Inorg. Chem. **2009**, *48*, 3832−3839

Inorganic Chemistry

Article

Synthesis and Characterization of Mixed Chalcogen Triangular Complexes with New $Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se_2)_3{}^{4+}$ and $M_3(\mu_3\text{-}S)(\mu_2\text{-}Se)_3{}^{4+}$ (M = Mo, W) Cluster Cores

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Received December 5, 2008

In our pursuit of mixed chalcogen-bridged cluster complexes, solids of the compositions $Mo_3SSe_6Br_4$ and $W_3SSe_6Br_4$ were prepared using high-temperature synthesis from the elements. Treatment of $Mo_3SSe_6Br_4$ with Bu_4NBr in a vibration mill yielded $(Bu_4N)_3\{[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se_2)_3Br_6]Br\}$ (**I**). Its all-selenide analogue $(Bu_4N)_3\{[Mo_3(\mu_3\text{-}Se)(\mu_2\text{-}Se_2)_3Br_6]Br\}$ (**II**) was prepared from $Mo_3Se_7Br_4$ in a similar way. Both compounds were characterized by IR, Raman, and ^{77}Se NMR spectroscopy. The structure of **II** was determined by X-ray single-crystal analysis. Compound **I** is isostructural with **II** and contains the new $Mo_3(\mu_3\text{-}S)Se_6{}^{4+}$ cluster core. By treatment of a 4 M Hpts solution of **I** with PPh_3 followed by cation-exchange chromatography, the new mixed chalcogenido-molybdenum aqua ion, $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se)_3(H_2O)_9]^{4+}$, was isolated and characterized using UV−vis spectroscopy and, after derivatization into $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se)_3(acac)_3(py)_3]^+$, electrospray ionization mass spectrometry. From HCl solutions of the aqua ion, a supramolecular adduct with cucurbit[6]uril (CB[6]), $\{[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se)_3(H_2O)_6Cl_3]_2CB[6]\}Cl_2 \cdot 11H_2O$ (**III**), was isolated and its structure determined using X-ray crystallography. $W_3SSe_6Br_4$ upon reaction with H_3PO_2 gave a mixture of all of the $[W_3S_xSe_{4-x}(H_2O)_9]^{4+}$ species. After repeated chromatography, crystals of $\{[W_3(\mu_3\text{-}S)(\mu_2\text{-}Se)_3(H_2O)_7Cl_2]_2CB[6]\}Cl_4 \cdot 12H_2O$ (**IV**) were crystallized from the fraction rich in $[W_3(\mu_3\text{-}S)Se_3(H_2O)_9]^{4+}$ and structurally characterized.

Introduction

The problem of selective synthesis of cluster complexes with mixed chalcogenide bridging ligands remains a daunting task. In the case of cluster cores with chalcogen atoms in structurally different bridging positions, the selectivity can be achieved either during the cluster self-assembly, when two different chalcogens go into their specific positions, or by selective chalcogen exchange in specific positions, due to the difference in the reactivity of structurally nonequivalent chalcogen atoms. To test these ideas, we have chosen to focus on the triangular clusters $M_3(\mu_3\text{-}Q)(\mu_2\text{-}Q_2)_3{}^{4+}$ (M = Mo, W; Q = S, Se, Te). They have three different chalcogen sites: one capping, one bridging residing almost in the M_3 plane (so-called equatorial position, Q_{eq}), and another bridging above the same plane, on the opposite side from the capping chalcogen (termed axial chalcogens, Q_{ax}). Thus, each $\mu_2\text{-}Q_2$ ligand is represented as $\mu_2\text{-}Q_{eq}Q_{ax}$. An additional interest in selecting the triangular clusters $M_3(\mu_3\text{-}Q)(\mu_2\text{-}Q_2)_3{}^{4+}$ (M = Mo, W; Q = S, Se) for the study lies in the possibility of the design of molecular conductors using multiple Q···Q interactions in the solid state. For example, a complex with 1,3-dithiol-2-thione-4,5-dithiolate (dmit), $[Mo_3S_7(dmit)_3]$, is a semiconductor with an activation energy of 12−22 meV, and its structure features the formation of columns of the $[Mo_3S_7(dmit)_3]$ molecules by means of $\mu_3\text{-}S\cdots\mu_2\text{-}S_2$ interactions.[1] The bis(ethylenedithio)tetrathiafulvalene charge-transfer salts of $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3Cl_6]^{2-}$ and $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_{ax}Se_{eq})_3Br_6]^{2-}$ exhibit properties ranging from semiconducting

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10.1021/ic8023327 CCC: $40.75

to insulating, which in turn are determined by various chalcogen−chalcogen and chalcogen−halogen interactions in the inorganic and organic sublattices.[2] It is obvious that, in order to better understand the individual contributions of each type of interaction into the conductivity path and to be able to optimize conducting behavior, ways of preparation of the $M_3(\mu_3\text{-}Q)(\mu_2\text{-}Q_2)_3^{4+}$ clusters with two different chalcogen atoms in clearly defined positions must be found.

Earlier work has shown that these clusters exchange their bridging chalcogens with $SePPh_3$ and KNCSe. In this way, it is possible to obtain heterochalcogenide complexes in which only equatorial atoms are substituted, the $M_3(\mu_3\text{-}S)(\mu_2\text{-}S_{ax}Se_{eq})_3^{4+}$ (M = Mo, W) and $W_3(\mu_3\text{-}Te)(\mu_2\text{-}Te_{ax}Se_{eq})_3^{4+}$ clusters.[3−5] Sulfur addition to the monochalcogenide-bridged $Mo_3Se_4^{4+}$ and $W_3Se_4^{4+}$ clusters gives $M_3(\mu_3\text{-}Se)(\mu_2\text{-}Se_{ax}S_{eq})_3^{4+}$ cluster cores.[6] These interconversions affect only the bridging ligand. The capping chalcogen atom is held very tightly and can be exchanged only under very drastic conditions.[5]

There are indications, however, that, in the presence of two different chalcogens, a cluster core preferentially assembles around the lighter chalcogen atoms, which thus go into the position with maximum connectivity (capping μ_3 in the case of the triangular clusters). This has been found for the Re_2O_7/OsO_4−S/$SeCl_2$ systems, which selectively yield the $\{M_3(\mu_3\text{-}S)(\mu_2\text{-}Se_2)_3\}$ clusters (M = Re, Os).[7] Recently, we have shown that it is possible to introduce S into the capping position of the square-planar tantalum selenide cluster. So, by heating Ta, Se, S, and I_2, the molecular complex $Ta_4(\mu_4\text{-}S)S_{0.5}Se_{7.5}I_8$ was obtained, where the capping position is occupied exclusively by the sulfur atom.[8]

A self-assembly reaction between Mo^{3+}, H_2Se (in situ), and $S_2P(OEt)_2^-$ (dtp) leads to the formation of $[Mo_3(\mu_3\text{-}Q)(\mu\text{-}Se_2)_3(dtp)_3]Cl$ (Q = 0.65S + 0.35Se), which is then converted into $[Mo_3(\mu_3\text{-}Q)(\mu\text{-}Se)_3(dtp)_4(py)]$—both products being obviously mixtures of the S- and Se-capped clusters. However, the individual complexes with $Mo_3(\mu_3\text{-}S)(\mu\text{-}Se_2)_3^{4+}$ and $Mo_3(\mu_3\text{-}Se)(\mu\text{-}Se_2)_3^{4+}$ cores were not isolated.[9] In this work, we have studied cluster high-temperature self-assembly reactions from the elements in stoichiometric ratios for Mo−S−Se−Br and W−S−Se−Br systems. A high degree of chalcogen discrimination between bridging and capping positions is observed in the case of molybdenum, which permits the isolation of new $Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se_2)_3^{4+}$ and $Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se)_3^{4+}$clusters. A lesser degree of selectivity is shown by tungsten.

Experimental Section

Materials and Methods. All operations were carried out in air. High-purity Mo, W, S, and Se powders were used. Br_2 was dried over P_4O_{10} and distilled. Cucurbit[6]uril decahydrate was synthesized according to the published protocol.[10] PPh_3 was recrystallized from hot ethanol. Bu_4NBr was thoroughly dried under vacuum. All the other reagents including concentrated hydrochloric acid and organic solvents were purchased from commercial sources and used without further purification. White crystalline 98.5% *p*-toluenesulfonic acid, $CH_3C_6H_4SO_3H\cdot H_2O$ (abbreviated Hpts·H_2O), from Sigma-Aldrich and Dowex 50W-X2, dry mesh size 200−400, a strongly acidic cation exchange resin, were used. Hypophosphorous acid (H_3PO_2) was available from Aldrich as a 1:1 w/w aqueous solution.

Elemental analyses were carried out by the Nikolaev Institute of Inorganic Chemistry microanalytical service. IR spectra (4000−400 cm^{-1}) were recorded on a Scimitar FTS 2000 Fourier-spectrometer. Raman spectra were obtained on a Triplimate SPEX spectrometer using a 632.8 nm line of a He−Ne laser for excitation. ^{77}Se NMR spectra were run on an SXP/300 spectrometer (Bruker) with a saturated aqueous solution of H_2SeO_3 as a standard. The chemical shifts for ^{77}Se spectra were recalculated versus Me_2Se. A Quattro LC mass spectrometer with an orthogonal Z-spray electrospray interface (Micromass, Manchester, U. K.) was used. The drying gas as well as the nebulizing gas was nitrogen at a flow rate of 400 and 80 L/h, respectively. Sample solutions in acetonitrile were infused via a syringe pump directly to the interface at a flow rate of 10 μL/min. A capillary voltage of 3.5 kV was used in the positive scan mode. The cone voltage (U_c) was set at 10 V (i.e., mild ionization conditions) to control the extent of fragmentation. Additional experiments were carried out by increasing U_c in order to explore the consecutive fragmentation of the identified species. The experimental isotope patterns were compared with theoretical ones calculated with the MassLynx 4.1 program.[10c]

High-Temperature Syntheses. The starting coordination polymers $Mo_3Se_7Br_4$ and "$M_3SSe_6Br_4$" (M = Mo, W) were prepared by heating stoichiometric mixtures of the elements (M/S/Se/Br = 3:1:6:4 for "$M_3SSe_6Br_4$") in a sealed glass ampule for 4 days at 350 °C, as described in the literature.[11] The solids thus obtained were washed with chloroform, vacuum-dried, and used as such.

Mechanochemical Synthesis. The construction of the vibration mill is described in ref 12. We used a simplified version of it without a gas outlet. All of the operations were in the air. A cylindrical titanium reactor was used (V = 100 mL, height = 50 mm). The reactor was filled with tungsten carbide balls (diameter 10 mm, total mass 320 g) and with a mixture of solid reagents. The reactions were run under the following conditions: reactor vibration frequency, 25 Hz; vertical movement amplitude, 1 cm; duration of the treatment, 12 h.

Synthesis of $(Bu_4N)_3\{[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se_2)_3Br_6]Br\}$ (I). A mixture of "$Mo_3SSe_6Br_4$" (2.0 g, 1.8 mmol) and Bu_4NBr (1.5 g, 4.7 mmol)

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(1) Llusar, R.; Uriel, S.; Vicent, C.; Coronado, E.; Gomez-Garcia, C. J.; Clemente-Juan, J. M.; Braida, B.; Canadell, D. *J. Am. Chem. Soc.* **2004**, *126*, 12076.

(2) Alberola, A.; Llusar, R.; Triguero, S.; Vicent, C.; Sokolov, M. N.; Gomez-Garcia, C. *J. Mater. Chem.* **2007**, *17*, 3440.

(3) Fedin, V. P.; Mironov, Yu. V.; Sokolov, M. N.; Kolesov, B. A.; Fedorov, V. Ye.; Yufit, D. S.; Struchkov, Yu. T. *Inorg. Chim. Acta* **1990**, *174*, 275.

(4) Fedin, V. P.; Sokolov, M. N.; Gerasko, O. A.; Kolesov, B. A.; Fedorov, V. Ye.; Mironov, Yu. V.; Yufit, D. S.; Slovohotov, Yu. L.; Struchkov, Yu. T. *Inorg. Chim. Acta* **1990**, *175*, 217.

(5) Sokolov, M. N.; Abramov, P. A.; Gushchin, A. L.; Kalinina, I. V.; Naumov, D. Yu.; Virovets, A. V.; Peresypkina, E. V.; Vicent, C.; Llusar, R.; Fedin, V. P. *Inorg. Chem.* **2005**, *44*, 8116.

(6) Hernandez-Molina, R.; Sokolov, M. N.; Nuñez, P.; Mederos, A. *Dalton Trans.* **2002**, 1072.

(7) Volkov, S. V.; Fokina, Z. A.; Yanko, O. G.; Pekhnyo, V. I.; Kharkova, L. B. *Zh. Neorg. Khim.* **2005**, *50*, 1244.

(8) Gushchin, A. L.; Sokolov, M. N.; Abramov, P. A.; Zakharchuk, N. F.; Fedin, V. P. *J. Cluster Sci.* **2008**, *19*, 659.

(9) Hu, J.; Zhuang, H.-H.; Liu, S.-X.; Huang, J.-L. *Trans. Met. Chem.* **1998**, *23*, 547.

(10) (a) Behrend, R.; Meyer, E.; Rusche, F. *Liebigs Ann. Chem.* **1905**, *339*, 1. (b) Freeman, W. A.; Mock, W. L.; Shih, N.-Y. *J. Am. Chem. Soc.* **1981**, *103*, 7367. (c) *MassLynx 4.1*; Micromass: Manchester, U. K., 2006.

(11) Fedin, V. P.; Sykes, A. G. *Inorg. Synth.* **2002**, *35*, 162.

(12) Volkov, V. V.; Myakishev, K. G. *Inorg. Chim. Acta* **1999**, *289*, 51.

was treated in the vibration mill as described above. Then, the reaction mixture was extracted with 15 mL of CH_2Cl_2. An equal volume of toluene was added to the filtered red extract, and the mixture was left overnight at −10 °C. The red crystals of **I** were collected by decantation, washed with toluene and ether, and air-dried. Yield: 0.35 g (10%). Anal. calcd for $C_{48}H_{104}Br_7Mo_3N_3Se_6S$: C, 27.76; H, 5.06; N, 2.02%. Found: C, 27.49; H, 4.85; N, 2.04%. IR (cm^{-1}): 3446 w, 2958 s, 2933 s, 2872 s, 1633 w, 1488 s, 1466 s, 1426 w, 1380 m, 1344 w, 1244 m, 1173 w, 1151 w, 1107 w, 1065 w, 1028 w, 1008 w, 927 w, 878 m, 801 w, 739 m, 523 w, 449 w. Raman (cm^{-1}): 448 w (Mo-μ_3-S), 373 w, 336 sh, 323 s, 292 w, 268 m, 253 w, 211 w, 186 sh, 178 s, 162 w, 139 s, 122 w, 103 m, 69 m, 52 m, 32 s. Raman (cm^{-1}) for $(Bu_4N)_3\{[Mo_3(\mu_3\text{-}^{34}S)(\mu_2\text{-}Se_2)_3Br_6]Br\}$: 437 w (Mo-$\mu_3$-^{34}S), 366 w, 337 sh, 321 s, 290 w, 267 m, 241 w, 210 w, 178 m, 161 w, 139 s, 122 w, 101 m, 69 m, 52 m, 33 s. ^{77}Se NMR (CH_2Cl_2, 25 °C): δ 256.3, −132.0 ppm.

Synthesis of $(Bu_4N)_3\{[Mo_3(\mu_3\text{-}Se)(\mu_2\text{-}Se_2)_3Br_6]Br\}$ (II). A mixture of $Mo_3Se_7Br_4$[13] (2.0 g, 1.7 mmol) and Bu_4NBr (1.5 g, 4.7 mmol) was treated in the vibration mill as described above. Then, the reaction mixture was extracted with acetonitrile (20 mL). An equal volume of toluene was added to the filtered red extract, and the mixture was left overnight at −10 °C. The red crystals of **II** were collected by decantation, washed with toluene and ether, and air-dried. Yield: 0.70 g (20%). Anal. calcd for $C_{48}H_{104}Br_7Mo_3N_3Se_7$: C, 27.10; H, 5.12; N, 1.98%. Found: C, 26.90; H, 5.00; N, 2.06%. IR (cm^{-1}): 3434 m, 3199 w, 3151 w, 2958 s, 2933 s, 2872 s, 1629 w, 1487 s, 1465 s, 1398 m, 1381 m, 1243 w, 1150 m, 1106 w, 1065 w, 1028 w, 878 m, 801 w, 739 m, 520 w. Raman (cm^{-1}): 336 w, 321 s, 291 w, 270 m, 254 w, 211 m, 187 w, 175 m, 158 m, 138 s, 121 w, 102 m, 68 m, 55 m. ^{77}Se NMR (CH_2Cl_2, 25 °C): δ 700.3, 286.6, −133.7 ppm.

Preparation of $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se)_3(H_2O)_9]^{4+}$. 250 mg of $(Bu_4N)_3\{[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se_2)_3Br_6]Br\}$ (**I**) (0.12 mmol) were dissolved in 25 mL of 4 M Hpts under magnetic stirring (which takes about 2 h). To the final orange solution of $[Mo_3SSe_6(H_2O)_6]^{4+}$ was added a solution of PPh_3 (95 mg, 0.36 mmol) in 10 mL of CH_2Cl_2. The mixture was left stirring for 20 h in an open beaker to remove methylene chloride. After the evaporation of CH_2Cl_2, the brown solution was diluted 2-fold with water. The white precipitate of $SPPh_3$ was filtered off. The filtrate was then diluted to 0.2 M Hpts and loaded on a Dowex 50W-X2 cation exchange column (2.2 cm × 20 cm) equilibrated with 0.2 M HCl. After washing 0.2 M HCl and then with 0.5 M HCl, a dark brown band was eluted with 1 M HCl. The eluted solution was further purified at ca. 4 °C on a second 50W-X2 column equilibrated with 0.1 M H_2SO_4. After washing with copious amounts of 0.1 and 0.2 M H_2SO_4, a brown band of $[Mo_3SSe_3(H_2O)_9]^{4+}$ was eluted with 0.5 M H_2SO_4. A small amount of uncharacterized species eluted prior to the $[Mo_3SSe_3(H_2O)_9]^{4+}$. The yield of $[Mo_3SSe_3(H_2O)_9]^{4+}$ was approximately 80%. UV−vis spectrum (1 M HCl, λ_{max}/nm ($\varepsilon/M^{-1}\cdot cm^{-1}$): 430 (7065), 650(630) based on Mo analysis by ICP-MS. Electrospray ionization mass spectrometry (ESI-MS) analysis was carried out on the acetylacetonate complex, $[Mo_3SSe_3(acac)_3(py)_3](PF_6)$, prepared from the aqua ion by reaction with acetylacetone and pyridine as described in the literature.[14] ESI-MS (CH_3CN): $[Mo_3SSe_3(acac)_3(py)_3]^+$ (35%, M/z = 1092), $[Mo_3SSe_3(acac)_3(py)_2]^+$ (100%, M/z = 1012), $[Mo_3SSe_3(acac)_3(py)]^+$ (50%, M/z = 932).

Synthesis of $\{[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se)_3(H_2O)_6Cl_3]_2CB[6]\}Cl_2\cdot 11H_2O$ (III). To 1.0 mL of a saturated (3.0 mM) solution of cucurbituril in 2 M HCl (0.0030 mmol) was added 2.0 mL of 3.2 mM $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se)_3(H_2O)_9]^{4+}$ (0.0064 mmol) in 2 M HCl. The final brown solution was mixed thoroughly and allowed to stand at room temperature. After 2 days, brown stick-shaped crystals of **III** were filtered off and washed with 1 mL of cold water, 1 mL of EtOH, and 2 mL of Et_2O and dried in air. Yield: 6 mg (68%). Anal. calcd for $C_{36}H_{36}N_{24}O_{12}\{(Mo_3Se_3SCl_3(H_2O)_6)Cl\}_2\cdot 11H_2O$: C, 15.65; H, 3.00; N, 12.17. Found: C, 15.83; H, 2.85; N, 12.26.

Preparation of $[W_3S_xSe_{4-x}(H_2O)_9]^{4+}$. To a suspension of the polymeric "$W_3SSe_6Br_4$" (2.0 g) in concentrated hydrochloric acid (20 mL, 11.4 M) was added excess H_3PO_2 (4 mL), and the mixture was heated on a steam bath (90 °C) under Ar for 10 h. The mixture turned green, and H_2Se was released. The dark green solution was cooled, diluted 2-fold with water, and filtered. The filtrate was diluted to 0.2 M HCl and then loaded onto a Dowex 50W-X2 cation exchange column (2.2 cm × 45 cm). Development and elution of the column was carried out at 4 °C. The column was washed with copious amounts of 0.1 and 0.2 M H_2SO_4, and purple, blue, and green (main) bands were eluted with 0.5 M H_2SO_4. Formation of red Se on the column was observed. UV−visible absorption spectra and ESI-MS analyses on the obtained fractions revealed that mixtures of $[W_3S_4(H_2O)_9]^{4+}$, $[W_3S_3Se(H_2O)_9]^{4+}$, $[W_3S_2Se_2(H_2O)_9]^{4+}$, $[W_3SSe_3(H_2O)_9]^{4+}$, and $[W_3Se_4(H_2O)_9]^{4+}$ aqua ions were present but were difficult to separate. The green fraction contained $[W_3SSe_3(H_2O)_9]^{4+}$ as the main product and $[W_3S_2Se_2(H_2O)_9]^{4+}$ and $[W_3Se_4(H_2O)_9]^{4+}$ as secondary products. ESI-MS analysis on the avetylacetonate complex obtained from the green fraction (in CH_3CN): $[W_3Se_4(acac)_3(py)_3]^+$ (35%, M/z = 1402), $[W_3SSe_3(acac)_3(py)_3]^+$ (100%, M/z = 1356), $[W_3Se_4(acac)_3(py)_2]^+$ (5%, M/z = 1323), $[W_3S_2Se_2(acac)_3(py)_3]^+$ (10%, M/z = 1310), $[W_3SSe_3(acac)_3(py)_2]^+$ (40%, M/z = 933).

Synthesis of $\{[W_3(\mu_3\text{-}S)(\mu_2\text{-}Se)_3(H_2O)_7Cl_2]_2CB[6]\}Cl_4\cdot 12H_2O$ (IV). To 1 mL of a 2.5 mM solution of cucurbituril in 2 M HCl was added 2 mL of the green solution obtained above (estimated concentration is 2 mM) in 2 M HCl. The final solution was mixed thoroughly and allowed to stand at room temperature over 4 days. During this time, green crystals of **IV** suitable for crystallography formed and were filtered off; washed with cooled water, MeOH, and Et_2O; and dried in the air. Yield: 3 mg (45%). Anal. calcd for $C_{36}H_{36}N_{24}O_{12}\{(W_3Se_3SCl_2(H_2O)_7)Cl_2\}_2\cdot 12H_2O$: C, 12.95; H, 2.66; N, 10.07. Found: C, 13.07: H, 2.34; N, 10.21.

X-Ray Structure Determinations. Data collection, data reduction, and absorption correction were performed using SMART, SAINT, and SADABS.[15,16] SHELXTL 95[17] was used to solve and refine the structures. Data collection and refinement details are listed in Table 1. Diffraction data for **II** were collected at room temperature on a Bruker X8APEX CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å). The crystals of **III** and **IV** were cooled to 120 K in an Oxford cryosystem nitrogen gas cooler system, and data were collected on a Bruker SMART platform CCD diffractometer using Mo Kα radiation. All structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data. Furthermore, in both structures **III** and **IV**, there are disordered water molecules present. This disorder does not, however, appear to affect either the triangular tungsten and molybdenum complexes or the cucurbituril, where also hydrogen

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(13) Fedin, V. P.; Sokolov, M. N.; Geras'ko, O. A.; Virovets, A. V.; Podberezskaya, N. V.; Fedorov, V. Ye. *Inorg. Chim. Acta* **1991**, *187*, 81.

(14) Hernandez-Molina, R.; Sokolov, M.; Clegg, W.; Esparza, P.; Mederos, A. *Inorg. Chim. Acta* **2002**, *331*, 52.

(15) *SMART*; *SAINT*, version 5.054; Bruker Analytical X-ray Instruments Inc.: Madison, WI, 1998.

(16) Sheldrick, G. M. *SADABS*, version 2.03; University of Göttingen: Göttingen, Germany, 2001.

(17) Sheldrick, G. M. *SHELXTL*, version 6.12; Bruker Analytical X-ray Instruments Inc.: Madison, WI, 2001.

Table 1. Crystallographic Data for $(Bu_4N)_3\{[Mo_3(\mu_3\text{-}Se)(\mu_2\text{-}Se_2)_3Br_6]Br\}$ (**II**), $\{[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se)_3(H_2O)_6Cl_3]_2CB[6]\}Cl_2\cdot 11H_2O$ (**III**), and $\{[W_3(\mu_3\text{-}S)(\mu_2\text{-}Se)_3(H_2O)_7Cl_2]_2CB[6]\}Cl_4\cdot 12H_2O$ (**IV**)

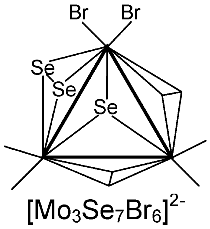
	II	**III**	**IV**
formula	$C_{48}H_{104}Br_7Mo_3N_3Se_7$	$C_{36}H_{82}Cl_8Mo_6N_{24}$ $O_{35}S_2Se_6$	$C_{36}H_{88}Cl_8N_{24}O_{38}S_2Se_6W_6$
fw	2123.25	2762.00	3337.48
T (°C)	293(2)	120(2)	120(2)
cryst syst, color	monoclinic, dark red	monoclinic, dark brown	monoclinic, dark green
cryst dimension (mm^3)	0.15 × 0.08 × 0.06	0.3 × 0.1 × 0.05	0.2 × 0.075 × 0.05
space group	$P2_1/c$	$C2/m$	$C2/m$
a (Å)	13.224(2)	16.585(1)	16.7347(9)
b (Å)	13.463(2)	18.521(1)	18.5128(10)
c (Å)	42.744(6)	14.984(1)	15.1361(8)
β (deg)	97.049(3)	104.483(1)	105.1420(10)
V (Å^3)	7552(2)	4456.2(5)	4526.5(4)
Z	4	2	2
D_{calcd} (g cm^{-3})	1.867	2.058	2.449
μ (Mo Kα, $\lambda = 0.71070$Å) (mm^{-1})	7.597	3.644	10.378
Θ range (deg)	0.96−26.36	1.97−27.94	1.96−28.01
no. measured reflns	37452	30263	30757
no. unique reflns	15372	5504	5616
no. reflns with $I > 2\sigma(I)$	7892	4559	4825
R(int)	0.0593	0.042	0.051
transmission factors	0.40−0.66	0.65−0.84	0.4−0.6
no. refined params	625	300	292
R_1 (obsd data)^a	0.0566	0.0669	0.0512
wR_2 (all data)^b	0.1576	0.2034	0.1389
GOF	0.946	1.009	1.007
max, min $\Delta\rho$ (e Å^{-3})	0.963, −0.886	3.292,-1.529	4.604,-2.004

^{a} $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^{b} $wR_2 = (\sum w|F_o^2 - F_c^2|^2 / \sum wF_o^4)^{1/2}$.

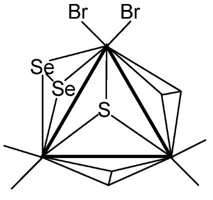
atoms could be observed and modeled at ideal positions. Hydrogen atoms were not modeled on the water molecules.

Results and Discussion

Synthesis and Characterization. The mechanochemical reactions of $Mo_3Se_7Br_4$ and "$Mo_3SSe_6Br_4$" with Bu_4NBr in a vibration mill resulted in the bromide complexes $[Mo_3Se_7Br_6]^{2-}$ and $[M_3(\mu_3\text{-}S)(\mu_2\text{-}Se_2)_3Br_6]^{2-}$, respectively. The latter complex contains a new mixed-chalcogenide $Mo_3(\mu_3\text{-}S)(Se_2)_3^{4+}$ cluster core where the sulfur atom is in the capping position. These complexes crystallize well as tetrabutylammonium salts, $(Bu_4N)_3\{[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se_2)_3Br_6]Br\}$ (**I**) and $(Bu_4N)_3\{[Mo_3(\mu_3\text{-}Se)(\mu_2\text{-}Se_2)_3Br_6]Br\}$ (**II**), from a CH_2Cl_2 (or CH_3CN)/toluene mixture.



$[Mo_3Se_7Br_6]^{2-}$



$[Mo_3(\mu_3\text{-}S)(Se_2)_3Br_6]^{2-}$

The mechanochemical reaction of $W_3Se_7Br_4$ and "$W_3SSe_6Br_4$" with Bu_4NBr initially produces, upon extraction with CH_3CN, a brown solution of $[W_3Q_7Br_6]^{2-}$, which is gradually transformed into a green solution of $[W_3Q_4(CH_3CN)_{6-x}Br_x]^{(4-x)+}$ with precipitation of red Se. A similar transformation was previously observed for the oxalate complex $[W_3Se_7(C_2O_4)_3]^{2-}$.[18]

$(Bu_4N)_3\{[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se_2)_3Br_6]Br\}$ (**I**) and $(Bu_4N)_3\{[Mo_3(\mu_3\text{-}Se)(\mu_2\text{-}Se_2)_3Br_6]Br\}$ (**II**) are well soluble in CH_2Cl_2 and form air-stable red solutions. The solutions in CH_3CN are less stable and decompose within hours to give yellow precipitates, which probably contain the neutral $[Mo_3Q_7Br_4(CH_3CN)_2]$ or oligomeric products.

The Raman spectrum of **I** shows the characteristic band at 448 cm^{-1} due to the Mo_3-μ_3−S vibrations.[4] To confirm this assignment, we have prepared the isotopomeric compound $(Bu_4N)_3\{[Mo_3(\mu_3\text{-}^{34}S)(\mu_2\text{-}Se_2)_3Br_6]Br\}$. The observed isotopic shift ($\Delta\nu = 448 - 437 = 11$ cm^{-1}) toward the lower wavelengths corresponds to that calculated for this band.

Three different types of Se atoms in the Mo_3Se_7 cluster core of the CH_2Cl_2 solution of **II** give three signals at +700.3, +286.6, and −133.7 ppm in the ^{77}Se NMR spectrum. There were some less intense satellite signals attributable to $[Mo_3Se_7Br_{6-x}Cl_x]^{2-}$ since adding an excess of PPNCl to the solution of **II** increases their intensities and decreases the signals from $[Mo_3Se_7Br_6]^{2-}$. Only two signals at +256.3 and −132.0 ppm due to μ_2-Se were observed in the ^{77}Se NMR spectrum of the CH_2Cl_2 solution of **II**. As expected, the signal from μ_3-Se in the 700 ppm area is absent. Some less intense satellite signals from $[Mo_3S(Se_2)_3Br_{6-x}Cl_x]^{2-}$ were also observed.

The chalcogen-rich cluster core in **I** can be further modified: after aquation in 4 M Hpts, triphenylphosphine abstracts three eqatorial selenium atoms from the Se_2 bridges in the $Mo_3S(Se_2)_3^{4+}$ core to give an incomplete cuboidal $Mo_3SSe_3^{4+}$ core, similar to the transformation of the $Mo_3Se_7^{4+}$ cluster into $Mo_3Se_4^{4+}$.[19] As expected, the reaction of the bromide complex **I** in 4 M Hpts acid with a stoichiometric amount of PPh_3 in CH_2Cl_2 followed by dilution with water and cation-exchange chromatography gives an aqua ion with the $Mo_3(\mu_3\text{-}S)Se_3^{4+}$ cluster core upon elution with 2 M HCl:

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[18] Sokolov, M. N.; Gushchin, A. L.; Naumov, D. Yu.; Gerasko, O. A.; Fedin, V. P. *Inorg. Chem.* **2005**, *44*, 2431.

$$[Mo_3(\mu_3\text{-}S)(Se_2)_3Br_6]^{2-} + 3PPh_3 + 9H_2O \rightarrow [Mo_3(\mu_3\text{-}S)Se_3(H_2O)_9]^{4+} + 3SePPh_3 + 6Br^-$$

This aqua ion, $[Mo_3(\mu_3\text{-}S)Se_3(H_2O)_9]^{4+}$, has never been reported previously. It was further purified by Dowex 50W-X2 cation-exchange chromatography under the following conditions: washing with 0.1 and 0.2 M H_2SO_4 and elution with 0.5 M H_2SO_4. Cation-exchange chromatography in dilute H_2SO_4 instead of dilute HCl was found to give efficient separation of the related $[Mo_3O_xS_{4-x}(H_2O)_9]^{4+}$ aqua ions.[20] Only a small amount of uncharacterized species (probably $[Mo_3(\mu_3\text{-}S)SSe_2(H_2O)_9]^{4+}$) was eluted prior to the $[Mo_3(\mu_3\text{-}S)Se_3(H_2O)_9]^{4+}$. The electronic spectrum of the purified solution in 1 M HCl (Figure 1) shows two characteristic absorption bands in the visible part at $\lambda_{max} = 430$ nm ($\varepsilon = 7065\ M^{-1}\cdot cm^{-1}$ per Mo_3) and 650 nm ($\varepsilon = 630\ M^{-1}\cdot cm^{-1}$ per Mo_3). The second band is expectedly shifted (by 31 nm) toward the shorter wavelength in comparison to the $[Mo_3Se_4(H_2O)_9]^{4+}$ (681 nm[19]).

To confirm the individuality of the aqua ion, it was converted into the acetylacetonate complex $[Mo_3SSe_3(acac)_3(py)_3]PF_6$ by reaction with acetylacetone and pyridine, as described in the literature,[14] and was analyzed by ESI-MS. The ESI mass spectrum of acetonitrile solutions of $[Mo_3(\mu_3\text{-}S)Se_3(acac)_3(py)_3]PF_6$ recorded at $U_c = 10$ V is shown in Figure 2.

Even though soft ionization conditions were used, that is, $U_c = 10$ V, the parent $[Mo_3(\mu_3\text{-}S)Se_3(acac)_3(py)_3]^+$ ion ($m/z = 1092$) was detected only as a minor species. Two additional peaks corresponding to the losses of one pyridine, namely, $[Mo_3(\mu_3\text{-}S)Se_3(acac)_3(py)_2]^+$ ($m/z = 1012$, corresponding to the base peak), or two pyridine molecules, $[Mo_3(\mu_3\text{-}S)Se_3(acac)_3(py)]^+$ ($m/z = 932$), were also observed. These results are indicative of pyridine being loosely coordinated to the Mo sites. Increasing the cone voltage (typically in the U_c 10−60 V range) results in the enhanced dissociation of pyridine molecules. For example, at $U_c = 60$ V, the base peak corresponds to the $[Mo_3(\mu_3\text{-}S)Se_3(acac)_3]^+$ ($m/z = 852$) cation where three pyridine molecules are released while the relative intensities of $[Mo_3(\mu_3\text{-}S)Se_3(acac)_3(py)_n]^+$ ($n = 1-3$) are significantly reduced. The trinuclear cluster core $Mo_3(\mu_3\text{-}S)Se_3^{4+}$ does not fragment under these experimental conditions, as is also seen for closely related trinuclear $Mo_3Q_4^{4+}$ (Q = S, Se) bearing chlorine or diphosphane ligands, thus demonstrating a high robustness of these Mo_3Q_4 cluster units.[21,22]

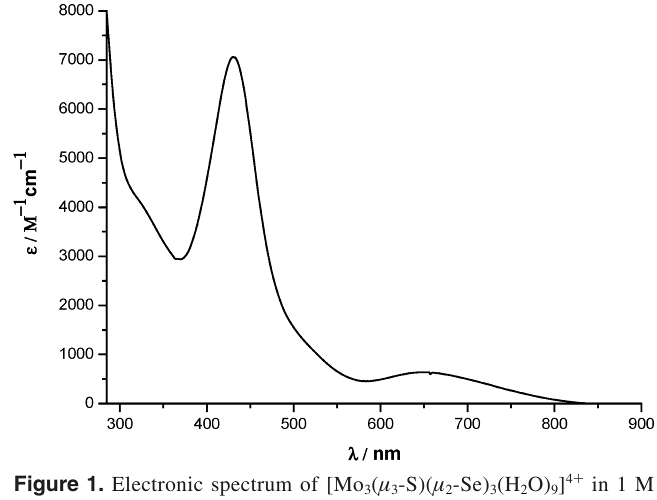


Figure 1. Electronic spectrum of $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se)_3(H_2O)_9]^{4+}$ in 1 M HCl.

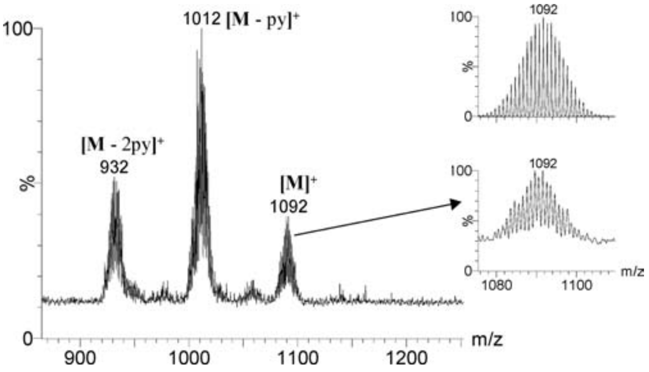
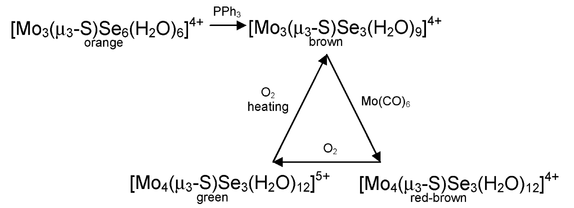


Figure 2. Positive ESI mass spectrum of acetonitrile solutions of $[Mo_3(\mu_3\text{-}S)Se_3(acac)_3(py)_3](PF_6)$ recorded at $U_c = 10$ V. The inset shows the simulated (top) and experimental (bottom) isotopic patterns for the $[Mo_3(\mu_3\text{-}S)Se_3(acac)_3(py)_3]^+$ cation. $[M]^+ = [Mo_3(\mu_3\text{-}S)Se_3(acac)_3(py)_3]^+$, $[M - py]^+ = [Mo_3(\mu_3\text{-}S)Se_3(acac)_3(py)_2]^+$, and $[M - 2py]^+ = [Mo_3(\mu_3\text{-}S)Se_3(acac)_3(py)]^+$.

Scheme 1. Transformations of Molybdenum Aqua Ions



The reactivity patterns of $[Mo_3(\mu_3\text{-}S)Se_3(H_2O)_9]^{4+}$ are similar to those of $[Mo_3Se_4(H_2O)_9]^{4+}$.[23] The brown solution of $[Mo_3(\mu_3\text{-}S)Se_3(H_2O)_9]^{4+}$ reacts with $Mo(CO)_6$ at 130 °C in a sealed ampule to form the red-brown solution of the cuboidal $[Mo_4(\mu_3\text{-}S)Se_3(H_2O)_{12}]^{4+}$, which converts to the green solution of the $[Mo_4(\mu_3\text{-}S)Se_3(H_2O)_{12}]^{5+}$ in the air (Scheme 1). The electronic spectrum of purified solutions of $[Mo_4(\mu_3\text{-}S)Se_3(H_2O)_{12}]^{5+}$ in 2 M HCl shows two bands at 323 and 662 nm. The electronic spectrum of $[Mo_4Se_4(H_2O)_9]^{5+}$ in 2 M Hpts also contains two bands in the visible part at 425 and 662 nm.[24] Heating of the $[Mo_4(\mu_3\text{-}S)Se_3(H_2O)_{12}]^{5+}$ at 90 °C in the air results in its degradation into starting incomplete cuboidal $[Mo_3(\mu_3\text{-}S)Se_3(H_2O)_9]^{4+}$ according to UV−vis spectra. Two different methods of degradation are theoretically possible for this cuboidal cluster. In the first case, the Mo_4 cube can lose one Mo vertex with the cleavage of both Mo−S and Mo−Se bonds to give a

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(19) Fedin, V. P.; Lamprecht, G. J.; Sykes, A. G. *J. Chem. Soc., Chem. Commun.* **1994**, 2685.

(20) Ooi, B.L. Unpublished work.

(21) Sokolov, M. N.; Chubarova, E. V.; Hernandez-Molina, R.; Clausén, M.; Naumov, D. Yu.; Vicent, C.; Llusar, R.; Fedin, V. P. *Eur. J. Inorg. Chem.* **2005**, 2139.

(22) Guillamón, E.; Llusar, R.; Pozo, O.; Vicent, C. *Int. J. Mass Spectrom.* **2006**, *254*, 28.

(23) Sokolov, M.; Esparza, P.; Hernandez-Molina, R.; Platas, J. G.; Mederos, A.; Gavin, J. A.; Llusar, R.; Vicent, C. *Inorg. Chem.* **2005**, *44*, 1132.

(24) Hernández-Molina, R.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1999**, *18*, 3137.

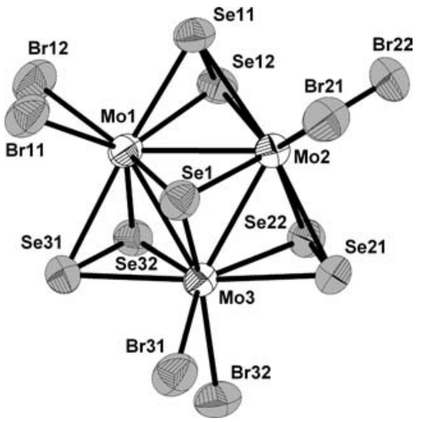

Figure 3. Structure of $[Mo_3Se_7Br_6]^{2-}$ in **II**. The thermal ellipsoids are drawn at a 50% probability level.

Table 2. Selected Bond Distances (Å) in $(Bu_4N)_3\{[Mo_3(\mu_3\text{-}Se)(\mu_2\text{-}Se_2)_3Br_6]Br\}$ (**II**), $\{[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se)_3(H_2O)_6Cl_3]_2CB[6]\}Cl_2\cdot 11H_2O$ (**III**), and $\{[W_3(\mu_3\text{-}S)(\mu_2\text{-}Se)_3(H_2O)_7Cl_2]_2CB[6]\}Cl_4\cdot 12H_2O$ (**IV**)

	I	III	IV
M−M	2.80−2.82	2.77−2.78	2.74−2.76
M−μ3-Q	2.47	2.36	2.38−2.39
M−Se_{eq}	2.60−2.62		
M−Se_{ax}	2.53	2.39−2.41	2.42−2.43
Mo−Br	2.64−2.68		
M−Cl		2.46−2.48	2.40−2.43
M−O		2.19−2.22	2.17−2.22
Se_{eq}−Se_{ax}	2.30−2.31		

new Mo_3 triangle with one S in the μ_2 position. In the second case, it can lose one Mo with the cleavage of three Mo−Se bonds to restore the initial triangular cluster. The UV−vis spectrum for the final product is the same as that for $[Mo_3(\mu_3\text{-}S)Se_3(H_2O)_9]^{4+}$. The second method of fragmentation is preferred, probably because of the relative ease of breaking the Mo−Se bonds.

The incomplete cuboidal aqua ions of the $M_3Q_4^{4+}$ (M = Mo, W) type are difficult to crystallize, but they are known to form supramolecular adducts with a macrocyclic cavitand, cucurbit[6]uril, which are easily obtainable in crystalline form even from dilute (millimolar) solutions.[25] Therefore, to characterize the resulting aqua ion, a supramolecular adduct with cucurbituril $\{[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se)_3(H_2O)_6Cl_3]_2CB[6]\}Cl_2\cdot 11H_2O$ (**III**) was crystallized from a concentrated solution of the aqua ions in 2 M HCl.

The behavior of the W analogue is more complicated. Polymeric "$W_3SSe_6Br_4$" reacts with H_3PO_2 (which is the best way of converting $W_3S_7Br_4$ and $W_3Se_7Br_4$ into the $[W_3Q_4(H_2O)_9]^{4+}$ aqua ions[26]) to give the whole range of $[W_3S_xSe_{4-x}(H_2O)_9]^{4+}$ species, which are extremely difficult to separate by conventional chromatography. Gel column chromatography on Sephadex G10, used to successfully separate mixtures of $[M_3O_xS_{4-x}(H_2O)_9]^{4+}$ (M = Mo, W) aqua ions,[27] fails in this case. Only separation on a Dowex cation-exchange column with very slow final elution with 0.5 M H_2SO_4 at 4 °C allowed isolation of a green fraction, containing $[W_3(\mu_3\text{-}S)Se_3(H_2O)_9]^{4+}$ (74%), $[W_3Se_4(H_2O)_9]^{4+}$ (20%), and $[W_3S_2Se_2(H_2O)_9]^{4+}$ (6%), as was shown by ESI-MS after derivatization into $[W_3Q_4(acac)_3(py)_3]PF_6$ in the usual way. However, complete separation of the three species was not achieved due to stability problems associated with Se loss (deposited as red Se), caused by very long elution times (days and weeks!).

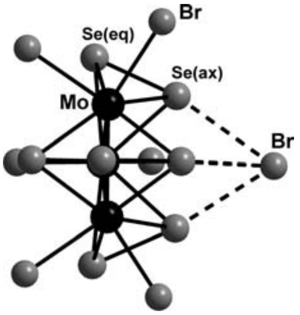

Figure 4. Structure of anionic associate $\{[Mo_3Se_7Br_6]Br\}^{3-}$ in **II**. Short contacts $Se_{ax}\cdots Br$ (3.02−3.14 Å) are shown as dashed lines.

$$W_3SSe_6Br_4 + 3H_3PO_2 + 12H_2O \rightarrow [W_3(\mu_3\text{-}S)Se_3(H_2O)_9]^{4+} + 3H_2Se + 3H_3PO_3 + 4Br^-$$

Instability of the Se-richer species toward oxidation with Se loss probably explains the fact that a *very* slow elution on a Dowex cation-exchange column with 0.2 M H_2SO_4 at 4 °C over several weeks gave mainly $[W_3S_2Se_2(H_2O)_9]^{4+}$ as dominant species instead of $[W_3(\mu_3\text{-}S)Se_3(H_2O)_9]^{4+}$.

Green crystals of $\{[W_3(\mu_3\text{-}S)(\mu_2\text{-}Se)_3(H_2O)_7Cl_2]_2CB[6]\}Cl_4\cdot 12H_2O$ (**IV**) were obtained in good yield by the reaction of cucurbituril with 2 equiv of $[W_3(\mu_3\text{-}S)Se_3(H_2O)_9]^{4+}$ in 2 M HCl.

It is interesting to note that the reaction of "$W_3S_4Se_3Br_4$", prepared under similar conditions to those for "$W_3SSe_6Br_4$" using appropriate stoichiometry, with H_3PO_2 leads to purple $[W_3S_4(H_2O)_9]^{4+}$.

$$W_3S_4Se_3Br_4 + 3H_3PO_2 + 12H_2O \rightarrow [W_3S_4(H_2O)_9]^{4+} + 3H_2Se + 3H_3PO_3 + 4Br^-$$

Structure Description. Crystal structures were determined for $(Bu_4N)_3\{[Mo_3(\mu_3\text{-}Se)(\mu_2\text{-}Se_2)_3Br_6]Br\}$ (**II**), $\{[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se)_3(H_2O)_6Cl_3]_2CB[6]\}Cl_2\cdot 11H_2O$ (**III**), and $\{[W_3(\mu_3\text{-}S)(\mu_2\text{-}Se)_3(H_2O)_7Cl_2]_2CB[6]\}Cl_4\cdot 12H_2O$ (**IV**). Compound **I** is isostructural with **II**, but good quality crystals could not be obtained. The view of $[Mo_3Se_7Br_6]^{2-}$ in **II** is shown in Figure 3. This is a first example of a structurally characterized halide complex $[M_3Se_7X_6]^{2-}$, though these complexes were first reported in 1991.[28] Geometrical characteristics of the $Mo_3Se_7^{4+}$ cluster are nonexceptional.[18] Main bond distances are given in Table 2. Anionic associates $\{[Mo_3Se_7Br_6]Br\}^{3-}$ via short contacts, $Se_{ax}\cdots Br$ (3.02−3.14 Å), are observed (Figure 4), similar to that found for the sulfur analogues. These contacts correspond to a weak donation of electron density from Br^- to σ^* orbitals of the Se_2 ligand and are considered in detail elsewhere.[29−31]

The crystal structures of **III** and **IV** are built of cluster cations $[M_3(\mu_3\text{-}S)Se_3(H_2O)_6Cl_3]^+$, which form adducts with

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(25) Gerasko, O. A.; Sokolov, M. N.; Fedin, V. P. *Pure Appl. Chem.* **2004**, *76*, 1633.

(26) Fedin, V. P.; Sokolov, M. N.; Virovets, A. V.; Podberezskaya, N. V.; Fedorov, V. E. *Inorg. Chim. Acta* **1998**, *269*, 292.

(27) Shibahara, T.; Yamada, T.; Kuroya, H.; Hills, E. F.; Kathirgamanathan, P.; Sykes, A. G. *Inorg. Chim. Acta* **1986**, *113*, L19.

(28) Fedin, V. P.; Myakishev, K. G.; Geras'ko, O. A.; Fedorov, V. Ye.; Macicek, J. *Polyhedron* **1991**, *10*, 1311.

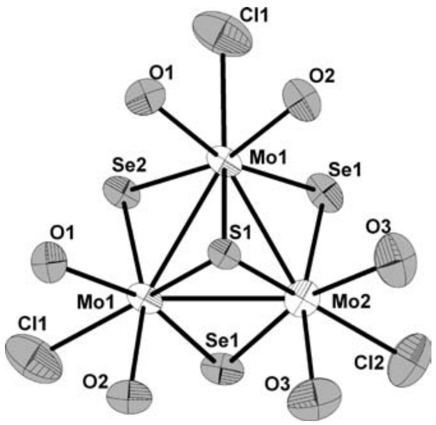

Figure 5. Structure of $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}Se)_3(H_2O)_6Cl_3]^+$ in **III**. The thermal ellipsoids are drawn at a 50% probability level.

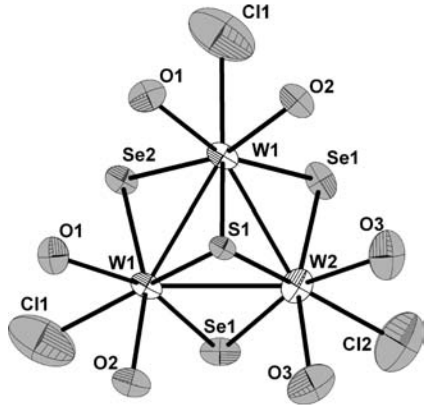

Figure 6. Structure of $[W_3(\mu_3\text{-}S)Se_3(H_2O)_7Cl_2]^{2+}$ in **IV**. The thermal ellipsoids are drawn at a 50% probability level. The chloride ligands positions are only partly occupied (2/3 chloride and 1/3 water).

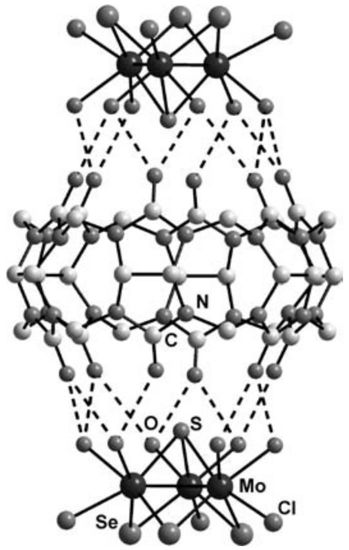

Figure 7. Structure of supramolecular adduct $\{[Mo_3(\mu_3\text{-}S)Se_3(H_2O)_6Cl_3]_2CB[6]\}^{2+}$ in **III**. O···O interections are shown as dashed lines.

CB[6], together with outer-sphere Cl anions and solvent H_2O molecules. The structures of $[Mo_3(\mu_3\text{-}S)Se_3(H_2O)_6Cl_3]^+$ and $[W_3(\mu_3\text{-}S)Se_3(H_2O)_7Cl_2]^{2+}$ are shown in Figures 5 and 6, respectively. The cluster cations contain the M_3 triangle (Mo−Mo, 2.76−2.77 Å; W−W, 2.74−2.76 Å), capped with the μ_3-S (Mo−S, 2.36 Å; W−S, 2.38−2.39 Å) and bridged by three μ_3-Se ligands (Mo−Se, 2.39−2.41 Å; W−Se, 2.42−2.43 Å). The coordinated Cl^- ions are trans to the μ_3-S (Mo−Cl, 2.46−2.48 Å; W−Cl, 2.40−2.43 Å), which is the typical arrangement to ensure the complementary of the hydrogen bonding between the aqua ion and the cavitand. Each metal atom of the cation is coordinated by two water molecules in the positions cis to the μ_3-S (Mo−O, 2.17−2.22 Å; W−O, 2.20−2.22 Å). The same Cl^- and H_2O ligand arrangement is observed in $[Mo_3(\mu_3\text{-}O)(\mu_2\text{-}O)_3Cl_3(H_2O)_6]^+$, $[Mo_3(\mu_3\text{-}Se)(\mu_2\text{-}O)_3Cl_3(H_2O)_6]^+$, and $[M_3(\mu_3\text{-}Q)(\mu_2\text{-}Q)_3Cl_3(H_2O)_6]^+$ (Q = S, Se; M = Mo, W) in their CB[6] adducts.[32−37] The Mo−Mo distances in **III** are, by 0.04 Å, shorter than those found in $[Mo_3(\mu_3\text{-}Se)(\mu_2\text{-}Se)_3Cl_3(H_2O)_6]^{+}$[34] due to the shortness of the Mo−S bonds, which draw more closely together the Mo atoms, but are much longer than those in $[Mo_3(\mu_3\text{-}O)(\mu_2\text{-}O)_3Cl_3(H_2O)_6]^+$ (2.51 Å[32]) and $[Mo_3(\mu_3\text{-}Se)(\mu_2\text{-}O)_3Cl_3(H_2O)_6]^+$ (2.57 Å[37]). As expected, the W−W distances in **IV** are slightly longer than those found in $[W_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3Cl_2(H_2O)_7]^{2+}$ (2.71−2.73 Å[38]) and slightly shorter than those in $[W_3Se_4(H_2O)_9](pts)_4\cdot 12H_2O$ (2.75−2.77 Å[39]). Mo−μ_3-S distances are almost identical to the ones found in $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3Cl_3(H_2O)_6]^+$.[38] The W−$\mu_3$-S distances are somewhat longer than those in $[W_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3Cl_2(H_2O)_7]^{2+}$ (2.33−2.35 Å[38]).

Six coordinated H_2O molecules form hydrogen bonds with portal oxygen atoms of cucurbituril (O···O, 2.70−3.04 Å for **III** and 2.70−2.92 for **IV**) to yield supramolecular 2:1 adducts (two clusters per CB[6], Figure 7). Similar 2:1 adducts are found in $\{[Mo_3(\mu_3\text{-}O)(\mu_2\text{-}O)_3Cl_3(H_2O)_6]_2CB[6]\}Cl_2\cdot 14H_2O$[32] and $\{[Mo_3(\mu_3\text{-}Se)(\mu_2\text{-}O)_3Cl_3(H_2O)_6]_2CB[6]\}Cl_2\cdot 15H_2O$,[37] though the three compounds are not isostructural.

To conclude, reliable selective procedures have been identified for the preparation of triangular Mo clusters with mixed chalcogenide bridging ligands, $Mo_3(\mu_3\text{-}S)(\mu\text{-}Se_2)_3{}^{4+}$ and $Mo_3(\mu_3\text{-}S)(\mu\text{-}Se)_3{}^{4+}$, starting from the stoichiometric mixtures of the elements. The selectivity is less in the case of tungsten. In this latter case, other synthetic approaches can be more efficient.

Acknowledgment. The authors thank Dr. Dmitriy Yu. Naumov (Nikolaev Institute of Inorganic Chemistry) for carrying out an X-ray diffraction experiment on **II**,

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(29) Gushchin, A. L.; Sokolov, M. N.; Peresypkina, E. V.; Virovets, A. V.; Kozlova, S. G.; Zakharchuk, N. F.; Fedin, V. P. *Eur. J. Inorg. Chem.* **2008**, 3964.

(30) Mayor-Lopez, M. J.; Weber, J.; Hegetschweiler, K.; Meienberger, M.; Joho, F.; Leoni, S.; Nesper, R.; Reiss, G. J.; Frank, W.; Kolesov, B. A.; Fedin, V. P.; Fedorov, V. E. *Inorg. Chem.* **1998**, *37*, 2633.

(31) Virovets, A. V.; Gushchin, A. L.; Abramov, P. A.; Alferova, N. I.; Sokolov, M. N.; Fedin, V. P. *J. Struct. Chem.* **2006**, *47*, 326.

(32) Samsonenko, D. G.; Virovets, A. V.; Sharonova, A. A.; Fedin, V. P.; Fenske, D. *Russ. Chem. Bull. Int. Ed.* **2001**, *50*, 494.

(33) Sokolov, M. N.; Hernandez-Molina, R.; Dybtsev, D. N.; Chubarova, E. V.; Solodovnikov, S. F.; Pervukhina, N. V.; Vicent, C.; Llusar, R.; Fedin, V. P. *Z. Anorg. Allg. Chem.* **2002**, *628*, 2335.

(34) Fedin, V. P.; Sokolov, M. N.; Dybtsev, D. N.; Gersako, O. A.; Virovets, A. V.; Fenske, D. *Inorg. Chim. Acta* **2002**, *331*, 31.

(35) Sokolov, M. N.; Gerasko, O. A.; Dybtsev, D. N.; Chubarova, E. V.; Virovets, A. V.; Vicent, C.; Llusar, R.; Fenske, D.; Fedin, V. P. *Eur. J. Inorg. Chem.* **2004**, 63.

Mr. Sergey Tkachev (Nikolaev Institute of Inorganic Chemistry) for recording NMR spectra, Dr. Jens E. T. Andersen for help with ICP-MS analysis, and the Technical University of Denmark for an H.C. Ørsted Postdoctoral Fellowship (to A.L.G.).

Supporting Information Available: CIF files for the structures **II**, **III**, and **IV**. ^{77}Se NMR and Raman spectra for **I**. UV−vis spectrum for $[Mo_4(\mu_3\text{-}S)Se_3(H_2O)_{12}]^{5+}$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC8023327

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(36) Gerasko, O. A.; Virovets, A. V.; Sokolov, M. N.; Dybtsev, D. N.; Gerasimenko, A. V.; Fenske, D.; Fedin, V. P. *Izv. Akad. Nauk. Ser. Khim.* **2002**, 1654.

(37) Abramov, P. A.; Sokolov, M. N.; Virovets, A. V.; Peresypkina, E. V.; Fedin, V. P. *J. Cluster Sci.* **2007**, *18*, 597.

(38) Fedin, V. P.; Virovets, A. V.; Sokolov, M. N.; Dybtsev, D. N.; Gerasko, O. A.; Clegg, W. *Inorg. Chem.* **2000**, *38*, 2227.

(39) Hernandez-Molina, R.; Elsegood, M. R. J.; Clegg, W.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **2001**, *14*, 2173.