Russian Chemical Bulletin, International Edition, Vol. 56, No. 9, pp. 1707—1711, September, 2007

Reactivity of triangular oxalate cluster complexes $[M_3Q_7(C_2O_4)_3]^{2-}$ (M = Mo or W; Q = S or Se)*

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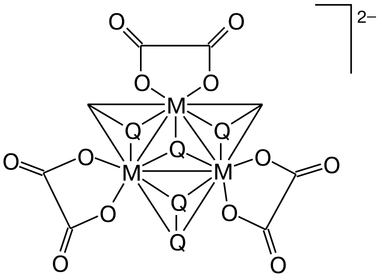
The reactions of the oxalate complexes $[M_3Q_7(C_2O_4)_3]^{2-}$ (M = Mo or W; Q = S or Se) with Mn^{II}, Co^{II}, Ni^{II}, and Cu^{II} aqua and ethylenediamine complexes in aqueous and aqueous ethanolic solutions were studied. The previously unknown heterometallic complexes $[Mo_3Se_7(C_2O_4)_3Ni(H_2O)_5]\cdot3.5H_2O$ (**1**) and $K_3\{[Cu(en)_2H_2O]([Mo_3S_7(ox)_3]_2Br)\}\cdot5.5H_2O$ (**2**) were synthesized. In these complexes, the oxalate clusters serve as monodentate ligands. The $K(H_2en)_2[W_3S_7(C_2O_4)_3]_2Br\cdot4H_2O$ salt (**3**) was isolated from solutions containing Co^{II}, Ni^{II}, or Cu^{II} aqua complexes and ethylenediamine. The reaction of $[Mo_3Se_7(C_2O_4)_3]^{2-}$ with HBr produced the bromide complex $[Mo_3Se_7Br_6]^{2-}$, which was isolated as $(Bu_4N)_2[Mo_3Se_7Br_6]$ (**4**). Complexes **1—3** were characterized by X-ray diffraction, IR spectra, and elemental analysis. The formation of **4** was detected by electrospray mass spectrometry.

Key words: molybdenum, tungsten, chalcogenide clusters, oxalate complexes, heterometallic complexes, X-ray diffraction study.

Mononuclear metal oxalate complexes are widely used for the preparation of heterometallic molecular complexes, supramolecular structures, and coordination polymers.[1—5] The oxalate ligand has a unique ability to transfer strong electronic interactions between paramagnetic metal ions spaced at more than 5 Å.[6] Oxalate cluster complexes have been poorly studied. The triangular molybdenum and tungsten chalcogenide complexes $[M_3Q_7(C_2O_4)_3]^{2-}$ have been synthesized in recent years, and their chemical properties remain to be studied.[7—9]



In the present study, we investigated the reactions of the $[M_3Q_7(C_2O_4)_3]^{2-}$ clusters (M = Mo or W; Q = S or Se) with 3d metal complexes. The heterometallic complexes $[Mo_3Se_7(C_2O_4)_3Ni(H_2O)_5]\cdot3.5H_2O$ (**1**) and $K_3\{[Cu(en)_2H_2O]([Mo_3S_7(ox)_3]_2Br)\}\cdot5.5H_2O$ (**2**), in which the oxalate clusters serve as monodentate ligands, were synthesized. These are the first examples of heterometallic complexes prepared from triangular molybdenum oxalate clusters. The reaction of $[Mo_3Se_7(C_2O_4)_3]^{2-}$ with HBr leads to the nucleophilic substitution of the bidentate coordinated oxalate ligands. This is a convenient procedure for the synthesis of the selenobromide complexes $[Mo_3Se_7Br_6]^{2-}$.

Results and Discussion

Due to the ability of the oxalate ligand coordinated to molybdenum or tungsten atoms of the cluster core M_3Q_7 (M = Mo or W; Q = S or Se) to bind other transition metals, these complexes are attractive for the synthesis of heterometallic coordination polymers and discrete nanosized complexes. The mixing of aqueous solutions of potassium salts of oxalate complexes with aqua complexes of 3d metals (Mn^{II}, Co^{II}, Ni^{II}, or Cu^{II}) in different ratios generally gives rise to amorphous precipitates, which are difficult to identify. Only in the case of Ni, red crystals with the composition $[Mo_3Se_7(C_2O_4)_3Ni(H_2O)_5]\cdot3.5H_2O$ (**1**) were obtained in 12% yield. These crystals have a molecular structure. The nickel atoms are monodentate coordinated by one of the three oxalate groups, which are coordinated to the cluster core Mo_3Se_7:

$$[Mo_3Se_7(C_2O_4)_3]^{2-} + [Ni(H_2O)_6]^{2+} = \\ = [Mo_3Se_7(C_2O_4)_3Ni(H_2O)_5] + H_2O.$$

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* Dedicated to Academician G. A. Abakumov on the occasion of his 70th birthday.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1645—1649, September, 2007.

The reactions of aqueous solutions of the ethylenediamine complexes $[M(en)_2]^{2+}$ (M = Co, Ni, or Cu) with aqueous solutions of the oxalate complexes produce amorphous precipitates. However, $K_3\{[Cu(en)_2H_2O]([Mo_3S_7(C_2O_4)_3]_2Br)\} \cdot 5.5H_2O$ (**2**) was isolated in 5% yield by heating aqueous ethanolic solutions of $[Cu(en)_2(H_2O)_2]^{2+}$ and $\{[Mo_3S_7(C_2O_4)_3]_2Br\}^{5-}$ at 50 °C followed by evaporation of the filtrate:

$$\{[Mo_3S_7(C_2O_4)_3]_2Br\}^{5-} + [Cu(en)_2(H_2O)_2]^{2+} =$$
$$= \{[Cu(en)_2H_2O]([Mo_3S_7(C_2O_4)_3]_2Br)\}^{3-} + H_2O.$$

This reaction affords the mononuclear oxalate complex $K_2[Cu(C_2O_4)_2] \cdot 2H_2O$ as the major product, which is indicative of the transfer of the coordinated oxalate ligand from the cluster core to the Cu^{II} atom. The analogous reaction of $[Mo_3Se_7(C_2O_4)_3]^{2-}$ with $[Cu(en)_2(H_2O)_2]^{2+}$ gives only the Cu^{II} oxalate complex.

In compounds **1** and **2**, the anionic oxalate cluster complexes serve as monodentate ligands, one of the oxalate ligands acting as a bridge between two metal atoms.

Another possible route to heterometallic complexes is based on the addition of aqua complexes of M'^{II} (M′ = Co, Ni, or Cu) and ethylenediamine (in a ratio of 1 : 1 and 1 : 2) to $[M_3Q_7(C_2O_4)_3]^{2-}$ in an aqueous solution. In all cases, we obtained needle-like crystals of mixed potassium ethylenediammonium salts of $[M_3Q_7(C_2O_4)_3]^{2-}$ with variable cation composition containing no heterometals in spite of variations in both the M_3Q_7 : M′ molar ratio and the concentrations of the reagents. According to the X-ray diffraction study, these salts contain the triple associate $\{[M_3Q_7(C_2O_4)_3]_2Br\}^{5-}$ as the anionic structural unit. In the case of Co^{II} and ethylenediamine (1 : 1), the mixed salt $K(H_2en)_2[W_3S_7(C_2O_4)_3]_2Br \cdot 4H_2O$ (**3**) was isolated in 11% yield. The structure of **3** was determined by X-ray diffraction.

The reaction of the potassium salt of $[Mo_3Se_7(C_2O_4)_3]^{2-}$ with a concentrated HBr solution is accompanied by the replacement of the oxalate ions with bromide ions, and the subsequent addition of Bu_4NBr affords $(Bu_4N)_2[Mo_3Se_7Br_6]$ (**4**, 67% yield).

$$[Mo_3Se_7(C_2O_4)_3]^{2-} + 6HBr \rightarrow [Mo_3Se_7Br_6]^{2-} + 3H_2C_2O_4$$

The electrospray mass spectrum of the reaction solution provides evidence that the solution contains the mixed-ligand complexes $[Mo_3Se_7Br_4(C_2O_4)]^{2-}$ (giving a peak of $[Mo_3Se_7Br_3(C_2O_4)]^-$) along with$[Mo_3Se_7Br_6]^{2-}$ (giving a peak of $[Mo_3Se_7Br_5]^-$ in ESI-MS), which is indicative of the stepwise mechanism of the substitution reaction. The $(Bu_4N)_2[Mo_3Se_7Br_6]$ complex isolated in good yield is of interest as the convenient starting compound for the synthesis of derivatives containing the metal selenide cluster fragment $Mo_3Se_7^{4+}$.[10]

Table 1. Selected bond lengths (*d*) in the structures of complexes **1**—**3**

1		2		3	
Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
Mo—Mo	2.77	Mo—Mo	2.72	W—W	2.70
Mo—μ_3-Se	2.49	Mo—μ_3-S	2.36	W—μ_3-S	2.37
Mo—Se_{ax}	2.54	Mo—S_{ax}	2.40	W—S_{ax}	2.41
Mo—Se_{eq}	2.62	Mo—S_{eq}	2.49	W—S_{eq}	2.50
Mo—O	2.13	Mo—O	2.12	W—O	2.11
Ni—O	2.07	Cu—O	2.63		
		Cu—N	2.03		

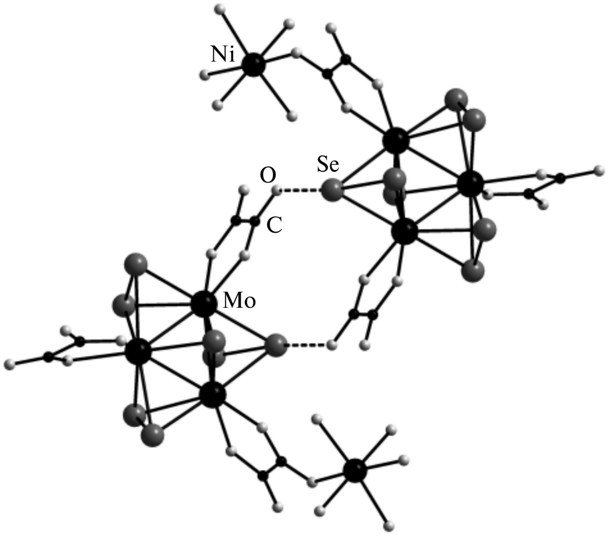

Fig. 1. Structure of the heterometallic complex $[Mo_3Se_7(C_2O_4)_3Ni(H_2O)_5]$ in the crystal structure of compound **1**.

Structures of the complexes. Selected bond lengths in structures **1**—**3** are given in Table 1. Compounds **1**—**3** contain the trinuclear anions $[M_3Q_7(C_2O_4)_3]^{2-}$ (M = Mo or W; Q = S or Se), whose structures have been discussed in detail in the earlier study.[8] In the crystal structure of compound **1**, the $[Mo_3Se_7(C_2O_4)_3Ni(H_2O)_5]$ molecules form dimers through cooperative interactions between the terminal oxygen atoms of the oxalate group and the equatorial selenium atoms of the diselenide ligands (chalcogen atoms lying in the plane of the M_3 triangle are referred to as equatorial; other chalcogen atoms of the asymmetrically coordinated dichalcogenide ligands are called axial) (Fig. 1). The O...Se distance (2.69 Å) is substantially smaller than the sum of the van der Waals radii of the O and Se atoms (3.29 Å). In the starting $[Mo_3Se_7(C_2O_4)_3]^{2-}$ anion, the corresponding distance is ~2.79 Å. Short O...Se contacts were found also in selenazoles and vary in a range of 2.554—2.725 Å.[11—13] The nickel atom is in an octahedral environment formed by five water molecules and the terminal oxygen atom of one of the oxalate ligands. The Ni—O(H_2O) distances (2.05—2.07 Å) are typical of nickel aqua complexes. About

20 $[Ni(H_2O)_5L]$-type structures, in which L is a relatively simple ligand (NH_3, NO_3^-, pyridine, carboxylate, or imidazole), or a rather complex molecule, such as guanosine phosphate or analogous derivatives of nitrogen bases, a polyoxometallated anion, or the nitrogen atom of the cyanide complex, were documented.[14] Interestingly, the crystals of the $[Ni(H_2O)_6][Pt(C_2O_4)_2]$ compound contain isolated $[Ni(H_2O)_6]^{2+}$ ions. In the latter structure, the oxygen atoms of the coordinated oxalate ligand are not involved in the coordination sphere of Ni^{II}.[15]

The crystal structure of **2** contains the neutral $[Mo_3S_7(C_2O_4)_3Cu(en)_2(H_2O)]$ complexes (Fig. 2) formed as a result of the axial coordination of $[Cu(en)_2]^{2+}$ by the oxygen atom of one of the oxalate ligands of the cluster complex and the water molecule (Cu—O(H_2O), 2.49 Å; Cu—O(C_2O_4), 2.63 Å). The coordination environment of Cu^{II} can be described as an octahedron with a strong tetragonal distortion along the O—Cu—O coordinate (Jahn—Teller effect). The crystal structure contains also potassium and bromide ions. The potassium ions are disordered, and their nearest environment is formed by the oxygen atoms of the oxalate ligands or water molecules of crystallization.

The $K(H_2en)_2[W_3S_7(C_2O_4)_3]_2Br \cdot 4H_2O$ compound (**3**) is structurally similar to potassium salts of oxalate complexes described earlier.[8] The structures of compounds **2** and **3** are characterized by the presence of the bent sandwich $\{[M_3S_7(ox)_3]_2Br\}^{5-}\cdot$(M = Mo or W), which is formed between two cluster anions $[M_3S_7(C_2O_4)_3]^{2-}$ and the bromide anion *via* specific nonbonded interactions, resulting in the formation of S...Br...S bridging bonds (Fig. 3). The S...Br distance (~3.2 Å) is smaller than the sum of the van der Waals radii of these elements (3.78 Å). These ionic associates are observed also in the structures of the starting $K_2[M_3(\mu_3\text{-}Q)(\mu_2\text{-}Q_2)_3(C_2O_4)_3] \cdot 0.5KBr \cdot xH_2O$ compounds (M = Mo or W; Q = S or Se)[8]. Short nonbonded contacts are often observed in such systems and were discussed in detail in the study.[16]

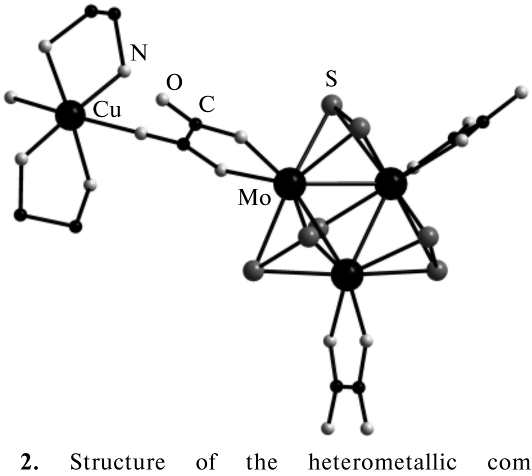

Fig. 2. Structure of the heterometallic complex $[Mo_3S_7(C_2O_4)_3Cu(en)_2H_2O]$ in the crystal structure of compound **2**.

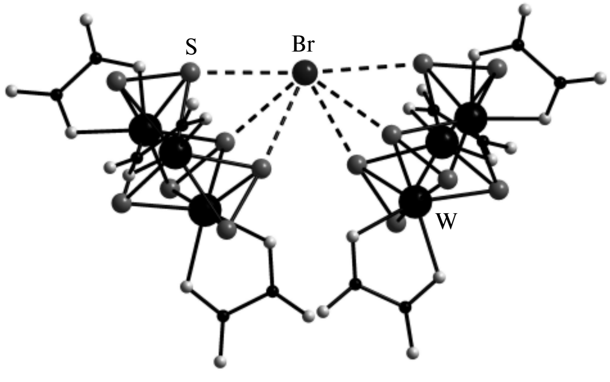

Fig. 3. Structure of the anionic associate $\{[Mo_3S_7(C_2O_4)_3]_2Br\}^{5-}$ in the crystal structure of compound **3**.

To summarize, we synthesized first heterometallic complexes based on the oxalate cluster anions $[Mo_3Q_7(C_2O_4)_3]^{2-}$ (Q = S or Se). Numerous heterometallic complexes and coordination polymers containing mononuclear oxalate complexes, which have interesting physicochemical properties, are known. New rich chemistry would be expected for heterometallic compounds consisting of oxalate cluster building blocks.

Experimental

All operations associated with the synthesis of compounds **1—4** were carried out in air. The $K_2[M_3(\mu_3\text{-}Q)(\mu_2\text{-}Q_2)_3(C_2O_4)_3] \cdot 0.5KBr \cdot xH_2O$ complexes (M = Mo or W; Q = S or Se) were prepared according to a procedure described earlier.[8] The solvents were purified according to standard procedures.[17] Other compounds of reagent grade were used as received. The vibrational spectra (KBr pellets) were recorded in the 4000—400 cm^{-1} range on a Scimitar FTS 2000 instrument at 1 cm^{-1} resolution. Analyses for C, H, and N were carried out in the Laboratory of Microanalysis of the N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry of the Siberian Branch of the Russian Academy of Sciences. The electrospray mass spectra (ESI-MS) were obtained on a Quattro LC (quadrupole—hexapole—quadrupole) mass spectrometer (Micromass, Manchester, UK).[18]

X-ray diffraction study. The structures of the heterometallic $[Mo_3Se_7(C_2O_4)_3Ni(H_2O)_5] \cdot 3.5H_2O$ (**1**), $K_3\{[Cu(en)_2H_2O]([Mo_3S_7(C_2O_4)_3]_2Br)\} \cdot 5.5H_2O$ (**2**), and $K(H_2en)_2[W_3S_7(C_2O_4)_3]_2Br \cdot 4H_2O$ (**3**) complexes were determined by X-ray diffraction. The X-ray diffraction data were collected on a four-circle automated Bruker X8APEX diffractometer equipped with a CCD area detector (Mo-Kα radiation, λ = 0.71073 Å, graphite monochromator). The crystallographic data 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.[19] The structures were solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters for nonhydrogen atoms with the use of the SHELXTL program

Table 2. Crystallographic data and the X-ray data collection and refinement statistics for complexes **1—3**

Parameter	1	2	3
Molecular formula	$C_6H_{17}Mo_3NiO_{20.50}Se_7$	$C_{16}H_{29}BrCuK_3Mo_6N_4O_{30.50}S_{14}$	$C_{16}H_{28}BrKN_4O_{28}S_{14}W_6$
Mr	1316.45	2050.66	2395.37
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	14.2662(8)	20.4875(11)	16.0394(17)
b/Å	14.5634(8)	19.1943(11)	18.5994(19)
c/Å	13.7132(6)	15.7056(6)	18.861(3)
α/deg	90	90	90
β/deg	103.3620(10)	111.2250(10)	114.866(2)
γ/deg	90	90	90
V/Å^3	2772.0(2)	5757.2(5)	5105.2(10)
Z	4	4	4
ρ_{calc}/g cm^{-3}	3.154	2.366	3.117
μ/mm^{-1}	11.268	3.130	14.988
$2\theta_{max}$/deg	52.74	51.36	55
Temperature/K	293	293	295
Number of measured/ independent/observed ($I > 2\sigma(I)$) reflections	18956/5537/4418	39993/10800/4917	32728/11635/6569
R_{int}	0.0339	0.0603	0.0825
Number of variables	343	727	644
R_1 ($I > 2\sigma(I)$)	0.0283	0.0545	0.0613
wR_2 (based on all reflections)	0.0713	0.1498	0.1860

package.[20] The hydrogen atoms of ethylenediamine were located in difference electron density maps and refined with geometric constraints. The hydrogen atoms of the water molecules were not located. Selected bond lengths are given in Table 1.

[Trioxalatoheptaselenidotrimolybdenumpentaaquanickel] hydrate, $[Mo_3Se_7(C_2O_4)_3Ni(H_2O)_5]\cdot3.5H_2O$ (1). The $Ni(NO_3)_2\cdot6H_2O$ compound (0.21 g, 0.72 mmol) was added to an aqueous solution of $K_2[Mo_3Se_7(C_2O_4)_3]\cdot0.5KBr\cdot4H_2O$ (10 mL, $7.2\cdot10^{-2}$ mol L^{-1}). After storage of the solution at room temperature for 1 day, dark-red crystals were separated by decantation, washed with cold water and ethanol, and dried in air. The yield was 0.11 g (12%). Found (%): C, 5.34; H, 1.66. $C_6H_{17}Mo_3Ni_1O_{20.5}Se_7$. Calculated (%): C, 5.47; H, 1.30. IR, ν/cm^{-1}: 3380 s, 1667 s, 1467 m, 1395 s, 1253 m, 909 m, 792 s, 608 m, 525 m, 468 w.

[Tripotassium-bis(trioxalatoheptasulfidotrimolybdenum)diethylenediaminomonoaquacopper] bromide hydrate, $K_3\{[Cu(en)_2H_2O]([Mo_3S_7(C_2O_4)_3]_2Br)\}\cdot5.5H_2O$ (2). A solution of $K_2[Mo_3S_7(C_2O_4)_3]\cdot0.5KBr\cdot3H_2O$ (207 mg) in H_2O (7 mL) was added to a solution of *trans*-$[Cu(en)_2Cl_2]\cdot0.5H_2O$ (56 mg) in C_2H_5OH (5 mL) and H_2O (1 mL). The aqueous-ethanolic solution was stirred at 50 °C for 3 h, filtered, and concentrated in air until orange crystals formed. The yield was 10 mg (5%). The further evaporation of the solution resulted in the crystallization of $K_2[Cu(C_2O_4)_2]\cdot2H_2O$. The composition and structure of **2** were determined by X-ray diffraction.

[Bis(ethylenediammonium)potassium-bis(trioxalatoheptasulfidotrimolybdenum)] bromide tetrahydrate, $K(H_2en)_2[W_3S_7(C_2O_4)_3]_2Br\cdot4H_2O$ (3). An aqueous solution of $CoCl_2\cdot6H_2O$ and ethylenediamine (1 : 1) (0.4 mL, 0.025 mol L^{-1}) was added dropwise to an aqueous solution of $K_2[W_3S_7(C_2O_4)_3]\cdot0.5KBr\cdot4H_2O$ (10 mL, 0.004 mol L^{-1}). After storage of the solution at room temperature for 3 days, the wine-red crystals were separated by decantation, washed with ethanol, and dried in air. The yield was 5 mg (11%). Found (%): C, 8.04; H, 1.24; N, 2.26. $C_{16}H_{24}BrKN_4O_{28}S_{14}W_6$. Calculated (%): C, 8.04; H, 1.01; N, 2.34. IR, ν/cm^{-1}: 3420 s, 2958 m, 2921 m, 2853 m, 1700 s, 1673 s, 1383 s, 1233 m, 1050 m, 984 m, 907 m, 796 m, 593 m, 537 m, 467 m.

Bis(tetrabutylammonium)hexabromidoheptaselenidotrimolybdenum, $(Bu_4N)_2[Mo_3Se_7Br_6]$ (4). Concentrated HBr (10 mL) was added to $K_2[Mo_3Se_7(C_2O_4)_3]\cdot0.5KBr\cdot4H_2O$ (0.076 g, 0.058 mmol). The reaction mixture was stirred for 30 min. The solution was filtered, and then a solution of Bu_4NBr (0.30 g, 0.93 mmol) in HBr (5 mL) was added. After storage of the reaction solution at room temperature for 1 h and at 10 °C for 4 h, the crystals were filtered off and washed with water, a 1 : 10 methanol—diethyl ether mixture, and diethyl ether. The yield was 0.070 g (67%). Found (%): C, 21.62; H, 4.01; N, 1.70. $C_{32}H_{72}Br_6Mo_3N_2Se_7$. Calculated (%): C, 21.29; H, 4.02; N, 1.55. IR, ν/cm^{-1}: 3447 m, 2959 s, 2872 s, 1629 m, 1465 s, 1381 m, 1151 m, 1029 m, 879 m, 734 m. The major peak in ESI-MS (in CH_2Cl_2), *m*/*z*: 1239 ($[Mo_3Se_7Br_5]^-$).

We thank C. Vicent (Jaume I University, Castello, Spain) for performing the ESI-MS experiment. L. Gushchin thanks the Haldor Topsøe Company for the scholarship.

This study was financially supported by the Russian Foundation for Basic Research (Project No. 05-03-32126).

References

1. Y. Q. Sun, J. Zhang, and G. Y. Yang, *J. Chem. Soc., Dalton Trans.*, 2006, 1685.
2. E. Coronado and J. R. Galan-Mascaros, *J. Mater. Chem.*, 2005, **15**, 66.
3. J. C. Trombe and A. Mohanu, *Solid State Sciences*, 2004, **6**, 1403.
4. E. Coronado and P. Day, *Chem. Rev.*, 2004, **104**, 5419.
5. Y. Q. Sun, J. Zhang, and G. Y. Yang, *J. Chem. Soc., Dalton Trans.*, 2004, 971.
6. O. Kahn, *Molecular Magnetism*; VCH: Weinheim, Germany, 1993.
7. J. M. Garriga, R. Llusar, S. Uriel, C. Vicent, A. J. Usher, N. T. Lucas, M. G. Humphrey, and M. Samoc, *J. Chem. Soc., Dalton Trans*, 2003, 4546.
8. M. N. Sokolov, A. L. Gushchin, D. Yu. Naumov, O. A. Gerasko, and V. P. Fedin, *Inorg. Chem.*, 2005, **44**, 2431.
9. M. N. Sokolov, A. L. Gushchin, D. Y. Naumov, O. A. Gerasko, and V. P. Fedin, *J. Cluster Science*, 2005, **16**, 309.
10. V. P. Fedin, M. N. Sokolov, O. A. Gerasko, A. V. Virovets, N. V. Podberezskaya, and V. Ye. Fedorov, *Inorg. Chim. Acta*, 1991, **187**, 81.
11. M. J. Laws, C. H. Schiesser, J. M. White, and Shi-Long Zheng, *Aust. J. Chem.*, 2000, **53**, 277.
12. M. Piatek, B. Oleksyn, and J. Sliwinski, *Acta Cryst., Sect. C: Cryst. Struct. Commun.*, 1995, **51**, 298.
13. L. Dupont, O. Dideberg, and P. Jacquemin, *Acta Cryst., Sect. C: Cryst. Struct. Commun.*, 1990, **46**, 484.
14. F. H. Allen, *Acta Cryst. A58*, 2002, 380.
15. A. Kobayashi, H. Kondo, Y. Sasaki, H. Kobayashi, A. E. Underhill, and D. M. Watkins, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2074.
16. A. V. Virovets, A. L. Gushchin, P. A. Abramov, N. I. Alferova, M. N. Sokolov, and V. P. Fedin, *Zh. Strukt. Khim.*, 2006, **47**, 340 [*J. Struct. Chem.*, 2006, **47** (Engl. Transl.)].
17. A. Gordon and R. Ford, *Chemist's companion*, A Wiley-Interscience Publication, New York—London—Sydney—Toronto, 1972.
18. *Masslynx 3.2*, Micromass, Manchester, UK, 1998.
19. *APEX2 (Version 1.08), SAINT (Version 7.03), and SADABS (Version 2.11), Bruker Advanced X-ray Solutions*, Bruker AXS Inc., Madison, Wisconsin, USA, 2004.
20. G. M. Sheldrick, *SHELXS-97 and SHELXL-97*, Programs for the Refinement of Crystal Structures, Göttingen University, Göttingen, Germany, 1997.

Received July 7, 2006;
in revised form March 23, 2007