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CLUSTER SPECIES.

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REACTIONS AND CHARACTERIZATION OF COMPOUNDS CONTAINING

TUNGSTEN HALIDE CLUSTER SPECIES

by

Ronald Dean Hogue

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INTRODUCTION

Throughout history the development of the chemistry of tungsten has closely paralleled or preceded that of the other second and third row transition elements. In recent years, however, the knowledge of compounds containing tungsten in lower oxidation states has lagged behind the advancements being made in other areas of transition metal chemistry. Preparation, properties, structures, and reactions of metal-metal bonded clusters of niobium, tantalum, molybdenum, and rhenium have been elucidated in many recent studies, but the tungsten derivatives have generally not received a thorough treatment.

The purpose of this investigation was to expand the knowledge in the areas of preparation, properties, and reactions of lower tungsten halides containing the W_6X_8 cluster, and to compare and contrast the results with known compounds of molybdenum containing Mo_6X_8 clusters as well as niobium and tantalum containing M_6X_{12} clusters.

Review of Previous Work

Chlorides and bromides of tungsten in oxidation states from 6+ to 2+ are known. Iodides are known in the 4+, 3+, and 2+ oxidation states. Reviews by Sidgwick (1), Parish (2), and Fergusson (3) summarize the early literature dealing generally with these compounds so only the literature specifically

pertaining to lower oxidation states will be discussed here.

Syntheses and reactions

A variety of methods have been used to synthesize lower oxidation state molybdenum and tungsten halides. Higher halides have been reduced thermally and with metals, hydrogen and other known reducing agents, whereas halides of intermediate oxidation state have been disproportionated, and the metals have been oxidized in controlled halogen atmospheres.

Hill (4) reduced tungsten(VI) chloride with sodium amalgam to prepare derivatives of tungsten(II) chloride. Lindner and Kohler (5) found aluminum gave better yields of tungsten (II) chloride than lead, zinc, or magnesium when reducing the hexachloride. Lindner (6) also used aluminum to reduce molybdenum(V) chloride to molybdenum(II) chloride and Murray (7) used aluminum for the reduction of tungsten(V) bromide to tungsten(II) bromide in a temperature gradient furnace. Hellriegel (8) and Senderoff and Brenner (9) used molybdenum metal to reduce molybdenum(V) chloride to molybdenum(II) chloride. Hydrogen reduction of tungsten(V) bromide at 400-450°C. led to tungsten(II) bromide for Emeleus and Gutman (10). Thermal decomposition of molybdenum(III) iodide to molybdenum (II) iodide in the absence of oxygen has been reported by Lewis et al. (11).

Disproportionation of the tungsten tetrahalides led to the corresponding tungsten(II) chlorides and bromides for

McCarley and Brown (12) whereas Robinson (13) and Couch and Brenner (14) disproportionated the trihalides of molybdenum to prepare the analogous molybdenum(II) chlorides and bromides.

Lindner and Hellwig (15) and Durand (16) prepared molybdenum(II) bromide from the elements at 600-700°C. Lindner et al. (17) prepared molybdenum(II) chloride by reacting molybdenum metal with $COCl_2$ at 600°C. in the absence of moisture.

The reactions of the lower halides have been studied in a variety of aqueous and non-aqueous media. Anionic complexes have been prepared from acidic solutions and neutral complexes from solutions in donor solvents. Oxidation, thermal decomposition and chemical disruption of the halides have also been studied.

Hill (4), by extracting tungsten(II) chloride into hydrochloric acid, prepared a chloroacid he formulated as $W_6Cl_{12} \cdot 2HCl \cdot 9H_2O$ on the basis of analytical data. Lindner (6,18) prepared additional haloacids of molybdenum and tungsten although he formulated them as trimeric clusters, $H(Mo_3Cl_7 \cdot H_2O)$, $H(Mo_3Cl_4Br_3 \cdot H_2O)$, $H(W_3Cl_7 \cdot H_2O)$ and $H(W_3Br_4Cl_3 \cdot H_2O)$. By adding a cation to these acidic solutions, Lindner and coworkers (5,15) found they could precipitate salts such as $(C_5H_5NH)^+(Mo_3Cl_7 \cdot H_2O)^-$ and $(C_5H_5NH)^+(Mo_3Br_7)^-$ which gave molecular weights in nitrobenzene (17) supporting the trimeric formulation.

Sheldon (19-22) prepared a number of anionic derivatives

$M_2^i[(Mo_6X_8)Y_6]$, $(M' = M(I)^+$, H_3O^+, $C_5H_5NH^+$, Ph_3PH^+, NH_4^+, R_4N^+; $X = Cl$, Br, I; $Y = Cl$, Br, I, OH), of the molybdenum clusters and found them to be 2:1 electrolytes in nitrobenzene. The observed molecular weights corresponded to those calculated for three ions per molecule based on the hexanuclear structure. Mackay (23) and Cotton et al. (24) prepared similar salts with cesium or tetraalkylammonium cations. Clark et al. (25) and Hartley and Ware (26) made further acid derivatives from hydrohalic acid solutions and Opalovskii and Samoilov (27) prepared the anionic bromide derivatives of molybdenum(II) bromide utilizing iodine monobromide as solvent.

Lindner and Kohler (5) observed the loss of hydrogen chloride upon heating the tungsten chloroacid, $H(W_3Cl_7 \cdot H_2O) \cdot aq$. The same observation was made on the molybdenum chloroacid, $(Mo_3Cl_6 \cdot H_2O) \cdot HCl \cdot 3H_2O$, by Rosenheim and Kohn (28). Thermal decomposition of the acids, $(H_3O)_2[(M_6X_8)Y_6] \cdot nH_2O$ led to an entire series of pure and mixed anhydrous derivatives of molybdenum and tungsten dihalide clusters, $(M_6X_8)Y_4$, ($M = Mo$, W; $X = Cl,Br,I$; $Y = Cl,Br,I,OH$), for Sheldon (20,22), Mackay (23), and Mattes (29).

Lindner and Hellwig (15) prepared the neutral complex, $Mo_3Br_6 \cdot py$ from molybdenum(II) bromide and pyridine. Sheldon (20,22,30) prepared the pyridine adducts of the mixed molybdenum iodides, $[(Mo_6I_8)X_4(py)_2]$, ($X = Cl,Br,I$), and the water, ethanol, pyridine, triethylamine, triphenylphosphine oxide,

and triphenylarsine oxide adducts of molybdenum(II) chloride
which were non-electrolytes formulated as $[(Mo_6Cl_8)Cl_4L_2]$.
In liquid ammonia Edwards (31) found that four ammonia mole-
cules add to the cluster forming $(Mo_6Cl_8)Cl_4 \cdot 4NH_3$ but that two
molecules of ammonia were lost on gentle heating. Cotton and
Curtis (32) formed bis(dimethylsulphoxide) and bis(dimethyl-
formamide) adducts from molybdenum(II) chloride in excess
ligand. Molybdenum(II) chloride was reacted with a series of
nitrogen donor ligands in excess ligand or in methylene chlo-
ride solution by Carmichael and Edwards (33). Methyl cyanide,
ethyl cyanide, n-propyl cyanide, trimethylamine, triethylamine,
pyridine, γ-picoline, quinoline, and pyrazine all formed bis
adducts, $[(Mo_6Cl_8)Cl_4L_2]$.

Fergusson et al. (34,35), investigating complexes with
more than two coordinated unidentate ligands and with bi- and
tridentate ligands, prepared the 1:1 electrolyte $[(Mo_6Cl_8)$
$Cl_3L_3]Cl$ with triphenylphosphine. Bidentate ligands bipyridyl,
0-phenanthroline, and 0-phenylenebis(dimethylarsine) gave
complexes of the type $[(Mo_6Cl_8)X_2B_2]X_2$, (X = Cl,I), which were
2:1 electrolytes and the tridentate ligand, terpyridyl,
yielded $[(Mo_6Cl_8)X_3T]X$, (X = Cl,I), a 1:1 electrolyte. Walton
and Edwards (36) found the potentially bidentate ligand, 2,5-
dithiahexane yielded a bis adduct with molybdenum(II) chloride,
$Mo_6Cl_{12}(DTH)_2$, and suggested that it was either ionic $[(Mo_6Cl_8)$
$Cl_2(DTH)_2]Cl_2$ with bridging dithiahexane or neutral $[(Mo_6Cl_8)$
$Cl_4(DTH)_2]$ with unidentate ligands.

Although oxidation of niobium and tantalum clusters is well documented, little success has been met in oxidizing derivatives of molybdenum and tungsten clusters. McCarley and Brown (37) utilized liquid bromine as solvent and reactant to oxidize tungsten(II) bromide to tungsten(III) bromide. Siepmann and Schäfer (38,39,40) studied the system in more detail and found the compounds W_6Br_{14}, W_6Br_{16}, and W_6Br_{18} were all derivatives of the $W_6Br_8^{6+}$ cluster. Thermal decomposition of any of the oxidized forms produced W_6Br_{12} and bromine. Siepmann et al. (41) found that liquid chlorine at 100°C. converted $(W_6Cl_8)Cl_4$ to $(W_6Cl_{12})Cl_6$ rather than simply oxidizing the W_6Cl_8 cluster.

Lindner and Kohler (5) reported that tungsten(II) chloride was hydrolyzed in basic solutions, but was stable in sulfuric acid from which they isolated the compound $W_3Cl_4SO_4$. Sheldon (22,42,43) suggested $(Mo_6X_{8-n}(OH)_n)$ intermediates in the hydrolysis of the molybdenum(II) halides with dilute base and proposed a mechanism for the hydroxide attack on the cluster. Addition of tetraethylammonium chloride to a basic solution of molybdenum(II) chloride which had subsequently been acidified with hydrochloric acid caused precipitation of $(Et_4N)_2[(Mo_6Cl_7 (OH)Cl_6]$ (44). He also found (19) that fluoride, thiocyanate, and strong hydroxide solutions completely disrupt the cluster. In acidic solution Sheldon (21) used hydrochloric and hydrobromic acid labelled with radioactive halide to show that the

outer halogens of the $[(Mo_6Cl_8)X_6]^{2-}$ group were exchanged quite rapidly through an aquo intermediate, $[(Mo_6Cl_8)X_5(H_2O)]^-$, but that the internal halogens were not exchanged over long periods, even with heating.

Lindner et al. (17) removed the outer chlorides from molybdenum(II) chloride with silver nitrate to prepare the compound they formulated as $Mo_3Cl_4(NO_3)_2$. Durand et al. (16) similarly prepared $Mo_3Br_4(NO_3)_2$. Cotton and Curtis (32) used silver perchlorate in excess dimethylsulphoxide or dimethylformamide to remove outer chlorides from Mo_6Cl_{12} and prepare hexasubstituted $[(Mo_6Cl_8)L_6](ClO_4)_4$.

At higher temperatures, Sheldon (19) found that the molybdenum chloride cluster was decomposed above $300^\circ C$. in air and above $800^\circ C$. in vacuum. In fused salts (22), the cluster was unaffected by boiling lithium iodide trihydrate at $200^\circ C$., but was slowly disproportionated in fused lithium chloride at $610^\circ C$. and rapidly disproportionated in fused potassium chloride at $770^\circ C$. to molybdenum metal and hexachloromolybdate(III). Fused lithium bromide or iodide converted molybdenum(II) chloride to the corresponding molybdenum(II) bromide or iodide while preserving the hexanuclear cluster of metal atoms.

Physical characterizations

Many physical measurements have been recorded for the anhydrous molybdenum and tungsten dihalides and the derivatives already described. Some conductivities and molecular

weights have been measured. Magnetic susceptibility data and visible-ultraviolet spectra have been interpreted in terms of the electronic configurations of the molecules. A limited number of x-ray single crystal studies have been complemented with powder diffraction studies to elucidate the hexanuclear molecular structure of the clusters. This structural information has been extended to similar clusters with far infrared and Raman spectral studies and normal coordinate analyses Finally, theoretical interpretations of the molecular orbitals and bonding involved in the clusters have shed light upon all of the chemical and physical properties of the hexanuclear metal atom clusters.

The pure and mixed anhydrous dihalides of molybdenum and tungsten, $(M_6X_8)Y_4$, $(M = Mo,W; X = Cl,Br,I; Y = Cl,Br,I)$, were found to be diamagnetic by Tjabbes (45), Klemm and Steinberg (46), Sheldon (20,22), Schäfer and Schnering (47), and Schäfer and Siepmann (40). Sheldon (20,44) and Edwards (31) found that derivatives such as $H_2[(Mo_6Cl_8)X_6]\cdot nH_2O$, $(X = Cl,Br,I)$, $R_2[(Mo_6Cl_8)Cl_6]$, and $(Mo_6Cl_8)Cl_4\cdot 4NH_3$ were also diamagnetic. However, Brown (48) and Schäfer and Siepmann (40) found that the oxidized forms, W_6Br_{14}, W_6Br_{16} and W_6Br_{18} were paramagnetic.

The visible-untraviolet spectra of the dihalides and their derivatives have been investigated by a number of workers. Sheldon (19,20,22), Edwards (31), Carmichael and Edwards (33),

and Fergusson et al. (35) studied derivatives of the molybde-
num(II) halides as hexahalo anions, neutral adducts, and the
anhydrous dihalides. Murray (7) and Schäfer and Siepmann (39,
40) studied tungsten(II) bromide. All of the workers observed
one or more charge transfer bands, generally in the 300-360 mμ
range, and no indication of the ligand field spectra one might
expect from a d^4 ion.

Single crystal x-ray structural determinations have con-
firmed the formulation of the molybdenum and tungsten di-
halides and their derivatives as hexanuclear metal-atom
clusters. Brosset (49,50) analyzed single crystals of
$(Mo_3Cl_4)(OH)_2 \cdot 8H_2O$ and $(Mo_3Cl_4)Cl_2 \cdot 4H_2O$ and found both con-
tained $[(Mo_6Cl_8)X_6]$ groups (X = chloride or the oxygen of
hydroxide or water). The inner Mo_6Cl_8 cluster consists of a
nearly regular octahedron of molybdenum atoms with a Mo-Mo
distance of 2.63Å. A chlorine atom is symmetrically located
above each of the eight triangular faces of the metal octa-
hedron forming three molybdenum-chlorine bonds at 2.56Å. The
outer constituents, X, are centrifugally directed from each of
the six molybdenum atoms. For X = Cl the Mo-Cl distance is
2.43Å. Brosset (51) also found the x-ray radial distribution
curves of $H(Mo_3Cl_2 \cdot H_2O) \cdot 3H_2O$ in concentrated ethanol solution
consistent with the formulation as $[(Mo_6Cl_8)Cl_6]^{2-}$ ions
present in the acid. Vaughan (52) applied the radial distri-
bution method to a powdered sample of $(NH_4)_2[(Mo_6Cl_8)Cl_6] \cdot H_2O$

and found the results also consistent with the presence of the $[(Mo_6Cl_8)Cl_6]^{2-}$ group having the above bond lengths. Single crystal studies led Schäfer et al. (53) to formulate molybdenum(II) chloride as $[(Mo_6Cl_8)Cl_{4/2}Cl_2]$ indicating the internal $Mo_6Cl_8^{4+}$ cluster with Mo-Mo bond lengths of 2.61Å, and Mo-Cl bond lengths of 2.47Å. The four external chlorides which bridge to adjacent clusters had a Mo-Cl distance of 2.50Å and the two non-bridging, terminal chlorides had a Mo-Cl distance of 2.38Å.

Siepmann and Schäfer (54) found that single crystals of W_6Br_{16} contained the polynuclear $W_6Br_8^{6+}$ cluster and polybromide anions, $(Br_4)^{2-}$. The structural formula $[(W_6Br_8)Br_4(Br_4)_{2/2}]$, indicates that the cluster is surrounded by four terminal bromides and two bridging polybromide anions. Bond lengths found were: W-W = 2.64Å, W-Br (cluster) = 2.58Å, W-Br (terminal) = 2.58Å.

Powder data by Schäfer et al. (53) encompassed previous work by Brown (48) on W_6X_{12}, (X = Cl,Br), Schäfer et al. (47) on M_6X_{12}, (M = Mo,W; X = Cl,Br), Murray (7) on W_6Br_{12}, and Clark et al. (25) on $(Mo_6Cl_8)Cl_4$, $(Mo_6Cl_8)Br_4$, and $(W_6Cl_8)Cl_4$ in showing that all of the dichlorides, dibromides, and diiodides of molybdenum and tungsten are isostructural, having the $[(Mo_6Cl_8)Cl_{4/2}Cl_2]$ structure. Sheldon (22) used powder patterns to show that $[(Mo_6Br_8)(OH)_4]\cdot 14H_2O$ was isomorphous with $[(Mo_6Cl_8)(OH)_4]\cdot 14H_2O$ reported in Brosset's (49) single

crystal studies. Mackay (23) found that the Cs $[(Mo_6Cl_8)X_6]$, X = Cl,Br,I), salts were isomorphous. The series of haloacids $H_2[(M_6Cl_8)X_6] \cdot 8H_2O$, (M = Mo,W; X = Cl,Br), were found isomorphous by Clark et al. (25), who also found the bidentate ligand derivatives $[(M_6Cl_8)Cl_2(O-phen)_2]Cl_2$, (M = Mo,W), isomorphous.

Recently, the far infrared spectra of a number of cluster derivatives have been investigated. Hexahaloanions, $[(M_6X_8)Y_6]^{2-}$, have been studied by Mackay (23), Cotton et al. (24), Clark et al. (25), and Hartley and Ware (26). Mackay (23), Clark et al. (25), and Mattes (29) also investigated the spectra of the anhydrous compounds $(M_6X_8)Y_4$. Clark et al. (25) and Walton and Edwards (36) found that the bidentate ligand adducts of the clusters, $[(M_6Cl_8)Cl_2B_2]Cl_2$ yielded spectra similar to the hexahaloanions and the anhydrous derivatives.

Although there are some differences in the assignments, the spectra are grossly similar and the authors generally assign the results on the basis of octahedral symmetry with two M-X modes, one M-M mode, one M-Y mode, and one X-M-Y mode allowed. The purity of each mode and the degree of mixing among modes is somewhat open to question presently.

Sheldon (19) discussed the bonding in $[(Mo_6X_8)Y_6]^{2-}$ clusters in terms of a tetragonal pyramid of halogens around each metal atom which used $d_{x^2-y^2}$ sp^3 hybrid orbitals for Mo-X and Mo-Y bonding. The $d_{xz,yz}$ orbitals were then used for Mo-Mo bonding and the remaining molybdenum electrons were considered

to occupy the remaining metal d orbitals. Gillespie (55),
using a similar approach for $Mo_6Cl_8^{4+}$ and $Nb_6Cl_{12}^{2+}$, looked at
the structures in terms of a distorted square antiprism of
bonding electrons around the metals and arrived at a descrip-
tion which utilized all of the metal electrons in the bonding,
but resulted in severely bent, localized Mo-X bonds.

Crossman et al. (56) first proposed a molecular orbital
treatment for the bonding in $Mo_6Cl_8^{4+}$ and $Ta_6Cl_{12}^{2+}$ clusters.
The available electrons just filled the chosen bonding orbitals
constructed from hybrid metal orbitals on each cluster. Cotton
and Haas (57) used a similar approach, but reserved some of the
available orbitals for specific bonds. Metal orbitals used to
bind the internal halogens were $d_{x^2-y^2}$, s, p_x, and p_y. The
metal p_z orbital was used for bonding to atoms located centri-
fugally from the six metals. LCAO-MO wave functions of the
proper symmetry were constructed from the remaining metal d
orbitals. The resulting molecular orbital energy level diagram
accounted for the observed spectra, the diamagnetism, the
metal-metal bond order, and the relative chemical reactivity
of internal and external halogens in the M_6X_8 clusters. Kettle
(58) employed a forty electron model including metal-halogen
interactions to show the similarity in the bonding of $Mo_6Cl_8^{4+}$
and $Ta_6Cl_{12}^{2+}$. In $Mo_6Cl_8^{4+}$ 24 electrons were used in metal-
metal bonding along the octahedral edges and 16 electrons in
metal-halogen bonding on the octahedral faces whereas in

$Ta_6Cl_{12}{}^{2+}$ 16 electrons were used in metal-metal bonding and 24 electrons in metal-halogen bonding.

EXPERIMENTAL

Materials

All air and moisture sensitive compounds in this study were handled only with a standard Pyrex glass vacuum system or in an argon atmosphere dry box maintained at a dew point less than $-60^\circ C$. Reactions involving these air or moisture sensitive compounds were carried out in sealed, evacuated Pyrex or Vycor glass reaction tubes. All other products were stored in a desiccator over Drierite.

Temperature gradients were maintained on reaction tubes as desired with separately wound, double-controlled, tubular furnaces.

All chemicals not specifically mentioned were of at least reagent grade.

Metals

High purity tungsten metal was obtained in the form of 200 mesh powder from the Lamp Metals and Components Department of the General Electric Company. Spectrographic analysis detected no aluminum, antimony, boron, gold, iridium, lead, manganese, molybdenum, silver, tantalum, tin, titanium, or vanadium. A very faint trace of calcium, chromium, and nickel, a faint trace of iron, magnesium, and silicon and a trace of copper were detected. Vacuum fusion analysis showed 128 ppm oxygen in the sample. The metal was subsequently treated with a stream of hydrogen gas at $950^\circ C$. to lower the oxygen content

and stored in the dry box for further use. The hydrogen reduced metal contained 20 ppm oxygen.

Turnings were machined from a block of 99.999% nominal purity aluminum from laboratory stock for use in aluminum reductions. Spectrographic analysis showed less than 16 ppm iron.

Halogens

Reagent grade chlorine was obtained in lecture size cylinders, distilled into the reaction vessel, and outgassed at -196°C. before beginning a reaction. Reagent grade bromine was dried for two days under vacuum over well outgassed phosphorous(V) oxide. It was then vacuum distilled into a clean, evacuated storage flask from which it was vacuum distilled as needed. Reagent grade iodine was resublimed in vacuo before use.

Organic solvents

Spectro grade cyclohexane was refluxed over sodium for 24 hours and outgassed by repeatedly freezing and thawing the solvent while pumping away the dissolved gases. The dried solvent was then vacuum distilled onto freshly prepared WBr_5 in a clean, evacuated flask for storage.

Analytical Procedures

Tungsten

Tungsten was determined gravimetrically as the oxide, WO_3. Binary halides in higher oxidation states which were easy to

convert to the oxide, were generally analyzed by placing a weighed sample into a tared crucible. The sample was then decomposed with hot nitric acid, slowly evaporated to dryness, and ignited to the oxide in a muffle furnace at 550°C.

Less reactive halides and compounds containing elements not volatilized by the nitric acid treatment were analyzed by homogeneous precipitation of WO_3 from a peroxy-acid solution following the method of Dams and Haste (59). Weighed samples were hydrolyzed in hot 0.5M KOH with hydrogen peroxide added as needed to speed the hydrolyses. The resultant clear tungstate solutions, or aliquots thereof, were treated with an equal volume of concentrated nitric acid, making them approximately 6N in acid. Addition of 30% hydrogen peroxide, as needed, redissolved all of the precipitated oxide as a peroxy-acid complex. The hydrated oxide was then completely precipitated in filterable form by slowly decomposing this complex at 80°C. for 4 hours. When cooled, the hydrated oxide was collected in a tared, fine porosity, porcelain filtering crucible, washed with dilute nitric acid, and ignited to WO_3 at 550°C. in a muffle furnace.

Halogens

Samples for halogen analysis were also hydrolyzed in hot 0.5M KOH with added hydrogen peroxide. The hydrolyzed samples were made just neutral with dilute nitric acid and reheated to expel excess peroxide. The samples or aliquots thereof, were

then potentiometrically titrated with a standard silver nitrate solution. When both chloride and iodide (or bromide and iodide) were present in a sample, good results were obtained by assigning the first of the two breaks in the graph of the potentiometric titration to iodide and the second to chloride (or bromide). However, when both chloride and bromide were present in a sample, only total halide could be determined by potentiometric titration since the two breaks in the graph were not well resolved.

Separate samples or aliquots were analyzed for bromide in the presence of chloride by the method of Kolthoff and Yutzy (60). The bromide was oxidized to bromate with sodium hypochlorite in a buffered solution. Potassium iodide was added and the solution was acidified with hydrochloric acid, liberating iodine which was titrated with standard sodium thiosulfate solution.

Derivatives of tungsten(II) iodide were generally very difficult to hydrolyze. Stronger base and peroxide along with vigorous boiling were usually needed to effect complete hydrolysis and oxidation. As a result, tungsten and halogen analyses for iodide derivatives were generally less accurate.

Carbon and hydrogen

Carbon and hydrogen were determined by Mr. J. J. Richard of the Ames Laboratory Analytical Service Group, Iowa State University of Science and Technology, Ames, Iowa.

Physical Measurements

X-ray diffraction

X-ray powder patterns were obtained with a 114.59 mm. Debye-Scherrer camera. Finely powdered samples were packed and sealed into 0.2 mm. Lindemann glass capillaries and exposed to Ni-filtered copper $K\alpha$ radiation for twenty to thirty hours.

Infrared spectra

Infrared absorption spectra were measured by Miss Evelyn Conrad of the Ames Laboratory Spectrochemistry Group, Iowa State University of Science and Technology, Ames, Iowa. Spectra were obtained in the 4000-600 cm^{-1} region on a Beckman IR-7 spectrophotometer and in the 800-33 cm^{-1} region on a Beckman IR-11 spectrophotometer in double beam operation. Air sensitive compounds, mulled with nujol in the dry box, were sealed between cesium iodide windows for the normal region of the infrared and between thin polyethylene windows in a specially designed O-ring holder for the far infrared.

Synthesis

Tungsten(VI) chloride

Tungsten(VI) chloride was prepared by distilling chlorine gas at 600 mm. pressure over tungsten metal maintained at $550^{\circ}C$. in a sealed, evacuated Pyrex tube. Quantities up to 250 grams were prepared and stored in the dry box for further use.

Tungsten(V) bromide

Tungsten(V) bromide was prepared in similar quantities by distilling bromine gas at 200 mm. pressure over tungsten metal maintained at 700°C. in a sealed, evacuated Vycor tube. The product was purified by sublimation at 300°C. under dynamic vacuum.

Tungsten(IV) halides

Tungsten(IV) chloride and bromide were prepared by reduction of the higher halides with aluminum or tungsten. A Pyrex tube containing 50-100 grams of higher halide was charged with the stoichiometric amount of aluminum turnings, evacuated, and sealed. The chloride was then reacted for three days in a temperature gradient furnace with the aluminum maintained at 475°C. and the other end, containing the tungsten(VI) chloride, at 200°C. The bromide was similarly prepared with a temperature gradient of 475°C./240°C.

A preferred method of preparing tungsten(IV) chloride was the reduction of 50-100 grams of tungsten(VI) chloride with tungsten metal in a Vycor tube maintained at 675°C./300°C. for three days.

Tungsten(II) halides[1]

$(W_6Cl_8)Cl_4$ Tungsten(II) chloride was prepared by disproportionation of the tetrachloride at 425°C. or by reduction

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[1]The tungsten(II) halides are properly named tetrahalo-octa-μ_3-halohexatungsten. For convenience the chemical formulas rather than the names will be used.

of the hexachloride with a stoichiometric amount of aluminum in the same temperature gradient maintained for preparation of the tetrachloride. Although the aluminum reduction was more direct, explosions of reaction tubes caused by excessive pressure of aluminum chloride were frequent, and finely divided, pyrophoric tungsten metal, as evidenced by the x-ray powder patterns and the low chlorine to tungsten ratios, was always present in the product.

Disproportionation of tungsten(IV) chloride was a rather indirect and inefficient method of preparing tungsten(II) chloride, but the success rate was much better. The products were somewhat purer although the powder patterns and the low chlorine to tungsten ratios showed that they also contained tungsten metal.

Tungsten metal could be removed and the purity of the dichloride increased substantially by a recrystallization process. Impure tungsten(II) chloride was dissolved in hot, concentrated, aqueous hydrochloric acid containing a few ml. of ethanol. The solution was filtered to remove insoluble impurities and the filtrate was cooled in an ice water bath. Bright yellow needles of the chloroacid, $(H_3O)_2[(W_6Cl_8)Cl_6] \cdot nH_2O$, precipitated from the cold solution. The chloroacid was collected and recrystallized from fresh hydrochloric acid by the same procedure except that the solution was saturated with hydrogen chloride gas during the cooling and precipitation

process. The recrystallized chloroacid was immediately trans-
ferred to a Pyrex tube, evacuated, and thermally decomposed
under dynamic vacuum by slowly raising the temperature to a
final 12 hour treatment at $325^{\circ}C$.

Analysis of one preparation made by each of the methods
gave the following results. Anal. calcd. for W_6Cl_{12}: W,
72.17; Cl, 27.83; Cl/W, 2.00. Found (Al reduction): W, 76.94;
Cl, 23.73; Cl/W, 1.60. Found (Disproportionation): W, 72.86;
Cl, 26.43; Cl/W, 1.88. Found (Recrystallized): W, 72.23; Cl,
27.62; Cl/W, 1.98.

<u>$(W_6Br_8)Br_4$</u>   Tungsten(II) bromide was prepared by direct
aluminum reduction of tungsten(V) bromide using a temperature
gradient of $475^{\circ}C./240^{\circ}C.$ for 5 days. Tungsten metal was found
as a contaminant in the products by x-ray powder patterns and
by low bromine to tungsten ratios.

The dibromide could be purified, when required, by a solu-
tion process. Impure tungsten(II) bromide was dissolved with
stirring in a hot 50-50 solution of ethanol and concentrated,
aqueous hydrobromic acid. The solution was filtered to remove
insoluble impurities and the filtrate was evaporated nearly to
dryness with gentle heating under aspirator vacuum. The re-
sultant orange precipitate was redissolved in water and again
evaporated nearly to dryness precipitating the yellow hydrate,
$W_6Br_{12} \cdot 2H_2O$. The hydrated tungsten(II) bromide was washed with
water, dried, and thermally decomposed under dynamic vacuum

with a final 24 hour treatment at 350°C.

Analysis of one preparation made by each of the methods gave the following results. Anal. calcd. for W_6Br_{12}: W, 53.50; Br, 46.50; Br/W, 2.00. Found (Al reduction): W, 54.86; Br, 44.36; Br/W, 1.86. Found (Solution): W, 53.93; Br, 45.92; Br/W, 1.96.

$(W_6I_8)I_4$ Tungsten(II) iodide was prepared by the exchange reaction between pure tungsten(II) chloride and a 10-fold excess of a molten solution of 70 mole % KI and 30 mole % LiI at 540°C. for 15 minutes. The reaction products were cooled and leached thoroughly with water to remove KI, LiI, KCl, and LiCl. Most of the rust-colored residue was soluble in ethanol, producing an orange solution which was filtered and evaporated nearly to dryness with gentle heating under aspirator vacuum. The resultant orange precipitate of W_6I_{12}· 2EtOH was thermally decomposed under dynamic vacuum with a final 24 hour treatment at 500°C. yielding orange tungsten(II) iodide. Anal. calcd. for W_6I_{12}: W, 42.01; I, 57.99; I/W, 2.00. Found: W, 41.79; I, 56.45; I/W, 1.96.

$(W_6X_8)Y_4.(X{\neq}Y)$ Mixed anhydrous tungsten(II) halides were prepared by dissolving anhydrous tungsten(II) halides $(W_6X_8)X_4$, in different hydrohalic acids, HY, $(X{\neq}Y)$, with a few ml. of ethanol added. The resultant solutions were heated and stirred for 4-12 hours to insure exchange of the outer halides. The solutions were then filtered and cooled to precipitate

yellow crystals of the mixed haloacids, $(H_3O)_2[(W_6X_8)Y_6]\cdot nH_2O$. The acids were recrystallized by the same procedure, washed with cold HY, transferred to the vacuum line, and thermally decomposed under dynamic vacuum with a final 12 hour treatment at $325°C$. Mixed tungsten(II) halides prepared in this manner were $(W_6Cl_8)Br_4$, $(W_6Cl_8)I_4$, and $(W_6Br_8)Cl_4$. Anal. calcd. for $(W_6Cl_8)Br_4$: W, 64.65; Cl, 16.62, Br, 18.73; Cl/W, 1.33; Br/W, 0.67. Found: W, 63.77; Cl, 16.19; Br, 18.01; Cl/W, 1.32; Br/W, 0.65. Anal. calcd. for $(W_6Cl_8)I_4$: W, 58.23; Cl, 14.97; I, 26.80; Cl/W, 1.33; I/W, 0.67. Found: W, 58.11; Cl, 14.17; I, 26.81; Cl/W, 1.27; I/W, 0.67. Anal. calcd. for $(W_6Br_8)Cl_4$: W, 58.55; Br, 33.93; Cl, 7.53; Br/W, 1.33; Cl/W, 0.67. Found: W, 58.67; Br, 33.77; Cl, 7.36; Br/W, 1.32; Cl/W, 0.65.

Another mixed anhydrous derivative was prepared by thermal decomposition of $(W_6Br_8)F_4(H_2O)_5$ under dynamic vacuum with a final treatment at $400°C$. for 4 hours. Anal. calcd. for $(W_6Br_8)F_4$: W, 60.66; Br, 35.16; Br/W, 1.33. Found: W, 61.72; Br, 35.04; Br/W, 1.31.

Neutral adducts of tungsten(II) halides

Water[1]   Hydrated derivatives of tungsten(II) chloride having the general formula $[(W_6Cl_8)Y_4(H_2O)_2]$, (Y = Cl,Br,I), were prepared by thermal decomposition of the corresponding

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[1]The hydrated tungsten(II) halides are properly named diaquotetrahalo-octa-μ_3-halohexatungsten. For convenience the chemical formulas rather than the names will be used.

haloacids at 200°C. The analytical data for the bis adducts, $[(W_6Cl_8)Cl_4(H_2O)_2]$, $[(W_6Cl_8)Br_4(H_2O)_2]$, and $[(W_6Cl_8)I_4(H_2O)_2]$, are summarized in Table 1.

Hydrated derivatives of tungsten(II) bromide and iodide were prepared by dissolving the dihalide in dilute base, filtering, and acidifying the filtrate strongly with the desired hydrohalic acid. The yellow precipitates were dried under dynamic vacuum at 200°C.yielding the bis adducts. Analytical data for $[(W_6Br_8)Cl_4(H_2O)_2]$, $[(W_6Br_8)Br_4(H_2O)_2]$, and $[(W_6I_8)I_4 H_2O)_2]$ are given in Table 1.

A hydrated fluoride derivative was prepared by titrating the external bromides of tungsten(II) bromide in aqueous solution with silver perchlorate until the potentiometric equivalence point. The silver bromide precipitate was coagulated and filtered away leaving a clear yellow solution which was acidified with aqueous hydrofluoric acid in Teflon labware. A cesium fluoride solution was then added in an attempt to prepare the hexafluoro salt, but no precipitation occurred. When the volume of the solution was reduced with gentle heating a yellow and a white solid precipitated. The white precipitate, apparently $CsClO_4$, was removed by repeated washings with hot water. The bright yellow precipitate which remained was rinsed with ether and vacuum dried. Anal. calcd. for $(W_6Br_8)F_4(H_2O)_5$: W, 57.80; Br, 33.50; F, 3.98; Br/W, 1.33; F/W, 0.67. Found: W, 57.62; Br, 33.34; F, 3.95; Br/W, 1.33; F/W, 0.66.

<u>Ethanol</u>[1] A bis-ethanol adduct was prepared by evaporating an ethanol solution of tungsten(II) iodide nearly to dryness. The resultant orange precipitate was washed with ethanol and vacuum dried. The analytical data are presented in Table 1.

The product of one exchange reaction, carried out between tungsten(II) chloride and lithium iodide that was not completely anhydrous, was much less soluble than normal. Overnight stirring and heating in a 50-50 solution of ethanol and aqueous HX, (X = F,Cl,Br), produced little coloration of the solutions. The insoluble residues were washed with ethanol and vacuum dried to provide the bis-ethanol adducts of the partially exchanged derivatives of tungsten(II) iodide. The analytical data are summarized in Table 1.

Attempts to prepare a bis-ethanol adduct of tungsten(II) chloride produced only a black, glassy, solvolyzed product. Anal. calcd. for $[(W_6Cl_8)Cl_2(C_2H_5O)_2(C_2H_5OH)_2]$: W, 67.27; Cl, 21.62; Cl/W, 1.67; (C,H,O), 11.11. Found: W, 67.07; Cl, 21.88; Cl/W, 1.69; (C,H,O) (by difference), 11.05.

<u>Acetonitrile</u>[2] A yellow bis-acetonitrile adduct was prepared by stirring pure tungsten(II) chloride in acetonitrile.

[1]The ethanol adducts of the tungsten(II) halides are properly named bis(ethanol)tetrahalo-octa-μ_3-halohexatungsten. For convenience the chemical formulas rather than the names will be used.

[2]The acetonitrile adduct of tungsten(II) chloride is properly names bis(acetonitrile)tetrachloro-octa-μ_3-chlorohexatungsten. For convenience the chemical formula rather than the name will be used.

Table 1. Analytical data for neutral adducts of tungsten(II) halides,
$[(W_6X_8)Y_4L_2]$

Compound	W		X		Y	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
$[(W_6Cl_8)Cl_4(H_2O)_2]$	70.51	70.88	27.19	27.10	---	---
$[(W_6Cl_8)Br_4(H_2O)_2]$	63.31	63.15	16.28	16.06	18.34	17.79
$[(W_6Cl_8)I_4(H_2O)_2]$	57.14	58.15	14.69	14.46	26.30	25.84
$[(W_6Br_8)Cl_4(H_2O)_2]$	57.45	57.85	33.29	33.33	7.39	7.51
$[(W_6Br_8)Br_4(H_2O)_2]$	52.58	52.21	45.70	44.58	---	---
$[(W_6I_8)I_4(H_2O)_2]$	41.44	40.42	57.21	55.23	---	---
$[(W_6I_8)I_4(C_2H_5OH)_2]$	40.58	40.24	56.03	55.42	---	---
$[(W_6I_8)I_3Br(C_2H_5OH)_2]$	41.30	40.75	52.26	51.91	2.99	2.86
$[(W_6I_8)I_3Cl(C_2H_5OH)_2]$	42.00	41.87	53.15	53.70	1.35	1.17
$[(W_6I_8)I_3F(C_2H_5OH)_2]$	42.26	41.21	53.48	54.27		
$[(W_6Cl_8)Cl_4(CH_3CN)_2]$	68.49	68.74	26.41	26.53	---	---

The analytical data are given in Table 1.

Hexahalo anions of tungsten(II) halides[1]

$R_2[(W_6X_8)X_6]$ The appropriate tungsten(II) halide, $(W_6X_8)X_4$, was dissolved in the corresponding hot hydrohalic acid, HX. Addition of a few ml. of ethanol hastened dissolution of the chloride, more ethanol was needed to dissolve the bromide, and ca. 50% ethanol was required to prepare solutions of the iodide. The solutions were filtered and the hexahalo complexes were precipitated by the addition of cesium or tetraalkylammonium halide. The products were washed with hydrohalic acid and vacuum dried. The analytical data are summarized in Table 2.

$R_2[(W_6X_8)Y_6]$ An extra step was necessary to insure complete exchange of outer halides when preparing complexes having different outer halides than those originally present on the cluster. The appropriate tungsten(II) halide, $(W_6X_8)X_4$, was dissolved in hydrohalic acid, HY, $(X \neq Y)$ as previously described with the addition of ethanol. The resultant solution was filtered and evaporated nearly to dryness with moderate heating under aspirator vacuum. The residue was collected and redissolved in hydrohalic acid, HY, as above, filtered, and treated with cesium or tetraalkylammonium halide to precipitate

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[1] The hexahalo salts of the tungsten(II) halides are properly named bis(tetraalkylammonium)hexahalo-octa-μ_3-halohexatungsten. For convenience the chemical formulas rather than the names will be used.

Table 2. Analytical data for hexahalo salts of tungsten(II) halides, $R_2[(W_6X_8)Y_6]$

R	X	Y	W		X		Y		C		H	
			Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
Cs	Cl	Cl	59.14	58.98	26.61	26.52	---	---	---	---	---	---
Me$_4$N	Cl	Cl	63.11	63.22	28.40	27.85	---	---				
Et$_4$N	Cl	Cl	59.31	59.23	26.69	26.60	---	---	10.33	10.65	2.17	2.23
Bu$_4$N	Cl	Cl	52.92	52.07			---	---				
Cs	Cl	Br	51.74	52.36	13.30	13.40	22.50	22.68	---	---	---	---
Me$_4$N	Cl	Br	54.76	54.46	14.08	14.29	23.82	23.92	4.77	4.37	1.20	1.21
Et$_4$N	Cl	Br	51.87	51.63	13.34	13.18	22.54	22.14	9.04	9.31	1.90	1.94
Bu$_4$N	Cl	Br	46.92	45.26								
Cs	Cl	I	45.70	44.70	11.75	11.57	31.54	32.29	---	---	---	---
Et$_4$N	Cl	I	45.80	45.88	11.78	11.99	31.61	32.21	7.98	7.87	1.67	1.74
Cs	Br	Cl	49.67	49.14	28.78	28.51	9.58	9.81	---	---	---	---
Et$_4$N	Br	Cl	49.79	50.00	28.85	28.45	9.60	9.25	8.67	9.90	1.82	1.75
Cs	Br	Br	44.34	44.58	44.97	45.32	---	---	---	---	---	---
Me$_4$N	Br	Br	46.54	45.48	47.20	45.42	---	---				
Et$_4$N	Br	Br	44.44	44.34	45.07	44.56	---	---	7.74	7.84	1.62	1.51

Table 2. (Continued)

R	X	Y	W Calcd.	W Found	X Calcd.	X Found	Y Calcd.	Y Found	C Calcd.	C Found	H Calcd.	H Found
Cs	Br	I	39.83	39.48	23.08	23.67	27.49	27.44	---	---	---	---
Et$_4$N	Br	I	39.91	40.07	23.13	22.96	27.54	27.34	6.95	6.50	1.46	1.34
Et$_4$N	I	Cl	42.57	42.00	39.17	39.08	8.21	7.41				
Bu$_4$N	I	Cl	39.17	39.17	36.05	33.50	7.55	7.35	13.65	12.73	2.58	2.44
Et$_4$N	I	Br	38.59	37.75								
Bu$_4$N	I	Br	35.78	35.60	32.93	32.16	15.55	15.18	12.47	12.45	2.35	2.40
Me$_4$N	I	I			58.67	57.28	---	---				
Et$_4$N	I	I	35.13	34.85	56.58	55.21	---	---				
Bu$_4$N	I	I	32.78	32.87	52.80	51.52	---	---	11.42	10.78	2.16	2.14

the hexahalo complex. The products were washed with hydro-halic acid and vacuum dried. $(Et_4N)_2[(W_6Br_8)I_6]$, $(Bu_4N)_2$ $[(W_6I_8)Cl_6]$, and $(Bu_4N)_2[(W_6I_8)Br_6]$ were purified by recrystal-lization from acetonitrile. The analytical data are presented in Table 2.

$R_2[(W_6X_8)X_4Y_2]$ Less rigorous conditions than those just described produced little or no exchange of the terminal halides originally present on a cluster. Dissolution of tungsten(II) iodide in ethanol-10% aqueous hydrochloric acid with gentle heating followed by immediate addition of tetra-alkylammonium chloride solution produced a yellow precipitate of $(Et_4N)_2[(W_6I_8)I_4Cl_2]$, which was washed with hydrochloric acid and vacuum dried. Anal. calcd. for $(Et_4N)_2[(W_6I_8)I_4Cl_2]$: W, 37.30; I, 51.49; Cl, 2.40; I/W, 2.00; Cl/W, 0.33. Found: W, 37.04; I, 51.42; Cl, 1.75; I/W, 2.01; Cl/W, 0.25.

Oxidized derivatives of tungsten clusters

$[(W_6Cl_{12})Cl_6]$ This compound was prepared by a slight modification of the method of Siepman et al. (41). Tungsten (II) chloride was shaken with liquid chlorine in a heavy-walled Pyrex tube at room temperature for three days. The chlorine was distilled away and the product was thoroughly extracted with cyclohexane to remove tungsten(VI) chloride which also formed. The product was left as an insoluble green-brown solid. Anal. calcd. for W_6Cl_{18}: W, 63.35; Cl, 36.65; Cl/W, 3.00. Found: W, 62.71; Cl, 36.75; Cl/W, 3.04.

W_6Br_{18} Tungsten(III) bromide was made by the method of McCarley and Brown (37). Tungsten(II) bromide was reacted with liquid bromine at 50°C. and extracted away from unreacted material with liquid bromine. The bromine was distilled away and the black product was vacuum dried at room temperature. Anal. calcd. for W_6Br_{18}: W, 43.40; Br, 56.60; Br/W, 3.00. Found: W, 43.17; Br, 54.93; Br/W, 2.93.

$[(W_6Br_8)Br_6]$ Following the method of Siepmann and Schafer (38), W_6Br_{18} was thermally decomposed under dynamic vacuum at 110°C. for one hour. Liberated bromine was collected in a cold trap and the product was recovered as a black residue. Anal. calcd. for W_6Br_{14}: W, 49.65; Br, 50.35; Br/W, 2.33. Found: W, 49.38; Br, 49.45; Br/W, 2.30.

RESULTS AND DISCUSSION

Synthesis

Starting materials

Since substantial quantities of pure, anhydrous tungsten (II) halides were required for this study, some effort was devoted to improving synthetic schemes with respect to quantity and quality of dihalides produced. The dihalides themselves were then characterized by x-ray powder patterns, far infrared spectra, and chemical reactivity in addition to routine chemical analyses.

Brown (48) synthesized tungsten(VI) chloride by passing chlorine gas over tungsten metal at $600^{\circ}C$. in an evacuated Vycor tube. This synthesis was improved in the present study by lowering the reaction temperature to $550^{\circ}C$. so that a less expensive and easier to handle Pyrex tube could replace the Vycor tube. To achieve a comparable chlorination rate at the lower temperature, the pressure of chlorine during the reaction was increased from 70 mm. to 600 mm. by using an 80% isopropanol-20% water-dry ice slush bath ($-40^{\circ}C$.) instead of an acetone-dry ice slush bath ($-78^{\circ}C$.) around the chlorine reservoir.

Many alternatives are available for the reduction of tungsten(VI) chloride to tungsten(II) chloride. Aluminum is generally a good, fast reducing agent in transition metal chloride systems, but the vapor pressure of the aluminum

chloride produced rises steeply as a function of temperature. When reducing tungsten(VI) chloride with aluminum in a temperature gradient furnace, explosions were frequent whenever the cooler temperature was raised high enough (225°C.) to sustain rapid reactions. If the reaction was performed at lower temperatures (180°C.), 4-5 days were required to complete the reduction and evidence for contamination by tungsten metal was always found in the elemental analyses and in the x-ray powder patterns. X-ray powder pattern data for one of these products are listed in the Appendix.

With respect to tungsten(VI) chloride, the most efficient conversion to tungsten(II) chloride is reduction with tungsten metal in a temperature gradient furnace. However, at temperatures sufficiently high to perform this reduction (400°C.), the vapor pressure of tungsten(V,VI) chloride in the cool end of the reaction tube was excessive and caused several explosions. Maintaining a lower temperature (300°C.) on the tungsten(VI) chloride end of the reaction tube did, however, produce good yields of pure tungsten(IV) chloride. The tungsten(IV) chloride was subsequently disproportionated to afford the desired tungsten(II) chloride and a byproduct of tungsten (V) chloride which could be reused in future reductions. Tungsten(II) chloride prepared by disproportionation was somewhat purer than that prepared by aluminum reduction, but still contained tungsten metal as an impurity. The x-ray powder

patterns of products prepared by either method were substantially the same.

Tungsten(II) chloride was always purified before further use by recrystallization of the chloroacid, $(H_3O)_2[(W_6Cl_8)Cl_6] \cdot nH_2O$, from hydrochloric acid saturated with hydrogen chloride gas following the method Sheldon (20) used with molybdenum(II) chloride. The bright yellow crystals of chloroacid faded to pale yellow during thermal decomposition at $325^\circ C$. under dynamic vacuum. Decomposition at lower temperatures yielded the hydrate, $W_6Cl_{12} \cdot 2H_2O$.

Tungsten(II) chloride prepared by thermal decomposition of the chloroacid was pyrophoric, more reactive toward halogens, amorphous to x-rays, and gave broad, poorly resolved bands in the far infrared spectrum. This is interpreted as meaning that there is considerable disorder produced by the random loss of chlorides in the thermally decomposed products. Reactive metal atoms, left without terminal or bridging external chlorides, then may account for the pyrophoric nature and the enhanced reactivity of the material.

To obtain pure, crystalline tungsten(II) chloride, a sample of amorphous tungsten(II) chloride was sealed in a pyrex ampoule, heated to $550^\circ C$., and cooled slowly to room temperature. An x-ray powder pattern revealed the crystalline nature of this annealed product which showed only the lines of tungsten(II) chloride with no lines of tungsten metal

impurity. The infrared spectrum of crystalline tungsten(II) chloride was better resolved than the amorphous material and exhibited eleven of the thirteen predicted bands for $[(W_6Cl_8) Cl_{4/2}Cl_2]$ in D_{4h} symmetry.

Apparently, the annealing process converted the disordered tungsten(II) chloride from the thermal decomposition into the crystalline form containing tungsten atoms which are fully coordinated by utilizing bridging chlorides between clusters. Variations in reactivity of different preparations of thermally decomposed tungsten(II) chloride were subsequently attributed to variations in the amount of annealing that took place during the thermal decomposition process.

Tungsten(II) bromide was prepared by the direct reduction of tungsten(V) bromide with aluminum in a temperature gradient furnace. An x-ray powder pattern agreed well with that previously reported by Murray (7) and showed tungsten metal as an impurity.

Tungsten(II) bromide was purified, when required, by recrystallization, first from an ethanol-hydrobromic acid solution, then from water. The hydrate was thermally decomposed forming fairly crystalline tungsten(II) bromide with no tungsten metal impurity. X-ray powder pattern data are given in the Appendix.

Tungsten(II) iodide was prepared by exchanging both the internal and the external halogens of tungsten(II) chloride

for iodides in a molten lithium iodide-potassium iodide solution. After alkali metal halides were leached away with water, the product was dissolved in ethanol and precipitated as an ethanol adduct. The adduct was thermally decomposed at 500°C. forming fairly crystalline tungsten(II) iodide. X-ray powder pattern data are given in the Appendix.

Owing to the complex scheme necessary to prepare tungsten (II) iodide by the halide exchange process, other methods were sought for preparing a tungsten iodide for use as a starting material. Iodination of tungsten hexacarbonyl in a sealed tube using the method of Djordjevic et al. (61) was not satisfactory because of the limits which the CO pressure places on the quantity of reactants that may be used. Iodination of tungsten metal was not successful below 700°C. at iodine pressures up to two atmospheres.

The mixed derivatives of the tungsten(II) halides, $(W_6X_8)Y_4$, X $\neq$ Y, prepared by thermal decomposition of the mixed haloacids or the mixed hydrates, were found to be amorphous to x-rays.

Terminal halogen exchange

The ease with which the outer halides could be removed or exchanged from a tungsten(II) halide varied considerably for chlorides, bromides, and iodides. In aqueous hydrohalic acid, HY, exchange of the terminal chlorides of tungsten(II) chloride for bromides or iodides was rapid and complete under fairly

mild conditions. This agrees with Sheldon's (21) findings for molybdenum(II) chloride. For tungsten(II) bromide exchange was slower, and for tungsten(II) iodide boiling in concentrated HY, (Y = Cl,Br), for several hours was necessary to insure complete exchange of the terminal iodides. Lower solubility of the bromide and iodide could be partly responsible for these results.

Terminal halogen exchange was also affected by dissolving tungsten(II) bromide or iodide in dilute base and filtering the solution into concentrated hydrohalic acid, HY. The chloride cluster, however, was immediately decomposed in basic solutions.

Terminal bromides were also extracted from tungsten(II) bromide in aqueous solution with silver perchlorate. Hydrofluoric acid was then added to the solution to prepare a derivative of the tungsten bromide cluster containing terminal fluorides. Similar attempts to precipitate the terminal chlorides from tungsten(II) chloride solutions in water, ethanol, or acetonitrile with silver nitrate, perchlorate, or fluoride resulted in immediate precipitation and oxidation of the tungsten containing species.

Attempts to exchange the terminal halides of $(Et_4N)_2$ $[(W_6Cl_8)Y_6]$ for fluorides in concentrated aqueous hydrofluoric acid, in dilute ethanol-hydrofluoric acid, or in acetonitrile containing excess tetraethylammonium fluoride resulted in dis-

ruption and oxidation of the tungsten chloride cluster.

Oxidation reactions

The oxidation of tungsten(II) chloride was studied under
a variety of conditions with numerous oxidizing agents. The
reaction of tungsten(II) chloride with liquid chlorine to pre-
pare tungsten(III) chloride was performed under nearly the
same conditions reported by Siepmann et al. (41). X-ray
powder pattern data are given in the Appendix.

Tungsten(III) chloride was also prepared by exposing
solid tungsten(II) chloride to chlorine gas. The reactivity
of the dichloride varied considerably in the reaction among
various preparations. Some reactions proceeded rapidly and
exothermally, whereas others proceeded only slowly and par-
tially to green-brown tungsten(III) chloride, even under a
variety of temperatures, chlorine pressures, and reaction
times. Chlorine to tungsten ratios for the products, after
extraction with cyclohexane to remove higher oxidation state
tungsten chlorides, varied from 2.15 for the unreactive mater-
ial to 3.03 for the highly reactive material. In all cases,
however, the x-ray powder patterns showed that tungsten(III)
chloride was the only new product formed.

Exposure of tungsten(II) chloride to vapors of sulfur(II)
chloride or thionyl chloride also produced materials with
chlorine to tungsten ratios of approximately 3.00, but both
products appeared to retain small quantities of sulfur con-

taining impurities after cyclohexane extraction. Anal. calcd. for W_6Cl_{18}: W, 63.35; Cl, 36.65; Cl/W, 3.00. Found (for $SOCl_2$ product): W, 63.34; Cl, 34.85; Cl/W, 2.85. The x-ray powder pattern data (Appendix) showed only the lines of tungsten(III) chloride.

In antimony trichloride solution at $110^{\circ}C.$, antimony penta-chloride was another effective chlorinating agent for convert-ing tungsten(II) chloride to tungsten(III) chloride. Materials having chlorine to tungsten ratios from 2.19 to 3.03 were produced depending upon the nature of the dihalide and the amount of antimony pentachloride used. All products gave x-ray powder patterns with only the lines of tungsten(III) chloride.

Thermal decomposition of tungsten(III) chloride at $375^{\circ}C.$ under dynamic vacuum produced a sublimate of tungsten(V) chloride and a residue of tungsten(II) chloride, both con-firmed by elemental analysis and x-ray powder patterns.

Tungsten(II) bromide was oxidized to W_6Br_{18} in liquid bromine by the method of McCarley and Brown (37). X-ray powder diffraction data are given in the Appendix.

Thermal decomposition of W_6Br_{18} at $110^{\circ}C.$ under dynamic vacuum led to the oxidized bromide cluster formulated as $[(W_6Br_8)Br_6]$ by Siepmann and Schäfer (38). X-ray powder pat-tern data are given in the Appendix.

Many other attempts were made to halogenate the tungsten (II) halides, $(W_6X_8)X_4$, and the mixed tungsten(II) halides,

$(W_6X_8)Y_4$, with X_2 or Y_2, but no pure derivatives of the W_6Cl_{18} or W_6Br_{14} types were isolated. Most complications seemed to be due to polyhalide formation. The infrared spectra, although not always well defined, were generally consistent with the presence of oxidized derivatives of tungsten clusters.

Far Infrared Spectra

Far infrared data and assignments

The infrared spectra of representative compounds reported in this study are shown for comparison in Figures 1-7. All of the infrared data, collected as wavenumber in cm^{-1} and relative intensities, are summarized in Tables 3-9. Assignment of the infrared bands was made on the basis of the octahedral model of the $[(W_6X_8)Y_6]^{2-}$ anion shown in Figure 8.

Reduction of the representation formed using the 60 Cartesian displacement coordinates of the $[(W_6X_8)Y_6]$ group as a basis set leads to the following irreducible representation:

$$\Gamma_{tot.} = 3A_{1g} + 3E_g + 3T_{1g} + 4T_{2g} + A_{2u} + E_u + 6T_{1u} + 3T_{2u}. \tag{1}$$

Subtraction of the representations for translation and rotation leaves the representations to which the 54 normal vibrations belong.

$$\Gamma_{trans.} = T_{1u} \tag{2}$$

$$\Gamma_{rot.} = T_{1g} \tag{3}$$

$$\Gamma_{vib.} = 3A_{1g} + 3E_g + 2T_{1g} + 4T_{2g} + A_{2u} + E_u + 5T_{1u} + 3T_{2u} \tag{4}$$

Since only T_{1u} modes are infrared active in octahedral symmetry, infrared spectra of $[(W_6X_8)Y_6]^{2-}$ anions should contain
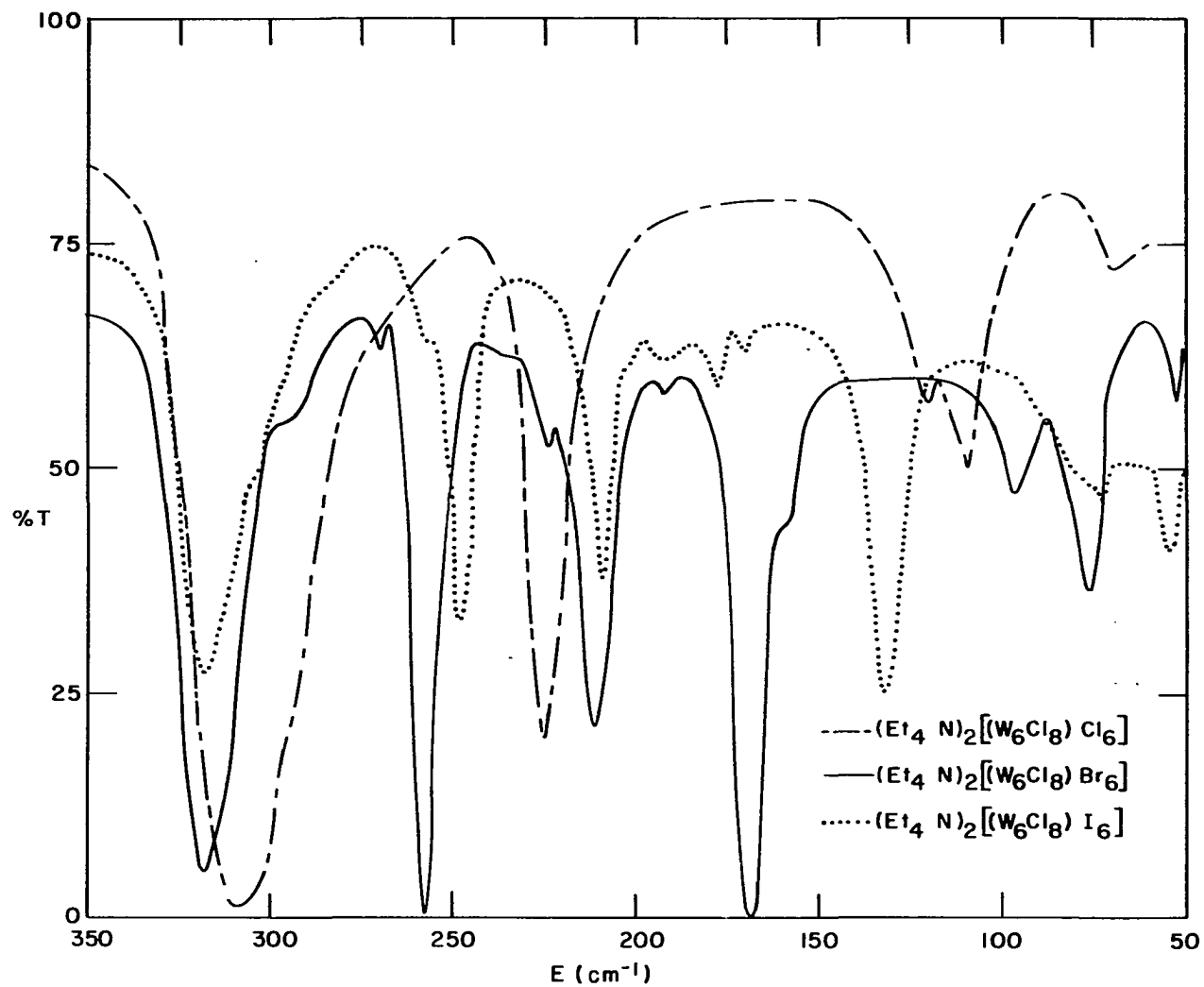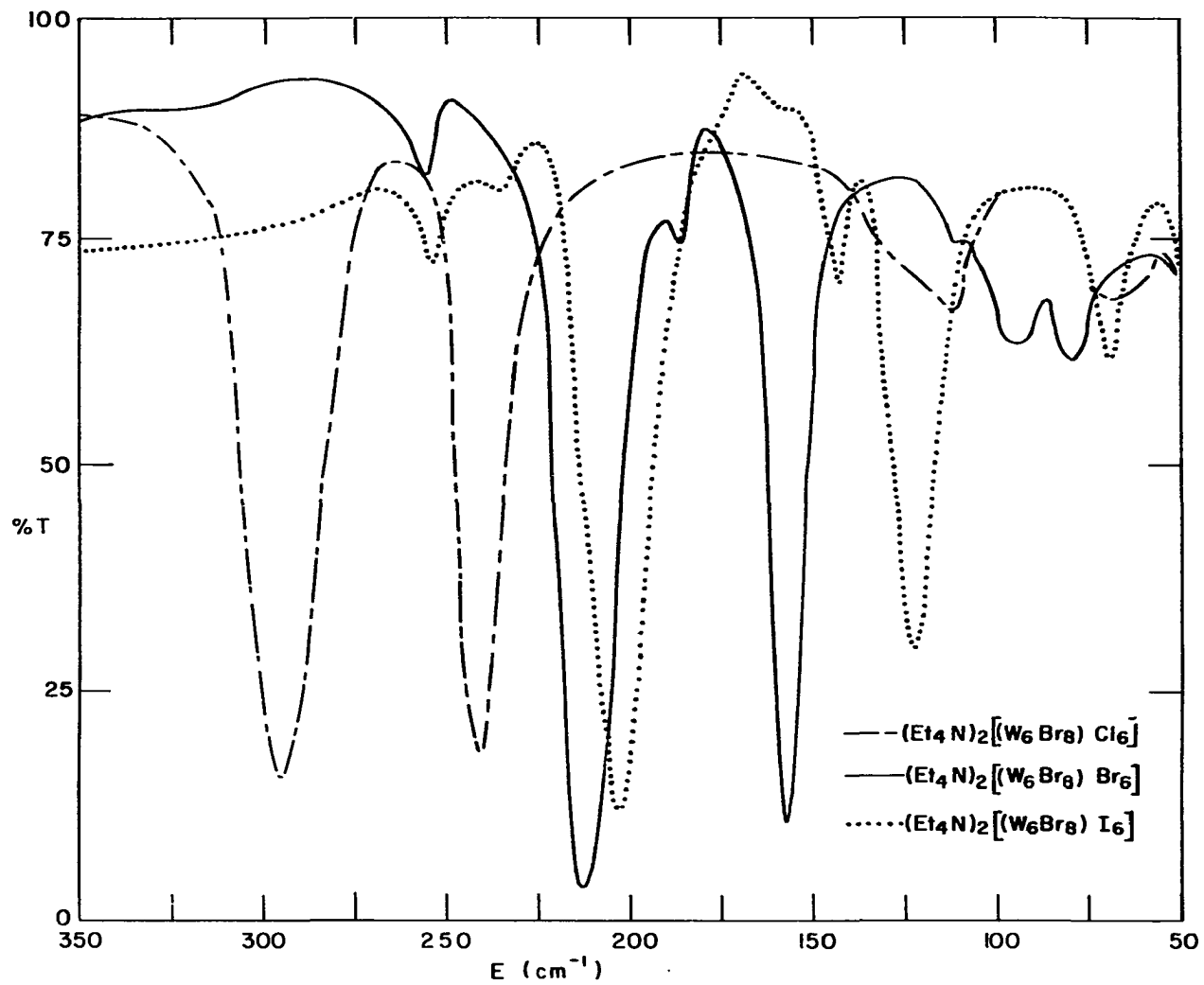
Figure 1. Far infrared spectra of the $(Et_4N)_2[(W_6Cl_8)Y_6]$ series

Figure 2. Far infrared spectra of the $(Et_4N)_2[(W_6Br_8)Y_6]$ series

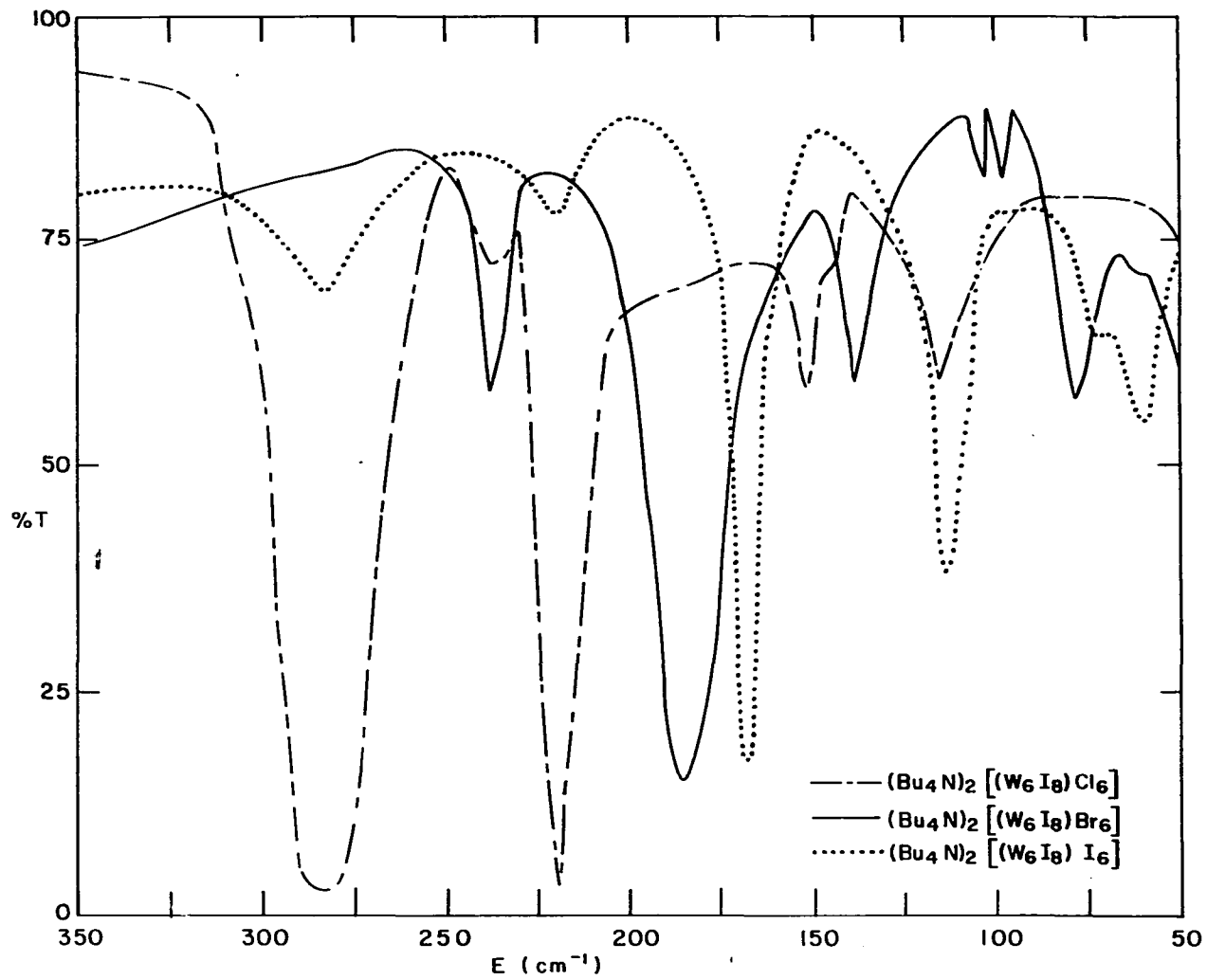Figure 3. Far infrared spectra of the $(Bu_4N)_2[(W_6I_8)Y_6]$ series

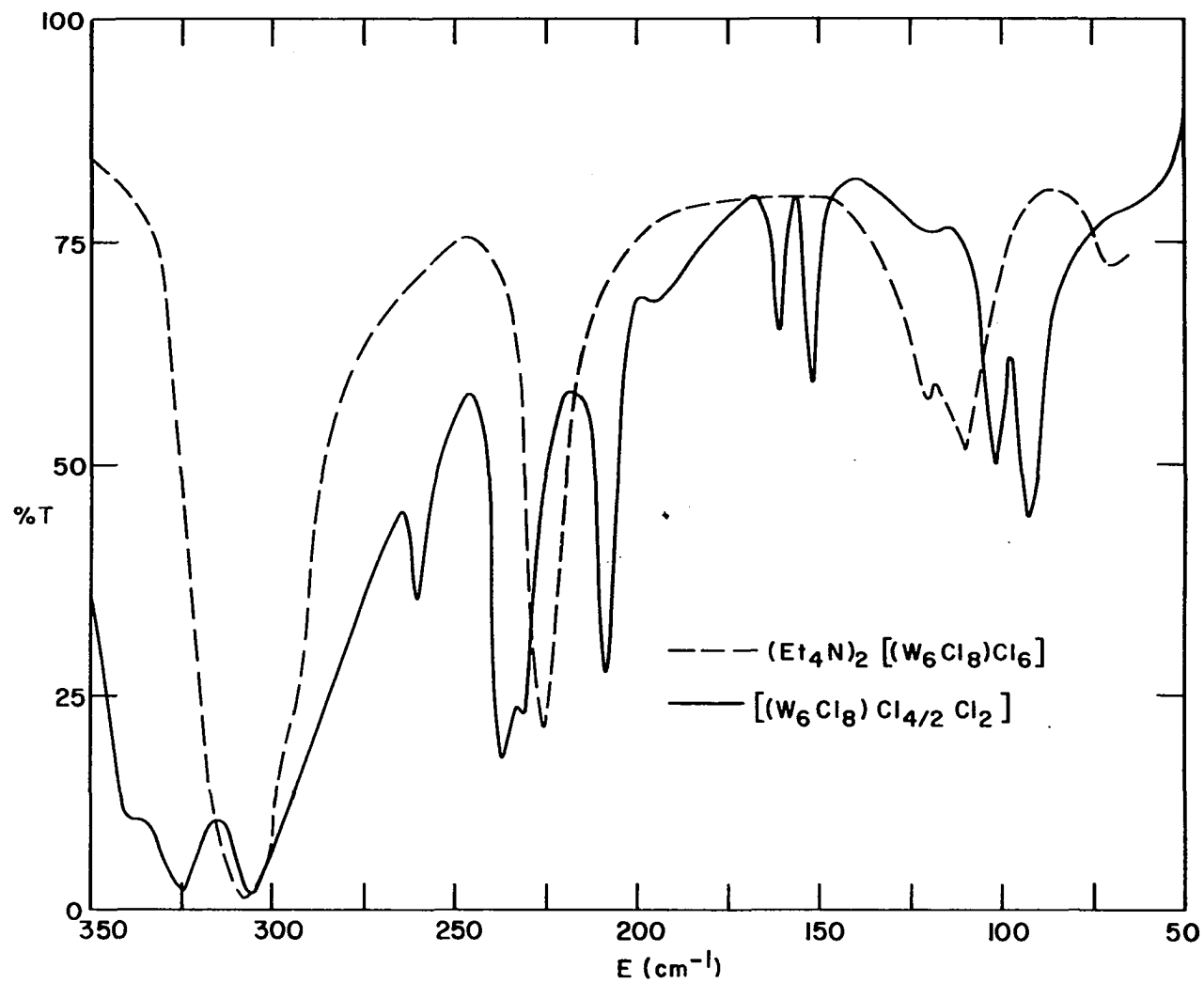Figure 4. Far infrared spectra of $(Et_4N)_2[(W_6Cl_8)Cl_6]$ and $[(W_4Cl_2)Cl_{4/2}Cl_2]$
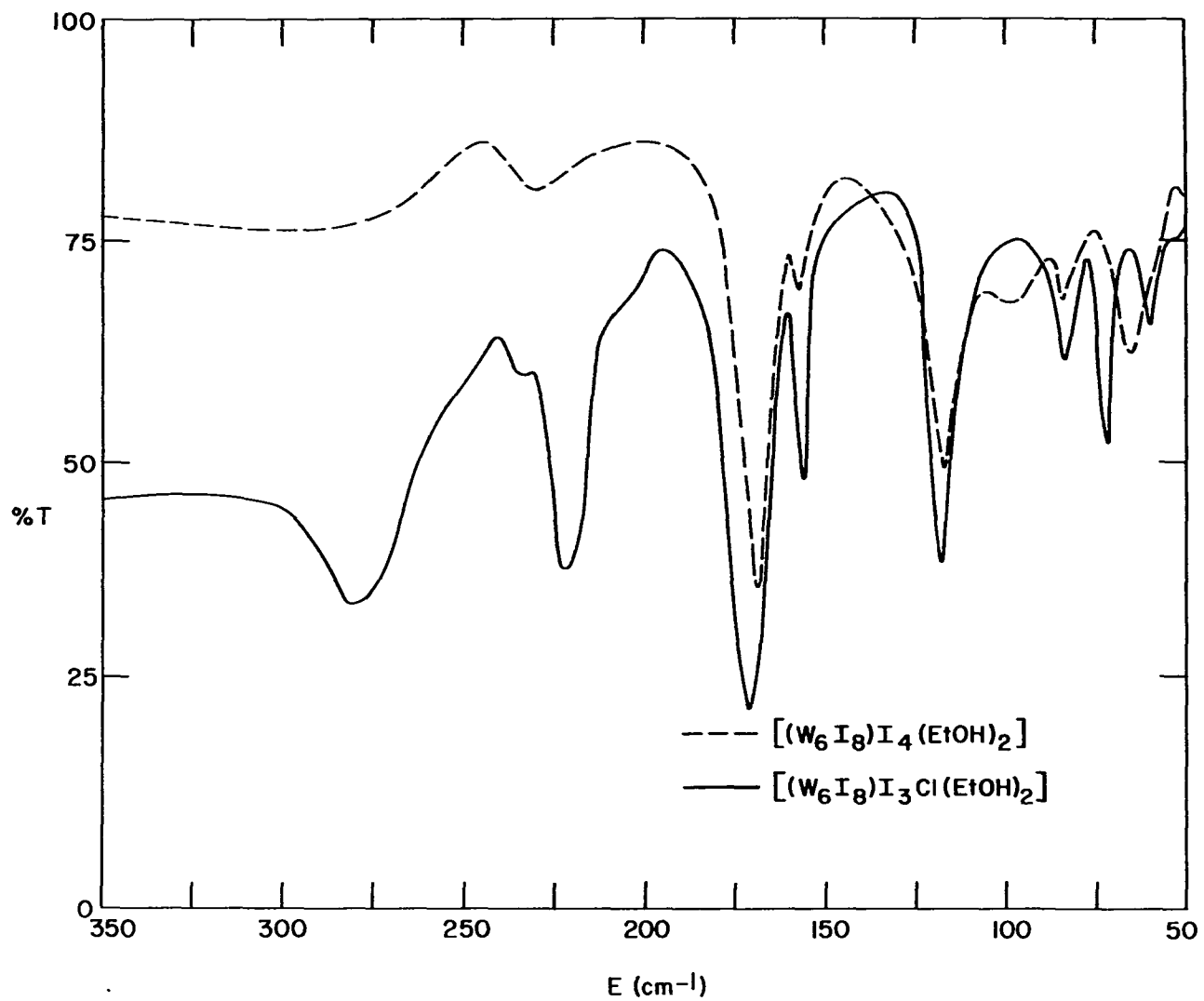
Figure 5. Far infrared spectra of $[(W_6I_8)I_4(EtOH)_2]$ and $[(W_6I_8)I_3Cl(EtOH)_2]$
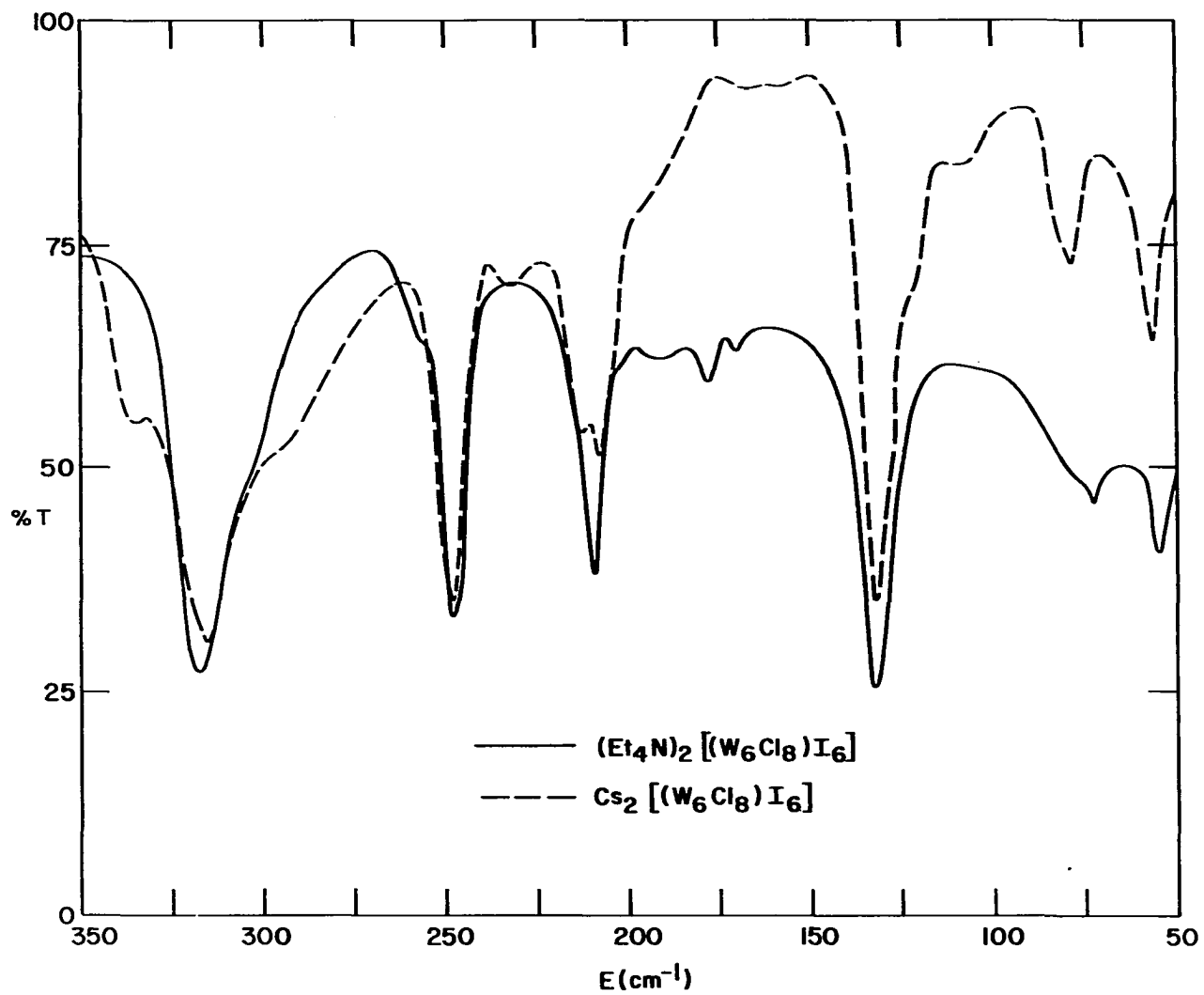
Figure 6. Far infrared spectra of some $R_2[(W_6Cl_8)I_6]$ salts

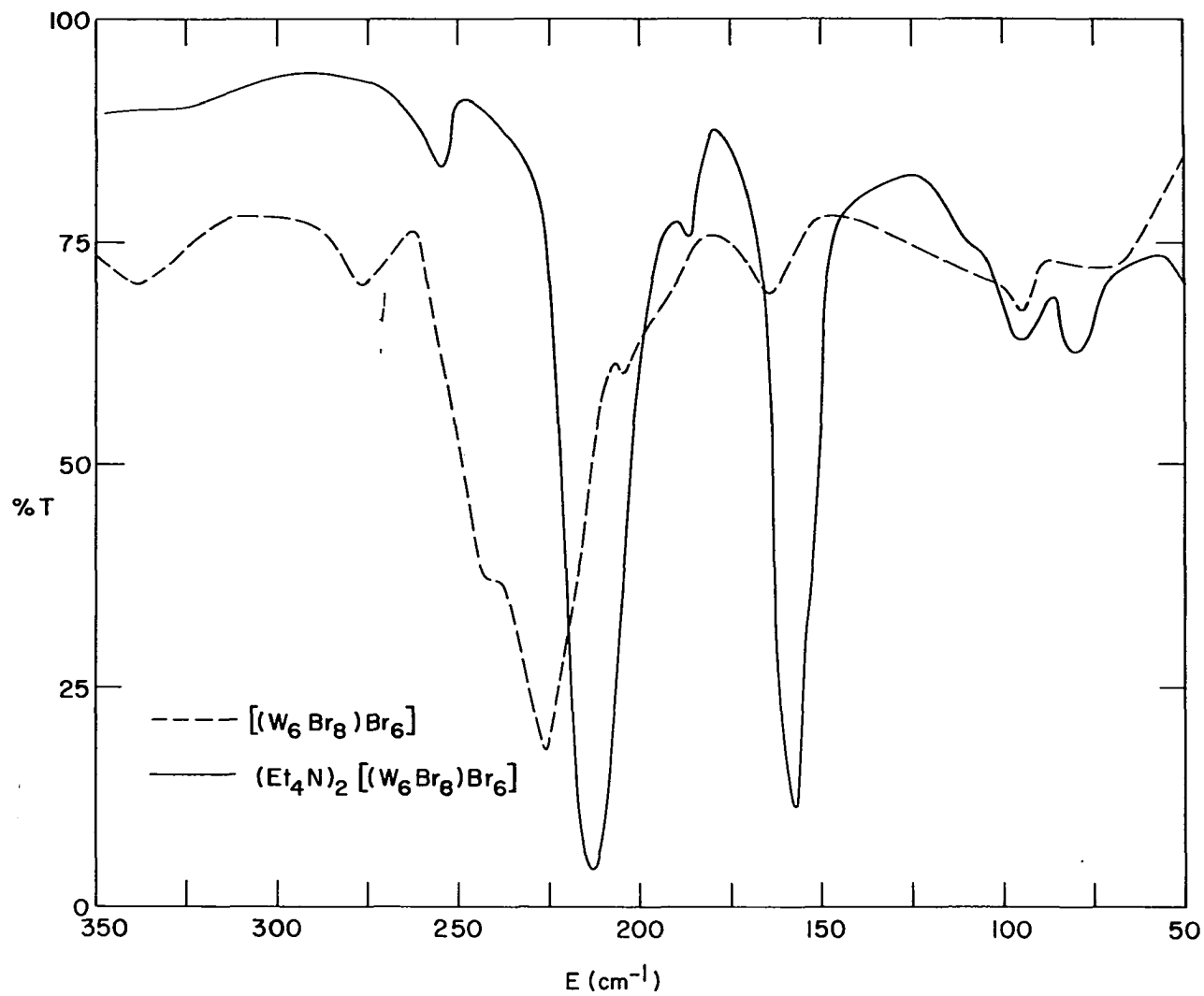Figure 7. Far infrared spectra of $[(W_6Br_8)Br_6]$ and $(Et_4N)_2$ $[(W_6Br_8)Br_6]$

●   M = metal atoms
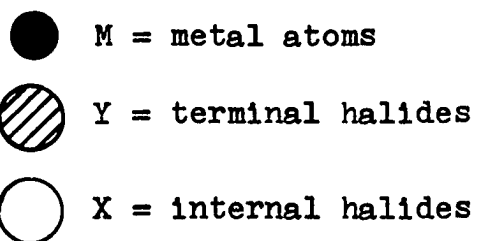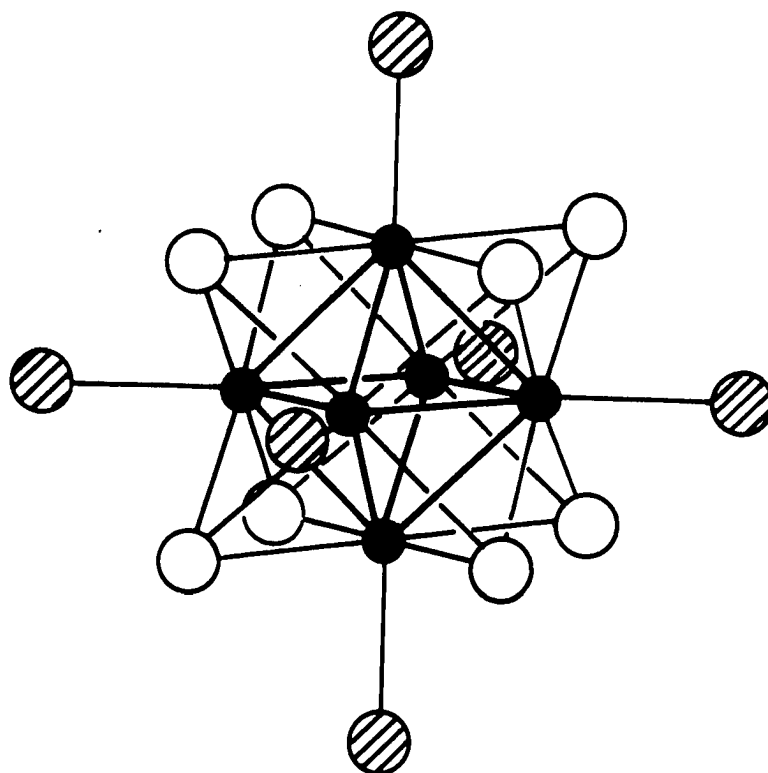
◐   Y = terminal halides

○   X = internal halides

Figure 8. Model of the $[(M_6X_8)Y_6]^{2-}$ anion

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Table 3. Far infrared spectra of some $R_2[(W_6Cl_8)Y_6]$ salts

Y = Cl	Y = Br	Y = I	
	$(Et_4N)_2[(W_6Cl_8)Y_6]$		$(Me_4N)_2[(W_6Cl_8)Br_6]$
306b(vs)i,ts[a,b,c]	317(s)i	318(s)i	319(s)i
	293sh(w)		
287sh(m)i	258(vs)i	248(s)i	258(vs)i
	225sh(w)		
225(ms)i	211(ms)i	210(ms)i	214(ms)i
	169(vs)ts		169(s)ts
	158sh(w)	132(s)ts	158sh(w)
120sh(wm)tb	97sh(w)tb	72(w)tb	90b(m)tb
109(m)tb	76(m)tb	57(vw)tb	
68(w)			
53(w)	54(wm)	47(vw)	52(wm)
	$Cs_2[(W_6Cl_8)Y_6]$		
328sh(m)	329sh(m)	335sh(m)	
303b(vs)i,ts	314(s)i	315(s)i	
	293sh(w)	293sh(m)	
284sh(m)i	258(vs)i	248(s)i	
231sh(m)	233(w)	213sh(ms)	
224(ms)i	215(m)i	207(ms)i	
	169(vs)ts	132(s)ts	
	158sh(w)		
122(wm)tb	90(w)tb	79(m)tb	
101(m)tb	68(w)tb	57(wm)tb	
51(m)	50(wm)	46(w)	
	45(wm)		

[a] Band positions are in cm^{-1}.

[b] Relative intensities are: s = strong, m = medium, w = weak, v = very, b = broad, sh = shoulder.

[c] Band assignments are: i = internal W_6X_8 mode, ts = terminal W-Y stretching mode, tb = terminal X-W-Y bending mode.

Table 4. Far infrared spectra of some $R_2[(W_6Br_8)Y_6]$ salts

Y = Cl	Y = Br	Y = I
	$(Et_4N)_2[(W_6Br_8)Y_6]$	
296(vs)ts[a]		
241(vs)i	265(w)i	254(w)i
	212(vs)i	204(vs)i
	186(w)i	142(m)i
	157(vs)ts	123(s)ts
112b(m)tb	95(m)tb	75(m)tb
	80(m)tb	69(m)tb
	50(w)	
	$Cs_2[(W_6Br_8)Y_6]$	
292(vs)ts		
243(vs)i		256(w)i
	213(vs)i	203(s)i
193(vw)i	189(vw)i	144(wm)i
152(wm)	160(s)ts	125(s)ts
129sh(w)		
116sh(wm)tb	88(m)tb	78(m)tb
105(wm)tb	72(wm)tb	57(m)tb
55(m)	49(m)	47(w)

[a]Band positions, relative intensities, and band assignments are as given in Table 3.

Table 5. Far infrared spectra of some $R_2[(W_6I_8)Y_6]$ salts

Y = Cl	Y = Br	Y = I
	$(Bu_4N)_2[(W_6I_8)Y_6]$	
283(vs)ts[a]		284(w)imp
237(w)i	237(m)i	221(w)i
219(s)i	185(vs)i	168(vs)i
151(wm)i		
	138(m)ts	113(s)ts
114(m)tb	78(m)tb	70(vw)tb
		59(w)tb

$(Et_4N)_2[(W_6I_8)I_4Cl_2]$

287(m)ts
222(wm)i
183sh(m)i
169(ms)i
115(m)ts,tb
85(w)
62(w)tb

[a]Band positions, relative intensities, and band assignments are as given in Table 3.

Table 6. Far infrared spectra of some anhydrous derivatives, $(W_6Cl_8)Y_4$, and some adducts, $[(W_6Cl_8)Y_4L_2]$ of $(W_6Cl_8)^{4+}$

Y = Cl[a]	Y = Cl[b]	Y = Br	Y = I
		$(W_6Cl_8)Y_4$	
339sh(s)[c]			
324(vs)l	321(vs)l,ts	321(s)l	326(s)l
306(vs)ts		292sh(m)	284sh(m)
260(m)l	294sh(s)l	252(m)l	231(m)l
237(ms)l	233(m)l	211(m)l	212(wm)l
231sh(ms)			
209(ms)	208(w)		
161(wm)	161(w)		168(w)
152(m)		177(wm)ts	119(w) ts
102(m)tb	98(m)tb	101(w)	
93(ms)tb		88(w)tb	
		$[(W_6Cl_8)Y_4L_2]$	
		412b(vw)[d]	415b(vw)[d]
	316b(vs)l,ts[e]	322(s)l	322(s)l
		271sh(m)	261sh(wm)
	284(m)l	257(ms)l	249(s)l
		236(w)	
	226(s)l	211(m)l	210(s)l
		173(ms)ts	137(s)ts
	108(m)tb	85b(vw)tb	72b(vw)tb
	69(w)		57(vw)

[a]Annealed at 550°C to crystallize bridged form.

[b]Prepared by thermal decomposition of chloroacid.

[c]Band positions, relative intensities, and band assignments are as given in Table 3.

[d]$L = H_2O$; bands in the 410-440 cm^{-1} region are assigned as W-O stretching modes in hydrates.

[e]$L = CH_3CN$; bands due to coordinated acetonitrile were observed in the infrared at 2313, 2280, 1348, 1023, 947, 399, and 390 cm^{-1}.

Table 7. Far infrared spectra of some anhydrous derivatives, $(W_6Br_8)Y_4$, and some adducts $[(W_6Br_8)Y_4L_2]$, of $(W_6Br_8)^{4+}$

Y = F	Y = Cl	Y = Br[a]	Y = Br[b]
625(wm)[c]			
518b(s)ts	320(s)ts		
	296sh(ms)		266(w)
256(ms)1	250(s)1	258(s)1	255(vw)1
			226(s)
219(s)1	220(m)1	218(ms)1	214(vs)1
198sh(m)1	205sh(m)1	183(m)1	202(s)1
	180(vw)		171(ms)
158(vw)	166(vw)	168(ms)ts	166(ms)ts
			143(wm)
			112(w)
$[(W_6Br_8)Y_4L_2]$		90(wm)tb	104(wm)
			72(m)tb
502(s)ts[d]			63(m)
482(s)ts			50(wm)
439(s)[e]	427b(w)[e]		
358(wm)			
301b(w)	316(s)ts		
273b(w)	297sh(s)		
254(s)1	248(vs)1		
214(m)1	209(w)1		
194(ms)1	196(wm)1		
133(w)	120(wm)tb		
70(vw)	84(wm)		

[a]Prepared by thermal decomposition of tungsten(III) bromide.

[b]Crystalline compound prepared by aluminum reduction of tungsten(V) bromide.

[c]Band positions, relative intensities, and band assignments are as given in Table 3.

[d]Analysis indicated this compound was $(W_6Br_8)F_4(H_2O)_5$, but infrared bands at 3468, 3135, 1630 and 1586 cm-1 show coordinated and lattice water are present.

[e]L = H_2O; bands in the 410-440 cm^{-1} region are assigned as W-O stretching modes in hydrates.

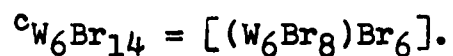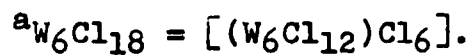Table 8. Far infrared spectra of some adducts, $[(W_6I_8)I_3YL_2]$, of $(W_6I_8)^{4+}$ and of anhydrous $(W_6I_8)I_4$

Y = I	Y = Br	Y = Cl	Y = F
			472(w)ts[a]
394(w)[b]	394(w)[b]	397(w)[b]	397(wm)[b]
		278(m)tx	321b(wm)
			235(vw)
229(vw)i	225(w)i	222(m)i	225(w)i
	181sh(ms)		
169(s)i	173(s)i	171(s)i	170(s)i
157(w)i	156(m)i	156(m)i	157(m)i
	137(m)ts		
117(m)ts	118(s)ts	118(s)ts,tb	117(s)ts
	84(wm)	84(w)	84(w)
	71(wm)tb	71(w)	72(wm)
65(m)tb	61(w)tb	60(w)tb	61(wm)tb
50(w)			

$(W_6I_8)I_4$

235(w)i
174(s)i
165(s)i
129sh(m)
122(ms)ts
110(w)
89(w)
61(vw)tb
51(w)

[a]Band positions, relative intensities, and band assignments are as given in Table 3.

[b]L = EtOH: bands in the 395 cm^{-1} region are assigned as W-O stretching modes in ethanol adducts; bands due to coordinated ethanol were observed in the infrared at 3327 and 1584 cm^{-1}.

Table 9. Far infrared spectra of some oxidized tungsten clusters

W_6Cl_{18}[a]	W_6Br_{18}[b]	W_6Br_{14}[c]
359(vs)1[d]		337(vw)
325(s)1	277(wm)1	277(w)1
305sh(m)ts	248(wm)1	242sh(ms)1
272(s)1	225b(s)1	226(s)1
236(m)1		205(vw)
208(wm)	164(m)ts	165(w)ts
173(wm)tb	157(m)ts	
	93(m)tb	96(w)tb

[a] $W_6Cl_{18} = [(W_6Cl_{12})Cl_6]$.

[b] $W_6Br_{18} = [(W_6Br_8)(Br_4)_{4/2}Br_2]$.

[c] $W_6Br_{14} = [(W_6Br_8)Br_6]$.

[d]Band positions, relative intensities, and band assignments are as given in Table 3.

five fundamental bands.

Additional information about the symmetry type of specific bond length stretching or bond angle bending vibrations is gained by using internal displacement coordinates instead of Cartesian coordinates. The irreducible representations, spanned by the representations formed using the 24 metal-internal halogen bond lengths, 12 metal-metal bond lengths, 6 metal-terminal halogen bond lengths, and 12 internal halogen-metal-terminal halogen bond angles as basis sets, are found to be:

$$\Gamma_{W-X} = A_{1g}+E_g+T_{1g}+2T_{2g}+A_{2u}+E_u+2T_{1u}+T_{2u} \qquad (5)$$

$$\Gamma_{W-W} = A_{1g}+E_g+T_{2g}+T_{1u}+T_{2u} \qquad (6)$$

$$\Gamma_{W-Y} = A_{1g}+E_g+T_{1u} \qquad (7)$$

$$\Gamma_{X-W-Y} = T_{1g}+T_{2g}+T_{1u}+T_{2u} \qquad (8)$$

These irreducible representations show that the five infrared active T_{1u} modes predicted for octahedral $[(W_6X_8)Y_6]^{2-}$ anions are two W-X stretches, one W-W stretch, one W-Y stretch, and one X-W-Y bend.

Reevaluation of the internal modes chosen, however, reveals that these five modes are not completely independent. For instance, the metal-internal halogen stretching modes and the metal-metal stretching mode must necessarily contain some bending character. The metal-metal mode must also contain some metal-internal halogen character since the metal-metal bonds cannot stretch without stretching and bending the metal-internal halogen bonds. Similarly, the metal-metal bonds can-

not be stretched without also affecting the metal-terminal halogen bond lengths. The conclusion then, is that these modes can be mixed in varying degrees. If any modes occur sufficiently close to one another, they can also interact through Fermi resonance to change the position and/or the intensity of the fundamental modes since they are all of the same symmetry (62).

With these cautionary notes in mind, the bands in the infrared spectra were assigned by comparing the systematic differences that occur upon changing the internal and the terminal halide in the complete ($[W_6X_8)Y_6]^{2-}$ series, (X,Y = Cl,Br,I). In many cases compounds of lower symmetry were studied to provide support for the assignments. The bands were designated $\underline{i}$ when assigned to a mode consisting primarily of motion of the internal W_6X_8 unit of the cluster including either W-X or W-W contributions; $\underline{ts}$ for a mode consisting primarily of the W-Y terminal halide stretch; and $\underline{tb}$ for a mode consisting primarily of the X-W-Y terminal halide bend.

The spectra of the $(Et_4N)_2[(W_6Cl_8)Y_6]$ series in Figure 1 and Table 3 show strong bands at 169 cm^{-1} in the Y = Br spectrum and 132 cm^{-1} in the Y = I spectrum. Since no absorption occurs in this region of the Y = Cl spectrum, these bands are associated with the terminal halides, Y. They are assigned as the terminal halide stretching modes while the associated terminal halide bending modes appear at lower energies as the split bands at 120, 109 cm^{-1} for Y = Cl; 97, 76 cm^{-1} for Y = Br;

and 72, 57 cm^{-1} for Y = I. The splitting may be due to crys-
tallographic non-equivalence of cation distribution surrounding
the terminal halides of the cluster. In the Y = Br spectrum
other bands occur at 317, 258, and 211 cm^{-1} while in the Y = I
spectrum bands remain at 318, 248, and 210 cm^{-1} corresponding
to the three predicted internal modes. The spectrum of
$[(W_6Cl_8)Cl_6]^{2-}$ presents a special problem because the requi-
site number of bands is not observed. In this spectrum the
band at 225 cm^{-1} may correspond to the internal bands at 211
and 210 cm^{-1} in the Y = Br and Y = I spectra. The band aris-
ing from an internal mode and corresponding to those at 258 and
248 cm^{-1} in the Y = Br and Y = I spectra, if present at all,
appears as a shoulder near 287 cm^{-1} on the broad absorption at
306 cm^{-1} in the Y = Cl spectrum. The last internal band in
the Y = Cl spectrum must also be located under the broad 306
cm^{-1} absorption and correspond to the 317 and 318 cm^{-1} bands
in the Y = Br and Y = I spectra. This leaves only a terminal
halide stretching mode to assign in the Y = Cl spectrum. By
comparison with the remaining series, it also is assigned
under the broad absorption at 306 cm^{-1}.

The spectra of the $(Et_4N)_2[(W_6Br_8)Y_6]$ series in Figure 2
and Table 4 show similarities in terminal halide modes as well
as some marked differences in internal cluster modes. Bands
at 157 and 123 cm^{-1} in the Y = Br and Y = I spectra clearly
correspond to the bands assigned as terminal halide stretching
modes in the $[(W_6Cl_8)Y_6]^{2-}$ series. The strong band at 296 cm^{-1}

is assigned as the terminal halide stretching vibration in the Y = Cl spectrum. Broadened or split bands at 112 cm^{-1} for Y = Cl; 95, 80 cm^{-1} for Y = Br; and 75, 69 cm^{-1} for Y = I are assigned as the terminal halide bending modes, split by the cations as previously described. Assignment of the three internal W_6X_8 modes in the $[(W_6Br_8)Y_6]^{2-}$ series is complicated because only one strong band in each spectrum remains to be assigned. However, two quite weak bands in the Y = Br and Y = I spectra can also be considered as fundamental modes. The strong bands at 241 cm^{-1} for Y = Cl, 212 cm^{-1} for Y = Br, and 204 cm^{-1} for Y = I, in addition to the weaker bands at 256 and 186 cm^{-1} for Y = Br and 254 and 142 cm^{-1} for Y = I, are assigned to the three internal W_6X_8 modes. These abnormal intensity relationships involving the fundamental internal modes may be partly a consequence of Fermi resonance, since these modes are all of the same symmetry and have similar energies.

The spectra of the $(Bu_4N)_2[(W_6I_8)Y_6]$ series in Figure 3 and Table 5 present the same difficulties in assignment found for the $[(W_6Br_8)Y_6]^{2-}$ series. Bands at 283, 138, and 113 cm^{-1} for Y = Cl, Br, and I respectively, correspond to the terminal halide stretching modes assigned in the other series. The terminal halide bending modes are assigned as the broadened or split bands at 114 cm^{-1} for Y = Cl, 78 cm^{-1} for Y = Br, and 70, 59 cm^{-1} for Y = I. Again, only one strong band in each spectrum remains to be assigned to internal W_6X_8 modes.

Weaker bands in each of the spectra are candidates for the remaining fundamentals. The strong bands at 219 cm^{-1} for Y = Cl, 185 cm^{-1} for Y = Br, and 168 cm^{-1} for Y = I, in addition to the weaker bands at 237 and 151 cm^{-1} for Y = Cl, 237 cm^{-1} for Y = Br, and 221 cm^{-1} for Y = I, are assigned to the three internal W_6X_8 modes. The weak band at 284 cm^{-1} for Y = I is assigned as terminal chloride containing impurity because of the method of preparation of the compound. Fermi resonance again may explain the weakening or complete absence of some of the fundamental internal W_6X_8 modes.

The effect of a major difference in symmetry is shown in Figure 4 and Tables 3 and 6. $(Et_4N)_2[(W_6Cl_8)Cl_6]$, in octahedral symmetry, should exhibit five infrared active modes compared to thirteen predicted in D_{4h} symmetry for tungsten (II) chloride which has been annealed to crystallize the externally bridged form, $[(W_6Cl_8)Cl_{4/2}Cl_2]$. Both the internal and the terminal modes are split in the lower symmetry compound so that eleven of the predicted bands are observed. The five bands in best agreement with the octahedral $[(W_6Cl_8)Cl_6]^{2-}$ spectrum are assigned as internal and terminal modes with the remaining bands attributed to the lower symmetry splitting.

Another such comparison can be made between the spectrum of crystalline tungsten(II) bromide, $[(W_6Br_8)Br_{4/2}Br_2]$, (Table 7) as prepared by aluminum reduction, and the spectrum of the octahedral $[(W_6Br_8)Br_6]^{2-}$ anion (Table 4). The spectrum of

the dibromide contains all thirteen bands predicted with strong peaks falling near each of the fundamentals assigned in the $[(W_6Br_8)Br_6]^{2-}$ spectrum. The unassigned bands are again attributed to the lower symmetry splitting.

The spectra (Tables 6, 7, 8) of the unannealed, anhydrous dihalides, $(W_6X_8)Y_4$, prepared by thermal decomposition of haloacids, hydrates, or oxidized derivatives, do not show the splitting expected for D_{4h} symmetry. Instead, these amorphous compounds exhibit spectra very similar to the analogous octahedral anions. This is interpreted to mean that the disorder introduced by the random loss of terminal halides is not sufficient to distort the octahedral symmetry of the internal W_6X_8 unit and the infrared spectrum retains the simplicity of the octahedral species. The assignments were made, therefore, on the basis of the analogous octahedral $[(W_6X_8)Y_6]^{2-}$ anions.

The minor splittings observed in the spectrum of anhydrous tungsten(II) iodide (Table 8) are attributed to partial crystallization (also observed in the x-ray powder pattern) during its preparation by thermal decomposition at $500^\circ C$. Assignments are made in relation to the analogous octahedral $[(W_6I_8)I_6]^{2-}$ anion.

The adducts, $[(W_6X_8)Y_4L_2]$, although also formally D_{4h} symmetry, have essentially the same spectra (Tables 6, 7, 8) as the octahedral complexes. This is interpreted to mean that ligands like acetonitrile, ethanol, and water in some of the terminal positions do not introduce serious enough distortions

of the cluster unit to lower the internal symmetry and split the infrared modes assigned to the W_6X_8 unit. Consequently, these spectra are also assigned in terms of the related octahedral $[(W_6X_8)Y_6]^{2-}$ anions.

The effect of an intermediate change in symmetry is shown in Figure 5 and Table 8. $[(W_6I_8)I_4(EtOH)_2]$ and $[(W_6I_8)I_3Y(EtOH)_2]$, although nominally D_{4h} or lower in symmetry, all have spectra similar to the octahedral compounds. Exchanging one of the terminal iodides for some other halide does have the effect, however, of enhancing the strength of the bands previously assigned as weak fundamentals in the octahedral $[(W_6I_8)I_6]^{2-}$ anion and in the pseudo-octahedral complex, $[(W_6I_8)I_4(EtOH)_2]$, without splitting these bands as would be expected in a lower symmetry.

–A minor symmetry change, due to different cations, is shown in Figure 6. Although the strongest peaks of the two $[(W_6Cl_8)I_6]^{2-}$ salts are at essentially the same positions, crystallographic lowering of the symmetry causes some minor splittings. The cesium salts studied exhibit more split bands than their tetraalkylammonium counterparts.

The effect of oxidation on the infrared spectra of tungsten clusters is shown in Figure 7 and Table 9. Oxidation of tungsten(II) bromide to W_6Br_{14} or W_6Br_{18}, containing $(W_6Br_8)^{6+}$, causes the infrared bands assigned to the internal $(W_6Br_8)^{4+}$ unit of $[(W_6Br_8)Br_6]^{2-}$ or $(W_6Br_8)Br_4$ to shift 20-40 cm^{-1} higher in energy while bands assigned to the terminal bromide

stretching and bending modes remain nearly constant.

The spectrum of tungsten(III) chloride, however, cannot be assigned on the basis of a simple oxidized W_6Cl_8 unit because of the appearance of additional infrared bands. The spectrum is assigned on the $[(W_6Cl_{12})Cl_6]$ model with four internal W_6Cl_{12} modes, one terminal W-Cl stretch, and one terminal W-Cl bend.

Some correlations and generalizations concerning the assignment of the spectra of $(W_6X_8)Y_n$ derivatives are readily apparent from the summary of these assignments presented in Table 10.

Table 10. Assignment of infrared spectral bands in $(W_6X_8)Y_n$ compounds

	Assignment	Y = Cl	Y = Br	Y = I
	W_6X_8	318	319	320
	W_6X_8	284	257	248
X = Cl	W_6X_8	225	212	210
	W-Y	305	170	134
	X-W-Y	105	76	57
	W_6X_8	245	256	255
	W_6X_8	215	214	204
X = Br	W_6X_8	198	186	143
	W-Y	294	159	124
	X-W-Y	108	76	63
	W_6X_8	237	237	229
	W_6X_8	219	185	170
X = I	W_6X_8	154	156	158
	W-Y	283	138	116
	X-W-Y	114	78	61

For X = Cl, Br, and I respectively, the terminal chloride stretching frequencies are 305, 294 and 283 cm^{-1}, the terminal bromide stretching frequencies are 170, 159, and 138 cm^{-1}, and the terminal iodide stretching frequencies are 134, 124, and 116 cm^{-1}. The lowering of these frequencies by $\underline{ca}$. 10 cm^{-1} as the internal halide is varied indicates a definite mixing of internal W-X character into the terminal halide stretching modes. The terminal halide bending modes, on the other hand, are not shifted appreciably by changing internal halides, but are moderately responsive to variations in cations.

Of the three bands assigned to internal W_6X_8 modes in each series, two seem to be relatively independent of the terminal halides present whereas the third has a rather strong terminal halide dependence. This, presumably, is the internal mode that contributed the W-X character to the terminal halide stretching modes and, in return, has acquired some W-Y character.

Fermi resonance, in addition to affecting the intensity of some of the fundamental modes as already described, has caused some shifts in band positions. When a heavier halide is introduced into the internal W_6X_8 unit, the terminal halide stretching frequency is found $\underline{ca}$. 10 cm^{-1} lower except for the terminal bromide stretching frequency in W_6I_8 derivatives which is $\underline{ca}$. 20 cm^{-1} lower than in W_6Br_8 compounds. The proximity of an internal W_6I_8 mode at 156 cm^{-1} apparently causes the

terminal bromide stretching frequency to shift downward from its expected position at $\underline{ca}$. 149 cm^{-1}.

The internal W_6I_8 bands observed at 237 cm^{-1} for Y = Cl and Y = Br are apparently shifted upward from their position at 229 cm^{-1} in the Y = I compounds because of the closer proximity of the internal W_6I_8 bands at 219 and 185 cm^{-1} respectively compared to the internal band at 170 cm^{-1} in the Y = I compounds. The band at 237 cm^{-1} in the Y = Cl derivatives might be shifted still higher because of the nearness of the band at 219 cm^{-1} except for the presence of the strong terminal chloride stretching mode above it at 283 cm^{-1}.

Similarly, the internal W_6Cl_8 bands at 212 and 210 cm^{-1} respectively for the Y = Br and Y = I derivatives have been shifted downward in comparison to the 225 cm^{-1} band in the Y = Cl compounds by the closer proximity of the internal modes at 257 and 248 cm^{-1} respectively whereas the band at 284 cm^{-1} in the Y = Cl compounds does not seriously affect the position of the band at 225 cm^{-1}.

With the complications introduced by mixing of T_{1u} infrared active modes as well as Fermi resonance effects in both band positions and intensities, these assignments of the infrared spectra may seem somewhat questionable without the added support of Raman data and a complete normal coordinate analysis, but the assignments are the most consistent for the data available.

Comparison of infrared results
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Mackay (23), Cotton et al. (24), Clark et al. (25),
Hartley and Ware (26), and Mattes (29) have previously re-
ported infrared or Raman investigations of M_6X_8 cluster deriv-
atives, but the variety of compounds for which data has been
reported is limited to $(Mo_6X_8)L_n$, (X = Cl,Br; L = Cl,Br,I,OH,
DMSO), and $(W_6Cl_8)L_n$, (L = Cl,Br) derivatives. Although the
molybdenum and tungsten species exhibit apparently analogous
spectra, most of the work has been devoted to the molybdenum
compounds.

Mackay (23), after assigning the spectra of Mo_6Cl_8 and
Mo_6Br_8 derivatives, suggested that the bands at 307 cm^{-1} and
226 cm^{-1} in $[(W_6Cl_8)Cl_4(H_2O)_2]$ supported his assignment of
comparable bands in the molybdenum compounds as internal
M_6X_8 modes. He did not observe or assign any other modes for
the tungsten compound.

Cotton et al. (24) also studied the infrared spectra of
$[(Mo_6X_8)Y_6]^{2-}$ anions, (X = Cl,Br; Y = Cl,Br,I) and of the
$[(W_6Cl_8)Cl_6]^{2-}$ anion. In contrast to Mackay, they assigned
two internal W_6Cl_8 modes in the 290-320 cm^{-1} region and a
terminal chloride stretching mode at 225 cm^{-1}. They tenta-
tively assigned a terminal chloride bending mode at 205 cm^{-1}
and a metal-metal stretching mode at 150 cm^{-1}. The spectrum
from which they derived these data must certainly be questioned
when it is compared to the spectrum of $(Et_4N)_2[(W_6Cl_8)Cl_6]$

reported in this study, which shows no absorption at 205 cm^{-1} or at 150 cm^{-1}.

Clark et al. (25) studied haloacids, anhydrous derivatives, and adducts of Mo_6Cl_8 and W_6Cl_8, but only over the 200-500 cm^{-1} range. They assigned bands at 225 and 308 cm^{-1} in $(W_6Cl_8)Cl_n$ derivatives and bands at 257 and 321 cm^{-1} in $(W_6Cl_8)Br_n$ derivatives as internal W_6Cl_8 modes, but could draw no further conclusions.

Mattes (29) observed the infrared spectra of $(Mo_6Cl_8)Y_4$, (Y = Cl,Br,I); $Cs_2[(Mo_6Cl_8)Cl_6]$; $(M_6Br_8)Br_4$, (M = Mo,W); and $(W_6Cl_8)Y_4$, (Y = Cl,Br) and performed a normal coordinate analysis to assign the observed bands. The spectra reported for the tungsten compounds are almost identical to those reported in this study, but the assignments are different. He assigns bands at 322 and 210 cm^{-1} for Y = Cl and bands at 291 and 212 cm^{-1} for Y = Br to the internal W_6Cl_8 modes. He assigns bands at 236 and 157 cm^{-1} respectively, as the terminal chloride and bromide stretching modes and the bands at 100 and 86 cm^{-1} respectively as the terminal chloride and bromide bending modes. He then calculates that a metal-metal stretching mode should occur around 75 cm^{-1} with a force constant of 0.3 md/Å.

In comparison to the assignments of infrared spectra of tungsten clusters made by other workers, some major differences are uncovered in this study. First, the position of the terminal tungsten-chloride stretching mode is shown to

be in the 280-310 cm^{-1} region in W_6X_8 derivatives instead of around 200-230 cm^{-1} as assigned by the other workers. Evidence from the wider variety of compounds, particularly the $[(W_6I_8)Cl_6]^{2-}$ and $[(W_6I_8)I_3Y(EtOH)_2]$ derivatives, unequivocally shows that this is the correct position of the terminal tungsten-chloride stretching mode. There seems to be general agreement on the position of the other terminal halide stretching modes.

Second, no bands were observed to remain relatively constant as would be expected from a pure metal-metal stretching mode, over the entire range of $[(W_6X_8)Y_6]^{2-}$ derivatives, (X,Y = Cl,Br,I). This demonstrates that prime consideration must be given to the mixing of the metal-metal mode with the other infrared active modes.

Finally, the mixing of the other internal and terminal modes and the effects of Fermi resonance in shifting band positions and intensitive changes some of the observed spectra so drastically that the five bands expected of $[(W_6X_8)Y_6]$ groups in octahedral symmetry are not always readily discerned.

The infrared spectra of the oxidized tungsten clusters can best be explained by comparison with recent infrared investigations of $(M_6X_{12})^{n+}$ systems, (M = Nb,Ta; X = Cl,Br; n = 2,3,4), by Fleming (63). He observed upward shifts of 18-32 cm^{-1} in the internal M_6X_{12} modes upon a 2 electron oxidation of the M_6X_{12} clusters. This agrees well with the

observed increases of 20-40 cm^{-1} in the internal modes upon oxidizing $(W_6Br_8)^{4+}$ to $(W_6Br_8)^{6+}$.

The infrared spectrum of tungsten(III) chloride as $[(W_6Cl_{12})Cl_6]$ is found to agree well with spectra of $[(M_6Cl_{12})Cl_6]^{n-}$ derivatives assigned by Fleming. Strong bands at 354, 336, 302, 267, 196, 190 and 142 cm^{-1} in $(Et_4N)_2[(Nb_6Cl_{12})Cl_6]$, for instance, compare very favorably with the bands observed at 359, 325, 305, 272, 236, 208 and 173 cm^{-1} in $[(W_6Cl_{12})Cl_6]$.

SUMMARY

A wide variety of lower oxidation state tungsten halides was synthesized and characterized chemically and physically. Derivatives were prepared by sealed tube reductions, from fused salt exchange reactions, from aqueous and non-aqueous solutions, and by oxidation in liquid halogens. All but one of the compounds studied was shown to contain W_6X_8 cluster units. The chemical and physical properties of these low oxidation state compounds were governed by the high stability of this polynuclear grouping.

Far infrared spectral data were used to characterize the similarities, as well as the differences, in these cluster derivatives. The spectral shifts upon changing internal and external halides in the complete chloride, bromide, and iodide series were observed and explained. The effect on the spectra of changing the symmetry, slightly and grossly, was also observed. Oxidation of the clusters was seen to cause upward shifts, as expected, in the positions of the infrared bands assigned to internal cluster modes.

Assignments, although somewhat tenuous in the absence of Raman data and a complete normal coordinate analysis, were then made for the bands attributed to internal W_6X_8 modes, to terminal W-Y stretching modes, and to terminal X-W-Y bending modes.

SUGGESTIONS FOR FUTURE WORK

New methods for preparing tungsten(II) halides directly from the higher chlorides and bromides should be sought. Tin(II) chloride, tungsten hexacarbonyl, or hydrogen iodide might be effective reducing agents for this purpose.

Oxidation of the mixed tungsten(II) halides like $(W_6Cl_8)Br_4$, $(W_6Cl_8)I_4$, $(W_6Br_8)Cl_4$, and $(W_6I_8)Cl_4$ with the appropriate halogen should prove interesting in establishing the conditions conducive to simple oxidation of the $(W_6X_8)^{4+}$ unit to $(W_6X_8)^{6+}$ as with tungsten(III) bromide and the conditions necessary for conversion to $(W_6X_{12})^{6+}$ as with tungsten(III) chloride.

More derivatives, especially those containing dissimilar terminal halides in the form of $[(W_6X_8)X_nY_m]^{x\pm}$ or those containing terminal fluoride, hydroxide, or other oxygen containing ligands might prove helpful in confirming the infrared assignments just made. Raman data and a normal coordinate analysis would certainly help remove the uncertainties present in the vibrational assignments.

New cluster derivatives, containing mixed metals, mixed halogens, or both would be interesting for infrared study as well as for magnetic, electronic spectral, and x-ray crystallographic studies.

Reactions designed to exchange the internal halides of W_6X_8 clusters for other known bridging groups such as OR^-, SH^-, SR^-, SCN^-, or bidentate oxygen or sulfur donor ligands capable

of bridging the internal W_6 unit could produce a wide variety
of new compounds for study.

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APPENDIX

Table 1A. X-ray powder pattern data for tungsten(II) halides

W_6Cl_{12}	W_6Br_{12}	W_6I_{12}
6.94(10)[a]	7.30 (10)	8.42(1)
5.64(7)	5.89(5)	7.77(6)
3.48(3)	3.63(1)	7.00(1)
2.85(5)	2.74(3)	6.33(3)
2.62(2)	2.64(2)	3.63(1)
2.54(2)	2.48(2)	3.41(1)
2.38(3)	2.42(1)	3.18(1)
2.35(3)	2.31(4)	3.14(1)
2.32(3)	2.18(4)	2.96(2)
2.25(5)[b]	2.15(3)	2.84(2)
2.21(5)	2.09(1)	2.73(1)
2.11(1)	2.06(1)	2.65(1)
2.06(4)	1.996(5)	2.49(3)
2.01(2)	1.861(3)	2.30(2)
1.941(1)	1.822(2)	2.23(1)
1.920(2)	1.751(1)	2.16(1)
1.794(3)	1.667(1)	2.12(1)
1.763(2)	1.539(2)	2.07(1)
1.746(2)	1.460(1)	1.999(10)
1.589(2)[b]	1.429(1)	1.944(1)
1.572(2)	1.316(1)	1.875(1)
1.478(4)	1.249(1)	1.844(1)
1.296(3)[b]	1.160(1)	1.791(1)
1.186(1)[b]	1.123(1)	1.735(3)
	1.103(1)	1.643(1)
		1.335(1)
		1.240(1)

[a]d spacing in angstroms (relative intensity).

[b]Tungsten metal line.

Table 2A. X-ray powder pattern data for some oxidized
tungsten clusters

W_6Cl_{18}[a]	W_6Cl_{18}[b]	W_6Br_{18}		W_6Br_{14}
7.44(8)[c]	7.48(4)	9.21(5)	1.953(2)	7.93(7)
7.04(10)	6.99(10)	8.07(10)	1.869(1)	7.17(6)
5.67(2)	5.73(3)	7.56(6)	1.814(1)	5.93(2)
5.13(2)	5.11(1)	7.21(6)	1.738(3)	4.33(1)
4.22(2)	4.23(1)	6.13(1)	1.710(1)	3.96(1)
4.01(1)		5.92(1)	1.609(1)	3.60(1)
3.72(1)		5.36(3)	1.552(1)	2.98(1)
3.29(1)	3.27(1)	4.31(3)	1.499(2)	2.81(1)
3.18(1)	3.18(1)	3.73(2)	1.412(1)	2.73(1)
3.01(1)	3.03(1)	3.63(1)	1.328(1)	2.65(2)
2.82(2)	2.82(2)	3.49(1)	1.292(1)	2.45(1)
2.73(1)		3.43(2)	1.276(1)	2.35(1)
2.63(1)	2.62(2)	3.22(1)	1.180(1)	2.10(1)
2.48(1)		3.10(4)	1.158(1)	1.993(10)
2.42(5)	2.41(3)	3.00(4)	1.129(1)	1.735(2)
2.34(1)	2.33(1)	2.85(1)		1.538(1)
2.31(1)	2.31(1)	2.72(1)		1.238(1)
2.24(1)		2.68(1)		1.126(2)
2.11(1)	2.11(1)	2.52(2)		
2.08(1)		2.42(2)		
2.06(1)	2.06(1)	2.30(1)		
2.03(1)		2.26(1)		
1.992(4)	1.994(1)	2.16(5)		
1.895(2)	1.897(1)	2.11(1)		
1.862(1)		2.06(1)		
1.713(3)	1.712(1)			
1.393(1)				
1.257(1)				
1.127(1)				

[a]Prepared from tungsten(II) chloride and liquid chlorine.

[b]Prepared from tungsten(II) chloride and thionyl chloride.

[c]d spacing in angstroms (relative intensity).