Syntheses and Structures of Raft-Type Hexanuclear Molybdenum Chloro Chalcogenido Cluster Complexes $[Mo_6E_8Cl_6(PEt_3)_6]$ (E = S, Se)

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Introduction

The chemistry of molybdenum chalcogenide cluster complexes has been developed remarkably in recent years,[1] and structural relations to Chevrel phases[2] and nitrogenase[3] and application to hydrodesulfurization catalysts[4] have aroused particular interest. Triangular, cubane, and octahedral frameworks are typical in the known molybdenum clusters. In contrast, hexanuclear raft-type cluster chalcogenide complexes of molybdenum are still very rare, and we have reported the formation of $[Mo_6S_{10}(SH)_2(PEt_3)_6]$ in the reaction of $[NH_4]_2[Mo_3S_{13}]$ with triethylphosphine.[5]

During the course of our study of controlled reduction by magnesium of triangular cluster complexes formed by the reaction of $Mo_3S_7Cl_4$ (E = S, Se) with triethylphosphine, we have obtained other raft-type hexanuclear cluster complexes. They have similar molybdenum cluster cores to that of $[Mo_6S_{10}(SH)_2(PEt_3)_6]$, and the average oxidation state of molybdenum is identical. The syntheses and structural characterizations are described in this paper.

Experimental Section

General Procedures. All manipulations were carried out under dinitrogen or argon atmosphere using standard Schlenk techniques. Solvents were dried and distilled under argon from appropriate drying agents. $Mo_3S_7Cl_4$[6] and PEt_3[7] were prepared by the literature methods. $Mo_3Se_7Cl_4$ was prepared by the reaction of $MoCl_3$ with selenium at 400 °C.

Preparation of $[Mo_6S_8Cl_6(PEt_3)_6]$ (1). $Mo_3S_7Cl_4$ (0.50 g, 0.76 mmol) was treated with PEt_3 (18.8% w/w in THF, 4 mL, 5.6 mmol) in 20 mL of THF at room temperature for 24 h. After the solid disappeared, the solution was cooled to −20 °C and stirred with magnesium (turnings, 0.10 g, 4.1 mmol) for 3 h. When the color became purple, the solvent and unreacted PEt_3 were removed under reduced pressure. After being washed with 20 mL of hexane, the residue was extracted with 20 mL of benzene. Dark brown crystals (0.19 g) were obtained in 26% yield. Anal. Calcd for $C_{36}H_{90}Cl_6Mo_6P_6S_8$: C, 24.65; H, 5.17; S, 14.63; Cl, 12.13. Found: C, 24.42; H, 5.12; S, 14.81; Cl, 12.00. UV−vis (CH_2Cl_2 soln)/nm (M^{-1} cm^{-1}): 340 (1.9×10^4), 410 (1.3×10^4), 570 (sh), 680 (sh), 880 (9.3×10^2), 1300 (7.3×10^2).

Table 1. Crystal Parameters and X-ray Diffraction Data for $[Mo_6S_8Cl_6(PEt_3)_6]\cdot CH_2Cl_2$ ($\mathbf{1}\cdot CH_2Cl_2$) and $[Mo_6Se_8Cl_6(PEt_3)_6]\cdot C_6H_6$ ($\mathbf{2}\cdot C_6H_6$)

	$\mathbf{1}\cdot CH_2Cl_2$	$\mathbf{2}\cdot C_6H_6$
formula	$C_{37}H_{92}Cl_8Mo_6P_6S_8$	$C_{42}H_{96}Cl_6Mo_6P_6Se_8$
fw	1838.8	2207.1
space group	$P2_1/c$	$C2/c$
a, Å	13.609(5)	32.562(4)
b, Å	24.323(12)	12.067(2)
c, Å	22.011(5)	24.935(3)
β, deg	94.11(3)	133.189(7)
V, Å^3	7267(5)	7143(2)
Z	4	4
μ, cm^{-1}	16.56	54.24
T, K	297	297
λ, Å	0.7107	0.7107
transm coeff	0.855−0.990	0.598−0.988
R,[a] R_w[b]	0.060, 0.058	0.059, 0.045

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = 1/\sigma^2(F_o)$.

Preparation of $[Mo_6Se_8Cl_6(PEt_3)_6]\cdot C_6H_6$ ($\mathbf{2}\cdot C_6H_6$). $Mo_3Se_7Cl_4$ (1.0 g, 1.0 mmol) was treated with PEt_3 (18.5% w/w in THF, 8 mL, 11 mmol) in 40 mL of THF at room temperature for 48 h, and the resulting mixture was filtered at −72 °C. The filtrate was stirred with magnesium (turnings, 0.2 g, 8.2 mmol) at −20 °C for 24 h. The solvent and unreacted PEt_3 were removed under reduced pressure. After being washed with 40 mL of hexane and 20 mL of diethyl ether, the residue was extracted with 10 mL of benzene. Dark brown crystals (0.12 g) were obtained in 11% yield. Anal. Calcd for $C_{42}H_{96}Cl_6Mo_6P_6Se_8$: C, 22.86; H, 4.38; Cl, 9.64. Found: C, 23.17; H, 4.35; Cl, 9.68. UV−vis (CH_2Cl_2 soln)/nm (M^{-1} cm^{-1}): 380 (sh), 460 (sh), 590 (sh), 700 (sh), 950 (9.5×10^2), 1420 (8.6×10^2).

X-ray Crystallography. Crystals were sealed in glass capillaries under argon atmosphere and mounted on a Rigaku AFC-5R diffractometer equipped with a Rotaflex rotating anode X-ray generator. The radiation used was Mo Kα monochromatized with graphite. The structures were solved by direct methods using the SHELXS86[8] program, and least-squares and Fourier syntheses were done with the SHELX76[9] and ANYBLK[10] programs. Atomic scattering factors were taken from a standard source.[11]

Structure Determination of $[Mo_6S_8Cl_6(PEt_3)_6]\cdot CH_2Cl_2$ ($\mathbf{1}\cdot CH_2Cl_2$). The crystals suitable for X-ray analysis were obtained by recrystallization from dichloromethane. The intensity data were collected by the ω-scan method in the range $5° \le 2\theta \le 55°$ ($0 \le h \le 19$, $0 \le k \le 34$, $-31 \le l \le 31$). The cell parameters were refined with 24 reflections in the range $37° \le 2\theta \le 40°$. A total of 18 199 reflections were collected, 10 137 of which were counted as observed with $F_o^2 > 5\sigma(F_o^2)$. An empirical absorption correction based on the ψ-scan was applied. Systematic absences showed that the space group was $P2_1/c$. All the positions of the heavy atoms were determined by direct methods, and carbon atoms were found by iterative application of least-squares and difference Fourier maps. Two crystallographically independent molecules were found, but their structures were essentially the same. All non-hydrogen atoms in the cluster molecules except a

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Table 2. Atomic Coordinates and Equivalent Isotropic Temperature Factors[a] for $[Mo_6S_8Cl_6(PEt_3)_6]\cdot CH_2Cl_2$ (**1**$\cdot CH_2Cl_2$)

atom	10^4x	10^4y	10^4z	10^2U_{eq}	atom	10^4x	10^4y	10^4z	10^2U_{eq}
Mo1	4319.6(4)	−398.7(2)	4666.7(2)	30.5(3)	P4	9177.8(15)	−844.5(7)	1348.0(8)	44.2(12)
Mo2	5075.2(4)	−984.5(2)	5672.9(2)	32.8 (3)	P5	12056.6(15)	1343.3(8)	1328.8(9)	47.7(12)
Mo3	3659.5(4)	−1486.9(2)	4957.1(3)	36.0(3)	P6	8025.8(16)	1209.3(8)	2131.4(9)	52.7(13)
Cl1	3332.4(12)	477.5(6)	4363.5(7)	40.7(10)	C19	9104(6)	−597(3)	2126(3)	56(5)
Cl2	5410.0(13)	−917.9(7)	6812.0(7)	46.4(10)	C20	8967(7)	−1072(3)	2602(3)	87(7)
Cl3	3998.6(15)	−2355.3(7)	4514.3(9)	60.5(13)	C21	8080(5)	−1259(3)	1217(3)	50(5)
S1	4290.0(12)	−104.2(6)	5699.5(7)	33.6(9)	C22	7137(6)	−977(3)	1297(4)	69(6)
S2	5226.0(12)	−1202.6(6)	4653.0(7)	35.5(9)	C23	10065(6)	−1401(3)	1407(3)	53(5)
S3	2692.0(13)	−767.3(7)	4707.9(8)	41.0(10)	C24	11108(6)	−1207(3)	1678(3)	61(5)
S4	3737.4(13)	−1443.9(7)	5971.8(8)	42.7(11)	C25	12990(5)	1651(3)	866(3)	56(5)
P1	3993.7(14)	−636.9(7)	3489.7(8)	41.0(11)	C26	13882(6)	1897(4)	1258(4)	88(7)
P2	6252.9(15)	−1844.9(8)	5862.4(9)	47.3(12)	C27	11744(6)	1885(3)	1887(3)	59(5)
P3	2021.7(16)	−1978.2(8)	5081.9(10)	53.6(13)	C28	11405(6)	2438(3)	1593(4)	76(6)
C1	3627(5)	−1359(3)	3359(3)	50(4)	C29	12746(5)	879(3)	1877(3)	54(5)
C2	3451(6)	−1529(3)	2691(3)	70(6)	C30	13326(6)	450(3)	1558(4)	72(6)
C3	3054(5)	−227(3)	3044(3)	42(4)	C31	7114(5)	1584(3)	1663(3)	56(5)
C4	2001(5)	−324(3)	3226(3)	56(5)	C32	6314(5)	1868(3)	2013(3)	65(6)
C5	5018(5)	−531(3)	3008(3)	48(4)	C33	7271(7)	715(4)	2582(4)	89(7)
C6	5896(6)	−915(3)	3167(3)	66(6)	C34A	6717(14)	422(8)	2334(9)	86(7)
C7	7358(5)	−1695(3)	6378(3)	56(5)	C34B	7762(13)	396(8)	3112(8)	94(6)
C8	8042(5)	−2200(3)	6523(3)	63(5)	C35	8440(7)	1723(4)	2702(4)	82(7)
C9	5662(6)	−2466(3)	6179(4)	76(6)	C36	8924(7)	2220(4)	2453(4)	98(8)
C10	5407(7)	−2388(3)	6859(4)	96(8)	C37A	6287(15)	786(18)	−243(7)	80
C11	6740(6)	−2198(3)	5185(3)	67(6)	C37B	6079(27)	1107(13)	−101(5)	80
C12	7475(6)	−1846(4)	4889(4)	76(6)	C37C	6191(27)	710(13)	−339(5)	80
C13	1240(5)	−1607(3)	5579(3)	63(5)	Cl7A	6093(23)	982(23)	−1015(8)	80
C14	251(6)	−1907(4)	5691(4)	101(8)	Cl7B	5838(34)	934(16)	−876(6)	80
C15	1295(6)	−2160(3)	4391(4)	83(7)	Cl7C	5761(34)	849(18)	−1099(6)	80
C16	855(7)	−1698(4)	4057(4)	103(8)	Cl8A	5257(19)	934(32)	173(9)	80
C17	2078(7)	−2703(4)	5366(4)	88(7)	Cl8B	5424(46)	682(22)	380(9)	80
C18	2625(9)	−2753(4)	5938(5)	128(10)	Cl8C	5660(48)	1154(20)	181(8)	80
Mo4	9492.5(4)	−26.5(2)	581.8(3)	33.1(3)	C38A	1568(11)	4924(5)	893(21)	80
Mo5	10533.6(4)	950.6(2)	661.8(3)	34.4(3)	C38B	1143(7)	−5088(6)	698(21)	80
Mo6	9376.5(5)	730.4(2)	1571.9(3)	37.0(3)	C38C	1518(18)	4633(15)	654(9)	80
Cl4	8148.5(13)	−534.5(7)	−78.3(7)	42.4(10)	Cl9A	342(16)	5096(10)	1027(36)	80
Cl5	10836.0(13)	1810.7(7)	63.1(8)	46.3(11)	Cl9B	1155(16)	−5802(7)	553(30)	80
Cl6	10156.0(15)	734.1(8)	2586.2(8)	59.2(12)	Cl9C	769(29)	4571(25)	−31(13)	80
S5	9392.8(13)	691.4(6)	−158.2(7)	35.9(9)	Cl10A	1719(19)	4210(6)	792(33)	80
S6	10742.6(13)	195.4(6)	1309.7(7)	37.0(10)	Cl10B	−66(9)	−4823(8)	673(37)	80
S7	8094.9(13)	352.8(7)	1039.8(8)	44.5(11)	Cl10C	997(44)	5080(20)	1176(13)	80
S8	9458.4(14)	1525.1(7)	1085.3(8)	43.9(11)					

[a] The isotropic equivalent temperature factors are defined as $U_{eq} = {}^1/_3\sum_{i,j}U_{ij}a_i^*a_j^*(\mathbf{a}_i\cdot\mathbf{a}_j)$.

disordered methyl carbon (C34A, C34B; occupancy factors, $^1/_2$) were refined anisotropically. Hydrogen atoms were not included in the calculation. Six dichloromethane molecules were found on the Fourier map. Due to disorder, the occupancy factors of the dichloromethanes were set to $^1/_6$ and the temperature factors fixed. The final difference Fourier map was featureless with the highest peak of 1.1 e Å^{-3}. Additional crystallographic data are presented in Table 1. Atomic parameters are listed in Table 2, and selected bond distances and angles in Table 4.

Structure Determination of $[Mo_6Se_8Cl_6(PEt_3)_6]\cdot C_6H_6$ (2$\cdot C_6H_6$). The intensity data were collected by the ω-scan method in the range $5° \leq 2\theta \leq 60°$ ($0 \leq h \leq 46$, $0 \leq k \leq 17$, $-35 \leq l \leq 35$). The cell parameters were refined with 25 reflections in the range $34° \leq 2\theta \leq 35°$. A total of 11 097 reflections were collected, 7246 of which were counted as observed with $F_o^2 > 3\sigma(F_o^2)$. An empirical absorption correction based on the ψ-scan was applied. Systematic absences narrowed down the space group choices to *Cc* and *C*2/*c*. The structure was successfully solved in *C*2/*c* following the procedure described above for **1**. Two benzene molecules were found on the Fourier map. Due to disorder, the occupancy factors of benzene were set to $^1/_2$ and the temperature factors fixed. The final difference Fourier map was featureless with the highest peak of 1.8 e Å^{-3}. Additional crystallographic data are presented in Table 1. Atomic parameters are listed in Table 3, and selected bond distances and angles in Table 4.

Results and Discussion

Syntheses. The raft-type hexanuclear cluster complexes **1** and **2** are obtained by reduction of trinuclear cluster complexes $[Mo_3E_4Cl_4(PEt_3)_x(thf)_{5-x}]$ (E = S, Se). These trinuclear cluster complexes are generated by the excision reaction of solid state cluster compounds $Mo_3E_7Cl_4$ with PEt_3 in tetrahydrofuran. When magnesium reacts with the trinuclear complexes, one chlorine atom is reductively abstracted, and electron-excess trinuclear intermediates $[Mo_3E_4Cl_3(PEt_3)_x(thf)_{6-x}]$ are likely to form. As we have described, the addition of dppe (= 1,2-bis(diphenylphosphino)ethane) to the solution containing this species formed the seven-electron trinuclear cluster $[Mo_3S_4Cl_3(dppe)_2(PEt_3)]$.[12] However, when they are extracted by noncoordinative solvents such as benzene or dichloromethane after removal of tetrahydrofuran, two cluster molecules are bound by chalcogenido and chloro bridges by dissociating tetrahydrofuran ligands. It is conceivable that the excess cluster valence electrons on the reduced trinuclear units are used for the formation of another Mo−Mo bond between the two trinuclear units. The reaction must be stopped at the stage when the trinuclear units are reduced by one electron. The reaction could be controlled by lowering the reaction temperatures to −20 °C and monitoring the color change of the solution. Otherwise the octahedral cluster complexes $[Mo_6E_8(PEt_3)_6]$ (E = S, Se)[2a] are formed by abstraction of four chloro ligands from the trinuclear cluster complexes. The present dimerization reactions of trinuclear chalcogenide cluster complexes in a horizontal

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[12] Mizutani, J.; Imoto, H.; Saito, T. *J. Cluster Sci.*, in press.

Table 3. Atomic Coordinates and Equivalent Isotropic Temperature Factors[a] for $[Mo_6Se_8Cl_6(PEt_3)_6]\cdot C_6H_6$ (**2**·C_6H_6)

atom	10^4x	10^4y	10^4z	10^2U_{eq}
Mo1	2997.0(1)	1812.2(3)	221.2(2)	23.71(16)
Mo2	2943.2(2)	3662.5(3)	−533.0(2)	26.17(17)
Mo3	3825.9(2)	2193.4(3)	105.2(2)	28.91(18)
Cl1	3102.6(4)	1285.8(8)	1311.0(5)	28.3(4)
Cl2	2872.4(5)	5741.8(9)	−564.1(6)	42.2(6)
Cl3	3947.5(5)	1260.4(10)	−633.6(6)	48.2(6)
Se1	3029.4(2)	3792.8(4)	543.4(2)	26.46(19)
Se2	2806.3(2)	1701.7(4)	−912.3(2)	28.37(19)
Se3	4056.9(2)	1842.7(4)	1219.8(2)	32.52(20)
Se4	3901.1(2)	4142.9(4)	147.4(2)	37.48(23)
P1	3153.9(5)	−359.9(9)	231.9(6)	33.2(6)
P2	2599.4(5)	4000.6(10)	−1831.9(6)	34.1(6)
P3	4907.5(5)	2261.1(12)	993.1(7)	49.6(7)
C1	2534.7(17)	−1256(4)	−453(2)	39(2)
C2	2220.8(18)	−1019(4)	−1272(2)	48(3)
C3	3450.8(19)	−1165(4)	1059(2)	44(2)
C4	4061.0(19)	−859(4)	1779(2)	50(2)
C5	3634.2(18)	−666(4)	104(2)	41(2)
C6	3817.7(20)	−1889(4)	197(3)	54(3)
C7	2314.5(19)	5378(4)	−2265(2)	47(2)
C8	1769.3(20)	5681(4)	−2479(3)	60(3)
C9	2044.9(18)	3022(4)	−2540(2)	46(2)
C10	1780.9(20)	3262(4)	−3335(2)	59(3)
C11	3150.9(19)	3768(4)	−1865(2)	50(3)
C12	3545.2(21)	4748(5)	−1608(3)	74(4)
C13	5273.9(20)	939(4)	1545(3)	77(3)
C14	5174.0(22)	−32(5)	1073(3)	105(4)
C15	5235.2(18)	3263(4)	1765(2)	60(3)
C16	5874.0(18)	3436(5)	2278(2)	65(3)
C17	5219.7(21)	2530(6)	617(3)	82(4)
C18	5031.7(26)	3524(5)	165(4)	98(4)
C19	0	911(6)	2500	144
C20	−315(2)	1085(11)	1752(1)	144
C21	−42(5)	1338(13)	1513(5)	144
C22	545(5)	1416(11)	2023(7)	144
C23	860(3)	1243(14)	2771(6)	144
C24	587.7(4)	990(12)	3010(3)	144

[a] See footnote *a* of Table 2.

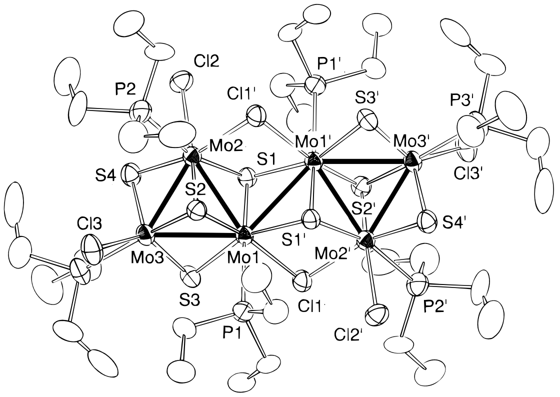

Figure 1. ORTEP drawing of $[Mo_6S_8Cl_6(PEt_3)_6]$ (**1**). One of two crystallographically independent molecules is shown. All atoms are represented by the thermal ellipsoids at the 50% probability.

fashion are other examples of the type of reactions reported so far for *μ*-sulfido-bridged trinuclear cluster complexes.[5,13]

Structures. The ORTEP drawing of one of the cluster molecules in **1** is shown in Figure 1. There is a crystallographic inversion center at the middle point of Mo1−Mo1′ and the molecule has $\bar{1}(C_i)$ point group symmetry. The cluster framework consists of six molybdenum atoms located on a plane within the deviation of 0.2 Å. Two incomplete-cubane-type Mo_3S_4 cluster units are bound by one Mo−Mo bond, two μ_3-S, and two μ_2-Cl. One triethylphosphine coordinates to each molybdenum atom, and a terminal chloro ligand coordinates to Mo2, Mo2′, Mo3, and Mo3′. The arrangement of the ligands around each molybdenum is octahedral for Mo1 and Mo2 and trigonal bipyramidal for Mo3. If the distances in the range 2.69−3.00 Å are assigned to seven Mo−Mo bonds, they are consistent with 14 cluster valence electrons. The Mo−Mo distances in the two trinuclear units (Mo1−Mo2, 2.77 Å; Mo1−Mo3, 2.87 Å; Mo2−Mo3, 2.69 Å) are similar to those in the Mo_3S_4 cluster complexes reported so far (2.73−2.83 Å).[1d] On the other hand, the distance of the Mo1−Mo1′ bond, which connects two trinuclear units, is relatively long (3.00 Å) as compared with those in the trinuclear units. The distance between Mo1 and Mo2′ is fairly long (3.55 Å), and the bonding interaction is unlikely. The Mo−S bond lengths in the two Mo_3S_4 units (Mo−(μ_3-S), 2.32−2.38 Å; Mo−(μ_2-S), 2.22−2.40 Å) are similar to those in the reported Mo_3S_4 cluster complexes (Mo−(μ_3-S), 2.31−2.36 Å; Mo−(μ_2-S), 2.28−2.34 Å),[1d] but those between the two Mo_3S_4 units (Mo1−S1′, 2.44 Å) are relatively long. The Mo−(μ_2-Cl) bond distances are 2.58 Å for Mo1−Cl1 and 2.50 Å for Mo2′−Cl1, and the angle of the Mo1−Cl1−Mo2′ bridge is 88.8°. This Mo−Cl−Mo bridge is relatively stretched in comparison with those in $Mo_3(\mu_3-O)(\mu-Cl)_3$-type cluster complexes (Mo−Cl, 2.40−2.44 Å; Mo−Cl−Mo, 64−66°).[14] The absence of the Mo1−Mo2′ bond and the elongation of S1′ and Cl1 bridges between the two Mo_3S_4 units may be understandable by the comparison of structure between **1** and the isoelectronic hexanuclear cluster complex $[Mo_6S_{10}(SH)_2(PEt_3)_6]$ (**3**).[5] Both **1** and **3** have the same mean oxidation state of +3.67 and 14 cluster valence electrons. The whole arrangement of molybdenum atoms in **3** is similar to that of the present cluster complex **1**. But the distance of Mo−Mo in **3** corresponding to Mo1−Mo2′ is 3.06 Å, which is much shorter than that of **1** (3.55 Å). This difference of Mo−Mo distance may be attributed to the coordination number of Mo2. The molybdenum atom in **3** corresponding to Mo2′ is pentacoordinated, and there is little steric repulsion between the ligands on Mo1 and those on Mo2′. In **1**, on the other hand, Mo2 is hexacoordinated and the repulsion between the terminal chloro ligand on Mo2 and the triethylphosphine on Mo1′ would become significant if the two molybdenum atoms approached closer. This steric repulsion may result in the larger distance between Mo1 and Mo2′ and the long ligand bridges between the two trinuclear cluster units.

The selenido complex **2** is almost isostructural with the sulfido complex **1**. The Mo−chalcogenido bond lengths are longer by 0.12−0.14 Å than those of **1**, as expected from the difference in the covalent radii of S (1.04 Å) and Se (1.17 Å). Though the Mo−Cl and Mo−P lengths are almost the same as those in **1**, the seven Mo−Mo bond distances in **2** are in the range 2.77−3.09 Å, which is longer by 0.07−0.10 Å than those of **1**. This difference of Mo−Mo distances may be the result of the elongation of Mo−chalcogenido bond distances by going from S to Se.

Spectra. The UV−visible spectra of **1** and **2** have two characteristic absorption bands in the near-infrared region (880 and 1300 nm for **1**, 950 and 1420 nm for **2**), which are absent in those of the trinuclear $Mo_3S_4^{4+}$ complexes.[15] These absorp-

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Table 4. Selected Interatomic Distances (Å) and Angles (deg) for [$Mo_6E_8Cl_6(PEt_3)_6$] (E = S (**1**), Se (**2**))[a]

	E = S (**1**)					E = S (**1**)			
bond	molecule A	molecule B[b]	av	E = Se (**2**)	bond	molecule A	molecule B[b]	av	E = Se (**2**)
Mo1−Mo1′	2.993(1)	2.999(1)	2.996	3.092(1)	Mo1−Mo3	2.881(1)	2.866(1)	2.874	2.941(1)
Mo1−Mo2	2.769(1)	2.766(1)	2.768	2.847(1)	Mo2−Mo3	2.693(1)	2.689(1)	2.691	2.771(1)
Mo1···Mo2	3.556(1)	3.540(1)	3.548	3.683(1)					
Mo1−E1	2.386(2)	2.385(2)	2.386	2.501(1)	Mo1−E2	2.313(2)	2.316(2)	2.315	2.447(1)
Mo1−E1′	2.438(2)	2.447(2)	2.443	2.572(1)	Mo2−E2	2.330(2)	2.330(2)	2.330	2.473(1)
Mo2−E1	2.395(2)	2.380(2)	2.388	2.505(1)	Mo3−E2	2.382(2)	2.374(2)	2.378	2.506(1)
Mo1−E3	2.397(2)	2.400(2)	2.399	2.520(1)	Mo2−E4	2.273(2)	2.271(2)	2.272	2.387(1)
Mo3−E3	2.235(2)	2.228(2)	2.232	2.368(1)	Mo3−E4	2.231(2)	2.217(2)	2.224	2.360(1)
Mo1−Cl1	2.582(2)	2.570(2)	2.576	2.574(1)	Mo2−Cl2	2.521(2)	2.522(2)	2.522	2.516(2)
Mo2−Cl1′	2.500(2)	2.494(2)	2.497	2.514(1)	Mo3−Cl3	2.385(2)	2.402(2)	2.394	2.412(2)
Mo1−P1	2.661(2)	2.663(2)	2.662	2.667(2)	Mo3−P3	2.561(2)	2.564(2)	2.563	2.577(2)
Mo2−P2	2.651(2)	2.632(2)	2.642	2.636(2)					
Mo1′−Mo1−Mo2	76.11(2)	75.66(2)	75.89	76.53(2)	Mo2′−Mo1−Mo3	175.05(3)	176.23(3)	175.64	175.26(2)
Mo1′−Mo1−Mo2′	49.10(2)	49.20(2)	49.15	48.74(1)	Mo1−Mo2−Mo1′	54.79(2)	55.14(2)	54.97	54.74(1)
Mo1′−Mo1−Mo3	132.72(3)	132.52(3)	132.62	133.46(2)	Mo1−Mo2−Mo3	63.67(2)	63.36(2)	63.52	63.13(2)
Mo2−Mo1−Mo2′	125.21(2)	124.86(3)	125.04	125.27(2)	Mo1′−Mo2−Mo3	118.24(2)	118.39(3)	118.32	117.69(2)
Mo2−Mo1−Mo3	56.89(2)	57.01(2)	56.95	57.17(2)	Mo1−Mo3−Mo2	59.44(2)	59.63(2)	59.54	59.70(2)
E1−Mo1−Cl1	87.39(6)	87.85(6)	87.62	87.19(3)	E1′−Mo1−P1	82.33(6)	83.09(6)	82.71	82.61(4)
E1−Mo1−E1′	103.34(6)	103.30(6)	103.32	104.91(2)	E2−Mo1−Cl1	164.28(6)	164.00(6)	164.14	161.93(4)
E1−Mo1−E2	108.15(6)	107.75(6)	107.95	110.16(3)	E2−Mo1−E3	100.34(6)	100.65(7)	100.50	103.61(2)
E1−Mo1−E3	89.86(6)	89.85(6)	89.85	86.58(2)	E2−Mo1−P1	81.67(6)	83.08(7)	82.38	81.57(4)
E1−Mo1−P1	168.47(6)	167.35(7)	167.91	166.03(4)	E3−Mo1−Cl1	81.57(6)	82.47(6)	82.02	81.80(3)
E1′−Mo1−Cl1	84.38(6)	84.40(6)	84.39	83.08(3)	E3−Mo1−P1	82.26(6)	81.54(6)	81.90	83.17(4)
E1′−Mo1−E2	89.57(6)	88.45(6)	89.01	87.39(2)	Cl1−Mo1−P1	83.15(6)	81.87(6)	82.51	81.99(5)
E1′−Mo1−E3	160.24(6)	161.02(7)	160.63	160.51(3)					
E1−Mo2−Cl1′	87.09(6)	87.48(6)	87.29	85.67(4)	E2−Mo2−P2	82.98(6)	83.56(6)	83.27	82.21(4)
E1−Mo2−Cl2	88.14(6)	86.88(6)	87.51	84.90(4)	E4−Mo2−Cl1′	165.00(7)	165.75(7)	165.38	164.41(4)
E1−Mo2−E2	107.29(6)	107.44(6)	107.37	109.17(3)	E4−Mo2−Cl2	80.51(6)	80.68(7)	80.60	80.06(4)
E1−Mo2−E4	93.69(6)	94.00(7)	93.85	95.13(3)	E4−Mo2−P2	93.10(7)	93.02(7)	93.06	94.89(4)
E1−Mo2−P2	165.36(7)	164.58(7)	164.97	161.58(4)	Cl1′−Mo2−Cl2	84.54(6)	85.26(6)	84.90	84.51(5)
E2−Mo2−Cl1′	86.85(6)	86.24(6)	86.55	86.23(4)	Cl1′−Mo2−P2	83.03(6)	82.41(6)	82.72	80.57(5)
E2−Mo2−Cl2	161.92(6)	163.00(7)	162.46	162.51(4)	Cl2−Mo2−P2	80.22(6)	80.74(6)	80.48	81.66(5)
E2−Mo2−E4	107.13(7)	106.73(7)	106.93	108.06(3)					
E2−Mo3−Cl3	86.51(7)	85.78(7)	86.15	84.98(4)	E3−Mo3−E4	101.18(7)	99.79(7)	100.49	100.71(3)
E2−Mo3−E3	103.12(7)	104.09(7)	103.61	106.40(3)	E3−Mo3−P3	83.67(7)	83.03(7)	83.35	81.25(5)
E2−Mo3−E4	106.75(7)	107.04(7)	106.90	107.83(3)	E4−Mo3−Cl3	117.00(7)	114.31(7)	115.66	115.67(5)
E2−Mo3−P3	165.65(7)	165.10(7)	165.38	164.15(5)	E4−Mo3−P3	83.91(7)	84.18(7)	84.05	83.74(5)
E3−Mo3−Cl3	136.15(7)	140.09(7)	138.12	136.61(5)	Cl3−Mo3−P3	79.98(7)	80.56(7)	80.27	80.14(6)
Mo1−E1−Mo1′	76.66(5)	76.70(5)	76.68	75.10(2)	Mo1−E2−Mo3	75.69(5)	75.32(6)	75.51	72.83(2)
Mo1−E1−Mo2	70.76(5)	70.97(5)	70.87	69.31(2)	Mo2−E2−Mo3	69.70(5)	69.71(5)	69.71	67.61(2)
Mo1′−E1−Mo2	94.72(6)	94.33(6)	94.53	92.98(2)	Mo1−E3−Mo3	76.85(6)	76.41(6)	76.63	73.91(2)
Mo1−E2−Mo2	73.21(5)	73.07(6)	73.14	70.70(2)	Mo2−E4−Mo3	73.44(6)	73.62(6)	73.53	71.41(2)
Mo1−Cl1−Mo2′	88.81(6)	88.70(6)	88.76	92.73(4)					

[a] Primed atoms are related by a crystallographic center of inversion positioned at the center of the molecule. [b] Mo4−Mo6, S5−S8, Cl4−Cl6, and P4−P6 in molecule B correspond to Mo1−Mo3, S1−S4, Cl1−C13, and P1−P3 in molecule A, respectively.

tion bands may be related to the extension of the metal core from trinuclear to hexanuclear. All absorption bands of the selenium complex **2** are red-shifted by 20−120 nm from the corresponding bands of the sulfur complex **1**. Parallel trends of the red-shift of absorption bands by going from S to Se have been observed for the trinuclear [$Mo_3E_4(H_2O)_9$]$^{4+}$ and the tetranuclear [$Mo_4E_4(H_2O)_{12}$]$^{5+}$ (E = S, Se) cluster complexes.[15f]

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Supporting Information Available: Listing of interatomic distances and angles and anisotropic temperature factors for **1**·CH_2Cl_2 and **2**·C_6H_6 (15 pages). Ordering information is given on any current masthead page.

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