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Synthesis, Structure, Vibrational Spectra and Chemical Properties of the Triangular Molybdenum and Tungsten Complexes $M_3(\mu_3\text{-S})(\mu_2\text{-SSe})_3X_6^{2-}$ (M = Mo, W; X = Cl, Br)

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Abstract

Salts containing $M_3(\mu_3\text{-S})(\mu_2\text{-}S_2)_3X_6^{2-}$ (M = Mo, W; X = Cl, Br) anions interact with $SePPh_3$ upon heating in acetonitrile to form $SPPh_3$ and $M_3(\mu_3\text{-S})(\mu_2\text{-SSe})_3X_6^{2-}$. The stereochemisty of this reaction has been studied. In the reaction of $SePPh_3$ with $Mo_3(\mu_3\text{-}^{34}S)(\mu_2\text{-}^{34}S_a{}^{32}S_e)_3X_6^{2-}$ replacement of the equatorial sulfur atoms takes place, and $^{32}SPPh_3$ and $Mo_3(\mu_3\text{-}^{34}S)(\mu_2\text{-}^{34}S_aSe_e)_3X_6^{2-}$ are produced.

The structure of $(PPh_3Et)_2Mo_3(\mu_3\text{-S})(\mu_2\text{-SSe})_3Cl_6$ (I) was established by X-ray diffraction analysis. The crystals of I are triclinic, space group $P\bar{1}$ (a = 13.547(2), b = 13.755(2), c = 15.736(3) Å; α = 101.79(1), β = 97.71(1), γ = 110.49(1)°, Z = 2). A total of 5721 independent reflections has been collected on an automated diffractometer, and the structure was solved to R = 0.051 (R_w = 0.062). The selenium atoms are essentially in the plane of the Mo_3 triangle. The S–Se distances are 2.157(5)–2.163(4) Å. Complex I is the first compound containing a S–Se ligand that has been structurally characterized.

IR and Raman spectra of $M_3S_4Se_3X_6^{2-}$ have been studied. For $Mo_3S_4Se_3Cl_6^{2-}$ an analysis of the normal vibrations has been performed. The force constant of the S–Se bond in complex I is 2.3 mdyn/Å.

Heating of $(Et_4N)_2Mo_3S_4Se_3Br_6$ under vacuum at 450 °C gave rise to MoSSe.

Introduction

The complexes of transition metals that contain chalcogenide ligands have been intensively studied recently. The most interesting cases are those in which the polychalcogenide ions participate in the coordination exhibiting an astonishing diversity of coordination types [1–4]. Polysulfides are the most studied ligands; in the last two or three years polyselenide and polytelluride complexes have also been studied [5–7]. However, almost nothing is known about mixed polychalcogenides containing, for example, S–Se, S–Te or Se–Te bonds.

It should be noted that even the synthesis of binary compounds, S_xSe_{8-x}, is not an easy task, and progress in this direction has been achieved only relatively recently [8–10]. The simplest binary sulfide, SSe, has been observed only in the gaseous phase [11]. Several organic selenosulfides, RSSeR, have been described [12]. There has been no report about the simple salts of the SSe^{2-} anion. The preparation of the $(Bu_4N)_4Nb_2(\mu_2\text{-SSe})_2(NCS)_8$ salt by the reaction of $NbSe_2Cl_2$ with a KNCS melt is reported in ref. 13, but structural evidence for the presence of the μ_2-SSe ligand is lacking. Rauchfuss *et al.* [14] have proved the formation of $Ir(\eta^2\text{-SSe})(dppe)_2^+$ by NMR and the FI-MS method but the complex was not obtained in pure form.

In the present paper we report the synthesis and an X-ray diffraction study of the first compounds of molybdenum and tungsten with the SSe ligand.

Experimental

Materials and Apparatus

The syntheses were carried out in a Schlenk apparatus under argon. Acetonitrile was distilled over P_4O_{10}, and toluene and ether over metallic sodium. The isotope-containing compounds were prepared from sulfur which contained 99.95% ^{34}S. The salts containing the $M_3S_7X_6^{2-}$ anions were prepared as described earlier [15, 16]. $SePPh_3$ was obtained in a high yield by boiling PPh_3 and a Se powder in CH_3CN. All other reagents were chemically pure.

Determination of C, H, N, Cl and Br was performed in the Laboratory of Microanalysis of the

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Institute of Organic Chemistry (Novosibirsk). Determination of Mo, S and Se was by the weight method as $Mo(C_9H_6NO)_2$, $BaSO_4$ and elemental Se.

The IR spectra were taken on a IFS-113 Fourier spectrometer (Bruker) in polyethylene. The Raman spectra were obtained on a DFS-24 spectrometer with excitation by the 632.8 nm line of a He–Ne laser. The mass spectra were measured on an MI-1305 instrument.

Preparation of $(Et_4N)_2Mo_3S_4Se_3Br_6$ (a general procedure of the synthesis)

A suspension of $(Et_4N)_2Mo_3S_7Br_6$ (0.25 g, 0.20 mmol) and $SePPh_3$ (0.34 g, 1.0 mmol) in CH_3CN (30 ml) was boiled for 1 h. Then 30 ml of toluene was slowly added dropwise to the filtrate, and the solution was allowed to stay at -5 °C for 12 h. Then the crystals were filtered off, washed with toluene and dried *in vacuo*. Yield 0.25 g, 90%.

Anal. Calc. for $C_{16}H_{40}Br_6Mo_3N_2S_4Se_3$: C, 13.80; H, 2.89; Br, 34.42; Mo, 20.66; N, 2.01; S, 9.21; Se, 17.01. Found: C, 13.98; H, 2.96; Br, 35.08; Mo, 21.10; N, 1.97; S, 8.99; Se, 17.70%.

Analogously, $Q_2Mo_3S_4Se_3X_6$ ($Q = Et_4N^+$, PPh_4^+, PPN^+, PPh_3Et^+; X = Cl, Br) and $Q_2W_3S_4Se_3X_6$ ($Q = PPh_4^+$, PPN^+; X = Cl, Br) have been obtained starting from the corresponding salts of $Q_2M_3S_7X_6$. The yields of the molybdenum complexes are 80–90%; those of the tungsten complexes about 40%. The analysis of the complexes for C, H, N and halogen was satisfactory. The complexes were also characterized by IR and Raman spectra.

Interaction of $(PPh_4)_2Mo_3S_4Se_3Cl_6$ with PPh_3

$(PPh_4)_2Mo_3S_4Se_3Cl_6$ (33.2 mg, 0.021 mmol) and PPh_3 (17 mg, 0.065 mmol) in 20 ml of acetonitrile were stirred for 1 h. Then the acetonitrile was removed under vacuum and the dry solid was treated with toluene. $SePPh_3$ (18.6 mg) was obtained from toluene, yield 85% (identified by the melting point and the IR spectrum).

Preparation of MoSSe

$(Et_4N)_2Mo_3S_4Se_3Br_6$ (445 mg) was heated under vacuum at 450 °C for 1 h; 203 mg of a black powder was produced (the theoretical yield of MoSSe is 198 mg).

Anal. Calc. for MoSSe: Mo, 46.35; S, 15.49; Se, 38.15. Found: Mo, 46.50; S, 15.72; Se, 38.04%.

X-ray diffraction analysis

$(PPh_3Et)_2Mo_3S_4Se_3Cl_6$ (I) suitable for an X-ray diffraction analysis was obtained by diffusing ether vapours into an acetonitrile solution of the complex. Crystallographical data for I are listed in Table 1. The structure was solved by the direct method and refined by the block-diagonal least-squares method in the anisotropic approximation for all non-hydrogen atoms. The hydrogen atoms were placed into the calculated sites with a fixed B_{iso} of 7 Å^2 and were not refined. A correction for absorption (μ = 34.8 cm^{-1}) was introduced by the DIFABS program. All calculations were performed on the 'Eslipse S/200' computer using the INEXTL programms [17]. The coordinates for the non-hydrogen atoms are given in Table 2. Table 3 lists the interatomic distances and valence angles for the $M_3S_4Se_3Cl_6^{2-}$ anion. In the PPh_3Et^+ cations the interatomic distances and the angles are the usual ones. Using the automated diffractometer the parameters were also determined for $(PPN)_2Mo_3S_4Se_3Cl_6$ (a = 13.650(2), b = 18.159(1), c = 19.009(3) Å, α = 99.48(1), β = 109.23(1), γ = 109.32(1); Z = 2, $P\bar{1}$, ρ_{calc} = 1.62 g/cm^3.

TABLE 1. Crystallographic data for $(PPh_3Et)_2Mo_3S_4Se_3Cl_6$

Formula	$C_{40}H_{40}Cl_6Mo_3P_2S_4Se_3$
Formula weight	1448.38
Space group	$P\bar{1}$
a (Å)	13.547(2)
b (Å)	13.755(2)
c (Å)	15.736(3)
α (°)	101.79(1)
β (°)	97.71(1)
γ (°)	110.49(1)
Z	2
Diffractometer	Hilger-Watts
Radiation	Mo Kα
Monochromator	graphite
No. independent reflections ($I \geq 2\sigma(I)$)	5721
Scanning method	$\theta/2\theta$ ($\theta < 26°$)
R	0.051
R_w	0.062

Results and Discussion

Synthesis and Properties of Salts Containing $M_3(\mu_3\text{-}S)(\mu_2\text{-}SSe)_3X_6^{2-}$ (M = Mo, W; X = Cl, Br)

To prepare compounds containing SSe ligands we made use of the readily available $M_3S_7Cl_6^{2-}$ salts [15, 16] as starting materials. We studied the interaction of these salts in acetonitrile with different selenium-containing compounds: (i) with elemental selenium upon heating; (ii) the reaction of elemental Se with $M_3S_4^{4+}$, solv. generated in the interaction of 3 equivalents of PPh_3 with $M_3S_7X_6^{2-}$. These conditions did not produce any complexes containing SSe ligands.

We found that the triangular thiohalide complexes of molybdenum and tungsten, $M_3S_7X_6^{2-}$, react with $SePPh_3$ upon heating in acetonitrile producing $SPPh_3$, obtainable in a quantitative yield, and triangular thioselenohalide complexes of molybdenum and tungsten (eqn. (1)).

TABLE 2. Atomic coordinates (×10^3 for C and ×10^4 for remaining atoms) and equivalent isotropic termal parameters

Atom	x	y	z	B_{iso}	Atom	x	y	z	B_{iso}
Mo(1)	1262(1)	2955(1)	2020(1)	2.05(4)	C(12)	391(1)	587(1)	856(1)	7.1(8)
Mo(2)	2392(1)	1706(1)	2412(1)	2.33(4)	C(13)	351(1)	582(1)	770(1)	7.1(9)
Mo(3)	1977(1)	1906(1)	686(1)	2.30(4)	C(14)	255(1)	493(1)	721(1)	5.6(7)
Se(1)	1716(1)	2767(1)	3624(1)	2.94(5)	C(15)	139(1)	200(1)	649(1)	3.3(5)
Se(2)	3169(1)	877(1)	1139(1)	3.71(6)	C(16)	200(1)	222(1)	587(1)	3.5(5)
Se(3)	1017(1)	3197(1)	414(1)	3.35(6)	C(17)	228(1)	139(1)	538(1)	4.2(6)
Cl(11)	1999(3)	4929(3)	2591(2)	3.4(1)	C(18)	199(1)	44(1)	556(1)	5.5(7)
Cl(12)	−422(3)	3192(3)	2285(2)	3.3(1)	C(19)	142(2)	23(1)	621(1)	6.4(8)
Cl(21)	4178(3)	2527(3)	3443(3)	4.0(1)	C(20)	111(1)	97(1)	667(1)	4.6(6)
Cl(22)	2239(3)	212(3)	3132(3)	4.4(2)	C(21)	−440(1)	−270(1)	212(1)	4.2(6)
Cl(31)	3383(3)	2855(3)	−30(3)	4.2(1)	C(22)	−505(2)	−383(1)	209(2)	9(1)
Cl(32)	1194(3)	719(3)	−901(2)	3.3(1)	C(23)	−570(1)	−183(1)	317(1)	3.1(5)
S(1)	577(3)	1396(3)	2573(2)	2.8(1)	C(24)	−676(1)	−197(1)	317(1)	5.1(7)
S(3)	125(3)	1678(3)	661(2)	2.7(1)	C(25)	−701(1)	−184(1)	402(1)	6.2(8)
S(2)	1460(3)	241(3)	1102(2)	3.0(1)	C(26)	−632(1)	−162(1)	479(1)	5.1(7)
S(4)	3075(3)	3296(3)	1961(2)	2.5(1)	C(27)	−529(1)	−145(2)	476(1)	6.3(8)
P(1)	918(3)	2973(3)	7005(2)	2.9(1)	C(28)	−499(1)	−158(2)	395(1)	6.4(8)
P(2)	−5228(3)	−1893(3)	2150(3)	3.4(1)	C(29)	−437(1)	−53(1)	220(1)	3.1(5)
C(1)	10(1)	243(1)	775(1)	4.2(6)	C(30)	−467(1)	28(1)	256(1)	4.5(6)
C(2)	−37(1)	321(1)	822(1)	4.8(7)	C(31)	−401(1)	135(1)	263(1)	5.0(7)
C(3)	14(1)	327(1)	616(1)	2.7(5)	C(32)	−306(1)	157(1)	233(1)	4.8(7)
C(4)	−23(1)	257(1)	529(1)	3.6(5)	C(33)	−283(1)	68(1)	191(1)	5.2(7)
C(5)	−85(1)	278(1)	464(1)	4.1(6)	C(34)	−345(1)	−33(1)	186(1)	4.0(6)
C(6)	−113(1)	366(1)	486(1)	4.1(6)	C(35)	−636(1)	−242(1)	121(1)	3.6(6)
C(7)	−77(1)	434(1)	572(1)	4.1(6)	C(36)	−722(1)	−345(1)	105(1)	5.3(7)
C(8)	−15(1)	414(1)	635(1)	3.3(5)	C(37)	−807(1)	−385(1)	35(1)	5.3(7)
C(9)	206(1)	416(1)	762(1)	3.2(5)	C(38)	−811(1)	−333(1)	−24(1)	5.6(7)
C(10)	256(1)	429(1)	849(1)	4.7(7)	C(39)	−732(2)	−233(1)	−15(1)	6.6(9)
C(11)	345(1)	512(1)	896(1)	5.6(7)	C(40)	−642(1)	−185(1)	58(1)	5.5(7)

TABLE 3. Bond lengths and angles in $(PPh_3Et)_2Mo_3S_4Se_3Cl_6$

Bond lengths (Å)			
Mo(1)–Mo(2)	2.774(2)	Mo(2)–S(1)	2.403(4)
Mo(1)–Mo(3)	2.778(2)	Mo(2)–S(2)	2.393(4)
Mo(1)–Se(1)	2.603(2)	Mo(2)–S(4)	2.354(4)
Mo(1)–Se(3)	2.609(2)	Mo(3)–Se(2)	2.613(2)
Mo(1)–Cl(11)	2.459(4)	Mo(3)–Se(3)	2.609(2)
Mo(1)–Cl(12)	2.490(4)	Mo(3)–Cl(31)	2.457(4)
Mo(1)–S(1)	2.408(4)	Mo(3)–Cl(32)	2.537(4)
Mo(1)–S(3)	2.392(4)	Mo(3)–S(3)	2.410(4)
Mo(1)–S(4)	2.352(4)	Mo(3)–S(2)	2.403(4)
Mo(2)–Mo(3)	2.788(2)	Mo(3)–S(4)	2.353(4)
Mo(2)–Se(1)	2.622(2)	Se(1)–S(1)	2.163(4)
Mo(2)–Se(2)	2.625(2)	Se(2)–S(2)	2.157(5)
Mo(2)–Cl(21)	2.459(4)	Se(3)–S(3)	2.161(4)
Mo(2)–Cl(22)	2.503(4)		
Angles (°)			
Mo(2)–Mo(1)–Mo(3)	60.29(4)	Cl(21)–Mo(2)–S(4)	82.0(1)
Mo(2)–Mo(1)–Se(1)	58.27(5)	Cl(22)–Mo(2)–S(1)	85.6(1)
Mo(2)–Mo(1)–Se(3)	118.01(6)	Cl(22)–Mo(2)–S(2)	82.9(1)
Mo(2)–Mo(1)–Cl(11)	123.2(1)	Cl(22)–Mo(2)–S(4)	163.0(1)
Mo(2)–Mo(1)–Cl(12)	138.0(1)	S(1)–Mo(2)–S(2)	81.9(1)

(continued)

TABLE 3. *(continued)*

Mo(2)-Mo(1)-S(1)	54.69(9)	S(1)-Mo(2)-S(4)	108.6(1)
Mo(2)-Mo(1)-S(3)	95.25(9)	S(2)-Mo(2)-S(4)	107.9(1)
Mo(2)-Mo(1)-S(4)	53.90(9)	Mo(1)-Mo(3)-Mo(2)	59.80(4)
Mo(3)-Mo(1)-Se(1)	118.55(6)	Mo(1)-Mo(3)-Se(2)	117.67(6)
Mo(3)-Mo(1)-Se(3)	57.84(5)	Mo(1)-Mo(3)-Se(3)	57.84(5)
Mo(3)-Mo(1)-Cl(11)	122.4(1)	Mo(1)-Mo(3)-Cl(31)	123.4(1)
Mo(3)-Mo(1)-Cl(12)	139.4(1)	Mo(1)-Mo(3)-Cl(32)	137.30(9)
Mo(3)-Mo(1)-S(1)	93.53(9)	Mo(1)-Mo(3)-S(3)	54.35(9)
Mo(3)-Mo(1)-S(3)	54.97(9)	Mo(1)-Mo(3)-S(2)	95.2(1)
Mo(3)-Mo(1)-S(4)	53.82(9)	Mo(1)-Mo(3)-S(4)	53.82(9)
Se(1)-Mo(1)-Se(3)	174.12(7)	Mo(2)-Mo(3)-Se(2)	58.06(5)
Se(1)-Mo(1)-Cl(11)	90.7(1)	Mo(2)-Mo(3)-Se(3)	117.53(6)
Se(1)-Mo(1)-Cl(12)	91.1(1)	Mo(2)-Mo(3)-Cl(31)	123.9(1)
Se(1)-Mo(1)-S(1)	50.96(9)	Mo(2)-Mo(3)-Cl(32)	139.38(9)
Se(1)-Mo(1)-S(3)	132.0(1)	Mo(2)-Mo(3)-S(3)	94.48(3)
Se(1)-Mo(1)-S(4)	88.1(1)	Mo(2)-Mo(3)-S(2)	54.28(9)
Se(3)-Mo(1)-Cl(11)	88.0(1)	Mo(2)-Mo(3)-S(4)	53.69(9)
Se(3)-Mo(1)-Cl(12)	94.4(1)	Se(2)-Mo(3)-Se(3)	171.07(7)
Se(3)-Mo(1)-S(1)	131.8(1)	Se(2)-Mo(3)-Cl(31)	88.4(1)
Se(3)-Mo(1)-S(3)	50.97(9)	Se(2)-Mo(3)-Cl(32)	95.43(9)
Se(3)-Mo(1)-S(4)	86.0(1)	Se(2)-Mo(3)-S(3)	134.6(1)
Cl(11)-Mo(1)-Cl(12)	80.9(1)	Se(2)-Mo(3)-S(2)	50.7(1)
Cl(11)-Mo(1)-S(1)	138.5(1)	Se(2)-Mo(3)-S(4)	85.3(1)
Cl(11)-Mo(1)-S(3)	135.1(1)	Se(3)-Mo(3)-Cl(31)	88.5(1)
Cl(11)-Mo(1)-S(4)	81.8(1)	Se(3)-Mo(3)-Cl(32)	92.34(9)
Cl(12)-Mo(1)-S(1)	84.1(1)	Se(3)-Mo(3)-S(3)	50.80(9)
Cl(12)-Mo(1)-S(3)	84.7(1)	Se(3)-Mo(3)-S(2)	134.7(1)
Cl(12)-Mo(1)-S(4)	162.7(1)	Se(3)-Mo(3)-S(4)	86.0(1)
S(1)-Mo(1)-S(3)	81.0(1)	Cl(31)-Mo(3)-Cl(32)	80.8(1)
S(1)-Mo(1)-S(4)	108.5(1)	Cl(31)-Mo(3)-S(3)	135.4(1)
S(3)-Mo(1)-S(4)	108.5(1)	Cl(31)-Mo(3)-S(2)	135.2(1)
Mo(1)-Mo(2)-Mo(3)	59.91(4)	Cl(31)-Mo(3)-S(4)	82.7(1)
Mo(1)-Mo(2)-Se(1)	57.58(5)	Cl(32)-Mo(3)-S(3)	83.4(1)
Mo(1)-Mo(2)-Se(2)	117.34(6)	Cl(32)-Mo(3)-S(2)	85.2(1)
Mo(1)-Mo(2)-Cl(21)	120.9(1)	Cl(32)-Mo(3)-S(4)	163.4(1)
Mo(1)-Mo(2)-Cl(22)	140.1(1)	S(3)-Mo(3)-S(2)	84.1(1)
Mo(1)-Mo(2)-S(1)	54.88(9)	S(3)-Mo(3)-S(4)	107.9(1)
Mo(1)-Mo(2)-S(2)	95.5(1)	S(2)-Mo(3)-S(4)	107.6(1)
Mo(1)-Mo(2)-S(4)	53.85(9)	Mo(1)-Se(1)-Mo(2)	64.14(5)
Mo(3)-Mo(2)-Se(1)	117.48(6)	Mo(1)-Se(1)-S(1)	59.9(1)
Mo(3)-Mo(2)-Se(2)	57.62(5)	Mo(2)-Se(1)-S(1)	59.4(1)
Mo(3)-Mo(2)-Cl(21)	125.0(1)	Mo(2)-Se(2)-Mo(3)	64.32(5)
Mo(3)-Mo(2)-Cl(22)	137.0(1)	Mo(2)-Se(2)-S(2)	59.1(1)
Mo(3)-Mo(2)-S(1)	93.4(1)	Mo(3)-Se(2)-S(2)	59.6(1)
Mo(3)-Mo(2)-S(2)	54.62(9)	Mo(1)-Se(3)-Mo(3)	64.32(5)
Mo(3)-Mo(2)-S(4)	53.65(9)	Mo(1)-Se(3)-S(3)	59.3(1)
Se(1)-Mo(2)-Se(2)	172.58(7)	Mo(3)-Se(3)-S(3)	59.8(1)
Se(1)-Mo(2)-Cl(21)	87.2(1)	Mo(1)-S(1)-Mo(2)	70.4(1)
Se(1)-Mo(2)-Cl(22)	94.8(1)	Mo(1)-S(1)-Se(1)	69.2(1)
Se(1)-Mo(2)-S(1)	50.75(9)	Mo(2)-S(1)-Se(1)	69.9(1)
Se(1)-Mo(2)-S(2)	132.6(1)	Mo(1)-S(3)-Mo(3)	70.7(1)
Se(1)-Mo(2)-S(4)	87.6(1)	Mo(1)-S(3)-Se(3)	69.7(1)
Se(2)-Mo(2)-Cl(21)	91.6(1)	Mo(3)-S(3)-Se(3)	69.4(1)
Se(2)-Mo(2)-Cl(22)	92.3(1)	Mo(2)-S(2)-Mo(3)	71.1(1)
Se(2)-Mo(2)-S(1)	132.3(1)	Mo(2)-S(2)-Se(2)	70.3(1)
Se(2)-Mo(2)-S(2)	50.7(1)	Mo(3)-S(2)-Se(2)	69.7(1)
Se(2)-Mo(2)-S(4)	85.0(1)	Mo(1)-S(4)-Mo(2)	72.2(1)
Cl(21)-Mo(2)-Cl(22)	81.3(1)	Mo(1)-S(4)-Mo(3)	72.4(1)
Cl(21)-Mo(2)-S(1)	134.6(1)	Mo(2)-S(4)-Mo(3)	72.7(1)
Cl(21)-Mo(2)-S(2)	138.1(1)		

$$Q_2M_3S_7X_6 + 3SePPh_3 \longrightarrow 3SPPh_3 + Q_2M_3S_4Se_3X_6 \qquad (1)$$

M = Mo; X = Cl, Br; Q = Et_4N^+, PPh_4^+, PPN^+, PPh_3Et^+

M = W; X = Cl, Br; Q = PPh_4^+, PPN^+

It appears that the driving force of the reaction is the difference in bond energy primarily between $>$P=S and $>$P=Se. Thus reaction (1) turned out to be practically irreversible, and boiling the thioselenohalide complexes with $SPPh_3$ in CH_3CN did not produce the starting thiohalide complexes. Also, heating of the $(Et_4N)_2Mo_3S_7Cl_6$ complex with 10 equivalents of $^{34}SPPh_3$ did not show any isotopic effect.

Thioselenohalide complexes of molybdenum and tungsten form red–brown air-stable complexes while the solutions of these complexes slowly decompose. The complexes are soluble in CH_3CN and DMF but not soluble in hydrocarbons and ether.

In the starting thiohalide molybdenum complexes the sulfur atoms of the μ_2-S_2 ligands are structurally non-equivalent [18, 19]. Three of them lie essentially in the Mo_3 plane (equatorial atoms S_e) while the other three occupy the side opposite to the μ_3-S side of the Mo_3 triangle (axial atoms S_a). We have studied the stereochemistry of reaction (1) proceeding from compounds containing ^{34}S isotopes $(Et_4N)_2$-$Mo_3(\mu_3\text{-}^{34}S)(\mu_2\text{-}^{34}S_a{}^{32}S_e)_3X_6$ (X = Cl, Br). The reactions proceeded with replacement of the equatorial sulfur atoms to form $^{32}SPPh_3$ and $(Et_4N)_2Mo_3(\mu_3\text{-}^{34}S)(\mu_2\text{-}^{34}S_aSe_e)_3X_6$ (eqn. (2)).

$$(Et_4N)_2Mo_3(\mu_3\text{-}^{34}S)(\mu_2\text{-}^{34}S_a{}^{32}S_e)_3X_6 + 3SePPh_3 \longrightarrow 3\,{}^{32}SPPh_3 + (Et_4N)_2Mo_3(\mu_3\text{-}^{34}S)(\mu_2\text{-}^{34}S_aSe_e)_3X_6 \qquad (2)$$

The formation of $^{32}SPPh_3$ has been proved by mass spectroscopy, and the IR and Raman spectra of the thioselenohalide complexes fully coincide with the spectra of the compounds obtained by reaction (3)

$$(Et_4N)_2Mo_3(\mu_3\text{-}^{34}S)(\mu_2\text{-}^{34}S_2)_3X_6 + 3SePPh_3 \longrightarrow 3\,{}^{34}SPPh_3 + (Et_4N)_2Mo_3(\mu_3\text{-}^{34}S)(\mu_2\text{-}^{34}S_aSe_e)_3X_6 \qquad (3)$$

On the other hand, the thioselenohalide complexes of molybdenum react with 3 equivalents of PPh_3 producing $SePPh_3$ in a 85% yield (eqn. (4)). The electronic spectrum of the bright-green reaction mixture fully coincides with that of $Mo_3S_4{}^{4+}$,solv. obtained by reaction (5) [16].

$$(PPh_4)_2Mo_3S_4Se_3Cl_6 + 3PPh_3 \longrightarrow 3SePPh_3 + Mo_3S_4{}^{4+}\text{,solv.} \qquad (4)$$

$$(PPh_4)_2Mo_3S_7Cl_6 + 3PPh_3 \longrightarrow 3SPPh_3 + Mo_3S_4{}^{4+}\text{,solv.} \qquad (5)$$

Thus, the $Mo_3S_4{}^{4+}$ cluster fragment with the sulfur atoms in the axial position relative to the Mo_3 plane is preserved in all of the studied reactions.

Thermal Properties of $(Et_4N)_2Mo_3S_4Se_3Br_6$

The soluble transition metal chalcogenides complexes are of interest due to their potential use for obtaining, for example, highly dispersed sulfides. In previous work [20] we have shown that the thermal decomposition of $H_2[Mo_2(\mu_2\text{-}S_2)_2Cl_8]\cdot 6H_2O$ produces MoS_2 with a specific surface area of 134 m^2/g. In the present work a mixed chalcogenide of composition MoSSe was formed upon heating $(Et_4N)_2Mo_3$-$S_4Se_3Br_6$ *in vacuo* at 450 °C. According to the X-ray powder diffraction patterns MoSSe is X-ray amorphous. No noticeable crystallization took place after MoSSe was kept in a sealed quartz ampoule at 800 °C for 7 days. In an earlier study [21] the synthesis of another molybdenum chalcogenide $MoS_{1.5}Se_{0.5}$ has been reported. The compound was obtained by heating Mo_2S_3 and Se at 1000 °C.

The structure of $(PPh_3Et)_2Mo_3S_4Se_3Cl_6$

The structure of the $Mo_3S_4Se_3Cl_6{}^{2-}$ anion is shown in Fig. 1. The three molybdenum atoms form an almost equilateral triangle with the average Mo–Mo distance 2.777(2) Å. The short Mo–Mo distances and the diamagnetism of the complex suggest a single Mo–Mo bonding in this Mo^{4+} complex. In addition, an estimation of the number of valence electrons according to the EAN rule shows that the anion contains 48 cluster valence electrons (the μ_2-SSe ligand, as μ_2-S_2 and μ_2-Se_2, is a donor of 6 electrons).

The μ_3-S(4) atom occupies a position that is almost above the center of the triangle (Table 4). There are two types of chlorine atoms. For the chlorine atoms occupying the same side of the Mo_3 plane as the μ_3-S ligand, the average Mo–Cl bond length is 2.458(4) Å which is somewhat smaller than for the remaining chlorines (the average distance 2.510(4) Å). Such difference in bond length is due to the sterical effect of the μ_2-SSe ligands whose Se atoms practically lie in the Mo_3 plane (Table 4). The average SSe distance in complex **I** is 2.160(4) Å. For the complexes of niobium, molybdenum and tungsten known from the literature the Y–Y dis-

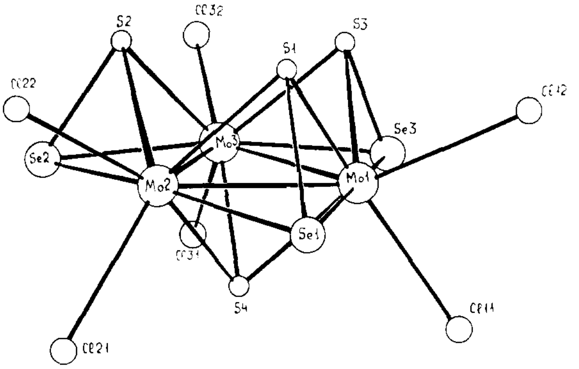

Fig. 1. Structure of the $Mo_3S_4Se_3Cl_6{}^{2-}$ anion.

TABLE 4. Deviation of the $Mo_3S_4Se_3Cl_6^{2-}$ dianion atoms from the plane of the three Mo atoms

Atom	Deviation (Å)
Se(1)	−0.054(2)
Se(2)	−0.198(2)
Se(3)	−0.155(2)
Cl(11)	−1.916(4)
Cl(12)	1.234(4)
Cl(21)	−1.910(4)
Cl(22)	1.253(4)
Cl(31)	−1.891(4)
Cl(32)	1.286(4)
S(1)	1.712(4)
S(2)	1.633(4)
S(3)	1.662(4)
S(4)	−1.720(4)

tance in the cluster fragment $M_2(\mu_2\text{-}Y_2)_2{}^{n+}$ is 1.97–2.03 Å (Y = S) and 2.26–2.30 Å (Y = Se) [22].

Vibrational Spectra

Figure 2 shows IR and Raman spectra of $(Et_4N)_2Mo_3S_4Se_3Cl_6$ and $(Et_4N)_2Mo_3S_4Se_3Br_6$. To assign the forms of the observed vibrations a calculation of the vibrational spectrum of $Mo_3S_4Se_3Cl_6^{2-}$ has been performed using the programs of ref. 23. The experimental basis of the calculation were: (i) the values of the frequencies of the IR and Raman-active modes; (ii) the isotope shifts upon going from $Mo_3{}^{32}S_4Se_3Cl_6^{2-}$ to $Mo_3{}^{34}S_4Se_3Cl_6^{2-}$; (iii) comparison of the vibrational spectra for $Mo_3S_4Se_3Cl_6^{2-}$ and $Mo_3S_4Se_3Br_6^{2-}$. The force constants from ref. 24 were taken as the first approximation. In calculating the spectra the main attention was given to the valence vibrations ($\nu > 200$ cm^{-1}) since the deformational inner vibrations occurring at lower frequencies are strongly mixed with the external

TABLE 5. Force constants in $Mo_3(\mu_3\text{-}S)(\mu_2\text{-}SSe)_3Cl_6^{2-}$

Bond	Force constant (mdyn/Å)
Mo–Mo	1.0
Mo–Se	1.1
Mo–S(1)	1.7
Mo–S(4)	1.9
Mo–Cl(11)	1.7
Mo–Cl(21)	1.5
S–Se	2.3

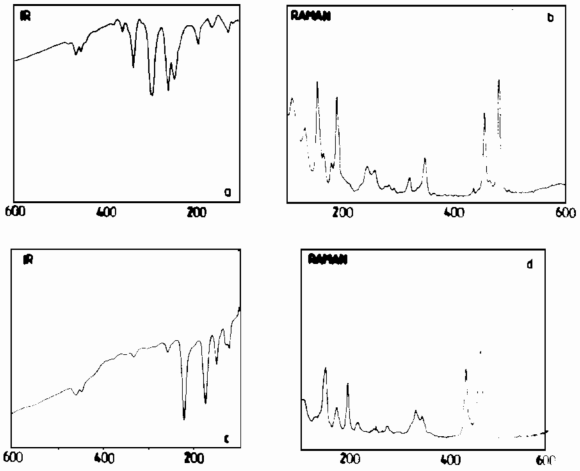

Fig. 2. IR (polyethylene) and Raman spectra of triangular thioselenohalide complexes of molybdenum: (a) and (b) $(Et_4N)_2Mo_3S_4Se_3Cl_6$; (c) and (d) $(Et_4N)_2Mo_3S_4Se_3Br_6$.

TABLE 6. Experimental (Et_4N^+ salt) and calculated vibrational frequencies of $Mo_3S_4Se_3Cl_6^{2-}$ and their shifts upon isotope exchange

ν_{exp} (cm^{-1})	ν_{calc} (cm^{-1})	$\Delta\nu$ for $Mo_3{}^{32}S_4Se_3Cl_6^{2-}$ and $Mo_3{}^{34}S_4Se_3Cl_6^{2-}$	
		Experimental	Calculated
260, Raman	266	5	6.1
260, IR		0	
292, Raman, IR	287	2	1.2
297, IR	293	2	0.5
321, Raman	321	4	5.1
335, IR	330	4	4.7
	339		3.0
348, Raman	351	4	3.1
	355		2.5
360, IR	360	4	3.1
434[a], Raman			
452, Raman, IR	453	10	10.3
461, Raman, IR	464	10	10.7
478, Raman, IR	476	11	10.1

[a] Band of weak intensity.

TABLE 7. Distribution of the potential energy (%) among the groups of equivalent vibrational coordinates

Bands (cm^{-1})	Mo–Mo	Mo–Se	Mo–μ_2-S	Mo–μ_3-S	Mo–Cl(11)	Mo–Cl(12)	S–Se
99, E	78	16	2	3	0	0	0
132, E	6	88	0	0	2	3	0
141, A_1	9	83	1	1	3	2	1
172, A_2	0	70	30	0	0	0	0
180, A_1	79	3	2	7	0	9	0
184, E	10	69	17	0	0	0	3
267, E	1	3	75	4	1	14	2
287, E	0	0	7	8	40	45	0
293, A_1	2	0	1	2	44	52	0
320, A_1	2	5	39	1	25	12	16
330, E	1	0	7	70	21	0	0
339, A_2	0	31	69	0	0	0	0
351, A_1	6	1	15	4	25	21	28
355, E	3	3	12	9	29	30	13
360, E	0	18	36	2	9	8	26
453, A_1	2	0	13	66	0	0	18
464, E	1	1	47	0	0	0	52
476, A_1	5	1	32	25	2	3	33

modes. This hinders, in particular, determination of the Mo–Mo bond force constant.

Table 5 presents the final variant of the set of valence force constants. Table 6 compares the calculated vibrational frequencies and isotope shifts with the experimental values. Table 7 shows the distribution of the potential energy among the groups of equivalent vibrational coordinates showing the extent of participation of specific bonds in each vibration. The force constants of the Mo–S and Mo–Cl bonds of the $Mo_3S_4Se_3Cl_6^{2-}$ and $Mo_3S_7Cl_6^{2-}$ complexes [16] practically coincide. Noteworthy is the great difference in force constants between the Mo–S and Mo–Se bonds of the $Mo_3S_4Se_3Cl_6^{2-}$ complex as well as a rather high value of the force constant of the S–Se bond which practically coincides with the force constants of the S–S bonds in the $Mo_3S_7Cl_6^{2-}$ [16] and $Mo_3S_{13}^{2-}$ [25] complexes. This appears to be due to a smaller (as compared with Mo–S) overlap of the Mo and Se atomic orbitals resulting in a smaller electronic density in the π^* orbitals of the S–Se fragments.

The data of Table 7 show that only vibrations involving chlorine atoms (symmetrical and degenerated) can be considered to be characteristic. The rest of the observed modes are mixed ones. In contrast to this, in the earlier studied $Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3Cl_6^{2-}$ and $Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_2(S_2)_3^{2-}$ the S–S vibrations are predominantly valence vibrations [16, 25].

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