Synthesis, Characterization, and Structure of Mixed Chloride−Selenide Tungsten Cluster Complexes

Xiaobing Xie and Robert E. McCarley*

Ames Laboratory, USDOE, and Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received January 10, 1997[⊗]

The first examples of mixed halide−chalcogenide hexatungsten clusters as the molecular complexes, $[W_6Se_{8-x}Cl_x(PEt_3)_6]^+$, were prepared via the reaction of W_6Cl_{12} with Na_2Se and PEt_3 in refluxing toluene. Single crystals of the mixed chloride−selenide cluster cationic complexes were grown from chloroform solution. The structures of two crystals from different preparations, using Na_2Se and K_2Se as reagents, were determined and found to have different compositions, $[W_6Se_{7.0}Cl_{1.0}(PEt_3)_6][Cl(CHCl_3)_6]$ and $[W_6Se_{6.4}Cl_{1.6}(PEt_3)_6][Cl(CHCl_3)_6]$, respectively. In the latter case the crystal contains both the 20-electron cluster $[W_6Se_7Cl(PEt_3)_6]^+$ and the 21-electron cluster $[W_6Se_6Cl_2(PEt_3)_6]^+$ in the mole fractions 0.40 and 0.60, respectively. The two crystals were isomorphous: hexagonal, $R\bar{3}$, $Z = 3$, $a = 18.921(4)$ Å, $c = 21.275(4)$ Å and $a = 18.908(5)$ Å, $c = 21.306(5)$ Å, respectively. The bridging chlorine and selenium atoms are disordered over all the bridging ligand sites in both structures. In the unique $[Cl(CHCl_3)_6]^-$ anion unit, six chloroform solvent molecules are octahedrally coordinated to a chloride anion via hydrogen bonding.

Introduction

The chemistry of molecular hexanuclear molybdenum−chalcogenide cluster complexes of general formulation $Mo_6Q_8L_6$ (Q = S, Se, Te) has undergone extensive development in recent years[1−6] because of their close relationship with the important materials known as Chevrel phases.[7,8] The essential structural element in these complexes is a strongly bonded Mo_6 octahedron with eight chalcogenide atoms capping the faces and six organic donor ligands occupying the terminal positions. In the Chevrel phases the organic donor ligands are replaced by bonds to the capping chalcogenide atoms of neighboring cluster units. Also in the Chevrel phases this cluster unit, Mo_6Q_8, can have a variable electron population of 20−24 electrons in the metal−metal bonding orbitals.[9−11] Therefore, these cluster complexes often support multisequential electron transfer reactions. The chemically reversible addition or removal of electrons from the clusters can result in measurable changes in the core dimensions.

In this laboratory, research has focused on the hexamolybdenum (Mo_6) and hexatungsten (W_6) chalcogenide cluster compounds. We have developed routes for preparation of the metal cluster complexes, $M_6Q_8L_6$ (M = Mo, W), by converting M_6Cl_{12}, which contains the $(M_6Cl_8)^{4+}$ cluster unit, through substitution of chalcogenide for chloride.[12−16] The preparation and structural characterization of $W_6Q_8L_6$ molecular complexes, where L is an organic donor ligand such as pyridine,[12,13,15] piperidine,[14,15] triethylphosphine,[13,14] or tetrahydrothiophene,[13] have been achieved. Likewise, the chemistry of molybdenum sulfide cluster complexes, $Mo_6S_8L_6$, was also developed by similar methods.[8]

Crystalline solid-state compounds in the mixed halide−chalcogenide series $(Mo_6X_{8-x}Q_x)X_{4-x}$ have been known for many years.[17] However, examples of the molecular hexanuclear cluster complexes with mixed halide−chalcogenide bridging ligands were rare. The first molecular Mo_6X_8 cluster compound with mixed bridging ligands, $(pyH)_3[(Mo_6Cl_7S)Cl_6]$, was reported by Michel and McCarley.[18] This mixed chloride−sulfide molecular cluster was established by substituting one chlorine ligand in the $Mo_6Cl_8{}^{4+}$ cluster unit of molybdenum(II) chloride with a sulfur ligand. Additional substitutions have led to the discovery of molecular complexes of $Mo_6S_xCl_{8-x}L_6$, where x varies from 3 to 8.[19] The products of these preparations were not single stoichiometric clusters but, rather, mixtures of cluster products which had a range of values of x. Therefore, the individual complexes have not been well characterized.

No example of a mixed tungsten chloride−chalcogenide molecular complex such as $W_6Q_{8-x}Cl_xL_6$ has been reported. Considering the difficulty in differentiating sulfur and chlorine atoms by X-ray diffraction, mixed chloride−selenide cluster complexes should be a better system to be explored. The present paper describes the syntheses, characterization, and structures of the first two new molecular complexes of the mixed chloride−selenide tungsten clusters, isolated as the compounds $[W_6Se_{7.0}Cl_{1.0}(PEt_3)_6][Cl(CHCl_3)_6]$ and $[W_6Se_{6.4}Cl_{1.6}(PEt_3)_6][Cl(CHCl_3)_6]$.

[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1997.

(1) Müller, A. *Polyhedron* **1986**, *5*, 323.
(2) Saito, T. In *Early Transition Metal Clusters with p-Donor Ligands*; Chisholm, M. H., Ed.; VCH: New York, 1995; p 63.
(3) Dance, I.; Fisher, K. *Prog. Inorg. Chem.* **1994**, *41*, 637.
(4) Shibahara, T. *Adv. Inorg. Chem.* **1991**, *37*, 143.
(5) Shibahara, T. *Coord. Chem. Rev.* **1993**, *123*, 73.
(6) Roof, L. C.; Kolis, J. W. *Chem. Rev.* **1993**, *93*, 1037.
(7) Saito, T.; Yamamoto, N.; Nagase, T.; Kobayashi, K.; Yamagata, T.; Imoto, H.; Unoura, K. *Inorg. Chem.* **1990**, *29*, 764.
(8) Hilsenbeck, S. J.; Young, V. G., Jr.; McCarley, R. E. *Inorg. Chem.* **1994**, *33*, 1822.
(9) Yvon, K. In *Current Topics in Materials Science*; Kaldis, E., Ed.; Elsevier: Amsterdam, 1979; Vol. 3, p 53.
(10) Andersen, O. K.; Klose, W.; Nohl, H. *Phys. Rev. B: Solid State* **1978**, *B17*, 1209.
(11) Hughbanks, T.; Hoffman, R. *J. Am. Chem. Soc.* **1983**, *105*, 1150.
(12) Zhang, X.; McCarley, R. E. *Inorg. Chem.* **1995**, *34*, 2678.
(13) Zhang, X. Ph.D. Dissertation, Iowa State University, Ames, IA, 1991.
(14) Xie, X.; McCarley, R. E. Unpublished results.
(15) Xie, X.; McCarley, R. E. *Inorg. Chem.* **1995**, *34*, 6124.
(16) Xie, X.; McCarley, R. E. *Inorg. Chem.* **1996**, *35*, 2713.
(17) (a) Perrin, C.; Sergent, M.; Le Fraon, A. *J. Solid State Chem.* **1978**, *25*, 197. (b) Perrin, C.; Sergent, M. *J. Chem. Res.* **1983**, 449. (c) Perrin, C.; Potel, M.; Sergent, M. *Acta Crystallogr. C* **1983**, *39*, 415. (d) Sergent, M.; Fischer, O.; De Croux, U.; Perrion, C.; Chevrel, R. *J. Solid State Chem.* **1978**, *22*, 87. (e) Perrin, A.; Perrin, C.; Sergent, M. *J. Less-Common Met.* **1988**, *137*, 241. (f) Perrin, C.; Sergent, M. *J. Less-Common Met.* **1986**, *123*, 117.
(18) Michel, J. B.; McCarley, R. E. *Inorg. Chem.* **1982**, *21*, 1864.
(19) Michel, J. B.; McCarley, R. E. Ph.D Dissertation, Iowa State University, Ames, IA, 1979.

S0020-1669(97)00038-4 CCC: $14.00

Experimental Section

Materials. The reagents and products are air and moisture sensitive. Therefore, all manipulations were performed by the use of an inert-atmosphere drybox, a high-vacuum manifold, and Schlenk techniques, unless otherwise stated. W_6Cl_{12} was prepared by literature methods.[13,20] Na_2Se and K_2Se were prepared by the reaction of the corresponding alkali metal and selenium in refluxing tetrahydrofuran with catalytic amounts of naphthalene.[21] All solvents were purified and dried prior to use and then distilled onto Linde 3- or 4-Å molecular sieves and stored under vacuum or a nitrogen atmosphere. Pyridine (Fisher), piperidine (Fisher), and triethylphosphine (Strem) were purified by refluxing over calcium hydride for at least 4 h. Toluene (Fisher) and chloroform were refluxed over phosphorus pentoxide. Without heating, tetrahydrofuran (Fisher) was dried by stirring with sodium metal and a benzophenone indicator. Methanol (Mallinckrodt) was dried by refluxing over sodium methoxide. When used, the solvents were vacuum-distilled or syringed under a flowing nitrogen gas atmosphere.

Physical Measurements. Mid-infrared (4000−200 cm^{-1}) spectra were recorded with a Bomem MB-102 Fourier transform infrared spectrometer. Samples were prepared as Nujol mulls and pressed between two cesium iodide plates. Far-infrared (650−100 cm^{-1}) spectra were recorded separately with an IBM IR/98 Fourier transform infrared spectrometer. Thick sample mulls were placed on a polyethylene film. XP spectra were collected with a Physical Electronics Industries 5500 multitechnique surface analysis system, and binding energies were calibrated with C 1s = 284.6 eV. The magnetic susceptibility measurements were obtained on powder samples with a Quantum SQUID magnetosusceptometer operating over the range 4−300 K at 3 T.

Chemical Analyses. Tungsten was determined gravimetrically as the trioxide after treatment of the samples with concentrated nitric acid and ignition at 800 °C. Chlorine was determined by potentiometric titration with a standardized silver nitrate solution after dissolving the sample in $KOH-H_2O_2$ solution and neutralization.

Reactions in Piperidine. Attempts to prepare mixed halide−chalcogenide cluster complexes as amine adducts were conducted in piperidine. Reactions between W_6Cl_{12} (*ca.* 0.50 g) and Na_2Se in 1:1, 1:2, 1:4, and 1:6 mole ratios were performed in refluxing piperidine (40 mL, 106 °C) under N_2 for 3−4 days. In all cases the reaction mixtures were filtered to provide some white to tan solid and a brown-red solution, from which black solids were recovered on removal of solvent. The black solids in all cases contained 42−48% W and 4−5% Cl with Cl:W ratios of 0.4−0.6. Crystalline $W_6Se_8(pip)_6\cdot 8pip$ could be recovered from the 1:4 and 1:6 reactions by recrystallization of the black solid from piperidine.

Preparation of $[W_6Se_{7.0}Cl_{1.0}(PEt_3)_6][Cl(CHCl_3)_6]$ (1). W_6Cl_{12} (0.250 g, 0.164 mmol) and Na_2Se (0.164 g, 1.31 mmol) were weighed in the drybox and transferred into a 100-mL Schlenk reaction flask equipped with a water-cooled condenser. By vacuum distillation, 40 mL of toluene was transferred into the flask. Then 0.25 mL of triethylphosphine was added to the reactants and the mixture was refluxed for 3 days. The color of the reaction mixture was light gray to start with, and then it slowly turned light brown and then darker brown as the reaction proceeded. About 0.19 g of tan solid and a reddish brown solution were separated by filtration. The filtrate was evaporated and dried overnight under dynamic vacuum to remove the solvent. About 0.30 g of dark brown oily material was thus recovered. This oily material was then washed with 5 mL of Et_2O, and about 0.12 g of yellow brown powder was obtained. IR (Nujol, cm^{-1}): 1414 (m), 1247 (w), 1032 (s), 863 (w), 760 (s), 712 (m), 620 (ms), 404 (s), 368(w), 332 (w), ν(W−Se) 254 (m). About 0.030 g of this brown material was refluxed in 10 mL of $CHCl_3$ for 1 day. The resulting yellow-brown solution was allowed to stand at −20 °C for 1 week. A few dark brown rhombohedral crystals of $[W_6Se_{7.0}Cl_{1.0}(PEt_3)_6][Cl(CHCl_3)_6]$ **(1)** were thus obtained.

The insoluble product obtained by filtration of the reaction mixture was washed with methanol for 2−3 days to remove NaCl, and about 0.035 g of brown powder was recovered. XPS data for this brown powder indicated that WSe_2 was the major component.

Table 1. Crystallographic Data for the Mixed Selenide−Chloride Tungsten Cluster Complexes

	compound	
	$[W_6Se_{7.0}Cl_{1.0}(PEt_3)_6]$-$[Cl(CHCl_3)_6]$	$[W_6Se_{6.4}Cl_{1.6}(PEt_3)_6]$-$[Cl(CHCl_3)_6]$
chem formula	$C_{42}Cl_{20.0}H_{96}P_6Se_{7.0}W_6$	$C_{42}Cl_{20.6}H_{96}P_6Se_{6.4}W_6$
fw	3151.94	3125.50
space group	$R\bar{3}$ (No. 148)	$R\bar{3}$ (No. 148)
a, Å	18.921(4)	18.908(5)
c, Å	21.275(4)	21.306(5)
V, $Å^3$	6596.(2)	6596.(3)
Z	3	3
ρ_{calcd}, g cm^{-3}	2.380	2.360
μ, cm^{-1}	114.67	112.32
radiation (Mo K), Å	0.710 69	0.710 69
T, C	−70.0	−70.0
R^a	0.0347	0.0329
$R_w{}^b$	0.0321	0.0297

[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 $[W_6Se_{6.4}Cl_{1.6}(PEt_3)_6][Cl(CHCl_3)_6]$ (2). W_6Cl_{12} (0.50 g, 0.327 mmol) and K_2Se (0.51 g, 3.2 mmol) were weighed in the drybox and transferred into a 100-mL Schlenk reaction flask equipped with a water-cooled condenser. By vacuum distillation, 50 mL of toluene was transferred into the flask. Then 0.23 mL of triethylphosphine was added to the reactants and the mixture was refluxed for 3 days. The color of the reaction mixture was light gray to start with, and then it slowly turned light brown and then darker brown as the reaction proceeded. About 0.80 g of tan solid and a reddish brown solution were separated by filtration. The filtrate was evaporated and dried overnight under dynamic vacuum to remove the solvent. About 0.25 g of dark orange-powder was thus recovered. IR (Nujol, cm^{-1}): 1414 (w), 1255 (w), 1033 (s), 759 (s), 712 (ms), 622 (m), 404 (m), 368 (m), 334 (m), 280 (m), ν(W−Se) 254 (m). About 0.050 g of this brown material was refluxed in 10 mL of $CHCl_3$ for 1 day. The resulting yellow-brown solution was allowed to stand at −20 °C for 1 week. Some dark brown rhombohedral crystals of $[W_6Se_{6.4}Cl_{1.6}(PEt_3)_6]$-$[Cl(CHCl_3)_6]$ **(2)** were obtained.

X-ray Structure Determinations

In each case, a crystal was chosen from material still in contact with the mother solution. The crystal was encased in epoxy cement, attached to the tip of a glass fiber, and immediately inserted into the low-temperature nitrogen stream of the diffractometer for data collection. The cell constants were determined from 25 randomly located and centered reflections. The structures were solved by direct methods using SHELXS[22] and refined on *F* by full-matrix, least-squares techniques with the TEXSAN package.[23] Pertinent crystallographic data are listed in Table 1.

$[W_6Se_{7.0}Cl_{1.0}(PEt_3)_6][Cl(CHCl_3)_6]$ (1). A dark brown crystal, with dimensions of 0.20 × 0.20 × 0.30 mm^3, was mounted on a glass fiber, and data collection proceeded at −70 °C. Data were collected with a Rigaku AFC6R diffractometer using Mo K radiation, over the range $3 < 2\theta < 55°$ in the quarter-sphere $(+h,+k,\pm l)$, using the $\omega-2\theta$ scan technique. Three standard reflections were monitored every 200 reflections and showed a 3.89% intensity decrease over the collection period. A total of 3695 reflections were collected, of which 3391 were unique ($R_{int} = 0.075$) and 1577 were observed with $I > 4\sigma(I)$. The linear absorption coefficient, μ, for Mo K radiation is 114.67 cm^{-1}. First, an empirical absorption correction using the φ scan technique was applied after the structure solution. After all of the atoms were located and refined isotropically, the φ scan absorption correction was removed and an absorption correction using the DIFABS program[24] was applied and resulted in the relative transmission factors ranging from 0.86 to 1.20. The data were corrected for Lorentz and polarization effects.

---

(20) Ehrlich, G. M.; Rauch, P. E.; DiSalvo, F. J. *Inorg. Synth.* **1995**, *30*, 1.

(21) Thompson, D. P.; Boudjouk, P. *J. Org. Chem.* **1988**, *53*, 2109.

(22) Scheldrick, G. M. *Crystallographic Computing 3*; Oxford University Press: Oxford, U.K., 1985.

(23) *TEXSAN: Single Crystal Structure Analysis Software*, Version 1.6c; Molecular Structure Corp.: The Woodlands, TX 77381, 1985, 1992.

(24) DIFABS: Walker, N., Stuart, *Acta Crystallogr.* **1983**, *A39*, 158.

Table 2. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) of the Non-Hydrogen Atoms for $[W_6Se_{7.0}Cl_{1.0}(PEt_3)_6][Cl(CHCl_3)_6]$

atom	x	y	z	B_{eq}[a]	pop.
W(1)	0.25912(4)	0.57806(4)	0.11490(3)	1.25(1)	
Se(1)	0.1654(1)	0.6389(1)	0.11776(8)	1.57(4)	0.867(12)
Cl(11)	0.1654	0.6389	0.11776	1.57	0.133(12)
Se(2)	0.3333	0.6667	0.0193(1)	1.63(3)	0.920(6)
Cl(12)	0.3333	0.6667	0.0193	1.63	0.080(6)
Cl(01)	0.0000	0.0000	0.0000	2.3(1)	
Cl(1)	0.1183(3)	0.2364(3)	−0.1218(2)	5.3(1)	
Cl(2)	−0.0176(4)	0.1883(4)	−0.0420(3)	7.5(2)	
Cl(3)	−0.0353(5)	0.0980(4)	−0.1551(3)	8.6(2)	
P(1)	0.1565(2)	0.4604(2)	0.0481(2)	1.68(9)	
C(01)	0.029(1)	0.153(1)	−0.0934(8)	3.3(4)	
C(11)	0.194(1)	0.399(1)	0.0133(7)	2.7(4)	
C(12)	0.261(1)	0.440(1)	−0.0342(8)	3.9(5)	
C(21)	0.121(1)	0.492(1)	−0.0208(7)	3.0(4)	
C(22)	0.060(1)	0.427(1)	−0.0626(8)	4.2(5)	
C(31)	0.067(1)	0.382(1)	0.0893(7)	3.0(4)	
C(32)	0.012(1)	0.412(1)	0.1160(7)	3.8(5)	

[a] $B_{eq} = (8/3)^2[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\alpha + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\gamma]$.

Table 3. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) of the Non-Hydrogen Atoms for $[W_6Se_{6.4}Cl_{1.6}(PEt_3)_6][Cl(CHCl_3)_6]$

atom	x	y	z	B_{eq}[a]	pop.
W(1)	0.25929(3)	0.57841(3)	0.11502(2)	1.71(1)	
Se(1)	0.16576(8)	0.63906(8)	0.11777(5)	2.24(2)	0.778(7)
Cl(11)	0.16576	0.63906	0.11777	2.24	0.222(7)
Se(2)	0.33333	0.66667	0.01946(8)	2.14(2)	0.862(11)
Cl(12)	0.33333	0.66667	0.01946	2.14	0.138(11)
Cl(01)	0.0000	0.0000	0.0000	2.78(8)	
Cl(1)	0.1183(3)	0.2364(2)	−0.1220(2)	6.0(1)	
Cl(2)	−0.0181(3)	0.1888(3)	−0.0416(2)	8.4(2)	
Cl(3)	−0.0352(3)	0.0984(3)	−0.1552(3)	9.1(1)	
P(1)	0.1572(2)	0.4605(2)	0.0480(1)	2.28(7)	
C(01)	0.0275(9)	0.1535(8)	−0.0940(6)	4.6(4)	
C(11)	0.1944(9)	0.3974(8)	0.0147(5)	4.0(4)	
C(12)	0.2613(9)	0.4393(9)	−0.0337(5)	5.2(4)	
C(21)	0.1209(8)	0.4935(8)	−0.0200(5)	3.9(4)	
C(22)	0.0584(9)	0.4242(9)	−0.0636(5)	5.3(4)	
C(31)	0.0663(7)	0.3825(8)	0.0892(5)	3.5(3)	
C(32)	0.0113(8)	0.4130(9)	0.1158(5)	5.4(4)	

[a] $B_{eq} = (8/3)^2[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\alpha + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\gamma]$.

The trigonal space group $R\bar{3}$ was chosen on the basis of systematic absences and intensity statistics. Initial tungsten atom positions were input on the basis of the SHELXS direct methods output. Subsequently, the atomic positions for Se, Cl (from chloroform molecules), P, and C were located directly from the electron density difference maps. After location of those atoms, a large peak (19 e/Å^3) remained at the origin of the unit cell. Consideration of the chemical reactions indicated that a chlorine atom should be tried in that position. After the subsequent refinement cycles, the unweighted and weighted agreement factors dropped from 0.076 and 0.078 to 0.057 and 0.058, respectively. At this point, it was noted that isotropic thermal parameters of the two unique selenium atoms were relatively large. Therefore, two chlorine atoms were introduced at positions identical to those of the two selenium atoms with their total population constrained to unity. The unweighted and weighted agreement factors dropped to 0.054 and 0.052, respectively, after the subsequent refinement cycles. Then all non-hydrogen atoms were refined with anisotropic thermal parameters. Idealized hydrogen positions were calculated and placed in the refinement with C−H distances equal to 1.04 Å, but their parameters were held constant during subsequent cycles. The final cycle of full-matrix least-squares refinement was based on 1577 observed reflections and 123 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.035$ and $R_w = 0.032$, respectively. The final formula from the refinement for this complex was found to be $[W_6Se_{7.04}Cl_{0.96}(PEt_3)_6][Cl(CHCl_3)_6]$. Considering the standard deviation and chemistry, this complex can be formulated as $[W_6Se_{7.0}Cl_{1.0}(PEt_3)_6][Cl(CHCl_3)_6]$. The atomic coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms are given in Table 2.

$[W_6Se_{6.4}Cl_{1.6}(PEt_3)_6][Cl(CHCl_3)_6]$ (2). A dark brown crystal, with dimensions of 0.30 × 0.30 × 0.40 mm^3, was mounted on a glass fiber, and data collection proceeded at −70 °C. Data were collected with a Rigaku AFC6R diffractometer using Mo K radiation, over the range 3° < 20 < 45° in the quarter-sphere ($+h,+k,\pm l$), using the $\omega-2\theta$ scan technique. Three standard reflections were monitored every 200 reflections and showed a 3.89% intensity decrease over the collection period. A total of 6061 reflections were collected, of which 2004 were unique ($R_{int} = 0.060$) and 1335 were observed with $I > 4\sigma(I)$. The linear absorption coefficient for Mo K radiation is 112.32 cm^{-1}. An empirical absorption correction based on azimuthal scans of four reflections was applied and resulted in transmission factors ranging from 0.27 to 1.00. The data were corrected for Lorentz and polarization effects.

The trigonal space group $R\bar{3}$ was chosen on the basis of systematic absences and intensity statistics. Initial tungsten atom positions were input on the basis of the SHELXS direct methods output. Subsequently, the atomic positions for Se, Cl, P, and C were located directly from the electron density difference maps. The unweighted and weighted agreement factors were 0.064 and 0.061, respectively, when every atom was refined with isotropic thermal parameters. At this point, it was noted that isotropic thermal parameters of the two unique selenium atoms were relatively large. Therefore, two chlorine atoms were introduced at positions identical to those of the two selenium atoms with their total population constrained to unity. The unweighted and weighted agreement factors dropped down to 0.060 and 0.056, respectively, after the subsequent refinement cycles. Then all non-hydrogen atoms were refined with anisotropic thermal parameters. Idealized hydrogen positions were calculated and placed in the refinement with C−H distances equal to 1.04 Å, but their parameters were held constant during subsequent cycles. The final cycle of full-matrix least-squares refinement was based on 1335 observed reflections and 123 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.033$ and $R_w = 0.030$, respectively. The final formula for this complex was found to be $[W_6Se_{6.4}Cl_{1.6}(PEt_3)_6][Cl(CHCl_3)_6]$. The atomic coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms are given in Table 3.

Results and Discussion

Preparation of Mixed Chloride−Selenide Complexes. It was found that $W_6Se_8L_6$ is the major product when 1 mol of W_6Cl_{12} reacts with 8 mol, or more, of Na_2Se in amine solvents.[15] In an effort to obtain the partially substituted complexes, such as $W_6Se_{8-x}Cl_xL_6$ ($0 < x < 8$), a series of reactions with differing Na_2Se/W_6Cl_{12} mole ratios (Na_2Se/W_6Cl_{12} = 1, 2, 4, 6, 8) was performed in refluxing piperidine. In general, the starting materials were refluxed in the amine solvent for 3−4 days, then the mixtures were filtered while still hot, and the desired products were obtained from the filtrate as black solids. Without addition of any Na_2Se, W_6Cl_{12} readily dissolved in piperidine to form a dark brown solution and yellow-green solid. On the basis of elemental analyses, this insoluble yellow-green solid was identified as the adduct $(W_6Cl_8)Cl_4{\cdot}2pip$. For reactions where the Na_2Se/W_6Cl_{12} mole ratios were varied over the range 1−6, the major products were soluble and all contained about 42−48% of tungsten and 4−5% of chlorine.

Photoelectron spectra of the black solids from these reactions clearly show two $W4f_{7/2,5/2}$ doublets in variable relative intensity. One component with $W4f_{7/2}$ BE = 30.8 eV clearly corresponds to that of $W_6Se_8(pip)_6$ with increasing relative intensity as the Na_2Se:W_6Cl_{12} mole ratio increased. The other component with $W4f_{7/2}$ BE = 32.8 eV must be associated with the Cl-containing species. Compare $W4f_{7/2}$ BE = 32.4 eV for W_6Cl_{12}. However, the only compound that could be successfully isolated from these mixtures was $W_6Se_8(pip)_6{\cdot}8pip$, identified by single-crystal

X-ray diffraction measurements.[15] We conclude that the substitution of Se for Cl in W_6Cl_{12} must proceed rapidly to W_6Se_8 even in reactions with low $Na_2Se:W_6Cl_{12}$ ratios. Thus, piperidine proved to be a poor reaction medium to promote formation of mixed halide−chalcogenide cluster compounds.

Synthesis of $[W_6Se_{7.0}Cl_{1.0}(PEt_3)_6][Cl(CHCl_3)_6]$ (1). The isolation of the ionic compound, $[W_6Se_{7.0}Cl_{1.0}(PEt_3)_6][Cl(CHCl_3)_6]$, was a surprise. Originally, the neutral phosphine complex, $W_6Se_8(PEt_3)_6$, was expected to form in a manner similar to that of the piperidine and pyridine analogues. Thus, in the presence of triethylphosphine, the reaction between 1 mol of W_6Cl_{12} and 8 mol of Na_2Se in toluene was expected to provide the neutral phosphine complex, $W_6Se_8(PEt_3)_6$. However, after recrystallization of the product from $CHCl_3$ single crystals of the ionic complex, $[W_6Se_{7.0}Cl_{1.0}(PEt_3)_6][Cl(CHCl_3)_6]$, were obtained. Nevertheless, it is possible that the initial material recovered from the toluene reaction filtrate was a mixture of the neutral, $W_6Se_8(PEt_3)_6$, and ionic, $[W_6Se_7Cl(PEt_3)_6]^+$, complexes. In that case, only the ionic complex was crystallized from the chloroform solution.

Although it is still unclear about the mechanism of the formation of this ionic complex, the solvent toluene must play an important role in formation of this mixed chloride−selenide cluster complex. In comparison, for reaction ratios of 1:8 or greater, the substitution reactions conducted in amine solvents, such as pyridine and piperidine, only provided the complete substitution product, $W_6Se_8L_6$.[15] As noted above, even when a lesser amount of Na_2Se was used as a reactant, the neutral complex, $W_6Se_8L_6$, was always identified as one of the products.

Synthesis of $[W_6Se_{6.4}Cl_{1.6}(PEt_3)_6][Cl(CHCl_3)_6]$ (2). In an effort to produce a larger quantity of the ionic complex, $[W_6Se_7Cl(PEt_3)_6]^+$, a similar reaction on a larger scale was conducted. However K_2Se was used rather than Na_2Se. After 3 days, only about 0.25 g of brown powder was recovered from the reaction filtrate, while the majority of materials remained insoluble. In this case recrystallization of the former provided single crystals of $[W_6Se_{6.4}Cl_{1.6}(PEt_3)_6][Cl(CHCl_3)_6]$ instead of $[W_6Se_{7.0}Cl_{1.0}(PEt_3)_6][Cl(CHCl_3)_6]$. It seems apparent that the two ionic species, $[W_6Se_7Cl(PEt_3)_6]^+$ and $[W_6Se_6Cl_2(PEt_3)_6]^+$, cocrystallized in the lattice and resulted in an average composition of $[W_6Se_{6.4}Cl_{1.6}(PEt_3)_6]^+$. The formation of a different composition for crystals from the second preparation suggested that the reaction conditions are crucial for the formation of different compounds. In the second preparation, a different source of selenide was used and the amounts of the starting materials were doubled while keeping a constant reaction time of 3 days. These differences could be important to the occurrence of the less selenium substituted cluster cation, $[W_6Se_6Cl_2(PEt_3)_6]^+$, in the isolated product.

Crystal Structures. The ionic complexes, $[W_6Se_{7.0}Cl_{1.0}(PEt_3)_6][Cl(CHCl_3)_6]$ **(1)** and $[W_6Se_{6.4}Cl_{1.6}(PEt_3)_6][Cl(CHCl_3)_6]$ **(2)**, both crystallize in the trigonal space group $R\bar{3}$ with 3 molecules per unit cell. These two complexes are thus isomorphous. The $[W_6Se_{8-x}Cl_x(PEt_3)_6]^+$ cationic cluster unit is centered on a $\bar{3}$ position (3b site symmetry), with two of the eight face capping atoms on the 3-fold axis. Chlorine and selenium atoms are randomly distributed among the eight bridging positions. Six triethylphosphine molecules were coordinated to the tungsten atoms at terminal positions strongly enough to replace all terminal chloride ions. The anionic unit, $[Cl(CHCl_3)_6]^-$, is centered on another $\bar{3}$ position (3a site symmetry), and the chlorine anion is located at the origin of the unit cell. These positions in the unit cell diagram of $[W_6Se_{8-x}Cl_x(PEt_3)_6][Cl(CHCl_3)_6]$ are shown in Figure 1.

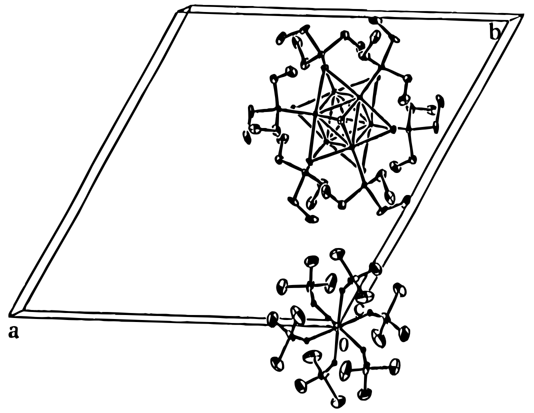

Figure 1. Unit cell of $[W_6Se_7Cl(PEt_3)_6][Cl(CHCl_3)_6]$ depicted with thermal ellipsoids at 35% probability.

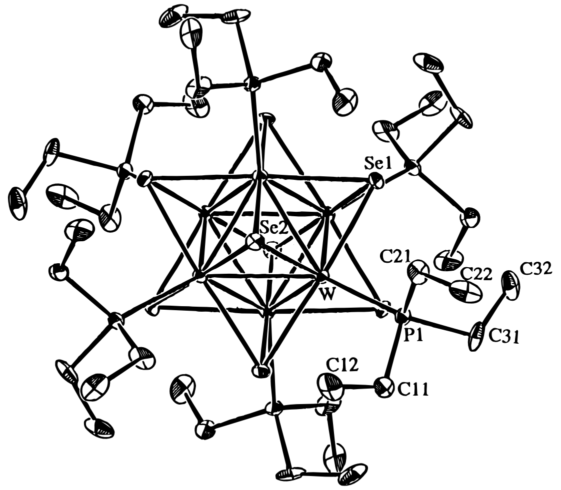

Figure 2. Molecular structure of $[W_6Se_7Cl(PEt_3)_6]^+$. Thermal ellipsoids are shown at 35% probability level. Hydrogen atoms have been omitted for clarity. The atom numbering scheme is the same for $[W_6Se_{6.4}Cl_{1.6}(PEt_3)_6]^+$.

A picture of the cationic unit $[W_6Se_{7.0}Cl_{1.0}(PEt_3)_6]^+$ is shown in Figure 2. Selected bond distances and bond angles within the cluster are listed in Table 4. From this table, it can be seen that the deviations from strict octahedral symmetry are very small. The average bond distances (Å) and maximum deviation are as follows: W−W, 2.699(1) average, 0.001; W−Se(Cl), 2.558(2) average, 0.006; W−P, 2.535(4) average, 0.000. This regular metal octahedron indicates that the cluster unit formally has 20 electrons involved in the metal−metal bonding and is confirmation that $[W_6Se_7Cl(PEt_3)_6]^+$ is the correct formula for this complex. In comparison, $W_6Se_8(py)_6$ has similar W−W bond distances but a slightly longer average W−Se bond distance of 2.578(2) Å than that of the mixed chloride−selenide complex. As expected, the random disorder of a smaller chlorine atom with seven selenium atoms should result in shortening of the average W−Se bond distance.

For the averaged cationic unit in **2**, $[W_6Se_{6.4}Cl_{1.6}(PEt_3)_6]^+$, selected bond distances and bond angles within the cluster are listed in Table 5. The average W−W, W−Se(Cl), and W−P bond distances are 2.691(1), 2.554(2), and 2.537(3) Å, respectively. It is believed that these data arise from a mixture of the 21-electron cluster, $[W_6Se_6Cl_2(PEt_3)_6]^+$, and the 20-electron cluster, $[W_6Se_7C\ l(PEt_3)_6]^+$, in a ratio of 60:40. Therefore, the observed bond distances are the weighted average values of these two types of cluster units. On the basis of Pauling's relation,[25] $d(n) = d(1) - 0.6\log(n)$, the calculated W−W bond distance difference (Δd) between a 20 e cluster and a 21 e cluster

Table 4. Selected Bond Lengths (Å) and Angles (deg) in $[W_6Se_{7.0}Cl_{1.0}(PEt_3)_6][Cl(CHCl_3)_6]^a$

W(1)−W(1A)	2.698(1)	W(1)−Se(1)	2.552(2)
W(1)−W(1C)	2.699(1)	W(1)−Se(2)	2.562(2)
av W−W	2.699(1)	W(1)−Se(1A)	2.562(2)
		W(1)−Se(1B)	2.554(2)
W(1)−P(1)	2.535(4)	av W−Se	2.558(2)
P(1)−C(11)	1.80(2)	C(11)−C(12)	1.50(2)
P(1)−C(21)	1.84(2)	C(21)−C(22)	1.49(2)
P(1)−C(31)	1.82(2)	C(31)−C(32)	1.51(2)
Cl(01)−C(01)	3.33(2)	Cl(01)−H(01)	2.41
W(1A)−W(1)−W(1B)	60.00(3)	W(1)−W(lD)−W(lA)	90.00(2)
W(1A)−W(1)−W(1D)	59.99(2)	W(1A)−W(1B)−W(1C)	90.00(4)
W(1B)−W(1C)−W(1)	60.02(3)		
av W−W−W	60.00(3)	Se(1)−W(1)−Se(1B)	89.98(5)
		Se(1A)−W(1)−Se(1B)	89.77(5)
W(1C)−Se(1)−W(1B)	63.66(5)	Se(1A)−W(1)−Se(2)	89.84(5)
W(1)−Se(1)−W(1B)	63.72(6)	Se(1)−W(1)−Se(2)	90.05(5)
W(1)−Se(1)−W(1C)	63.79(5)	av Se−W−Se	89.91(6)
W(1)−Se(2)−W(1A)	63.58(6)		
av W−Se−W	63.69(6)	Se(2)−W(1)−P(1)	93.4(1)
		Se(1A)−W(1)−P(1)	94.1(1)
Se(1A)−W(1)−Se(1)	175.37(6)	Se(1B)−W(1)−P(1)	91.1(1)
Se(1B)−W(1)−Se(1)	175.54(6)	Se(1)−W(1)−P(1)	90.5(1)
av Se−W−Se	175.46(6)	av Se−W−P	92.2(1)

[a] Equivalent atoms generated by symmetry transformation: A, $1 - y, 1 + x - y, z$; B, $-x + y, 1 - x, z$; C, $y - {}^1/_3, 1/3 - x + y, {}^1/_3 - z$; D, ${}^2/_3 + x - y, {}^1/_3 + x, {}^1/_3 - z$.

Table 5. Selected Bond Lengths (Å) and Angles (deg) in $[W_6Se_{6.4}Cl_{1.6}(PEt_3)_6][Cl(CHCl_3)_6]^a$

W(1)−W(1A)	2.688(1)	W(1)−Se(1)	2.545(2)
W(1)−W(1C)	2.693(1)	W(1)−Se(2)	2.560(2)
av W−W	2.691(1)	W(1)−Se(1A)	2.556(2)
		W(1)−Se(1B)	2.554(2)
W(1)−P(1)	2.537(3)	av W−Se	2.554(2)
P(1)−C(11)	1.81(1)	C(11)−C(12)	1.51(2)
P(1)−C(21)	1.84(1)	C(21)−C(22)	1.56(2)
P(1)−C(31)	1.83(1)	C(31)−C(32)	1.53(2)
Cl(01)−C(01)	3.35(1)	Cl(01)−H(01)	2.42
W(1A)−W(1)−W(1B)	60.00(5)	W(1)−W(lD)−W(lA)	90.00(4)
W(1A)−W(1)−W(1D)	60.06(3)	W(1A)−W(1B)−W(1C)	90.00(4)
W(1B)−W(1C)−W(1)	59.88(3)		
av W−W−W	59.98(4)	Se(1)−W(1)−Se(1B)	90.01(4)
		Se(1A)−W(1)−Se(1B)	89.76(4)
W(1C)−Se(1)−W(1B)	63.61(5)	Se(1A)−W(1)−Se(2)	89.82(4)
W(1)−Se(1)−W(1B)	63.61(4)	Se(1)−W(1)−Se(2)	90.07(4)
W(1)−Se(1)−W(1C)	63.77(5)	av Se−W−Se	89.92(4)
W(1)−Se(2)−W(1A)	63.34(5)		
av W−Se−W	63.58(5)	Se(2)−W(1)−P(1)	93.03(8)
		Se(1A)−W(1)−P(1)	93.69(8)
Se(1A)−W(1)−Se(1)	175.52(4)	Se(1B)−W(1)−P(1)	91.30(8)
Se(1B)−W(1)−Se(2)	175.66(4)	Se(1)−W(1)−P(1)	90.79(8)
av Se−W−Se	175.59(6)	av Se−W−P	92.20(8)

[a] Equivalent atoms generated by symmetry transformation: A, $1 - y, 1 + x - y, z$; B, $-x + y, 1 - x, z$; C, $y - {}^1/_3, {}^1/_3 - x + y, {}^1/_3 - z$; D, ${}^2/_3 + x - y, {}^1/_3 + x, {}^1/_3 - z$.

is 0.013 Å, [$\Delta(d) = 0.6 \log(21/20) = 0.013$ Å]. The fact that the observed average W−W bond distance of 2.691(1) Å for **2** is only 0.008(1) Å shorter than the average W−W distance in **1** is in agreement that the second crystal contained a mixture of 21 and 20 electron clusters.

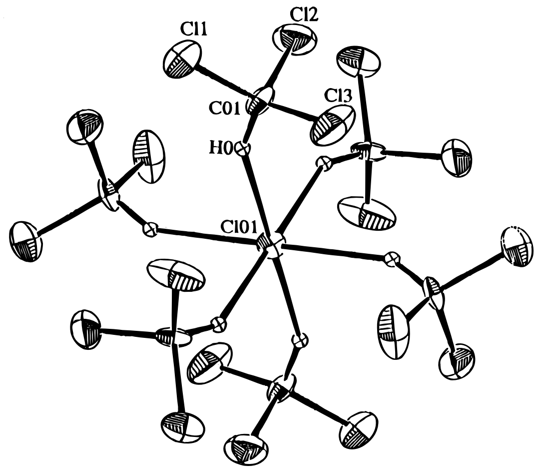

Figure 3. ORTEP drawing of the anion unit $[Cl(CHCl_3)_6]^-$ with thermal ellipsoids at the 35% probability level. H atoms shown have been placed in calculated positions.

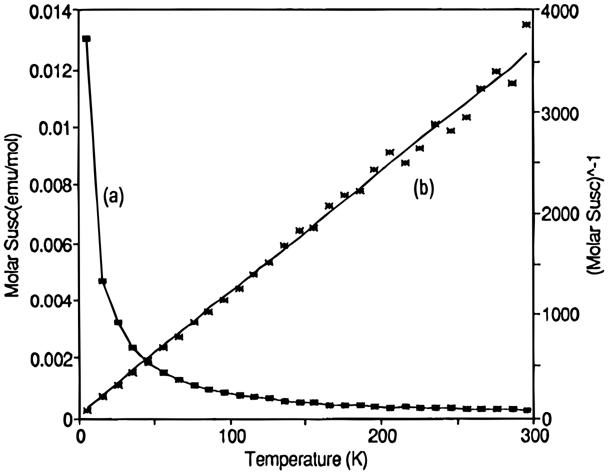

Figure 4. (a) Molar susceptibility versus temperature of $[W_6Se_{6.4}Cl_{1.6}(PEt_3)_6]Cl$. (b) Reciprocal molar susceptibility versus temperature of $[W_6Se_{6.4}Cl_{1.6}(PEt_3)_6]Cl$. The points are experimental data points, and the straight line is the linear regression fitting.

As shown in Figure 3, the interesting and unique $[Cl(CHCl_3)_6]^-$ anion unit exhibits six chloroform solvent molecules octahedrally coordinated to a chloride anion through the hydrogen atoms of the chloroform solvent. The distance between the calculated hydrogen positions and the chloride anion for compounds **1** and **2** are 2.41 and 2.42 Å, respectively. The summation of the ionic radius for Cl^- and the van der Waals radius for H [$r(Cl)_{ion} + r(H)_{VDW} = 1.70 + 1.20 = 2.90$ Å] produces a value that is larger than the experimental value. Also the distance between the chlorine anion and carbon atoms of the chloroform is 3.34(2) Å. The summation of the ionic radius for Cl^- and the van der Waals radius for C, [$r(Cl)_{ion} + r(C)_{VDW} = 1.70 + 1.65 = 3.35$ Å] produces a value that is very close to the experimental value. These results suggest that the chloroform molecules are interacting with the chloride anion through strong hydrogen bonding. However, because the H atom positions are not experimentally established, the bonding interactions between chloride anion and six chloroform molecules in this anion unit are not completely clear. The $[Cl(CHCl_3)_6]^-$ anion is, to our knowledge, the first documented example of a chloride anion octahedrally coordinated with six chlorohydrocarbon molecules.

Magnetic Measurement. The composition of the bulk product recovered from the toluene reaction solution was not established by chemical analysis. In the reaction using K_2Se as source of selenium the composition of the single crystals obtained after recrystallization of a portion of this product was

---

(25) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell Univ. Press: Ithaca, NY, 1960; p 400.

(26) Selwood, P. W. *Magnetochemistry*, 2nd ed.; Interscience Publishers: New York, 1988, p 78.

established as $[W_6Se_{6.4}Cl_{1.6}(PEt_3)_6]Cl$ by the X-ray structure refinement. This composition dictates that both 20-electron $[W_6Se_7Cl(PEt_3)_6]^+$ and 21-electron $[W_6Se_6Cl_2(PEt_3)_6]^+$ cluster cations are present in mole fractions of 0.40 and 0.60, respectively. Thus, magnetic susceptibility measurements to confirm the presence of paramagnetic 21-electron species were conducted. The molar and reciprocal molar susceptibilities for the bulk product recovered from toluene are shown in Figure 4. The data are fit by the Curie−Weiss relationship $X = C(T + \Theta)^{-1} + X_o$ from 6 to 297 K. Thus derived are the values $C = 0.084$ emu·K mol^{-1}, $\Theta = -2.28$ K, and $\mu = 0.82\ \mu_B$. From the moment of 0.82 μ_B we calculate that this bulk sample must contain only 23 mol % of the paramagnetic $[W_6Se_6Cl_2(PEt_3)_6]^+$. The compositions of the bulk product recovered from toluene and the crystals grown from chloroform are thus somewhat different. However, the susceptibility measurements confirm the presence of the paramagnetic 21-electron clusters in this product.

Acknowledgment. We wish to thank James Anderegg for aid with the XP spectra. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, through Ames Laboratory operated by Iowa State University under Contract No. W-7405-Eng-82.

Supporting Information Available: Complete tables of crystallographic data, hydrogen atom coordinates and isotropic thermal parameters, and anisotropic thermal parameters for non-hydrogen atoms (5 pages). Ordering information is given on any current masthead page.

IC970038L