Triangular $M_3Se_7^{4+}$ and $M_3Se_4^{4+}$ complexes (M = Mo, W). An X-ray study of $Mo_3Se_7(Et_2NCS_2)_4$ and $W_3Se_7(Et_2NCS_2)_4$

V. P. Fedin*, M. N. Sokolov, O. A. Geras'ko, A. V. Virovets, N. V. Podberezskaya and V. Ye. Fedorov

Institute of Inorganic Chemistry, Siberian Branch of the Academy of Sciences of the USSR, Prospekt Lavrentyeva 3, 630090 Novosibirsk (U.S.S.R)

Abstract

New methods for the synthesis of triangular $M_3Se_7^{4+}$ and $M_3Se_4^{4+}$ complexes soluble in organic solvents have been developed which proceed from polymeric $M_3Se_7X_4$ (M = Mo, W; X = Cl, Br). Heating of $Mo_3Se_7Cl_4$ in a PPh_4Cl melt has produced the $(PPh_4)_2Mo_3Se_7Cl_6$ salt. Selenobromide complexes of molybdenum and tungsten are less stable and have been converted to $M_3Se_7(dtc)_4$ complexes by reacting them with $NaS_2NCEt_2 \cdot 3H_2O$ ($Nadtc \cdot 3H_2O$) in CH_3CN. The structure of $M_3Se_7(dtc)_4$ (M = Mo, W) has been determined by X-ray structural analysis: $a = 16.728(5)$, $b = 18.604(7)$, $c = 13.324(3)$ Å, $\beta = 99.12(3)°$, $Z = 4$, $P2_1/c$, $R_F = 0.1344$ for $W_3Se_7(dtc)_4$; $a = 16.652(5)$, $b = 18.614(8)$, $c = 13.337(3)$ Å, $\beta = 99.11(2)°$, $Z = 4$, $P2_1/c$, $R_F = 0.0628$ for $Mo_3Se_7(dtc)_4$. Heating of $M_3Se_7X_4$ in a melt of 1,10-phenanthroline (phen) produces salts containing $M_3Se_7(phen)_3^{4+}$ with different anions (Cl^-, Br^-, $ZnCl_4^{2-}$, $ZnBr_4^{2-}$). The action of phosphines on $M_3Se_7^{4+}$ complexes gave $M_3Se_4^{4+}$ complexes $Mo_3Se_4(dtc)_4(PPh_3)$ and $Mo_3Se_4(dppe)_3Cl_4$ (dppe is $Ph_2PCH_2CH_2PPh_2$).

Introduction

The work of the last decade has resulted in the discovery of a large new area of specifically built polymeric thio complexes of transition metals. The largest number of the syntheses have been obtained for homometallic thio complexes of Mo and W [1–4]. In particular, different methods for the synthesis of triangular $M_3S_7^{4+}$ and $M_3S_4^{4+}$ complexes (M = Mo, W) [5–10] have been developed. Recently highly effective methods have been reported for the synthesis of mixed-chalcogen $M_3S_4Se_3^{4+}$ complexes containing a μ_2-SSe ligand [11, 12]. On the other hand, the $M_3Se_7^{4+}$ and $M_3Se_4^{4+}$ complexes (M = Mo, W) have been rarely studied. In 1986 Sykes and co-workers proposed the preparation of $Mo_3Se_4^{4+}$, and also of $Mo_3O_3Se^{4+}$, by electrolysis of aqueous solutions of $Mo_2O_4(cys)_2^{2-}$ using a cathode of selenium [13]. The $Mo_{12}Se_{56}^{12-}$ complex containing $Mo_3(\mu_3\text{-}Se)(\mu_2\text{-}Se_2)_3^{4+}$ has been obtained recently proceeding from metallic Mo and K_2Se_4 in H_2O and has been structurally characterized [14].

In a previous study [15] we were able to obtain a series of $M_3Se_7^{4+}$ and $M_3Se_4^{4+}$ complexes using as starting materials polymeric $M_3Se_7X_4$ (M = Mo, W; X = Cl, Br) which were subjected to a mechanochemical activation. In the present study we have investigated other methods for the synthesis of $M_3Se_7^{4+}$ complexes from polymeric selenohalogenides $M_3Se_7X_4$ and determined the structure of $M_3Se_7(dtc)_4$ (M = Mo, W). $W_3Se_7(dtc)_4$ is the first structurally characterized complex containing a $W_3Se_7^{4+}$ core.

Experimental

The materials and experimental equipment of the present work were those normally used in our laboratory [5, 6]. The $^{31}P\{^1H\}$. NMR spectra were obtained on a Brucker 400 instrument (at a working frequency of 161.977 mHz for P). Electrical conductivity measurements were performed on 10^{-4} M solutions in nitromethane. The synthesis of $M_3Se_7Br_4$ occurred by heating stoichiometric amounts of the elements in evacuated quartz ampoules at temperatures of 300–350 °C for 60–80 h.

The reactions at temperatures above the ambient one were conducted under argon. Isolation and purification of the complexes were carried out in air.

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*Author to whom correspondence should be addressed.

Preparation of (PPh$_4$)$_2$Mo$_3$Se$_7$Cl$_6$ (1)

Mo$_3$Se$_7$Cl$_4$ (1.0 g) was heated in a melt of PPh$_4$Cl at 280 °C for 3 h. The dark-red melt was ground, washed with ethanol and then extracted with hot acetonitrile and precipitated with ether. The precipitated solid was recrystallized from an acetonitrile–ethyl acetate mixture. Yield: 0.54 g of complex 1, 31%.

Anal. Calc. for C$_{48}$H$_{40}$Cl$_6$Mo$_3$P$_2$Se$_7$: C, 33.29; H, 2.33; Cl, 12.28; Se, 31.91. Found: C, 34.28; H, 2.35; Cl, 12.25; Se, 31.48%. Raman: 334, 312, 263, 250, 231, 194, 146 cm^{-1}.

Preparation of W$_3$Se$_7$(dtc)$_4$ (2)

W$_3$Se$_7$Br$_4$ (1.0 g) was heated in a melt of PPh$_4$Br (1.0 g) at 300 °C for 3 h. The cold melt was ground, washed from PPh$_4$Br using alcohol and extracted with DMF. Adding ether to the extract afforded 0.56 g of a brown powder which was then boiled for 3 h in 50 ml of CH$_3$CN containing 0.8 g of NaS$_2$CNEt$_2$·3H$_2$O. The precipitated solid was washed with water, alcohol and extracted with CH$_2$Cl$_2$. Ether was added to the extract to produce a red crystalline substance. Yield: 0.48 g of complex 2, 40%.

Anal. Calc. for C$_{20}$H$_{40}$N$_4$S$_8$Se$_7$W$_3$: C, 14.14; H, 2.36; N, 3.30; Se, 32.57; W, 32.51. Found: C, 14.26; H, 1.94; N, 3.36; Se, 32.80; W, 32.21%.

IR (4000–100 cm^{-1}) and Raman (1000–100 cm^{-1}) data are practically the same as those for complex 3 [15].

Preparation of Mo$_3$Se$_7$(dtc)$_4$ (3)

Complex 3 in a 64% yield was prepared by a procedure analogous to that just described. The IR and Raman spectra for 3 completely coincide with those obtained for the same complex in ref. 15.

Preparation of [Mo$_3$Se$_7$(dtc)$_3$]PF$_6$ (4)

Complex 3 (0.43 g) in CH$_2$Cl$_2$ (30 ml) was stirred with a solution of NH$_4$PF$_6$ (1.0 g) in 30 ml of H$_2$O for 3 h. The aqueous layer was removed, the solution in CH$_2$Cl$_2$ dried over CaCl$_2$ and then 30 ml of ether was added. Yield: 0.33 g of complex 4, 86%.

Anal. Calc. for C$_{15}$H$_{30}$N$_3$F$_6$S$_6$Se$_7$Mo$_3$P: C, 12.58; H, 2.10; N, 2.94; F, 7.97. Found: C, 12.73; H, 2.18; N, 3.19; F, 8.47%. The IR (4000–400 cm^{-1}) spectrum coincides with that of 3 with extra bands at 833 and 550 cm^{-1} (PF$_6^-$).

Preparation of [Mo$_3$Se$_7$(phen)$_3$]Br$_4$ (5)

Mo$_3$Se$_7$Br$_4$ (5.7 g) was heated in a melt of *o*-phen·H$_2$O (8.0 g) at 230–250 °C for 5 h. The red–brown melt was ground and extracted with hot CF$_3$COOH and then a threefold volume of ether was added to the solution. The precipitated powder was recrystallized from conc. HBr. Yield: 5.3 g of complex 5, 63%.

Anal. Calc. for C$_{36}$H$_{24}$N$_6$Br$_4$Mo$_3$Se$_7$: C, 25.43; H, 1.41; N, 4.93; Br, 18.81. Found: C, 25.70; H, 1.48; N, 4.93; Br, 18.90%.

Preparation of [Mo$_3$Se$_7$(phen)$_3$]Cl$_4$ (6)

Recrystallization of complex 5 from conc. HCl gives complex 6 in quantitative yield.

Anal. Calc. for C$_{36}$H$_{24}$N$_6$Cl$_4$Mo$_3$Se$_7$: C, 28.37; H, 1.58; N, 5.52; Cl 9.32; Mo, 18.90; Se, 36.31. Found: C, 28.70; H, 1.64; N, 5.41; Cl, 9.46; Mo, 19.00; Se, 36.30%. Details of the IR and Raman spectra of 6 coincide with those for complex 5.

Preparation of [Mo$_3$Se$_7$(phen)$_3$](ZnCl$_4$)$_2$ (7)

Complex 6 (0.20 g) was dissolved in conc. HCl (10 ml) and ZnO (0.20 g) was added. The precipitated red solid was separated and recrystallized from an HCl/HCOOH mixture Yield: 0.26 g of complex 7, 98%.

Anal. Calc. for C$_{36}$H$_{24}$N$_6$Cl$_8$Mo$_3$Se$_7$Zn$_2$: C, 24.08; H, 1.35; N, 4.67; Cl, 15.80. Found: C, 24.07; H, 1.47; N, 4.49; Cl, 15.67.

Preparation of [Mo$_3$Se$_7$(phen)$_3$](ZnBr$_4$)$_2$ (8)

Complex 8 was obtained in quantitative yield in a conc. HBr medium by a procedure analogous to that used to prepare 7.

Anal. Calc. for C$_{36}$H$_{24}$N$_6$Br$_8$Mo$_3$Se$_7$Zn$_2$: C, 20,09; H, 1.12; N, 3.91. Found: C, 20.01; H, 1.30; N, 3.44%. The IR spectrum (4000–100 cm^{-1}) corresponds to the spectra of 5 and 6 and shows an extra band at 213 cm^{-1} (ZnBr$_4^{2-}$).

Preparation of [W$_3$Se$_7$(phen)$_3$]Cl$_4$ (9)

Complex 9 was obtained in a 36% yield by a procedure analogous to that used to prepare 6.

Anal. Calc. for C$_{36}$H$_{24}$N$_6$Cl$_4$W$_3$Se$_7$: C, 24.17; H, 1.94; N, 4.70; Cl, 7.95; Se, 30.95. Found: C, 24.20; H, 2.40; N, 4.78; Cl, 8.96; Se, 30.45%. The vibrational spectra of complex 9 coincide with those of the molybdenum analogs 5 and 6.

Preparation of Mo$_3$Se$_4$(dtc)$_4$(PPh$_3$) (10)

Mo$_3$Se$_7$(dtc)$_4$ (1.01 g) was boiled with PPh$_3$ (1.50 g) in CH$_2$Cl$_2$ (30 ml) for 2 h. The solution was added to ether to produce a brown finely crystalline substance at −5 °C. Yield: 0.80 g of complex 10, 82%.

Anal. Calc. for C$_{38}$H$_{55}$Mo$_3$PS$_8$Se$_4$: C, 31.71; H, 3.82; P, 2.16%. Found: C, 31.31; H, 3.67; P, 2.31%. ^{31}P{^{1}H} NMR spectrum: 5.6 ppm relative to H$_3$PO$_4$.

Preparation of Mo₃Se₄(dppe)₃Cl₄ (11)

Mo₃Se₇Cl₄ (0.50 g) and dppe (1.00 g) were boiled in acetonitrile (30 ml) for 6 h. Ether was added to the filtrate until it became turbid and the mother liquor was allowed to stand overnight at −5 °C. The precipitated crystals were separated and washed with ether. Yield: 0.15 g of complex 11, 29%.

Anal. Calc. for $C_{52}H_{48}Cl_4Mo_3P_6Se_4$: C, 46.30, H, 3.86, Cl, 7.61. Found: C, 46.31, H, 3.69, Cl, 7.97%.

X-ray structural analysis

The reddish-brown crystals of complex 2 and the red–brown crystals of 3 in the form of flat needles suitable for X-ray structural analysis were obtained by diffusing ether vapours into solutions of the complexes in CH_2Cl_2. The crystallographic parameters are listed in Table 1. The structures were solved by the direct method using the SHELX-86 program [16]. The absorption was taken into account from an azimuthal scanning curve in 3 and using the DIFABS program [17] for complex 2. The hydrogen atoms have not been taken into account in the calculation. The positional and heat parameters of the atoms in both structures have been refined by full-matrix least-squares technique in an anisotropic (M atoms, Se, S, some light atoms)–isotropic approximation with a unit weighting scheme. Because of the large heat motion of the ethyl groups the refinement of their coordinates has been performed

in 3 with a restriction on the C–C and C–N bond lengths (1.52 and 1.45 Å, respectively). In 2 the thermal parameters of the ethyl group carbons were fixed ($U_{iso} = 0.08$ Å^2). The coordinates and equivalent temperature parameters of the atoms are given in Tables 2 and 3. All calculations were performed on a EC-1037 computer using the set of programs YANX [18].

Results and discussion

Selenohalogenide complexes of molybdenum of composition $Mo_3Se_7X_4(X = Cl, Br)$ were first obtained

TABLE 2. Position parameters and equivalent temperature parameters for $W_3Se_7(dtc)_4$

Atom	x	y	z	U
W(1)	0.8511(3)	0.8565(3)	0.2289(4)	0.084(4)[a]
W(2)	0.7073(3)	0.8109(3)	0.2289(4)	0.086(4)[a]
W(3)	0.7908(3)	0.9155(3)	0.3920(4)	0.084(4)[a]
Se(1)	0.7705(5)	0.7488(4)	0.1315(5)	0.031(5)[a]
Se(2)	0.7207(5)	0.8623(4)	0.1036(5)	0.033(5)[a]
Se(3)	0.6596(5)	0.8584(4)	0.4408(5)	0.032(5)[a]
Se(4)	0.6475(5)	0.9349(4)	0.3017(6)	0.040(5)[a]
Se(5)	0.9358(5)	0.9442(4)	0.3565(6)	0.033(5)[a]
Se(6)	0.82265(5)	0.9897(4)	0.2450(5)	0.032(5)[a]
Se(7)	0.8362(4)	0.7871(3)	0.3852(5)	0.018(4)[a]
S(11)	0.675(1)	0.687(1)	0.329(1)	0.04(1)[a]
S(21)	0.675(1)	0.687(1)	0.329(1)	0.04(1)[a]
S(22)	0.366(1)	0.770(1)	0.191(2)	0.07(2)[a]
S(31)	0.851(1)	0.906(1)	0.576(1)	0.03(1)[a]
S(32)	0.775(1)	1.033(1)	0.481(1)	0.04(1)[a]
S(41)	0.675(1)	1.022(1)	0.117(2)	0.05(1)[a]
S(42)	0.735(2)	1.149(2)	0.238(2)	0.10(2)[a]
C(1)	0.991(7)	0.817(6)	0.119(8)	0.02(3)
N(1)	1.043(3)	0.796(3)	0.066(4)	0.03(1)
C(11)	1.045(5)	0.821(4)	−0.05(6)	0.05(2)
C(12)	1.115(6)	0.875(5)	−0.027(7)	0.08(3)
C(13)	1.050(6)	0.664(5)	0.064(7)	0.08(3)
C(2)	0.579(5)	0.698(5)	0.244(6)	0.09(3)
N(2)	0.533(4)	0.640(3)	0.240(4)	0.08(2)
C(21)	0.452(6)	0.638(5)	0.177(7)	0.08(3)
C(22)	0.446(5)	0.585(4)	0.083(6)	0.10(2)
C(23)	0.556(6)	0.558(6)	0.294(8)	0.10(3)
C(24)	0.569(6)	0.497(5)	0.199(8)	0.14(3)
C(3)	0.88(5)	1.000(4)	0.600(6)	0.02(2)
N(3)	0.847(5)	1.031(4)	0.678(6)	0.05(2)
C(31)	0.889(6)	0.996(5)	0.763(7)	0.07(3)
C(32)	0.837(6)	0.969(5)	0.829(7)	0.08(3)
C(33)	0.842(6)	1.108(6)	0.674(6)	0.10(3)
C(34)	0.761(6)	1.120(6)	0.718(8)	0.09(3)
C(4)	0.63(4)	1.110(5)	0.133(5)	0.04(2)
N(4)	0.645(3)	1.158(3)	0.072(4)	0.07(2)
C(41)	0.621(6)	1.245(5)	0.082(7)	0.0800
C(42)	0.666(6)	1.45(5)	0.022(7)	0.0800
C(43)	0.607(6)	1.132(5)	−0.029(7)	0.0800
C(44)	0.534(6)	1.084(5)	−0.070(7)	0.0800

[a]$U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$.

TABLE 1. Crystallographic data for $W_3Se_7(dtc)_4$ (2) and $Mo_3Se_7(dtc)_4$ (3)

	2	3
Formula	$C_{20}H_{40}N_4S_8Se_7W_3$	$C_{20}H_{40}Mo_3N_4S_8Se_7$
Formula weight	1697.4	1433.7
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	16.728(5)	16.652(5)
b (Å)	18.604(7)	18.614(8)
c (Å)	13.324(3)	13.337(3)
β (°)	99.12(3)	99.11(2)
V (Å³)	4094(2)	4082(2)
Z	4	4
D_{calc} (g cm⁻³)	2.754	2.333
Dimensions (mm)	0.05 × 0.09 × 0.4	0.03 × 0.04 × 0.75
Diffractometer	Syntex P2₁	Syntex P2₁
Radiation	Cu Kα	Cu Kα
Monochromator	graphite	graphite
Scan mode	θ/2θ, $V_{min} = 4°$/min	θ/2θ, $V_{min} = 4°$/min
2θ range	3–90	3–80
μ (cm⁻¹)	199	306
Temperature	room	room
Total reflections	3400	2715
Independent reflections $I > 3\sigma(I)$	2242	1433
R_F	0.1344	0.0628

TABLE 3. Position parameters and equivalent temperature parameters for $Mo_3Se_7(dtc)_4$

| Atom	x	y	z	U
Mo(1)	0.2078(3)	0.4157(2)	0.1075(3)	0.063(3)[a]
Mo(2)	0.1472(3)	0.3573(2)	0.2711(3)	0.062(3)[a]
Mo(3)	0.2967(3)	0.3114(2)	0.2265(3)	0.072(4)[a]
Se(1)	0.0612(4)	0.4440(3)	0.1418(4)	0.078(5)[a]
Se(2)	0.1715(4)	0.4905(3)	0.2533(4)	0.082(5)[a]
Se(3)	0.2295(4)	0.2501(3)	0.3686(4)	0.083(5)[a]
Se(4)	0.2778(4)	0.3642(3)	0.3969(4)	0.089(5)[a]
Se(5)	0.3398(3)	0.3591(3)	0.0587(4)	0.087(3)[a]
Se(6)	0.3509(4)	0.4355(3)	0.1973(5)	0.091(5)[a]
Se(7)	0.1635(4)	0.2877(3)	0.1161(4)	0.064(4)[a]
S(11)	0.147(1)	0.4061(7)	−0.0745(8)	0.08(1)[a]
S(12)	0.224(1)	0.5238(7)	0.016(1)	0.10(1)[a]
S(21)	0.026(1)	0.2799(8)	0.271(1)	0.08(1)[a]
S(22)	0.075(1)	0.3380(8)	0.418(1)	0.09(1)[a]
S(31)	0.326(1)	0.187(1)	0.172(1)	0.10(1)[a]
S(32)	0.436(1)	0.272(1)	0.309(1)	0.13(2)[a]
S(41)	0.323(1)	0.520(1)	0.384(1)	0.11(1)[a]
S(42)	0.261(2)	0.649(1)	0.260(2)	0.21(3)[a]
C(1)	0.177(3)	0.491(3)	−0.091(4)	0.09(5)[a]
C(2)	0.008(3)	0.320(3)	0.385(3)	0.07(4)[a]
C(3)	0.401(5)	0.190(4)	0.238(5)	0.13(7)[a]
C(4)	0.324(5)	0.601(5)	0.372(6)	0.15(3)
N(1)	0.156(3)	0.526(2)	−0.182(4)	0.09(4)[a]
N(2)	−0.049(3)	0.294(2)	0.433(3)	0.08(3)[a]
N(3)	0.465(3)	0.131(6)	0.262(5)	0.24(8)[a]
N(4)	0.373(7)	0.650(4)	0.447(9)	0.3(1)[a]
C(11)	0.106(4)	0.489(3)	−0.266(4)	0.13(2)
C(13)	0.168(4)	0.605(3)	−0.186(5)	0.13(2)
C(21)	−0.050(4)	0.326(3)	0.534(3)	0.11(2)
C(23)	−0.105(3)	0.35(3)	0.395(4)	0.10(2)
C(31)	0.431(9)	0.059(5)	0.222(9)	0.39(7)
C(33)	0.549(4)	0.139(4)	0.314(6)	0.19(3)
C(41)	0.378(7)	0.725(5)	0.418(7)	0.22(4)
C(43)	0.46(1)	0.63(1)	0.53(1)	0.7(1)
C(12)	0.169(4)	0.45(3)	−0.318(4)	0.13(2)
C(14)	0.49(4)	0.614(4)	−0.23(5)	0.16(3)
C(22)	−0.111(4)	0.388(3)	0.527(5)	0.14(3)
C(24)	−0.069(4)	0.163(3)	0.432(5)	0.14(3)
C(32)	0.464(7)	0.057(6)	0.114(8)	0.46(5)
C(34)	0.539(8)	0.136(7)	0.431(7)	0.56(6)
C(42)	0.306(8)	0.752(7)	0.46(1)	0.33(7)
C(44)	0.39(1)	0.604(8)	0.58(1)	0.55(8)

[a] $U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$.

more than 20 years ago upon heating the lower halogenides of molybdenum and selenium [19]

$$MoX_n + Se \longrightarrow Mo_3Se_7X_4 \qquad (1)$$
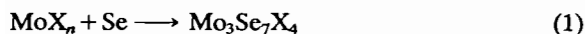
$(X = Cl, Br; n = 2, 3)$

In a previous work we obtained $M_3Se_7Br_4$ (M = Mo, W) from the elements (eqn. (2)) [15]

$$3M + 7Se + 2Br_2 \longrightarrow M_3Se_7Br_4 \qquad (2)$$
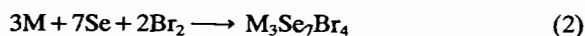
No X-ray structural determination of the $M_3Se_7X_4$ structure has been made. The same stoichiometry,

common methods of synthesis, regular changes in the vibrational spectra and a comparison of the chemical properties of $M_3Y_7X_4$ (M = Mo, W; Y = S, Se; X = Cl, Br) suggest that they all have a polymeric structure $M_3(\mu_3\text{-}Y)(\mu_2\text{-}Y_2)_3X_2X_{4/2}$, the same as the structurally characterized $Mo_3S_7Cl_4$ [20] and $W_3S_7Br_4$ [8].

Earlier the polymeric $M_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3X_2X_{4/2}$ were shown to be convenient starting materials for the preparation of different complexes containing $M_3(\mu_3\text{-}S)(\mu_2\text{-}SSe)_3^{4+}$ and $M_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3^{4+}$ [5, 6, 11, 12]. In the present study, as a continuation of our results already obtained [15], it is shown that the polymeric $M_3Se_7X_4$ are convenient starting materials for the synthesis of complexes containing $M_3(\mu_3\text{-}Se)(\mu_2\text{-}Se_2)_3^{4+}$ and $M_3(\mu_3\text{-}Se)(\mu_2\text{-}Se)_3^{4+}$ fragments.

Synthesis and properties of the diethylthiocarbamate complexes $M_3Se_7(dtc)_3^+$ (M = Mo, W)

The polymeric $M_3Se_7X_4$ (X = Cl, Br) complexes do not interact with $NaS_2CNEt_2 \cdot 3H_2O$ upon boiling in acetonitrile or benzonitrile. Heating of these complexes in a melt of PPh_4X results in the destruction of the polymer and in the case of M = Mo, X = Cl this afforded the $(PPh_4)_2Mo_3Se_7Cl_6$ (1) salt in analytically pure form (eqn. (3))

$$Mo_3Se_7Cl_4 + 2PPh_4Cl \longrightarrow (PPh_4)_2Mo_3Se_7Cl_6 \qquad (3)$$
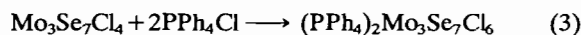
The vibrational (IR and Raman) spectra of complex 1 coincide to within 5 cm^{-1} with those of the starting $Mo_3Se_7Cl_4$. The tetraphenylphosphonium salts of tungsten and selenobromide complexes of molybdenum turned to be rather unstable and could not be obtained in analytically pure form. Heating of all these tetraphenylphosphonium salts with Nadtc·3H₂O in acetonitrile produces complexes of composition $M_3Se_7(dtc)_4$ (M = Mo, W) (eqn. (4)).

$$(PPh_4)_2Mo_3Se_7X_6 + 4Nadtc \longrightarrow$$
$$M_3Se_7(dtc)_4 + 4NaX + 2PPh_4X \qquad (4)$$
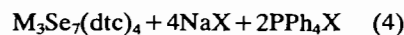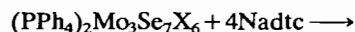
M = Mo(3), W(2)

The structure of these complexes was established by X-ray analysis and is discussed below. The vibrational spectra of these compounds completely coincide.

Complexes 2 and 3 in nitromethane do not dissociate and 10^{-4} M solutions do not conduct an electrical current. In the two-phase system CH₂Cl₂/H₂O the dtc$^-$ anion is replaced by PF$_6^-$ to form salt 4 (eqn. (5)).
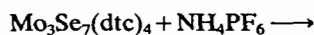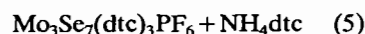
$$Mo_3Se_7(dtc)_4 + NH_4PF_6 \longrightarrow$$
3
$$Mo_3Se_7(dtc)_3PF_6 + NH_4dtc \qquad (5)$$
4

Description of the structures

The clusters $(M_3Se_7dtc_3)^+dtc^-$ (M = Mo (3), W (2)) are isostructural. The structure of the ion pair in 3 is shown in Fig. 1, the packing of the ions in the crystal lattice is shown in Fig. 2. The bond lengths and angles for 3 are given in Table 4 and for 2 in Table 5.

The cluster metal core represents a practically equilateral triangle M_3 with an average Mo–Mo bond length of 2.778(7) Å and average W–W bond length of 2.764(8) Å which somewhat exceeds the values in the metals (2.73 Å for Mo and 2.74 Å for W [21]). The (μ_2-Se$_2$) ligands coordinate the M–M bonds in such a way that deviations of Se(1), Se(3), Se(5) from the M_3 plane do not exceed 0.3 Å. Three other selenium atoms of this ligand occupy axial positions deviating from the M_3 plane on the side opposite to that occupied by the (μ_3-Se) ligand, the latter being symmetrically coordinated at the metals at a distance of 2.502(7) Å for Mo and 2.500(8) Å for W (deviations of the cluster cation atoms from the metal core plane are listed in Table 6). The W–Se distances for the axial Se atoms (average values are 2.532(7) Å in 3 and 2.534(9) Å in 2) are substantially smaller than for the equatorial ones (average values 2.617(7) Å in 3 and 2.613(9) Å in 2; the difference of 0.08 Å being an order of magnitude greater than the r.m.s. deviations in bond lengths). The average Se–Se bond lengths of 2.312(8) Å in 3 and 2.31(1)

Å in 2 are somewhat smaller than in the elemental selenium (2.37 Å [22]) and considerably greater than in the Se$_2$ molecule in the gas phase (2.19 Å [22]). The dtc ligands are terminally coordinated to the M atoms to form practically planar four-membered chelate cycles perpendicular to the M_3 plane.

The S atoms occupy semi-axial non-symmetrical positions relative to the M_3 plane (the average M–M–S angles are 126.5(4)° in 3 and 126.6(5)° in 2 for the S atoms occupying the side with the (μ_3-Se) ligand and 143.0(4)° in 3 and 142.8(8)° in 2 for S on the opposite side; deviations of sulfur atoms from this plane are ~1.8 and 1.0 Å, respectively). The bond lengths in the MS_2CNEt_2 fragment have normal values (according to CCSDB [23] the average bond lengths are S–C = 1.72(4), C(CS$_2$)–N = 1.33(4), C(Et)–N = 1.50(5) Å from 193 structures; Mo–S = 2.50(3) Å from 13 structures; W–S = 2.52(3) Å from 8 structures). The dtc$^-$ counterion is situated in the crystal in such a way that one of the S atoms lies at a rather short distance (2.89(2)–3.09(2) Å in 3 and 2.88(2)–3.04(2) Å in 2) from the axial Se atoms of the (μ_2-Se$_2$) ligands (the sum of van der Waals radii of Se and S is 3.85 Å [24]). In 3 there is a strong shortening of the S–C bond in dtc$^-$ (to 1.53(9) Å) for the S(41) atom which is in contact with Se relative to the 'free' S(42) (1.90(8) Å). The corresponding distances in the W compound are practically equal.
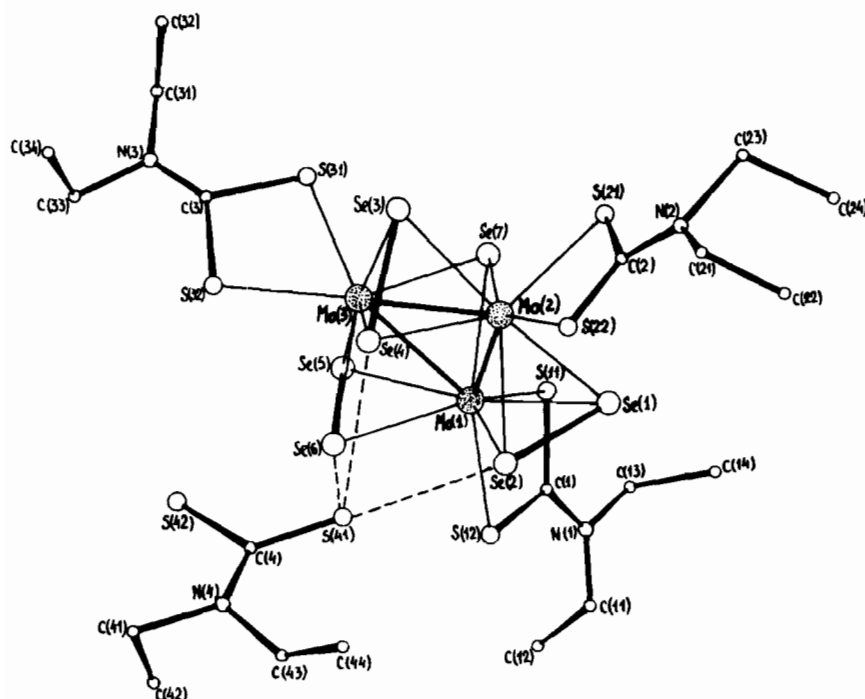

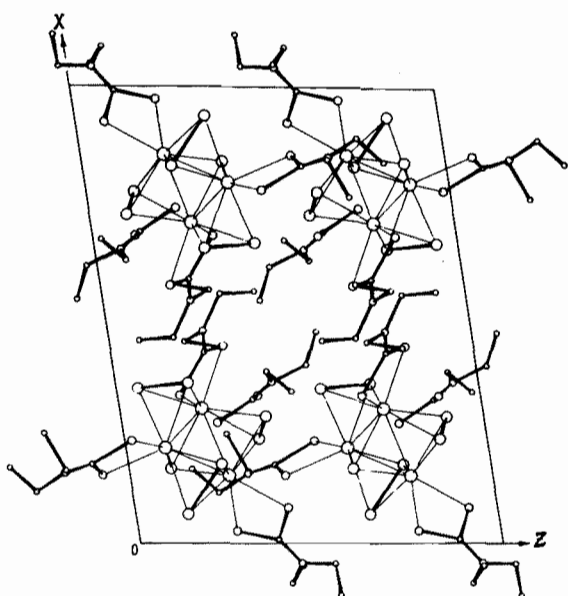Fig. 1. Structure of Mo$_3$Se$_7$(dtc)$_4$.

Fig. 2. Unit cell of $Mo_3Se_7(dtc)_4$.

A cluster anion of composition $Mo_{12}S_{56}^{12-}$ has been described in the literature [14] in which four $Mo_3(\mu_3\text{-Se})(\mu_2\text{-Se}_2)_3$ may be singled out with a geometry close to that observed in the **2** and **3** structures.

On the whole, the $M_3Se_7S_6$ fragment can be represented by a distorted octahedron of the M atoms and axial $Se(\mu_2\text{-Se}_2)$ ligands with edges of length ≈ 2.8, 2.5 and 3.3 Å for M–M, M–Se$_{ax}$, Se$_{ax}$...Se$_{ax}$, respectively. With respect to the M_3Se_3 octahedron the equatorial Se atoms of the $(\mu_2\text{-Se}_2)$ ligands and the $(\mu_3\text{-Se})$ ligand are acting as caps above the M_2Se and M_3 faces, respectively. Lying above the Se_2M and Se_3 faces of the octahedron are the S atoms of the dtc ligands that are on the opposite side of the $(\mu_3\text{-Se})$ ligand and the S atom of the counterion. The remaining S atoms of the chelate dtc ligands occupy terminal positions with respect to the M_3Se_3 octahedron, the M–S bond lengths being similar to each other (2.50(2) Å in **3** and 2.50(1) Å in **2**). An analogous treatment can also be applied to other known compounds containing fragments of the general formula $M_3(\mu_3\text{-X})(\mu_2\text{-X}_{ax}Y_{equ})_3L_6$ where M = Mo, W; X, Y = S, Se; L is a terminal ligand containing either N or S donor atoms, or a halogen. For these compounds the octahedral face formed by the X_{ax} atoms has been found, by X-ray structural analysis [6, 11, 25], to be capped by a symmetrically lying atom X' of the counterion, as in our case, or even by an atom from another ion of the same charge (in this case the distance $X_{ax}...X'$ might be somewhat larger, 3.3–3.4 Å, which is easily explained by Coulomb repulsion). Occurrence of such a contact could

TABLE 4. Selected lengths and selected angles in $W_3Se_7(dtc)_4$

Bond lengths (Å)

W(1)–W(2)	2.770(8)	W(1)–W(3)	2.763(8)
W(1)–Se(1)	2.639(9)	W(1)–Se(2)	2.531(9)
W(1)–Se(5)	2.606(9)	W(1)–Se(6)	2.525(9)
W(1)–Se(7)	2.495(8)	W(1)–S(11)	2.48(2)
W(1)–S(12)	2.53(2)	W(2)–W(3)	2.757(7)
W(2)–Se(1)	2.636(9)	W(2)–Se(2)	2.540(9)
W(2)–Se(3)	2.586(9)	W(2)–Se(4)	2.53(1)
W(2)–Se(7)	2.494(8)	W(2)–S(21)	2.48(2)
W(2)–S(22)	2.52(2)	W(3)–Se(3)	2.612(9)
W(3)–Se(4)	2.531(9)	W(3)–Se(5)	2.60(1)
W(3)–Se(6)	2.542(9)	W(3)–Se(7)	2.512(8)
W(3)–S(31)	2.50(2)	W(3)–S(32)	2.51(2)
Se(1)–Se(2)	2.28(1)	Se(3)–Se(4)	2.32(1)
Se(5)–Se(6)	2.33(1)		

Bond angles (°)

W(2)–W(1)–W(3)	59.8(2)	W(2)–W(1)–Se(1)	58.3(2)
W(2)–W(1)–Se(2)	57.0(2)	W(2)–W(1)–Se(5)	117.2(3)
W(2)–W(1)–Se(6)	96.8(3)	W(2)–W(1)–Se(7)	56.3(2)
W(2)–W(1)–S(11)	125.5(4)	W(2)–W(1)–S(12)	141.9(5)
W(3)–W(1)–Se(1)	117.8(3)	W(3)–W(1)–Se(2)	96.8(3)
W(3)–W(1)–Se(5)	57.8(2)	W(3)–W(1)–Se(6)	57.2(2)
W(3)–W(1)–Se(7)	56.8(2)	W(3)–W(1)–S(11)	128.7(4)
W(3)–W(1)–S(12)	143.3(4)	Se(1)–W(1)–Se(2)	52.3(2)
Se(1)–W(1)–Se(5)	168.1(3)	Se(1)–W(1)–Se(6)	135.2(3)
Se(1)–W(1)–Se(7)	84.6(3)	Se(1)–W(1)–S(11)	85.4(4)
Se(1)–W(1)–S(12)	92.8(4)	Se(2)–W(1)–Se(5)	136.6(3)
Se(2)–W(1)–Se(6)	83.1(3)	Se(2)–W(1)–Se(7)	112.5(3)
Se(2)–W(1)–S(11)	130.3(4)	Se(2)–W(1)–S(12)	86.1(4)
Se(5)–W(1)–Se(6)	53.9(2)	Se(5)–W(1)–Se(7)	84.0(3)
Se(5)–W(1)–S(11)	89.8(4)	Se(5)–W(1)–S(12)	95.7(4)
Se(6)–W(1)–Se(7)	113.4(3)	Se(6)–W(1)–S(11)	135.1(5)
Se(6)–W(1)–S(12)	87.1(5)	Se(7)–W(1)–S(11)	83.6(4)
Se(7)–W(1)–S(12)	153.0(5)	S(11)–W(1)–S(12)	69.4(6)
W(1)–W(2)–W(3)	60.0(2)	W(1)–W(2)–Se(1)	58.4(2)
W(1)–W(2)–Se(2)	56.7(2)	W(1)–W(2)–Se(3)	118.0(3)
W(1)–W(2)–Se(4)	96.6(3)	W(1)–W(2)–Se(7)	56.3(2)
W(1)–W(2)–S(21)	124.7(5)	W(1)–W(2)–S(22)	140.9(6)
W(3)–W(2)–Se(1)	118.1(3)	W(3)–W(2)–Se(2)	96.7(3)
W(3)–W(2)–Se(3)	58.4(2)	W(3)–W(2)–Se(4)	57.0(2)
W(3)–W(2)–Se(7)	56.9(2)	W(3)–W(2)–S(21)	127.0(5)
W(3)–W(2)–S(22)	146.2(6)	Se(1)–W(2)–Se(2)	52.2(3)
Se(1)–W(2)–Se(3)	168.7(3)	Se(1)–W(2)–Se(4)	135.1(3)
Se(1)–W(2)–Se(7)	84.7(3)	Se(1)–W(2)–S(21)	85.9(5)
Se(1)–W(2)–S(22)	90.3(6)	Se(2)–W(2)–Se(3)	136.7(3)
Se(2)–W(2)–Se(4)	83.0(3)	Se(2)–W(2)–Se(7)	112.3(3)
Se(2)–W(2)–S(21)	131.6(5)	Se(2)–W(2)–S(22)	86.3(6)
Se(3)–W(2)–Se(4)	53.9(4)	Se(3)–W(2)–Se(7)	84.8(3)
Se(3)–W(2)–S(21)	88.6(5)	Se(3)–W(2)–S(22)	97.0(6)
Se(4)–W(2)–Se(7)	113.3(3)	Se(4)–W(2)–S(21)	135.3(6)
Se(4)–W(2)–S(22)	90.3(6)	Se(7)–W(2)–S(21)	82.0(5)
Se(7)–W(2)–S(22)	150.9(6)	S(21)–W(2)–S(22)	69.1(7)
W(1)–W(3)–W(2)	60.2(2)	W(1)–W(3)–Se(3)	117.4(3)
W(1)–W(3)–Se(4)	96.8(3)	W(1)–W(3)–Se(5)	58.1(2)
W(1)–W(3)–Se(6)	56.7(2)	W(1)–W(3)–Se(7)	56.2(2)
W(1)–W(3)–S(31)	127.0(5)	W(1)–W(3)–S(32)	142.4(5)
W(2)–W(3)–Se(3)	57.5(2)	W(2)–W(3)–Se(4)	57.1(2)
W(2)–W(3)–Se(5)	117.9(3)	W(2)–W(3)–Se(6)	96.7(3)
W(2)–W(3)–Se(7)	56.3(2)	W(2)–W(3)–S(31)	126.7(5)

(continued)

TABLE 4. (*continued*)

W(2)–W(3)–S(32)	142.3(5)	Se(3)–W(3)–Se(4)	53.6(3)
Se(3)–W(3)–Se(5)	166.9(3)	Se(3)–W(3)–Se(6)	136.2(3)
Se(3)–W(3)–Se(7)	83.9(3)	Se(3)–W(3)–S(31)	87.3(5)
Se(3)–W(3)–S(32)	94.6(5)	Se(4)–W(3)–Se(5)	136.5(3)
Se(4)–W(3)–Se(6)	82.9(3)	Se(4)–W(3)–Se(7)	112.8(3)
Se(4)–W(3)–S(31)	132.8(5)	Se(4)–W(3)–S(32)	86.5(5)
Se(5)–W(3)–Se(6)	53.8(3)	Se(5)–W(3)–Se(7)	83.8(3)
Se(5)–W(3)–S(31)	87.1(5)	Se(5)–W(3)–S(32)	94.5(5)
Se(6)–W(3)–S(32)	86.9(5)	Se(7)–W(3)–S(31)	83.9(5)
Se(7)–W(3)–S(32)	153.7(5)	S(31)–W(3)–S(32)	69.8(6)
W(1)–Se(1)–W(2)	63.4(2)	W(1)–Se(1)–W(2)	61.4(3)
W(2)–Se(1)–Se(2)	61.7(3)	W(1)–Se(2)–W(2)	66.2(2)
W(1)–Se(2)–Se(1)	66.3(3)	W(2)–Se(2)–Se(1)	66.1(3)
W(2)–Se(3)–W(3)	64.1(2)	W(2)–Se(3)–Se(4)	61.9(3)
W(3)–Se(3)–Se(4)	61.4(3)	W(2)–Se(4)–W(3)	66.0(2)
W(2)–Se(4)–Se(3)	64.2(3)	W(3)–Se(4)–Se(3)	65.0(3)
W(1)–Se(5)–W(3)	64.1(2)	W(1)–Se(5)–Se(6)	61.3(3)
W(3)–Se(5)–Se(6)	61.9(3)	W(1)–Se(6)–W(3)	66.1(2)
W(1)–Se(6)–Se(5)	64.8(3)	W(3)–Se(6)–Se(5)	64.4(3)
W(1)–Se(7)–W(2)	67.4(2)	W(1)–Se(7)–W(3)	67.0(2)
W(2)–Se(7)–W(3)	66.8(2)		

be explained by the interaction of the unshared pairs of the X' atom with σ*MO of the Se_2 fragment. In an indirect way, this is confirmed by the linearity of the fragment X_{equ}–X_{ax}...X' (166.4(6)–169.2(6) for **2** and 165.3(5)–168.2(5) for **3**).

Synthesis and properties of 1,10-phenanthroline complexes $M_3Se_7(phen)_3^{4+}$ (M=Mo, W)

Heating of $M_3Se_7X_4$ in a melt of 1,10-penanthroline produces salts of composition $[M_3Se_7(phen)_3]X_4$ (eqn. (6))

$$M_3Se_7X_4 + 3phen \longrightarrow M_3Se_7(phen)_3X_4 \qquad (6)$$

6: X = Cl, M = Mo; **9**: X = Cl, M = W; **5**: X = Br, M = Mo.

Complexes of molybdenum were obtained in good yields. Those of the tungsten complexes are not so high and poorly reproducible. Recrystallization of bromide salts from concentrated HCl affords the corresponding chloride salts in quantitative yields. Analogously, recrystallization of chloride salts from concentrated HBr results in quantitative yield of bromide salts. Salts **7** and **8** were obtained on adding zinc oxide to solutions of complexes **5** and **6** in the corresponding HX acids. Noteworthy is the stability of the $M_3Se_7(phen)_3^{4+}$ complexes in concentrated HX acids — there is no protonation of the 1,10-phenanthroline ligands or of the selenium atoms of the μ_2-Se_2 ligands. A high stability of M_2S_2 and M_2SSe tetrahedral fragments has been observed previously in the triangular complexes $M_3S_7X_6^{2-}$ and $M_3S_4Se_3X_6^{2-}$ (M=Mo, W) [5, 11].

TABLE 5. Bond lengths and selected angles in $Mo_3Se_7(dtc)_4$

Bond lengths (Å)

Mo(1)–Mo(2)	2.767(6)	Mo(1)–Mo(3)	2.783(6)
Mo(1)–Se(1)	2.607(8)	Mo(1)–Se(2)	2.541(7)
Mo(1)–Se(5)	2.612(8)	Mo(1)–Se(6)	2.520(8)
Mo(1)–Se(7)	2.503(7)	Mo(1)–S(11)	2.49(1)
Mo(1)–S(12)	2.53(1)	Mo(2)–Mo(3)	2.785(7)
Mo(2)–Se(1)	2.616(7)	Mo(2)–Se(2)	2.528(7)
Mo(2)–Se(3)	2.644(7)	Mo(2)–Se(4)	2.531(7)
Mo(2)–Se(7)	2.492(6)	Mo(2)–S(21)	2.49(2)
Mo(2)–S(22)	2.52(2)	Mo(3)–Se(3)	2.611(8)
Mo(3)–Se(4)	2.541(7)	Mo(3)–Se(5)	2.612(8)
Mo(3)–Se(6)	2.533(8)	Mo(3)–Se(7)	2.500(7)
Mo(3)–S(31)	2.49(2)	Mo(3)–S(32)	2.51(2)
Se(1)–Se(2)	2.339(8)	Se(3)–Se(4)	2.282(9)
Se(5)–Se(6)	2.315(8)	S(11)–C(1)	1.68(6)
S(12)–C(1)	1.71(5)	S(21)–C(2)	1.75(5)
S(22)–C(2)	1.70(5)	S(31)–C(3)	1.41(8)
S(32)–C(3)	1.85(8)	S(41)–C(4)	1.53(9)
S(42)–C(4)	1.90(8)	C(1)–N(1)	1.38(7)
C(2)–N(2)	1.33(7)	C(3)–N(3)	1.52(9)
C(4)–N(4)	1.49(9)	N(1)–C(11)	1.47(7)
N(1)–C(13)	1.47(7)	N(2)–C(21)	1.48(6)
N(2)–C(23)	1.48(7)	N(3)–C(31)	1.53(9)
N(3)–C(33)	1.47(8)	N(4)–C(41)	1.46(9)
N(4)–C(43)	1.74(9)	C(11)–C(12)	1.52(9)
C(13)–C(14)	1.51(9)	C(21)–C(22)	1.52(9)
C(23)–C(24)	1.52(8)	C(31)–C(32)	1.62(9)
C(33)–C(34)	1.59(9)	C(41)–C(53)	1.53(9)
C(43)–C(44)	1.54(9)		

Bond angles (°)

Mo(2)–Mo(1)–Mo(3)	60.2(2)	Mo(2)–Mo(1)–Se(1)	58.2(2)
Mo(2)–Mo(1)–Se(2)	56.7(2)	Mo(2)–Mo(1)–Se(5)	117.7(2)
Mo(2)–Mo(1)–Se(6)	96.8(2)	Mo(2)–Mo(1)–Se(7)	56.2(2)
Mo(2)–Mo(1)–S(11)	126.7(4)	Mo(2)–Mo(1)–S(12)	143.0(4)
Mo(3)–Mo(1)–Se(1)	118.0(2)	Mo(3)–Mo(1)–Se(2)	96.6(2)
Mo(3)–Mo(1)–Se(5)	57.8(2)	Mo(3)–Mo(1)–Se(6)	56.8(2)
Mo(3)–Mo(1)–Se(7)	56.2(2)	Mo(3)–Mo(1)–S(11)	127.3(4)
Mo(3)–Mo(1)–S(12)	141.8(5)	Se(1)–Mo(1)–Se(2)	54.0(2)
Se(1)–Mo(1)–Se(5)	166.8(3)	Se(1)–Mo(1)–Se(6)	136.8(2)
Se(1)–Mo(1)–Se(7)	83.9(2)	Se(1)–Mo(1)–S(11)	86.3(4)
Se(1)–Mo(1)–S(12)	95.0(5)	Se(2)–Mo(1)–Se(5)	136.3(2)
Se(2)–Mo(1)–Se(6)	83.0(2)	Se(2)–Mo(1)–Se(7)	112.3(2)
Se(2)–Mo(1)–S(11)	132.6(4)	Se(2)–Mo(1)–S(12)	87.4(4)
Se(5)–Mo(1)–Se(6)	53.6(2)	Se(5)–Mo(1)–Se(7)	83.8(2)
Se(5)–Mo(1)–S(11)	87.6(4)	Se(5)–Mo(1)–S(12)	93.8(5)
Se(6)–Mo(1)–Se(7)	112.4(2)	Se(6)–Mo(1)–S(11)	133.2(4)
Se(6)–Mo(1)–S(12)	86.3(4)	Se(7)–Mo(1)–S(11)	84.1(4)
Se(7)–Mo(1)–S(12)	153.7(4)	S(11)–Mo(1)–S(12)	69.5(5)
Mo(1)–Mo(2)–Mo(3)	60.2(2)	Mo(1)–Mo(2)–Se(1)	57.9(2)
Mo(1)–Mo(2)–Se(2)	57.1(2)	Mo(1)–Mo(2)–Se(3)	117.3(2)
Mo(1)–Mo(2)–Se(4)	96.9(2)	Mo(1)–Mo(2)–Se(7)	56.5(2)
Mo(1)–Mo(2)–S(21)	128.7(3)	Mo(1)–Mo(2)–S(22)	143.3(4)
Mo(3)–Mo(2)–Se(1)	117.6(2)	Mo(3)–Mo(2)–Se(2)	96.9(2)
Mo(3)–Mo(2)–Se(3)	57.4(2)	Mo(3)–Mo(2)–Se(4)	56.9(2)
Mo(3)–Mo(2)–Se(7)	56.2(2)	Mo(3)–Mo(2)–S(21)	125.3(4)
Mo(3)–Mo(2)–S(22)	142.1(4)	Se(1)–Mo(2)–Se(2)	54.0(2)
Se(1)–Mo(2)–Se(3)	167.6(2)	Se(1)–Mo(2)–Se(4)	136.8(3)
Se(1)–Mo(2)–Se(7)	83.9(2)	Se(1)–Mo(2)–S(21)	89.8(4)
Se(1)–Mo(2)–S(22)	95.3(4)	Se(2)–Mo(2)–Se(3)	135.1(3)
Se(2)–Mo(2)–Se(4)	83.1(2)	Se(2)–Mo(2)–Se(7)	113.1(2)
Se(2)–Mo(2)–S(21)	135.3(4)	Se(2)–Mo(2)–S(22)	87.3(4)
Se(3)–Mo(2)–Se(4)	52.3(2)	Se(3)–Mo(2)–Se(7)	84.2(2)
Se(3)–Mo(2)–S(21)	85.5(4)	Se(3)–Mo(2)–S(22)	93.6(4)

(*continued*)

TABLE 5. *(continued)*

Se(4)–Mo(2)–Se(7)	112.4(3)	Se(4)–Mo(2)–S(21)	130.1(4)
Se(4)–Mo(2)–S(22)	86.5(4)	Se(7)–Mo(2)–S(21)	83.9(4)
Se(7)–Mo(2)–S(22)	153.0(5)	S(21)–Mo(2)–S(22)	69.1(5)
Mo(1)–Mo(3)–Mo(2)	59.6(2)	Mo(1)–Mo(3)–Se(3)	117.9(3)
Mo(1)–Mo(3)–Se(4)	96.3(2)	Mo(1)–Mo(3)–Se(5)	57.8(2)
Mo(1)–Mo(3)–Se(6)	56.3(2)	Mo(1)–Mo(3)–Se(7)	56.3(2)
Mo(1)–Mo(3)–S(31)	126.2(4)	Mo(1)–Mo(3)–S(32)	145.3(5)
Mo(2)–Mo(3)–Se(3)	58.6(2)	Mo(2)–Mo(3)–Se(4)	56.5(2)
Mo(2)–Mo(3)–Se(5)	117.1(2)	Mo(2)–Mo(3)–Se(6)	96.1(2)
Mo(2)–Mo(3)–Se(7)	56.0(2)	Mo(2)–Mo(3)–S(31)	124.8(5)
Mo(2)–Mo(3)–S(32)	142.3(4)	Se(3)–Mo(3)–Se(4)	52.6(2)
Se(3)–Mo(3)–Se(5)	168.0(3)	Se(3)–Mo(3)–Se(6)	135.6(3)
Se(3)–Mo(3)–Se(7)	84.7(2)	Se(3)–Mo(3)–S(31)	86.2(5)
Se(3)–Mo(3)–S(32)	91.7(5)	Se(4)–Mo(3)–Se(5)	136.4(3)
Se(4)–Mo(3)–Se(6)	83.3(2)	Se(4)–Mo(3)–Se(7)	111.8(3)
Se(4)–Mo(3)–S(31)	132.7(4)	Se(4)–Mo(3)–S(32)	87.6(5)
Se(5)–Mo(3)–Se(6)	53.5(2)	Se(5)–Mo(3)–Se(7)	83.9(2)
Se(5)–Mo(3)–S(31)	88.3(5)	Se(5)–Mo(3)–S(32)	96.5(5)
Se(6)–Mo(3)–Se(7)	112.0(2)	Se(6)–Mo(3)–S(31)	135.1(5)
Se(6)–Mo(3)–S(32)	90.2(5)	Se(7)–Mo(3)–S(31)	82.0(5)
Se(7)–Mo(3)–S(32)	151.5(5)	S(31)–Mo(3)–S(32)	69.6(6)
Mo(1)–Se(1)–Mo(2)	64.0(2)	Mo(1)–Se(1)–Se(2)	61.5(2)
Mo(2)–Se(1)–Se(2)	61.1(2)	Mo(1)–Se(2)–Mo(2)	66.2(2)
Mo(1)–Se(2)–Se(1)	64.4(2)	Mo(2)–Se(2)–Se(1)	64.9(2)
Mo(2)–Se(3)–Mo(3)	64.0(2)	Mo(2)–Se(3)–Se(4)	61.3(2)
Mo(3)–Se(3)–Se(4)	62.2(2)	Mo(2)–Se(4)–Mo(3)	66.6(2)
Mo(2)–Se(4)–Se(3)	66.4(2)	Mo(3)–Se(4)–Se(3)	65.3(2)
Mo(1)–Se(5)–Mo(3)	64.4(2)	Mo(1)–Se(5)–Se(6)	61.1(2)
Mo(3)–Se(5)–Se(6)	61.5(2)	Mo(1)–Se(6)–Mo(3)	66.8(2)
Mo(1)–Se(6)–Se(5)	65.3(2)	Mo(3)–Se(6)–Se(5)	65.0(2)
Mo(1)–Se(7)–Mo(2)	67.3(2)	Mo(1)–Se(7)–Mo(3)	67.6(2)
Mo(2)–Se(7)–Mo(3)	67.8(2)		

TABLE 6. Deviation of the $W_3Se_7(dtc)_4$ **(2)** and $Mo_3Se_7(dtc)_4$ **(3)** atoms from the plane of the three M atoms

| Atom	Deviation (Å)	
	2	**3**
Se(1)	−0.217	−0.289
Se(2)	1.786	1.795
Se(3)	−0.269	−0.230
Se(4)	1.797	1.784
Se(5)	−0.286	−0.279
Se(6)	1.791	1.778
Se(7)	−1.926	−1.915
S(11)	−1.777	−1.786
S(12)	1.012	1.014
S(21)	−1.827	−1.782
S(22)	0.929	0.992
S(31)	−1.802	−1.852
S(32)	1.009	0.920
S(41)	4.082	4.041
S(42)	4.510	4.506

The vibrational spectra of the phenanthroline complexes 5–9 coincide with each other. As an example, Fig. 3 shows IR and Raman spectra for the complex $[W_3Se_7(phen)_3]Cl_4$. The frequencies in the vibrational

spectra of $[Mo_3{}^{76}Se_7(phen)_3]Br_4$ and the shifts of these frequencies in $[Mo_3{}^{82}Se_7(phen)_3]Br_4$ are given in Table 7. A small shift of most of the bands in the vibrational spectra of these isotopomeric compounds indicates a strong mixing of the vibrations involving the Se atoms with other vibrations. This makes the qualitative interpretation of the spectra of the studies complexes difficult. At the present time we are performing a calculation of the normal vibrations which will be reported elsewhere.

The methods for the synthesis of triangular seleno complexes from elements proposed in this study allow an easy preparation of isotopomeric compounds which are important for the description of vibrational spectra and for the interpretation of NMR spectra.

Synthesis and properties of $Mo_3Se_4{}^{4+}$ complexes

It is well known that the complexes $M_3S_7{}^{4+}$ interact with phosphines with the elimination of the equatorial sulfur atoms of unsymmetrically coordinated μ_2-S_2 ligands to form sulfides of phosphines and the $M_3S_4{}^{4+}$ complexes [5, 8, 25]. Analoguously, $M_3S_4Se_3{}^{4+}$ complexes interact with PPh_3 to form Se=PPh_3 and $M_3S_4{}^{4+}$ complexes [11, 12]. We have found that such reactions easily take place also for the $Mo_3Se_7{}^{4+}$ complexes containing an unsymmetrically coordinated ligand μ_2-Se_2. Thus $Mo_3Se_7(dtc)_4$ **(2)** easily interacts with PPh_3 in methylene chloride. The reaction produced complex **10** and Se=PPh_3 (eqn. (7)).

$$Mo_3Se_7(dtc)_4 + 4PPh_3 \longrightarrow$$

$$Mo_3Se_4(dtc)_4PPh_3 + 3Se=PPh_3 \quad (7)$$
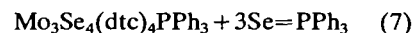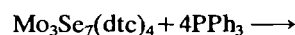
The IR spectrum of complex **10** shows bands of the dtc and PPh_3 ligands. In the $^{31}P\{^1H\}$ NMR spectrum there is a singlet of the P atoms of the PPh_3 ligand. We propose the following structure for complex **10** analogous to those of a wide range of structurally characterized $Mo_3S_4(dtp)_4L$ and $Mo_3S_4(dtc)_4L$ complexes [26] (dtp is diethyldithiophosphate anion).

$$S\!\!\frown\!\!S = S_2CN(C_2H_5)_2$$
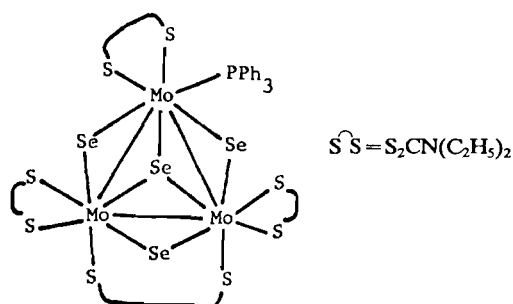
The polymeric $Mo_3Se_7Cl_4$ interacts with dppe upon boiling in acetonitrile (eqn. (8)).
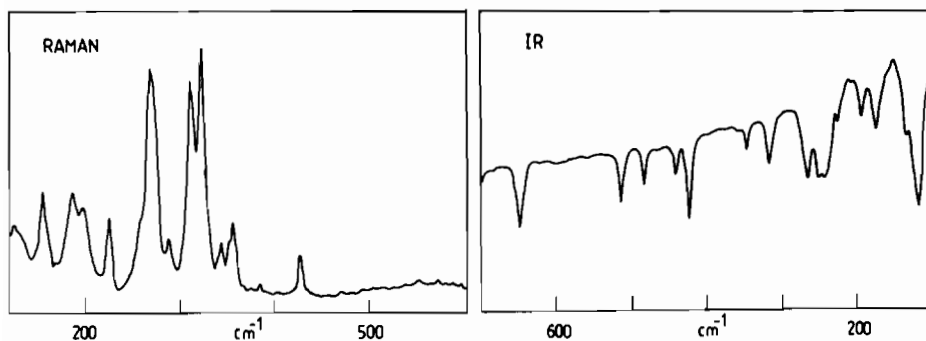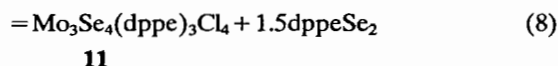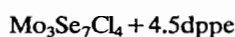
Fig. 3. IR and Raman spectra for the complex $[W_3Se_7(phen)_3]Cl_4$.

TABLE 7. Experimental vibrational frequencies in the Raman and IR spectra of the $[Mo_3{}^{76}Se_7(phen)_3]Br_4$ complex and their shifts for $[Mo_3{}^{82}Se_7(phen)_3]Br_4$ complex

ν (cm^{-1})	$\Delta\nu$ (cm^{-1})
505 IR	0
492 IR	0
441 IR	0
427 IR, Raman	0
357 Raman	3
347 IR, Raman	3
322 Raman	1
310 IR, Raman	2
287 Raman	5
268 IR, Raman	1
253 IR, Raman	4
241 IR	0
227 Raman	5
199 IR, Raman	4
187 IR, Raman	6
156 IR, Raman	5
139 IR	0

Fig. 4. $^{31}P\{^1H\}$ NMR spectrum of the complex Mo_3Se_4-$(dppe)_3Cl_4$ in CD_2Cl_2 at 25 °C.

$$Mo_3Se_7Cl_4 + 4.5dppe$$

$$= Mo_3Se_4(dppe)_3Cl_4 + 1.5dppeSe_2 \qquad (8)$$

11

The IR spectrum of complex **11** contains bands of coordinated dppe. The $^{31}P\{^1H\}$ NMR spectrum of **11** is shown in Fig. 4. It shows two symmetrical signals of equal intensity which does not contradict the presence of two types of P atoms coordinated at a molybdenum atom in *cis*- and *trans*-position with respect to μ_3-Se. Such a coordination of bidentate ligands is characteristic of all earlier studied complexes $M_3S_4(\widehat{P\,P})_3X_3{}^+$ (M = Mo, W; $\widehat{P\,P}$ = dmpe, dppe; X = Cl, Br) [5, 8, 9]. An analogous splitting of signals in the $^{31}P\{^1H\}$ NMR spectra, a doublet of doublets, has been observed by Cotton and co-workers in the spectra of $[Mo_3S_4(dmpe)_3Cl_3]Cl$ [8]. By analogy with this structurally characterized complex we propose the following structure for the $Mo_3Se_4(dppe)_3Cl_3{}^+$ cation of complex **11**.
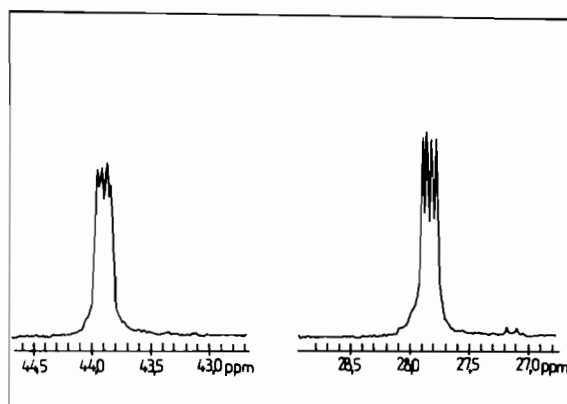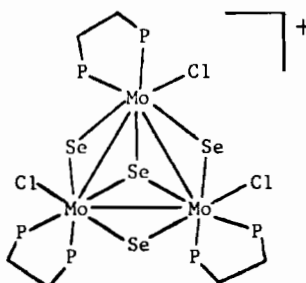

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