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Chemistry of Polynuclear Metal Halides. IV. Electronic Spectra of Some Niobium and Tantalum $M_6X_{12}^{n+}$ Cluster Derivatives[1a,b]

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The absorption spectra of $Nb_6X_{12}^{n+}$ and $Ta_6Cl_{12}^{n+}$ derivatives (where X = Cl, Br; n = 2, 3, 4) have been measured over the range 4–50 kK under conditions where the oxidation state ($n+$) and coordination sphere of the clusters are carefully controlled. Measurements on solutions of the anions $(Nb_6Cl_{12})Cl_6^{n-}$ (n = 2, 3, 4) were made at *ca.* −100 to 25° to facilitate resolution of the spectra into Gaussian component bands by computer analysis. Errors in previously published spectra for these systems are elucidated and suggestions for assignment of the individual bands are discussed in the light of recent structural findings and MO bonding schemes.

Introduction

The previous paper[2] in this series was concerned with the preparation of numerous $Nb_6X_{12}^{n+}$ and $Ta_6X_{12}^{n+}$ (X = Cl, Br; n = 2, 3, 4) derivatives. In this paper we describe the results of a detailed study of the electronic spectra of these cluster complexes under carefully controlled conditions where the oxidation state and composition of the absorbing species are determined with confidence.

As shown in previous work[3-7] it is possible to prepare well-defined complexes of the type $(M_6X_{12})Y_nL_{6-n}^{(m-n)+}$, where Y = F, Cl, Br, I, or OH; L is a neutral electron pair donor molecule, and m is the oxidation state of the central M_6X_{12} cluster. Because these compounds have very rich electronic spectra throughout the uv–visible–near-infrared region, which depend on M, X, Y, L, and m, systematic studies of the spectra should provide insight into the molecular orbital levels of the M_6X_{12} cluster units. In fact several papers dealing with this subject have already appeared.[8-11] However many of the results have been suspect because the compounds and particularly the oxidation state of the cluster units were not adequately defined.

It was obvious that much work needed to be done before attempts to relate the electronic spectra to the MO bonding schemes would be fruitful. This work, along with the recent work of Spreckelmeyer,[12] should remove most of the experimental uncertainties and provide the basis for a more rigorous treatment of the spectra.

Experimental Section

Compounds.—Preparation of the compounds used in this study is described elsewhere.[2-4]

Spectra.—Electronic spectra were measured on solutions of cluster-containing compounds in a variety of solvents and at low temperatures and room temperature (25°) with a Cary Model 14 recording spectrophotometer. All spectra were obtained in 10-mm fused quartz cells and were measured using a solvent reference. A base line was recorded for each spectrum so that accurate absorbance values could be obtained at any desired wavelength.

Diffuse reflectance spectra were measured at 25° with a Beckman DU spectrophotometer fitted with a Beckman 2580 reflectance attachment. The samples were diluted with KX (X = Cl, Br), and the same KX was used as a reference.

Low-temperature measurements were made by placing a quartz spectrophotometer cell in a cryostat consisting of a bored-out copper rod with a surrounding jacket which could be evacuated. The copper heat-transfer rod extended up into a stainless dewar which contained a frozen slush of the same solvent in which the cluster species was measured. Solvents used in this regard were ethanol, mp −115°, propionitrile, mp −92°, and acetone, mp −95°.

Solution Preparations.—Solution preparation was the same for low- and room-temperature measurements except that solutions run at low temperature were hermetically sealed in a quartz cell so that solvent loss did not occur when the cryostat was evacuated. In many cases a specified cluster compound was simply dissolved in the appropriate solvent. For this purpose n-propylammonium cluster complexes were generally used because of their greater solubility as compared to $(C_2H_5)_4N^+$ salts. Some measurements on the $Nb_6Cl_{12}^{n+}$ derivatives (n = 3, 4) were made in absolute ethanol saturated with hydrogen chloride. These solutions were made by dissolving $Nb_6Cl_{14}\cdot 8H_2O$ in ethanol, saturating with hydrogen chloride, and oxidizing the cluster with O_2 or halogen to provide the 3+ or 4+ cluster units, respectively.

Solvents.—Certain criteria were established to allow selection of the most advantageous solvents. These criteria were: a solvent should have a broad absorption-free range, the integrity of an anionic cluster species, $(Nb_6X_{12})Y_6^{n-}$, should be preserved through the time it takes to obtain a spectrum, the solvent should have a low freezing point to allow for low-temperature measurements, and the maximum cluster concentration should be at least 10^{-3} M. Two solvent systems satisfied all four of the above, *viz.*, ethanol saturated with hydrogen chloride and propionitrile. Acetone was an excellent solvent for measurements above 300 nm, and other solvents, *e.g.*, acetonitrile, dimethyl sulfoxide, and nitromethane, were used for some room-temperature measurements.

Analysis of Solutions.—Samples for analysis were taken as aliquots of a solution prior to dilution and loading into a cell, or for the more concentrated solutions aliquots of the solution

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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 155th National Meeting, American Chemical Society, San Francisco, Calif., 1968. (c) A part of the Ph.D. thesis of P. B. Fleming, Department of Chemistry, Iowa State University, Ames, Iowa.

[2] B. G. Hughes, J. L. Meyer, P. B. Fleming, and R. E. McCarley, *Inorg. Chem.*, **9**, 1343 (1970).

[3] P. B. Fleming, T. A. Dougherty, and R. E. McCarley, *J. Am. Chem. Soc.*, **89**, 159 (1967).

[4] P. B. Fleming, L. A. Mueller, and R. E. McCarley, *Inorg. Chem.*, **6**, 1 (1967).

[5] R. A. Mackay and R. F. Schneider, *ibid.*, **6**, 549 (1967).

[6] R. A. Mackay and R. F. Schneider, *ibid.*, **7**, 455 (1968).

[7] R. A. Field and D. L. Kepert, *J. Less-Common Metals*, **13**, 378 (1967).

[8] R. F. Schneider and R. A. Mackay, *J. Chem. Phys.*, **42**, 843 (1968).

[9] M. B. Robin and N. A. Kuebler, *Inorg. Chem*, **4**, 978 (1965).

[10] R. J. Allen and J. C. Sheldon, *Australian J. Chem.*, **18**, 277 (1965).

[11] W. van Bronswyk, *J. Chem. Soc., A*, 692 (1968).

[12] B. Spreckelmeyer, *Z. Anorg. Allgem. Chem.*, **365**, 225 (1969).

TABLE I

MAJOR ABSORPTION MAXIMA (kK) FOR SOME $Nb_6Cl_{12}^{n+}$ SPECIES

Compound[a]	H_2O	C_2H_5OH	DMSO	C_2H_5OH + HCl(g)[b]	CH_3CN	CH_3NO_2[c]	Acetone	Solid reflectance
$R_4[(Nb_6Cl_{12})Cl_6]$	25.2	. . .	24.2	24.1	24.3	22.7	23.9	23.9
			10.7	10.5	10.7	9.90	10.3	10.3
						7.60		
$[Nb_6Cl_{12}]Cl_2 \cdot 8H_2O$	25.3	24.7[d]	24.3	. . .	. . .		24.4	24.9
	11.2	23.5	10.7				10.7	11.0
$R_3[(Nb_6Cl_{12})Cl_6]$	. . .	23.1	22.6	22.8	22.7	22.6	22.6	22.7
		10.3		10.1	9.90	9.90	9.89	9.95
		7.97			7.64	7.65	7.67	
$R_2[(Nb_6Cl_{12})Cl_6]$	. . .	22.0	22.6	21.9	21.8	21.9	21.8	21.5
		10.6		10.6	10.6	10.7	10.5	10.4

[a] R is Li^+ and K^+ for 2+ (reflectance only); R is $n\text{-}C_3H_7NH_3^+$ and $(C_2H_5)_4N^+$ for 3+ and 4+ (reflectance only). [b] Ethanol saturated with HCl; solutions prepared as in the Experimental Section. [c] Data for 2+ and 4+ according to Schneider and Mackay.[8] [d] Data taken from Schneider and Mackay[8] or Robin and Kuebler.[9]

actually measured were analyzed. Analyses were accomplished by hydrolyzing the cluster solution with ammonia and determining niobium by the standard Nb_2O_5 gravimetric technique and/or by spectrophotometric determination of niobium[13] in sulfuric acid solution. Analyses by the two methods were generally in good agreement.

Data Processing.—Resolution of some spectra into Gaussian error components was carried out on the Iowa State University IBM 360/50 computer using a program developed by the Ames Laboratory Computer Services Group. The program fitted the experimental spectra with components defined in eq 1.[14]

$$\epsilon = \epsilon_0 \exp\left(-\frac{(\nu - \nu_0)^2}{\theta^2}\right) \tag{1}$$

For this purpose only the spectra measured at room temperature were used. In order to obtain a more reliable estimation of the position of weak bands and those evidenced only by shoulders, use was made of the spectra taken at low temperatures. For example at −100° the spectra were sharpened sufficiently so that the shoulders were either resolved into maxima or had become much more pronounced. The initial estimates of all such band positions were then used as input to the computer program for least-squares refinement of the spectra. In all cases the program was limited to refinement on this number of input bands, for which there was direct experimental evidence from the spectra.

Results and Discussion

Results of Present Investigation.—The electronic spectra obtained in this study are reported in Tables I–V and Figures 1 and 2. The tables are self-explanatory, but we point out here that in all except Table I the data are given as: frequency in kilokaisers (1 kK = 1000 cm^{-1}), extinction coefficient, ϵ, in liters per mol per centimeter, and band half-width at half-height, δ, in kilokaisers, all at 25°.

In Table I the spectra obtained for some $Nb_6Cl_{12}^{n+}$ derivatives in various solvents are presented. These data were obtained to help establish in which solvents anionic species of the type $(Nb_6X_{12})Y_6^{n-}$ could be studied. Earlier work by Mackay and Schneider[5,6] had established, through conductance measurements and comparison of far-infrared spectra of solutions with those of the solids $((C_2H_5)_4N)_n[(Nb_6Cl_{12})Cl_6]$ (n = 2, 3, 4), that these were n:1 electrolytes and the terminal chloride ions remained associated in nitromethane. In view of these results, the presence of a hexahalo cluster anion in a solvent was ascertained by comparing the positions of the prominent bands in the reflectance spectra with those in the solution spectra.

The nitromethane solutions were measured only for the 3+ and 4+ cluster complexes[15] but Schneider and Mackay's data[8] could not be duplicated for the 4+ compound because of an apparent reaction with the solvent. However, maxima at 21.8 and 10.6 kK were obtained in nitroethane. Because these latter data and those for the 3+ cluster agree fairly well with the solid state, no appreciable dissociation of the hexahalo cluster anion is indicated. Note that the 2+ cluster spectrum obtained by Schneider and Mackay[8] in nitromethane appears identical with that reported for the 3+ cluster. The correspondence extends over the entire spectrum and will be commented on in more detail later. At this point it is also appropriate to note that Mackay and Schneider[5] prepared their 2+ complex, $((C_2H_5)_4N)_4[(Nb_6Cl_{12})Cl_6]$, by a method in which some air oxidation of the cluster to the 3+ state is almost inevitable. We attempted the preparation of the 2+ hexachloro cluster by a similar approach but where all manipulations were carried out *in vacuo* and specially prepurified hydrogen chloride was used, and we were still unable to prevent some oxidation of the cluster.

Further comparison of the data in Table I allows the following conclusions regarding the cluster species present. Close agreement of the solid-state spectra with those in acetone suggests the presence of $(Nb_6Cl_{12})Cl_6^{n-}$ in acetone. Data not reported here also indicated that only very slow displacement of the terminal chlorides (except for the 2+ cluster) took place in acetonitrile and DMSO at 25°. It is seen also that the cluster is probably nearly completely anated in ethanol saturated with hydrogen chloride, the solvent from which most of the $(M_6X_{12})Y_6^{n-}$ derivatives were crystallized.

The primary problem was to determine reliably for each species the number of bands and their position in the spectra. Any interpretation is vitally dependent upon this. In Table II data obtained for the $(Nb_6Cl_{12})Cl_6^{n-}$ anions are listed. There is a 1:1 corre-

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(13) These analyses were performed by the Ames Laboratory Analytical Service Group, Ames, Iowa.

(14) C. K. Jørgensen, *Acta Chem Scand.*, **8**, 1495 (1954).

(15) A notation where the cluster in a given oxidation state, $M_6X_{12}^{n+}$, is designated by $n+$ is established here.

TABLE II

ABSORPTION BAND PARAMETERS FOR $(Nb_6Cl_{12})Cl_6^{n-}$ SPECIES[a]

	$(Nb_6Cl_{12})Cl_6^{4-}$ [b]			$(Nb_6Cl_{12})Cl_6^{3-}$ [c]			$(Nb_6Cl_{12})Cl_6^{2-}$ [c]		
Band	ν, kK	$10^{-3}\epsilon$	δ, kK	ν, kK	$10^{-3}\epsilon$	δ, kK	ν, kK	$10^{-3}\epsilon$	δ, kK
A	10.02	1.83	0.98	7.16	1.14	0.69	...	...	...
B	11.27	2.09	1.24	8.23	1.26	0.74	...	...	...
C	...	...	...	...	...	...	8.65	0.15	1.15
D	...	...	...	9.93	1.51	0.58	10.57	0.94	0.53
E	16.8	0.57	2.2	15.5	0.27	1.4	15.2	0.56	1.6
F	20.3	1.10	1.4	18.6	0.69	1.5	17.8	0.65	1.3
G	23.9	10.27	1.5	22.8	7.35	1.3	21.9	13.56	1.1
H	30.1	3.1	2.4	28.1	1.8	3.2	27.4	3.9	3.2
I	35.5	10.3	2.1	35.1	20	2.8	33.3	26.5	2.3
J	...	...	...	...	...	...	39	20	...
K	42.7	27	2.6	43.0	79	3.3	42.7	84	2.8
L	46.8	48	2.2	46.2	43	2.0	46.4	(45)[d]	1.1

[a] Maxima are resolved Gaussian components. [b] Spectrum of $Li_4Nb_6Cl_{18}$–acetone solution for bands A–G; bands H–L obtained from ethanol-saturated HCl solution. [c] Spectra obtained from ethanol-saturated HCl solutions. [d] Value is only approximate.

spondence between the spectra of the different oxidation states at energies >15.0 kK (bands E through L) except for the extra band in the 4+ ultraviolet spectrum (band J). These data, excluding band J, are in general agreement with those of Schneider and Mackay,[8] although they did not locate some of the weaker bands reported here. The data given in Table III, when compared to those in Table II, show that there is also a 1:1 correspondence between the spectra of the $Nb_6X_{12}^{4+}$ clusters (X = Cl, Br) and that substitution of Br for Cl in the terminal positions Y of $(Nb_6X_{12})Y_6^{2-}$ has a much smaller effect than substitution in the inner positions X.

TABLE III

ABSORPTION BAND PARAMETERS FOR $(Nb_6Cl_{12})Br_6^{2-}$ AND $(Nb_6Br_{12})Br_6^{2-}$

	$(Nb_6Cl_{12})Br_6^{2-}$ [a,b]			$(Nb_6Br_{12})Br_6^{2-}$ [b]		
Band	ν, kK	$10^{-3}\epsilon$	δ, kK	ν, kK	$10^{-3}\epsilon$	δ, kK
C	9.00	0.15	...	7.75	0.40	1.20
D	10.79	1.00	0.48	9.43	1.19	0.57
E	15.5	0.51	...	14.0	0.50	1.5
F	17.9	0.76	...	16.6	0.97	1.3
G	21.6	15.2	1.3	20.5	14.5	1.3
H	28.2	...[c]	...	25.4	3.2	2.2
I	32.0	21.6	...	29.6	13.8	3.2
J	39	30	...	33	...	...
K	41.2	75	...	36.3	50	2.5
L	46.9	95	...	41.1	85	2.2
M	...	...	...	47.9	126	4.8

[a] Data not subjected to computer analysis. [b] Spectra obtained on solutions of $n\text{-}C_3H_7NH_3^+$ salts in acetone (bands C–H) and acetonitrile (bands I–M). [c] Shoulder; ϵ could not be estimated.

Further consideration of the ultraviolet spectra of the $Nb_6X_{12}^{n+}$ has led to an important conclusion. In Table IV the band maxima obtained for the 3+ and 4+ niobium chloride and bromide clusters are listed for comparison. The difference between the energy of the chloride and bromide bands is listed in columns three and six. With the exception of M all of the bands at greater than 29 kK (I through L) exhibit shifts of from 4–7 kK to lower energy on changing from chloride to bromide. These bands are in the region where charge-transfer bands are usually found, and they are assigned in that manner. The reason for assigning these bands as halogen-to-metal charge-transfer bands is the magnitude of the energy shift on changing halide ligands. In general, charge-transfer bands of octahedral hexahalo metalate complexes show a shift to lower energy of *ca.* 6–8 kK on going from chloride to bromide.[16] In fact, this shift also is observed for the halide ions in aqueous solution or in alkali metal halide crystals and thus appears to be nearly independent of the halide environment.

TABLE IV

COMPARISON OF ABSORPTION MAXIMA FOR $[(Nb_6X_{12})X_6]^{2,3-}$ (X = Cl, Br)

	$(Nb_6X_{12})X_6^{2-}$			$(Nb_6X_{12})X_6^{3-}$		
Band	ν(X = Cl)[a]	ν(X = Br)[a]	$\Delta\nu$(Cl − Br)	ν(X = Cl)[a]	ν(X = Br)[b]	$\Delta\nu$(Cl − Br)
A	...	...	...	7.16	7.0	0.16
B	...	...	...	8.23	8.1	0.13
C	8.65	7.75	0.90	...	...	...
D	10.57	9.43	1.14	9.93	9.01	0.92
E	15.2	14.0	1.2	15.5	14.3	1.2
F	17.8	16.6	1.2	18.6	17.5	1.1
G	21.9	20.5	1.4	22.8	21.4	1.4
H	27.4	25.4	2.0	28.1	...[c]	...
I	33.3	29.6	3.7	35.1	31.0	4.1
J	39	33	6	...	...	...
K	42.7	36.3	6.4	43.0	35.8	7.2
L	46.4	41.1	5.3	46.2	39.4	6.8
M	...	47.9	...	...	...	...

[a] Maxima are resolved Gaussian components in kK. [b] Maxima estimated from recorder data; spectrum obtained in DMSO. [c] Band is present as shoulder, but position not located accurately.

Comparison of the data for the $(Nb_6X_{12})X_6^{2-}$ (X = Cl, Br) species with those obtained for $(Nb_6Cl_{12})Br_6^{2-}$ (Table III) further suggests that the charge-transfer transitions are from inner halide to metal and that the terminal halide has little effect on the spectra.

A question might be raised as to the nature of band M in the spectrum of $(Nb_6Br_{12})Br_6^{2-}$. This band was near the solvent cut off and although there is a greater uncertainty in its position, we feel this band also should be viewed as arising from a charge-transfer transition.

The near-infrared region of the spectrum undergoes

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(16) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Addison-Wesley Publishing Co., Reading, Mass., 1962, p 146 ff.

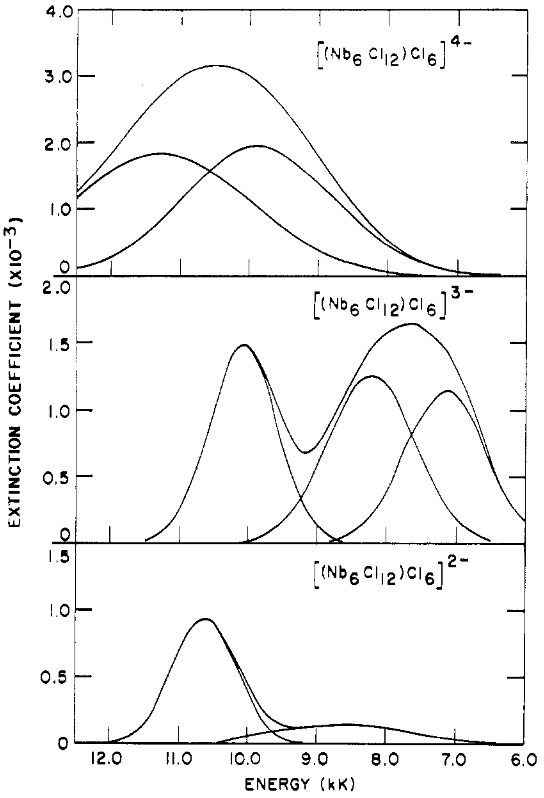

Figure 1.—Near-infrared spectra of $Nb_6Cl_{12}^{n+}$ clusters in acetone. Lower curves are resolved Gaussian components.

profound changes when the cluster oxidation state is varied. We have found two bands (C and D) in the near-infrared region for the 4+ cluster. These are clearly defined as presented in Figure 1, where the near-infrared spectra of the hexachloro $n+$ niobium chloride clusters are shown resolved into Gaussian components. Schneider and Mackay[8] have not reported the weak band at 8.65 kK, but Spreckelmeyer[12] found a corresponding band at 9.3 kK.

The situation in the 3+ and 2+ cluster spectra is not as simple. As shown in Figure 1 the 3+ cluster gives rise to two absorption regions, a sharp high-energy one and a broad low-energy one. In this region the 2+ cluster spectrum exhibits only one broad symmetrical absorption.

For the 3+ cluster the sharp higher energy absorption, band D, is assigned as corresponding to the sharp 4+ absorption at 10.6 kK because of the similar band parameters, ν, ϵ, and δ (Table II). In fact, these bands are significantly more narrow than any other bands in the spectra (δ = 0.53–0.58 kK) and a corresponding band in the 2+ cluster is notably absent. This correlation is based on the assumption that transitions between the same two energy levels should give rise to similar band parameters regardless of the oxidation state of the cluster. The overall similarity between the spectra, Table II, indicate that this is the case.

A consideration of the 3+ cluster band at lower energy shows that it cannot be fit with one Gaussian-shaped band but that two Gaussians yield a good fit with experimental data (Figure 1). The 2+ cluster spectrum can also be resolved into two Gaussian components in the near-ir region. In each case the component bands have reasonable half-width parameters (Table II). The most convincing evidence in favor of the above description of the experimental spectra comes from an examination of the $Ta_6Cl_{12}^{n+}$ spectra and also the electronic structure.

Spectra obtained for the $Ta_6Cl_{12}^{n+}$ clusters are reported in Table V. Note that the 2+ and 3+ spectra here arise from at least partially solvated clusters (not hexachloro anions), and hence the band positions are at *ca.* 500–1000 cm^{-1} higher energy than for the hexachloro complexes. This estimate is made from a consideration of similar solutions in the $Nb_6X_{12}^{n+}$ systems.

The establishment of the individual bands in the experimental spectra is more obvious in the $Ta_6Cl_{12}^{n+}$ systems. Through the visible and ultraviolet regions of the spectra there is an obvious 1:1 correspondence between the niobium and tantalum spectra (compare Tables II and V). Most important, however, are the well-defined near-infrared spectra (Figure 2) which show the bands noted in Table V. Espenson and McCarley[17] do not report the two weakest $Ta_6Cl_{12}^{4+}$ bands, but this was because of the more limited scope of their study. Thus the near-infrared spectra show two bands for the 2+ cluster, three bands for the 3+ cluster, and three bands for the 4+ cluster.

Table V

Absorption Maxima of $Ta_6Cl_{12}^{n+}$-Containing Species[a]

	$Ta_6Cl_{12}^{2+}$ [b]			$Ta_6Cl_{12}^{3+}$ [c]			$(Ta_6Cl_{12})Cl_6^{2-}$ [d]		
Band	ν, kK	$10^{-3}\epsilon$	δ, kK	ν, kK	$10^{-3}\epsilon$	δ, kK	ν, kK	$10^{-3}\epsilon$	δ, kK
0	...	...	...	...	...	...	8.64	0.05	0.5
C	...	...	...	..	...	...	10.1	0.32	0.5
A	12.7	2.2	1.1	10.6	1.5	0.9	...	...	...
B	15.2	3.8	1.5	12.1	2.0	0.95	...	...	...
D	...	...	...	13.6	1.7	0.9	11.85	1.3	0.8
E	20.4	1.2	...	...	...	...	19.2	1.0	1.4
F	25.0	6	...	23.2	2.2	...	22.5	2.5	1.7
G	29.9	30	...	29.0	14.5	...	27.1	26.5	1.2
H	34.5	8	...	36.4	8	...	35.1	8.4	1.9
I	42.2	20	...	42.5	16	...	40.3	18.5	2.7

[a] Data reported are estimated from the raw data and are not resolved bands. [b] Measured in DMSO as a solvated cation. [c] Measured in C_2H_5OH as a solvated cation. [d] Measured in acetone as the hexachloro anion; bands H and I measured in acetonitrile.

These data, then, bring the niobium and tantalum spectra into a 1:1 correspondence over the entire spectral region except for the lowest energy tantalum 4+ cluster band. This latter band (with ϵ ~50) would probably not be observed in the niobium cluster system due to an even lower expected intensity, since, in general, $\epsilon(Nb)/\epsilon(Ta) \approx$ 0.5–0.8.

There is good reason to believe *a priori* that the niobium and tantalum spectra should have a 1:1 correspondence in bands. This derives from new preliminary structural work on $K_4[(Nb_6Cl_{12})Cl_6]$,[18] $((CH_3)_4N)_2[(Nb_6Cl_{12})Cl_6]$,[19] and $H_2[(Ta_6Cl_{12})Cl_6] \cdot nH_2O$[20] which

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(17) J. H. Espenson and R. E. McCarley, *J. Am. Chem. Soc.*, **88**, 1063 (1966).

(18) A. Simon, H. G. von Schnering, and H. Schafer, *Z. Anorg. Allgem. Chem.*, **361**, 235 (1968).

(19) F. W. Koknat and R. E. McCarley, to be submitted for publication.

(20) R. A. Jacobson, private communication.

indicate that the metal atom clusters have nearly ideal O_h symmetry. It is reasonable to suppose if these complexes were retained as the hexahalo anions in solution that little distortion of the metal octahedron would occur. In fact, the spectra of the clusters are qualitatively the same regardless of the solvent, thus, leading to the conclusion that either no distortion of the metal octahedron occurs or that any distortion present has little effect on the spectra. Additionally, other physical data, *viz.*, magnetic susceptibilities, suggest that the gross features of the cluster electronic structure are the same for niobium and tantalum.

Comparison with Previous Investigations.—Prior to a discussion of the electronic structure it is appropriate to consider some of the spectra reported by other workers. The earliest attempt at interpreting the cluster electronic spectra was made by Allen and Sheldon,[10] who reported data for $M_6X_{12}^{2+}$(aq) species and assigned all of their bands (up to 50 kK) as metal–metal transitions on the basis of the Cotton and Haas[21] MO treatment. The assignments in the ultraviolet region are clearly unreasonable in view of our data.

Robin and Kuebler[9] have reported the spectra of the $M_6X_{12}^{2+}$ (M = Nb, Ta; X = Cl, Br) and $Ta_6X_{12}^{4+}$ species in ethanol. They assigned their bands as either halogen-to-metal charge transfer (if $\Delta\nu(\mathrm{Cl} - \mathrm{Br}) > 1000\ \mathrm{cm}^{-1}$) or metal–metal transitions (if $\Delta\nu(\mathrm{Cl} - \mathrm{Br}) < 1000\ \mathrm{cm}^{-1}$). As discussed earlier we believe that the downward energy shift for charge-transfer bands in the clusters should be close to that observed for other systems. The important point is that Robin and Kuebler's $Ta_6X_{12}^{4+}$ spectrum corresponds most closely to that of $Ta_6X_{12}^{3+}$ (this has been recognized by Schneider and Mackay[8]). As a consequence of these erroneous experimental data and recently obtained magnetic and structural data the arguments of Robin and Kuebler concerning the cluster electronic structure are seen to be incorrect.

Recently, Field and Kepert[7] reported the partial electronic spectra of some $(Nb_6Cl_{12})Cl_2L_4$ (L = oxygen donor, *e.g.*, DMSO) derivatives and commented on the relative merits of the Allen and Sheldon[10] *vs.* Robin and Kuebler assignment schemes. They argued that their L donors should have the greatest perturbing effect on MO's derived from the d_{z^2}, d_{xz}, and d_{yz} atomic orbitals (AO's) since these ligands are bound to the cluster along the local *z* direction of each metal atom. Considering the possible MO transitions giving rise to the intense absorptions at *ca.* 10, 25, and 35 kK and the ligand dependency of their bands, Field and Kepert stated that their data were more consistent with the assignments of Robin and Kuebler than with the assignments of Allen and Sheldon. It is apparent, however, from a detailed consideration of their magnetic and electronic spectral data that the compounds and solutions used by Field and Kepert contained significant amounts of 3+ cluster. First, the *positive* gram-susceptibilities, χ_g, which they reported lead to high values of μ_{eff} and hence indicate the presence of paramagnetic impurities,[22] *i.e.*, 3+ cluster. Second, we have never obtained a near-ir band at lower energy than *ca.* 10.3 kK for a 2+ niobium cluster; this was for the hexachloro cluster anion which shows bands at lower energy than the cluster with bound oxygen donors, *e.g.*, H_2O or C_2H_5OH in Table I. A similar correlation holds for the band at *ca.* 25 kK. A more complete spectrum than was published would unequivocally answer the questions raised above. However it is apparent that the arguments of Field and Kepert, which were based on band shifts as a function of the ligand L, are cast in doubt because small amounts of 3+ impurity could cause band shifts of the magnitude observed.

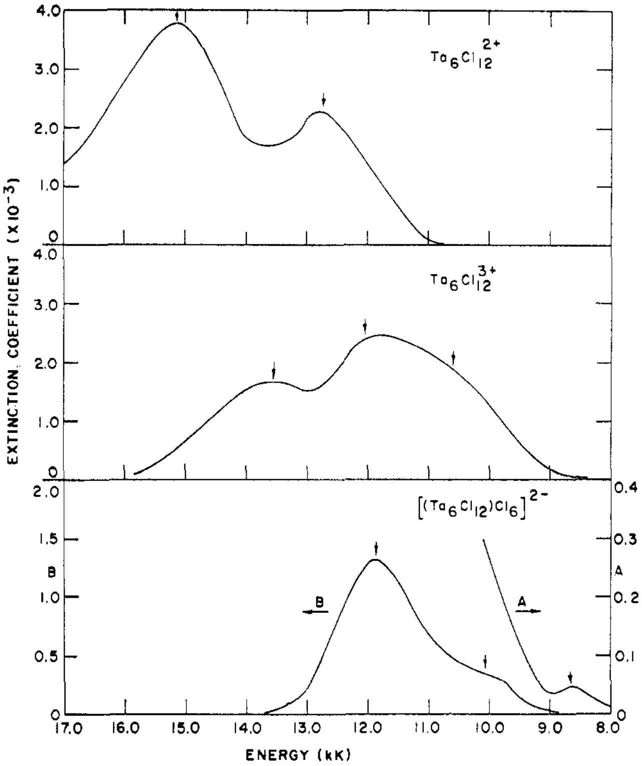

Figure 2.—Near-infrared spectra of $Ta_6Cl_{12}^{n+}$ clusters. $Ta_6Cl_{12}^{2+}$ in DMSO, $Ta_6Cl_{12}^{3+}$ in ethanol, and $(Ta_6Cl_{12})Cl_6^{2-}$ in acetone.

van Bronswyk[11] has reported a photolysis experiment in which it was hoped irradiation of the cluster species at the energy of the charge-transfer bands would test the validity of earlier spectral assignments. A simple replacement reaction (eq 2) was assumed as a model for

$$Nb_6Cl_{12}^{2+} + OH^- \longrightarrow Nb_6Cl_{11}OH^{2+} + Cl^- \qquad (2)$$

the photochemical experiment. It was further hypothesized that irradiation of the "metal–chlorine" charge-transfer bands should accelerate hydrolytic decomposition. The result, which showed no increase in the decomposition in basic solution upon irradiation, was proposed as invalidating the use of spectral shifts between $M_6X_{12}^{n+}$ (X = Cl, Br) clusters for assigning charge-transfer bands, at least in the sense that these shifts were used by Robin and Kuebler. We disagree with this interpretation and believe our data are strong

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(21) F. A. Cotton and T. E. Haas, *Inorg. Chem.*, **3**, 10 (1964).

(22) J. G. Converse and R. E. McCarley, *ibid.*, **9**, 1361 (1970). In this reference it is shown that derivatives of $Nb_6Cl_{12}^{2+}$ are diamagnetic ($\chi_g < 0$) when they are carefully prepared to avoid air oxidation and contamination with paramagnetic $Nb_6Cl_{12}^{3+}$.

evidence in favor of using spectral shifts as an aid in assigning cluster spectra. The photochemical experiment does open a new area of study in cluster chemistry and in the future may provide some interesting data.

Schneider and Mackay[8] have reported a more comprehensive study of the spectra and bonding of the M_6X_{12} clusters. Their measurements of spectra dealt entirely with $Nb_6Cl_{12}^{n+}$ clusters. In the case of the 3+ and 4+ species their data are in general agreement with those given here. However their data given for the 2+ cluster, $(Nb_6Cl_{12})Cl_6^{4-}$, in nitromethane are clearly in error and should be attributed to the 3+ cluster. In this regard we are in agreement with Spreckelmeyer.[12] Since Schneider and Mackay believed thus that the bands of 3+ at 7.6 and 9.9 kK belonged to 2+, they used this information to justify assigning two bands under the broad absorption at 10.8 kK for the 2+ cluster in ethanol. The spectra of $Nb_6Cl_{12}^{2+}$ and $Ta_6Cl_{12}^{2+}$ were thus brought into a 1:1 correspondence. We also believe the band at *ca.* 10.8 kK of $Nb_6Cl_{12}^{2+}$ consists of two components, but experimental proof is lacking (*vide infra*).

Finally we note that wherever similar compounds were measured the spectra given here are in substantial agreement with those given by Spreckelmeyer.[12] However there are some differences in actual values for absorption maxima because of measurements in different solvents, and in the case of $(Nb_6X_{12})X_6^{n-}$ ions, our values are for the resolved Gaussian components.

In the paper by Schneider and Mackay[8] it was mentioned that a further band for $(Nb_6Cl_{12})Cl_6^{2-}$ at *ca.* 5 kK had been observed by us. We did indeed observe this band in acetone or acetonitrile solutions, but further work has shown that it arises from a small content of water in these solvents. In no case have we observed genuine absorption bands for any of the $M_6X_{12}^{n+}$ cluster species at energies of less than *ca.* 7 kK.

Discussion of Spectral Assignments.—Three significant attempts to understand the cluster electronic structure have been reported. They have been summarized in quite some detail in the recent paper by Schneider and Mackay[8] and hence only the major and relevant points will be discussed here.

Cotton and Haas[21] have discussed the cluster electronic structure in terms of MO's arising from only the d_{z^2}, d_{xy}, d_{xz}, and d_{yz} metal atomic orbitals. They were able to arrive at an MO ordering scheme which allowed accommodation of the 16 $M_6X_{12}^{2+}$ d electrons in bonding MO's. These authors did not make any attempt to rationalize or predict physical properties of the clusters.

Robin and Kuebler[9] extended the above treatment by including chlorine 3p orbitals and the niobium $d_{x^2-y^2}$ orbital and calculating an MO ordering. Their final MO ordering was arrived at by *a priori* consideration of the experimental spectra, which had certain errors included,[8] thus invalidating the treatment.

Schneider and Mackay in their paper[8] have proposed an MO ordering similar to that of Cotton and Haas.[21] They considered the species $(Nb_6Cl_{12})Cl_6^{n-}$ and arrived at their electronic structure scheme in a semiempirical fashion so that they had a self-consistent set of band assignments. Possible spectral transitions were considered on the basis of symmetry selection rules but the orthogonality of the various d orbitals was not taken into account explicitly. Bands were assigned as shown in Table VI.

Table VI

Band Assignments for $Nb_6Cl_{12}^{n+}$ by Schneider and Mackay[8]

ν_{max}, kK	Assignment
5 (weak)[a,b]	$t_{2g}(xz, yz) \rightarrow a_{2u}(xy)$
10 (1.5)	$a_{2u}(xy) \rightarrow t_{2g}(xy)^c$
11 (1.5)	$t_{2g}(xz, yz) \rightarrow t_{2u}(xz, yz)^c$
17 (0.3)	$t_{1u}(xz, yz) \rightarrow t_{2g}(xy)^c$
20 (0.9)	$t_{1u}(xz, yz) \rightarrow t_{1g}(xz, yz)^c$
25 (12)	. . .[d]
31 (4)	a_{1g}, t_{2g}, or $t_{1u} \rightarrow t_{1u}$ or $e_g{}^c$
35 (16)	. . .[d]
44 (39)	. . .[d]
47 (83)	. . .[d]

[a] Approximate $\epsilon_{max} \times 10^{-3}$ are listed in parentheses. [b] This near-infrared band was discussed earlier and has been found to be spurious. [c] Metal to metal transitions. [d] Assigned generally as either ligand-to-metal or metal-to-ligand charge-transfer bands.

Examination of these assignments led to the suggestion that metal–metal bands should have ϵ values of a relatively constant magnitude as ligand field bands of a given type do. *A posteriori* considerations led to the proposed criteria that metal–metal transitions within a given d-orbital subsystem should have $\epsilon \geq (1-3) \times 10^3$ l. mol^{-1} cm^{-1} and transitions between different d-orbital subsystems, *e.g.*, $\Gamma(d_{xy}) \rightarrow \Gamma(d_{z^2})$, should have $\epsilon < \sim 2 \times 10^3$ l. mol^{-1} cm^{-1}. The more intense absorptions were then assigned as charge-transfer bands (Table VI) of an unspecified type mainly because of their high ϵ. This is in disagreement with our proposals, especially for band G.

Prior to a consideration of our suggestions for assignment of the spectra, some important structural features of the $M_6X_{12}^{n+}$ cluster compounds need to be discussed. First, as mentioned earlier, the structure determinations of $K_4[(Nb_6Cl_{12})Cl_6]$,[18] $(Ta_6Cl_{12})Cl_3$,[23] $((CH_3)_4N)_2[(Nb_6Cl_{12})Cl_6]$,[19] and $H_2[(Ta_6Cl_{12})Cl_6] \cdot nH_2O$[20] indicate there is no significant distortion of the M_6X_{12} unit from O_h symmetry in any of the three oxidation states. Thus the MO levels appropriate to O_h symmetry must be valid.

Second, even though O_h symmetry may be retained, there may be profound changes in bonding parameters on change of oxidation state of the cluster unit. This is indicated by the change in the Nb–Nb bond distance which accompanies oxidation of the discrete cluster anions, *viz.*, d(Nb–Nb) = 2.92 Å in $K_4[(Nb_6Cl_{12})Cl_6]$[18] and 3.017 Å in $((CH_3)_4N)_2[(Nb_6Cl_{12})Cl_6]$.[19] At the same time the terminal Nb–Cl bond distance changes from 2.59 Å (average) in the 2+ salt to 2.46 Å in the 4+ salt. Hence we conclude that on oxidation of the clus-

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(23) D. Bauer and H. G. von Schnering, *Z. Anorg. Allgem. Chem.*, **361**, 259 (1968).

ter unit there is a considerable weakening of the Nb–Nb bonding and strengthening of the terminal halide bonds.

Third, the magnetic properties[3,5,22] show that the 2+ and 4+ compounds are diamagnetic, whereas the 3+ compounds are paramagnetic with moments consistent with one unpaired electron per M_6X_{12} unit. This means that the highest occupied MO's in the 2+ and 3+ clusters must be orbital singlets. The epr spectrum[5] of $(Nb_6Cl_{12})Cl_6^{3-}$ also indicates the ground state of the 3+ compounds is an orbital singlet, and the isotropic hyperfine structure shows that the unpaired electron is symmetrically delocalized over the Nb_6 octahedron. Based on this information and the results of the Cotton and Haas calculations, Schneider and Mackay[8] arrived at $a_{2u}(xy)$ as the highest bonding MO.

We proceed now to some tentative band assignments based on the spectra reported here. First, because of the large band shifts noted earlier, we assign bands I through M to halogen-to-metal charge-transfer transitions. Intensities of $>10^4$ l. mol^{-1} cm^{-1} for these bands support this assignment. Bands A through H and band 0 then are assigned to the transitions between the "metal–metal" orbitals.

Taking the set $a_{1g}(z^2)$, $a_{2u}(xy)$, $t_{1u}(xz, yz)$, and $t_{2g}(xz, yz)$ as the bonding MO's,[21] the following transitions are symmetry allowed

Type I	Type II
$a_{2u}(xy) \longrightarrow t_{2g}^*(xy)$	$t_{1u}(xz, yz) \longrightarrow a_{1g}(z^2)$
$t_{2g}(xz, yz) \longrightarrow t_{2u}^*(xz, yz)$	$t_{2g}(xz, yz) \longrightarrow a_{2u}(xy)$
$t_{1u}(xz, yz) \longrightarrow t_{1g}^*(xz, yz)$	$t_{2g}(xz, yz) \longrightarrow e_u^*(xy)$
$a_{1g}(z^2) \longrightarrow t_{1u}^*(z^2)$	$t_{2g}(xz, yz) \longrightarrow t_{1u}^*(z^2)$
	$t_{1u}(xz, yz) \longrightarrow t_{2g}^*(xy)$
	$t_{1u}(xz, yz) \longrightarrow e_g^*(z^2)$

The first two transitions given in the right-hand column are between bonding orbitals; all others terminate in antibonding orbitals. The transitions between the bonding orbitals become possible only in the 3+ or 4+ clusters. In the left-hand column the transitions stay within the same AO subset (type I), and these may exhibit enhanced intensities as maintained by Robin and Kuebler.[9] These authors also imply the remaining "allowed" transitions (type II) should have negligible intensities because of the orthogonality of the different AO subsets. It should be noted, however, that there is ample opportunity for mixing of subsets *via* configuration interaction between MO's of the same representation, *e.g.*, $t_{2g}(xz, yz)$ and $t_{2g}^*(xy)$.

Schneider and Mackay[8] have suggested that ϵ should be as high as $(1\text{–}4) \times 13^3$ l. mol^{-1} cm^{-1} for transitions of type I and less than this range for transitions of type II. An example for a different system is found in the discussion of the spectra of $Re_2Cl_8^{2-}$ by Cotton and Harris.[24] They assigned two bands, at 19.7 kK (ϵ 5600) and 34.8 kK (ϵ 8800)[25] as electric dipole allowed transitions, but the transition at 18.7 kK (ϵ 1500) was assigned as being dipole forbidden. These bands, in the above order, were assigned as the metal–metal transitions $b_{2g}(xy) \rightarrow b_{1u}(xy)$, $e_g(xz, yz) \rightarrow a_{2u}(z^2)$, and $b_{2g}(xy) \rightarrow a_{2u}(z^2)$. No account of AO orthogonality was noted. It is thus apparent that band intensities may be useful in making assignments only in the case of the strongest bands where all factors governing the intensity are optimized.

We propose that band D, because it appears as the unique band in spectra of the 3+ and 4+ clusters, arises from a transition within the bonding MO's, *viz.*, $t_{2g} \rightarrow a_{2u}$ or $t_{1u} \rightarrow a_{1g}$. Schneider and Mackay did not consider the latter assignment and assigned the former at *ca.* 5 kK, which as noted above is a spurious band. The intensity of band D is consistent with either assignment. We prefer the latter assignment, and hence a_{1g} as the uppermost bonding MO for the following reason.

In the Cotton–Haas calculations no account was taken of the effect of the metal–halogen MO's on the metal orbitals. Clearly, among the orbitals used to construct the metal–metal MO's, the one most disturbed by bonding to halogens is the d_{z^2} orbital on each metal. The changes in the Nb–Nb and Nb–Cl (terminal) bond distances on oxidation of the $(Nb_6Cl_{12})Cl_6^{n-}$ unit indicate that this is the case, *i.e.*, the d_{z^2} orbital is extracted from metal–metal bonding and used in Nb–Cl bonding as the oxidation state increases. The large hyperfine interaction in the epr spectrum of $(Nb_6Cl_{12})Cl_6^{3-}$ also is consistent with a_{1g} as the topmost bonding level.

Bands A and B must arise from transitions out of the uppermost level (a_{1g}) since both of these are absent from the spectra of 4+ derivatives. Only one such transition is symmetry allowed, *viz.*, $a_{1g}(z^2) \rightarrow t_{1u}^*(z^2)$, but the intensities of these bands suggest that both transitions are allowed. This dilemma would remain even if a_{2u} were the topmost level, since the transition $a_{2u}(xy) \rightarrow t_{2g}^*(xy)$ is similarly the only such allowed transition. Thus an exact assignment is not possible for these bands, although surely one must be assigned as noted. Any of the usual mechanisms[26] by which a forbidden transition may attain a high intensity may be operative in the case of the other band, or the two bands may result from Jahn–Teller splitting of the excited state.

The other bands (0 and C) in the low-energy spectrum are the weak bands observed for the 4+ clusters. These bands are not observed for the 2+ or 3+ clusters, but even if present they would not be seen for the 3+ cluster due to the strong absorption in this region. These bands are suggested as being transitions from the remaining two bonding MO's ($a_{2u}(xy)$ and $t_{2g}(xz, yz)$) into the $a_{1g}(z^2)$ MO. These transitions are formally forbidden which correlates with the very low observed intensity.

There remain four bands (E through H) in the niobium and tantalum spectra which are common to all oxidation states and are not assigned as charge-transfer bands. Band G, at *ca.* 23 and 28 kK in the niobium and tantalum spectra, respectively, is much more intense than the other metal–metal bands. This transition must be fully allowed, and we have ruled out metal–

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(24) F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **6**, 926 (1967).

(25) F. A. Cotton and C. B. Harris, *ibid.*, **4**, 330 (1965).

(26) B. N. Figgis, "Introduction to Ligand Fields," Interscience Publishers, New York, N. Y., 1966, p 203.

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.

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

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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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