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# Synthesis, Structure, and Properties of the $[Mo_2Q_2(\mu\text{-}Se)_2(\eta^2\text{-}Se_2)_2]^{2-}$ (Q = O, Se) Ions: Influence of Mo–Q $\pi$-Bonding

**Bryan W. Eichhorn,***[,1a] **Donna R. Gardner,**[1a] **Ann Nichols-Ziebarth,**[1a] **Kazi J. Ahmed,**[1b] **and Simon G. Bott**[1c]

Departments of Chemistry, University of Maryland,
College Park, Maryland 20742, University of Vermont,
Burlington, Vermont 05405, and University of North Texas,
Denton, Texas, 76203

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Herein we report the preparation, structure, and properties of two polyselenide complexes: $[Mo_2Se_2(\mu\text{-}Se)_2(\eta^2\text{-}Se_2)_2]^{2-}$ (**1**) and its oxo analog $[Mo_2O_2(\mu\text{-}Se)_2(\eta^2\text{-}Se_2)_2]^{2-}$ (**2**). Both **1** and **2** have polysulfide analogs,[2,3] and the *trans* Te analog of **2** was recently prepared in a concurrent study by Kolis et al.[4] The structural and spectroscopic features of **1** and **2** and their sulfur analogs provide an unambiguous illustration of $\pi$-bonding effects in complexes containing terminal Mo–Q functions [Q = O, S, Se].

## Experimental Section

**General Procedures.** All reactions were conducted under dry oxygen-free $N_2$ atmospheres by using standard Schlenk techniques or a Vacuum Atmospheres Co. drybox. The mid-IR spectra were obtained from pressed KBr pellets using a Nicolet 283 infrared spectrophotometer under $N_2$. Far-IR spectra were obtained from high-density polyethylene pellets using a Perkin-Elmer FTIR 1800 spectrophotometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY, and Desert Analytics, Tucson, AZ. $^{77}Se$ NMR spectra were recorded on a Bruker AM-400 (76.3 MHz) spectrometer. Spectra were run locked [dimethyl-$d_6$ sulfoxide (DMSO-$d_6$)] or unlocked [*N,N*-dimethylformamide (DMF)] and referenced to an external $(PPh_4)_2[MoSe_4]$ standard in DMF ($\delta$ = 1643 ppm).[5a] Cyclic voltammograms were run in a standard three-electrode glass cell with an SCE reference electrode, a Pt-wire counter electrode, and a Pt-wire microelectrode (20-$\mu$m diameter). The cyclic voltammograms were referenced against the $Fe(C_5H_5)_2/Fe(C_5H_5)_2^+$ couple, which is defined as 0.0 V, and were run with no supporting electrolyte. Approximately 2.5 mL of 1 mM solutions of compounds **1** and **2** in DMF were loaded into airtight glass cells in a drybox.

**Chemicals.** $(PPh_4)_2[MoSe_4]$ and $Mo_2(O_2CMe)_4$ were prepared according to published procedures.[5,6] $K_2Se_4$ was prepared in an $N_2$ atmosphere by reacting stoichiometric ratios of K and Se in liquid $NH_3$ distilled from Na metal. Solvents were purified, dried, distilled, and stored under $N_2$ with molecular sieves. Crystalline 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (2,2,2-crypt), *N*-methylmorpholine *N*-oxide (NMO) and $PPh_4Br$ were purchased from Aldrich and used without further purification.

**Synthesis. $(PPh_4)_2[Mo_2Se_2(\mu\text{-}Se)_2(\eta^2\text{-}Se_2)_2]\cdot{}^1/_2en$.** $Mo_2(O_2CMe)_4$ (100 mg, 0.23 mmol) and $K_2Se_4$ (276 mg, 0.70 mmol) were dissolved in ethylenediamine (en) (4 mL), forming a dark brown solution. The mixture was stirred for 3 h and filtered twice through glass wool to remove the colorless $KO_2CMe$ precipitate. After filtration, an en solution (~2 mL) of $PPh_4Br$ (245 mg, 0.58 mmol) was added to the reaction mixture. The solution was concentrated to *ca.* 2 mL and refiltered, and after 2 weeks at room temperature, well-formed dark block-shaped crystals were isolated (202-mg total crystalline yield, 57% based on Mo). Anal. Calcd for $Mo_2Se_8P_2NC_{49}H_{44}$: C, 38.46; H, 2.90; N, 0.92. Found: C, 39.18; H, 3.06; N, 1.22. Pertinent IR data (cm$^{-1}$): 370 (m), 301 (m). $^{77}Se$ NMR (DMF, 296 K) (ppm): 290, 1133, 2376.

**Table I.** Summary of Crystallographic Data[a]

| | A | B |
|---|---|---|
| formula | $C_{49}H_{44}Mo_2NP_2Se_8$ | $C_{36}H_{72}K_2Mo_2N_4O_{14}Se_6$ |
| space group | $P\bar{1}$ | $P\bar{1}$ |
| $a$ (Å) | 11.048(1) | 11.135(3) |
| $b$ (Å) | 12.206(1) | 12.349(4) |
| $c$ (Å) | 20.380(2) | 21.785(8) |
| $\alpha$ (deg) | 90.504(8) | 78.37(3) |
| $\beta$ (deg) | 99.469(8) | 79.40(2) |
| $\gamma$ (deg) | 105.568(7) | 74.48(2) |
| $V$ (Å$^3$) | 2607.1(5) | 2799(1) |
| $Z$ | 2 | 2 |
| $D_c$ (g/cm$^3$) | 1.959 | 1.813 |
| $\mu$ (cm$^{-1}$) | 60.94 | 53.2 |
| $2\theta$ range | 2–44 | 4–55 |
| no. of reflns collcd | 6362 | 13578 |
| no. of unique reflns | 6362 | 12877 |
| $R_{merg}$ | N/A | 3.99 |
| no. of obsd reflns | 2840 [$I > 3\sigma(I)$] | 6155 [$F > 6\sigma(F)$] |
| $R^b$ | 0.0561 | 0.051 |
| $R_w{}^b$ | 0.0669 | 0.068 |
| GOF | 0.96 | 0.90 |
| refn:param | 9.2 | 10.7 |

[a] A = $(PPh_4)_2[Mo_2Se_2(\mu\text{-}Se)_2(\eta^2\text{-}Se_2)_2]\cdot{}^1/_2en$; B = $[K(2,2,2\text{-}crypt)]_2[Mo_2O_2(\mu\text{-}Se)_2(\eta^2\text{-}Se_2)_2]$. [b] $R = \sum||F_o|-|F_c||/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|) + 0.004(|F_o|^2)$.

**$[K(2,2,2\text{-}crypt)]_2[Mo_2O_2(\mu\text{-}Se)_2(\eta^2\text{-}Se_2)_2]$.** The procedure is the same as that described for $(PPh_4)_2[Mo_2Se_2(\mu\text{-}Se)_2(\eta^2\text{-}Se_2)_2]\cdot{}^1/_2en$ except NMO (55 mg, 0.47 mmol) was added as a solid to the en solution of $Mo_2(O_2CMe)_4$ and $K_2Se_4$. After filtration, 2,2,2-crypt (176 mg, 0.48 mmol) was added to the filtrate as a solid. After 6 days, well-formed dark needles were isolated (197-mg total crystalline yield, 55% based on Mo). Anal. Calcd for $K_2Mo_2Se_6O_{14}C_{36}H_{72}N_4$: C, 28.28; H, 4.75; N, 3.66. Found: C, 28.98; H, 5.07; N, 4.18. Pertinent IR data (cm$^{-1}$): 1006 (m), 351 (m), 312 (m), 233 (b, w), 144 (m). $^{77}Se$ NMR (DMSO-$d_6$, 296 K) (ppm): 130, 702.

**Crystallography.** Summaries of the single-crystal X-ray studies for compounds **1** and **2** are given in Table I. Experimental details and fractional coordinates have been deposited in the supplementary material.

**$(PPh_4)_2[Mo_2Se_2(\mu\text{-}Se)_2(\eta^2\text{-}Se_2)_2]\cdot{}^1/_2en$.** The cell parameters for a black elongated block crystal were based on a least-squares refinement of 25 reflections with $2\theta > 26°$. A total of 6362 reflections were collected in the range $2° < 2\theta < 44°$, of which 2840 ($I > 3\sigma$(I)) were used for structure solution and refinement. The data indicated the triclinic space group $P\bar{1}$ (No. 2). The data were corrected for polarization and absorption (DIFABS),[7] but no correction was made for extinction.

The structure was solved by using MULTAN,[8] which revealed the positions of the Mo and Se atoms. All remaining non-hydrogen atoms were located using difference Fourier maps and least-squares refinement (MOLEN).[9] The Mo, Se, and P atoms were refined with anisotropic thermal parameters. Hydrogen atoms were generated and allowed to ride on the appropriate carbon [$U(H) = 1.3U_{eq}(C)$]. After the final cycle of least-squares refinement, the maximum shift of a parameter was less than 0.02 of its estimated standard deviation, and the final difference map showed no feature higher than 1.19 e/Å$^3$ close to Mo(1).

**$[K(2,2,2\text{-}crypt)]_2[Mo_2O_2(\mu\text{-}Se)_2(\eta^2\text{-}Se_2)_2]$.** A black needle-shaped crystal was coated with epoxy, glued onto a glass fiber, and mounted on the goniometer. The cell constants and orientation matrix for data collection were based on 25 carefully centered reflections in the range $20° < 2\theta < 30°$. Acceptable $\omega$–$2\theta$ scans over the $2\theta$ range 4.5–55° produced 12 877 unique reflections, of which 6155 ($I > 3\sigma(I)$) were used for structure refinement. The data indicated the triclinic space group $P\bar{1}$

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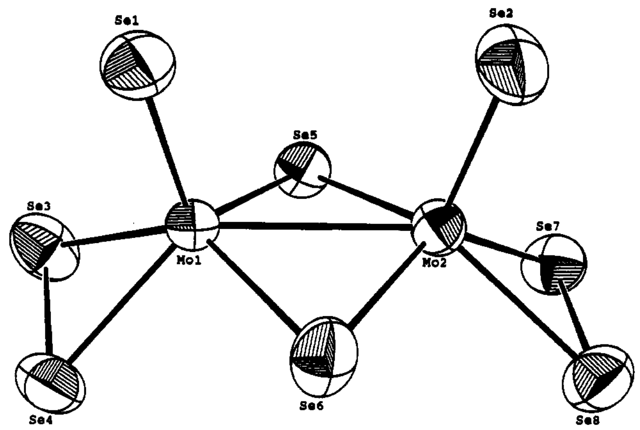

**Figure 1.** ORTEP drawing of the $[Mo_2Se_2(\mu\text{-}Se)_2(\eta^2\text{-}Se_2)_2]^{2-}$ ion (**1**). A common atomic numbering scheme is used for **1** and **2** in Table I.

(No. 2). The structure was solved by a combination of direct methods and heavy-atom Fourier techniques (Siemens SHELXTL PLUS crystallographic package). The hydrogen atoms were placed in calculated positions. The maximum shift/esd in the last cycle of refinement was less than 0.03, and the maximum residual electron density in the final difference Fourier map was <1.52 e/Å$^3$. No absorption correction was applied.

## Results

**Synthesis and Reactivity.** The $[Mo_2Se_2(\mu\text{-}Se)_2(\eta^2\text{-}Se_2)_2]^{2-}$ anion (**1**) was prepared from $Mo_2(O_2CMe)_4$ and 3.0 equiv of $K_2Se_4$ in ethylenediamine (en). Crystals of the $PPh_4^+$ salt of **1** were isolated in 57% yield. The $[Mo_2O_2(\mu\text{-}Se)_2(\eta^2\text{-}Se_2)_2]^{2-}$ ion (**2**) was prepared in a similar manner except 2 equiv of *N*-methylmorpholine *N*-oxide (NMO)/equiv of $Mo_2(O_2CMe)_4$ was added as an oxygen atom source. The $[K(2,2,2\text{-crypt})]^+$ salt of **2** was isolated in 55% yield. Both compounds are stable to air over short periods of time and have been characterized by energy-dispersive X-ray analysis (EDX), cyclic voltammetry, microanalysis, $^{77}$Se NMR and far-IR spectroscopy, and single-crystal X-ray diffraction.

Spectroscopic studies (IR and $^{77}$Se NMR) on crude products from the synthesis of **1** often revealed small quantities (<15%) of $[MoSe_4]^{2-}$ (**3**).[5a] To determine if **3** is formed as an intermediate in the synthesis of **1** or as a competitive byproduct, alternative synthetic procedures were attempted. Coyle, Stiefel, and coworkers have shown that $[MoS_4]^{2-}$ reacts cleanly with RSSR reagents to form the polysulfide complex $[Mo_2S_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)_2]^{2-}$ (**4**) according to eq 1.[2,10]

$$2[MoS_4]^{2-} + RSSR \rightarrow \underset{\mathbf{4}}{[Mo_2S_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)_2]^{2-}} + 2RS^- \qquad (1)$$

Analogous reactions between **3** and PhSeSePh did not yield **1** even after 6 h at 135 °C. IR analysis of the reaction mixture revealed **3** as the only Mo═Se-containing species. Identical results were obtained from reactions between **3** and en solutions of excess $Se_4^{2-}$. Previous studies[5] have shown that **3** reacts with Se metal to form $[MoSe(Se_4)_2]^{2-}$, which was also not observed in the reactions just described.

**Structural Considerations.** The ORTEP drawing of **1** shown in Figure 1 is given as an example of the isostructural $[Mo_2Q_2(\mu\text{-}Se)_2(\eta^2\text{-}Se_2)_2]^{2-}$ ions where Q = O, Se. A listing of selected bond distances and angles for both compounds is given in Table II. Both compounds possess terminal Mo–Q functions and symmetrically bound $\eta^2\text{-}Se_2^{2-}$ ligands on each Mo atom. The two Mo atoms are bridged by two $Se^{2-}$ ligands. The Mo–O distances in **2** (1.69(2) Å (average)) are identical to those of $[Mo_2O_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)_2]^{2-}$ (**5**)[3] and related *cis*-dioxo $Mo_2$ complexes[11] whereas the terminal Mo–Se bonds in **1** (2.237(9) Å (average)) are quite short in comparison with those of $[MoSe(Se_4)_2]^{2-}$ (2.270(4) Å) and $[MoSe_4]^{2-}$ (2.293(1) Å).[5] The Mo–Mo distances of 2.876(3) Å for **1** and 2.888(2) Å for **2** are typical of d$^1$–d$^1$ dimers with Mo–Mo single bonds. The ions have virtual $C_{2v}$ point symmetry and are essentially isostructural with their polysulfide analogs.[2,3]

**Table II.** Selected Bond Distances (Å) and Angles (deg) for $[Mo_2Q_2(\mu\text{-}Se)_2(\eta^2\text{-}Se_2)_2]^{2-}$ Ions Where Q = Se (1) and Q = O (2)[a]

| | Q = Se | Q = O |
|---|---|---|
| Mo(1)–Mo(2) | 2.876(3) | 2.888(2) |
| Mo(1)–Se(3) | 2.491(4) | 2.538(2) |
| Mo(1)–Se(4) | 2.548(4) | 2.545(2) |
| Mo(1)–Q(1) | 2.243(3) | 1.672(6) |
| Mo(1)–Se(5) | 2.415(3) | 2.456(1) |
| Mo(1)–Se(6) | 2.430(3) | 2.445(2) |
| Mo(2)–Se(5) | 2.442(3) | 2.453(2) |
| Mo(2)–Se(6) | 2.436(4) | 2.446(2) |
| Mo(2)–Q(2) | 2.231(4) | 1.702(6) |
| Mo(2)–Se(7) | 2.527(3) | 2.540(2) |
| Mo(2)–Se(8) | 2.528(3) | 2.544(2) |
| Se(3)–Se(4) | 2.317(4) | 2.342(2) |
| Se(7)–Se(8) | 2.334(4) | 2.338(2) |

| | Q = Se | Q = O |
|---|---|---|
| Mo(2)–Mo(1)–Se(4) | 131.0(1) | 138.8(1) |
| Mo(2)–Mo(1)–Se(3) | 137.8(1) | 137.0(1) |
| Mo(2)–Mo(1)–Q(1) | 105.9(1) | 104.2(3) |
| Mo(2)–Mo(1)–Se(5) | 54.11(8) | 53.9(1) |
| Mo(2)–Mo(1)–Se(6) | 53.86(9) | 53.8(1) |
| Se(4)–Mo(1)–Se(3) | 54.7(1) | 54.9(1) |
| Se(4)–Mo(1)–Q(1) | 114.1(1) | 105.6(3) |
| Se(4)–Mo(1)–Se(5) | 127.9(1) | 135.7(1) |
| Se(4)–Mo(1)–Se(6) | 86.8(1) | 90.2(1) |
| Se(3)–Mo(1)–Se(5) | 88.6(1) | 88.5(1) |
| Se(3)–Mo(1)–Se(6) | 137.2(1) | 135.4(1) |
| Q(1)–Mo(1)–Se(5) | 110.2(1) | 109.4(2) |
| Q(1)–Mo(I)–Se(6) | 107.8(1) | 107.5(2) |
| Se(5)–Mo(1)–Se(6) | 107.5(1) | 104.0(1) |
| Se(3)–Mo(1)–Q(1) | 105.2(1) | 108.2(3) |
| Mo(1)–Se(4)–Se(3) | 63.9(1) | 62.4(1) |
| Mo(1)–Se(3)–Se(4) | 61.4(1) | 62.7(1) |
| Mo(1)–Se(5)–Mo(2) | 72.6(1) | 72.1(1) |
| Mo(1)–Se(6)–Mo(2) | 72.5(1) | 72.4(1) |

[a] See Figure 1 for numbering scheme. For compound **2**, the same numbering scheme is used except Se(1) and Se(2) are replaced by O(1) and O(2).

**Spectroscopic Studies.** The $^{77}$Se NMR spectrum of **1** in DMF shows a downfield resonance at 1133 ppm due to the $\mu$-Se$^2$ ligands and an upfield resonance at 290 ppm due to the $\eta^2\text{-}Se_2^{2-}$ ligands. The peak for the terminal Se ligand of **1** appears at 2376 ppm. The $^{77}$Se NMR spectrum in DMSO-$d_6$ gave essentially the same chemical shifts at 300, 1134, and 2387 ppm. In a few of the samples, small amounts of $[MoSe_4]^{2-}$ (**3**) were detected in the $^{77}$Se NMR spectra of **1**, as evidenced by its characteristic 1643 ppm resonance.[5a] Its identity was confirmed by adding authentic **3** to the sample, which gave rise to a single peak. The $\mu\text{-}Se^{2-}$ and $\eta^2\text{-}Se_2^{2-}$ resonances of **2** (DMSO-$d_6$) appear at 702 and 130 ppm, respectively, and are shielded relative to those of **1**. These chemical shifts are in the range reported for other M–$\mu$-Se–M and M–$\eta^2$-Se$_2$ ligands.[12]

The IR spectrum of the $PPh_4^+$ salt of **1** shows two low-frequency bands at 370 and 301 cm$^{-1}$ associated with the anion. The former is assigned to the terminal Mo–Se stretch. For comparison, the $\nu$(Mo–Se) bands for $[MoSe(Se_4)_2]^{2-}$ and **3** appear at 360 and 340 cm$^{-1}$, respectively.[5a]

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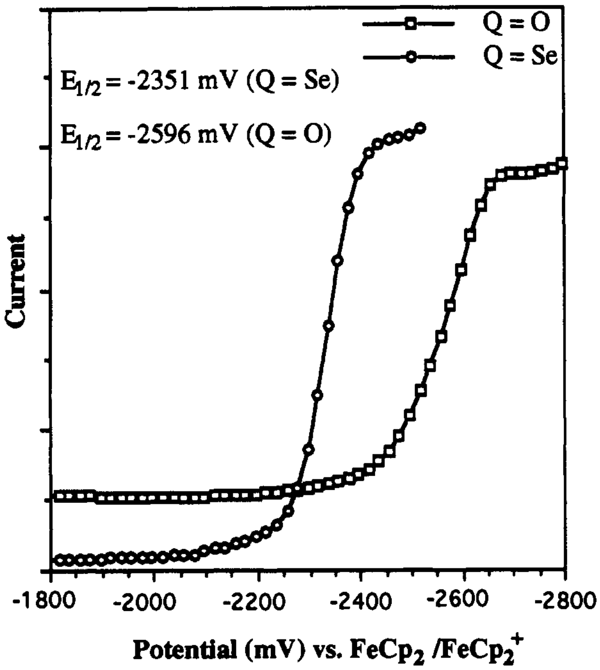

**Figure 2.** Reduction waves of 1 mM solutions (DMF, no electrolyte) of the $[Mo_2Q_2(\mu\text{-}Se)_2(\eta^2\text{-}Se_2)_2]^{2-}$ ions **1** (Q = Se) and **2** (Q = O) recorded using a Pt microelectrode (20 $\mu m^2$). The potentials are referenced to the $FeCp_2/FeCp_2^+$ couple (0.0 V) as described in the Experimental Section.

The IR spectrum of the $[K(2,2,2\text{-crypt})]^+$ salt of **2** shows a $\nu$(Mo–O) band at 1006 $cm^{-1}$ and medium-intensity bands at 351, 312, and 144 $cm^{-1}$.

**Electrochemistry.** The cyclic voltammetric studies of anions **1** and **2** were conducted to compare the effect of the terminal Mo–Q group on the redox behavior of these compounds. The compounds showed reductions at –2351 and –2596 mV, respectively, in DMF versus $Fe(C_5H_5)_2/Fe(C_5H_5)_2^+$ (microelectrode, no electrolyte). The reduction waves are shown in Figure 2 for comparison. The observed currents were consistent with one-electron processes, and no oxidation waves were detected out to the solvent cutoff (~+0.5 V versus $Fe(C_5H_5)_2/Fe(C_5H_5)_2^+$). It is interesting to note that it is significantly easier to reduce compound **1** than it is **2**, which is opposite to expectations based on electronegativity arguments.

## Discussion

The Mo–Mo, Mo–Se, and Se–Se contacts in the $Mo_2Se_6$ centers of both **1** and **2** are in the expected ranges[12] for compounds of this type. However, the bonds in $Mo_2Se_6$ center of **1** are without exception 0.008–0.040 Å shorter than the corresponding contacts in **2** (average difference = 0.021 Å). In fact, the same situation exits in sulfide[2] and oxide[3] analogues **4** and **5** where the Mo–Mo, Mo–S, and S–S contacts in the $Mo_2S_6$ center of the homoleptic sulfide complex **4** are on average 0.017 Å shorter[13] than the corresponding contacts in the oxo complex **5**. These trends are consistent with greater electron density in the $Mo_2^{10+}$ centers of the oxo compounds relative to their non-oxo counterparts. The Mo atoms in an electron-rich $Mo_2$ center would have larger effective atomic radii (longer Mo–Mo and Mo–Se bonds) and in turn would leave the $\eta^2\text{-}Q_2$ fragments in a more reduced state (longer Q–Q bonds). The relative electronegativities of oxygen versus sulfur and selenium would tend to produce the opposite effect. However, the superior $\pi$-bonding ability of an oxide ligand relative to a sulfide or a selenide ligand could produce the observed structural trends. The electrochemical studies show that it is easier to reduce **1** than **2** which is also consistent with $\pi$ bonding effects.

The $\nu$(Mo=Se) stretching frequencies and the $^{77}Se$ NMR chemical shifts of the terminal Se ligands of **1**, **3**, and $[MoSe(Se_4)_2]^{2-}$ correlate with the Mo—Se bond distances. The longer Mo—Se interactions give rise to upfield $^{77}Se$ chemical shifts and lower frequency $\nu$(Mo=Se) stretches.[5a] It has been well established that NMR chemical shift data are *not* reliable indications of absolute bond order or the electron density at a nucleus,[14–16] and the correlations observed thus far may be purely coincidental. Ibers and co-workers have noted similar trends in the related $[W_2Se_x]^{2-}$ complexes ($x$ = 9, 10) and other tungsten and molybdenum selenides.[5a,12,17] The $^{77}Se$ chemical shifts in the $Mo_2Se_6$ center of **1** are deshielded relative to those of **2**, which parallels the trend in $^{77}Se$ chemical shifts in the isostructural series of $[MoQ(Se_4)_2]^{2-}$ ions (Q = O, S, Se) and the $[W_3QSe_8]^{2-}$ compounds (Q = O, Se).[12] The inductive effects due to the $\pi$-bonding arguments just described are consistent with the trends in $^{77}Se$ chemical shifts in the $[MoQ(Se_4)_2]^{2-}$ and $[W_3QSe_8]^{2-}$ series as well as the $[Mo_2Q_2(\mu\text{-}Se)_2(\eta^2\text{-}Se_2)_2]^{2-}$ series; however, varying contributions from paramagnetic terms can clearly complicate chemical shift analyses such as these.[14,15]

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**Supplementary Material Available:** A textual presentation of the crystallographic experimental details, complete listings of crystallographic data, bond distances and angles, fractional coordinates, and anisotropic thermal parameters, and ORTEP diagrams of **1** and **2** (28 pages). Ordering information is given on any current masthead page.

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