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High-Yield Synthesis of the W_6S_8 Cluster Unit as the Pyridine Complex $(W_6S_8)(py)_6$ and Attempts To Prepare Tungsten Analogues of the Chevrel Phases

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A convenient high-yield synthesis of W_6Cl_{12} has been devised from the reaction of WCl_4 with iron powder at 500 °C. Conversion to $(W_6S_8)(py)_6$, py = pyridine, is effected in essentially quantitative yield by reaction of W_6Cl_{12} with NaSH and NaO-*n*-Bu in 1:12:6 mol ratio in refluxing pyridine (115 °C). Black crystals of the insoluble complex $(W_6S_8)(py)_6$ were grown from pyridine solution in a sealed tube at 200 °C: triclinic, $P\bar{1}$; $a = 9.397(2)$, $b = 11.932(3)$, $c = 10.624(2)$ Å; $\alpha = 114.28(1)$, $\beta = 108.88(1)$, $\gamma = 91.19(2)°$; $Z = 1$; R $(R_w) = 0.0267$ (0.0359). The average bond distances in the cluster molecule, W−W = 2.6617(2), W−S = 2.458(3), and W−N = 2.255(5) Å, are similar to those in $Mo_6S_8(py)_6$. IR spectra show strong bands at 378 cm^{-1}, attributable to the T_{1u} W−S stretching modes, and 232 cm^{-1} of uncertain assignment. Several unsuccessful approaches to deligation of $(W_6S_8)(py)_6$, in efforts to prepare W_6S_8 and $M_xW_6S_8$ analogs of the Chevrel phases, are discussed. Sulfidation of W_6Cl_{12} with variable ratios of NaSH and NaO-*n*-Bu provided evidence for materials with mixed sulfide−chloride cluster units of average composition $[(W_6Cl_6S_2)Cl_2(py)_4]\cdot 5py$ and $(W_6Cl_2S_6)(py)_6$.

Introduction

The chemistry of the ternary molybdenum chalcogenide (Chevrel) phases, $M_xMo_6X_8$ (X = S, Se, or Te), has been well-developed.[1] These phases are especially well-known for their superconducting properties.[2] The essential structural elements in these compounds are the Mo_6X_8 units with octahedral Mo clusters which have a variable electron population of 20−24 electrons in Mo−Mo bonding orbitals.[1b,3] Because these compounds are almost always prepared at high temperatures, there is little doubt that they are the thermodynamically favored phases.

In contrast to the plethora of these molybdenum compounds, there presently is no reported example of their tungsten analogues, $M_xW_6X_8$ (X = S, Se, or Te). Because they are not formed in high-temperature preparative attempts, the $M_xW_6X_8$ phases must be unstable toward formation of alternate phases, e.g. by disproportionation. Thus the metastable phases may exist only at lower temperatures where thermodynamic equilibrium can be kinetically denied. We thus initiated research toward preparation of these tungsten analogues at low temperatures through molecular precursors. The conversion of W_6Cl_{12}, which contains the $W_6Cl_8^{4+}$ cluster unit, by sulfide substitution was developed as reported here. While this work was in progress the papers by Saito *et al.* appeared, where a low-yield synthesis of $W_6S_8(PEt_3)_6$ via "reductive dimerization" of a complex formed between $W_3S_7Cl_4$ and triethylphosphine was reported,[4] following the earlier related preparation of $Mo_6X_8(PEt_3)_6$ and $(PPN)[Mo_6X_8(PEt_3)_6]$ (X = S, Se; PPN = $(Ph_3P)_2N$) by analogous procedures.[5] A convenient synthesis of W_6Cl_{12} has also been developed and is presented here.

Experimental Section

Reagents. WCl_6 was separated from more volatile oxyhalide impurities by sublimation at 160 °C in a sealed, evacuated Pyrex tube. The red and yellow oxyhalide compounds deposited in a region farther from the heated zone than the WCl_6 which deposited as blue-black needles. WCl_4 was prepared from WCl_6 by stoichiometric reduction with $W(CO)_6$ in refluxing chlorobenzene.[6] Volatile impurities, e.g. WCl_5 or $WOCl_4$, were removed from WCl_4 *in vacuo* by heating the latter to 250 °C overnight. Organic solvents were dried and distilled *in vacuo* or under nitrogen. NaSH was prepared by the method of Brauer.[7] NaO-*n*-Bu was prepared by adding pieces of Na to *n*-BuOH and recovery of the Na-O-*n*-Bu by vacuum removal of solvent. All other reagents were used as received.

Preparation of W_6Cl_{12}. In a typical reaction, 7.3 g of WCl_4 (0.022 mol) and 1.26 g of Fe (0.023 mol) were loaded into a Pyrex tube, which was subsequently evacuated, sealed, and placed in a horizontal tube furnace. The temperature was then raised slowly to 500 °C and held for 3 days. Upon cooling, the tube was removed and adjusted so that the sample remained in the furnace but the opposite end projected out of the furnace. The sample was then held at 450 °C for several hours so that volatile products were condensed in the cooler zone. A good yield of W_6Cl_{12} was indicated by the presence of a pale yellow powder left as the product in the hot zone. The tube was then broken in air and the product from the hot end dissolved in *ca.* 200 mL of 6 M HCl together with a small volume of ethanol. Anhydrous W_6Cl_{12} was then prepared from the $(H_3O)_2W_6Cl_{14}\cdot nH_2O$ crystallized from this solution by a procedure previously described.[8]

A temperature of 325 °C was used during thermal decomposition of the acid salt. A 60% yield of pale yellow powder, based on the amount of WCl_4 used, was achieved in the best reactions. This material was often pyrophoric and amorphous to X-ray diffraction. Anal. Calcd for W_6Cl_{12}: W, 72.2; Cl, 27.8. Found: W, 70.1; Cl, 27.6. IR (Nujol): 323 (vs, b) [ν(W−Cl)], 233(m) cm^{-1}.

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Synthesis of $(W_6S_8)(py)_6$. In a typical reaction, a mixture of W_6Cl_{12} (1.67 g, 1.09 mmol), NaSH (0.73 g, 13.0 mmol), and NaO-*n*-Bu (0.65 g, 6.77 mmol) was refluxed in pyridine for 2 days. In this case, filtration gave a nearly colorless filtrate essentially devoid of products. The insoluble dark solid was exhaustively extracted with methanol to remove NaCl and thus provide the dark red powder corresponding to $(W_6S_8)(py)_6$. Anal. Calcd: W, 60.2; S, 14.0; N, 4.58; C, 19.64; H, 1.65. Found: W, 60.0; S, 13.0; N, 4.36; C, 19.03; H, 1.70. A test for Cl was negative. Far-IR (Nujol): 634(w), 435(w), 378(vs), 231(s) cm^{-1}. Single crystals of this relatively insoluble compound were grown from pyridine by heating 0.1 g of the red powder in pyridine in a sealed Pyrex tube at 200 °C for 5 days, with the tube about one-fourth filled. (*Caution! High pressure!*) After slow cooling (*ca.* 10 deg h^{-1}), black crystals were attached to the walls of the tube just above the surface of the nearby colorless liquid. The major portion of the material remained as a black, finely crystalline powder at the bottom of the tube. This crystalline material is decomposed only slowly in air.

Other Reactions between W_6Cl_{12} and NaSH in Pyridine. In efforts to isolate mixed sulfide chloride clusters $(W_6Cl_{8-x}S_x)Cl_{4-x}$ reactions with W_6Cl_{12}, NaSH, and NaO-*n*-Bu in various mole ratios in refluxing pyridine were conducted. These are summarized below, with the mole ratios given for the reactants in the above order.

1:2:0 for 1 Day. Only a dark yellow, pyridine-soluble solid was recovered. IR bands at 637(w), 608(w), 406(vw), 306(vs), and 227(m) cm^{-1} corresponded to those of $[(W_6Cl_8)Cl_4(py)_2]\cdot n$py. Treatment with 1 M HCl in methanol yielded $(pyH)_2[(W_6Cl_8)Cl_6]$. Anal. Calcd: Cl, 28.2. Found: Cl, 28.0.

1:6:0 for 4 Days. After removal of some insoluble brown solid, the solution yielded a dark solid on removal of solvent. Anal. Calcd for $[W_6Cl_6S_2)Cl_2(py)_4]\cdot 5py$: W, 51.0; Cl, 13.1. Found: W, 51.5; Cl, 13.3. Far-IR: 637(vw), 608(m), 432(w), 399(m), 310(sh), 284(vs), 218(w) cm^{-1}.

1:8:0 for 3 Days. The major product as a red solid was filtered off and extracted with MeOH to remove NaCl. Anal. Calcd for $(W_6S_{6.3}Cl_{1.7})(py)_6$: W, 60.0; Cl, 3.3. Found: W, 58.9; Cl, 3.3. Far-IR: 634(w), 460(s,b), 434(w), 379(s), 300(w), 232(m) cm^{-1}. A small amount of red pyridine-soluble product corresponded to $[(W_6Cl_6S_2)Cl_2(py)_4]\cdot 5py$, as in the 1:6:0 reaction.

1:8:4 for 5 Days. After filtration and extraction with MeOH to remove NaCl, the red, insoluble product corresponding to $(W_6S_6Cl_2)(py)_6$ was obtained.

Thermal Decomposition of $(W_6S_8)(py)_6$. Samples of this compound were subjected to thermal treatment *in vacuo* at several temperatures. In a typical case, a portion of $(W_6S_8)(py)_6$ was placed in a Pyrex (or fused silica) ampule with joints for connection to the vacuum manifold. The ampule was then heated at constant temperature with a furnace for 12 h under working vacuum to remove pyridine and other volatiles to a cold trap. Experiments were conducted at 250, 300, and 640 °C. In all cases, the residue was a black solid for which tungsten analyses gave the following percentages: 69.1 (250 °C), 74.7 (300 °C), and 79.0 (640 °C), corresponding to $(W_6S_8)(py)_n$ with $n = 3$, 1.5, and 0.5, respectively. Infrared spectra also were obtained (Nujol mull).

Other Reactions. Reactions of $(W_6S_8)(py)_6$ with powdered lead (1:1 mole ratio) at 250 °C (1 day) and 350 °C (2 days) *in vacuo* and with zinc and $ZnCl_2$ (>1 mol of each/mol of sample) at 200 °C (1 day) *in vacuo* were conducted. Infrared spectra of the black powders indicated partial retention of pyridine ligands in each of these products, and the metal reducing agents appeared to remain essentially unchanged.

A reaction of $(W_6S_8)(py)_6$ with $AlCl_3$ (1:6 mole ratio) in a sealed Pyrex ampule was conducted at 225 °C for 5 days. The ampule was then adjusted so that the products could be held at 200 °C in one end, while the other end of the ampule was kept at room temperature. The white $AlCl_3\cdot py$ and excess $AlCl_3$ were thus sublimed away from the black residue. An IR spectrum of the residue showed a broad band at 400 cm^{-1} and weak bands of residual pyridine in the range 650–1600 cm^{-1}.

Two reactions of $(W_6S_8)(py)_6$ with CF_3SO_3H were conducted, one in acetonitrile and the other in methanol. For the first, 0.50 g (0.27 mmol) of $(W_6S_8)(py)_6$ was loaded into a 100 mL flask in the drybox. Subsequently, 50 mL of acetonitrile was transferred to the flask and the mixture stirred under nitrogen for several hours. The liquid remained colorless. Then 0.30 mL of CF_3SO_3H (>6 mol/mol of sample) was added by syringe, whereupon the solid dissolved and gave a dark green-yellow solution. No further change could be discerned after stirring this solution for several hours. Filtration showed that all of the solid had dissolved. Efforts to obtain crystals or solid from this solution provided only oily residues.

Table 1. Crystallographic Data for $(W_6S_8)(py)_6$

chem formula	$(W_6S_8)(C_5H_5N)_6$	space group	$P\bar{1}$
fw	1834.30	Z	1
a, Å	9.397(2)	ϱ(calc), g cm^{-3}	3.02
b, Å	11.932(3)	μ(Mo Kα), cm^{-1}	178.04
c, Å	10.624(2)	λ(Mo Kα), Å	0.710 73
α, deg	114.28(1)	T, °C	−70
β, deg	108.88(1)	$R(F)^a$	0.0267
γ, deg	91.19(2)	$R_w(F)^b$	0.0359
V, $Å^3$	1010.9(4)		

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

In the second reaction with CF_3SO_3H, 0.44 g (0.24 mmol) of $(W_6S_8)(py)_6$ was added to a 100 mL flask and 20 mL of methanol transferred by distillation. Then, with stirring, 0.13 mL of CF_3SO_3H was added. With continued stirring at room temperature, no evidence of reaction could be seen. The mixture was then brought to reflux for 2 days. Upon cooling, 0.34 g of a black solid was separated from the dark green solution by filtration and drying. Anal. Found: W, 66.4. Subsequently, this black solid was refluxed with pyridine for 2 days, and the mixture was filtered to provide a black solid and yellow filtrate. The latter provided a dark yellow solid upon removal of the solvent.

Physical Measurements. IR spectra were obtained on a IBM-IR/98-FT spectrometer. Samples prepared as Nujol mulls and pressed between CsI plates in the drybox were transferred to the sample chamber which was purged with dry nitrogen. Spectra were recorded separately over the ranges 600–4000 and 200–650 cm^{-1}. Magnetic susceptibility measurements were made on a Quantum Design SQUID magnetosusceptometer system, with samples sealed in fused silica tubes of 3 mm inside diameter and pressed between fused silica rods of 3 mm uniform outside diameter which fit inside the silica tubes.

X-ray Structure Determination. Single crystals of $(W_6S_8)(py)_6$ were grown from pyridine at 200 °C as described in the synthesis section. A black crystal of dimensions 0.2 × 0.1 × 0.1 mm^3 was mounted on a glass fiber and immediately transferred to the diffractometer in a cold stream of N_2 at −70 °C. Data were collected with an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation, over the range $4° < 2\theta < 55°$ using the $\theta-2\theta$ scan technique. Three standard reflections were monitored every 300 reflections and showed no intensity variation over the collection period. A total of 4621 unique reflections were collected, 3754 of which were counted as observed with $F_o^2 > 3\sigma(F_o^2)$. With an absorption coefficient for Mo Kα radiation of $\mu = 178.04$ cm^{-1}, an empirical absorption correction was applied using the ψ scan technique.

Twenty-five orientation reflections were automatically indexed to triclinic symmetry and used to determine the lattice parameters given in Table 1. Because these lattice parameters were very close to those of $Mo_6S_{6\pm x}Cl_{2\mp x}$,[9] the positional parameters for the Mo atoms of the latter were used as input for the W atom positions in an initial refinement in the space group $P\bar{1}$ with the CAD4-SDP program.[10] An R factor of <0.10 resulted after four cycles. Positional parameters for the other non-hydrogen atoms were derived from Fourier synthesis maps and subsequently refined anisotropically to residuals of $R = 0.034$, $R_w = 0.042$. Idealized H positions were calculated and put into the refinement, but their parameters were held constant during subsequent cycles. The final cycle of refinement reduced the residuals to $R = 0.0267$, $R_w = 0.0359$. The final electron density difference map showed the largest peak of 2.33 e $Å^{-3}$ and several peaks over 1.0 e $Å^{-3}$ located close to the W atom, all considered as artifacts caused by Fourier series termination errors. The crystallographic data are given in Table 1, positional parameters and isotropic equivalent temperature factors in Table 2, and important bond distances and bond angles in Table 3.

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Table 2. Positional Parameters and Equivalent-Isotropic Thermal Parameters (Å^2) of Non-Hydrogen Atoms for $(W_6S_8)(py)_6$

atom	*x*	*y*	*z*	B_{eq}[a]
W(1)	0.55952(3)	0.62566(2)	0.45353(3)	1.111(5)
W(2)	0.41813(3)	0.61419(2)	0.62958(3)	1.036(5)
W(3)	0.68993(3)	0.54498(2)	0.65627(3)	1.069(5)
S(1)	0.8035(2)	0.5530(2)	0.4807(2)	1.46(3)
S(2)	0.4552(2)	0.4663(2)	0.1919(2)	1.53(3)
S(3)	0.6556(2)	0.7625(1)	0.7230(2)	1.57 (3)
S(4)	0.3042(2)	0.6792(1)	0.4336(2)	1.65 (3)
N(1)	0.6346(7)	0.7770(5)	0.4004(6)	2.0(1)
N(2)	0.3137(6)	0.7524(5)	0.7778(6)	1.8(1)
N(3)	0.9172(6)	0.5944(5)	0.8406(6)	1.7(1)
C(1)	0.669(1)	0.7528(8)	0.281(1)	4.0(2)
C(2)	0.719(1)	0.844(1)	0.248(1)	5.3(3)
C(3)	0.736(1)	0.9692(9)	0.347(1)	5.8(3)
C(4)	0.693(2)	0.9944(9)	0.465(1)	7.2(4)
C(5)	0.646(1)	0.8966(8)	0.488(1)	4.9(3)
C(6)	0.1641(7)	0.7581(6)	0.7266(8)	1.8(2)
C(7)	0.0965(8)	0.8402(8)	0.8152(9)	2.9(2)
C(8)	0.1815(9)	0.9223(8)	0.957(1)	3.4(2)
C(9)	0.3351(9)	0.9185(9)	1.012(1)	3.4(2)
C(10)	0.3955(8)	0.8317(7)	0.9186(8)	2.3(2)
C(11)	1.0411(8)	0.5500(7)	0.8148(8)	2.3(2)
C(12)	1.1820(8)	0.5816(7)	0.9258(9)	2.5(2)
C(13)	1.1989(9)	0.6540(8)	1.0686(8)	2.7(2)
C(14)	1.074(1)	0.6989(9)	1.0992(9)	3.1(2)
C(15)	0.9354(8)	0.6679(8)	0.9823(8)	2.6(2)

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

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) in $(W_6S_8)(py)_6$

W(1)–W(2)	2.6634(4)	W(1)–S(1)	2.440(2)
W(1)–W(2′)	2.6610(4)	W(1)–S(2)	2.473(1)
W(1)–W(3)	2.6671(4)	W(1)–S(3)	2.469(2)
W(1)–W(3′)	2.6608(3)	W(1)–S(4)	2.461(2)
W(2)–W(3)	2.6641(4)	W(2)–S(1′)	2.453(2)
W(2)–W(3′)	2.6536(3)	W(2)–S(2′)	2.453(2)
av W–W	2.6617(2)	W(2)–S(3)	2.461(2)
		W(2)–S(4)	2.450(2)
W(1)–N(1)	2.263(8)	W(3)–S(1)	2.462(2)
W(2)–N(2)	2.257(6)		
		W(3)–S(2′)	2.465(2)
W(3)–N(3)	2.244(5)	W(3)–S(3)	2.452(2)
av W–N	2.255(5)	W(3)–S(4′)	2.452(2)
		av W–S	2.458(3)
W(2)–W(1)–W(3)	59.97(1)	S(1)–W(1)–S(2)	89.42(5)
W(2)–W(1)–W(3′)	59.79(1)	S(1)–W(1)–S(3)	89.64(5)
W(2′)–W(1)–W(3)	59.741(9)	S(2)–W(1)–S(4)	90.17(5)
W(2′)–W(1)–W(3′)	60.080(9)	S(3)–W(1)–S(4)	89.86(5)
W(1)–W(2)–W(3)	60.08(1)	S(1′)–W(2)–S(2′)	89.56(6)
W(1)–W(2)–W(3′)	60.06(1)	S(1′)–W(2)–S(4)	90.31(6)
W(1′)–W(2)- W(3)	59.956(9)	S(2′)–W(2)–S(3)	89.07(6)
W(1′)–W(2)–W(3′)	60.245(9)	S(3)–W(2)–S(4)	90.31(6)
W(1)–W(3)–W(2)	59.94(1)	S(1)–W(3)–S(3)	89.52(7)
W(1)–W(3)–W(2′)	60.104(9)	S(1)–W(3)–S(4′)	90.08(6)
W(1′)–W(3)–W(2)	59.964(9)	S(2′)–W(3)–S(3)	89.00(7)
W(1′)–W(3)–W(2′)	60.15(1)	S(2′)–W(3)–S(4′)	90.58(7)
av W–W–W	60.01	av S–W–S	89.79
W(1)–S(1)–W(2′)	65.89(4)	S(1)–W(1)–N(1)	92.5(2)
W(l)–S(1)–W(3)	65.94(5)	S(2)–W(1)–N(1)	94.3(1)
W(2′)–S(1)–W(3)	65.36(5)	S(3)–W(1)–N(1)	93.3(1)
W(1)–S(2)–W(2′)	65.40(4)	S(4)–W(1)–N(1)	94.4(2)
W(1)–S(2)–W(3′)	65.22(4)	S(1′)–W(2)- N(2)	93.0(1)
W(2′)–S(2)–W(3′)	65.60(5)	S(2′)–W(2)–N(2)	95.1(2)
W(1)–S(3)–W(2)	65.40(3)	S(3)–W(2)–N(2)	94.0(1)
W(1)–S(3)–W(3)	65.63(4)	S(4)–W(2)–N(2)	91.0(2)
W(2)–S(3)–W(3)	65.67(4)	S(1)–W(3)–N(3)	93.6(2)
W(1)–S(4)–W(2)	65.67(5)	S(2′)–W(3)–N(3)	93.6(2)
W(1)- S(4)–W(3′)	65.58(4)	S(3)–W(3)–N(3)	94.5(2)
W(2)–S(4)–W(3′)	65.55(5)	S(4′)–W(3)–N(3)	92.1(2)
av W–S–W	65.58	av S–W–N	93.5
W(2)–W(1)–W(2′)	89.78(1)	S(1)–W(1)–S(4)	173.09(7)
W(3)–W(1)- W(3′)	89.86(1)	S(2)–W(l)–S(3)	172.42(7)
W(1)–W(2)–W(1′)	90.22(1)	S(1′)–W(2)–S(3)	172.98(6)
W(3)–W(2)–W(3′)	90.08(1)	S(2′)–W(2)–S(4)	173.83(6)
W(1)–W(3)–W(1′)	90.14(1)	S(1)–W(3)–S(2′)	172.77(5)
W(2)–W(3)–W(2′)	89.923(9)	S(3)–W(3)–S(4′)	173.44(5)
av W–W–W	90.00	av S–W–S	173.09

Results and Discussion

Synthesis of W_6Cl_{12}. A convenient, high-yield synthesis of W_6Cl_{12} has been sought since the earliest work by Hill.[11] Many have worked on this problem with varying degrees of success.[12–16] Because larger quantities were desired for conversion to $W_6S_8L_6$ derivatives, a synthesis involving little danger of excessive pressures, reduction of higher halide at a sufficiently low temperature to make use of Pyrex glass practical, and attainment of yields >50% was sought. The synthesis devised here resulted from a study of the metallic reducing agents, including Mg, Zn, Sn, and Fe, acting on WCl_4 in sealed tubes at elevated temperatures. In contrast to Al, which generates high pressures of $AlCl_3$,[15,16] and W, which requires temperatures above 700 °C,[14] these elements were thought to be sufficiently active and to generate MCl_2 products which are sufficiently nonvolatile that these problems could be avoided. However, only powdered Fe gave good yields of W_6Cl_{12} under the desired conditions. Reductions in the stoichiometry of eq 1 in sealed Pyrex tubes

$$6WCl_4(s,g) + 6Fe(s) = W_6Cl_{12}(s) + 6FeCl_2(s) \tag{1}$$

at 500 °C for 3 days consistently gave yields of 50–60% with due attention to maintaining high purity of the starting materials. Reactions continued for more than 3 days did not improve yields. The preliminary synthesis of WCl_4 by reduction with $W(CO)_6$ in refluxing chlorobenzene according to eq 2,[6] which

$$2WCl_6 + W(CO)_6 = 3WCl_4 + 6CO \tag{2}$$

is essentially quantitative in production of WCl_4, means that total conversion of WCl_6 to W_6Cl_{12} is quite high. The separation of W_6Cl_{12} from Fe and $FeCl_2$, after completion of the initial reduction reaction, is facilitated by the easy solubility of all products in 6 M HCl and the easy crystallization of $(H_3O)_2W_6Cl_{14}{\cdot}nH_2O$ from these solutions after reduction of volume. A final step of decomposing this acid salt *in vacuo* at 300–350 °C gives W_6Cl_{12} as an amorphous, yellow to greenish yellow powder. It is air-sensitive, indeed often pyrophoric, and must be handled only under inert atmosphere. When desired, a product of improved purity can be prepared by crystallizing the chloro acid salt from 6 M HCl a second time prior to its conversion to W_6Cl_{12}.

Sulfidation Reactions and Synthesis of $(W_6S_8)(py)_6$. Although the primary goal here was the preparation of the W_6S_8 cluster complex, the possibility of isolating members of the mixed chloride–sulfide series $(W_6Cl_{8-x}S_x)Cl_{4-x}L_{2+x}$ and $(W_6Cl_{4-x}S_x)L_6$ with $1 \le x \le 4$ was also investigated. Pyridine was used as both a solvent with sufficiently high boiling point to conveniently promote the reactions at reflux (115 °C) and a good ligand for binding the terminal positions of the W_6X_8 cluster unit, thus solubilizing the cluster complexes. Previous investigation of the substitution of sulfide into the cluster unit of $(Mo_6Cl_8)Cl_4$ has shown that NaSH in pyridine or pyridine–*n*-butanol mixtures, especially when used in combination with

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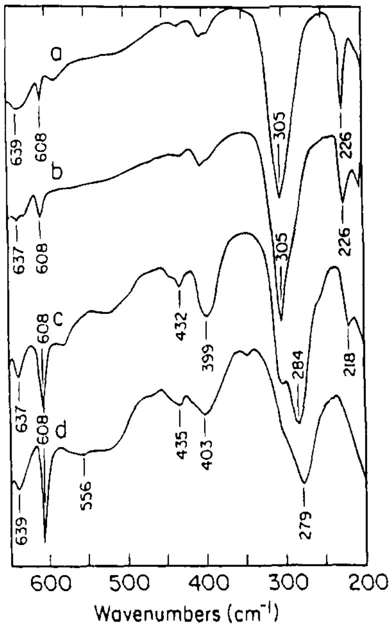

Figure 1. Comparison of the far-infrared spectra of (a) the pyridine adduct of W_6Cl_{12} and the soluble products of (b) the 1:2:0 reaction, (c) the 1:6:0 reaction, and d the (1:8:0) reaction.

NaO-*n*-Bu as a deprotonating agent, is an efficient combination for generation of $(Mo_6S_8)(py)_x$[17] or $(Mo_6Cl_{4-x}S_x)(py)_y$[18] complexes.

For preparation of $(W_6S_8)(py)_6$ the expected overall reaction is given in eq 3. Insolubility of NaCl in pyridine must enhance

$$W_6Cl_{12} + 8NaSH + 4NaOBu + 6py = (W_6S_8)(py)_6 + 12NaCl + 4BuOH + 2H_2 \quad (3)$$

the reaction. Unfortunately, the product $(W_6S_8)(py)_6$ is also insoluble and a prolonged extraction of the NaCl with methanol is necessary to obtain a pure product. However, the conversion of W_6Cl_{12} is essentially quantitative in one step when an excess of NaSH and NaOBu is used (1:12:6 reaction). In contrast to the behavior of the same system for conversion of Mo_6Cl_{12}, where an amorphous ligand-deficient material $(Mo_6S_8)(py)_x$ (with $x < 6$) is obtained, stoichiometric $(W_6S_8)(py)_6$ results from this procedure as a microcrystalline, red precipitate. Growth of single crystals large enough for X-ray diffraction structure determination was difficult and required temperatures in pyridine near the limit for safe handling of the sealed tubes and for stability of the complex. The structure shows that indeed the complex is a neutral molecule $(W_6S_8)(py)_6$ with all six terminal coordination sites occupied by pyridine donors. It is not obvious why such a complex should be so insoluble in pyridine; it is also insoluble in most other organic solvents with which it does not react.

Efforts to prepare mixed chloride−sulfide derivatives were less successful. At a ratio of 1:2 the reaction of W_6Cl_{12} with NaSH in pyridine yields no identifiable product analogous to the $(Mo_6SCl_7)^{3+}$ cluster unit derived in the related reaction of Mo_6Cl_{12}.[19] With increasing amounts of NaSH the 1:6:0 and 1:8:0 reactions provided the soluble product formulated as $[(W_6Cl_6S_2)Cl_2(py)_4]\cdot5py$. Growth of the IR bands at 284 and 399 cm⁻¹, shown in Figure 1, reflects the presence of the W−S bonds. On the basis of analytical data, the insoluble product from these reactions corresponds to a mixture of $(W_6S_6Cl_2)(py)_6$ and $(W_6S_7Cl)(py)_6$. The spectra shown in Figure 2 show a weak band at about 300 cm⁻¹ indicative of W−Cl stretching in addition to the stronger band at about 380 cm⁻¹ for W−S stretching. In the absence of NaOBu, higher amounts of NaSH lead to some decomposition of the cluster. In the 1:8:0 reaction this is evidenced by the broad, strong band at 460 cm⁻¹ in the

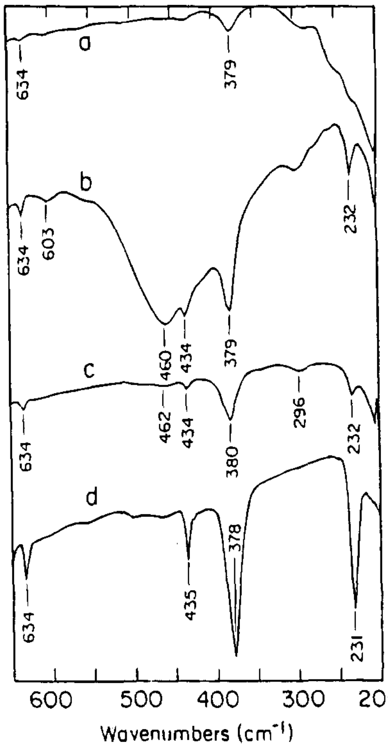

Figure 2. Far-infrared spectra of insoluble products of (a) the 1:2:0 reaction, (b) the 1:8:0 reaction, (c) the 1:8:4 reaction, and (d) the 1:12:6 reaction containing essentially pure $(W_6S_8)(py)_6$.

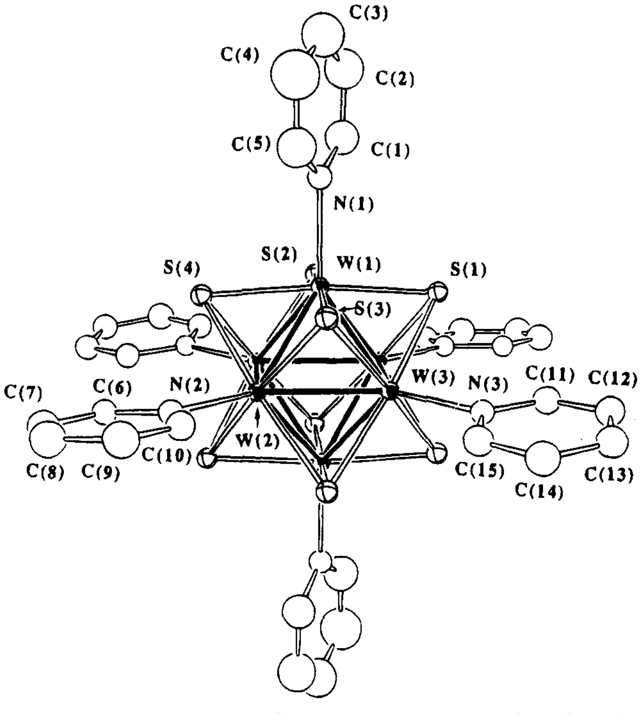

Figure 3. ORTEP drawing of the molecular structure of $(W_6S_8)(py)_6$. Thermal ellipsoids represent the 50% probability level. H atoms are omitted for clarity.

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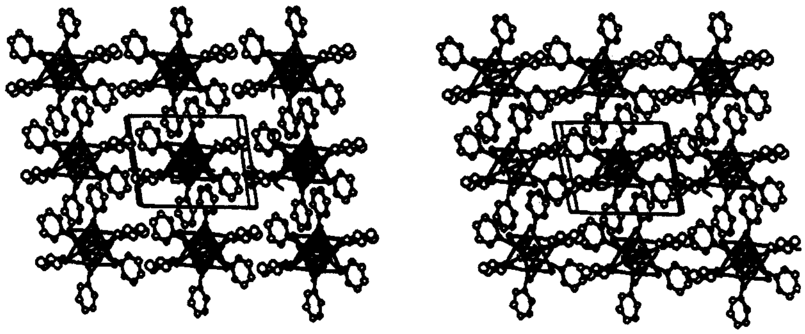

Figure 4. Stereographic view down the *c* axis of $(W_6S_8)(py)_6$ showing the packing of cluster molecules and interleaving of pyridine rings on neighboring molecules.

IR spectra, Figure 2b. The band at 460 cm^{-1} is indicative of the formation of WS_2 resulting from oxidation of the cluster by NaSH.

Structure of $(W_6S_8)(py)_6$. The structure consists of discrete molecules located on inversion centers in the simple unit cell with $Z = 1$. As shown in Figure 3, the central octahedral cluster of six W atoms is capped on its faces with eight S atoms, each triply bridging to three adjacent W atoms. These atoms thus compose the inner cluster positions. The outer or terminal positions, one on each W atom, are occupied by the pyridine ligands bound through the donor N atoms. The molecules are packed efficiently so that the pyridine rings of adjacent molecules interleave as shown in Figure 4.

Although only $\bar{1}$ symmetry is imposed, the cluster is quite regular. From the bond distances and angles in Table 3, it can be seen that the deviations from strict octahedral symmetry are quite small. The maximum deviations from the average bond distances (Å) are as follows: W–W, 2.6617(2) average, 0.0081; W–S, 2.458(3) average, 0.015; and W–N, 2.255(5) average, 0.011. The average W–W bond distance is close to that expected for a 20-electron cluster with average bond order of 20/24 = 0.833. On the basis of a single bond distance of 2.630 Å and Pauling's relation,[20] $d(n) = d(1) - 0.6 \log n$, the calculated W–W distance for $n = 0.833$ is 2.677 Å, only 0.015 Å longer than observed. The average W–W distance of 2.6617(2) Å compares with that of 2.679 Å for the isoelectronic $(W_6S_8)(PEt_3)_6$, the only other known derivative of this cluster unit.[4] As expected, this distance is longer than that for a 24-electron cluster, e.g. 2.626 Å in $(W_6Cl_8)Cl_4(PBu_3)_2$[21] and 2.607 Å in $(Bu_4N)_2\ W_6Cl_{14}$.[22]

The average W–S distance of 2.458(3) Å here compares with 2.458 Å in $(W_6S_8)(PEt_3)_6$, showing that the W–S distances are not very sensitive to change of the terminal ligands. In order to obtain a value for the covalent radius of W toward the nonmetallic atoms, we subtract the Pauling radius of S, $r(S) = 1.05$ Å, from the average W–S distance and obtain $r(W) = 1.41$ Å. Applying the latter to estimate W–N (bond order = 1), we derive $r(W) + r(N) = 1.41 + 0.70 = 2.11$ Å. The average observed W–N distance is 2.255 Å, corresponding to a low bond order of *ca.* 0.56. The same consideration applied to $(W_6S_8)(PEt_3)_6$, $d(W-P)_{obs} = 2.52$ Å and $d(W-P)_{calc} = 2.51$ Å, indicates the W–P bonds from PEt_3 are normal with bond order 1.0. Thus the N-donor ligand here definitely bonds more weakly to the cluster. Subsequent work[23] has shown that pyridine is easily displaced by PEt_3, but the reverse reaction does not occur to a detectable extent under reflux in liquid pyridine. A similar chemistry has developed for the corresponding Mo compounds.[17]

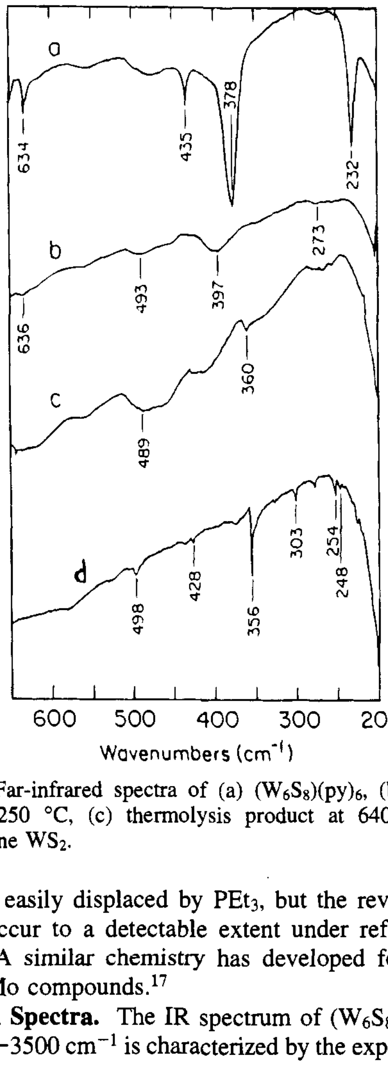

Figure 5. Far-infrared spectra of (a) $(W_6S_8)(py)_6$, (b) thermolysis product at 250 °C, (c) thermolysis product at 640 °C, and (d) polycrystalline WS_2.

Infrared Spectra. The IR spectrum of $(W_6S_8)(py)_6$ in the region 650–3500 cm^{-1} is characterized by the expected bands[24] arising from coordinated pyridine (with strong bands observed at 1597, 1213, 1148, 1067, 1040, 756, and 687 cm^{-1}). It is in the low-frequency region where distinctive vibrations of the cluster occur. The spectrum shown in Figure 2d for $(W_6S_8)(py)_6$ exhibits strong bands at 634, 435, 378, and 231 cm^{-1}. The bands at 634 and 435 cm^{-1} arise from torsional modes of the coordinated pyridine ligands. The strongest band at 378 cm^{-1} arises from the IR-allowed T_{1u} W–S stretching modes of the W_6S_8 unit. The occurrence of only one band in this region reflects the effective O_h symmetry of the cluster complex. The second band at 231 cm^{-1} must arise from another set of T_{1u} modes involving either W–W or W–N stretching or W–S

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bending vibrations, but the assignment here is uncertain. The strong band at 378 cm^{-1} also occurs, ± 10 cm^{-1}, in complexes with S- or P-donor ligands,[23] and the corresponding Mo−S stretching modes in $(Mo_6S_8)L_6$ complexes occur at slightly higher wavenumbers ($+5-10$ cm^{-1}).[17] This characteristic band of the M_6S_8 cluster units has been used to indicate survival of the cluster in the important reactions for exchange or removal of ligands, in cases where more direct structural evidence is lacking.

Magnetic Susceptibility. The magnetic susceptibility for $(W_6S_8)(py)_6$ was measured over the range 4−350 K. Above 200 K, the susceptibility is constant at $\chi_M = -59 \times 10^{-6}$ emu mol^{-1}. Below 50 K, the susceptibility increases rapidly, indicating the presence of a small amount of paramagnetic impurity. It is clear that the compound exists with a singlet ground state up to 350 K. If the MO scheme for $(W_6S_8)L_6$ is similar to that for $(Mo_6S_8)L_6$,[3] this is to be expected. Although the presence of Cl was not detected in analyzed samples of $(W_6S_8)(py)_6$, the presence of traces of $(W_6S_7Cl)(py)_6$, an odd-electron species, would account for the increase of χ_M at low temperatures.

Deligation Experiments. Efforts to remove the pyridine ligands from $(W_6S_8)(py)_6$ by thermolysis *in vacuo* did not result in formation of W_6S_8 as hoped. Only at the lower temperature does it appear that the cluster unit is retained. As shown in Figure 5, the broad band at 397 cm^{-1} for the residue from thermolysis at 250 °C indicates retention of the W_6S_8 unit. At higher temperatures the disappearance of that band and the appearance of the sharp band at 360 cm^{-1} herald the formation of WS_2 in the product. Thus stability of the W_6S_8 cluster at temperatures above *ca.* 250−300 °C is doubtful. Efforts to chemically remove the pyridine ligands with good acceptors, including the strong proton donor CF_3SO_3H (TSA) and the Lewis acids $AlCl_3$ and BF_3, also were unsuccessful. The products were difficult to characterize, and indeed it is uncertain whether the cluster unit survived any of these reactions.

The reactions of tin and lead with $(W_6S_8)(py)_6$ followed the same course as simple thermal deligation. At the low temperatures employed, the tin and lead remained unreacted. The prospect of preparing the ternary compounds $M_xW_6S_8$ as analogs of the Chevrel phases using such molecular precursors is still an attractive approach and will be the subject of further work in this laboratory.

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Supplementary Material Available: Tables giving an extended listing of crystallographic data, anisotropic thermal parameters, calculated hydrogen positional parameters, and C−C and C−N bond distances (4 pages). Ordering information is given on any current masthead page.

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