Mechanochemical synthesis and crystal structure of acetylacetonate complexes with the triangular $Mo_3Q_7^{4+}$ core (Q = S or Se)

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Mechanochemical reactions of inorganic polymers $^1{}_\infty[Mo_3Q_7Br_4]$ (Q = S or Se) with sodium acetylacetonate hydrate lead to excision of the $Mo_3Q_7^{4+}$ cluster core giving rise to the cationic complexes $[Mo_3Q_7(acac)_3]^+$. Extraction of the reaction mixture with acetone followed by recrystallization from a benzene—hexane mixture afforded the $\{[Mo_3S_7(CH_3COCHCOCH_3)_3]Br\}\cdot 2C_6H_6$ (**1**) and $\{[Mo_3Se_7(CH_3COCHCOCH_3)_3]Br\}\cdot 2C_6H_6$ (**2**) complexes. The structures of complexes **1** and **2** were studied by IR and ^{1}H NMR spectroscopy and X-ray diffraction. Compound **1** was characterized by electrospray mass spectrometry.

Key words: molybdenum, chalcogenide clusters, acetylacetonate complexes, mechanochemical synthesis, X-ray diffraction analysis.

Many halide and chalcogenide clusters of transition metals are readily available and can be prepared by the high-temperature synthesis from simple compounds in high yields. These reactions primarily produce coordination polymers, in which cluster fragments are linked to each other through bridging ligands to form one-, two-, or three-dimensional structures characterized by low reactivity.[1—4] The reactions of such polymers with melts of PPh_4X (X = Cl or Br), KNCS, or *o*-phenathroline are used for the synthesis of the discrete complexes $[M_3Q_7X_6]^{2-}$, $[Mo_3Q_7(phen)_3]^{4+}$, and $[Nb_2(S_2)_2(NCS)_8]^{4-}$ from one-dimensional compounds $[M_3Q_7X_{4/2}X_4]$ and two-dimensional compounds $[Nb_2(S_2)_2X_{8/2}]$ (M = Mo or W; Q = S or Se).[5—7] Another method for excision of the cluster core from solid coordination polymers is based on mechanochemical reactions with solid reagents.[8,9] The use of mechanochemistry in the synthesis of coordination compounds involves the preparation of boranes[10] and 3d-metal complexes (*β*-diketonates, cyclopentadienyls, and dithiocarbamates).[11—13] Earlier, we have used the mechanochemical synthesis for the preparation of derivatives with the cluster cores $M_3Se_7^{4+}$ (M = Mo or W) and $Nb_2Se_4^{4+}$.[8,14] In some cases, this is the only route to these complexes. In the present study, we performed mechanochemical reactions of the one-dimensional inorganic polymers $^1{}_\infty[Mo_3Q_7Br_{4/2}Br_2]$ with sodium acetylacetonate hydrate. These reactions followed by extraction with acetone and crystallization afforded new $\{[Mo_3Q_7(CH_3COCHCOCH_3)_3]Br\}\cdot 2C_6H_6$ complexes (Q = S or Se). The structures of the resulting compounds were established by X-ray diffraction.

Results and Discussion

The reactions of the coordination polymers $^1{}_\infty[Mo_3Q_7Br_4]$ with sodium acetylacetonate in a vibration mill lead to excision of the cluster fragments Mo_3Q_7 giving rise to the corresponding $[Mo_3Q_7(acac)_3]^+$ complexes (Q = S or Se):

$$Mo_3Q_7Br_4 + 3\ Na(acac) \rightarrow [Mo_3Q_7(acac)_3]Br + 3\ NaBr.$$

These complexes were extracted with acetone. After crystallization from a benzene—hexane mixture, the complexes were isolated as crystal solvates with two benzene molecules, $\{[Mo_3S_7(CH_3COCHCOCH_3)_3]Br\}\cdot 2C_6H_6$ (**1**) and $\{[Mo_3Se_7(CH_3COCHCOCH_3)_3]Br\}\cdot 2C_6H_6$ (**2**). Low yields of the mechanochemical reactions are compensated by the fact that the starting polymers can readily be prepared from simple compounds in evacuated sealed tubes[8] and the simplicity of the mechanochemical synthesis. Other acetylacetonate complexes containing the cluster cores M_3Q_4 (M = Mo or W; Q = S or Se) were synthesized from hydrochloric acid solutions of the aqua complexes $[M_3Q_4(H_2O)_9]^{4+}$, acetylacetonate, and pyridine and were isolated as the hexafluorophosphate salts $[M_3Q_4(acac)_3(Py)_3]PF_6$.[15]

The IR spectra of compounds **1** and **2** show two characteristic absorption bands at 1562—1574 and

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1522—1524 cm^{-1} corresponding to vibrations of the bidentate acetylacetonate group (ν(C=O+C=C)). The bands at 433—441 cm^{-1} can be assigned to both bending vibrations of the chelate ring and stretching vibrations of the Mo—O and C—CH_3 bonds. To make a more precise assignment of the bands in the near-IR region, it is necessary to analyze the isotope shifts.

The ^1H NMR spectra of solutions of complexes **1** and **2** in $CDCl_3$ and CD_3COCD_3 show two signals for the protons of two nonequivalent CH_3 groups of the acetylacetonate ligand and one signal for γ-H, which is consistent with the X-ray diffraction data (see below). The nonequivalence of the Me groups is attributed to their different geometric arrangement. The β-diketonate ligands are coordinated to the molybdenum atoms in such a way that one Me group is in the *cis* position with respect to the Mo—μ_3-Q bond, whereas another Me group is in the *trans* position.

The electrospray mass spectrum of a solution of compound **1** in acetone has a set of signals at *m/z* from 798 to 820 corresponding to the $[Mo_3S_7(acac)_3]^+$ cations with different natural H, C, O, S, and Mo isotope abandance (Fig. 1).

Compounds **1** and **2** are isostructural and contain trinuclear cations $[Mo_3Q_7(acac)_3]^+$, Br^- anions, and benzene solvent molecules. The structure of the $[Mo_3S_7(acac)_3]^+$ cation is shown in Fig. 2. In both compounds, the cationic complexes $[Mo_3Q_7(acac)_3]^+$ and the Br^- anions form the neutral associates $\{[Mo_3S_7(acac)_3]Br\}$ through rather short Q_{ax}...Br contacts (2.96—3.02 Å in the case of S_{ax}...Br and 2.99—3.05 Å in the case of Se_{ax}...Br; the chalcogen atoms lying in the plane of the Mo_3 triangle are called equatorial (Q_{eq}); the other chalcogen atoms of the asymmetrically coordinated dichalcogenide ligands are called axial (Q_{ax})). Analogous associates are present also in $[Mo_3S_7(dtc)_3]Br$ (dtc is dithiocarbamate),[16] $[Mo_3S_7(pipCS_2)_3]Br$ (pip is piperidyl),[17] and $[W_3Se_7(dtp)_3]Br$ (dtp is dithiophosphate; Se...Br, 3.03—3.08 Å).[18] In spite of the fact that the size of the selenium atom is larger than that of the sulfur atom (by ~0.25 Å), the Se...Br distance is virtually equal to the S...Br distance, which is indicative of stronger Se...Br contacts. Short nonbonded contacts are often observed in such systems and were discussed in detail in the study.[19] The benzene molecules occupy the cavities in the crystal structure and are not involved in essential nonbonded contacts. Principal geometric parameters of **1** and **2** are given in Table 1. The Mo—Mo distances are in the ranges of 2.72—2.74 Å (**1**) and 2.78—2.80 Å (**2**) and are typical of M_3Q_7 clusters. The Mo—O distances (2.10—2.13 Å in **1** and 2.10—2.14 Å in **2**) are somewhat shorter than those in the oxalate complexes $[Mo_3Q_7(C_2O_4)_3]^{2-}$ (Q = S or Se) (2.10—2.21 Å)[20] and are virtually equal to those in $[M_3Q_4(acac)_3(Py)_3]^+$ (2.10—2.12 Å).[15]

In the case of the bidentate coordination of acetylacetonate ligands to molybdenum atoms, the C—C_γ and C—O bond lengths in the metallocycle vary only slightly. For example, the C—O and C—C_γ distances in compound **2** vary from 1.25 to 1.27 and from 1.37 to 1.39 Å, respectively. This is indicative of delocalization of the π interaction over the metallocycle in compounds **1** and **2**.

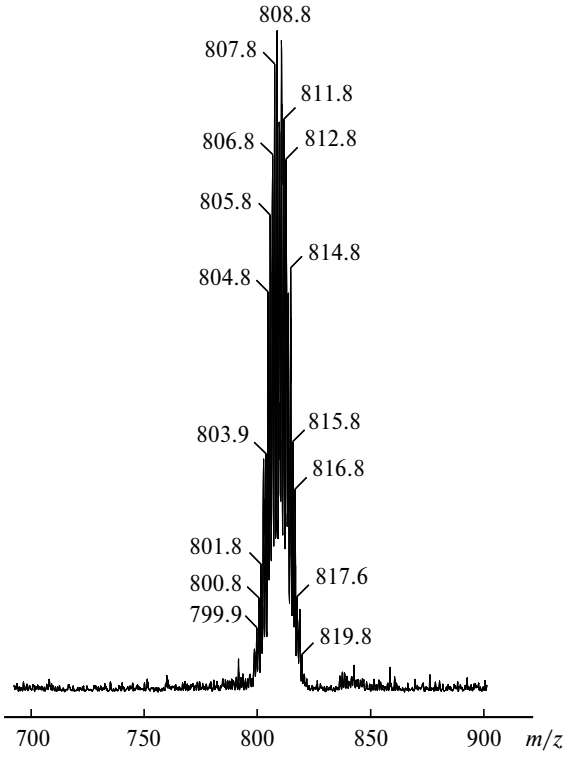

Fig. 1. Electrospray mass spectrum of a solution of compound **1** in acetone.

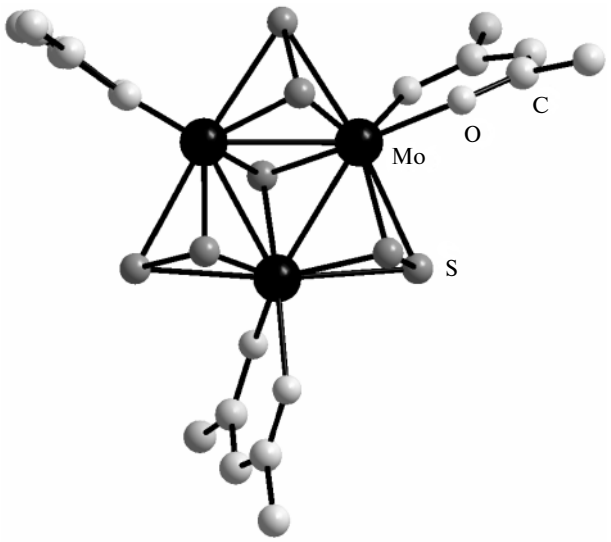

Fig. 2. Structure of the cluster complex $[Mo_3S_7(CH_3COCHCOCH_3)_3]^+$.

Table 1. Selected bond lengths (*d*) in the structures of **1** and **2**

1		**2**	
Bond	*d*/Å	Bond	*d*/Å
Mo(1)—Mo(3)	2.720(1)	Mo(1)—Mo(3)	2.777(1)
Mo(1)—Mo(2)	2.737(2)	Mo(1)—Mo(2)	2.795(2)
Mo(1)—S(21)	2.478(1)	Mo(1)—Se(21)	2.610(1)
Mo(1)—S(22)	2.397(1)	Mo(1)—Se(22)	2.536(1)
Mo(1)—S(31)	2.499(1)	Mo(1)—Se(31)	2.627(1)
Mo(1)—S(32)	2.402(1)	Mo(1)—Se(32)	2.534(1)
Mo(1)—S(4)	2.357(1)	Mo(1)—Se(4)	2.477(1)
Mo(1)—O(11)	2.096(3)	Mo(1)—O(11)	2.110(4)
Mo(1)—O(12)	2.133(3)	Mo(1)—O(12)	2.141(5)
Mo(2)—Mo(3)	2.721(1)	Mo(2)—Mo(3)	2.776(1)
Mo(2)—S(11)	2.489(1)	Mo(2)—Se(11)	2.623(1)
Mo(2)—S(12)	2.397(1)	Mo(2)—Se(12)	2.534(1)
Mo(2)—S(31)	2.482(1)	Mo(2)—Se(31)	2.606(1)
Mo(2)—S(32)	2.401(1)	Mo(2)—Se(32)	2.537(1)
Mo(2)—S(4)	2.356(1)	Mo(2)—Se(4)	2.480(1)
Mo(2)—O(21)	2.090(3)	Mo(2)—O(21)	2.120(4)
Mo(2)—O(22)	2.127(3)	Mo(2)—O(22)	2.145(3)
Mo(3)—S(11)	2.485(2)	Mo(3)—Se(11)	2.609(2)
Mo(3)—S(12)	2.400(1)	Mo(3)—Se(12)	2.538(1)
Mo(3)—S(21)	2.486(2)	Mo(3)—Se(21)	2.612(1)
Mo(3)—S(22)	2.397(1)	Mo(3)—Se(22)	2.534(1)
Mo(3)—S(4)	2.359(1)	Mo(3)—Se(4)	2.477(1)
Mo(3)—O(31)	2.096(3)	Mo(3)—O(31)	2.098(4)
Mo(3)—O(32)	2.128(3)	Mo(3)—O(32)	2.139(5)

This phenomenon is observed in most of octahedral transition metal β-diketonates with equal M—O bonds, for example, in $[Mn(acac)_2(H_2O)_2]$ (Mn—O, 2.15—2.18 Å).[21] At the same time, asymmetric coordination of the ligand (for example, in $[Cu(hfac)_2Bipy]$, where hfac is hexafluoroacetylacetonate; the Cu—O distance is 1.97—2.30 Å)[22] leads to the nonequivalence of the C—C_γ and C—O bonds in the metallocycle, *i.e.*, to partial localization of the π interaction in the β-diketonate ligand.

In the crystal structure, the cluster cations form zigzag chains through shortened $S_{eq}...S_{eq}$ (3.58—3.63 Å) and $Se_{eq}...Se_{eq}$ (3.54—3.56 Å) contacts (Fig. 3). In the structure of compound **2**, there are also C...Se nonbonded contacts between the acetylacetonate and diselenide ligands (C(CH)...Se_{eq}, 3.69 Å; C(Me)...Se_{ax}, 3.68 Å; the sum of the van der Waals radii of the selenium and carbon atoms is 3.7 Å).

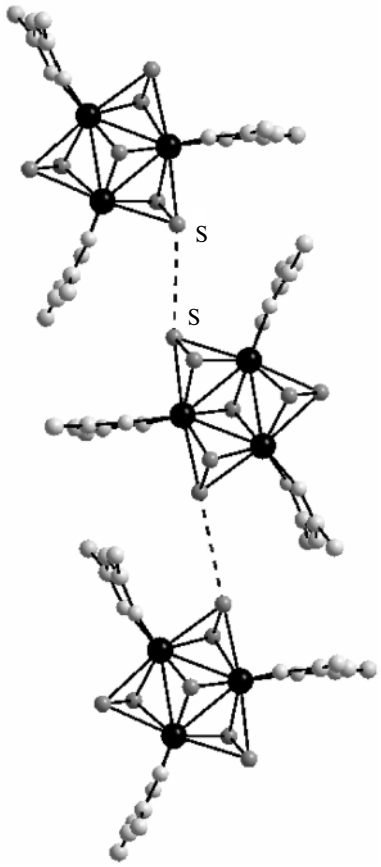

Fig. 3. Fragment of the packing of compound **1**.

Experimental

All operations associated with the synthesis of compounds **1** and **2** were performed in air. The solvents were purified according to standard procedures. Polymeric cluster chalcogenides $Mo_3Q_7Br_4$ (Q = S or Se) were synthesized according to known procedures by the reactions of stoichiometric amounts of metal, chalcogen, and bromine in evacuated glass tubes at 350 °C for 6—7 days.[8] Other compounds of reagent grade were used without additional purification. Sodium acetylacetonate monohydrate was prepared from sodium ethoxide and acetylacetone in ethanol.[23,24]

Mechanochemical syntheses were carried out in a vibration mill, whose design has been described earlier.[10] A titanium cylindrical reactor was used (volume was 100 ml, the height was 50 mm) with tungsten carbide balls 10 mm in diameter (weight was 300 g). The degree of filling of the reactor with balls was 65%. Mechanical activation was performed by vibrating the reactor at a frequency of 25 Hz and an amplitude of 1 cm for 15 h.

The vibrational spectra were measured in the 4000—400 cm^{-1} region in KBr pellets on a Scimitar FTS 2000 instrument at 1 cm^{-1} resolution. The ^1H NMR spectra were recorded on a Bruker MSL300 spectrometer in $CDCl_3$ and CD_3COCD_3 at room temperature with Me_4Si as the internal standard. The electrospray mass spectra were obtained on a Quattro LC (quadrupole—hexapole—quadrupole) mass spectrometer (Micromass, Manchester, UK).[25]

[Tri(acetylacetonato)heptasulfidotrimolybdenum monobromide] dibenzene solvate, $\{[Mo_3S_7(CH_3COCHCOCH_3)_3]Br\}\cdot 2C_6H_6$ (1). After mechanical treatment of a mixture of $Mo_3S_7Br_4$ (1.05 g, 1.26 mmol) and sodium acetylacetonate monohydrate (0.68 g, 4.85 mmol), the resulting powder was extracted with acetone (30 mL). The dark-red extract was concentrated on a rotary evaporator. The resulting compound was recrystallized from a benzene—hexane mixture. Single crystals were grown by diffusion of hexane into a solution of the complex

in benzene. The yield was 0.160 g (14%). Found (%): C, 31.29; H, 3.40. $C_{27}H_{33}BrMo_3O_6S_7$. Calculated (%): C, 31.01; H, 3.18. IR (KBr), cm^{-1}: 2921 ($\nu(CH_3)$), 1562 ($\nu(C{=}C) + \nu(C{=}O)$), 1522 ($\nu(C{=}O) + \nu(C{=}C)$), 1416 ($\delta_d(CH_3)$), 1358 ($\delta_s(CH_3)$), 1278 ($\nu(C{-}CH_3) + \nu(C{=}C)$), 1187 ($\delta(CH) + \nu(C{-}CH_3)$), 1132, 1025 ($\rho_r(CH_3)$), 931 ($\nu(C{=}C) + \nu(C{=}O)$), 875, 785 ($\pi(CH)$), 672, 577, 533, 441. Electrospray mass spectrum: $m/z = 809$. ^{1}H NMR (CD_3COCD_3), δ: 3.45 (α-H), 3.47 (α-H), 6.08 (γ-H).

[Tri(acetylacetonato)heptaselenidotrimolybdenum monobromide] dibenzene solvate, $\{[Mo_3Se_7(CH_3COCHCOCH_3)_3]Br\}\cdot 2C_6H_6$ (2). After mechanochemical treatment of a mixture of $Mo_3Se_7Br_4$ (0.79 g, 0.68 mmol) and sodium acetylacetonate monohydrate (0.44 g, 3.14 mmol), the resulting powder was extracted with acetone (30 mL). The dark-red extract was concentrated on a rotary evaporator. The resulting compound was recrystallized from a benzene—hexane mixture. Single crystals were grown by diffusion of hexane into a solution of the complex in benzene. The yield was 25 mg (3%). Found (%): C, 23.79; H, 2.62. $C_{27}H_{33}BrMo_3O_6Se_7$. Calculated (%): C, 23.60; H, 2.42. IR (KBr), cm^{-1}: 2922 ($\nu(CH_3)$), 1574 ($\nu(C{=}C) + \nu(C{=}O)$), 1524 ($\nu(C{=}O) + \nu(C{=}C)$), 1418 ($\delta_d(CH_3)$), 1360 ($\delta_s(CH_3)$), 1277 ($\nu(C{=}CH_3) + \nu(C{=}C)$), 1024 ($\rho_r(CH_3)$), 932 ($\nu(C{=}C) + \nu(C{=}O)$), 895, 779 ($\pi(CH)$), 669, 572, 515, 433. ^{1}H NMR ($CDCl_3$), δ: 2.05 (α-H), 2.16 (α-H), 5.50 (γ-H). ^{1}H NMR (CD_3COCD_3), δ: 3.45 (α-H), 3.47 (α-H), 5.93 (γ-H).

Table 2. Crystallographic data and X-ray data collection and refinement statistics for compounds **1** and **2**

Parameter	**1**	**2**
Molecular formula	$C_{27}H_{33}BrMo_3O_6S_7$	$C_{27}H_{33}BrMo_3O_6Se_7$
Molecular weight	1045.68	1373.98
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	12.3612(4)	12.5189(4)
b/Å	18.9516(7)	19.2347(4)
c/Å	16.9753(6)	17.2244(7)
α/deg	90	90
β/deg	111.070(1)	111.290(1)
γ/deg	90	90
V/Å^3	3710.8(2)	3864.5(2)
Z	4	4
ρ_{calc}/g cm^{-3}	1.872	2.362
μ/mm^{-1}	2.506	8.622
$2\theta_{max}$/deg	55	50.7
Temperature/K	293	293
Number of measured/ independent/ observed ($I > 2\sigma(I)$) reflections	27347/9109/5940	26620/6942/5221
R_{int}	0.0350	0.0300
Number of parameters in refinement	403	403
R_1 ($I > 2\sigma(I)$)	0.0360	0.0369
wR_2 (for all reflections)	0.0850	0.0979

X-ray diffraction study. The crystal structures of $\{[Mo_3S_7(CH_3COCHCOCH_3)_3]Br\}\cdot 2C_6H_6$ (**1**) and $\{[Mo_3Se_7(CH_3COCHCOCH_3)_3]Br\}\cdot 2C_6H_6$ (**2**) were established by X-ray diffraction. The X-ray diffraction data sets were collected on an automated Bruker X8APEX diffractometer equipped with a CCD area detector (Mo-Kα radiation, $\lambda = 0.71073$ Å; graphite monochromator). The crystallographic characteristics and the X-ray data collection and refinement statistics are given in Table 2. Semiempirical absorption corrections were applied based on the intensities of equivalent reflections with the use of the SADABS program.[26] The structures were solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters for nonhydrogen atoms using the SHELX97 program package.[27] The hydrogen atoms were located in difference electron density maps and refined with geometric constraints. The selected bond lengths are given in Table 1.

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