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## Note

# Oxoselenide triangular molybdenum clusters: Synthesis and characterization of $[Mo_3SeO_3(acac)_3(py)_3]PF_6$

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#### 1. Introduction

Triangular clusters  $Mo_3Q_4^{4+}$  (Q = S, Se) are key compounds in the synthesis of a vast range of homo and heterometal chalcogenide clusters. They can undergo reduction to give tetra-, hexa- and heptanuclear clusters of different types, and they are capable of incorporating some 20 transition and post-transition metals to give heterometal cuboidal clusters with unique reactivity and promising catalytic properties [1-3]. Their oxygen analogs with the Mo<sub>3</sub>O<sub>4</sub><sup>4+</sup> core are also known [4]. They possess a completely different reactivity and show neither tendency to clustering upon reduction nor to the incorporation of heterometals. Chemistry of the mixed oxo-sulfido, and especially of the oxo-selenido clusters is poorly explored, mainly because of the lack of the convenient and selective synthetic routes to the individual  $Mo_3Q_{4-x}O_x^{4+x}$ (x = 1-3) species [5]. Recently we have reported a simple and selective synthesis of Mo<sub>3</sub>SeO<sub>3</sub><sup>4+</sup> clusters by reductive self-assembly from  $[MoOCl_5]^{2-}$  and  $H_2Se$  in situ. The aqua complex  $[Mo_3SeO_3$  $(H_2O)_9$ <sup>4+</sup> now can be easily and selectively prepared in this way in moderate yields [6]. In this paper we report derivatization of

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#### ABSTRACT

New cluster complex  $[Mo_3SeO_3(acac)_3(py)_3]^+$  was obtained by ligand substitution in the aqua complex  $[Mo_3SeO_3(H_2O)_9]^{4+}$ . Crystal structure was determined for  $[Mo_3SeO_3(acac)_3(py)_3]PF_6\cdot C_6H_5CH_3$ . The complex was characterized by <sup>77</sup>Se NMR, electrospray mass-spectrometry, and cyclic voltammetry. DFT calculations were used to confirm the assignment of chemical shift and to study Mo–Mo bonding in the cluster core.

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the aqua complex and preparation and characterization of the first complex of the  $Mo_3SeO_3^{4+}$  cluster core with organic ligands,  $[Mo_3SeO_3(acac)_3(py)_3]PF_6 \cdot C_6H_5CH_3$ .

#### 2. Experimental

#### 2.1. Synthesis

The starting cluster aqua complex  $[Mo_3(\mu_3-Se)(\mu-O)_3(H_2O)_9]^{4+}$  was prepared as described in [6]. The stock solutions were kept at 4 °C under Ar. All the manipulations were done in air. Pyridine was distilled over BaO, and acetylacetone was distilled *in vacuo*. Other reagents were of commercial quality and used as purchased. DMF (Fluka) for electrochemical studies was dehydrated over so-dium carbonate for 1 week, and was doubly distilled thereafter under N<sub>2</sub> atmosphere and reduced pressure.

### 2.2. Synthesis of $[Mo_3(\mu_3-Se)(\mu_2-O)_3(acac)_3(py)_3]PF_6 \cdot C_6H_5CH_3$ (1)

To a stirred red solution of  $[Mo_3(\mu_3-Se)O_3(H_2O)_9]^{4+}$  in 4 M HCl (15 ml, 0.8 mM) 100 µl of Hacac (0.97 mmol) was added, followed by portionwise addition of KHCO<sub>3</sub> (ca. 1 g) until the color of the solution turned brown. Then 100 µl of pyridine (1.2 mmol) and



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 Table 1

 Crystal data, data collection and structure solution details.

Crystal data	
Chemical formula	C <sub>37</sub> H <sub>44</sub> M0 <sub>3</sub> N <sub>3</sub> O <sub>9</sub> SeF <sub>6</sub> P
$M_{ m r}$	1232.57
Crystal system, space group	triclinic, P1
Temperature (K)	100
a (Å)	14.1567(3)
b (Å)	15.1171(5)
c (Å)	15.4344(8)
α (°)	111.584(1)
β(°)	110.983(1)
γ (°)	100.690(1)
$V(Å^3)$	2669.51(17)
Ζ	2
$F(0\ 0\ 0)$	1226
Radiation type	Μο Κα
$\mu$ (mm <sup>-1</sup> )	1.47
Crystal size (mm)	0.27  imes 0.23  imes 0.15
Data collection	
Diffractometer	Bruker X8Apex CCD detector diffractometer
Absorption correction	empirical (using intensity measurements) based on intensities (sADABS,
	Bruker, 2005)
I <sub>min</sub> , I <sub>max</sub>	0.663, 0.802
Number of measured, independent and observed $[1 > 2\sigma(1)]$	30 126, 12 069, 9759
reflections	0.020
$\Lambda_{\text{int}}$	$b_{-} = 12 + 12 k_{-} = 10 + 10 k_{-} = 10 + 20$
Rafinement	$1110 \rightarrow 13, \ \kappa15 \rightarrow 19, \ 115 \rightarrow 20$
$P[F^2 > 2\sigma(F^2)] \rightarrow P(F^2) \leq C$	0.040 0.146 1.00
Number of reflections	12 069
Number of parameters	653
Number of restraints	5
H-atom treatment	H-atom parameters constrained
Weighting scheme	$w = 1/(\sigma^2(F_0^2) + (0.0781P)^2 + 7.6908P)$ , where $P = (F_0^2 + 2F_c^2)/3$
$\Delta \rho_{\rm max}, \Delta \rho_{\rm min}  ({\rm e}  {\rm \AA}^{-3})$	1.23, -0.46

Computer programs: Apex2 V.1.27 (Bruker, 2005), SHELXS97 (Sheldrick, 1990), SHELXL97 (Sheldrick, 1997), SHELXTL V6.22 (Bruker, 2000–2005), local programs.

 $0.07 \text{ g of NH}_4\text{PF}_6$  (0.43 mmol) were added in a quick succession and the solution was left stirring for 1 h. The brownish slurry was extracted with 20 ml of CH<sub>2</sub>Cl<sub>2</sub> for 30 min. The extract was separated, dried over CaCl<sub>2</sub> and the volume was reduced to 3 ml by rota-

evaporation. This solution was carefully layered with 2 ml of toluene in a thin tube, to give a crop of brown single crystals of **1** in a few days. Yield 70%. The solid can be handled for some time in air, but slowly converts into  $[Mo_3(\mu_3-O)(\mu_2-O)_3(acac)_3(py)_3]PF_6$  and



Fig. 1. View of the cluster cation  $[Mo_3(\mu_3-Se)(\mu_2-O)_3(acac)_3(py)_3]^+$ . Ellipsoids are shown with 50% probability.

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Selected bond	lengths	and	valence	angles (	(Å,	°)	ex	perimental	)
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2.6107 (5)	Mo2-03	1.908 (3)
2.6050 (5)	Mo2-N2	2.227 (4)
2.4983 (5)	Mo2-021	2.102 (3)
1.911 (3)	Mo2-022	2.085 (3)
1.917 (3)	Mo3-Se1	2.4996 (6)
2.239 (4)	Mo3-01	1.913 (3)
2.099 (3)	Mo3-O3	1.908 (3)
2.071 (3)	Mo3-N3	2.239 (4)
2.6033 (5)	Mo3-031	2.086 (3)
2.5006 (5)	Mo3-032	2.095 (4)
1.912 (3)		
104.01 (9)	021-Mo2-N2	84.20 (13)
95.36 (13)	022-Mo2-Se1	87.98 (8)
81.61 (13)	O22-Mo2-N2	86.01 (13)
88.68 (13)	022-Mo2-021	81.05 (12)
163.87 (13)	01-Mo3-Se1	103.90 (9)
103.39 (9)	01-Mo3-N3	83.41 (13)
83.43 (13)	01-Mo3-031	165.56 (14)
166.66 (13)	01-Mo3-032	89.36 (15)
91.86 (13)	O3-Mo3-Se1	103.89 (9)
170.52 (9)	03-Mo3-01	94.39 (12)
87.88 (9)	O3-Mo3-N3	81.67 (13)
84.60 (13)	03-Mo3-031	91.65 (14)
88.25 (9)	O3-Mo3-O32	165.55 (14)
84.93 (13)	N3-Mo3-Se1	170.25 (10)
81.24 (13)	O31-Mo3-Se1	87.30 (9)
103.45 (9)	O31-Mo3-N3	84.51 (13)
82.76 (13)	O31-Mo3-O32	81.71 (16)
165.99 (13)	O32-Mo3-Se1	88.68 (10)
92.95 (12)	O32-Mo3-N3	84.92 (14)
103.83 (9)	Mo1-Se1-Mo2	62.968 (15)
95.75 (12)	Mo1-Se1-Mo3	62.830 (15)
80.91 (13)	Mo3-Se1-Mo2	62.750 (15)
87.19 (12)	Mo1-01-Mo3	85.88 (12)
163.23 (13)	Mo2-O2-Mo1	85.97 (12)
171.59 (10)	Mo3-O3-Mo2	86.02 (12)
89.06 (9)		
	$\begin{array}{c} 2.6107 \ (5) \\ 2.6050 \ (5) \\ 2.4983 \ (5) \\ 1.911 \ (3) \\ 1.917 \ (3) \\ 2.239 \ (4) \\ 2.099 \ (3) \\ 2.071 \ (3) \\ 2.6033 \ (5) \\ 2.5006 \ (5) \\ 1.912 \ (3) \\ 104.01 \ (9) \\ 95.36 \ (13) \\ 81.61 \ (13) \\ 88.68 \ (13) \\ 163.87 \ (13) \\ 103.39 \ (9) \\ 83.43 \ (13) \\ 166.66 \ (13) \\ 91.86 \ (13) \\ 170.52 \ (9) \\ 84.60 \ (13) \\ 88.25 \ (9) \\ 84.60 \ (13) \\ 88.25 \ (9) \\ 84.60 \ (13) \\ 88.25 \ (9) \\ 84.93 \ (13) \\ 105.99 \ (13) \\ 85.75 \ (12) \\ 103.83 \ (9) \\ 95.75 \ (12) \\ 103.83 \ (9) \\ 95.75 \ (12) \\ 103.83 \ (9) \\ 95.75 \ (12) \\ 80.91 \ (13) \\ 87.19 \ (12) \\ 163.23 \ (13) \\ 171.59 \ (10) \\ 89.06 \ (9) \end{array}$	2.6107 (5)Mo2-O32.6050 (5)Mo2-N22.4983 (5)Mo2-O211.911 (3)Mo2-O221.917 (3)Mo3-Se12.239 (4)Mo3-O12.099 (3)Mo3-O32.071 (3)Mo3-N32.6033 (5)Mo3-O312.5006 (5)Mo3-O321.912 (3)104.01 (9)O21-Mo2-N295.36 (13)O22-Mo2-Se181.61 (13)O22-Mo2-N288.68 (13)O22-Mo2-N288.68 (13)O1-Mo3-Se1103.39 (9)O1-Mo3-O31166.66 (13)O1-Mo3-O31166.66 (13)O3-Mo3-O3187.88 (9)O3-Mo3-O384.60 (13)O3-Mo3-O3188.25 (9)O3-Mo3-O3284.93 (13)N3-Mo3-Se1103.45 (9)O31-Mo3-Se1103.45 (9)O31-Mo3-O3284.93 (13)N3-Mo3-Se181.24 (13)O31-Mo3-Se1103.45 (9)O31-Mo3-N382.76 (13)O32-Mo3-Se192.95 (12)O32-Mo3-Se195.75 (12)Mo1-Se1-Mo295.75 (12)Mo1-Se1-Mo380.91 (13)Mo3-Se1-Mo380.91 (13)Mo2-O2-Mo1171.59 (10)Mo3-O3-Mo289.06 (9)Set

must be kept under Ar. IR (KBr, cm<sup>-1</sup>): 1608s, 1568s, 1529s, 841s, 558m. ESI-MS (+) (CH<sub>2</sub>Cl<sub>2</sub>):  $[Mo_3(\mu_3-Se)(\mu_2-O)_3(acac)_3(py)_3]^+$  (*m*/*z* = 950),  $[Mo_3(\mu_3-Se)(\mu_2-O)_3(acac)_3(py)_2]^+$  (*m*/*z* = 870),  $[Mo_3(\mu_3-Se)(\mu_2-O)_3(acac)_3(py)_2]^+$  (*m*/*z* = 870),  $[Mo_3(\mu_3-Se)(\mu_2-O)_3(acac)_3(py)_2]^+$  (*m*/*z* = 792). <sup>77</sup>Se NMR ( $\delta$ , ppm, CDCl<sub>3</sub>, standard D<sub>2</sub>SeO<sub>3</sub>): 1356. *Anal.* Calc. for **1**: C, 36.0; H, 3.6; N, 3.4. Found: C, 35.4; H, 3.1; N, 3.2%.

#### 2.3. NMR studies

NMR studies of  $[Mo_3(\mu_3-Se)(\mu_2-O)_3(acac)_3(py)_3]^+$  in CDCl<sub>3</sub> solution at room temperature were carried out on a Bruker Avance 500 spectrometer operating at 95.38 MHz for <sup>77</sup>Se nucleus. <sup>77</sup>Se chemical shift was referenced to external H<sub>2</sub>SeO<sub>3</sub> ( $\delta$  = 1282 ppm) and then recalculated versus SeMe<sub>2</sub> ( $\delta$  = 0 ppm). The total range of scanned <sup>77</sup>Se shifts runs from –1000 to 2000 ppm.

#### 2.4. DFT calculations

Geometries of  $[Mo_3(\mu_3-Se)(\mu_2-O)_3(acac)_3(py)_3]^+$  cation and of the reference compounds SeMe<sub>2</sub> and H<sub>2</sub>SeO<sub>3</sub> were optimized with

Table 3		
Selected	ond lengths and valence angles (Å, °) (optimized	).

ADF2008 [7]. We used zero order regular approximation (ZORA) [8] to account for scalar relativistic effects together with BP density functionals [9–11]. Basis set consisted of relativistic Slater type orbitals of triple- $\zeta$  quality augmented with a set of polarized orbitals (TZP/ADF). Inner atomic shells were treated with frozen core approximation (Mo – 3d; Se – 3p; C, N, and O – 1s). NMR shieldings were calculated with DFT–GIAO method [12].

To characterize chemical bonding in the system we used topological analysis of Electron Localization Function (ELF) [13,14]. This method allows partitioning of the real space into chemically meaningful regions: core electrons, lone pairs, and covalent bonds. Values of ELF are unitless. The upper limit ELF = 1 corresponds to perfect localization and the value ELF = 0 means that no electrons are localized at this point. Since ELF is a scalar function, analysis of its gradient field can be carried out in order to locate its attractors (the local maxima) and corresponding basins (the region of space around the attractor that contains all ELF gradient trajectories that end at this attractor). Core basins (surrounding nuclei) are denoted by C(A) where A stands for the atomic symbol of the atom to which it belongs. V(A, B, ..., X) denotes a valence basin shared by atomic centers A, B, ..., X. Synaptic order of a valence basin is the number of core basins that have a common boundary with it. If there is a proton within this valence basin, it counts one for the synaptic order. Localization domain is the volume surrounded by the isosurface ELF = const. At low values of ELF, there is a single localization domain that contains the whole molecule. While ELF value increases, the single domain divides into several domains, enabling definition of chemical units within the system.

#### 2.5. X-ray crystallography

Crystallographic data and refinement details are given in Table 1. Crystals of **1** quickly lose solvent and become amorphous in air. Mineral oil was used to suppress the decay. The diffraction data were collected on a Bruker X8Apex CCD diffractometer with Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) by doing  $\phi$  and  $\omega$  scans of narrow (0.5°) frames at 100 K. Structure of 1 was solved by direct methods and refined by full-matrix least-squares treatment against  $|F|^2$  in anisotropic approximation with SHELXTL programs set [15]. Absorption corrections were applied empirically with sadabs program [16]. All non-hydrogen atoms of main structural units were refined anisotropically. The hydrogen atoms were refined in their geometrically calculated positions; a riding model was used for this purpose. The PF<sub>6</sub><sup>-</sup> anion was found to be disordered over two close positions with 0.6/0.4 occupancy ratio. Since solvent toluene molecules are severely disordered, most of their carbon atoms were refined in isotropic approximation, while the hydrogen atoms were not localized.

#### 2.6. Electrochemistry

Electrochemical measurements were carried with a Mod House 273 A EG and G PARC potentiostate/galvanostate. Glassy carbon electrode (GC, CHI 104, geometrical exposed area 12.6 mm<sup>2</sup>) was

Bond	Bond length (Å)	Angle	Angle value (°)	Angle	Angle value (°)
Mo1-Mo2	2.66	O1-Mo1-Se1	103	011-Mo1-Se1	89
Mo1-Se1	2.55	01-Mo1-02	95	O11-Mo1-N1	85
Mo1-01	1.94	01-Mo1-N1	82	012-Mo1-011	82
Mo1-011	2.12	01-Mo1-011	90	Mo1-Se1-Mo2	63
Mo1-N1	2.28	01-Mo1-012	165	Mo1-O1-Mo3	87
		N1-Mo1-Se1	172		



**Scheme 1.** ELF domain reduction in  $[Mo_3(\mu_3-Se)(\mu_2-O)_3(acac)_3(py)_3]^+$ .

**Table 4**Calculated $^{77}$ Se isotropic shielding  $\sigma^{iso}$  and chemicalshifts  $\delta^{calc}$  compared to experimental values  $\delta^{exp}$  (ppm).

	SeMe <sub>2</sub>	H <sub>2</sub> SeO <sub>3</sub>	[Mo <sub>3</sub> (μ <sub>3</sub> -Se)(μ <sub>2</sub> - O) <sub>3</sub> (acac) <sub>3</sub> (py) <sub>3</sub> ] <sup>+</sup>
$\sigma^{ m iso} \ \delta^{ m calc} \ \delta^{ m exp}$	1665	350	275
	0	1315	1390
	0	1282	1356

used as working electrode, and Pt wire as counter electrode. The reference electrode was Ag/AgCl/TMA chloride (saturated solution in 3:1 acetonitrile–DMF), however the potentials reported are referred to SCE in water. Scans were run at 5, 10, 25, 50, 100, 250, 350, 500 and 750 mV s<sup>-1</sup>. The parameters used in SWV were: frequency 2 Hz, pulse height 25 mV and scan increment of 4 mV. Background electrolyte was 0.1 M (Bu<sub>4</sub>N)ClO<sub>4</sub>. Ten milliliters of 0.53 mM solution of **1** in DMF was used in the experiments.

#### 3. Results and discussion

The preparation of **1** is based upon general approach for preparation of  $[M_3Q_4(acac)_3(py)_3]PF_6$  salts from the aqua complexes  $[M_3Q_4(H_2O)_9]^{4^+}$  (M = Mo, W; Q = S, Se) as described in [19]. The only-chalcogenide bridged  $M_3Q_4^{4+}$  cores are more robust then their mixed oxo-chalcogenide derivatives. Neutralization with KHCO<sub>3</sub> during the preparation must be done by very careful portionwise addition of the reagent with the amount just enough to make the pH sufficiently high for complexation to proceed, and the intermediate species, presumably  $[Mo_3SeO_3(acac)_3(H_2O)_3]^+$ , must be immediately converted into the pyridine-substituted derivative  $[Mo_3SeO_3(acac)_3(py)_3]^+$ , followed by rapid precipitation with NH<sub>4</sub>PF<sub>6</sub>. In this way formation of the oxo-cluster Mo<sub>3</sub>O<sub>4</sub><sup>4+</sup> through Se loss is averted.

The IR spectrum of **1** shows bands at 1608 cm<sup>-1</sup> attributable to coordinated py ( $\nu$  (C=C + C=N)), and two characteristic *acac* bands ( $\nu$  (C=C + C=O)) at 1568 and 1529 cm<sup>-1</sup>. The PF<sub>6</sub><sup>-</sup> anion gives very intense bands at 841 and 558 cm<sup>-1</sup>. ESI mass spectrum at low cone voltages shows dominant presence of the intact cluster cationic species [Mo<sub>3</sub>SeO<sub>3</sub>(acac)<sub>3</sub>(py)<sub>3</sub>]<sup>+</sup>. Upon harsher ionization conditions the spectra show characteristic fragmentation patterns from the sequential loss of the coordinated pyridine molecules, up to [Mo<sub>3</sub>SeO<sub>3</sub>(acac)<sub>3</sub>(py)<sub>3</sub>]<sup>+</sup>. Aged samples also show a signal from [Mo<sub>3</sub>O<sub>4</sub>(acac)<sub>3</sub>(py)<sub>3</sub>]<sup>+</sup>.

The crystal structure of **1** is built of triangular cluster cations  $[Mo_3(\mu_3-Se)(\mu_2-O)_3(acac)_3(py)_3]^+$  (Fig. 1,  $Mo-Mo_{(av)} = 2.606$  [3] Å) with three  $\mu_2$ -bridged oxo-ligands  $(Mo-\mu_2-O_{(av)} = 1.912[4]$  Å) and one apical selenium ligand  $(Mo-\mu_3-Se_{(av)} = 2.500$  [1] Å). The PF<sub>6</sub><sup>-</sup>



**Fig. 2.** ELF plots for selected planes: (a) plane containing three Mo atoms, (b) the plane containing one Se and two Mo atoms, and (c) the plane containing Se, Mo and  $\mu_2$ -O atoms (the plane is perpendicular to Mo-Mo bond). Isoline step is 0.05.

anions and toluene solvent molecules occupy the voids of the cationic arrangement. Selected bond distances and angles in the cluster complex are listed in Table 2. The Mo<sub>3</sub>SeO<sub>3</sub><sup>4+</sup> core in **1** appears to be slightly expanded in comparison with the same core in the supramolecular adduct with cucurbit[6]uril (Q6) {[Mo<sub>3</sub>( $\mu_3$ -Se)( $\mu$ -O)<sub>3</sub>(H<sub>2</sub>O)<sub>6</sub>Cl<sub>3</sub>]<sub>2</sub>{Q6}{Cl<sub>2</sub>·15H<sub>2</sub>O} (Mo-Mo 2.565(1) Å, Mo- $\mu_2$ -O<sub>(av)</sub> = 1.908(6) Å, Mo- $\mu_3$ -Se<sub>(av)</sub> = 2.492(2) Å) [6]. In all the known [M<sub>3</sub>Q<sub>4</sub>(acac)<sub>3</sub>(py)<sub>3</sub>]<sup>+</sup> complexes [19], the *acac*<sup>-</sup> ligands occupy



Fig. 3. Bonding between molybdenum atoms: valence basins V(Mo, Mo) and V(Mo, Mo, Mo). Isosurface ELF = 0.395.



Fig. 4. CV for freshly prepared solution of 1 in DMF at different scan rates.



Fig. 5. CV for freshly prepared solution of 1 in DMF at different scan rate in terms of normalized current.



Fig. 6. Square wave voltammetry of 1.

*cis*-positions to the capping selenium atom  $(Mo-O_{(av)} = 2.09(2) \text{ Å})$ , and the pyridine ligands occupy the trans-positions (Mo-N<sub>(av)</sub> = 2.233(6) Å). The Mo-O and Mo-N bonds in **1** are distinctively shorter than in the sulfide cluster cation  $[Mo_3S_4(acac)_3 (py)_3]^+$  (2.121(3) and 2.262(5) Å), respectively.

We found one narrow <sup>77</sup>Se NMR signal at  $\delta$  = 1356 ppm in solutions of **1** in CDCl<sub>3</sub>. Half-width of the signal was 4.3 Hz. This proves that only one type of Se-containing species is present in the solution. Observed shift value is much higher then known  $\mu_3$ -Se chemical shifts in the trinuclear molybdenum clusters with one capping Se and three bridging Se<sub>2</sub> ligands (76.9 ppm in [Mo<sub>3</sub>( $\mu_3$ -Se)( $\mu_2$ -Se<sub>2</sub>)<sub>3</sub>(Se<sub>2</sub>P(OCH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>]Br [13], 666.4 ppm in [Mo<sub>3</sub>( $\mu_3$ -Se)( $\mu_2$ -Se<sub>2</sub>)<sub>3</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>2-</sup> [14]). Nevertheless, it falls in the known range of NMR shifts for  $\mu_3$ -Se atoms in transition metal clusters (from –608.1 ppm [17] to 2066 ppm [18]).

In order to confirm that the observed value of <sup>77</sup>Se chemical shift really corresponds to the  $[Mo_3(\mu_3-Se)(\mu_2-O)_3(acac)_3(py)_3]^+$  species, DFT calculations have been carried out. The geometry of  $[Mo_3(\mu_3-Se)(\mu_2-O)_3(acac)_3(py)_3]^+$  was optimized starting from atomic coordinates taken from the X-ray data. Resulting cluster has C<sub>3</sub> symmetry. Interatomic distances (Table 3) turned out to be slightly longer then the experimental values (Table 2), while valence angles were almost the same. We calculated <sup>77</sup>Se isotropic magnetic shielding and NMR chemical shifts in the optimized  $[Mo_3(\mu_3-Se)(\mu_2-O)_3(acac)_3(py)_3]^+$  cation, and in two reference compounds SeMe<sub>2</sub> and H<sub>2</sub>SeO<sub>3</sub> (Table 4). All calculated values are in good agreement with experimental data and thus unequivocally confirm the identity of the Se-containing species in solution as  $[Mo_3(\mu_3-Se)(\mu_2-O)_3(acac)_3(py)_3]^+$ .

Bonding hierarchy inside the  $[Mo_3(\mu_3-Se)(\mu_2-O)_3(acac)_3(py)_3]^+$ cation is shown by electron localization domain reduction scheme (Scheme 1). Core domains of light atoms and valence domains of pyridine and acetylacetone separate form  $\{Mo_3(\mu_3-Se)(\mu_2-O)_3\}^{4+}$ cluster core at ELF = 0.15–0.16, thus indicating that the {Mo<sub>3</sub>( $\mu_3$ -Se)( $\mu_2$ -O)<sub>3</sub>}<sup>4+</sup> core is an individual chemical unit. If we further assume that, like  $\mu_2$ -O atoms,  $\mu_3$ -Se atom takes up two electrons to become Se<sup>2–</sup>, there are two electrons left for each molybdenum atom. In consequence, we might expect three ordinary two-center two-electron Mo-Mo bonds and no multicenter bonds (the concept of multicenter bonding was developed for electron deficient systems [20]). Absence of V(Se, Mo) valence basins confirms essentially ionic nature of bonding between selenium and three molybdenum atoms. Nevertheless, along with three disynaptic V(Mo, Mo) basins, there is a trisynaptic basin V(Mo, Mo, Mo) that indicates presence of three-center bond (Fig. 2) [22]. The V(Mo, Mo)

**Table 5** Peak potential variations ( $E_p$  and  $\Delta E_p$ ) as function of scan rate.

$v/(V s^{-1})$	$E_p a^1 1/V$	$E_p a^{II} 1/V$	$E_p a_2/V$	$E_p a_3 / V$	$E_p c1/V$	$E_p c2/V$	$E_p c3/V$	$\Delta E_p^2$ (a2–c2)	$\Delta E_p^3$ (a3–c3)
0.005	0.009	-	-0.623	-	-0.333	-0.705	-0.881	0.082	-
0.01	0.0043	-	-0.620	-	-0.322	-0.697	-0.883	0.077	-
0.025	0.000	-	-0.627	-	-0.362	-0.702	-0.880	0.075	-
0.05	-0.005	-0.184	-0.621	-	-0.415	-0.697	-0.883	0.076	-
0.1	-0.011	-0.166	-0.620	-0.812	-0.445	-0.689	-0.894	0.074	0.082
0.250	-	-0.126	-0.604	-0.811	-	-0.686	-0.907	0.082	0.096
0.350	-	-0.114	-0.598	-0.801	-	-0.698	-0.905	0.100	0.104
0.5	-	-0.096	-0.589	-0.798	-	-0.708	-0.917	0.119	0.119
0.7	-	-0.071	-0.567	-0.768	-	-0.731	-0.939	0.164	0.171

basins have common borders with the V(Mo, Mo, Mo) basin and the difference between ELF values at the turning points and at the attractors is 0.02 (Fig. 3). Thus, as it was suggested in [21], it is more chemically meaningful to consider the union of the corresponding basins rather than the individual basins themselves. Similar bonding picture was observed in model sulfide cluster  $[Mo_3(\mu_3-S)(\mu_2-S)_3(PH_3)_6Cl_3]^+$  [22].

#### 3.1. Cyclic voltammetry

Fig. 4 shows CV for freshly prepared solution of 1 in DMF at different scan rate. Three cathodic peaks (c1, c2 and c3) and four anodic peaks (**a**<sup>I</sup>1, **a**<sup>II</sup>1, **a**2 and **a**3) are observed at low scan rates. Increase in the scan rate causes gradual disappearance of **c1** and **a<sup>1</sup>1**, as can be better seen in Fig. 5, where normalized current value (i.e., divided by  $v^{1/2}$ ), is given. Fig. 6 shows square wave voltammetry results. Clearly distinguishable are two reversible peaks in the negative area and one quasi reversible peak in the positive area. The negative peaks agree well with the two most negative peaks in the CV. All the results are summarized in Table 5, where the values of  $\Delta E_p (E_p^a - E_p^c)$  are also given. From all these observations we can conclude that c2/a2 and c3/a3 couples correspond to quasi reversible processes. At low scan rates the peak potentials are virtually the same in both cases, however,  $\Delta E_p$  is higher than is required for a perfectly reversible couple. Increase in scan rates displaces the potentials to more negative, and more positive values, respectively. Standard redox potentials for both systems,  $E_{\rm redox}^{\circ}$ , were determined as  $-0.650 \pm 0.005$  V and  $-0.855 \pm 0.002$  V, respectively. In agreement with the published electrochemical behavior of various  $M_3Q_4^{4+}$  clusters, including those with the closely related  $\{Mo_3(\mu_3-S)(\mu_2-O)_3\}^{4+}$  core [23], we can assign the negative potential waves to two consecutive one-electron reductions in the cluster core:

$$Mo_3^{IV}SeO_3^{4+} \rightarrow Mo_2^{IV}Mo^{III}SeO_3^{4+} \rightarrow Mo^{IV}Mo_2^{III}SeO_3^{4+}.$$

In  $[Mo_3Se_4(acac)_3(py)_3]^+$  corresponding processes were observed at  $E_{1/2}$  -0.85 and -0.98 V, respectively [19]. As could be expected, when more electronegative oxide ligands replace selenides in the cluster core, the latter becomes more easily reducible. The **c1** and **a**<sup>1</sup>**1** peaks can be tentatively assigned to cluster core oxidation which gives unstable species.

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#### Appendix A. Supplementary material

CCDC 786056 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011. 05.007.

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