halogen charge transfer because the band is shifted by only 1.4 kK when Br is substituted for Cl in the $Nb_6X_{12}^{4+}$ cluster (Table IV). There are two plausible assignments: $t_{2g}(xz, yz) \rightarrow t_{2u}^*(xz, yz)$ and $t_{1u}(xz, yz) \rightarrow t_{1g}^*(xz, yz)$. These cannot be differentiated until a more accurate MO calculation can be made. Although bands E, F, and H are thought to be metal–metal bands, a more specific assignment is not possible; their intensities (by comparison with band G) indicate that they arise from forbidden transitions.

The above discussion indicates the very tenuous nature of these assignments. We hope, however, that this work will stimulate the necessary experimental and theoretical investigations which are needed to verify the assignments and further the understanding of bonding in these complicated systems.

Contribution No. 2604 from the Institute for Atomic Research and Department of Chemistry,
Iowa State University, Ames, Iowa 50010

Chemistry of Polynuclear Metal Halides. V. Reactions and Characterization of Compounds Containing Tungsten Halide Cluster Species[1a,b]

By R. D. HOGUE[1c] and R. E. McCARLEY

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Many new complexes of the tungsten(II) halides containing the $W_6X_8^{4+}$ cluster species (X = Cl, Br, I) have been prepared and characterized both physically and chemically. The anhydrous halides $(W_6X_8)X_4$, prepared by reduction or disproportionation of higher halides, were treated in acidic, basic, nonaqueous, and fused-salt media to prepare principally derivatives of $(W_6X_8)Y_4$, $(W_6X_8)Y_6^{2-}$, and $(W_6X_8)Y_4L_2$, where X or Y = Cl, Br, I and L = a neutral electron pair donor molecule Infrared spectra of these compounds in the region 50–600 cm^{-1} showed bands characteristic of the W_6X_8 cluster unit and of the ligands Y or L. Assignment of the observed bands to discrete modes arising from the stretching or bending of pure metal–metal or metal–halogen bonds was precluded because of mixing and interaction of the vibrational modes. However, some definite assignments to the W_6X_8 cluster modes or modes of the terminal ligands Y could be made by observing the changes in the spectra that occurred upon varying both X and Y in the complete series for the $(W_6X_8)Y_6^{2-}$ derivatives. Data supporting these assignments were obtained from the other types of derivatives.

Introduction

A thorough study of the preparation, reactions, and properties of compounds containing the molybdenum(II) halide cluster species $Mo_6X_8^{4+}$ has been made by Sheldon,[2] who prepared anhydrous halides $(Mo_6X_8)Y_4$, salts of $(Mo_6X_8)Y_6^{2-}$, and adducts of the type $(Mo_6X_8)Y_4L_2$, where X = Cl, Br, I; Y = Cl, Br, I, OH; and L = neutral donor ligand. Additional derivatives of the $Mo_6Cl_8^{4+}$ cluster have been prepared by other workers.[3–5]

Structure determinations by Brosset,[6] Vaughan,[7] and Schäfer, *et al.*,[8] have shown the $Mo_6X_8^{4+}$ unit to have essentially a perfect cubic arrangement with the eight bridging halogen atoms located over each face of the octahedron formed by the six metal atoms. The Mo–Mo distance of 2.61 Å,[8] diamagnetic susceptibility, and great stability of the cluster unit support strong metal–metal bonding, which is augmented by unusually strong metal-bridging halogen bonding indicated by the Mo–Cl_b distance of 2.47 Å. Another important structural feature is the bonding of each metal atom to an additional ligand in a terminal (nonbridging) position over each face of the Mo_6X_8 cube. This accounts for the formation of the complex derivatives such as $(Mo_6X_8)Y_6^{2-}$ and $(Mo_6X_8)Y_4L_2$. The structure attained by the anhydrous halides $(Mo_6X_8)X_4$ results in complete occupation of these six coordination sites by sharing of terminal halide atoms between cluster units, as indicated by the formula $(Mo_6Cl_8)Cl_{4/2}Cl_2$. That the tungsten(II) halides have the same structure and, hence, contain the $(W_6X_8)^{4+}$ units has been demonstrated by Schäfer, *et al.*[8]

Several authors have examined the vibrational spectra of $Mo_6X_8^{4+}$ derivatives, both by infrared[9–12] and Raman[13] methods. Assignment of the spectra in terms of the various vibrational modes of the cluster species has been difficult because the requisite number of bands has not always been observed and because serious inter-

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[1] (a) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. (b) Presented in part at the 157th National Meeting, American Chemical Society, Minneapolis, Minn., 1969. (c) A portion of the Ph.D. thesis of R. D. Hogue, Department of Chemistry, Iowa State University.

[2] (a) J. C. Sheldon, *Nature*, **184**, 1210 (1959); (b) *J. Chem. Soc.*, 1007, 3106 (1960); (c) *ibid.*, 750 (1961); (d) *ibid.*, 410 (1962); (e) *ibid.*, 4183 (1963); 1287 (1964).

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action between modes of the same symmetry representation may result in marked changes in position or intensity of absorption bands. In this paper we describe the preparation and characterization, principally by infrared spectra, of an extensive series of $W_6X_8^{4+}$ derivatives. The results show that the tungsten compounds are quite stable and chemically similar to their molybdenum analogs, and the large body of infrared data has permitted a more positive interpretation of the vibrational spectra.

Experimental Section

Measurements.—Infrared absorption 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 drybox, were sealed between cesium iodide windows for the normal region of the infrared spectrum and between thin polyethylene windows in a specially designed O-ring holder for the far-infrared spectrum.

Tungsten analyses were performed by hydrolysis of samples in basic solution, followed by homogenous precipitation of tungsten trioxide from hydrogen peroxide–nitric acid solution. The oxide was weighed as WO_3 after ignition in air at 500°. Halides were determined by potentiometric titration with standard silver nitrate in compounds containing only one halide and in compounds containing both chloride and iodide or bromide and iodide. Bromide was determined in compounds containing chloride by the method of Kolthoff and Yutzy.[14] Carbon and hydrogen were determined by Mr. J. J. Richard of the Ames Laboratory Analytical Service Group.

Preparation of Compounds.—Tungsten(II) chloride was prepared by disproportionation of tungsten(IV) chloride[15] at 425° or by reduction of tungsten(VI) chloride with aluminum in a temperature gradient of 475–200°. Finely divided, pyrophoric tungsten metal, a contaminant in both methods, was removed by recrystallization of the chloro acid $(H_3O)_2[(W_6Cl_8)Cl_6]\cdot nH_2O$ from hydrochloric acid containing a few milliliters of ethanol following essentially the method Sheldon used for the chloro acid of molybdenum.[2b] The bright yellow crystals of chloro acid faded to pale yellow tungsten(II) chloride during thermal decomposition *in vacuo* at 325°.

Tungsten(II) bromide was prepared by aluminum reduction of tungsten(V) bromide in a temperature gradient of 475–240°. This product was dissolved in hot ethanol–50% concentrated hydrobromic acid, which was filtered and evaporated nearly to dryness with gentle heating under aspirator vacuum. The resultant orange precipitate was redissolved in water and again evaporated to precipitate the yellow hydrate $(W_6Br_8)Br_4(H_2O)_2$, which was decomposed *in vacuo* at 350° to provide $(W_6Br_8)Br_4$.

Tungsten(II) iodide was prepared by the exchange reaction between pure tungsten(II) chloride and a 10-fold (moles of I^- per mole of Cl^-) excess of a molten solution of 70 mol % KI and 30 mol % LiI at 540° for 15 min. The cooled reaction products were leached thoroughly with water to remove alkali metal halides and dissolved in ethanol. The solution was evaporated nearly to dryness with gentle heating under aspirator vacuum precipitating an orange ethanol adduct. Thermal decomposition of the adduct under dynamic vacuum at 500° produced orange tungsten(II) iodide. The corresponding reaction between tungsten(II) bromide and molten KI–LiI was only partially complete after 15 min.

Mixed Anhydrous Halides.—Mixed 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 milliliters of ethanol added. The resultant solutions were heated and stirred for 4–12 hr, filtered, and cooled to precipitate the mixed halo acids $(H_3O)_2[(W_6X_8)Y_6]\cdot nH_2O$. The acids were recrystallized by the same procedure to ensure complete exchange of the terminal halides Y and thermally decomposed at 325°. Mixed tungsten(II) halides prepared in this manner were $(W_6Cl_8)Br_4$, $(W_6Cl_8)I_4$, and $(W_6Br_8)Cl_4$.

A derivative containing terminal fluorides was prepared by titrating the terminal bromides from an ethanol solution of $(W_6Br_8)Br_4$ with silver perchlorate. After removing the silver bromide precipitate, the solution was acidified with aqueous hydrofluoric acid in Teflon labware. Upon reducing the volume, a yellow hydrated derivative having the analytical composition $(W_6Br_8)F_4(H_2O)_5$ precipitated. The hydrate was thermally decomposed at 400° *in vacuo* to provide anhydrous $(W_6Br_8)F_4$. Tungsten(II) chloride decomposed when treated with silver perchlorate under similar conditions.

Neutral Adducts.—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 halo acids at 200° *in vacuo*. Hydrated derivatives of tungsten(II) bromide and iodide were prepared by dissolving the dihalide in dilute base (tungsten(II) chloride decomposed in base), filtering, and acidifying the filtrate strongly with the desired hydrohalic acid. The yellow precipitates were dried at 200° yielding the bis-aquo adducts.

A yellow bis-acetonitrile adduct $(W_6Cl_8)Cl_4(CH_3CN)_2$ was prepared by stirring pure anhydrous tungsten(II) chloride in acetonitrile, filtering, and drying the product *in vacuo*.

An orange bis-ethanol adduct $(W_6I_8)I_4(C_2H_5OH)_2$ was prepared by reducing the volume of an ethanol solution of tungsten(II) iodide with gentle heating, filtering, and drying. Because of apparent solvolysis of the compound an attempt to prepare $(W_6Cl_8)Cl_4(C_2H_5OH)_2$ was unsuccessful.

One preparation of tungsten(II) iodide, prepared from 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 bis-ethanol adducts of the partially exchanged derivatives of tungsten(II) iodide, formulated as $(W_6I_8)I_3Y(C_2H_5OH)_2$ (Y = F, Cl, Br), on the basis of analytical and infrared evidence.

Hexahalo Salts.—The appropriate tungsten(II) halide, $(W_6X_8)X_4$, was dissolved in the corresponding hot, concentrated hydrohalic acid, HX. Addition of a few milliliters 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 salts $M_2[(W_6X_8)X_6]$ (M = Cs, R_4N; X = Cl, Br, I) were precipitated by the addition of cesium or tetraalkylammonium halide. The products were washed with hydrohalic acid and vacuum dried.

An extra step was necessary to ensure 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 the exchanged hexahalo salts $M_2[(W_6X_8)Y_6]$ (M = Cs, R_4N; $X \neq Y$ = Cl, Br, I). The products were washed with hydrohalic acid and vacuum dried. $((C_2H_5)_4N)_2[(W_6Br_8)I_6]$, $((C_4H_9)_4N)_2[(W_6I_8)Cl_6]$, and $((C_4H_9)_4N)_2[(W_6I_8)Br_6]$ were purified by recrystallization from acetonitrile.

Less rigorous exchange conditions than those just described produced little or no exchange of the terminal halides originally present on a cluster. For example, dissolution of tungsten(II) iodide in ethanol–10% aqueous hydrochloric acid with gentle heating, followed by immediate addition of tetraalkylammonium chloride solution, produced a yellow precipitate which analytical and infrared data indicated was the compound $((C_2H_5)_4N)_2[(W_6I_8)I_4Cl_2]$.

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Table I

Analytical Data for $(W_6X_8)X_4$, $(W_6X_8)Y_4$, $(W_6X_8)X_4L_2$, and $(W_6X_8)Y_4L_2$

	% W		% X		% Y	
Compound	Calcd	Found	Calcd	Found	Calcd	Found
$(W_6Cl_8)Cl_4$	72.17	72.23	27.83	27.62	...	...
$(W_6Cl_8)Br_4$	64.65	63.77	16.62	16.19	18.73	18.01
$(W_6Cl_8)I_4$	58.23	58.11	14.97	14.17	26.80	26.81
$(W_6Br_8)F_4$	60.66	61.72	35.16	35.04	...	...
$(W_6Br_8)Cl_4$	58.55	58.67	33.93	33.77	7.53	7.36
$(W_6Br_8)Br_4$	53.50	53.93	46.50	45.92	...	...
$(W_6I_8)I_4$	42.01	41.79	57.99	56.45	...	...
$(W_6Cl_8)Cl_4(CH_3CN)_2$	68.49	68.74	26.41	26.53	...	...
$(W_6Cl_8)Cl_4(H_2O)_2$	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
$(W_6Br_8)F_4(H_2O)_5$	57.80	57.62	33.50	33.34	3.98	3.95
$(W_6Br_8)Cl_4(H_2O)_2$	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	...	...
$(W_6I_8)I_3F(C_2H_5OH)_2$	42.26	41.21	53.48	54.27	...	...
$(W_6I_8)I_3Cl(C_2H_5OH)_2$	42.00	41.87	53.15	53.70	1.35	1.17
$(W_6I_8)I_3Br(C_2H_5OH)_2$	41.30	40.75	52.26	51.91	2.99	2.86

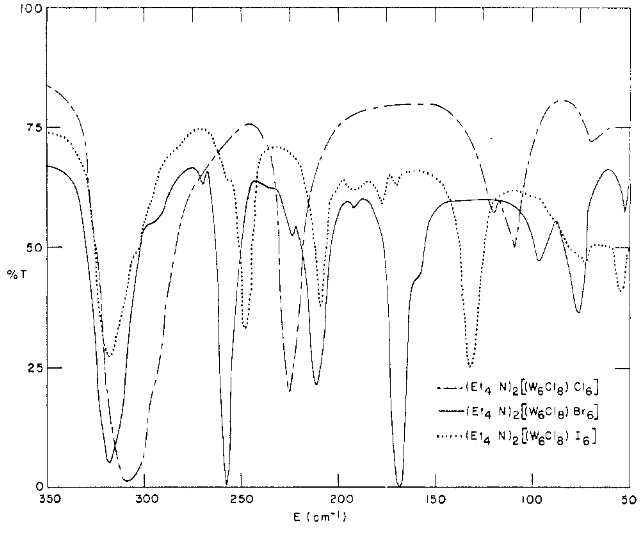

Figure 1.—Far-infrared spectra of the $((C_2H_5)_4N)_2[(W_6Cl_8)Y_6]$

Table II

Analytical Data for $M_2[(W_6X_8)X_6]$ and $M_2[(W_6X_8)Y_6]$

	% W		% X		% Y		% C		% H	
Compound	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$Cs_2[(W_6Cl_8)Cl_6]$	59.14	58.98	26.61	26.52	...	...	...	...	...	...
$((CH_3)_4N)_2[(W_6Cl_8)Cl_6]$	63.11	63.22	28.40	27.85	...	...	...	...	...	...
$((C_2H_5)_4N)_2[(W_6Cl_8)Cl_6]$	59.31	59.23	26.69	26.60	...	...	10.33	10.65	2.17	2.23
$Cs_2[(W_6Cl_8)Br_6]$	51.74	52.36	13.30	13.40	22.50	22.68	...	...	...	...
$((CH_3)_4N)_2[(W_6Cl_8)Br_6]$	54.76	54.46	14.08	14.29	23.82	23.92	4.77	4.37	1.20	1.21
$((C_2H_5)_4N)_2[(W_6Cl_8)Br_6]$	51.87	51.63	13.34	13.18	22.54	22.14	9.04	9.31	1.90	1.94
$Cs_2[(W_6Cl_8)I_6]$	45.70	44.70	11.75	11.57	31.54	32.29	...	...	...	...
$((C_2H_5)_4N)_2[(W_6Cl_8)I_6]$	45.80	45.88	11.78	11.99	31.61	32.21	7.98	7.87	1.67	1.74
$Cs_2[(W_6Br_8)Cl_6]$	49.67	49.14	28.78	28.51	9.58	9.81	...	...	...	...
$((C_2H_5)_4N)_2[(W_6Br_8)Cl_6]$	49.79	50.00	28.85	28.45	9.60	9.25	8.67	9.90	1.82	1.75
$Cs_2[(W_6Br_8)Br_6]$	44.34	44.58	44.97	45.32	...	...	...	...	...	...
$((C_2H_5)_4N)_2[(W_6Br_8)Br_6]$	44.44	44.34	45.07	44.56	...	...	7.74	7.84	1.62	1.51
$Cs_2[(W_6Br_8)I_6]$	39.83	39.48	23.08	23.67	27.49	27.44	...	...	...	...
$((C_2H_5)_4N)_2[(W_6Br_8)I_6]$	39.91	40.07	23.13	22.96	27.54	27.34	6.95	6.50	1.46	1.34
$((C_2H_5)_4N)_2[(W_6I_8)Cl_6]$	42.57	42.00	39.17	39.08	8.21	7.41	...	...	...	...
$((C_4H_9)_4N)_2[(W_6I_8)Cl_6]$	39.17	39.17	36.05	33.50	7.55	7.35	13.65	12.73	2.58	2.44
$((C_4H_9)_4N)_2[(W_6I_8)Br_6]$	35.78	35.60	32.93	32.16	15.55	15.18	12.47	12.45	2.35	2.40
$((C_2H_5)_4N)_2[(W_6I_8)I_6]$	35.13	34.85	56.58	55.21	...	...	...	...	...	...
$((C_4H_9)_4N)_2[(W_6I_8)I_6]$	32.78	32.87	52.80	51.52	...	...	11.42	10.78	2.16	2.14
$((C_2H_5)_4N)_2[(W_6I_8)I_4Cl_2]$	37.30	37.04	51.49	51.42	2.40	1.75	...	...	...	...

Analytical data for all of the compounds described are collected in Tables I and II.

Results

Representative infrared spectra for the various compounds are presented in Figures 1–4. Figure 1 shows how the spectra change as Y is varied in the $M_2[(W_6Cl_8)Y_6]$ series (Y = Cl, Br, I). Figures 2 and 3 show the same for the $M_2[(W_6Br_8)Y_6]$ and $M_2[(W_6I_8)Y_6]$ series. Figure 4 shows the effects of symmetry changes around the W_6Cl_8 unit by comparing $((C_2H_5)_4N)_2[(W_6Cl_8)Cl_6]$ and annealed, crystalline $[(W_6Cl_8)Cl_{4/2}Cl_2]$. All of the infrared data, collected as wave number in cm^{-1}, and relative intensities are summarized in Tables III and IV.

Discussion

Stability and Exchange of Terminal Halides.—Thermal decomposition of the tungsten halo acids $(H_3O)_2[(W_6X_8)Y_6]\cdot nH_2O$ below 200° yielded the corresponding dihydrates $(W_6X_8)Y_4(H_2O)_2$. Further heating to 350° gave anhydrous tungsten(II) halides which were sometimes pyrophoric, amorphous to X-rays, and more reactive toward coordinating ligands and which gave broad, poorly resolved bands in their infrared spectra. These observations indicate that considerable disorder is produced by the random loss of halides during thermal decomposition. Reactive metal atoms, perhaps left without terminal or bridging external halides, then may account for the pyrophoric nature and the enhanced reactivity of these materials. The amorphous products could be crystallized, however, by heating them to 550° and cooling them slowly to room temperature in evacuated, sealed ampoules. Tungsten(II) chloride so treated gave a good X-ray powder pattern and an infrared spectrum containing 11 well-resolved bands compared to 13 bands predicted for $(W_6Cl_8)Cl_{4/2}Cl_2$ in D_{4h} symmetry.[16] The annealing process apparently con-

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[16] The structure of $(W_6Cl_8)Cl_{4/2}Cl_2$ is assumed to be the same as that of $(Mo_6Cl_8)Cl_{4/2}Cl_2$ as described in ref 8. In this structure the two unshared terminal chlorine atoms are in *trans* positions of the coordination sphere of the $Mo_6Cl_8^{4+}$ unit with Mo–Cl = 2.38 Å. The four remaining chlorine atoms are shared between cluster units, with Mo–Cl = 2.50 Å.

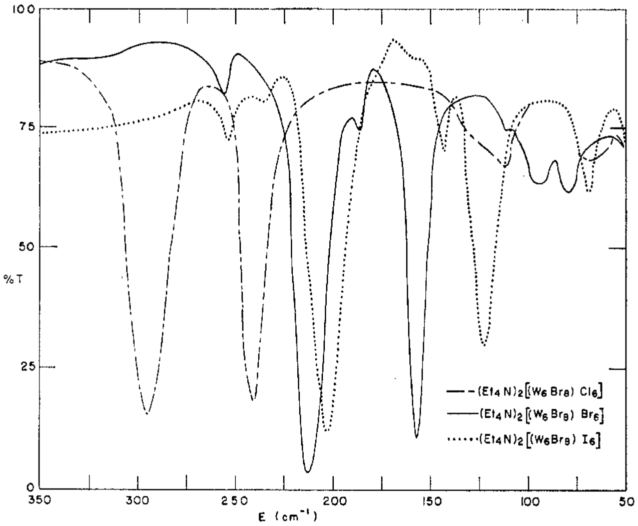

Figure 2.—Far-infrared spectra of the $((C_2H_5)_4N)_2[(W_6Br_8)Y_6]$.

TABLE III

FAR-INFRARED SPECTRA OF SOME $M_2[(W_6X_8)X_6]$ AND $M_2[(W_6X_8)Y_6]$ SALTS

$(C_2H_5)_4N$ Cl Cl[a]	Cs Cl Cl	$(C_2H_5)_4N$ Cl Br[c]	Cs Cl Br	$(C_2H_5)_4N$ Cl I	Cs Cl I
	328 m, sh		329 m, sh		335 m, sh
306 vs, b[b]	303 vs, b	317 s	314 s	318 s	315 s
		293 w, sh	293 w, sh		293 m, sh
287 m, sh	284 m, sh	258 vs	258 vs	248 s	248 s
	231 m, sh	225 w, sh	233 w		213 ms, sh
225 ms	224 ms	211 ms	215 m	210 ms	207 ms
		169 vs	169 vs		
		158 w, sh	158 w, sh	132 s	132 s
120 wm, sh	122 wm	97 w, sh	90 w	72 w	79 m
109 m	101 m	76 m	68 w	57 vw	57 wm
68 w					
53 w	51 m	54 wm	50 wm	47 vw	46 w
			45 wm		

$(C_2H_5)_4N$ Br Cl	Cs Br Cl	$(C_2H_5)_4N$ Br Br	Cs Br Br	$(C_2H_5)_4N$ Br I	Cs Br I
296 vs	292 vs				
241 vs	243 vs	256 w		254 w	256 w
		212 vs	213 vs	204 vs	203 s
	193 vw	186 w	189 vw	142 m	144 wm
	152 wm	157 vs	160 s	123 s	125 s
112 m, b	116 wm, sh	95 m	83 m	75 m	78 m
	105 wm	80 m	72 wm	69 m	57 m
	55 m	50 w	49 m		47 w

$(C_4H_9)_4N$ I Cl	$(C_2H_5)_4N$ I I Cl[d]	$(C_4H_9)_4N$ I Br	$(C_4H_9)_4N$ I I
283 vs	287 m		284 w
237 w	222 wm	237 m	221 w
219 s	183 m, sh	185 vs	168 vs
151 wm	169 ms		
		138 ms	113 s
114 m	115 m	78 m	70 vw
	85 w		59 w
	62 w		

[a] Abbreviations used stand for M, X, and Y in $M_2[(W_6X_8)Y_6]$; *e.g.*, $(C_2H_5)_4N$ Cl Cl indicates $((C_2H_5)_4N)_2[(W_6Cl_8)Cl_6]$. [b] Band maxima are in wave numbers; relative intensities: s, strong; m, medium; w, weak; v very; b, broad; sh, shoulder. [c] Band positions for $((CH_3)_4N)_2[(W_6Cl_8)Br_6]$ agree within 2 cm^{-1}. [d] Analysis indicates this compound is $(C_2H_5)_4N)_2[(W_6I_8)I_4Cl_2]$.

verted the disordered tungsten(II) chloride into the crystalline form containing tungsten atoms which are fully coordinated by utilizing bridging chlorides between clusters.

The ease with which external 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 findings for molybdenum(II) chloride.[2b] However, terminal halide exchange from tungsten(II) bromide was slower, and for tungsten(II) iodide, boiling in concentrated HY (Y = Cl, Br) for several hours was necessary to ensure complete exchange of the terminal iodides. Lower solubility of the bromide and iodide could be partly responsible for these results.

TABLE IV

FAR-INFRARED SPECTRA OF ANHYDROUS DERIVATIVES, $(W_6X_8)Y_4$, AND SOME ADDUCTS, $(W_6X_8)Y_4L_2$

(W_6Cl_8)-Cl_4[a]	(W_6Cl_8)-Cl_4L_2[b]	(W_6Cl_8)-Br_4	(W_6Cl_8)-Br_4L_2[c]	$(W_6Cl_8)I_4$	(W_6Cl_8)-I_4L_2[c]
			412 vw, b		415 vw, b
321 vs	316 vs, b	321 s	322 s	326 s	322 s
294 s, sh	284 m	292 m, sh	271 m, sh	284 m, sh	261 wm, sh
		252 m	257 ms	231 m	249 s
233 m			236 w		
208 w	226 s	211 m	211 m	212 wm	210 s
161 w		177 wm	173 ms	168 w	137 s
98 m	108 m	101 w		119 w	72 vw, b
	69 w	88 w	85 vw, b		57 vw

$(W_6Br_8)F_4$	(W_6Br_8)-F_4L_5[d]	(W_6Br_8)-Cl_4	(W_6Br_8)-Cl_4L_2[c]	(W_6Br_8)-Br_4
625 wm				
518 s, b	502 s			
	482 s			
	439 s		427 w, b	
	358 wm	320 s	316 s	
	301 w, b	296 ms, sh	297 s, sh	
	273 w, b			
256 ms	254 s	250 s	248 vs	258 s
219 s	214 m	220 m	209 w	218 ms
198 m, sh	194 ms	205 m, sh	196 wm	183 m
158 vw		180 vw		168 ms
	133 w	166 vw	120 wm	
	70 vw		84 wm	90 wm

(W_6I_8)-I_3FL_2[e]	(W_6I_8)-I_3ClL_2[e]	(W_6I_8)-I_3BrL_2[e]	$(W_6I_8)I_4$	(W_6I_8)-I_4L_2[e]
472 w				
397 wm	397 w	394 w		394 w
321 wm, b	278 m			
235 vw				
225 w	222 m	225 w	235 w	229 vw
		181 ms, sh		
170 s	171 s	173 s	174 s	169 s
157 m	156 m	156 m	165 s	157 w
		137 m	129 m	
117 s	118 s	118 s	122 ms	117 m
			110 w	
84 w	84 w	84 wm	89 w	
72 wm	71 w	71 wm	61 w	65 m
61 wm	60 w	61 w		50 w

[a] Band positions and relative intensities are as given in Table III. [b] L = CH_3CN; additional bands due to coordinated acetonitrile were observed in the infrared spectrum at 2313, 2280, 1348, 1023, 947, 399, and 390 cm^{-1}. [c] L = H_2O; bands in the 410–440-cm^{-1} region were attributed to W–O stretching modes in hydrates. [d] L = H_2O; analysis indicates this compound is $(W_6Br_8)F_4(H_2O)_5$. Infrared bands at 3468, 3135, 1630, and 1586 cm^{-1} show coordinated and free water implying the compound is incompletely dried $(W_6Br_8)F_4(H_2O)_2$. [e] L = C_2H_5OH; additional bands due to coordinated ethanol were observed in the infrared spectrum at 3327 and 1584 cm^{-1}; bands in the 395-cm^{-1} region were attributed to W–O stretching modes in ethanol adducts.

Terminal halogen exchange was also effected 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 ethanol–water solution with silver perchlorate. Addition of hydrofluoric acid and reduction of the volume caused precipitation of a tungsten bromide cluster containing terminal fluorides. Similar attempts to precipitate the terminal chlorides from tungsten(II) chloride in water, ethanol, or acetonitrile with silver nitrate, perchlorate, or fluoride resulted in immediate precipitation and oxidation of the tungsten-containing species. Likewise, attempts to exchange the terminal halides of $((C_2H_5)_4N)_2[(W_6Cl_8)Y_6]$ for fluorides in concentrated aqueous hydrofluoric acid, in dilute ethanol–hydrofluoric acid, or in acetonitrile containing excess tetraethylammonium fluoride resulted in disruption and oxidation of the tungsten chloride cluster.

Far-Infrared Spectra.—Reduction of the representation formed using the 60 Cartesian displacement coordinates of the $(W_6X_8)Y_6$ group as a basis set and subtraction of the representations for translation and rotation leaves the following irreducible representation to which the 54 normal vibrations belong

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

Since only T_{1u} modes are infrared active in octahedral symmetry, infrared spectra of $(W_6X_8)Y_6^{2-}$ anions should contain five fundamental bands. Additional information about the symmetry type of specific bond length stretching or bond angle bending vibrations can be 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 independent internal halogen–metal–terminal halogen bond angles as basis sets are found to be

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

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

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

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

These irreducible representations show that the five infrared-active T_{1u} fundamental bands predicted for octahedral $(W_6X_8)Y_6^{2-}$ anions may be classified as two W–X stretching, one W–W stretching, one W–Y stretching, and one X–W–Y bending fundamentals. Reevaluation of the internal modes chosen, however, reveals that these five modes are not completely independent. For instance, the metal–metal stretching modes must contain some metal–internal halogen character since the metal–metal bonds cannot stretch without simultaneously stretching and bending the metal–internal halogen bonds. Similarly, the metal–metal bonds cannot be stretched without also affecting the metal–terminal halogen bond lengths. The conclusion then is that these modes can be mixed in varying degrees, and assignment of the infrared bands to the various pure (unmixed) modes may be misleading, at least for the internal W_6X_8 unit.

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 halides in the complete $(W_6X_8)Y_6^{2-}$ series (X, Y = Cl, Br, I). Spectra of the lower symmetry $(W_6X_8)Y_4$ and $(W_6X_8)Y_4L_2$ compounds were used to provide support for the assignments. The spectra of the $((C_2H_5)_4N)_2[(W_6Cl_8)Y_6]$ series in Figure 1 and Table III 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 assigned as the terminal bromide and iodide stretching modes. The associated terminal halide bending or wagging modes appear at lower energies as the split bands of 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 crystallographic nonequivalence of cation distribution surrounding the terminal halides of the cluster. In the Y = Br spectrum other strong bands occur at 317, 258, and 211 cm^{-1}, while in the Y = I spectrum strong bands remain at 318, 248, and 210 cm^{-1}. Because these bands are least sensitive to the terminal halide substitution, they must correspond to the three predicted internal fundamentals of the W_6Cl_8 cluster.

The spectrum of $(W_6Cl_8)Cl_6^{2-}$ presents a special problem because the requisite number of bands is not observed. In this spectrum the band at 225 cm^{-1} we believe corresponds to the internal bands at 211 and 210 cm^{-1} in the Y = Br and Y = I spectra, respectively. This assignment differs from that made by Mattes,[12] who assigned it as the terminal W–Cl stretching mode. However strong evidence against the latter assignment may be found in the spectra of the $(W_6X_8)Cl_6^{2-}$ (X = Br or I) derivatives, which each exhibit a strong band at 283–296 cm^{-1}. This band disappears when the Cl is completely displaced with Br or I but remains in the interesting $(W_6I_8)I_4Cl_2^{2-}$ derivative. Thus we conclude the terminal W–Cl stretching mode should be located near 300 cm^{-1} in the $(W_6Cl_8)Cl_6^{2-}$ spectra. Very likely the broad band at 306 cm^{-1} contains at least two components, one of which corresponds to the terminal W–Cl mode. The other component should correspond to the internal W_6Cl_8 mode which occurs at highest wave number and which is found at 314–317 cm^{-1} and 315–318 cm^{-1} in the Y = Br and Y = I spectra, respectively. Coupling between one of the internal modes and the terminal W–Cl mode may be partly responsible for this near coincidence of the two bands. Even if such coupling is ignored these two bands are indicated to occur at similar wave number by comparison with data from other derivatives.

The third band arising from an internal W_6Cl_8 mode of $(W_6Cl_8)Cl_6^{2-}$ and corresponding to the bands at 258 and 248 cm^{-1} in the Y = Br and Y = I spectra, respectively, is found as a shoulder at 284–287 cm^{-1}. This band is more evident in the spectrum of $(W_6Cl_8)Cl_4(CH_3CN)_2$ (Table IV), which is otherwise remarkably

TABLE V

ASSIGNMENT OF INFRARED SPECTRAL BANDS IN $(W_6X_8)Y_n$ COMPOUNDS

Assignment		Y = F	Y = Cl	Y = Br	Y = I
			X = Cl		
i	W_6X_8		318	319	320
i	W_6X_8		284	257	248
i	W_6X_8		225	212	210
ts	W–Y		305	170	134
tb	X–W–Y		105	76	57
			X = Br		
i	W_6X_8	255	245	256	255
i	W_6X_8	217	215	214	204
i	W_6X_8	198	198	186	143
ts	W–Y	510	294	159	124
tb	X–W–Y	158	108	76	63
			X = I		
i	W_6X_8	225	237	237	229
i	W_6X_8	170	219	185	170
i	W_6X_8	157	154	156	158
ts	W–Y	472	283	138	116
tb	X–W–Y		114	78	61

similar to the spectrum of $(W_6Cl_8)Cl_6^{2-}$. A summary of these assignments is given in Table V.

The spectra of the $((C_2H_5)_4N)_2[(W_6Br_8)Y_6]$ series given in Figure 2 and Table III 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 these terminal halide stretching modes in the $(W_6Cl_8)Y_6^{2-}$ series. As noted above the strong band at 296 cm^{-1} is assigned as the terminal halide stretching mode 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_6Br_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 possible 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_6Br_8 modes. The corresponding lower symmetry compounds show stronger bands in these positions and thus corroborate these assignments. The lower symmetry compounds with Y = Cl and Y = F show the internal and terminal modes in the $(W_6Br_8)Cl_n$ and $(W_6Br_8)F_n$ series. For Y = Cl bands at 248, 215, and 198 cm^{-1} correspond to the internal modes. The terminal halide stretching mode is found at 296 cm^{-1} with the corresponding terminal halide bending mode at 120 cm^{-1}. For Y = F internal bands are observed at 255, 217, and 198 cm^{-1}. The terminal halide stretching mode is assigned around 510 cm^{-1} with the bending mode at 158 cm^{-1}.

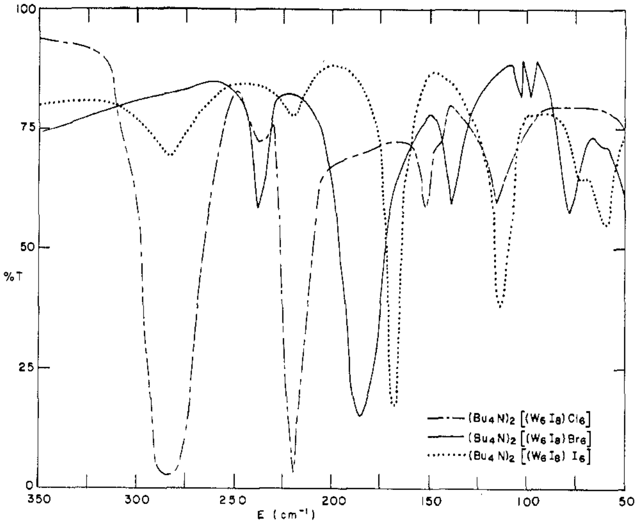

Figure 3.—Far-infrared spectra of the $((C_4H_9)_4N)_2[(W_6I_8)Y_6]$.

The spectra of the $((C_4H_9)_4N)_2[(W_6I_8)Y_6]$ series in Figure 3 and Table III 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_6I_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_6I_8 modes. The lower symmetry compounds confirm these assignments and locate the remaining internal W_6I_8 modes at 156 and 158 cm^{-1}, respectively, for Y = Br and I. 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. The terminal fluoride containing material shows the same internal W_6I_8 bands with the W–F stretching mode located at 472 cm^{-1}.

The effect of changing symmetry around the internal W_6Cl_8 unit is shown in Figure 4 and Tables III and IV. Comparison of the spectra of the hexahalo anions $(W_6X_8)Y_6^{2-}$ with those of $(W_6X_8)Y_4L_2$ and amorphous $(W_6X_8)Y_4$ prepared by thermal decomposition reveals only minor differences. For the compounds with the nonequivalent terminal ligands, at least 13 infrared-active modes are predicted. However, the overall similarity and simplicity of the spectra indicate that the cluster behaves as if it were in octahedral symmetry with equivalent terminal ligands in *all* of these complexes. Thus, varying halides or oxygen- or nitrogen-donor ligands in the terminal positions does not grossly affect the symmetry of the internal W_6X_8 or terminal tungsten–ligand vibrational modes. However, both the internal and terminal modes are split in the spectrum of annealed, crystalline tungsten(II) chloride, $(W_6Cl_8)Cl_{4/2}Cl_2$, as shown in Figure 4 so that 11 of the 13 bands predicted in D_{4h} symmetry are observed.

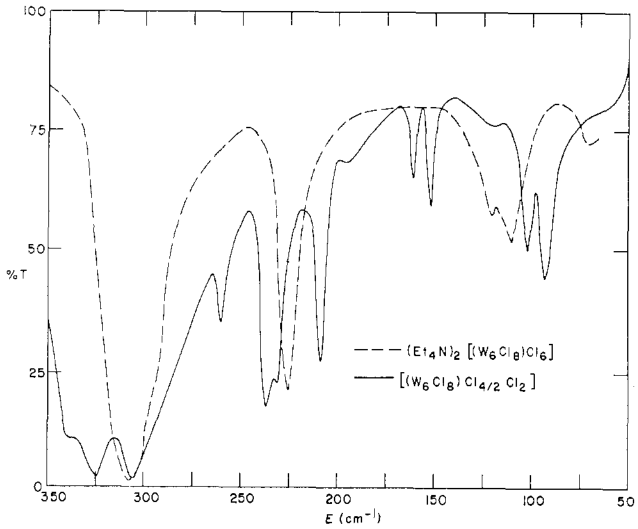

Figure 4.—Far-infrared spectra showing the effect of gross distortion of the $(W_6Cl_8)L_6$ cluster complex.

This more effective shift to lower symmetry is apparently due to the gross nonequivalence of bridging and terminal external halides.

Some correlations and generalizations concerning the assignment of the spectra of these $(W_6X_8)Y_n$ derivatives are readily apparent from the summary of assignments presented in Table V. The bands were designated 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, ts for a mode consisting primarily of W–Y terminal halide stretching, and tb for a mode consisting primarily of terminal halide bending or wagging.

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 *ca.* 10 cm^{-1} as the mass of the internal halide is increased 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.

In these compounds the normal relationship of metal–halogen stretching frequencies, $\nu(M–Br)/\nu(M–Cl) \approx 0.7$ and $\nu(M–I)/\nu(M–Cl) \approx 0.5$, does not pertain. Thus for the terminal halogen stretching modes ν(W–Br) and ν(W–I) are abnormally low compared to ν(W–Cl), which is near the range of values found for WCl_6^{2-}.[17] This abnormal relationship is especially surprising in view of the chemical evidence which indicates the W–Br and W–I terminal bonds are strong and broken with difficulty. We may only speculate on the reasons for this. It should be noted however that the terminal W–Cl mode is at higher energy than two of the W_6Cl_8 modes and all of the W_6Br_8 or W_6I_8 modes. Any interaction between these modes should *increase* the energy of ν(W–Cl). On the other hand ν(W–Br) or ν(W–I) occur at lower energy than the W_6X_8 modes; hence they will be *decreased* in energy by any interaction with the latter modes. Also, as noted above, one of the W_6X_8 modes in each series does appear to be shifted by a change of terminal halogen. Finally, we note that Hartley and Ware[13] have found evidence from the Raman spectra of the $(Mo_6Cl_8)Y_6^{2-}$ ions that the symmetric Mo–Y stretch is extensively mixed with one of the symmetric breathing modes of the Mo_6Cl_8 cluster.

In general there is nearly a 1:1 correspondence between the spectra of previously reported molybdenum compounds[9–12] and the analogous tungsten compounds reported in this paper. The frequencies observed in the tungsten compounds generally fall a few reciprocal centimeters lower than the molybdenum compounds as predicted on the basis of the relative masses. The wider range of compounds investigated in the present study helps remove the ambiguity from previous assignments. Specifically, the location of the terminal halide stretching modes at 470–510, 283–305, 138–170, and 116–134 cm^{-1}, respectively, for Y = F, Cl, Br, and I has not been conclusively demonstrated previously. Additionally, the wider range of compounds shows that the three internal modes of the cluster are so thoroughly mixed that no band can be identified as remaining constant enough throughout the entire series to merit the connotation of the metal–metal stretching mode. Due to this mixing and possible resonance shifts in band positions and intensities, the specific assignments of the internal modes must be considered tentative without the added support of Raman data and a complete normal-coordinate analysis. Work along this line has been undertaken in cooperation with Professor Michael Ware.

Acknowledgment.—We are grateful to Miss Evelyn Conrad for her services in the measurement of the infrared spectra reported here.

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[17] See, for example, D. M. Adams, "Metal-Ligand and Related Vibrations," St. Martin's Press, New York, N. Y., 1968, and references therein.