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Article

Cluster Oxalate Complexes $[M_3(\mu_3\text{-}Q)(\mu_2\text{-}Q_2)_3(C_2O_4)_3]^{2-}$ and $[Mo_3(\mu_3\text{-}Q)(\mu_2\text{-}Q)_3(C_2O_4)_3(H_2O)_3]^{2-}$ (M = Mo, W; Q = S, Se): Mechanochemical Synthesis and Crystal Structure

Maxim N. Sokolov,* Artyom L. Gushchin, Dmitrii Yu. Naumov, Olga A. Gerasko, and Vladimir P. Fedin

A. V. Nikolayev Institute of Inorganic Chemistry, Russian Academy of Sciences, pr. Lavrentyeva 3, Novosibirsk 630090, Russia

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Mechanochemical reaction of cluster coordination polymers $^1_\infty[M_3Q_7Br_4]$ (M = Mo, W; Q = S, Se) with solid $K_2C_2O_4$ leads to cluster core excision with the formation of anionic complexes $[M_3Q_7(C_2O_4)_3]^{2-}$. Extraction of the reaction mixture with water followed by crystallization gives crystalline $K_2[M_3Q_7(C_2O_4)_3]\cdot 0.5KBr\cdot nH_2O$ (M = Mo, Q = S, $n = 3$ (**1**); M = Mo, Q = Se, $n = 4$ (**2**); M = W, Q = S, $n = 5$ (**3**)). $Cs_2[Mo_3S_7(C_2O_4)_3]\cdot 0.5CsCl\cdot 3.5H_2O$ (**4**) and $(Et_4N)_{1.5}H_{0.5}K\{[Mo_3S_7(C_2O_4)_3]Br\}\cdot 2H_2O$ (**5**) were also prepared. Close Q···Br contacts result in the formation of ionic triples $\{[M_3Q_7(C_2O_4)_3]_2Br\}^{5-}$ in **1**–**4** and the 1:1 adduct $\{[Mo_3S_7(C_2O_4)_3]Br\}^{3-}$ in **5**. Treatment of **1** or **2** with PPh_3 leads to chalcogen abstraction with the formation of $[Mo_3(\mu_3\text{-}Q)(\mu_2\text{-}Q)_3(C_2O_4)_3(H_2O)_3]^{2-}$, isolated as $(Ph_4P)_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3(C_2O_4)_3(H_2O)_3]\cdot 11H_2O$ (**6**) and $(Ph_4P)_2[Mo_3(\mu_3\text{-}Se)(\mu_2\text{-}Se)_3(C_2O_4)_3(H_2O)_3]\cdot 8.5H_2O\cdot 0.5C_2H_5OH$ (**7**). All compounds were characterized by X-ray structure analysis. IR, Raman, electronic, and ^{77}Se NMR spectra are also reported. Thermal decomposition of **1**–**3** was studied by thermogravimetry.

Introduction

Many transition metal halide and chalcohalide clusters are easily available via high-temperature synthesis from the elements in high yields. These reactions generally result in chemically inert coordination polymers in which the desired cluster units are connected by bridging ligands into 1D, 2D, and 3D frameworks.[1−4] Therefore, it is necessary to find a compromise between the elevated temperatures needed to overcome the inert nature of the clusters, and the obvious goal is to excise the desired cluster unit intact, in a discrete molecular or ionic form, from the extended solid framework. Ligand melts (such as molten PPh_4X (X = Cl, Br), KNCS, and *o*-phenanthroline) were applied to obtain discrete complexes of $[M_3Q_7X_6]^{2-}$, $[Mo_3Q_7(phen)_3]^{4+}$, and $[Nb_2(S_2)_2(NCS)_8]^{4-}$ from 1D $[M_3Q_7X_{4/2}X_4]$ and 2D $[Nb_2(S_2)_2X_{8/2}]$ (M = Mo, W; Q = S, Se).[5−7] Under milder conditions, these cluster coordination polymers were found to be too inert. It is clear, however, that many ligands would not withstand required prolonged heating without decomposition. We have introduced an alternative method of cluster excision from the solids based on the mechanochemical reaction of cluster coordination polymers with an appropriate ligand.[8,9] We consider the reactions occurring during deformation, friction, and fracture of solids to be mechanochemical.[10] Applications of mechanochemistry to inorganic synthesis (solid-state chemistry not included) include borane synthesis[11] and 3d element coordination chemistry (carbollides, β-diketonates and iminoanalogues, cyclopentadienyls, and dithiocarbamates).[12−14] We have successfully applied mechanochemical synthesis as an entry route into $M_3Se_7^{4+}$

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* To whom correspondence should be addressed. E-mail: cluster@che.nsk.su.

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and $Nb_2(Se_2)_2^{4+}$ coordination chemistry.[8,9] In this paper, we report mechanochemical reactions of 1D coordination cluster polymers $^{1}_{\infty}[M_3Q_7X_{4/2}X_2]$ with solid $K_2C_2O_4$ which produce, after water extraction and crystallization, isostructural $K_2[M_3Q_7(C_2O_4)_3]\cdot 0.5KBr\cdot nH_2O$ (M = Mo, W; Q = S, Se). The crystal structures of both Mo derivatives and the W/S cluster were determined.

Experimental Section

Materials and Methods. The starting cluster coordination polymers $M_3Q_7Br_4$ were prepared by heating stoichiometric mixtures of elements in sealed glass tubes (350 °C, 4 days).[5,6,8] All other reagents were of commercial purity.

The construction of the vibration mill is described in ref 11. We used a simplified version without a gas outlet. All the operations were in air. A cylindrical titanium reactor (stainless steel was found to be unsatisfactory because considerable amounts of $[Fe(C_2O_4)_3]^{3-}$ formed during the treatment) was used (V = 100 mL, height = 50 mm). The reactor was filled with tungsten carbide balls (diameter = 10 mm, total mass = 320 g) and a mixture of solid reagents. The reactions were run under the following conditions: reactor vibration frequency, 25 Hz; vertical movement amplitude, 1 cm; and duration of treatment, 15 h.

Elemental analyses were carried out by the Novosibirsk Institute of Organic Chemistry microanalytical service. IR spectra (4000−400 cm^{-1}) were recorded on an IFS-85 Fourier spectrometer (Bruker). Raman spectra were obtained on a Triplimate SPEX spectrometer using a 632.8 nm 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 vs Me_2Se. Thermogravimetric studies were done in an He atmosphere on a TGD-7000RH apparatus at a rate of 10 °C min^{-1}.

Synthesis of $K_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3(C_2O_4)_3]\cdot 0.5KBr\cdot 3H_2O$ (1). A mixture of solid $Mo_3S_7Br_4$ (1.42 g, 1.71 mmol) and $K_2C_2O_4$ (1.02 g, 6.14 mmol) was treated in the vibration mill as described above. After extraction with 50 mL of water and cooling to 5 °C, a crop of red crystals of **1** was obtained, filtered, washed with a water−ethanol mixture (1:1 v/v) and diethyl ether, and dried. Yield: 0.77 g (47%). Anal. Calcd for $C_6H_6Br_{0.5}Mo_3O_{15}K_{2.5}S_7$: C, 7.44; H, 0.62. Found: C, 7.08; H, 0.56. IR (KBr, 4000−400 cm^{-1}): 3460 s, 1667 s, 1379 s, 1235 vw, 1070 vw, 1026 w, 904 m, 789 s, 587 vw, 530 s, 465 m. Raman (cm^{-1}): 531 s, 455 w, 399 m, 364 s, 345 w, 291 s, 237 vs, 209 m, 190 m, 171 sh, 157 m, 98 sh, 71 s, 59 sh. DTG: 48−156 °C, Δm = 5.9% ($-3H_2O$); 276−381 °C, Δm = 24.1% ($-3CO_2$, $-3CO$).

Synthesis of $K_2[Mo_3(\mu_3\text{-}Se)(\mu_2\text{-}Se_2)_3(C_2O_4)_3]\cdot 0.5KBr\cdot 4H_2O$ (2). A mixture of solid $Mo_3Se_7Br_4$ (3.01 g, 2.59 mmol) and $K_2C_2O_4$ (1.51 g, 9.09 mmol) was treated in the vibration mill as described above. After extraction with 50 mL of water and cooling to 5 °C, dark-red, almost black, crystals of **2** were obtained, filtered, washed with a water−ethanol mixture (1:1 v/v) and diethyl ether, and dried. Yield: 1.20 g (35%). ^{77}Se NMR (57 MHz, H_2O, 25 °C): δ 666.4, 287.1, −85.8. Anal. Calcd for $C_6H_8Br_{0.5}Mo_3O_{16}K_{2.5}Se_7$: C, 5.48; H, 0.61. Found: C, 5.67; H, 0.62. IR (KBr, 4000−400 cm^{-1}): 3388 s, 1670 s, 1395 s, 1317 w, 1246 w, 1073 vw, 1037 vw, 909 m, 792 s, 525 m, 470 m. Raman (cm^{-1}): 521 w, 355 m, 315 s, 273 s, 224 vw, 169 s, 141 s, 59 m. DTG: 43−156 °C, Δm = 6.1% ($-4H_2O$); 291−376 °C, Δm = 16.8% ($-3CO_2$, $-3CO$).

Synthesis of $K_2[W_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3(C_2O_4)_3]\cdot 0.5KBr\cdot 5H_2O$ (3). A mixture of solid $W_3S_7Br_4$ (1.29 g, 1.18 mmol) and $K_2C_2O_4$ (0.71 g, 4.27 mmol) was treated in the vibration mill as described above. After extraction with 100 mL of water and cooling to 5 °C, red crystals of **3** were obtained and treated as above. Yield: 0.15 g (10%). Anal. Calcd for $C_6H_{10}Br_{0.5}O_{17}K_{2.5}S_7W_3$: C, 5.68; H, 0.79. Found: C, 5.75; H, 0.62. IR (KBr, 4000−400 cm^{-1}): 3499 s, 1677 s, 1380 s, 1227 w, 1068 vw, 908 m, 792 s, 538 s, 458 m. Raman (cm^{-1}): 521 s, 429 w, 368 sh, 362 m, 328 s, 317 sh, 295 s, 244 sh, 234 vs, 215 sh, 188 w, 169 m, 98 sh, 71 s, 56 s. DTG: 31−194 °C, Δm = 6.7% ($-5H_2O$); 243−411 °C, Δm = 18.0% ($-3CO_2$, $-3CO$).

Synthesis of $Cs_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3(C_2O_4)_3]\cdot 0.5CsCl\cdot 3.5H_2O$ (4). CsCl (0.24 g, 1.43 mmol) was added to a solution of **1** (0.30 g, 0.31 mmol) in 10 mL of H_2O. Red crystals of **4** were obtained after ethanol vapor diffusion into the solution, filtered, washed with ethanol and diethyl ether, and dried. Yield: 0.32 g (87%). Anal. Calcd for $C_6H_7Cl_{0.5}Cs_{2.5}Mo_3O_{15.5}S_7$: C, 6.05; H, 0.59. Found: C, 5.86; H, 0.63. IR (KBr, 4000−400 cm^{-1}): 3438 s, 1676 s, 1379 s, 1233 w, 905 m, 790 s, 590 vw, 530 s, 471 m, 401 vw.

Synthesis of $(Et_4N)_{1.5}H_{0.5}[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3(C_2O_4)_3]\cdot KBr\cdot 2H_2O$ (5). Et_4NBr (6.00 g, 28 mmol) was added to a solution of **1** (0.30 g, 0.31 mmol) in 10 mL of H_2O. Red crystals of **5** were obtained by a slow evaporation of the solution. Yield: 0.30 g (88%). Anal. Calcd for $C_{18}H_{34.5}BrMo_3O_{14}KS_7$: C, 19.54; H, 3.14. Found: C, 19.19; H, 3.22. IR (KBr, 4000−400 cm^{-1}): 3416 s, 1677 s, 1483 m, 1440 w, 1373 s, 1224 w, 1173 w, 1053 vw, 998 m, 902 m, 789 s, 596 w, 529 s, 465 m, 405 w.

Synthesis of $(Ph_4P)_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3(C_2O_4)_3(H_2O)_3]\cdot 11H_2O$ (6). A solution of PPh_3 (0.57 g, 2.17 mmol) in 50 mL of CH_2Cl_2 was added to a solution of **1** (0.64 g, 0.66 mmol) in 70 mL of H_2O. The mixture was stirred for 2 h. After evaporation of CH_2Cl_2 and filtration of the white precipitate of $SPPh_3$, PPh_4Cl (1.20 g, 3.2 mmol) was added to the green solution. Some brown precipitate appeared, which was filtered off. Green platelike crystals of **6** were obtained by a slow evaporation of the filtrate. Yield: 0.71 g (67%). Anal. Calcd for $C_{54}H_{68}Mo_3O_{26}P_2S_4$: C, 40.26; H, 4.25. Found: C, 40.49; H, 3.86. IR (KBr, 4000−400 cm^{-1}): 3424 s, 1700 w, 1670 s, 1587 sh, 1483 m, 1437 s, 1369 s, 1246 w, 1188 w, 1165 w, 1108 s, 996 m, 899 m, 787 m, 757 m, 722 s, 689 s, 616 vw, 527 s, 496 w, 460 w, 439 vw. Absorption spectrum (water) λ_{max} (ϵ_M): 363 (7290), 626 (430) nm.

Synthesis of $(Ph_4P)_2[Mo_3(\mu_3\text{-}Se)(\mu_2\text{-}Se)_3(C_2O_4)_3(H_2O)_3]\cdot 8.5H_2O\cdot 0.5C_2H_5OH$ (7). A solution of PPh_3 (0.40 g, 1.52 mmol) in 50 mL of CH_2Cl_2 was added to a solution of **2** (0.65 g, 0.67 mmol) in 70 mL of H_2O. The mixture was stirred for 2 h. After separation of the CH_2Cl_2 layer, PPh_4Cl (1.20 g, 3.2 mmol) was added to the brown solution. A precipitate appeared and was filtered off. Dark-brown platelike crystals of **7** were obtained by a slow evaporation of the solution, to which ethanol (1:3 by volume) was added. Yield: 0.53 g (60%). Anal. Calcd for $C_{55}H_{66}Mo_3O_{24}P_2Se_4$: C, 37.18; H, 3.74. Found: C, 36.93; H, 3.44. IR (KBr, 4000−400 cm^{-1}): 3416 s, 1699 w, 1670 s, 1586 sh, 1481 m, 1436 s, 1371 s, 1317 vw, 1243 w, 1188 w, 1164 w, 1108 s, 1027 w, 995 m, 897 m, 785 m, 756 m, 722 s, 688 s, 616 vw, 526 s, 469 vw. Absorption spectrum (water) λ_{max} (ϵ_M): 423 (5330), 679 (650) nm.

X-ray Structure Determinations. Crystals of complexes **1**−**7** suitable for X-ray diffraction were obtained as described in the Experimental Section. The data were collected on a Brucker-Nonius

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Table 1. Crystal Data and Structure Refinement for **1**−**7**

	1	**2**	**3**	**4**	**5**	**6**	**7**
formula	$C_6H_6Br_{0.5}Mo_3O_{15}K_{2.5}S_7$	$C_6H_8Br_{0.5}Mo_3O_{16}K_{2.5}Se_7$	$C_6H_{10}Br_{0.5}O_{17}K_{2.5}S_7W_3$	$C_6H_7Cl_{0.5}Cs_{2.5}Mo_3O_{15.5}S_7$	$C_{18}H_{34.5}Br_1Mo_3O_{14}K_1S_7$	$C_{54}H_{68}Mo_3O_{26}P_2S_4$	$C_{55}H_{66}Mo_3O_{24}P_2Se_4$
fw	968.05	1314.37	1267.82	1189.36	1127.22	1611.08	1776.68
T (°C)	20(2)	20(2)	−123(2)	23(2)	20(2)	−123(2)	20(2)
space group, *Z*	$P2_1/c$, 8	$P2_1/c$, 8	$P2_1/c$, 8	$P2_1/n$, 8	$P\bar{1}$,2	$P2_1/n$, 4	$P2_1/n$, 4
a (Å)	14.7810(8)	15.0725(8)	14.9237(6)	14.0054(3)	11.0139(8)	14.8766(7)	15.3693(10)
b (Å)	13.1362(7)	13.5246(8)	13.2375(8)	16.1190(4)	12.6133(12)	14.5692(5)	14.6896(6)
c (Å)	26.7804(14)	27.3192(15)	26.9304(16)	23.8186(5)	13.9776(13)	30.5265(13)	31.1011(19)
α (deg)	90	90	90	90	107.069(2)	90	90
β (deg)	99.154(1)	100.8780(10)	101.3970(10)	91.3310(10)	93.029(3)	102.976(8)	102.2850(10)
γ (deg)	90	90	90	90	94.690(2)	90	90
V	5133.6(5)	5468.9(5)	5215.3(5)	5375.7(2)	1844.0(3)	6447.4(5)	6860.9(7)
μ(Mo Kα) (mm^{-1})	3.258	11.847	14.999	5.371	2.656	0.835	2.782
d_{calc} (g cm^{-3})	2.505	3.193	2.229	2.939	2.030	1.660	1.720
number of reflns	21374	23210	48681	35905	13236	52342	39670
final R1 and wR2 $[I > 2\sigma(I)]^a$	0.0431, 0.0995	0.0374, 0.0945	0.0417, 0.1008	0.0333, 0.0948	0.0351, 0.1013	0.0440, 0.1087	0.0515, 0.1328

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, $w = s_F^{-2}$

×8 APEX CCD diffractometer equipped with graphite-monochromated (Mo Kα radiation $\lambda = 0.71073$ Å). The data were collected at 293 K for **1**, **2**, **4**, **5**, and **7** and 150 K for **3** and **6**. Experimental details are described in Table 1. The *ω*- and *φ*-scan technique was employed to measure intensities. Decomposition of the crystals did not occur during data collection. Corrections were applied for Lorentz and polarization effects and for absorption.[15] The structures were solved by direct methods using SHELXS-97,[16] and the missing atoms were located in the difference Fourier map and included in subsequent refinement cycles. The structures were refined by full-matrix least-squares refinement on F^2, using anisotropic displacement parameters for all non-hydrogen atoms using SHELXL-97.[17] Restraints were imposed on crystalline water molecules and disordered cations to reduce the sphericity of anisotropic displacement parameters. In all cases, hydrogen atoms were included using a riding model with C−H distances of 0.93−0.97 Å and fixed isotropic thermal parameters. The hydrogen atoms from the water molecules are not located. ORTEP drawings were made using ORTEP III for Windows.[18]

Results and Discussion

Synthesis and Spectra. In a vibration mill, the intercluster halide linkages are efficiently broken and, in the presence of oxalate, discrete anionic complexes $[M_3Q_7(C_2O_4)_3]^{2-}$ result. They can be extracted with water, giving stable solutions, from which, after concentrating, double salts $K_2[M_3Q_7(C_2O_4)_3]\cdot 0.5KBr\cdot nH_2O$ (**1**−**3**) crystallize. One exception is red $[W_3Se_7(C_2O_4)_3]^{2-}$, which in aqueous solutions easily loses selenium to give green $[W_3Se_4(C_2O_4)_3(H_2O)_3]^{2-}$ ($\lambda_{max} = 652$ nm), and was not isolated pure. Similar transformation of the sulfide derivative **3** is much slower, while the molybdenum clusters are perfectly stable with no tendency to lose chalcogen in solution. However, adding PPh_3 brings about rapid and quantitative transformation, such as

$$[Mo_3S_7(C_2O_4)_3]^{2-} + 3PPh_3 + 3H_2O = [Mo_3S_4(C_2O_4)_3(H_2O)_3]^{2-} + 3SPPh_3$$

The electronic spectra of the heptachalcogenide species are featureless, while the spectra of the tetrachalcogenide clusters have characteristic bands to follow the reaction. Adding Ph_4PCl to the solution allowed us to isolate crystalline $(Ph_4P)_2[Mo_3S_4(C_2O_4)_3(H_2O)_3]\cdot 11H_2O$ (**6**). The selenide analogue $(Ph_4P)_2[Mo_3(\mu_3\text{-Se})(\mu_2\text{-Se})_3(C_2O_4)_3(H_2O)_3]\cdot 8.5H_2O\cdot 0.5C_2H_5OH$ (**7**) was obtained similarly.

An alternative method, used recently to make $(Bu_4N)_3\{[Mo_3S_7(C_2O_4)_3]Br\}$, made use of ligand substitution in the reaction of $(Bu_4N)_2[Mo_3S_7Br_6]$ with $H_2C_2O_4$ in the presence of Et_3N in high yield.[19] The oxalate complexes with other M_3Q_7 cores have not been reported.

There are several derivatives of M_3Q_7 clusters with other O-donor ligands, such as aqua complexes $[M_3Q_7(H_2O)_6]^{4+}$ and tris-chelates of Mo_3S_7 with 3,4-dihydroxybenzoic acid, pyrocatechol, and its bis(sulfonated) derivative.[20−23] They are easily obtained from corresponding $[M_3Q_7Br_6]^{2-}$ by ligand substitution. Structural characterization of all of them, with the sole exception of $(Bu_4N)_3\{[Mo_3S_7(C_2O_4)_3]\}Br$, is lacking.

Thermogravimetric studies on **1**−**3** show that after removal of the water of crystallization before 160−190 °C the complexes are stable up to 243 °C (**3**), 291 °C (**2**), and 276 °C (**1**) when the decomposition of the oxalate ligands starts. Infrared spectra show strong characteristic bands of

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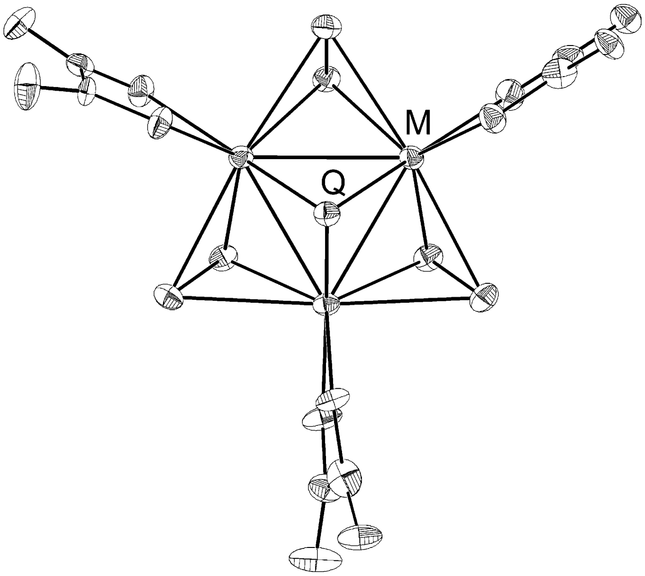

Figure 1. View of $[W_3S_7(C_2O_4)_3]^{2-}$ in **3**.

bidentate oxalate at 1667−1670 cm^{-1} (ν_{as}(C=O)), 1379−1395 cm^{-1} (ν_s(C−O) + ν(C−C)), 904−909 cm^{-1} (ν_s(C−O) + δ(O−C−O)), and 789−792 cm^{-1} (δ(O−C−O) + ν(M−O)), which are also routinely observed in the IR spectra of other complexes. M−O vibrations contribute to the bands at 525−530 cm^{-1}.[24] Raman spectra show characteristically strong ν(S−S) bands at 531 and 521 cm^{-1} for **1** and **3**, respectively.[25] The ^{77}Se NMR spectrum for aqueous solution of **2** shows three signals with δ = 666.4, 287.1, and −85.8 according to the three types of selenium atoms in the structure; one corresponds to μ_3-Se (δ = 666.4), and the asymmetrically coordinated μ_2-Se$_2$ ligands give two sets of nonequivalent selenium atoms (δ = 287.1 and −85.8): three Se lying in the M$_3$ plane and the other three Se lying out of the plane, in perfect agreement with the solid-state structure. The scale of the observed chemical shifts is more than 700 ppm. Close values were reported for $[Mo_3Se_7(N(SePPh_2))_3]Br$, where the signal at 605 ppm was assigned to the μ_3-Se, and the two peaks at 210 and 97 ppm were assigned to the asymmetrically coordinated μ-Se$_2$ ligand. The assignments are based on the peak relative intensity.[26]

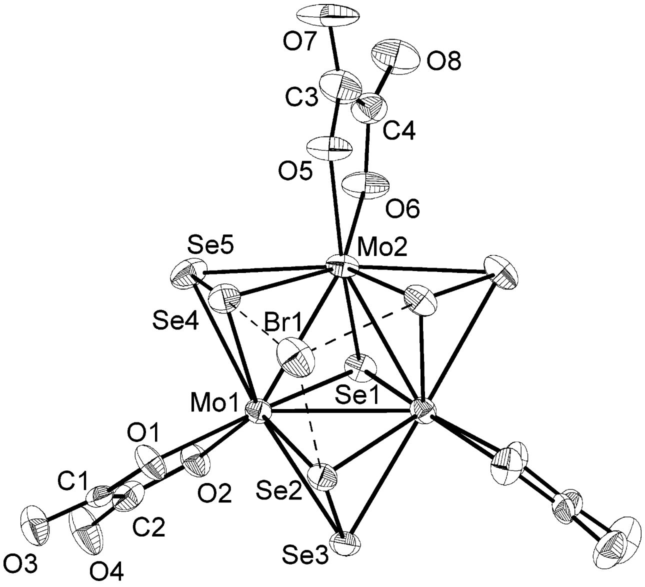

Figure 2. ORTEP drawing of adduct $\{[Mo_3Se_7(C_2O_4)_3]Br\}^{3-}$ in complex **2** with the atom-labeling scheme and 50% probability thermal ellipsoids.

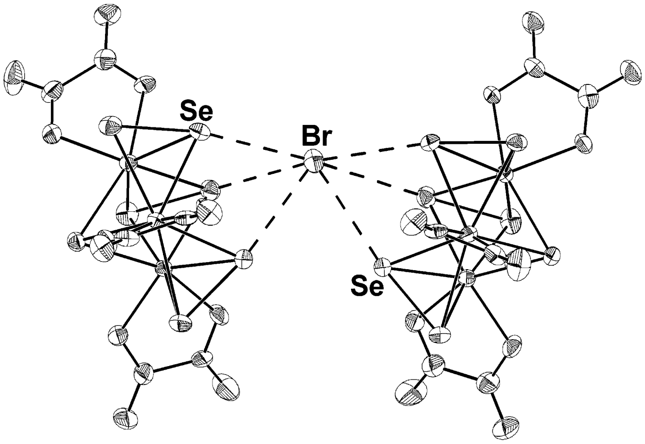

Figure 3. Sandwich formation in structure **2**.

Structure Description. Complexes **1**−**3** are isostructural. They contain K$^+$ cations, $[M_3Q_7(C_2O_4)_3]^{2-}$ anions (Figure 1), Br$^-$, and the water of crystallization. The same building units are found in the crystals of **4** and **5** except that the cationic part is represented by Cs$^+$ in **4**, and by Et$_4$N$^+$/K$^+$ in **5**. However, in all cases $[M_3Q_7(C_2O_4)_3]^{2-}$ and Br$^-$ are not isolated from each other but form either ionic triplets $\{[M_3Q_7(C_2O_4)_3]_2Br\}^{5-}$ (as in **1**−**4**, Figure 2) or 1:1 adducts, as in **5** (Figure 3), through Q···Br interactions. Main geometrical parameters of the cluster anions are given in Table 2. The M−M distances in the cluster anions vary from 2.72 to 2.78 Å for the Mo clusters in **1**, **2**, **4**, and **5**, and are somewhat shorter in $[W_3S_7(C_2O_4)_3]^{2-}$ in **3** (2.70 Å). This slight shortening of the W−W bond vs the Mo−Mo bond is also found in other M$_3$Q$_7$ clusters.[27] Note the absence of any appreciable lengthening of the Mo−Mo bonds on going from **1** (sulfide bridges) to **2** (selenide bridges). Each M$_3$ triangle is capped by one μ_3-Q atom. The μ_2-Q$_2$ ligands are asymmetrically bonded so that one of them (Q$_{eq}$) lies almost in the M$_3$ plane, while the other (Q$_{ax}$) is above the plane. The M−Q$_{eq}$ bond distances are always longer, by about 0.1 Å, than those of the M−Q$_{ax}$ bond, and Br$^-$ is attached to the Q$_{ax}$ atoms. All of these features are typical for all M$_3$Q$_7$ clusters.[3] Three bidentate oxalates coordinate M atoms to give almost planar MOCCO rings, strictly perpendicular to the M$_3$ plane. The two oxygen atoms of the coordinated oxalate are designated O$_{cis}$ and O$_{trans}$ with respect to the μ_3-Q (Figure 1). The M−O$_{cis}$ bonds are always shorter than the M−O$_{trans}$ bonds ($\Delta \approx$ 0.05 Å). Thus, the coordination mode of the oxalate groups in **1**−**5** is slightly asymmetric. The K$^+$ ions in **1**−**3** are disordered and are surrounded by both

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Table 2. Selected Bond Lengths (Å) for **1**−**5** and $(Bu_4N)_3\{[Mo_3S_7(ox)_3]Br\}$

compound	$[Mo_3S_7(ox)_3]^{2-}$ [19]	**1**	**2**	**3**	**4**	**5**
M−M	2.73	2.76−2.79	2.77−2.78	2.70	2.72−2.73	2.72
M−μ_3-Q	2.36	2.37−2.44	2.49−2.50	2.38−2.39	2.36	2.37
M−Q_{eq}	2.49	2.54−2.56	2.59−2.64	2.49−2.51	2.48−2.49	2.49−2.50
M−Q_{ax}	2.41	2.41−2.47	2.53−2.54	2.40−2.42	2.40−2.41	2.39−2.40
M−O_{trans}[a]	2.12	2.15−2.21	2.14−2.15	2.12−2.14	2.12−2.14	2.11−2.13
M−O_{cis}[b]	2.08	2.11−2.14	2.10−2.12	2.08−2.09	2.09−2.11	2.09−2.10
Q_{eq}−Q_{ax}	2.06	2.05−2.10	2.31−2.32	2.06−2.07	2.03−2.04	2.05−2.06
Q···Br	2.99−3.06	3.14−3.33	3.13−3.33	3.10−3.30	2.88−2.99[c]	2.99−3.06

[a] M−O_{trans} distance trans to M−μ_3-Q bond. [b] M−O_{cis} distance cis to M−μ_3-Q bond. [c] S···Cl.

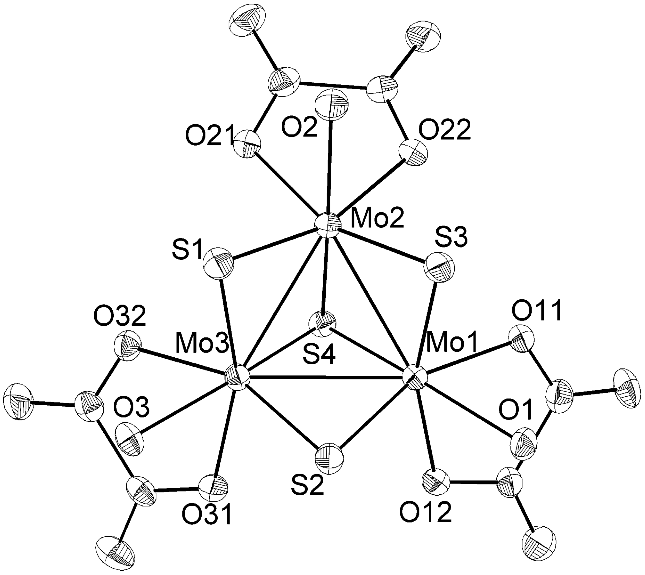

Figure 4. Molecular structure of **6** with the atom-labeling scheme and 50% probability thermal ellipsoids.

Table 3. Selected Bond Lengths [Å] for **6**, **7**, $Cs_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3(C_2O_4)_3(H_2O)_3]\cdot 3H_2O$, and $(\gamma,\gamma'\text{-bipyH})_2[W_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3(C_2O_4)_3(H_2O)_3]\cdot 5H_2O$[29]

compound	**6**	**7**	$[Mo_3S_4(C_2O_4)_3(H_2O)_3]^{2-}$ [29a]	$[W_3S_4(C_2O_4)_3(H_2O)_3]^{2-}$ [29b]
M−M	2.71−2.75	2.81−2.83	2.72−2.74	2.72
M−μ_3-Q	2.30−2.33	2.45−2.46	2.32	2.36−2.39
M−Q	2.26−2.28	2.40−2.41	2.27−2.29	2.25−2.29
M−$O_{oxalate}$	2.11−2.15	2.13−2.16	2.08−2.16	2.12−2.20
M−O_{water}	2.15−2.22	2.19−2.22	2.18−2.20	2.11−2.18

oxalate oxygens and water molecules. The water molecules and oxalate ligands participate in a hydrogen bond network. In **4**, Cs^+ is surrounded by both water and oxalate oxygen atoms, while in **5**, the coordination requirements of K^+ are satisfied only by oxalates. To balance the charge, we had to assume one acidic proton per two formula units of **5**, but it could not be localized.

Chalcogen abstraction from $[Mo_3Q_7(C_2O_4)_3]^{2-}$ leads to $[Mo_3Q_4(C_2O_4)_3(H_2O)_3]^{2-}$ (Figure 4) isolated as $(Ph_4P)_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3(C_2O_4)_3(H_2O)_3]\cdot 11H_2O$ (**6**) and as $(Ph_4P)_2[Mo_3(\mu_3\text{-}Se)(\mu_2\text{-}Se)_3(C_2O_4)_3(H_2O)_3]\cdot 8.5H_2O\cdot 0.5C_2H_5OH$ (**7**). The chalcogen atoms are always removed from the equatorial positions.[25,28] The geometrical parameters of the $Mo_3Q_4^{4+}$ clusters in **6** and **7** are nonexceptional.[3] The change from $Mo_3S_7^{4+}$ to $Mo_3S_4^{4+}$ leads to some shortening of the Mo−Mo bond lengths, while in the case of Se-bridged clusters they lengthen by ca. 0.05 Å, thus causing a significant matrix effect in the $M_3Q_4^{4+}$ clusters. There is also drastic shortening of the Mo-μ_3-Q and Mo-μ_2-S bonds, by 0.10−0.15 Å (Tables 2 and 3). The transformation also includes a ca. 90° reorientation of the coordinated oxalate so that its oxygens now occupy all-cis positions with respect to the μ_3-Q. The same configuration is found when $C_2O_4^{2-}$ enters the coordination sphere of $[Mo_3S_4(H_2O)_9]^{4+}$ by a ligand substitution reaction and was confirmed by X-ray analyses of $Cs_2[Mo_3S_4(C_2O_4)_3(H_2O)_3]\cdot 3H_2O$ and $(\gamma,\gamma'\text{-bipyH})_2[W_3S_4(C_2O_4)_3(H_2O)_3]\cdot 5H_2O$.[29] The all-cis coordination of a bidentate ligand is also exhibited by the $[M_3Q_4(acac)_3(py)_3]^+$ complexes,[30] but in all the other known cases the preferred mode is cis, trans.[3]

Q_{ax}···Br^- Contacts. A constant feature of structures **1**−**5** is close attachment of Br^- to the Q_{ax} atoms of $[M_3Q_7(C_2O_4)_3]^{2-}$. The resulting S···Br and Se···Br distances still fall beyond the limits of "normal" covalent bonding, but they also are far shorter than the sum of the van der Waals radii (S + Br, 3.78 Å; Se + Br, 3.89 Å).[31] Such contacts are typical for M_3Q_7 cores.[3] They were reviewed and given a theoretical treatment.[32,33] In the structures of **1**−**3**, there are rare "sandwich"-type ionic triplets in which Br^- forms six contacts with two cluster anions (Figure 3). They were previously observed in $\{[Mo_3S_7(Hmsa)_3][Mo_3S_7(Hmsa)_2(msa)]Br\}^{6-}$ (S_{ax}···Br, 3.30 Å).[34] At the same time $(Bu_4N)_3\{[Mo_3S_7(C_2O_4)_3]Br\}$ contains the 1:1 adducts (S···Br, 2.99−3.06 Å),[19] which is a far more common manner of association between cluster units and anionic species (Table 4). Obviously, the nature of cations influencing the crystal packing is crucial for the preference of 1:1 vs 2:1 (sandwich) associates. Going from K^+ and Br^- (complex **1**) to Cs^+ and Cl^- (complex **4**) preserves the sandwich structure while contracting the S_{ax}···X^- distances,

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Table 4. Interatomic Distances $d(Q_{ax}\cdots Br)$ and Covalence Index f_{cov} for the $Q_{ax}\cdots Br$ Interactions[a] in the $M_3Q_7^{4+}$ Clusters

formula	$d(Q_{ax}\cdots Br)$ (Å)	f_{cov}	ref
$[Mo_3S_7(Et_2NCS_2)_3]Br$	3.11	0.42	35
$\{H_5[Mo_3S_7(msa)_3]_2Br\}^{6-}$	3.30	0.30	34
$(Bu_4N)_3\{[Mo_3S_7(C_2O_4)_3]Br\}$	3.03	0.47	19
$(Et_4N)\{[Mo_3S_7Br_3(PhNH_2)_3]Br\}Br$	2.93−3.32	0.53	36
$[Mo_3S_7(n\text{-}Pr_2PS_2)_3]Br$	3.05	0.46	37
$\{[Mo_3S_7Br_5(DMSO)]Br\}^{2-}$	3.02−3.19	0.48	38
$[Mo_3S_7(N(P(S)Ph_2)_2)_3]Br$	2.99	0.49	39
$[Mo_3S_7(N(P(Se)Ph_2)_2)_3]Br$	3.22	0.35	39
$[Mo_3S_4Se_3(Et_2NCS_2)_3]Br$[b]	2.94−3.01	0.43	40
$[W_3Se_7((EtO)_2PS_2)_3]Br$	3.03−3.07	0.54	41
$[Mo_3Se_7((EtO)_2PSe_2)_3]Br$	3.05	0.53	26
$[Mo_3Se_7(N(P(Se)Ph_2)_2)_3]Br$	3.04	0.54	26
1	3.14−3.33	0.40	this work
2	3.13−3.33	0.48	this work
3	3.10−3.30	0.43	this work
4	2.88−2.99[c]	0.47	this work
5	2.99−3.06	0.49	this work

[a] $f_{cov} = [R_{vdW}(Q) + R_{vdW}(X) - d(Q_{ax} - X)][R_{vdW}(Q) + R_{vdW}(X) - R_{cov}(Q) - R_{cov}(X)]^{-1}$, where R_{vdW} and R_{cov} are the van der Waals radii and covalent radii, respectively, of the corresponding atoms.[31] [b] Q_{ax} = S. [c] S⋯Cl.

as expected (by 0.25 Å, if only the shortest contacts are taken into account). Even partial introduction of the far bulkier Et_4N^+ (complex **5**) is enough to make the structure prefer a 1:1 aggregation, as in the Bu_4N^+ salt; the S⋯Br contacts are practically identical in both cases (2.99−3.00 Å).[19]

To analyze such contacts (termed "specific noncovalent interactions"[32,33]), a semiempirical parameter covalence factor (f_{cov}) was found to be useful (Table 4). $f_{cov} = 0$ corresponds to no bonding, and $f_{cov} = 1$ corresponds to normal covalent bonding.[31,33] The S⋯Br contacts of about 3.0−3.1 Å represent a significant degree of bonding (f_{cov} = 0.4−0.5), and the Se⋯Br contacts do so even more.

The ionic triples in **1**−**3** interact with each other through shortened $Q_{eq}\cdots Q_{ax}$ contacts of 3.42−3.57, 3.32−3.55, and 3.34−3.54 Å in **2**, **1**, and **3**, respectively, to form layers in which K^+ and H_2O are located.

The importance of specific interactions between heavier nonmetals is increasingly being recognized. In addition to halogen−halogen[42] and chalcogen−chalcogen[43] interactions (and, of course, to already classical H-bonding and $\pi-\pi$ stacking), the chalcogen−halogen contacts must be added to the list of noncovalent interactions essential for specific packing and supramolecular aggregation.

There are no close Q⋯Q contacts in **6** and **7**. However the cluster anions dimerize by virtue of hydrogen bonding between coordinated water molecules and oxalate groups. Further linking the dimers through water molecules leads to the formation of layered structures. The cations occupy the interlayer space.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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