

# Solid state synthesis, structure and optical limiting properties of seleno cuboidal clusters $[M_3Se_4X_3(\text{diphosphine})_3]^+$ ( $M = \text{Mo}, \text{W}; X = \text{Cl}, \text{Br}$ )

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## Abstract

The trinuclear complexes  $[M_3(\mu_3\text{-Se})(\mu\text{-Se})_3X_3(\text{dppe})_3]PF_6$  [ $M = \text{Mo}, X = \text{Cl}$  (**1**), **Br** (**2**);  $M = \text{W}, X = \text{Br}$  (**3**)] have been prepared by both solid state and solution syntheses. A structural study of **1** confirms the presence of an incomplete cuboidal  $\text{Mo}_3\text{Se}_4$  core. The electrochemical, linear optical and optical limiting properties of **1–3** and the previously reported  $[M_3(\mu_3\text{-Q})(\mu\text{-Q})_3X_3(L_2)_3]PF_6$  ( $M = \text{Mo}, Q = \text{Se}, X = \text{Cl}, L_2 = \text{dmpe}$  (**4**);  $M = \text{Mo}, Q = \text{Se}, X = \text{Br}, L_2 = \text{dmpe}$  (**5**);  $M = \text{W}, Q = \text{Se}, X = \text{Br}, L_2 = \text{dmpe}$  (**6**);  $M = \text{Mo}, Q = \text{S}, X = \text{Cl}, L_2 = \text{dppe}$  (**7**);  $M = \text{Mo}, Q = \text{S}, X = \text{Br}, L_2 = \text{dppe}$  (**8**);  $M = \text{W}, Q = \text{S}, X = \text{Br}, L_2 = \text{dppe}$  (**9**)) have been examined. Two different kinds of electrochemical behavior are proposed for the trinuclear  $[M_3Q_4X_3(\text{diphosphine})_3]^+$  complexes upon reduction: (i)  $M^{IV}_3 \leftrightarrow M^{IV}M_2^{III} \rightarrow M^{III}_3$  for all complexes except **5** and **6** (ii)  $M^{IV}_3 \rightarrow M^{IV}M_2^{III} \rightarrow M^{IV}M_2^{III} \rightarrow M^{III}_3$  for **5** and **6**. The ease of reduction within the  $[M_3Q_4Br_3(\text{dppe})_3]^+$  series follows the trend  $\text{Mo}_3\text{S}_4 > \text{Mo}_3\text{Se}_4 > \text{W}_3\text{Se}_4 \approx \text{W}_3\text{S}_4$ , while the ease of reduction for the analogous dmpe derivatives follows the trend  $\text{Mo}_3\text{S}_4 \approx \text{Mo}_3\text{Se}_4 > \text{W}_3\text{Se}_4 \approx \text{W}_3\text{S}_4$ . A quasi-reversible oxidation process at half-wave potential close to approximately 1.2 V vs. Ag | AgCl has been identified for the first time in  $[\text{W}_3\text{Q}_4]$  cluster compounds. Linear optical absorption spectra are broadly similar, with intense bands at high energy and weaker bands at lower energy. The longest wavelength absorption maximum is red-shifted in this series of complexes upon replacing chloride by bromide, sulfur by selenium, and tungsten by molybdenum. Complexes **4–6** have weak absorption from 500 to 800 nm. Optical limiting in **1–9** has been assessed by open-aperture Z-scan at 523 nm using 40 ns pulses, all nine clusters exhibiting optical limiting (values of the excited state cross-sections  $\sigma_{\text{eff}}$  are larger than those of the ground-state cross-sections  $\sigma_0$ ) at fluences approximately  $100 \text{ mJ cm}^{-2}$ . © 2003 Elsevier Science B.V. All rights reserved.

**Keywords:** Crystal structures; Molybdenum clusters; Tungsten clusters; Selenide clusters; Trinuclear clusters

## 1. Introduction

Optical limiting materials are attracting much attention due to a growing interest in developing new protective optical devices [1,2]. Recently, transition metal clusters have been shown to possess significant optical limiting capability [3,4]. These compounds are of considerable interest because they combine the advantages of the presence of heavy atoms with structural versatility of the coordination environment [5].

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Strong optical limiting effects have recently been observed in sulfur-containing clusters possessing cubane-type structures, and also in selenium-containing clusters, although the number of studies in the latter case is much more limited [6–8]. Systematic investigations of the optical limiting properties of transition metal clusters have shown that changes in the skeleton atoms have a much larger effect on the nonlinear optical (NLO) response than modifications to the peripheral ligands [9]. For example, substitution of Cu by Ag in  $[MM'_{3}(\mu_{3}\text{-S})_{3}(\mu_{3}\text{-Br})\text{SBr}_{2}]^{3+}$  ( $M = \text{Mo}, \text{W}; M' = \text{Cu}, \text{Ag}$ ) complexes leads to a significant improvement of the limiting performance. We have also observed that replacement of W by Mo in incomplete cuboidal trimers  $[\text{M}_{3}\text{S}_{4}\text{X}_{3}(\text{dmpe})_{3}]^{+}$  and heterobimetallic cubane-like  $[\text{M}_{3}\text{CuS}_{4}\text{X}_{3}(\text{dmpe})_{3}]^{+}$  clusters decreases the threshold limiting fluence in these optical limiters, and that replacement of Cl by Br also affects the optical limiting capability.

In our search for better NLO materials, we have undertaken a systematic study of the optical limiting properties of trinuclear clusters with formula  $[\text{M}_{3}\text{Q}_{4}\text{X}_{3}(\text{diphos})_{3}]^{+}$  ( $M = \text{Mo}, \text{W}; Q = \text{S}, \text{Se}; X = \text{Cl}, \text{Br}; \text{diphos} = \text{dmpe}, \text{dppe}$ ). Of particular interest is the S/Se substitution, because of the use of selenium-containing compounds in the preparation of low band gap semiconductors. We report herein solid state low temperature synthetic procedures for the selenido trimers  $[\text{M}_{3}\text{Se}_{4}\text{X}_{3}(\text{dppe})_{3}]^{+}$ , together with a comprehensive study of electrochemical and optical properties of these  $[\text{M}_{3}\text{Q}_{4}]$  incomplete cuboidal complexes.

## 2. Results and discussion

### 2.1. Synthesis and structure

The development of transition metal cluster chemistry is closely related to the availability of rational synthetic routes for the preparation of these compounds. Among the different strategies available, cluster excision has proved to be of great utility for the synthesis of molecular trinuclear clusters from their corresponding polymeric solid state phases [10,11]. In the current work we present the excision of the selenido polymeric phases  $\{\text{M}_{3}\text{Se}_{7}\text{X}_{4}\}_{x}$  with dppe [1,2-bis(diphenylphosphino)ethane] both in the solid state and in solution, as a direct route for the preparation of cluster cations of formula  $[\text{M}_{3}\text{Se}_{4}\text{X}_{3}(\text{dppe})_{3}]^{+}$  ( $M = \text{Mo}, \text{W}; X = \text{Cl}, \text{Br}$ ).

The synthesis of the molybdenum-containing cluster cation  $[\text{Mo}_{3}\text{Se}_{4}\text{Cl}_{3}(\text{dppe})_{3}]^{+}$  ( $\mathbf{1}^{+}$ ) and of the tungsten-containing cluster cation  $[\text{W}_{3}\text{Se}_{4}\text{Br}_{3}(\text{dppe})_{3}]^{+}$  ( $\mathbf{3}^{+}$ ) from their corresponding solid state polymers  $\{\text{M}_{3}\text{Se}_{7}\text{X}_{4}\}_{x}$  using excision solution methods, in low to moderate yields (30% for  $\mathbf{1}^{+}$ , 50–70% for  $\mathbf{3}^{+}$ ), was first reported by Fedin et al. [11–13]. We have reinvestigated this

procedure based on our previous findings on the pivotal role of the solvent on the excision products' yields, and have observed that complexes  $\mathbf{1}$ ,  $\mathbf{2}$  and  $\mathbf{3}$  can be prepared in higher yields, between 67 and 85%, using acetonitrile as solvent under reflux conditions and reaction times of approximately 48 h. This work extends our previous conclusion on the validity of the excision reaction in acetonitrile as a general route for the synthesis of  $[\text{M}_{3}\text{Q}_{4}\text{Cl}_{3}(\text{dmpe})_{3}]^{+}$  ( $M = \text{Mo}, \text{W}; Q = \text{S}, \text{Se}$ ) and  $[\text{M}_{3}\text{S}_{4}\text{Cl}_{3}(\text{dppe})_{3}]^{+}$  cluster complexes to the selenido  $[\text{M}_{3}\text{Se}_{4}\text{Cl}_{3}(\text{dppe})_{3}]^{+}$  series. In contrast to the observation for the sulfido clusters, the reaction with dppe gives better yields than that with dmpe while, as observed for the sulfido complexes,  $\{\text{Mo}_{3}\text{Se}_{7}\text{Cl}_{4}\}_{x}$  is more reactive than the corresponding molybdenum and tungsten bromides.

In recent years special attention had been paid to the use of low-heating solid state reactions for the preparation of homo and heterobimetallic sulfido and selenido transition metal clusters [8,14,15]. Compounds  $\mathbf{1}$ ,  $\mathbf{2}$  and  $\mathbf{3}$  can be readily synthesized by direct solid state reactions of the polymeric  $\{\text{M}_{3}\text{Se}_{7}\text{X}_{4}\}_{x}$  phases in molten diphosphine (dppe) in low to moderate yields, 43% for  $\mathbf{1}$ , 38% for  $\mathbf{2}$  and 62% for  $\mathbf{3}$ . Although the yields obtained for the molecular molybdenum clusters are lower than those obtained in solution, this procedure has the advantages of simplicity and a lower solvent consumption. This synthetic method has more interest in the case of tungsten, as  $\{\text{W}_{3}\text{Se}_{7}\text{Br}_{4}\}_{x}$  has been shown to be more reactive than its homologous molybdenum polymers, in contrast to the solution findings.

All complexes reported in this work have a  $[\text{M}_{3}\text{Q}_{4}]$  ( $M = \text{Mo}, \text{W}; Q = \text{S}, \text{Se}$ ) incomplete cuboidal unit, as can be seen in Fig. 1 for the X-ray crystallographically-characterized cluster cation  $\mathbf{1}^{+}$ .

Each metal atom is coordinated to a chlorine atom which is *trans* to a bridging selenium, while the phosphorus atoms of the dppe ligand occupy the remaining 'outer' positions of the pseudooctahedral metal environment, a ligand disposition observed in other diphosphine complexes  $[\text{M}_{3}\text{Q}_{4}\text{X}_{3}(\text{diphos})_{3}]^{+}$  ( $X = \text{Cl}, \text{Br}; \text{diphos} = \text{dmpe}, \text{dppe}$ ). This coordination mode, with one P atom *trans* to the capping  $\mu_{3}\text{-Se}$  atom and the other *trans* to the bridging  $\mu\text{-Se}$  atom, yields chiral cations, although the non-stereospecificity of the synthetic procedure results in racemic mixtures and compound  $\mathbf{1}$  crystallizing in the centrosymmetric space group  $C2/c$ . Complex  $\mathbf{1}$  is isostructural with the previously-reported analogous sulfide cluster  $[\text{Mo}_{3}\text{S}_{4}\text{Cl}_{2.25}\text{Br}_{0.75}(\text{dppe})_{3}](\text{BF}_{4})_{0.5}\text{Cl}_{0.5}$ ; and a selected list of bond distances for both complexes, together with the equivalent distances for the cluster cation  $[\text{Mo}_{3}\text{Se}_{4}\text{Cl}_{3}(\text{dmpe})_{3}]^{+}$ , is presented in Table 1 [16,17].

The Mo–Mo bond distance in  $\mathbf{1}$  is 0.07 Å longer than the corresponding distance in the isostructural sulfur derivative, and essentially the same as the intermetallic

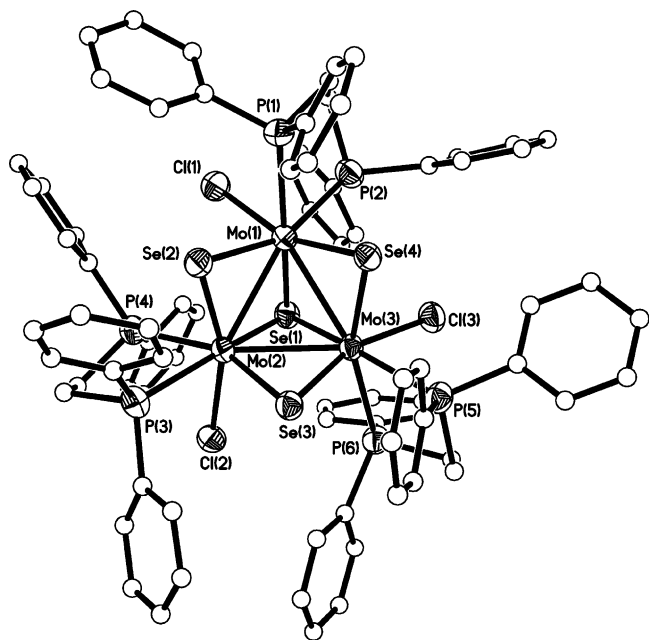


Fig. 1. ORTEP representation of  $[\text{Mo}_3\text{Se}_4\text{Cl}_3(\text{dppe})_3]^+$  ( $1^+$ ) (50% probability ellipsoids) with carbon atoms depicted as spheres.

distance in the homologous selenido dmpe complex. The Mo–Se bond lengths are unexceptional. The Mo–P bond distances in compound **1** are approximately 0.04 Å for P(1) and 0.07 Å for P(2) longer than the corresponding distances in the analogous dmpe complex, attributable to the lower basicity of the phosphine. The cations in **1** and the analogous dmpe derivative do not show intermolecular Se...Se contacts linking  $[\text{Mo}_3\text{Se}_4]$  units in pairs, as commonly observed in these incomplete cuboidal clusters [18,19].

$^{31}\text{P}$  NMR studies confirm the preservation of the solid state structure in solution. All complexes are air-stable and a molecular ion is observed as the base peak under ESI MS conditions at 35 V. Increasing the ionization energy results in successive losses of the terminal diphosphine ligands.

## 2.2. Redox properties

The electrochemical behavior of compounds **1–3** have been studied by cyclic voltammetry and compared with that previously reported for their homologous sulfide and dmpe derivatives. Two different kinds of electrochemical behavior have been proposed for the trinuclear  $[\text{M}_3\text{Q}_4\text{X}_3(\text{diphosphine})_3]^+$  complexes upon reduction: (i) a quasi-reversible two-electron process followed by an irreversible one-electron reduction (ii) a quasi-reversible one-electron process followed by two irreversible one-electron reductions. Complexes **1**, **2** and **3**, with one quasi-reversible and one irreversible reduction waves, belong to the first type, which is the most common for these trinuclear phosphino complexes. The second type has only been observed for the phosphino molybdenum and tungsten selenides,  $[\text{M}_3\text{Se}_4\text{Br}_3(\text{dmpe})_3]^+$ ,  $\text{M} = \text{Mo}$  (**5**) and  $\text{W}$  (**6**), although the existence of three mono-electronic reduction steps has also been reported for other trinuclear clusters, namely  $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$  and  $[\text{Mo}_{3-x}\text{WS}_4(\text{Hnta})_3]^{3-}$  ( $\text{nta}^{3-} = \text{nitrilotriacetate}$ ,  $x = 0-3$ ) [20,21]. The trinuclear clusters  $[\text{M}_3\text{Q}_4(\text{acac})_3(\text{py})_3]^+$  ( $\text{M} = \text{Mo}$ ,  $\text{W}$ ;  $\text{Q} = \text{S}$ ,  $\text{Se}$ ) only show two one-electron quasi-reversible reduction waves, within the potential range investigated, whose values range between  $-0.75$  and  $-1.36$  V for the first reduction process and between  $-0.97$  and  $-1.56$  V for the second one [18]. A summary of the electrochemical data for clusters **1–12** is listed in Table 2.

Substitution of molybdenum by tungsten causes a cathodic shift of the first half-wave potential  $E_{1/2}$  which is more pronounced for the dppe derivatives (460 mV for Se and 550 mV for S) than for the dmpe derivatives (370 mV for Se and 390 mV for S). The same tendency is observed for the  $[\text{Mo}_{3-x}\text{W}_x\text{S}_4(\text{Hnta})_3]^{3-}$  and for the  $[\text{M}_3\text{Q}_4(\text{acac})_3(\text{py})_3]^+$  trimers. The replacement of selenium by sulfur in homologous coordination compounds most often results in increased difficulty in reduction, as observed for complexes **3–6** where cathodic shift potentials between 20 and 90 mV have been measured

Table 1

Selected bond distances in  $[\text{Mo}_3\text{Se}_4\text{Cl}_3(\text{dppe})_3]\text{PF}_6 \cdot 0.5\text{CH}_3\text{CN}$  (**1**),  $[\text{Mo}_3\text{S}_4\text{Cl}_{2.25}\text{Br}_{0.75}(\text{dppe})_3](\text{BF}_4)_{0.5}\text{Cl}_{0.5}$  and  $[\text{Mo}_3\text{Se}_4\text{Cl}_3(\text{dmpe})_3]\text{PF}_6$

d (Å)	$[\text{Mo}_3\text{Se}_4\text{Cl}_3(\text{dppe})_3]\text{PF}_6$	$[\text{Mo}_3\text{S}_4\text{Cl}_{2.25}\text{Br}_{0.75}(\text{dppe})_3](\text{BF}_4)_{0.5}\text{Cl}_{0.5}$	$[\text{Mo}_3\text{Se}_4\text{Cl}_3(\text{dmpe})_3]\text{PF}_6$
Mo–Mo	2.850[3]	2.777[6]	2.836[2]
Mo–( $\mu_3$ -Q)	2.4709[2]	2.359[5]	2.478[3]
Mo–( $\mu$ -Q) <sup>a</sup>	2.436[5]	2.320[4]	2.450[2]
Mo–( $\mu$ -Q) <sup>b</sup>	2.393[4]	2.280[5]	2.404[2]
Mo–P(1) <sup>c</sup>	2.639[8]	2.658[12]	2.601[5]
Mo–P(2) <sup>d</sup>	2.571[8]	2.576[6]	2.512[5]

Standard deviations for averaged values are given in square brackets.

<sup>a</sup> Distance *trans* to the Mo–P bond.

<sup>b</sup> Distance *trans* to the Mo–X bond.

<sup>c</sup> Distance *trans* to the Mo–( $\mu$ -Q) bond.

<sup>d</sup> Distance *trans* to the Mo–( $\mu_3$ -Q) bond.

Table 2  
Electrochemical data for complexes **1–12** in acetonitrile <sup>a</sup>

Compound	Reduction		Oxidation
	$E_{1/2}(\Delta E^b)$ or $E_c^c$ (V)		$E_{1/2}(\Delta E^a)$ (V)
	$M_3^{IV}/M^{IV}M_2^{III}$ or $M_3^{IV}/M_2^{IV}M^{III}$ and $M_2^{IV}M^{III}/M^{IV}M_2^{III}$	$M^{IV}M_2^{III}/M_3^{III}$	$M_3^{IV}/M^{IV}M_2^V$
[Mo <sub>3</sub> Se <sub>4</sub> Cl <sub>3</sub> (dppe) <sub>3</sub> ](PF <sub>6</sub> ) ( <b>1</b> )	−0.52 (0.078)		−1.25
[Mo <sub>3</sub> Se <sub>4</sub> Br <sub>3</sub> (dppe) <sub>3</sub> ](PF <sub>6</sub> ) ( <b>2</b> )	−0.46 (0.07)		−1.09
[W <sub>3</sub> Se <sub>4</sub> Br <sub>3</sub> (dppe) <sub>3</sub> ](PF <sub>6</sub> ) ( <b>3</b> )	−0.92 (0.068)		−1.43
[Mo <sub>3</sub> Se <sub>4</sub> Cl <sub>3</sub> (dmpe) <sub>3</sub> ](PF <sub>6</sub> ) ( <b>4</b> )	−0.60 (0.078)		−1.21
[Mo <sub>3</sub> Se <sub>4</sub> Br <sub>3</sub> (dmpe) <sub>3</sub> ](PF <sub>6</sub> ) ( <b>5</b> )	−0.54 and −0.87		−1.20
[W <sub>3</sub> Se <sub>4</sub> Br <sub>3</sub> (dmpe) <sub>3</sub> ](PF <sub>6</sub> ) ( <b>6</b> )	−0.91 and −1.12		−1.41
[Mo <sub>3</sub> S <sub>4</sub> Cl <sub>3</sub> (dppe) <sub>3</sub> ](PF <sub>6</sub> ) ( <b>7</b> )	−0.50 (0.068)		−1.34
[Mo <sub>3</sub> S <sub>4</sub> Br <sub>3</sub> (dppe) <sub>3</sub> ](PF <sub>6</sub> ) ( <b>8</b> )	−0.39 (0.068)		−1.15
[W <sub>3</sub> S <sub>4</sub> Br <sub>3</sub> (dppe) <sub>3</sub> ](PF <sub>6</sub> ) ( <b>9</b> )	−0.94 (0.095)		−1.62
[Mo <sub>3</sub> S <sub>4</sub> Cl <sub>3</sub> (dmpe) <sub>3</sub> ](PF <sub>6</sub> ) ( <b>10</b> )	−0.69 (0.068)		−1.38
[Mo <sub>3</sub> S <sub>4</sub> Br <sub>3</sub> (dmpe) <sub>3</sub> ](PF <sub>6</sub> ) ( <b>11</b> )	−0.56 (0.102)		−1.20
[W <sub>3</sub> S <sub>4</sub> Br <sub>3</sub> (dmpe) <sub>3</sub> ](PF <sub>6</sub> ) ( <b>12</b> )	−0.95 (0.110)		−1.34

<sup>a</sup>  $E_{1/2}(\text{ferrocene}/\text{ferrocene}^+) = 0.44$  V ( $\Delta E = 66$  mV).

<sup>b</sup>  $\Delta E = |E_a - E_c|$ .

<sup>c</sup> Potentials measured at 100 mV s<sup>−1</sup>.

when Se is replaced by S [16]. However, the opposite trend is observed for the selenido clusters **1** and **2**, which are 20 and 70 mV, respectively, more difficult to reduce than their homologous sulfides. These differences in tendencies upon Se/S substitution are also observed when comparing the reduction potential values within the [M<sub>3</sub>Q<sub>4</sub>(acac)<sub>3</sub>(py)<sub>3</sub>]<sup>+</sup> series, for which ease of reduction decreases as Mo<sub>3</sub>S<sub>4</sub> > Mo<sub>3</sub>Se<sub>4</sub> > W<sub>3</sub>S<sub>4</sub> > W<sub>3</sub>Se<sub>4</sub>. This ease of reduction has been related to the relative affinities of the different cores for metals such as Sn [22], although the opposite way in which the Se/S substitution manifests itself in the Mo and in the W systems is difficult to explain with the information available. The ease of reduction within the [M<sub>3</sub>Q<sub>4</sub>Br<sub>3</sub>(dppe)<sub>3</sub>]<sup>+</sup> series decreases as Mo<sub>3</sub>S<sub>4</sub> > Mo<sub>3</sub>Se<sub>4</sub> > W<sub>3</sub>Se<sub>4</sub> ≈ W<sub>3</sub>S<sub>4</sub>, while the reducibility order for the analogous dmpe derivatives follows the tendency Mo<sub>3</sub>S<sub>4</sub> ≈ Mo<sub>3</sub>Se<sub>4</sub> > W<sub>3</sub>Se<sub>4</sub> ≈ W<sub>3</sub>S<sub>4</sub>. Again, the differences in redox potentials upon Se/S substitution are not straightforward.

The phosphino trimers reported in the current work are much easier to reduce than the corresponding acetylacetonate or nitrilotriacetate trimers [18,21]. Changes in the peripheral ligands in the [M<sub>3</sub>Q<sub>4</sub>X<sub>3</sub>(diphos)<sub>3</sub>]<sup>+</sup> cationic clusters, diphosphine or halide, also affect the reduction potential values. Substitution of dppe by the more basic dmpe in the molybdenum clusters results in a cathodic shift of 80 mV for Se and 170–190 mV for S, in good agreement with the increase in basicity of the phosphine. However, no significant change of the  $E_{1/2}$  is observed for the tungsten compounds when dppe is substituted by dmpe. Replacement of chlorine by bromine in the molybdenum complexes shifts  $E_{1/2}$  between 60 and 130 mV towards more anodic potentials, respectively.

The oxidation behavior of the [M<sub>3</sub>Q<sub>4</sub>] cuboidal clusters has been investigated for the first time. While the molybdenum clusters do not show a well-defined oxidation process within the potential range investigated (0–1.2 V), a quasi-reversible oxidation wave has been

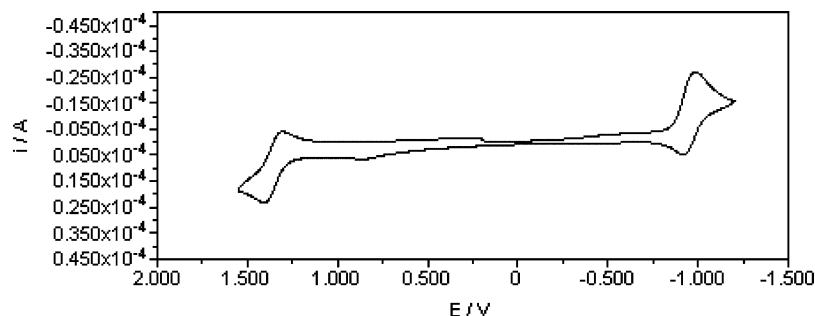


Fig. 2. Cyclic voltammogram of [W<sub>3</sub>S<sub>4</sub>Br<sub>3</sub>(dppe)<sub>3</sub>](PF<sub>6</sub>) (**9**) in CH<sub>3</sub>CN at a scan rate of 500 mV s.

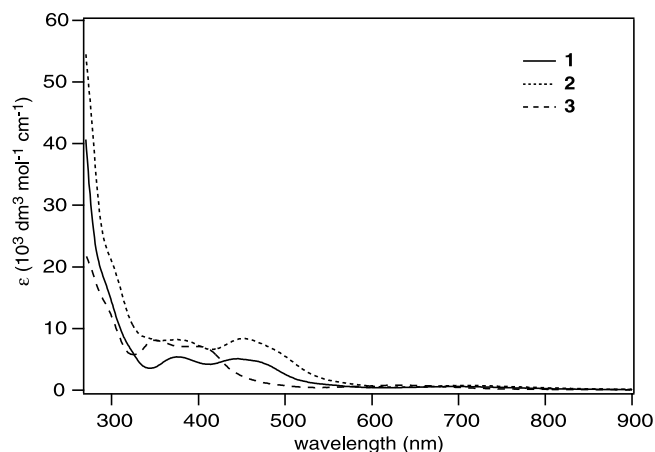


Fig. 3. Linear optical spectra for complexes 1–3.

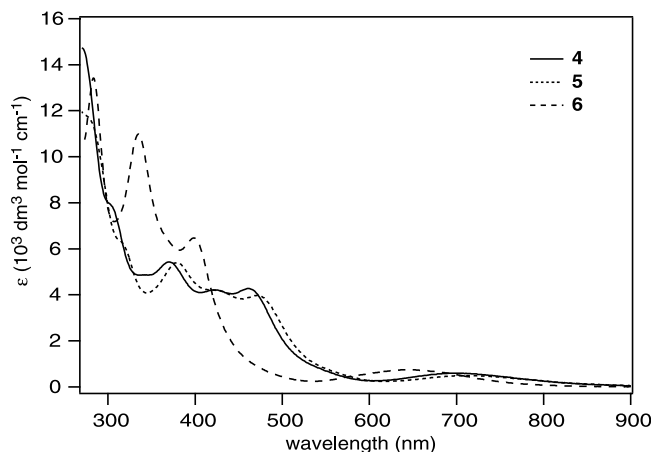


Fig. 4. Linear optical spectra for complexes 4–6.

observed for the tungsten compounds **3**, **6** and **9**, as show in Fig. 2 for complex **9** together with its first reduction wave. The intensities of these two waves are approximately equal. One can tentatively assign the oxidation process to a two-electron transfer ( $M^{IV}_3 \rightarrow M^V_2M^{IV}$ ). The selenido clusters **3** and **6** are slightly easier to oxidize than their sulfido counterparts **9** and **12** by approximately 80–90 mV. Replacement of dppe by dmpe causes an anodic shift of 105 mV, as expected based on the ligand basicity increase.

### 2.3. Optical limiting properties

The linear and NLO properties of clusters **1–9** have been assessed, the results from which are collected in Table 3 together with the previously-reported data for **10–12** which were obtained under similar experimental conditions [6].

Linear optical spectra for **1–9** are displayed in Figs. 3–5. The spectra of all complexes are broadly similar, with intense bands at high energy and weaker bands at lower energy. The wavelength of the lowest energy transition in these clusters is shifted in a systematic fashion upon cluster substitutions: a red-shift in this transition is observed on replacing dmpe by dppe (in proceeding from **4**, **5**, or **6** to **1**, **2**, or **3**, respectively), Cl by Br (in proceeding from **1**, **4**, or **7** to **2**, **5**, or **8**, respectively), W by Mo (in proceeding from **3**, **6**, or **9** to **2**, **5**, or **8**, respectively), and S by Se (in proceeding from **7**, **8**, or **9** to **1**, **2**, or **3**, respectively); with the exception of the dmpe for dppe replacement for which a blue-shift in the low-energy transition is observed on proceeding from **12** to **9**, the same trends are observed when the series of clusters is expanded to embrace the previously-reported **10–12**. These clusters have broad low-intensity absorptions extending through the visible region, and hence have potential as broad-band optical limiters.

Table 3  
Linear optical and optical limiting data for clusters **1–12**

Cluster	Optical absorption $\lambda(\epsilon)$ (nm) ( $10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) <sup>a</sup>	Cross-section ( $\times 10^{-18} \text{ cm}^2$ )	
		Ground-state, $\sigma_0$	Excited state, $\sigma_{\text{eff}}$
[Mo <sub>3</sub> Se <sub>4</sub> Cl <sub>3</sub> (dppe) <sub>3</sub> ]PF <sub>6</sub> ( <b>1</b> )	302 (sh, 13), 375 (5.4), 445 (5.1), 478 (sh, 4.2), 693 (0.59)	5.3	7.5
[Mo <sub>3</sub> Se <sub>4</sub> Br <sub>3</sub> (dppe) <sub>3</sub> ]PF <sub>6</sub> ( <b>2</b> )	305 (sh, 19), 375 (8.2), 453 (8.4), 498 (sh, 5.7), 707 (0.73)	1.2	14
[W <sub>3</sub> Se <sub>4</sub> Br <sub>3</sub> (dppe) <sub>3</sub> ]PF <sub>6</sub> ( <b>3</b> )	301 (sh, 12), 349 (8.1), 400 (sh, 7.1), 629 (0.80)	1.8	11
[Mo <sub>3</sub> Se <sub>4</sub> Cl <sub>3</sub> (dmpe) <sub>3</sub> ]PF <sub>6</sub> ( <b>4</b> )	302 (sh, 8.0), 369 (5.4), 423 (4.2), 461 (4.3), 545 (sh, 0.77), 698 (0.60)	4.5	9.0
[Mo <sub>3</sub> Se <sub>4</sub> Br <sub>3</sub> (dmpe) <sub>3</sub> ]PF <sub>6</sub> ( <b>5</b> )	322 (sh, 5.9), 379 (5.4), 420 (4.0), 471 (4.0), 553 (sh, 0.76), 711 (0.49)	5.4	11
[W <sub>3</sub> Se <sub>4</sub> Br <sub>3</sub> (dmpe) <sub>3</sub> ]PF <sub>6</sub> ( <b>6</b> )	335 (11), 398 (6.5), 640 (0.75)	1.0	6.2
[Mo <sub>3</sub> S <sub>4</sub> Cl <sub>3</sub> (dppe) <sub>3</sub> ]PF <sub>6</sub> ( <b>7</b> )	309 (sh, 16), 357 (8.5), 409 (7.9), 486 (sh, 1.3), 643 (0.61)	1.9	11
[Mo <sub>3</sub> S <sub>4</sub> Br <sub>3</sub> (dppe) <sub>3</sub> ]PF <sub>6</sub> ( <b>8</b> )	353 (sh, 9.5), 419 (8.9), 458 (sh, 6.5), 653 (0.51)	3.5	10
[W <sub>3</sub> S <sub>4</sub> Br <sub>3</sub> (dppe) <sub>3</sub> ]PF <sub>6</sub> ( <b>9</b> )	327 (14), 364 (12), 578 (0.80)	2.1	8.6
[Mo <sub>3</sub> S <sub>4</sub> Cl <sub>3</sub> (dmpe) <sub>3</sub> ]PF <sub>6</sub> ( <b>10</b> ) <sup>b</sup>	341 (6.0), 398 (4.6), 634 (0.42)	1.1	6.3
[Mo <sub>3</sub> S <sub>4</sub> Br <sub>3</sub> (dmpe) <sub>3</sub> ]PF <sub>6</sub> ( <b>11</b> ) <sup>b</sup>	353 (5.5), 410 (sh, 4.0), 642 (0.37)	1.1	6.8
[W <sub>3</sub> S <sub>4</sub> Br <sub>3</sub> (dmpe) <sub>3</sub> ]PF <sub>6</sub> ( <b>12</b> ) <sup>b</sup>	317 (sh, 13), 348 (sh, 8.1), 583 (0.71)	1.1	5.8

<sup>a</sup> Optical absorption maxima to lower energy of 300 nm.

<sup>b</sup> Ref. [6].

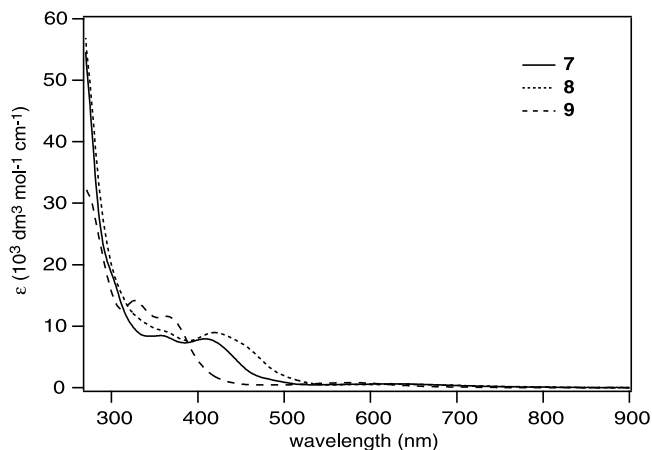


Fig. 5. Linear optical spectra for complexes 7–9.

Optical limiting has been assessed for the present series of clusters using the Z-scan technique. We have previously discussed the utility and shortcomings of this experimental procedure to evaluate power limiting [6]. Representative open and closed aperture Z-scan traces [for  $[\text{Mo}_3\text{Se}_4\text{Cl}_3(\text{dppe})_3]\text{PF}_6$  (**1**)] are displayed in Fig. 6. Our earlier report found a decrease in threshold limiting fluence on proceeding from a tetranuclear cluster derivative to trinuclear cluster **10–12**, and on replacing W by Mo. In the present study, power limiting was observed in **1–9** at fluences of the order of  $100 \text{ mJ cm}^{-2}$ , similar to the results we previously presented for **10–12**, and confirming that complexes of general composition  $[\text{M}_3\text{Q}_4\text{X}_3(\text{L}_2)_3]^+$  are efficient limiters. We reiterate here that, with about 40 ns pulses from the laser, the limiting is likely to involve several different contributions, the thermal contribution being likely to be important or even to dominate the process.

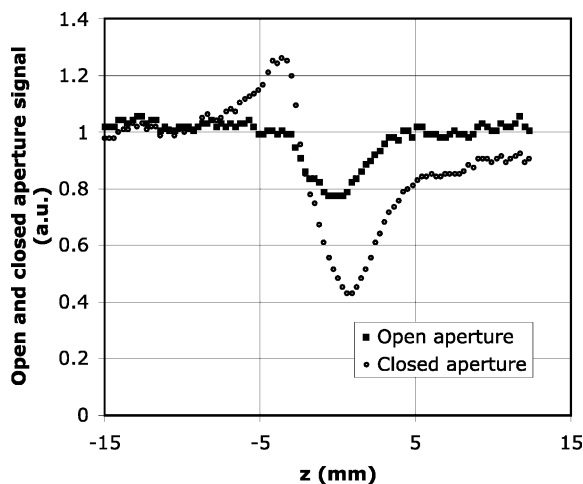


Fig. 6. Open and closed aperture Z-scans in solution of  $[\text{Mo}_3\text{Se}_4\text{Cl}_3(\text{dppe})_3]\text{PF}_6$  (**1**).

Transmission vs. fluence plots were generated for all clusters, a representative example (that for **1**) being shown in Fig. 7. We have analyzed the power limiting by literature procedures to provide quantitative comparisons between the different compounds [23]. The transmittance of the cell is taken as:

$$T = (1 - R)^2 \frac{\exp(-\alpha_0 L)}{q} \ln(1 + q)$$

where

$$q = (1 - R)[1 - \exp(-\alpha_0 L)] \delta_{\text{eff}} F_0 / 2F_s$$

and  $R$  is the reflection coefficient,  $\alpha_0$  is the low power absorption coefficient,  $F_0$  is the fluence and  $F_s$  is the saturation fluence defined as

$$F_s = \frac{h\omega}{\sigma_0}$$

and

$$\delta_{\text{eff}} = \frac{\sigma_{\text{eff}} - \sigma_0}{\sigma_0}$$

The effective excited-state cross-section  $\sigma_{\text{eff}}$  should only be treated as a measure of the power limiting ability of the substance under our specific experimental conditions: it may contain contributions from several different excited states with different properties (e.g. from both a singlet and a triplet state). The values of  $\sigma_{\text{eff}}$  derived in these experiments are comparable to those presented by us before; however, comparisons between values obtained in different data collection runs should be cautious, since the  $\sigma_{\text{eff}}$  values are likely to depend to a

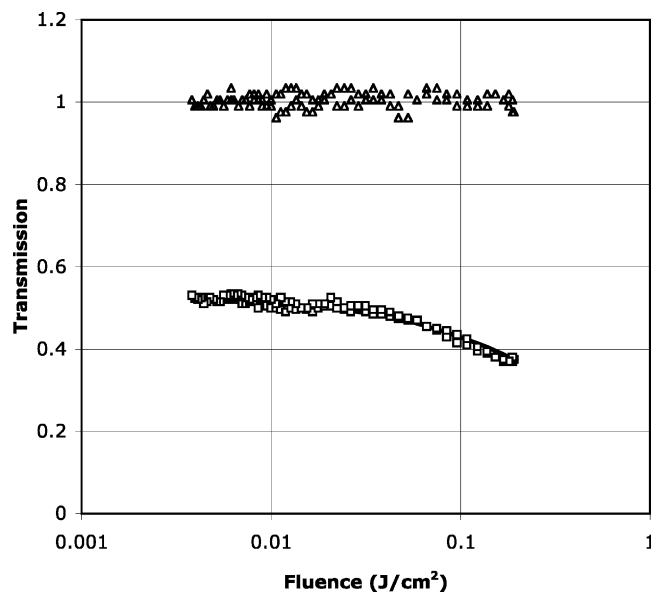


Fig. 7. Power limiting plots for  $[\text{Mo}_3\text{Se}_4\text{Cl}_3(\text{dppe})_3]\text{PF}_6$  (**1**) together with the theoretical fit.  $\Delta$ , Solvent;  $\square$ , **1**.

certain degree on the details of a power limiting experiment such as the pulse duration, the geometric parameters of the laser beam, etc. A large ratio of  $\sigma_{\text{eff}}$  to ground-state absorption cross-section  $\sigma_0$  is one criterion for assessing potential as optical limiters. Values of  $\sigma_{\text{eff}}/\sigma_0$  lie in the range 1.4 (**1**)–12 (**2**). While these clusters are all efficient optical limiters, no systematic trends in  $\sigma_{\text{eff}}/\sigma_0$  upon molecular modification are apparent. Indeed, the values of  $\sigma_{\text{eff}}$  for **1**–**12** all lie within an order of magnitude of each other suggesting a common power limiting mechanism, possibly purely thermal in origin.

### 3. Conclusion

A low temperature synthetic route for the preparation of molecular clusters with formula  $[\text{M}_3\text{Se}_4\text{X}_3(\text{dppe})_3]^+$  ( $\text{M} = \text{Mo}, \text{W}$ ;  $\text{X} = \text{Cl}, \text{Br}$ ) has been developed based on the cluster excision of  $\{\text{M}_3\text{Se}_7\text{X}_4\}_x$  polymeric phases in molten diphosphines. These molecular clusters as well as their dppe derivatives can also be prepared by excision of the solid precursors in acetonitrile under reflux conditions following the synthetic strategy developed for the corresponding sulfide cluster trimers. A systematic study on the electrochemical, linear optical and optical limiting properties on the  $[\text{M}_3\text{Q}_4\text{X}_3(\text{diphos})_3]^+$  ( $\text{Q} = \text{Se}, \text{S}$  and  $\text{diphos} = \text{dppe}, \text{dmpe}$ ) has been undertaken. The existence of a quasi-reversible oxidation process has been identified for the first time in clusters with  $[\text{W}_3\text{Q}_4]$  central units. All clusters investigated are efficient optical limiters ( $\sigma_{\text{eff}} > \sigma_0$ ) although no systematic trend upon molecular modification is apparent, suggesting a common power limiting mechanism.

## 4. Experimental section

### 4.1. General remarks

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Compound **4**–**9** were obtained according to literature methods [16,17]. We report modified methods to the synthesis of compounds **1** [12] and **3** [11] in which we have improved the yields. New low temperature solid state synthetic procedures with simplified workups are also presented for clusters **1**, **2** and **3**. The polymeric phases  $\{\text{Mo}_3\text{Se}_7\text{Cl}_4\}_x$ ,  $\{\text{Mo}_3\text{Se}_7\text{Br}_4\}_x$  and  $\{\text{W}_3\text{Se}_7\text{Br}_4\}_x$  which were used as precursors were prepared by solid state reactions following published procedures [12,22]. Solvents for synthesis and electrochemical measurements were dried and deoxygenated by standard methods before use. Chromatographic work was performed on Silica gel 60 Å.

$^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded on a Varian 300 MHz spectrometer, using  $\text{CH}_3\text{CN}$  with a reference scale

of 85%  $\text{H}_3\text{PO}_4$ . IR spectra were recorded on a Perkin-Elmer System 2000 FTIR spectrophotometer using KBr pellets. Cyclic voltammetry experiments were performed with a Echochemie Pgstat 20 electrochemical analyzer. All measurements were carried out with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and a  $\text{Ag}|\text{AgCl}$  reference electrode containing aqueous 3 M KCl. The solvent used in all experiments was  $\text{CH}_3\text{CN}$  (Merck isocratic grade). The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate, synthesized by reaction of tetrabutylammonium bromide and  $\text{HPF}_6$ , recrystallized from ethanol and dried under vacuum.  $E_{1/2}$  values were determined as  $1/2 (E_a + E_c)$ , where  $E_a$  and  $E_c$  are the anodic and cathodic peak potentials, respectively. All potentials reported were not corrected for the junction potential.

Optical measurements of sample solutions in acetonitrile were carried out in 1 mm thick glass cells. Linear optical spectra were obtained on a Cary 4 spectrophotometer over the spectral range 320–900 nm. The system for optical limiting studies employed a Q-switched diode-pumped Nd:YLF laser with a fundamental wavelength of 523 nm, pulse length 40 ns, repetition rate 20 Hz. The experiments were performed on solutions of concentrations such as to give transmission close to 50%. The power limiting curves were obtained by the open-aperture Z-scan technique [24], and the data were then converted into transmittance–fluence plots assuming Gaussian character of the beam, the  $w_0$  parameter of the beam being determined from the closed aperture Z-scan results.

### 4.2. Syntheses

#### 4.2.1. $[\text{Mo}_3\text{Se}_4\text{Cl}_3(\text{dppe})_3](\text{PF}_6)$ (**1**)

**4.2.1.1. Method 1.** To a suspension of  $\{\text{Mo}_3\text{Se}_7\text{Cl}_4\}_x$  (0.12 g, 0.11 mmol) in  $\text{CH}_3\text{CN}$  (25 ml) was added an excess of dppe (0.3 g, 0.75 mmol) under nitrogen and the reaction mixture was refluxed for 48 h. The colour of solution turned brown after 15 min. After filtration, the resulting brown solution was taken to dryness under reduced pressure, redissolved in  $\text{CH}_2\text{Cl}_2$  and adsorbed onto a silica gel column. The column was washed with  $\text{CH}_2\text{Cl}_2$  and acetone, after which elution with a  $\text{KPF}_6$  solution in acetone ( $1 \text{ mg ml}^{-1}$ ) afforded a very concentrated brown solution. This solution was taken to dryness, and redissolved in  $\text{CH}_2\text{Cl}_2$  in order to remove the insoluble KBr and  $\text{KPF}_6$ . Finally, diethylether was added to precipitate the desired air-stable brown product characterized as **4**. Yield: 0.21 g (85%).

**4.2.1.2. Method 2.** A mixture of  $\{\text{Mo}_3\text{Se}_7\text{Cl}_4\}_x$  (0.12 g, 0.11 mmol) and dppe (0.3 g, 0.75 mmol) was charged and sealed in a pyrex tube under vacuum and heated at

140 °C for 48 h. The desired cluster was extracted from the resulting brown residue with  $\text{CH}_2\text{Cl}_2$ , filtered, adsorbed onto a silica gel column and purified as described in method 1. Yield: 0.10 g (43%). *Anal.* Found: C, 45.44; H, 3.67%. Calc. for  $\text{C}_{78}\text{H}_{72}\text{Cl}_3\text{F}_6\text{Mo}_3\text{P}_7\text{Se}_4$ : C, 45.69; H, 3.54%. IR (KBr) ( $\text{cm}^{-1}$ ) 1484s, 1433s, 1190m, 1096m, 1026m, 998m, 840s (P–F), 740s, 693m, 557s (P–F), 513s, 486w, 410w, 370w.  $^{31}\text{P}$  NMR (121.47 MHz,  $\text{CH}_3\text{CN}$ ):  $\delta$  –140.7 (septet, 1P,  $J_{\text{P-F}} = 705$  Hz), 28.17 (dd, 3P), 43.49 (dd, 3P) (AA'A' BB'B' system). MS (ES+65 V):  $m/z = 1908 [M]^+$ ,  $1410 [M-\text{dppe}]^+$ .

#### 4.2.2. $[\text{Mo}_3\text{Se}_4\text{Br}_3(\text{dppe})_3](\text{PF}_6)$ (2)

This compound was prepared following Method 1 and Method 2 (described for **1**) by using dppe (0.4 g, 1 mmol) and  $\{\text{Mo}_3\text{Se}_7\text{Br}_4\}_x$  (0.20 g, 0.17 mmol) instead of  $\{\text{Mo}_3\text{Se}_7\text{Cl}_4\}_x$ . Yield: 0.25 g (67%) for Method 1 and 0.07 g (38%) for Method 2. *Anal.* Found: C, 42.97; H, 3.41%. Calc. for  $\text{C}_{78}\text{H}_{72}\text{Br}_3\text{F}_6\text{Mo}_3\text{P}_7\text{Se}_4$ : C, 42.90; H, 3.32%. IR (KBr) ( $\text{cm}^{-1}$ ) 1484s, 1434s, 1190m, 1097m, 1026m, 999m, 840s (P–F), 740s, 693m, 557s (P–F), 512s, 485w, 407w, 370w.  $^{31}\text{P}$  NMR (121.47 MHz,  $\text{CH}_3\text{CN}$ ):  $\delta$  –140.7 (septet, 1P,  $J_{\text{P-F}} = 705$  Hz), 23.85 (dd, 3P), 43.37 (dd, 3P) (AA'A' BB'B' system). MS (ES+65 V):  $m/z = 2039 [M]^+$ ,  $1641 [M-\text{dppe}]^+$ .

#### 4.2.3. $[\text{W}_3\text{Se}_4\text{Br}_3(\text{dppe})_3]\text{PF}_6$ (3)

This compound was prepared following Method 1 and Method 2 (described for **1**) by using dppe (0.2 g, 0.5 mmol) and  $\{\text{W}_3\text{Se}_7\text{Br}_4\}_x$  (0.13 g, 0.09 mmol) instead of  $\{\text{Mo}_3\text{Se}_7\text{Cl}_4\}_x$ . Yield: 0.17 g (75%) for Method 1 and 0.11 g (62%) for Method 2. *Anal.* Found: C, 38.34; H, 2.96%. Calc. for  $\text{C}_{78}\text{H}_{72}\text{Br}_3\text{F}_6\text{P}_7\text{Se}_4\text{W}_3$ : C, 38.28; H, 2.97%. IR (KBr) ( $\text{cm}^{-1}$ ) 1484s, 1434s, 1191m, 1096m, 1025m, 1000m, 840s (P–F), 740s, 693m, 557s (P–F), 518s, 493w, 419w, 371w.  $^{31}\text{P}$  NMR (121.47 MHz,  $\text{CH}_3\text{CN}$ ):  $\delta$  –140.7 (septet, 1P,  $J_{\text{P-F}} = 705$  Hz), –0.8 (s, 3P,  $J_{\text{P-W}} = 145$  Hz), 9.77 (s, 3P,  $J_{\text{P-W}} = 150$  Hz). MS (ES+65 V):  $m/z = 2301 [M]^+$ ,  $1903 [M-\text{dppe}]^+$ .

### 4.3. X-ray crystallographic study

Crystals of compound **1** suitable for X-ray studies were grown from an acetonitrile solution by slow evaporation at room temperature. The air-stable crystal was mounted on the tip of a glass fiber with the use of epoxy cement. The X-ray diffraction experiment was carried out on a Bruker SMART CCD diffractometer using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at room temperature. The data were collected with a frame width of  $0.3^\circ$  in  $\omega$  and a counting time of 20 s per frame at a crystal-to-detector distance of 4 cm. The diffraction frames were integrated using the SAINT package and corrected for absorption with SADABS [25,26].

The structure was solved by direct methods and refined by the full-matrix method based on  $F^2$  using the SHELXTL software package [27]. The crystal parameters and basic information relating data collection and structure refinement for compound **1** are summarized in Table 4.

Compound **1** is isostructural with  $[\text{Mo}_3\text{S}_4\text{Cl}_{2.25}\text{Br}_{0.75}(\text{dppe})_3](\text{BF}_4)_{0.5}\text{Cl}_{0.5}$  [17], both crystallizing in the monoclinic space group  $C2/c$ . The non-hydrogen atoms in the cation were refined anisotropically. Three disordered  $\text{PF}_6^-$  anions were found in general positions and were included in the model with partial occupancy to assure that the ratio cluster: $\text{PF}_6^-$  equals unity, compatible with the observed cluster charge. One of the  $\text{PF}_6^-$  anions was refined isotropically, and the phosphorus atoms of the other highly disordered  $\text{PF}_6^-$  anions were placed on the highest electronic density peak and refined isotropically; the fluorine atoms were geometrically generated, assigned isotropic thermal parameters and allowed to ride on their parent phosphorus atoms. The positions of methyl, methylene and phenyl hydrogen atoms were generated geometrically, assigned isotropic thermal parameters and allowed to ride on their respective parent carbon atoms. At this moment the difference Fourier map showed the presence of a half molecule of  $\text{CH}_3\text{CN}$ , which was refined isotropically leaving peaks with intensities ranging between 1.17 and  $-0.62 \text{ e } \text{Å}^3$  (see Table 4) in the final difference Fourier map. The largest electron density

Table 4  
Crystallographic data for  $[\text{Mo}_3\text{Se}_4\text{Cl}_3(\text{dppe})_3](\text{PF}_6) \cdot 0.5\text{CH}_3\text{CN}$  (**1**)

Empirical formula	$\text{C}_{79}\text{H}_{73.50}\text{Cl}_3\text{F}_6\text{Mo}_3\text{N}_{0.50}\text{P}_7\text{Se}_4$
Formula mass	2070.68
Crystal system	monoclinic
Space group	$C2/c$
$a$ (Å)	44.2012(14)
$b$ (Å)	13.9118(4)
$c$ (Å)	30.2126(9)
$\beta$ (°)	98.5660(10)
$V$ (Å <sup>3</sup> )	18371.0(10)
$Z$	8
$D_c$ (g cm <sup>-3</sup> )	1.497
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	2.248
$\theta$ Range (°)	0.93–24.71
Absorption correction	SADABS
Ratio of min. to max. apparent transmission	0.76
Refinement method	Full-matrix least-squares on $F^2$
Reflections collected	50037
Unique reflections $R_{\text{int}}$	15670/0.1006
Goodness-of-fit	0.968
$R_1^a/wR_2^b$ ( $I > 2\sigma$ )	0.0558/0.1457
$R_1^a/wR_2^b$ (all data)	0.1357/0.1786
Residual $\rho$ (e Å <sup>-3</sup> )	1.165/–0.622

<sup>a</sup>  $R_1 = \sum |F_o| - |F_c| / \sum F_o$ .

<sup>b</sup>  $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ .

residual is not connected to any of the cluster, anion or solvent molecules.

## 5. Supplementary material

Crystallographic data has been deposited with the Cambridge Crystallographic Data Center, CCDC No. 185999. These data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk/conts/retrieving.html>).

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