et₄N]₂[4] (0.15 g, 38%).

4.11. X-ray structural characterization of [Et₄N]₂[1]–[Et₄N]₂[4]

The selected crystallographic data for [Et₄N]₂[1]–[Et₄N]₂[4] are given in Table 3. All crystals were mounted on glass fibers with epoxy cement. Data collection for [Et₄N]₂[1], [Et₄N]₂[2] and [Et₄N]₂[4] was carried out on a Nonius (CAD-4) diffractometer using graphite-monochromated Mo K α radiation at 293 K using the θ –2 θ scan mode, and an empirical absorption correction by azimuthal (ψ) scans was applied [17]. Data collection for [Et₄N]₂[3] was carried out on a Bruker-Nonius Kappa CCD diffractometer using graphite-monochromated Mo K α radiation at 293 K employing the θ –2 θ scan mode and an empirical absorption correction by multiscans was applied. The structures of [Et₄N]₂[1]–[Et₄N]₂[4] were refined by SHELXL packages [18]. All of the non-hydrogen atoms were refined with anisotropic temperature factors. For [Et₄N]₂[2], the

refinement of the X-ray data led us to consider one tungsten and two chromium positions in the M₃ plane as slightly disordered, with very small occupancy of Cr for the W site and W for the two Cr sites; however, elemental analysis further confirmed its formulation. The selected distances and angles for [Et₄N]₂[1]–[Et₄N]₂[4] are listed in Table 4.

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Appendix A. Supplementary data

CIF tables for the structural analyses of compounds [Et₄N]₂[1]–[Et₄N]₂[4] have been deposited with the Cambridge Crystallographic Data Center. The deposit numbers

are CCDC 281314–281317. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.10.039.

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